

Nanometrology for Controlling and Probing Organic Semiconductors and Devices

Jessica Alice Feinmann Wade

Department of Physics, Imperial College London

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Abstract

Organic semiconductors continue to attract interest due to their potential applications in printable, low-cost, high throughput, flexible electronic devices, which could profoundly impact the large area electronics and semiconductor industries. The performance and stability of such devices is strongly influenced by the chemical composition and molecular packing of the organic semiconducting material. This thesis considers a range of solution processing techniques, which can be used to control the molecular packing of polymeric and small molecular organic semiconductors, and employs a range of complementary spectroscopic and electronic characterisation techniques to elucidate the complex relationships between thin film morphology and optoelectronic device performance. By understanding these effects, we are able to control the deposition processes in order to yield optimised morphologies for high-performance organic field effect transistors, magnetic tunnel junctions, and photovoltaic devices.

We first develop a highly controlled solution deposition system that offers precise control of the thermal conditions and rate of solution deposition. The zone-casting technique is optimised to print uniaxially aligned needle-like domains of small molecule organic semiconductors. We establish a robust structural probe, Raman spectroscopy, to interpret the well-defined packing motifs.

The characterisation of molecular packing is extended to vacuum deposited organic thin films. For both pentacene and phthalocyanine materials, we identify strong interactions between the organic layer and the substrate, which can be modified using self-assembled monolayers, inorganic interlayers and temperature control. We are able to produce films with uniform molecular packing and an optimised molecular orientation such that the charge carrier mobility or magnetoresistance of transistor or tunnel junction devices are increased by several orders of magnitude.

Finally we consider organic photovoltaic devices, where modifications to the chemical structures of conjugated polymers provide an effective means of controlling both molecular packing and device stability. We investigate the impacts of a number of structural modifications on the molecular packing and stability of the benchmark material poly(3-hexyl)thiophene. We consider the operational stability of these materials and find that increased planarity of the conjugated backbone and a deeper ionisation potential do not necessarily result in long device lifetimes. For polymer/fullerene blend films, we identify how the size and loading of the acceptor molecules influences the polymer molecular packing.

Both the specific conclusions drawn in this thesis and the techniques for morphological control and characterisation are highly relevant to a broad range of organic semiconducting materials and device architectures. Our findings have particular relevance to the issues of optimised solution deposition and device stability, which are of critical importance to the emerging industry of printed electronics.

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Declaration of Originality

Except where specific reference is made to the work of others, and has not been already submitted either wholly or in part to satisfy any degree requirement at this or any other university.

Jess Wade, April 2016

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Table of Contents

Abstract	3
Acknowledgements	4
Declaration of Originality	5
Table of Contents	6
List of Figures	9
List of Tables	16
Frequently Used Abbreviations	18
1 Introduction	20
<i>Motivation</i>	20
<i>Aims</i>	20
<i>Bibliography</i>	23
2 Review	24
2.1 <i>Organic Semiconductors</i>	25
2.1.1 Conjugated Molecules	25
2.1.2 Optoelectronic Properties	26
2.1.3 H- and J- aggregation	28
2.2 <i>Organic Field Effect Transistors</i>	29
2.2.1 Operating Principles	30
2.2.2 Device Characterisation	32
2.2.3 Factors limiting device performance	33
2.2.4 Anisotropy	34
2.3 <i>Organic Solar Cells</i>	35
2.3.1 Operating Principles	36
2.3.2 Device Characterisation	40
2.3.3 Blend Morphology	40
2.3.4 Device Stability	41
2.4 <i>Bibliography</i>	43
3 Experimental Details	49
3.1 <i>Sample Preparation</i>	49
3.2 <i>Solution Preparation</i>	49
3.3 <i>Substrate Preparation</i>	49
3.3.1 SAM Treatment	50
3.3.2 Spin Coating	50
3.3.3 Zone Casting	50
3.3.4 Bottom-Gate Bottom-Contact Transistors	50
3.4 <i>Characterisation Techniques</i>	51
3.4.1 Optical Microscopy	51
3.4.2 Atomic Force Microscopy	52
3.4.3 UV-Visible Absorption Spectroscopy	53
3.4.4 X-Ray Techniques	54

3.4.5	Photoluminescence	55
3.4.6	Raman Spectroscopy	55
3.4.7	Electrical Characterisation	68
3.5	Bibliography	70
4	Molecular Packing in Zone-Cast Solution Processed Small Molecule Devices	73
4.1	Motivation and Aim	74
4.2	Development of the Zone-Casting Technique	75
4.2.1	Solution Temperature	77
4.2.2	Substrate Temperature	78
4.2.3	Solution Concentration	79
4.2.4	Substrate Displacement Rate	79
4.2.5	Meniscus Height	80
4.3	Impact of Molecular Packing on Charge Transport Anisotropy	81
4.3.1	Experimental Details	83
4.3.2	Optoelectronic Properties of Zone-Cast TIPS and TES pentacene thin films	84
4.3.3	Charge Transport Anisotropy in Zone-Cast Organic Field-Effect Transistors	88
4.3.4	Impact of Intermolecular Interactions on Molecular Packing and Optoelectronic Properties	99
4.3.5	Summary	111
4.4	Impact of Chemical Structure on Molecular Packing in Zone-Cast Phthalocyanines	112
4.4.1	Experimental Details	113
4.4.2	Optoelectronic Properties	113
4.4.3	Investigation into the Stability of Molecular Packing in Spin-Coated Phthalocyanines	123
4.4.4	Controlling H- and J-aggregation using Zone-Casting	124
4.4.5	Summary	127
4.5	Conclusions	128
4.6	Bibliography	130
5	Interfacial Molecular Packing in Vacuum-Evaporated Small Molecule Devices	136
5.1	Motivation and Aim	137
5.2	Impact of Surface Treatment on Molecular Packing and Device Performance in Pentacene Organic Field-Effect Transistors	138
5.2.1	Experimental Details	146
5.2.2	Effect of SAM Treatment on Pentacene Packing on the Gold Electrode	146
5.2.3	Effect of SAM Treatment on Pentacene Packing in the Active Channel	155
5.2.4	Effect of SAM Treatment on the Pentacene Packing at the Electrode/ Channel Interface	156
5.2.5	Effect of SAM treatment on Charge Transport Characteristics	159
5.2.6	Summary	160
5.3	Impact of MgO Interlayers on Molecular Packing and Device Performance in Copper Phthalocyanine Magnetic Tunnel Junctions	161
5.3.1	Experimental Details	163
5.3.2	Developing a Structural Probe for Molecular Packing of Copper Phthalocyanine	165
5.3.3	Impact of Substrate on Copper Phthalocyanine Molecular Packing in Magnetic Tunnel Junctions	169
5.3.4	Impact of Film Thickness on Copper Phthalocyanine Molecular Packing	171
5.3.5	Impact of Substrate Temperature on Copper Phthalocyanine Molecular Packing	173
5.3.6	Summary	179
5.4	Conclusions	180
5.5	Bibliography	181
6	Influence of Chemical Structure on Polymer Molecular Order and Device Stability in Polythiophene Derivatives	187

6.1	<i>Motivation and Aims</i>	188
6.2	<i>Operational Electrochemical Stability of Thiophene-Thiazole Copolymers</i>	189
6.2.1	Experimental Details	189
6.2.2	Optoelectronic properties.....	190
6.2.3	<i>In situ</i> electrochemical degradation of P3HT	195
6.2.4	Impact of Electrochemical Degradation of P3HT, PTTTz and PTTz	202
6.2.5	Summary	207
6.3	<i>Effect of Side-Chain Branching on the Morphological Stability of Polythiophenes</i>	208
6.3.1	Experimental Details	209
6.3.2	Optoelectronic Properties.....	209
6.3.3	Summary	213
6.4	<i>Conclusions</i>	214
6.5	<i>Bibliography</i>	216
7	The Control of Polymer/Fullerene Interactions and its Impact on Blend Morphology and Operational Stability.....	219
7.1	<i>Motivation and Aims</i>	220
7.2	<i>Impact of Acceptor Size on Polymer Molecular Order</i>	224
7.3	<i>Impact of Fullerene Loading Ratio on Polymer Molecular Order</i>	229
7.4	<i>Impact of Polymer Side-Chain Length on Molecular Packing in a Blend</i>	232
7.5	<i>Probing the Nature of the Interfacial Interaction using in situ Resonant Raman Spectroscopy</i>	234
7.5.1	Impact of Intercalation on Thermal Properties of a Polymer/Fullerene Blend.....	235
7.5.2	Impact of Intercalation on Electrochemical Stability of a Polymer/Fullerene Blend	244
7.6	<i>Summary</i>	250
7.7	<i>Conclusions</i>	251
7.8	<i>Bibliography</i>	252
8	Conclusions and Further Work	254
8.1	<i>Conclusions</i>	255
8.1.1	Molecular Orientation in Solution Processed Small Molecule Devices	255
8.1.2	Interfacial Molecular Orientation	256
8.1.3	Stability of Organic Solar Cells.....	257
8.2	<i>Further Work</i>	259
8.3	<i>Bibliography</i>	261
9	Presentations, Publications and Prizes	262
9.1	<i>Publications</i>	262
9.2	<i>Presentations</i>	262
9.3	<i>Grants and Prizes</i>	264
9.3.1	Prizes	264
9.3.2	Grants.....	264

List of Figures

Figure 2.1:(a) Molecular orbital diagrams of high-energy anti-bonding (π^*) and low energy bonding (π) molecular orbitals. The two lobes of the p_z orbital can interact constructively (bonding) or destructively (anti-bonding). When two lobes meet constructively there is increased electron density between the nuclei. (b) σ and π bonds in ethene. Adapted from reference [3] (c) Energy levels of an organic small molecule. The green arrows represent an optical absorption.	25
Figure 2.2: Localised Frenkel exciton on one molecule and a pair of charges sitting around 10 Å apart on different molecules. Adapted from reference [3]	26
Figure 2.3: A schematic representation of optical absorption spectra for pentacene molecules in different environments. Vibronic replicas are indicated. The blue arrows from crystal to isolated molecules represent the solvent shift. The right hand side illustrates radiative and non-radiative decay processes in a polyatomic molecule that obeys Kasha's rule. The positions of the electrons are included. Absorption from the ground state (S_0) leaves the molecule in an excited singlet state (S_1 , S_2). Adapted from reference [5]	28
Figure 2.4: Molecular orientations within J- and H-aggregates. The sign of the excitonic coupling constant ' J_0 ' is > 0 in H-aggregates, < 0 in J-aggregates. Polymer HJ-aggregates contain both $J_0 > 0$ between chains and $J_0 < 0$ within chains. This figure is adapted from reference [8]	29
Figure 2.5: Typical OFET architecture.	29
Figure 2.6: Common OFET Device Architectures.	30
Figure 2.7: Band diagram of metal-insulator-(p-type) semiconductor interface at (a) $V_G = 0$, flat band, and (b) $V_G < 0$, accumulation mode. The metal work function (ϕ) and molecular HOMO and LUMO are indicated. Adapted from reference [19]	30
Figure 2.8: Operating Principles of OFETs.	31
Figure 2.9: (a) Output and (b) transfer characteristics in the linear ($V_D = -10V$) and saturation ($V_D = -40V$) for a solution processed TIPS pentacene OFET characterised in air.	32
Figure 2.10: (a) PHYSIOSORPTION Charge density close to the metal surface before organic molecules are deposited. (b) Metal electron states are pushed back due to physisorption reducing the surface dipole (c) CHEMISORPTION Interfacial density of states forms at metal/ organic interface. Within induced states, charge neutrality level $\neq$ mid-gap. (d) Charge transfer takes place from the organic material to the metal generating an interfacial dipole. Adapted from references [37,39]	34
Figure 2.11: Stages of OPV operation: exciton formation and diffusion, exciton dissociation, charge transport and charge collection.	36
Figure 2.12: The formation of geminate and non-geminately bound polaron pairs during charge generation. Red arrows show the processes responsible for photocurrent generation. Blue arrows show the loss processes. Here, ΔE_{CS} is the energy of the charge separated state and ΔG is the difference in free energy between the excited and charge separated state. This figure is adapted from reference [48]	37
Figure 2.13: Illustration of heterojunctions for OPV devices. The first heterojunction was (a) planar bilayer of donor and acceptor materials. To increase the active volume of the OPV, heterojunctions must exist within an exciton diffusion length such as in an (b) bulk heterojunction or (c) an ordered interdigitated heterojunction.	38
Figure 2.14: Illustration of current density-voltage for an operational solar cell indicating the parameters described in Table 2.2.	40
Figure 2.15: Chain oxidation process of polymers (PH) reproduced from reference [111]	42
Figure 3.1: (a) Layout of a Fraunhofer test substrate. (b) BG BC device architecture.	51
Figure 3.2:(a) Non-polarised and (b) cross-polarised optical images taken of a spin-coated thin film.	52
Figure 3.3: Schematic of AFM apparatus.	52
Figure 3.4: (a) Schematic of UV-Visible Spectrophotometer (b) modification to beam path for polarised UV-Visible absorption measurements.	54
Figure 3.5: Energy Diagram representing elastic Rayleigh scattering (light blue), anti-Stokes Raman scattering (dark blue) and Stokes Raman scattering (red) with ν_0 , ν_s and ν_R representing the frequencies of the incident light, Raman scattered light and molecular vibration respectively. Adapted from reference [14]	56
Figure 3.6: Vibrational internal coordinates and definition of totally symmetric A mode, adapted from reference [24]	58
Figure 3.7: Harmonic potential curves for the ground and excited state, indicating the occurrence of Resonant Raman scattering via the A-term. If the electronic state is not displaced (left) there A-term will be zero. A displacement of the electronic excited state (right) with respect to the ground state (Δ) allows non-vanishing vibrational overlap for totally symmetric upward and downward transitions.	59

Figure 3.8: Molecular structure and atom numbering of RR-P3HT. (a) Normalised absorption spectrum and (b) Normalised Raman spectrum of a 40 mg ml ⁻¹ RR-P3HT thin film in the 1300 – 1600 cm ⁻¹ range. The positions of the excitation wavelengths are indicated.	60
Figure 3.9: Normalized non-resonant Raman spectra of RR and RRa P3HT	61
Figure 3.10: Molecular structure, (a) Thin Film UV-Visible Absorption and (b) Raman spectrum under 785, 488 and 457 nm excitation energies. Raman modes related to the TBT, T, BT and F8 units are indicated.....	62
Figure 3.11: Schematic of angle-dependent polarized Raman apparatus, showing the placement of the half-wave plate in the beam path.	64
Figure 3.12: Schematic of the electrochemical cell used in this work.	66
Figure 3.13: (a) Geometry optimised structure of a pentacene molecule and F8TBT D-A-D oligomer and (b) simulated (black) and experimental (red) non-resonant Raman spectrum.	68
Figure 3.14: Schematic of electrical characterisation of OFETs using an Agilent B2902A	69
Figure 4.1: Schematic of the zone-casting apparatus with tilted, narrow nozzle (width = 0.25 mm). The maximum substrate width in the present set-up is 15 cm. The zone-casting direction is indicated.	76
Figure 4.2: Optical microscope images of zone-cast TIPS-pentacene films deposited at a range of solution temperatures. The substrate temperature is maintained at 70 °C. These images were obtained with David T James.	77
Figure 4.3: Optical microscope images of zone-cast TIPS-pentacene films deposited at a range of substrate temperatures. The solution temperature is maintained at 60 °C. These images were obtained with David T James.	78
Figure 4.4: Optical microscope images of zone-cast TIPS-pentacene films deposited at a range of concentrations. The solution temperature is maintained at 60 °C and substrate temperature at 70 °C. These images were obtained with David T James.	79
Figure 4.5: Optical microscope images of zone-cast TIPS-pentacene films deposited at a range of substrate displacement rates. The solution temperature is maintained at 60 °C, substrate temperature at 70 °C and concentration at 7 mg ml ⁻¹ . These images were obtained with David T James.	79
Figure 4.6: Optical microscope images (10 x optical zoom) of zone-cast TIPS-pentacene films deposited at a range of substrate displacement rates. The solution temperature is maintained at 60 °C, substrate temperature at 70 °C, substrate displacement rate at 500 μm s ⁻¹ and concentration at 7 mg ml ⁻¹ . These images were obtained with Samuel de Malprade... ..	80
Figure 4.7: Cartoon representations of (a) herringbone packing for unsubstituted pentacene (b) Brick-wall type packing for TIPS-pentacene (c) slipped-stack packing for TES pentacene.	81
Figure 4.8: Molecular and orthographic projections of the triclinic unit cells of TIPS- (a,c,e,g) and TES- (b,d,f,h) pentacene. The red, green and blue colours correspond to x, y and z directions, respectively. This figure is reproduced from our published work. ^[1] Crystal structures for TIPS-pentacene are generated using unit cell parameters from Ostroverkhova et al and can be obtained via Cambridge Crystallographic Data Centre (CCDC). ^[5] The TES-pentacene structure has been calculated from the force-field Molecular Mechanics calculations.....	82
Figure 4.9: Normalised absorption spectra for TIPS-pentacene solutions in toluene (black solid line) and spin-coated thin films (red, dashed). The inset displays the unnormalised absorption of the dilute solution up to 250 nm.	85
Figure 4.10: DFT simulated Raman spectra for unsubstituted and TIPS-pentacene molecules in the gas phase. Geometries were optimised using the B3LYP functional and 6-31 G(d,p) basis set. The identities of the strongest vibrational modes are shown in the inset.	86
Figure 4.11: (a) Solid-state Raman spectra for TIPS pentacene at a range of excitation energies (457 – 785 nm) and the DFT simulated Raman spectra (black dashed line). (b) Non-resonant solid-state Raman spectra for TIPS (black), TES-(red) and unsubstituted (blue) pentacene measured at 785 nm.	87
Figure 4.12: Montage of 8 cross-polarised optical images (50x optical zoom) of TIPS-pentacene (first row) and TES-pentacene (second row) FETs cast at 50, 100, 500 and 1000 μm s ⁻¹ . The horizontal stripes are source and drain electrodes pre-patterned on the Si/SiO ₂ substrate. The zone-casting direction is indicated by the arrow. This figure is reproduced from our published work. ^[1]	88
Figure 4.13: (a) TIPS-pentacene and (b) TES-pentacene FET transfer curves taken in the saturation regime (V _D = -40 V) for polycrystalline devices zone-cast parallel to the S and D direction, channel length (L) = 2.5 μm. This figure is reproduced from our published work. ^[1]	89
Figure 4.14: Representative output characteristics for TIPS-pentacene FETs at a series of gate voltages (0 - -40V) for (a) and (b) polycrystalline and (c) and (d) needle-like domains. (a) and (c) represent devices zone-cast parallel to the direction of charge transport, whereas (b) and (d) are perpendicular.....	90
Figure 4.15: Saturation mobility as a function of substrate displacement rate in (a) TIPS- and (b) TES-pentacene FETs for L = 2.5 μm. Measurements are taken from devices with needles oriented parallel (open) and perpendicular (closed) to the charge transport direction. Charge mobility anisotropy (μ μ _⊥) as a function of substrate displacement rate for different channel lengths for (c) TIPS- and (d) TES-pentacene FETs. This figure is reproduced from our published work. ^[1]	91

Figure 4.16: (left, upper) image of FET substrate attached to translation stage. (left, lower) Cross-polarised images of TIPS-pentacene transistors with different relative needle to charge transport direction alignments, characterised by the angle 'θ'. Logarithmic mobility as a function of the angle (θ) between crystalline grain a-axis and charge-transport directions for (a) TIPS-pentacene and (b) TES-pentacene. Simulated (black) and experimental (red) data are fit with a $\cos^2\theta$ peak. The zone-casting direction is 0°. This figure is reproduced from our published work. ^[1]	94
Figure 4.17: Montage of cross-polarised optical images (50× optical zoom) of TIPS-pentacene FETs cast at 55, 70, 90, 100 and 115° C. The substrate displacement rate is fixed (500 $\mu\text{m s}^{-1}$) to print highly aligned needles. The horizontal stripes are source and drain electrodes pre-patterned on the Si/SiO ₂ substrate.	95
Figure 4.18: Transfer curves taken in the saturation regime ($V_{\text{SD}} = -40\text{V}$) for (a) parallel and (b) perpendicular TIPS-pentacene FETs. (c) Average saturation mobility as a function of substrate temperature for parallel (black) and perpendicular (red) devices.	96
Figure 4.19: Mobility anisotropy ($\mu_{\text{parallel}}/\mu_{\text{perpendicular}}$) for devices with 20, 10, 5 and 2.5 μm channel lengths and average (b) film thickness as a function of substrate temperature	97
Figure 4.20: Orientation of the C – C _{LONG} (red) and C – C _{SHORT} (black) Raman modes at various points down a needle (a, c, e) on the channel and (b, d) on the contact.	98
Figure 4.21: (a) Relative intensity of C – C _{SHORT} /C – C _{LONG} across the contact-channel-contact. Angle-dependent polarised Raman plots of the C – C _{LONG} (Black) and C – C _{SHORT} (red) on the (b) channel and in the (c) contact.	99
Figure 4.22: Experimental and simulated Raman spectra for a pentacene thin film and isolated molecule. The main vibrational modes are indicated. Simulated Raman spectra are scaled by 0.971.	101
Figure 4.23: Normalised UV-Visible absorption spectra of pentacene in a p-terphenyl lattice (black) and TIPS pentacene solutions (red).	102
Figure 4.24: (a) Absorption of isolated pentacene in p-terphenyl lattice (b) Normalised Raman spectra of pentacene in a p-terphenyl lattice collected at 785, 633, 514, 488, 457 nm and the simulated Raman spectra of pentacene and p-terphenyl.	103
Figure 4.25: (a) Molecular structure of p-terphenyl (b) uncorrected DFT simulated Raman spectra of pentacene and p-terphenyl and Raman spectra acquired at 785, 633, 514 and 457 nm of crystals of (c) pure p-terphenyl (d) p-terphenyl doped with pentacene (0.01 %), normalised to the 1591 cm^{-1} p-terphenyl mode.	104
Figure 4.26: Raman spectra of (a,b) pentacene doped and (d,e) pure p-terphenyl at different tilt angles. The spectra is (a) and (d) are collected parallel to the direction of zone-translation and (b) and (e) are perpendicular. All Raman spectra are normalised to the 770 cm^{-1} p-terphenyl vibrational mode (c) shows the intensities of the pentacene modes at 795, 1335 and 1404 cm^{-1} relative to p-terphenyl as a function of tilt angle. When the electric field of the laser is in the plane of the vibrational mode, the Raman signal is enhanced. The photograph of the zone-refined crystal was obtained by Ke Jie Tan.	106
Figure 4.27: (a) Simulated Raman spectra of pentacene, p-terphenyl and DAP-1. (b) Raman spectra acquired at 785 and 514 nm for DAP-1 compared to the simulated spectra. (c) Molecular structures and bond lengths.	108
Figure 4.28: (a) Normalised absorption spectra of 0.1 % pentacene and DAP-1 in p-terphenyl. Inset: raw absorption spectra. (b) A comparison of the crystal and solution absorption spectra of DAP-1. The solvent (chloroform) absorption is also included.	108
Figure 4.29: Mulliken charges for (a) pentacene and (b) DAP-1. The isosurfaces of the HOMO and LUMO and simulated energy levels are provided. Nitrogen substitution reduces the HOMO energy level. The isovalue is 0.02.	109
Figure 4.30: Normalised Raman spectra of DAP-1 polymorphs: polycrystalline (dark blue), dissolved in a 0.1 mg ml^{-1} chloroform solution (pale blue) and isolated in a p-terphenyl lattice (green). The red dashed box indicates the region of interest for study of DAP-1 molecules.	110
Figure 4.31: The molecular structures of the three materials considered in this work: Zinc Phthalocyanine (ZnPc, black solid) and Thiophene Zinc Phthalocyanine (TZnPc, red dashed) and metal-free Thiophene Phthalocyanine (TPc, blue dotted) and their associated UV-visible absorption spectra in the solution (left) and solid state (right), normalised to the Qx-band absorption peak ($\approx 600\text{ nm}$). The TZnPc is one of four regioisomers, discussed further below.	113
Figure 4.32: TD-DFT calculation of UV-visible absorption spectrum showing two strong contributions from S ₁ and S ₂ states. Table shows the contributions to these states from different molecular orbitals and the electron isodensity surfaces (isovalue = 0.04 atomic units).	115
Figure 4.33: Isodensity surfaces for the LUMO + 1, LUMO, HOMO and HOMO – 1 of ZnPc, TPc and TZnPc generated using TD-DFT with the CAM-B3LYP functional at the 6-31G+(d,p) basis set. The isovalue is 0.04.	116
Figure 4.34: Cartoon illustrating H- and J-aggregation of phthalocyanine materials.	117
Figure 4.35: Simulated Raman spectra for four structural isomers of TZnPc. The intensity has been normalized to the main peak.	119

Figure 4.36: DFT Simulations (black, solid) and experimental Raman spectra obtained at 457, 488, 514 and 633 nm excitation for thin films of (a) ZnPc, (b) TPc and (c) TZnPc.	120
Figure 4.37: Schematic indicating main vibrational modes of the materials considered here.	121
Figure 4.38: (a) UV-Visible absorption spectra and the (b) associated resonant Raman spectra for pristine thin films of TZnPc and after aging for 72 hours in N ₂	123
Figure 4.39: (a) UV-Visible absorption spectra and the (b) associated resonant Raman spectra for pristine thin films of TZnPc and after annealing at 200, 270 and 310 °C.	124
Figure 4.40: Summary of deposition parameters for the solute-solvent systems described in text. Optical microscope images of thin films zone-cast at 100 $\mu\text{m s}^{-1}$	125
Figure 4.41: Absorption spectra of TZnPc thin films deposited from chlorobenzene (black), chloroform (red), dichlorobenzene (blue) and toluene (purple) and (b) absorption after 7 days storage in nitrogen. All spectra are normalised to the Q band maxima.	126
Figure 4.42: Absorption spectra of TZnPc thin films deposited from chlorobenzene at 100 (black), 500 (red) and 1000 $\mu\text{m s}^{-1}$ (blue), normalised to Q band maximum, and (b) resonant Raman spectra under 514 nm excitation normalised to 1503 cm^{-1} intensity.	126
Figure 4.43: Peak intensity of C = C _{aza} (1474) and C = N in PC ring (1504) as a function of incident laser polarisation (a) before and (b) after annealing, obtained using angle-dependent polarised Raman spectroscopy.	127
Figure 5.1: The 'a' and 'b' Davydov absorption peaks arising due to coupling of dipoles within a unit cell.	139
Figure 5.2: Absorption of isolated and solid-state pentacene. The absorption peaks between 500 – 700 nm represent the 'a' and 'b' transitions illustrated in Figure 1. Close-up Raman spectra of C-H stretching modes on the sides and ends of the molecule at different excitation wavelengths: 785, 633, 514 and 488 nm.	140
Figure 5.3: Raman spectra taken at 5 positions across pentacene films evaporated through the (a) square and (b) circular apertures. The aperture width is 1 μm . For the square aperture (a) there is evidence of splitting of both the 1158 cm^{-1} and 1371 cm^{-1} Raman modes.	141
Figure 5.4: AFM images (20 μm x 20 μm) of pentacene films deposited through square apertures of (a) 1 μm and (b) 0.2 μm width. These AFM were acquired by Pavlo Fesenko at IMEC.	141
Figure 5.5: Raman spectra of pentacene C-H modes with Gaussian peaks fitted to 1155, 1158 (ν_0 and ν_1) and 1179 cm^{-1}	142
Figure 5.6: Angle dependent polarised Raman scattering intensity of C – C _{SHORT} and C – C _{LONG} Raman active modes taken from four crystals. Crystal 3 demonstrates isotropic scattering of both modes.	142
Figure 5.7: The structure of the pentacene polymorph formed from a (a) circular and (b) square aperture of 1 μm . Adapted from reference ^[34]	144
Figure 5.8: AFM images of 50 nm thick vacuum evaporated pentacene thin films on (a) untreated Au (b) TP treated Au (c) PFBT treated Au (5 x 5 μm).	147
Figure 5.9: Normalised UV-Visible absorption spectra of pentacene thin films (~50 nm) on quartz and Au substrates and pentacene isolated in a p-terphenyl lattice (black dotted). Au substrates were also compared with/ without SAM (PFBT and TP). Molecular orientation within the unit-cell on (b) unmodified and (c) surface treated gold (where $\theta_1 < \theta_2$).	147
Figure 5.10: Raman spectra of pentacene on unmodified Au (black solid) and Au treated with PFBT (red dashed) and TP (blue dotted) when excited with (a) 785 nm (b) 633 nm (c) 457 nm. The highlighted modes are C – C _{SHORT} (grey) and C – C _{LONG} (blue). All spectra are normalised to the 1372 cm^{-1} C – C _{SHORT} mode.	150
Figure 5.11: (a) Relative Raman scattering intensity of C – C _{SHORT} / C – C _{LONG} axis stretch mode under 457, 488, 514, 633 and 785 nm excitation for 100 nm thick pentacene films and a pentacene single crystal. Illustrations of edge-on and end-on packing on untreated and surface treated pentacene films	153
Figure 5.12: (a) Relative intensity C – C _{SHORT} / C – C _{LONG} under 514 nm excitation for pentacene films of different thicknesses. Graphical illustrations of molecular packing on (b) untreated and (b),(c) surface treated Au.	154
Figure 5.13: Non-resonant Raman spectra (785 nm excitation) collected from different points on the device: in the channel, at the electrode/channel interface and on the electrode for (a) untreated Au (b) PFBT treated Au and (c) TP treated Au. Modes shaded green are related to stretches of the SAMs and are discussed in text.	156
Figure 5.14: Raman spectra from different points on the device, on the contact (purple), at the interface (green, orange) and in the channel (dark red) for 60 nm pentacene on (a) untreated (b) TP treated and (c) PFBT treated Au.	157
Figure 5.15: (a) DFT simulation of Raman spectra of PFBT (blue) and TP (red). Pentacene packing at the electrode/ channel interface for (b) PFBT treated and (c) TP treated Au.	157
Figure 5.16: (a) Proposed TP molecular orientation at edge of contact. Simulated dipole moments and orientations for (b) PFBT and (c) TP at LanL2DZ basis set.	158
Figure 5.17: Transfer Curves of pentacene OTFTs in bottom gate bottom contact architecture, W=1000 μm , L=50 μm , measured in nitrogen. V _{SD} = -30 V, V _G = 10 to -30 V (a) with no treatment and (b) with ODTs treatment to the channel. The active layer thickness is 60 nm. (c) – (e) Proposed molecular packing for pentacene on untreated and thiol treated Au.	159

Figure 5.18: A schematic of (a) parallel FM ₁ and FM ₂ and (b) anti-parallel FM ₁ and FM ₂ . Electrons (purple) passing through the layers either have a spin-polarised up or down. The resistivity of each configuration is also indicated ($\rho_{\uparrow\uparrow}, \rho_{\downarrow\downarrow}$).	162
Figure 5.19: Resonant Raman spectra of CuPc excited in the Q-band (black) and B-band (red). The Raman spectra are normalised to the 1528 cm ⁻¹ mode.	164
Figure 5.20: Molecular arrangement of CuPc in α - and β -phase.	165
Figure 5.21: Raman spectra of 5 nm CuPc on (a) SiO ₂ and (b) PTCDA/ SiO ₂ substrates excited at 457, 488, 514, 633 and 785 nm. The peaks marked with an asterisk correspond to Raman scattering from the substrate (SiO ₂ , broad mode centred at 1206 cm ⁻¹ , PTCDA, modes at 1381, 1573, 1592, 1617 cm ⁻¹). The Raman spectra are normalised to the most intense vibration (1530 cm ⁻¹ for CuPc).	166
Figure 5.22: Relative intensities of (a) 1611 cm ⁻¹ , (b) 681 cm ⁻¹ and (c) 1450 cm ⁻¹ Raman modes as a function of excitation wavelength (457, 488, 514, 633 and 785 nm).	167
Figure 5.23: (black) 457 nm excitation, resonant with PTCDA layers, of 5 nm CuPc/ PTCDA/ SiO ₂ thin films and (red) the simulated Raman spectrum for PTCDA calculated at the 6-31 G(d,p) basis set.	168
Figure 5.24: Schematic of intermolecular and molecule – substrate interactions as a function of distance from the inorganic interface.	169
Figure 5.25: (a) Raman spectra measured under 633 nm excitation of 1.6 nm CuPc films deposited on mica, SiO ₂ /MgO/Fe and SiO ₂ /MgO/Fe/MgO substrates. Spectra normalised to the 520 cm ⁻¹ Si peak. Illustration of CuPc packing on (b) a reactive substrate (Fe) and (c) an unreactive substrate (Mica, SiO ₂ , MgO).	169
Figure 5.26: AFM images of the surfaces of 1.6 nm CuPc films on (a) mica (b) MgO and (c) Fe substrates.	170
Figure 5.27: Raman spectra measured under 633 nm excitation for 1.6 (black) and 5 nm (red) CuPc films on (a) MgO (b) Fe surfaces at 293 K. The impact of cooling 1.6 nm CuPc to 77 K on (c) MgO (d) Fe surfaces are also provided. Spectra normalised to the 520 cm ⁻¹ Si peak. Peaks discussed in text (1106, 1143, 1306, 1340, 1452 and 1528 cm ⁻¹) are highlighted. The MR response of MgO/Fe/MgO/CuPc/Co where CuPc thickness is varied from 2.5 to 5 nm is illustrated at (e) 293 and (f) 77 K. The inset of (e) shows the MR of MgO/Fe/CuPc/Co devices at 77 K. MR for 1.6 nm thick CuPc.	173
Figure 5.28: Magnetoresistance at 77 (black) and 300 K (red) of (a) 1.6 nm and (b) 1.2 – 5 nm CuPc. The applied current is 50 nA.	174
Figure 5.29: in situ temperature dependent Raman spectra measured under 633 nm excitation for 1.6 nm CuPc films on (a) MgO (b) Fe surfaces. The heating/ cooling rate is 10 K/ minute.	174
Figure 5.30: Peak parameters extracted from Lorentzian fits to in situ measurements taken every 10 K for 1.6 nm CuPc on MgO (left) and Fe (right) (a) Maximum peak shift of 1528 cm ⁻¹ , (b) I_{1528}/I_{1452} and (c) FWHM of 1528 cm ⁻¹ mode.	176
Figure 5.31: Angle-dependent polarised Raman spectroscopy of CuPc on Fe (black) and MgO (red) surfaces reveals isotropic vibrational modes at 293 K (a). When samples are cooled to 77K, the 1528 cm ⁻¹ (C = N stretch) of CuPc on MgO becomes highly anisotropic (b) revealing a change in the packing structure or size of domains.	178
Figure 5.32: Schematic of CuPc packing on an MgO (green) interlayer at (a) 293 and (b) 77 K.	178
Figure 6.1: Molecular structures of materials considered in this chapter. The materials are all isostructural to P3HT. The main changes are indicated in red.	187
Figure 6.2: Molecular structures of P3HT, PTTTz and PTTz. The calculated Mulliken charges for P3HT, PTTTz and PTTz are shown. For thiazole containing polymers, electrostatic attraction between the nitrogen and sulphur atoms planarize the polymer chain.	189
Figure 6.3: Normalized absorption spectra of pristine thin films of P3HT, PTTTz and PTTz on FTO/glass substrates.	190
Figure 6.4: Calculated HOMO-LUMO isosurfaces for oligomers of (a) P3HT, (b) PTTTz and (c) PTTz. For the thiazole containing polymers, the frontier molecular orbitals include contributions from the nitrogen atoms.	191
Figure 6.5: Experimental (black) and simulated Raman (red) spectra from DFT calculations at the 6-31 G(d,p) basis set for P3HT, PTTTz and PTTz. The spectra are simulated from oligomers of seven repeat units. The nature of the main vibrational modes are described in the text. Experimental Raman spectra are acquired at 488 nm excitation.	192
Figure 6.6: Resonant Raman spectra for pristine thin films of P3HT, PTTTz and PTTz measured under 488 nm excitation. Normalised to the strongest Raman peak (~1460 cm ⁻¹).	193
Figure 6.7: Minimum energy configurations of oligomers of P3HT, PTTTz and PTTz with key dihedrals (θ_{Th-Th} , θ_{Tz-Th} , θ_{Th-Tz}) highlighted. (lower) potential energy scans of the polymers as a function of θ_{Th-Th} , θ_{Tz-Th} , θ_{Th-Tz}	195
Figure 6.8: Three-probe (working, counter and reference) experimental set-up for in situ chronoamperometry measurements. Raman spectra are acquired through a clean quartz window. There is a diagram of the set-up in Section 3.4.6.4.	196
Figure 6.9: Cyclic voltammogram of a neat P3HT film. The red arrow indicates the shift of polymer oxidation during repeat cycles.	196
Figure 6.10: Simulated Raman spectra for P3HT oligomers as a function of inter-unit dihedral torsion. The increase in dihedral torsion (all in a helical conformation) shifts the C = C bond to higher frequencies and increases the energy of the HOMO.	197

Figure 6.11: Calculated isosurfaces of HOMO and LUMO of (a) planar and (b) twisted P3HT. Increasing the inter-unit torsion decreases π -electron conjugation.	197
Figure 6.12: (a) Current as a function of time for a chronoamperometry measurement. Integration of the area under the curve allows calculation of the polaron density created in the polymer films. (b) Resonant Raman spectra of P3HT pre (black), during (red) and after 60 s pulses of 0.65 V (blue).	198
Figure 6.13: (a) Current as a function of time for a range of potential differences (0.5 – 1.05 V). The bias time is fixed at $t = 60$ s. Resonant Raman scans for (b,c) during potential application (d) after the potential is removed and the film is held at 0 V. The Raman spectra in (c) and (d) are normalized to the main C = C peak, (≈ 1489 cm^{-1}).	199
Figure 6.14: (a) Relative intensity of C – C vs C = C modes and (b) relative quinoidal fraction as a function of polaron concentration for P3HT films. The relative quinoidal fraction is found using a linear fit of the neutral (N) and quinoidal polymer (Q) spectra, as illustrated in (c).	201
Figure 6.15: UV-Visible absorption spectra for pristine (black solid line) and electrochemically degraded (red dashed line) films of P3HT, PTTTz and PTTz.	202
Figure 6.16: Raman spectra of pristine and degraded films of PTTz measured with 457, 488, 514 and 785 nm excitations.	203
Figure 6.17: Maximum peak position (cm^{-1}) and FWHM (cm^{-1}) of the main C = C mode in PTTz at 785, 633, 514, 488 and 457 nm excitations for pristine (black) and degraded (red) thin films.	204
Figure 6.18: Resonant Raman spectra for pristine (black solid line) and degraded films (red dashed line) of P3HT, PTTTz, and PTTz measured using 488 nm excitation.	204
Figure 6.19: Lorentzian peak fitting for the main vibrational modes of pristine P3HT, PTTTz and PTTz films measured at 488 nm excitation. The experimental spectra (black line), individual peaks (red dotted line) and cumulative peak (blue dashed line) fit is indicated. The same FWHM (20 cm^{-1}) and peak centres of individual peaks are used for pristine and degraded samples and only the peak intensity allowed to vary.	205
Figure 6.20: Optimised molecular structures of degraded PTTz polymer chains and simulated Raman spectra. All simulations were performed at the 6-31 G(d,p) basis set.	207
Figure 6.21: Molecular structure of P3HT and P3EHT.	208
Figure 6.22: (a) Normalized absorption and (b) resonant Raman spectra of P3HT (black) and P3EHT (red) thin films. Raman spectra are normalized to the C = C vibrational mode.	209
Figure 6.23: Raw (a,c) and normalized (b,d) absorption and resonant Raman spectra of pristine (purple) and quenched (blue) P3EHT. The recrystallization of P3EHT occurs over several hours and is illustrated by the coloured curves.	210
Figure 6.24: Absorption band maxima and C = C peak position as a function of time after quench for thin films of P3EHT extracted from Figure 6.23.	211
Figure 6.25: (a) Lorentzian fits of ordered and disordered components of C = C mode for P3EHT. (b) Integrated peak intensity of $C = C_{\text{ORDER}}/C = C_{\text{DISORDER}}$	212
Figure 6.26: (left) CV scans of thin films of P3EHT on FTO/glass. The oxidation peak has two components at high and low energy representing ordered and disordered material. The relative intensity of these two peaks is illustrated (right) as a function of time after quench.	213
Figure 7.1: Energy level diagram of an organic solar cell at the donor acceptor interface. The photocurrent generation processes are indicated.	220
Figure 7.2: Common organic photovoltaic device architectures: (a) the bilayer device (b) bulk heterojunction and (c) ordered bulk heterojunction.	221
Figure 7.3: Molecular structures of donor polymers considered in this work.	221
Figure 7.4: Raman spectra of PBTtT in as a thin film and in the gas phase, simulated using the B3LYP functional and 6-311 G(d,p) basis-set. The geometry is optimized for an oligomer of at least three repeat units. The table and figure details the bond-lengths and dihedral angles resulting from the geometry optimization. The Mulliken charges are also provided.	223
Figure 7.5: UV-Visible Absorption and associated isosurfaces simulated using TD-DFT with the CAM-B3LYP functional and 6-31 G(d,p) basis set. For the simulation, 9 states were considered.	224
Figure 7.6: Molecular structure of acceptor molecules used in this work.	224
Figure 7.7: Absorbance (a,b) and normalized absorbance (c,d) of thin films of 1:1 blends of PBTtT-C14 with: (a) and (c) 4 small molecule acceptors (bis-PC ₆₀ BM, PC ₇₀ BM, ICBA and ICTA), (b) and (d) PC ₇₀ BM at different loading ratios.	226
Figure 7.8: (a) Normalized absorption and emission spectra of thin films of PC ₇₀ BM. (b) Raman spectra of PC ₇₀ BM excited at 457, 488, 514 and 785 nm and the simulated Raman spectrum for a PC ₇₀ BM molecule. (c) Thin film Raman spectra of a 1:1 PBTtT:PC ₇₀ BM blend and neat PC ₇₀ BM excited at 488 nm.	227
Figure 7.9: (a) Experimental Raman spectra for neat PBTtT and the cumulative fit of a convolution of planar and twisted polymer chains. (b) Potential energy scan as a function of dihedral angle between $\angle_{\text{T-T}}$ and $\angle_{\text{T-}\pi}$ (indicated by red and blue arrows). The simulated Raman spectra arising from an oligomer of PBTtT with frozen dihedral angles between (c) $\angle_{\text{T-T}}$ and (d) $\angle_{\text{T-}\pi}$	228

Figure 7.10: Resonant Raman spectra (488 nm) for blends of PBTTC-C14 with: (a) 4 small molecule acceptors (bis-PC ₆₀ BM, PC ₇₀ BM, ICBA and ICTA), (b) PC ₇₀ BM at different loading ratios. Raman spectra are acquired with a 488 nm laser and normalized to the 1425 cm ⁻¹ Raman mode.	229
Figure 7.11: Schematic of the donor: acceptor interaction in intercalated and high fullerene loading blends	231
Figure 7.12: Normalized absorption and Raman spectra for PBTTC-C16 blends with (a,b) ICBA and (d,e) PC ₇₀ BM. The Raman spectra are normalized to the delocalised C = C mode at 1415 cm ⁻¹ . The associated PL spectra of the pristine films are provided in (c) and (d). The inset spectra focus on the blends > 40 % fullerene.	233
Figure 7.13: (left) optical microscope images of the annealed 1:1 blends with PC ₇₀ BM (middle) the corresponding Raman spectra off (black) and on (red) the crystal structures (positions indicated with circles on microscope images). Annealing the films causing crystallization of the PC ₇₀ BM, allowing characterization in the blend film. The raw PL spectra of neat films of the blends (black) and acceptors (red), along with PL of the annealed samples off (green) and on (blue) the crystals.	234
Figure 7.14: Phase Diagram for PBTTC:PC ₇₀ BM, constructed from references ^[6,26]	235
Figure 7.15: (upper) in situ Resonant Raman spectra acquired on heating at 10 °C/minute for the four fullerenes discussed in the text. (middle) The extracted peak shift of the C = C _T Raman active vibrational mode. (lower) Relative intensity of C = C _{order/disorder} , corresponding to the proportion of planar/twisted polymer chains. The numbers (3, 4, 5...) correspond to the diagrams in Figure 7.18. Stages 1 and 2 happen before the heating/ cooling cycle.	235
Figure 7.16: (upper) in situ Resonant Raman spectra acquired on heating at 10 °C/minute for four PC ₇₀ BM loading ratios (0, 9:1, 1:1, 1:4) discussed in the text. (middle) The extracted peak shift of the C = C _T Raman active vibrational mode. (lower) Relative intensity of C = C _{order/disorder} , corresponding to the proportion of planar/twisted polymer chains.	236
Figure 7.17: The peak shift of the C = C _T Raman active vibrational mode extracted from in situ Resonant Raman spectra acquired on heating at 10 °C/minute for the -C ₁₄ (upper) and -C ₁₆ (lower) PBTTC blends with PC ₇₀ BM.	237
Figure 7.18: The mechanism of heating and cooling an intercalated blend.	239
Figure 7.19: Absorption spectra for pristine and annealed (inset) films of PBTTC blended with (left) PC ₇₀ BM and (right) ICBA, normalized to the main polymer absorption band.	240
Figure 7.20: (upper) in situ Resonant Raman spectra acquired on heating at 10 °C/minute for PBTTC-C ₁₆ blends with ICBA discussed in the text. (middle) The extracted peak shift of the C = C _T Raman active vibrational mode. (lower) Relative intensity of C = C _{order/disorder} , corresponding to the proportion of planar/twisted polymer chains.	241
Figure 7.21: AFM images of the (upper) as-prepared spin-coated PBTTC:PC ₇₀ BM blend films at the loading ratios described above. (b) Topography of the blend films after annealing to 270 °C and slow cooling to room temperature. These images were acquired with Minwon Suh at Imperial College London.	243
Figure 7.22: AFM images of the (upper) spin-coated PBTTC:ICBA blend films at the loading ratios 0 – 60 % after annealing to 270 °C and slow cooling to room temperature. These images were acquired with Oliver Holmes at Imperial College London.	244
Figure 7.23: Cyclic voltammograms for neat, intercalated and non-intercalated PBTTC. For the neat material, the resonant Raman spectrum is plotted at each of the potentials indicated (pre, black solid, post, red dotted and after reduction, blue dashed). The Raman spectra are normalised to the 915 cm ⁻¹ Raman active mode.	245
Figure 7.24: Molecular structures of PBTTC-C ₁₆ and F-PBTTC-C ₁₆ , synthesised by Pierre Boufflet in the Department of Chemistry. ^[12]	245
Figure 7.25: UV-Visible Absorption and associated isosurfaces simulated using TD-DFT with the CAM-B3LYP functional and 6-31 G(d,p) basis set. 9 states were considered.	246
Figure 7.26: Experimental Raman spectra of PBTTC (black) and F-PBTTC (red) normalized to their maximum intensity and corresponding DFT simulation (blue dashed) using the B3LYP functional and 6-311 G(d,p) basis-set. The geometry is optimised for an oligomer of at least three repeat units. The table and figure details the bond-lengths and dihedral angles resulting from the geometry optimization for both PBTTC and F-PBTTC.	247
Figure 7.27: Resonant Raman spectra acquired during hold at 0 V (left) and potential application (right) for thin films of (a, b) neat, (c, d) non-intercalated blends with bisPC ₆₀ BM and (e,f) intercalated blends with PC ₇₀ BM. The spectra are normalized to the 915 cm ⁻¹ of the electrolyte solution.	248
Figure 7.28: Maximum peak shift of the C – C and C = C modes as a function of polaron concentration for neat (black), intercalated (blue) and non-intercalated blends (red) extracted from Figure 7.27.	250

List of Tables

Table 2.1 Electrical characteristics of OFETs:	32
Table 2.2: Photovoltaic device parameters.	40
Table 3.1: Non-resonant Raman active vibrational modes of P3HT and their observed nature from DFT simulations and literature.	61
Table 3.2: Excitation wavelengths used in this work.	63
Table 4.1: The unit cell parameters of TIPS- and TES- pentacene used in this study from the work of Ostroverkhova et al. ^[5] This table is reproduced from our published work. ^[1]	82
Table 4.2: Peak positions of the vibronic replicas of various electronic transition dipoles (indicated) for dilute TIPS-pentacene solutions.	85
Table 4.3: Summary of TIPS-, TES- and unsubstituted pentacene vibrational modes in wavenumbers (cm^{-1}) calculated using DFT and non-resonant Raman spectra of thin-films. Calculated wavenumbers have been scaled by 0.96.	86
Table 4.4: Transfer characteristics parameters for TIPS- and TES-pentacene devices, extracted from the linear regime ($V_D = -40$ V) of the drain current- gate voltage curves (Figure 4.13).	89
Table 4.5: Calculated charge transfer integrals and inner-sphere reorganisation energies between HOMO levels for TIPS- and TES-pentacene. TIPS-pentacene has two high transfer integrals (100, 110) indicating 2-dimensional transport while TES-pentacene has only one relatively high one which implies 1-dimensional transport. These calculations were completed by Florian Steiner at Imperial College London and have been published in our previous work. ^[1]	93
Table 4.6: UV-Visible absorption peaks of TIPS-pentacene in toluene solution and pentacene in a p-terphenyl lattice. All values are quoted in nm.....	103
Table 4.7: Observed Raman frequencies and approximate descriptions for p-terphenyl and pentacene doped p-terphenyl, excited with a 514 nm excitation.	105
Table 4.8: UV-Visible absorption peaks of pentacene and DAP-1 in a p-terphenyl lattice and in a dilute chloroform solution and their spacing in cm^{-1}	109
Table 4.9: Summary of positions of Q- and B-band absorption maxima in solution and thin films of ZnPc, TPc and TzPc extracted from the absorption spectra in Figure 4.31.	118
Table 4.10: Calculated bond lengths ($\text{\AA}$) of the ZnPc, TzPc and TPc molecules.	121
Table 5.1: Simulated and observed Raman frequencies and an approximate description.	140
Table 5.2: Peak positions in eV of absorption transitions for the samples discussed in text.	148
Table 5.3: Peak positions (cm^{-1}) of Raman active vibrational modes at 457, 633 and 785 nm excitation for isolated pentacene and thin films deposited on untreated Au, TP treated Au and PFBT treated Au, extracted from Figure 5.10.	149
Table 5.4: Resonant excitation (514 nm), peak positions (cm^{-1}) of Raman active vibrational modes on untreated Au, TP treated Au and PFBT treated Au.	149
Table 5.5: Intensities of B_{3g} and A_{1g} modes for incident light parallel to the pentacene long-axis.	153
Table 5.6 Integrated Peak Area $C - C_{\text{SHORT}} / C - C_{\text{LONG}}$ in resonant 514 nm excitation for 60 nm thick pentacene films.	155
Table 5.7: Device characteristics of BG BC transistors.	159
Table 5.8: Selection of intensity ratios that can be used as polymorphic markers for CuPc thin films, extracted from reference ^[93]	164
Table 5.9: Relative peak intensities of I_{1106}/I_{1143} , I_{1305}/I_{1340} , I_{1528}/I_{1452} for 30 and 100 nm thick films of CuPc on SiO_2 and PTCD.	168
Table 5.10: I_{1106}/I_{1143} , I_{1305}/I_{1340} and I_{1528}/I_{1452} extracted from Raman spectra at 633 nm excitation for CuPc on mica, MgO and Fe surfaces at 293 and 77 K.	171
Table 5.11: Raman bands and shifts observed for CuPc on SiO_2 , PTCD, Mica, MgO and Fe. Peak positions in α and β - phase from ref ^[106]	171
Table 6.1: DFT Calculated HOMO-LUMO energies and band gaps for thin films of P3HT, PTTz and PTTz. HOMO levels calculated by CV (from reference ^[2]) and optical band gaps (extracted from onset of absorption) are shown for comparison. All values quoted are in eV.....	191
Table 6.2: Bond lengths ($\text{\AA}$) and dihedral angles ($^\circ$) from DFT simulations at 6-31G(d,p) basis set.....	192
Table 6.3: $C = C$ max peak shift, FWHM and $C = C/C - C$ during potential application and when the film is held at 0 V. The polaron density is calculated from integration of the current vs. time and are also provided for reference.	200
Table 6.4: Peak position, FWHM and I_{1447}/I_{1464} collected at 785, 633, 514 and 488 nm for pristine and degraded films. Δ indicates the percentage change of the ratio after electrochemical degradation.	204
Table 6.5: Relative peak intensity ratios (integrated) for the main vibrational modes of pristine and degraded P3HT, PTTz and PTTz films extracted from Lorentzian fits to Raman spectra measured with 488 nm excitation (Figure 6). Δ indicates the percentage change of the ratio after electrochemical degradation.	206

Table 6.6: Absorption band maxima and C = C peak position as a function of time after quench for thin films of P3EHT. The FWHM of the C = C mode and relative fractions of order and disorder also included.	211
Table 7.1: Lamellar Spacing ($\text{\AA}$)*, Absorption band maximum (nm), C = C shift (cm^{-1}) and relative increase in planarity for PBTTT blends with respect to the neat material. Lamellar Spacing (*) from ref ^[13]	226
Table 7.2: Absorption band maximum (nm), integrated PL, C = C shift (cm^{-1}) and relative increase in planarity for PBTTT blends with respect to the neat material.	230
Table 7.3: Surface roughness (r_q) for PBTTT: PC ₇₀ BM blends pre and post-annealing extracted from AFM images of the film surface.	244
Table 7.4: C = C peak position as a function of polaron density for neat PBTTT and 1:1 blends with bis PC ₆₀ BM and PC ₇₀ BM.	249

Frequently Used Abbreviations

Abbreviation	Full Description
2D	Two Dimensional
3D	Three Dimensional
AFM	Atomic Force Microscopy
AMM	Amplitude Mode Model
BG BC	Bottom Gate Bottom Contact
bis-PC₆₀BM	Bis-[6,6]-Phenyl C61 Butyric Acid Methyl Ester
BT	Benzothiadiazole
C – C	Carbon – Carbon Single Bond
C = C	Carbon = Carbon Single Bond
CAM	Coulomb Attenuated Method
CT	Charge Transfer State
CuPc	Copper Phthalocyanine
CV	Cyclic Voltammetry
CW	Continuous Wave
DAP	Diazopentacene
DFT	Density Functional Theory
DSC	Differential Scanning Calorimetry
ECCM	Effective Conjugation Coordinate Model
F8	Poly(9,9- Dioctylfluorene)
FET	Field-Effect Transistors
FM	Ferromagnetic Layers
FWHM	Full Width Half Maximum
GIXD	Grazing-Interface X-Ray Diffraction
HMDS	Hexamethyldisilazane
HOMO	Highest Occupied Molecular Orbitals
ICBA	Indene-C60 Bisadduct
ICTA	Indene-C60 Triadduct
IPA	Isopropylalcohol
ITO	Indium Tin Oxide
LCAO	Linear Combination Of Atomic Orbitals
LUMO	Lowest Unoccupied Molecular Orbitals
MASER	Microwave Amplification By Stimulated Emission Of Radiation
MR	Magnetoresistance
MTJ	Magnetic Tunnelling Junctions
NEXAFS	Near-Edge X-Ray Absorption Fine Structure
OFET	Organic Field Effect Transistor
OPV	Organic Photovoltaic
P3EHT	Poly(3-Ethylhexylthiophene)
P3HT	Poly(3-Hexylthiophene)
Pc	Phthalocyanine
PC₇₀BM	[6,6]-Phenyl-C-71-Butyric Acid Methyl Ester
PCE	Power Conversion Efficiency
PFBT	Pentfluorobenzene Thiol
PL	Photoluminescence
PTTz	2:1 Thiophene Thiazole Co Polymer
PTTz	1:1 Thiophene Thiazole Co Polymer
rpm	Revolutions Per Minute
RR	Regio-Regular
RRa	Regio-Random

SAMs	Self-Assembled Monolayers
T	Thiophene
TAS	Transient Absorption Spectroscopy
TCPS	Trichlorophenylsilane
TD-DFT	Time Dependent Density Functional Theory
TES	6,13-Bis(Triethylsilylethynyl)Pentacene
TIPS	6,13-Bis(Triisopropylsilylethynyl)Pentacene
TMR	Tunneling Magnetoresistance
TPc	Thiophene Phthalocyanine
T_{sol}	Solution Temperature
T_{subs}	Substrate Temperature
TT	Thieno[3,2-B]Thiophene
Tz	Thiazole
TZnPc	Thiophene Zinc Phthalocyanine
UV-Vis	Uv-Visible
ZnPc	Zinc Phthalocyanine

1 Introduction

Motivation

The field of organic electronics has a lot to offer the modern world, ranging from low-cost, clean energy, to roll-up large-area lighting and flexible displays. Whilst inorganic technologies continue to dominate the field of micro-electronics, academic and industrial efforts have provided exciting alternatives for the charge-transporting layer in the form of 'organic semiconductors'. Compared to inorganic semiconductors, organic semiconductors offer numerous advantages, including their solubility in common organic solvents, cheap production costs and flexibility of chemical design. Semiconducting organic inks can be deposited onto large-area flexible substrates using conventional printing techniques in ambient conditions. Early research of high-performance electroluminescent materials has led to the first commercial products incorporating organic light emitting diodes.^[1–3] Very recently, small molecule Organic Field Effect Transistors (OFETs) have achieved hole mobilities of $19.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and electron mobilities of $12.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in air, and organic photovoltaic (OPV) efficiency has exceeded 12 %.^[4–6] Despite immense promise, commercial organic solar cells and transistors have yet to be realised.

Organic transistors and solar cells trail conventional inorganic devices in practical applications due to poor device performance and operational stability.^[7–10] The aim of this thesis is to better understand the relationships between molecular packing, conjugated polymer molecular order and both the device performance and operational stability.

Aims

A general review of organic semiconductors and their optoelectronic properties are described in Chapter 2. Here, the operational principles of OFETs and OPV are discussed. There is a review of current literature regarding the relationships between thin film morphology (< 100 nm), device performance and stability. We introduce the main characterisation techniques important for this work.

Chapter 3 details the experimental techniques used throughout this thesis to control and characterise the thin film morphology.

Chapter 4 identifies the principal solution-processing parameters for control of thin film morphology using the zone-casting technique; making use of intermolecular interactions, controlled solvent evaporation and substrate

temperature to control the molecular packing of the thin films. For thin films of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) and 6,13-bis(triethylsilylethynyl)pentacene (TES-pentacene) the relationship between molecular packing and charge transport mobility is evaluated, showing a simple approach to improving device performance. We develop techniques to characterise molecular packing across a device, from electrode to the active channel, which are applied to a number of OFET configurations. We attribute the improvement of device performance and increase in charge transport anisotropy to the formation of ordered, uniaxially aligned domains. We compare the optoelectronic properties of the TIPS- and TES-pentacene thin films, where intermolecular interactions determine both charge transport and molecular packing, to isolated pentacene molecules dispersed in a *p*-terphenyl matrix for Microwave Amplification by Stimulated Emission of Radiation (MASER) applications. Having identified the crucial parameters required to deposit uniaxially aligned thin films, we apply our understanding to a series of soluble phthalocyanines. Zone-casting is established as an appropriate technique for the formation of ordered phthalocyanine domains, with improved thermal stability and control of aggregation.

Chapter 5 explores the impact of the organic-inorganic interface on the molecular packing in vacuum evaporated small molecule thin films. The interfacial molecular packing of the organic small molecules is controlled using a range of self-assembled monolayers and interlayers. The molecular packing is correlated to device performance for both pentacene OFETs and copper phthalocyanine (CuPc) Magnetic Tunnel Junctions (MTJs). Clean, reactive metals are demonstrated to interact with the small molecules, forming an interfacial dipole which dominates the strong intermolecular interactions and governs the molecular packing close to the interface. For pentacene OFETs, uniform molecular packing is achieved with thiol and silane treatment on the electrodes and channel, respectively, which is found to significantly improve charge-transport mobility. In MTJs, an MgO interlayer is identified as an approach to inhibit dipole formation at the interface CuPc/Fe interface, preventing CuPc from lying face-down. The more upright packing is found to be beneficial for the preservation of spin polarised charge transport, revealed by an increase in the magnetoresistance. We evaluate molecular packing as a function of organic layer thickness and relate this to the preservation of spin-polarisation. Finally, we establish the relationship between molecular packing and operating temperature. We find that at 77 K molecular reorganisation forms large CuPc domains with uniform molecular packing, which permits spin-polarised charge to move through the oriented organic layer without being scattered and increases the magnetoresistance.

Chapter 6 studies the impact of chemical structures on the polymer molecular order and stability of polythiophene derivatives for OPV applications. First we consider the incorporation of electronegative nitrogen (thiazole units) on the molecular order and operational electrochemical stability of poly(3-hexyl)thiophene (P3HT). Increasing thiazole content results in reduced inter-unit torsion and a deeper HOMO level, but leaves the polymers more susceptible to degradation during device operation. We identify the spectroscopic signature of quinoidal P3HT and develop a structural probe to detect the formation hole polarons. In an effort to understand the crystallisation mechanism of P3HT, we study the morphological stability of a branched side chain derivative already established to have slow re-crystallisation kinetics. Using a range of characterisation techniques a two-step process is identified, whereby the rearrangement of the flexible side-chains completes before the backbone configuration is optimised.

Chapter 7 is focussed on the polymer molecular order in polymer/fullerene blend films used as the active layer in OPV devices. The polymer molecular order is studied as a function of fullerene size and loading ratio. We consider operational and thermal stability of donor/acceptor blends, correlating phase transitions observed in differential scanning calorimetry (DSC) with polymer molecular packing. The optimum blend ratio and conditions for thermal annealing conditions are identified. Finally, we compare the process of charge injection into the polymer/fullerene blends on the molecular order of the polymer backbone. In an effort to understand our findings, the effect of fluorination on the backbone conformation is examined and used. From this research we propose chemical design rules for high-performance stable copolymer photovoltaic materials.

Chapter 8 summaries the main results of this work and outlines future investigations that could be undertaken.

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2 Review

A general review of organic semiconductors and the development of field-effect transistors and photovoltaic devices based on small molecules and conjugated polymers. We discuss the operational principles behind device operation, and the morphological requirements for efficient performance.

2.1 Organic Semiconductors

Semiconductors, a class of materials with small energy gaps (1 – 2.5 eV) between valence and conduction bands, are the basis of all modern day microelectronics. To date the technological revolution has been dominated by inorganic semiconductors like silicon or germanium, whose high-purity crystals have particularly appropriate energy gaps for light absorption and fast charge transport. Since the detection of electroluminescence in the 1960s, covalently bonded organic semiconductors have attracted interest from researchers around the world.^[1,2]

2.1.1 Conjugated Molecules

There are two main classes of conjugated molecular semiconductors; small molecules with low molecular weights and polymers with high molecular weights. In both cases, the semiconducting properties arise from the conjugated molecular structure, where overlapping p_z orbitals of sp^2 -hybridised carbon (or sometimes sp -hybridised carbon), allow the formation of a delocalised π -electron system alongside the polymer backbone. The relative phases of overlapping adjacent p_z orbitals result in the creation of either π - 'bonding' or π^* 'anti-bonding' orbitals for in-phase and out-of-phase interactions, respectively (Figure 2.1). The anti-bonding orbitals have a higher energy than the bonding orbitals and so in the ground state, only the bonding orbitals are occupied by electrons. The Highest Occupied Molecular Orbital is known as the HOMO and the Lowest Unoccupied Molecular Orbital is the LUMO. Compared to the strong σ -bonds that make up the polymer backbone, the π -bonds are weaker. The gap between the bonding and anti-bonding π -orbitals ($\pi - \pi^*$) is the optical energy gap.

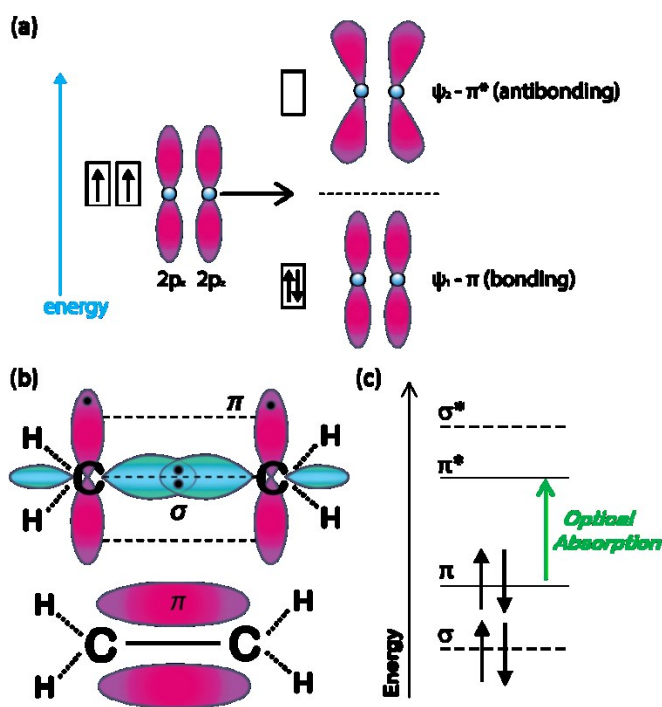


Figure 2.1:(a) Molecular orbital diagrams of high-energy anti-bonding (π^*) and low energy bonding (π) molecular orbitals. The two lobes of the p_z orbital can interact constructively (bonding) or destructively (anti-bonding). When two lobes meet constructively there is increased electron density between the nuclei. (b) σ and π bonds in ethene. Adapted from reference [3] (c) Energy levels of an organic small molecule. The green arrows represent an optical absorption.

2.1.2 Optoelectronic Properties

When light of the appropriate wavelength is absorbed by a molecule an electron is promoted from the π -bonding orbitals to the empty anti-bonding π^* orbitals. The edge of the absorption band therefore corresponds to the gap between the HOMO and LUMO. The size of the optical energy gap ($\Delta E = E_{HOMO} - E_{LUMO}$) is controlled by the extent of π -conjugation, or amount of π -electron delocalisation, often described in terms of the effective conjugation length which may be shorter than the length of chemical conjugation, particularly in disordered polymeric materials. Typically, the size of the HOMO – LUMO energy gap decreases with increasing effective conjugated length.

The intermolecular bonds in organic crystals (van der Waals) are weaker than their covalently bonded inorganic counterparts, which is apparent in their reduced hardness, lower melting point and weaker delocalisation of electron wave functions amongst neighbouring molecules. The reduced delocalisation of electronic wave functions results in particularly interesting optoelectronic properties. In comparison to inorganic semiconductors, where high dielectric constants act to effectively screen charges from one another, organic semiconductors have low dielectric constants. Excitation of an organic semiconductors creates a localised neutral excited state of bound electrons and holes (binding energy 0.5 – 1 eV), called a Frenkel exciton, radius ≈ 10 Å, which can be strongly localised on a single molecule or across adjacent molecules ('Charge-Transfer'). Figure 2.2 illustrates the differences between these two excited states. Optical excitations preserve spin and create singlet excitons, whereas electrical excitation can lead to the formation of singlet or triplet excitons.^[4] The Mott-Wannier type excitons that form in inorganic semiconductors are significantly more delocalised and more weakly bound, with binding energies of < 50 meV and radii ≈ 100 Å.

In organic crystals and isolated molecules, electronic transitions are strongly coupled to molecular vibrations. This accounts for vibronic structure observed in spectroscopic measurements of ordered samples. The spectral broadening and loss of this structure often observed in the optical absorption and luminescence spectra can be used to infer the extent of energetic disorder in the sample.

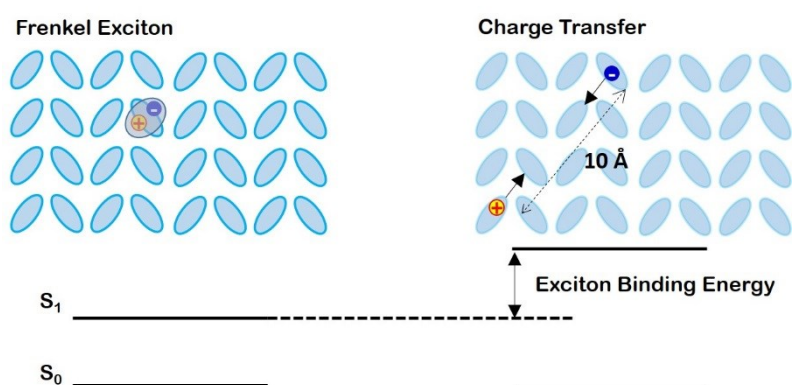


Figure 2.2: Localised Frenkel exciton on one molecule and a pair of charges sitting around 10 Å apart on different molecules.

Adapted from reference ^[3]

Figure 2.3 illustrates the electronic and vibrational transitions within a molecule. Electronic transitions are in the UV or visible region (300 – 700 nm), vibrational in the IR (700 – 1000 nm) and rotational in the far IR ($\approx 10 \text{ cm}^{-1}$).^[5] For small molecules it is sometimes possible to observe vibrational structure within the electronic absorption spectra. The first ‘vertical’ transition ‘0 $\rightarrow$ 0’ corresponds to the energy required to move from the lowest energy vibrational level of the ground state ($n = 0$) to the lowest energy vibrational level of the electronically excited state. The transition is vertical because of the Franck-Condon principle and Born-Oppenheimer approximation. Born-Oppenheimer explains that the mass of the electron is much less than that of the protons or neutrons and as a consequence move much faster- i.e. electronic transitions occur before the nuclei have time to respond. Franck-Condon is simply the application of Born-Oppenheimer to electronic transitions; that is, the most likely electronic transition will occur without any change in nuclear position between the ground and excited electronic states, on a timescale that is effectively instantaneous.^[6] The molecular reorganisation that occurs after a change in electron configuration sets up a molecular vibration.^[6] After 0 $\rightarrow$ 0, the next transition (0 $\rightarrow$ 1) relates to the transition to the first vibrationally excited energy level of the excited electronic state and the subsequent (0 $\rightarrow$ 2) to the second vibrational state.

Even in the case of solution absorption, the peaks are not always sharp and distinct. Inhomogeneous broadening can arise due to intermolecular interactions, temperature and electronic coupling between the organic semiconductor and the solvent. When a sample has a broad distribution of molecular orientations, it absorbs light differently across the various molecular environments. Increasing the temperature of the sample populates higher vibrational levels of the ground state, which can undergo transitions to higher vibrational levels of the first excited electronic state.^[6] The absorption spectra become broad and vibrational fine structure is lost.

An electronically excited molecule has a short excited state lifetime and will return quickly to the ground state, giving out energy in the form of fluorescence (nanoseconds), phosphorescence (milliseconds) or heat. Kasha’s rule explains that excited molecules relax quickly to the lowest vibrational energy level before emitting light- photon emission can only occur from the lowest lying electronically excited singlet states.^[6] At fast time scales, radiative depopulation of the electronic excited states occurs via the spontaneous emission of fluorescence photons that also obeys the Franck-Condon principle.^[6] Application of Kasha’s rule and the Franck-Condon principle mean that vibrational energy is lost during the absorption – re-emission process, so fluorescence always occurs at a lower energy to absorption.^[6]

In most organic semiconductors, the intermolecular coupling (electron-transfer integrals) is much weaker than the electronic-vibrational coupling (reorganisation energy). The magnitude of the molecular coupling determines the Stoke’s shift and reorganisation of molecules after the movement of charge. Moving charges and a ‘hopping model’ is the most appropriate method to describe the movement of charge.^[7] The charge and associated distortion of the surrounding crystal structure is referred to as a polaron. To create a hole polaron an electron is removed from a neutral state, which can move coherently along the conjugated sections of the polymer chain. The hole polaron then hops from the polaronic state on one molecule to one on a nearby molecule. The fields of the moving charges polarise the surrounding molecules, and stabilise the charged states of organic semiconductors. In disordered solids and non-aligned thin films the organic molecules are arranged in different environments with significant variations in molecular

orientations and intermolecular distances, which leads to a Gaussian density of states for the distribution of sites where charge transport can take place.^[4] The stabilisation of the ionic states leads to an optical band gap smaller than that of an isolated molecule (Figure 2.3).^[3] Even in highly purified molecular crystals, the weak electronic delocalisation leads to a small bandwidth and thus minimal band transport even at low temperatures, with molecular crystals achieving mobilities up to $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The intrinsic charge-transport rates for holes and electrons rely upon:

Inner Reorganisation Energy: Change in energy due to geometric relaxation of the molecule. The majority of the inner reorganisation energy arises due to the energetic change of adding/ removing charge on a single molecule as these dominate electronic and nuclear polarisation/relaxation of surroundings.

External Reorganisation Energy: Change in energy due to polarisation of the surrounding medium. The electronic coupling is highly sensitive to the relative positions of adjacent molecules and the intermolecular orientations.

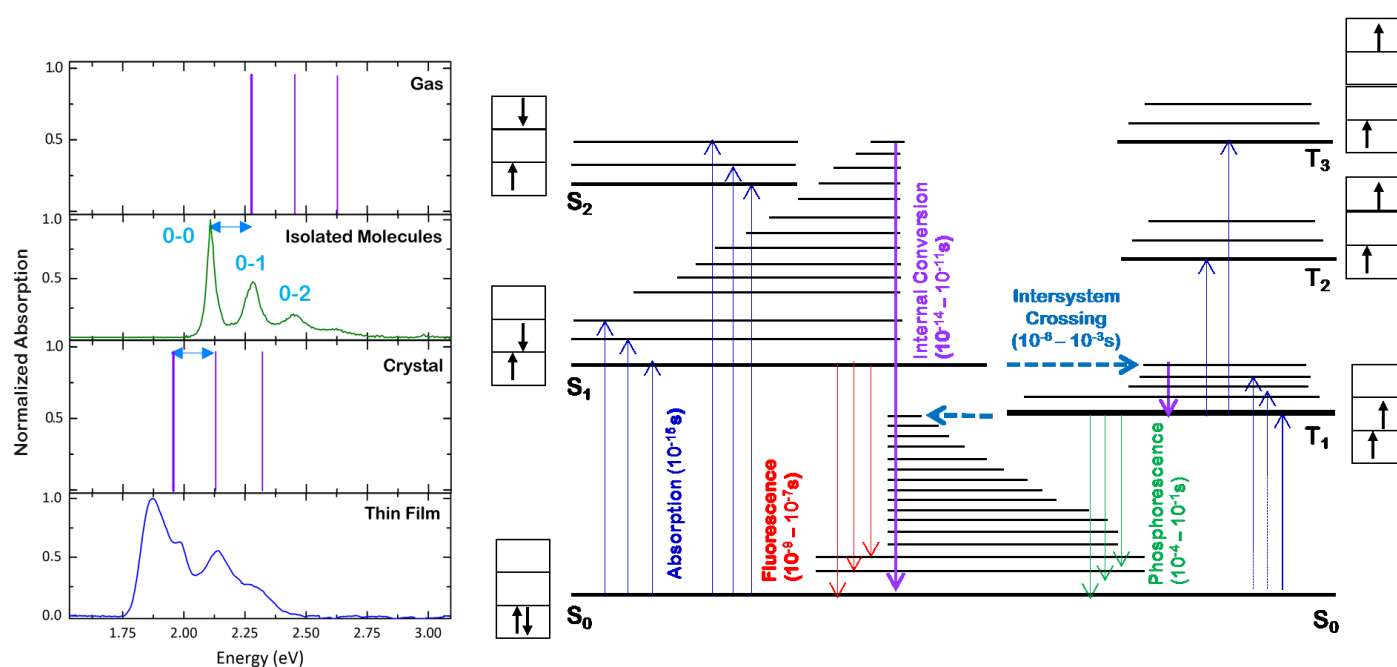


Figure 2.3: A schematic representation of optical absorption spectra for pentacene molecules in different environments. Vibronic replicas are indicated. The blue arrows from crystal to isolated molecules represent the solvent shift. The right hand side illustrates radiative and non-radiative decay processes in a polyatomic molecule that obeys Kasha's rule. The positions of the electrons are included. Absorption from the ground state (S_0) leaves the molecule in an excited singlet state (S_1 , S_2). Adapted from reference ^[5]

2.1.3 H- and J- aggregation

In organic molecular assemblies the coupling of electronic excitations to intramolecular vibrations results in polaronic states surrounded by a field of vibrational distortion.^[8] This vibronic coupling acts to increase the effective mass of a polaron, which, in combination with the multiple defect sites within a molecular crystal, acts to localise the

exciton even further.^[8] The extent of coupling is highly dependent on the morphology and defines the photophysics as described by Kasha *et al.*^[8–10]

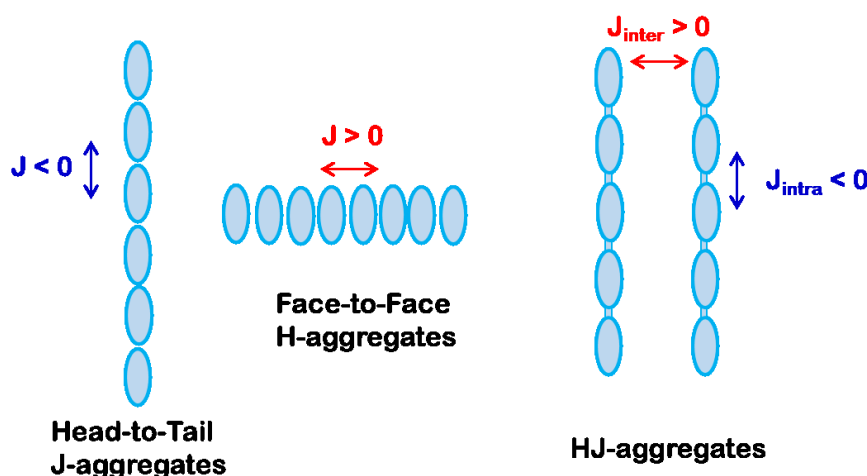


Figure 2.4: Molecular orientations within J- and H-aggregates. The sign of the excitonic coupling constant ' J_0 ' is > 0 in H-aggregates, < 0 in J-aggregates. Polymer HJ-aggregates contain both $J_0 > 0$ between chains and $J_0 < 0$ within chains. This figure is adapted from reference ^[8].

Compared to isolated molecules, the electronic interactions between neighbouring molecules in H-aggregates (or J-) induce relatively delocalised excitons, which cause a blue-shift (red-) of the main absorption peak and an suppression (enhancement) of the excited state decay (Figure 2.4).^[8,11] In H-aggregates, the neighbouring molecules are oriented side-by-side. This causes a positive coupling of excitons ($J_0 > 0$) and places an optically active *crystal wave vector* ($k = 0$) exciton at the top of the exciton band.^[8] After absorption, H-aggregates rapidly relax to the lowest energy $k = \pi$ exciton, which cannot radiatively couple to the ground state and forbids 0-0 emission.^[8] On the other hand, J-aggregates have a negative coupling, the $k = 0$ exciton is at the bottom of the band and the 0-0 emission is allowed.

2.2 Organic Field Effect Transistors

Since their inception in the 20th century, Field-Effect Transistors (FETs) have become one of the most abundant electronic components in modern-day society, with there being an estimated 400×10^6 for every single person on earth.^[12,13] An FET is a three-terminal device, which acts as either a signal amplifier or electronic switch. The active layer in an FET is a semiconducting material whose conductivity changes on application of an electric field. Current then flows through the semiconducting layer, from a 'source' to a 'drain' electrode, under an imposed bias.

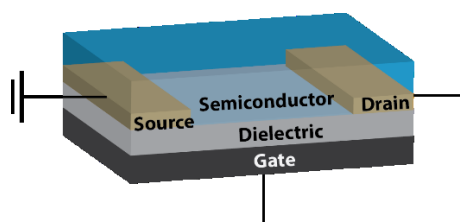


Figure 2.5: Typical OFET architecture.

In an organic field effect transistor (OFET), the gate electrode (typically Si) is insulated from the active channel by an insulating material (the 'dielectric'), shown in Figure 2.5.^[14] The source – drain distance is the channel length (L) and source or drain width the channel width (W). The insulating dielectric material thickness (d) is much less than the channel length. The ease of charge injection and conductivity along the organic semiconductor-dielectric interface is dependent on the location of the electrodes (either top- or bottom-contact) and overall device architecture (Figure 2.6).^[15] Contact resistance arises due to the high electron-density at the metal surface, which forms an interfacial dipole at the metal-organic interface and presents an energetic barrier to charge injection. Top-contact devices require patterning of electrodes on top of the sensitive organic layer, but can result in lower contact resistances.^[16,17]

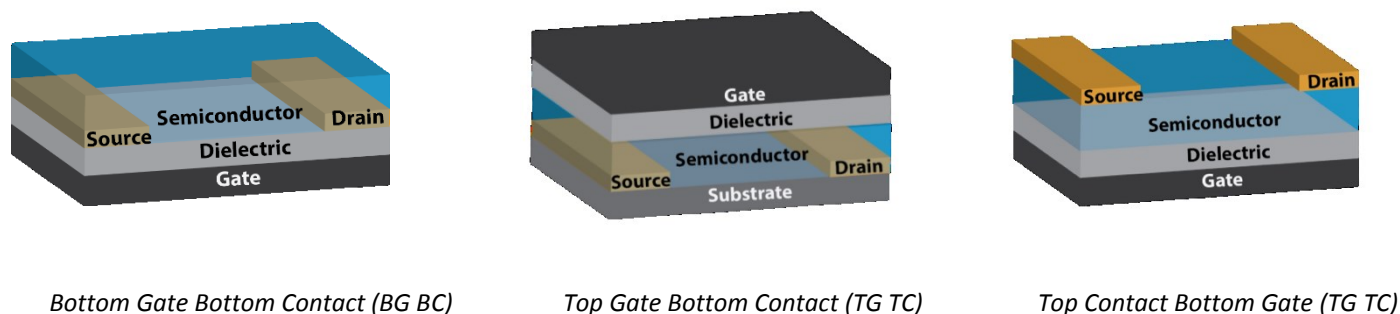


Figure 2.6: Common OFET Device Architectures.

2.2.1 Operating Principles

Most organic semiconductors are 'p-type', where the application of a negative gate voltage forms an accumulation layer of positive charge-carriers (holes).^[18] The lack of many ambipolar or n-type organic materials could be due to charge trapping and impurities causing low electron mobilities. Depending on the sign of the applied gate voltage (V_G), the electrodes may act as source or drain and so the same material must be used for both.^[18] The OFET is essentially a capacitor and can be understood as an inorganic FET operating in accumulation mode (Figure 2.7), where application of a voltage to the gate results in equal charges of opposite polarity accumulating on either side of the dielectric material. The band bending which takes place on contact with a metal is discussed below (Figure 2.10).

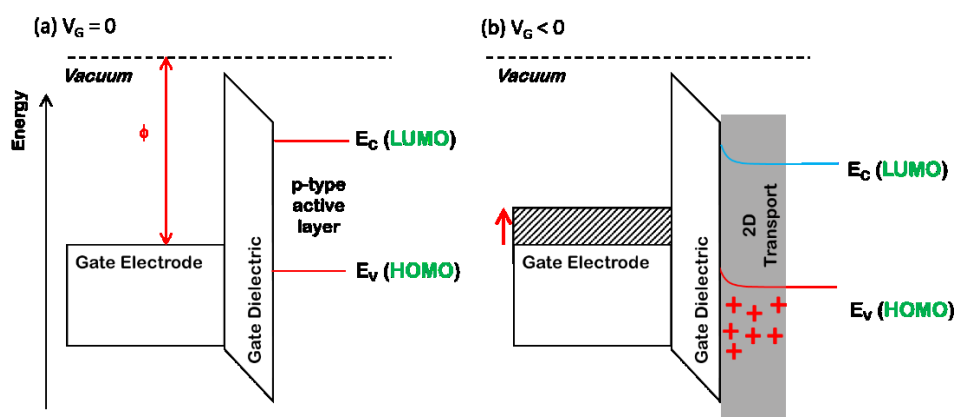


Figure 2.7: Band diagram of metal-insulator-(p-type) semiconductor interface at (a) $V_G = 0$, flat band, and (b) $V_G < 0$, accumulation mode. The metal work function (ϕ) and molecular HOMO and LUMO are indicated. Adapted from reference ^[19]

On application of a positive voltage to the gate ($V_G > 0$), negative charges are created in the organic semiconductor at the source electrode. For the purposes of this description the source electrode is held at ground ($V_S = 0$ V). The Fermi Level of Gold ($E_{F, Au} \approx 5.1$ eV), a common electrode material, is quite far from the LUMO level of most conjugated p-type materials and only a small 'leakage' electron current can flow.

On the other hand, a negative $V_G (< 0)$ results in a low barrier to hole injection into the organic layer. This is illustrated in Figure 2.7 (b). The valence band of the organic semiconductor bends closer to the metal E_F , which induces holes at the semiconductor/dielectric interface.^[19] V_G is increased until charge-traps within the organic layer are full. The accumulation region near the drain electrodes becomes increasingly narrow as the potential difference between the gate and drain ($V_G \rightarrow V_D$) decreases. Charges are confined within this conductive channel close to the interface, and the movement from source to drain results in two-dimensional (2D) charge transport.

When $V_G = V_{Th}$, the threshold voltage of the device and the charge density within the active channel is uniform. The conductance of the organic layer is proportional to the charge density and therefore proportional to the applied V_G . Application of a second voltage to the drain electrode (V_D) causes the charge-carriers to be driven from source to drain, generating a current (I_{SD}). The movement of charges at fixed V_G as a function of V_D are displayed in Figure 2.8 and can be summarised as follows:

1. **Linear:** When $V_D < V_G - V_{Th}$: I_{SD} obeys Ohm's Law: $I_{SD} \propto V_G$ and V_D
As $V_D \rightarrow V_G$, the potential difference between the drain and gate decreases
2. **Pinch-Off:** When $V_D = V_G - V_{Th}$: the accumulation layer of generated charges is 'pinched off'. The gradient of $\frac{\partial I_{SD}}{\partial V_D} = 0$ (Figure 2.9 (a)).
3. **Saturation:** When $V_D > V_G - V_{Th}$: the accumulation region does not change shape and so I_{SD} becomes independent of V_D .

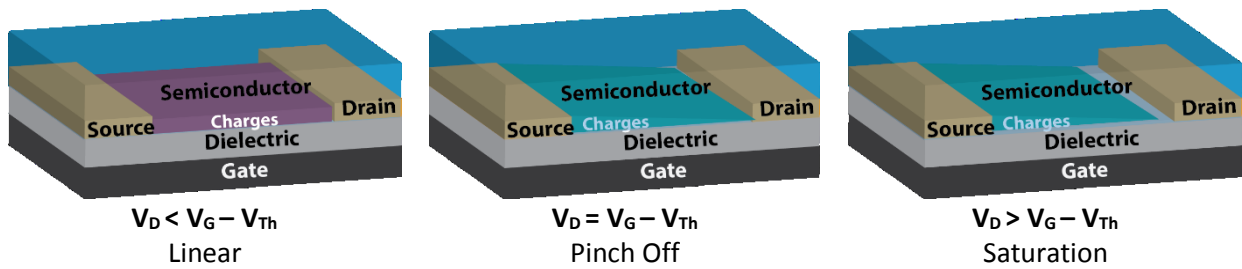


Figure 2.8: Operating Principles of OFETs.

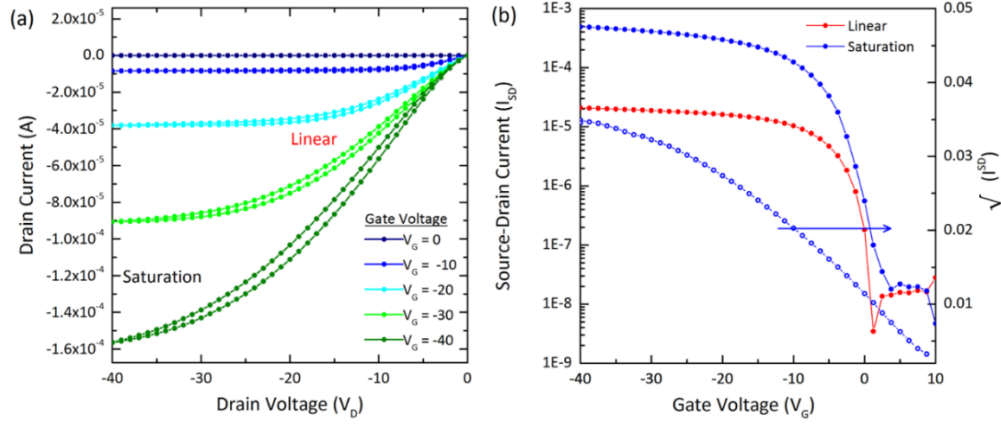


Figure 2.9: (a) Output and (b) transfer characteristics in the linear ($V_D = -10V$) and saturation ($V_D = -40V$) for a solution processed TIPS pentacene OFET characterised in air.

2.2.2 Device Characterisation

The utility of OFETs as switches in modern day circuitry is determined by their ‘switching speed’, which depends of the ease of charge movement through a device under the influence of an electric field.^[20] The ratio of current in the ‘on’ and ‘off’ states (I_{ON}/I_{OFF}) is a measure of the switching performance.^[20]

The capacitance of the dielectric (C_i) determines the charge accumulation at the semiconductor-dielectric interface:

$$C_i = \frac{\epsilon_0 \epsilon_r}{d} \quad \text{Equation 2.1}$$

Here, ϵ_0 is the permittivity of free-space, ϵ_r the relative permittivity of the dielectric and d the dielectric thickness.

In the gradual channel approximation, where the electric field along the channel is much lower than across it (i.e. $L \gg d$), we define the linear (μ_{Lin}) and saturation mobility (μ_{Sat}), along with the threshold voltage (V_{Th}) and On/Off (I_{ON}/I_{OFF}) Ratio:

Table 2.1 Electrical characteristics of OFETs:

Parameters			
Linear	$I_{SD} = \frac{W}{L} \mu_{Lin} C_i (V_G - V_{Th}) V_D$	$\mu_{Lin} = \left. \frac{\partial I_{SD}}{\partial V_G} \right _{V_D=const} \frac{L}{W V_D C_i}$	Equation 2.2
Saturation	$I_{SD} = \frac{W}{L} \mu_{Sat} C_i (V_G - V_{Th})^2$	$\mu_{Sat} = \left(\left. \frac{\partial I_{SD}}{\partial V_G} \right _{V_D=const} \right)^2 \frac{2L}{W C_i}$	Equation 2.3
V_{Th}	Threshold Voltage	– Voltage at which trap states in active layer are populated and free carrier density can form (Q_{trap}/C_i) – Charges can move through delocalised molecular orbitals under influence of V_D. - Intercept of $\sqrt{I_{SD}}$ vs. V_G	
I_{ON}/I_{OFF}	On/Off Ratio	– Ratio of maximum ‘on’ and ‘off’ current – Switching Performance	

The electrical characteristics described above (Table 2.1) are typically extracted from ‘transfer curves’ ((Figure 2.9 (b)), which are generated from the measurement of I_{SD} vs. V_G .

2.2.3 Factors limiting device performance

For small conjugated organic molecules similar to those considered in this thesis, it has been demonstrated that charge transport occurs in the first few monolayers above the dielectric interface.^[21–29] Particular emphasis has been placed on achieving high charge carrier mobilities with a high degree of molecular alignment. Our studies will focus on the interaction between the organic layer and the dielectric, contact electrodes and adjacent organic layers.

2.2.3.1 Organic- Dielectric Interface

Organic molecules can interact with the dielectric, which results in variation in the relative orientation of molecular units.^[30] Non-zero threshold voltages (V_{Th}) can be caused by built-in charge in the organic semiconducting layer, the presence of external impurities or formation of undesirable interfacial states. Hysteresis, the shift of current-voltage curves depending on the direction of the voltage sweep, is attributed to mobile charges within the dielectric forming moving dipoles within the organic layer.^[31] The deposition of the dielectric can result in interfacial roughness between the organic and dielectric, restricting the formation of extended crystalline domains and forming valleys within the channel region which act as charge traps.^[30] Several studies have considered the use of self-assembled monolayers (SAMs) to treat the surface of the dielectric layer resulting in significant performance improvements.^{[30,32–34][35,36]}

2.2.3.2 Organic- Contact Interface

To generate high I_{SD} there must be negligible voltage drop across the contacts- the so-called ‘ohmic’ injection of charges.^[37,38] The organic molecules can interact with the metal contact; either forming chemical bonds (chemisorption) or by modifying the surface dipole (physisorption).^[37,39] The π -electron system of organic molecules push the electron system of the metal close to the metal surface (Figure 2.10 (b)), which decrease the metal work function. Chemisorption refers to the metal-hybridisation of molecular orbitals that occurs when organic molecules interact with metal surfaces, which shifts and broadens the energy levels of the organic molecule and creates an induced density of interfacial states (Figure 2.10 (c)). The broadening of energy levels that occurs on metal hybridisation means that the charge neutrality of this induced density of states may not coincide with the mid-gap. The charge transfer at the interface is determined by the position of this charge neutrality level with respect to the Fermi level of the metal.^[37] SAM treatment of metals with thiol anchoring groups can result in the formation of strong metal/organic covalent bonds which can generate additional dipoles and further enhance charge injection.^[38]

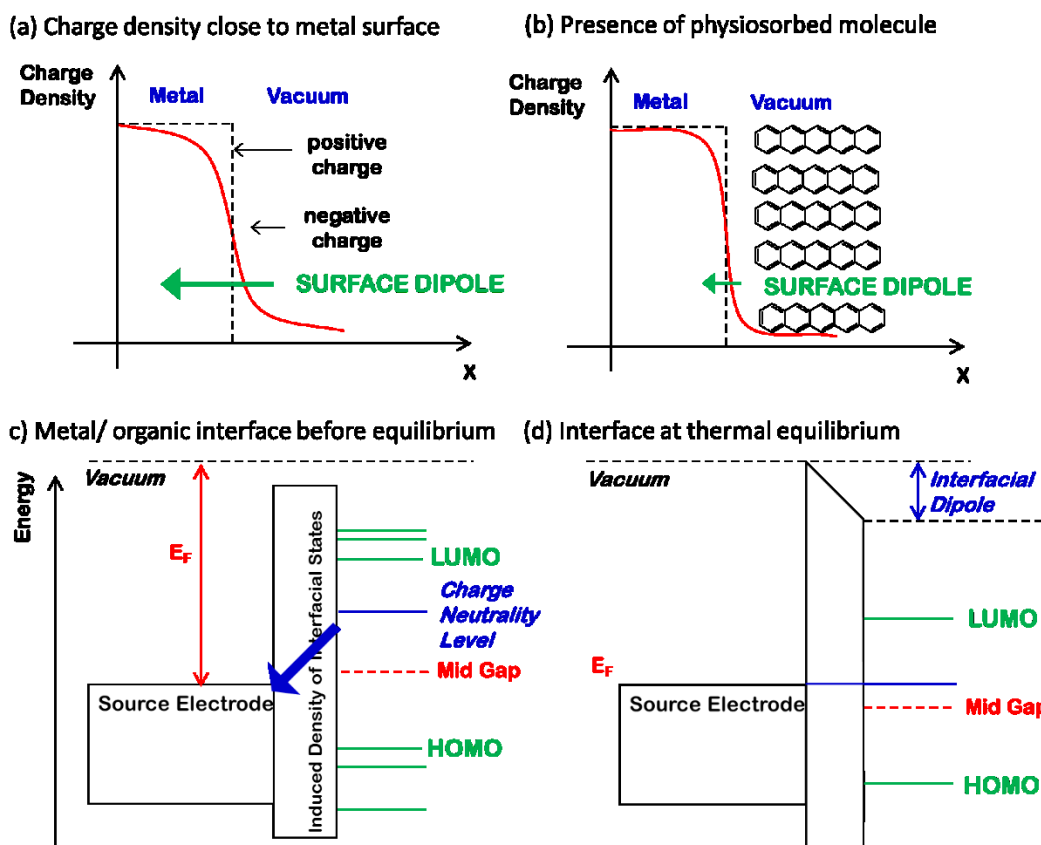


Figure 2.10: (a) PHYSIORPTION Charge density close to the metal surface before organic molecules are deposited. (b) Metal electron states are pushed back due to physisorption reducing the surface dipole (c) CHEMISORPTION Interfacial density of states forms at metal/ organic interface. Within induced states, charge neutrality level $\neq$ mid-gap. (d) Charge transfer takes place from the organic material to the metal generating an interfacial dipole. Adapted from references^[37,39]

2.2.3.3 Thickness of Organic Layer

The solid-state interactions of conjugated small molecules such as pentacene cause them to pack together with their conjugated cores facing one another, in a layered stack. Molecules that are within the same layer are much closer to each other than those in adjacent layers, and as a result charge-transport is more effective *along* the layers rather than *across* them.^[34] In theory, increasing the thickness of the organic layer at the same gate voltage should increase the number of injected carriers and reduce the number of induced charge carriers as the electric field strength decreases, but in practise increased thicknesses result in molecular packing that is difficult to control. As a result, the charge-carrier mobility and contact resistance are highly dependent on the film thickness.^[40–42] The impact of molecular domain size and boundaries between grains on device performance is well documented.

2.2.4 Anisotropy

Organic molecular crystals often display directionally dependent material properties, referred to as 'anisotropy'. The shapes of organic crystals are dictated by their intermolecular interactions. One widely studied family of anisotropic molecules is the linear polyacenes, where interactions between adjacent functionalising side groups has been used to determine the solid-state arrangement. With regards to molecular packing within a molecular crystal or

thin film, a disordered arrangement is described as isotropic structure, whereas an ordered packing is anisotropic. This work will consider the optical, vibrational and charge transport anisotropy:

2.2.4.1 Optical Anisotropy

Anisotropy of the optical absorption is observed in samples where molecules adopt an anisotropic packing motif and have a uniform arrangement of electronic dipoles. The orientation of linearly polarised light can be used to extract the dichroic ratio of a uniaxially aligned chromophore. The Dichroic Ratio, D_R , can be simply calculated from:

$$D_R = \frac{A_{Parallel}}{A_{Perpendicular}} \quad \text{Equation 2.4}$$

Where $A_{Parallel}$ and $A_{perpendicular}$ are the absorption when the polarisation is parallel and perpendicular to the chromophore.

2.2.4.2 Vibrational Anisotropy

Raman anisotropy refers to the anisotropic scattering of vibrational modes. Raman anisotropy is measured by considering the Raman scattering as a function of the excitation laser polarisation:^[43,44] In our set-up the excitation is polarised parallel to the z-axis and directed at a sample in the x, y plane. The scattered light from the molecular plane is symmetric with respect to the z-axis, which explains the factor of '2' in the denominator.

$$A_{Raman} = \frac{I_{PLL} - I_{PRP}}{I_{PLL} + 2I_{PRP}} \quad \text{Equation 2.5}$$

Where I_{PLL} and I_{PRP} are the parallel and perpendicular polarisations.

2.2.4.3 Charge Transport Anisotropy

The anisotropic packing motifs and the associated π -orbital overlap within organic semiconductor crystals results in anisotropic charge transport. The transistor devices made in this work are all bottom-gate, bottom-contact, allowing direct observation of the anisotropic charge transport by arranging organic molecular crystals parallel and perpendicular to the charge transport direction. The anisotropy of field-effect mobility (A_μ) depends on intrinsic structural anisotropy, the orientation and density of grain boundaries, the distribution and density of defects and the interaction potentials (organic – metal interactions). A_μ is calculated using:

$$A_\mu = \frac{\mu_{Parallel}}{\mu_{Perpendicular}} \quad \text{Equation 2.6}$$

2.3 Organic Solar Cells

In a photovoltaic devices, light of a higher energy than the band gap of a semiconducting material is absorbed, allowing electrons to access the conduction band and leave behind a positively charged hole. The electron-hole pair is subsequently spatially separated by an electric field, and the charge carriers are guided into an external circuit. In *organic* photovoltaic devices, photon absorption forms a spatially-localised exciton that must be split into electron and hole polarons. This is achieved by blending the active organic absorber with an electron accepting material, such as a fullerene. Research in organic polymer solar cells dates back to the 1990s, and there are now certified efficiencies

of over 12 %.^[45] The first successful operation of an OPV device combined two organic layers, a 'donor' and an 'acceptor', where one had a stronger affinity for electrons.^[46] Despite the progress, commercially available OPV is yet to become a reality, and considerable work must be done to understand the implications of nanostructure on the operation of organic solar cells.

2.3.1 Operating Principles

Successful operation of OPV devices comprises of several stages which are illustrated Figure 2.11, each of which are discussed briefly below.

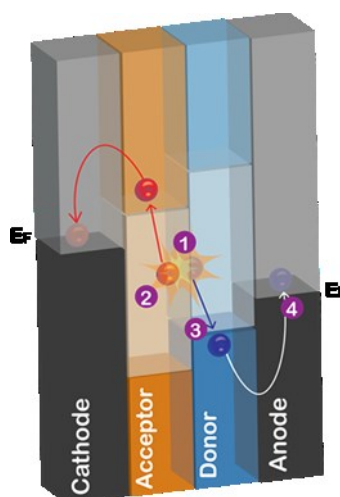


Figure 2.11: Stages of OPV operation: exciton formation and diffusion, exciton dissociation, charge transport and charge collection.

2.3.1.1 Exciton Formation

In order to produce promote electrons in the organic semiconductor, the incident radiation must exceed the energy gap and light harvesting must be as efficient as possible. To avoid energetic losses through internal conversion and vibrational relaxation, the absorption range must be optimised.^[9] Optical absorption is determined by the polymer energy gap, and numerous efforts have been made to extend the absorption range of OPV materials:^[47,48]

Morphology

Chemical structure and device fabrication conditions can be tuned to extend the delocalisation of π -electrons through the conjugated units. Planarisation of the polymer backbone can be achieved synthetically through use of bridging atoms, control of molecular weight, incorporation of electron-rich units such as thiophene, or reduction of steric hindrance through manipulation of side-chains.^[47,49–52] The planar chains can arrange into ordered π -stacks which reduces the energy gap even further. The choice of solvent, blend composition and post deposition treatments such as thermal annealing can also influence the blend microstructure.^[47] Increasing the active layer thickness also

increases the exciton yield but opposes efficient charge transport meaning that an optimum thickness must be found. The morphology of the donor – acceptor blend system dictates the device performance, illustrated in Figure 2.13.

Energy Level Modification

An increase in electron delocalisation reduces the HOMO – LUMO gap of the organic polymer which can be detrimental for the V_{oc} and PCE.^[53,54] Replacing sulphur with low ionisation potential atoms like selenium atoms stabilises the LUMO energy level whilst maintaining the HOMO energy level.^[55] The popular combination of electron-rich and electron-poor units in the polymer backbone, so-called donor-acceptor copolymers, allows control of the HOMO and LUMO energy levels with carefully chosen push-pull units minimising energy losses.^[56–58] The dominant acceptor materials in OPV blends are fullerenes, but optical absorption in the visible band is weak on account of many absorption transitions being forbidden from the highly symmetric C60 cage and their deep energy level for electron conduction limits V_{oc} .^[48,59]

2.3.1.2 Charge Separation

The low dielectric constant of organic semiconductors makes it unlikely that the strongly bonded photo-generated exciton will dissociate into free charges. Spatial separation of the Coulombically bound electron-hole pair occurs at the interface between donor and acceptor molecules, where electrochemical potential differences can generate a driving force that dissociates the excitons and allows ultrafast electron transfer.^[47] The electron and hole polarons formed after exciton dissociation are often still Coulombically bound and must be dissociated by electric field and are known as geminate pairs (see Figure 2.12).^[60–65] The Coulombically bound electron and hole polaron residing on the donor and acceptor units are referred to as a charge transfer state (CT). The CT states can be beneficial or detrimental for the generation of free carriers, depending on their ability to create free polarons.^[66]

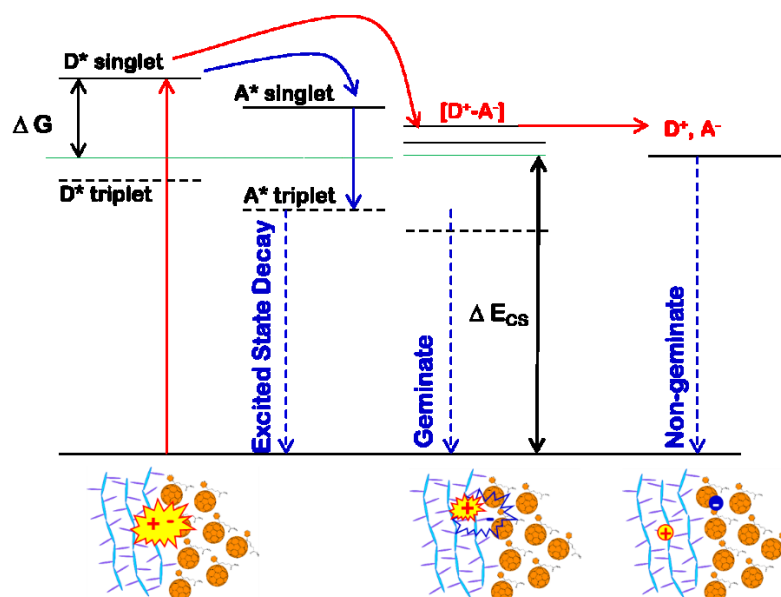


Figure 2.12: The formation of geminate and non-geminately bound polaron pairs during charge generation. Red arrows show the processes responsible for photocurrent generation. Blue arrows show the loss processes. Here, ΔE_{cs} is the energy of the charge separated state and ΔG is the difference in free energy between the excited and charge separated state. This figure is adapted from reference ^[48]

The first promising OPV devices were heterojunctions comprising of two organic layers, shown in Figure 2.13 (a). To utilise all of the excitons, a heterojunction must exist within the distance the exciton can diffuse before decaying ($\approx 3 - 10$ nm).^[67–70] As excitons that are formed further from the interface have a lower probability of being harvested, efforts have been focussed on controlling the nanostructure of this heterojunction. Sandwich-like heterojunctions such as those in Figure 2.13 (a) are only active in a very small volume close to the polymer/fullerene interface. The ‘bulk heterojunction’ has proved the most effective device architecture, where throughout the thickness of the active layer intermixing of donor and acceptor materials happens on a length scale less than the exciton diffusion length (Figure 2.13 (b)).^[71,72]

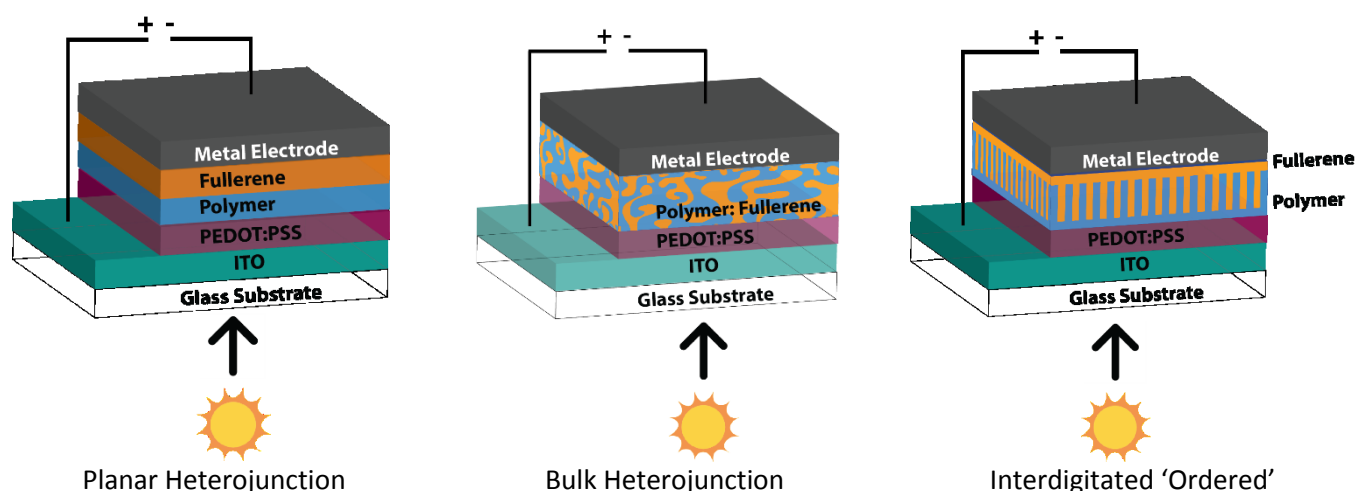


Figure 2.13: Illustration of heterojunctions for OPV devices. The first heterojunction was (a) planar bilayer of donor and acceptor materials. To increase the active volume of the OPV, heterojunctions must exist within an exciton diffusion length such as in an (b) bulk heterojunction or (c) an ordered interdigitated heterojunction.

2.3.1.3 Charge Transport

The presence of energetic disorder and trap states prevent the passage of charges to the electrodes. In ordered materials, charge transport can occur efficiently through the donor and acceptor networks. A number of studies have revealed that the yield of charge generation increases when one of the phases is well ordered, as the charges can delocalise more effectively which reduces the Coloumbic binding energy.^[73–75] The ease of charge movement through the device is characterised by the electron and hole mobilities, μ_e and μ_h [$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$], which must be high enough to overcome the back-transfer rate and balanced to avoid the build-up of one carrier which opposes the built-in field.^[76] Non-geminate or bimolecular recombination refers to the recombination of spatially separated charges (Figure 2.12) and occurs because low μ_e and μ_h mean charges are likely to meet before they reach the electrodes.

The device efficiency is therefore limited by the nanostructure of the network that forms during rapid solvent evaporation, which suffers due to the different phase segregation kinetics of the two components. Isolated large domains that are poorly ordered are effectively dead zones and cannot contribute to the photocurrent.^[77–79] If the domains of one semiconductor connect both sides of the active layer, the OPV can short-circuit, which is known as a shunt.^[72,80] The ideal OPV is described by Figure 2.13 (c) where the two materials form connected, ordered domains

with no shunt connections. The degree of segregation is strongly depend on the chemical structure of the polymer, which can be manipulated to allow fullerene molecules to fit between the side-chains.^[49,81] The impact of this molecular packing is explored in Chapter 6.

2.3.1.4 Charge Extraction

For efficient devices, electrodes must be chosen with sufficiently different work functions to allow formation a built-in electric field that encourages collection of electrons at one electrode and holes at the other.^[82] Crucially in OPV applications one of the electrodes must be transparent to allow light to enter the device. Interfacial layers can be applied to the electrodes to reduce barrier heights ('transport' layers) and reduce unfavourable recombination ('blocking layers').^[80,83–85] In Figure 2.13, PEDOT:PSS is a doped conducting polymer that is used to raise the work function of the bottom electrode (ITO) and encourage it to accept holes.^[48] A metal interlayer with a low work function can be used to lower the work function of the top electrode to aid accept electrons, but this can lead to device degradation.^[82]

2.3.2 Device Characterisation

Once the above criteria are fulfilled, the performance of a solar cell can be extracted from the ‘current density-voltage’ characteristics (Figure 2.14).

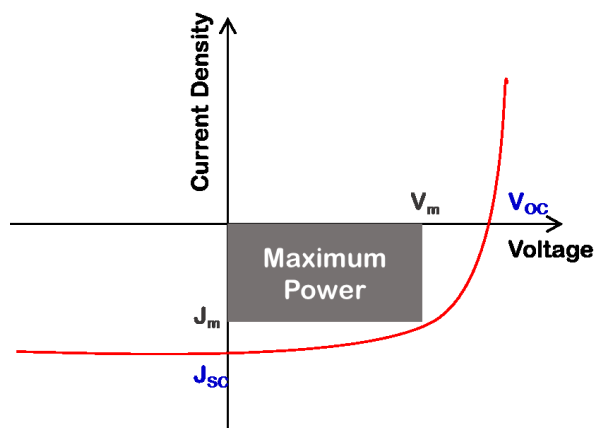


Figure 2.14: Illustration of current density-voltage for an operational solar cell indicating the parameters described in Table 2.2.

Table 2.2: Photovoltaic device parameters.

Quantity	Description
V_{oc} Open-circuit voltage	Voltage when terminals are isolated.
I_{sc} Short-circuit current	Current when terminals are connected in short-circuit
J_{sc} Current Density $J_{sc} = q \int b(E)EQE(E)dE$ Equation 2.7 <i>q</i> = electron charge, <i>b</i> (<i>E</i>) = incident photon flux	Current is proportional to illuminated area
EQE External Quantum Efficiency	The probability of a photon inducing an electron in the external circuit. Depends on: – Efficiency of charge separation – Absorption of donor-acceptor blend – Efficiency of charge collection – Efficiency of charge extraction
P Power Density $P = J_m V_m$	Maximum when $J = J_m$, $V = V_m$
FF Fill Factor $FF = \frac{J_m V_m}{J_{sc} V_{oc}}$ Equation 2.8	The ‘squareness’ of the J-V curve Competition between photocurrent generation and charge recombination
PCE Power Conversion Efficiency $PCE = \frac{J_m V_m}{P_s} = \frac{J_{sc} V_{oc} FF}{P_s}$ Equation 2.9	Power density output as a function of incident power density

2.3.3 Blend Morphology

The most efficient OPV devices come from polymer/fullerene blends, but bulk heterojunctions comprising of blends with other polymers, small molecule, inorganic nanoparticle and metal oxide acceptors have been reported.^[86–88] The role of ‘morphology’ is the topic of ongoing discussion and central to every aspect of OPV operation. The ideal morphology, comprising of both the local molecular order of each component within a blend and global phase separation into traversable networks, is unachievable from most single solution deposition techniques. The polymer

molecular weight, solvent choice, processing conditions and post-deposition conditions are strongly correlated to changes in morphology and charge carrier mobilities.^[47,89–95] A detailed discussion and evaluation of the implications of local-scale molecular order and general OPV morphology can be found elsewhere.^[86,90,96–98] This work primarily addresses the relationship between morphology and charge generation in polymer/fullerene blends. The polymer/fullerene blend is described as combining three morphological phases; pure domains of polymer or fullerene or an intermixed blend of both, where size and purity of phase effects the rate of exciton quenching, generation and charge separation.^[94,99–102] Morphological control is achieved *via* chemical structure of component molecules, with a particular emphasis on those that have a tendency to self-organize into ordered molecular domains.

2.3.4 Device Stability

Chapters 6 and 7 of this thesis is particularly concerned with the impact of polymer conformation on the stability of the OPV devices. Indeed, even the most state-of-the art morphologies suffer during long-term operation.^[103] Organic materials are inherently more susceptible to degradation than inorganic materials.^[104] It is well established that device lifetime is governed by the initial morphology and morphological stability, extent of photo-oxidation or chemical degradation and diffusion of oxygen or water into the OPV device.^[104–109] The interaction with light and oxygen alone can destroy the π -conjugation, which result in chain scissions, crosslinking or modification of the morphology and the catastrophic loss of absorption.^[105,110,111] The morphological benefits achieved by incorporation of additives can even prove detrimental to device lifetimes as they initiate chain oxidation reactions within the polymer backbone.^[108,112–115] The side chains that make polymers soluble increase their vulnerability toward photooxidation, and recent work has focussed on achieving mechanical stability through functionalisation of the polymer or fullerene side-groups.^[111,116,117]

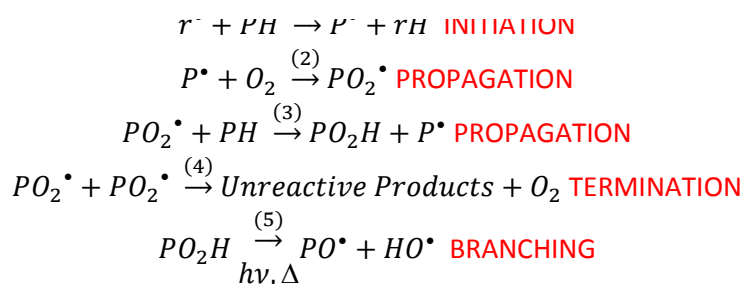
Morphological Stability

Achieving well-ordered conjugated polymer morphologies has proven very difficult. Detailed understanding of the precise crystallisation mechanism requires an accessible melt phase and is still poorly understood.^[118,119] For example, the temperature required to melt P3HT is close to the temperature at which it degrades, precluding further study of recrystallisation. Morphological stability can be achieved through optimisation of microstructure using techniques such as thermal annealing, which promotes chain reorganisation and crystallisation.^[92,120–123] In the blends used for OPV devices, the fullerene molecules have been observed to aggregate into microcrystallites over time.^[103,124] An understanding of the precise structural mechanics and kinetics of recrystallisation in neat and blend systems is essential for understanding the structural requirements of efficient charge transport.

Photostability

Light exposure is one of the main triggers to the degradation of polymers materials. Photobleaching on exposure to light directly impacts the first step of OPV operation and has been observed in both the presence and absence of oxygen.^[110,111] The role of singlet oxygen in the degradation mechanism is still fiercely debated.^[125,126] Photonic excitation of the chromophore can create free radicals, which react with the polymer backbone, producing a macroradical that goes on to react with oxygen (Figure 2.15).^[111] This initiation step is referred to as hydrogen abstraction and can occur at several potential sites along a polymer chain. It eventually leads to the formation of hydroperoxide which can decompose thermally or photochemically.^[111] It is clear that identification of the potential degradation sites of degradation is of paramount importance in chemical design. The instability observed for P3HT based polymers is attributed to the oxidizability of the carbon atom in the α -position of the thiophene ring.^[127,128]

Figure 2.15: Chain oxidation process of polymers (PH) reproduced from reference ^[111]



Operational Electrochemical Stability

To date, most degradation studies consider the stability of the neutral polymer, but for the majority of OPV devices the conjugated polymers are partially oxidised during operation, and there has been little investigation into how the oxidised species themselves degrade. The impact of polaron formation within organic semiconductors is being actively studied in the field of OFETs, where field-induced polaronic charge densities within the accumulation layer are high ($> 10^{18} \text{ cm}^{-3}$), enabling the observation of charge-induced absorption.^[129] The complexity of the behaviour of the polaronic species can be understood using spectroscopic techniques. Using chronoamperometry it is possible to control the extent of oxidation within a polymer film, allowing a series of spectroscopic measurements to be performed *in situ*.^[130,131]

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3 Experimental Details

3.1 Sample Preparation

The majority of the materials considered in this thesis are soluble and thin films were deposited via spin coating and zone-casting from solution. To prevent contamination, solution and substrate preparation was carried out in the Experimental Solid State Physics Cleanroom, a class 1000 environment in the Blackett Laboratory. The cleanroom contains optical filters to minimise exposure to short wavelength light. Zone-casting was carried out in the Undercroft Laboratory at Imperial College, in a fume cupboard in ambient conditions. Vacuum deposition and zone-refining has been performed by collaborators elsewhere and their contributions are detailed in the text.

3.2 Solution Preparation

Glass vials were first flushed with a nitrogen line and solute was weighed out using a Mettler Toledo microbalance (0.1 mg resolution). An Eppendorf Research adjustable micro-pipette (1 μ l resolution) was used to measure solvent volume. For small molecule work toluene was the typical solvent, at concentrations 7 – 10 mg ml⁻¹. Polymers were generally dissolved in a chlorinated solvent (chlorobenzene, chloroform or dichlorobenzene) at 20 – 30 mg ml⁻¹ concentrations. Each component in blend samples were dissolved separately and mixed at given ratios. Solvents were all supplied by Sigma-Aldrich. To increase solubility the solutions were left overnight on a hot plate at 60 °C with magnetic stirrer bars. To remove any solute aggregates, solutions were filtered through a 0.45 μ m pore size PTFE filter into a clean vial prior to deposition.

3.3 Substrate Preparation

Substrates were cleaned prior to deposition using ultrasonication in a variety of solutions and solvents. The substrates were loaded into a substrate rack and placed into a detergent bath (2 % Hellmanex solution) to remove any large residue on the surface (30 minutes). These were then rinsed or soaked in deionised water (15 minutes), and rinsed with acetone. This was followed by sequential 15 minute ultrasonication cycles in isopropanol (IPA), acetone, IPA and finally acetone. The samples were then dried with the nitrogen line. Immediately prior to solution deposition the substrates were placed in an Emitech K1050X oxygen plasma asher at 80 – 100 W for 1 – 5 minutes. For spectroscopic samples fused silica substrates (quartz) were used (Spectrosil 2000, 12 × 12 × 1.5 mm, UQG Optics). For

transistor fabrication bottom-gate, bottom-contact pre-patterned wafers (IPMS Fraunhofer) were used. For *in situ* electrochemical studies, conductive FTO coated glass substrates (TEC15, Corning, 13 x 26 x 22 mm) were used.

3.3.1 SAM Treatment

Self-assembled monolayers (SAMs) are used in transistor fabrication to improve device performance. SAM materials were purchased from Sigma Aldrich. For the work in this thesis, trichlorophenylsilane (TCPS) and hexamethyldisilazane (HMDS) were used for channel passivation and pentafluorobenzene thiol (PFBT) was used for modification of the metal electrodes. The SAMs were deposited immediately after the plasma treatment.

TCPS and PFBT were deposited using an immersion technique, by placing the cleaned substrates in low concentration solutions of TCPS in toluene (8 drops/ 10 ml) for 5 minutes and PFBT in IPA (8 drops/ 10 ml) for 15 minutes. Each step was followed by an IPA rinse and blast of the nitrogen jet. HMDS was deposited from spin coating for 60 s at 4500 rpm followed by baking at 180 °C for 2 minutes.

3.3.2 Spin Coating

Spin-coating was performed in a fume hood using a Laurell Technologies Corporation spin coater (model number- WS-650SZ-6NPP/LITE). The sample was held onto the rotating chuck using a low vacuum. The typical conditions for spin-coating were 1000 – 2000 rpm spin speeds for 60 s but were varied to produce film thicknesses of ≈ 100 nm. The film thicknesses were checked using a Tencor Instruments Alphastep 200 profilometer.

3.3.3 Zone Casting

The zone casting procedure is described in Section 4.2. The equipment was designed and built in-house at Imperial College London by David T. James, Steve Cussell and Dave Bowler. Designs for the heater power supply was provided by Rafal M. Gisko at the University of Lodz, Poland. Thin films were zone cast as soon as possible after oxygen plasma treatment. The typical zone-casting conditions are substrate shift-speeds of 100 – 2000 $\mu\text{m s}^{-1}$, substrate temperatures of 70 – 90 °C and solution temperatures of 50 – 70 °C.

3.3.4 Bottom-Gate Bottom-Contact Transistors

To ensure the only variation between devices was in the morphology of the organic layer, pre-patterned interdigitated bottom-gate, bottom-contact (BG BC) transistor substrates were purchased from IPMS Fraunhofer, Germany. The end-of-line test substrates comprise of an n-doped ($n \approx 3 \times 10^{17} \text{ cm}^{-3}$) 150 mm Si wafer with 230 ± 10

nm thermally grown SiO₂ dielectric. The lift-off technique was used to structure the 30 nm Au source/drain contacts (contact size = 0.5 mm²) with a high work function 10 nm ITO adhesion layer. The individual 15 × 15 mm test substrates contain 16 devices, each with 2 mm channel widths (W). There are 4 transistors of various channel lengths (L = 20, 10, 5, 2.5 μm). Each test substrate contains two orthogonal devices per channel length in order to characterise any anisotropy in the organic materials. Schematics of the test substrate and device architecture are shown in Figure 3.1.

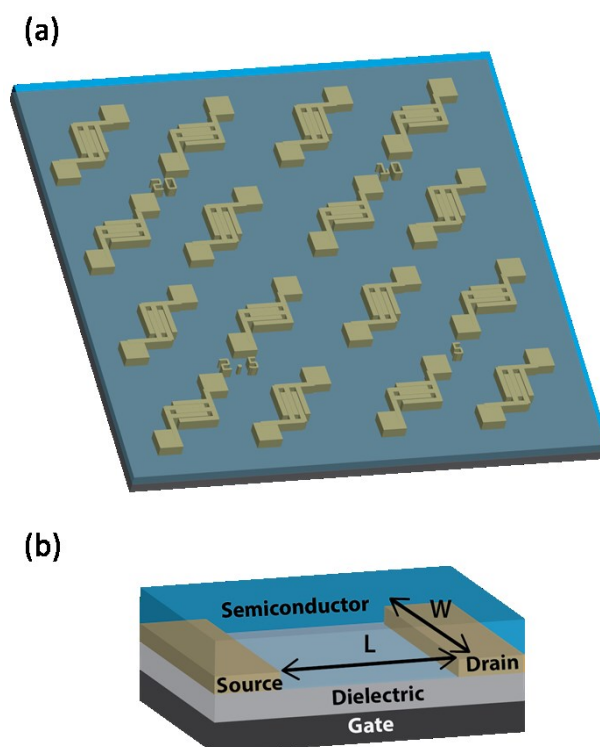


Figure 3.1: (a) Layout of a Fraunhofer test substrate. (b) BG BC device architecture.

3.4 Characterisation Techniques

The orientation and reorganisation of molecules during solution processing and device operation is likely to influence the mechanical and electrical properties of organic electronic devices. In this work a range of characterisation techniques are used to describe the growth and morphology of small molecules and polymers on untreated and surface treated substrates. The topography of the samples is imaged using atomic force microscopy (AFM) and cross-polarized optical microscopy (POM). The intra- and intermolecular interactions are understood using UV-Visible absorption and Raman spectroscopy.

3.4.1 Optical Microscopy

The microstructure of the thin film samples was initially evaluated using optical microscopy in reflection mode. The non-polarised microscope images were acquired using a Leica DM 2500M microscope with 5 – 50 x magnification.

The cross-polarised images were taken using the Olympus BX51-P polarising microscope in the Glovebox Lab at Imperial College and analysed using Olympus OlyVia software. The cross-polariser provides contrast to uniaxially crystalline domains, where adjacent crystals exhibit birefringent light scattering (Figure 3.2). Through cross-polarisers the highly crystalline regions are bright and dark regions are amorphous.

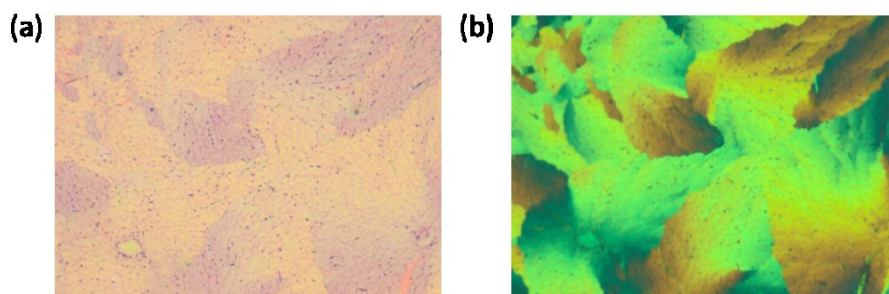


Figure 3.2:(a) Non-polarised and (b) cross-polarised optical images taken of a spin-coated thin film.

3.4.2 Atomic Force Microscopy

For the morphological effects that occur on length-scales < the optical diffraction limit, high-resolution surface topography was measured using AFM. The NX10 scanning probe system is manufactured by Park (South Korea) and surfaces were imaged using the non-contact mode to avoid damaging the soft organic layer. A schematic of the AFM apparatus is shown in Figure 3.3.

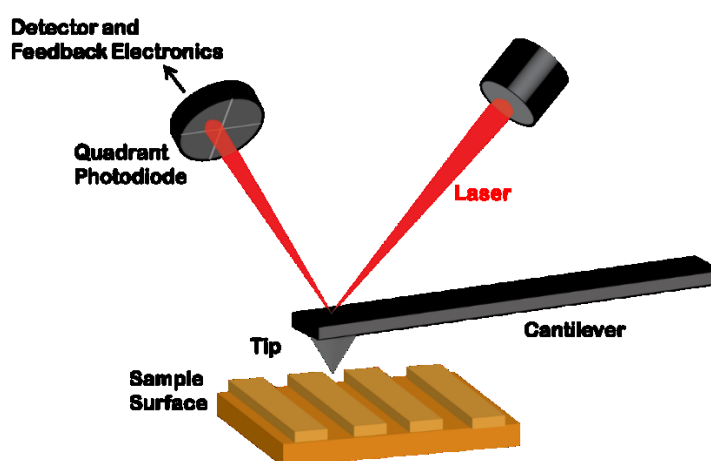


Figure 3.3: Schematic of AFM apparatus.

Non-contact mode AFM involves sensitive sharp tip mounted to a cantilever which is driven close to its resonant frequency ($f = 330 \text{ kHz}$). AFM measures the deflection of the cantilever (the tip-sample distance, 'z') by reflecting a laser beam off the back onto a quadrant photodiode. The AFM contains two independent piezoelectric scanners, in the XY and Z planes. The XY scanner moves the sample through two-dimensional space and the changing interactions between the tip and the sample modifies the resonant frequency of the cantilever. In non-contact mode

AFM, the cantilever is oscillated at the resonant frequency and the amplitude of oscillation is kept constant. A feedback loop is used to adjust the tip-sample distance (Z) *via* a piezoelectric z-scanner, so that the Z-height maps out the surface of the film. The PointProbe Plus (PPP) tips used in this thesis have a < 7 nm radius and a high mechanical Q-factor and offer superior sensitivity to the surfaces below. On the detector side, they are coated with 30 nm Al to increase the reflectivity of the laser beam and they are highly doped to prevent the build-up of static charge. The image composed by AFM is a convolution of the shape of the sharp tip and the surface of the sample.^[1] In order to avoid resolution limiting artefacts, which arise when the tip becomes contaminated with parts of sample, the tip must be sharper than the length-scales over which features change on the sample. AFM is a measure of the morphology of the surface of a sample and provides little information on the interactions below.^[2] It cannot measure the order or crystallinity of a thin-film, but can accurately measure step-heights and details of surface roughness for a range of complex nanostructures. In this thesis it is used in combination with other structural probes.

3.4.3 UV-Visible Absorption Spectroscopy

UV-Visible (UV-Vis) absorption spectroscopy is the measurement of the near-UV and visible light by a sample. UV and near UV light contains enough energy to promote outer electrons to excited energy levels. UV-Vis absorption can be used to characterise the molecular packing and electronic interactions in thin-films or dilute solutions. For polymer materials, UV-Vis spectra generally contain broad features that are particularly useful for quantitative analysis, but can also contain some information on the degree of polymer molecular order.

Absorption spectra were measured using a Shimadzu UV-2550 spectrophotometer. The spectrophotometer passes broadband light through a monochromator, which separates the light into specific wavelengths. The beam of light is split so that half passes through the sample and half passes through a reference cell where it is collected by two independent photodiodes. The instrument measures the intensity of light transmitted through a sample (I) and compares it to light that passes through the reference cell (I₀). The ratio (I/I₀) is called the transmittance, which is converted to absorbance (A) using Beer's law.

$$A = -\log\left(\frac{I}{I_0}\right) \quad \text{Equation 3.1}$$

Measurements comprise of many steps to minimise ambient light and variations in results. First a baseline measurement is performed without any sample present. Subsequently, the transmittance of a clean substrate (glass

or quartz) is measured, followed by the transmittance of the substrate and thin film. The absorbance of the film itself is found by subtracting the substrate absorbance from that of the substrate and film. Absorbance spectra often contain some evidence of light scattering, which is removed by subtracting a baseline absorbance such that the long wavelength absorption is equal to 0.

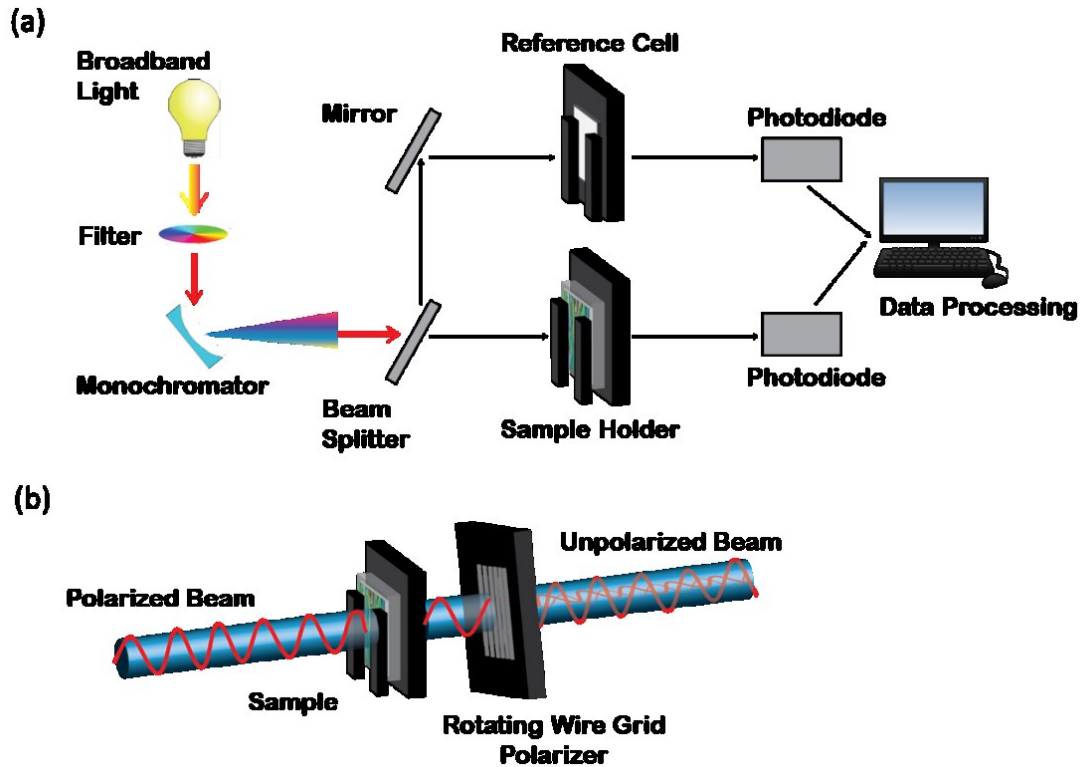


Figure 3.4: (a) Schematic of UV-Visible Spectrophotometer (b) modification to beam path for polarised UV-Visible absorption measurements.

Polarized UV-Visible absorption Spectroscopy

The polarisation of the incident light beam was controlled using an Edmund Optics broadband wire grid polarizer, which is placed inside an optical mount before the sample itself. Transmittance spectra of both the thin film + substrate and bare substrate are acquired every 10 °, allowing the determination of the dichroic properties of the sample under test.

3.4.4 X-Ray Techniques

Grazing-interface X-Ray diffraction (GIXD) characterises the surfaces of crystal structures and the global microstructure within thin films.^[9] An X-Ray travels through the sample and some of the plane wave is diffracted, with the diffraction being related to the spacing of the crystal planes by application of Bragg's Law. GIXD patterns consist of a number of 'bright spots' at a given rotation angle, which allow extraction of crystal plane spacings and orientations.

The integrated intensity of the ‘diffraction spots’ corresponds to the amount of crystalline material, and can be used to characterise local order and relative film crystallinity. Analysis of the in-plane and out-of-plane scattering allows calculation of the lamellar and π - π stacking distances in polymer thin-films, and can be used to determine whether the polymers pack ‘edge-on’ or ‘face-on’.^[10–12]

Near-edge X-ray absorption fine structure (NEXAFS) probes the core shell electrons in a material using soft-X-Rays. NEXAFS is comparable to UV-Vis absorption spectroscopy- it probes the specific energy that the core electrons are excited to and provides information on molecular bonding. NEXAFS can be used to estimate the fraction of crystallinity within a sample, and study chemical composition or molecular orientation within a unit-cell.

3.4.5 Photoluminescence

In the active layer of organic solar cells, measurements of photoluminescence (PL) can provide information about the proximity of molecules in amorphous and crystalline domains.^[3–8] Laser excitation forms an exciton within the donor – acceptor blend (Chapter 2), which can radiatively recombine and emit light. On the other hand, excitons that quickly reach a donor-acceptor interface cannot radiatively recombine and do not result in a PL signal. Intimately mixed donor – acceptor blends have low photoluminescence, as all photogenerated excitons are very close to an interface and are unlikely to recombine radiatively before being separated, whereas pure regions of donor and acceptor typically have high photoluminescence.

3.4.6 Raman Spectroscopy

Theory

The bonds between organic molecules have translational (all in same direction), rotational (about principle axis of inertial ellipsoid) and vibrational degrees of freedom (changes in lengths and inter-unit dihedrals of chemical bonds). The collective movements of these molecular systems can be described by their ‘normal coordinate’ – a superposition of ‘normal’ vibrations in which all atoms are vibrating with the same phase and normal frequency. The vibrational spectra of organic molecules can be observed using either Raman or Infrared (IR) spectroscopy, where molecular symmetry defines the nature of particular vibrations (bonds) and whether they be Raman or Infrared (IR) active. The principle difference between Raman and IR spectroscopy is that Raman is based on the scattering of light as opposed to the absorption of light.

In the following equations μ = molecular dipole moment, q = normal coordinate (i.e. motion of atoms during vibration) and α = molecular polarisability (i.e. freedom of motion of electrons and nuclei).

Infrared Spectroscopy refers to the absorption by a vibrating molecule irradiated with infrared radiation.^[13] If the electric vector of the radiating field (light) vibrates at the same frequency as the dipole moment of the molecule it is 'infrared active'- i.e. the molecular dipole is modulated by the normal vibration:

$$\left(\frac{\partial \mu}{\partial q}\right)_0 \neq 0 \quad \text{Equation 3.2}$$

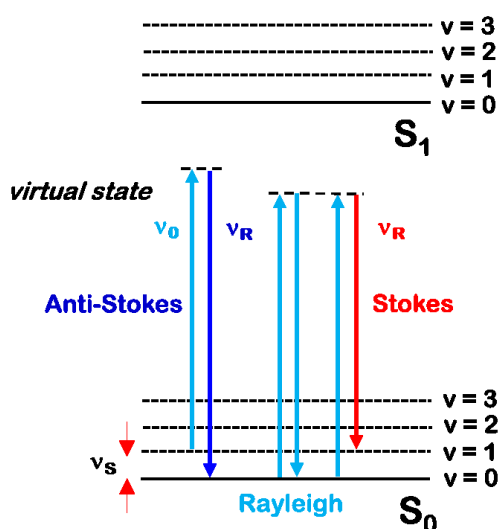


Figure 3.5: Energy Diagram representing elastic Rayleigh scattering (light blue), anti-Stokes Raman scattering (dark blue) and Stokes Raman scattering (red) with ν_0 , ν_s and ν_R representing the frequencies of the incident light, Raman scattered light and molecular vibration respectively. Adapted from reference ^[14]

Raman Spectroscopy refers to the inelastic scattering of light upon interaction with a vibrating molecule, where electrons and nuclei move on interaction with an electric field. The oscillating electric field vector ($\vec{E}$) of the incident radiation can induce a dipole in the molecule proportional to the electric field strength and molecular polarisability (α):

$$\vec{\mu} = \tilde{\alpha}(\nu) \cdot \vec{E} \quad \text{Equation 3.3}$$

Here $\tilde{\alpha}(\nu)$, the polarisability tensor, describes the response of the electron to the nuclear moment on oscillation at the normal mode frequency ν_s . The molecular polarisability is modulated by the molecular vibration:

$$\left(\frac{\partial \alpha}{\partial q}\right)_0 \neq 0 \quad \text{Equation 3.4}$$

When the molecule is excited with monochromatic light ($h\nu_0$), there is an exchange of vibrational energy with the molecular system ($h\nu_s$), resulting in the inelastic scatter of light at higher or lower energy: ^[13]

$$h\nu_R = h\nu_0 \pm h\nu_s \quad \text{Equation 3.5}$$

Scattering that leaves the incident frequency unchanged is referred to as elastic or Rayleigh scattering (Figure 3.5). The ‘Raman shift’ refers to the energetic difference between inelastically and elastically scattered light and is usually quoted in wavenumbers (cm^{-1}). At room temperature most molecules are in their vibrational ground state, and so Raman processes that transfer vibrational energy to the molecule ($h\nu_0 - h\nu_s$) or ‘Stokes’ processes dominate the reverse (Figure 3.5). ^[13,15] At high temperatures when there is a non-zero population of excited vibrational states the scattered photon can gain energy (‘anti-Stokes’). ^[15]

Raman Spectroscopy of Polymers and Small Molecules

Raman spectroscopy is a particularly applicable tool for the study of both polymers and small molecules, as $\partial\alpha/\partial q$ is very large for conjugated systems owing to the delocalisation of the π -electrons.

The polarisability tensor ($\tilde{\alpha}$) contains components defined by the fixed x, y and z coordinates of the molecule:

$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \cdot \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \quad \text{Equation 3.6}$$

With molecule-fixed coordinates (ρ, σ), the Raman-scattering cross-section for a particular mode ($\sigma_{i \rightarrow j}$) can be used to determine the intensity of scattered radiation, and is defined by:

$$\sigma_{i \rightarrow j} \propto (\nu_0 \pm \nu_s)^4 \cdot \sum_{\rho, \sigma} |\alpha_{\rho, \sigma}|^2 \quad \text{Equation 3.7}$$

The orientation of the molecule with respect to the highly polarised incident electric field ($\vec{E}$) and components of the polarisability tensor ($\alpha_{\rho, \sigma}$) determine the polarisation of the Raman scattered light. Raman scattered radiation includes components polarised parallel and perpendicular polarised to the incident field. The anisotropic structural properties of organic molecules and thin films can be examined using angle-dependent polarised Raman spectroscopy, where the polarisation of an incident excitation is controlled using a half-wave plate connected to a software trigger. Every small molecule has an associated point group which describes the symmetry operations that it can perform. The symmetry properties of a given point group are tabulated in character tables, which determine the individual

components of $\alpha_{\rho,\sigma}$ and permit the interpretation of molecular orientation from the relative intensities and polarisation of Raman modes.^[16]

Effective Conjugation Coordinate Model

Conjugated polymers display very few strong Raman modes which are typically associated with stretches along the optically-active backbone. They also display a so-called 'Raman dispersion', where the vibrational frequencies shift as a function of excitation wavelength. These changes are attributed to the coupling of electrons and phonons, and has been qualitatively approached by different groups. Albrecht's Theory was the first to apply an empirical distribution function for the conjugation length to finite sections of the polymer backbone and successfully reproduce line shapes and intensities at different excitation wavelengths. The matrix elements and reproduced intensities are correlated to the number of double bonds within a chain.^[17–20] In the Amplitude Mode Model (AMM), chains are instead assumed to be infinitely long with an electron-phonon coupling constant, $\overline{\lambda}$.^[21–23] AMM is inapplicable to complex polyconjugated molecules, as it relies on a knowledge of the bare phonon frequencies and individual coupling constants of each mode and assumes a distributed electron-phonon coupling constant along an infinitely long, perfect chain.

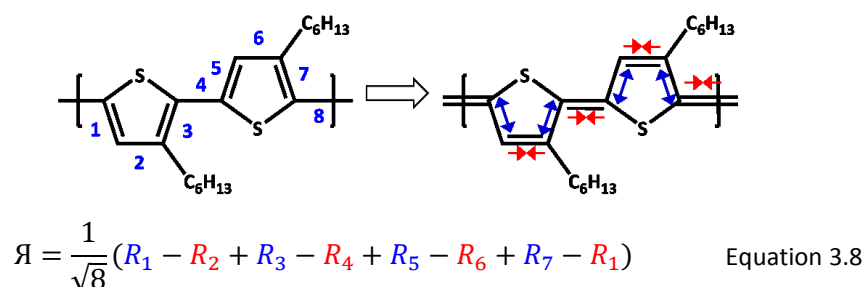


Figure 3.6: Vibrational internal coordinates and definition of totally symmetric R mode, adapted from reference ^[24]

There is a narrowing of the HOMO – LUMO energy gap on increased delocalisation of π -electrons along a molecular backbone of sp^2 hybridised carbon atoms.^[25] In addition, Raman spectra of polyconjugated molecules show very few characteristic features, a strong C = C stretching mode that cannot be assigned a traditional 'group frequency' but instead the collective skeletal stretching of the whole conjugated chain (R).^[25] This Effective Conjugation Coordinate Model (ECCM) considers only a single dipole allowed transition, $\pi \rightarrow \pi^*$, mainly involving the HOMO/LUMO orbitals, and does not consider resonance or pre-resonance phenomena.^[26–28] ECCM originally was used to describe *trans*-polyacetylene as having a totally symmetric normal mode ' Q_R ' (where $\nu = \nu_R$) which involves the simultaneous stretching of C = C and C – C bonds. The Raman dispersion is described by an effective force constant (f_R). Figure 3.6

shows the ‘ $\mathcal{R}$ ’ modes for polythiophene, which occur where there is the largest modulation of π -electron delocalisation, or where the electron-phonon coupling is strongest.^[24,26,27,29] Accordingly, the ECCM defines $\mathcal{R}$ for conjugated polymers as the movement of the π -system going from the aromatic to the quinoidal structure, i.e. the trajectory along which electron-phonon coupling is strongest. The ground and excited electronic states can be defined by these two extremes, with different weights ‘ a ’ and ‘ b ’:^[24]

$$\Psi = a\psi_{\text{Quinoid}} + b\psi_{\text{Aromatic}} \quad \text{Equation 3.9}$$

Longer conjugation (i.e. smaller $f_{\mathcal{R}}$) shifts the modes to lower frequency, allowing a measure of Raman dispersion vs. effective conjugation length.^[30] Therefore ECCM allows the measurement of conjugation within a system by measurement of the frequencies and intensities of Raman modes, providing information on the molecular conformation.^[29–33]

3.4.6.1 Resonant Raman Spectroscopy

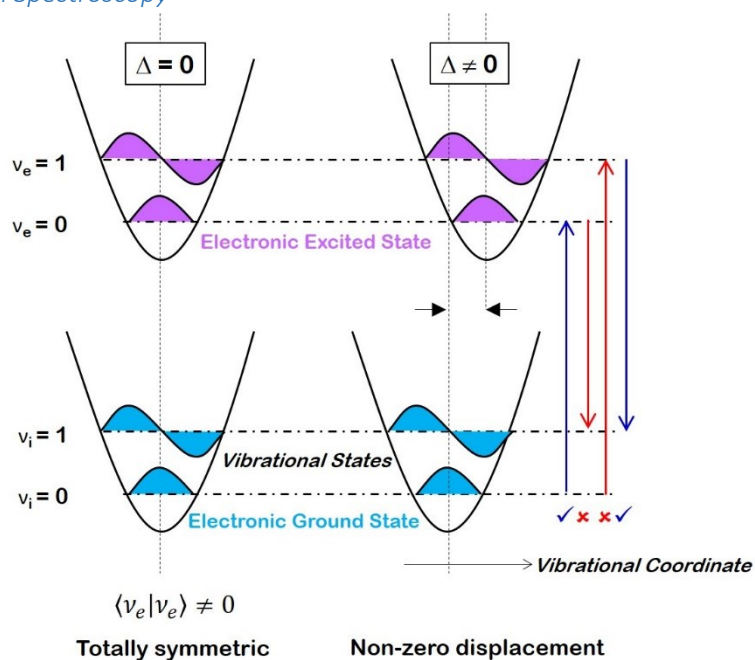


Figure 3.7: Harmonic potential curves for the ground and excited state, indicating the occurrence of Resonant Raman scattering via the A-term. If the electronic state is not displaced (left) there A-term will be zero. A displacement of the electronic excited state (right) with respect to the ground state (Δ) allows non-vanishing vibrational overlap for totally symmetric upward and downward transitions.

The resonant Raman spectrum is mainly populated by $\mathcal{R}$ modes. Resonant Raman spectroscopy is the occurrence of markedly enhanced Raman scattering cross-section of phonon modes coupled to particular electronic transitions, and occurs when absorption to an electronic excited state coincides with the excitation wavelength.^[13] The

scattering tensors for resonant Raman transitions were developed by Albrecht *et al* using a Taylor series expansion for the electronic dipole moments (from ground to excited state) with respect to the electronically excited state. Within the harmonic oscillator approximation, only the two lowest order terms are important which represent different scattering mechanisms.^[34–38] When the resonant electronic transition exhibit a large oscillator strength (i.e. large dipole transition moment) it is referred to as a ‘Franck-Condon’ enhancement and the A-term dominates the B-term. For the Franck-Condon term to be non-zero the transition must be totally symmetric and the electronic excited state must be displaced with respect to the ground state (Figure 3.7).^[34,35] The absorption spectra of a conjugated polymer typically displays a strong band originating from the $\pi \rightarrow \pi^*$ transition of the C = C bond.^[14] When the π^* orbital is occupied, the C = C bond order lowers from 2 to 1- i.e. in the excited state, the C – C bond length increases. The increase in C – C displaces the potential energy curve with respect to the ground state along the internal coordinate. Raman scattering is proportional to this displacement (Δ^2). Resonant Raman spectroscopy allows selective identification of individual components within a sample according to their absorption spectra; distinguishing different materials within a blend, different morphological phases within a single material and the identification of the nature of electronic transitions.

Morphological Phases and Raman Dispersion

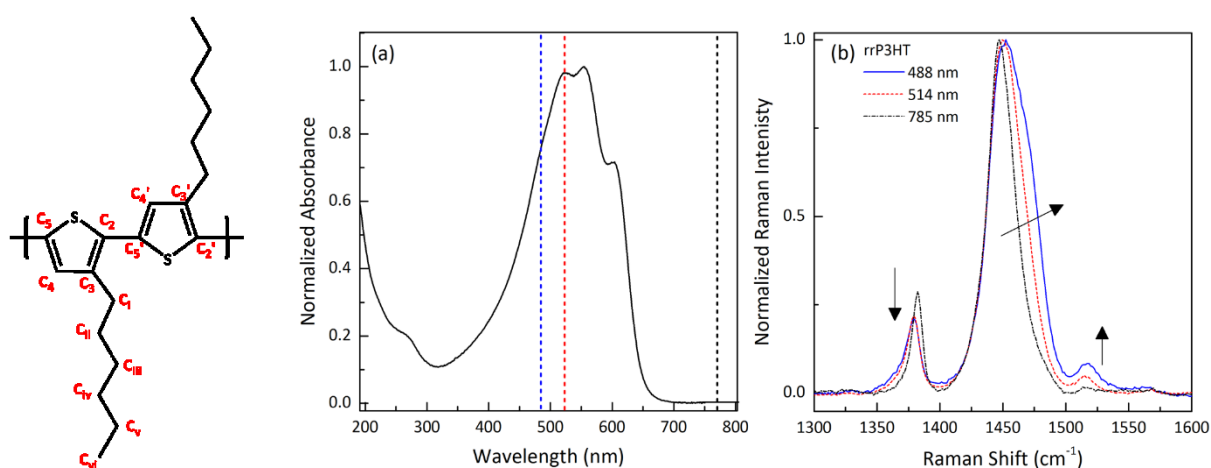


Figure 3.8: Molecular structure and atom numbering of RR-P3HT. (a) Normalised absorption spectrum and (b) Normalised Raman spectrum of a 40 mg ml⁻¹ RR-P3HT thin film in the 1300 – 1600 cm⁻¹ range. The positions of the excitation wavelengths are indicated.

Figure 3.8 displays the Raman spectra of Regio-Regular (RR)-P3HT in different excitation conditions. 488 and 514 nm lie within the main absorption band and are highly resonant. The Raman spectrum is dominated by stretches

from the C – C and C = C bonds along the main backbone. The nature of the Raman modes (Table 3.1) have been identified extensively in literature and our simulation is similar.^[25]

Table 3.1: Non-resonant Raman active vibrational modes of P3HT and their observed nature from DFT simulations and literature.

Experiment	Simulation * 0.978	Approximate description
785 nm)	<i>6-31 G(d,p)</i>	
727 cm⁻¹	710 cm ⁻¹	C – S
1091 cm⁻¹	985 cm ⁻¹	C – C intra-ring coupled to C ₃ – C _i stretch
1170 cm⁻¹		
1183 cm⁻¹	1190 cm ⁻¹	C – C coupled to C – H wag
1230 cm⁻¹	1216 cm ⁻¹	
1382 cm⁻¹	1372 cm ⁻¹	C – C intra-ring
1447 cm⁻¹	1448 cm ⁻¹	C = C symmetric stretch
1514 cm⁻¹	1536 cm ⁻¹	C = C asymmetric stretch

Comparing the Raman spectrum in the non-resonant (785 nm) and highly resonant (488 nm) regime; the C = C mode at 1450 cm⁻¹ broadens to higher energy, the intensity of the C – C mode at 1380 cm⁻¹ (relative to the C = C) increases and the asymmetric C = C stretch at 1515 cm⁻¹ increases. The strength of electron delocalisation in polyconjugated chains depends strongly on the geometry of the system and the overlap of adjacent p_z orbitals.^[25] The spectral differences occur because the high energy excitation wavelengths interact with segments of the polymer chain with shorter conjugation lengths and can therefore be used as spectroscopic markers for the molecular packing structure of polymer chains. The Raman activity of the modes depend on the extent of coupling to the π (C = C) mode.^[27,39–42] Figure 3.9 shows the non-resonant Raman spectra of thin films of RR and regio-random (RRa) P3HT. Compared to the semi-crystalline RR-P3HT, RRa-P3HT contains 1:1 head-to-head: head-to-tail linkages and is considered to be amorphous.^[43]

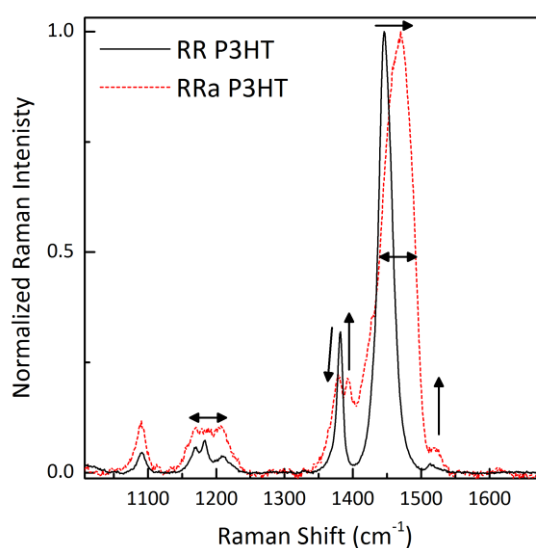


Figure 3.9: Normalized non-resonant Raman spectra of RR and RRa P3HT

This simple comparison shows obvious differences in the Raman spectra between the two extremes.

Considering RRa relative to RR:

1. C = C stretch: Shifts toward higher energy 1446 to 1470 cm^{-1} and broadens ($\text{FWHM}_{\text{RR}} = 23 \text{ cm}^{-1}$, $\text{RRa} = 52 \text{ cm}^{-1}$)
2. Intra-ring C – C stretch: Decrease in relative intensity, two peaks at 1378 and 1393 cm^{-1}
3. Asymmetric C = C: Increase in relative intensity, shifts to higher energy to 1513 to 1521 cm^{-1}
4. Alkyl chain peaks 1000 – 1250 cm^{-1} : become broad and less well-defined

The frequency of the ν mode (planar = 1446 cm^{-1}) can be used as an unambiguous marker of the shape of the polymer backbone, with the shift to high energy indicating a disruption of effective conjugation length. This confines the π -electron density to within the thiophene rings (instead of along the whole backbone), which increases the C = C force constant (f_{R}). The increased Raman scattering from the asymmetric C = C stretch indicates an asymmetric geometry of the polymer backbone. The broad distribution of conformational states for the adjacent thiophene units in RRa-P3HT is also evident in the Raman spectra, with large FWHM and splitting of the intra-ring C – C into two components. The existence of conformational disorder in the hexyl side chains is clear for RRa-P3HT, which show broad scattering in the region 1000 – 1250 cm^{-1} . On the other-hand, the conformationally ordered alkyl chains in RR-P3HT display a well-defined pattern of sharp, distinct peaks.^[25]

Nature of Electronic Transitions

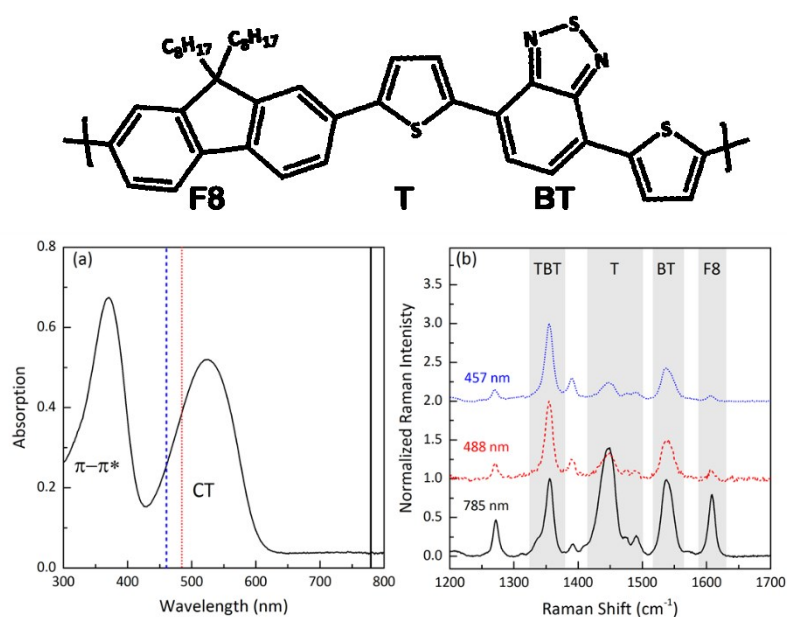


Figure 3.10: Molecular structure, (a) Thin Film UV-Visible Absorption and (b) Raman spectrum under 785, 488 and 457 nm excitation energies. Raman modes related to the TBT, T, BT and F8 units are indicated.

The nature of the low energy CT absorption band (450 – 650 nm) of F8TBT (Figure 3.10 (a)) can be interpreted by measuring the non-resonant and resonant Raman spectra. The non-resonant Raman spectrum is populated by vibrational modes (Figure 3.10 (b)), which are assigned to the C = C and C – C stretches located on the F8 (1609 cm⁻¹), BT (1537 cm⁻¹), T (1447 cm⁻¹) and collectively across the T-BT (1355 cm⁻¹) unit. As the excitation wavelength gets shorter, F8TBT shows a strong resonant enhancement of the BT and TBT modes. These resonant enhancements of these modes within the CT- excitation regime indicates that this low electronic transition is highly localised on the T-BT unit.

Materials within a blend

Resonant Raman spectroscopy allows identification of the individual components within a blend film. By tuning the excitation wavelength with the absorption bands of one material, it is possible to selectively excite one material within the blend. This will be explored in Section 4.4.

3.4.6.2 Experimental Details

Raman spectra were measured using a Renishaw inVia Confocal Raman spectrometer coupled to a Leica DM2500M microscope. All spectra were acquired in the back scattering configuration with a 50 × objective focussing the laser spot to $\approx 1 \mu\text{m}$. The resolution of the spectrometer is $\pm 1 \text{ cm}^{-1}$. The laser sources and their powers measured at the sample are detailed in Table 3.2. Five wavelength specific edge filters were used to remove the Rayleigh scattering and ensure the Stokes Raman signal was measured.

Table 3.2: Excitation wavelengths used in this work.

Wavelength (nm)	Description, <i>Manufacturer</i>	Power at Sample (mW)
785	Diode, <i>Renishaw HPNIR785</i>	130
633	He-Ne, <i>Renishaw RL633</i>	12
514	Argon-Ion	11
488	<i>Modu-Laser Stellar-REN</i>	9
457		2

Where possible, measurements were taken in an inert atmosphere; a purged chamber filled with nitrogen.

The specific excitation conditions are detailed in the relevant results chapters. The laser spot was often defocussed to minimise degradation of sensitive samples.

To measure isolated molecules/ polymers, Raman spectra are measured of very dilute solutions. The solutions are made in the clean room and transferred to the spectrometer in sealed clean quartz vials.

3.4.6.3 Calibration

Prior to any experiments, the lasers were allowed to warm up and stabilise for at least 30 minutes. The spectra were calibrated based on the sharp 520.5 cm^{-1} Raman peak of a silicon reference sample. Acquisition and analysis of Raman spectra was performed using the WiRE 3.2 and 3.4 software packages supplied by Renishaw.

Polarized Raman Spectroscopy

Polarized Raman measurements are taken by inserting a wavelength specific half-wave plate into the beam path. The half-wave plate is mounted on an automated rotated stage, where the rotation is controlled by a C++ based computer program (compiled by David T. James, Department of Physics, Imperial College London). A software trigger is sent from the WiRE software between measurements to set the rotation angle and a Raman spectrum is acquired at every interval. A typical experiment comprises of 36 measurements taken at 5° increments to rotate the half-wave plate from $0 - 360^\circ$. The change in laser polarisation (θ_L) is equal to two times the half-wave plate ($\theta_L = 2\theta_{\text{HWP}}$).

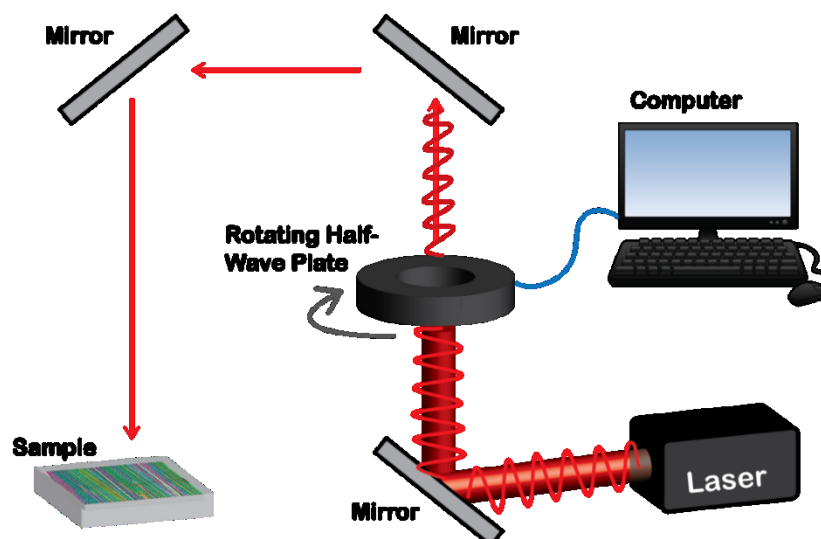


Figure 3.11: Schematic of angle-dependent polarized Raman apparatus, showing the placement of the half-wave plate in the beam path.

3.4.6.4 *In situ* Raman spectroscopy

Raman spectroscopy relies on the scattering of light and is both non-destructive and non-invasive, which lends it well to *in situ* investigations of chemical and structural processes. In this thesis we have considered the photo-, thermal and operational electrochemical stability of conjugated polymers and their morphology in thin films. Other work has investigated the impact of pressure and operation of FETs.

Photostability

For the study of photo-stability, the Raman excitation laser is used as both a probe for the collection of Raman spectra and source of photo-degradation. Measurements are recorded from a sample in a sealed chamber purged with nitrogen. It is possible to identify the photo-degradation mechanism through analysis of the Raman signal of vibrational modes as a function of exposure time or excitation wavelength. In order to understand wavelength specific degradation of conjugated polymers, the exposure time and number of accumulations is based on the excitation wavelength to ensure similar intensities of light are incident upon the sample.

Thermal Stability

A Linkam THMS6000 heating-freezing stage is used to control the temperature of the sample. The cell is purged with nitrogen. The rate of temperature change is fixed at 10 °C/ minute and samples are left to stabilise at a given temperature for at least 30 seconds before any measurements are taken. In this thesis, temperatures in the range of – 196 – 300 °C (77 – 578 K) have been considered. For temperatures below room temperature, liquid nitrogen was used to chill the sample with a LNP95 cooling pump. To prevent photo-degradation, the sample is moved using an XY stage and the laser spot is defocused between measurements.

Electrochemical stability

A custom-built spectroelectrochemical cell (Figure 3.12) was built for *in situ* cyclic voltammetry (CV) and chronoamperometry measurements. The cell was built by Steve Cussell in the Blackett Laboratory. A macrosampling kit is used to navigate the laser beam through the apparatus. The cell is a 3-electrode system consisting of a counter electrode (platinum gauze), reference electrode (Ag/ AgCl aqueous electrode) and working electrode (FTO substrate). The ion transporting electrolyte solution is 0.1 m KCl / acetonitrile. The potential difference was maintained using a potentiostat (Autolab, PGSTAT 101) and controlled using Nova software. *In situ* electrochemical Raman spectroscopy allows direct interpretation of energy level shifts during repeated CV sweeps. Raman spectra were acquired as a function of oxidising potential (V_{probe} quoted with respect to Ag/AgCl reference electrode) or oxidative stress time (at a fixed potential). The injected charge/ polaron density formed is calculated from the integral of current vs. time.

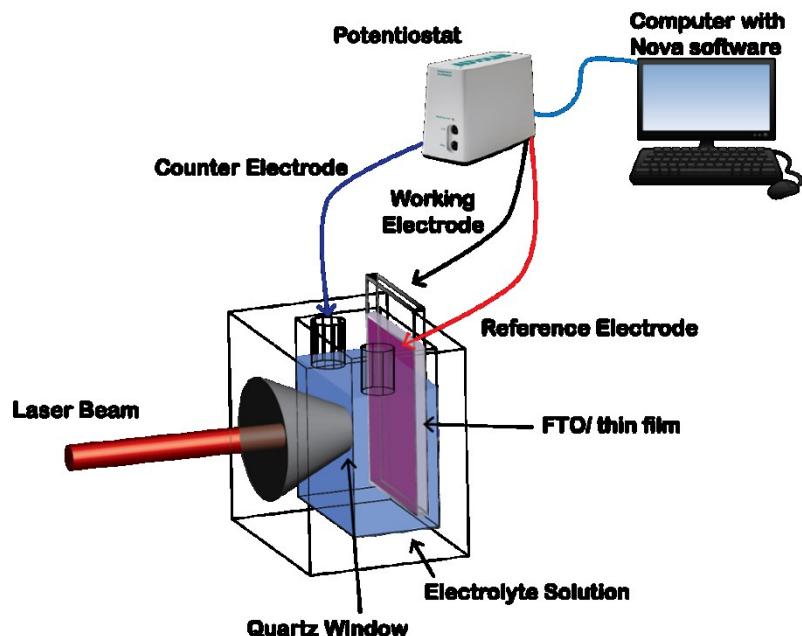


Figure 3.12: Schematic of the electrochemical cell used in this work.

Density Functional Theory

Quantum-chemical computations are essential for interpretation of experimental spectra. Density Functional Theory (DFT) is an efficient and unbiased tool to describe the electronic and structural properties of small molecules and polymer systems.^[44–46] DFT considers isolated molecular systems in the gas phase and is frequently used to determine the nature of Raman-active vibrational modes or the molecular orbitals involved in electronic transitions based on a determination of electron density.^[47] DFT gives the bond lengths of large molecules with a 1 – 2 % accuracy and the vibrational frequencies with a 5 – 10 % accuracy.^[48] DFT starts calculations based on a basis set which approximately represents the atomic orbitals, then calculates molecular orbitals using the linear combination of atomic orbitals (LCAO) approximation. Hybrid functionals (such as B3LYP) combines the *ab initio* description of single electron wavefunctions with the DFT description of the combined electron density, which a function with three variables (x, y and z position of electrons) that can be used to describe the properties of molecular systems.^[49–53] This thesis primarily uses the B3LYP hybrid functional and 6-31G(d,p) basis set, which has been demonstrated to give chemically meaningful results at relatively low computational cost. The 6-31 G(d,p) basis set is comprised of a series of Gaussian functions which accommodate the polarisation induced distortion of atomic orbitals during the formation of molecules.^[54] All calculations were performed on the High Performance Computer service at Imperial College London using the GAUSSIAN09 software suite.^[55,56]

Extreme computational costs arise from performing DFT on conjugated polymers owing to the large number of atoms and as a result polymer chains are often approximated to oligomeric model compounds comprising 3 – 5 repeat units. For these materials the majority of the electron density is located on the conjugated backbone, so to further reduce computational time the alkyl side chains are replaced by methyl groups. For both small molecules and polymers the geometry is first optimised, i.e. the molecular system adopts the lowest potential energy conformation, followed by frequency calculations to reveal the positions and approximate descriptions of Raman-active vibrational modes. The description of a Raman-active vibrational mode is based upon approximations of the bonds which show the greatest vibrational amplitude. To accommodate for discrepancies arising from *ab initio* approximations with finite basis sets, the calculated frequencies of Raman-active vibrational modes are empirically scaled.^[48,57] The B3LYP/6-31 G(d,p) vibrational frequency scaling factor is 0.9611 ± 0.0201 .^[57]

Figure 3.13 compares the Raman spectrum measured experimentally for a pentacene molecule and the simulated Raman spectrum following a geometry optimisation. The main vibrational mode is both calculated and measured at 1370 cm^{-1} , along with an accurate prediction of positions and relative intensities of other vibrational modes. For the donor-acceptor copolymer F8TBT, a chain of donor (D) and acceptor (A) units (DADAD) is simulated illustrated. The long conjugated chain contains many more atoms than the small molecule, and the lower overall symmetry results in an accurate modelling of the main vibrational mode (1446 cm^{-1}) but mismatch in simulated and measured Raman activity. Throughout this work we find that DFT methods reproduce vibrational frequencies well but often inaccurately predicts calculated peak intensities.

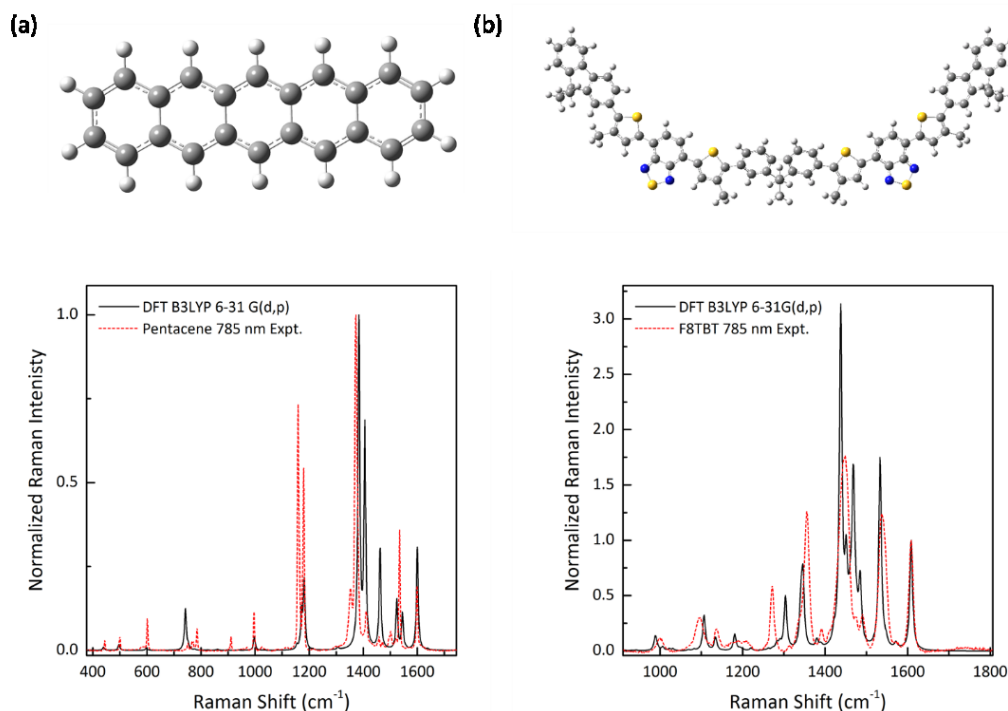


Figure 3.13: (a) Geometry optimised structure of a pentacene molecule and F8TBT D-A-D oligomer and (b) simulated (black) and experimental (red) non-resonant Raman spectrum.

B3LYP is the most widely cited model in computational chemistry, but cannot account for the polarisability of long conjugated chains, excitations using time dependent theory (TD-DFT) or CT excitations.^[58,59] TD-DFT can be used to compute the low-lying electronic excitations and is crucial for understanding absorption spectra. For these simulations the 'Coulomb Attenuated Method' CAM-B3LYP is employed, correcting B3LYP for the long range decrease in non-Coulomb exchange functional.

3.4.7 Electrical Characterisation

Electrical characterisation of small molecule FETs was performed in air using a home-built system. The source and drain electrodes of each transistor device (16 per substrate) were visible through the organic layer and directly contacted using probes. To contact the common n-doped Si gate electrode, the substrate was cleaved and painted with conductive silver paste (RS Electronics).

An Agilent dual source/measure unit (B2902A) was used to measure output and transfer characteristics. The B2902A has two SMU channels on the front and back of the device (Figure 3.14). The source electrode was held at ground (low force) for both Channels 1 and 2, whilst the drain and gate were connected to the bias (high force) terminals (see Figure 3.14). Measurements are programmed using the Quick IV Measurement software suite provided by Agilent. To determine the output characteristics, the source-drain current is measured during a forward-reverse

sweep of the drain voltage at fixed gate voltages. A linear plot of source-drain current vs. drain voltage is produced. At a fixed drain voltage, the transfer characteristics are measured during a forward-reverse sweep of the gate voltage. The drain voltage is either in the linear or saturation regime, determined based on the output characteristics. The logarithmic source-drain current is plot against the gate voltage.

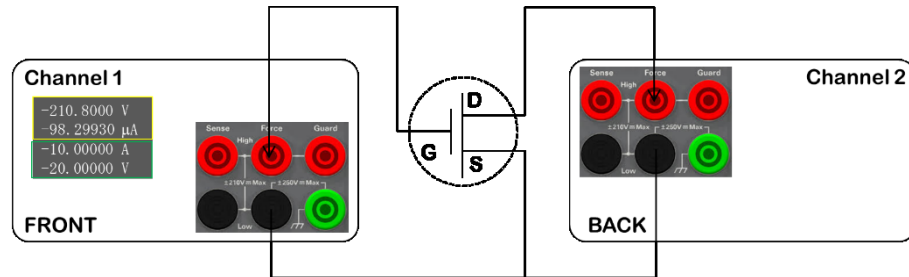


Figure 3.14: Schematic of electrical characterisation of OFETs using an Agilent B2902A

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4 Molecular Packing in Zone-Cast Solution Processed Small Molecule Devices

We investigate the relationship between thin film microstructure and device performance for small molecule organic devices, typified by a series of soluble pentacene and phthalocyanine derivatives. For both cases, we compare the influence of functionalising side groups on molecular packing, thin-film microstructure and optoelectronic properties.

The solution processing technique ‘zone-casting’ is adapted for each material set in order to form highly aligned molecular domains. For the soluble pentacene derivatives we evaluate the anisotropy of charge transport in bottom-gate, bottom-contact field effect transistors. Explicitly the effects of substrate displacement rate, substrate temperature and grain orientation on the device performance are investigated. The experimental data are compared with theoretical simulations using a multi-scale modelling approach. Having identified the conditions required for the formation of aligned films, we extend our investigation to soluble phthalocyanine materials. Here we study the sensitivity of the morphological and thermal stability to the substrate displacement rate and solvent composition. Throughout the chapter, angle-dependent polarised Raman spectroscopy is used to interpret molecular conformation.

The results shown in Section 4.3 have been published previously.^[1–4] The majority of these experiments were performed in collaboration with Dr David T. James at Imperial College London, who assisted with the solution deposition, OFET fabrication and characterisation. The simulated angle-dependent mobilities were calculated by Dr Florian Steiner and Dr Dorota Niedzialek at Imperial College London using crystallographic data provided by Dr Yongsuk Jung at Samsung Advanced Institute of Technology, South Korea. The zone-casting apparatus was build and developed in collaboration with David T. James, Steve Cussell and Dave Bowler in the Mechanical Instrumentation Workshop, Department of Physics, Imperial College London. The investigation in Section 4.3.4 was carried out with Ke Jie Tan, Mark Oxborrow and co-workers, Department of Materials, Imperial College London, and is in preparation for a publication. The materials in Section 4.4 were provided by Abigail Casey and Martin Heeney, Department of Chemistry, Imperial College London.

4.1 Motivation and Aim

Solution-processing techniques for low-cost plastic electronic devices have attracted intense study over the past decade, with efforts focussed on understanding and optimising molecular design, molecular orientation and device architecture. For high performance small molecule devices the control of molecular orientation is of the utmost importance as charge transport through crystalline domains is inherently anisotropic.^[5] Charge carriers must be able to hop between molecules without becoming trapped or scattered.^[6] Device characteristics are determined by the local molecular order, molecular alignment, crystal packing and thin-film morphology.^[3,5,7–13]

A variety of solution-based deposition methods have been used to investigate thin-film morphology, with recent efforts focussed on the precise control of solvent evaporation *via* techniques such as: dip-coating, blade-coating, solution-shearing, spray coating, alignment of liquid crystals and zone-casting.^[9,10,14–24] For the small-molecules considered here, zone-casting has been proven as a particularly appropriate technique.^[1–3,23] The zone-casting apparatus was designed and developed in-house and has since been adapted to improve control of the evaporation rate.^[3]

The first part of this investigation is concentration on the differences in charge carrier mobility due to crystal structure and thin-film morphology for two, well-characterised, model materials: 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) and 6,13-bis(triethylsilylethynyl)pentacene (TES-pentacene) (Figure 4.8). The bulky TIPS- and TES- side groups improve the solubility of pentacene and modify its packing structure.^[25,26] Whilst TIPS-pentacene has been extensively studied in the field of organic electronics, TES-pentacene is largely overlooked due to inferior charge transport properties.^[5,8,18,23,25,27–31]

There has been little activity in understanding the charge transport anisotropy imposed by the molecular packing structure of the two molecules in working organic field-effect transistors. Specifically, the significance of grain alignment and domain density for a given molecular packing has not yet been addressed. We have previously demonstrated the use of angle-dependent polarised Raman spectroscopy and absorption spectroscopy to characterise the molecular orientation and anisotropic optoelectronic properties of thin-films of TIPS- and TES-pentacene.^[3,8]

The charge transport and optoelectronic properties of TIPS- and TES- pentacene, and in fact all organic semiconductors, are determined by the relative strengths of the intermolecular interactions. We establish the spectral

signatures of a non-interacting solid-state system, where non-functionalised pentacene cores are isolated from one another within a *p*-terphenyl lattice. The electronic isolation of pentacene molecules permits excitons to undergo intersystem crossing and populate their triplet sub-levels, and, under appropriate conditions, can provide microwave amplification of stimulated emission of radiation (MASER) at room temperature. This investigation compares the optoelectronic and structural properties of pentacene with nitrogen substituted 6,13-diazopentacene.

The third part of this chapter considers a series of phthalocyanine materials, renowned for their morphological and thermal stability. To impart solubility to the small molecules long alkyl side-chains (C_8H_{17}) are attached to the side groups of the inner phthalocyanine core. This investigation compares the optoelectronic and structural properties of soluble zinc phthalocyanine (ZnPc), metal-free thiophene phthalocyanine (TPc) and thiophene zinc phthalocyanine (TZnPc). The optoelectronic properties of TZnPc are reported for the first time. This study considers the impact of solution processing techniques and choice of solvent on molecular aggregation. Finally, we test the hypothesis that phthalocyanines possess morphological stability using *in situ* Raman spectroscopy during heating/ cooling.

4.2 Development of the Zone-Casting Technique

Innovation in new materials and processing techniques continues to improve OFET device performance, with field-effect mobilities for both small molecules and polymers in excess of $10\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.^[32–34] For further progress there is a need to establish accurate and robust control over the microstructure of the organic thin films. Development of techniques to control and characterise in-plane orientation will be particularly useful for future circuit design; as charge transport in OFETs occurs in the plane of the substrate at the semiconductor-dielectric interface and the best performing materials, small molecules, are usually highly anisotropic. Zone-casting is a well-established, reproducible technique in the preparation of small molecule films.^[18,19,23,35–37] Unlike drop-casting, spin-coating or ink-jet printing, zone-casting can achieve precise control of the contact-line permits the formation of aligned crystalline domains.

During zone-casting, a heated solution is injected out of a stationary nozzle onto a moving substrate. The solution is continuously supplied through a slit-like nozzle and the solvent evaporates at the drying-edge (meniscus). Independent control of the substrate and solution temperature can be used to control the solvent evaporation rate. The substrate displacement rate, solution injection-rate, meniscus height and substrate displacement rate can be independently maintained to control grain size and quality. As the solvent evaporates from the solution meniscus, the

concentration gradient increases. At the contact line, when the critical concentration for solute-solvent phase separation is reached, nucleation occurs at the contact line. After initial random nucleation at the contact edge, the direction of solution-supply and substrate-displacement rate preferentially elongates crystals aligned with the zone-casting direction, forming crystals aligned parallel to the direction of the moving substrate. When the deposition conditions are optimised to obtain a stationary drying front, grains of variable widths (tens to hundreds of μm wide) and lengths ($\gg 2\text{ mm}$) can be produced.

The zone-casting apparatus used in this work have been comprehensively described elsewhere.^[30] The substrate displacement rate and solution injection rate are controlled via a PC using Labview software. The heater power supplies were created by Rafal M. Gisko, from the Technical University of Lodz, Poland. The design and development of the hardware was completed by Dr David T. James, Dave Bowler and Steve Cussell from the Department of Physics, Imperial College London.

Nozzle Design

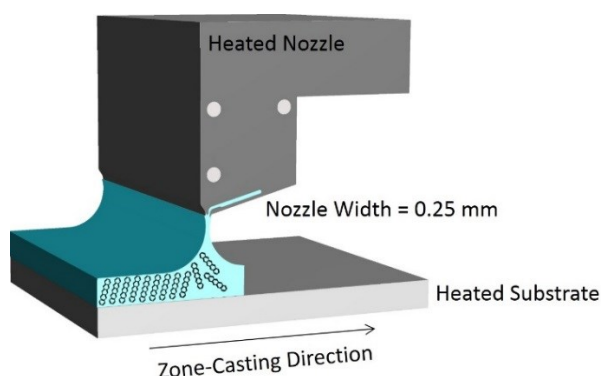


Figure 4.1: Schematic of the zone-casting apparatus with tilted, narrow nozzle (width = 0.25 mm). The maximum substrate width in the present set-up is 15 cm. The zone-casting direction is indicated.

Zone-casting from the former wide, flat nozzle resulted in a build-up of solution behind the meniscus and imprecise manipulation of the contact line. We have since made efforts to improve microstructural control by means of a tilted, narrow slit-like nozzle. The second generation nozzle features a narrower width, reduced from ≈ 1 to 0.25 mm, and a nozzle-substrate tilt of 30° compared to parallel (Figure 4.1). We have also developed an *in situ* stage to allow the simultaneous operation of OFETs and monitoring of molecular vibrations using Raman spectroscopy.

Zone-Casting Parameters

Zone-casting is a highly flexible deposition technique that offers manipulation of an extensive range of processing parameters, permitting morphological control of complicated organic systems. These include:

- i. Solvent
- ii. Solution injection rate
- iii. Meniscus height
- iv. Solution temperature
- v. Solution concentration
- vi. Substrate displacement rate
- vii. Substrate temperature

Nanostructure Control

The formation of aligned films requires materials that can self-assemble into ordered crystalline, or semi-crystalline, structures.^[20,35] Despite the choice of zone-casting parameters, if the solvent-solute system prevents such ordering, aligned domains cannot form.^[30] The suitability of a solvent-solute system is first assessed by evaluating the morphology of drop-cast films. When crystal structures are observed, the system is considered appropriate for zone-casting. After this has been established, the meniscus height and solvent injection rates (i.e. the meniscus volume) are crucial for achieving stationary solidification conditions.^[20]

We have considered the impact of solution and substrate temperature on the microstructure of TIPS-pentacene thin films. Next the implications of solution concentration and substrate displacement rate are explored.

4.2.1 Solution Temperature

To encourage the dissolution of poorly-soluble organic semiconductors and prevent aggregation before film formation, thin-film deposition often occurs from high temperature solutions onto heated substrates.^[36,38–42] Here, the impact of solution and substrate temperatures on TIPS-pentacene microstructure is evaluated.

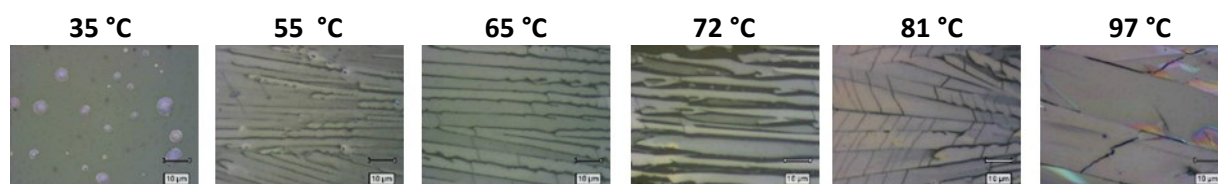


Figure 4.2: Optical microscope images of zone-cast TIPS-pentacene films deposited at a range of solution temperatures. The substrate temperature is maintained at 70 °C. These images were obtained with David T James.

The optical microscope images in Figure 4.2 illustrate the evolution of microstructure on increasing solution temperature from 35 to 97 °C. For these measurements the substrate temperature is held at 70 °C. The upper limit of the solution temperature is determined by both the solvent boiling point and thermal properties of the solute.

At low solution temperatures ($T_{\text{sol}} = 35\text{ }^{\circ}\text{C}$) the solution cannot effectively wet the substrate and random aggregate structures (many μm wide) cover the film surface. In general, if the solution temperature is less than the substrate temperature ($T_{\text{sol}} < T_{\text{subs}}$), the injected solutions cool the substrate, reducing the overall system temperature and control of the contact line.^[38,43,44] A more precise control of the contact line comes with increasing solution temperature, which permits the molecules to self-arrange into aligned needle-like structures. As the solution temperature is increased to $\approx 50\text{ }^{\circ}\text{C}$ the contact line becomes more stable and this results in the formation of crystal domains parallel to the zone-casting direction.

At $T_{\text{sol}} > T_{\text{subs}}$ the heat exchange is reversed and the contact line once again becomes unstable. The increased evaporation increases the overall film thickness and larger platelet like domains form. The needle-like grains increase in width with increasing temperature, from $2 - 3\text{ }\mu\text{m}$ at $T_{\text{sol}} = 55\text{ }^{\circ}\text{C}$ to $> 10\text{ }\mu\text{m}$ at $T_{\text{sol}} = 80\text{ }^{\circ}\text{C}$. The boiling point of toluene is $110\text{ }^{\circ}\text{C}$, and the contact line becomes impossible to maintain approaching this ($> 100\text{ }^{\circ}\text{C}$). Rapid evaporation of the solvent and the high system temperature (due to the heat exchange discussed previously) increase the temperature of the crystallising film. The evidence for this heat exchange arises in the diagonal lines appearing at $81\text{ }^{\circ}\text{C}$: despite the solid-state phase transition of TIPS-pentacene being well above this temperature, cracks start to appear along the long-axis of the pentacene cores.^[27]

4.2.2 Substrate Temperature

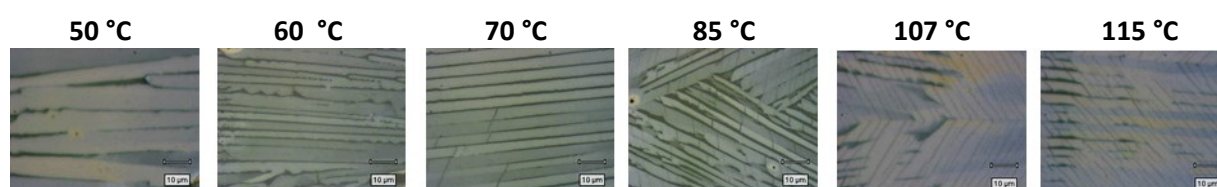


Figure 4.3: Optical microscope images of zone-cast TIPS-pentacene films deposited at a range of substrate temperatures. The solution temperature is maintained at $60\text{ }^{\circ}\text{C}$. These images were obtained with David T James.

At a set solution temperature chosen to optimise film thickness and grain width ($T_{\text{sol}} = 60\text{ }^{\circ}\text{C}$), the impact of substrate temperature is now evaluated (Figure 4.3). When $T_{\text{sol}} > T_{\text{subs}}$ ($50, 60\text{ }^{\circ}\text{C}$) inadequate control of the contact line forms a non-aligned network of domains. The solution evaporation rate and contact line control increase for higher substrate temperatures $T_{\text{sol}} < T_{\text{subs}}$ ($70, 85\text{ }^{\circ}\text{C}$). At $T_{\text{subs}} = 107\text{ }^{\circ}\text{C}$ there is evidence of large platelet-like cracked domains with a random arrangement of needle structures on top. Despite the relatively cold solution attempting to minimise the overall energy of the system, the drying process occurs from the bottom which is approaching the solid-state phase transition of pentacene. On the top surface of the film where the solvent is evaporating, the molecules adopt needle

like domains, whereas below, in the bulk, cracks start to form. The formation of cracks at the substrate interface would be particularly damaging to device performance as charges are reported to transport only in the first few monolayers above a substrate.^[14,45] Beyond the boiling point of the solvent ($T_{\text{subs}} = 115\text{ }^{\circ}\text{C}$), the number of needle like domains decreases. This is accompanied by an increase in the size of the large platelets beneath, where the uniform crack orientation (from top left to bottom right) indicate that all the molecules in the platelet are arranged in the same direction.^[27] For these reasons, the substrate temperature is maintained at $T_{\text{subs}} = 70\text{ }^{\circ}\text{C}$ to prevent cracking and promote uniform molecular packing throughout the whole film thickness.

4.2.3 Solution Concentration

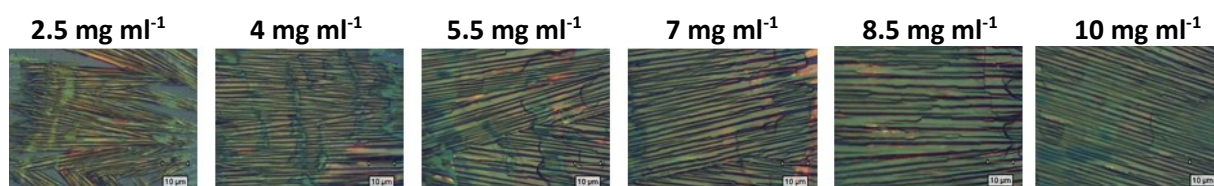


Figure 4.4: Optical microscope images of zone-cast TIPS-pentacene films deposited at a range of concentrations. The solution temperature is maintained at $60\text{ }^{\circ}\text{C}$ and substrate temperature at $70\text{ }^{\circ}\text{C}$. These images were obtained with David T James.

The solution and substrate temperatures are maintained $T_{\text{subs}} = 70\text{ }^{\circ}\text{C}$, $T_{\text{sol}} = 60\text{ }^{\circ}\text{C}$ and the solution concentration varied from $2.5 - 10\text{ mg ml}^{-1}$ (Figure 4.4). At low concentrations, solvent evaporation occurs faster than the self-assembly of TIPS-pentacene resulting in poor surface coverage. Poor control of the contact line and the low solution viscosity causes waves of material to spread across the otherwise aligned needle domains, resulting in thick and rough surfaces. Increasing concentration beyond 5.5 mg ml^{-1} increases film coverage and the needle-like domains align ($7, 8.5\text{ mg ml}^{-1}$). It is interesting that above the conditions required for uniform film coverage, the nucleation density of the crystals does not change much. The 8.5 mg ml^{-1} films show slightly wider domains, implying that during needle-formation the molecules accumulate into larger clusters. Above this (10 mg ml^{-1}) needle alignment and morphological uniformity across a sample decreases, as the high concentration TIPS-pentacene molecules start to aggregate.

4.2.4 Substrate Displacement Rate

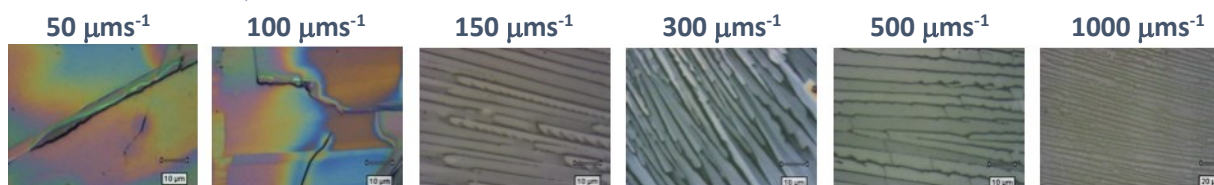


Figure 4.5: Optical microscope images of zone-cast TIPS-pentacene films deposited at a range of substrate displacement rates.

The solution temperature is maintained at $60\text{ }^{\circ}\text{C}$, substrate temperature at $70\text{ }^{\circ}\text{C}$ and concentration at 7 mg ml^{-1} . These images were obtained with David T James.

At low substrate displacement rates (50, 100 $\mu\text{m s}^{-1}$), thick films (>200 nm) of large crystalline domains are formed which extend over the entire substrate (crystal width $\gg 200 \mu\text{m}$ and length $\gg 2 \text{ mm}$) as displayed in Figure 4.5. At such slow displacement rates the films resemble drop-cast morphologies, with a poor control over the alignment of crystal grains. When the substrate displacement rate exceeds 100 $\mu\text{m s}^{-1}$ the morphology evolves into the elongated needle-like structures, which can extend across the entire length of the substrate. As the displacement rate is increased further, we see an improvement in the needle alignment from $35 \pm 3^\circ$ to almost perfectly parallel with the zone-casting direction ($1.3 \pm 0.7^\circ$ at 1000 $\mu\text{m s}^{-1}$). The increased concentration gradient within the meniscus encourages crystal growth along the zone-casting direction (solution-supply direction) and controls the density of grains (i.e. a higher density ensues when needles become increasingly narrow). The narrow needles deposited at 1000 $\mu\text{m s}^{-1}$ are accompanied by areas where needles have not formed, perhaps due to excessive substrate displacement rates.

4.2.5 Meniscus Height

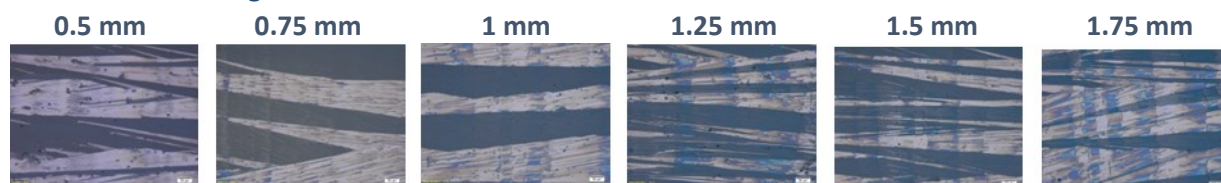


Figure 4.6: Optical microscope images (10 x optical zoom) of zone-cast TIPS-pentacene films deposited at a range of substrate displacement rates. The solution temperature is maintained at 60 $^\circ\text{C}$, substrate temperature at 70 $^\circ\text{C}$, substrate displacement rate at 500 $\mu\text{m s}^{-1}$ and concentration at 7 mg ml^{-1} . These images were obtained with Samuel de Malprade.

The delicate balance of the factors determining the zone-cast morphology discussed above must be completely readdressed when considering the height of the meniscus (Figure 4.6). The changes occur at a larger scale than the parameters explored previously an optical zoom x 10 must be used to evaluate the evolving microstructure. The large birefringence demonstrated by these structures indicates the formation of twin-boundaries. The brightness of each 'twin' (i.e. group of needles) depends on the relative orientation of the crystal optical axis and the polarisation of the light. For meniscus heights $\approx 1 \text{ mm}$, there is very good control of the contact line and the twin boundaries align with the zone-casting direction. Very low meniscus heights (0.5, 0.75 mm) and the resultant narrow 'drying front' hinder the ability of molecules to arrange in regular, aligned domains. As the surface area for evaporation is decreased, needles with random orientations populate the width of the substrate. Increasing the meniscus height $> 1 \text{ mm}$ results in a very unstable contact line with excessive build-up of solution behind the contact line. The surface of the films are covered in patches visible through a microscope, where solution has been deposited on already-dry material.

4.3 Impact of Molecular Packing on Charge Transport Anisotropy

TIPS- and TES-pentacene

To evaluate the impact of the molecular packing and thin film morphology on charge transport, we consider two pentacene derivatives, where the size of the solubilizing (TIPS- and TES-) side groups has been chosen to modify the solid-state packing motif.^[26] Unsubstituted pentacene is a p-type transporting 14 Å long linear acene consisting of five fused benzene rings.^[46] The crystal packing structures of linear acenes are well reported in literature and depend on the C-H and C – C interactions.^[47] For acenes with a large number of H atoms like pentacene, molecules pack in a ‘herringbone’ arrangement, with the C–H bonds on one molecule pointing toward the π -conjugated core of their nearest neighbour (Figure 4.7 (a)). In the solid-state the pentacene unit cell orientation is determined by the relative strengths of intermolecular and molecule-substrate interactions and is investigated in Chapter 5.

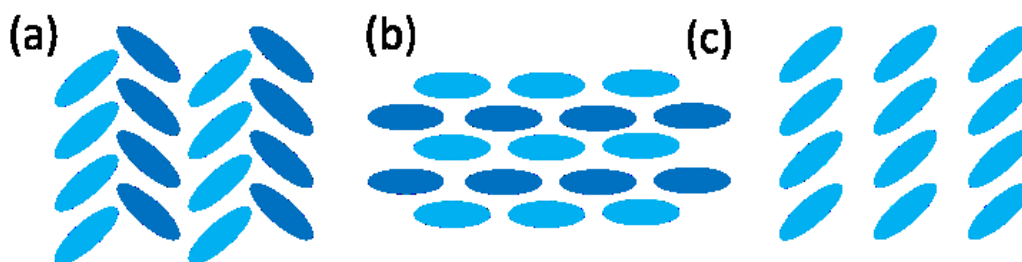


Figure 4.7: Cartoon representations of (a) herringbone packing for unsubstituted pentacene (b) Brick-wall type packing for TIPS-pentacene (c) slipped-stack packing for TES pentacene.

Pentacene	Unit Cell Parameters					
	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]
TIPS	7.66	7.75	16.84	89.2	78.4	83.6
TES	7.20	9.99	11.33	80.8	89.1	82.2

Table 4.1: The unit cell parameters of TIPS- and TES- pentacene used in this study from the work of Ostroverkhova et al.^[5] This table is reproduced from our published work.^[1]

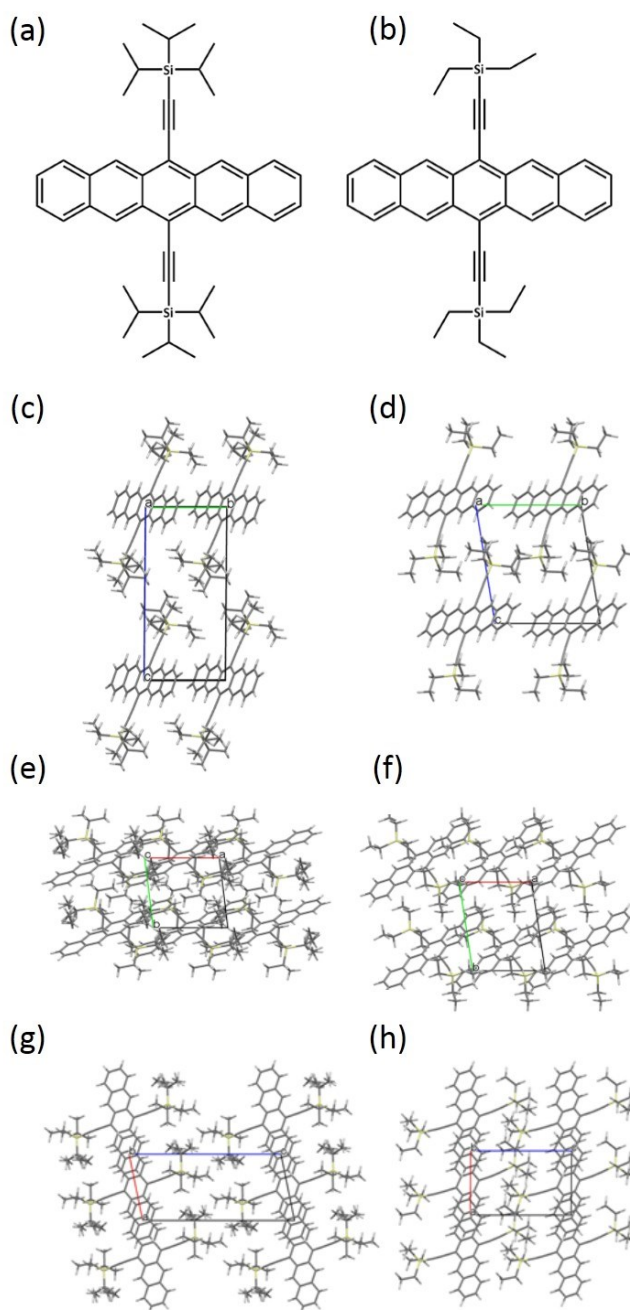


Figure 4.8: Molecular and orthographic projections of the triclinic unit cells of TIPS- (a,c,e,g) and TES- (b,d,f,h) pentacene. The red, green and blue colours correspond to x, y and z directions, respectively. This figure is reproduced from our published work.^[1] Crystal structures for TIPS-pentacene are generated using unit cell parameters from Ostroverkhova et al and can be obtained via Cambridge Crystallographic Data Centre (CCDC).^[5] The TES-pentacene structure has been calculated from the force-field Molecular Mechanics calculations.

Solubilising side-groups can modify the pentacene packing as follows:

- i. Disrupt the edge-to-face interactions and promote π -stacked order. I.e. the relative bulk of side-groups can supports co-facial staking (face-to-face) of pentacene cores and prevent the functionalised pentacene molecules from packing in a herringbone arrangement. The 2D arrangement improves π -orbital overlap, or the electronic communication between aromatic pentacene molecules.^[26]
- ii. Promote an 'edge-on' arrangement, with the pentacene short-axis and functional groups touching down on the substrate.^[48]

The size of the side-group determines the amount of π - π overlap along the pentacene long axis, whilst slippage along the short axis is a slightly more subtle relationship. If the diameter of the side-groups is than half the length of the pentacene core (i.e. TES ≈ 6.6 Å), the pentacene molecules arrange in a 1D "slipped-stack structure".^[26] The larger TIPS- side groups (diameter ≈ 7.5 Å) encourage a 2D "brick-wall" motif.^[26] The molecular structure and orthographic projections of the TIPS- and TES- pentacene unit cells are illustrated in Figure 4.8. We have confirmed the favourable 2D network for TIPS-pentacene from X-Ray analysis provided by Dr Youngsuk Jung at Samsung Advanced Institute of Technology, South Korea, where a peak corresponding to the (120) plane suggests an order in the ab-direction.^[1] The unit cell parameters are detailed in Table 4.1.

4.3.1 Experimental Details

TIPS- and TES- pentacene were purchased from High Force Research and dissolved in toluene at a concentration of 7 mg ml⁻¹, unless otherwise specified. The solutions were stirred overnight on a hot plate at a temperature of 70 °C. The solutions were filtered through using a 0.45 μ m pore size. For initial studies of microstructure, borosilicate microscope slides were used as purchased.

Evaporated thin films of pentacene were provided by collaborators at SNU. The fabrication details of these can be found in our published work, and are detailed in the next chapter.^[49] For the preliminary characterisation of optoelectronic properties, thin-films were spin-coated onto quartz substrates.

The solution and substrate temperatures of the zone-casting apparatus were stabilised for at least 30 minutes before commencing experiments. The solutions were loaded into a glass syringe. The glass syringes were thoroughly cleaned before use in an ultrasonic bath using acetone and IPA. The substrate displacement rate was 500 μ m s⁻¹ unless

otherwise stated. The optical images of the zone-cast films are at a 50 x magnification ($\text{—} = 10\ \mu\text{m}$) unless otherwise specified.

4.3.2 Optoelectronic Properties of Zone-Cast TIPS and TES pentacene thin films

UV-Visible Absorption

In highly conjugated materials such as the pentacene derivatives considered here the photo-generated excitons are delocalised across several molecules, and as a result UV-Vis absorption spectra provide details on both transition dipoles and local packing. The comparison between TIPS and TES-pentacene has been made previously and the absorption spectra are similar, resulting from their identical pentacene cores.^[30]

The absorption spectra in Figure 4.9 is characteristic of dilute TIPS-pentacene and other pentacene derivative solutions.^[3,30,50,51] Toluene starts absorbing at $\approx 250\text{ nm}$ and the absorption is flat for the regions for considered here. In fact, even at high concentrations the absorption spectra of TIPS-pentacene barely changes, indicating that in solution TIPS-pentacene molecules remain electronically decoupled.^[50] Isolated TIPS-pentacene displays a sharp peak at 643 nm (1.93 eV) with a series of vibronic replicas ($591, 548, 508\text{ nm}$), which arise from the fundamental transition $S_0 \rightarrow S_1 (\pi\text{-}\pi^*)$. This transition dipole is reported to lie along the short-axis of the pentacene core.^[52–54] The energetic spacing of the vibronic replicas is 1369 cm^{-1} . At high energies there is a second set of electronic transitions can be seen ($439, 413, 391\text{ nm}$) with a spacing of 1483 cm^{-1} . The inset of Figure 4.9 shows the solution absorption into up to the onset of toluene absorption, revealing a third family of transitions at 353 nm (vibronic replicas: $329, 309\text{ nm}$). These peak positions are detailed in Table 4.2.

For comparison, the solid-state absorption is included (red dashed line, Figure 4.9) of a TIPS-pentacene film spin-coated from a toluene solution. The solid-state spectra shows both red and blue-shifted absorption peaks indicating that both H and J-aggregation is present within these films. Red- and blue-shifted absorption peaks indicate the coexistence of H- and J-aggregates and has been observed previously for pentacene thin films.^[52] The nature of these absorption peaks in TIPS and TES-pentacene have been thoroughly investigated by our group previously using polarised UV-visible spectroscopy and time-dependent density functional theory.^[3,30] We found that the 2D brick-wall packing of TIPS-pentacene promoted H-aggregate formation, formed by a network of strongly interacting J-aggregate pentacene cores, whereas weaker intermolecular interactions for TES-pentacene restricted H-aggregate formation. In

the solid-state, the J-aggregate like red-shifted peak (690 – 700 nm) is found to be aligned along the crystallographic a-axis, and the H-aggregate like blue-shifted peak (560 – 585 nm) aligned along the crystallographic b-axis.^[3,30]

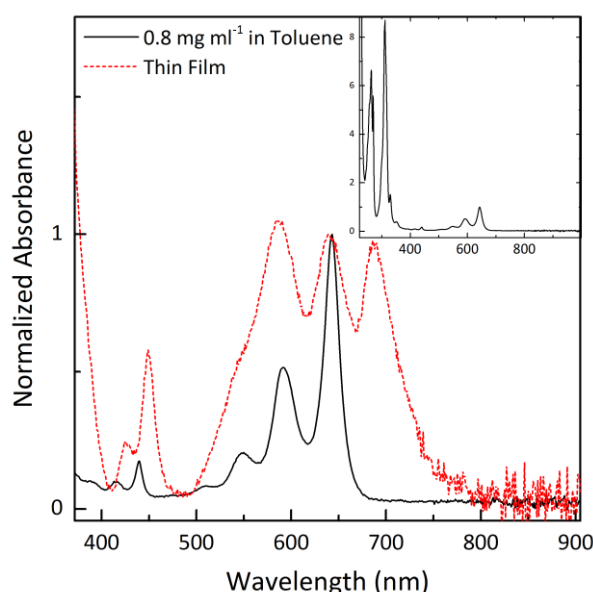


Figure 4.9: Normalised absorption spectra for TIPS-pentacene solutions in toluene (black solid line) and spin-coated thin films (red, dashed). The inset displays the unnormalised absorption of the dilute solution up to 250 nm.

Vibronic	Solution Absorption Transition Dipoles		
	S0 → S1 (nm)	S0 → S2 (nm)	S0 → S3 (nm)
0-0	643	439	353
0-1	591	413	329
0-2	548	391	309
0-3	508		

Table 4.2: Peak positions of the vibronic replicas of various electronic transition dipoles (indicated) for dilute TIPS-pentacene solutions.

Raman Spectroscopy

Raman spectroscopy is used as a local probe of molecular packing within the TIPS- and TES-pentacene thin films. The DFT simulated Raman spectra for gas phase molecules are calculated using the B3LYP/ 6-31 G (d,p) level of theory. Our group have previously compared the simulated and experimental Raman spectra of TIPS and TES-pentacene and found them to be very similar due to the identical pentacene cores.

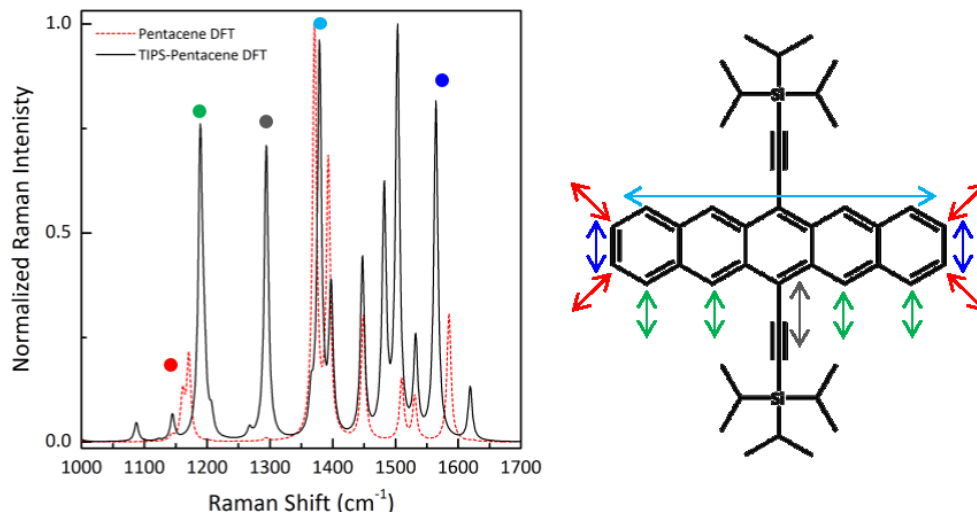


Figure 4.10: DFT simulated Raman spectra for unsubstituted and TIPS-pentacene molecules in the gas phase. Geometries were optimised using the B3LYP functional and 6-31 G(d,p) basis set. The identities of the strongest vibrational modes are shown in the inset.

Figure 4.10 compares the simulated spectra of TIPS-pentacene (black) and unsubstituted pentacene (red) in the *fingerprint* region for C – C bonds. An empirical scaling factor of 0.96 is applied to the calculated wavenumbers to allow direct comparison to experimental spectra, illustrated in Figure 4.11.^[55] The Raman spectrum of unsubstituted and TIPS-pentacene show similar peak positions. The vibrations indicated with coloured circles are identified on the adjacent TIPS-pentacene molecule. The Raman modes of TIPS-pentacene are identified as C—C stretches along the long-axis (dark blue, 1564 cm⁻¹), C—C stretches along the short-axis (pale blue, 1378 cm⁻¹), C—C to side groups (grey, 1293 cm⁻¹), and C—H_{SIDES} (1189 cm⁻¹), C—H_{ENDS} (1145 cm⁻¹). The details are provided in Table 4.3, along with the positions of the vibrational modes of unsubstituted pentacene.

	DFT Simulation		Non-resonant Raman spectra (785 nm)		
	<i>TIPS-Pentacene</i>	<i>Unsubstituted Pentacene</i>	<i>TIPS-Pentacene</i>	<i>TES Pentacene</i>	<i>Unsubstituted Pentacene</i>
C-H ends rocking	1145	1144	1158	1156	1158
C-H sides rocking	1189	1170	1194	1192	1179
C – C > side groups stretch	1293	n/a	1303	1303	n/a
C – C_{SHORT} stretch	1378	1370	1373	1374	1372
C – C_{LONG} stretch	1564	1585	1578	1578	1598

Table 4.3: Summary of TIPS-, TES- and unsubstituted pentacene vibrational modes in wavenumbers (cm⁻¹) calculated using DFT and non-resonant Raman spectra of thin-films. Calculated wavenumbers have been scaled by 0.96.

The solid-state Raman spectra of TIPS-pentacene using various excitation energies is indicated in Figure 4.11 (a), and the non-resonant absorption of thin films of TIPS, TES- and unsubstituted pentacene in (b). The peak positions

for non-resonant spectra are detailed in Table 4.3. The vibronic spacing of the absorption peaks arising from the $S_0 \rightarrow S_1$ transition dipole, discussed above, corresponds well to the C – C stretch along the short axis ($C-C_{\text{SHORT}} = 1370 \text{ cm}^{-1}$) of unsubstituted pentacene cores. At excitation energies corresponding to this transition dipole (633 nm, red solid line) there is a preferential enhancement of these short-axis vibrations relative to those along the long-axis.^[56] At excitation energies corresponding to the $S_0 \rightarrow S_2$ transition (457 nm) there is a strong enhancement of both the C-H rocking motions on the sides of the molecules and the C – C stretch to the TIPS-side groups.

In comparison to unsubstituted pentacene, in the non-resonant Raman spectra of TIPS- and TES- pentacene the relative intensity of the C – C stretch along the long axis relative to C – C along the short axis ($C-C_{\text{LONG}}$ vs. $C-C_{\text{SHORT}}$) is much larger. As discussed above, the bulky side groups change the packing from face-to-face to a more edge-on motif, where the side groups touch-down on the substrate (i.e. the molecules lie flat). In this situation, the electric field of the excitation laser would be in the plane of the $C-C_{\text{LONG}}$ (i.e., $C-C_{\text{LONG}} > C-C_{\text{SHORT}}$). On the other hand, for unsubstituted pentacene the face-to-face configuration results in the $C-C_{\text{SHORT}}$ being more in-plane (i.e. $C-C_{\text{LONG}} < C-C_{\text{SHORT}}$). Comparing the non-resonant Raman spectra of TIPS- and TES-pentacene in the solid-state reveals that the Raman peaks of C-H rocking modes in TES-pentacene are shifted to slightly lower energies ($\approx 2 \text{ cm}^{-1}$). These frequency shifts are likely due to the different overlaps of the pentacene cores resulting from the 1D and 2D packing structures.

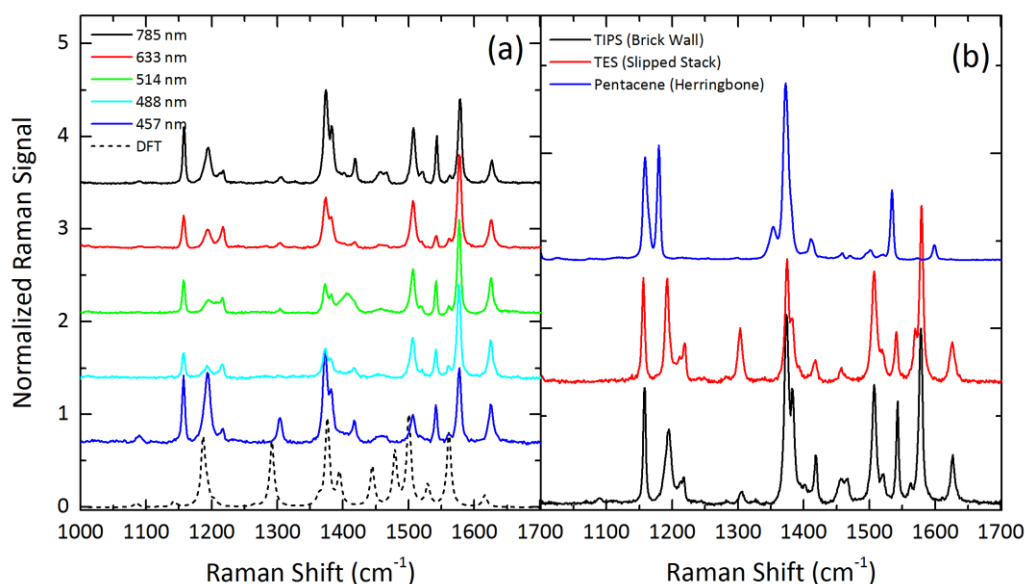


Figure 4.11: (a) Solid-state Raman spectra for TIPS pentacene at a range of excitation energies (457 – 785 nm) and the DFT simulated Raman spectra (black dashed line). (b) Non-resonant solid-state Raman spectra for TIPS (black), TES-(red) and unsubstituted (blue) pentacene measured at 785 nm.

4.3.3 Charge Transport Anisotropy in Zone-Cast Organic Field-Effect Transistors

To investigate the impact of these morphological changes on charge transport properties within different packing structures, we first investigate the effect of molecular packing structure (TIPS- vs. TES-pentacene) using large ‘single-crystal’ devices (zone-cast at $50 \mu\text{m s}^{-1}$) and second the effect of grain density (density of needles) on charge transport.

As we are interested in correlating the differences in anisotropic charge carrier mobility with the different packing structures, thin films are cast both parallel and perpendicular to the source-drain (and thus charge-transport) direction. The thin film and grain orientation are defined in relation to the zone-casting and charge-transport directions at an angle ‘ θ ’. Parallel grains are aligned parallel to the direction of charge transport ($\theta = 0^\circ$) whereas perpendicular devices are obtained by rotating the zone-casting direction such-that $\theta = 90^\circ$. Figure 4.12 presents a montage of cross-polarised optical images of the different morphologies obtained by zone-casting at different substrate displacement rates.

Controlling the Molecular Packing using the Substrate Displacement Rate

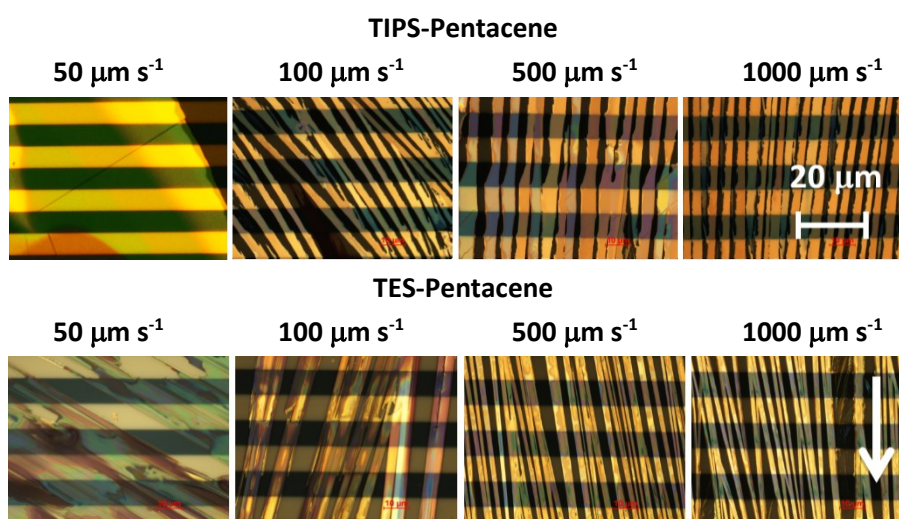


Figure 4.12: Montage of 8 cross-polarised optical images (50 $\times$ optical zoom) of TIPS-pentacene (first row) and TES-pentacene (second row) FETs cast at 50, 100, 500 and $1000 \mu\text{m s}^{-1}$. The horizontal stripes are source and drain electrodes pre-patterned on the Si/SiO₂ substrate. The zone-casting direction is indicated by the arrow. This figure is reproduced from our published work.^[1]

Charge Carrier Mobility

The transfer curves for FET devices cast at $50 \mu\text{m s}^{-1}$ of TIPS- and TES-pentacene in the saturation regime are presented in Figure 4.13. Output characteristics of parallel and perpendicular polycrystalline and needle-like ($500 \mu\text{m s}^{-1}$) devices were measured to confirm that this source drain voltage ($V_{\text{SD}} = -40\text{V}$) represented the saturation regime for

charge transport, irrespective of microstructure. Without further analysis it is evident that both crystal structure (TIPS- vs. TES-pentacene) and grain density (increasing with higher substrate displacement rates) influence charge transport; the sub-threshold slope, ON/OFF ratio and ON-current are improved in highly aligned TIPS- relative to TES-pentacene (Table 4.4).

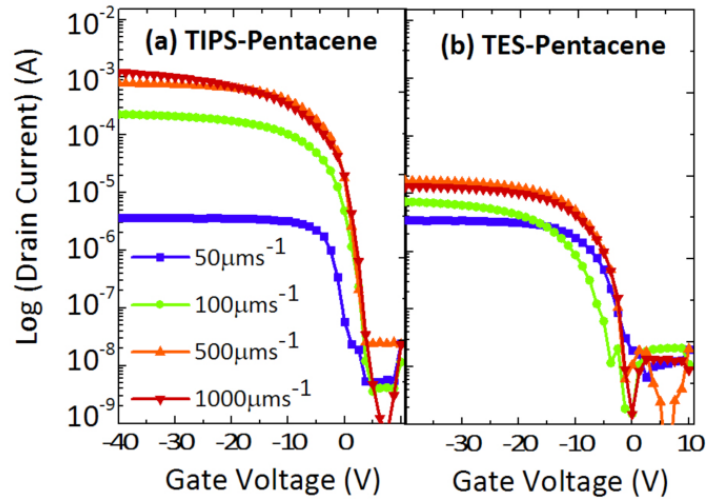


Figure 4.13: (a) TIPS-pentacene and (b) TES-pentacene FET transfer curves taken in the saturation regime ($V_D = -40$ V) for polycrystalline devices zone-cast parallel to the S and D direction, channel length (L) = $2.5 \mu\text{m}$. This figure is reproduced from our published work.^[1]

	TIPS-pentacene		TES-pentacene	
Substrate Displacement Rate	$50 \mu\text{ms}^{-1}$	$1000 \mu\text{ms}^{-1}$	$50 \mu\text{ms}^{-1}$	$1000 \mu\text{ms}^{-1}$
ON/OFF ratio	$\approx 10^2$	$> 10^5$	$\approx 10^2$	$\approx 10^3$
ON-current	$3.7 \mu\text{A}$	1.23 mA	$3.45 \mu\text{A}$	$13.33 \mu\text{A}$

Table 4.4: Transfer characteristics parameters for TIPS- and TES-pentacene devices, extracted from the linear regime ($V_D = -40$ V) of the drain current- gate voltage curves (Figure 4.13).

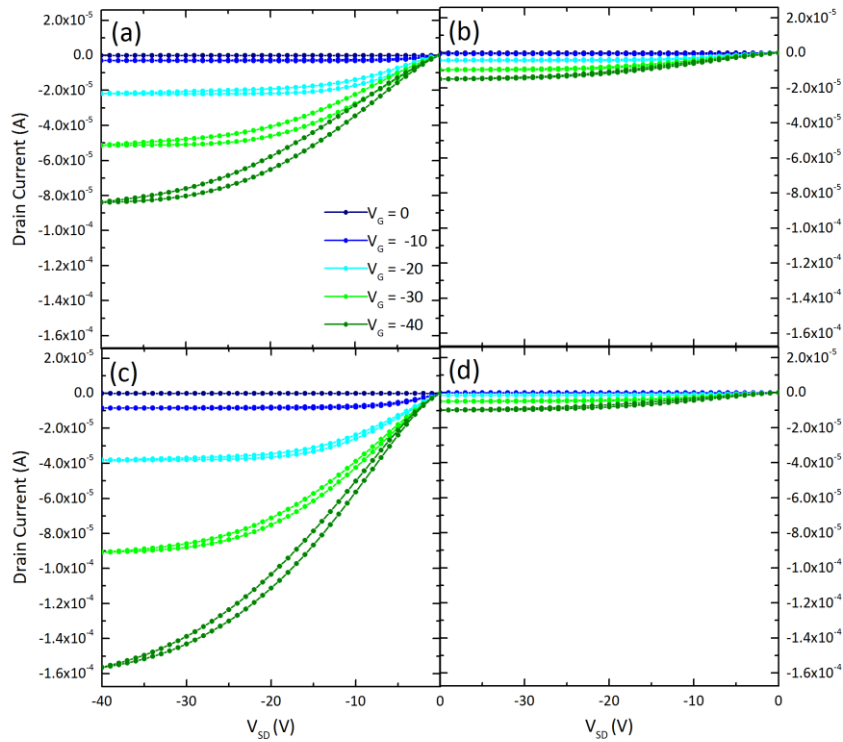


Figure 4.14: Representative output characteristics for TIPS-pentacene FETS at a series of gate voltages (0 - -40V) for (a) and (b) polycrystalline and (c) and (d) needle-like domains. (a) and (c) represent devices zone-cast parallel to the direction of charge transport, whereas (b) and (d) are perpendicular.

The saturation mobilities were calculated using simple MOSFET equations^[57] from a linear fit to a plot of $I_{DS}^{1/2}$ vs. V_G , in the saturation regime ($V_{SD} = -40$ V) for parallel devices are shown in Figure 4.15(a) and (b) for TIPS- and TES-pentacene respectively. All devices were characterised in air at room temperature. The TIPS-pentacene mobilities are one order of magnitude higher ($\mu_{SAT MAX} = 0.670 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for a $L = 2.5 \text{ }\mu\text{m}$ device) than those of TES-pentacene ($\mu_{SAT MAX} = 0.064 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for a $L = 2.5 \text{ }\mu\text{m}$ device).

As the needle density and width are the same for both (Figure 4.12), the considerably different mobility values are attributed to different packing structures for the two molecules (brick-wall and slipped-stack, illustrated in Figure 4.7) which control the π - π interactions between the pentacene conjugated cores. It is interesting to note that if the effective channel width (W) is defined only by the crystal dimensions covering the substrate, we obtain $\mu_{TIPS} = \approx 1.28 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\mu_{TES} = \approx 0.13 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in $L = 2.5 \text{ }\mu\text{m}$ devices due as $\mu \propto 1/W$.^[28]

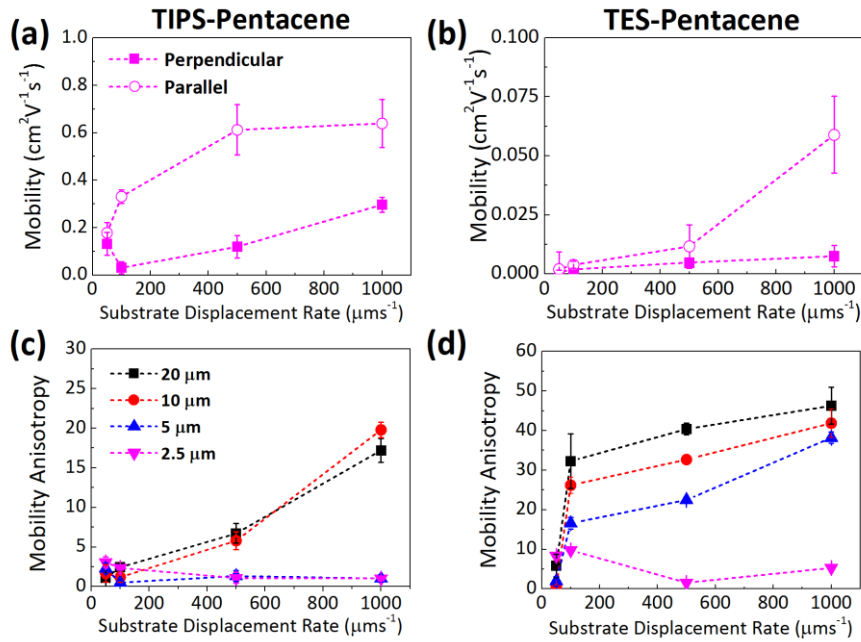


Figure 4.15: Saturation mobility as a function of substrate displacement rate in (a) TIPS- and (b) TES-pentacene FETs for $L = 2.5 \mu\text{m}$. Measurements are taken from devices with needles oriented parallel (open) and perpendicular (closed) to the charge transport direction. Charge mobility anisotropy ($\mu_{\parallel}/\mu_{\perp}$) as a function of substrate displacement rate for different channel lengths for (c) TIPS- and (d) TES-pentacene FETs. This figure is reproduced from our published work.^[1]

Mobility Anisotropy

For both pentacene derivatives, saturation mobility increases with substrate displacement-rate and peaks as needle-like domains align with the direction of charge transport. The mobility measured at low substrate displacement-rates could be due to increase disorder in thicker films, but it is widely understood that charge-transport occurs within the first few monolayers of material in the direct contact with a gate dielectric layer.^[58,59] When the charge transport direction is aligned parallel to the zone-casting direction the mobility is greater than when they are aligned perpendicular (Figure 4.15 (a) and (b)). The parallel and perpendicular mobilities are defined as $\mu_{\parallel}$ and $\mu_{\perp}$, respectively and the mobility anisotropy is equal to $\mu_{\parallel}/\mu_{\perp}$. The mobility anisotropy values as a function of substrate displacement rate are shown in Figure 4.15 (c) and (d). At the same substrate displacement-rate (i.e. for a similar number of grain boundaries), the TES-pentacene devices show significantly greater maximum mobility anisotropies ($\mu_{\parallel}/\mu_{\perp} \approx 45$) than the TIPS-pentacene ($\mu_{\parallel}/\mu_{\perp} \approx 20$) devices.

To differentiate the influence of molecular packing from that of increasing grain density, which dominates charge-transport for long channel length devices fabricated by high substrate displacement rates, large crystalline domains ($50 \mu\text{m s}^{-1}$) are considered in further detail. The polarised optical microscopy images (Figure 4.12) show that

these contain very few grain boundaries in the active channel allowing evaluation of the intra-grain mobility anisotropy. The mobility anisotropy of TES-pentacene is still higher than TIPS-pentacene ($\mu_{\parallel}/\mu_{\perp\text{TES}} = 4.2 \pm 1.8$ vs. $\mu_{\parallel}/\mu_{\perp\text{TIPS}} = 2.0 \pm 0.4$, respectively) suggesting that the charge transport within the grain is more directional in TES-pentacene than TIPS-pentacene. These results are comparable with transient photoconductivity measurements of single crystals reported to have mobility anisotropy values of 12 ± 6 and 3.5 ± 0.6 for TES- and TIPS-pentacene, respectively, and the optical dichroism we measured previously.^[3,5]

To resolve the differences between TIPS- and TES-pentacene intra-grain charge transport properties it is important to consider their different molecular packing. TIPS-pentacene, which packs in a 2D “brick-wall” arrangement, exhibits a lower mobility anisotropy. Strong π - π interactions along both the crystallographic *a*- and *b*-axis allow significant charge transport in both directions (Figure 4.7).^[7] TES-pentacene, on the other hand, packs in a 1D “slipped-stack” structure, which produces much higher mobility anisotropy. The 1D nature of this stacking promotes charge transport along the pentacene-pentacene stacks (*a*-axis) but limits inter-stack charge transport due to weak π - π interactions along the *b*-axis. To appreciate the consequences of these packing structures on charge transport, the electronic structures of TIPS- and TES- pentacene have been simulated with DFT using the B3LYP functional and 6-31G* basis set. The transfer integrals (*J*) have been calculated by considering a pair of neighbouring molecules and applying a projective method.^[60] TIPS-pentacene has two high transfer integrals along the (100) and (110) directions, suggesting that charge transport can occur in two dimensions, whilst TES-pentacene has only one (100) which indicates 1D transport. The calculated values of *J* are detailed in Table 4.5 and are consistent with other reports.^[61,62] The inner-sphere reorganisation energies have been calculated using the minimum energies of the neutral or cation geometries simulated using DFT (Figure 4.8) using well-established methods described in our published work.^[63]

	TIPS-pentacene	TES-pentacene
Charge Transfer Integrals (J) (meV)		
(100)	53.7	66.1
(010)	0.21	0.02
(001)	1.17	3.32
(110)	64.8	6.51
Inner-Sphere Reorganisation Energy (meV)		
	138	142

Table 4.5: Calculated charge transfer integrals and inner-sphere reorganisation energies between HOMO levels for TIPS- and TES-pentacene. TIPS-pentacene has two high transfer integrals (100, 110) indicating 2-dimensional transport while TES-pentacene has only one relatively high one which implies 1-dimensional transport. These calculations were completed by Florian Steiner at Imperial College London and have been published in our previous work.^[1]

When the zone-casting and charge-transport directions are parallel and the substrate displacement rate is optimised to achieve produce aligned needles, the movement of charges is not obstructed by grain boundaries. Grain boundary limited transport is most clearly illustrated by the mobility anisotropy at long channel lengths ($> 10 \mu\text{m}$, Figure 4.15 (c) and (d)) and can be considered as being a combination in series of the high (needle) and low (between the needles) conductivity regions.^[64] For devices cast at $1000 \mu\text{ms}^{-1}$ there are almost one hundred times more grain boundaries than for those cast at $50 \mu\text{ms}^{-1}$. This results in an increase in $\mu_{\parallel}/\mu_{\perp}$ from ≈ 4.2 to ≈ 20 and ≈ 2.0 to ≈ 42 for TIPS- and TES-pentacene respectively. To probe the nature of the low conductivity material between the needles, we consider resonant Raman line scans across the transistor channel.

In order to obtain any perpendicular mobility (i.e. non-zero values in Figure 4.15 (a) and (b)) there must be some material (possibly disordered) between the needle-like domains. By comparing the conventional microscope image (see Figure 4.17) with that seen through cross polarisers, the clear bright needles indicate aligned material. Between the needles the cross polarised image is black, indicating either no or disordered material. The channel profile is evaluated using AFM and resonant Raman spectroscopy. AFM cross-sectional mapping is complicated by the sharp edges of the crystals and are therefore non-conclusive. When taking Raman spectra ($\pm 1 \mu\text{m}$ lateral resolution) along a line perpendicular to multiple needle domains ($\approx 1\text{-}2 \mu\text{m}$ width) there is a very weak (yet non-zero) Raman activity between needles, indicating the possible presence of some material.

Grain orientation

It is evident from Figure 4.12 and Figure 4.15 that the angle between the crystals (needles) and charge-transport direction, ' θ ', has profound implications on charge transport. The unique uniaxial control of domain alignment offered by zone-casting at high substrate displacement rates is used to elucidate the nature of this angular dependence. This investigation develops upon the work started by Chen *et al* using a larger-area system with enhanced microstructure control.^[65] By fixing the FET substrates to the zone-casting translation stage at different orientations and the fastest substrate displacement rates ($1000 \mu\text{ms}^{-1}$), proven to produce the smallest variation in domain orientation, needles were deposited at a range of θ .

Figure 4.16 plots the saturation mobilities of these devices against needle-orientation, θ , the maximum mobility for TIPS- and TES-pentacene is at needle alignments of $\theta \approx 30^\circ$ and $\theta \approx 0^\circ$. These results support the greater higher mobility anisotropy measured for TES-pentacene; $\cos^2\theta$ curves fitted to polar plots of θ vs. μ reveal anisotropies ($\mu_\theta = \mu_{\text{Max}}/\mu_{\text{Min}}$) of ≈ 35 for TES-pentacene and ≈ 5 for TIPS-pentacene.

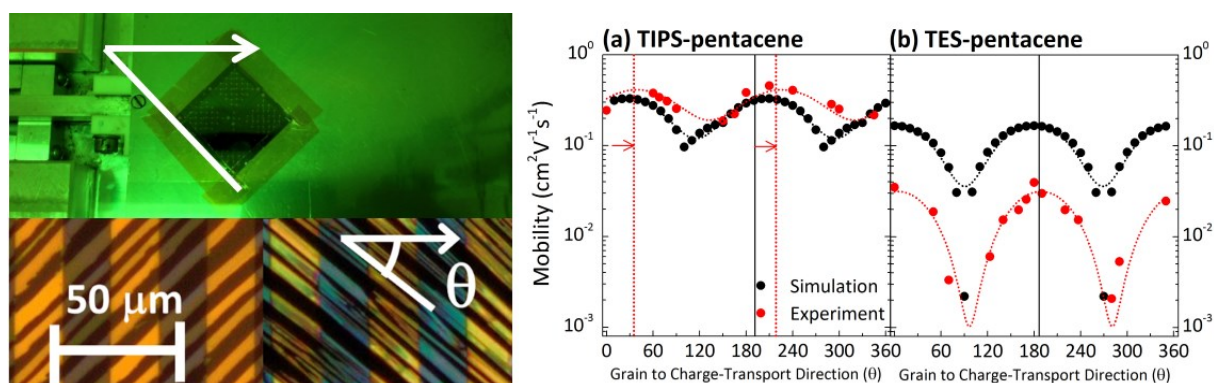


Figure 4.16: (left, upper) image of FET substrate attached to translation stage. (left, lower) Cross-polarised images of TIPS-pentacene transistors with different relative needle to charge transport direction alignments, characterised by the angle ' θ '. Logarithmic mobility as a function of the angle (θ) between crystalline grain a-axis and charge-transport directions for (a) TIPS-pentacene and (b) TES-pentacene. Simulated (black) and experimental (red) data are fit with a $\cos^2\theta$ peak. The zone-casting direction is 0° . This figure is reproduced from our published work.^[1]

The optimum needle orientation is correlated to the polar plots of absorbance as a function of polarization angle for single domains of TIPS- and TES- pentacene.^[3] In this study, a combination of angle-dependent polarised UV-Visible absorption and Raman spectroscopy were used to correlate the orientation of the various transition dipoles within the crystal structure. The 695 nm absorption peak, common to both TIPS- and TES- pentacene and red-shifted

from solution, is aligned with the pentacene-pentacene core stacking (crystallographic a-) axis. On the other hand, the high-energy 440 nm transition dipole lies along the pentacene short (crystallographic b-) axis. The extracted anisotropies ($\mu_0 \approx 5$ and ≈ 35 for TIPS- and TES-pentacene, respectively) are again similar to the dichroic ratios of the 695 nm absorption (≈ 3.2 and 16) as expected within a simple model.

The strong dependence of angular mobility encouraged us to re-examine the simulations. The internal reorganisation energies of TIPS- and TES- (Table 4.5) are significantly larger than that of pentacene (95 meV) and are expected to be much less than the total reorganisation energy (λ).^[66] Based on this assumption, the angular dependent mobilities could be calculated using a multi-scale modelling approach and a master equation non-adiabatic Marcus transfer rates.^[67–73] Further details of these calculations can be found in our published work.^[1] The crystal structures of TIPS-pentacene is well-known whereas the crystal structure of TES-pentacene had to be determined using a molecular mechanics approach (see Figure 4.16).^[1,7,26] The highest mobility for single-crystalline TIPS-pentacene structures was found at 33° relative to the a-vector of the unit cell ($\mu_{\text{TIPS}} = 0.33 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), whereas TES-pentacene exhibits best transport at an angle of $\approx 0^\circ$ ($\mu_{\text{TES}} = 0.16 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). These are indicated by the vertical lines on Figure 4.16. The over-estimation of mobility for modelled TES-pentacene could be due to crystal defects being particularly disruptive for one-dimensional charge transport.

Controlling the Molecular Packing using the Substrate Temperature

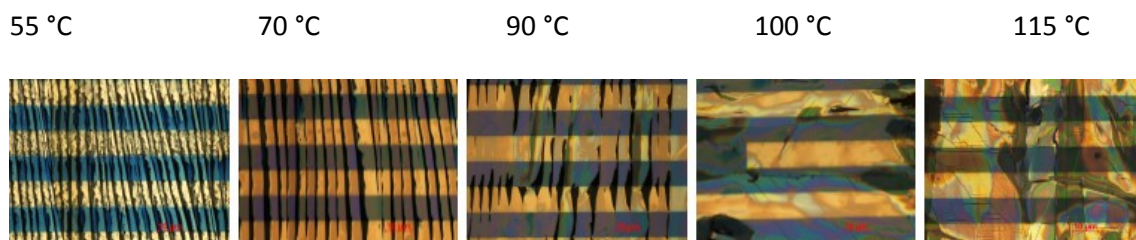


Figure 4.17: Montage of cross-polarised optical images (50× optical zoom) of TIPS-pentacene FETs cast at 55, 70, 90, 100 and 115° C. The substrate displacement rate is fixed ($500 \mu\text{m s}^{-1}$) to print highly aligned needles. The horizontal stripes are source and drain electrodes pre-patterned on the Si/SiO₂ substrate.

Having established that the substrate displacement rate has a profound impact on charge transport properties, the influence of substrate temperature on device performance is now examined. As demonstrated in Figure 4.3, increasing the substrate temperature increases the width of the needle-like domains, eventually resulting in the formation of transport-limiting cracks. Figure 4.17 shows cross-polarised images of TIPS-pentacene FETs fabricated at a range of substrate temperatures and show comparable features to the initial studies on microscope

slides. The substrate displacement rate is maintained at $500 \mu\text{ms}^{-1}$. At high substrate temperatures large platelet-like crystals cover the entire transistor channel and cracks start to appear along the long-axis of the pentacene core.

Charge Carrier Mobility

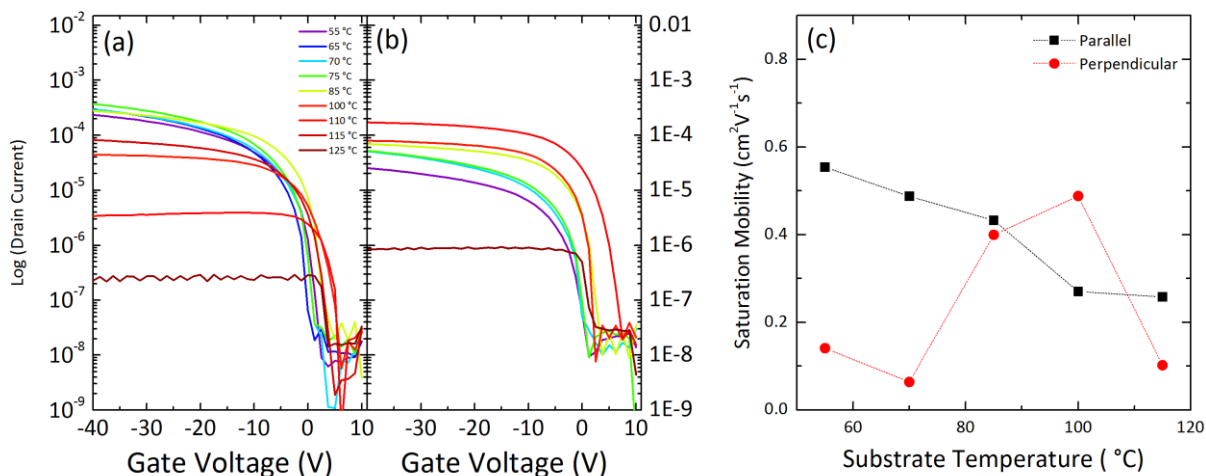


Figure 4.18: Transfer curves taken in the saturation regime ($V_{SD} = -40\text{V}$) for (a) parallel and (b) perpendicular TIPS-pentacene FETs. (c) Average saturation mobility as a function of substrate temperature for parallel (black) and perpendicular (red) devices.

It is interesting to compare the transfer curves for needles zone-cast parallel (a) and perpendicular (b) to the source-drain direction, as demonstrated in Figure 4.18. For parallel devices, the maximum ON-current and steepest sub-threshold slopes occur for the low substrate temperatures. This results in an average saturation mobility that decreases with increasing substrate temperatures. On the other hand, for perpendicular devices, the ON-current increases with increasing temperature until $\approx 100 \text{ }^\circ\text{C}$. The average saturation mobility peaks at $100 \text{ }^\circ\text{C}$, when the platelet-like crystals cover the entire device, and then decreases as pronounced cracking starts to occur. These findings demonstrate how detrimental thermally induced cracks are on charge transport.^[27]

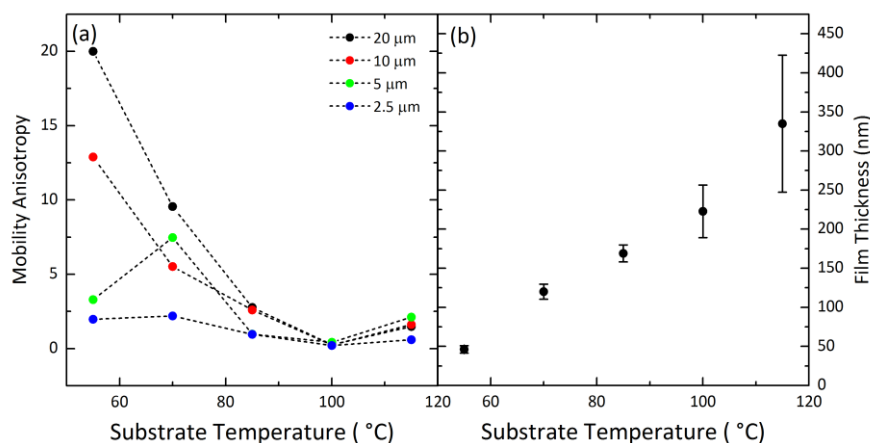


Figure 4.19: Mobility anisotropy ($\mu_{\text{parallel}}/\mu_{\text{perpendicular}}$) for devices with 20, 10, 5 and 2.5 μm channel lengths and average (b) film thickness as a function of substrate temperature

In Section 4.2 we established that the relative orientation between the zone-casting and charge transport direction determines the charge carrier mobility. When it comes to substrate temperature, the mobility anisotropy (Figure 4.19) is largest for devices deposited at low substrate temperatures, where narrow aligned needles result in a high mobility when the charge-transport is oriented in the direction parallel to the crystal domains and low mobility when it is perpendicular. High substrate temperatures increase the width of the crystal domains, which permit some charge transport perpendicular to the zone-casting direction and decreases the mobility anisotropy ($\mu_{\parallel} \approx \mu_{\perp}$). It is interesting to note that increasing the substrate temperature results in a significant increase in film thickness (Figure 4.19). For devices deposited at high temperatures there is a substantial variation in film thicknesses between devices, as the contact line is difficult to maintain. As charge is transported laterally in these BG BC FETs, film thickness is not expected to influence charge-transport, however increased disorder in thick films deposited at high temperatures could hinder the movement of charge carriers.

Uniformity of Molecular Packing in Zone-Cast Thin Films

The most efficient charge transport occurs when the molecules within the aligned needles are all oriented in the same direction. The homogeneity of molecular orientation and local molecular order across the zone-cast is evaluated by measuring the polarised Raman spectra at 10 ° intervals both in the channel and on the gold contacts. The small laser spot size ($\sim 1 \mu\text{m}$) allows us to investigate individual crystal domains. As the laser polarisation angle rotates from 0 – 360 °, the intensities of Raman active vibrational modes change. The intensity of the Raman modes

oriented along the $C - C_{\text{LONG}}$ and $C - C_{\text{SHORT}}$ can then be monitored function of excitation polarisation angle. The orientation of the pentacene core can be deduced from such polar plots.

In all cases, 0° is aligned along the zone-casting direction. Our group have previously demonstrated that the twinned molecular crystals result in mirror images of the polarised Raman plots, as the twin boundary is an axis of symmetry for the two grain orientations.^[3] To quantify the local molecular order the Raman anisotropy (Equation 2.5) can be calculated by evaluating the maximum and minimum Raman scattering intensity. Here, perfectly anisotropic = 1 and perfectly isotropic = 1. This investigation has been performed on both the TIPS-pentacene FETs considered here and zone-cast needles deposited on plastic substrates.^[2,3]

Figure 4.20 illustrates the polarised Raman spectra measured at 5 positions down a needle-like domain cast at $500 \mu\text{ms}^{-1}$. The orientation of $C - C_{\text{LONG}}$ (red) is maintained across the entire length of the crystal, aligned at $50 - 60^\circ$ to the zone-cast direction. The variation in $C - C_{\text{SHORT}}$ orientation is attributed to variations in the out-of-plane tilt down the needle. The Raman anisotropy of $C - C_{\text{LONG}}$ is greater on the contacts (b,d) (0.55 ± 0.1) than in the channel (a, c, e) (0.25 ± 0.2) indicating that the gold contacts impose a higher degree of molecular order, perhaps due to an interaction with the pentacene core.

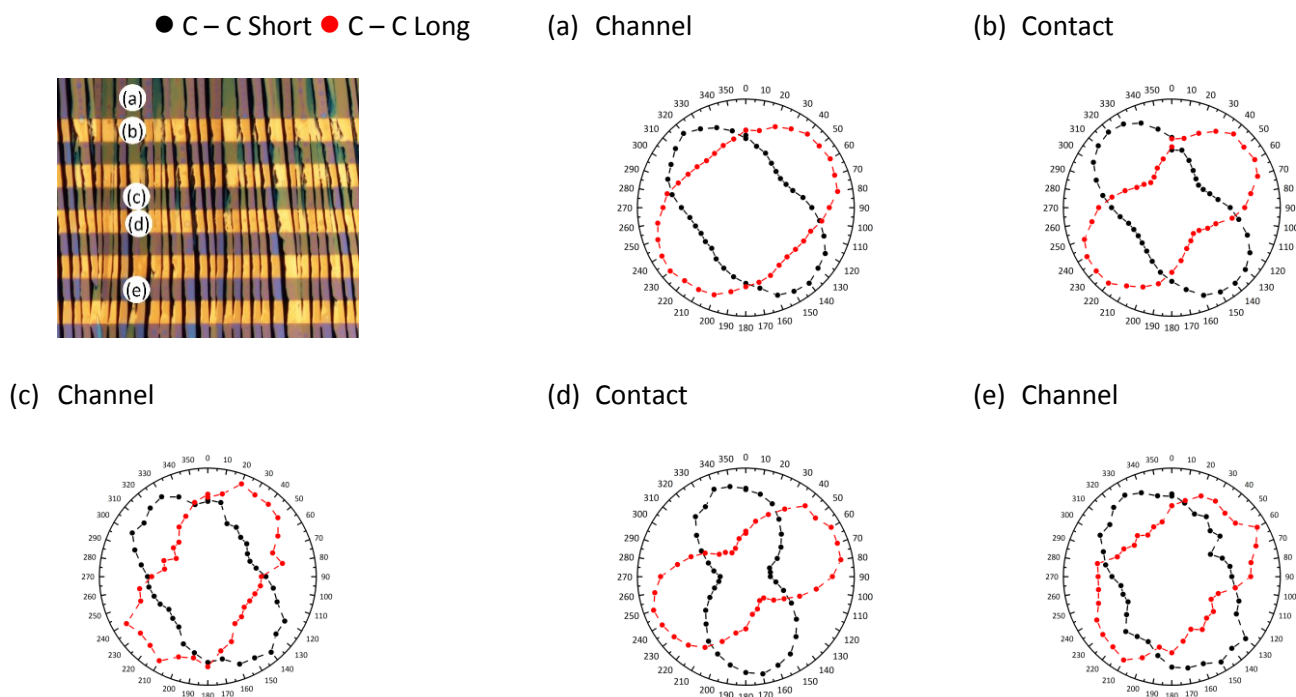


Figure 4.20: Orientation of the $C - C_{\text{LONG}}$ (red) and $C - C_{\text{SHORT}}$ (black) Raman modes at various points down a needle (a, c, e) on the channel and (b, d) on the contact.

In collaboration with Stuart Higgins, Department of Physics Imperial College London, needle-like domains of TIPS-pentacene ($500 \mu\text{m s}^{-1}$) were deposited on flexible plastic substrates.^[2] Narrow transistor channels ($L = 3 \mu\text{m}$) were defined using ultraviolet nanoimprint lithography, further details of which can be found in our published work.^[2] To confirm homogeneity across the device, the relative peak intensity of $C - C_{\text{SHORT}}$ relative to $C - C_{\text{LONG}}$ is measured at regular intervals across substrate (Figure 4.21 (a)). In these polar plots, perfectly anisotropic modes have an anisotropy (see Section 2.2.4.2) $= 1$ and isotropic modes $A_R = 0$. The step-like progression at the edges of the electrodes indicates that the molecules are not oriented in the same direction. In the channel, the $C - C_{\text{LONG}}$ and $C - C_{\text{SHORT}}$ vibrational modes were oriented $65 \pm 4^\circ$ to one another (Figure 4.21 (b)), whereas they were near perpendicular on the contact (Figure 4.21 (c)). Since these vibrational modes are orthogonal within the plane of the pentacene molecule, the relative orientation on the contact indicates that the pentacene core lies parallel to the substrate on the contact, whereas in the channel they are tilted out-of-plane. The maximum mobility achieved is $0.06 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, an order of magnitude lower than the typical values we expect for zone-cast needles. This is attributed to this mismatch in molecular orientation between the channel and contact, perhaps arising due to an unfavourable interaction between TIPS-pentacene and the surface treated plastic substrate.

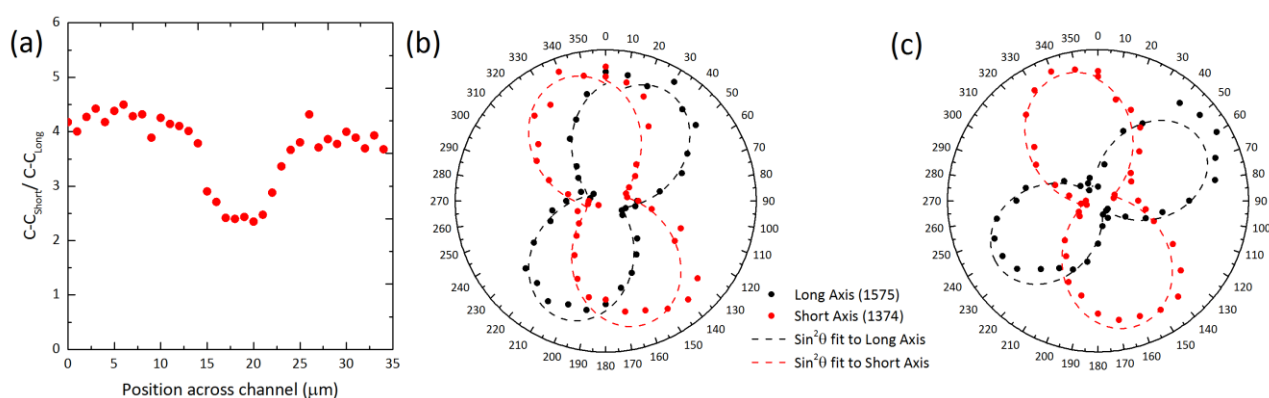


Figure 4.21: (a) Relative intensity of $C - C_{\text{SHORT}}/C - C_{\text{LONG}}$ across the contact-channel-contact. Angle-dependent polarised Raman plots of the $C - C_{\text{LONG}}$ (Black) and $C - C_{\text{SHORT}}$ (red) on the (b) channel and in the (c) contact.

4.3.4 Impact of Intermolecular Interactions on Molecular Packing and Optoelectronic Properties

We have established that TIPS- and TES- side groups can be attached to the 6,13 positions of the pentacene core to impart solubility, modify intermolecular interactions and control molecular packing in the solid-state. The electronic interactions between adjacent molecules, determined by the substituent diameter, was demonstrated to have strong implications on the optoelectronic and charge transport properties. We now apply our understanding of the spectroscopic signatures of intermolecular interactions of pentacene to identify the extent of isolation within a

host matrix. The guest-host system allows us to experimentally uncover the optoelectronic properties of non-interacting π -conjugated cores and exploit otherwise inaccessible electronic energy levels for novel device applications.

This study was performed in collaboration with Ke-Jie Tan and Iain Andrews in the Departments of Materials and Chemistry at Imperial College London, and considers the orientation of guest molecules pentacene and diazapentacene (DAP-1) within a *p*-terphenyl lattice is evaluated for use in room temperature MASERs. Organic molecules have been demonstrated as appropriate candidates to produce pulsed amplification of microwaves, but continuous wave (CW) operation has yet to be achieved.^[74,75] MASER operation exploits the accessible triplet sub-levels of pentacene molecules. A 585 nm laser is used to excite pentacene from ground to the first-excited singlet state (S_1), where it undergoes spin-selective intersystem crossing into the triplet ground states (T_1). The splitting of the T_x , T_y and T_z sub-levels is on the microwave length scale. The population inversion between the populous T_x and underpopulated T_z sub-levels ($x \leftrightarrow z$) that provides the conditions required for masing. In order to design a resonator cavity that optimises the output power, an understanding of molecular orientation of the guest-host system within the resonator cavity and guest (pentacene) within the host (*p*-terphenyl) lattice is essential. In an effort to identify an organic molecule suitable for CW operation DAP-1 is also considered.

Experimental Details

Pentacene doped *p*-terphenyl and diazopentacene (DAP) doped *p*-terphenyl crystals were grown in an open system zone-melting technique.^[76,77] 0.1 mol/mol % pentacene or DAP in *p*-terphenyl were loaded into the in-house zone-melting system. The melt zone was sweep up along the pentacene doped *p*-terphenyl at a rate of 1mm/hour in flowing purified argon gas (99.999%) at 1 atmospheric pressure. The pentacene was purified by vacuum ($\sim 10^{-5}$ - 10^{-6} mbar) sublimation and *p*-terphenyl was purified by close system zone refinement technique. The resulting crystals are 10 – 20 cm long and 1 – 2 cm in diameter, containing ≈ 0.01 % pentacene and DAP-1 molecules.^[75]

Reference single crystals of millimeter-size neat pentacene single crystals were grown using physical vapour transport (PVT) method.^[78] Purified pentacene was sublimed and crystallised at a cooler region in a lab-made two zone furnace under the flow of purified Argon gas (99.999%) at 1 atmospheric pressure. Commercial pentacene powder (99%) bought from Sigma Aldrich was purified by vacuum ($\sim 10^{-5}$ - 10^{-6} mbar) sublimation prior the crystal growth.

DFT Simulation

The Raman spectrum of pentacene is well-known from literature and our assignments are based upon DFT simulations at the 6-31G(d,p) level of theory.^[23,59,79,80] Akin to TIPS- and TES-pentacene in 4.3.2, under non-resonant conditions the intramolecular vibrational modes observed in the range 1100-1200 cm^{-1} (Figure 4.22) originate from in-plane bending of the C – H bonds on the ends (1) and sides (2) of the molecule. In the range 1300 – 1650 cm^{-1} the Raman spectrum is dominated by aromatic C – C symmetric stretching modes, along the short (3, 4, 5) ($\text{C} - \text{C}_{\text{SHORT}}$) and long (6) axis ($\text{C} - \text{C}_{\text{LONG}}$) of the molecule.

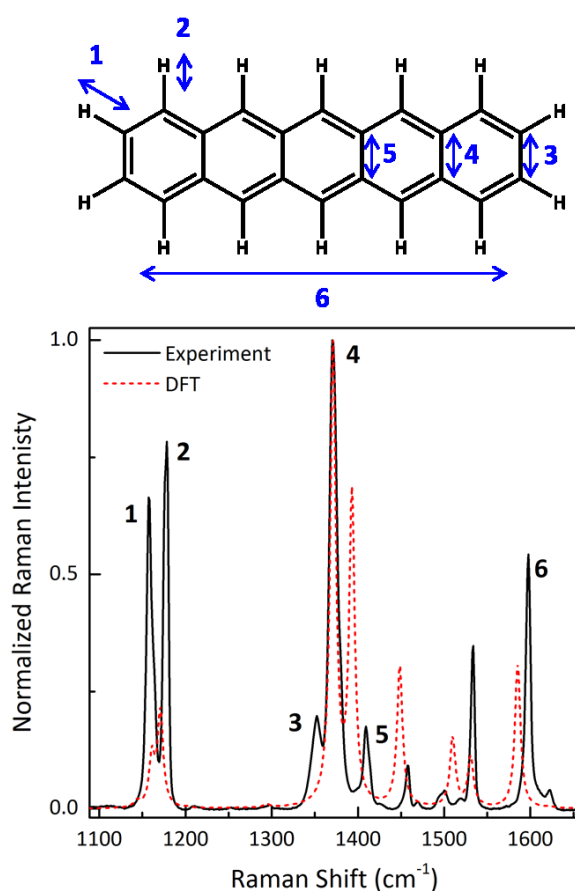


Figure 4.22: Experimental and simulated Raman spectra for a pentacene thin film and isolated molecule. The main vibrational modes are indicated. Simulated Raman spectra are scaled by 0.971.

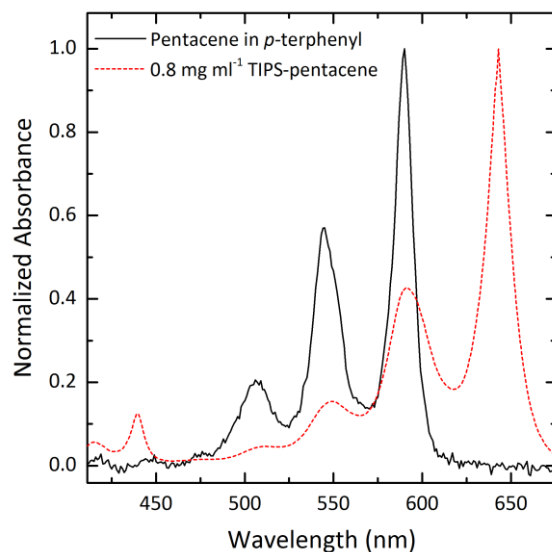


Figure 4.23: Normalised UV-Visible absorption spectra of pentacene in a *p*-terphenyl lattice (black) and TIPS pentacene solutions (red).

The similar lengths of pentacene and *p*-terphenyl (pentacene ≈ 14 Å, *p*-terphenyl ≈ 12.5 Å) result in pentacene molecules which are physically and electronically isolated from one another when dispersed in a *p*-terphenyl lattice. The absorption of isolated pentacene is compared to solution absorption of dilute TIPS-pentacene (Figure 4.23). The *p*-terphenyl lattice absorbs at high energy (< 300 nm) and is negligible in this region. It is interesting to note that the nature of the singlet excited state changes as acene length increases; for naphthalene S_1 is polarised along the long-axis of the acene core, whereas for anthracene and above it is polarised along the short-axis.^[81] The energetic spacing of the first absorption band is similar for unsubstituted and TIPS-pentacene, because the acetylene linker effectively insulates the TIPS- side groups from the pentacene core. The first electronic transition (centred at 590 nm) is much narrower than the rest of the vibronic progression. This occurs because within a *p*-terphenyl lattice pentacene can adopt one of four sites, where differences in local environment change the vibrational energy levels.^[82,83] For pentacene, the spacing of the vibronic replicas corresponds to vibrational modes at 1433 and 1380 cm^{-1} , which correspond to the short-axis stretch. The bulky side groups change the oscillator strengths of the absorption bands.

Vibronic	TIPS-Pentacene	Pentacene
	$S_0 \rightarrow S_1$	
0-0	643	590
0-1	591	544
0-2	548	506
0-3	508	475

Table 4.6: UV-Visible absorption peaks of TIPS-pentacene in toluene solution and pentacene in a p-terphenyl lattice. All values are quoted in nm.

Raman Spectroscopy

P-terphenyl is a highly Raman active small molecule where three phenyl rings are connected by single bonds.

Table 4.7 details the nature of the main vibrational modes based on a DFT simulation (B3LYP at 6-31 G(d,p) level of theory) and literature.^[84] Strong vibrational modes are assigned to inter-unit stretch modes (1273 cm^{-1}) and long-axis vibrations in the phenyl rings (Figure 4.24 (b)) $1604, 1591\text{ cm}^{-1}$). *P*-terphenyl is not resonant in any of the excitation wavelengths used here (785, 633, 514, 488 and 457 nm) and neither the positions nor relative intensities of the Raman bands change Figure 4.24 (c). The high relative concentration compared to pentacene means that irrespective of the choice of laser their Raman peaks dominate the blend spectra.

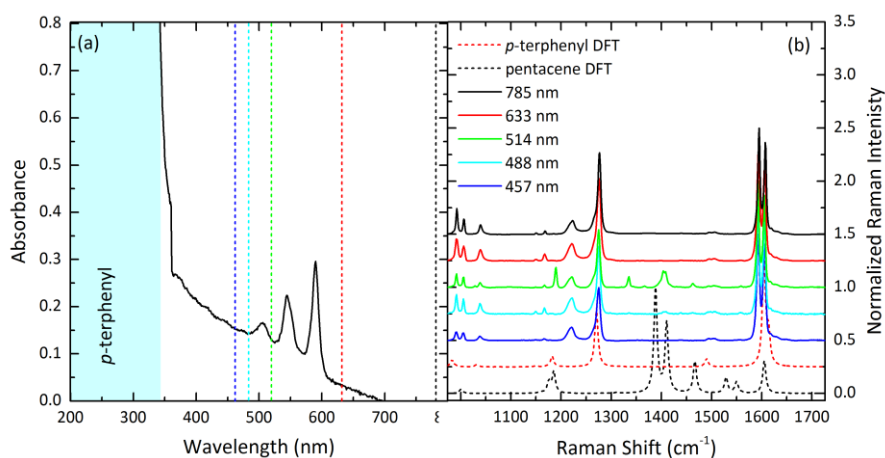


Figure 4.24: (a) Absorption of isolated pentacene in p-terphenyl lattice (b) Normalised Raman spectra of pentacene in a p-terphenyl lattice collected at 785, 633, 514, 488, 457 nm and the simulated Raman spectra of pentacene and p-terphenyl.

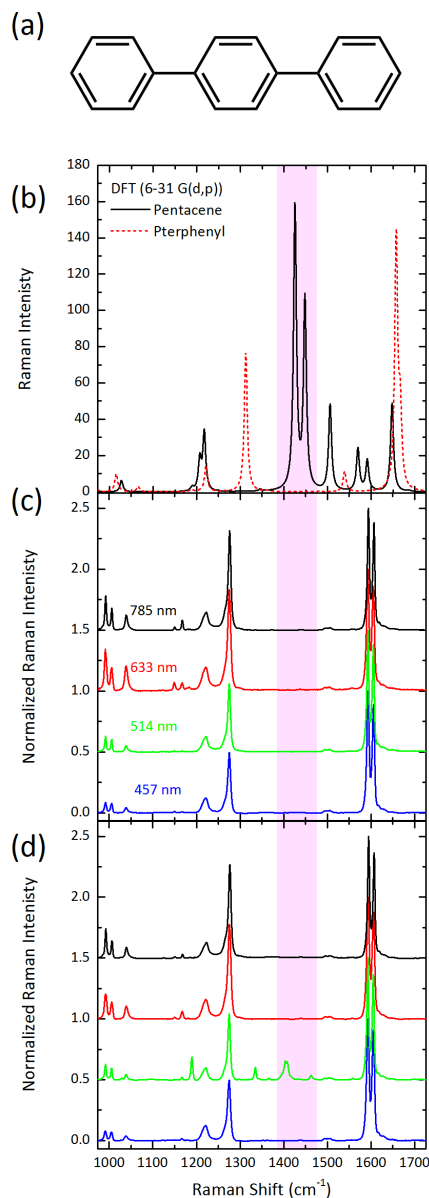


Figure 4.25: (a) Molecular structure of *p*-terphenyl (b) uncorrected DFT simulated Raman spectra of pentacene and *p*-terphenyl and Raman spectra acquired at 785, 633, 514 and 457 nm of crystals of (c) pure *p*-terphenyl (d) *p*-terphenyl doped with pentacene (0.01 %), normalised to the 1591 cm^{-1} *p*-terphenyl mode.

Compared to the pure *p*-terphenyl lattice, pentacene doped *p*-terphenyl excited at 514 nm displays a new feature at 1404 cm^{-1} . 514 nm resonantly excites the $S_0 \rightarrow S_1$ transition of pentacene, shown above to be directed along the short-axis of the pentacene core, and is close to the MASER excitation wavelength (585 nm). This vibrational mode is assigned to the short-axis C – C stretch of isolated pentacene. The Raman frequencies of C – C_{SHORT} are slightly higher than in the thin-film and are comparable to the simulated unscaled gas-phase Raman spectra. The main changes are detailed below (Table 4.7). The enhancement of Raman scattering associated with resonant excitation allows detection of the low concentration guest (pentacene) in the host (*p*-terphenyl) matrix.

Table 4.7: Observed Raman frequencies and approximate descriptions for p-terphenyl and pentacene doped p-terphenyl, excited with a 514 nm excitation.

<i>p</i> -terphenyl	Pentacene doped <i>p</i> -terphenyl	Vibrational Mode
cm⁻¹		
773	773	In-plane ring vibration
	795	<i>In-plane ring vibration</i>
991	991	In-plane ring deformation
1005	1005	C-H deformation
	1028	
1038	1038	C-H deformation
	1167	<i>C-H ends</i>
	1189	<i>C-H sides</i>
1221	1221	C-H sides
1273	1273	Inter-ring C – C Stretch
	1335	
	1404	<i>C – C_{SHORT} Stretch (central)</i>
	1408	<i>C – C_{SHORT} Stretch (middle)</i>
	1462	<i>C – C_{SHORT} Stretch (ends)</i>
1591	1591	C – C_{LONG} Axis Stretch
1604	1604	C – C_{LONG} Axis Stretch

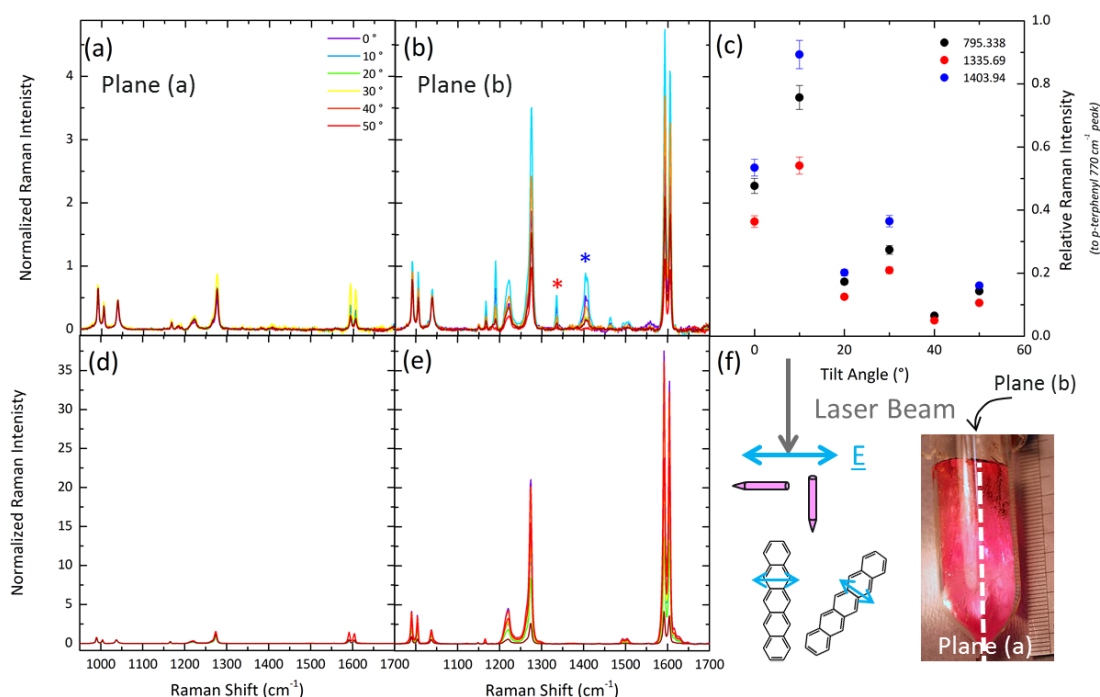


Figure 4.26: Raman spectra of (a,b) pentacene doped and (d,e) pure *p*-terphenyl at different tilt angles. The spectra in (a) and (d) are collected parallel to the direction of zone-translation and (b) and (e) are perpendicular. All Raman spectra are normalised to the 770 cm⁻¹ *p*-terphenyl vibrational mode. (c) shows the intensities of the pentacene modes at 795, 1335 and 1404 cm⁻¹ relative to *p*-terphenyl as a function of tilt angle. When the electric field of the laser is in the plane of the vibrational mode, the Raman signal is enhanced. The photograph of the zone-refined crystal was obtained by Ke Jie Tan.

The cylindrical crystals have two planes, parallel and perpendicular to the direction of zone-translation. The Raman scattering from both pentacene and *p*-terphenyl is markedly weaker when the excitation is parallel to zone-translation (a,d) as opposed to perpendicular (b,e). The detection of the C – C_{SHORT} dopant pentacene molecules (blue and red asterisk) is only possible in (b), and decreases with increasing tilt out-of-plane (c). When evaluating Raman spectra from tilted molecules, it is important to remember that the Raman signal is strongest when the electric field of the laser is parallel to a particular vibrational mode. These results indicate that the pentacene molecules are standing upright in the *p*-terphenyl lattice, with their long axes parallel to the direction of zone-translation. As pentacene molecules are understood to adopt one of four *p*-terphenyl lattice sites, it is reasonable to assume a similar orientation for *p*-terphenyl molecules.^[83] This also explains the reduced Raman scattering of both doped and pure *p*-terphenyl when the Raman excitation is parallel to the direction of zone-melting.

Molecular Orientation within the *p*-terphenyl lattice

In order to determine which lattice site pentacene occupies within the *p*-terphenyl lattice the FWHM of the *p*-terphenyl molecules is measured before and after doping. The FWHM of a Raman active mode is sensitive to the range of conformational states that the molecules within the thin film adopt. The *p*-terphenyl modes are narrower in the doped crystals ($\text{FWHM}_{1591} \approx 4 \text{ cm}^{-1}$) than the pure crystal ($\text{FWHM}_{1591} \approx 5.5 \text{ cm}^{-1}$), which indicates that pentacene adopts a site that minimises the disorder of *p*-terphenyl. Applying this understanding to the *p*-terphenyl configuration described by Güttler *et al*, we predict pentacene preferentially adopts one of only two positions within the crystal (explicitly the 'M₃ or M₄ position' described in the reference).^[83]

Impact of Nitrogen Substitution on Molecular Packing

In an effort to achieve CW MASER operation, we manipulate the guest molecule chemical structure to increase intersystem crossing rates. In diaza-substituted oligoacenes two C – H moieties are replaced with nitrogen atoms, which decreases the reorganisation energy for electron transfer, increases solubility and promotes sheet-like packing in the solid state with short interlayer distances.^[85] Whilst they are reported to show accelerated ISC compared to unsubstituted forms, effective isolation has not yet been reported and this study looks to evaluate their potential in MASER devices.^[86]

DFT Simulation

Geometrical optimisation at the B3LYP/6-31 G(d,p) level of theory reveals that substitution with electronegative nitrogen at the 6,13 positions has negligible effects on the lengths of the C – C_{LONG} or C – C_{SHORT} bonds (Figure 4.27). On the other hand, the C-N bonds are shorter than the C – C bonds and the CNC angles are below 120 ° ($\approx 116^\circ$), which maximises the *s* character of the nitrogen lone-pair orbitals. The simulated Raman spectra for DAP-1 and pentacene are compared in Figure 4.27 (a) and are markedly similar, with DAP-1 displaying additional modes arising from the C – N bonds (simulated: 1315, 1500 cm^{-1} , observed: 1354, 1475 cm^{-1}). The nature of the simulated Raman modes of DAP-1 are confirmed by comparing the non-resonant (785 nm) and resonant (514 nm) Raman spectra of a polycrystalline sample to DFT simulations (Figure 4.27 (b)). The C – C_{SHORT} axis is composed of three modes representing contributions from the 1 (1460 cm^{-1}), 3 (1402 cm^{-1}) and 7 (1388 cm^{-1}) bonds indicated in Figure 4.27 (c).

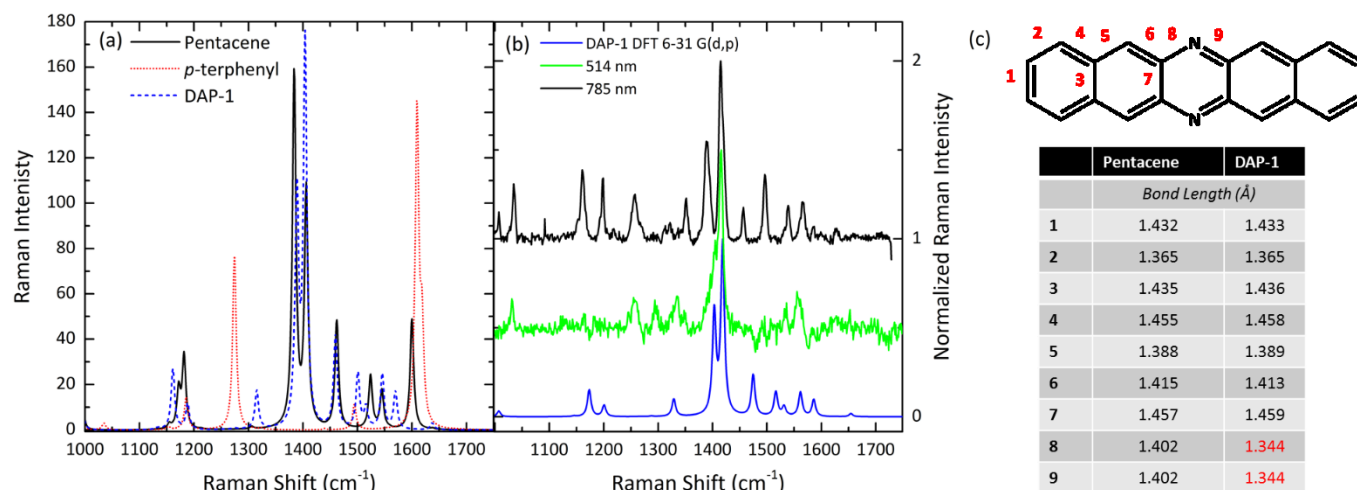


Figure 4.27: (a) Simulated Raman spectra of pentacene, p-terphenyl and DAP-1. (b) Raman spectra acquired at 785 and 514 nm for DAP-1 compared to the simulated spectra. (c) Molecular structures and bond lengths.

UV-Visible Absorption

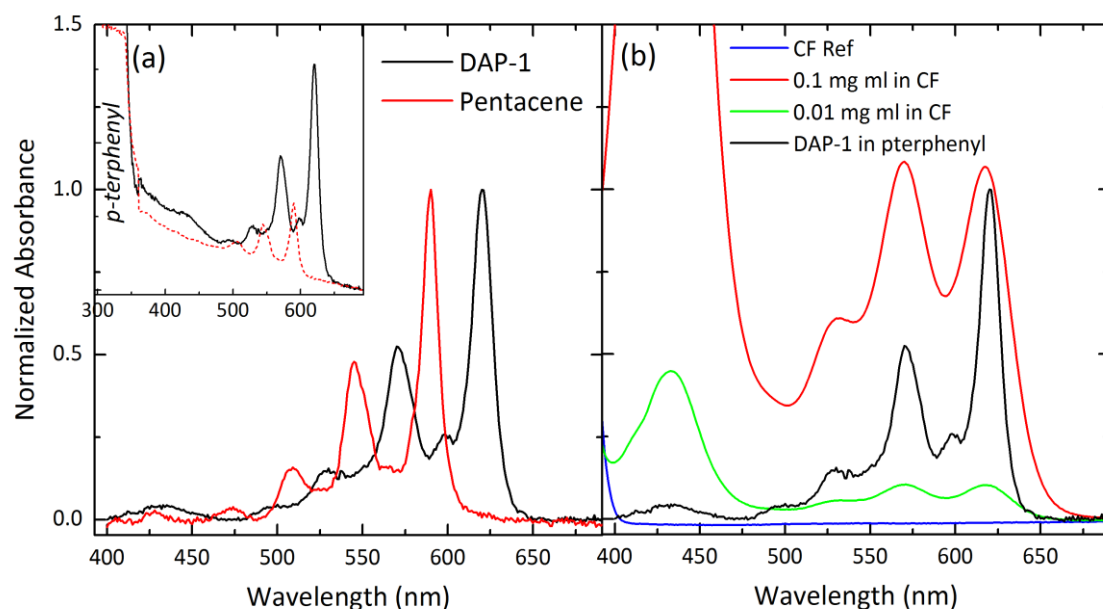


Figure 4.28: (a) Normalised absorption spectra of 0.1 % pentacene and DAP-1 in p-terphenyl. Inset: raw absorption spectra. (b) A comparison of the crystal and solution absorption spectra of DAP-1. The solvent (chloroform) absorption is also included.

Figure 4.28 compares the absorption of isolated DAP-1 and pentacene. The absorption spectra of DAP-1 is red-shifted compared to pentacene, but the vibronic spacing is maintained ($\approx 1400 \text{ cm}^{-1}$) and corresponds to a vibrational mode along the C–C_{SHORT} axis. The energetic similarities between the $S_0 \rightarrow S_1$ transition for DAP-1 and pentacene make it a promising candidate for maser applications, as excess energy can heat the system via non-radiative internal conversion and ISC. The HOMO-LUMO energy levels and associated isosurfaces of DAP-1 and pentacene are simulated using TD-DFT (Figure 4.29). Introduction of electronegative nitrogen atoms stabilises the HOMO level compared to the

LUMO. The calculated HOMO – LUMO energy gap is 2.17 eV for pentacene and 2.22 eV for DAP-1, which corresponds to a calculated red-shift of ≈ 8 nm (observed ≈ 29 nm). Compared to unsubstituted pentacene, DAP-1 contains the same total number of π -electrons and whilst the π -electron distribution in the LUMO is similar, the contribution of the outer rings to the HOMO energy level is more significant (Figure 4.29). This increase in electron density results in increase resonant Raman scattering from the outer ring C – C_{SHORT} bonds compared to the inner rings (i.e. bonds 1 and 3 in Figure 4.27 (c)).

Vibronic	Pentacene		DAP-1		DAP-1	
	λ	Splitting	λ	Splitting	λ	Splitting
$S_0 > S_1$	nm	cm ⁻¹	nm	cm ⁻¹	nm	cm ⁻¹
0-0	590	1433	619	1420	617	1336
0-1	544	1380	569	1401	570	1324
0-2	506	1379	527	1186	530	
0-3	475		496			

Table 4.8: UV-Visible absorption peaks of pentacene and DAP-1 in a p-terphenyl lattice and in a dilute chloroform solution and their spacing in cm⁻¹

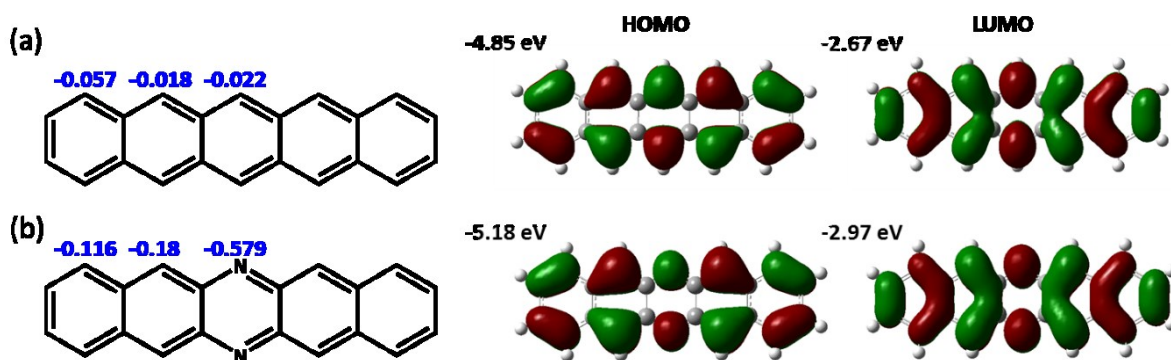


Figure 4.29: Mulliken charges for (a) pentacene and (b) DAP-1. The isosurfaces of the HOMO and LUMO and simulated energy levels are provided. Nitrogen substitution reduces the HOMO energy level. The isovalue is 0.02.

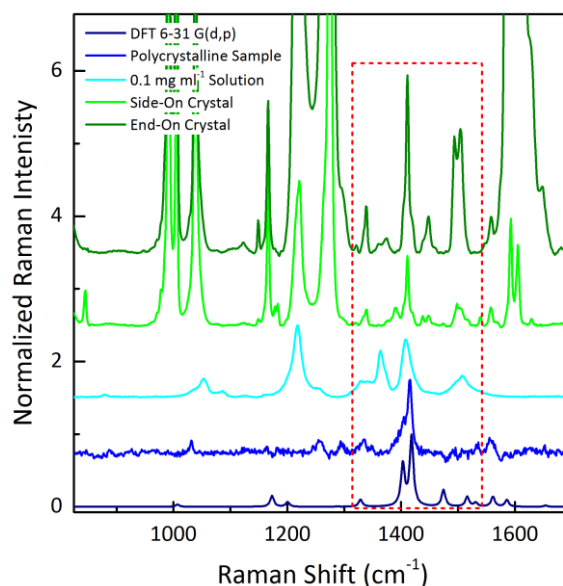


Figure 4.30: Normalised Raman spectra of DAP-1 polymorphs: polycrystalline (dark blue), dissolved in a 0.1 mg ml⁻¹ chloroform solution (pale blue) and isolated in a *p*-terphenyl lattice (green). The red dashed box indicates the region of interest for study of DAP-1 molecules.

Compared to insoluble pentacene, the ability to solution process DAP-1 allows investigation in thin-film and polycrystalline structures, as well as isolated in dilute solution (chloroform) and zone-melted in a *p*-terphenyl lattice. Equivalent to unsubstituted pentacene, the main Raman mode is the C – C_{SHORT} axis stretch. The resonant enhancement of Raman scattering at 514 nm also allows detection of DAP-1 in the isolated *p*-terphenyl lattice (Figure 4.30). When DAP-1 is isolated from neighbouring molecules (dissolved in chloroform and in the guest-host system) the dominant peaks are from the surrounding medium, nevertheless, Raman modes from DAP-1 are observed between 1300 – 1500 cm⁻¹ (indicated by a red box in Figure 4.30). In the guest-host system DAP-1 exists in a particularly narrow range of conformational states, as evidenced by the narrow FWHM of the C – C_{SHORT DAP-1} Raman modes. The broader peaks in the solution state indicate even at these low concentrations there is some aggregation of the DAP-1 molecules, which is likely due to strong bonds between the lone pair of nitrogen and adjacent DAP-1 molecules. These attractive N-C(H) bonds have been described elsewhere as providing the sheet-like stacking of aza-acenes.^[85] Equivalent to unsubstituted pentacene, the Raman scattering of the DAP-1 is strongest when excited in the plane perpendicular to the direction of zone-translation (dark green vs light green in Figure 4.30). In order to evaluate the DAP-1 orientation within the *p*-terphenyl lattice, the FWHM of *p*-terphenyl modes is monitored in neat and doped zone-melted crystals.

The FWHM of the main C – C_{LONG} vibration at 1591 cm⁻¹ increases on doping with DAP-1 (FWHM₁₅₉₁ neat ≈ 5.5 cm⁻¹, FWHM₁₅₉₁ DAP-1 ≈ 6.9 cm⁻¹) which implies that DAP-1 disrupts the packing of *p*-terphenyl.

4.3.5 Summary

The charge transport anisotropy of pentacene-based molecular thin films was investigated using bottom-gate bottom-contact FET substrates onto which TIPS- and TES-pentacene were zone-cast. For both materials, devices with needles oriented parallel to the charge transport direction had a higher mobility ($\mu_{|| \text{ TIPS}} = 0.67 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_{|| \text{ TES}} = 0.037 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) than those oriented perpendicular ($\mu_{\perp \text{ TIPS}} = 0.11 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_{\perp \text{ TES}} = 0.0048 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). In longer channel length ($L \geq 10 \text{ }\mu\text{m}$) devices with a dense population of needles, the mobility perpendicular to the needles decreases $\mu_{\perp} = 0.07$ to $0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ as needle width decreases from 2.20 to $0.97 \pm 0.25 \text{ }\mu\text{m}$. The highest mobility of TIPS-pentacene is obtained when needles are cast at $\sim 30^\circ$ to the charge-transport direction, whereas in TES-pentacene the highest mobility is obtained when the needles are parallel. The measured optimum orientation and associated charge-transport anisotropies agree well with simulations using a multi-scale modelling approach with Marcus transfer rates. The differences in mobility and mobility anisotropy between TIPS- and TES- pentacene can be explained with calculation of the direction dependent hole mobility in single crystals of the materials using a hopping transport formalism. The substantial agreement between experimental and theoretical results confirms zone-casting as a reliable and reproducible solution processing technique that enables control to be exercised over the morphology and molecular alignment within working organic devices. These studies help us to confirm the origin of the charge-transport anisotropy within crystalline organic thin films; controlled predominantly by the packing structure (and hence direction of the π - π interactions) within the crystal grains. By addressing the issues of molecular alignment across the device, we can better optimise performance and further our understanding of how calculated packing structures link to charge-transport anisotropy.

We have identified the spectroscopic signatures of isolated molecules, namely pentacene and DAP-1. The sensitivity provided by resonant Raman spectroscopy allows the detection of isolated π -conjugated core within a *p*-terphenyl lattice. The electronegative nitrogen atom in DAP-1 stabilizes the HOMO energy level and decreases π -electron delocalisation across the central ring, providing a relative increase in the resonant Raman scattering from C – C_{SHORT} bonds at the ends of the molecule. Attractive N-C(H) interactions promote short interlayer packing between sheets of π -stacked DAP-1 molecules and causes even dilute solutions to aggregate. The Raman scattering from

isolated pentacene and DAP-1 is stronger when excited perpendicular to the direction of zone-translation, which can be used as a simple marker of molecular orientation within a MASER crystal. The *p*-terphenyl lattice site occupied by pentacene is identified as one which minimises conformational disorder of the host system, whereas for DAP-1 the opposite is true. The distinct electronic and vibrational signatures of isolated acenes makes these promising candidates as analytical tools to probe the interactions between guest molecules within an organic crystalline host, alongside determining the optimal crystal orientation for masing applications.

4.4 Impact of Chemical Structure on Molecular Packing in Zone-Cast Phthalocyanines

Amongst the numerous high performance small molecule organic semiconductors that have been reported, electron-rich phthalocyanines (PCs) afford great popularity in organic electronics owing to their extraordinary stability, unique electronic structures and strong intermolecular interactions. Akin to the functionalised pentacene derivatives in Section 4.3, functionalising the phthalocyanines with side groups can improve solubility and determine the molecular packing. We have previously demonstrated the use of zone-casting to achieve highly aligned thin-films of small organic molecules with impressive charge carrier mobilities. For phthalocyanines deposited from solution the device performance is strongly related to the molecular packing motif and degree of π -orbital overlap.^[87–90]

To establish zone-casting as a robust technique that can be applied to a range of small molecule systems, not just the functionalized pentacenes considered previously, we compare three phthalocyanine derivatives, where thiophene has been incorporated at the α -positions (on the outer 5 member rings): TPc (metal free thiophene fused porphyrazine), soluble zinc phthalocyanine (ZnPc) and TZnPc, a structural isomer of TPc with a central metal atom^[90] The molecular structures are illustrated in Figure 4.31. Solubilising at the α -position of the PC does not inhibit the conjugated molecular packing, leaving the high electron density cores of adjacent molecules free to interact, but does result in four regioisomers. The small central Zinc atom is not expected to modify the molecular symmetry (D_{4h}). The high electron-density donor thiophene side groups in TZnPc (vs. benzene in ZnPc) modify the shapes of the frontier molecular orbitals, which in turn impact the strength of intermolecular interactions between neighbouring phthalocyanines. Zone-casting has been demonstrated as an appropriate technique to process highly oriented films of soluble phthalocyanines over large areas and is used here to deposit aligned films of TZnPc.^[35] Finally, we evaluate the morphological and thermal stability of the aligned samples.

4.4.1 Experimental Details

TPc, ZnPc and TzPc, were provided by Abby Casey, Department of Chemistry, Imperial College London. Unless otherwise stated, the materials were dissolved in chlorobenzene at a concentration of 20 mg ml^{-1} . The solutions were left to stir overnight at $T = 90^\circ \text{C}$. For basic characterisation of the optoelectronic properties, films were spin coated onto clean quartz substrates. Cleaned quartz substrates were plasma ashed before being covered with polymer solution, before being spun at 1500 rpm for 60 seconds. Unless otherwise stated, substrate displacement rate was fixed at $100 \mu\text{ms}^{-1}$, to ensure similar thicknesses to spin-coated films.

4.4.2 Optoelectronic Properties

UV-Visible Absorption

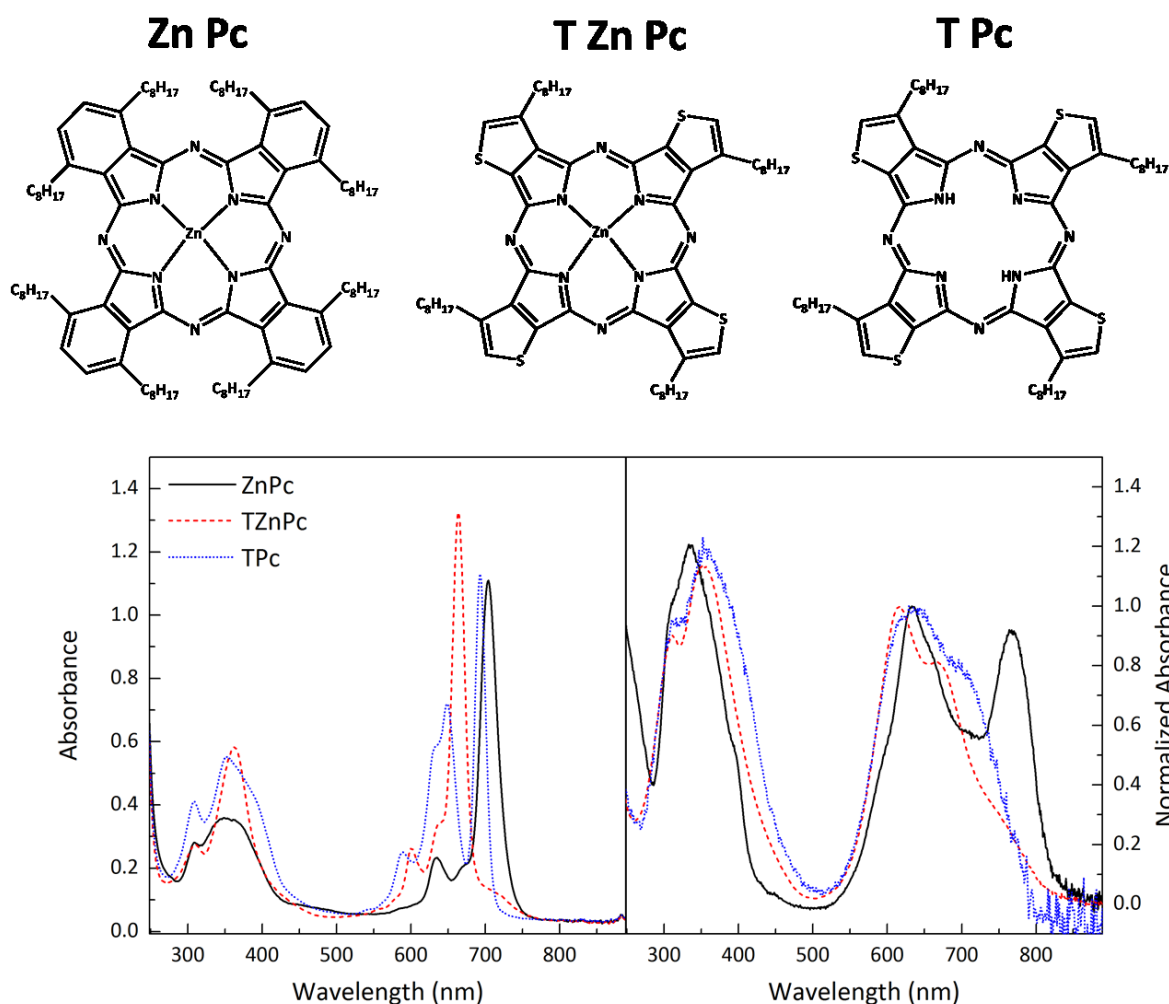


Figure 4.31: The molecular structures of the three materials considered in this work: Zinc Phthalocyanine (ZnPc, black solid) and Thiophene Zinc Phthalocyanine (TZnPc, red dashed) and metal-free Thiophene Phthalocyanine (TPc, blue dotted) and their associated UV-visible absorption spectra in the solution (left) and solid state (right), normalised to the Qx-band absorption peak ($\approx 600 \text{ nm}$). The TZnPc is one of four regioisomers, discussed further below.

The highly delocalised π -electron phthalocyanine core results in a particularly low energy gap compared to other small molecules.^[91] All three materials considered here display two prominent absorption bands; the Q- and B-bands. Q-band absorption occurs in the visible region (800 – 500 nm), whereas the B-band is responsible for the strong absorption in the ultra-violet between 450 – 250 nm (Figure 4.31). The Q-band absorption arises from a π - π^* HOMO-LUMO transition.^[92] The splitting of the Q-band, most pronounced in ZnPc, is due to the difference in symmetry of the frontier molecular orbitals (HOMO – a_{1u} and LUMO – e_g) that results in a doubly degenerate first excited state (Q_x and Q_y bands).^[93]

TD-DFT provides a means to confirm the nature of these electronic transitions for the novel material (TZnPc). For these simulations the CAM-B3LYP/6-31G+(d,p) level of theory were used. Considering the first 12 excited states of the small molecule, three transitions are identified with oscillator strengths > 0.4 at 630 nm (0.48), 574 nm (0.37) and 322 nm (0.85), described in Figure 4.32. The two absorption bands correspond well with the Q- and B-band described above. The lowest energy transition corresponds to the HOMO-LUMO transition. The associated isosurfaces shows that the HOMO is mainly localised on the C – N bonds in the pyrrole units, with some density on the adjacent thiophene rings, and the LUMO is localised over the C = N bonds of the inner macrocycle and C = C pyrrole bonds. Significantly, this transition does not have any charge transfer to the outer thiophene units. The nature of the higher energy transition (HOMO – 1 and HOMO – 2 to LUMO) has significant contributions from the outer thiophenes. The isodensity surfaces of the deeper occupied orbitals (HOMO – 1, HOMO -2) are mainly located on the outer rings.

State	Configuration	Oscillator Strength	Transition Energy (eV)	λ (nm)
S1	167 $\rightarrow$ 168 (68 %)	0.467	1.97	630
S1	167 $\rightarrow$ 169 (67 %)	0.368	2.16	574
S2	164 $\rightarrow$ 168 (65 %)	0.856	3.83	323

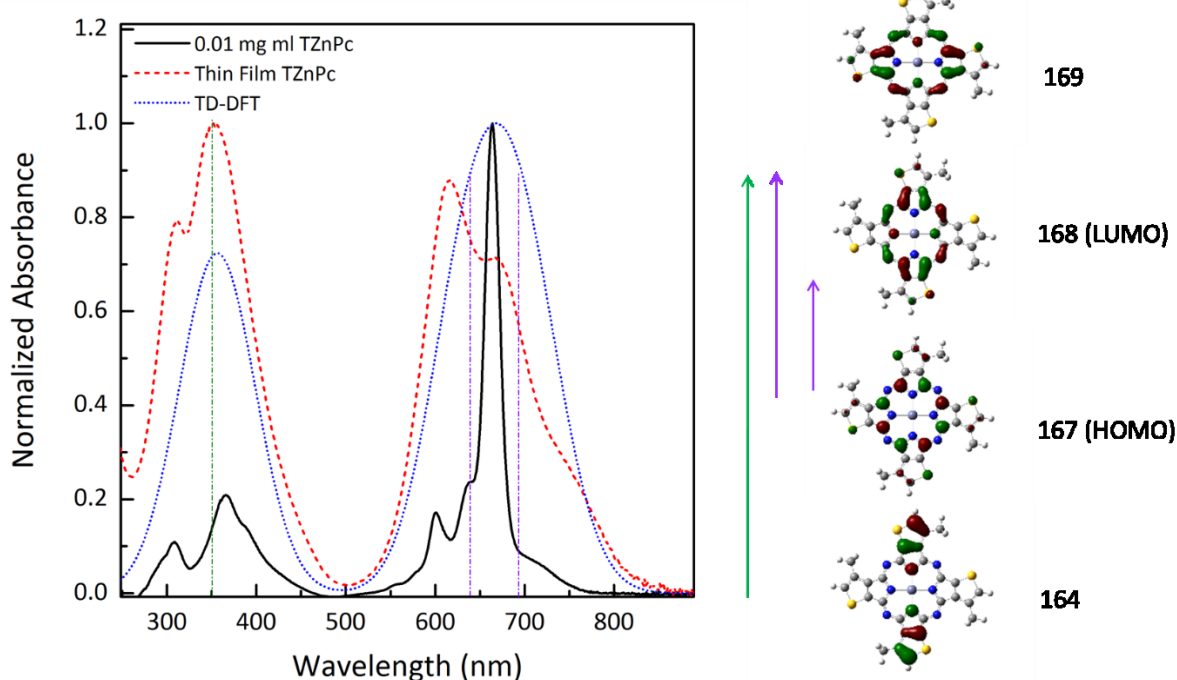


Figure 4.32: TD-DFT calculation of UV-visible absorption spectrum showing two strong contributions from S_1 and S_2 states. Table shows the contributions to these states from different molecular orbitals and the electron isodensity surfaces (isovalue = 0.04 atomic units).

Isodensity surfaces of the HOMO – 1, HOMO, LUMO and LUMO + 1 of ZnPc and TPc are provided for comparison (Figure 4.33). The surfaces are similar for TZnPc and TPc. For ZnPc, our simulations correspond well to published results.^[93] The HOMO shows increased delocalisation across the benzene rings compared to thiophene units, which predicts a wider-band gap for ZnPc vs. TZnPc.

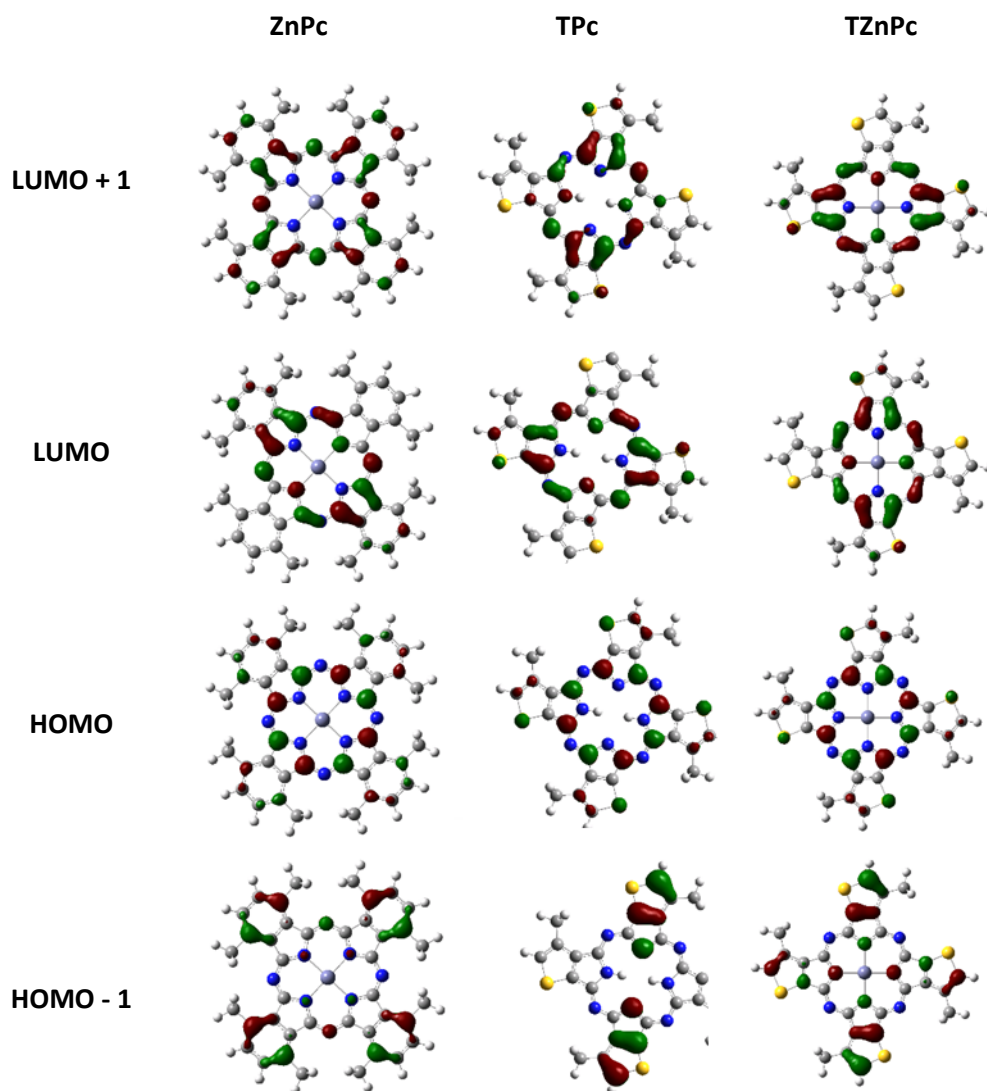


Figure 4.33: Isodensity surfaces for the LUMO + 1, LUMO, HOMO and HOMO – 1 of ZnPc, TPc and TZnPc generated using TD-DFT with the CAM-B3LYP functional at the 6-31G+(d,p) basis set. The isovalue is 0.04.

In the solid-state PCs arrange in a herringbone structure, self-assembling in a series of columnar stacks where the central PC ring is tilted relative to the axis of the stack.^[94] Within this herringbone arrangement a range of polymorphs exist, categorised by their tilt-angles between molecules and stacking axes.^[94,95] The most common α - and β -phases of ZnPc possess identical inter-planar distances (3.4 Å) with tilt-angles of 26.5 and 45.8 °, respectively.^[94] The tilt-angle determines the relative orientation of adjacent transition dipole moments, which in turn determine the positions of the frontier molecular orbitals and describe how the thin films will absorb light.^[96–98] It is even possible to deduce the inclination of phthalocyanine stacks (i.e. the phase) from the relative intensities of the absorption peaks of the Q_x and Q_y bands. For example, a low intensity high-energy absorption peak (Q_x) indicates the stable β -phase polymorph.^[94,99–101] As for TIPS- and TES-pentacene described in 4.3.2, the deposition conditions during solution processing determine the solid-state packing structure.^[1,3,99,102–104]

For the majority of phthalocyanine derivatives, the strong interaction between neighbouring electron-rich π -systems forces adjacent phthalocyanines to stack face-to-face (H-aggregation, Figure 4.34).^[105,106] Self-assembly in head-to-tail structures results in π -electron states that can delocalise over only parts of the aggregate (J-aggregation).^[107–110] H-type face-to-face stacked PC dimers are non-photoactive, while J-aggregates are photoactive.^[111] The energy can then be transferred between molecules resonantly over long distances before exciton relaxation occurs, making them of particular interest in organic photonics. J-aggregation is occasionally observed for phthalocyanines and is characterised by additional low-energy absorption red-shifted from the Q band.^[112,113]

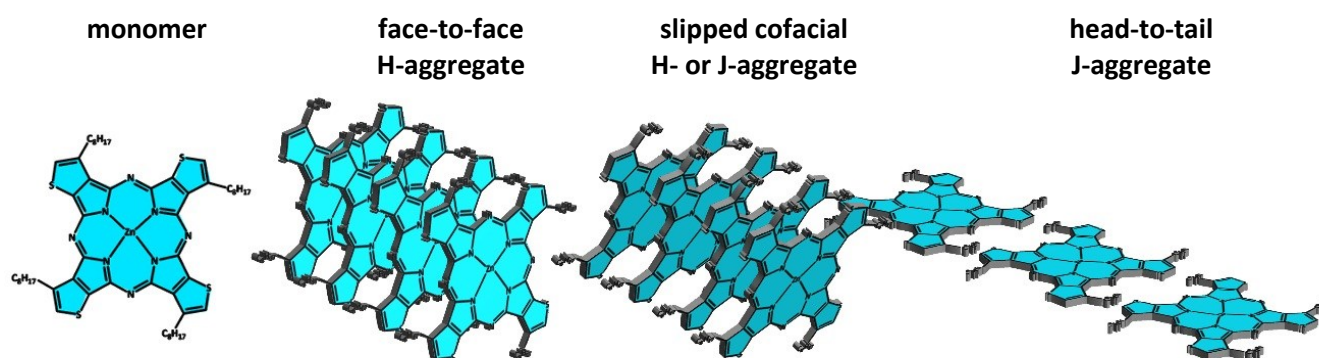


Figure 4.34: Cartoon illustrating H- and J-aggregation of phthalocyanine materials.

First we compare TZNpC and TPc to identify the role of the central metal atom on the electronic transitions. The solution absorption in Figure 4.31 is characteristic of absorption from metalated and metal-free phthalocyanines, and reveal the differences in molecular symmetry (TZNpC vs ZnPc).^[114] In the case of metal-free TPc, the electronic states are non-degenerate and the major transitions are polarised in the x-, y- and z-directions. As our excitation source is non-polarised, this results in a number of absorption peaks in the Q-band. Aside from these extra allowed transitions due to a lifting of degeneracy for TPc, the overall shape of the solution absorption spectra are similar indicating that molecular symmetry dominates the electronic transitions when intermolecular interactions are eliminated. The positions of the main absorption bands are described in Table 4.9. If we assume all four regioisomers of TZNpC (Figure 4.35) are present and their transition energies similar it is possible to determine whether or not the molecular symmetry has been modified compared to ZnPc. From the similar shapes of the Q-bands of TZNpC and ZnPc, we can see that the peripheral substituents do not disrupt the molecular symmetry of unsubstituted ZnPc. The Q-band absorption maxima blue shift while the B-band absorption maxima red shift when benzene groups (ZnPc) are replaced with thiophene units (TZNpC). The solid-state UV-Visible absorption spectra in Figure 4.31 display characteristics of both the H- and J-aggregates described above. Compared to metal-free TPc, metalated TZNpC displays a more resolved

vibronic absorption (narrower Q_x and Q_y bands), indicating a more ‘ordered’ molecular arrangement. The ordered film is surprising considering the chemical synthesis is not selective with respect to the direction of the thiophene units, which results in the TZnPc comprising four regioisomers. This suggests that sulphur is a crucial factor in the intermolecular interactions, perhaps by coordinating to a nearby Zn²⁺ molecule. Coordination is a particularly strong, directional, type of non-covalent bonding. Changing the benzene ring (ZnPc) to a thiophene (TZnPc) blue-shifts the absorption onset and supports the reduced electron delocalisation over the thiophene rings. The intensity pattern films of ZnPc correlate well with the spectra of metastable α -polymorph of ZnPc (high intensity Q_x absorption) reported in literature.^[101,115]

	Q-band (nm)		B-band (nm)	
	Solution	Thin Film	Solution	Thin Film
ZnPc	703	632, 768	353	335
TPc	692	637	351	352
TZnPc	663	616	362	357

Table 4.9: Summary of positions of Q- and B-band absorption maxima in solution and thin films of ZnPc, TPc and TZnPc extracted from the absorption spectra in Figure 4.31.

Raman Spectroscopy

A more detailed comparison of the molecular conformations for the three small molecules is provided by the resonant Raman spectra in Figure 4.36. The peak positions and relative intensities under different excitation frequencies of Raman active vibrational modes are sensitive to the molecular symmetry of the system. The materials described here all possess a twofold symmetry axis orthogonal to the principle molecular axis (C₂) and a horizontal mirror plane (σ_h). Compared to TPc, the central Zn in TZnPc and ZnPc means these molecules possess two-twofold symmetry axes and two vertical mirror planes aligned with the axis of principle symmetry (D_{2h}). ZnPc is of a highly planar molecule of the D_{4h} point group. The assignments of TZnPc are made by considering the simulated spectra for each other the four regioisomers, all with distinct molecular symmetries and simulated Raman spectra, however for the vibrational modes described here the identifications are the same (Figures 4.35).

Selected vibrations are illustrated in Figure 4.37. The presence, or size, of the central metal atom modifies the strength of bonds within the inner ring, changing bond lengths.^[116] When an excitation is tuned to the same frequency as an electronic transition, there is a strong resonant enhancement revealing the location of π -electrons. The changes in intensity of vibrational modes are due to changes in the electron density localisation across the molecule under

difference excitations. For all three materials, 457 and 488 nm excitation are resonant with the B-band, 514 nm pre-resonant with the B-band and 633 nm resonant with the Q-band. The Raman spectra of each molecule in Figure 4.35 and Figure 4.36 were simulated using DFT at the B3LYP/ 6-31 G(d,p) level of theory. The main vibrational modes and approximate descriptions, based upon these simulations, are provided in Table 4.10. The vibrational modes of metal-free and zinc phthalocyanine are extensively discussed in literature.^[116,117]

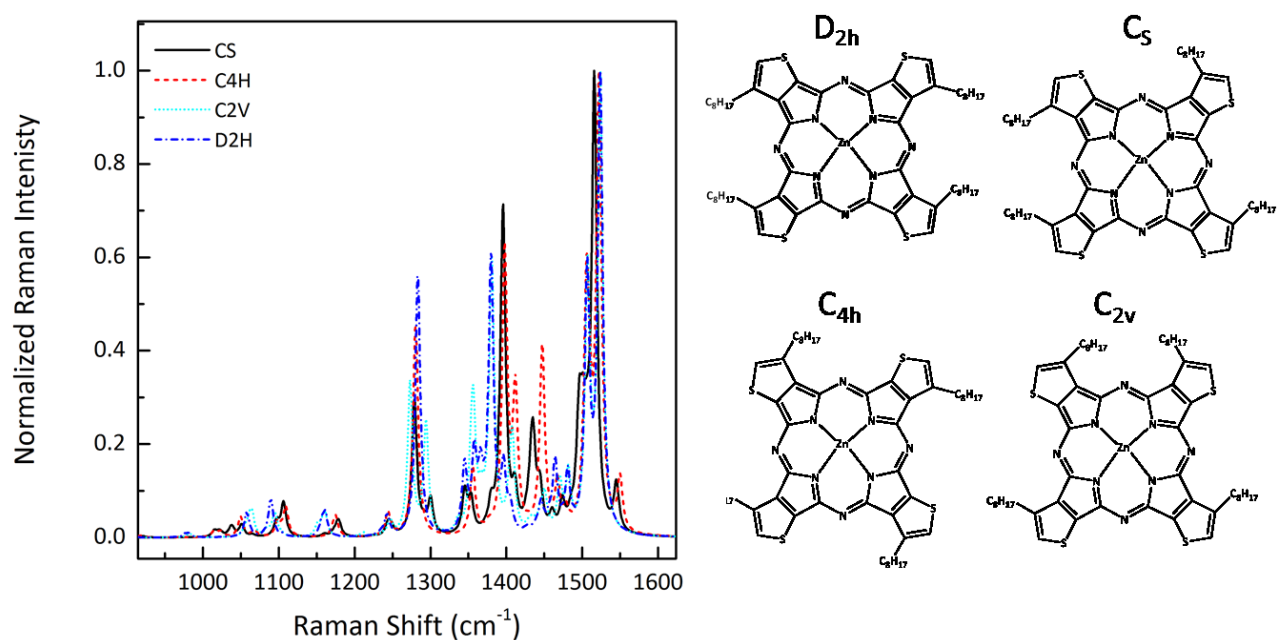


Figure 4.35: Simulated Raman spectra for four structural isomers of TZnPc. The intensity has been normalized to the main peak.

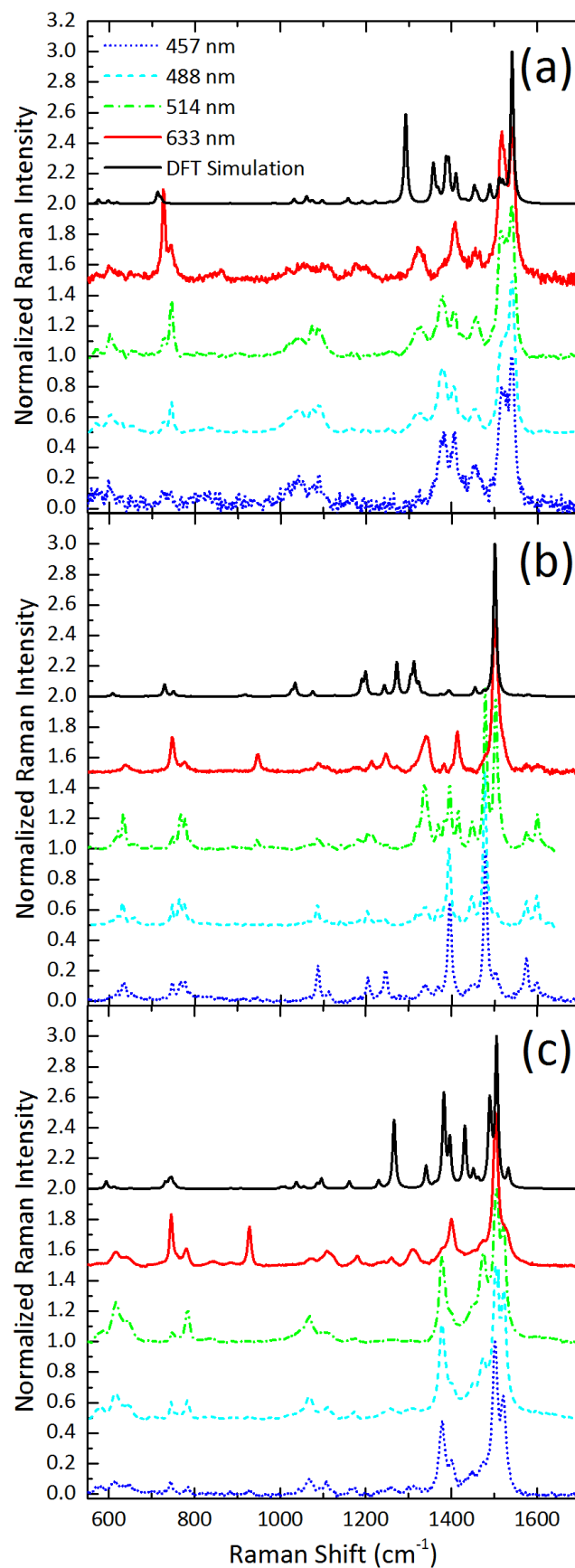
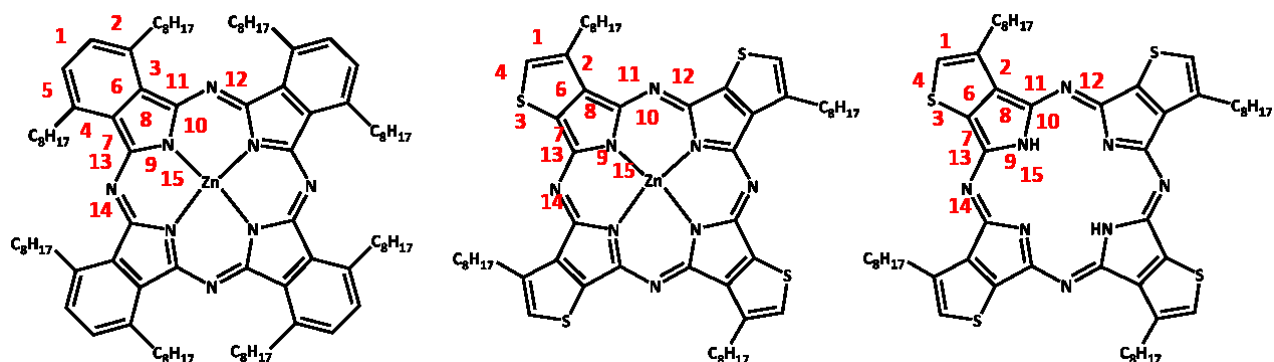


Figure 4.36: DFT Simulations (black, solid) and experimental Raman spectra obtained at 457, 488, 514 and 633 nm excitation for thin films of (a) ZnPc, (b) TPc and (c) TZnPc.



Bond Lengths (Å)

	ZnPc	TZnPc	TPc		ZnPc	TZnPc	TPc
1	1.401	1.373	1.372	9	1.374	1.380	1.385
2	1.398	1.437	1.431	10	1.374	1.376	1.381
3	1.410	1.724	1.724	11	1.336	1.333	1.319
4	1.410	1.754	1.755	12	1.336	1.333	1.336
5	1.398			13	1.336	1.330	1.319
6	1.418	1.385	1.390	14	1.336	1.330	1.336
7	1.468	1.446	1.440	15	2.009	1.988	1.012
8	1.468	1.456	1.446				

Table 4.10: Calculated bond lengths (Å) of the ZnPc, TZnPc and TPc molecules.

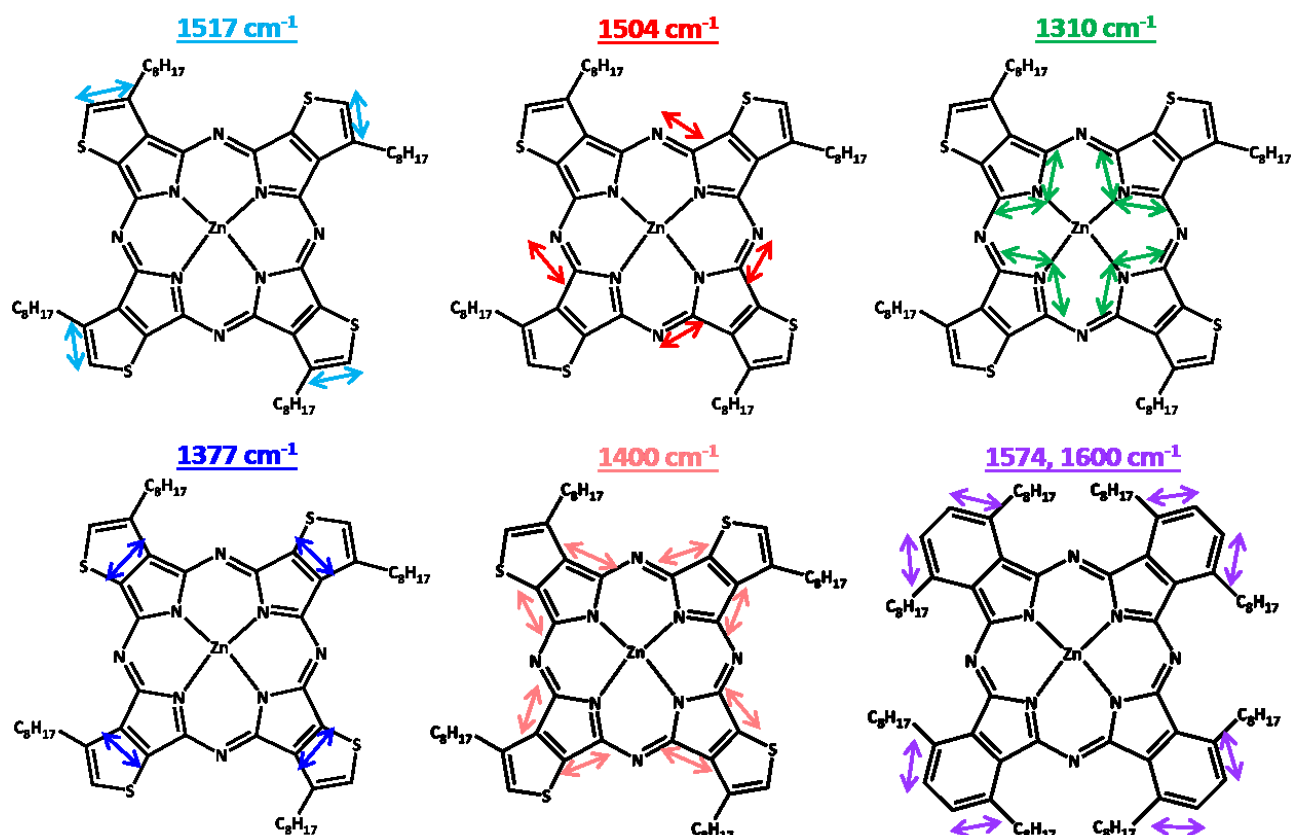


Figure 4.37: Schematic indicating main vibrational modes of the materials considered here.

For all three materials, the most intense Raman scattering modes under 633 nm excitation belong to vibrations of the inner-ring, notably the C = N bonds.^[118,119] Sulphur donates electrons to the system (thiophene is a stronger donor than benzene), and the highly delocalised system results in their effects being felt on the inner-ring. The length of the C = N bond in the aza group is longer in ZnPc than TPc or TZnPc (ZnPc – 1.34 Å, TZnPc – 1.32 Å, TPc – 1.33 Å, Table 4.10) and as a result the vibration is at a slightly lower energy (ZnPc – 1500, TPc – 1516, TZnPc – 1504 cm⁻¹). This vibration (B_{1g}) derives its intensity from the stretching of the C = N in the aza unit and expansion of the pyrrole groups. It is interesting to compare the scattering intensity of particular vibrational modes when the exciting frequency is varied from the vicinity of the Q-band to the B-band:

B-band resonant excitations (488, 457 nm)

For the ZnPc, the vibrational modes at 1202 (B_{2g}), 1245 (B_{1g}) and 1574 (B_{1g}) and 1600 cm⁻¹ (B_{2g}) are quadrant and sextant stretches of the outer benzene rings, respectively.^[116] The vibrational mode at 1086 cm⁻¹ (E_g) is C-H wagging of the benzene rings. The aza vibration (1500 cm⁻¹) is very weak in the B-band. The strongest Raman scattering comes from the mode located at 1477 cm⁻¹ (A_{1g}, 1474 cm⁻¹ for TZnPc), which is of the same origin as the 1500 cm⁻¹ mode (C = N on inner ring, pyrrole expansion, C – C_{aza}).

For TPc, B-band resonant spectra display a symmetric thiophene C = C stretch (C = C_{Thiophene}) at 1527 cm⁻¹. The broad FWHM indicates this mode is comprised of multiple peaks. C = C_{Thiophene} is at a lower energy (1522 cm⁻¹) in the case of the more planar TZnPc. Only macrocycle deformations (ZnPc- 765, TZnPc- 784, TPc - 744 cm⁻¹) and pyrrole stretches (C – C_{pyrrole} ZnPc- 1392, TZnPc- 1378, TPc - 1378 cm⁻¹) with strong contributions from the outer groups are particularly strong. The deformation mode of the isoindole (benzene/thiophene and pyrrole) unit stretch is only present in B-band resonance (ZnPc – 1446, TPc – 1457, TZnPc – 1448 cm⁻¹). It has been reported for metal-free PC systems that only totally symmetric modes derive their intensity in the B-band.^[120]

Q-band resonant excitations (633 nm)

Q-band resonance selects vibrations from the inner ring. For ZnPc, the weakly donating benzene ring results in a shorter pyrrole C-N bond (1.37 Å) which is only apparent in the Q-band at high wavenumber (1413 cm⁻¹) (A_{1g}). Under these conditions the macrocycle deformation (ZnPc- 747, TZnPc- 746, TPc - 726 cm⁻¹) that are predominantly related to the inner ring dominate those coupled to outer ring vibrations. The strong scattering between 1460 – 1300

cm^{-1} are related to motions of the N atoms. These modes are broader in the case of TPc as there are two pyrrole environments (Figure xx (a)), isolated and bonded to hydrogen. Pyrrole (ZnPc- 1316, TZnPc- 1311, TPc - 1322 cm^{-1}) and aza ring stretches (ZnPc- 1414, TZnPc- 1401, TPc - 1407 cm^{-1}) concentrated on the inner-ring dominate over similar vibrations coupled to the outer-units. The 7 cm^{-1} downshift of the pyrrole stretch on metalation indicates a reduction in the force constant. The stretching of the pyrrole is downshifted from 1322 cm^{-1} in TPc to 1310 cm^{-1} in TZnPc as the N-Zn-N bonds allow the C = C bonds to lengthen (TPc – 1.44 Å, TZnPc – 1.45 Å).

4.4.3 Investigation into the Stability of Molecular Packing in Spin-Coated Phthalocyanines

Ageing

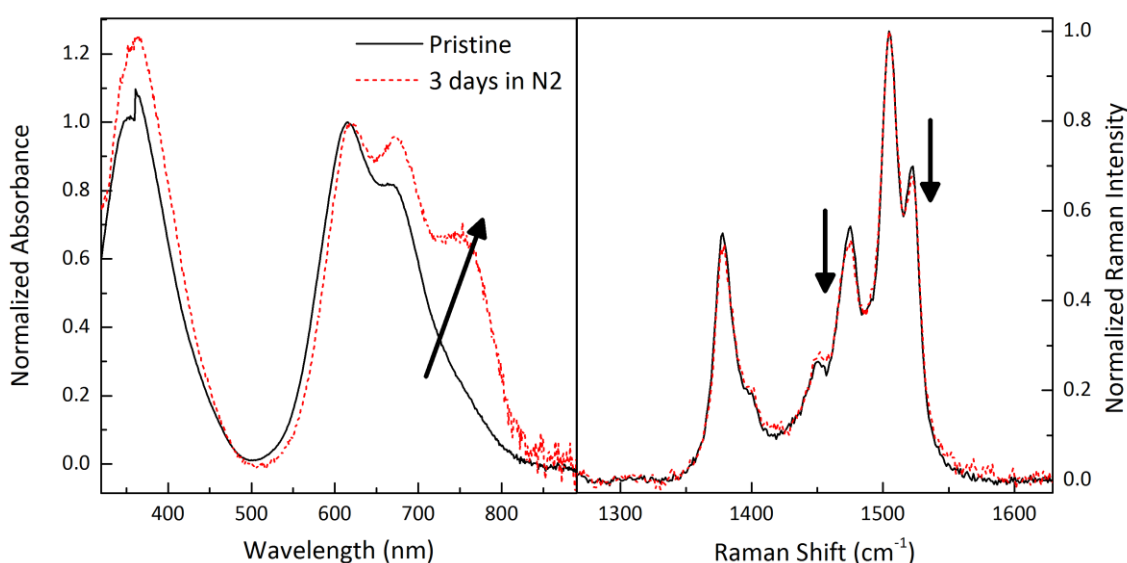


Figure 4.38: (a) UV-Visible absorption spectra and the (b) associated resonant Raman spectra for pristine thin films of TZNpC and after aging for 72 hours in N_2 .

The thin-films described above were all fabricated using spin-coating from solutions using chlorobenzene. Uniquely for the spin-coated TZNpC films, after 72 hours storage in a nitrogen environment a particularly interesting morphological transition occurs. There is an increase in the relative absorption of the high energy B-band (to the Q-band) and appearance of broad low energy absorption band (750 nm) which increases over time. This is accompanied by a decrease in the monomer absorption Q-band (615 nm), implying the species responsible for the 750 nm absorption has been transformed from the monomer form. The fact that the transformation occurs long-after the solvent has left the film indicates the new species is more thermodynamically stable than the monomer species. Crucially, this morphological instability is not observed for ZnPc or TPc, indicating that both the central metal atom and substituents are very important in the aggregation process. These changes indicate the spontaneous nano-

assembly of TZnPc into J-aggregates (Figure 4.38 Figure 4.39(a)) and has never been reported for non-oxygen containing ZnPc derivatives. J-aggregate formation significantly changes the molecular orientation (see Figure 4.34). The aggregated J-aggregate resonant Raman spectra (Figure 4.38 (b)) show a decrease in Raman scattering from the outer thiophene rings ($C = C_{\text{Thiophene}}$), indicating these are no longer in the plane of the electric field of the laser. Slow recrystallization kinetics have been reported for semiconducting polymers, but details of their changes in microstructure have never been described.^[121]

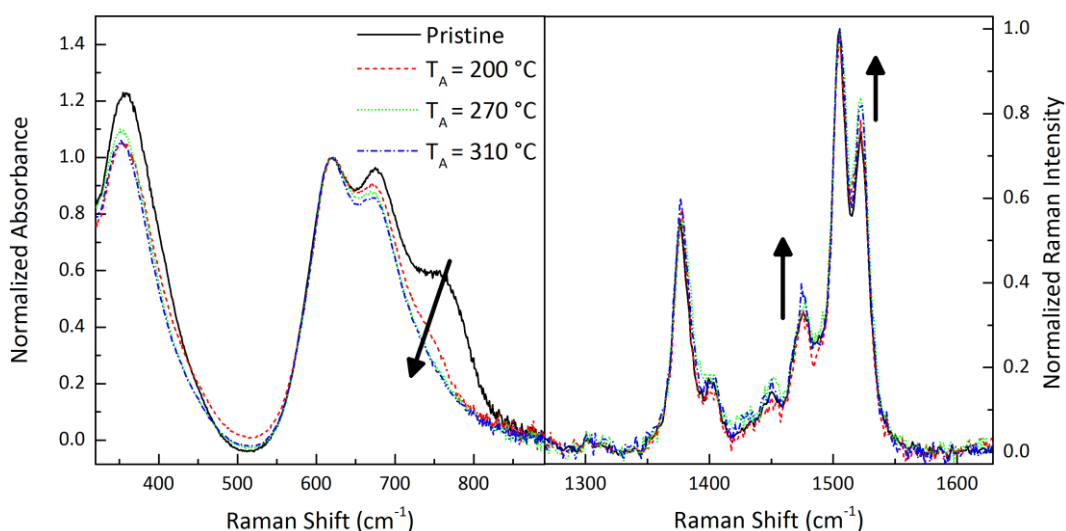


Figure 4.39: (a) UV-Visible absorption spectra and the (b) associated resonant Raman spectra for pristine thin films of TZnPc and after annealing at 200, 270 and 310 °C

The aggregation is found to be reversed on thermal annealing at temperatures > 500 K (200 °C), which is consistent with transition temperatures of other phthalocyanines.^[101] After such annealing films display a sharp decrease in the ‘J-band’ (750 nm). This is accompanied by a blue-shift in both the Q_x (675 nm $\rightarrow$ 671 nm) and B-band (358 nm $\rightarrow$ 351 nm) absorbance bands, or a more H-type aggregation (Figure 4.34 (a)). On increasing H-aggregate formation (i.e. with increasing annealing temperature) there is a systematic increase in Raman scattering from modes involving the outermost parts of the PC molecule. This could indicate the non-covalent sulphur-zinc bonds between neighbouring macrocycles are broken and the thiophene rings re-assemble into a face-to-face structure.

4.4.4 Controlling H- and J-aggregation using Zone-Casting

Phthalocyanines exhibit excellent self-assembling properties and are therefore suitable candidates for zone-cast deposition. The elevated substrate temperatures during deposition should improve wetting of TZnPc and forms uniform thin-films over large areas (5 cm²). As with other solution processing techniques, the solvent is critical in determining the quality of the zone-cast film. When the intermolecular PC-solvent interactions are weaker than the

PC-PC associations, aggregation has been observed in PC solutions.^[123] Metal-free PCs are very sensitive to the solvent system, while metalated PCs demonstrate very slight solvent effects on absorption or emission spectra.^[123]

Solvent

We have established that for a stable contact line, certain requirements must be met: $T_{\text{sol}} < T_{\text{subs}}$ and $T_{\text{sol}}, T_{\text{subs}} <$ the boiling point of the solvent. The temperatures detailed in Figure 4.40 were chosen as the starting point for zone-cast studies. Based on previous reports, slow substrate displacement rates were investigated ($100 \mu\text{ms}^{-1}$).^[35]

	Chloroform	Toluene	Chlorobenzene	Dichlorobenzene
Dipole Moment	1.04	0.36	1.54	2.14
Hildebrand Parameter	9.3	8.9	9.5	10.0
BP_{Solvent}	61	110	131	174
T_{subs} (°C)	40	80	100	140
T_{sol} (°C)	35	70	90	100
Optical Microscope Images ZC Films 100 μms^{-1}				

Figure 4.40: Summary of deposition parameters for the solute-solvent systems described in text. Optical microscope images of thin films zone-cast at $100 \mu\text{ms}^{-1}$.

For the majority of the solvent systems considered here there are very few surface features visible through the microscope. Immediately after deposition (less time to nano-assemble) thin films of TZnPc display increased H-aggregation in highly polar solvents (dichlorobenzene, chlorobenzene) and increased J-aggregation in low polarity solvents (chloroform, toluene) (Figure 4.41). The face-to-face π - π aggregation in highly polar solvents has been reported previously.^[124] It occurs because the solvent-solvent interactions are so strong the PC molecules are excluded from solution, forcing them to aggregate.^[125] In this case it is particularly interesting for the thin-films zone-cast from toluene, because the elevated substrate temperatures should inhibit J-aggregate formation in a similar way to the thermal annealing described previously.^[126] The J-aggregation (750 nm absorption) increases after the films are stored in nitrogen for 7 days. This implies the intermolecular interactions that allow J-aggregate formation to occur are restricted when thin films are deposited from low polarity solvents.

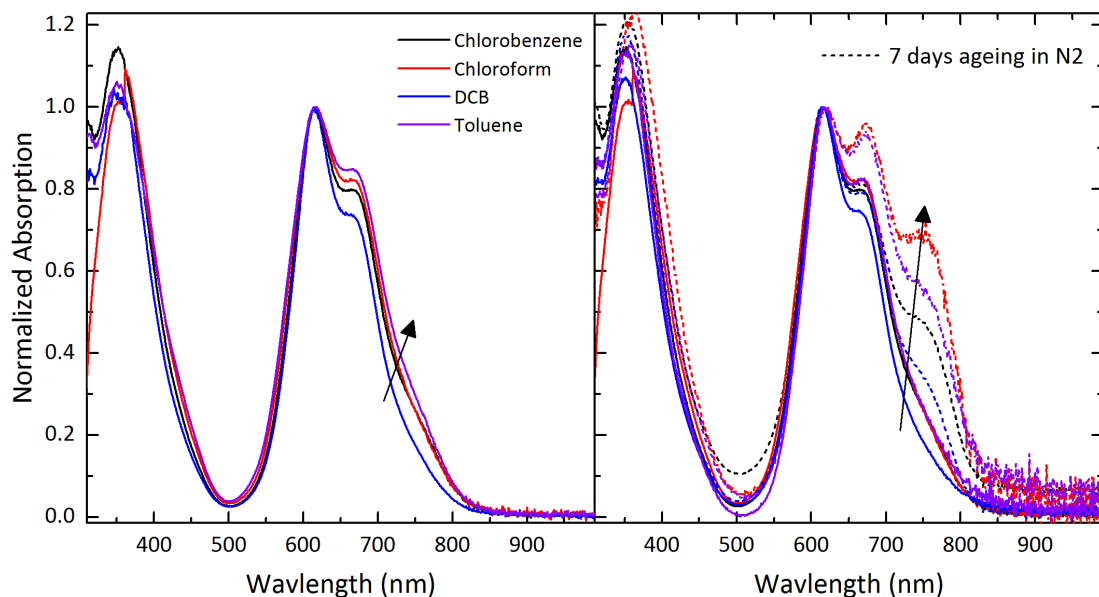


Figure 4.41: Absorption spectra of TZNpC thin films deposited from chlorobenzene (black), chloroform (red), dichlorobenzene (blue) and toluene (purple) and (b) absorption after 7 days storage in nitrogen. All spectra are normalised to the Q band maxima.

Substrate Displacement Rate

For the high polarity chlorobenzene system, the substrate displacement rate can also be used to tune J-aggregate formation (Figure 4.42). High displacement rates produces disordered films with both H- and J-aggregate formation: a broad Q-band absorption, increase in the 750 nm absorption and decrease in Raman scattering from the thiophene rings.

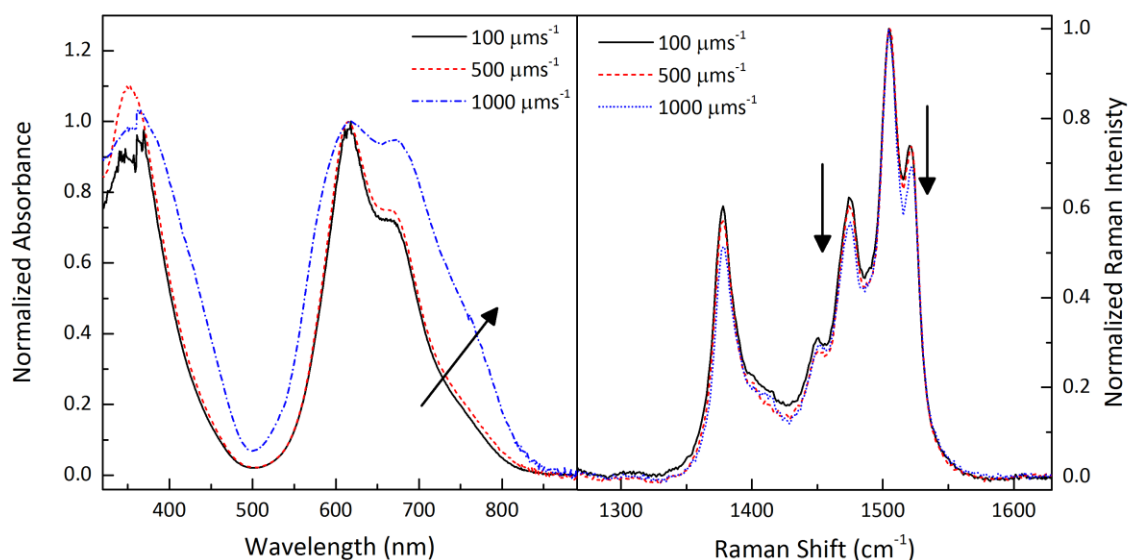


Figure 4.42: Absorption spectra of TZNpC thin films deposited from chlorobenzene at 100 (black), 500 (red) and 1000 $\mu\text{m/s}$ (blue), normalised to Q band maximum, and (b) resonant Raman spectra under 514 nm excitation normalised to 1503 cm^{-1} intensity.

For thick H-aggregate films deposited at $100 \mu\text{ms}^{-1}$ it is possible to quantify the role of thermal annealing at 543 K, previously shown to eliminate J-Aggregation. By placing a half-wave plate in the path of the laser, the incoming photon polarisation can be controlled and the Raman intensity of vibrational modes plot as a function of polarisation angle. For the two vibrational modes deriving their intensity from the same units (C = N, pyrrole expansion), it is interesting to compare their polarisation dependence. Figure 4.43 illustrates the Raman intensity of the 1475 cm^{-1} (A_g) and 1504 cm^{-1} (B_g) Raman modes as at 298 K in (a) spin-coated and (b) zone-cast samples. The intensity of Stokes Raman scattered radiation is proportional to the Raman tensor of a particular mode (R) and the polarisations of the incoming and scattered photons (e_i and e_s) and is described by: $I \propto |e_i^* R e_s|^2$. The highly anisotropic Raman scattering from zone-cast samples reflects an increase in the proportion of molecules within the laser-spot size ($1 \mu\text{m}^2$). The orthogonal scattering from these modes confirm their different natures ('B' and 'A' type).

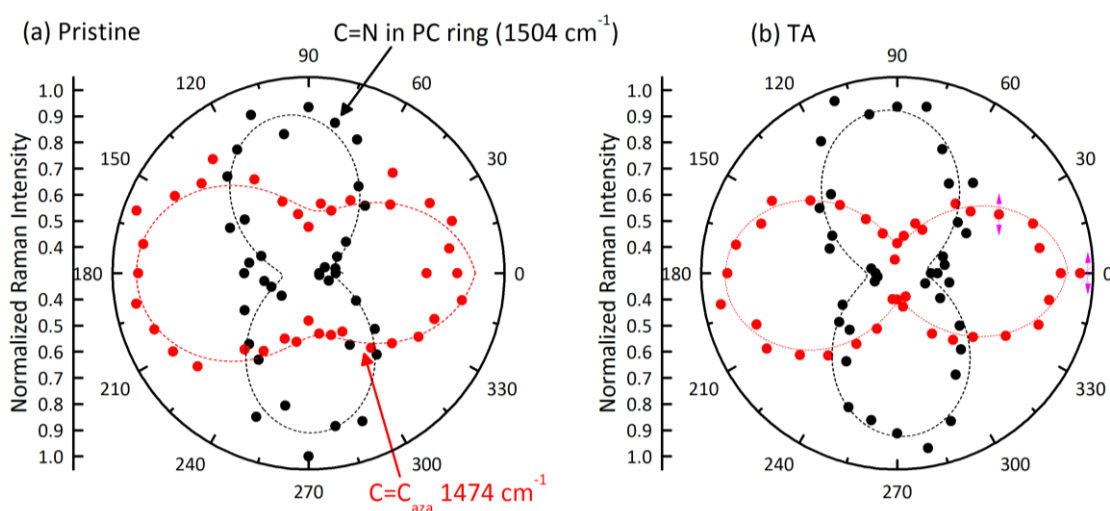


Figure 4.43: Peak intensity of C = C_{axa} (1474) and C = N in PC ring (1504) as a function of incident laser polarisation (a) before and (b) after annealing, obtained using angle-dependent polarised Raman spectroscopy.

4.4.5 Summary

Resonant Raman has been used to investigate the nature of electronic transitions of three soluble phthalocyanines: TznPc, TPc, ZnPc. The origin of vibrational and electronic transitions have been identified using a combination of quantum chemistry and experimental results. For the novel material, TznPc, J-aggregation occurs upon: ageing, deposition from a low polarity solvent, and fast substrate displacement rates. J-aggregation could occur due to the spontaneous formation of non-covalent sulphur-zinc interactions, which would disrupt the packing of the outer thiophene units. Annealing at 540 K is found to promote H-aggregation and a more uniaxial orientation, as indicated by reduction in J-aggregate absorption, increase in Raman scattering from outer thiophene rings. Zone-

casting is presented as a technique to control aggregation in phthalocyanine films. Compared to spin-coated samples, zone-cast H-aggregate phthalocyanine films show highly anisotropic Raman scattering which indicate improved in-plane molecular order. The control of aggregation during solution processing will be crucial in the fabrication of efficient devices.

4.5 Conclusions

We have systematically evaluated the impact of solvent composition, meniscus height, substrate temperature, solution temperature, substrate displacement rate and concentration on the microstructure of a zone-cast thin films.

The influence of substrate displacement rate, substrate temperature and grain orientation on charge transfer characteristics is determined for two pentacene derivatives (TIPS- and TES-pentacene). We find that for both pentacene derivatives, deposition from fast substrate displacement rates results in narrow, aligned needles parallel to the zone-casting direction. In these aligned films, the charge carrier mobility is highest when measured parallel to the direction of zone-casting. The absolute mobility is greater for the 2D transporting TIPS-pentacene, whereas the mobility anisotropy is greatest for 1D TES-pentacene. The impact of needle orientation on charge transport is considered by comparing experimental results to those generated by a multi-scale modelling approach. For 1D transporting TES-pentacene the optimum needle orientation is parallel to the source-drain direction compared to $\approx 30^\circ$ for 2D transporting TIPS-pentacene.

Increasing substrate temperature is found to increase film thickness and grain width. For needle-like domains the highest parallel mobility is obtained at low substrate temperatures whereas perpendicular devices show an improved device performance for the wider grains deposited at high temperatures. As a result the mobility anisotropy

The molecular orientation across a device has been examined using angle-dependent polarised Raman spectroscopy at regular intervals from on top of the electrodes to in the channel. For devices zone-cast on Si/SiO₂, the molecular packing is maintained both on the electrode and in the active channel. For short channel length devices zone-cast on plastic substrates, a disruption in molecular packing at the electrode/ channel interface is identified as the cause of poor device performance.

Resonant Raman spectroscopy has been identified as a mechanism to probe isolated molecules of pentacene and DAP-1 in a *p*-terphenyl lattice used in room temperature solid-state masers. The Raman modes and electronic

transitions of 6,13-diazapentacene have been identified using DFT simulations. Nitrogen substitution stabilises the HOMO energy level compared to unsubstituted pentacene but the HOMO-LUMO energy gap remains similar, which is an encouraging finding for CW masing. Unsubstituted pentacene occupies a *p*-terphenyl lattice site that minimises conformational disorder of the host system, however DAP-1 increases disorder. The Raman scattering intensity increases when the excitation is perpendicular to the direction of zone-translation. These results allow evaluation of the crystal quality and interactions of the guest molecule, which can better inform designers of maser systems.

The microstructure of solution processed thin-films of three soluble phthalocyanine materials (ZnPc, TPc and TZnPc) was evaluated. The nature of the electronic transitions of all three materials was probed using resonant Raman spectroscopy. Vibrational modes located on the inner ring are resonantly enhanced when resonantly excited by the Q-band, whereas vibrations on the outer rings are resonantly enhanced by B-band excitations. Zone-casting has been demonstrated as an appropriate technique to control the molecular packing of soluble phthalocyanine materials. The vibrational modes of the novel phthalocyanine derivative (TZnPc) are reported for the first time. The morphological stability on ageing and during *in situ* heating/cooling is considered. Spontaneous J-aggregation of TZnPc on ageing occurs in thin-films that have been deposited from a low polarity solvent, or at a fast substrate displacement rate. Annealed H-aggregated zone-cast phthalocyanine films show a strong increase in in-plane molecular alignment, which we expect to be an important consideration for the fabrication of future devices.

4.6 Bibliography

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5 Interfacial Molecular Packing in Vacuum-Evaporated Small Molecule Devices

Optimisation of device performance is possible with careful consideration of molecular packing, thin film uniformity and surface coverage close to the organic/ inorganic interface. Small changes in molecular packing determined by the interplay between the strengths of molecule-molecule (intermolecular) and molecule-substrate interactions have been demonstrated to cause large variations in the transfer integrals between neighbouring molecules and hence charge transport properties.^[1–9]

Here we investigate the influence of self-assembled monolayers (SAMs), organic and inorganic interlayers on the interfacial molecular packing of the well-studied organic semiconductors pentacene and copper phthalocyanine, and develop a robust structural probe of thin film orientation and quality that can accurately predict device performance.

The pentacene single-crystals in 5.1 were prepared by Pavlo Fesenko at IMEC, Brussels. The investigation in Section 5.2 was performed in collaboration with Jeonkyun Roh and Chan-Mo Kan at Korea Advanced Institute of Science and Technology, South Korea. These results have either been published or are awaiting publication.^[10] The investigation in Section 5.3 was performed in collaboration with Alex Ramadan at Imperial College London and Yu Jeong Bae at EWha Woman's University, Seoul. It is being prepared for publication.

5.1 Motivation and Aim

Interfacial layers are a common feature of all organic electronic devices, where they are used to adjust the energetic barrier height between the organic layer and electrodes, selectively form a contact for one type of charge carrier, determine the device polarity, act as an optical spacer and minimise chemical and physical interactions between the contact and organic layer.^[11] In this chapter, we consider the molecular packing of vacuum evaporated small organic molecules at a variety of interfaces including reactive metals to surface treated oxides. The molecular packing of the vacuum evaporated small molecules is strongly dependent on the properties of the substrate below, which in turn dictates their ability to transport charge.^[12,13]

First the impact of SAM treatment on the molecular packing of pentacene in organic field-effect transistors is evaluated. SAMs are renowned for their applications in surface modification; where fine tuning of the SAM chemical structure can be used to control the uniformity, packing, conformation and charge density in the subsequent organic layers.^[12,14] SAMs are used in an organic electronic stack to modify both the contact and channel regions of a device, to increase grain size and wetting on the channel and improve charge injection from the electrode. The molecular packing of the organic layer on top of the SAM is particularly important for device performance as the formation of grain boundaries are highly disruptive for charge carrier transport. The ideal molecular packing for high performing OFETs would be a single crystal, with uniform molecular alignment and minimal grain boundaries.^[13] With consideration of the device geometry we can tune molecular packing to ensure high current flow through the active channel; i.e. for FETs with in-plane electrodes charge transport occurs parallel to the substrate plane, and so π - π stacking should be too.^[13] Whilst study of the re-organisation of the organic layer on interacting with SAM layers is nothing new, *in situ* non-destructive characterisation of molecular packing is rarely reported and a clear understanding of molecular orientation across a device is hard to come by.^[15,16] This work looks to find a robust, highly sensitive structural probe to uncover molecular packing on the contact, at the contact/channel interface and in the active channel, and correlate these to charge carrier mobility in working devices.

The second part of this chapter evaluates the impact of the underlying substrate on molecular packing of vacuum deposited copper phthalocyanine in magnetic tunnel junctions. The low spin-orbit coupling of organic semiconductors ensures long spin relaxation lengths, which allow spin-polarised charge to pass through the organic layers of organic spintronic devices without being scattered, retaining their spin identity and achieving high values of

magnetoresistance.^[17] Spin-polarised charge transport through the organic layer depends upon the molecular packing and thin film morphology of the small molecules- defects in the organic layer scatter spin-polarised electrons and reduce magnetoresistance. We first look to establish spectroscopic signatures of phthalocyanine polymorphs in organic thin-films and then use these to unravel the dependence of device performance on device architecture, organic layer thickness and operating temperature.

5.2 Impact of Surface Treatment on Molecular Packing and Device Performance in Pentacene Organic Field-Effect Transistors

This section considers the molecular packing of vacuum evaporated pentacene thin films. First a structural probe for molecular order is established using pentacene single crystals. The distance between organic molecules within a single crystal determines the extent of intermolecular coupling between the π -conjugated cores, and can be probed using spectroscopic techniques.^[18] We apply our understanding of the spectroscopic markers for molecular order and orientation to uncover the origin of enhanced charge carrier mobilities in surface treated pentacene OFETs.

Developing a Structural Probe for Molecular Order

Pentacene Polymorphs in Single Crystal Samples

Single-crystal organic devices offer high electronic performance owing to the lack of grain boundaries and low energetic disorder. As shown for aligned films of TIPS- and TES-pentacene, charge-transport within molecular crystals is highly anisotropic and is particularly sensitive on the quality of organic layer. We have demonstrated the quantification of molecular order across a crystal by measuring the ‘anisotropy’ of Raman-active vibrational modes, by controlling the polarisation of the incident laser beam. This technique is first developed to probe the quality of single-crystal pentacene devices.

Pentacene molecules adopt the herringbone packing described in Chapter 4. In the solid-state each pentacene cell contains two molecules and as a result the dipoles of each molecule interact according to whether they are aligned parallel or antiparallel. This results in a so-called ‘Davydov’ splitting of absorption bands into two components polarised along the a- and b- crystal axes (Figure 5.1).^[19] The magnitude of Davydov splitting depends on the distance between molecules, and is not observed when pentacene molecules are held apart from one another; either dispersed in solution or an amorphous matrix.^[19,20] Davydov splitting has been observed for a range of single crystals and thin films where there is more than one molecule per unit cell.^[19–25]

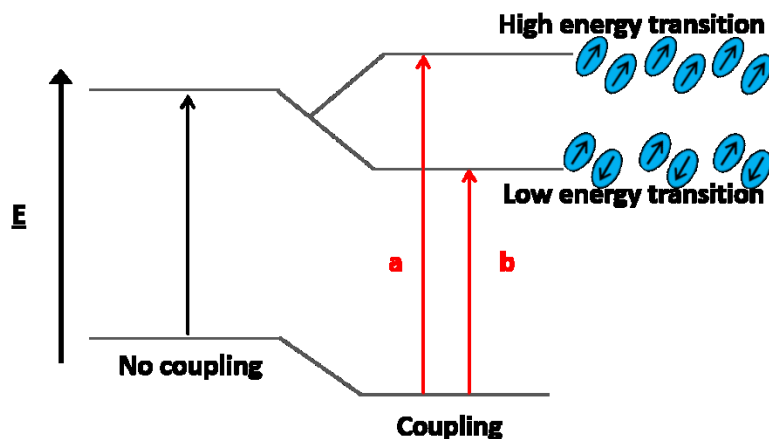


Figure 5.1: The 'a' and 'b' Davydov absorption peaks arising due to coupling of dipoles within a unit cell.

The presence of more than one molecule in a unit cell can result in a splitting of each Raman-active vibrational mode. Within a molecular crystal, herringbone packed pentacene molecules arrange in layers with small tilt angles with respect to the substrate normal. Between the molecular layers it is the ends of molecules that are most likely to interact with one another. Analogous to the splitting observed in absorption bands, the splitting of the two components can be identified by changing the polarization of the laser, as each Raman band has a different depolarization ratio. The depolarization ratio is the ratio between the Raman signal obtained in cross-polarisation to the signal obtained in a parallel configuration.^[26] The strength of intermolecular interactions determines the extent of Davydov splitting, and therefore the magnitude of the splitting can be used as a marker of the intermolecular forces between pentacene molecules.^[18,20,27]

Experimental Details

With this in mind, we investigate the molecular interactions within single crystal pentacene thin films vacuum deposited by Pavlo Fesenko at IMEC. For the vacuum deposition, a mask was patterned by electron beam lithography and dry etching. The stencil consists of two regions of square and circular apertures of a range of sizes. The thin films are evaporated onto a SiO₂ substrate held at 40 °C. To avoid degradation of the single crystals, Raman spectra were all acquired in a nitrogen enclosure. Angle-dependent polarised Resonant Raman spectra (633 nm) were performed on single crystals of pentacene at low laser power (1 %).

The strongest Raman active vibrational modes of pentacene are described in Table 5.1. Further details of the Raman simulation are provided in Section 4.

Table 5.1: Simulated and observed Raman frequencies and an approximate description.

Peak Position (cm ⁻¹)		Raman mode assignment
<i>Simulation</i> (scaled 0.961)	<i>Observed</i>	
1158	1158	C—H Ends
1169	1178	C—H Sides
1369	1371	C—C _{SHORT}
1583	1598	C—C _{LONG}

Development of the Structural Probe

A comparison of the absorption spectra of isolated pentacene molecules and those packed in the solid-state reveals a clear splitting of the 0-0 band in absorption into two Davydov components (Figure 5.2). Instead of a narrow, well-defined single band centred at 590 nm, two new bands are seen at 627 and 662 nm ('a' and 'b', see next section). For a pentacene single crystal we have compared the angle-dependent Raman spectra collected in non-resonant (785 nm) and resonant (488, 514, 633 nm) excitation wavelengths.

Davydov splitting in the Raman spectrum is only evident when resonant with the Davydov absorption bands (see Figure 5.2, 633 nm) and presents as a splitting of the C-H wagging mode on the ends of the pentacene molecule. The Davydov splitting of the C-H_{Ends} mode results in two components at 1155 cm⁻¹ and 1158 cm⁻¹ with opposite depolarisation ratios. The splitting indicates the strength of intermolecular interactions between adjacent layers.

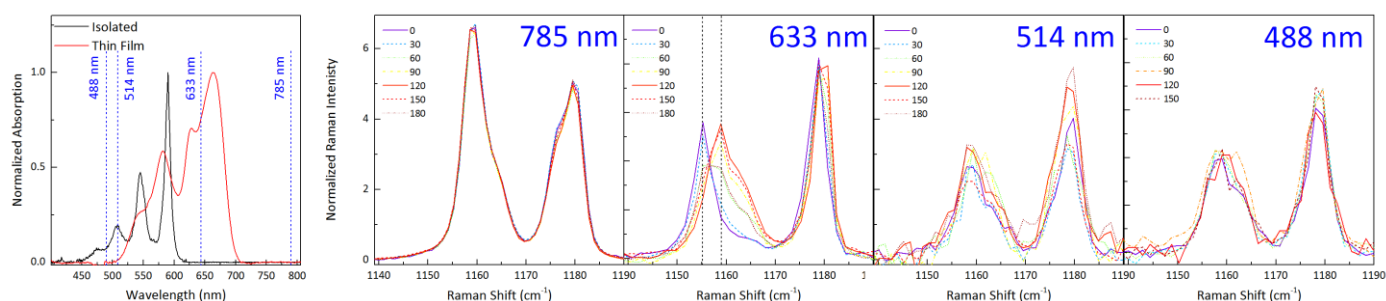


Figure 5.2: Absorption of isolated and solid-state pentacene. The absorption peaks between 500 – 700 nm represent the 'a' and 'b' transitions illustrated in Figure 1. Close-up Raman spectra of C-H stretching modes on the sides and ends of the molecule at different excitation wavelengths: 785, 633, 514 and 488 nm.

Using Angle-Dependent Polarised Raman Spectroscopy to probe the Uniformity of Molecular Order across a Sample

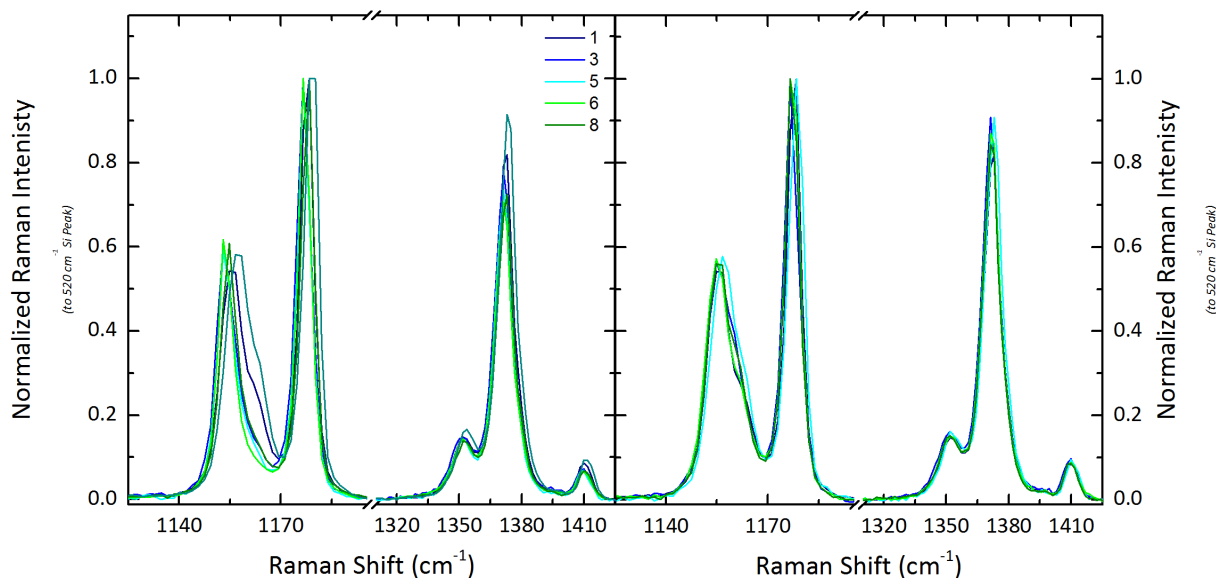


Figure 5.3: Raman spectra taken at 5 positions across pentacene films evaporated through the (a) square and (b) circular apertures.

The aperture width is 1 μm . For the square aperture (a) there is evidence of splitting of both the 1158 cm^{-1} and 1371 cm^{-1} Raman modes.

Thin layers of pentacene were evaporated through a patterned mask with circles and squares of a variety of widths (0.2 – 10 μm). The evaporation through the square and circular mask results in difference in the quality and thickness of the evaporated pentacene thin film. Figure 5.3 compares the Raman spectra from 20 nm thick pentacene films evaporated through (a) square and (b) circular apertures of 1 μm width/ radius. The sample is kept at the same orientation relative to the excitation beam, and no efforts are made to control the laser polarisation.

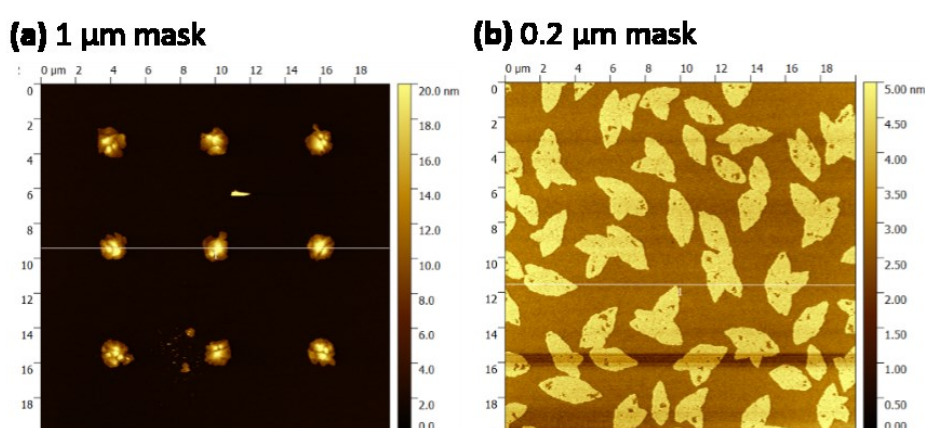


Figure 5.4: AFM images (20 μm x 20 μm) of pentacene films deposited through square apertures of (a) 1 μm and (b) 0.2 μm width.

These AFM were acquired by Pavlo Fesenko at IMEC.

AFM (Figure 5.4) shows that the evaporated film consists of island 'domains' that are 2-3 μm wide. The thickness of the domains were measured using AFM, and are either $\approx$ 20 nm (1 μm aperture) or $\approx$ 1.5 nm thick (0.2 μm

aperture). Unfortunately it was difficult to locate the thinner crystals (0.2 μm aperture) under the Raman microscope, and their thickness, size and random positions limited further structural evaluation. The lateral resolution of the Raman microscope is equivalent to the width of each domain (1 μm). In the absence of control of incident polarisation, the 1 μm wide circular aperture results in no variations of Raman spectra between domains, which points to a similar molecular orientation within each domain. For the domains evaporated through square apertures, the variation in Raman spectra across different domains indicate that there is some variation in the orientation of the pentacene crystals within each unit cell. The angle-dependent polarised Raman spectra were acquired from more than 10 domains across the substrate. In the region of the C-H wagging modes (ends and sides of the molecule) Gaussian peaks of the same FWHM are fitted to the two components of the C-H_{end} mode (1155, 1158 cm^{-1}) and their maximum intensity extracted as a function of polarisation angle (Figure 5.5).

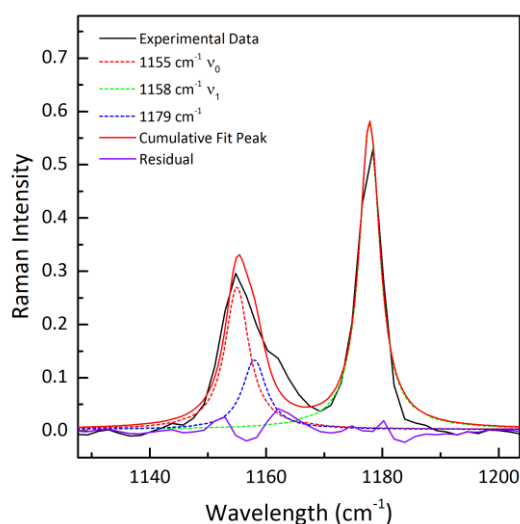


Figure 5.5: Raman spectra of pentacene C-H modes with Gaussian peaks fitted to 1155, 1158 (v_0 and v_1) and 1179 cm^{-1} .

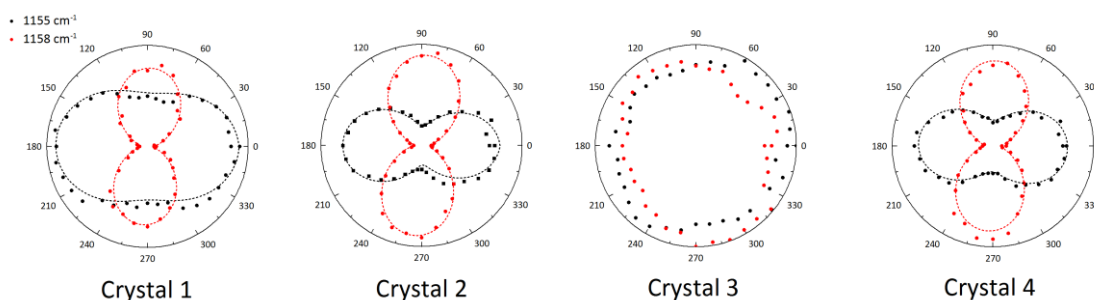


Figure 5.6: Angle dependent polarised Raman scattering intensity of C – C_{SHORT} and C – C_{LONG} Raman active modes taken from four crystals. Crystal 3 demonstrates isotropic scattering of both modes.

The 1 μm wide apertures produce films of ≈ 20 nm, which are expected to consist of about 14 layers of pentacene (14 $\text{\AA}$ long). Changing the polarization of the incident radiation changes the intensity of the 1155 and 1158

components. Figure 5.6 shows polar plots of the intensity of the 1155 and 1158 cm⁻¹ modes typical of spectra recorded across the domains from both the square and circular apertures and correspond to the same lateral position on the sample. It is clear the depolarisation ratio of the high energy component (1158 cm⁻¹) is always greater than that of the low energy component (1155 cm⁻¹), indicating the different symmetry of these modes. The depolarisation ratio (ρ) of a particular mode is calculated by:

$$\rho = \frac{I_{\text{Perpendicular}}}{I_{\text{Parallel}}} \quad \text{Equation 5.1}$$

The variation in the peak position of the C-H_{ends} vibration and of the intensities of the 1155 and 1158 cm⁻¹ components in unpolarised and polarised light indicate that the different shaped apertures promote different crystallographic polymorphs.^[28–31] The intra-layer structure of pentacene films depends on the strength of interactions between the highly aromatic carbons and hydrogens at the edge and those between neighbouring molecules.^[32] When the interactions with the outer hydrogens dominate, pentacene adopts a typical herringbone motif, with neighbouring molecules tilted with respect to one another. Increasing the strength of intermolecular carbon – carbon interactions results in ‘sandwich’ herringbone structure with tilted dimers.^[20,32,33] The relative strengths of these interactions depend on temperature, thickness and surface energy.

For films evaporated through the square aperture there are two possible positions (i.e. Figure 5.3(b)) of the pentacene molecules with respect to the substrate surface and the incident excitation. These molecules are both excited with nearly equal likelihood and exchange the depolarisation ratios from parallel to perpendicular. This polymorph is the so-called ‘sandwich herringbone’; with a shift between adjacent vertically stacked layers.^[21,34] For the non-polarised Raman spectra, the lack of variations across the sample imply that for the circular apertures, only one geometrical orientation is expected, i.e. the layers are aligned.^[21] These two arrangements are illustrated in Figure 5.7. As the temperature, film thickness and surface energy remains constant for the square and circular apertures, the shift in layer alignment must be due to slightly different intermolecular interactions. We propose that after the formation of the first monolayer, pentacene molecules deposited at the edges of the apertures diffuse inward, lowering the level of saturation required for subsequent layers. The diffusion is likely to be different depending on whether the perimeter is circular or square. For the circular aperture, diffusion from the perimeter all starts equally far from the centre so molecules travel similar distances before nucleating.

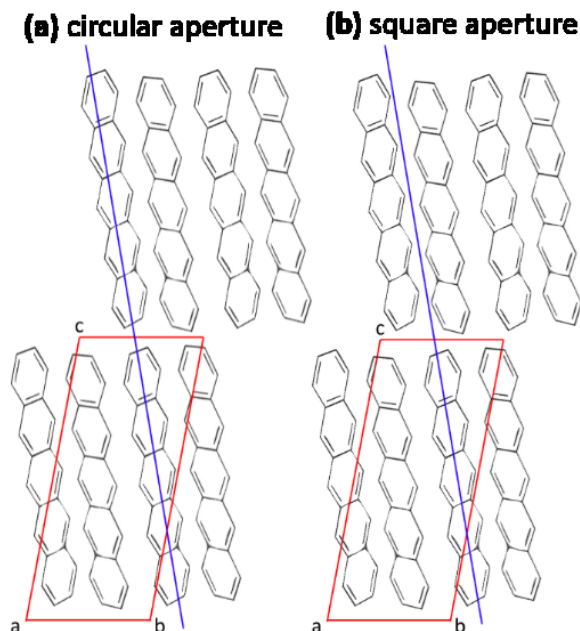


Figure 5.7: The structure of the pentacene polymorph formed from a (a) circular and (b) square aperture of 1 μm . Adapted from reference^[34].

The Control of Pentacene Molecular Packing using Self-Assembled Monolayers

Charge transport in organic thin film transistors occurs within the first few monolayers of semiconductor adjacent to the insulator interface.^[35] This work evaluates the impact of the influence of different self-assembled monolayers (SAMs) on the interfacial molecular packing of the organic semiconductor pentacene. The impact of surface treatment on molecular packing at the interface and the extent to which this packing motif is retained in the bulk of the film. The devices considered here are thin-film transistors in the BG BC architecture, which provides optical access to both the metal/semiconductor interface on top of the source/drain electrodes as well as the dielectric/semiconductor interface in the channel.

The most common electrodes for hole transporting pentacene devices are gold (Au), as it offers good Fermi-level alignment with the highest occupied molecular orbital (HOMO) of pentacene, but still result in a slight barrier to charge injection.^[36–39] The highly delocalised π -electron system of conjugated small molecules can interact with clean metal surfaces. At a gold interface, molecule-substrate interactions dominate intermolecular pentacene-pentacene interactions: the organic molecules form Van de Waals bonds with the metal, where the π -system aligns parallel to the d-orbitals of the gold.^[40,41] SAMs can be used to modify the Au-pentacene interactions, resulting in pentacene film growth dominated by intermolecular interactions. Unlike for the single-crystals, π -stacking of pentacene results in the lowest energy (001) crystal surface arranging parallel to the substrate, such that the molecules have their long-axes perpendicular to the substrate plane.^[1,2,16]

Alongside molecular packing, SAMs can be used to influence energy level offset with the injecting electrodes.^[42,43] Thiol treatments (such as those used for the TIPS and TES- study in Chapter 4) lower the Schottky barrier, whilst silane monolayers lower the surface energy and hydrophobicity of the channel, increasing surface coverage and grain sizes.^[14,41,44,45] A polar monolayer formed by the self-assembly of a layer of molecules with an intrinsic dipole moment can induce a potential energy shift in the Au electrode, raising or lowering the work function. The work function of the untreated Au is ≈ 5.05 eV, resulting in a 0.45 eV hole injection barrier into the HOMO of pentacene.^[46] The charges must first tunnel across the SAM molecules and then be transported into the bulk organic layer.^[47]

For this study we consider aromatic SAMs, thiophenol (TP) and 2,3,4,5,6-pentafluorobenzenethiol (PFBT), which exhibit π - π stacking between their conjugated systems and result in less resistance to electron tunnelling than long-chain alkane thiols.^[48,49]

Atomic force microscopy (AFM), ultraviolet photoemission spectra (UPS) and x-ray diffraction (XRD) are common nanoanalysis tools used to elucidate the morphology, work function and molecular orientation of pentacene.^[50] AFM can provide detailed top surface topographical information, which is not appropriate for interpretation of molecular conformation at the interface, whilst XRD provides information on the long-range (intermolecular) packing structure throughout the bulk of the film and is not sensitive to the subtle changes in molecular packing occurring at interfaces.

To experimentally probe the relationship between pentacene interfacial molecular packing and charge carrier mobility, we used non-invasive resonant Raman spectroscopy directly on complete, electrically characterised devices.^[51–53] The impact of fluorinated and non-fluorinated thiol SAM (PFBT vs. TP) treatments on microstructure and charge transport properties are compared. Optimum device performance is achieved when thiols are used in combination with silane monolayers, which improve wetting to the channel and ensure uniform, homogeneous molecular packing of the semiconductor across both the electrode and dielectric surfaces. Spatial chemical mapping across the contacts and channel areas is used to directly observe allows direct observation of morphological differences between pentacene deposited on the electrode and in the channel. The step-like edge of electrode causes a distinct surface enhancement effect in the Raman scattering, providing strong Raman signals in a very thin pentacene

layer (< 10 nm), and serving as a sensitive chemical and structural probe to the first few layers of pentacene packing at the interface.

5.2.1 Experimental Details

For the fabrication of bottom-gate bottom-contact OTFTs, heavily doped Si and thermally grown 100 nm of silicon dioxide (SiO_2) were used as a gate and dielectric, respectively. For the source and drain electrodes, 50 nm of Au was thermally evaporated with a rate of $1 \text{ \AA s}^{-1}$ with a channel width of 1000 μm and length of 50 μm . For the modification of Au electrodes, thiophenol (TP) and 2,3,4,5,6-Pentafluorothiophenol (PFBT) were purchased from Sigma Aldrich. The substrates with Au electrodes were soaked in a toluene solution containing 10 mM L^{-1} of either TP or PFBT for 1 minute and then were rinsed with toluene to remove residue. Due to the high reactivity of the SAMs, the TP-treated or PFBT-treated Au substrates were stored in a desiccator separately for 30 min under low-vacuum to eliminate vaporised SAM molecules surrounding the samples and prevent cross-contamination. The samples were then transferred to the vacuum chamber and 50 nm of pentacene was evaporated onto the SAM-treated Au electrodes at a rate of $0.5 \text{ \AA s}^{-1}$. The electrical characteristics for the fabricated devices were measured by a semiconductor parameter analyzer (Agilent 4155 C) in a N_2 -filled glove box. The transfer characteristics were obtained in a saturation regime where $V_{\text{GS}} = -30 \text{ V}$.

5.2.2 Effect of SAM Treatment on Pentacene Packing on the Gold Electrode

First, the impact of thiophenol (TP) and pentafluorobenzenethiol (PFBT) treatment on pentacene polymorphism is evaluated. AFM images of a typical $5 \times 5 \mu\text{m}$ area of the thin films prepared on various substrates (untreated gold, Au/ TP and Au/PFBT) are shown in Figure 5.8. On untreated gold surfaces the grains are $\approx 300 \text{ nm}$ wide with no preferential orientation. The grains are smaller for TP treated gold (100 nm) and larger after PFBT treatment ($\approx 500 \text{ nm}$ wide). The grain sizes are significantly smaller than the lateral resolution of the Raman microscope ($\approx 1 \mu\text{m}$), and therefore any measurement represents an average spectrum taken over several grain orientations.

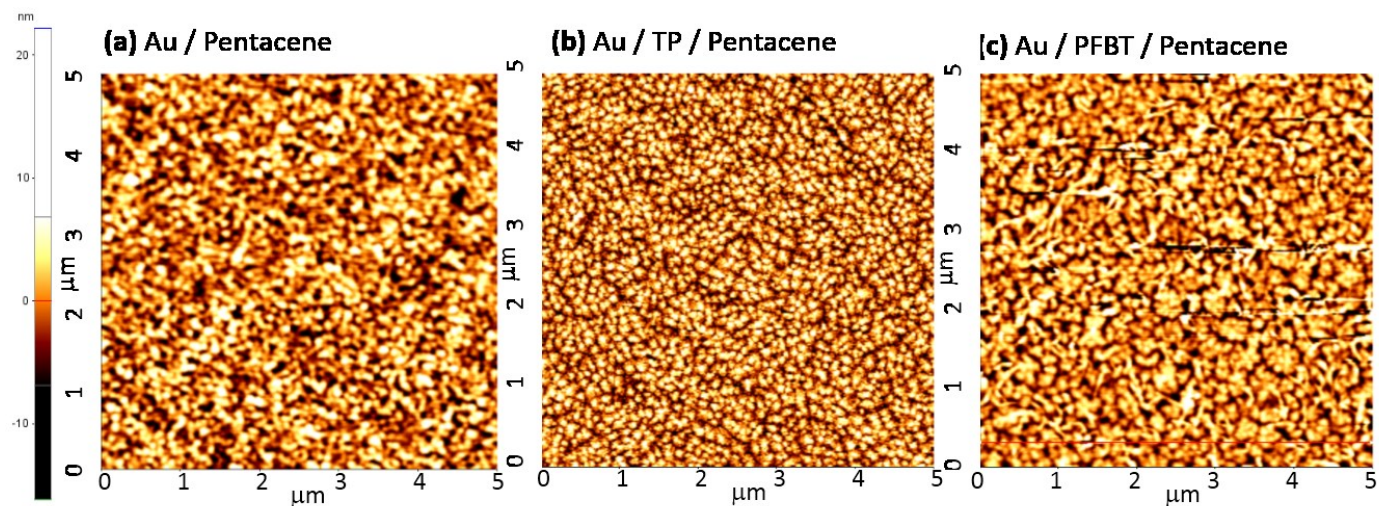


Figure 5.8: AFM images of 50 nm thick vacuum evaporated pentacene thin films on (a) untreated Au (b) TP treated Au (c) PFBT treated Au (5 x 5 μm).

Figure 5.9 shows the absorption spectra obtained from representative samples to those in Figure 5.8. The eV scale is used to emphasise the narrow vibronic features of the isolated pentacene molecule. For this measurement a thin gold layer (15 nm) was deposited on quartz and the resulting substrates were treated with TP and PFBT. 50 nm of pentacene was then deposited on top of the quartz / Au/ SAM stack. The resulting absorption is plotted together with the absorption of pentacene isolated in a *p-terphenyl* lattice. The absorption of bare gold (15 nm) has been removed to allow comparison of the pentacene layer above. The crystal growth within a *p-terphenyl* lattice results in isolated pentacene molecules and is described in detail elsewhere.^[54,55]

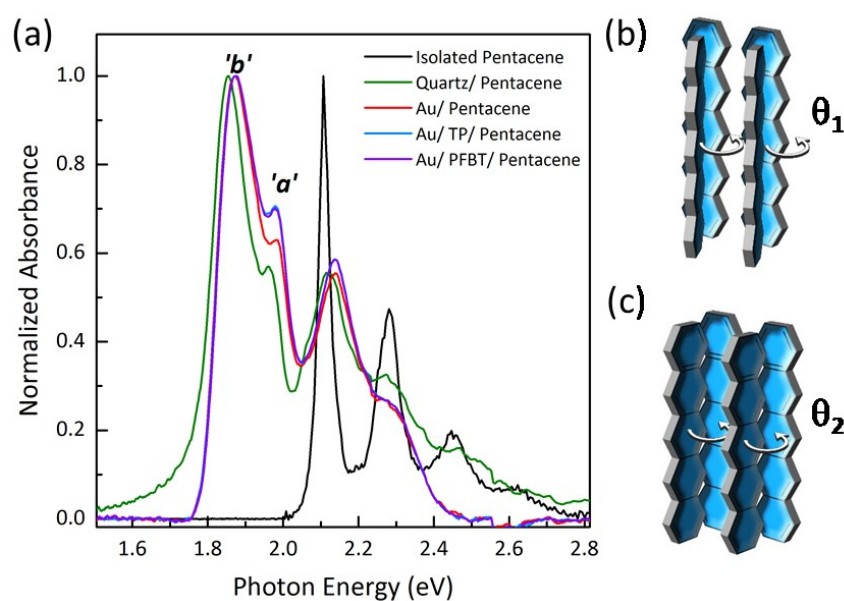


Figure 5.9: Normalised UV-Visible absorption spectra of pentacene thin films (~50 nm) on quartz and Au substrates and pentacene isolated in a *p-terphenyl* lattice (black dotted). Au substrates were also compared with/ without SAM (PFBT and TP). Molecular orientation within the unit-cell on (b) unmodified and (c) surface treated gold (where $\theta_1 < \theta_2$).

Electronic Transition	Isolated Pentacene	Quartz	Quartz/ Au	Quartz/ Au/TP	Quartz/Au /PFBT
b		1.85	1.87	1.87	1.87
a		1.96	1.99	1.98	1.98
0-0	2.10	2.12	2.15	2.14	2.14
0-1	2.28	2.27	2.28	2.28	2.28
0-2	2.45				

Table 5.2: Peak positions in eV of absorption transitions for the samples discussed in text.

The absorption peaks at 2.11, 2.28 and 2.45 eV correspond to electronic transitions from the ground to the first excited singlet state with clear vibronic features (0-0, 0-1, 0-2 and 0-3) of pentacene. Equivalent to TIPS pentacene in Section 4.3, the energetic spacing (0.17 eV) is roughly equivalent to the vibrational energy of a C – C_{SHORT} stretching mode (1372 cm⁻¹).^[52] The most striking feature when moving from the isolated molecules (described in to the solid-state thin film ones is the splitting of the 0-0 band in absorption. Instead of a narrow, well-defined single band centred at 2.10 eV, two new bands are seen at 1.96 eV and 1.85 eV (indicated as ‘a’ and ‘b’ components). The relative intensities of the ‘a’ and ‘b’ peaks is different for untreated surfaces and those treated by SAMs. These doublets coincide well with the Davydov components reported previously, and occur due to the absorption of herringbone-packed polycrystalline pentacene films.^[19,20] The splitting of the two components can also be used to elucidate the distribution of orientations of crystallites in the sample, with narrower splitting suggesting a broader distribution of orientations.^[56] In order to compare our results to published work, the energies are converted into wavenumbers. Davydov splitting ranges from 850 cm⁻¹ to 1100 cm⁻¹ depending on whether pentacene adopts the quasi-amorphous or single-crystalline phase.^[57] The largest Davydov splitting (i.e. most ordered phase) is seen here on an untreated gold substrate, which indicates the strongest intermolecular interactions occur without SAM treatment (Au- 935 cm⁻¹, Au/TP- 863 cm⁻¹, Au/PFBT- 863 cm⁻¹, Quartz- 870 cm⁻¹).^[58]

The relative strengths of the ‘a’ and ‘b’ bands are controlled by relative molecular orientations, which determine the molecular orbital overlap within a unit cell.^[57,59–62] Pentacene molecules tilted at 45 ° to one another would have similar relative intensities of the two components, whereas parallel molecules would show one broad absorption band. A lower intensity ‘a’ to ‘b’ band for unmodified Au indicates a smaller tilt angle between adjacent pentacene cores (Figure 5.9 (b)). The absorption spectra of the films deposited on Au treated with either TP or PFBT are indistinguishable and correspond with a maximum tilt angle between molecules (Figure 5.9 (c)), indicating that the molecular orientations are similar irrespective of the type of thiol used.

Figure 5.10 (a-c) compares the Raman spectra of pentacene thin films deposited on untreated, PFBT and TP-treated Au substrates under (a) 785, (b) 633 and (c) 457 nm excitation wavelengths. Pentacene belongs to a D_{2h} point group and the C – C_{SHORT} stretch is an A_g fundamental bands with Raman scattering tensor components along α_{xx} , α_{yy} and α_{zz} .^[22,23,63–66] The C – C_{LONG} stretch (1596 cm⁻¹) is a B_{3g} mode and only has a tensor component along α_{yz} .^[63,64]

	Single Crystal			Au			TP			PFBT		
Excitation λ (nm)	457	633	785	457	633	785	457	633	785	457	633	785
C-H_{Ends}	1157	1159	1158	1158	1158	1157	1156	1157	1156	1156	1158	1156
C-H_{Sides}	1176	1179	1177	1176	1178	1178	1178	1178	1178	1178	1178	1178
C – C_{SHORT}	1369	1371	1370	1371	1371	1370	1371	1371	1370	1371	1372	1370
C – C_{LONG}	1595	1598	1597	1597	1597	1597	1596	1597	1597	1596	1597	1597

Table 5.3: Peak positions (cm⁻¹) of Raman active vibrational modes at 457, 633 and 785 nm excitation for isolated pentacene and thin films deposited on untreated Au, TP treated Au and PFBT treated Au, extracted from Figure 5.10.

	Au			TP			PFBT		
	Channel	Channel + ODTS	Contact	Channel	Channel + ODTS	Contact	Channel	Channel + ODTS	Contact
C-H_{Ends}	1157	1156	1155	1154	1155	1157	1156	1156	1157
C-H_{Sides}	1178	1178	1175	1177	1178	1178	1178	1178	1178
C – C_{SHORT}	1371	1371	1368	1371	1371	1371	1371	1371	1371
C – C_{LONG}	1597	1598	1594	1597	1598	1597	1597	1597	1597

Table 5.4: Resonant excitation (514 nm), peak positions (cm⁻¹) of Raman active vibrational modes on untreated Au, TP treated Au and PFBT treated Au.

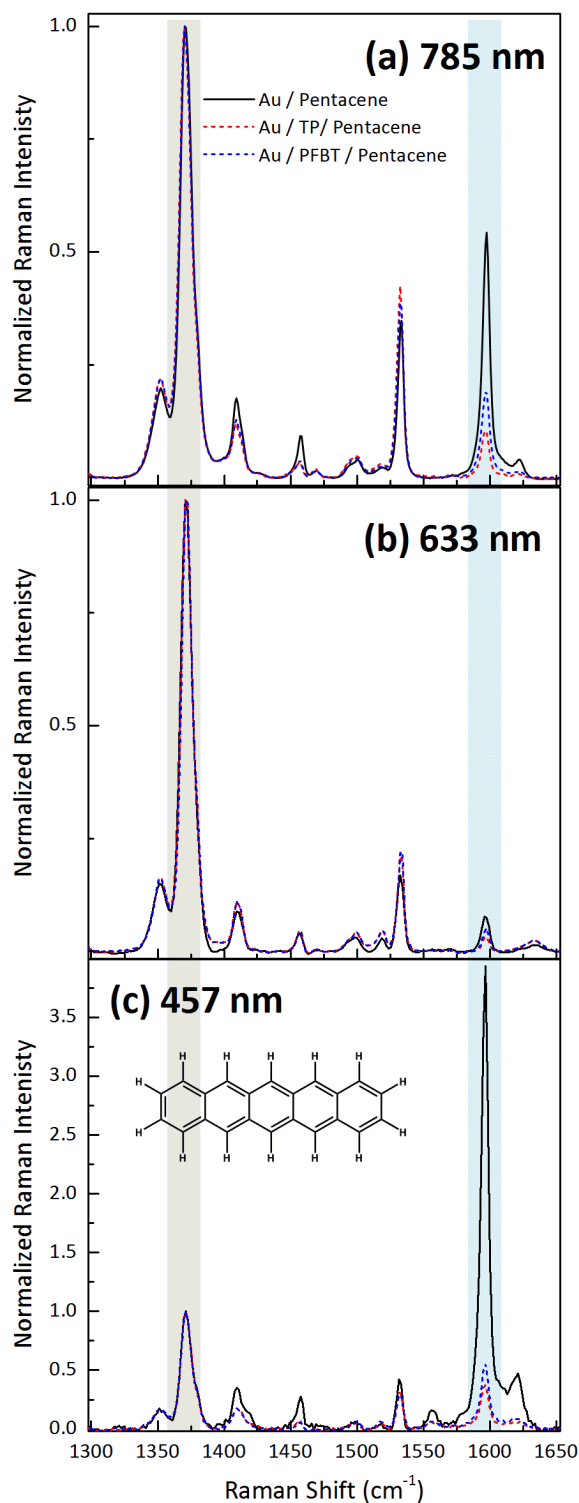


Figure 5.10: Raman spectra of pentacene on unmodified Au (black solid) and Au treated with PFBT (red dashed) and TP (blue dotted) when excited with (a) 785 nm (b) 633 nm (c) 457 nm. The highlighted modes are C – C_{SHORT} (grey) and C – C_{LONG} (blue). All spectra are normalised to the 1372 cm^{-1} C – C_{SHORT} mode.

The Raman shifts of the main vibrational modes at each excitation wavelength (457, 633, 785 nm) for pentacene deposited on surface treated Au extracted from Figure 5.10 are detailed in Table 5.3. The peak positions of a single crystal are shown for comparison. The peak positions are relatively consistent between the devices ($1 - 2 \text{ cm}^{-1}$

variation) irrespective of surface treatment, which indicates that this is not an appropriate means to characterise the morphological differences. In general, non-resonant excitations (785 nm) probe both the ordered and disordered molecules at the same time, and the Raman peaks are at slightly lower energy than when resonant (633 nm). It is interesting to compare the peak positions when excited with 457 and 633 nm, which are either resonant with the Davydov absorption band or higher electronic states. Resonance with the Davydov absorption band (633 nm) appears to be selective to disordered pentacene molecules and Raman peaks appear at a higher energy, whilst higher excitation energies (457 nm) select the ordered molecules (C – C_{SHORT} Single Crystal, 785 nm – 1370, 633 nm – 1371, 457 nm – 1369 cm⁻¹). The negligible changes in frequency are all within the error of our apparatus (± 1 cm⁻¹) and instead we consider variations in relative peak intensity.

The Raman scattering intensity of the B_{3g} (C – C_{LONG}) mode at 1596 cm⁻¹, relative to that of the A_g (C – C_{SHORT}) mode at 1372 cm⁻¹ show a strong dependence on both the excitation conditions (resonant or non-resonant) and the molecular interaction with the underlying surface (Au or SAM on Au). Non-resonant 785 nm excitation does not preferentially enhance any particular vibrational modes and detect all vibrations of the molecule. In contrast, Figure 5.10 (b) illustrates that under 633 nm (1.96 eV) excitation, Raman scattering from C – C stretching modes aligned along the short-axis are strongly enhanced (*i.e.* the largest C – C_{SHORT}/C – C_{LONG} value). Such enhancement is due to a surfaced enhanced Raman scattering effect allowing more sensitive observation of the interfacial packing of pentacene on top of Au surface, note that a 633 nm excitation matches with the plasmonic absorption of Au.^[4,67] Resonant Raman spectra predominantly enhances the totally symmetric A_g modes.^[68] The Raman activity of certain modes is determined by the D_{2h} point group of the pentacene molecule. For pentacene, 633 nm excitation corresponds to excitation from the HOMO π (B_{2g}) to the LUMO (B_{3u}). On the other hand, the Raman spectrum measured with 457 nm (2.71 eV) excitation shows an enhancement of the C – C_{LONG} mode intensity (Figure 5.10 (c)). The 457 nm excitation is now in resonance with a higher-energy electronic transition, whose dipole aligns with the long-axis of pentacene molecule and is perpendicular with that of the low energy absorption transition.^[69] Whilst the different resonant conditions affect the relative peak intensities, the trend is the same for the samples considered here, which permits the use of resonant excitations to accurately determine the packing of thin pentacene thin films.

Figure 5.11 summarizes the Raman scattering intensity of the C – C_{LONG} relative to the C – C_{SHORT} axis stretch modes measured under various excitation wavelengths. The absorption spectra (Figure 5.9 (a)) illustrate that surface

treatment has no impact on the position of the absorption bands but slight variations in the relative intensities, which could result in the association of resonant enhancement with different parts of the molecule being dependent surface treatment. However the same trend is observed irrespective of surface treatment, $C - C_{\text{SHORT}}/C - C_{\text{LONG}} \text{ TP} > \text{PFBT} > \text{untreated Au}$, implying that molecular packing dominates the effects of resonance.

The intensity of Stokes Raman scattered radiation is proportional to:

$$I \propto |\mathbf{e}_i^* R \mathbf{e}_s|^2 \quad \text{Equation 5.2}$$

where R is the Raman tensor of a particular mode and $\mathbf{e}_i$ and $\mathbf{e}_s$ are the polarisations of the incoming and scattered photons, respectively. By considering the Raman scattering tensors of the D_{2h} point group it is possible to determine which modes will scatter light based on the molecular orientation with respect to the substrate plane. Raman scattering tensors for the B_{3g} and A_{1g} modes in the D_{2h} point group appear as:^[70]

$$A_g = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}, B_{3g} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{yz} \\ 0 & \alpha_{yz} & 0 \end{pmatrix} \quad \text{Equation 5.3}$$

Given that pentacene molecules align parallel along the a and b - crystal axes of the unit cell, if the molecule are lying in the plane of the substrate, the polarisations of the incoming and scattered photons are only polarised in x - and y - and can be simplified as:^[28]

$$\mathbf{x} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \mathbf{y} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \text{Equation 5.4}$$

In non-resonant Raman spectroscopy, the intensity of a B_{3g} can then be estimated for various combinations of incident and scattered photon polarisations (see Table 5.5) therefore be described as follows:

$$I_{B_{3g}} \propto \left| \mathbf{e}_i^* \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{yz} \\ 0 & \alpha_{yz} & 0 \end{pmatrix} \mathbf{e}_s \right|^2 \quad \text{Equation 5.5}$$

For incoming y -polarised light and scattered x -polarised light, this simplifies to:

$$I_{B_{3g}} \propto (100) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{yz} \\ 0 & \alpha_{yz} & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0 \quad \text{Equation 5.6}$$

e_i	e_s	$\propto I_{B_{3g}}$	$\propto I_{A_g}$
Photon Polarisation			
Incoming	Outgoing		
x	x	0	α_{xx}
x	y	0	0
y	x	0	0
y	y	0	α_{yy}

Table 5.5: Intensities of B_{3g} and A_{1g} modes for incident light parallel to the pentacene long-axis.

The only case where $I_{B_{3g}}$ will be non-zero is when there is some 'z' component of the incident or scattered photon (the B_{3g} mode is tilted out of the substrate plane). There is very little discussion in literature about how resonant excitations affect the polarisation dependence of scattered light, but Figure 5.10 (b) suggests they makes $C - C_{SHORT}/C - C_{LONG}$ more sensitive to molecular orientation. This is likely because the HOMO-LUMO transition is directed along the short axis.^[52,71]

The relative Raman intensity of the $C - C_{SHORT}$ stretch mode with respect to the $C - C_{LONG}$ mode is greatest in single crystals of pentacene, followed by films deposited on TP-treated Au, PFBT and finally untreated Au (Figure 5.11). A decrease in $C - C_{SHORT}/C - C_{LONG}$ intensity on untreated Au indicates that pentacene molecules are mainly lying flat (edge-on, Figure 5.11 (b)) so their $C - C_{LONG}$ stretch is aligned mainly parallel to the substrate, providing the strongest enhancement of this mode with the electric field of the laser. The surface treatment limits molecule-substrate interactions and allows the pentacene molecules to pack in a 'standing up' fashion (end on, Figure 5.11 (c)).

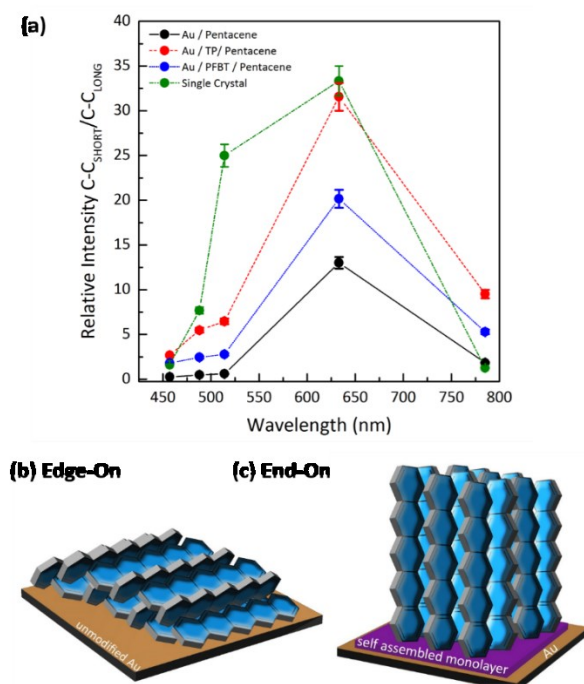


Figure 5.11: (a) Relative Raman scattering intensity of $C - C_{SHORT}/C - C_{LONG}$ axis stretch mode under 457, 488, 514, 633 and 785 nm excitation for 100 nm thick pentacene films and a pentacene single crystal. Illustrations of edge-on and end-on packing on untreated and surface treated pentacene films

To investigate the extent to which the edge-on and end-on orientations (Figure 5.11 (b) and (c)) are retained close to the interface, a series of pentacene films of varying thicknesses were considered. The overall Raman signal is strongest from 100 nm thick films on untreated Au, owing to the greatest number of scattering centres in the path of the laser-beam when the molecules are lying flat.

The resonant enhancement of Raman scattering achieved at a 514 nm excitation allows determination of molecular orientation in very thin (≈ 10 nm) layers of pentacene. Figure 5.12 (a) illustrates the relative intensity of $C-C_{\text{SHORT}}/C-C_{\text{LONG}}$ for film thicknesses ranging from 10 – 100 nm on untreated (black) and treated (red, blue) gold surfaces. For pentacene deposited on untreated gold there is very little difference in the $C-C_{\text{SHORT}}/C-C_{\text{LONG}}$ relative intensity (≈ 0.60), irrespective of film thickness. For TP treated Au, an increase in $C-C_{\text{SHORT}}/C-C_{\text{LONG}}$ relative intensity from 4.60 to 7.47 ± 0.30 is observed when increasing the film thickness from 10 to 100 nm, indicating that the molecules furthest from the interface are standing more upright than those close to the substrate interface. In the case of PFBT (Figure 5.12 (d)), the opposite is true: molecules close to the substrate are standing more upright than those far away, and could be due to the stronger dipole moment of PFBT (2.34 Debye) vs. TP (1.23 Debye).^[72] The results in this section demonstrate the unique capability of resonant Raman spectroscopy to directly probe the impact of substrates on interfacial packing of pentacene in thin films.

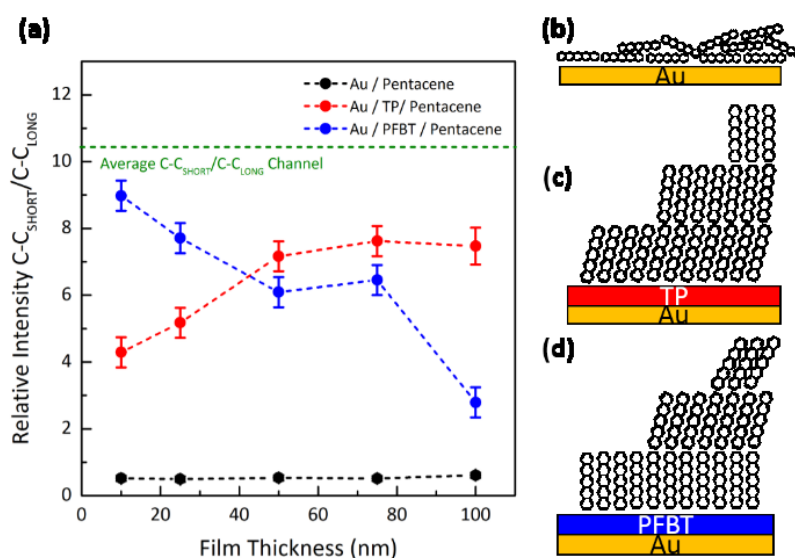


Figure 5.12: (a) Relative intensity $C-C_{\text{SHORT}}/C-C_{\text{LONG}}$ under 514 nm excitation for pentacene films of different thicknesses. Graphical illustrations of molecular packing on (b) untreated and (b),(c) surface treated Au.

5.2.3 Effect of SAM Treatment on Pentacene Packing in the Active Channel

As this work focuses on the lateral charge transport in FETs, it is important to consider the molecular orientation in the active channel where charges move from the source to drain electrodes. Silane treatments such as octadecyltrichlorosilane (ODTS) passivate the polar species formed in the channel after oxygen plasma treatment during device fabrication.^[73]

The peak positions of the main vibrational modes of pentacene on the three surfaces considered here, excited with a resonant 514 nm, measured (i) in the untreated channel (ii) in the ODTS treated channel and (iii) on the contact are detailed in Table 5.4. This is a clearly an inappropriate means to compare the pentacene morphology as all the changes are within the equipment error ($\pm 1 \text{ cm}^{-1}$). The comparison of 514 nm (on the contact) and 633 nm excitation (Table 5.3, Table 5.4) highlights the different natures of the Davydov and $S_0 \rightarrow S_1$ transitions. The Davydov absorption band only occurs in the solid state and particularly sensitive to disorder, resulting in Raman scattering at high frequencies. On the other hand, the $S_0 \rightarrow S_1$ is less sensitive to energetic disorder. These differences are particularly strong for untreated Au, perhaps due to the arrangement of the molecules relative to the excitation beam.

The ratio of the integrated relative peak areas of the $C - C_{\text{SHORT}}/C - C_{\text{LONG}}$ under a resonant 514 nm excitation is given in Table 5.6. Raman spectroscopy of pentacene in the active channel (on top of the SiO_2 dielectric) indicates that pentacene is in the end-on configuration (very weak scattering from the $C - C_{\text{LONG}}$ mode). In BG BC devices with untreated Au electrodes pentacene molecules pack edge-on (lying down) on the Au surface and end-on (standing-up) in the channel. This discontinuous growth of pentacene molecules at the electrode-channel interface is expected to hinder efficient charge injection/ transport. From these results, it is expected the most uniform interfacial molecular packing occurs in devices where the Au electrodes are treated with TP and the channel with ODTS (smallest mismatch of relative intensities, $C - C_{\text{SHORT}}/C - C_{\text{LONG}} \approx 6.7$ for the electrodes and 7.6 for the channel).

	Integrated Peak Area: $C - C_{\text{SHORT}}/C - C_{\text{LONG}}$			
	Untreated SiO_2		ODTS Treatment	
	Channel	Contact	Channel	Contact
	± 0.45			
Untreated Au	7.35	0.61	7.75	0.62
TP	12.82	7.47	7.56	6.69
PFBT	11.36	2.79	7.13	3.56

Table 5.6 Integrated Peak Area $C - C_{\text{SHORT}}/C - C_{\text{LONG}}$ in resonant 514 nm excitation for 60 nm thick pentacene films.

This molecular packing can be understood by considering the roles of the thiol (TP, PFBT) and silane surface treatment (ODTS). Whilst TP and PFBT SAMs are effective at blocking the dipole formed at Au electrode-semiconductor interface, thiol groups do not chemically bond to the SiO₂ dielectric nor influence molecular packing in the transistor channel. On the other hand, ODTS treatment removes –OH groups left on the dielectric surface after O₂ plasma treatment, which improves wetting of the dielectric and results in an increased grain size of the active material.^[13,74,75] The unreactive surfaces of dielectrics allow the inter-molecular forces to dominate over the substrate-molecule forces, and hence pentacene molecules pack with the lowest energy (001) surface (along the short-axis) parallel to the substrate plane (end-on).

5.2.4 Effect of SAM Treatment on the Pentacene Packing at the Electrode/ Channel Interface

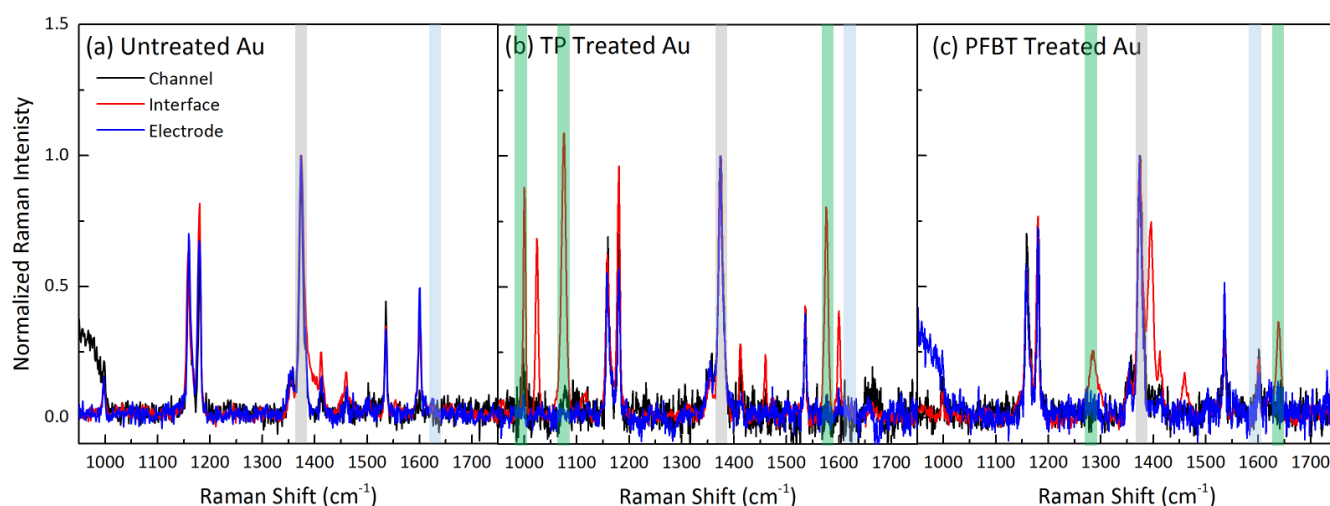


Figure 5.13: Non-resonant Raman spectra (785 nm excitation) collected from different points on the device: in the channel, at the electrode/channel interface and on the electrode for (a) untreated Au (b) PFBT treated Au and (c) TP treated Au. Modes shaded green are related to stretches of the SAMs and are discussed in text.

Figure 5.13 compares the Raman spectra of pentacene in the channel, at the electrode-channel interface and on top of the electrode. One dimensional Raman maps (line scans) were performed laterally across the device (from electrodes to channel areas) to confirm of the formation of a ‘SAM’ with effective surface coverage and the impact of boundary between the Au electrode and dielectric channel on molecular packing. In contrast to the smooth electrode surface, the sharp edge at the electrode-channel interface provides efficient electromagnetic field enhancement and localization.^[76] The large enhancement of Raman signal allows direct observation of the first few layers above the substrate. For devices with untreated Au electrodes the interface shows an abrupt change in pentacene molecular

orientation from lying-down (edge-on) to standing up (end-on) on the dielectric, clearly demonstrated in Figure 5.14 by the increase relative intensity of $C - C_{\text{SHORT}}/C - C_{\text{LONG}}$ and change in shape of the $C - C_{\text{SHORT}}$ axis stretch.

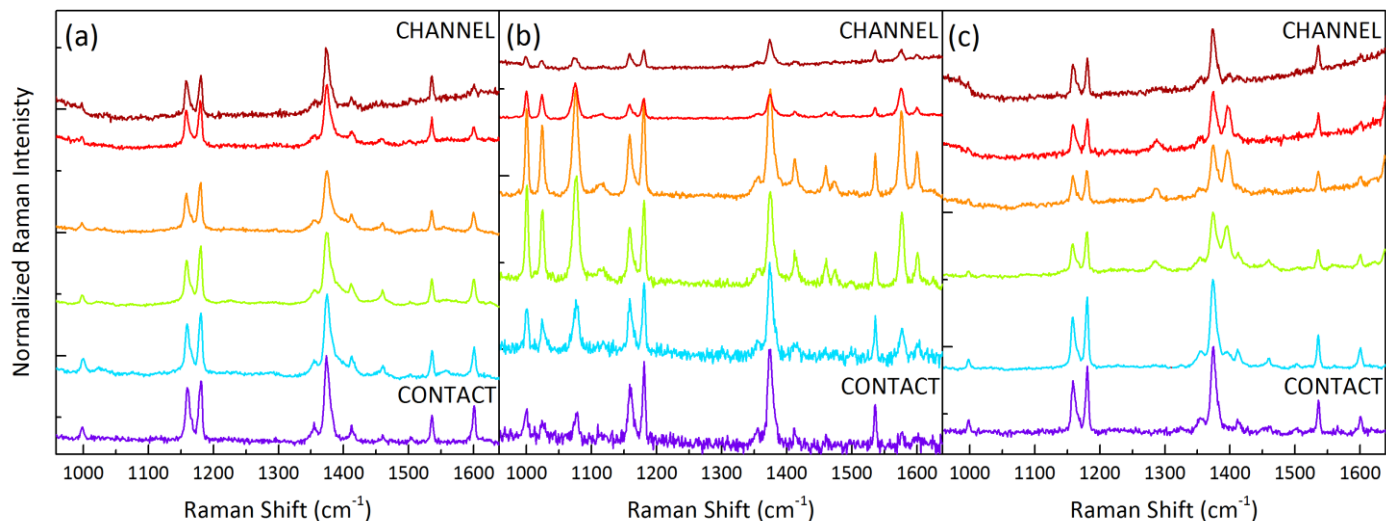


Figure 5.14: Raman spectra from different points on the device, on the contact (purple), at the interface (green, orange) and in the channel (dark red) for 60 nm pentacene on (a) untreated (b) TP treated and (c) PFBT treated Au.

The Raman spectra of TP and PFBT (Figure 5.15) were simulated using quantum chemical calculations at the B3LYP/6-31G(d,p) and B3LYP/LanL2DZ levels of theory and compared to published work.^[72] In the case of TP SAM-treated Au, the Raman intensity of the 1076 cm^{-1} mode, which originates from a TP molecule (in-plane C-S stretch), increases from negligible on the electrode to much stronger than that of pentacene at the interface (Figure 5.14(b)). Additional peaks at 1001, 1024, 1460, 1473 and 1575 cm^{-1} relate to stretching modes of the benzene ring in TP.^[77]

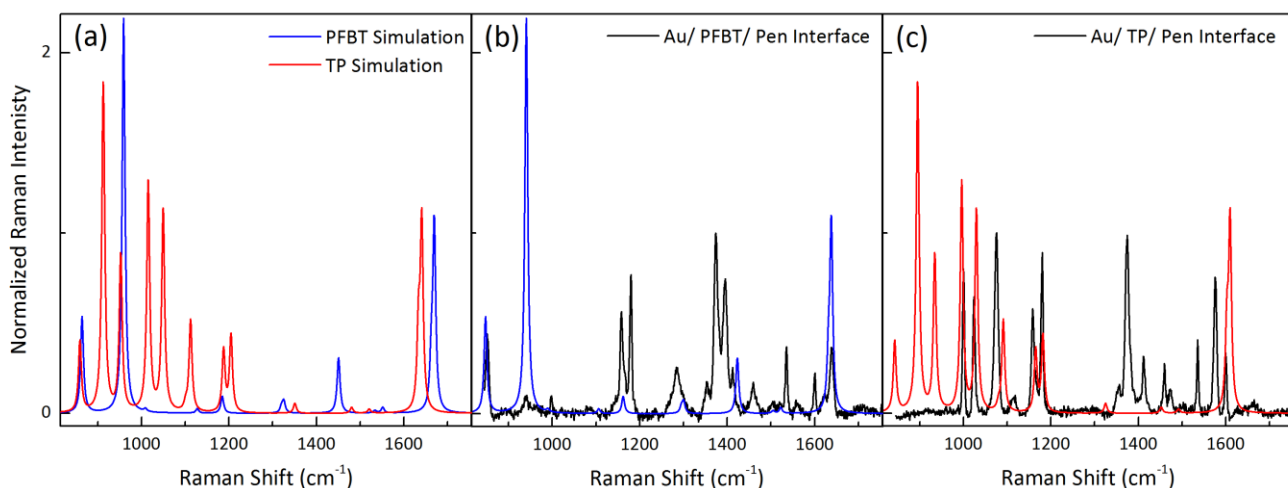


Figure 5.15: (a) DFT simulation of Raman spectra of PFBT (blue) and TP (red). Pentacene packing at the electrode/ channel interface for (b) PFBT treated and (c) TP treated Au.

The Raman signal of PFBT is significantly weaker than that of TP, but quadrant stretches of the benzene ring of PFBT are also observed at 1638, 1621 cm^{-1} along with other modes at 851 and 1285 cm^{-1} . Raman scattering from TP is larger than that from PFBT indicating a more polarizable chemical bond formed between the sulphur atom in the thiol and gold surface. The highly electronegative fluorine atoms in PFBT are more effective at withdrawing charge from the benzene ring, resulting in less polarizable Au-S bonds. The proposed packing of the SAM layers on the Au electrode is illustrated in Figure 5.16.

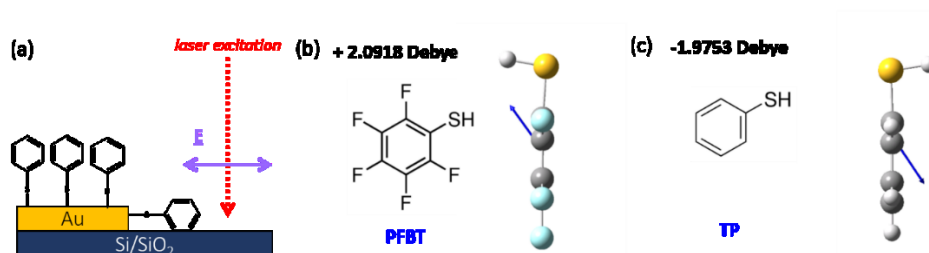


Figure 5.16: (a) Proposed TP molecular orientation at edge of contact. Simulated dipole moments and orientations for (b) PFBT and (c) TP at LanL2DZ basis set.

There is evidence for pentacene molecules with disturbed sp^3 carbons at the interface between the electrode and channel, which presents as an increase in the intensity of the C-H bending mode on the sides of the molecule (1179 cm^{-1}) relative to those at the ends (1158 cm^{-1}) and shift of the C – C_{SHORT} mode to 1381 cm^{-1} .^[67] The disruption is due to the formation of sp^3 hybridised carbon atoms in pentacene (additional hydrogens on the sides and ends of the molecule) confirmed by Adil *et al* using DFT, and is enhanced after periods of long bias stress.^[67] This is likely due to the pentacene molecules attempting to stand-upright on both the side of the treated electrode and in the channel. The molecular packing across a complete device are illustrated in Figure 5.17 (c-e).

5.2.5 Effect of SAM treatment on Charge Transport Characteristics

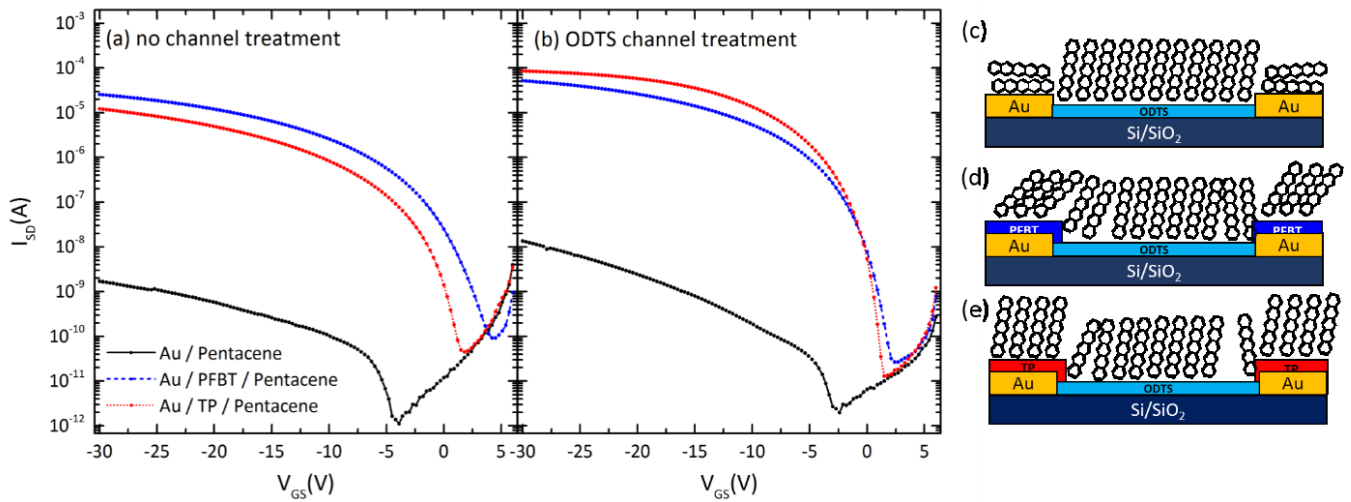


Figure 5.17: Transfer Curves of pentacene OTFTs in bottom gate bottom contact architecture, $W=1000\ \mu\text{m}$, $L=50\ \mu\text{m}$, measured in nitrogen. $V_{SD} = -30\ \text{V}$, $V_G = 10\ \text{to} -30\ \text{V}$ (a) with no treatment and (b) with ODTS treatment to the channel. The active layer thickness is 60 nm. (c) – (e) Proposed molecular packing for pentacene on untreated and thiol treated Au.

To correlate the changes in morphology with device performance, the charge transport characteristics of BG BC transistors devices with and without self-assembled monolayers were measured. Representative transfer characteristics are compared in

Figure 5.17 and are summarised in Table 5.7. Without any surface treatment to the channel or electrodes, the charge-carrier mobility of pentacene in the saturation regime is $\approx 10^{-6}\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and a large negative voltage ($\approx -5\ \text{V}$) must be applied to the gate for charge injection to occur. The threshold voltage represents the voltage required to switch the transistors 'on'. To avoid the need to applying positive voltages to turn the devices 'off', this voltage should ideally be zero.

	No ODTS Treatment			ODTS Treatment		
	Mobility	Threshold Voltage	$I_{ON/OFF}$	Mobility	Threshold Voltage	$I_{ON/OFF}$
	$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	V		$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	V	
Untreated	$9.62 \times 10^{-6} (\pm 7.38 \times 10^{-7})$	$-9.66 (\pm 2)$	10^3	$6.72 \times 10^{-5} (\pm 4 \times 10^{-5})$	$-3.60 (\pm 1)$	10^3
TP	$4.70 \times 10^{-2} (\pm 3.17 \times 10^{-2})$	$-4.89 (\pm 1)$	10^5	$6.34 \times 10^{-1} (\pm 1.04 \times 10^{-1})$	$-2.00 (\pm 1)$	10^5
PFBT	$1.00 \times 10^{-1} (\pm 1.75 \times 10^{-2})$	$-1.17 (\pm 0.2)$	10^5	$1.61 \times 10^{-1} (\pm 3.67 \times 10^{-2})$	$-1.70 (\pm 0.5)$	10^5

Table 5.7: Device characteristics of BG BC transistors.

Thiol treatment is reported to improve charge carrier mobility by five orders of magnitude.^[43] To investigate the change for the devices considered here, the dipole moments of the two thiol SAM molecules were calculated using DFT in the Gaussian '09 software package, with the B3LYP method and LanL2DZ basis set.^[72] The work function change

depends on the both the magnitude and orientation molecular dipole of the SAM. The electronegative fluorine atoms in PFBT result in a large dipole moment (+ 2.1 Debye), which points in the opposite direction to TP (- 1.98 Debye, see Figure 5.16). The work function change after the formation of a polar monolayer was measured using photoelectron spectroscopy, the details of which are reported in our published work. TP treatment decreases the Au work function from 4.78 to 4.67 eV, whereas PFBT increases the work function to 5.02 eV.

When pentacene is deposited on PFBT treated Au, there is an electron transfer from the weakly bound pentacene HOMO to the polar monolayer and the Fermi energies align.^[43] This improves the energy alignment with pentacene and brings the threshold voltage close to zero (see Table 5.7). The improved charge transport characteristics are due to both the reduced barrier to hole injection and more uniform molecular packing from the contact to the channel (Figure 5.17). The upright orientation of pentacene on SAM treated Au electrode results in the most effective lateral charge transport and injection in the direction of π -stacking across the channel, increasing mobility from $\approx 10^{-6}$ (bare Au) to $0.10 \pm 0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (PFBT). On the other hand, the improved wetting after treatment with ODTS promotes intermolecular interactions and an therefore end-on packing, which results in a further increase in charge carrier mobility with the TP-treated Au device increasing from a mobility of 0.05 to $0.63 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This order-of-magnitude increase in mobility is due to the consistent configuration of pentacene packing across the Au electrodes and in the channel.

5.2.6 Summary

The molecular packing on different substrates can be understood simply by comparing the relative intensity of the long and short-axis C – C modes of the pentacene molecule. We have demonstrated that surface treatments not only improve device performance due to increased grain sizes and minimised injection barriers but also via control of interfacial molecular packing. Thiol monolayers are shown to minimize dipole formation at a metal/organic interface, allowing pentacene molecules to stand-up. This upright orientation is maintained on the SiO_2 dielectric channel reducing molecular disruption across the device, allowing for more efficient lateral charge transport and dramatic improvements in device performance. The most consistent molecular packing across electrode – interface – channel is observed with both TP treated Au and ODTS treated SiO_2 . Charge carrier mobility is found to increase from 9.6×10^{-6} for untreated Au/ SiO_2 to $0.047 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for TP-treated Au. Furthermore ODTS treatment to the SiO_2 , which only affects molecular conformation in the channel and so not the energy barrier to injection, improves this further to

$0.63 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Raman spectroscopy is demonstrated as an effective, non-destructive, direct probe of molecular packing of both the active organic semiconducting molecules and the SAM molecules used in organic thin-film transistors.

5.3 Impact of MgO Interlayers on Molecular Packing and Device Performance in Copper Phthalocyanine Magnetic Tunnel Junctions

Organic Spintronics

The field of organic spintronics has attracted a large amount of interest since the discovery of magnetoresistance (MR) in organic devices in 2002.^[78] Spintronics combines spin-physics with organic chemistry, allowing molecular level engineering of spin-based electronic devices. Organic magnetic tunnelling junctions (MTJs) consist of two ferromagnetic layers (FM_1 and FM_2) separated by thin layers of an organic semiconductor.^[79,80] Organic semiconductors are composed of light elements without magnetic moments (mainly carbon and hydrogen), which result in long spin diffusion lengths due to weak spin orbit-coupling and hyperfine interactions.^[80–82] We have previously introduced the ‘hopping mechanism’ with regards to charge transport in organic semiconductors, whereby charges movement occurs *via* hopping between localised states and is restricted by impurities and traps at grain boundaries. The mobility is greatly improved by forming a highly ordered structure, where closer packing of molecules improves the π -orbital overlaps and facilitates charge transport.^[83–85]

Phthalocyanines continue to attract significant research efforts owing to their high chemical stability, synthetic adaptability, and ability to transport charges efficiently.^[86] They can be used as donor materials in OPV, interlayers or emitters in OLEDs, as the active layers in OFETs and even as spin-transporters in MTJs.^[87–89] The electronic structure of the prototype semiconducting small molecule CuPc, has a highly polarisable system of delocalised π -electrons, with a HOMO-LUMO energy gap in the visible range (1.7 eV).^[90] In the crystal form, planar CuPc molecules stack in columns and can exhibit many different polymorphs (α , β , δ , γ , ϵ ...), characterised by the angle between the normal to the surface and the stacking axis.^[91] The unit cell dimensions of the two most common, orthorhombic like ‘ α -phase’ or monoclinic ‘ β -phase’ with 26.1 and 44.8 ° tilt angles respectively.^[92] Equivalent to the soluble ZnPc derivatives evaluated in Chapter 4, CuPc has optical absorption bands at 500- 800 nm (‘Q-band’) and below 460nm (‘B-band’). The Q-band arises from $\pi - \pi^*$ transitions, which are localised on the inner ring system, whereas the B-Band (or Soret) transitions involve movement of electrons on the inner and outer ring systems.^[93]

Magnetic Tunnel Junctions

An MTJ comprises of two ferromangets (FM₁ and FM₂) separated by a non-magnetic layer. MR depends on the relative orientation of the magnetization of FM₁ and FM₂, with a high electrical resistance for anti-parallel alignment (R_{AP}) and lower resistance for parallel alignment (R_P).

The basic mechanism of magnetoresistance is described in Figure 5.18. If the FM₁ and FM₂ are aligned (a), spin-up electrons have a spin parallel to the magnetization of the layers and consequentially can pass through the stack without scattering. On the other hand, spin-down electrons are scattered within both the FM₁ and FM₂. The overall conductivity (including contributions from spin up and down electrons) is mainly determined by the highly conductive spin-up electrons, and as a result resistivity is low. In case (b), when the FM₁ and FM₂ are anti-parallel, both spin-up and spin-down electrons are scattered within one of FM₁ and FM₂, because the spin is anti-parallel to the direction of magnetization. The resultant resistance is very high (Figure 5.18).

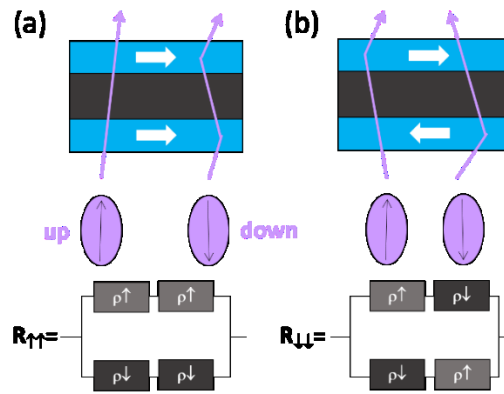


Figure 5.18: A schematic of (a) parallel FM₁ and FM₂ and (b) anti-parallel FM₁ and FM₂. Electrons (purple) passing through the layers either have a spin-polarised up or down. The resistivity of each configuration is also indicated (ρ_↑, ρ_↓).

If the non-magnetic layer is thin enough (< a few nm), electrons can quantum mechanically tunnel from FM₁ to FM₂. This tunnelling is more likely to occur when the magnetisations of FM₁ and FM₂ are oriented parallel to one another. Julliere's model describes the spin polarizations (P₁ and P₂) of the electrodes, which are calculated using the density of states and the Fermi energy for spin-up and spin-down electrons.^[94] TMR can then be calculated using Equation 5.7.

$$MR = \frac{R_{AP} - R_P}{R_P} = \frac{2P_1P_2}{1 - P_1P_2} \quad \text{Equation 5.7}$$

When cooling from 293 to 77 K, there is an increase of MR from ~ 5 % to > 130 % in Si/MgO/Fe/MgO/CuPc/Co MTJs.^[95] Here we establish the causes for this improvement in spin-transport, by evaluating both the role of the

organic/ inorganic interface and operating temperature (293, 77 K) on the molecular packing of CuPc. Crystalline MgO is well-known to have very different decay lengths for spin-up and spin-down electrons, and is widely used as a spin-filter in organic spintronics demonstrated to improve MR by an order of magnitude.^[96–98] *In situ* temperature dependent Raman spectroscopy reveals that this is due to a rearrangement of CuPc molecules.^[95]

As for pentacene described at the beginning of this chapter, the packing of CuPc is strongly influenced by the relative strengths of substrate-molecule and molecule-molecule (intermolecular) interactions.^[87,99] When organic materials are deposited on a highly reactive metal surface such as Fe, gap states are induced in the organic layer due to the decaying tail of the surface electronic wave function within the metal.^[100] The Fermi levels of the organic semiconductor and Fe align, forming an interfacial dipole layer that interacts with the highly polarizable electron cloud of CuPc and forces the molecules close to the interface to pack ‘face-on’. The strength of this dipole layer is understood by comparing different thicknesses of CuPc. The MgO layer does not only act to filter spin but also to prevent dipole formation allowing ‘edge-on’ packing of CuPc. Without this interfacial dipole CuPc can rearrange into an ordered crystalline layer at 77 K, demonstrated by increases in anisotropy measured using angle-dependent resonant Raman spectroscopy. MR values > 130 % when CuPc molecules are uniaxially aligned edge-on indicates that spin-polarised charges are moving freely through the organic layer, rather than just by quantum tunnelling. A combination of appropriate nano-analysis techniques and engineering of the molecular interface offer further enhancements of MR values, broadening the scope of applications of organic materials in spintronic devices.

5.3.1 Experimental Details

The experimental details are reported elsewhere.^[87] The organic layers were vacuum deposited at a pressure of $\approx 8 \times 10^{-8}$ mbar. The deposition rate for 3,4,9,10-perylenetetracarboxylic (PTCDA) was $0.1 - 0.2 \text{ \AA s}^{-1}$. The deposition rate of the CuPc was maintained at $1 \text{ \AA s}^{-1}$.

To prepare the MTJs, an ultra-high vacuum (UHV)-molecular beam epitaxy film evaporation system was used to stack successively inorganic elements beyond chemically etched p-type Si(001) wafers. The base pressure of the UHV-MBE chamber was lower than approximately 2.6×10^{-10} mbar. The epitaxial MgO(001)/Fe(001)/MgO(001) multilayers were formed at 250°C with low deposition rate of 0.003 nm s^{-1} . During the organic layer deposition, the pressure was kept no more than 2.6×10^{-6} mbar, and the deposition rate was fixed at $0.3 \text{ \AA s}^{-1}$. The layer thickness was obtained by

a quartz thickness monitor and verified after deposition by a profilometer. A more comprehensive description can be found elsewhere.^[95,101]

Impact of Excitation Wavelength on Raman Scattering

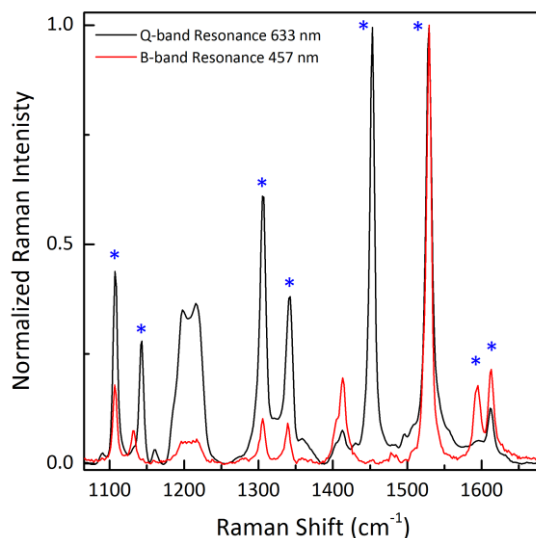


Figure 5.19: Resonant Raman spectra of CuPc excited in the Q-band (black) and B-band (red). The Raman spectra are normalised to the 1528 cm^{-1} mode.

Raman spectroscopy is widely used to study the photochemical and photo-physical properties of phthalocyanines and has been used to distinguish four different H_2Pc (metal free phthalocyanine) polymorphs.^[102–105] The peak positions, full width half maximum (FWHM) and relative peak intensities of particular pairs of Raman active vibrational modes are sensitive to whether CuPc molecules adopt the ' α -' or ' β -' conformation.^[106] The sensitivity afforded by resonant Raman spectroscopy makes it an appropriate tool for the ultra-thin organic layers. The main Raman active modes of CuPc are assigned using Density Functional Theory (DFT) and previously published reports.^[93,107] The most intense in-plane Raman active modes are associated with C = N stretches (B_{1g} - 1528, 1340 cm^{-1}), outer ring C – C stretches ($\text{A}_{1g}, \text{B}_{1g}$ - 1452 cm^{-1}), outer ring rotations ($\text{B}_{1g}, \text{B}_{2g}$ - 1305 cm^{-1}), outer-ring breathing (B_{2g} - 1142 cm^{-1}) and N-Cu-N bends (A_{1g} - 1106 cm^{-1}), see Figure 5.19.^[107–109] The vibrations at 1594 and 1613 cm^{-1} are related to benzene stretches of the outer rings.

	α -phase	β -phase
I_{1106}/I_{1143}	> 1	< 1
I_{1305}/I_{1340}	> 1	< 1
I_{1528}/I_{1452}	≥ 1	$\gg 1$

Table 5.8: Selection of intensity ratios that can be used as polymorphic markers for CuPc thin films, extracted from reference ^[93].

As the Raman spectra reported here are recorded in the backscattering configuration, it is appropriate to consider this measurement as probing a projection of the molecule onto the substrate plane, which changes with molecule-

substrate tilt angle or crystal polymorph. For accurate analysis of tilted molecules, the Raman tensors of each mode must be transformed into the laboratory reference frame.^[102,108,110,111] CuPc belongs to the D_{4h} point group symmetry and the crystal space group is C_{2h} .^[102,108] There are marked differences in relative intensities of Raman modes depending on whether the excitation is resonant with the Q- or B-band (Figure 5.19). In a Q-band resonant excitations, the relative intensity ratios of the pairs of peaks at 1528 and 1452, 1340 and 1305, and 1143 and 1105 cm^{-1} strongly depend on the particular CuPc polymorph.^[106] For α -CuPc the characteristic peak intensity ratios are: $I_{1106}/I_{1143} > 1$, $I_{1305}/I_{1340} > 1$, and $I_{1528}/I_{1452} \geq 1$. The inverse of these ratios are observed for β -phase (except that $I_{1528}/I_{1452} \gg 1$). This is summarised in Table 5.8 and illustrated in Figure 5.20.

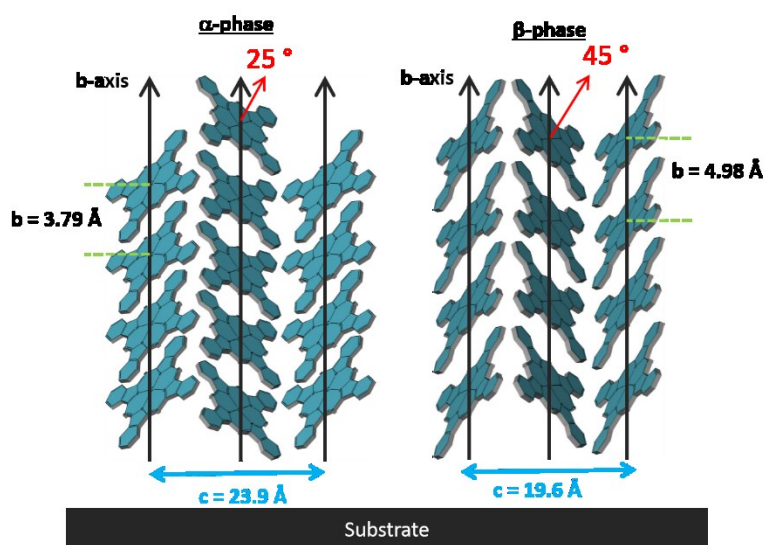


Figure 5.20: Molecular arrangement of CuPc in α - and β -phase.

5.3.2 Developing a Structural Probe for Molecular Packing of Copper Phthalocyanine

In order to establish a robust structural probe that can be used to reliably predict the CuPc polymorph in MTJs containing very thin films (< 5 nm), we first consider an ideal case where templating with another organic small molecule is known to determine the microstructure. When CuPc is grown on unreactive substrates at room temperature it arranges into highly one-dimensional molecular stacks in the α -polymorph.^[112,113] The small molecule PTCDA is often used to control molecular packing of phthalocyanine thin films, as it lies parallel to the surface on unreactive substrates and can interact with the electrons in π -orbitals.^[114–118] Sullivan *et al.* monitor the XRD signature of α -phase CuPc (single intense diffraction peak at 6.8°) and confirm that with no PTCDA interlayer, CuPc arranges with the stacking axis parallel to the substrate, whereas with PTCDA the strong interactions force the molecules to lie flat.^[87,119]

Resonant Raman Signatures of Controlled Molecular Packing

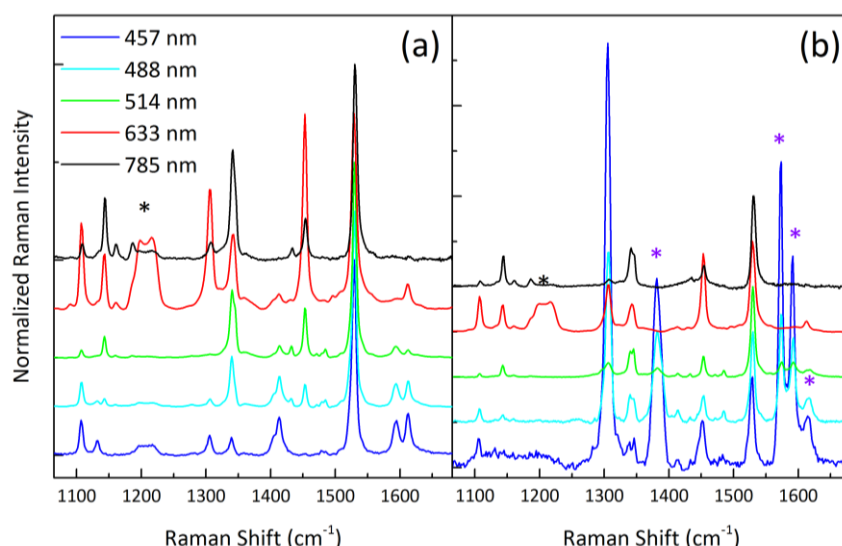


Figure 5.21: Raman spectra of 5 nm CuPc on (a) SiO₂ and (b) PTCDA/ SiO₂ substrates excited at 457, 488, 514, 633 and 785 nm. The peaks marked with an asterisk correspond to Raman scattering from the substrate (SiO₂, broad mode centred at 1206 cm⁻¹, PTCDA, modes at 1381, 1573, 1592, 1617 cm⁻¹). The Raman spectra are normalised to the most intense vibration (1530 cm⁻¹ for CuPc).

In order to determine the appropriate excitation source for our characterisation of very thin organic films, the Raman spectra of both samples was collected as a function of excitation wavelength. Figure 5.21 shows the Raman spectra acquired at 457, 488, 514 and 633 nm for 5 nm CuPc on (a) SiO₂ and (b) PTCDA/ SiO₂. As can be seen from Figure 5.21 (a), for CuPc/ SiO₂ the peak positions and FWHM are relatively unchanged by excitation wavelength. On the other hand, resonant enhancement clearly determines relative intensities. The peak positions correspond well to reported values for α -CuPc (1528, 1305, 1141, 1106, 953, 255 cm⁻¹).^[106,120] We can assess the impact of resonance on different Raman modes by normalizing to the vibration least affected by resonance: 1341 cm⁻¹, which is consistent with resonant analysis for metal free phthalocyanine.^[121]

The variations in peak intensity with excitation wavelength reveal distinct differences in the involvement of vibrational modes with the Q- and B-bands.^[93] For vibrations where the B-band is the dominant absorption transition (Figure 5.22 (a)), the intensity decreases with increasing excitation wavelength; 1611, 1528, 1434, 1008, 940, 834, 780, 594 cm⁻¹. For vibrations enhanced by both the B- and Q- bands, the intensity decreases between the two resonances 457 – 633 nm (Figure 5.22 (b)); 1553, 1306, 1106, 953, 746, 680 cm⁻¹. Whereas when the principal transition is the Q-band, the relative intensity increases with increasing excitation wavelength (Figure 5.22 (c)); 1450, 1141 cm⁻¹. As discussed in Chapter 4, the changes in electron-density that are involved with the B-band are involved with the outer

rings whereas the Q-band is localised on the central phthalocyanine macrocycle. Modes that are predominantly involved with the outer-rings are strong in the B-band- i.e. the outer ring stretches at 1611 and 1434 cm^{-1} . On the other hand, vibrations common to both the inner- and outer- rings the intensity decreases between the two- i.e. 1305, 1553 cm^{-1} , which involve pyrrole deformations and benzene ring stretches. For modes that are strongly localised on the macrocycle the relative intensity increases when resonant with the Q-band, i.e. the pyrrole vibrations at 1141 and 1450 cm^{-1} .

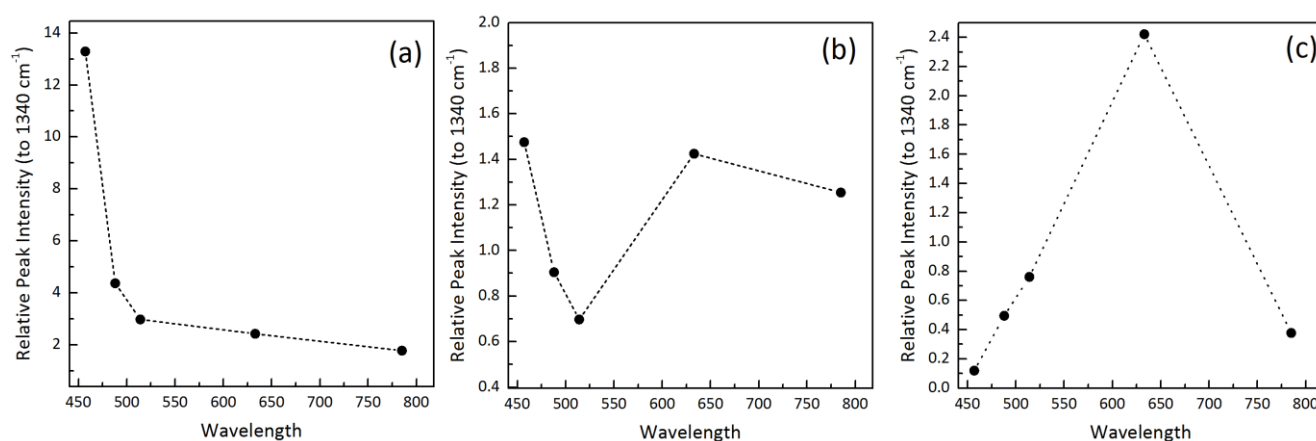


Figure 5.22: Relative intensities of (a) 1611 cm^{-1} , (b) 681 cm^{-1} and (c) 1450 cm^{-1} Raman modes as a function of excitation wavelength (457, 488, 514, 633 and 785 nm).

In non-resonant conditions (785, 633 nm), PTCDA appears to have a very small Raman scattering cross-section, so only vibrations from the CuPc on top are detected. In resonant conditions (i.e. ≥ 514 nm) PTCDA displays strong Raman scattering from several vibrational modes: 1381 (A_g), 1573 (A_g), 1592 (A_g), 1617 cm^{-1} (B_{3g}).^[122] The modes have identified using the B3LYP/6-31 G(d,p) level of theory, and they correspond to C—C stretches of the conjugated perylene core. SiO_2 is relatively Raman inactive in this region, displaying a strong mode at 520 cm^{-1} and a collection of low intensity vibrational modes at 1200 – 1250 cm^{-1} . From this analysis, it is clear the only appropriate excitation for characterisation of CuPc morphology is 633 nm (i.e. resonant with the Q-band whilst non-resonant with the PTCDA).

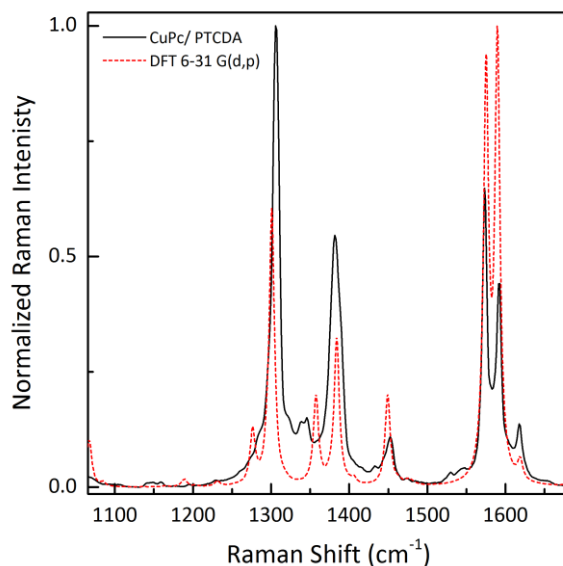


Figure 5.23: (black) 457 nm excitation, resonant with PTCDA layers, of 5 nm CuPc/ PTCDA/ SiO₂ thin films and (red) the simulated Raman spectrum for PTCDA calculated at the 6-31 G(d,p) basis set.

The peak intensities relevant for determining the CuPc packing structure for both thin and thick films on SiO₂ with and without PTCDA interlayers extracted from the spectra obtained at 633 nm are detailed in Table 5.9.

			SiO ₂		PTCDA	
	CuPc Thickness (nm)		30	100	30	100
	α -phase	β -phase				
I ₁₁₀₆ /I ₁₁₄₃	> 1	< 1	1.48	1.57	0.91	1.32
I ₁₃₀₅ /I ₁₃₄₀	> 1	< 1	1.14	1.60	0.97	1.68
I ₁₅₂₈ /I ₁₄₅₂	≥ 1	>> 1	1.03	1.00	1.44	1.15

Table 5.9: Relative peak intensities of I_{1106}/I_{1143} , I_{1305}/I_{1340} , I_{1528}/I_{1452} for 30 and 100 nm thick films of CuPc on SiO₂ and PTCDA.

The results of this simple comparison of relative intensities support XRD results for thin films.^[87] For the thin layers (30 nm) on unreactive substrates CuPc clearly arranges in the α -phase polymorph. This is retained for increasing film thickness (100 nm), which implies that when intermolecular interactions between phthalocyanines dominate the molecules arrange in the α -phase. On top of PTCDA interlayers, the CuPc arranges into a conformation that more closely resembles β -phase (smaller tilt angle with respect to substrate plane). Given the backscattering geometry of our Raman measurements, this observation is equivalent to the CuPc molecules lying flat due to strong π - π interactions with the PTCDA layer below measured using XRD.^[87] For thick films on top of PTCDA (100 nm) this arrangement is no longer observed and the film becomes more α -phase like. This can be understood as follows: far from the interface the intermolecular phthalocyanine interactions dominate packing and the arrangement is equivalent to that on unreactive SiO₂. These results are similar to our observations made of pentacene on different SAMs.

In summary, the molecular arrangement of CuPc can be determined by evaluating the intensity ratios: I_{1106}/I_{1143} , I_{1305}/I_{1340} , I_{1528}/I_{1452} . On unreactive substrates (SiO_2) CuPc adopts the α -phase (I_{1106}/I_{1143} , I_{1305}/I_{1340} , $I_{1528}/I_{1452} \geq 1$) due to intermolecular interactions between phthalocyanine molecules. On top of PTCDA interlayers CuPc is forced to lie flat (I_{1106}/I_{1143} , $I_{1305}/I_{1340} < 1$, $I_{1528}/I_{1452} \gg 1$) due to strong π - π interactions. This is not retained far from the interface, where phthalocyanine interactions dominate (see Figure 5.24).

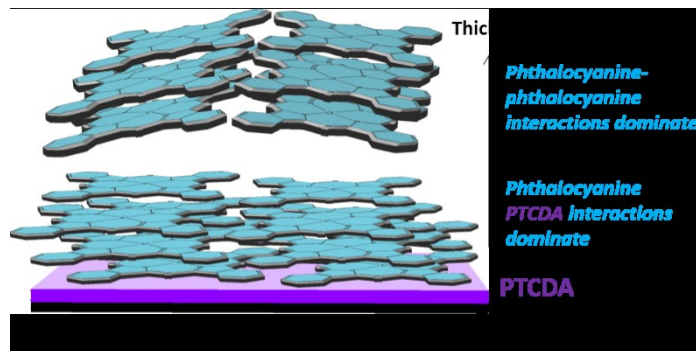


Figure 5.24: Schematic of intermolecular and molecule – substrate interactions as a function of distance from the inorganic interface.

5.3.3 Impact of Substrate on Copper Phthalocyanine Molecular Packing in Magnetic Tunnel Junctions

Having designed a means to accurately assess phthalocyanine packing in ultra-thin films, we extend our investigation to the MTJ device architecture.

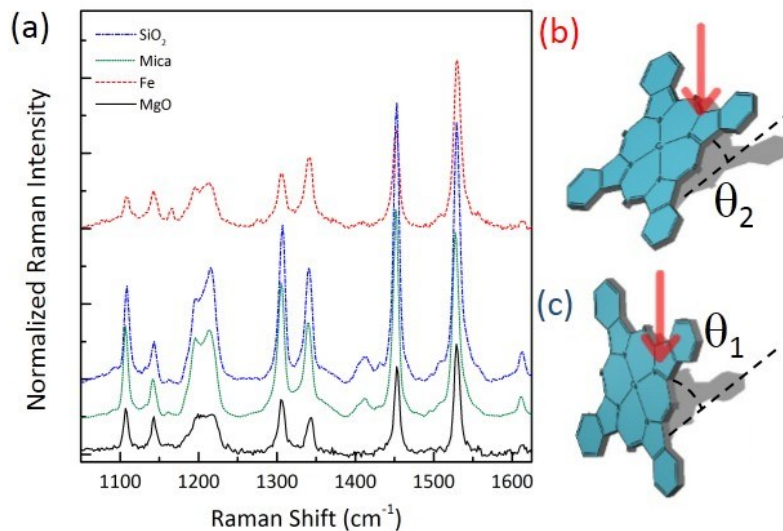


Figure 5.25: (a) Raman spectra measured under 633 nm excitation of 1.6 nm CuPc films deposited on mica, $\text{SiO}_2/\text{MgO}/\text{Fe}$ and $\text{SiO}_2/\text{MgO}/\text{Fe}/\text{MgO}$ substrates. Spectra normalised to the 520 cm^{-1} Si peak. Illustration of CuPc packing on (b) a reactive substrate (Fe) and (c) an unreactive substrate (Mica, SiO_2 , MgO).

Figure 5.25 compares the Raman spectra of CuPc (1.6 nm) on MgO, Fe, SiO₂ mica substrates. On mica substrates, we find that I_{1305}/I_{1340} and $I_{1106}/I_{1143} > 1$, indicating that CuPc adopts the less stable α -phase conformation. The same is observed for CuPc on MgO (see Table 5.10 and Figure 5.25) and SiO₂. In all three cases the substrates have non-reactive surfaces and the intermolecular interaction dominates the molecule-substrate interaction, causing the molecules to tilt at the characteristic angle of the α -phase ($\approx 26.5^\circ$) to the substrate plane.^[123] For CuPc on Fe substrates, $I_{1528}/I_{1452} \gg 1$, $I_{1305}/I_{1340} < 1$ and $I_{1106} \approx I_{1143}$, indicating that the more stable β -phase CuPc packing is adopted. β -phase corresponds to a more ‘lying-flat’ configuration, as the molecules are tilted at a higher angle from the stacking axis (i.e. more parallel to the substrate plane). Equivalent to the PTCDA-CuPc interaction, the strong molecule-substrate interaction between the electron cloud of CuPc and the reactive Fe surface pulls the molecule face-on, flat to the substrate plane. We have compared to peak positions of thin films of CuPc on SiO₂, PTCDA, Mica, MgO and Fe in Table 5.11. The Raman modes for pure α - and β -phase CuPc were reported by Shaibat *et al*, who report the largest differences for the Cu-N deformation at 255 cm^{-1} ($\Delta\alpha \rightarrow \beta = +4.0\text{ cm}^{-1}$) and C-H deformation at 1109 cm^{-1} ($\Delta\alpha \rightarrow \beta = 2.2\text{ cm}^{-1}$). We find that in the case of more planar CuPc (PTCDA, Fe) compared to more α -phase, the $\Delta_{\text{Cu-N}} \approx +2\text{ cm}^{-1}$ and the $\Delta_{\text{C-H}} \approx +1.9\text{ cm}^{-1}$. AFM measured at room temperature indicates an increased surface roughness for 1.6 nm CuPc/MgO or 1.6 nm CuPc/ mica vs. CuPc/ Fe (Figure 5.26). In all cases, the domain sizes are much smaller than the lateral resolution of the Raman microscope, i.e. multiple domains are probed with one excitation. Planar CuPc on Fe surfaces appear to aggregate into larger flat regions. According to AFM and relative ratios from Raman spectroscopy, Mica promotes larger crystal formation- a strong Pc-Pc interaction (more α -phase) and higher aspect ratio domains.

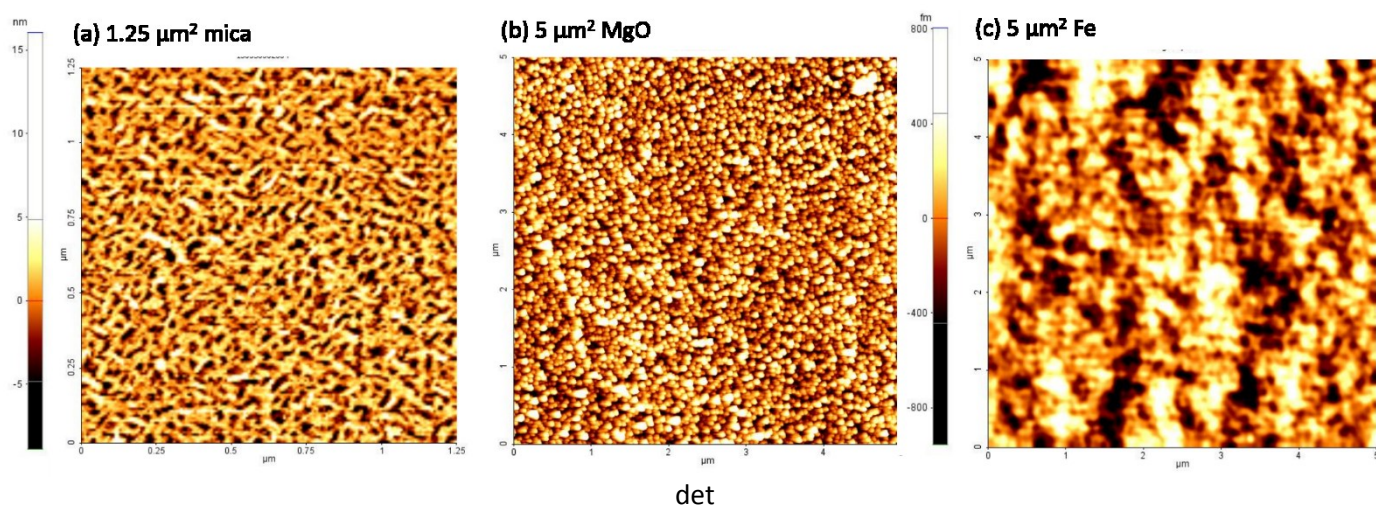


Figure 5.26: AFM images of the surfaces of 1.6 nm CuPc films on (a) mica (b) MgO and (c) Fe substrates.

	α -phase	Planar CuPc	Mica	MgO	SiO ₂	Fe	MgO	Fe	MgO	Fe
Film Thickness (nm)			1.6	1.6	1.6	1.6	5	5	1.6	1.6
Temperature (K)			293	293	293	293	293	293	77	77
I_{1106}/I_{1143}	> 1	< 1	$2.41 \pm .05$	$1.34 \pm .05$	$2.38 \pm .05$	$0.86 \pm .05$	$1.25 \pm .03$	$1.31 \pm .02$	0.75 ± 0.1	$0.74 \pm .05$
I_{1305}/I_{1340}	> 1	< 1	$1.42 \pm .05$	$1.76 \pm .05$	$1.37 \pm .05$	$0.82 \pm .05$	$1.51 \pm .03$	$1.11 \pm .02$	0.95 ± 0.1	$0.65 \pm .05$
I_{1528}/I_{1452}	≥ 1	$\gg 1$	$0.89 \pm .05$	1.19 ± 0.1	$1.08 \pm .05$	1.75 ± 0.1	$1.19 \pm .03$	$1.14 \pm .02$	$1.95 \pm .05$	2.19 ± 0.1

Table 5.10: I_{1106}/I_{1143} , I_{1305}/I_{1340} and I_{1528}/I_{1452} extracted from Raman spectra at 633 nm excitation for CuPc on mica, MgO and Fe

surfaces at 293 and 77 K.

Substrate	α^i	β^i	SiO ₂	PTCDA	Mica	MgO	Fe
CuPc Thickness			30 nm	30 nm	1.6 nm	1.6 nm	1.6 nm
Cu-N	255.9	259.90	255.9	256.9	256.5	256.0	257.5
			680.2	680.2	680.0	680.3	680.5
			745	748.9	747.4	748.1	749.0
	954.3	955.3	953.7	953.7	951.7	953.4	953.3
	1109.1	1111.3	1106.8	1107.9	1106.8	1107.1	1108.6
			1142.9	1142.8	1142.5	1142.5	1142.6
			1306.2	1306.3	1304.6	1305.6	1306.1
			1342.8	1342.1	1340.2	1343.4	1340.6
	1455.7	1453.8	1453.0	1453.0	1451.4	1452.9	1451.7
			1529.6	1529.6	1527.2	1529.0	1529.4

Table 5.11: Raman bands and shifts observed for CuPc on SiO₂, PTCDA, Mica, MgO and Fe. Peak positions in α and β - phase from ref^[106].

5.3.4 Impact of Film Thickness on Copper Phthalocyanine Molecular Packing

In vertically stacked devices, charges are transported between electrodes through the bulk of the organic layer. It is well established that the packing of organic small molecules depends on the strengths of intermolecular and molecule-substrate interactions as thickness increases, and above we have observed CuPc far from the PTCDA interface experiences stronger Pc-Pc interactions.^[23] In organic MTJs the thickness is of great importance as it determines whether charges tunnel quantum mechanically or exploit the low spin-orbit coupling or organic semiconductors. It has been well established that the efficiency of spin-polarised injection into CuPc decreases significantly with increasing film thickness.^[78,124–126]

To evaluate the thickness dependent evolution of CuPc polymorphism and the implications of this on MR in MTJs 1.6 nm and 5 nm thick CuPc grown on both Fe and MgO surfaces were considered (Figure 5.27 (a) and (b), respectively). The changes in relative peak intensity, listed in Table 5.10, indicate that on MgO surfaces the α -phase CuPc conformation is maintained with increasing CuPc thickness. In contrast, for the Fe surfaces we find that the 5 nm thick sample shows a strong component of CuPc molecules tilted out of the plane of the substrate, which is consistent

with the α -phase conformation (see Figure 5.25 (c)). This indicates that the dipole interaction on Fe substrates affects only the interfacial layer of CuPc and that the planar molecules at the interface do not template the subsequently deposited CuPc. In complete devices there is a 5 nm Co electrode on top of the CuPc layer, which could also cause strong molecule-substrate interactions. Whilst this reduces the measurable intensity of Raman scattering from the organic layer in complete devices (Fe/MgO/CuPc/Co), for 1.6 nm CuPc the same α -like packing structure is largely observed, with the slight reduction in I_{1106}/I_{1143} and I_{1305}/I_{1340} indicating a more planar molecule-substrate tilt angle due to interactions between the CuPc and Co. The impact of this thickness dependent microstructure on MR is considered in Figure 5.27, where the MR response is measured for 300 K. An increase in CuPc thickness from 2.5 to 5 nm decreases MR values from $\approx 8\%$ to $\approx 4\%$, indicating that despite similar molecular conformation the spin-polarisation is not maintained through the bulk, reducing the MR ratio. Without the MgO interlayer there is no MR response due to mismatches of conductivity and spin-scattering through the organic layer. ^[17,127]

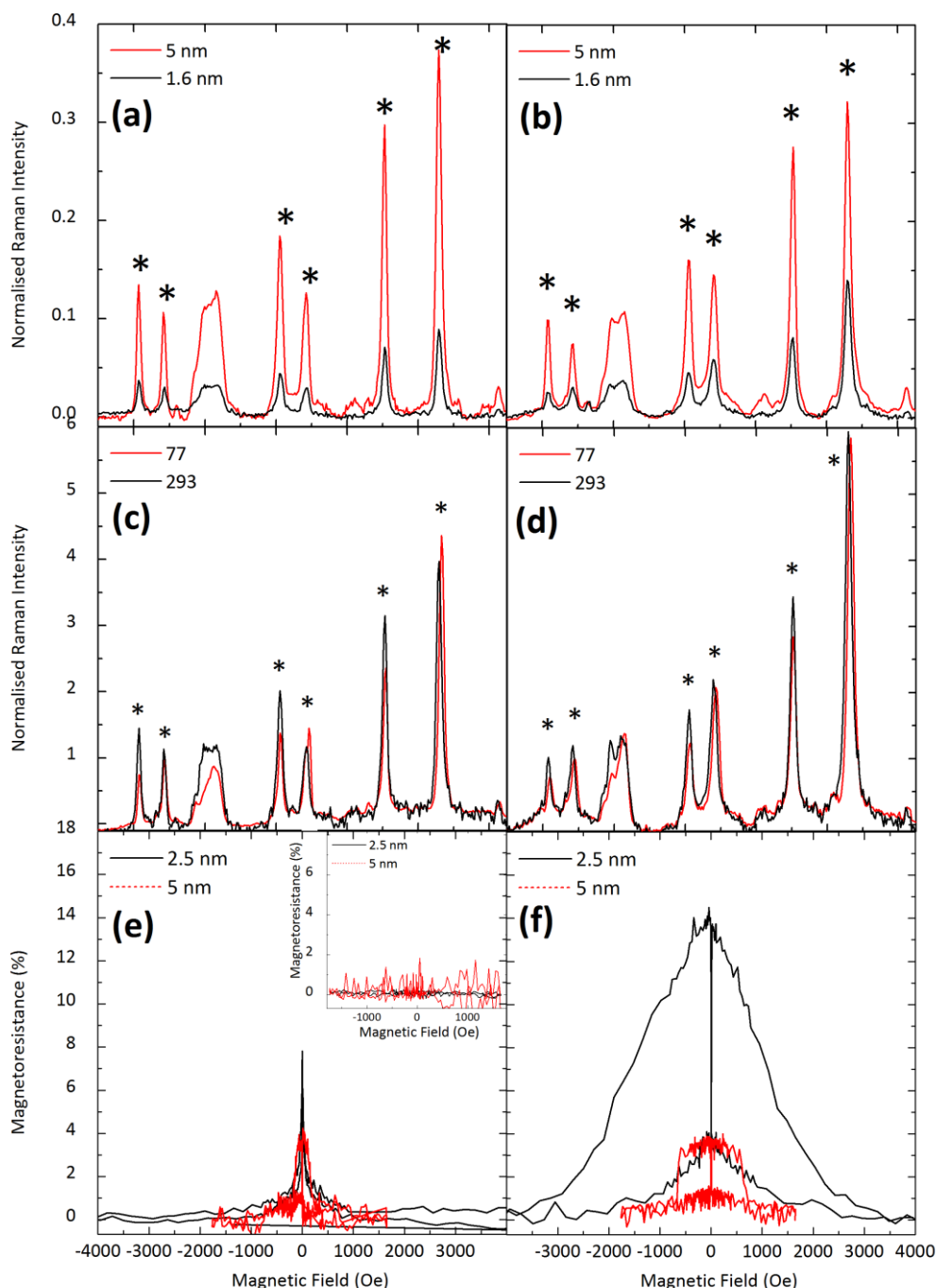


Figure 5.27: Raman spectra measured under 633 nm excitation for 1.6 (black) and 5 nm (red) CuPc films on (a) MgO (b) Fe surfaces at 293 K. The impact of cooling 1.6 nm CuPc to 77 K on (c) MgO (d) Fe surfaces are also provided. Spectra normalised to the 520 cm^{-1} Si peak. Peaks discussed in text (1106, 1143, 1306, 1340, 1452 and 1528 cm^{-1}) are highlighted. The MR response of MgO/Fe/MgO/CuPc/Co where CuPc thickness is varied from 2.5 to 5 nm is illustrated at (e) 293 and (f) 77 K. The inset of (e) shows the MR of MgO/Fe/CuPc/Co devices at 77 K. MR for 1.6 nm thick CuPc.

5.3.5 Impact of Substrate Temperature on Copper Phthalocyanine Molecular Packing

In collaboration with coworkers in EWA, South Korea, we observed that when 1.6 nm CuPc MTJs with a MgO interlayer were cooled to 77 K, the MR increases from 5 to 130 % (see Figure 5.28). Figure 5.28 (b) shows the average MR values obtained at 77 and 300 K as CuPc thickness is increased from 1.2 to 5 nm. Temperature dependent changes

in the phase of CuPc have been reported elsewhere in literature, but only at temperatures above 500 K.^[128] Using *in situ* Raman spectroscopy it is possible to probe the temperature-induced molecular reorganisation of the CuPc molecules on the MgO and Fe substrates (Figure 5.29). The characteristics (maximum peak shift, relative intensities and FWHM) of relevant vibrational modes were extracted from Lorentzian peak fits as a function of temperature with spectra recorded every 10 K. In general, we measure an increase in the overall Raman scattering intensity as the temperature decreases. This could be due to bond contraction, as Raman intensity is determined by the derivative of polarizability, which depends on bond length.^[129]

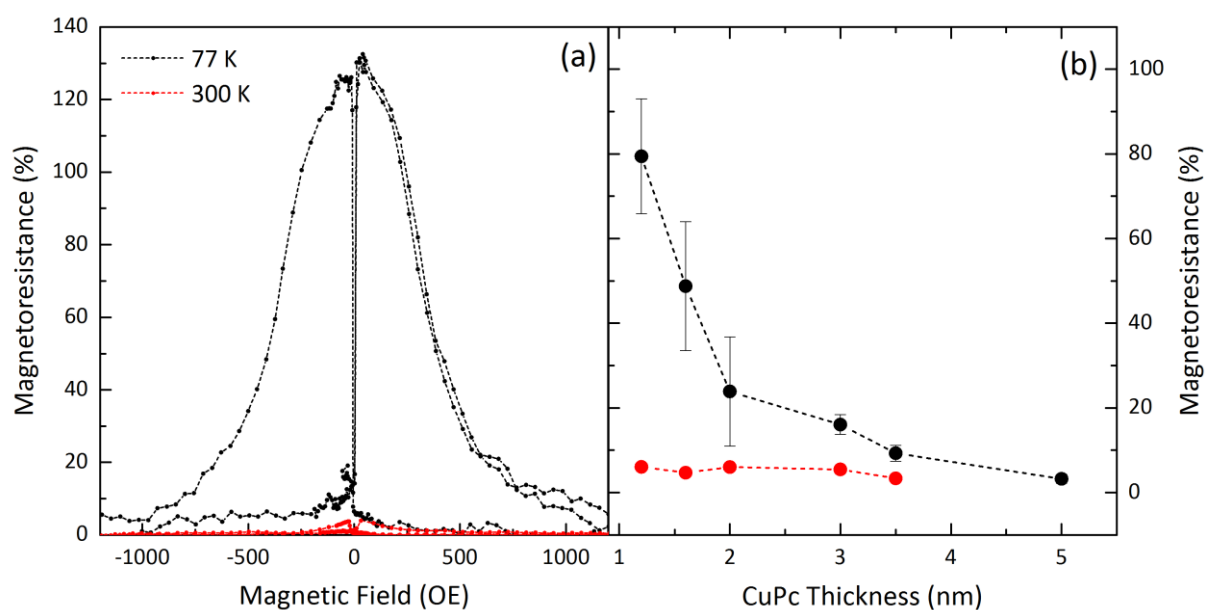


Figure 5.28: Magnetoresistance at 77 (black) and 300 K (red) of (a) 1.6 nm and (b) 1.2 – 5 nm CuPc. The applied current is 50 nA.

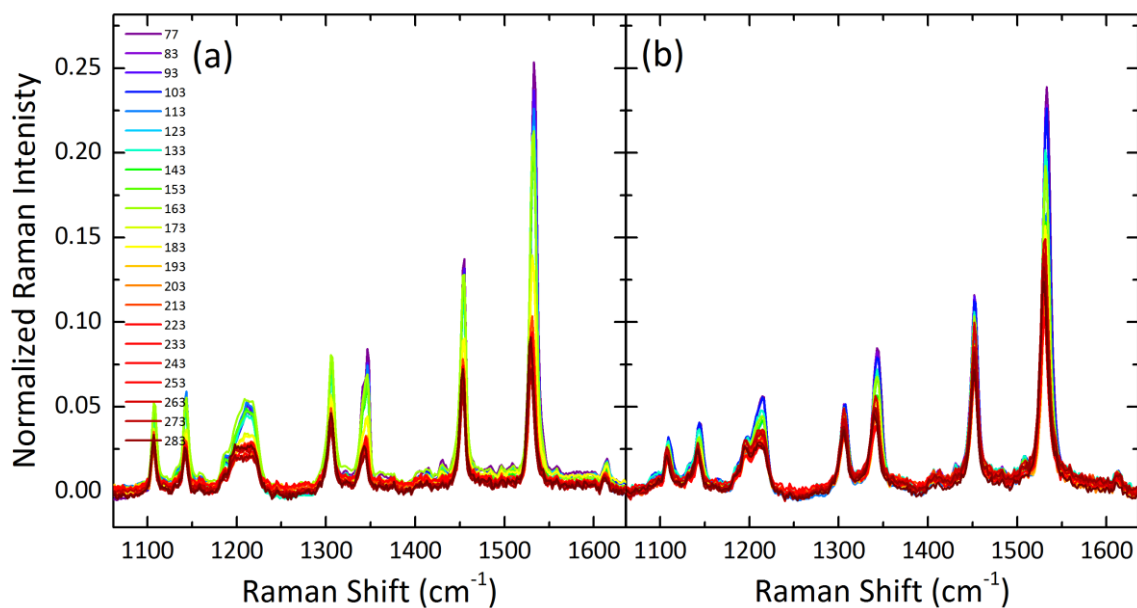


Figure 5.29: *in situ* temperature dependent Raman spectra measured under 633 nm excitation for 1.6 nm CuPc films on (a) MgO (b) Fe surfaces. The heating/ cooling rate is 10 K/ minute.

Figure 5.30 (a) illustrates the shift of vibrational modes extracted from Figure 5.29 (heating and cooling from 293 to 77K) on MgO (left) and Fe (right). The shift of peaks to higher wavenumber are entirely reversible on heating. The vibrational modes involving bonds the outer-rings ($681, 748, 1450 \text{ cm}^{-1}$) are the least affected by changes in temperature, whereas modes on the inner-ring ($1528, 1142 \text{ cm}^{-1}$) are shifted by up to 4 cm^{-1} . The shift to higher wavenumber is attributed to a lattice contraction and increase in the harmonicity interactions between phonon modes at lower temperature.^[130] For 1.6 nm CuPc on MgO at 77 K, I_{1106}/I_{1143} and I_{1305}/I_{1340} decrease to < 1 whilst I_{1528}/I_{1452} increases to $\gg 1$ (see Figure 5.30 (b) and Table 5.10) typical of the more planar/ β -phase polymorph adopted on Fe substrates.^[106] The changes in relative intensity occur linearly and recover on heating with negligible hysteresis. As the molecules occupy the less stable α -phase on MgO at room temperature, and there is no interfacial dipole to polarize the electron cloud as there is for Fe surfaces, they have sufficient freedom to rearrange. For CuPc on Fe I_{1528}/I_{1452} the extracted relative intensities indicate that the molecules resist any significant changes in conformation and still adopt the stable β -phase, with the interfacial dipole forcing the CuPc molecules to lie flat on the substrate.^[100] On heating these samples (Fe/CuPc) from 77 K to 293 K (Figure 5.30 (c)) we observe a strong hysteresis between 150-240 K. This temperature range has been described in literature as corresponding to a change in the packing of CuPc molecules.^[92]

Raman spectroscopy probes the bulk of the film, so the FWHM of a particular mode represents the full distribution of conformational molecular states that throughout the whole film thickness. For CuPc on MgO interlayers, the FWHM of the strongest mode (1528 cm^{-1} C = N stretch) decreases from 10 cm^{-1} at 293 K to 8 cm^{-1} at 77 K (see Figure 5.30 (c)). For CuPc on Fe, the FWHM at 293K is significantly larger, 12 cm^{-1} , decreasing to 10 cm^{-1} when it is cooled. In agreement with the changes in I_{1528}/I_{1452} (noted above), the FWHM of the 1528 cm^{-1} mode of CuPc / MgO recovers with negligible hysteresis, whereas for CuPc / Fe there is a hysteresis in the recovery of relative intensities. The larger FWHM on Fe (11.7 cm^{-1} on Fe vs. 9.6 cm^{-1} on MgO) and increased I_{1528}/I_{1452} hysteresis is likely due to the presence of two different orientations: face-on at the interface with Fe and edge on further from the interface where the molecular packing is dominated by intermolecular interactions.^[131] To overcome the rotational barriers imposed by a boundary between face- and edge-on molecules, a significant amount of energy (thermal energy in our case) must be put into the system, which is finally achieved at 250 K.^[132]

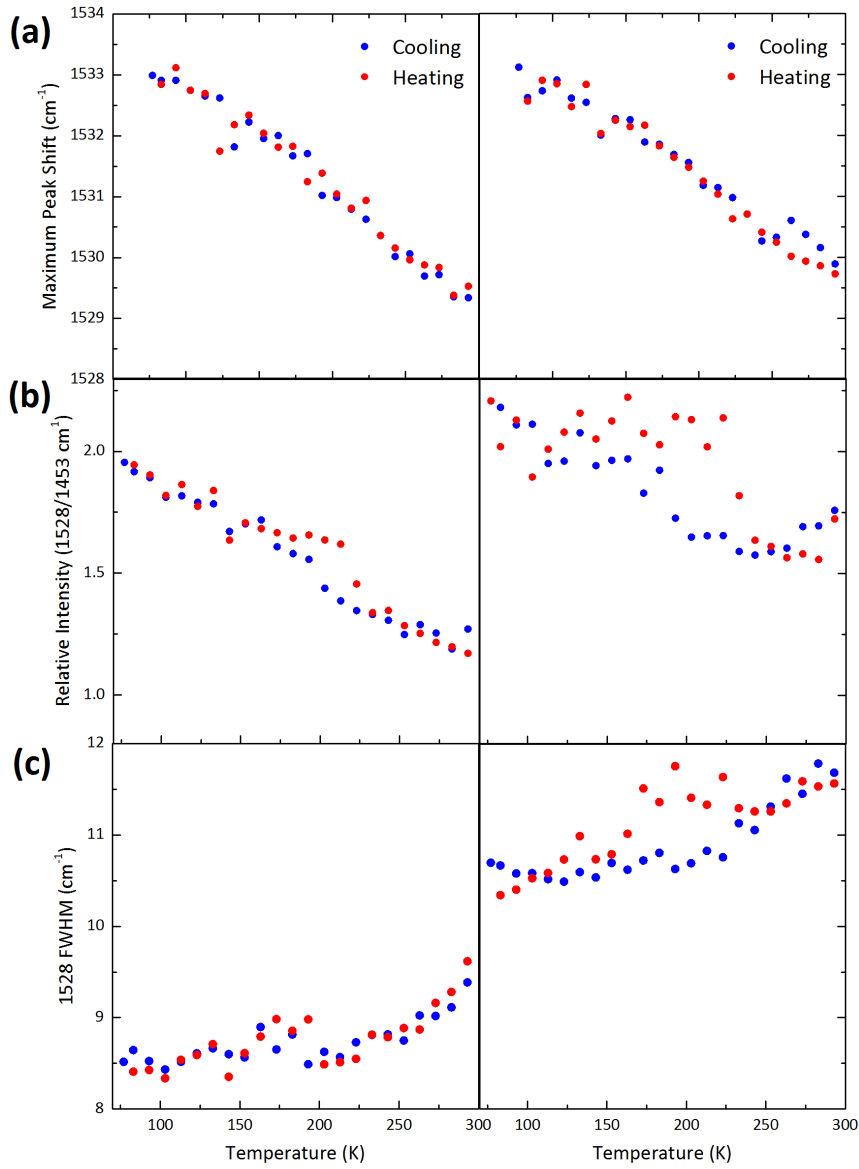


Figure 5.30: Peak parameters extracted from Lorentzian fits to in situ measurements taken every 10 K for 1.6 nm CuPc on MgO (left) and Fe (right) (a) Maximum peak shift of 1528 cm^{-1} , (b) I_{1528}/I_{1452} and (c) FWHM of 1528 cm^{-1} mode.

In order to evaluate the impact of the change in morphology, Figure 5.27 compares the MR response of 2.5 and 5 nm thick CuPc in MTJs at 77 K with and without the MgO interlayer (Fe/MgO/CuPc/Co, Fe/CuPc/Co). Without the MgO interlayer to polarise spin currents and combination of lying-flat CuPc at the interface and α -phase CuPc in the bulk on Fe results in 0 % MR. With the MgO interlayer spin-polarised currents are injected into the ordered CuPc molecules and transported from FM_1 to FM_2 , increasing the MR from 8 % to 14 % as the devices are cooled from 293 to 77 K. It is evident from Figure 5.28 (b) that there is a loss of spin-polarisation through increasingly thick layers of CuPc. Even with the enhanced molecular order observed at low temperatures, increasing the thickness of the organic layer results in a decrease of MR (MR 1.6 nm $\sim$ 130 %, 2.5 nm $\sim$ 14 %, 5 nm $\sim$ 4 %).

The comparison of Raman spectra and MR values at 293 and 77 K indicate a structural change of CuPc on MgO surfaces on cooling. To investigate this change in molecular packing we used angle-dependent polarised Raman spectroscopy, a powerful probe for the local molecular orientation in organic semiconductor films.^[52,108,133] When the CuPc / MgO samples are cooled to 77K we detect some anisotropy of the high wavenumber 1528 cm^{-1} vibrational mode, which appears to align at $\sim 40^\circ$ to the laser beam (see Figure 5.31 (b)). In the case of non-resonant Raman, with an understanding of the shape of the B_{1g} scattering tensor it would be possible to use the intensity of the 1528 cm^{-1} mode in parallel and perpendicular polarisations to extract the average tilt angle between the molecule and the substrate plane.^[108] The resonant excitation required to detect the ultra-thin 1.6 nm CuPc modifies the form of the Raman scattering tensor and so this simple analysis is not valid.^[93,134,135] Instead, this observation of anisotropy at 77 K implies that: within the laser spot size ($\approx 1\text{ }\mu\text{m}$) the majority of the CuPc molecules have the same orientation, and they are standing up with their edge to the substrate. The lack of anisotropic scattering from CuPc on Fe (Figure 5.31 (a)), even at 77 K, could indicate small domains of CuPc with different orientations or multiple packing motifs. At 293 K we evaluate the topography using atomic force microscopy, which reveals a rough surface ($r_q = 2.47\text{ nm}$, larger than the film thickness) covered in 100 nm wide domains (see Figure 5.26). This indicates that when the polarised Raman spectrum is measured at room temperature, it is sampling a large number of grains in which CuPc adopts different orientations. The Raman scattering appears to be almost completely isotropic (Figure 5.31 (a)). The increase in anisotropy of the 1528 cm^{-1} vibrational mode at 77 K indicates an increase in the number of neighbouring domains with the same molecular alignment (Figure 5.31, Figure 5.32). The highest measured anisotropy is 0.45 for the C = N vibrational mode implies that through the bulk film within the $1 \times 1\text{ }\mu\text{m}$ laser spot size more molecules have the same tilt angle with respect to the substrate plane. In the sandwich junction structure, the spin (and charge) is transferred vertically through the CuPc layer due to π -electrons perpendicular to the molecular plane (like p_z orbitals in conjugated polymers). We expect that the improved alignment between both neighbouring molecules and adjacent intermolecular layers reduces the change of a spin-flip occurring, increasing the MR. The changes in molecular alignment at low temperatures are likely due to changes in the surface energy of MgO. As the temperature increases from 77 K atoms of MgO begin to vibrate, their cohesive binding forces decrease and as a result the surface energy reduces- the CuPc molecules are more free to move.^[136] Without the MgO interlayer the interfacial dipole between Fe and CuPc holds the molecules flat to the surface.

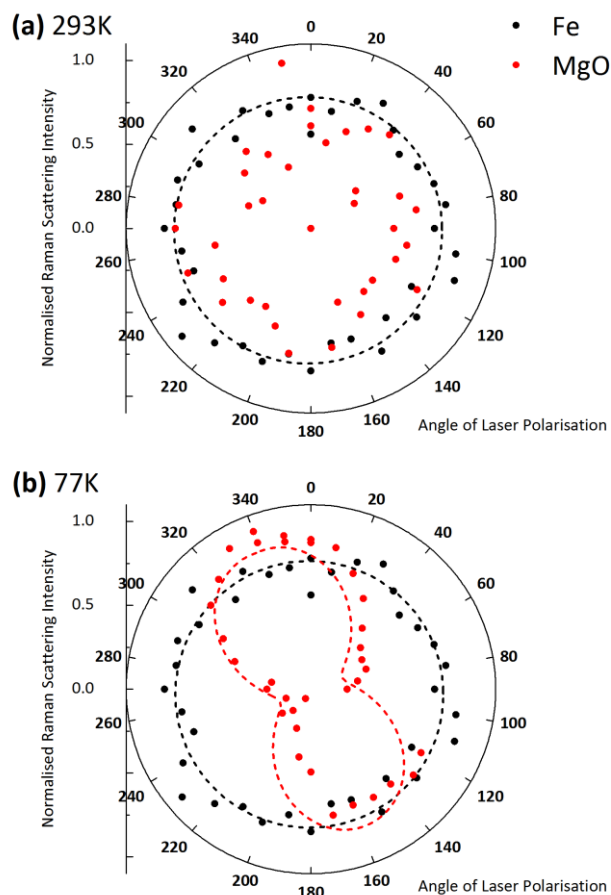


Figure 5.31: Angle-dependent polarised Raman spectroscopy of CuPc on Fe (black) and MgO (red) surfaces reveals isotropic vibrational modes at 293 K (a). When samples are cooled to 77K, the 1528 cm^{-1} (C = N stretch) of CuPc on MgO becomes highly anisotropic (b) revealing a change in the packing structure or size of domains.

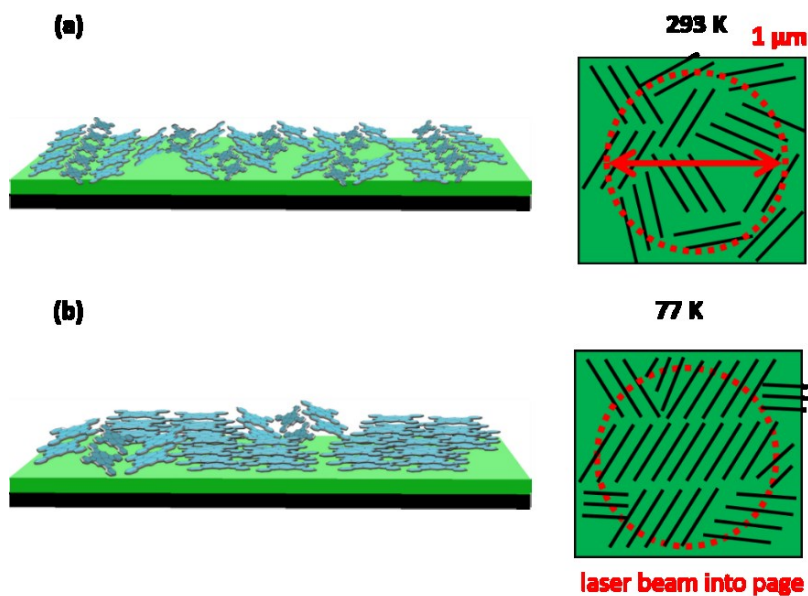


Figure 5.32: Schematic of CuPc packing on an MgO (green) interlayer at (a) 293 and (b) 77 K.

5.3.6 Summary

A means to probe the molecular packing of CuPc thin films was first established using samples of well-established morphology. The nature of CuPc Raman bands has been established using resonant Raman spectroscopy. A 'fingerprint' of α -phase CuPc was determined using Q-band resonant (633 nm) Raman spectroscopy, relative intensities of the Raman bands: I_{1106}/I_{1143} , I_{1305}/I_{1340} , $I_{1528}/I_{1452} \geq 1$. This molecular packing was observed when the intermolecular phthalocyanine (Pc-Pc) interaction dominated the Pc-substrate interaction. For thin films of CuPc on PTCD, interaction with the small organic molecule caused the CuPc to lie-flat (i.e. more like β -phase), which results in a change in the relative intensities of the Raman bands: I_{1106}/I_{1143} , $I_{1305}/I_{1340} < 1$, $I_{1528}/I_{1452} \gg 1$. As the CuPc thickness increased we found a more α -phase like CuPc (i.e. far from the interface, Pc-Pc interactions dominate).

With a spin-filtering MgO layer, we have investigated the cause of the record MR of 130% at 77 K in an organic MTJ. By exciting CuPc in the Q_x vibration band (633 nm) we can distinguish between different polymorphs in ultra-thin films of CuPc; the metastable α -phase on MgO and stable β -phase on Fe. An interaction at the CuPc – Fe interface that polarizes the electron-rich CuPc molecule and forces it to lie flat on the surface of the Fe. Intermolecular interactions dominate the packing structure on MgO surfaces. The FWHM of the CuPc inner-ring vibrational modes are 3 cm^{-1} wider on Fe than those on MgO surfaces. On MgO surfaces the CuPc is not affected by an interfacial dipole and at low temperatures we observe a more ordered film with significant anisotropy of the highly symmetric C = N vibrational mode (1528 cm^{-1}). This increased anisotropy is attributed to an increased the fraction of uniaxially aligned CuPc domains, which is lost as temperature increases and surface energy decreases. We can correlate the changes in MR at low temperatures for CuPc on MgO to this increase in the number of aligned grains (8 to 14 % for 2.5 nm thick CuPc), Increasing film thickness from 1.6 to 5 nm decreases the value of MR from 130 % to 4 % at 77 K. Far from the interfacial dipole on Fe surfaces CuPc adopts the bulk packing structure (similar to on MgO). These two distinct packing motifs are expected to form traps, which when out of the tunnelling regime will hinder the transport of charge and spin across the layer, and results in negligible MR. This study shows that MgO does not only act as a spin-filter; but also prevents the polarization of CuPc at the organic metal interface. This gives the domains freedom to rearrange at lower temperatures into a highly crystalline layer, improving MR by an order of magnitude.

5.4 Conclusions

We have demonstrated the use of non-destructive *in situ* resonant angle-dependent polarised Raman spectroscopy to determine the molecular orientation of thin-films of pentacene and copper phthalocyanine in working electronic devices. The molecular orientation is particularly sensitive to the relative strengths of intermolecular vs. molecule-substrate interactions.

The signature of single crystals has been identified using angle-dependent polarised Raman spectroscopy, which allows interpretation of molecular orientation of single crystals evaporated through a shadow mask. The molecular packing on surface treated Au and SiO₂ is evaluated. In OFET devices with pentacene as the active layer, the conjugated π -electron system interacts with untreated gold and forms an interfacial dipole which forces them to lie flat on the electrode. Surface treatment can be used to shield the organic layer from the interfacial dipole and permits pentacene molecules to pack in their lowest energy arrangement, standing upright. Pentacene stands upright within the active channel. The molecular packing is investigated close to the organic-inorganic interface and within the bulk organic film. With this exceptional control of molecular packing on the electrode, at the electrode-channel interface and within the active channel, the device performance of pentacene OFETs is explored. When the molecular packing is maintained across the device (TP treatment to the electrode, ODTS treatment to the SiO₂) the charge transfer mobility increases from $\approx 10^{-6}$ to $0.63 \text{ m}^2\text{s}^{-1}\text{V}^{-1}$.

CuPc is identified as an appropriate material for the fabrication of high MR organic MTJs. In order to evaluate the impact of molecular packing on spin-selective charge transport, the characteristics of well-established phthalocyanine polymorphs were identified. Resonant Raman spectroscopy was used to reveal the subtle differences in molecular packing of CuPc on unreactive and reactive substrates (mica, SiO₂, MgO and Fe). Within the SiO₂/MgO/Fe/CuPc/Co device stack the MgO interlayer is found to filter the spin-polarised current and prevent CuPc interacting with the Fe below. The impact of organic layer thickness and temperature on molecular packing and MR are investigated. When the molecule-substrate interaction is strong, the high density of π -electrons for the CuPc more flat to the substrate, or in the β -phase, where molecules are tilted furthest away from their stacking axis. When CuPc is deposited on the unreactive MgO interlayer, it packs in the meta-stable α -phase and is free to re-arrange when the films are cooled. Uniaxial molecular orientation is found to increase the MR from 5 % at 298 K to 130 % at 77 K.

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6 Influence of Chemical Structure on Polymer Molecular Order and Device Stability in Polythiophene Derivatives

This chapter describes the use of quantum chemical methods to understand the structure-property relationships in a range of polymer systems. The relationships are used to interpret the molecular packing and operational stability of OPV blends. We have considered a range of thiophene derivatives, where chemical structure has been modified to in an attempt to enhance the oxidative stability or planarity. The materials are all derivatives of the benchmark semiconducting polymer, poly(3-hexylthiophene) incorporating thiazole units, branched side chains and unsubstituted thienothiophenes (Figure 6.1) into the conjugated backbone.

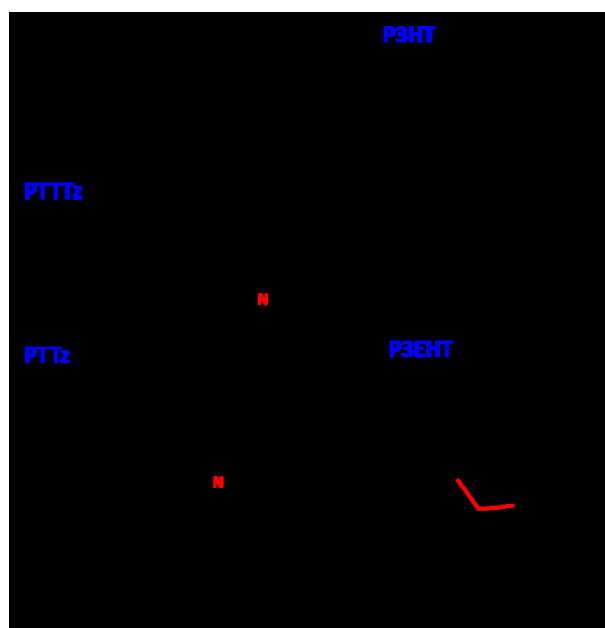


Figure 6.1: Molecular structures of materials considered in this chapter. The materials are all isostructural to P3HT. The main changes are indicated in red.

Section 6.2.2 explores the impact of thiazole incorporation into a P3HT chain on the conjugated backbone conformation and optoelectronic properties (**P3HT**, **PTTz**, **PTTz**).

Section 6.2.4 monitors the polymer molecular order in these materials during charge injection and subsequent hole polaron formation.

Section 6.3 considers the morphological stability of a branched side-chain poly-thiophene derivative (**P3EHT**).

The investigation in Section 6.2 was performed in collaboration with Daniel Beatrup, James Durrant and co-workers in the Department of Chemistry, Imperial College London and has been published elsewhere.^[1,2] The electrochemical cell introduced in Section 6.2.3 was designed in collaboration with Steph Pendlebury, Sarah Holliday, Steve Cussell and co-workers in the Departments of Chemistry and Physics, Imperial College London.

6.1 Motivation and Aims

To fully realise the commercialisation of polymer organic solar cells there is an urgent need to address the issue of stability and lifetime. Degradation studies of polymer electronic devices reported in literature consider chemical and morphological stability under various external stresses, such as temperature or humidity.^[3,4] However, there has been very little study on the operational stability of the charge carriers injected into the active material of polymer devices. The energy level of the HOMO represents the energy required to remove an electron from a neutral molecule, so at this potential, charge (hole) is injected into the polymer forming a hole polaron, and the polymer is reversibly oxidised. When used as an electron donor, polymers with a similar LUMO energy level but a deeper HOMO level typically demonstrate organic photovoltaic performance due to their increased energy level offsets with fullerene LUMO, and improve their stability to electrochemical reactions in air.^[5–7]

P3HT is one of the most widely studied polymer materials and remains important for fundamental studies in the field of organic photovoltaics and in tandem solar cells.^[8–11] Stability/ degradation of P3HT has been investigated extensively and its consequences are well-documented, yet the mechanism is still under debate.^[12–15] In general, exposure to light, heat or oxygen can destroy the π -conjugation of P3HT and reduce light absorption.^[13,14,16] Singlet oxygen is understood to degrade polymer solutions, whilst in the solid-state it is proposed that the alkyl side chains are attacked leading to a reactive peroxide species which oxidises the sulphur and breaks apart the thiophene ring.^[12,16–18] Madsen *et al.* compared the stability of RR and RRa P3HT under simulated sunlight and found that photo-degrading radicals attack the polymer at points in the chain where conformational conjugation is broken.^[19]

This chapter will establish the backbone conjugation, morphological, thermal and operational stability of a series of P3HT derivatives. The optoelectronic properties and molecular order of each material will be compared to P3HT. In order to evaluate the impact of polaron formation on the molecular order of the conjugated backbone, we design apparatus to allow *in situ* spectroscopic characterisation during charge injection. Electronegative elements like nitrogen are often incorporated into the backbones of conjugated polymers, as they attract electrons away from the conjugated backbone and stabilise the polymer HOMO level.^[20] We consider the systematic introduction of nitrogen at the 4-position of the five membered ring on backbone planarity and operational stability. Next we establish the impact of branched alkyl side-chains on molecular order and morphological stability of a polythiophene chain.

6.2 Operational Electrochemical Stability of Thiophene-Thiazole Copolymers

The materials considered are all isostructural to P3HT, where thiazole units have been included to systematically deepen the energy level of the HOMO. The copolymers of thiophene and thiazole have different proportions: P3HT is all thiophene units, PTTTz has every third unit substituted with thiazole, and PTTz has alternate units substituted with thiazole (see Figure 6.2). Thiazole is a commonly used electron-accepting heterocyclic compound due to electron-withdrawing nitrogen in the C = N bond.^[6,21,22]

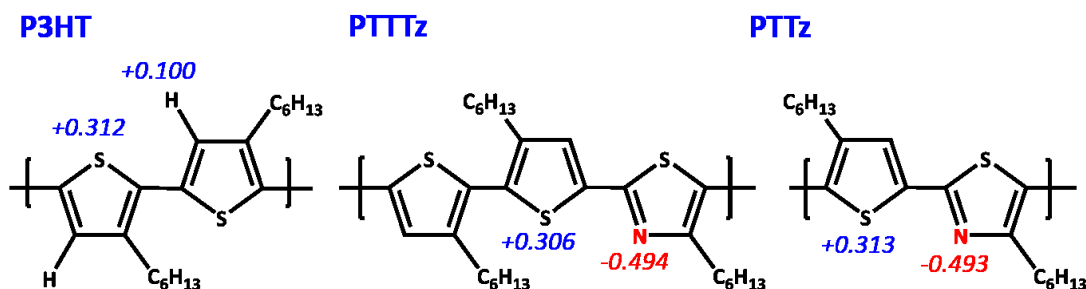


Figure 6.2: Molecular structures of P3HT, PTTTz and PTTz. The calculated Mulliken charges for P3HT, PTTTz and PTTz are shown. For thiazole containing polymers, electrostatic attraction between the nitrogen and sulphur atoms planarize the polymer chain.

Using DFT calculations, the effect of incorporation of thiazole units on the conformation and optoelectronic properties of a thiophene backbone is evaluated. Increasing the thiazole content is found to planarize the conjugated polymer backbone and improves the ground state electrochemical stability. However, these more planar thiazole containing polymers are increasingly susceptible to electrochemical degradation in the polaronic excited state. The degradation mechanism is identified, which targets the C = N bond in the thiazole units and results in disruption of the main polymer backbone conjugation. The introduction of thiazole units to deepen the HOMO energy level and increase the conjugated backbone planarity can be beneficial for the performance of certain optoelectronic devices, but the reduced electrochemical stability of the hole polaron may compromise their operational stability. This work was carried out in collaboration with Daniel Beatrup, Imperial College London (who provided the thin films) and is published in references ^[1,2].

6.2.1 Experimental Details

Films were spin-coated from solutions of polymer dissolved in chloroform (P3HT), chlorobenzene (PTTTz) and *ortho*-dichlorobenzene for (PTTz). FTO/glass substrates were covered with polymer solution, before being spun for 60 s at 2000 rpm in a nitrogen atmosphere. Films were then dried under vacuum for 24 hours.

UV-Visible Absorption

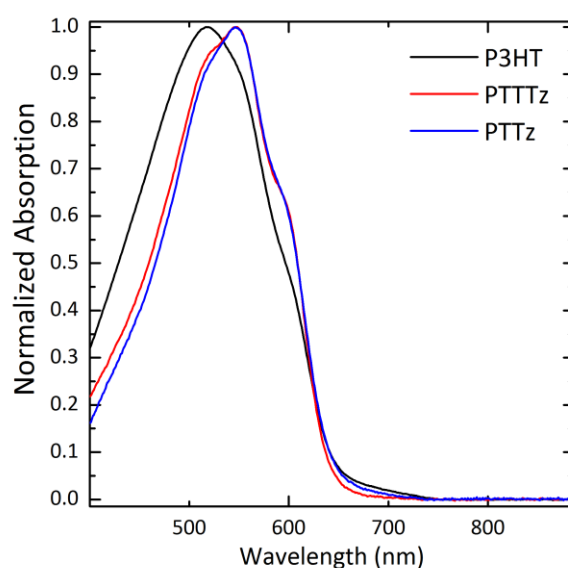


Figure 6.3: Normalized absorption spectra of pristine thin films of P3HT, PTTTz and PTTz on FTO/glass substrates.

The three polymers have different HOMO energy levels (P3HT, -4.8 eV; PTTTz, -5.1 eV; PTTz, -5.2 eV from CV) and so will require different potentials to inject holes.^[2,20] The UV-Visible absorption spectra of pristine and films of the three polymers are shown in Figure 6.3. For the pristine polymer films, the absorption onsets are similar, indicating that the increasingly deeper HOMO energy level is accompanied by a deepening of the LUMO energy level such that the optical band gap is unchanged. Compared to P3HT, the thiazole containing co-polymers have a red shifted absorption band maxima (P3HT -517 nm, PTTTz, PTTz -546 nm) and low energy shoulder (601 nm). For PTTTz, there is evidence of some high energy disorder within the conjugated chain (519 nm). The calculated HOMO and LUMO isosurfaces for the material series are illustrated in Figure 6.4 and detailed in Table 6.1. The systematic introduction of thiazole units into the thiophene chain deepens the HOMO energy level and reduces steric interactions between the adjacent heterocycles (removes C-H...C-H interactions) leading to the a planar polymer backbone.^[6] The antibonding (π^*) orbital energy levels of the electron-withdrawing thiazole units are similar to those of other π -conjugated materials, resulting in efficient mixing of orbitals and a deeper LUMO level.^[6,22] For the thiazole containing polymers, both the HOMO and LUMO overlap with the nitrogen atom, which explain the why they become systematically deeper on incorporation of thiazole units into the polythiophene chain. The narrow range of HOMO/LUMO energy levels is consistent with the similar onset of absorption of these materials. The bond lengths ($\text{\AA}$) and dihedral angles ($^\circ$) from DFT simulations at 6-31G(d,p) basis set are detailed in Table 6.2.

Table 6.1: DFT Calculated HOMO-LUMO energies and band gaps for thin films of P3HT, PTTTz and PTTz. HOMO levels calculated by CV (from reference ^[2]) and optical band gaps (extracted from onset of absorption) are shown for comparison. All values quoted are in eV.

	HOMO	LUMO	BG(DFT)	HOMO(CV)	Optical BG
	eV				
P3HT	-4.59	-1.97	2.62	-4.8	1.91
PTTTz	-4.64	-2.33	2.31	-5.1	1.93
PTTz	-4.84	-2.27	2.57	-5.2	1.93

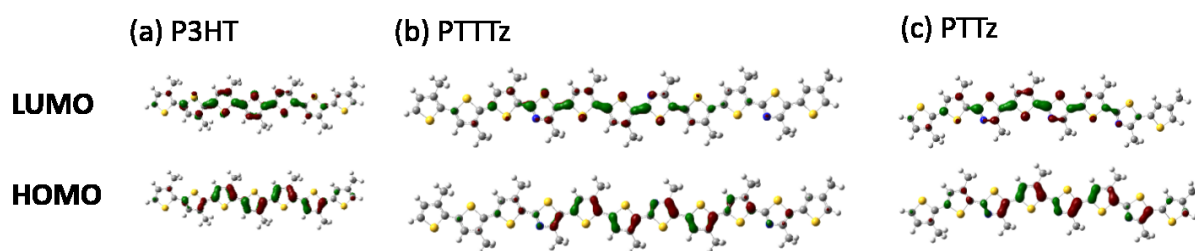


Figure 6.4: Calculated HOMO-LUMO isosurfaces for oligomers of (a) P3HT, (b) PTTTz and (c) PTTz. For the thiazole containing polymers, the frontier molecular orbitals include contributions from the nitrogen atoms.

Raman Spectroscopy

A more detailed comparison of the molecular conformations for the three polymers is provided by the resonant Raman spectra (Figure 6.5). A resonant excitation (488 nm) was used to obtain a strong Raman scattering signal and enhanced sensitivity to morphological changes.^[23] The resonant Raman spectra of conjugated molecules are typically dominated by a small number of vibrational modes describing stretches of the main conjugated backbone of the molecules. The vibrational modes of large molecules such as the polymers studied here typically involve nuclear motion of many atoms, thus producing collective motions of many bonds, but they can be understood more simply in terms of the dominant bond vibrations.

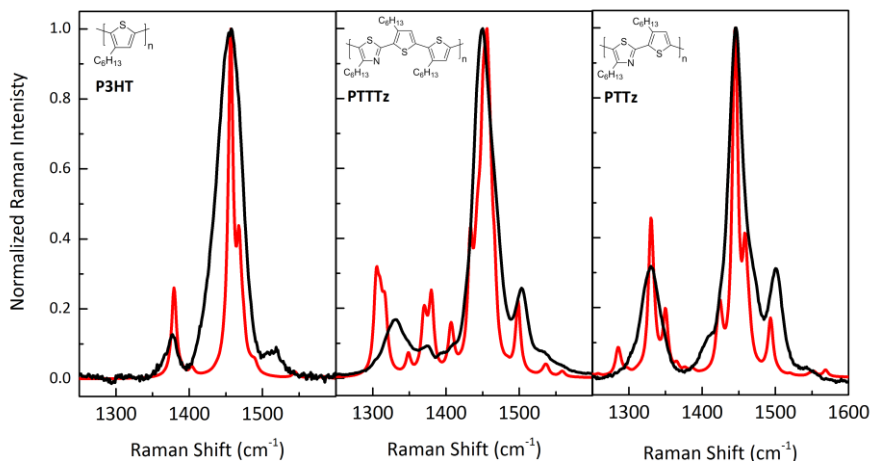


Figure 6.5: Experimental (black) and simulated Raman (red) spectra from DFT calculations at the 6-31 G(d,p) basis set for P3HT, PTTTz and PTTz. The spectra are simulated from oligomers of seven repeat units. The nature of the main vibrational modes are described in the text. Experimental Raman spectra are acquired at 488 nm excitation.

	P3HT	PTTTz	PTTz
Bond Lengths (Å)			
a	1.382	1.391	1.391
b	1.418	1.420	1.416
c	1.390	1.386	1.385
d	1.445	1.444	1.442
e	1.382	1.392	1.391
f	1.418	1.420	1.365
g	1.390	1.383	1.316
h	1.445	1.442	1.438
i	1.382	1.391	1.392
j	1.418	1.365	1.414
k	1.390	1.315	1.387
Dihedral Angles (°)			
A	17.857	9.842	1.773
B	16.163	1.545	0.183
C	16.982	0.275	0.130

Table 6.2: Bond lengths (Å) and dihedral angles (°) from DFT simulations at 6-31G(d,p) basis set.

The Raman spectrum of P3HT is well known, and in this frequency range ($1300\text{--}1600\text{ cm}^{-1}$) consists of in-plane symmetric C – C (1380 cm^{-1}), symmetric C = C (at 1450 cm^{-1}) and anti-symmetric C = C (1525 cm^{-1}) stretching modes of the thiophene rings.^[23–28] A combination of analysis of the changes in bond-length and dihedral angle and comparison of the features in the simulated and experimental Raman spectra allowed vibrational assignments to be made for the novel thiophene derivatives. The new peaks that are only present in PTTTz and PTTz are assigned to the C – N (1331 cm^{-1}) and C = N (1501 cm^{-1}) stretch modes of the thiazole units in these polymers.^[29] Increasing the number of thiazole

units in the polymer backbone (from P3HT to PTTTz to PTTz) results in distinct differences in the Raman spectra (Figure 6.6).

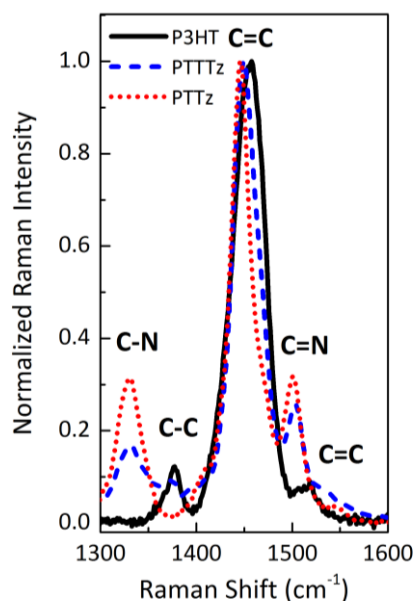


Figure 6.6: Resonant Raman spectra for pristine thin films of P3HT, PTTTz and PTTz measured under 488 nm excitation. Normalised to the strongest Raman peak ($\sim 1460 \text{ cm}^{-1}$).

The effects of incorporation of thiazole units into a P3HT chain in its Raman spectrum are summarised below:

Raman scattering intensities of the C – N (1331 cm^{-1}) and C = N (1501 cm^{-1}) modes increase relative to the C – C mode in PTTTz and PTTz. Such an increase corresponds with the increased proportion of thiazole units in the polymer chain, which these modes belong to.

Raman scattering intensity of the C – C mode (1380 cm^{-1}) reduces relative to the C = C mode (1450 cm^{-1}) in PTTTz and PTTz. The C – C bond is only found in thiophene units, whereas the C = C bond is present in both thiophene and thiazole, so the reduction in this ratio corresponds with the increasing proportion of thiazole units in the polymer chain. The apparent absence of this peak in PTTz, despite half of the units being thiophene, can be understood to indicate that the stretching modes of the thiazole ring have much larger Raman scattering cross sections under 488 resonant excitation than those in the thiophene unit (see a significant increase in the C-N and C = N mode intensities), or alternatively the C – C mode in the thiophene could shift to higher energy when adjacent to a thiazole unit, which would explain a slight increase in intensity of the shoulder observed at 1408 cm^{-1} in the PTTz spectrum.

The peak position of the main symmetric C = C stretch mode shifts to lower energy with increasing thiazole content (P3HT – 1456 cm^{-1} ; PTTTz – 1450 cm^{-1} ; PTTz – 1446 cm^{-1}). Shifts in the position of this mode towards lower

energy (lower vibrational frequency) have previously been attributed to increases in planarity of the main conjugated backbone.^[23–25,27,30,31] Here, we find that this effect correlates with an increase in the proportion of thiazole units, supporting the hypothesis that the reduced steric interactions between neighbouring thiazole and thiophene units leads to increased planarity and longer effective conjugation length.^[6] This is supported by both Mulliken charges and inter-unit dihedral angles following a geometry optimisation (see Table 6.2), predicting much smaller inter-unit torsion angle for PTTz (1 °) than for P3HT (17 °). An interaction between the nitrogen lone-pair and C-S anti-bonding orbitals has been described by Bronstein et al.^[20] From our simulations (Figure 6.2), in PTTTz and PTTz there is an electrostatic attraction of electronegative nitrogen with electron donating sulphur (partial charges, S— +0.256, N— -0.464). On the other hand, there is an electrostatic repulsion between adjacent thiophene units (S— +0.256, H-C — +0.101). Whilst absolute values of Mulliken charges must be used with caution in highly conjugated systems, they at least provide some sense of the polarity of the atoms.

Width (FWHM) of the C = C symmetric stretch mode (1460 cm⁻¹) reduces with increasing thiazole content (P3HT – 39 ± 1 cm⁻¹, PTTTz – 32 ± 1 cm⁻¹, PTTz – 26 ± 1 cm⁻¹). A reduced FWHM indicates that the distribution of C = C modes in different conformational environments is narrower indicating an increase in energetic order.^[23,32,33] The narrowing observed here when thiazole units are present is consistent with the increased backbone planarity mentioned above. This reduction in FWHM primarily results from a reduction in intensity in the higher energy part of this Raman peak, which is particularly associated with the disordered polymer phase, so this result indicates an overall increase in the degree of molecular order with increasing thiazole content.^[23]

Impact of Nitrogen on Energetic Barrier to Inter-Unit Torsion

The planarising effect of the nitrogen atom is particularly evident when scanning the potential energy as a function of dihedral torsion for the oligomers, as shown in Figure 6.7. The barrier to rotation is much larger between neighbouring thiazole and thiophene units and the *syn*- conformation is strongly disfavoured. The barrier to rotation of adjacent thiophene – thiophene is much smaller.

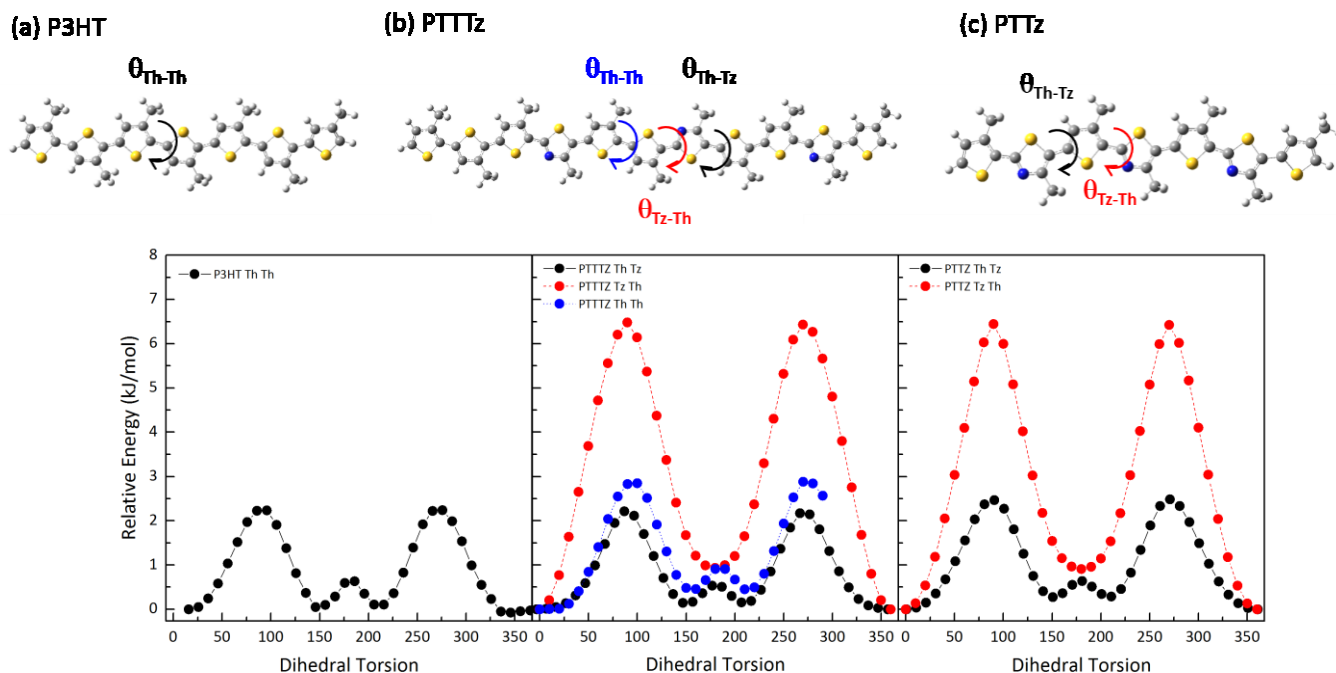


Figure 6.7: Minimum energy configurations of oligomers of P3HT, PTTTz and PTTz with key dihedrals ($\theta_{\text{Th-Th}}$, $\theta_{\text{Tz-Th}}$, $\theta_{\text{Th-Tz}}$) highlighted. (lower) potential energy scans of the polymers as a function of $\theta_{\text{Th-Th}}$, $\theta_{\text{Tz-Th}}$, $\theta_{\text{Th-Tz}}$.

This study comprises of two components, one studying the effect of the P3HT polaron *in situ*, and the other looking at the long-lasting impact of chemical degradation of the polaronic species. Whilst UV-visible absorption measurements can provide some evidence for morphological differences and optical property changes in the polymer thin film due to the degradation effect, it provides limited information about the chemical and conformational changes at a molecular level. To investigate this further, we have employed resonant Raman spectroscopy, which is sensitive to molecular structure and conformation.^[23–25,27,28,31,34–37] We have previously demonstrated the use of resonant Raman spectroscopy to quantify the degree of molecular order in P3HT induced by thermally annealing P3HT:fullerene blend films.^[24]

6.2.3 *In situ* electrochemical degradation of P3HT

Experimental Details

30 mg/ml solutions of RR-P3HT were dissolved in chlorobenzene, left to stir overnight at 100 °C and passed through a 0.45 μm filter. The FTO coated glass substrates were cleaned (detergent, deionised water, acetone, IPA (x 2), plasma ashing for 3 minutes at 80 W) prior to spinning the polymer film at 2000 rpm for 60 s under a nitrogen atmosphere. Measurements were carried out in a 3-electrode spectroelectrochemical cell, consisting of a platinum gauze counter electrode, Ag/AgCl reference electrode, with the polymer film/FTO/glass substrate forming the working

electrode, as well as two quartz windows suitable for absorption spectroscopy measurements. The working electrode was held in a neutral state by applying a starting potential (V_0) of 0.00 V. The electrolyte was a 0.1 m KCl solution dissolved in acetonitrile. The solutions were prepared in a degassed environment. Raman spectra were taken as a function of oxidising potential (V_{probe} quoted with respect to Ag/AgCl reference electrode) or oxidative stress time using a Renishaw macrosampling kit, as shown in Figure 6.8. Spectra were acquired in resonant (488 nm excitation) conditions with a nitrogen line bubbling through the electrolyte to prevent degradation.

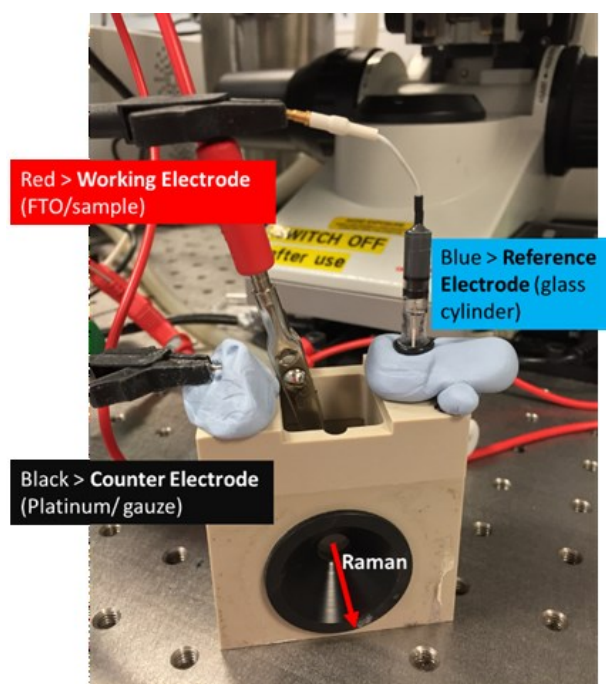


Figure 6.8: Three-probe (working, counter and reference) experimental set-up for in situ chronoamperometry measurements.

Raman spectra are acquired through a clean quartz window. There is a diagram of the set-up in Section 3.4.6.4.

Results and Discussion

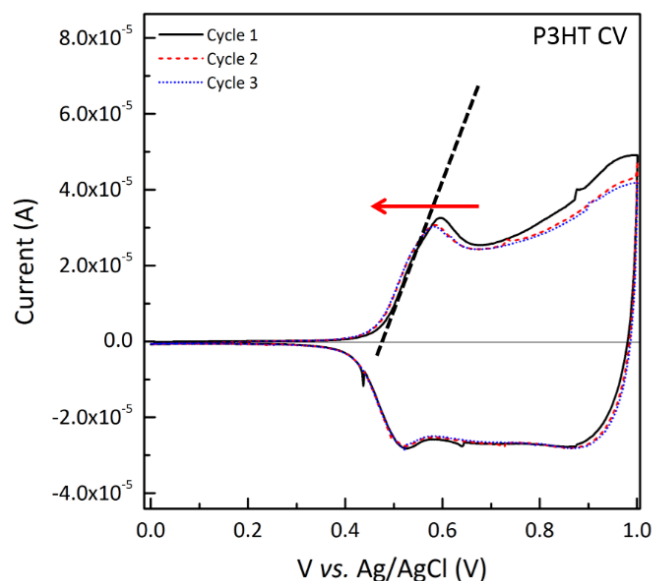


Figure 6.9: Cyclic voltammogram of a neat P3HT film. The red arrow indicates the shift of polymer oxidation during repeat cycles.

The first CV sweep (oxidation and reduction) leads to an extracted HOMO energy level for P3HT thin-films of -4.81 eV (Figure 6.9). For every system considered here, repeat CV cycles shifts (red, blue) the onset to lower values, which implies the films become easier to oxidise. In order to understand the cause of this reduction of the HOMO energy level, a series of P3HT oligomers were simulated with controlled inter-unit torsion angles. Using the optimised torsion angle as a reference (16 °) increasing the planarity of the polymer chain shifts the C = C to lower wavenumbers and decreases the HOMO energy level (Figure 6.10). The isosurfaces of electron density for the HOMO illustrate an increased delocalisation of electron density along the backbone for the planar vs. twisted P3HT (Figure 6.11).

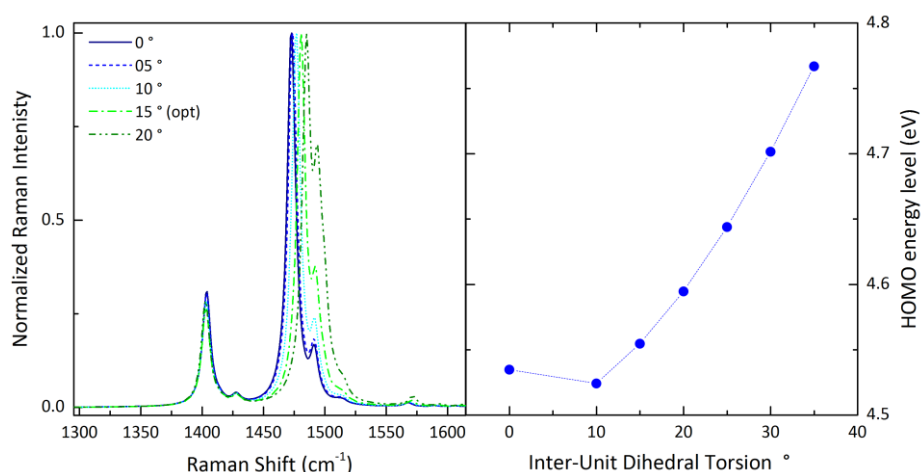


Figure 6.10: Simulated Raman spectra for P3HT oligomers as a function of inter-unit dihedral torsion. The increase in dihedral torsion (all in a helical conformation) shifts the C = C bond to higher frequencies and increases the energy of the HOMO.

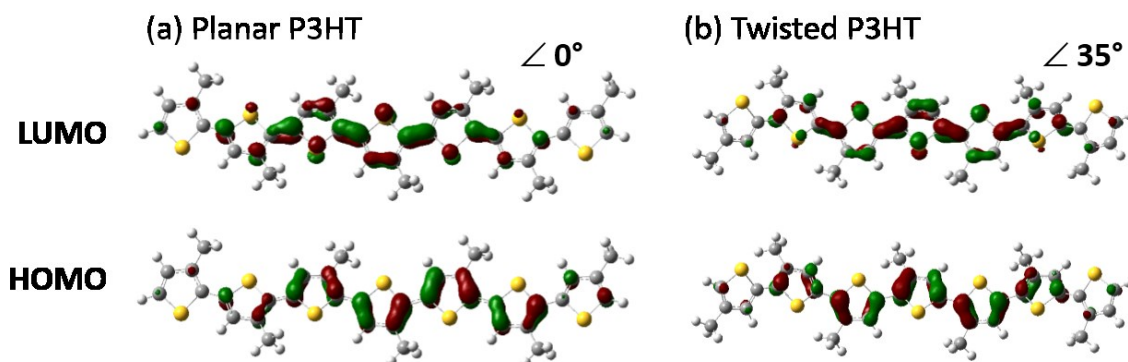


Figure 6.11: Calculated isosurfaces of HOMO and LUMO of (a) planar and (b) twisted P3HT. Increasing the inter-unit torsion decreases π -electron conjugation.

To establish the impact of polaron formation in the polymer film but avoid significant degradation of the polymer backbone, a series of short ($t = 60 - 90$ s), low potential pulses (0.65 V with respect to Ag/AgCl) are first considered, each corresponding to the formation of 10^{20} cm⁻³ polaron density (p).^[2] The polaron density is estimated by integrating the area underneath the current – time curve (Figure 6.12).

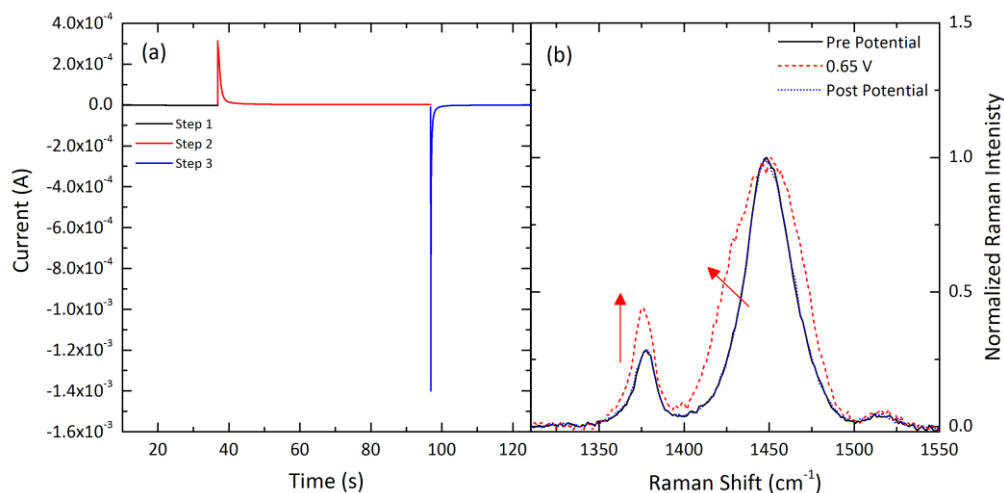


Figure 6.12: (a) Current as a function of time for time for a chronoamperometry measurement. Integration of the area under the curve allows calculation of the polaron density created in the polymer films. (b) Resonant Raman spectra of P3HT pre (black), during (red) and after 60 s pulses of 0.65 V (blue).

Current vs time for a representative pulse 0.65 V pulse is illustrated in Figure 6.12. The films are held at 0 V for 60 s after the potential application to allow the charged polymers to return to their neutral state. Immediately after the potential is applied (Figure 6.12 (b)) the C = C stretch (1489 cm^{-1}) broadens to high and low energy and there is an increase in the relative intensity of C – C/C = C ($1379/1489 \text{ cm}^{-1}$). The instantaneous response to charge injection is not surprising as the in-plane ring skeletal modes are sensitive to π -electron delocalisation (see HOMO/LUMO in Figure 6.11). Short timescale pulses and the associated polaron formation appears to cause reversible changes to the polymer backbone, which recovers to the original FWHM and relative intensity almost immediately.

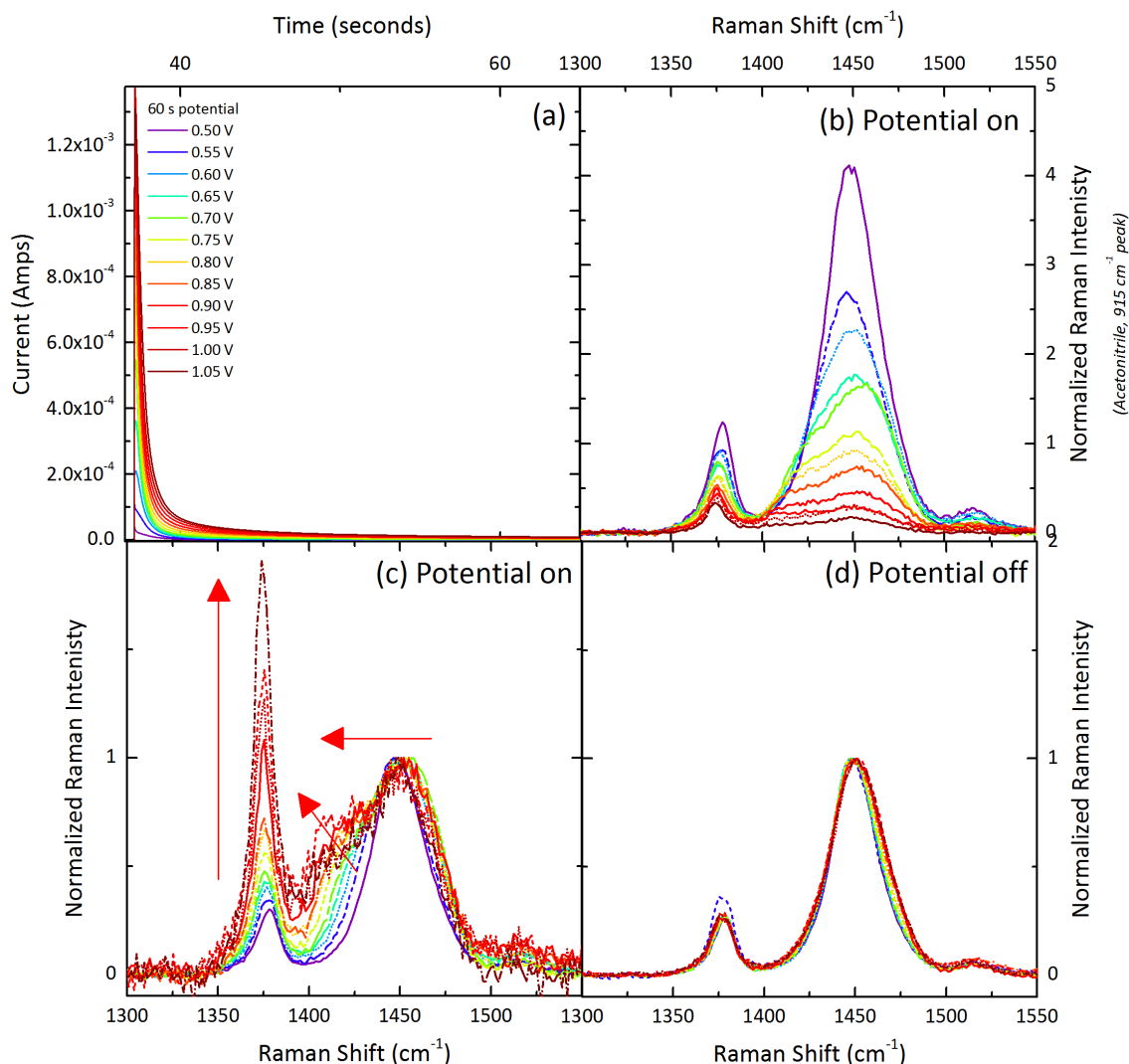


Figure 6.13: (a) Current as a function of time for at a range of potential differences (0.5 – 1.05 V). The bias time is fixed at $t = 60$ s. Resonant Raman scans for (b,c) during potential application (d) after the potential is removed and the film is held at 0 V. The Raman spectra in (c) and (d) are normalized to the main C = C peak, ($\approx 1489 \text{ cm}^{-1}$).

Next we evaluate the impact of increasing the polaron density on polymer molecular order. A series of $t = 60$ s potential pulses ranging from pre- to post-oxidation (-4.7 to -5.4 eV), corresponding to $p \approx 10^{19} - 10^{21} \text{ cm}^{-3}$ are considered. A simple comparison is made by normalizing the spectra (Figure 6.13). Oxidative stress decreases the absolute Raman scattering intensity, consistent with our previous observation of loss of the polymer chromophore (bleaching in absorption spectra) as the laser is resonant with the neutral polymer (488 nm).^[2] For high polaron densities ($p \approx 10^{21} \text{ cm}^{-3}$) there is an immediate loss of Raman activity, shift of C = C to lower wavenumber and increase in the relative intensity of C – C/C = C. When oxidised at potentials greater than 0.85 V (energy levels ≈ -5.2 eV), the Raman spectra of P3HT are similar to that obtained by Yu *et al* for photo-oxidized P3HT.^[38]

The new mode near 1420 cm^{-1} is assigned to the ‘quinoidal stretch’, symmetric stretching of the $\text{C} = \text{C}$ bond of radical cations and the increase of $\text{C} - \text{C}/\text{C} = \text{C}$ indicates the oxidised P3HT is in a more planar conformation.^[38–40] The breadth of the $\text{C} = \text{C}$ mode implies it is not purely quinoidal but contains contributions from the neutral and oxide state. This indicates that even at these high polaron densities not all the P3HT chains are oxidised.

Applied potential	Polaron Density	Potential On			Post Potential (0 V)		
		$\text{C} = \text{C}$ max	FWHM	$\text{C} - \text{C}/\text{C} = \text{C}$	$\text{C} = \text{C}$ max	FWHM	$\text{C} - \text{C}/\text{C} = \text{C}$
V	cm^{-3}	cm^{-1}	cm^{-1}		cm^{-1}	cm^{-1}	
0.5	5.03E+19	1447.2	36.7	0.27	1449.3	26.4	0.26
0.55	1.24E+20	1447.3	41.8	0.30	1449.2	27.5	0.36
0.6	2.40E+20	1449.2	48.4	0.34	1449.4	26.6	0.27
0.65	4.13E+20	1449.9	52.6	0.40	1449.2	27.7	0.29
0.7	6.23E+20	1450.5	55.6	0.43	1449.3	27.3	0.28
0.75	8.41E+20	1451.3	59.6	0.48	1449.7	28.4	0.27
0.8	1.04E+21	1452.0	69.7	0.56	1450.1	29.1	0.26
0.85	1.23E+21	1453.6	78.9	0.66	1450.3	31.4	0.28
0.9	1.39E+21	1452.8	94.1	0.72	1450.9	30.5	0.26
0.95	1.51E+21	1449.8	123.0	1.08	1451.2	32.0	0.29
1	1.56E+21	1452.0	108.5	1.40	1451.6	31.2	0.25
1.05	1.49E+21	1449.8	125.8	1.91	1451.5	31.2	0.28

Table 6.3: $\text{C} = \text{C}$ max peak shift, FWHM and $\text{C} = \text{C}/\text{C} - \text{C}$ during potential application and when the film is held at 0 V. The polaron density is calculated from integration of the current vs. time and are also provided for reference.

The $\text{C} = \text{C}$ peak position, FWHM and relative intensity of $\text{C} - \text{C}/\text{C} = \text{C}$ (from Figure 6.13) are evaluated for a series of applied potentials (and thus polaron densities) in Table 6.3, during polaron formation (‘Potential On’) and when the film is held at 0 V after application (‘Post Potential’). As the polaron density increases, the FWHM of the $\text{C} = \text{C}$ mode and the relative intensity of $\text{C} - \text{C}/\text{C} = \text{C}$ increases as it contains both neutral and quinoidal portions of the polymer chain. After the potential is removed, when the films are allowed to return to their neutral state, the effects of the polaron formation can be observed. Repeated applications of potential result in an increase in the high energy (disordered) component of the $\text{C} = \text{C}$ mode, indicating an increase in conformational disorder.

The amounts of quinoidal polymer can be monitored by either extracting $\text{C} - \text{C}/\text{C} = \text{C}$, or fitting a linear combination of the quinoidal (1420 cm^{-1}) and neutral (1489 cm^{-1}) structures (Figure 6.14).

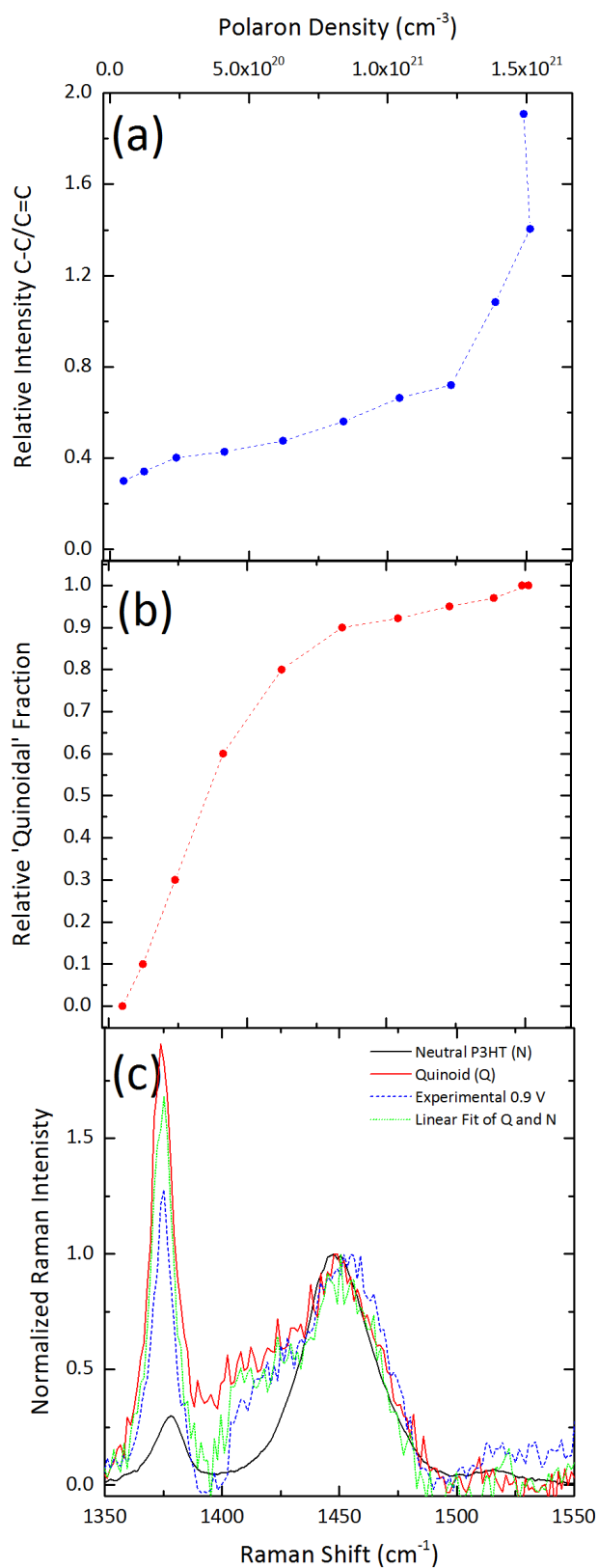


Figure 6.14: (a) Relative intensity of C – C vs C = C modes and (b) relative quinoidal fraction as a function of polaron concentration for P3HT films. The relative quinoidal fraction is found using a linear fit of the neutral (N) and quinoidal polymer (Q) spectra, as illustrated in (c).

6.2.4 Impact of Electrochemical Degradation of P3HT, PTTTz and PTTz

We consider the long-term structural changes occurring in these materials after hole polaron formation. To ensure the different HOMO level polymers are subject to the same extent of oxidative stress, the degree of polymer electrochemical oxidation is controlled using chronoamperometry at different potentials in order to create the same polaron density (10^{20} cm^{-3}) in each sample.^[2] The measurements were carried out using the same set-up as above (*in situ* of P3HT), with an oxidising potential (V_{probe}) of +0.65 V, +0.80 V, and +1.05 V to the working electrode, for P3HT, PTTTz, and PTTz, respectively (all potentials quoted with respect to Ag/AgCl reference electrode) for 10,000 s (just under 3 hours). Subsequently, absorption spectra were measured *in situ* to monitor the quinoidal polymer and Raman spectra acquired *ex situ* to observe the results of polaron formation in the polymer film.

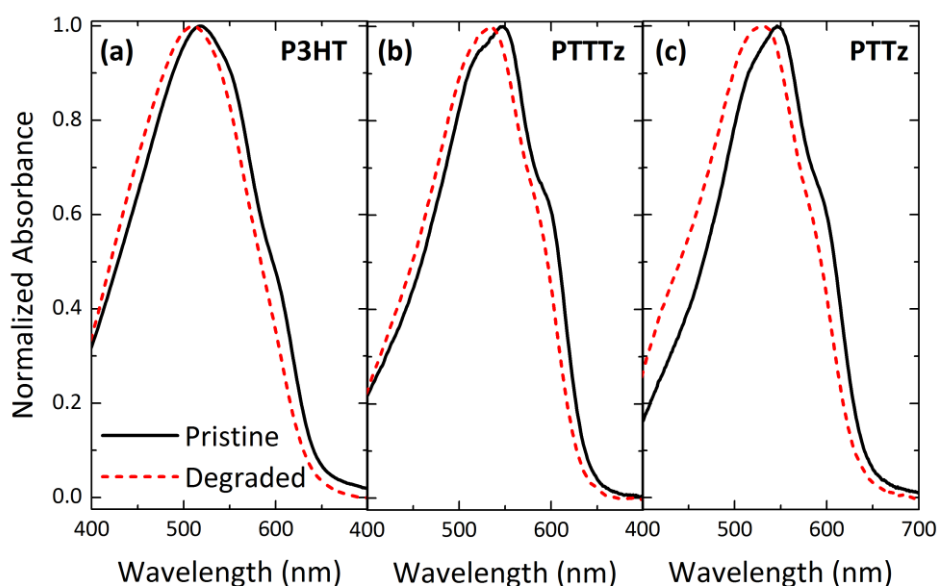


Figure 6.15: UV-Visible absorption spectra for pristine (black solid line) and electrochemically degraded (red dashed line) films of P3HT, PTTTz and PTTz.

Figure 6.15 compares the UV-Visible absorption of pristine and electrochemically degraded (after polaron injection of $\approx 10^{20} \text{ cm}^{-3}$) films of the three polymers. After the electrochemical degradation, all three materials show a blue shift of the absorption onset and band maxima and the absorption shoulder at around 590 nm is lost. These changes indicate an increase in conformational disorder in each case.^[23] P3HT is the least blue-shifted ($\approx 7 \text{ nm}$) followed by PTTTz ($\approx 14 \text{ nm}$) and finally PTTz ($\approx 19 \text{ nm}$). It is clear that the polymer with the deepest HOMO (and therefore most 'stable') experiences the most severe morphological changes after charge injection. A more detailed

comparison of the molecular conformations for the three polymers is provided by the resonant Raman spectra in Figure 6.18.

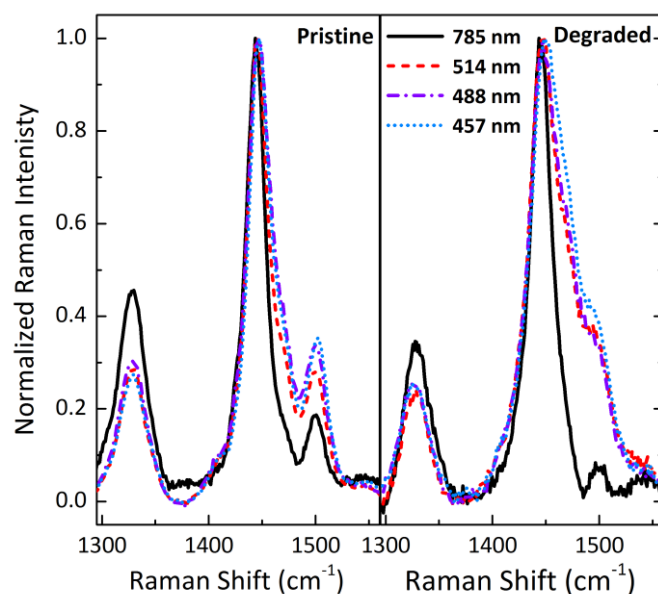


Figure 6.16: Raman spectra of pristine and degraded films of PTTz measured with 457, 488, 514 and 785 nm excitations.

Figure 6.16 compares the Raman spectra of pristine and degraded PTTz films using several excitation wavelengths ranging from the non-resonant (785 nm) to the highly resonant (514, 488, 457 nm). The Raman scattering cross-section is determined by the polarisability of a particular mode, which in turn depends upon the molecular conformation and effective conjugation length.^[36,41] Therefore, the differences in the Raman spectra measured with different excitation wavelengths can provide information about particular morphological phases (ordered or disordered) present in polymer films.^[23] The shorter wavelength excitations selectively probe more disordered portion of the polymer chains, corresponding to the relative shift in the main C = C peak position to higher energy^[23,24,31] As a result the FWHM of the C = C peak for both pristine and degraded PTTz films increases with decreasing excitation wavelength (Figure 6.17). The dependence on excitation energy of the FWHM of the degraded PTTz film is much larger than that of the pristine film (from 25.1 to 64.0 cm⁻¹ for 457 nm excitation). This is accompanied by an overall shift in the peak position to higher frequency (from 1446 to 1449 cm⁻¹ for 457 nm excitation). Both the large increase in FWHM and peak shift to higher frequency arise from an increased higher energy portion of the main C = C peak. The changes are detailed in Table 6.4. This result clearly shows that the degradation mechanism induced by the electrochemical hole injection results in an increase in the fraction of disordered phase of the PTTz polymer, with reduced effective

conjugation length potentially associated with increased inter-unit torsion angle (or breaking) of the conjugated polymer backbone.^[23]

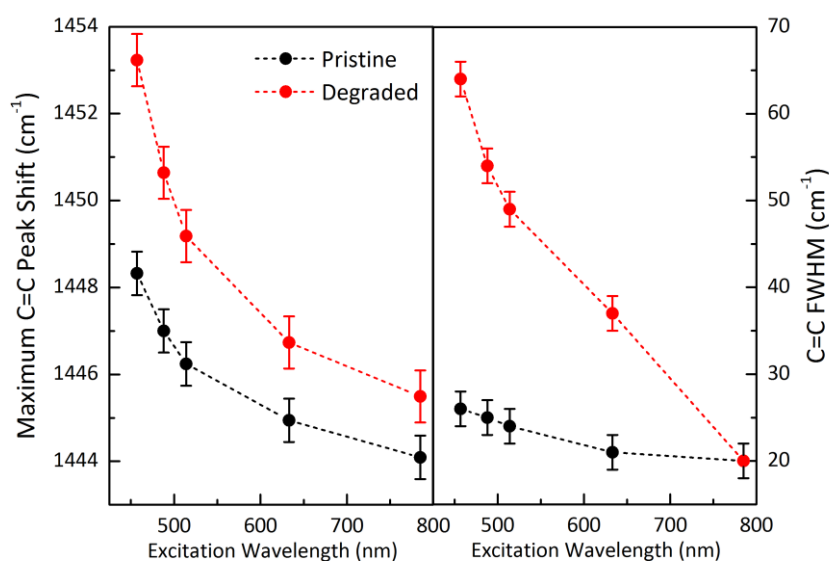


Figure 6.17: Maximum peak position (cm^{-1}) and FWHM (cm^{-1}) of the main C = C mode in PTTz at 785, 633, 514, 488 and 457 nm excitations for pristine (black) and degraded (red) thin films.

	C = C Peak Position		FWHM		I_{1447}/I_{1464}		Δ
	Pristine	Degraded	Pristine	Degraded	Pristine	Degraded	
785 nm	1444.1	1445.5	26	64	1.3	1.0	-24 %
514 nm	1444.9	1446.7	25	54	9.6	2.5	-73 %
488 nm	1446.2	1449.2	24	49	7.0	1.1	-85 %
457 nm	1447.0	1450.6	21	37	5.4	1.6	-70 %

Table 6.4: Peak position, FWHM and I_{1447}/I_{1464} collected at 785, 633, 514 and 488 nm for pristine and degraded films. Δ indicates the percentage change of the ratio after electrochemical degradation.

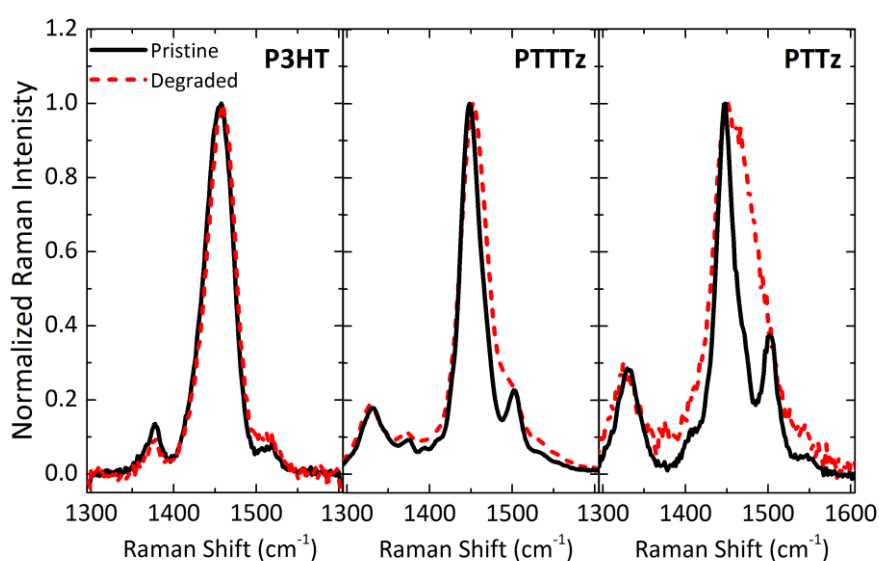


Figure 6.18: Resonant Raman spectra for pristine (black solid line) and degraded films (red dashed line) of P3HT, PTTTz, and PTTz measured using 488 nm excitation.

Resonant Raman spectroscopy is used to study the local impact of electrochemical degradation on the conjugated backbone of P3HT, PTTTz and PTTz films. The increase in the high energy component of the C = C stretching mode peak ($\sim 1460 \text{ cm}^{-1}$) is minimal for the P3HT film, though there is also a clear decrease in the intensity of the C–C stretch mode relative to the C = C peak, which indicates an increase in polymer disorder (Figure 6.18).^[23] When thiazole units are incorporated into the chain (PTTTz, PTTz) the electrochemical degradation results in more significant changes, the most obvious being a larger increase in the high energy component of the main C = C vibration mode, showing that these polymers are more strongly affected. More subtle effects are detected using peak fitting to distinguish the contributions from the overlapping peaks.

Lorentzian peaks with fixed FWHM (20 cm^{-1}) and peak centres were fitted to the C–N (1331 cm^{-1}), C = C_{Ordered} (1447 cm^{-1}), C = C_{Disordered} (1464 cm^{-1}), and C = N (1501 cm^{-1}) modes (Figure 6.19). This allows us to extract ratios of the integrated peak intensities for the ordered and disordered components contributing to the C = C mode, providing a quantitative measure of the degree of polymer molecular order, and also to monitor degradation induced changes in the bonds involving the N atom (Table 6.5). The I_{1447}/I_{1464} value is the ratio of the integrated intensities of the 1447 cm^{-1} peak (C = C in the ordered phase) to the 1464 cm^{-1} peak (C = C in the disordered phase). The I_{1501}/I_{1331} value is the ratio of integrated intensities of the C = N stretching mode (1501 cm^{-1}) to the C–N stretching mode (1331 cm^{-1}).

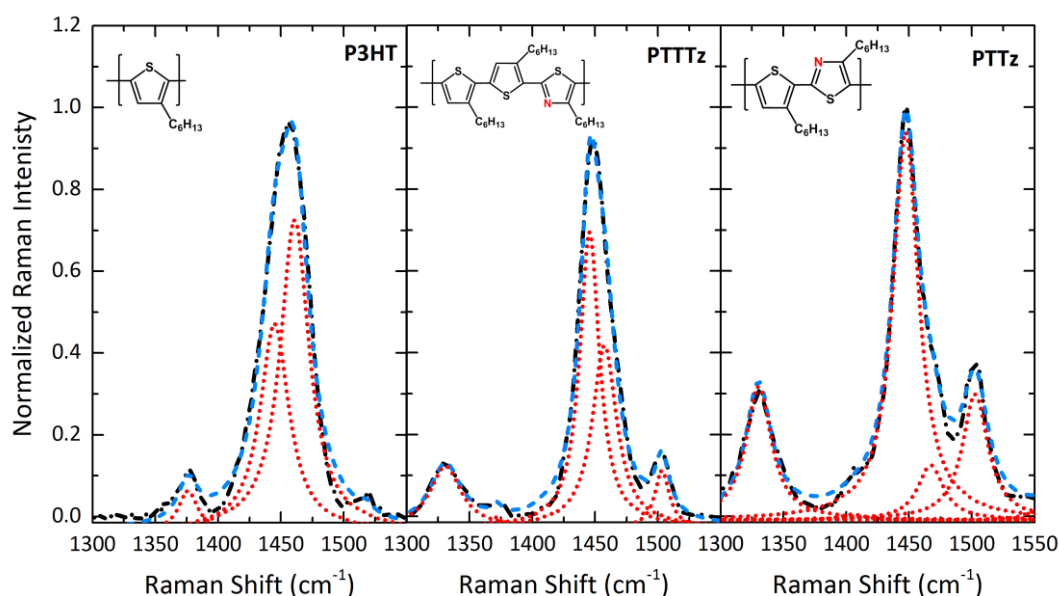


Figure 6.19: Lorentzian peak fitting for the main vibrational modes of pristine P3HT, PTTTz and PTTz films measured at 488 nm excitation. The experimental spectra (black line), individual peaks (red dotted line) and cumulative peak (blue dashed line) fit is indicated. The same FWHM (20 cm^{-1}) and peak centres of individual peaks are used for pristine and degraded samples and only the peak intensity allowed to vary.

	P3HT			PTTTz			PTTz		
	Pristine	Degraded	$\Delta(\%)$	Pristine	Degraded	$\Delta(\%)$	Pristine	Degraded	$\Delta(\%)$
I_{1447}/I_{1464}	1.0 ± 0.2	0.7 ± 0.2	- 30	4.2 ± 0.4	1.3 ± 0.2	- 69	7.0 ± 0.5	1.1 ± 0.4	- 85
I_{1501}/I_{1331}				0.43 ± 0.04	0.40 ± 0.04	- 7	0.20 ± 0.02	0.13 ± 0.01	- 28

Table 6.5: Relative peak intensity ratios (integrated) for the main vibrational modes of pristine and degraded P3HT, PTTTz and PTTz films extracted from Lorentzian fits to Raman spectra measured with 488 nm excitation (Figure 6). Δ indicates the percentage change of the ratio after electrochemical degradation.

In the pristine case the I_{1447}/I_{1464} value is smallest for P3HT and increases with increased thiazole content (P3HT, 1.0; PTTTz, 4.2; PTTz, 7.0) confirming the increase in backbone coplanarity resulting from the thiazole unit (Table 6.5). In all three polymers the I_{1447}/I_{1464} value is largest for the pristine case and decreases once they are degraded, showing that the proportion of the disordered phase increases. In addition to this conformational changes induced by the electrochemical degradation, more specific information about particular bonds affected by this degradation can be gained from the relative intensities of the C–N (1331 cm^{-1}) and C = N (1501 cm^{-1}) vibrational modes. These bonds are only found in the thiazole unit so they are not observed for P3HT, but for both PTTTz and PTTz films this value (I_{1501}/I_{1331}) reduces after the sample is degraded. The significant decrease of C = N vs. C–N indicates that the electrochemical degradation affects the C = N bond more strongly than the C–N bond, and that the degradation mechanism involves either the p_z orbital of nitrogen or carbon. For the polymer containing the highest proportion of thiazole (PTTz) there is a significant reduction of integrated peak intensity of C = N vs. C–N. In this instance, we would expect this degradation to cause a potential breaking of the C = N bond and hence reduce effective conjugation length and coplanarity of the polymer backbone in the degraded material. The electron donating nitrogen lone pair (in an sp^2 orbital) could also have interactions with the cation portion of the polaron, forming C–N bond and thus decreasing the C = N/ C–N intensity value in the electrochemically degraded film. The reason why the nitrogen atom is particularly vulnerable in the polaronic state is not yet clear, though we consider alternating thiophene-thiazole form the unsymmetrical hole polarons with high charge density in the C = N bond and nitrogen lone pair.^[42] This leaves thiazole units more susceptible to radical degradation pathways centred on this site.

Analogous to our work with PTB7, in an effort to interpret the conformation changes that occur upon hole polaron formation a series of likely degradation products were investigated using quantum chemical calculations

(Figure 6.20).^[43] Similar studies have demonstrated the importance of modelling the complete molecule and considering intermolecular interactions.^[26,27] A range of molecular structures were considered, where the polymer chain had been broken or oxygenation had occurred at different positions. The results were not particularly conclusive (the results of a few are illustrated below). The precise degraded chemical structure is also a matter of hypothesis, so a rigorous DFT study would be a major undertaking, and the practical simplifications of considering truncated polymer backbones with reduced alkyl side chains as isolated molecules would also need careful consideration.

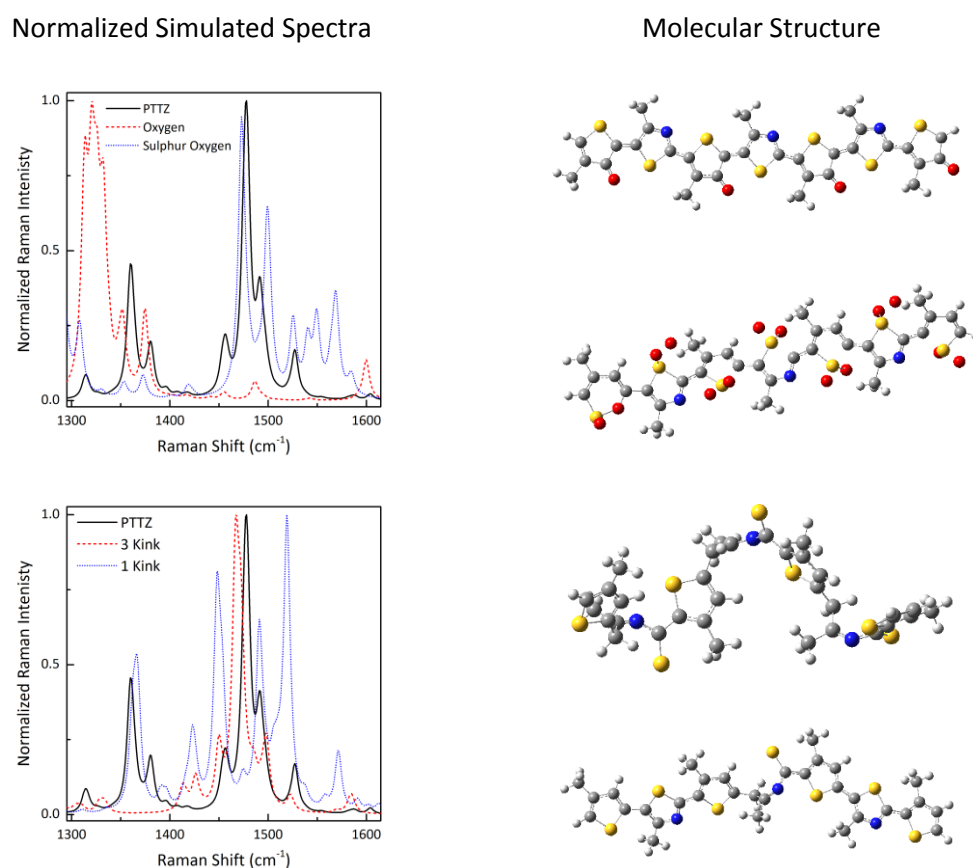


Figure 6.20: Optimised molecular structures of degraded PTTz polymer chains and simulated Raman spectra. All simulations were performed at the 6-31 G(d,p) basis set.

6.2.5 Summary

Incorporation of thiazole units into a polythiophene polymer chain is understood to deepen the HOMO energy level and planarise the conjugated polymer backbone by reducing the steric hindrance between neighbouring units. Whilst thiazole units improves the chemical stability of the polymer in the ground state, the formation of the polaronic state shows increased susceptibility to electrochemical degradation, which is problematic for application in photovoltaic devices under normal operational conditions. The Raman spectra of the three polymers (P3HT, PTTTz and PTTTz) confirm a systematic enhancement of molecular planarity with increasing thiazole content. The presence of

additional vibrational modes in the Raman spectra of PTTz and PTTz related to the thiazole unit (C–N and C = N bond stretching modes) provides an important means to probe chemical changes associated to this unit during electrochemical degradation. We find that increasing the thiazole content in the thiophene chain makes the polymer more susceptible to degradation of the polaronic species, resulting in a substantial increase in the conformationally disordered phase of the material. This is accompanied by a decrease in Raman scattering intensity of the C = N vibrational mode relative to the C–N mode, indicating the C = N bond is most vulnerable in the degraded polymer chain.

6.3 Effect of Side-Chain Branching on the Morphological Stability of Polythiophenes

Despite a range of new materials being developed for high performance organic solar cells, it remains a challenge to understand the mechanism of film growth and there has been little progress in describing the crystallisation mechanism polymers. As discussed in Section 6.2, thin films of P3HT and derivatives contain both ordered and disordered polymer chains, which contribute to the intricacy of the drying process. The microstructure of the majority of polymers deposited via conventional solution-processing techniques occurs on a timescale too short for in-depth characterisation. Poly(3-ethylhexylthiophene) (P3EHT) (Figure 6.21) has similar optoelectronic properties to P3HT and an accessible liquid crystalline phase. The liquid crystalline phase is unstable in P3HT because of close melting ($T_M \approx 180 - 220\text{ }^\circ\text{C}$, depending on drying mechanism) and degradation temperatures ($T_{\text{deg}} \approx 240 - 260\text{ }^\circ\text{C}$).^[44–46]

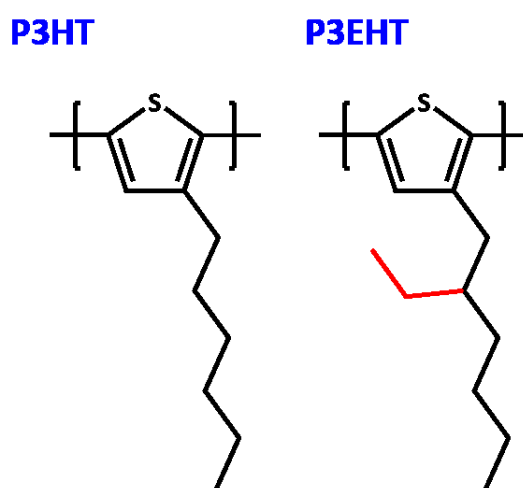


Figure 6.21: Molecular structure of P3HT and P3EHT.

P3EHT has been demonstrated as a material with exceptionally slow crystallisation kinetics only recrystallizing several hours after melt ($T_M \approx 90\text{ }^\circ\text{C}$).^[44,47,48] Using XRD and UV-Visible absorption, Duong *et al* monitored the growth

of anisotropic aggregates along the alkyl stacking and backbone direction.^[49] The growth along the alkyl direction occurs at a faster timescale (≈ 20 minutes), after which films continue to crystallise along the polymer backbone.

6.3.1 Experimental Details

Films were spin-coated from 30 mg ml⁻¹ solutions of P3EHT dissolved in chloroform. Clean quartz substrates were covered with polymer solution and spun at 1500 rpm for 60 s. The films were dried under vacuum for 24 hours.

For optoelectronic measurements, thin films of P3EHT on quartz were placed on a hot plate at 100 °C in a nitrogen atmosphere for 10 minutes. After melting each film they were quenched in the glovebox on a metal block. Absorption and resonant Raman spectra were recorded every 30 minutes for 3 hours. A separate control sample was held at 60 °C for 3.5 hours and slow-cooled to room temperature to promote crystallisation.

For cyclic voltammograms thin films were deposited on FTO/glass and were subjected to the same annealing conditions as for the samples prepared on quartz. The measurements were carried out in the same 3-electrode spectroelectrochemical cell described in Section 6.2.3. Voltammograms were recorded 30, 90, and 250 minutes after melt, along with that of the 'control sample'.

6.3.2 Optoelectronic Properties

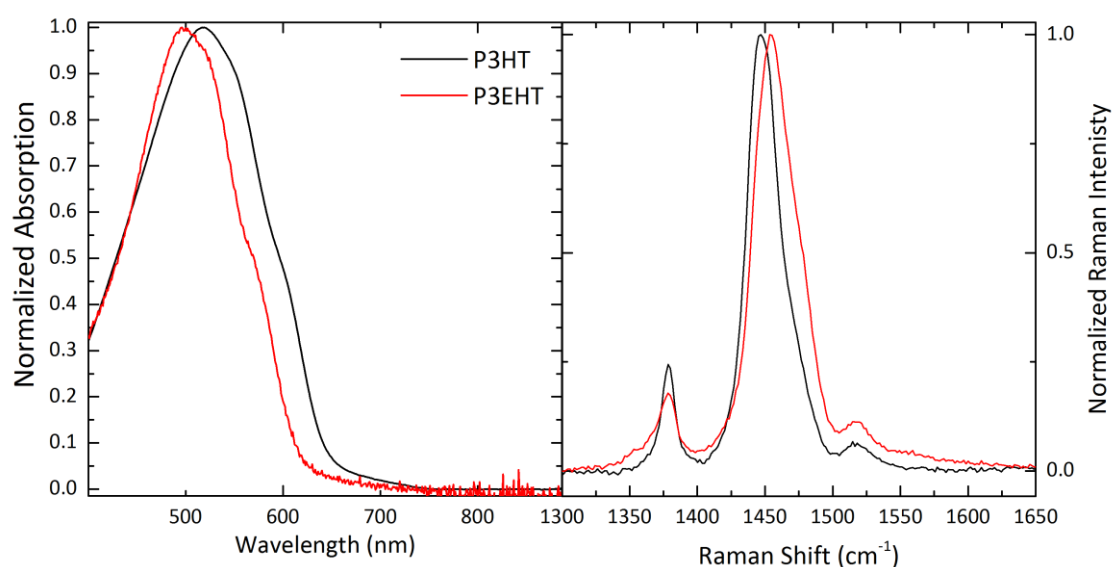


Figure 6.22: (a) Normalized absorption and (b) resonant Raman spectra of P3HT (black) and P3EHT (red) thin films. Raman spectra are normalized to the C = C vibrational mode.

Decreased molecular order of the polymer backbone for the branched side-chain P3EHT is illustrated by the blue-shift of the absorption maximum (P3HT ≈ 520 nm, P3EHT ≈ 500 nm) and loss of low-energy absorption shoulder

(Figure 6.22). The absorption onset is similar in both cases. Interestingly the high-energy polymer absorption is relatively unaffected. Using the C = C mode as a signature for backbone disorder, resonant Raman spectroscopy (457 nm excitation) reveal an increased number of conformational states (broadening to higher energy), reduction of C – C/C = C and shortening C = C bonds. The C = C peak position shifts from 1446 (P3HT) to 1454 (P3EHT) cm^{-1} .

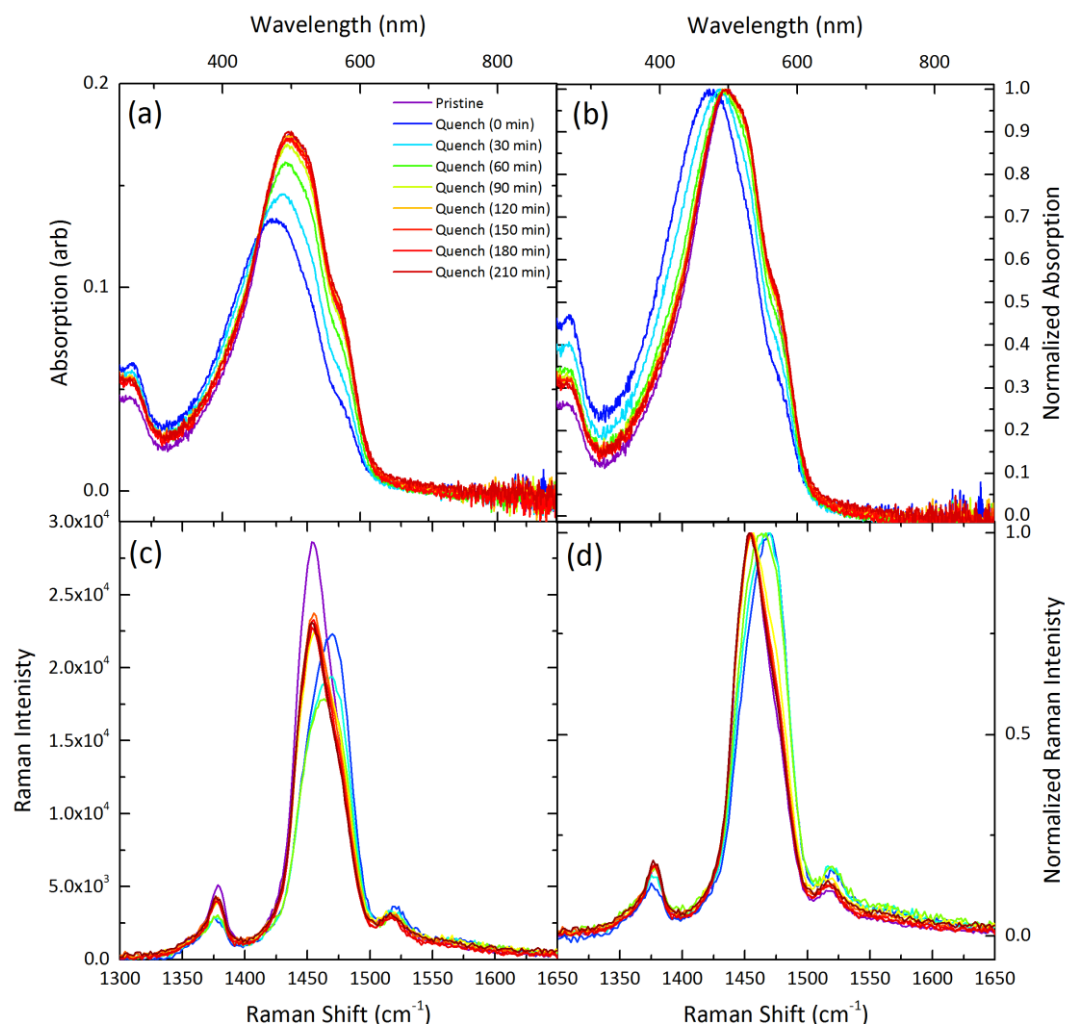


Figure 6.23: Raw (a,c) and normalized (b,d) absorption and resonant Raman spectra of pristine (purple) and quenched (blue) P3EHT. The recrystallization of P3EHT occurs over several hours and is illustrated by the coloured curves.

Figure 6.23 illustrates the raw (a,c) and normalized (b, d) absorption and resonant Raman spectra as a function of time after quench (every 30 minutes for 3.5 hours). Immediately after the film is removed from 100 °C the relatively ordered polymer absorption blue-shifts (500 nm to 474 nm) and broadens to high energy. The Raman spectra are accumulated at an excitation wavelength = 457 nm- an isobetic point of the absorption spectra, where the total absorbance of the sample does not change during recrystallization. The blue-shift is accompanied by an overall decrease of absorption and shift of the C = C mode to higher frequency (1453.4 to 1470.1 cm^{-1}), indicating that

effective conjugation is broken and the chromophore is diminished. These changes are summarized in Table 6.6 and illustrated in Figure 6.24. Whilst the chromophore recovers quickly (within 60 minutes), the conjugated backbone takes longer to rearrange; the C = C peak position and C = C_{Order}/C = C_{Disorder} recover within 120 minutes. This is consistent with observations that the alkyl chains rearrange first followed by crystallite growth along the backbone direction.^[49]

Time post quench <i>mins</i>	Absorption band maximum <i>nm</i>	C = C peak position <i>cm⁻¹</i>	C = C FWHM <i>cm⁻¹</i>	% Ordered <i>1451 cm⁻¹</i>	% Disordered <i>1472 cm⁻¹</i>	C = C _{Order} /C = C _{Disorder}
Pristine	499.6	1453.4	40.6	0.9	0.5	1.9
0	474.6	1470.1	43.5	0.6	1.0	0.6
30	487.6	1465.1	44.9	0.7	0.9	0.8
60	493.3	1463.4	45.6	0.7	0.9	0.8
90	496.3	1456.8	44.2	0.9	0.6	1.4
120	497.4	1455.1	43.1	0.9	0.6	1.6
150	497.7	1455.1	42.3	0.9	0.6	1.6
180	498.6	1453.4	42.1	0.9	0.5	1.8
210	499.3	1453.4	42.3	0.9	0.5	1.8

Table 6.6: Absorption band maxima and C = C peak position as a function of time after quench for thin films of P3EHT. The FWHM

of the C = C mode and relative fractions of order and disorder also included.

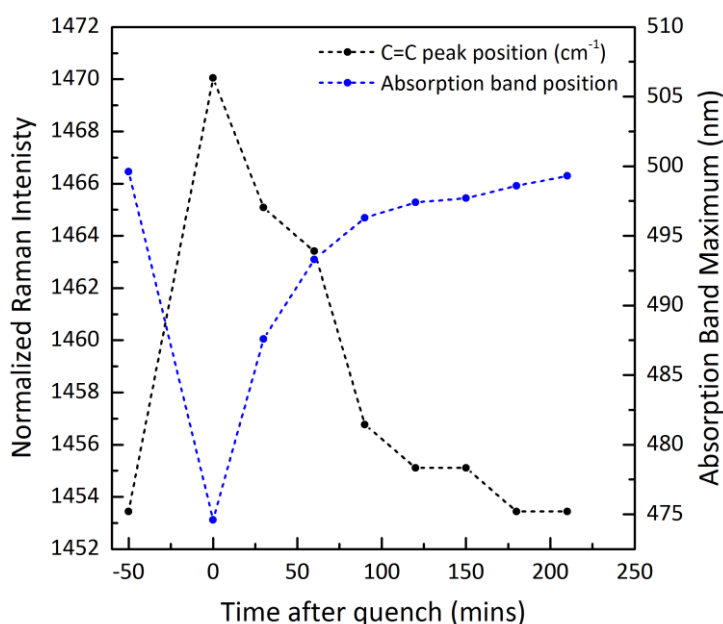


Figure 6.24: Absorption band maxima and C = C peak position as a function of time after quench for thin films of P3EHT extracted from Figure 6.23.

Analogous to our previous studies of polythiophene systems, we have fitted the C = C peak as a combination of ordered and disordered components.^[1,2,23,24] From the normalized Raman spectra in Figure 6.24 the C = C mode is fit as a convolution of ordered (1451 cm⁻¹) and disordered (1472 cm⁻¹) components with the same FWHM. The integrated peak intensity of the ordered relative to disordered fraction is plot in Figure 6.25.

Cyclic Voltammetry

Cyclic voltammetry was used to measure the oxidation potential as a function of time after quench. Two transient-shaped oxidation peaks are observed in each voltammogram with relative intensities correlating to time after quench. The two peaks represent planar (lower potential) and twisted (higher potential) portions of the polymer chain. The higher potential peak (0.87 V) is strongest for the most disordered films (30, 90 minutes after quench), whilst the lower potential (0.92 V) dominates the more ordered films (120 minutes after quench). The blue curve represents the morphologically stable control sample, annealed at 60 °C for 60 minutes, and shows no evidence of the higher oxidation potential. Equivalent to our study of the disordered and ordered components of the C = C mode, the CV curves have been fit as a linear combination of the 0.87 and 0.92 V peaks. Linear fits have been performed on each sample and show surprisingly similar gradients, Raman- $6.5 \pm 0.6 \times 10^{-3}$, CV- $6.9 \pm 1 \times 10^{-3}$. These findings illustrate the suitability of both resonant Raman spectroscopy and cyclic voltammetry in monitoring the *in situ* recrystallization of polymer thin films and confirm the longer time constant of backbone rearrangement in P3EHT. The rapid recrystallization of P3HT do not allow for such measurements.

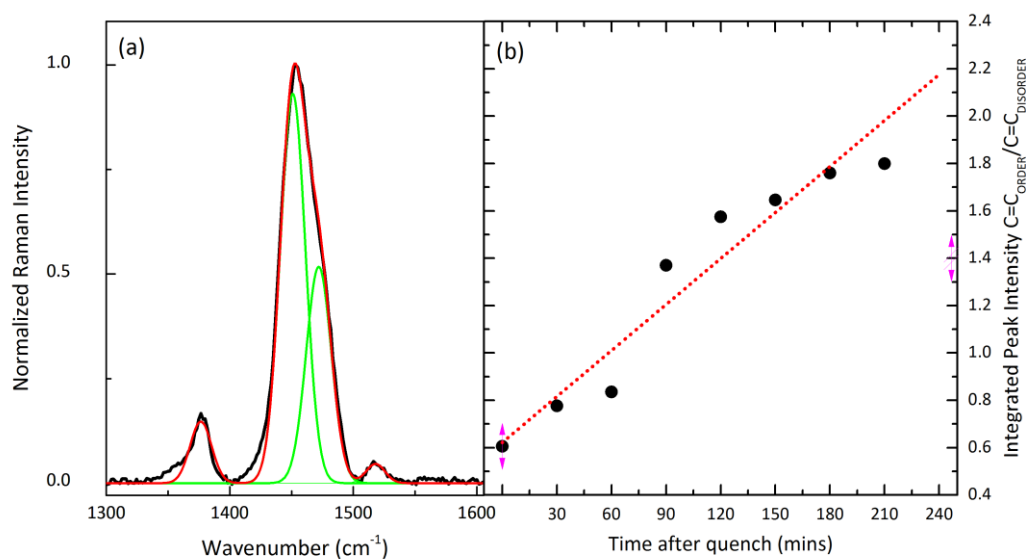


Figure 6.25: (a) Lorentzian fits of ordered and disordered components of C = C mode for P3EHT. (b) Integrated peak intensity of C

$= I_{C=C}^{ORDER}/I_{C=C}^{DISORDER}$

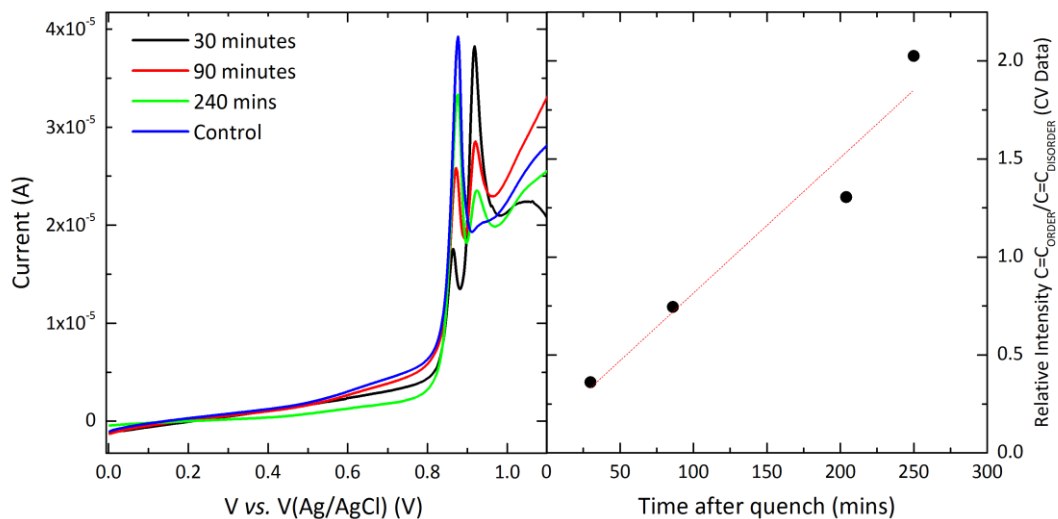


Figure 6.26: (left) CV scans of thin films of P3EHT on FTO/glass. The oxidation peak has two components at high and low energy representing ordered and disordered material. The relative intensity of these two peaks is illustrated (right) as a function of time after quench.

6.3.3 Summary

The impact of recrystallization on polymer backbone order and oxidation energy was investigated. P3EHT, a derivative of P3HT with a branched side chain, is well-known to exhibit slow recrystallization dynamics. Using DFT calculations, the impact of backbone torsion on the optoelectronic properties of P3HT is considered. Resonant Raman spectra, UV-Visible absorption and cyclic voltammetry were used to successfully probe the backbone conformation and oxidation potential as a function of time after melt.

The red-shift of the main absorption band of the polymer is complete within the first 30 minutes after recrystallization, and is attributed to alkyl chain rearrangement. The red shift and increased absorbance is attributed to the decrease in inter-unit torsion. By deconvoluting the resonant Raman peak representing the C = C bond into an ordered and disordered component, the recrystallization of P3EHT is monitored as a function of $C = C_{\text{order}}/C = C_{\text{disorder}}$. The linear relationship between time after melt and $C = C_{\text{order}}/C = C_{\text{disorder}}$ demonstrates the ability of Raman spectroscopy to locally probe the movements of the conjugated backbone.

Twisted P3EHT displays two oxidation peaks from ordered and disordered polymer chains. The relative intensity of the planar and twisted components is calculated as a function of time after quench and found to be strongly related to the inter-unit torsion monitored using resonant Raman spectroscopy.

6.4 Conclusions

For all the materials studied here, the structure-property relationships of the thin-films were explored using DFT methods. These techniques demonstrate that *in situ* resonant Raman spectroscopy can be used with quantum chemical calculations where the molecular structure has been systematically controlled to understand the nature of the conformational order of the polymer backbone.

In the first study, the effect of nitrogen substitution on the structural and opto-electronic properties of P3HT was studied. Electronegative nitrogen in thiazole units creates a donor-acceptor like polymer chain. Using resonant Raman spectroscopy as a structural probe, DFT calculations of the vibrational properties of oligomers of the donor-acceptor copolymers were able to accurately reproduce the experimental data. From the optimised oligomer molecules, it was determined that incorporation of nitrogen into the polymer backbone planarises the donor and acceptor units, increasing the electronic coupling and leading to a red-shift and increased oscillator strength of the main optical excitation.

The impact of polaron formation on polythiophene was considered using chronoamperometry. A systematic increase of polaron density within the backbone is found to increase the backbone planarity, with a shift of the main C = C stretch to lower wavenumbers as a function of injected charge. The vibrational changes were corroborated by comparing the experimental spectra to those of quantum chemical calculations where inter-unit torsion had been controlled.

We consider the impact of electrochemical degradation on the thiophene-thiazole copolymers. A series of potentials were chosen based on the HOMO energy level of the polymer and charges were injected for a fixed amount of time to form 10^{20}cm^{-3} of hole polarons in the thin films. We found that incorporation of electronegative nitrogen may lead to a deeper HOMO level and more planar backbone, but that the delocalised polarons formed in these films were of a highly reactive nature. Increasing thiazole content in polythiophene chains is found to systematically reduce the operational stability.

A further investigation into the morphological stability of a branched side-chain derivative of P3HT was performed by studying the effect of recrystallization on polymer backbone order and oxidation level. A red-shift of the main optical excitation and shift of the C = C to lower wavenumbers indicated recrystallization a significant increase in

polymer order. The red-shift of the main absorption band is complete 20 minutes after melt, which was attributed to the rearrangement of the alkyl side-chains. Using our understanding of inter-unit torsion on the vibrational frequencies of P3HT, slow recrystallization of P3EHT after melt resulted in a significantly more planar polymer backbone. The backbone is found to planarize after around 210 minutes. The HOMO level of twisted P3EHT is found to comprise of two distinct oxidation peaks at high and low potential. The relative intensities of these is found to vary linearly as a function of time after melt.

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7 The Control of Polymer/Fullerene Interactions and its Impact on Blend Morphology and Operational Stability

This chapter develops the study of polythiophene derivatives in Chapter 6. Here we establish the impact of acceptor small molecules on the conjugated backbone conformation of the organic polymers (PBTTT, F-PBTTT). We also consider the impact of hole polaron formation in these blend systems. This investigation was performed in collaboration with Elisa Collado-Fregaso, James Durrant, Pierre Boufflet, Martin Heeney and co-workers in the Department of Chemistry at Imperial College London, and is being prepared for a publication.

7.1 Motivation and Aims

In Chapter 6 we established the operational stability of neat polymer films. Here we consider the complete active layer, in a polymer/fullerene blend system. We use the size and loading ratio of the fullerene acceptors to control the blend film morphology. We employ a range of complementary techniques to characterise the polymer molecular order.

Organic photovoltaic devices typically comprise of a bulk heterojunction consisting of a blend of a donor (typically P3HT) and an acceptor material (typically [6,6]-phenyl-C₇₁-butyric acid methyl ester, PC₇₀BM). When the blend is excited in the donor absorption band, a tightly bound electron-hole pair (exciton) is formed in the donor material. The energy level offset between the donor and acceptor can split the exciton into free charges at the donor-acceptor interface, which then move through the donor and acceptor materials (Figure 7.1).

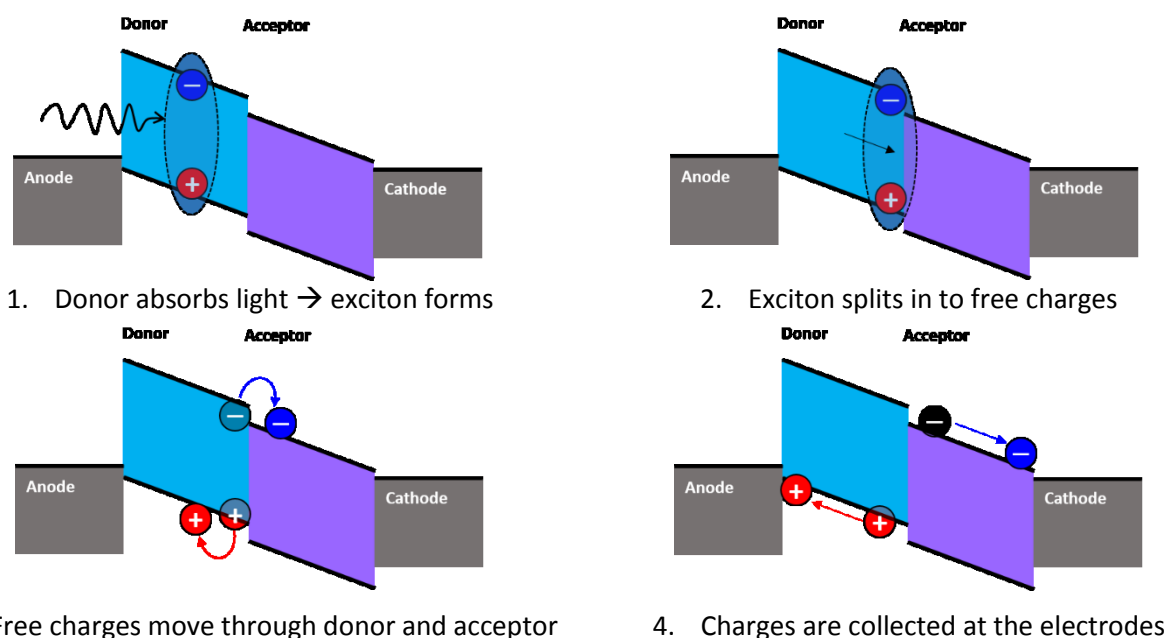


Figure 7.1: Energy level diagram of an organic solar cell at the donor acceptor interface. The photocurrent generation processes are indicated.

The mechanism of charge separation depends on a number of factors, namely:

1. Crystallinity and conjugation length of donor
2. Size of the donor and acceptor domains
3. Relative orientation of donor and acceptor
4. Hole and electron carrier mobility in donor and acceptor

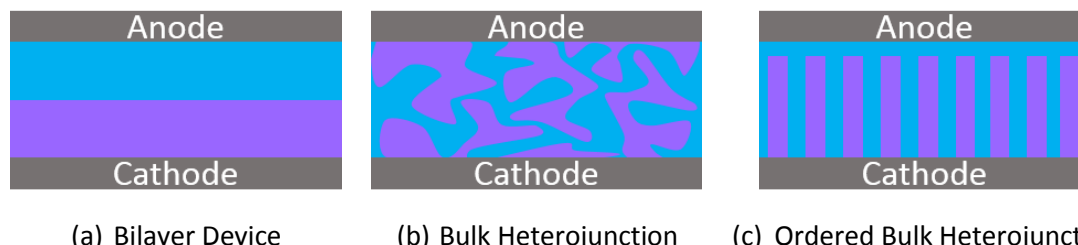


Figure 7.2: Common organic photovoltaic device architectures: (a) the bilayer device (b) bulk heterojunction and (c) ordered bulk heterojunction.

Bilayer devices (Figure 7.2) are typically fabricated *via* the thermal evaporation of the donor and acceptor molecules. A bulk heterojunction architecture, with domain sizes comparable to the diffusion length of excitons (≈ 10 nm), increase the interfacial area between the donor and acceptor molecules. The ordered bulk heterojunction has large domains of donor and acceptor units, where charges can quickly move to the electrodes.

The separated charges can recombine before generating any photocurrent by geminate or non-geminate (bimolecular) processes.^[1] Geminate recombination occurs immediately after exciton dissociation (less than 100 ns) and can be identified by the dependence on electric field.^[1] The application of an electric field can drive separation of the coulombically bound charges in intimately mixed blends. Non-geminate recombination of spatially separated free-charges from different parts of the blend occurs on a longer timescale (100s of ns).^[2] The complex morphology of the donor-acceptor interface is of crucial importance for the mechanism of carrier recombination: it must be large enough for bound pairs to separate, but have accessible pathways for the charges to move through the bulk material. The donor-acceptor ratio can be used to control crystallinity and phase separation of blend films.

PBTTT

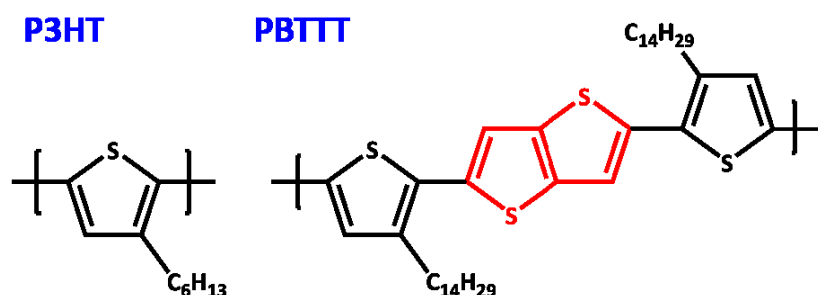


Figure 7.3: Molecular structures of donor polymers considered in this work.

This work considers PBTTT, a polymer designed by McCulloch et al when looking to improve the oxidative stability of P3HT (Figure 7.3).^[3] From a molecular design perspective, the linear conjugated thieno[3,2-b]thiophene unit has a larger resonance stabilisation energy than unfused thiophene. This means electrons do not delocalise into

the polymer backbone as readily, and the reduced delocalisation along the chain lowers the energy levels of the frontier molecular orbitals. The alkyl groups in unfused thiophene units donate electrons into the conjugated π -system, and reducing the number of alkyl units lowers the electron density.^[4] The position of the highest occupied molecular orbital (HOMO) is ≈ -5.1 eV, 0.3 eV deeper than P3HT.^[3] The free volume afforded by the side-chain free thienothiophene unit promotes self-organization and crystallisation.^[3] On cooling PBTTT from a liquid-crystal phase large crystalline domains can be formed. The extended planar π -system ensures close intermolecular π - π distances, which results in excellent two-dimensional charge transport.^[3] The optimised gas-phase geometry has an all anti-arrangement of sulphur across the short-axis, which promotes lamellar packing and allows small molecules to fit between the extended chains (so called 'intercalation').^[3,5]

For PBTTT OPV devices, the size, shape and loading fraction of the acceptor molecules are crucial in determining the interfacial morphology (Figure 7.2) of an organic solar cell. For example, for a 1:1 donor: acceptor blend switching from bis-PC₆₀BM to PC₇₀BM dictates whether the interface consists of intermixed (mixed crystals of polymer and fullerene) or phase-separated domains.^[5–10]

Whilst the donor-acceptor interface is on the nano-scale, the dynamics of charge separation are investigated using macro-scale transient techniques. This work seeks to correlate these distinct macro-scale photo-physical processes with the nano-scale molecular conformation of the donor polymer backbone. The effect of fullerene size on the polymer backbone planarity is considered using a combination of optoelectronic structural probes. The impact of both the fullerene loading fraction and length of the alkyl side-chain of the polymer on the nature of the donor-acceptor interface are considered. In addition to uncovering the conformational origins of phase transitions and evaluating the thermal stability of the complex blend structures, *in situ* resonant Raman spectroscopy provides further details of the mechanism of the donor-acceptor interaction, along with details on the requirements for successful thermal annealing.

Optoelectronic Properties

Geometry Optimization

XRD is an effective probe for long-range molecular order of the polymer films, however for studies of the donor-acceptor interface a more sensitive molecular level local probe of polymer order is required. The Raman spectra of PBTTT is described in literature, however these assignments were based upon a model of a simple monomer.^[11]

Instead we consider a PBTtT oligomer and calculate at B3LYP/6-311 G(d,p) level of theory using the Gaussian computational suite (Figure 7.4). To ease the computation the C₁₄ side chains were replaced with methyl groups. The bond-lengths and dihedral angles were used to assign vibrational modes.

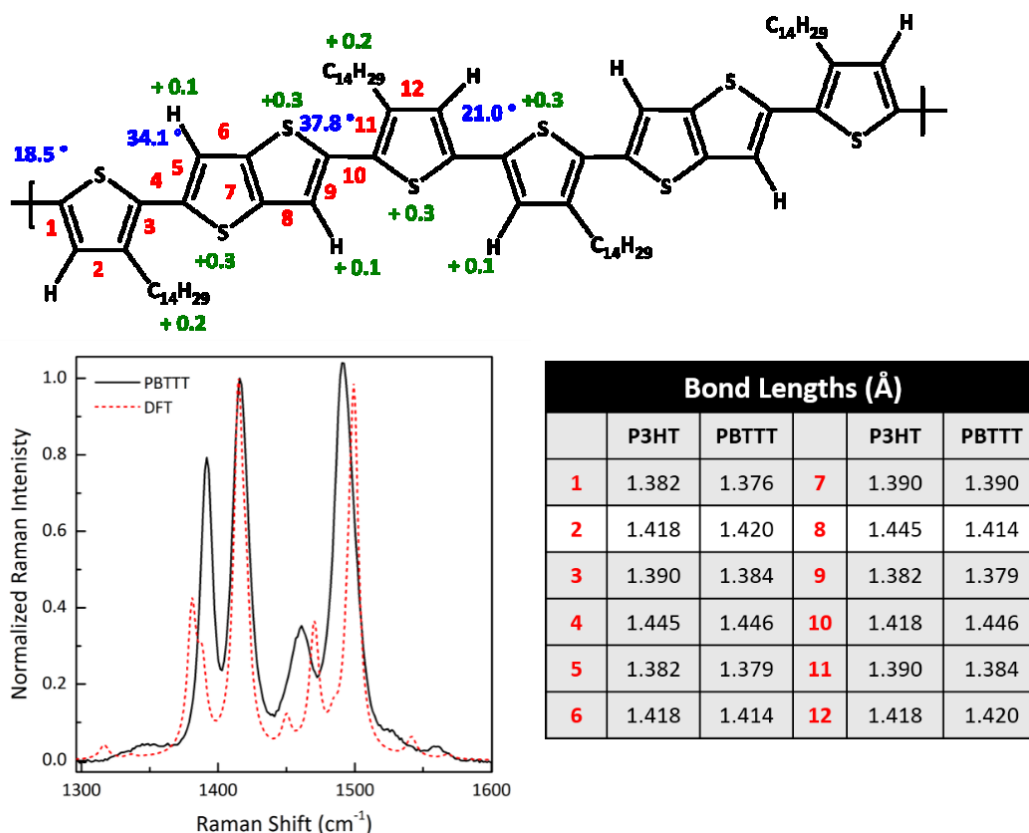


Figure 7.4: Raman spectra of PBTtT in as a thin film and in the gas phase, simulated using the B3LYP functional and 6-311 G(d,p) basis-set. The geometry is optimized for an oligomer of at least three repeat units. The table and figure details the bond-lengths and dihedral angles resulting from the geometry optimization. The Mulliken charges are also provided.

The backbone torsion is of a Coloumbic nature and arises due to partial positive charges on neighbouring sulphur and hydrogen atoms in the thiophene (T) and thienothiophene (TT) units, respectively (Figure 7.4). Neat PBTtT displays four main vibrational modes, which we assign to symmetric stretches of the C – C and C = C: C – C_T = 1389 cm⁻¹, C = C_{T,TT} 1415 cm⁻¹, C – C_{TT} 1467 cm⁻¹ and C = C_{T,TT} 1491 cm⁻¹. The mixed nature of the double bond (C = C) modes arises from four unique environments in one repeat unit; C = C_T neighbouring an unfused T, C = C_T adjacent to TT, C = C_{TT} adjacent to T and inner C = C_{TT}. The lower energy 1415 cm⁻¹ mode contains contributions from the shorter C = C bonds (inner C = C_{TT} – 1.390 Å, outer C = C_T – 1.384 Å), whilst the higher energy 1491 cm⁻¹ concerns the longer C = C bonds (inner C = C_{TT} – 1.379 Å, outer C = C_T – 1.376 Å). The extended spectra show Raman scattering from inter-unit vibrations between 1100 – 1250 cm⁻¹ and C-S bonds between 600 – 750 cm⁻¹. [UV-Visible Absorption](#)

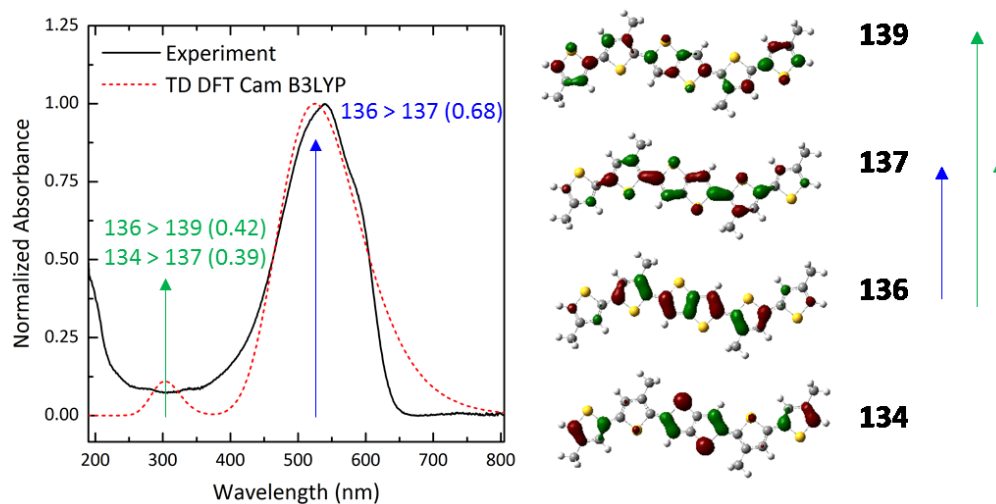


Figure 7.5: UV-Visible Absorption and associated isosurfaces simulated using TD-DFT with the CAM-B3LYP functional and 6-31 G(d,p) basis set. For the simulation, 9 states were considered.

Visual representations of the HOMO and LUMO of a PBTBT monomer is shown in Figure 7.5.^[12] Whilst the HOMO-LUMO transition is delocalized along the whole polymer backbone, the high energy absorption band appears to involve changes in electron density on the unfused T units.

7.2 Impact of Acceptor Size on Polymer Molecular Order

The backbone conformation of PBTBT in neat films and 1:1 blends with four different fullerene acceptors of varying diameters and symmetries are evaluated; namely the bis-adduct of [6,6]-phenyl-C₆₁-butyric acid methyl ester (hereafter bis-PC₆₀BM), PC₇₀BM, indene-C₆₀ bis-adduct (ICBA) and indene-C₆₀ tris-adduct (ICTA) (Figure 7.6).

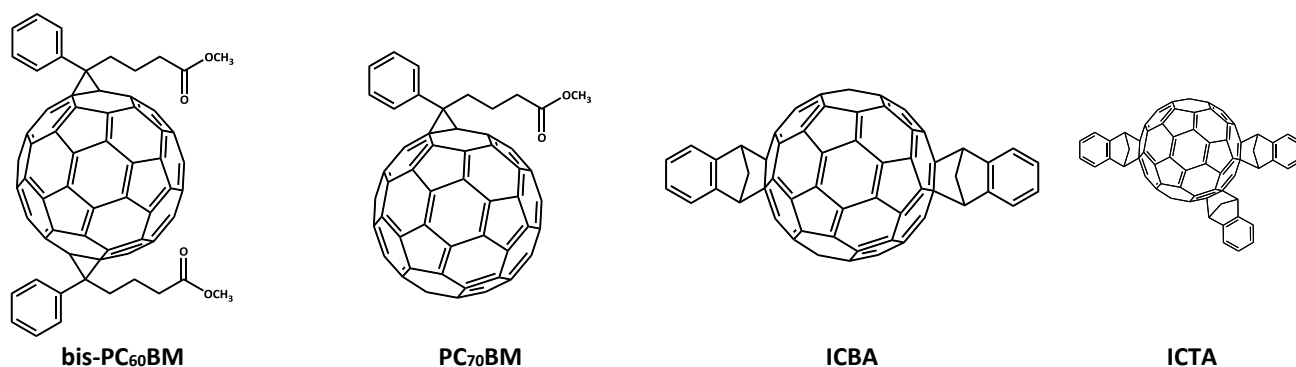


Figure 7.6: Molecular structure of acceptor molecules used in this work.

UV-Visible Absorption

First we consider the UV-Visible absorption of the 1:1 blends (Figure 7.7). All studies are pristine (i.e. not-annealed) unless otherwise stated. The neat polymer predominantly absorbs between 400 and 650 nm, with evidence of a shoulder at low energy (Figure 7.7 (a) and (c), Table 7.1). The majority of the fullerene absorption occurs at high

energy (wavelengths < 350 nm) as demonstrated in Figure 7.8. Considering first the bulky acceptors (bis-PC₆₀BM, ICTA), the main polymer absorption band broadens to broadens to high energy and there is a loss of the low energy shoulder without much shift of the absorption maxima. The high energy absorption comes from the twisted (low conjugation length) portions of the polymer chain. The weak absorption of the neat acceptor molecules occurs at high energies, as illustrated in Figure 7.7 (b), with an absorption peak at 485 nm. The resolved vibronic structure in the polymer absorption band for 1:1 blends with PC₇₀BM are typical of intimate donor-acceptor mixing.^[9] Increased conjugation of the polymer red-shifts the absorption band maxima (540 to 554 nm, see Table 7.1). Blends with ICBA lie intermediate between the two extremes; a somewhat resolved vibronic structure red-shifting (540 to 547 nm, see Table 7.1) accompanied by a broadening to high energy. This implies that the extent of π -electron delocalisation is less significant for blends with ICBA compared to PC₇₀BM.

Raman Spectroscopy

Despite their small Raman scattering cross-sections, in order to fairly evaluate the impact of the acceptors on the conjugated polymer backbone it is important to consider the Raman scattering of the neat fullerene. The experimental Raman scattering of PC₇₀BM accumulated at 785, 514, 488 and 457 nm excitation wavelengths are shown in Figure 7.8. The strong modes at 1188 and 1229 cm⁻¹, only visible in the resonant spectra (514, 488 nm), are C – C stretches around the equator of PC₇₀BM and pentagonal C = C stretches at the poles. The modes at 1426 and 1467 cm⁻¹ are equatorial quadrant and polar breathing modes. C = C bonds on the equator (1600 cm⁻¹) are also only visible in resonant conditions. Crucially for our study, even in resonant conditions (488 nm, Figure 7.8 (c)) the vibrations of PC₇₀BM do not overlap with the positions of the C = C_{T,TT} and C – C_T modes of PBTTT.

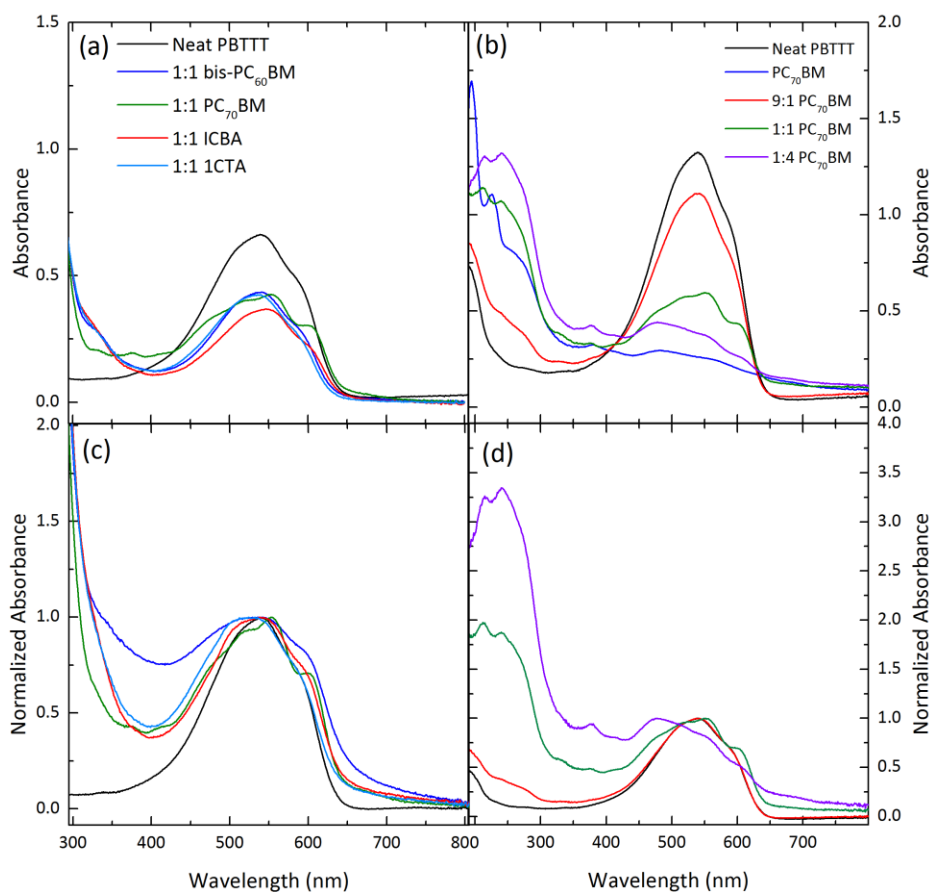


Figure 7.7: Absorbance (a,b) and normalized absorbance (c,d) of thin films of 1:1 blends of PBTBT-C14 with: (a) and (c) 4 small molecule acceptors (bis-PC₆₀BM, PC₇₀BM, ICBA and ICTA), (b) and (d) PC₇₀BM at different loading ratios.

1:1 Blends	Lamellar Spacing	Max absorption Peak	C = C	FWHM C = C	$\Delta C = C$ order/disorder vs. neat
	Å	nm	cm ⁻¹	cm ⁻¹	%
Neat PBTBT	21.5	540	1491.3	16.2	0
C ₁₄ -bisPC ₆₀ BM	22.0	538	1490.9	17.1	4.0
C ₁₄ -PC ₇₀ BM	30.9	554	1485.0	13.8	39.4
C ₁₄ -ICBA	26.0	547	1487.8	15.5	29.1
C ₁₄ -ICTA	23.1	535	1490.8	16.9	-0.5

Table 7.1: Lamellar Spacing (Å)*, Absorption band maximum (nm), C = C shift (cm⁻¹) and relative increase in planarity for PBTBT blends with respect to the neat material. Lamellar Spacing (*) from ref ^[13]

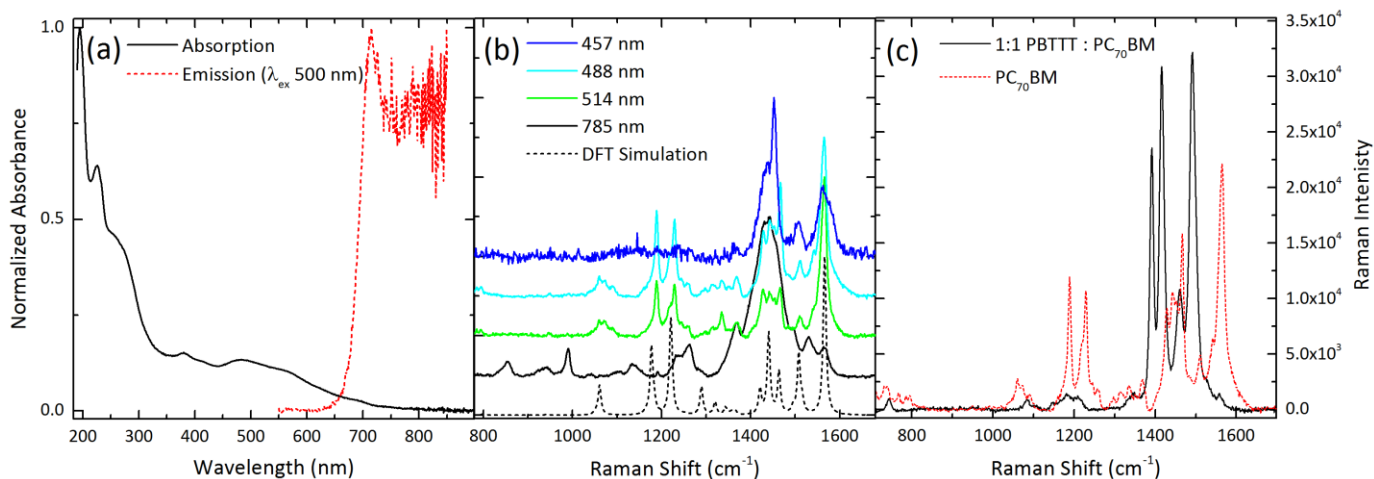


Figure 7.8: (a) Normalized absorption and emission spectra of thin films of PC₇₀BM. (b) Raman spectra of PC₇₀BM excited at 457, 488, 514 and 785 nm and the simulated Raman spectrum for a PC₇₀BM molecule. (c) Thin film Raman spectra of a 1:1 PBTBT:PC₇₀BM blend and neat PC₇₀BM excited at 488 nm.

In the steady-state, blending with the bulky acceptors (bisPC₆₀BM and ICTA) has negligible effects the position or shape of the vibrational modes (Figure 7.10). The situation is very different for the 1:1 blend with PC₇₀BM, with a downshift of $C = C_{T,TT}$ from 1491 cm⁻¹ for neat films to 1485 cm⁻¹ and narrowing of the FWHM (see Table 7.1). Equivalent to the absorption spectra, blending with ICBA appears to lie intermediate between that of bis-PC₆₀BM and PC₇₀BM ($C = C_{T,TT} = 1485$ cm⁻¹).

Impact of Inter-Unit Torsion on Optoelectronic Properties

The inter-unit torsion between T-T is $\angle_{T-T} = 18.5^\circ$ and between the T-TT units $\angle_{T-TT} = 34^\circ$ (Figure 7.4). We have previously demonstrated that the $C = C$ mode of P3HT can be interpreted from a simple convolution of disordered and ordered components.^[14–16] To evaluate the impact of inter-unit torsion in the polymer chain on the Raman spectrum, a series of polymer structures ranging from highly planar to highly twisted were simulated with frozen inter-unit dihedral angles ($\angle_{T-T}$ and $\angle_{T-TT}$) and their Raman spectra calculated (Figure 7.9). Irrespective of whether the inter-unit torsion is between the $\angle_{T-T}$ or $\angle_{T-TT}$, planarizing the chain shifts $C = C_{T,TT}$ (1491 cm⁻¹) to lower wavenumber, narrows the FWHM and increases the relative intensity of $C - C_T$ (1389 cm⁻¹). By calculating the potential energy as a function of dihedral angle it appears a reduction of $\angle_{T-TT}$ is the most likely cause of the improved backbone planarity. In any case, the $C = C_{T,TT}$ mode can be described as a superposition of planar and twisted phases of PBTBT (Figure 7.9 (a)). The planarity of the chain can then be quantified by calculating the relative ratio of the planar/twisted $C = C$ components ($C = C_{order/disorder}$).

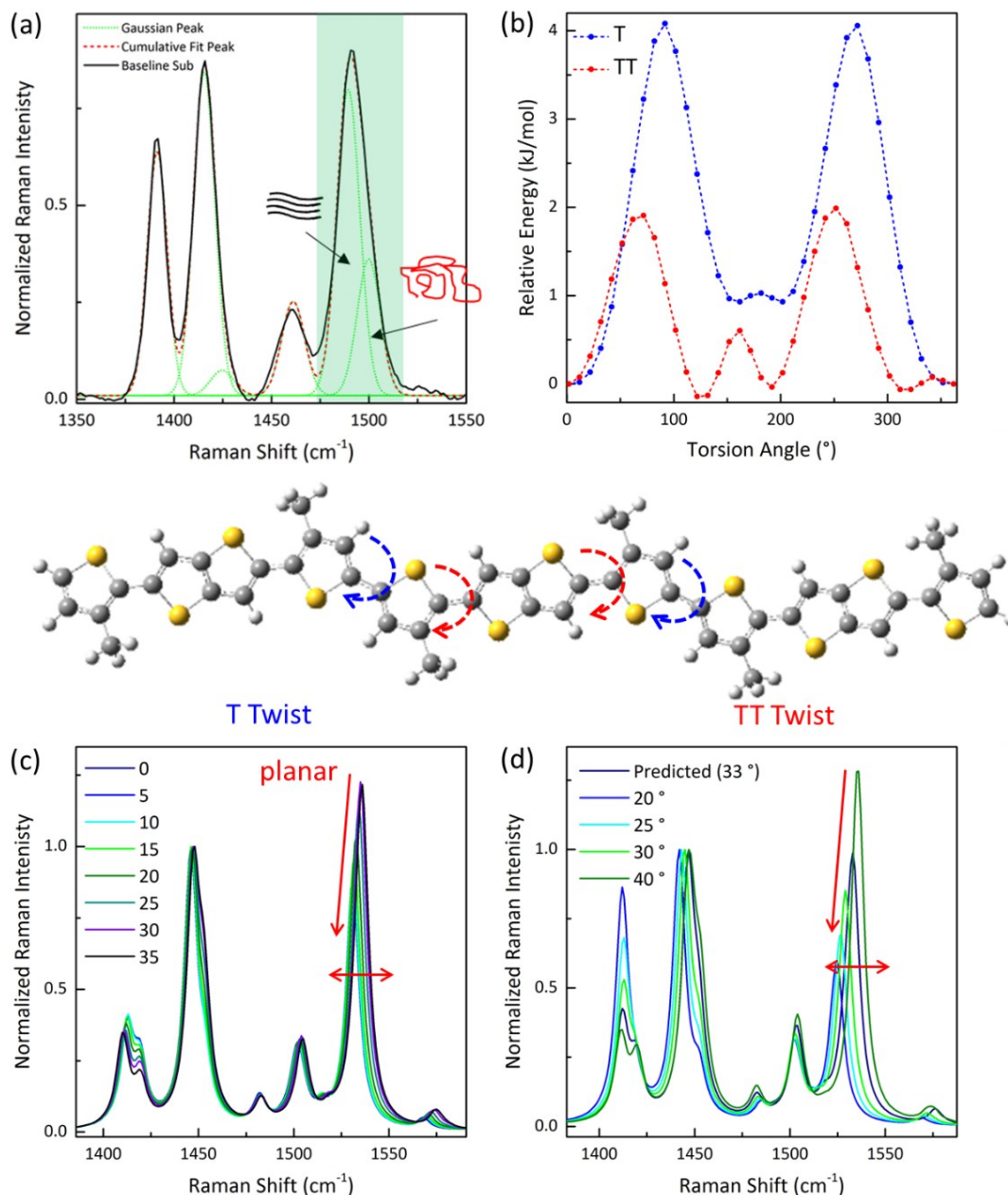


Figure 7.9: (a) Experimental Raman spectra for neat PBTBT and the cumulative fit of a convolution of planar and twisted polymer chains. (b) Potential energy scan as a function of dihedral angle between $\angle_{T-T}$ and $\angle_{T-TT}$ (indicated by red and blue arrows). The simulated Raman spectra arising from an oligomer of PBTBT with frozen dihedral angles between (c) $\angle_{T-T}$ and (d) $\angle_{T-TT}$.

Using this simple analysis for the blend films, it is evident the resolved red-shifted absorption spectra for 1:1 blends with PC₇₀BM occurs due to planarization of the polymer backbone. For smaller fullerenes, polymer backbone planarity increases on intercalation from by up to 40 % for blends with PC₇₀BM and 25 % for blends with ICBA, whereas for bulky fullerenes the increase is negligible (4 % for bisPC₆₀BM, $\approx$ 0.5 % ICTA). The narrow FWHM on blending with PC₇₀BM and ICBA indicates a narrower range of conformational states compared to the neat material (Table 7.1).^[17]

In summary, the bulky fullerenes (bis-PC₆₀BM, and ICTA) force the TT unit to adopt a twisted conformation, whereas smaller size fullerenes (ICBA, and PC₇₀BM) permit the polymer to adopt a planar conformation. The planar polymer backbone accommodates the fullerenes between the polymer side chains, resulting in an increase in the lamellar spacing (Table 7.1).

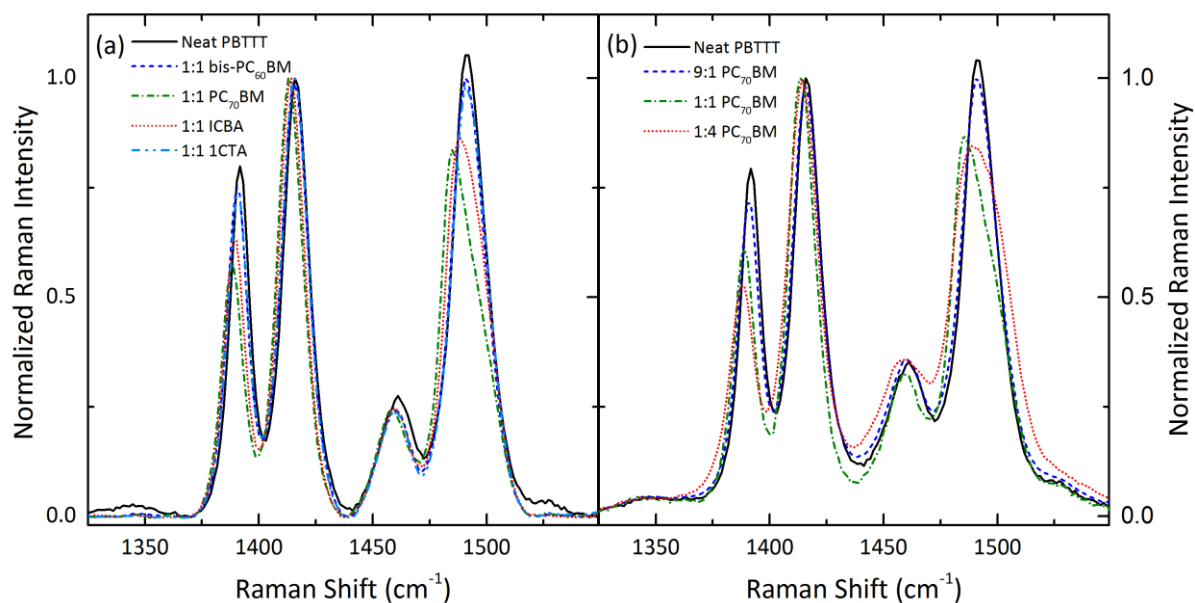


Figure 7.10: Resonant Raman spectra (488 nm) for blends of PBTTT-C14 with: (a) 4 small molecule acceptors (bis-PC₆₀BM, PC₇₀BM, ICBA and ICTA), (b) PC₇₀BM at different loading ratios. Raman spectra are acquired with a 488 nm laser and normalized to the 1425 cm⁻¹ Raman mode.

7.3 Impact of Fullerene Loading Ratio on Polymer Molecular Order

UV-Visible Absorption

Next we investigate the backbone packing as the fraction of PC₇₀BM is increased from 0 to 80 % by weight (neat, 9:1, 1:1, 1:4). As the polymer absorbs most of the light in the visible region, increasing the loading ratio dilutes the light absorption. There is also evidence of a polymer conformation change occurring in the 1:1 and 1:4 blend films. The main polymer absorption band red-shifts (from 540 to 554 nm at ratios up to 1:1) and the low energy shoulder becomes more resolved (Figure 7.7). The increased absorption for the intercalated blends is consistent with the higher photo-current observed compared to the non-intercalating blends reported in literature.^[5] For the 1:4 blends the absorption from the short conjugation-length (high energy) disordered polymer chains dominate, with some evidence for enhanced planarity in the fine structure (peaks at 552 and 603 nm). The absorption maxima (477 nm) is at higher energies than the absorption peak of neat PC₇₀BM (485 nm) indicating this blue-shift is from the polymer itself. Ultrafast pump-probe Transient Absorption Spectroscopy (TAS) should allow the selective excitation of donor and

acceptor units within these blends, but is complicated by these somewhat overlapping spectral signatures.^[8–10] For example, Scarongella *et al* choose 390 and 540 nm to excite the fullerene and polymer, respectively, whereas Gehrig *et al* use 520 nm to excite both components. Intercalated blends (1:1) charge dissociation is ultra-fast, irrespective of which component is initially excited (390 or 540 nm).^[10] Around 80 % of these photo-generated charges go on to geminately recombine.^[5,7,8,18] When only the donor is excited in 1:4 donor: acceptor blends dissociation is still ultra-fast but the majority of charges outlive the nanosecond time window.^[10] Excitation of the fullerene in 1:4 blends shows both ultra-fast and slow charge transfer dynamics due to the formation of extended fullerene domains.^[8,10] For the 1:4 blends, Gehrig *et al* observed electro-absorption (EA), which occurs because of oppositely charged carriers due to an electric field across the donor-acceptor interface.^[8,19] The absence of EA in the 1:1 blend films indicate that the electric field is confined to a very small volume between trapped charge close to the donor-acceptor interface.^[8] Large, pure, crystalline domains of PC₇₀BM increase the electron affinity of the acceptor, which in-turn increases the polymer—fullerene energy level offset and creates spatially separates long-lived free charges.^[20] For PBTTT:PC₇₀BM, pure domains increase the power conversion efficiency from 0.55 % (1:1) to 2.4 % (1:4).^[8]

	C ₁₄ -PC ₇₀ BM					C ₁₆ -PC ₇₀ BM				C ₁₆ -ICBA				
%	Max absorption		C = C	ΔC = C order/disorder	FWHM	Max absorption	Δ Integrated PL	C = C	ΔC = C order/disorder	Max absorption		Δ Integrated PL (%)	C = C	ΔC = C order/disorder
	nm		cm ⁻¹	%	cm ⁻¹	nm	%	cm ⁻¹	%	nm		%	cm ⁻¹	%
		TA									TA			
0	540	556	1491.4	0	16.2	540	100.00	1491.3	0	540	547	100.00	1491.1	0
10	540	556	1490.6	1.2	16.1	543	9.31	1490.0	2.4	541	547	3.70	1490.7	1.1
20						548	0.40	1486.1	8.5	544	551	1.65	1490.3	3.2
30						550	0.29	1485.9	9.8	545	553	1.11	1489.9	9.4
40						553	0.18	1485.7	27.2	547	557	0.71	1489.1	13.0
50	551	572	1485.4	37.2	14.0	554	0.17	1485.1	40.3	549	558	0.39	1488.2	30.4
60						555	0.16	1484.6	42.4	540	558	0.39	1490.8	-18.4
80	477	561	1489.5	-3.5	23.1	477	0.17	1487.0	-2.4					

Table 7.2: Absorption band maximum (nm), integrated PL, C = C shift (cm⁻¹) and relative increase in planarity for PBTTT blends with respect to the neat material.

Raman Spectroscopy

It is important to correlate the observation of improved device performance to a clear understanding of backbone conformation during the formation of these pure donor acceptor domains. The planarization of PBTTT backbones at different weight ratios for the intercalated blends (PC₇₀BM, ICBA) has been monitored using resonant Raman spectroscopy. For high fullerene loading, an upper limit for purely intercalated donor-acceptor interfaces becomes apparent (1:4) in the broadening of all vibrational modes to higher energy. For PC₇₀BM, the maximum C = C

peak position shifts to lower energy, $C = C_{\text{order/disorder}}$ and FWHM ($C = C$) increases with increasing fullerene fraction (2 % for 9:1, 40 % for 1:1,

%	C₁₄-PC₇₀BM					C₁₆-PC₇₀BM					C₁₆-ICBA				
	Max absorption		C = C	$\Delta C = C$ order/disorder	FWHM	Max absorption		Δ Integrated PL	C = C	$\Delta C = C$ order/disorder	Max absorption		Δ Integrated PL (%)	C = C	$\Delta C = C$ order/disorder
	nm		cm ⁻¹	%	cm ⁻¹	nm		%	cm ⁻¹	%	nm		%	cm ⁻¹	%
	TA										TA				
0	540	556	1491.4	0	16.2	540	100.00		1491.3	0	540	547	100.00	1491.1	0
10	540	556	1490.6	1.2	16.1	543	9.31		1490.0	2.4	541	547	3.70	1490.7	1.1
20						548	0.40		1486.1	8.5	544	551	1.65	1490.3	3.2
30						550	0.29		1485.9	9.8	545	553	1.11	1489.9	9.4
40						553	0.18		1485.7	27.2	547	557	0.71	1489.1	13.0
50	551	572	1485.4	37.2	14.0	554	0.17		1485.1	40.3	549	558	0.39	1488.2	30.4
60						555	0.16		1484.6	42.4	540	558	0.39	1490.8	-18.4
80	477	561	1489.5	-3.5	23.1	477	0.17		1487.0	-2.4					

Table 7.2). Compared to the intercalated blends, excess fullerene results in a shift of $C = C$ from 1484 cm⁻¹ (1:1) to 1489 cm⁻¹ (1:4) and 30 % reduction of $C = C_{\text{order/disorder}}$. Increasing the fraction of acceptor beyond 1:1 ratios results in a multi-phase polymer conformation, planar near the fullerene molecules that can intercalate and twisted around the larger fullerene domains. Whilst the $C = C$ peak positions are similar for 1:1 blends with ICBA and 1:4 blends with PC₇₀BM, the FWHM reveals the extent of twisted polymer domains at high fullerene loading.

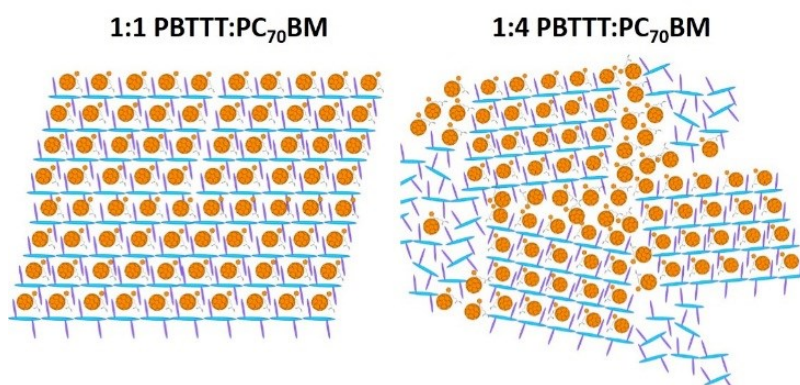


Figure 7.11: Schematic of the donor: acceptor interaction in intercalated and high fullerene loading blends

This comprehensive understanding of the polymer backbone can be used to explain the charge dynamics observed using TAS. The intercalated 1:1 blends have highly planar donor units that are very close to acceptor molecules. It is no surprise that charges generated at these interfaces quickly recombine. In 1:4 blends, large domains of pure fullerene disrupt the packing of polymer chains. The microstructure comprises of some intercalation between the more planar portions of the polymer chains accompanied by large regions of disordered polymer material.

7.4 Impact of Polymer Side-Chain Length on Molecular Packing in a Blend

The impact of blending the longer side-chain donor polymer (PBTTT-C₁₆) with PC₇₀BM and ICBA is also considered. Intercalation in 1:1 blends has been reported by many groups, irrespective of the side-chain length.^[5,9,10] Longer side chain PBTTT-C₁₆ demonstrates inferior device performance, but the same trend of improved efficiency with increased size of pure domains is observed (blends with PC₇₀BM; 1:4 = 1.8 % PCE, 1:1 = 0.3 %).^[21] Figure 7.12 shows the absorption and normalized resonant Raman spectra of the PBTTT-C₁₆ blend films, incrementally increasing the fullerene loading ratios by 10 %.

%	C14-PC70BM					C16-PC70BM					C16-ICBA				
	Max absorption		C = C	$\Delta C = C$ order/disorder	FWHM	Max absorption	Δ Integrated PL	C = C	$\Delta C = C$ order/disorder	Max absorption	Δ Integrated PL (%)	C = C	$\Delta C = C$ order/disorder		
	nm		cm ⁻¹	%	cm ⁻¹	nm	%	cm ⁻¹	%	nm	%	cm ⁻¹	%		
		TA									TA				
0	540	556	1491.4	0	16.2	540	100.00	1491.3	0	540	547	100.00	1491.1	0	
10	540	556	1490.6	1.2	16.1	543	9.31	1490.0	2.4	541	547	3.70	1490.7	1.1	
20						548	0.40	1486.1	8.5	544	551	1.65	1490.3	3.2	
30						550	0.29	1485.9	9.8	545	553	1.11	1489.9	9.4	
40						553	0.18	1485.7	27.2	547	557	0.71	1489.1	13.0	
50	551	572	1485.4	37.2	14.0	554	0.17	1485.1	40.3	549	558	0.39	1488.2	30.4	
60						555	0.16	1484.6	42.4	540	558	0.39	1490.8	-18.4	
80	477	561	1489.5	-3.5	23.1	477	0.17	1487.0	-2.4						

Table 7.2 compares the peak positions and relative fraction of ordered material ($C = C_T$ peak positions, $C = C_{\text{order/disorder}}$) for PBTTT-C₁₄:PC₇₀BM and -C₁₆ blends at increasing fullerene loading. This comparison reveals that, at least in the solid-state, increasing the length of the solubilising side-chains has minimal effect on donor-acceptor mixing. This is unsurprising as the change in length from C-14 to C-16 side chains is much smaller than the radius of an acceptor molecule.

The emissive recombination of photo-generated excitons, so-called photoluminescence (PL), is systematically quenched for increasing fullerene loading (Figure 7.12).^[9] Photoluminescence occurs when excitons recombine emissively prior to splitting and is often used as a means to gauge exciton diffusion.^[5] The integrated area underneath the PL spectrum can be used to estimate quenching efficacy. The decrease of integrated PL from neat to 60 % PC₇₀BM to 0.16 % of the original value (

	C14-PC70BM					C16-PC70BM					C16-ICBA				
	Max absorption		C = C	Δ C = C	FWHM	Max absorption		Δ Integrated PL	C = C	Δ C = C	Max absorption		Δ Integrated PL (%)	C = C	Δ C = C
	nm		cm ⁻¹	%	cm ⁻¹	nm		%	cm ⁻¹	%	nm		%	cm ⁻¹	%
	TA										TA				
0	540	556	1491.4	0	16.2	540	100.00	1491.3	0		540	547	100.00	1491.1	0
10	540	556	1490.6	1.2	16.1	543	9.31	1490.0	2.4		541	547	3.70	1490.7	1.1
20						548	0.40	1486.1	8.5		544	551	1.65	1490.3	3.2
30						550	0.29	1485.9	9.8		545	553	1.11	1489.9	9.4
40						553	0.18	1485.7	27.2		547	557	0.71	1489.1	13.0
50	551	572	1485.4	37.2	14.0	554	0.17	1485.1	40.3		549	558	0.39	1488.2	30.4
60						555	0.16	1484.6	42.4		540	558	0.39	1490.8	-18.4
80	477	561	1489.5	-3.5	23.1	477	0.17	1487.0	-2.4						

Table 7.2) indicates that a fullerene molecule sits close to the sites of the majority of photo-generated excitons.

The weak signals at 730 nm for the 40 and 50 % blends arise from recombination and emission of pure large, pure PC₇₀BM domains, displayed in the inset of Figure 7.13.^[20,22–24] Above these loading ratios (80 %) the changing shape of the PL spectrum confirms the system is no longer uniquely a bimolecular crystal but also contains pure fullerene domains.

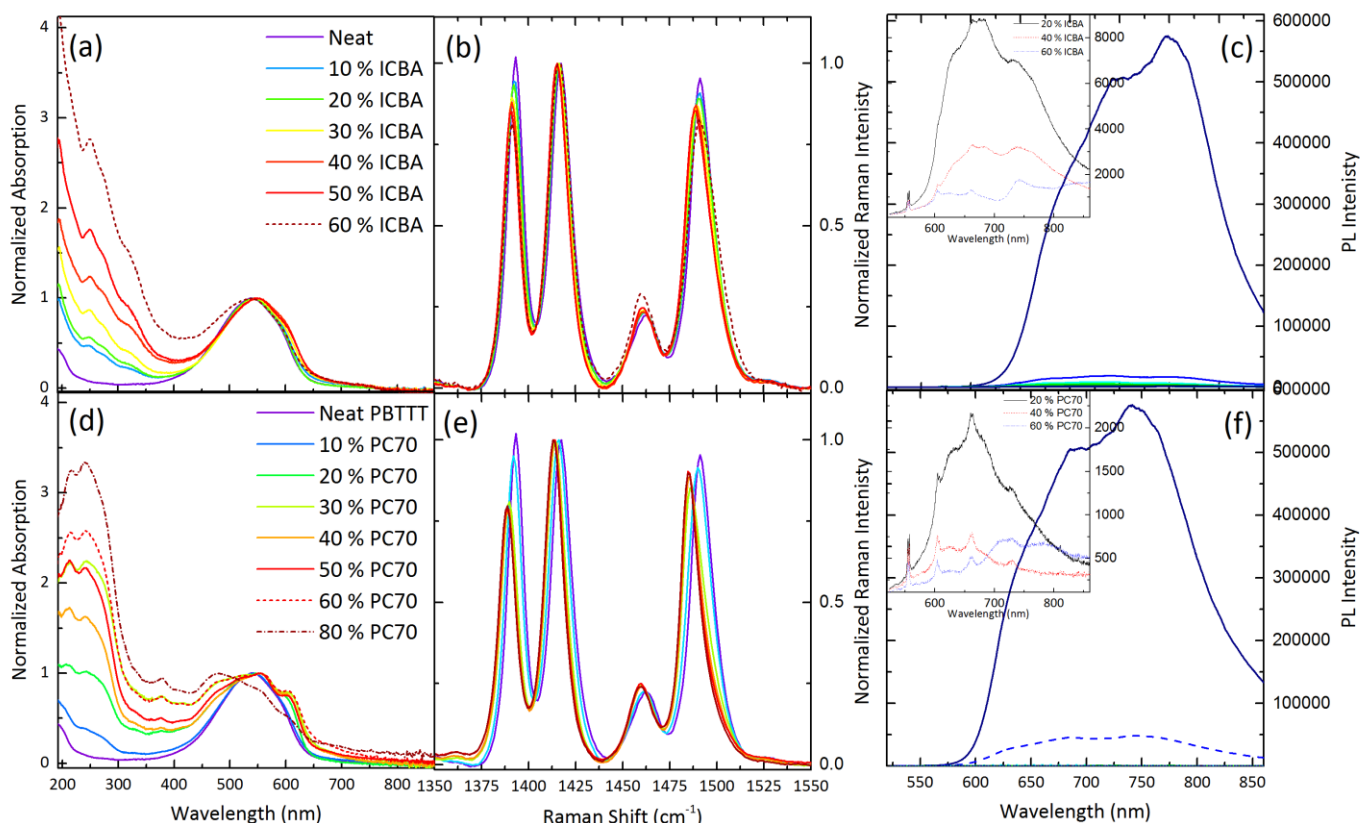


Figure 7.12: Normalized absorption and Raman spectra for PBTTT-C16 blends with (a,b) ICBA and (d,e) PC₇₀BM. The Raman spectra are normalized to the delocalised C = C mode at 1415 cm⁻¹. The associated PL spectra of the pristine films are provided in (c) and (d). The inset spectra focus on the blends > 40 % fullerene.

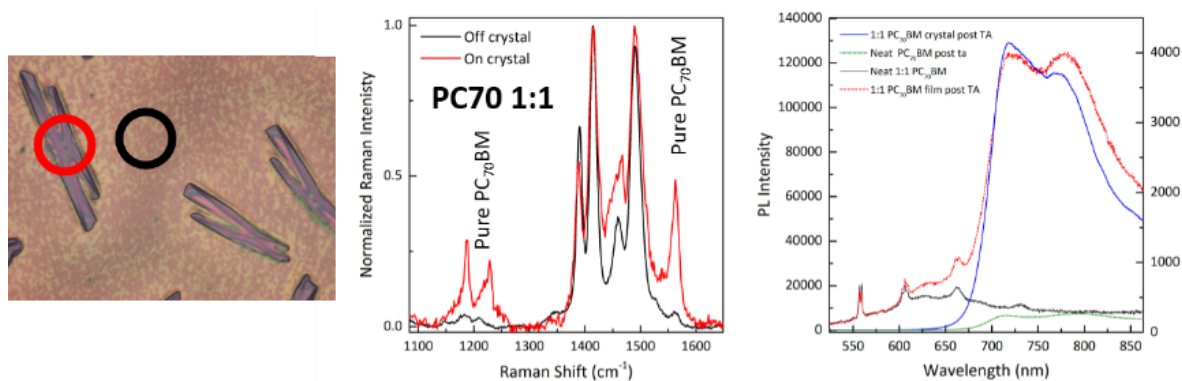


Figure 7.13: (left) optical microscope images of the annealed 1:1 blends with PC₇₀BM (middle) the corresponding Raman spectra off (black) and on (red) the crystal structures (positions indicated with circles on microscope images). Annealing the films causing crystallization of the PC₇₀BM, allowing characterization in the blend film. The raw PL spectra of neat films of the blends (black) and acceptors (red), along with PL of the annealed samples off (green) and on (blue) the crystals.

The weaker donor-acceptor interaction on blending with ICBA compared to PC₇₀BM is apparent in the lower overall peak shift (1491 to 1488 cm⁻¹), less significant quenching of PL (ICBA – 60 %, PC₇₀BM – 84 %) and increase in backbone order ($C = C_{\text{order/disorder}}$ ICBA – 30 %, PC₇₀BM – 40 %). This is consistent with XRD results, where intercalation with ICBA only increases lamellar spacing from 21.5 to 26.0 Å, and inferior device performance compared to PC₇₀BM (PCE = 1.2 % vs. 2.5 %).^[7,25] The maximum ICBA loading allowing ordered PBTTT chains is lower (50 %) than PC₇₀BM, probably due to the extra space required to fit the additional indene side group between adjacent side chains.

7.5 Probing the Nature of the Interfacial Interaction using *in situ* Resonant Raman Spectroscopy

A clear understanding of the phase behaviour on heating/cooling the blend system is of utmost importance, not only for optimising annealing conditions but in order to thoroughly understand the nature of the donor-acceptor interaction and how it is affected by the interfacial morphology. Previous studies have combined optical microscopy, differential scanning calorimetry (DSC), PL, XRD and cyclic voltammetry (CV) to determine the impact of thermal treatment on PBTTT-fullerene blend films.^[6,20] Using DSC scans and XRD basic phase diagrams (Figure 7.14) can be constructed for the PBTTT-PC₇₀BM system, allowing a comprehensive understanding of the composition of blend films as a function of temperature.^[6,26] These diagrams provide no information of the composition of the sample during cooling to room temperature. Whilst these studies effectively describe the behaviour of the acceptor and of the bulk, it is difficult to deduce the associated conformational changes of the polymer backbone.

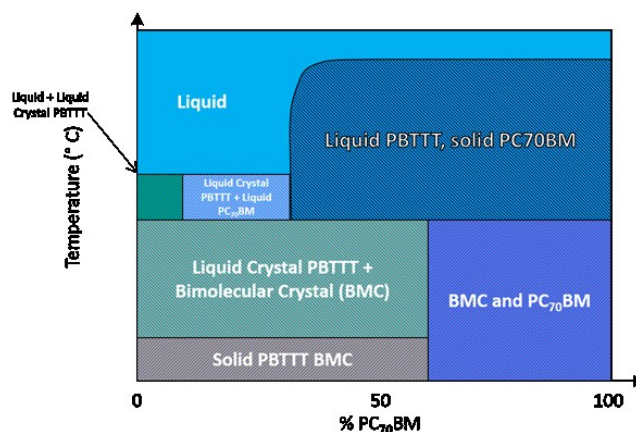


Figure 7.14: Phase Diagram for PBTTT:PC₇₀BM, constructed from references [6,26]

7.5.1 Impact of Intercalation on Thermal Properties of a Polymer/Fullerene Blend

In order to evaluate such changes a series of *in situ* resonant Raman measurements were performed. The maximum $C = C_T$ peak shift and $C = C_{\text{order/disorder}}$ were extracted from Gaussian fits to the experimental spectra acquired at every 10 °C (heating rate = 10 °C/ minute).

Acceptor Size in 1:1 Polymer/Fullerene Blends

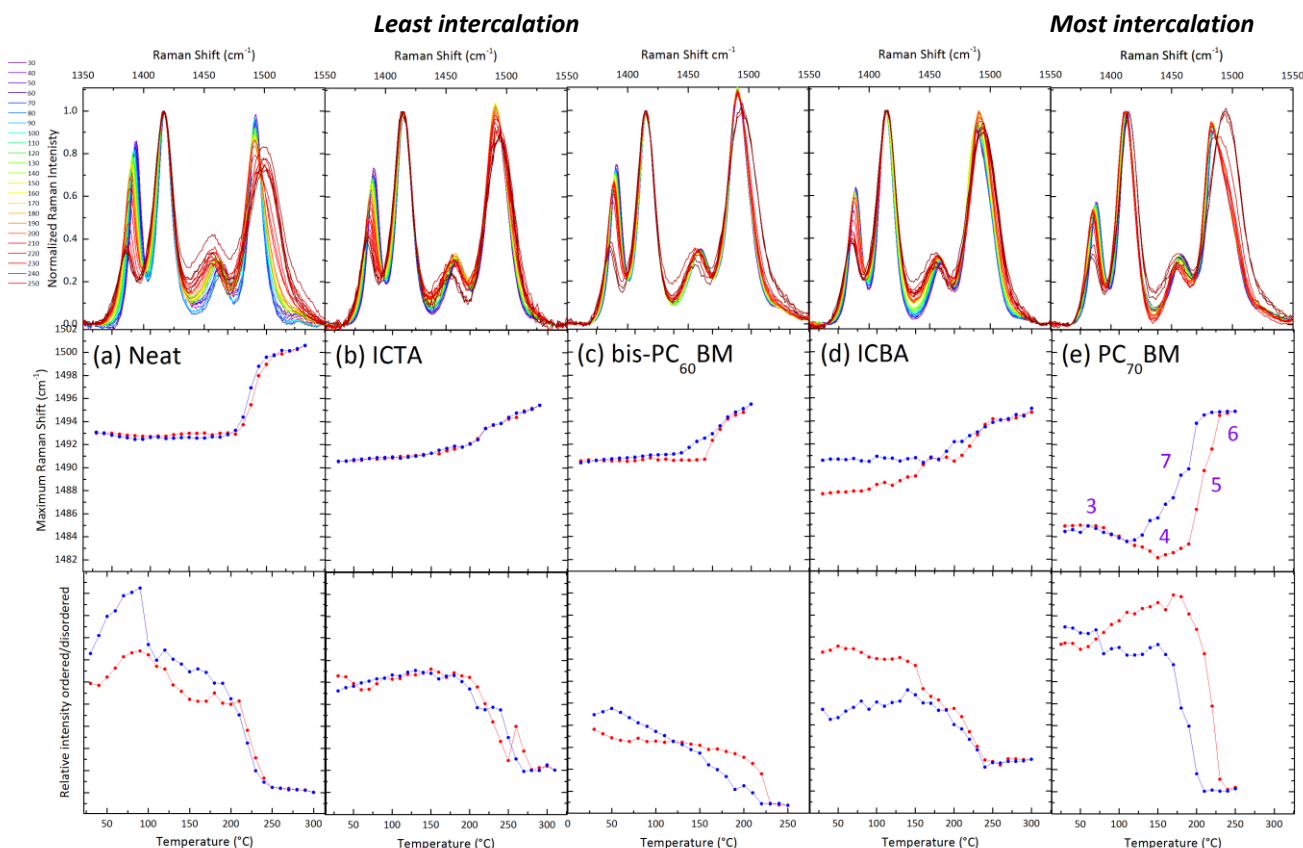


Figure 7.15: (upper) *in situ* Resonant Raman spectra acquired on heating at 10 °C/minute for the four fullerenes discussed in the text. (middle) The extracted peak shift of the $C = C_T$ Raman active vibrational mode. (lower) Relative intensity of $C = C_{\text{order/disorder}}$, corresponding to the proportion of planar/twisted polymer chains. The numbers (3, 4, 5...) correspond to the diagrams in Figure 7.18. Stages 1 and 2 happen before the heating/ cooling cycle.

On heating the neat polymer (Figure 7.15 (a)), the relative intensity of $C = C_{\text{order/disorder}}$ increases and peaks between 90 – 120 °C. This temperature is consistent with the side-chain melting temperature observed by Miller *et al.*^[6] Beyond this temperature the mobile side chains no longer maintain the regular packing of adjacent polymer backbones and disorder increases. We have performed similar measurements for a C_{16} -derivative and find this transition temperature increases with increasing chain length (Figure 7.17). The most significant phase transition occurs between 200 – 225 °C, consistent with the backbone melting temperature for PBTTC, displayed here as a large decrease in $C = C_{\text{order/disorder}}$ and shift of $C = C$ to a higher frequency. On cooling there is an increase in backbone order after the liquid-side chains re-crystallise (115 °C). The maximum peak position returns to the original value, but there is a slight increase in the $C = C_{\text{order/disorder}}$ ratio as the overall backbone order has improved.

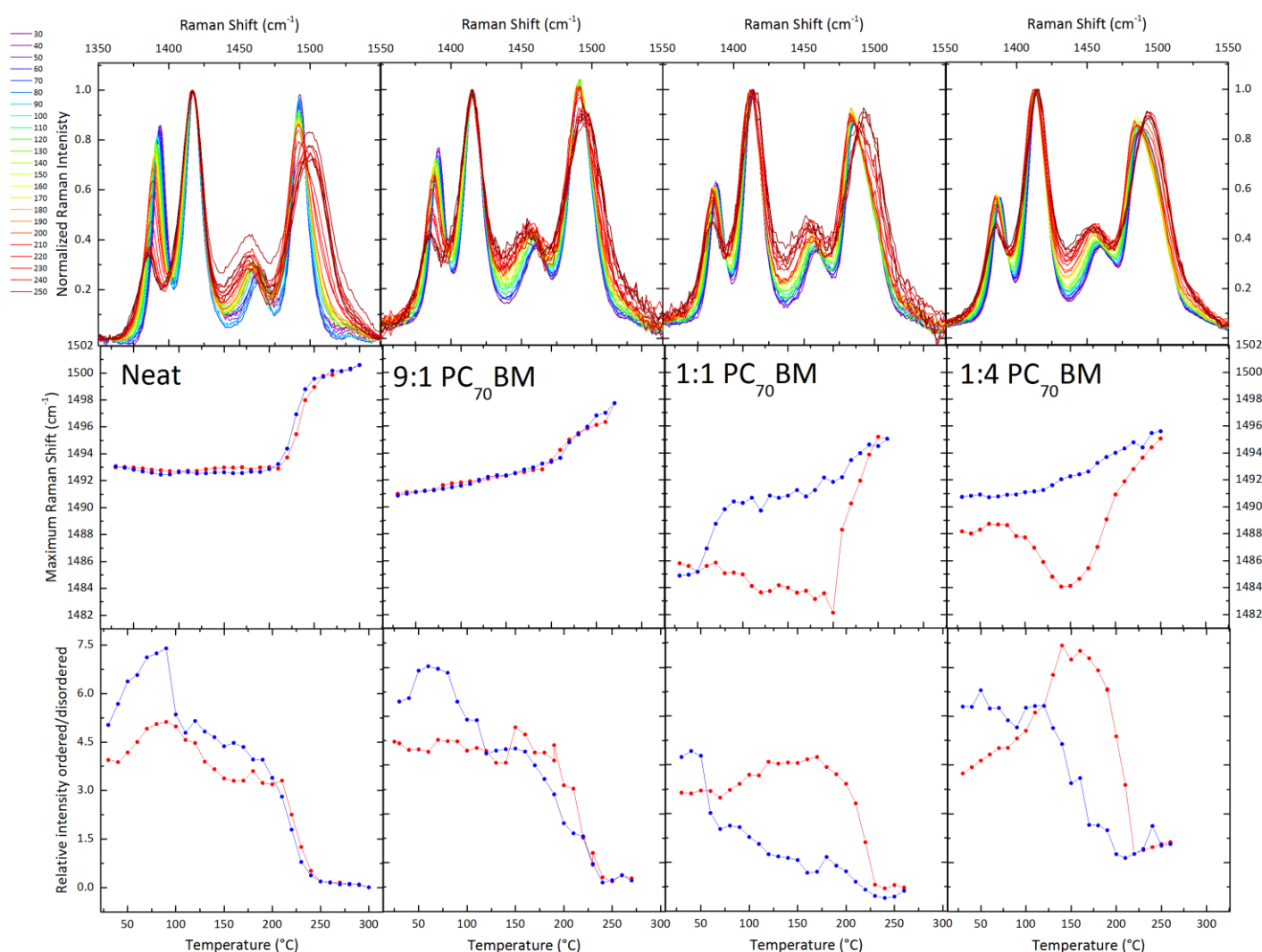


Figure 7.16: (upper) in situ Resonant Raman spectra acquired on heating at 10 °C/minute for four PC₇₀BM loading ratios (0, 9:1, 1:1, 1:4) discussed in the text. (middle) The extracted peak shift of the $C = C_T$ Raman active vibrational mode. (lower) Relative intensity of $C = C_{\text{order/disorder}}$, corresponding to the proportion of planar/twisted polymer chains.

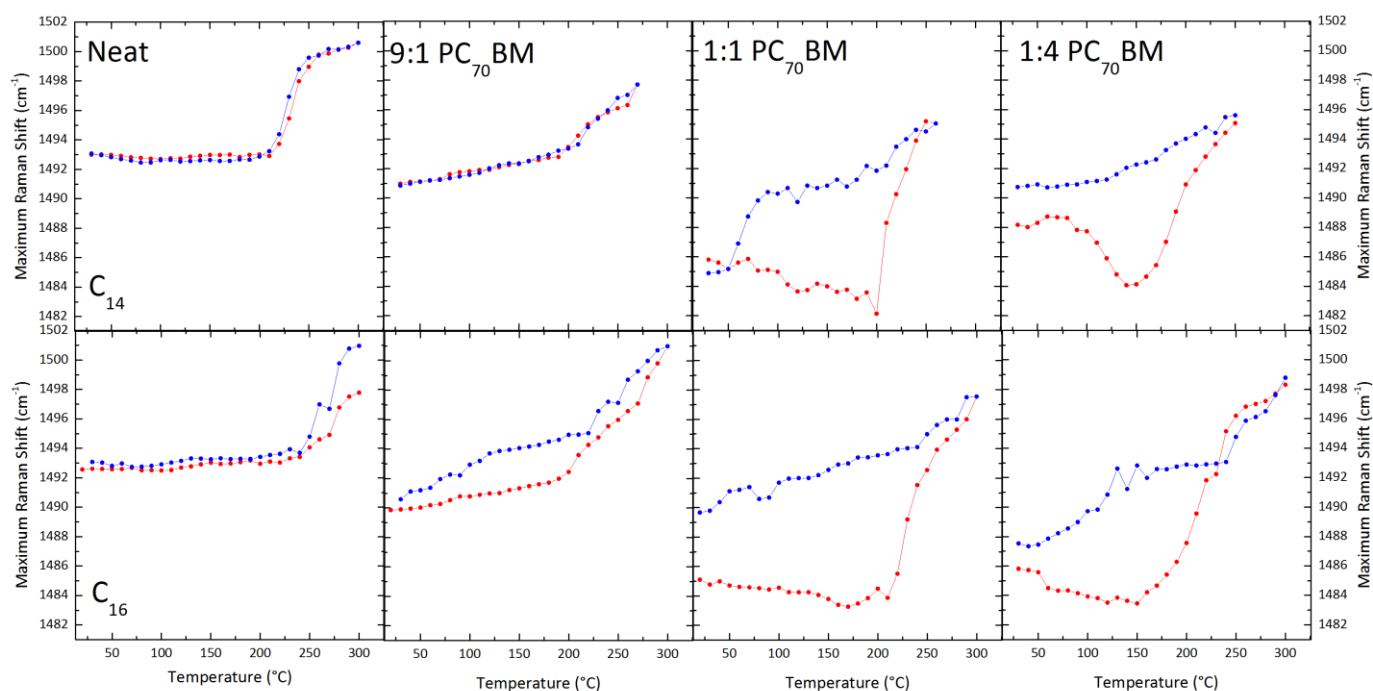


Figure 7.17: The peak shift of the $C = C_T$ Raman active vibrational mode extracted from in situ Resonant Raman spectra acquired on heating at $10\text{ }^{\circ}\text{C}/\text{minute}$ for the $-C_{14}$ (upper) and $-C_{16}$ (lower) PBTBT blends with $PC_{70}BM$

The blend films show strikingly different features dependent on fullerene size and loading (Figure 7.15, Figure 7.16). For 1:1 blends with large fullerenes that are too bulky to penetrate the polymer side chains (bis- $PC_{60}BM$, ICTA), thermal energy causes minimal structural changes to the polymer backbone until the melt temperature ($200 - 225\text{ }^{\circ}\text{C}$) which is similar to the neat material. The lack of any clear transition relating to the side-chain melt on heating or cooling could indicate a disruption of side-chain packing in these blend films, or that without intercalation occurring movement of the side-chains has little impact on backbone conformation. For ICTA (the largest acceptor considered here) the $C = C$ shift and evolution of $C = C_{\text{order/disorder}}$ is completely reversible on heating with negligible hysteresis, equivalent to the neat material. The hysteresis on cooling for bis- $PC_{60}BM$ blends indicates a stronger interaction with the polymer backbone. This observation supports our previous observations of the partially resolved vibronic absorption and slight increase in $C = C_{\text{order/disorder}}$ (4 %). As these fullerenes do not intercalate, these observations are equivalent to the neat polymer in Figure 7.14. In the case of the intercalated blend (1:1 with $PC_{70}BM$), after the side-chains becoming more flexible ($110\text{ }^{\circ}\text{C}$) the overall backbone order to increases on heating to $150\text{ }^{\circ}\text{C}$ (down shift from 1485 to 1482 cm^{-1}) as the polymer chains become more planar. We have previously demonstrated this as the onset for $PCBM$ to start to diffuse out of a P3HT matrix.^[27] The temperature at which PBTBT order is maximised ($150\text{ }^{\circ}\text{C}$) therefore indicates the optimum annealing temperature to optimise polymer fullerene phase separation at these

ratios. This is above typical annealing temperatures reported for this system, and perhaps why previous authors report a decreased device performance upon annealing.^[5,11,28]

Heating the blends beyond this temperature (150 – 190 °C) leaves both the polymer and fullerene more liquid, evident by the C = C shift to a higher energy and decrease of $C = C_{\text{order/disorder}}$. Above 190 °C, PC₇₀BM separates from the polymer side chains and crystallises.^[25] The disorder increases until the fullerene molecules have disentangled from the polymer matrix and formed macroscopic crystalline domains, visible in optical microscope images, completing by 230 °C. The film now represents a multi-phase system; with domains of pure fullerene, liquid polymer and a partially intercalated blend film. On cooling the multi-phase system, there is noticeable hysteresis, implying the now crystalline fullerene cannot effectively re-enter the polymer side chains.^[20] The extent of hysteresis correlates well with the amount of intercalation. The polymer becomes less flexible once the non-crystalline fullerenes become immobile (150 °C), but recovers the original C = C position. The macroscopic fullerene domains remain at room temperature, and are large enough to be characterised using resonant Raman and PL spectroscopy. Figure 7.13 compares regions of annealed film and aggregate crystal. The total recovery of the peak position and $C = C_{\text{order/disorder}}$ on cooling reveals *in situ* characterisation is necessary to understand the multi-phase blend. The cartoon in Figure 7.18 can be used to interpret the interactions in 1:1 blends with PC₇₀BM, and parts 3 – 7 correlate with the numbers on Figure 7.15. This result supports the decrease in lamellar spacing (≈ 30 to $23 \text{ \AA}$) and lack of improvement in solar cell performance on annealing reported by Miller et al.^[25]

Whilst ICBA causes some planarization of the polymer chains, the phase behaviour of these the 1:1 blend is remarkably different to that of blends with PC₇₀BM (Figure 7.16) and could be attributed to the indene units penetrating the PBTBT side chains.^[25,29] Heating 1:1 PBTBT: ICBA blends results in a gradually decrease of polymer backbone order as ICBA separates from the partially intercalated matrix. Macroscopic circular domains of μm wide domains of ICBA and disordered PBTBT are visible through the optical microscope. ICBA starts to become mobile slightly earlier (140 °C) than PC₇₀BM, completing by 240 °C. There is a noticeable loss of order once these films are cooled to room temperature, with the maximum peak shift increasing from 1488 to 1490 cm^{-1} .

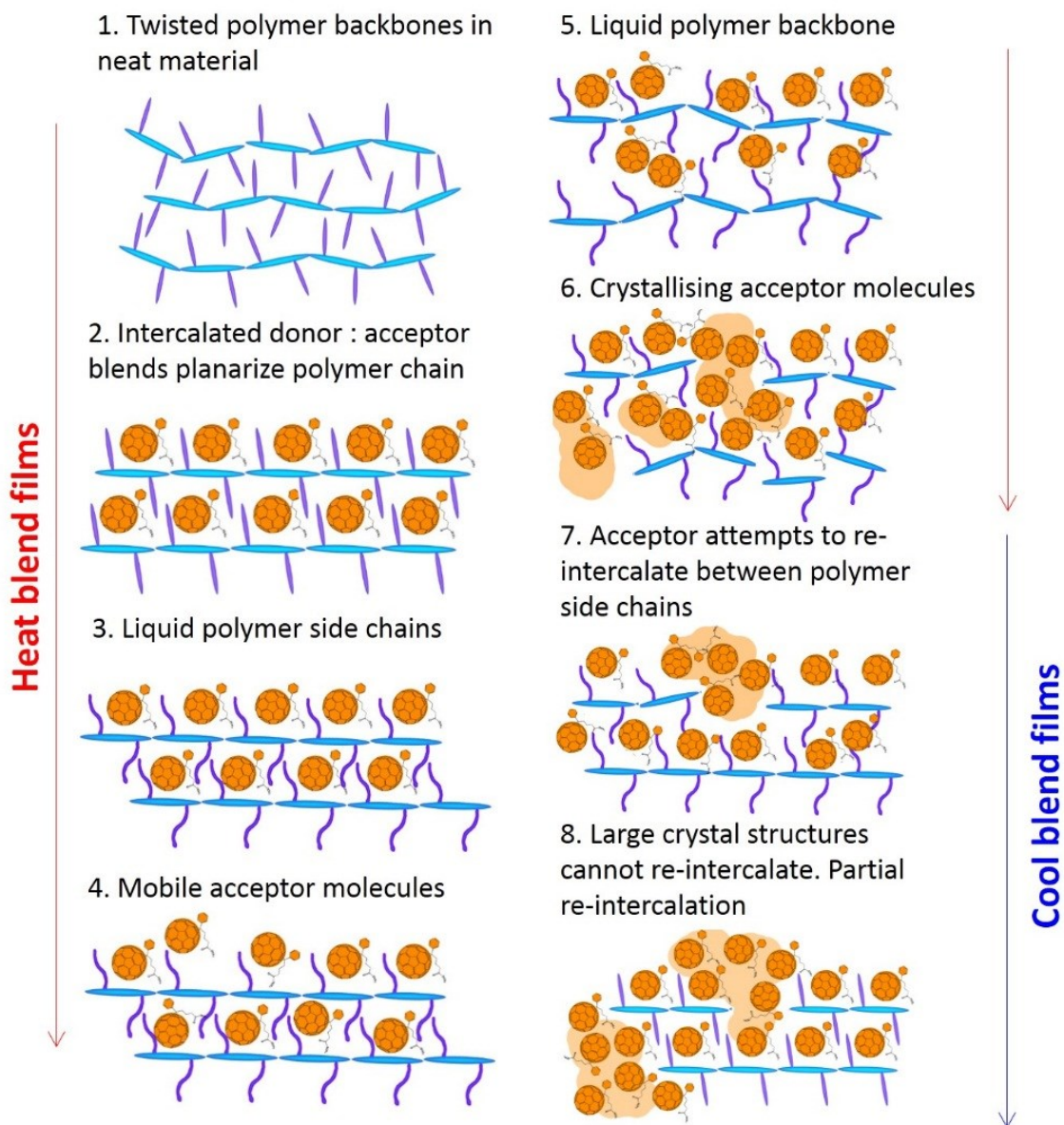


Figure 7.18: The mechanism of heating and cooling an intercalated blend.

Impact of Acceptor Loading Ratio: PC₇₀BM

The impact of fullerene loading on the phase behaviour is investigated in Figure 7.16. For small amounts of fullerene (9:1 blends) the disrupting effect of the polymer backbone melting is somewhat softened and complete by 240 °C. On cooling there is minimal hysteresis, and the re-organisation of the mobile side-chains results in an increase in returning to room temperature. For blends with excess fullerene (1:4) the polymer steadily becomes more ordered ($C = C_T$ max shifts from 1489 to 1484 cm^{-1}) until the intercalated acceptors start to mobilise (140-150 °C). The progression to a liquid polymer and solid PC₇₀BM system is complete by 220 °C.

Increased fullerene loading develops our cartoon as follows: the liquid polymer chains (≈ 100 °C) allow the disordered polymer backbones close to large fullerene domains to re-assemble, promoting backbone order (3). The

high fullerene loading results in a more significant loss of backbone order when these start to mobilise (4). The large hysteresis on cooling represents an increase in the proportion of solid fullerene domains that cannot re-intercalate into the polymer side chains (7). The process is irreversible; after the PC₇₀BM becomes immobile (150 °C) the backbone is frozen into a more twisted structure than the pristine film. The C = C frequency and C = C_{order/disorder} is now comparable to the neat PBTBT, indicating that the partial intercalation that was present in pristine 1:4 blends has been destroyed.

In the case of PC₇₀BM, heating to 270 °C and subsequently slow cooling allows partial disentanglement of the fullerene molecules from the polymer matrix and allows the remaining polymer to re-arrange. For the 1:1 samples, the fullerene absorption band (< 350 nm) represents a less intimately mixed donor-acceptor material. For 1:4 blends, it is interesting to compare the local changes observed with resonant Raman spectroscopy and the global-scale changes in absorption. The absorption maxima of the polymer in these blends red-shifts 480 nm to 555 nm and broadens to high energy, with vibronic structure from ordered polymer chains becoming increasingly apparent (Figure 7.19). Resonant Raman spectroscopy at $\lambda_{\text{ex}} = 488$ nm is particularly sensitive to short conjugation length portions of the polymer backbone, so the increase in polymer backbone disorder is enhanced. We predict that a combination of PC₇₀BM crystallisation out from the polymer side chains and thermal energy allows some portions of the polymer to become more ordered. These results support the loss of lamellar spacing observed after heating these blends above 250 °C.^[25]

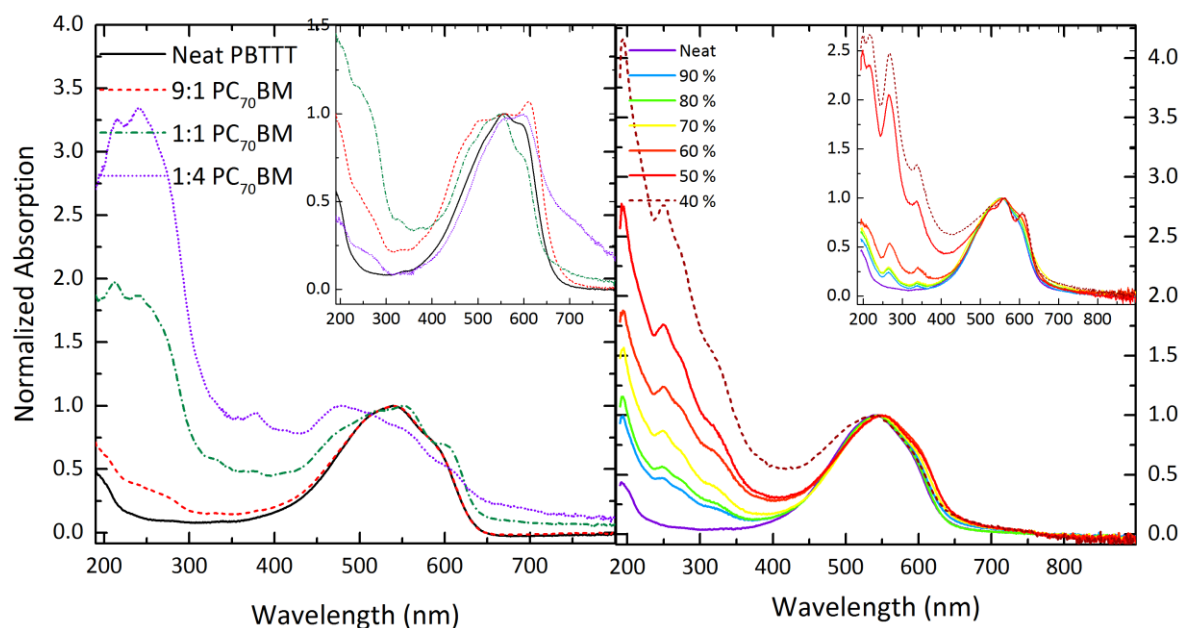


Figure 7.19: Absorption spectra for pristine and annealed (inset) films of PBTBT blended with (left) PC₇₀BM and (right) ICBA, normalized to the main polymer absorption band.

Impact of Acceptor Loading Ratio: ICBA

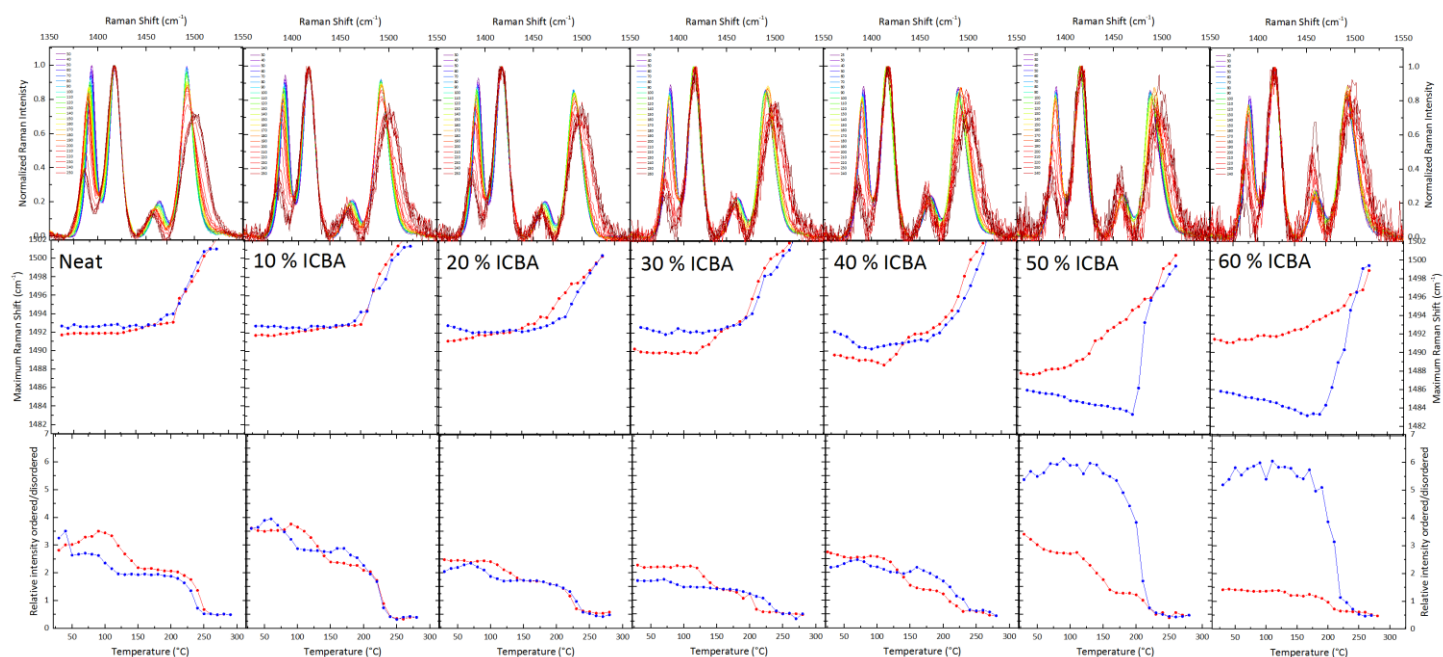


Figure 7.20: (upper) in situ Resonant Raman spectra acquired on heating at 10 °C/minute for PBTTC- C_{16} blends with ICBA discussed in the text. (middle) The extracted peak shift of the $C = C_T$ Raman active vibrational mode. (lower) Relative intensity of $C = C$ Order/disorder, corresponding to the proportion of planar/twisted polymer chains.

The impact of fullerene loading on the phase behaviour of the ICBA is examined in Figure 7.20. To the best of our knowledge, no phase diagram is available for this blend. In general, blends with ICBA content show similar characteristics to that observed for low loading levels of $PC_{70}BM$. However, the *in situ* analysis of the 1:1 PBTTC- C_{16} :ICBA blend is not consistent with the 1:1 PBTTC- C_{14} :ICBA blend. It is not entirely obvious why this may occur. The increased solubility of longer side-chains could promote intermixing in the solution state, causing the same extent of planarization at lower loading ratios. As these donor: acceptor ratios are calculated by weight, the same weight of PBTTC- C_{14} and PBTTC- C_{16} results in fewer backbone units per unit mass in the latter, which on intercalation would permit less acceptor molecules between the side-chains. It is possible to estimate the number of molecules of ICBA and monomer units of PBTTC- C_{14} and PBTTC- C_{16} per gram (~ 6.3 , 8.7 and 8.2×10^{20} respectively) of neat material, which allows estimation of the degree of intercalation. A 1:1 blend (by weight) will contain 1.38 (C_{14}) or 1.27 (C_{16}) ICBA molecules per PBTTC monomer. This means that for 1:1 blends by weight, the longer side-chain polymer is more likely to promote a better intercalated molecular packing.

For 0 – 40 % blends, the polymer order gradually increases until the onset of the side-chain melt (≈ 110 – 120 °C), which is slightly higher than the shorter side-chains, and subsequently decreases (until 150 °C). Beyond this (150 –

200 °C) there is no evidence of the polymer planarizing due to disentanglement of the fullerene, perhaps due to a higher crystallisation temperature of ICBA vs. PC₇₀BM.^[30] For blends with 0 – 40 % ICBA, the polymer solid-to-liquid phase transition of the polymer backbone is complete by 240 °C. The blends with 50 – 60 % ICBA emphasise the complexity of the donor-acceptor interaction. Whilst heating these blends shows the same transition temperatures as blends with low ICBA content, the polymer chains are fully liquid earlier (around 240 °C). Cooling the samples from 270 to 200 °C results in a significant increase in backbone order, down-shifting the position of $C = C_T$ (from 1500 to 1483 cm⁻¹) and increasing $C = C_{\text{order/disorder}}$. The transition is irreversible on cooling to room temperature, resulting in a large hysteresis of peak shift and increase in the proportion of ordered material. The polymer absorption in these thermally annealed samples display a red-shifted main absorption band (from pristine $\approx$ 550 nm to annealed $\approx$ 558 nm) with an increase in the low energy shoulder (right of Figure 7.19). The new high energy electronic transitions visible (263 and 332 nm) are typical of highly crystalline ICBA molecules.^[31]

Atomic Force Microscopy

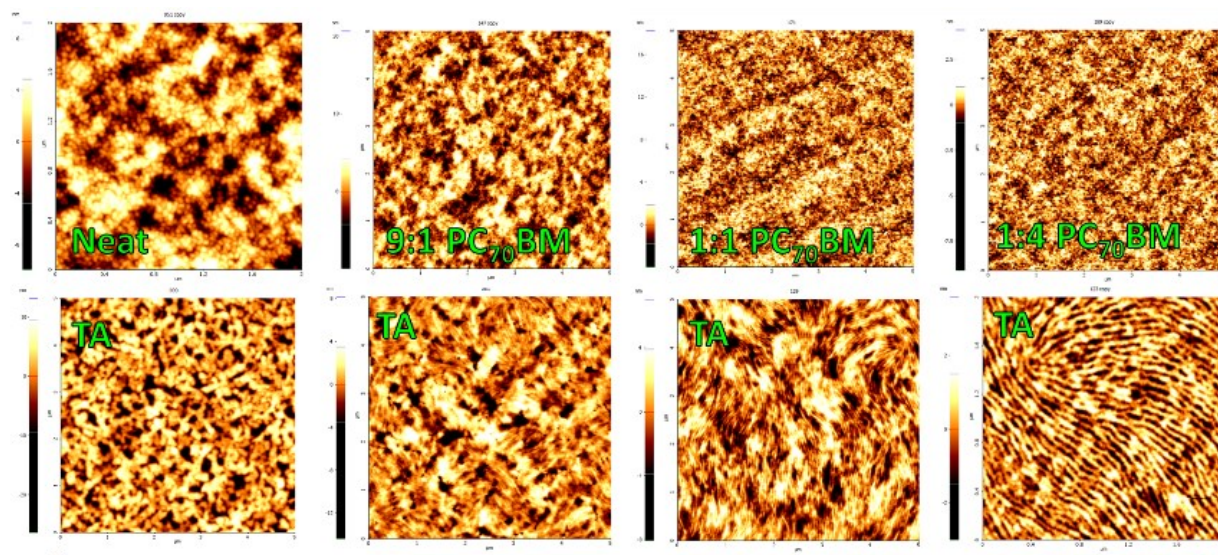


Figure 7.21: AFM images of the (upper) as-prepared spin-coated PBTTT:PC70BM blend films at the loading ratios described above. (b) Topography of the blend films after annealing to 270 °C and slow cooling to room temperature. These images were acquired with Minwon Suh at Imperial College London.

Whilst sensitive to local changes in molecular packing, resonant Raman spectroscopy considers the whole thickness of the polymer film, and for devices it is also important to consider the evolution of surface microstructure. Figure 7.21 displays AFM images (2 μm x 2 μm) for the pristine and annealed films discussed above. For the pristine films increasing loading ratios of PC₇₀BM decreases the surface roughness (r_q), as detailed in Table 7.3. After heating the samples to 270 °C and the subsequent slow-cooling to room temperature, high aspect ratio ribbons of material (1–2 nm high, 10s of nm wide, 100s of nm long) exist between the crystalline fullerene domains. The combination of AFM, absorption and *in situ* Raman spectroscopy provides a detailed picture of the vertical structure of these films. The broad polymer absorption with increased absorption from the low-energy shoulder but reversible changes detected by *in situ* Raman analysis indicate that for blends with low fullerene content annealing forms surface terraces of polymer domains but has minimal effects on the film below.^[32] The terraced morphology for pristine and 10 % blends is typical of annealed PBTTT, with the height of each terrace ($\approx$ 0.2 nm) representing the distance between in-plane π -stacked polymer backbones.^[32] For high fullerene content, annealing and subsequent removal of fullerenes from the polymer side-chains results in ordered ribbons of material that float to the surface. The nano-ribbon morphology has been described before for films of PBTTT heated beyond their second phase transition and is characteristic of fully extended PBTTT chains.^[32] The presence of high concentrations of fullerene molecules appear to align the nano-ribbons of PBTTT, similar to those obtained by zone-casting and dip-coating.^[32,33]

	Roughness (R_q , nm)	
PC ₇₀ BM	Pristine	TA
Neat	2.46 ± 0.35	4.78 ± 0.55
9:1	2.18 ± 0.34	1.80 ± 0.24
1:1	0.93 ± 0.03	2.00 ± 0.25
1:4	0.50 ± 0.02	0.75 ± 0.05

Table 7.3: Surface roughness (r_q) for PBTTT: PC₇₀BM blends pre and post-annealing extracted from AFM images of the film surface.

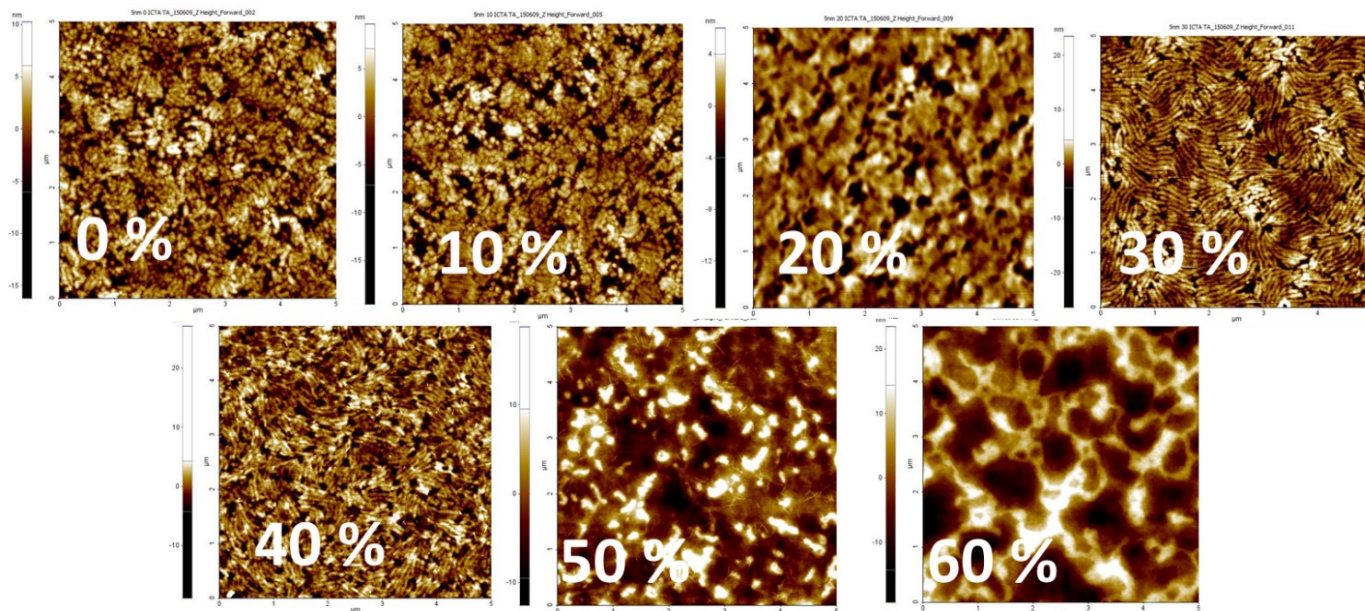


Figure 7.22: AFM images of the (upper) spin-coated PBTTT:ICBA blend films at the loading ratios 0 – 60 % after annealing to 270 °C and slow cooling to room temperature. These images were acquired with Oliver Holmes at Imperial College London.

AFM images of the annealed blends with ICBA are shown in Figure 7.22. For blends mainly composed of PBTTT; AFM reveals small circular aggregates (≈ 300 nm wide) on top of the distinctive terraced morphology of neat PBTTT (Figure 7.22) with step-heights of ≈ 10 nm. Increasing the ICBA content to 30 % allows the polymer chains to extend into nano-ribbons, 100 nm wide and 100s of nm long. Increasing the ICBA content decrease the width of the nano-ribbons and increases the density of circular aggregates on the film surface. For the high fullerene content blends (50, 60 %) the topography is markedly different, with both large islands of aggregated material and narrow wires, 10s of nm wide. The lack of any visible microscopic surface features in the optical microscope, strong ICBA absorption and low wavenumber $C = C_{T,TT}$ indicates ICBA is interacting with the ordered polymer chains below.

7.5.2 Impact of Intercalation on Electrochemical Stability of a Polymer/Fullerene Blend

In order to evaluate the impact of interfacial morphology on the operational stability of these blends, a series of cyclic voltammograms and chronoamperometry measurements were performed on neat, intercalating (1:1 PC₇₀BM) and non-intercalating (1:1 bis-PC₆₀BM) blends.

From the cyclic voltammograms in Figure 7.23 (a) the HOMO energy level of neat PBTBT is estimated to be -5.0 eV. The broad oxidation peak indicating multiple oxidation states due to disorder in the polymer chain.^[11,34] 1:1 blends with bis-PC₆₀BM and PC₇₀BM cause slight shifts to a lower onset (40 and 30 meV, respectively). For the intercalating blend (PC₇₀BM) the shape of the oxidation peak is much smoother demonstrating less energetic and morphological disorder for these films (Figure 7.23 (c)). This novel experimental technique allows observation of the polymer backbone conformation throughout the CV sweep; immediately after oxidation and during the subsequent reduction. For the neat material, before the oxidation onset (≈ 0.65 V), the Raman spectrum shows peaks (compared to that of a blend film) attributed to vibrational modes of the electrolyte solution (Figure 7.23 (d)). The spectra are normalised to the 915 cm^{-1} of the electrolyte solution allowing impartial evaluation of oxidation on different portions of the polymer chain. When the voltage exceeds the first oxidation peak of PBTBT (≈ 1.0 V) the Raman spectrum is very different to that of the neutral material, with new vibrational modes appearing at 1439 and 1484 cm^{-1} , and a decrease in scattering intensity due to resonance with the neutral portions of the polymer chain. On the return sweep (≈ 0.35 V), after the polymer has been reduced, the Raman spectrum of the neat polymer is restored with an almost total recovery of scattering intensity (Figure 7.23 (d)). The broad new vibrational modes of charged PBTBT could represent the collective backbone stretching of the T and TT units, where the C–C and C=C bonds are in a quinoidal structure.^[35]

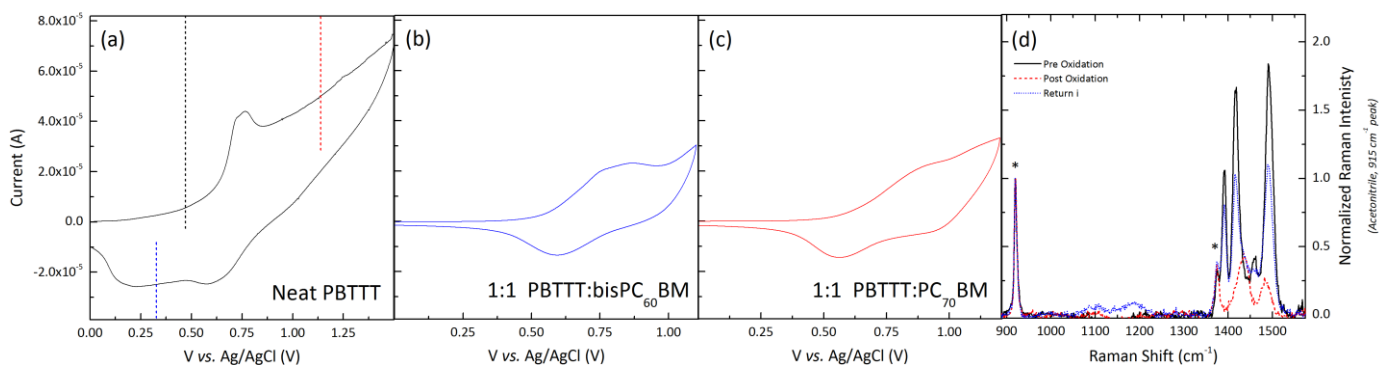


Figure 7.23: Cyclic voltammograms for neat, intercalated and non-intercalated PBTBT. For the neat material, the resonant Raman spectrum is plotted at each of the potentials indicated (pre, black solid, post, red dotted and after reduction, blue dashed). The Raman spectra are normalised to the 915 cm^{-1} Raman active mode.

F-PBTBT

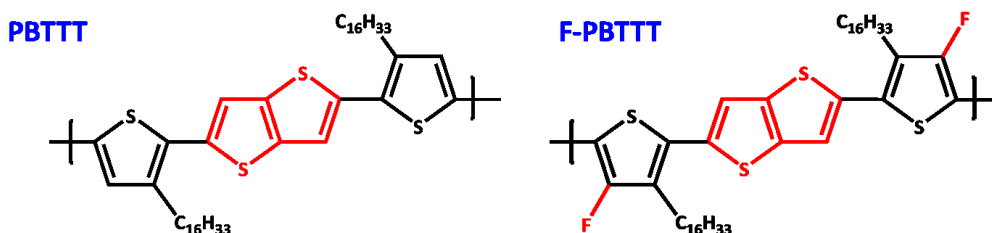


Figure 7.24: Molecular structures of PBTBT-C₁₆ and F-PBTBT-C₁₆, synthesised by Pierre Boufflet in the Department of Chemistry.^[12]

As the Raman spectrum of charged P3HT displays features typical of a planar P3HT backbone, the new vibrational modes observed here could be from very planar portions of the PBTTT chain. We have previously demonstrated that fluorination of the thiophene units, i.e. Poly(3-florothiophene), exhibits reduced inter-unit torsion between adjacent thiophene units and decreased intermolecular distances, which in turn increased charge-carrier mobility by a factor of 5.^[36] Non-bonding interactions between nearby sulphur and fluorine atoms promote planarization of the polymer backbone. Compared to their non-fluorinated counterparts (F-P3OT vs. P3OT) Raman spectra of the thin films showed a shift of the C – C and C = C modes to higher frequencies (1417, 1492 cm⁻¹) and an increase of C – C relative to C = C (C – C/C = C).^[36] It is therefore appropriate to compare the Raman spectra of fluorinated and non-fluorinated PBTTT. The site of fluorination, head-to-head on the alkylated bithiophene co-monomers, was chosen to enhance these S...F interactions.^[12] The optimised geometries of F-PBTTT produced by DFT simulations at the same level of theory to PBTTT (confirm 6-311 G(d,p)) confirm that between the unfused thiophene units the dihedral angles decrease from $\approx 20^\circ$ to $\approx 0^\circ$ (Figure 7.24).

The electronic absorption of F-PBTTT (Figure 7.25) is very similar to that of PBTTT with extended delocalisation of π -electrons along the whole conjugated backbone. The orbital distribution is only minimally effected by the substitution of fluorine atoms, and π -electron density is not delocalised across does not extend to the fluorine atom.

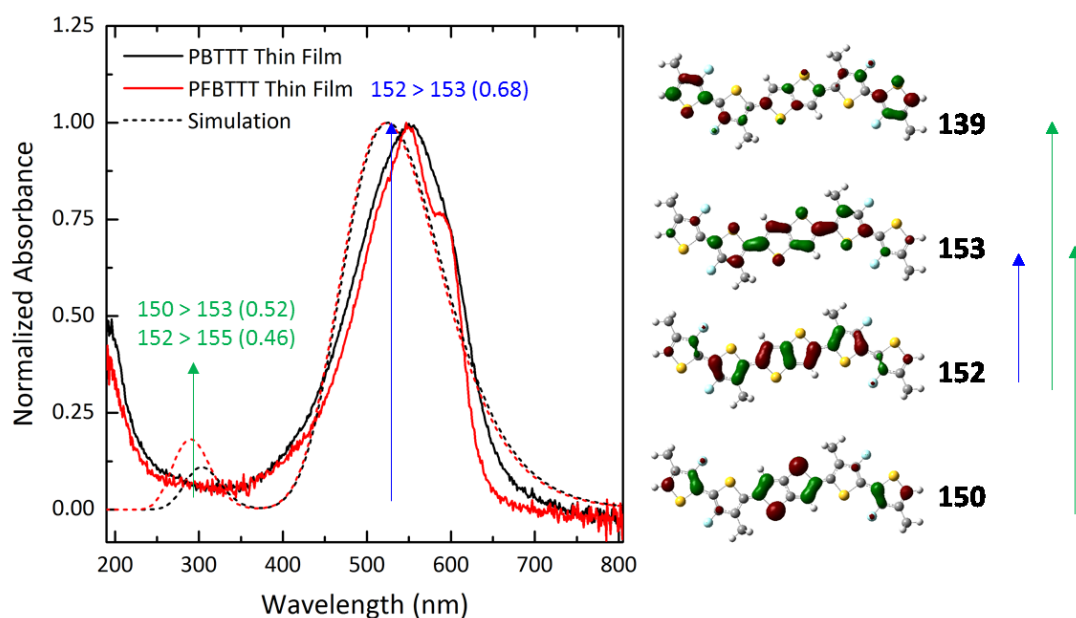
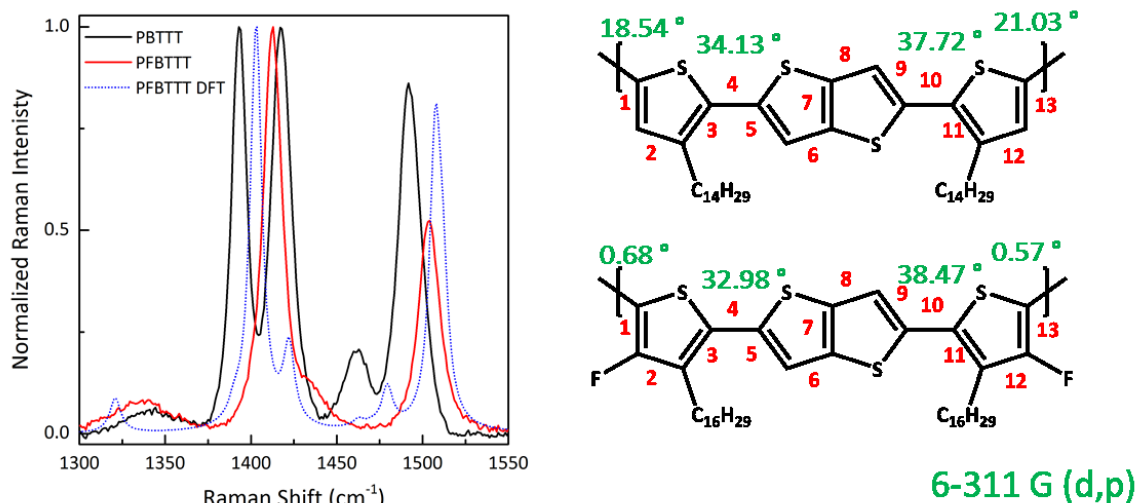


Figure 7.25: UV-Visible Absorption and associated isosurfaces simulated using TD-DFT with the CAM-B3LYP functional and 6-31 G(d,p) basis set. 9 states were considered.



	PBTtT	F-PBTtT		PBTtT	F-PBTtT		PBTtT	F-PBTtT
	Å			Å			Å	
1	1.376	1.377	5	1.379	1.384	9	1.379	1.384
2	1.420	1.415	6	1.414	1.414	10	1.446	1.445
3	1.384	1.387	7	1.390	1.394	11	1.384	1.388
4	1.446	1.444	8	1.414	1.413	12	1.420	1.415

Figure 7.26: Experimental Raman spectra of PBTtT (black) and F-PBTtT (red) normalized to their maximum intensity and corresponding DFT simulation (blue dashed) using the B3LYP functional and 6-311 G(d,p) basis-set. The geometry is optimised for an oligomer of at least three repeat units. The table and figure details the bond-lengths and dihedral angles resulting from the geometry optimization for both PBTtT and F-PBTtT.

Equivalent to fluorinated polythiophene, F-PBTtT has strong Raman peaks centred at 1412 and 1503 cm^{-1} .^[36] The nature of these peaks are established by comparison with the DFT calculations and appear to be collective stretches of the C – C and C = C bonds along the whole PBTtT backbone (i.e. from the thienothiophene and fluorinated bithiophene units). Improved backbone planarity results in both increased π -electron density in the C – C bond (increase in C – C/C = C) and particularly narrow peaks (narrower distribution of molecular conformations).^[15,36] On fluorination, the double bonds (1, 3, 5, 7, 9, 11 and 13) get longer whilst the single and inter-unit bonds stay the same or get shorter (2, 4, 6, 8, 10, 11) (Figure 7.26). The spectra of charged-PBTtT (Figure 7.27) are similar to the fluorinated case which supports the suggestion that the Raman scattering from the charged polymer arises from the more planar polymer chains.

Chronoamperometry

In order to compare the operational electrochemical stability of non-intercalated and intercalated blends of PBTtT, short timescale potential pulses (60 s) of increasing magnitude were applied to 1:1 blends with PC₇₀BM and

bisPC₆₀BM. The films were held at 0 V for 120 s before each cycle to minimise degradation of the polymer film. The current passing through the film was measured for each pulse, which allowed the polaron density to be calculated and the effect on the polymer backbone calibrated accordingly.

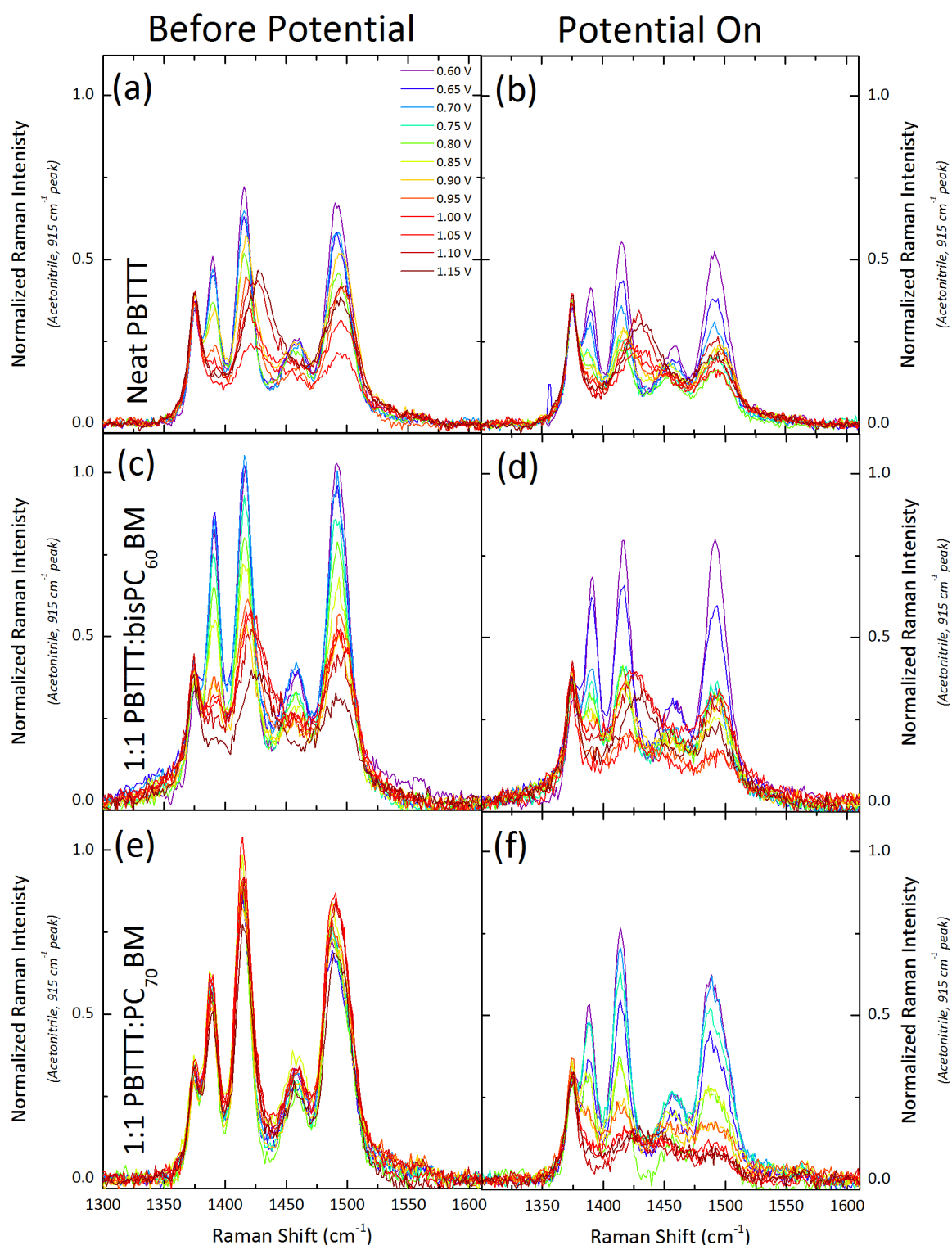


Figure 7.27: Resonant Raman spectra acquired during hold at 0 V (left) and potential application (right) for thin films of (a, b) neat, (c, d) non-intercalated blends with bisPC₆₀BM and (e, f) intercalated blends with PC₇₀BM. The spectra are normalized to the 915 cm⁻¹ of the electrolyte solution.

Figure 7.27 compares the Raman spectra before (left) and during (right) applications of a series of potentials (0.6 – 1.15 V) to the neat and blend films, normalized to the Raman peaks of the electrolyte solution (at 915 cm^{-1}). For the non-intercalating blends (Figure 7.27 (c) and (d)), excess charge injection has the same effect on the conjugated vibrations as oxidizing a neat film: a substantial loss of scattering from the C—C bonds (1390, 1452 cm^{-1}) and broadening of C = C to higher energy (1425, 1495 cm^{-1}). This remains even when the films are held at 0 V. At first glance, the intercalating blends (Figure 7.27 (e) and (f)) are more stable to charge injection: although the scattering intensity decreases, the neutral C – C modes are not instantly lost and the C = C shift is less significant. Once the potential is removed the relative intensities and peak positions recover (left). Even for the highest potential considered here (1.15 V), 1:1 blends with PC₇₀BM display comparable spectra to their neutral state. Figure 7.28 and Table 7.4 track the position of the C = C mode as a function of the density of the polaronic species for the intercalating and non-intercalating blends. Polaron density is calculated by integrating the relevant plots of current vs. time. As the polaron density is not independently controlled, only the size and duration of the applied potential, it is interesting to note the higher polaron densities in the intercalated blends. Figure 7.28 therefore highlights the relative stability of these blends to charge injection compared to the non-intercalated case, for intercalated blends the peak positions remain comparatively stable. The effect of oxidizing the blend films can be interpreted as an increase in co-planarity for the charged polymer. The enhanced stability of intercalated blends upon oxidation may be an important factor for widespread success in OPV devices.

Table 7.4: C = C peak position as a function of polaron density for neat PBTBT and 1:1 blends with bis PC₆₀BM and PC₇₀BM.

Polaron Density	Neat		Polaron Density	1:1 bis PC ₆₀ BM		Polaron Density	1:1 PC ₇₀ BM	
cm ⁻³	cm ⁻¹		cm ⁻³	cm ⁻¹		cm ⁻³	cm ⁻¹	
2.93E+20	1416.4	1491.9	2.16E+20	1416.6	1491.9	1.34E+21	1413.6	1487.4
6.75E+20	1416.6	1492.2	2.25E+20	1417.0	1492.2	1.59E+21	1413.1	1487.8
9.62E+20	1416.4	1492.6	2.60E+20	1416.6	1492.6	1.82E+21	1413.9	1488.1
1.23E+21	1417.0	1492.7	3.40E+20	1417.0	1492.6	2.16E+21	1414.8	1488.1
1.51E+21	1416.1	1492.7	4.46E+20	1417.6	1492.2	2.55E+21	1413.9	1488.4
1.90E+21	1417.3	1493.8	5.65E+20	1417.6	1493.5	2.96E+21	1414.3	1489.5
2.23E+21	1419.3	1494.3	8.59E+20	1417.9	1493.5	3.50E+21	1416.1	1490.2
2.40E+21	1421.1	1495.6	1.08E+21	1419.6	1494.0	5.16E+21	1417.3	1490.5
2.81E+21	1425.6	1495.6	1.25E+21	1421.6	1494.6	5.60E+21	1418.5	1490.9
3.22E+21	1428.8	1495.9	1.43E+21	1423.9	1494.7	6.07E+21	1423.0	1491.7
3.32E+21	1430.7	1496.7	1.68E+21	1426.2	1495.3	6.71E+21	1426.0	1491.8
3.50E+21	1433.6	1496.9	1.96E+21	1431.5	1496.0	6.71E+21	1429.6	1491.9

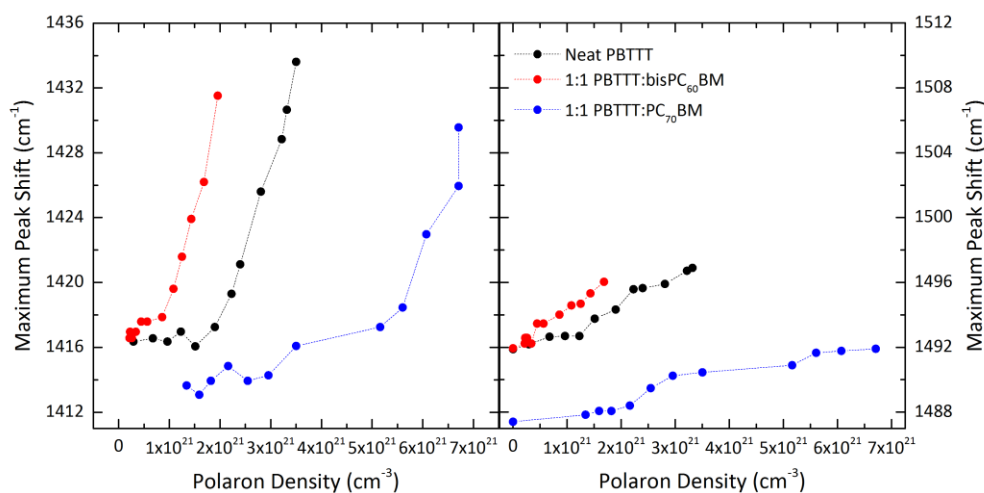


Figure 7.28: Maximum peak shift of the C – C and C = C modes as a function of polaron concentration for neat (black), intercalated (blue) and non-intercalated blends (red) extracted from Figure 7.27.

7.6 Summary

The conjugated backbone modes of PBTBT have been identified and the peak positions, relative intensities and shapes studied to assess the molecular conformation in intercalated and non-intercalated blends. Intercalation with small fullerenes (PC₇₀BM, ICBA) is found to planarise the polymer backbone. This was postulated to be the cause of the increase in OPV efficiency. High loading ratios (> 60 %) are found to decrease the co-planarity of adjacent units as polymer chains twist around large fullerene domains. On the other hand, large fullerene molecules (bisPC₆₀BM, ICTA) have no influence on the backbone packing.

The phase-behaviour of the intercalated and non-intercalated blends is explored using *in situ* Raman spectroscopy. For both intercalated and non-intercalated blends with PC₇₀BM, heating beyond the side-chain melt is found to improve backbone planarity. Heating to the second phase transition increases the relative proportion of disordered polymer units. For the non-intercalated blends, the transitions are found to be totally reversible with minimal hysteresis i.e. there is no interaction between the polymer and fullerene. For intercalated blends the observed hysteresis on heating arises due to the now-crystalline fullerene attempting to re-intercalate. The topography of the annealed intercalated films reveals a surface network of polymer nano-ribbons hundreds of nm long. Blends with ICBA have a less pronounced effect on improving polymer planarity and are found to be less effective at quenching photoluminescence. At high blending ratios an interesting microstructure results from annealing beyond the second phase transition: increasingly narrow nano-ribbons (tens of nm across) of highly ordered material, where there is a strong electronic interaction between the polymer and fullerene.

Finally, the operational stability of the blends is considered using *in situ* chronoamperometry. The technique is first established for P3HT, where resonant excitation of the charged species probes the planar poly-thiophene chains typical of a more quinoidal structure. Charged PBTTT displays two strong Raman modes, which we interpret to be collective C – C and C = C vibrations from a planar PBTTT chain. The positions and relative peak intensities of these modes in intercalated and non-intercalated blends are measured at different polaron concentrations. We report that whilst it is easier to inject charge into the intercalated blend (an increase in polaron concentration for a given potential difference and application time), the backbone conformation is more stable for these structures. This is likely due to the highly planar donor-acceptor interface, where every fullerene molecule sits between neighbouring side-chains.

7.7 Conclusions

Systematic DFT calculations were used to generate structure-property relationships, namely the shift of the C = C stretch modes as a signature of conformational disorder. The effect of blending with small fullerene molecules (PC₇₀BM, ICBA) was found to planarise the polymer backbone and increase molecular order. On the other hand, large fullerene molecules could not fit between the polymer side chains and as a result no change in backbone planarity was observed. The nature of the donor-acceptor interaction was investigated using *in situ* Raman spectroscopy, explaining the phase-diagram of intercalating and non-intercalating donor-acceptor blends. We found that heating, and subsequent slow cooling, the neat or non-intercalating systems to beyond the polymer backbone melting temperature had no impact on backbone order, only the rearrangement of the alkyl side chains (red-shift of UV-Visible spectra). On the other hand, heating the intercalating system beyond the temperature for the polymer side-chains and fullerene molecules to become mobile allowed the partial de-intercalation of these units from the polymer side chains. This resulted in a large hysteresis of the peak position of C = C or relative intensity of $C = C_{\text{order}} / C = C_{\text{disorder}}$. The electrochemical stability of these intercalating and non-intercalating blends was monitored. In order to understand the evolution of Raman spectrum as a function of hole polaron density, we compared the charged PBTTT to a highly planar fluorinated PBTTT derivative. Quinoidal, charged PBTTT displays two strong Raman active modes, equivalent to F-PBTTT. The intercalated blends are found to accommodate increased charge injection before the polaronic species degrade, which is attributed to their highly planar, delocalised polymer backbones.

7.8 Bibliography

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8 Conclusions and Further Work

This thesis considers the molecular packing and conformation of low and high-molecular weight organic semiconductors, and their implications on the optoelectronic properties and performance of thin-film devices. The first section looks to control the molecular packing and alignment of solution processed small molecules using the zone-casting technique. The optoelectronic properties are systematically investigated using a range of structural probes. The device performance of organic field-effect transistors (OFETs) is characterised in terms of charge carrier mobility and mobility anisotropy. The second part investigates the interactions at the organic-inorganic interface in vacuum evaporated small molecule devices. We consider the implications of molecular packing in pentacene OFETs and copper phthalocyanine magnetic tunnelling junctions (MTJs) on the charge carrier mobility and magnetoresistance. The molecular orientation and device performance are investigated as a function of film thickness and device temperature, which are relevant for real world applications with enhanced operational lifetimes. The final part considers the conformation and electrochemical stability of conjugated polymers for use in organic photovoltaic devices (OPV). Apparatus was built to enable to systematic injection of charge into polymer thin films in situ under the Raman microscope, allowing observation of the hole polaron formation through reorganisation of the polymer backbone. For OPV blends, quantum-chemical methods and structural probes were used to explore the interaction between the polymer donor and fullerene acceptor molecules as a function of acceptor size and loading ratio.

8.1 Conclusions

This study has demonstrated the critical importance of uniaxial molecular orientation for producing high-performance OFETs and MTJs. Additionally, it has uncovered the criteria required for optimally blended, stable, solar cells. To achieve these improvements a number of sample preparation and characterisation techniques have been investigated. Detailed conclusions can be found at the end of each section and are summarised below.

8.1.1 Molecular Orientation in Solution Processed Small Molecule Devices

For small molecule thin films, we have demonstrated that through simple control of processing conditions it is possible to increase the charge carrier mobility by an order of magnitude and on/off current by three orders of magnitude. For functionalized pentacene derivatives (TIPS- and TES-pentacene) uniaxial molecular alignment and high aspect ratio needle-like crystal structures were found to result in devices significant anisotropy in charge-carrier mobility; with mobility increasing by a factor of 45 depending on whether crystals of 1D packed TES-pentacene are oriented parallel or perpendicular to the charge transport direction. The discrepancy in anisotropy between 2D (TIPS) and 1D (TES-) was understood through an evaluation of the charge transfer integrals. To achieve a high charge-carrier mobility, the molecular alignment must be uniform across the device; on the electrode, in the channel and at the interface between the two. Angle-dependent polarized Raman spectroscopy is used to deduce the molecular order at regular intervals across the device on both Si/SiO₂ and plastic substrates. The PFBT-treated gold contacts act as nucleating sites, where pentacene cores arrange with the highest possible degree of molecular order.

TIPS- and TES- pentacene both represent materials where strong intermolecular interactions dominate the optoelectronic and charge transport properties, and it is therefore interesting to compare them to truly non-interacting systems. We have demonstrated resonant Raman spectroscopy as an appropriate tool to identify the orientation of isolated pentacene molecules within a *p*-terphenyl lattice for MASER applications. The introduction of nitrogen atoms at the 6,13 positions of pentacene core is proposed as a means to achieve continuous wave MASER operation, and the impacts of this substitution on the electronic, vibrational and structural properties within the *p*-terphenyl have been thoroughly investigated.

Resonant Raman spectroscopy and systematic quantum-chemical simulations were used to probe the nature of the two strong phthalocyanine absorption bands. The low energy absorption is localised on the inner rings whilst the high energy absorption band is the result of charge transfer to the outer rings. The impact of an inner metallic core

(Zn) and outer electron donating groups (thiophene) on the optoelectronic and structural properties have been examined. The optoelectronic signatures of H- and J-aggregated phthalocyanine films have been identified. In pristine, as-deposited, thin films the interactions between thiophene groups was found to result in J-aggregation between neighbouring molecules over a period of days, which relaxes on annealing at $T > 200\text{ }^{\circ}\text{C}$. The extent of J-aggregation was found to depend on the choice of solvent and substrate displacement rate during zone casting. The control of aggregation is expected to be beneficial for charge transport and operational device stability.

8.1.2 Interfacial Molecular Orientation

Having established the impact of molecular packing on the device performance of solution-processed small molecule devices, we consider its impact in vacuum evaporated small molecule FETs and MTJs. Particularly we have focussed on the interaction of vacuum evaporated molecules with the inorganic interface below. We first characterised an ideal system of vacuum evaporated pentacene single-crystals. Here we identified angle-dependent polarised Raman spectroscopy at an excitation wavelength resonant with the Davydov absorption band ($\lambda_{\text{ex}} = 633\text{ nm}$) as a means to evaluate the crystalline order. The shape of the aperture through which the single crystals are evaporated was found to determine the packing structure within the single-crystal domains.

As for the functionalised solution processed pentacene derivatives in Chapter 3, uniform molecular packing across vacuum evaporated BG BC FETs was demonstrated to be crucial in ensuring a high charge-carrier mobility. The molecular packing is found to depend strongly on the relative strengths of the interactions between neighbouring molecules and the underlying layers/ substrate. When pentacene was evaporated onto a reactive metal surface such as clean untreated gold, the formation of an interfacial dipole was demonstrated to cause the molecules to lie flat. On the other hand, within the active channel (the unreactive Si/SiO₂ dielectric) pentacene molecules were found to stand upright. At increasing film thicknesses, the substrate-molecule interaction becomes weaker and pentacene molecules were found to stand more upright. Surface-treatment of the electrode and channel (with thiol and silane SAMs, respectively) has been introduced as a means to achieve a high device performance; attributed to minimised interfacial dipoles and a constant molecular packing across the device. The combination of thiophenol and octadecyltrichlorosilane result in near-on identical molecular packing across the device, which is demonstrated to increase charge-carrier mobility by four orders of magnitude.

Next, we identified the morphological polymorph of copper phthalocyanine (CuPc) in vacuum evaporated thin-films. The optoelectronic properties of CuPc have been extensively examined and the nature of electronic transitions described in terms of π -electron distribution. Structural probes were developed to study the molecular packing of CuPc on a variety of reactive and non-reactive substrates and interlayers, and as a function of both film thickness and device temperature. First, we established the spectroscopic signatures of α - and β -phase. On unreactive substrates, ultra-thin (1.6 nm) films of CuPc were found to pack in the meta-stable α -phase polymorph. Strong interactions between CuPc and underlying PTCDA or Fe interlayers instead promoted the formation of more stable β -phase molecular packing close to the interface. The surface of the 1.6 nm thin films is comprised of a number of small ($\ll 1\ \mu\text{m}$) grains, with a higher surface roughness (i.e. smaller domains) detected on unreactive surfaces. As the thickness of the thin films increases the magnetoresistance dramatically decreases, which we expect is due to the loss of spin identity whilst charges navigate the thick organic layer. The stability imparted by β -phase molecular packing at room temperature is found to remain even on cooling to 77 K (-196 °C). Interestingly, the morphological freedom associated with the meta-stable α -phase CuPc allowed the molecules to form uniaxially aligned domains upon cooling, which were larger than the size of our laser spot (1 μm). This unique insight into the morphology was used to explain the improvement of magnetoresistance from 5 to 180 % when CuPc/MgO/Fe MTJs were cooled from 300 to 77 K. On heating/cooling unreactive surfaces, the structural changes were shown to be reversible with negligible hysteresis, whereas for reactive surfaces the combination of interfacial β -phase and bulk α -phase results in an energetic barrier.

8.1.3 Stability of Organic Solar Cells

In the final section, the backbone conformation and operational stability of a host of polythiophene derivatives were investigated for OPV applications. Quantum-chemical methods were used to determine spectroscopic signatures for improved backbone planarity. Systematic theoretical studies were applied to theoretical data to gain deeper insight into the changes in polymer molecular packing which occur during OPV operation; both on blending with the accepting fullerene molecules and during the formation of hole polarons after light absorption.

In the first study, the impact of nitrogen substitution into a polythiophene chain ($\text{S} \rightarrow \text{N}$) was investigated. Using a series of systematic quantum-chemical calculations and a set of novel thiophene-thiazole copolymers, the relationship between thiazole content and inter-unit torsion was established. Electronegative nitrogen withdraws

electrons from the conjugated backbone and deepens the position of the highest occupied molecular orbital. Interactions between nitrogen and hydrogen atoms in adjacent backbone units were found to result in reduced steric interactions for the thiazole containing copolymers, which resulted in a more planar backbone conformation compared to P3HT, and favourable electrostatics. The increased planarization and deeper HOMO energy level is somewhat misleading; the thiazole containing copolymers are the least stable under charge injection and subsequent hole polaron formation. The cause of this instability is two-fold; in the polaronic state the nitrogen lone pair is particularly susceptible to radical attack and the planar polymer backbone results in a highly delocalised polaron being formed. This study demonstrates that the combination of systematic DFT calculations and resonant Raman spectroscopy can aid polymer design for high performance OPV devices.

In situ Raman spectroscopy during the formation of hole polarons revealed that charge injection into a P3HT backbone significantly reduces inter-unit torsion. This feature is often observed in CV data, where the oxidation peak shifts to lower energy on repeat cycles, but is rarely discussed and has never been experimentally investigated. The planarization is found to occur immediately after charge injection but is largely reversible after the oxidising potential is removed. We have uncovered clear Raman signatures which can be used to evaluate the polaron density in the polythiophene films; the position and FWHM of the C = C and relative intensity of the C – C/C = C.

Next the morphological stability of a polythiophene chain was evaluated. Branched side-chain P3EHT displays slow re-crystallisation from the melt phase, which allowed a detailed investigation of the polymer backbone order as a function of time after melt. The crystallisation is a two-step process; first the alkyl chains rearrange (seen as a shift of the main absorption band) and then the backbone reorganises (a shift of C = C and increase in the order/disorder ratio). Cyclic voltammograms reveal that immediately after melt twisted disordered P3EHT displays two oxidation peaks, from planar and twisted chains at lower and higher energy. The rearrangement of the polymer backbone is a linear process, which is complete after 3 hours. The more ordered P3EHT films with improved alkyl-chain arrangement only show one lower energy oxidation peak (more planar portions of backbone).

Finally, DFT calculations were applied to understand the impact of blending the polythiophene derivative PBTTT with fullerene molecules on the optoelectronic and conformational properties of the conjugated polymer. Potential energy scans of the torsion angles between adjacent thiophene units and between the thiophene and bithiophene units revealed a significantly lower barrier to rotation in the latter case. Using quantum-chemical

methods, the relationship between the bithiophene C = C ring stretch peak position and inter-unit torsion was established. Smaller fullerene molecules (PC₇₀BM, ICBA) were found to planarise the PBTTT chain. The extent of planarization was investigated for a range of fullerene materials and loading ratios. A combination of resonant Raman spectroscopy, *in situ* Raman spectroscopy during heating/ cooling and photoluminescence revealed that 1:1 blends of PBTTTC₁₄ with PC₇₀BM contained highly planar polymer chains, where one fullerene molecule sits between each alkyl side-chain in a so-called 'intercalated' structure. As fullerene size is increased (PC₇₀BM → ICBA → ICTA → bisPC₆₀BM) the ability to intercalate decreases. This study also found that PBTTT with longer side-chains (C₁₆) could accommodate higher fullerene loading before becoming disordered, where polymer chains twist around excess fullerene molecules. We have used *in situ* electrochemical Raman spectroscopy to reveal that effective intercalation does not only reduce the inter-unit torsion between adjacent units in a polymer chain, but also imparts stability into the blend film, which will be important for OPV performance.

In addition to the study specific conclusions of this work, we have demonstrated a wide variety of techniques to control molecular packing and conformation of both small molecules and polymers. Resonant Raman spectroscopy has been established as a means to determine molecular packing and aid device design for OPV, OFET, MASER and MTJ applications. Raman spectroscopy has been developed beyond a probe of molecular order and conformation in the steady-state, to offering a particularly sensitive analysis of the operational stability of organic materials *in situ*.

8.2 Further Work

We have demonstrated the use of zone-casting to deposit uniaxially aligned crystals of soluble small molecules with a high charge-carrier mobility. It would be interesting to apply our understanding of the interactions between small molecules and self-assembled monolayers to deposit other highly oriented small molecule films. A natural extension of the zone-casting work would be to investigate the use of zone-casting to deposit aligned films of polymers and polymer/small molecule blends.^[1,2] The possibility to cross-link the needle-like crystal structure of TIPS- and TES-pentacene and deposit a subsequent layer of electro-active polymer or n-type conducting small molecule would permit novel bipolar device design. The modular apparatus offers a wide-range of promising investigations; with the redesign of the nozzle allowing unique microstructures and low-temperature controlled solution deposition of transparent electrode materials and active layers allowing the fabrication of flexible electronic devices.^[3]

Our characterisation of phthalocyanine layers in MTJs and pentacene molecules in MASERs demonstrated the versatility of Raman spectroscopy beyond the characterisation of conventional organic electronic devices. It would be interesting to consider a range of other small molecules for applications in spintronics, where precise control of the molecular orientation and order within the organic layer could permit room-temperature spin-polarised charge transport.^[4,5] The *in situ* characterisation of spin-polarised charge movement through an MTJ would be particularly worthwhile to determine the precise mechanism of charge transport through the ultra-thin organic layer. For MASER applications, relationships between the pentacene concentration within the *p*-terphenyl lattice and true extent of molecular 'isolation' will aid further crystal design, and be a simple extension of an exciting investigation.

With an ever-expanding catalogue of donor and acceptor materials that cover more of the solar spectrum than ever before, and published solar cell efficiencies that exceed 12 %, it is time to stop neglecting device stability.^[6] Our *in situ* studies in photodegradation, morphological, thermal and electrochemical stability reveal the extent of work required to identify the degradation mechanism and localise weak-spots along the polymer chain.^[7–9] A possible collaboration with synthetic chemists to create a road-map for the design of stable polymers and suitable fullerenes could aid further advances. A first rule would be to carefully consider the use of nitrogen to achieve deeper HOMO energy levels; as this has been demonstrated to be particularly detrimental to operational stability.^[10] For OPV devices, the choice of suitably sized fullerene molecules at appropriate loading ratios will enhance the molecular order and device stability beyond current reports. The results shown in this work suggest that polymer chains become planar during oxidation. Whilst tuning the excitation conditions to the main polymer absorption reveal the conformational changes within the conjugated backbone, excitation with the polaronic absorption band would constitute an important extension of this work.

8.3 Bibliography

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9 Presentations, Publications and Prizes

9.1 Publications

- 1-GHz pentacene diode rectifiers enabled by controlled film deposition on SAM-treated Au anodes C-M. Kang, J. Wade, S. Yun, J. Lim, H. Cho, J. Roh, H. Lee, S. Nam, D. D. C. Bradley, J-S. Kim, and C. Lee, *Adv. Electron. Mater.* **2**, 1500282, 2016 (Front Cover)
- Optimization and Analysis of Conjugated Polymer Side Chains for High Performance Organic Photovoltaic Cells, J-H. Kim, J-B. Park, J. Wade, S. Wood, M. Song, J-S. Kim, I-H. Jung, S-C. Cheol, D-H. Hwang. *Adv. Funct. Mater.* 2016 (Front Cover)
- Operational Electrochemical Stability of Thiophene-Thiazole Copolymers Probed by Resonant Raman Spectroscopy, J. Wade, S. Wood, D. Beatrup, M. Hurhangee, H. Bronstein, I. McCulloch, J. Durrant, and J-S. Kim, *Journal of Chemical Physics*, 2015
- Polaron stability in semiconducting polymer neat films, D. Beatrup, J. Wade, L. Biniek, H. Bronstein, M. Hurhangee, J-S. Kim, I. McCulloch and J. R. Durrant, *Chemical Communications*, 50, 14425, 2015
- Influence of Backbone Fluorination in Regioregular Poly(3-alkyl-4-fluoro)thiophenes, Z. Fei, P. Boufflet, S. Wood, J. Wade, J. Moriarty, E. Gann, E. Ratcliff, C. McNeill, H. Sirringhaus, J-S. Kim, M. Heeney, *J Am Chem Soc*, 137, 6866, 2015
- Self-Aligned Megahertz Organic Transistors Solution-Processed on Plastic, S. G. Higgins., B. V. O. Muir, J. Wade, J. Chen, B. Striedinger, H. Gold, B. Stadlober, M. Caironi, J-S. Kim, J. H. G. Steinke, A. J. Campbell, *Advanced Electronic Materials*, 1, 2015
- Excitation Energy Dependent Optical Transitions and Their Photostability of Diketopyrrolopyrrole (DPP)-Based Copolymers for Photovoltaic Application, *Energy & Environmental Science* S. Wood, J. Wade, M. Shahid, E. Collado-Fregoso, D. D. C. Bradley, J. Durrant, M. Heeney, J-S. Kim. *Energy Environ. Sci.*, 8, 3222-3232, 2015 (Front Cover)
- Charge mobility anisotropy of functionalized pentacenes in organic field effect transistors fabricated by solution processing, J. Wade, F. Steiner, D. T. James, D. Niedzialek, Y Jung, D-J. Yun, D. D.C. Bradley, J. Nelson, J-S. Kim, *Journal of Materials Chemistry C*, 2, 10110, 2014
- Photochemical stability of high efficiency PTB7:PC70BM solar cell blends, J. Razzell-Hollis, J. Wade, W. C. Tsoi, Y. Soon, J. Durrant, J-S. Kim, *Journal of Materials Chemistry A*, 2, 20189, 2014
- Controlling Microstructure of Pentacene Derivatives by Solution Processing: Impact of Structural Anisotropy on Optoelectronic Properties, D. T. James, J. M. Frost, J. Wade, J. Nelson, J-S. Kim, *ACS NANO*, 7, 79831, 2013
- Synthesis and morphology of asymmetric, alkyne-functionalised pentacene and 2-fluoroanthradithiophene, c. M. S. Combe, D. T. James, J. Wade, A. J. P. White, J-S. Kim, I. McCulloch, *Tetrahedron Letters*, 54, 6814, 2013
- Direct Imaging Pentacene Molecular Orientation Controlled by SAM layers and Its Impact on Thin Film Transistor Device Performance, *Advanced Electronic Materials*, J. Wade, J. Roh, C-M. Tan, C. Lee, J-S. Kim. *Submitted*
- Molecular Design of a Room-Temperature Maser, S. Bogatko, P. Haynes, J. Sathian, J. Wade, J-S. Kim, J. Breeze, E. Salvadori, A. Horsfield, M. Oxborrow, *Journal of the American Chemical Society*, *Submitted*
- Modulation of spin injection and Interface-Mediated Molecular Ordering in Organic Spintronic Devices, Y- J. Bae, N-J. Lee, J. Wade, J-S. Kim, I. Eisuke, T-H. Kim, *Advanced Materials*, *Submitted*

9.2 Presentations

- Operational Electrochemical Stability of Thiophene-Thiazole Copolymers Probed by Resonant Raman Spectroscopy, Brazil Materials Research Society, Rio de Janeiro, 2015, J. Wade, S. Wood, D. Beatrup, M. Hurhangee, H. Bronstein, I. McCulloch, J.Durrant, and J-S. Kim. *Oral presentation*
- UK-Korea Academic Conference, National Physics Laboratory, 2015, Direct Imaging Pentacene Molecular Orientation Controlled by SAM layers and Its Impact on Thin Film Transistor Device Performance, J. Wade, J. Roh, C-M. Tan, C. Lee, J-S. Kim. *Poster*
- The First International Symposium on Flexible Electronics, Nanjing, 2015, Operational Electrochemical Stability of Thiophene-Thiazole Copolymers Probed by Resonant Raman Spectroscopy, J. Wade, S. Wood, D. Beatrup, M. Hurhangee, H. Bronstein, I. McCulloch, J.Durrant, and J-S. Kim. *Oral presentation*
- The First International Symposium on Flexible Electronics, Nanjing, 2015, Impact of molecular orientation on device performance probed by Raman spectroscopy, J. Wade, J. Roh, C-M. Tan, C. Lee, J-S. Kim. *Poster*
- OPV Stability, Specific, 2014, Operational Electrochemical Stability of Thiophene-Thiazole Copolymers Probed by Resonant Raman Spectroscopy, J. Wade, S. Wood, D. Beatrup, M. Hurhangee, H. Bronstein, I. McCulloch, J.Durrant, and J-S. Kim. *Oral presentation*
- UK-Korea Academic Conference, Imperial College London, 2014, Direct Imaging Pentacene Molecular Orientation Controlled by SAM layers and Its Impact on Thin Film Transistor Device Performance, J. Wade, J. Roh, C-M. Tan, C. Lee, J-S. Kim. *Oral Presentation*
- E-MRS, Lille, 2014, Microstructure of Organic Semiconductors Controlled by Solution Processing and its Impact on Optoelectronic and Charge Transport Properties, J. Wade, J-S. Kim. *Oral presentation*
- CPE Workshop, Erlangen, 2014, Charge mobility anisotropy of functionalized pentacenes in organic field effect transistors fabricated by solution processing, J. Wade, F. Steiner, D. T. James, D. Niedzialek, Y Jung, D-J.Yun, D. D.C. Bradley, J. Nelson, J-S. Kim. *Oral presentation*
- ECME, London, 2013, Charge mobility anisotropy of functionalized pentacenes in organic field effect transistors fabricated by solution processing, J. Wade, F. Steiner, D. T. James, D. Niedzialek, Y Jung, D-J.Yun, D. D.C. Bradley, J. Nelson, J-S. Kim. *Poster*
- UK-Korea Student Exchange, KAIST, 2013 Charge mobility anisotropy of functionalized pentacenes in organic field effect transistors fabricated by solution processing, J. Wade, F. Steiner, D. T. James, D. Niedzialek, Y Jung, D-J.Yun, D. D.C. Bradley, J. Nelson, J-S. Kim. *Oral presentation*

9.3 Grants and Prizes

9.3.1 Prizes

- Shortlisted for Very Early Career Woman in Physics Prize (IOP) 2015
- Physics Department Postgraduate Research Symposium, Presentation Prize 2015
- Union Colour 2015
- Union Award for Contribution to College Life 2015
- Faculty of Natural Sciences Award for Excellence in Teaching and Learning 2015
- Student Academic Learning Choice Award 2014
- Physics Department Tyndall Prize for Best Final Year Project 2012

9.3.2 Grants

- RAEng Ingenious Award for Public Engagement £ 6200
- Armourers and Brasiers Gauntlet Trust travel to Brazil MRS 2015 £ 900
- Imperial College Trust travel to scientific conference 2015 £400
- Nanjing Tech Travel Grant for visit to The First International Symposium on Flexible Electronics 2015 £800
- Centre for Plastic Electronics Travel Grant travel to Erlangen 2014 £400
- Graduate School Funding: Professional Development Grants for Postgraduate Students £4000