

**A STRUCTURAL AND SPECTROSCOPIC
INVESTIGATION OF
POLYFLUORENE COPOLYMERS
IN SOLUTION AND THE SOLID STATE**

Robert Peter Stanley

Experimental Solid State Physics

Imperial College London

A thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

November 2012

I dedicate this work to my parents

Peter and Sue

Acknowledgements

There are many people I would like to thank, and without each and every one of them this work would not be completed to the standard it is. The constant support from my parents Sue and Peter over the last seven years has meant I have been able to complete this work, which sometimes did not seem likely. My wonderful girlfriend Hannah has been a constant source of encouragement during my time writing up and I thank her hugely for that. Alasdair Campbell has been an exceptional supervisor without his knowledge and guidance I could not have completed this. Although it has taken longer than anyone had anticipated when I first set out on this PhD journey, his belief in my ability to complete it, and occasional surprise at things I had completed made it a pleasure.

There have been many others in the Experimental Solid State Physics group at Imperial College who have helped me, both academically and personally. All those I worked and drank tea with in Huxley 724: Dan Farrell, Jeremy Smith, Markus Fuhrer, Matt Lumb, Matt Ng, Clare Dyer-Smith, Peter Spencer, Justin Dane, Thomas Wellinger, Jarvist Frost and more. There were many people whose assistance consisted of more than just warm caffeinated beverages, namely Colin Belton, Joachim Steinke, Alex Guite, and Natasha Shirshova for their generous help with equipment and theory and of course Donal Bradley. I could not have completed the work at RAL without generous help from Maximillian Skoda and Steve Parnell.

My time in America at Cornell University was spent very enjoyably, studying hard under the watchful eyes of George Malliaras and Detlef Smilgies. They were both incredibly helpful and generous in their assistance. The solvent annealing could not have been completed without use of Aram Amassian's vapour cell. I would also like to thank the other members of the Malliaras and Smilgies groups, namely Hon-Hang Fong and Ruipeng Li.

My time in London was rarely lonely, and my various housemates and friends all played a big part in allowing me to get this thesis completed. Thank you to Dave Lee, Dan Farrell, and Justin Dane. After my return to Littlehampton many friends old and new helped me to finally complete this work, the interesting discussions, constant encouragement and shared enjoyment in various places including the New Inn, were a welcome outlet away from constant physics!

Declaration of Originality

I declare that the work herein is my own
unless specific mention to the work of others is made.

Abstract

This thesis involves a structural and spectroscopic investigation of the electroluminescent polymer poly(9,9-dioctylfluorene), F8T2, and its copolymers poly(9,9-dioctyl)fluorene, PFO, and poly(9,9-dioctylfluorene-alt-benzothiadiazole), F8BT. Small angle neutron scattering (SANS) studies have shown that the three polymers take up very rigid, rod-like conformations in toluene and chloroform solutions. Aggregation effects of F8T2 in toluene were studied over 16 hours with a sheet-like aggregate structure suggested. Light-scattering (LS) measurements were used to investigate the molecular weight, backbone conformation on different length scales, coil size and the effect of chain aggregation in different solvents, and at different temperatures of the three polymers. Again, the polymers appear to be very rigid, with precise molecular weights and radii of gyration found.

F8T2 was extensively studied using optical absorption, photoluminescent (PL) emission, PL quantum efficiency (PLQE) and PL lifetime measurements of solutions and films deposited from them. Strong PL quenching effects were seen which have been attributed to interchain interactions at concentrations around 0.01 mg/ml, self-absorption effects dominate at higher concentrations above ~0.1 mg/ml. Large spectral changes were seen due to solvent choice, aggregation effects and thermal dissolution histories. Deposited films were also investigated with temperature dependent PL, which allowed some thermal transition temperatures to be found, atomic force microscopy and as bottom-gate/top-contact organic field-effect transistors.

Synchrotron Grazing Incidence Wide-Angle X-ray scattering (GIWAXS) studies were conducted on films deposited on flat substrates and polyimide alignment layers, as well as annealed within an in-situ vapour cell. F8T2 was found to be a poor scatterer of X-rays but F8BT appears to stack with a vertical interchain distance of 4.4 Å, with an interchain separation of 5.8 Å due to sidechains. Other copolymers of F8T2, poly[2,7-(9,9-dihexylfluorene)-alt-bithiophene] F6T2, and SC005 were found to be good candidates for GIWAXS study. Thermally treated PFO was very well indexed, with clear changes seen due to vapour exposure in situ.

Chapter 1 discusses vital, general concepts used to describe electro-conductive polymers, as well as a thorough review of the background of organic semiconductor characterisation. Further relevant details are covered in each results chapter.

Chapter 2 describes and defines the polymer samples and processing methods used throughout this thesis. The experimental techniques used are described in detail, as are the polymers involved and sample fabrication methods.

In **Chapter 3** small-angle neutron scattering undertaken at RAL is discussed, with results shown from F8T2 in various solvents, as well as studies of F8BT and PFO.

Chapter 4 covers both the results of multi-angle light scattering on F8T2 and other polyfluorenes in a variety of solvents. The effect of the passage of time of dissolved polymer solutions is investigated, along with size and molecular weight characteristics in different solvents. SAXS results from F8T2 solutions are also briefly discussed.

In **Chapter 5** a broad variety of spectroscopic investigations of F8T2 are discussed, both in solution and as thin-films. The effects of thermal treatments on thin-films are studied, including DSC results and the consequences on the electrical properties of thermal and solvent annealing on field-effect transistors.

In **Chapter 6** the results from a GIWAXS study on aligned and non-aligned thin-films of PFO and three co-polymers are shown. Unit cell size parameters are determined, and the effect of exposing PFO thin-films to solvent vapour is studied.

Table of Contents

Acknowledgements	3
Declaration of Originality	4
Abstract	5
Table of Contents	7
List of Figures	12
List of Tables	17
1 Background	19
1.1 Introduction to Semiconducting Polymers	20
1.2 History of Organic Semiconductors	20
1.3 Types of organic semiconductors	22
1.3.1 Categories of polymers	22
1.3.2 Polyfluorene Copolymers	23
1.4 Semiconduction	23
1.4.1 Origin of the Energy Gap	25
1.4.2 Peierls Instability and Conjugation Length	26
1.4.3 Excitons and Polarons	27
1.4.4 Charge Transport	27
1.4.5 Inorganic Semiconductors	28
1.4.6 OFETs	29
1.4.6.1 OFET Operation and Characterisation	29
1.5 Absorption and Fluorescence	31
1.6 Physical Characteristics	33
1.6.1 M_w , M_n , and Polydispersity	33
1.6.2 Radius of Gyration	33
1.6.3 Theta condition and good and bad solvents	34

1.6.4	Phases	35
1.7	Bibliography	38
2	<u>Materials and Experimental Methods</u>	<u>42</u>
2.1	Materials	43
2.1.1	F8T2	43
2.1.2	PFO/F8	43
2.1.3	F8BT	44
2.1.4	Solvents	45
2.2	Sample Processing	46
2.2.1	Solution Processing	46
2.2.2	Film Processing	47
2.2.2.1	Substrate Cleaning	47
2.2.2.2	Spin Coating	47
2.2.2.3	Contact Evaporation	48
2.2.2.4	HMDS	49
2.2.2.5	Rubbed Polyimide Layer	49
2.2.2.6	Surface Profilometry	49
2.2.2.7	Thermal Treatment	49
2.2.2.8	Optical Microscopy	50
2.3	Spectroscopy	50
2.3.1	Absorption Spectroscopy	50
2.3.2	Photoluminescence	51
2.3.3	Photoluminescence Quantum Efficiency (PLQE)	53
2.3.4	Photoluminescence Lifetime (PL (τ))	56
2.3.5	Photoluminescence with Temperature	58
2.4	Grazing Incident Wide-Angle X-Ray Scattering (GIWAXS)	58
2.4.1	In Situ Vapour Annealing	61
2.5	Small-Angle X-Ray Scattering (SAXS)	61
2.6	Small-Angle Neutron Scattering (SANS)	62
2.7	Multi-Angle Light Scattering (MALS)	63
2.7.1	Differential Refractometry	65
2.8	Field-Effect Transistors (FETs)	66

2.9 Other Techniques	67
2.9.1 Atomic Force Microscopy (AFM)	67
2.9.2 Differential Scanning Calorimetry (DSC)	67
2.9.3 Gel-Permeation Chromatography (GPC)	68
2.10 Bibliography	69
3 <u>Small Angle Neutron Scattering</u>	73
3.1 Introduction	74
3.2 Theory and Analytical Concerns	74
3.3 Previous Work	79
3.4 Results	81
3.4.1 F8T2	82
3.4.2 F8BT and PFO	88
3.5 Conclusions	89
3.6 Suggested Further Work	90
3.7 Bibliography	92
4 <u>Multi-Angle Light Scattering and Small Angle X-Ray Scattering</u>	97
4.1 Introduction	98
4.2 Theory and Analytical Concerns	98
4.2.1 Rayleigh Scattering	98
4.2.2 Light Scattering	99
4.2.3 Small Angle X-ray Scattering	102
4.3 Previous Work	102
4.4 Light Scattering Results	104
4.4.1 Differential Refractometry	104
4.4.2 Light Scattering	106
4.4.3 Light Scattering of F8T2 in THF	108
4.4.4 Light Scattering of F8T2 in Chloroform	112
4.4.5 Light Scattering of F8T2 in Toluene	112
4.4.6 Light Scattering of PFO	115
4.4.7 Light Scattering of F8BT	117
4.5 SAXS Results	118

4.6	Conclusions	120
4.7	Suggested Further Work	121
4.8	Bibliography	123
5	<u>Spectroscopy and Thin Films</u>	<u>127</u>
5.1	Introduction	128
5.2	Theory and analytical concerns	128
5.3	Previous Work	129
5.4	Results	130
5.4.1	Concentration Dependences of F8T2	130
5.4.1.1	F8T2 in THF Solutions	130
5.4.1.2	F8T2 Absorption and PL in THF Solutions and Thin Films	133
5.4.1.3	F8T2 in Toluene Solutions	135
5.4.1.4	F8T2 in Other Solvents	137
5.4.2	Solvatochromic Shifts of F8T2	139
5.4.2.1	Solvatochromism in Solution with Concentration	140
5.4.2.2	Time Dependent Effects of F8T2 in Solution	143
5.4.2.3	Spectral Results Summary and Conclusions	147
5.4.3	Lifetime Measurements of F8T2	147
5.4.4	PLQE Measurements of F8T2 Films	150
5.4.5	Thermal Treatment of F8T2 Films	152
5.4.5.1	Photoluminescence	152
5.4.5.2	DSC	154
5.4.5.3	AFM	156
5.4.6	Field-Effect Transistors	159
5.4.6.1	Ageing and Thermal Treatments	161
5.4.6.2	Ageing and Vapour Treatments	162
5.5	Conclusions	163
5.6	Further Work	164
5.7	Appendix A	165
5.8	Bibliography	167

6	<u>Grazing Incident Wide-Angle X-Ray Scattering (GIWAXS)</u>	170
6.1	Introduction	171
6.2	Theory and analytical concerns	171
6.3	Previous Work	172
6.4	Results	176
6.4.1	F8BT	177
6.4.2	PFO	179
6.4.2.1	In Situ Vapour Annealing	182
6.4.3	Other Polymers	185
6.4.3.1	F6T2	185
6.4.3.2	SC005	187
6.5	Conclusions	189
6.6	Further Work	190
6.7	Bibliography	191
7	<u>Conclusions and Further Work</u>	194
	Chapter 3: Small Angle Neutron Scattering	195
	Further Work	195
	Chapter 4: Multi-Angle Light Scattering and Small Angle X-ray Scattering	196
	Further Work	196
	Chapter 5: Spectroscopy and Thin Films	197
	Further Work	197
	Chapter 6: Grazing Incident Wide Angle X-Ray Scattering	198
	Further Work	198

List of Figures

Figure 1 Diagram showing energy levels involved for electron promotion and orbital hybridisation to sp^2 from (19)	24
Figure 2 Schematic of sp^2 hybridisation and double bonding of carbon atoms. The central sigma bond and outer pi bonds are shown. Bonding with H with the remaining sp^2 orbitals ethylene is formed. (23)	24
Figure 3 Showing that as the number of bonds N, increases the energy gap decreases from (6)	25
Figure 4 OFET geometries (23)	29
Figure 5 Output characteristics plot of F8T2 OFETs on OTS, showing the linear and saturation regimes, and the effect of increasing gate voltage.	30
Figure 6 Schematic showing vibronic energy levels in the S_0 and S_1 states and associated absorption and emission spectra. The increased intensity of 0-1 over 0-0 is due to longer bond length in the S_1 state. (23; 36)	32
Figure 7 Schematic diagrams of (a) Nematic (b) Smectic and (c) Chiral ordering	36
Figure 8 Structures of polymers used (a) PFO, (b) F8T2, (c) F8BT, (d) F6T2	45
Figure 9 Photospectrometer internal schematic	50
Figure 10 PL Intensity of F8T2 film to show the angular dependence of Fluoromax-3	52
Figure 11 Transmission of Hellma cuvettes (12)	52
Figure 12 Photoluminescence of 10 mg/ml F8T2 solution with exciton movement across cuvette towards detector. Increase in PL is towards detector.	53
Figure 13 Diagram showing the three measurements needed for PLQE. (a) No Sample, (b) Sample Off Beam, (c) Sample In Beam	54
Figure 14 Intensity x Wavelength against wavelength results for PLQE measurements of F8T2 thin film, with excitation peak at 450 nm shown inset	55
Figure 15 Schematic diagram of PL lifetime setup (16)	57
Figure 16 Example plots of (a) PL lifetime decay, (b) 1st moment by wavelength calculations of F8T2 in THF thin films described in <i>Chapter 5</i>	57
Figure 17 Layout of the CHESS facility at Cornell University	59
Figure 18 Real-space experimental setup for GIWAXS at d-line, CHESS (21)	60
Figure 19 Determination of sample-detector distance by similar triangles	60
Figure 20 Cross-section of Solvent Flow-Cell for GIWAXS (21)	61
Figure 21 Schematic of the LOQ detector	62

Figure 22 Internal schematic of Brookhave BI-DNDC flow cell and detectors (31)	65
Figure 23 Coherent scattering from two planes separated by d	75
Figure 24 Example of contrast improvement through deuteration	76
Figure 25 Different physical conformations for values of n in the Period regime (14)	78
Figure 26 Schematic description of the scattering data and proposed structures of PFs in toluene: (a) a network-like structure with cross-linked nodes; (b) a structure of rodlike particles forming Gaussian coils (scenario I) or sheet-like aggregates (scenario II) in the longer length scales, and (c) a structure of fully dissolved rodlike particles (essentially single polymer chains) (26)	80
Figure 27 Neutron scattering intensities against q for F8T2 in (a) d-THF, (b) CDCl ₃ , (c) d-Toluene. Variation in scattering with ageing solutions 24 hours is shown. Summary of magnitude of powers of q for each solvent is shown in (d).	83
Figure 28 Neutron scattering intensities against q for F8T2 in (a) d-THF, (b) CDCl ₃ . Variation in scattering with temperature of solutions is shown. The trend of the (mod) index n is shown for d-THF in (c) and CDCl ₃ in (d), with formulae for n from T in Kelvins.	86
Figure 29 Arrhenius plots of 10 mg/ml F8T2 in (a) THF and (b) CDCl ₃	87
Figure 30 Scattering intensity variation of F8T2 in d-THF against concentration is shown in (a), (b) graphically shows the power n against concentration, having a mean value of 0.95 ± 0.07 .	88
Figure 31 Neutron scattering intensity with q of 10mg/ml F8T2, PFO and F8BT in (a) d-toluene, (b) CDCl ₃ .	88
Figure 32 Example of grid-like structure in a Zimm Plot showing 4 concentrations (C1-C4) and 8 angular extrapolations (more horizontal lines) of F8T2 in THF	101
Figure 33 Differential Refractometry results, (a) direct voltage of F8T2 in THF, with C0,1,2,3,4,5,0 shown (b) n vs c of F8T2 in THF, (c) RI Area vs c of PFO in THF	105
Figure 34 Wyatt Astra strip chart example showing pure THF (solvent), 6 increasing concentrations of F8T2 in THF (C2-C6), 4K polystyrene standard in THF (PS) and pure THF	107
Figure 35 Initial Zimm plots of F8T2 in THF, showing robustness of R_g and M_w values despite what appear to be large changes in data and fit quality	109
Figure 36 Zimm Plots of 'high' sample F8T2 in THF with time (a) +1 day, (b) +2 days, (c) +3days (d) +6 days	110
Figure 37 Zimm Plots of F8T2 in chloroform solution (a) Freshly prepared, (b) +1 Week	112
Figure 38 Zimm Plots of F8T2 in toluene solution, showing the robustness of the analysis to loss/gain of a concentration	113

Figure 39 Zimm plots of F8T2 in toluene solution taken after 1 week. Analysed with (a) 3 concentrations, (b) 4 concentrations.	114
Figure 40 Schematic diagram of possible F8T2 configurations in (a) THF (b) fresh chloroform (c) 1 week old chloroform and (d) aggregated toluene solutions.	115
Figure 41 Zimm Plots of PFO in (a) THF and (b) toluene solutions.	116
Figure 42 Zimm plots of F8BT in toluene (a) Freshly made, (b) +24 hours	117
Figure 43 Scattering Intensities of F8T2 in THF. (a) absolute, (b) Background Subtracted (c) Pure THF scattering (d) F8T2 30 mg/ml scattering and integration range used	119
Figure 44 Scattering results for F8T2 in toluene (a) Perod plot (b) SAXS image of 30mg/ml problem	120
Figure 45 Overall absorption and PL spectra of F8T2 using THF as the solvent, showing labelled vibronic peaks	129
Figure 46 PL intensities of F8T2 in THF over 5 decades of concentrations (a) Low, (b) Mid, (c) High. Legend shows concnentraion in mg/ml. (d) Integrated PL intensity to gaussian fit of each peak	131
Figure 47 Absorption of F8T2 in THF (a) solution, note *scale to left for high concentrations with 1mm lightpath and (b) film by concentration (c) PL of films by concentration normalised to 0-1 peak	133
Figure 48 PL of F8T2 in toluene solution at concentrations from 0.0001 mg/ml to 1 mg/ml	135
Figure 49 PL Spectra of aged (~2 weeks) F8T2 in toluene solutions at (a) high and (b) low concentrations dashed are aged spectra	136
Figure 50 PL spectra with concentration of (a) THF (b) Toluene (c) Xylene (d) Chlorobenzene (e) Chloroform *0.01 mg/ml PL reduced by a factor of 15 **0.01 mg/ml PL reduced by a factor of 30 ***0.01 mg/ml PL reduced by a factor of 15, 10 mg/ml reduced by a factor of 2	138
Figure 51 Vials of F8T2 at concentrations of 10, 1 and 0.1 mg/ml (1) Freshly made and (2) after ~24 hours in (a) THF (b) Toluene (c) Xylene (d) Chlorobenzene (e) Chloroform	139
Figure 52 Vials of F8T2 at concentrations of 10, 1 and 0.1 mg/ml (1) Freshly made and (2) after ~24 hours in (f) Hexane (g) Acetone	140
Figure 53 PL intensities of F8T2 in five solvents at concentrations of (a) 0.01 mg/ml (b) 0.1 mg/ml (c) 1.0 mg/ml (d) 10 mg/ml	141
Figure 54 Absorption spectra of solutions of F8T2 in five solvents at (a) 0.01 mg/ml (b) 0.1 mg/ml (c) 1.0 mg/ml.	142

Figure 55 Offset PL of fresh (solid line) and old (dashed line) 1 mg/ml solutions of F8T2 in (a) THF (b) Toluene (c) Xylene (d) Chlorobenzene (e) Chloroform	143
Figure 56 PL of 10mg/ml solutions of (a) THF (b) Toluene (c) Xylene after (1) +0hrs (2) +20hrs (3) +42hrs (4) +70hrs (5) +92hrs (5*) sediment	144
Figure 57 PL of films of (a) THF (b) Toluene (c) Xylene and (d) absorption of same films spin coated	146
Figure 58 Absorption spectra of films made from fresh (full lines) and aged (dashed lines) F8T2 in solutions.	147
Figure 59 Lifetime Expectation Values with time of F8T2 in THF, toluene and xylene solutions	149
Figure 60 Single Exponential Decay Lifetimes of F8T2 in THF over a range of concentrations	150
Figure 61 PL intensity maps against temperature of (a) Spin Coated (b) Cooled and (c) Quenched F8T2 films. (d) Integrated PL	153
Figure 62 PL of films annealed and quenched, with the quenching temperature shown. The starred 290° C spectrum has been slowly cooled, and the unannealed is purely spin coated.	154
Figure 63 DSC results of F8T2, showing heating and cooling cycles	155
Figure 64 AFM images of F8T2 films from fresh solutions (1) 10x10µm (2) 1x1µm (a) Spin cast (b) Quenched (c) Cooled	157
Figure 65 AFM images of F8T2 films from aged solutions (1) 10x10µm (2) 1x1µm (a) Spin cast (b) Quenched (c) Cooled	158
Figure 66 Output Characteristics of F8T2 OFETS with (a) no treatment, (b) HMDS (c) OTS Output Characteristics and (d) Transfer characteristic. Solid and dashed lines indicated different devices	160
Figure 67 Transfer Characteristics for heat treated F8T2 toluene solutions, (a) fresh, (b) aged	161
Figure 68 (a) output (dashed have had vapour) and (b) transfer characteristics for a 10µm F8T2 OFET, made from freshly dissolved toluene solution	162
Figure 69 All spectra for (a) THF, (b) Toluene, (c) Xylene	165
Figure 70 All spectra for (d) Chlorobenzene (e) Chloroform	166
Figure 71 GIWAXS intensity plots of an annealed F8BT film on silicon. Showing (a) the vertical 90-120° integration region and (b) the in plane 150-180° region	172

Figure 72 (a) Likely packing structure of F8BT in thin films. (b) and (c) shown alternatives (3)	173
Figure 74 Suggested PFO repeat cell (a) along the backbone and (b) viewed from the b-axis from (8). PFO structure along the backbone with sidechain crystallinity is shown in (d) and interdigitation in dimer structure (e) from (8).	175
Figure 75 AFM images of rubbed alignment grooves on polyimide films (a) 5x5 μ m, (b) 2x2 μ m	177
Figure 76 GIWAXS scattering intensities of F8BT thin films, on (a) silicon, (b) incident beam parallel to the rubbing direction, and (c) with the incident beam perpendicular to the rubbing direction	177
Figure 77 GIWAXS image of annealed F8BT film on silicon substrate, with peaks assigned where possible.	178
Figure 78 GIWAXS images of PFO annealed on (a) Silicon substrate, and with (b) Beam parallel to alignment and (c) perpendicular.	179
Figure 79 PFO crystal planes	180
Figure 80 2D GIWAXS scattering intensity plot showing the indices of all peaks	182
Figure 81 Scattering intensity images of annealed PFO film, with solvent added at T = 0s	183
Figure 82 Lattice spacing changes of annealed PFO films with time from exposure to toluene vapour for (a) h axis, (b) k axis, (c) l axis	184
Figure 83 GIWAXS intensity images of annealed PFO films exposed to toluene vapour at T = 0s.	185
Figure 84 GIWAXS images of (a) the Kapton window background, (b) F6T2 film annealed at 90° and (c) 150°	186
Figure 85 GIWAXS image of F6T2 film annealed at 150° C, with peak indices shown	186
Figure 86 GIWAXS intensity images of SC005 annealed on (a) silicon substrate, and on grooved PI (b) parallel and (c) perpendicular to the incident beam direction	188

List of Tables

Table 1 Summary of polymers used	44
Table 2 Abbreviations, polarity and boiling points of solvents used. All data taken from Sigma Aldrich, except polarity. * Density at 20°C (8)	45
Table 3 Specification of pre-patterned substrates from Fraunhofer IPMS.	48
Table 4 Specification of evaporated FET contacts	48
Table 5 Summary of SANS experiments	63
Table 6 Detector angles in a Dawn EOS	64
Table 7 Scattering lengths of H, D and C atoms (6)	76
Table 8 Structural characteristics for Perod analysis	78
Table 9 Structural characteristics for Perod anlaysis with $1 < n < 3$	78
Table 10 Values of n for F8T2 in each solvent over time	85
Table 11 Values of n for each polymer/solvent combination studied	89
Table 12 Variations in slope and axis from different light scattering formulations (12)	101
Table 13 dn/dc values of the polymer.solvent combinations used in this work.	
*Visotek result	106
Table 14 Monomer size and weight of F8, F8T2 and F8BT used for light scattering (31) (32) (33)	108
Table 15 Radius of Gyration and Molecular Weight results for 3 seperate light scattering experiments on F8T2 in THF	109
Table 16 RMS radius and molecular weight of polymer samples as they dissolve determined by light scattering	111
Table 17 Calculated values for F8T2 in CHCl ₃	112
Table 18 R_g and M_w results for F8T2 in toluene with age	114
Table 19 R_g and M_w values expressed in RUs for PFO in THF and Toluene solutions	116
Table 20 GPC results of PFO in THF	116
Table 21 R_g and M_w values obtained by light scattering and in RUs, of F8BT in toluene over 1 week.	117
Table 22 Values of n for all available SAXS measurements.	120
Table 23 Peak positions of 0-0, 0-1, and 0-2 fluorescent transitions of F8T2 in F8T2 in THF soltuions	133
Table 24 Film thicknesses and feature sizes of F8T2 films spin coated from various solvents, freshly prepared and after 92 hours.	146

Table 25 Lifetime Expectation Values of F8T2 films spin coated from a range of solvents. *mean of 6 points, not 7.	148
Table 26 PLQE values for all F8T2 and solvent combinations studied	151
Table 27 Transistion temperatures of 3 F8T2 samples, determined by Kinder et al (2).	155
Table 28 Table showing RMS roughness and average heights of AFM images above	159
Table 29 Output characteristics for F8T2 films from 10mg/ml toluene solutions, for no treatments, HMDS and OTS	160
Table 30 OFET characteristics for F8T2 in toluene films, from fresh and aged solutions.	162
Table 31 Results of working F8T2 OFETs, with films made from fresh and old solutions in toluene	163
Table 32 F8BT unit cell dimensions from (3)	173
Table 33 Repeat unit cell values of PFO, from various groups	176
Table 34 Showing d-spacings for peaks in GIWAXS intensity of annealed F8BT	178
Table 35 Values for crystallographic planes, from experiment and for comparison with modelling (a) h, (b) k, (c) l.	181
Table 36 d-spacing of indexed peaks of an annealed F6T2 film	187
Table 37 d-spacing positions seen in SC005 annealed on silicon substrates and perpendicular aligned	188
Table 38 d-spacings seen in SC005 fim aligned parallel to the incident beam and likely assignments	189

Chapter 1

Background

This chapter discusses the background of the major topics covered in this work. Initially the history of semiconducting polymers is covered, with particular importance given to polyfluorenes, and then the vital properties of this interesting class of material are discussed. Due to their importance in this work the physical and spectroscopic characteristics are covered in detail, as well as the manifestation of electrical conductivity in polymers.

1.1 Introduction to Semiconducting Polymers

The understanding and practical application of semiconducting materials has changed the world in incredible and unexpected ways. The first recorded use of the word 'semiconducting' was by Alessandro Volta in 1782 (1), yet the first recorded observation of semiconduction in a material was by Michael Faraday in 1833 (2). Since those early days the understanding and usage of semiconducting devices has increased enormously. The most world changing development from these materials was the invention of the solid state transistor at AT&T's Bell Labs in 1947 by Bardeen and Brattain, in the Solid State Physics Group run by Shockley, these three later received the Nobel Prize in Physics in 1956 (3). Transistors were able to do things valves could do but faster, more cheaply and in a much smaller package. Without the discovery and subsequent developments in semiconductor technology the modern world would not exist. Transistors in particular, underpin almost all of the technological advances of the past 50 years, including mobile phones, solar cells, LEDs, computers and the internet.

Polymers have long been thought of insulating materials, but since the first report of organic electroluminescence in 1963 by Pope et al (4), this view has changed, and there has been a large amount of research effort directed at these new sorts of semiconductors. Organic semiconductors, both conduct in a different way to inorganic semiconductors and are processed and used differently. They are much simpler and cheaper to process than inorganic devices due to the ease of solution processing, and although they function more slowly are finding many uses in more niche devices particularly where their low power consumption and physical flexibility can be beneficial.

A polymer, coming from *poly* a Greek word meaning many and *meros* meaning parts, is a collection of single units (monomers) joined together to form a long molecule, usually containing a carbon based backbone. Chains made from small numbers of monomers are referred to as oligomers, such as a dimer (two repeat units), trimer (three repeat units) etc. Conjugated polymers are a particular class of polymeric materials with a strong σ -bonded backbone and alternating single and double π -bonds, leading to a delocalised electron cloud along the length of the polymer and eventually conduction.

1.2 History of Organic Semiconductors

The first report of electroluminescence (EL) in an organic semiconductor was in 1963 by Pope et al (4), showing EL from crystalline anthracene in very high electric fields. Other reports

followed, including Helfrich and Schneider in 1965 (5), among others. Unfortunately this did not cause the surge in research it perhaps deserved, due to the difficulties in growing millimetre sized single crystals of anthracene and the high applied fields needed (50–1000V).

The area of polymer electronics was really born by the discovery of metallic conduction in doped polyacetalene in 1977 by Shirakawa and Chiang (6). Shirakawa, MacDiarmid and Heeger (7) received the Nobel Prize in Chemistry in 2000 for “the discovery and development of conductive polymers”. Interest in organic materials for EL was increased during the 1980s, by the creation of the first organic light emitting diode (OLED), from evaporated small molecules films and which operated at low voltages (8). In 1986 researchers at the Mitsubishi Electric Corporation made the first organic FET device, with polythiophene as the semiconducting material (9; 10). At the same time C W Tang published the first organic photovoltaic device (11) while working at the Eastman Kodak Company.

The next important step in the now growing field of organic electronics was the development of a polymer light emitting diode (PLED) structure based on the conjugated polymer poly(2,5-diphenyl-1,4-phenylenevinylene) (PPV), by Burroughes et al (12) in 1990, with similar devices following. The development of a solution processable precursor to PPV (13) in 1992 made spin-cast devices from conjugated polymers an attractive prospect for simple LED fabrication. Since the first LED other devices including field effect transistors (FETs) and photovoltaic solar cells have been developed and improved from solution processed conjugated polymers. Although levels are unlikely to match those of inorganic semiconductors, organic electronics is attracting a lot of commercial interest.

Due to large increase in device efficiency over the last 20 years, organic solution processed LEDs and FETs are becoming more commonplace in the consumer field. RFID chips are an obvious example (14), but small screens on mobile phones (15), MP3 players and cameras have been produced, as well as much larger full HD (16) and even flexible displays, from many different companies.

An important benefit to using solution processable semiconducting polymers is the ease of deposition compared to the complex growth of an inorganic semiconductor crystal. Much research (17) is being focused on inkjet (18) and gravure printable devices (19).

1.3 Types of organic semiconductors

Small molecules are monomeric particles, and hence simplest to understand, and there is a lot of overlap in the understanding their properties and those of larger polymer materials. Most notably however, is that small molecules are usually deposit into films via vacuum deposition, where polymers are solution processed and spin coated.

Short polymer chains, usually below ~ 20 repeat units are referred to as oligomers, with particularly short chains called dimers (with two monomers) and trimers (with three), linear polymer lengths extend from ~ 20 to 10^{10} monomers.

A variety of organic materials are now being studied for their semiconducting properties including those based on fluorene polymers, polythiophenes, dendrimers (centrally branched polymers) and those containing Buckminsterfullerene.

1.3.1 Categories of polymers

When polymers are composed of only a single monomer species, they are referred to as homopolymers. Monomer is a slight misnomer here, as monomer specifically refers to a small molecule capable of polymerisation (20). From here on however, monomer is used to describe the repeat unit of a polymer, ie a polymerised monomer unit. Polyfluorene is a homopolymer used in this work. When polymer chains are composed of two types of monomer they are called copolymers, most of the polymers studied in this work are copolymers with polyfluorene. Additionally, if three varieties of monomer unit are combined they are called a terpolymer (21). Monomer distribution in copolymer chains can be divided into four main categories show below:

- Statistical copolymer – here the monomers in the chain are randomly distributed

~AAABBBABABABBBBABBBBBBAAAAB~

- Alternating copolymer – here the monomer species have a regular repeat placement along the chain

~ABABABABABABABABABABABABAAB~

- Block copolymer – these are composed of large ‘blocks’ of each monomer along the length of the polymer chain.

~AAAAAABBBBBBAAAAAAAAABBBBBBBB~

- Graft copolymers – these manifest as blocks of a monomer grafted onto a backbone comprised of a second monomer

Branching is a further structural property of polymers, leading to various architectures and properties.

1.3.2 Polyfluorene Copolymers

The polymers discussed in this thesis are all polyfluorene copolymers. The fluorene monomer was first isolated prior to 1883 by Barthelot (22), and named for its fluorescent properties, and fully polymerised into a conjugated form in 1972 (23). Substantial research into the material did not occur until after the publication of the work of Shirakawa et al (6).

1.4 Semiconduction

The vital property of conjugated polymers that gives rise to their semiconducting properties is the hybridisation of SP^2 orbitals in the material.

Carbon atoms have six electrons in $1s^2 2s^2 2p^2$ orbitals, indicating that the $2p_x$ and $2p_y$ orbitals have no electrons. This would be expected to give rise to a divalent element with two valence electrons available for covalent or ionic bonding. This however is not seen, and carbon is actually tetravalent, meaning four electrons are available for bonding. In this case one electron from the 2s orbital is promoted to 2p, creating four unpaired electrons in $1s^2 2s^1 2p^3$, and hybridisation of these occurs. Three levels of hybridisation may occur, sp^1 , sp^2 , or sp^3 , formed from the linear combinations of 2s and 2p orbitals.

sp^1 – This results in two sp and two p orbitals and triple bond formation. Here the two electrons in sp^1 orbitals lie in opposite directions along the z axis, with $2p_y$ and $2p_x$ lying along the x and y axis.

sp^3 – In sp^3 hybridisation the 2s mixes with all three 2p orbitals, resulting in four sp orbitals. To minimise electron-electron repulsion they are directed to the four corners of a tetrahedron. This allows carbon to make four sigma (single) bonds. Polymers with sp^3 hybridisation have strong sigma bonded backbones and do not conduct.

sp^2 – hybridisation is needed for conduction. In this hybridisation the 2s orbital mixes with two 2p orbitals leaving 1p and 3sp orbitals. This is shown below in *figure 1* and leads to double bonding between carbon atoms.

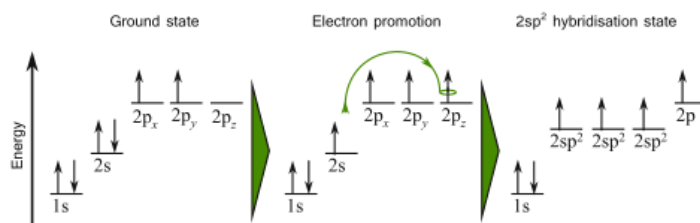


Figure 1 Diagram showing energy levels involved for electron promotion and orbital hybridisation to sp^2 from (19)

Here the three sp orbitals lie in a plane orthogonal to the unchanged p_z orbital, and two sp orbitals overlap and form a sigma bond. This strong backbone bonding means unbonded p orbitals come close enough above and below the sigma bond to form a π bond, and lead to conjugation. Sigma bonds are very strong and highly localised, whereas π bonds are not and this delocalisation is responsible for these materials' semiconducting properties. Materials with alternating single and double bonds in their structure are referred to as conjugated. Structurally, the formation of the π bond hinders rotation around the strong sigma bond (24), with hybridised double bonding shown schematically below in *figure 2*.

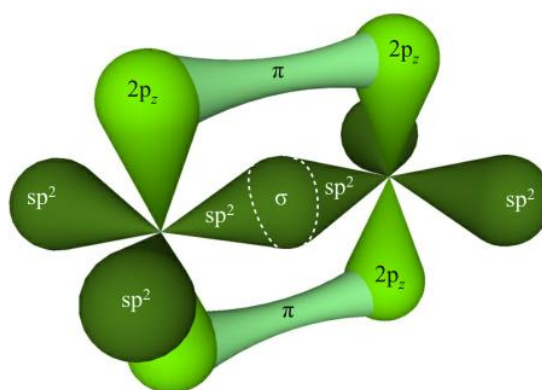


Figure 2 Schematic of sp^2 hybridisation and double bonding of carbon atoms. The central sigma bond and outer π bonds are shown. Bonding with H with the remaining sp^2 orbitals ethylene is formed.(19)

1.4.1 Origin of the Energy Gap

Combining the wavefunctions through a linear combination of atomic orbitals (LCAO) a molecular orbital (MO) can be built up. Superposition of φ_1 and φ_2 wavefunctions leads to two solutions, if both are sp atomic orbitals they lead to σ bonding and σ^* antibonding orbitals.

$$\psi_{\sigma} = \varphi_1 + \varphi_2 \quad [1.1]$$

$$\psi_{\sigma^*} = \varphi_1 - \varphi_2 \quad [1.2]$$

Sigma bonds are very strong as the electrons are highly localised, leading to energy gaps $\sim 8\text{eV}$ (25). As discussed in *Section 1.4*, carbon-carbon double (or triple) bonds are formed by electrons in the p_y and p_x orbitals, and known as π -bonds. In the simplest case, as above, π and π^* bonding and anti-bonding orbitals are formed. However, multiple carbon atoms form delocalised cloud around sigma bonds and many more bonding and antibonding states are formed. This leads to the highest occupied molecular orbital (HOMO) ie. the highest occupied π -bonding state, and lowest unoccupied molecular orbital (LUMO), the lowest unoccupied π -antibonding state. This transition from π to π^* defines the energy gap E_g , as seen in *figure 3*. When an electron is promoted from pi to pi* it can travel along the length of the chain, allowing the polymers to support an electric current. Typically E_g is 2-3 eV, allowing transitions in the optical region.

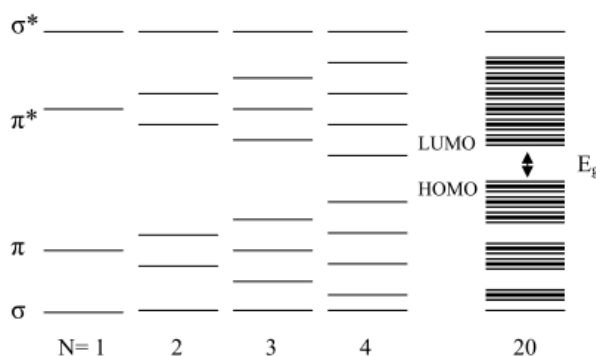


Figure 3 Showing that as the number of bonds N , increases the energy gap decreases from (26)

When an electron is promoted to the LUMO from the HOMO an empty electronic space is left, called a hole which is characterised as an electron with positive charge. These electron hole pairs are attracted by coulombic attraction, leading to excitons discussed in *Section 1.4.3* below.

1.4.2 Peierls Instability and Conjugation Length

As the length of the polymer extends N increases, and in an ideal case tends to infinity. In that case E_g would tend to zero as a continuum of filled and unfilled π and π^* states exist. The Peierls transition refers to instability in this hypothetical long chain, which causes the zero energy gap to not be achieved. Due to atomic displacement within the system it is disrupted and a lower energy state is achieved by delocalisation of the electrons along the chain combined with variations in bond length (27). In practice the E_g limit tends to 20-30 π -bonds(25).

Other deviations from ideal behaviour are caused by torsion along the polymer chain, as p_z orbitals must be parallel to each other to overlap. Angles between neighbouring carbon rings greater than $\sim 40^\circ$ from coplanar do not allow the conjugated structure to continue (28) as such long polymers are regarded as finite conjugated sections, with a conjugation length as the mean length over which π electrons delocalise, which is defined as the length of an oligimer which would have the same E_g (29). Variation in conjugation length over different physical chains leads to a broad featureless absorption peak.

Two obvious models can describe polymers in solution, the segment model where the backbone is broken up by large rotations, meaning a long chain is made up of many discrete, short segments. Or a worm like model, where the backbone slowly curves due to many small rotations around each bond. The curvature can be quantified by the effective conjugation length l_c , the length of an oligimeric segment which has the same value of E_g as the disordered polymer chain, clearly this has some physical meaning in the segment model. This is relationship is shown in [1.3], where $E_{g'}$ is the energy gap due to effective conjugation length, E_n is the energy gap of an oligimeric segment of length l_c and E_0 is the limit of the energy gap as the chain length tends to infinity.

$$E_{g'} \equiv E_n = E_0 + \frac{\text{constant}}{l_c} \quad [1.3]$$

This variation in energy gaps in amorphous materials due to variations in conformations leads to a broad absorption peak made up from absorption from a variety of chains with various E_g values.

1.4.3 Excitons and Polarons

After photoexcitation from the HOMO to the LUMO, the electron and hole are bound by coulombic attraction. There are various types of excitons in thin films. Inorganic semiconductors form Mott-Wannier excitons with a very low binding energy ~ 0.01 eV, so are very weakly bound. Organic materials have much more localised electrons, with larger binding energies. Frenkel electron-hole pairs have a binding energy of ~ 0.3 eV, meaning charge separation in photovoltaics is much harder in organic devices. Charge-transfer excitons are also found in organic semiconductors, but in this case the electron and hole are on different polymer chains and have lower binding energies, so are easier to separate into free charge carriers. Both types are seen in photoexcited films. Note that the energy gap seen in organic semiconductors measured by optical absorption is reduced by the small binding energy of the exciton.

Polarons are quasiparticles of chain distortions due to localised charge, from separated electrons and holes which have not formed an exciton. This additional charge causes the chain to deform, and as a charged particle it can move along the chain or between chains in the presence of an electric field. Polarons are an important field of study in donor-acceptor blends. To discuss charge transport more than just polaron models are needed, due to the distributed nature of polymer chains, charges must 'hop' between them.

1.4.4 Charge Transport

Although band like transport is found in highly crystalline organic films, such as anthracene it is not a good description of charge transport in the usually highly disordered amorphous systems seen in polymer films. Energetic and spatial disorder in the film leads to distribution of density of states. All organic semiconductors are intrinsic semiconducting materials, and due to the soft nature of the materials doping atoms can physically move in an electric field, so doping is very rare.

Charge carriers in disordered organic semiconductors are polaronic in nature, when charges hop from chain to chain it is then clearly from a site where a charge is with its associated polaronic distortion, to an undistorted free site on a neighbouring chain. The rate limiting step in charge transport is the thermally activated hopping between chains or molecules. 'Hopping' being thermally activated quantum mechanical tunnelling between sites. Various models of charge transport have been developed over the years. The earliest approximation for polaron hopping rate was based on semiclassical Marcus electron transfer theory (30; 31), but needed

unphysically large polaron binding energies to reproduce observed values, and the large amount of disorder in films needs to be taken into account. Bassler proposed a model in 1993 (32) where the density of states can be approximated by a gaussian distribution, with varying physical distances and orientations between localised states from which random hopping occurs. The variable range hopping model is also commonly used to model charge transport in polymers, where a gaussian density of states is still used, but hopping is not confined to nearest neighbour sites, assuming the activation energy needed is low (33). Poole-Frenkel type field dependence of charge mobility is regularly seen in devices.

1.4.5 Inorganic Semiconductors

It is worth briefly comparing conduction in organic semiconductors to those of inorganic semiconductors, as organics are being used to create devices initially developed with crystalline, doped inorganic semiconductors in mind. Dopants are rarely used in plastic electronic devices, as they can physically move during use, and large scale crystallinity is still very different to that seen in silicon etc. Some crystalline organic semiconductors are used, but in many ways this complex processing step can negate the benefits of using polymeric semiconductors for electronic devices.

In inorganic crystalline structures Bloch electrons move in a periodic potential of ion cores arranged in a Bravais lattice, with the periodicity of the lattice. Bloch electrons are independent electrons in this lattice which obey the Schrödinger equation in a periodic potential, and eigenstates have the form of a plane wave multiplied by a function with the periodicity of the lattice.

Inorganic semiconduction is described by band theory, of which the free electron model is the simplest. It assumes valence electrons do not interact with the ion-core potentials of the materials and there are no electron-electron interactions. The weak binding model describes the overall aspects of band structure. In this model, the electron wavevector satisfies the Bragg condition of $\underline{k} + \underline{G} = \underline{k}'$, and it undergoes Bragg scattering back on itself. Solving for E_k combining the incident and diffracted waves leads to an energy or band gap and energy bands of allowed electron states. As energy states are filled taking into account the Pauli Exclusion Principle the highest occupied energy level (at 0 K) is the Fermi Level. In metals this is above the band gap and conduction is easy, in insulators and semiconductors this is between the valence and conduction bands. If the energy gap is large, electrons cannot reach the

conduction band and this is an insulator. If the gap is smaller (~ 1 eV) electrons can gain enough energy to reach the conduction band, and if placed in an electric field will conduct.

1.4.6 OFETs

The transistor was one of the most important inventions of the 20th century. The modern world runs on them. Shockley Bardeen and Brattain received the 1956 Nobel Prize for their invention (3), and prior to their invention vacuum tubes were used as switching/amplification devices. The basic principle of a Field Effect Transistor (FET) was patented by Julius Edgar Lilienfeld in 1925, but practical devices were only achieved in the 1950s.

A transistor is effectively a switchable amplifier. The device architecture is that of a metal-insulator-semiconductor capacitor, where one plate is a semiconductor containing a channel of length L , with the addition of source and drain contacts on the semiconductor. Applying a voltage to the gate contact (the metal plate of the capacitor) allows current to flow from the source to the drain contacts. OFETs (Organic FETs) differ from inorganic FETs as the semiconducting material is organic.

There are four device geometries for an OFET, shown below in *figure 4* (19). The gate material is silicon, with a silicon dioxide insulating layer. In this work, I mostly used devices with the architecture seen in *figure 4(c)* with pre-patterned source and drain contacts. When evaporated source and drain contacts were used the architecture is shown in *figure 4(b)*.

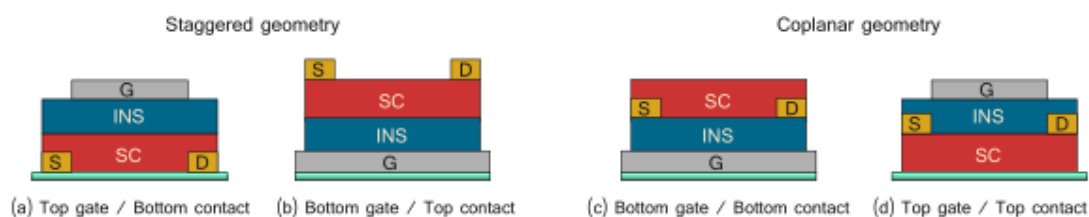


Figure 4 OFET geometries (19)

1.4.6.1 OFET Operation and Characterisation

I will discuss the operation of a hole-transporting, p-type device, as F8T2 used in OFETs in this work is a p-type material. OFETs are switched on and off by the accumulation of a layer of charge between the source and drain contacts at the semiconductor-insulator interface. With no voltage applied to the gate the transistor is off and no current can flow from the source to the drain. By applying a voltage to the gate electrode, a layer of charge is accumulated as in a capacitor. With a negative V_g holes are accumulated, and electrons with positive. The

semiconductor now has excess charge and can be used to modulate the conductivity of the channel. However, as not all charges can be used for conduction, due to trapping sites the gate voltage V_g must increase to above the so called threshold voltage V_{th} to accumulate mobile charges. More trapping sites lead to a higher threshold voltage. At this point the transistor can be turned on, and if a potential is applied at the drain contact V_D , (but $V_D \ll V_g - V_{th}$) a larger current than purely ohmic conduction of the bulk can flow. The FET is now operating in the linear regime, where drain current I_D , is directly proportional to V_D . Further increasing V_D to $V_g - V_{th}$ the conducting channel is 'pinched off', the local potential at the drain contact is $V_g - V_{th}$ and there are no mobile charge carriers anymore. Because of this a depletion region is formed between the point where pinch off occurs, where $V(\text{along the channel}) = V_g - V_{th}$ and the drain electrode. A space-charge limited current can flow across this region $I_{D, sat}$, and at this drain voltage the drain current begins to saturate. Increasing V_D further moves the depletion region towards the source electrode and I_D saturates at its maximum value. The OFET is now operating in the saturation regime. Clearly values V_D for saturation are dependent on applied V_g . *Figure 5* shows the linear and saturation regimes and the effect of increasing V_g . It is worth noting that in n-type devices, polarity is reversed, such that increasing positive V_D leads to an increased positive I_D .

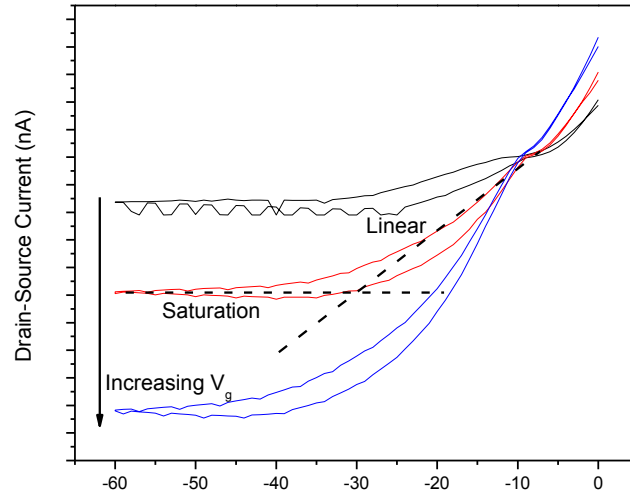


Figure 5 Output characteristics plot of F8T2 OFETs on OTS, showing the linear and saturation regimes, and the effect of increasing gate voltage.

In the linear regime source-drain current-voltage characteristics are described by [1.4](25), where μ_{lin} is the linear regime mobility, W and L are the width and length of the channel and C

is the capacitance of the insulating layer per unit area and $A = 0.5V_D^2$, which can be ignored for $V_D \ll V_g$ in the linear regime.

$$I_D = \frac{W}{L} \mu_{lin} C [(V_g - V_t)V_D - A] \quad [1.4]$$

From [1.4] it is clear that I_D is linear with respect to V_g and V_D . In the saturation regime I_D can be expressed as follows, with μ_{sat} being the mobility in the saturation regime.

$$I_{D,sat} = \frac{W}{2L} \mu_{sat} C (V_g - V_t)^2 \quad [1.5]$$

Saturation mobilities are calculated from transfer characteristics and [1.5], and by extrapolation of the linear section of V_g vs I_D V_{th} can be determined.

In addition to their use in OFET devices, organic semiconductors can be used as semiconducting material in organic light emitting diodes (OLEDs) (12), and organic photovoltaic cells (PV) (34).

1.5 Absorption and Fluorescence

Due to the extensive use of spectroscopic techniques in this work, discussion of the processes of absorption and fluorescence in polymers is important. Absorption and photoluminescence are discussed concurrently as both are due to vibronic transitions between the ground state of a molecule S_0 and the excited singlet state S_1 . It is also assumed that the molecule is capable of absorbing light and promoting an electron to the excited state without the physical breakdown of the molecule! Within the ground and excited state there are vibronic energy levels, and transitions occur between these levels specifically, schematically shown for a single molecule in *figure 6* (19). Absorption occurs from the $v = 0$ level in the lower energy, ground state to one of the vibronic levels in the excited state, with probabilities governed by wavefunction overlap. The importance of wavefunction overlap and the fact that nuclear transitions occur on timescales much greater than those of electronic transitions is the Frank-Condon Principle, as such nuclear positions readjust after the electronic transition has occurred. All emission occurs from the 0th vibronic state, as relaxation from higher energy states via phonon emission is very rapid and known as internal conversion. Ideally the absorption and emission spectra are mirror images separated by the Stokes's Shift, the change in energy due

to the physical readjustment of nuclear positions after absorption. In F8T2 studied here this is approximately 0.13 eV.

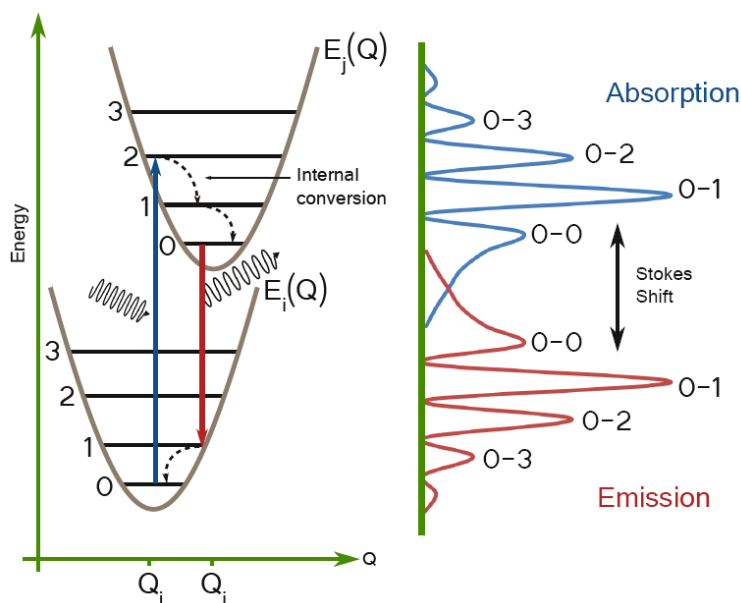


Figure 6 Schematic showing vibronic energy levels in the S_0 and S_1 states and associated absorption and emission spectra. The increased intensity of 0-1 over 0-0 is due to longer bond length (Q) in the S_1 state (19; 24).

The Stoke's shift means materials are largely transparent to their emissive spectra, however this is not always the case, especially in physically thick films or high concentration solutions. Excited states in polymers are localised, modelled as a gaussian disorder throughout the chain rather than truly continuous LUMO level. This allows excitons to hop to a particular physical position before decay leading to broad spectral features in less ordered materials. Increases in order lead to more defined vibronic spectral features.

The relative intensities of the 0-0 and 0-1 reflect differences in bond lengths after absorption, with 0-1 being longer. Fluorescent emission is discussed above, additionally phosphorescent emission is possible in some materials due to classically forbidden intersystem crossing to a triplet, spin = 1, excited state.

Molecular alignment can induce polarised emission, and can be seen by preferential polarised absorption. Emission and absorption from the polymer backbone are polarised along it. In well aligned samples parallel to perpendicular ratios of 20:1 can be seen.

1.6 Physical Characteristics

Obviously, polymers can be defined and differentiated by their physical characteristics. This section discusses a range of those characteristics.

1.6.1 M_w , M_n , and Polydispersity

Due to the statistical nature of polymerisation, giving an exact molar mass to a polymer is difficult. As such the polymer molar mass distribution is characterised by various mass averages, described below (21). [1.6] defines M_n , the number average molecular weight, where N_i is the number of molecules of mass M_i .

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad [1.6]$$

[1.7] describes M_w , the weight average molecular weight, where N_i is the number of molecules of mass M_i .

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad [1.7]$$

The number average molecular weight is often found by Gel Permeation Chromatography GPC, whereas weight average is found by Light Scattering techniques, and for most distributions is the larger of the two.

Polydispersity is defined as M_w/M_n , and gives an idea of the breadth of the distribution. Clearly monodisperse distributions, made of a single mass polymer would have a polydispersity of 1. The degree of polymerisation, the number of monomer units in each polymer is defined as M_x/M_0 where M_0 is the molar mass of the monomer, and M_x is the appropriate molecular weight average.

1.6.2 Radius of Gyration

Most polymer semiconducting devices are created by deposition from solution. The choice of solvent can have a large effect on the polymer in solution. One must choose a solvent which will dissolve the polymer being worked on, and different solvents affect the deposited film in various physical ways, manifested as spectral and/or electronic changes. Whether a solvent is

good will determine the coil size, R_g , in the solution. The average r.m.s radius of gyration, R_g , is defined as the average distance of a chain element from the centre of gravity of the coil.

These statistical parameters are influenced by a range of factors in solution, most notably the solvating power of the solvent and the temperature of the system, and are linked by the following equation in absence of excluded volume effects for simple chains

$$\langle \bar{r}^2 \rangle^{\frac{1}{2}} = \langle 6\bar{S}^2 \rangle^{\frac{1}{2}} \quad [1.8]$$

Where $\langle \bar{r}^2 \rangle^{\frac{1}{2}}$ is the average root mean square distance between chain ends and $\langle \bar{S}^2 \rangle^{\frac{1}{2}}$ is the root mean squared radius of gyration R_g . Two averages, denoted by a bar and brackets are averages for many conformational sizes and polydispersity respectively.

This is true for many traditional coiled polymers but conjugated polymers often take up rod like shapes (35). Polyfluorenes and other pi-bonded polymers are often not well described as coils, but in many cases are stiff, rigid rods.

Radii of gyration can be computed for other ideal chain types, including conjugated rod-like, rings, disks and cylinders (20).

1.6.3 Theta condition and good and bad solvents

Beyond this one of the simplest models is that of a freely jointed chain, where it is assumed that the polymer is made up of n units of length l , which can take up any angle at each joint, with an end to end distance of r_f . This leads to: (21)

$$r_f^2 = nl^2 \quad [1.9]$$

A further extension is that the bond angle between units is not free, but fixed leading to:

$$\langle \bar{r}^2 \rangle_0 = nl^2 \frac{(1 - \cos \theta)}{(1 + \cos \theta)} \cdot \frac{(1 - \langle \cos \theta \rangle)}{(1 + \langle \cos \theta \rangle)} \quad [1.8]$$

Where $\langle \bar{r}^2 \rangle_0$ is the average r.m.s. of the unperturbed dimension, a characteristic parameter for a given polymer chain, and $\langle \cos \theta \rangle$ is the cosine of the average bond angle along the chain, and is a measure of chain stiffness. The theta condition is defined as when the coil size is the

unperturbed dimension [1.8]. A solvent in which this occurs is a theta solvent, and the temperature a theta temperature. Above the Θ -temperature in a better solvent the chain expands, below or in a worse solvent the coil collapses and may precipitate. The coil size is also affected by the number of repeat units in a polymer chain and chain stiffness. Other effects cause the polymer size to deviate from its unperturbed dimension, such as excluded volume effects – where one polymer segment cannot take up the physical space of another, leading to a larger size, and osmotic swelling where in good solvents polymer-solvent interaction increase leading to more extended configurations.

A critical factor in allowing conjugated polymers to be solution processed is the addition of sidechains, to allow solubility in organic solvents. A very important factor to consider is aggregation when solution processing polymeric materials, as will be seen in this report. Prior to visible aggregation, spectroscopic changes can be seen due to interactions between polymer chains. These are most generally manifested as reduced photoluminescent efficiency, as non-radiative decay pathways become available.

1.6.4 Bulk Phase Behaviour

Polymers in the solid phase can be quenched into different physical states by rapid cooling after heating. In an amorphous polymer, at temperatures below the glass transition temperature T_G the solid is brittle and polymer chains are unable to move around. After heating to above T_G , the solid polymer becomes ‘rubbery’ and polymer chains are able to move around and take up lower energy configurations, chains can undergo rotations and slide over each other with mechanical deformation. With further heating positional order can be achieved and crystallinity is observed. Some polymers, including F8T2, exhibit liquid crystalline phase above T_c the crystalline melt temperature and prior to complete isotropic melting at T_m . Crystals have defined structural order in 3 dimensions; liquid crystals have order in just 1 or 2.

The most common liquid crystal phases are:

- Nematic, where long range orientational order within a single domain is seen, however without positional order.
- Smectic liquid crystallinity is observed at lower temperatures than nematic, where strongly defined ordered layers are seen. Smectic A liquid crystals have layers orientated at 90° to the chain direction, Smectic C liquid crystals are orientated tilted with respect to the layer. These layers can slide over each other easily.

- Chiral nematic liquid crystallinity, where chiral molecules show twisting order.

These three phases are shown below in *figure 7* (36).

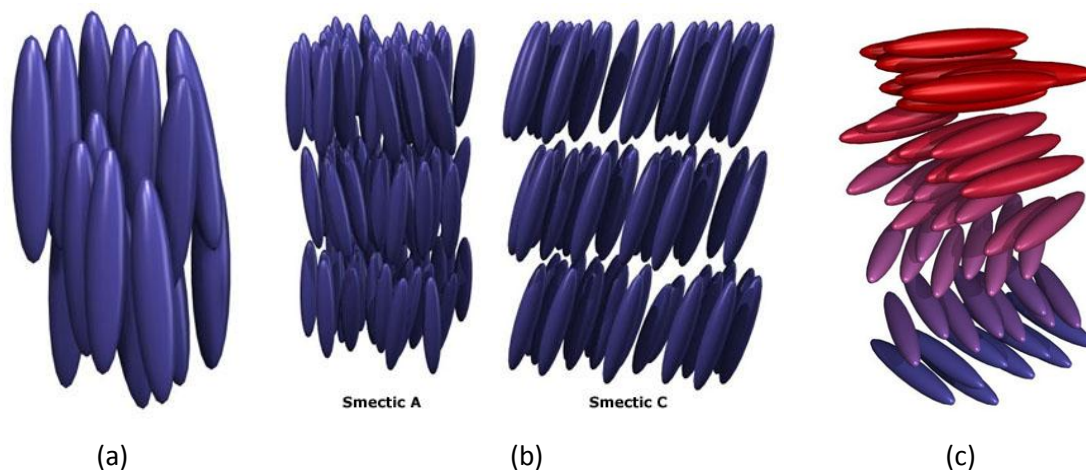


Figure 7 Schematic diagrams of (a) Nematic (b) Smectic and (c) Chiral ordering

Above the melt temperature, the solid melts and an amorphous liquid phase is observed. By quenching (quickly cooling) from the melt a glassy solid can be obtained, and quenching from within the other thermal domains leaves the solid ‘frozen’ in that state. Cooling slowly from the melt or liquid crystal phases allow crystal growth and a (many domained) crystalline solid is formed. By using this technique on a rubbed or aligned substrate, large domain sizes can be formed, and a preferential direction for nematic crystallinity can be obtained. This can be very useful in organic semiconductor research and average energy gap and distribution, and electronic properties will be changed (37).

Crystallinity in polymers is usually considered in long flexible chains as chain folded crystals, spherulites from dendritic growth or fringed micelles, small crystals imbedded within the amorphous solid. Many polymers need sidechains to allow them to be soluble, and sidechains can affect the physical properties of the polymer and can crystallise themselves if they are long enough. Their extent can strongly affect crystal packing in the solid state.

The amount of directional order is characterised by the order parameter S , varying from $S = 0$ for wholly isotropic random sample to $S = 1$ for one perfectly aligned. In practice, for films on alignment layers, such that the crystal director is known, the macroscopic order parameter can be calculated from the dichroic ratio in absorption measurements taken with polarised light parallel and perpendicular to the rubbing direction.

The use of polyimide (PI) alignment layers is common in polyfluorene and other polymer research (37; 38; 39), for structural studies and improvements to electrical properties in OFET, OLEDs and OPV.

1.7 Bibliography

1. **G Busch.** Early history of the physics and chemistry of semiconductors – from doubts to fact in a hundred years. *Eur. J. Phys.* 1989. Vol. 10, 4, pp. 254-264.
2. **M Faraday.** Experimental Researches in Electricity. *On Conducting Power Generally.* 1833.
3. **The Nobel Prize.** http://www.nobelprize.org/nobel_prizes/physics/laureates/1956/. July 2112. 1956.
4. **M Pope, H Kallmann, and P Magnante.** Electroluminescence in organic crystals. *J.Chem. Phys.* 1963. Vol. 38, 8, pp. 2042-2043.
5. **W Helfrich and W G Schneide.** Recombination radiation in anthracene crystals. *Phys. Rev. Lett.* 1965. Vol. 14, 7, pp. 229–231.
6. **H Shirakawa, E J Louis, AG MacDiarmid, C K Chiang, and A J Heeger.** Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene. *Journal of the Chemical Society, Chemical Communications.* 1977. Vol. 16, pp. 578-580.
7. **C K Chiang, C R Fincher, Y W Park, A J Heeger, H Shirakawa, E J Louis, S C Gau, and A G MacDiarmid.** Electrical conductivity in doped polyacetylene. *Phys. Rev. Lett.* 1998. Vol. 39, 17, pp. 1098-1101.
8. **C W Tang and S A VanSlyke.** Electroluminescence of doped organic thin-films. *Journal of Applied Physics.* 1989. Vol. 65, 9, pp. 3610-3616.
9. **A Tsumura, H Koezuka, and T Ando.** Macromolecular electronic device: Field-effect transistor with a polythiophene thin film. *Applied Physics Letters.* 1986. Vol. 49, pp. 1210-1212.
10. **H Koezuka, A Tsumura, and T Ando.** Field-effect transistor with polythiophene thin films. *Synthetic Metals.* 1987. Vol. 18, pp. 699-704.
11. **C W Tang.** Two-layer organic photovoltaic cell. *Appl. Phys. Lett.* 1986. Vol. 48, 2, pp. 183-186.

12. **J H Burroughes, D D C Bradley, A R Brown, R N Marks, K Mackay, R H Friend, P L Burns, and A B Holmes.** Light-emitting diodes based on conjugated polymers. *Nature*. 1990. Vol. 347, pp. 539-541.
13. **P L Burn, D D C Bradley, R H Friend, D A Halliday, A B Holmes, R W Jackson and A Kraft.** Precursor route chemistry and electronic-properties of poly(p-phenylene-vinylene), poly[(2,5-dimethyl-p-phenylene)vinylene] and poly[(2,5-dimethoxy-p-phenylene)vinylene]. *Journal of the Chemical Society. Perkin transactions 1*. 1992. Vol. 23, pp. 3225-3231.
14. **S Steudel, K Myny, V Arkhipov, C Deibel, S D Vusser, J Genoe, and P Heremans.** 50 MHz rectifier based on an organic diode. *Nat. Mater.* 2005. Vol. 4, pp. 597-600.
15. **Samsung.** <http://www.samsung.com/uk/consumer/mobile-devices/smartphones/android/GT-I9100RWAXEU>. July 2012.
16. **LG.** <http://www.lg.com/uk/tvs/lg-55EM960V-oled-tv>. July 2012.
17. **W Clemens, W Fix, J Ficker, A Knobloch, and A Ullmann.** From polymer transistors toward printed electronics. *J. Mater. Res.* 2004. Vol. 19, 7, pp. 1963-1973.
18. **H Sirringhaus.** High-resolution inkjet printing of all-polymer transistor circuits. *Science*. 2000. Vol. 290, 5499, pp. 2123-2126.
19. **A Guite.** Microstructure, morphology and device physics of gravure printed and solutionprocessed organic field-effect transistors. *Imperial College London*. 2011.
20. **M Rubinstein, R H Colby.** Polymer Physics. *Oxford*. 2006.
21. **J M G Cowie.** Polymers: Chemistry & Physics of Modern Materials. 2nd Edition. *Blackie Academic & Professional*. 1996.
22. **W R Hodgkinson and F E Matthews.** XXIII.-Note on some derivatives of fluorene, C₁₃H₁₀. *Journal of the Chemical Society, Transactions*. 1883. Vol. 43, pp. 163-172.

23. **V V Prey, H Schindlbauer, and D Cmelka.** Versuche zur Polymerisation von Fluoren. *Die Angewandte Makromolekulare Chemie*. 1973. Vol. 28, 1, pp. 137-143.
24. **W Barford.** Electronic and Optical Properties of Conjugated Polymers. *Oxford University Press*. 2005.
25. **A J Campbell.** Introduction to Organic Semiconductors. *Imperial College London*. 2005.
26. **J J Benson-Smith.** Spectroscopic studies of organic donor-acceptor blend films for organic solar cell applications . *Imperial College London*. 2007.
27. **T H Richardson.** Functional organic and polymeric materials: molecular functionality - macroscopic reality. *Wiley*. 2000.
28. **J L Brédas, G B Street, B Thémans, and J M André.** Organic polymers based on aromatic rings (polyparaphenylene, polypyrrole, polythiophene): Evolution of the electronic properties as a function of the torsion angle between adjacent rings. *J. Chem. Phys.* 1985. Vol. 83, pp. 1323-1329.
29. **D Campbell, J R White, and R A Pethrick.** Polymer Characterization: Physical Techniques 2nd ed. *CRC Press*. 2000.
30. **R A Marcus.** Exchange reactions and electron transfer reactions including isotopic exchange. Theory of oxidation-reduction reactions involving electron transfer. Part 4.A statistical-mechanical basis for treating contributions from solvent, ligands, and inert salt. *Discuss. Faraday Soc.* 1960. Vol. 29, pp. 21-31.
31. —. Electron transfer reactions in chemistry. Theory and experiment. *Rev. Mod. Phys.* 1993. Vol. 65, pp. 599-610.
32. **H Bässler.** Charge transport in disordered organic photoconductors: a monte carlo simulation study. *Phys. Status Solidi B*. 1993. Vol. 175, 15, pp. 15-56.
33. **S Roth, H Bleier, and W Pukacki.** Charge transport in conducting polymers. *Faraday Discuss. Chem. Soc.* 1989. Vol. 88, pp. 223-233.

34. **J Nelson.** Organic photovoltaic films. *Current Opinion in Solid State and Materials Science*. 2002. Vol. 6, pp. 87-95.
35. **K C Lim, C R Fincher, and A J Heeger.** Rod-to-coil transition of a conjugated polymer in solution. *Phys. Rev. Lett.* 1983. Vol. 50, pp. 1934-1937.
36. **C J Barrett and D Gray.** Introduction to Liquid Crystals. http://barrett-group.mcgill.ca/tutorials/liquid_crystal/LC01.htm. 2012.
37. **M Grell, D D C Bradley, G Ungar, J Hill, and K S Whitehead.** Interplay of Physical Structure and Photophysics for a Liquid Crystalline Polyfluorene. *Macromolecules*. 1999. Vol. 32, 18, pp. 5810–5817.
38. **A Zen, D Neher, C Bauer, U Asawapirom, U Scherf, R Hagen, S Kostromine, and R F Mahrt.** Polarization-sensitive photoconductivity in aligned polyfluorene layers. *Appl. Phys. Lett.* 2002. Vol. 80, pp. 4699-4701.
39. **M Knaapila, R Stepanyan, B P Lyons, M Torkkeli, and A P Monkman.** Towards General Guidelines for Aligned, Nanoscale Assemblies of Hairy-Rod Polyfluorene. *Advanced Functional Materials*. 2006. Vol. 16, 5, pp. 599-609.

Chapter 2

Materials and Experimental Methods

This chapter describes and defines the polymer samples and processing methods used throughout this thesis. The experimental techniques used are described in detail, as are the polymers involved and sample fabrication methods.

2.1 Materials

Three polymer samples were used regularly in this work; poly(9,9-dioctyl)fluorene, F8 or PFO polyfluorene, and two of its copolymers poly(9,9-dioctylfluorene-alt-bithiophene) F8T2, and poly(9,9-dioctylfluorene-alt-benzothiadiazole) F8BT. Occasional studies were undertaken on two other polyfluorene copolymers; poly[2,7-(9,9-dihexylfluorene)-alt-bithiophene] F6T2, and SC005 made of 80% poly(9,9-dioctyl)fluorene, 20% poly(9,9-dipentyl)fluorene. The other key materials used were the solvents, these are also briefly described below.

2.1.1 F8T2

The material used most in this work is the conjugated co-polymer poly(9,9-dioctylfluorene-alt-bithiophene), F8T2. A single batch of polymer was used in almost all experiments for consistency, if comparisons with a second batch of a different molecular weight are made this is noted in the text.

All polymer samples used in this work were provided by Sumitomo Chemical Company and used as received. Solution processing for films and devices led to typical concentration ranges of 10–30 mg/ml for spectroscopy and FETS. For multi-angle light scattering, MALS, much lower concentration ranges of 0.1–0.6 mg/ml were used.

A sample of poly[2,7-(9,9-dihexylfluorene)-alt-bithiophene] F6T2 was also measured with GIWAXS. F6T2 is analogous to F8T2 however shorter sidechains are seen in the polyfluorene monomer sections.

F8T2 can be seen to be a PFO monomer with two thiophene rings attached, and is shown graphically in *figure 8 (1)*.

2.1.2 PFO/F8

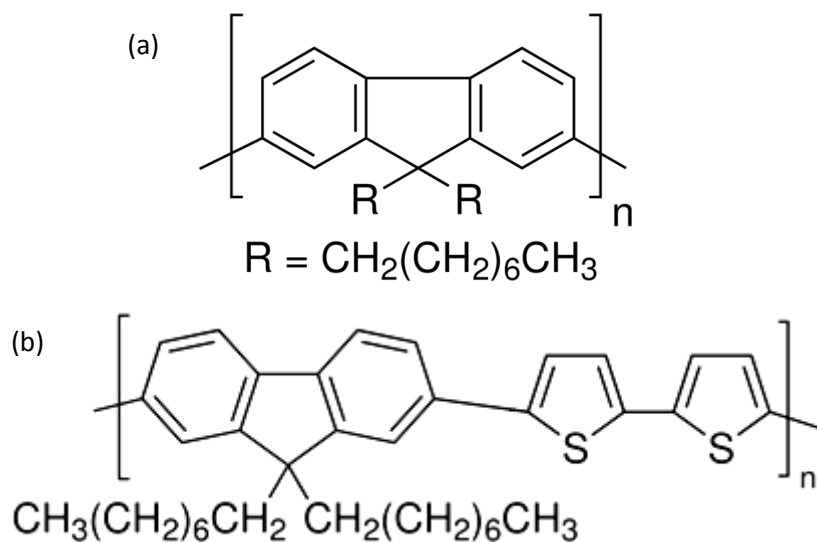
In addition to F8T2, the homopolymer poly(9,9-dioctyl)fluorene, PFO, was used for light scattering, SANS and GIWAXS experiments. PFO is a very well studied (2; 3; 4) light emitting polymer and was a useful addition to the investigation as it is the polymer on which F8T2 and F8BT are based and gives interesting results in comparison. Note the differences in side-chain lengths between the three polymers, as well as the co-polymer sections. PFO samples were received from Sumitomo Chemical Company. The structure of PFO is shown in *figure 8 (5)*. An additional PFO type polymer, SC005 was used in GIWAXS studies. Received from Sumitomo Chemical Company, and previously studied by Yap et al (6).

2.1.3 F8BT

The co-polymer poly(9,9-dioctylfluorene-co-benzothiadiazole), F8BT, was used in light scattering, SANS and GIWAXS experiments, and is described in *table 1* and *figure 8* (7)

Polymer	Full Name	Chemical Formula	Monomer Atomic Weight
PFO / F8	poly(9,9-dioctyl)fluorene	$(C_{29}H_{41})_n$	389
F6	poly(9,9-dihexyl)fluorene	$(C_{25}H_{33})_n$	333
F8T2	poly(9,9-dioctylfluorene-alt-bithiophene)	$(C_{37}H_{44}S_2)_n$	552
F8BT	poly(9,9-dioctylfluorene-alt-benzothiadiazole)	$(C_{35}H_{42}N_2S)_n$	522
F6T2	poly[2,7-(9,9-dihexylfluorene)-alt-bithiophene]	$(C_{33}H_{36}S_2)_n$	496
SC005	80% poly(9,9-dioctyl)fluorene, 20% poly(9,9-dipentyl)fluorene		

Table 1 Summary of polymers used



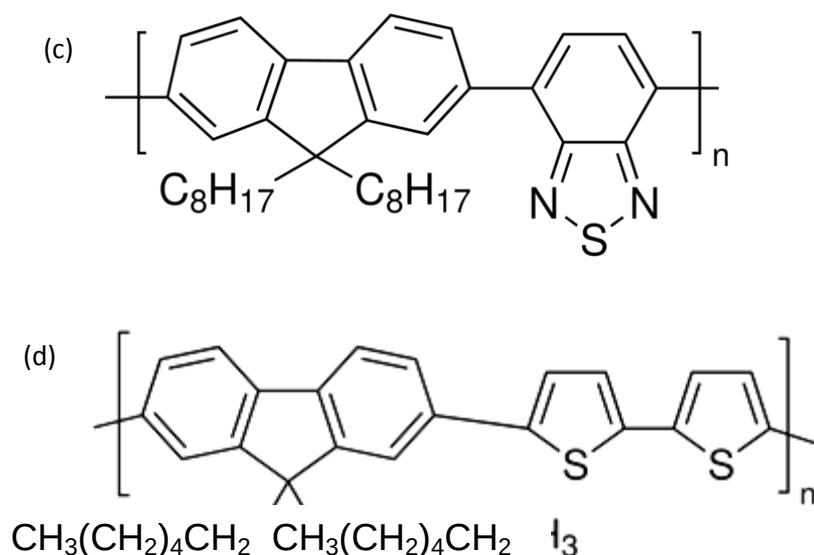


Figure 8 Structures of polymers used
(a) PFO, (b) F8T2, (c) F8BT, (d) F6T2

2.1.4 Solvents

A summary of the properties of the solvents used is shown below in *table 2* (8).

Name	Abbreviation	Formula	Dielectric Constant	Boiling Point [°C]	Density [g/ml] at 25°C	Purity
Tetrahydrofuran	THF	C ₄ H ₈ O	4.0	65 - 67	0.889	≥99.9%
Methylbenzene	Toluene	C ₆ H ₅ CH ₃	2.4	110 - 111	0.865	99.9%
Chloroform	-	CHCl ₃	4.1	60.5 - 61.5	1.48	≥98%
1,2-Dimethylbenzene	Xylene (σ)	C ₆ H ₄ (CH ₃) ₂	2.5	143 - 145	0.879*	98%
Chlorobenzene	-	C ₆ H ₅ Cl	2.7	132	1.106	99.9%
Deuterated Tetrahydrofuran	d-THF	C ₄ D ₈ O	-	65 - 66	0.985	99.5 D atom %
Deuterated Methylbenzene	d-Toluene	C ₆ D ₅ CD ₃	-	110	0.943	99.6 D atom %
Deuterated Chloroform	d-Chloroform	CDCl ₃	-	60.9	1.500	99.6 D atom %

Table 2 Abbreviations, polarity and boiling points of solvents used.
All data taken from Sigma Aldrich, except dielectric constant . * Density at 20°C (8)

Solvents used throughout this work were HPLC grade Chromasolv® obtained from Sigma-Aldrich, except for the SANS studies where deuterated (hydrogen replaced with deuterium) solvents were used, also from Sigma-Aldrich. The main solvents used in F8T2 processing were tetrahydrofuran, THF, used as a 'good' solvent, and toluene, used as a 'bad' solvent.

2.2 Sample Processing

Most samples were prepared in the class 1000 cleanroom facility (ISO 6 equivalent) at the Blackett Laboratory, Imperial College, London. Samples for SANS were prepared in the LOQ chemistry lab at the Rutherford Appleton Laboratory, Oxford, and GIWAXS and GISAXS samples were prepared in the Malliaras Laboratory for Organic Electronics at Cornell University, Ithaca. Most thermal treatment of films was done in a MBRAUN MB20G glovebox with nitrogen atmosphere and typical moisture levels <3 ppm and oxygen <0.1 ppm, except those at Cornell where a similar facility was used. Unless higher precision was needed for light scattering measurements all polymers were weighed to a precision of $\pm 5 \times 10^{-3}$ mg at ambient temperature in the cleanroom, with solvents added volumetrically, with a stated precision of $\pm 0.5 \times 10^{-3}$ ml, to create solutions primarily in the range 10–30 mg/ml. Solutions were occasionally heated, either as a deliberate change in processing, or to improve dissolution, this is mentioned when used.

2.2.1 Solution Processing

Solutions were processed using Sigma-Aldrich HPLC grade solvents. Glass vials were used for solutions to be processed, unless spectroscopy was to be undertaken on the solution, in which case optical glass cuvettes from Hellma were used. 1 mm light path, and 10 mm light path cuvettes were used, with internal volumes of 1 ml and 3 ml respectively.

Vials were cleaned with acetone and dried with a nitrogen gun, and then cleaned in IPA and dried with a nitrogen gun. Before use vials were rinsed with the solvent to be used and dried with a nitrogen gun.

If cuvettes were to be reused the following cleaning regime was used. On completion cuvettes were checked for polymer traces by fluorescence and absorption spectroscopy.

1. Drain cuvette of solution
2. Rinse and scrub with a good solvent
3. Sonicate in a good solvent for up to 1 hour
4. Repeat until cuvette appears clean of polymer
5. Sonicate cuvette for 10 minutes in acetone
6. Dry with nitrogen gun

7. Sonicate substrates for 10 minutes in IPA
8. Dry with nitrogen gun

Solutions used for Multi-angle Light Scattering needed more intense a cleaning regime, outlined below in *Section 2.7*.

2.2.2 Film Processing

Spectrosil B quartz substrates were used throughout this investigation for spectroscopic measurements. For GIWAXS n-type Si/SiO₂ substrates were used, with a polyimide alignment layer if film alignment was to be studied. Si/SiO₂ substrates with pre-patterned gold source and drain electrodes were used for FET measurements. If pre-patterned substrates were unavailable gold contacts were evaporated onto the films.

2.2.2.1 Substrate Cleaning

Substrate cleaning is vitally important for electronic measurements, as well as spectroscopic measurements on films. The following procedure was used throughout.

1. Sonicate substrates for 10 minutes in acetone
2. Dry with nitrogen gun
3. Sonicate substrates for 10 minutes in IPA
4. Dry with nitrogen gun

If the substrates were being reused such as those with pre-patterned gold electrodes, prior to the sonication in acetone, polymer was removed with a 'good' solvent, and sonicated for at least 10 minutes in that solvent, before being dried with a nitrogen gun. Additionally, before their first use, pre-patterned substrates were sonicated twice for 15 minutes in acetone to remove any photoresist layer remaining after manufacture.

2.2.2.2 Spin Coating

Spin coating is a technique used to create thin films from solution on substrates. A known volume of polymer solution, usually ~50 μ L, is pipetted onto a substrate held on a chuck by vacuum, which is then spun at high speed to spread the solution out radially, forcing solvent evaporation and the creation of a thin film. Care must be taken to ensure no air bubbles are introduced, as these can strongly affect the homogeneity of the film. Film thickness is dependant on the concentration and viscosity of the solution, the rate of rotation and very weakly on the initial volume to be spun. Spin coating was done at ambient temperature with spin speeds ~2000 rpm for ~60 s, unless otherwise stated.

2.2.2.3 Contact Evaporation

FETS were usually processed onto pre-patterned Si/SiO₂ substrates from Fraunhofer IPMS. The specification is shown below.

Layer Structure:	
Gate:	n-doped silicon (doping at wafer surface $n \sim 3 \times 10^{17} \text{ cm}^{-3}$)
Gate Oxide:	230±10 nm SiO ₂ (thermal oxidation)
Drain/Source:	10 nm Au, with a high work function adhesion layer
Protection	Resist AZ7217 soluble in AZ-thinner or acetone
Layout:	
Chip Size:	15 mm x 15 mm
Transistors:	16 per chip
	4 x transistors, L = 2.5 µm, W = 10 mm
	4 x transistors, L = 5 µm, W = 10 mm
	4 x transistors, L = 10 µm, W = 10 mm
	4 x transistors, L = 20 µm, W = 10 mm

Table 3 Specification of pre-patterned substrates from Fraunhofer IPMS.

If pre-patterned substrates were not used, gold contacts were evaporated directly onto the polymer film to give the following properties, *table 4*, 100 µm channel lengths were used exclusively.

The procedure for Au contact evaporation was undertaken under high vacuum $\sim 4 \times 10^{-6}$ and through a shadow mask. To prevent gold atoms penetrating the film the evaporation rate is kept very low for the first $\sim 100 \text{ Å}$ at $< 0.05 \text{ Å/s}$, after that layer has built up the evaporation rate is increased to 0.3-0.5 Å/s until the final thickness of $\sim 350 \text{ Å}$ is achieved.

Layer Structure:	
Gate:	n-doped silicon wafer
Gate Oxide:	200 nm SiO ₂
Drain/Source:	$\sim 35 \text{ nm}$ evaporated Au
Layout:	
Mask Size:	$\sim 35 \text{ mm} \times 35 \text{ mm}$
Transistors:	12 per chip
	4 x transistors, L = 50 µm, W = 2 mm
	4 x transistors, L = 100 µm, W = 2 mm
	4 x transistors, L = 150 µm, W = 2 mm

Table 4 Specification of evaporated FET contacts

2.2.2.4 HMDS

For transistor measurements, a Hexamethyldisilazane or HMDS layer was usually used to improve charge injection and film adhesion. The process used to form this layer is described below.

1. Bake for 15 minutes at 200° C in nitrogen
2. Allow to cool
3. Spin coat 75–100 μ L of HMDS at 3000 rpm for 60 s
4. Bake at 150° C for 10 minutes in air
5. Bake at 190° C for 10 minutes in air
6. Allow to cool

2.2.2.5 Rubbed Polyimide Layer

Some of the GIWAXS experiments required alignment layers made from rubbed polyimide (PI). Polyimide was deposited from the Merck Polyimide ZLI2650 kit, following the manufactures instructions, which are briefly described below.

1. Using ~30 mg/ml polyimide solution for a 30 – 40 nm layer
2. Spin coat 75–100 μ L of solution of 2500 rpm for 60 s
3. Anneal for 60 minutes at 300° C in air
4. Rub polyimide layer using velvet

A ‘rubbing machine’ with a rotating velvet covered barrel was used, with 20 passes forward and back.

Once polymer solutions are spin coated onto PI alignment layers, thermal annealing above the melt temperature can be used to induce alignment (9; 10; 11).

2.2.2.6 Surface Profilometry

All film thickness measurements were taken using a Dektac Surface Profilometer. A scratch through the film to the substrate in the area to be measured is made, and a needle is moved across the scratch by the profilometer, showing the profile in that area. Film thicknesses can be read from the scale. At least two profile measurements were made per film.

2.2.2.7 Thermal Treatment

Almost all thermal treatment was undertaken on a programmable Linkham hotstage, under nitrogen if polymer thin films were being heated, in air otherwise. Polymer films were either ‘quenched’ into their melt by placing on to a large, room temperature thermally conductive metal plate, or allowed to slowly cool on the hotstage over a period of hours. For *in situ* thermal photoluminescence

measurements a monochromated Benthall Xenon light-source was used to illuminate the samples at 420nm. The emission was collected by a silica fibre bundle, passed through a spectrograph and detected with an Instaspec IV CCD. All spectra were corrected for the CCD's response function.

2.2.2.8 Optical Microscopy

Occasionally films were reviewed for quality using an optical microscope. A Zeiss Axioplan microscope was used, with a Nikon Coolpix P5100 digital camera to capture micrograph images.

2.3 Spectroscopy

Solutions and films used for spectroscopic measurements were processed as described previously in *Section 2.2*.

2.3.1 Absorption Spectroscopy

Absorption measurements are one of the most useful and easily undertaken experiments used with organic semiconductors. In all cases a Jasco V-560 (12) spectrophotometer was used to determine absorption spectra (transmission is measured) in the UV and visual wavelength ranges, for both thin films and solutions. A deuterium lamp is used as a light source in the range 190–350 nm, and a halogen lamp for 330–900 nm. Light is passed through a monochromator to produce tunable monochromatic light with a wavelength accuracy of 0.3 nm, a wavelength bandwidth of 2 nm was used throughout. The monochromatic light is then split to give reference and sample beams, with either a cleaned but unused substrate or a cleaned cuvette filled with solvent in the reference path, and the sample to be studied placed in the sample beam. Wavelengths are incremented using the monochromator and transmittance through the sample is measured, removal of the reference beam and calculation of the sample absorption is then completed internally by the spectrophotometer. The internal experimental setup is shown in *figure 9*.

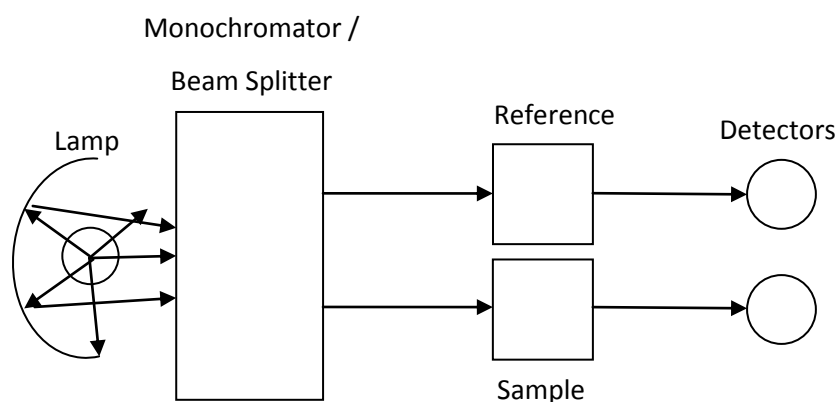


Figure 9 Photospectrometer internal schematic

When solution measurements were being taken a 10 mm light path was used if possible. Once concentrations were high enough to lead to detector output saturation 1 mm light path cuvettes were used. For F8T2 10 mm light paths were used for concentrations <0.5 mg/ml, for solutions >0.05 mg/ml 1mm light paths were used, with some completely blocked transmission still occurring at concentrations >1 mg/ml.

It is assumed reflections from either the film or the substrate can be ignored and absorption spectra were usually used as normalised to the peak of absorption.

2.3.2 Photoluminescence

Photoluminescence is another powerful and well used technique in the analysis of organic semiconductors, both as thin films and in solution.

All solution and thin-film photoluminescence measurements described in this work were taken using a Horiba Scientific, FluoroMax-3 spectrofluorometer with a xenon light source (13). Two monochromators are used, initially an excitation monochromator to set the excitation wavelength to an accuracy of 0.5 nm, the light is then passed through a slit, to illuminate the sample. Emitted light from the sample then passes through another slit and as the second monochromator scans across the wavelength range, counting the number of detected at each wavelength. Photon counts were corrected for detector response internally, and fluctuations in light source brightness.

F8T2 samples were usually excited at 450 nm, to coincide with the absorption peak, and scanned at 1 nm pitch from 450–800 nm to cover the full range of emission. Integration time and excitation slit width was chosen to keep the peak emission at below $\sim 10^6$ counts/second to maintain linearity of the detector response.

Thin films were always placed at an angle of 35° from the excitation beam, due to the strong angular dependence of the FluoroMax detector, and to make sure the excitation beam is not reflected in to the detector, as can be seen at 45° in *figure 10(b)*. The excitation angle is shown schematically in *figure 10(a)*.

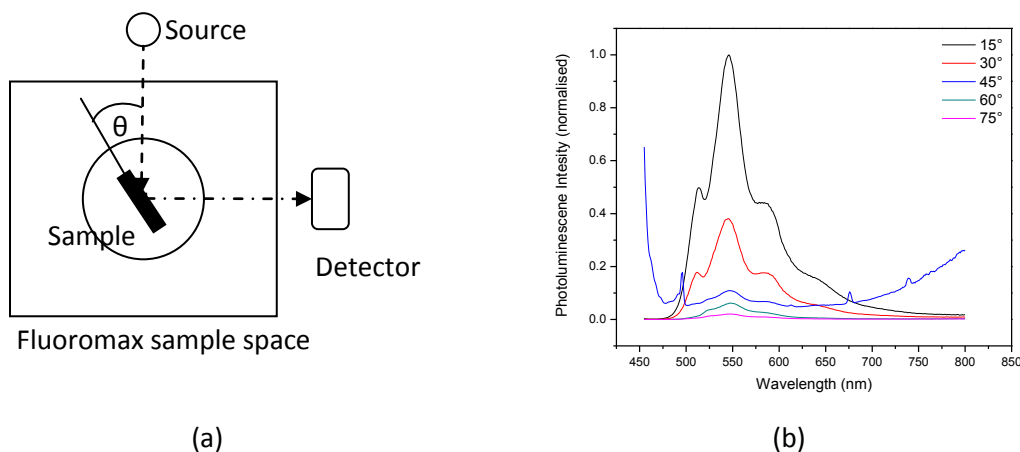


Figure 10 PL Intensity of F8T2 film to show the angular dependence of Fluoromax-3

Solution photoluminescence was measured with solutions in 10x10 mm optical glass 101-OS, cuvettes from Hellma Analytics, with transmission over 80% in the range 320 nm–2500 nm, shown below in *figure 11* (14).

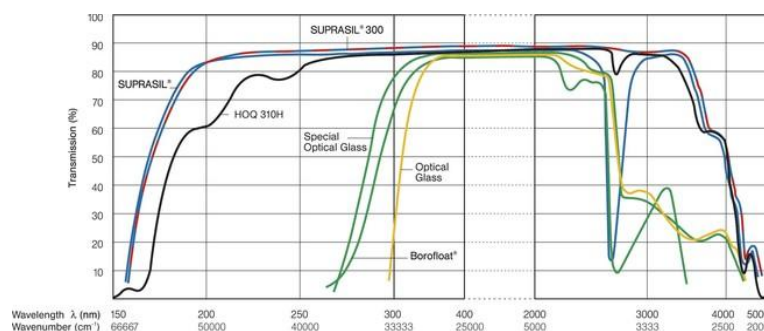


Figure 11 Transmission of Hellma cuvettes (14)

A holder was fabricated to ensure positional repeatability of the cuvettes and to be able to minimise self-absorption by the solution being studied. The cuvette holder was designed such that the excitation beam could illuminate the sample in the centre of the cuvette and anywhere up to 0.5 mm in from the cuvette edge nearest the detector, centred approximately 15 mm up from the cuvette base. The cuvette position was repeatable at the two extremes, an example of emission across the holder is shown in *figure 12*.

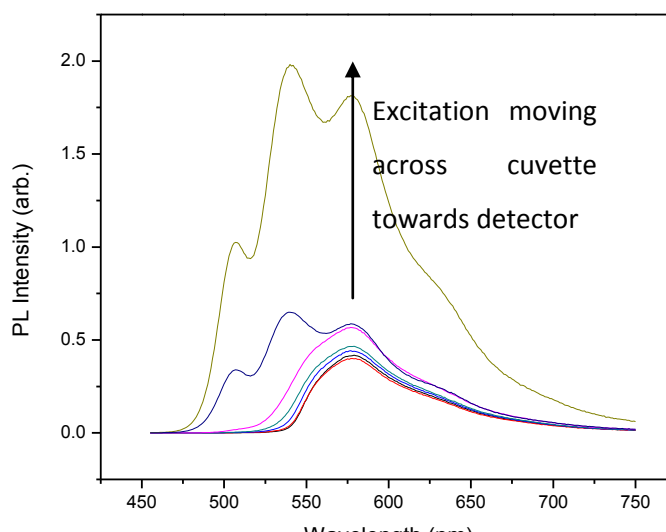


Figure 12 Photoluminescence of 10 mg/ml F8T2 solution with excitation movement across cuvette towards detector. Increase in PL intensity is movement towards detector.

2.3.3 Photoluminescence Quantum Efficiency (PLQE)

Photoluminescence quantum efficiency measurements were undertaken, using the methods described in J. De Mello et al (15). Three photoluminescence measurements are taken for each sample within an integrating sphere, shown in *figure 13*. A white PTFE integrating sphere was used in a Fluoromax-3 spectrophotometer. Initially a spectrum of the empty sphere, illuminated by the excitation beam is taken (a), followed by spectra with the sample directly in the beam (c) and within the sphere but out of the beam-path (b). Results were integrated using OriginPro 8.0. Thin-film samples were prepared as described in *Section 2.2.2*.

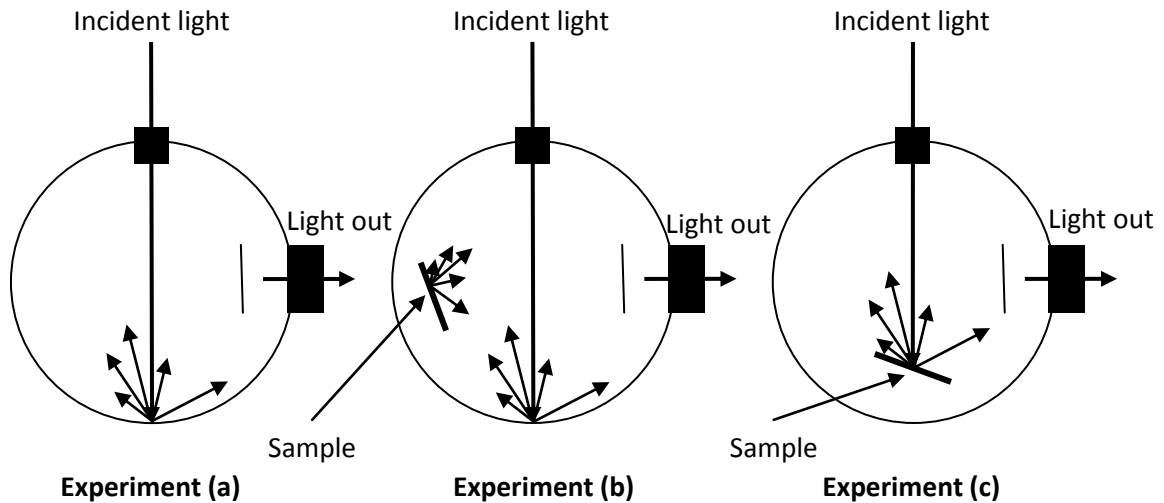


Figure 13 Diagram showing the three measurements needed for PLQE.
(a) No Sample, (b) Sample Off Beam, (c) Sample In Beam

The external radiative quantum efficiency η , is defined as

$$\eta = \frac{\sum \text{photons emitted}}{\sum \text{photons absorbed}} \quad [2.1]$$

Use of an integrating sphere, a hollow sphere internally coated with a diffusely reflecting material, is a standard procedure to measure η of thin-films. The technique outlined by de Mello et al is particularly useful as absorption and photoluminescence are measured simultaneously.

Three PL measurements must be taken and described in *figure 13(a), (b) and (c)*, examples of each are shown in *figure 14*.

The ordinate axis shows PL intensity x wavelength which is proportional to photon number at each wavelength, inset is the excitation peak, and clearly integration underneath each curve is the total number of photons.

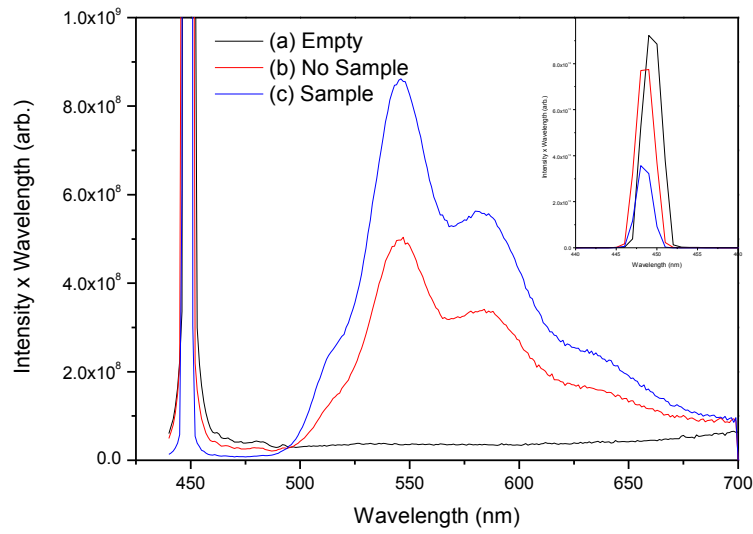


Figure 14 Intensity x Wavelength against wavelength results for PLQE measurements of F8T2 thin film, with excitation peak at 450 nm shown inset

To determine the fraction of incident light absorbed by the sample A , the measured excitation is needed, three terms are defined: L_a , L_b , and L_c each the integrated photon count for the three measurements shown in *figure 13*, no sample, sample off beam and sample in beam respectively. We can also define μ as the fraction of light internally scattered from the sphere wall that is absorbed by the sample, such as light that passes through the sample initially but is then scattered and absorbed. From this we can show that:

$$L_b = L_a(1 - \mu) \quad [2.1]$$

$$L_c = L_a(1 - A)(1 - \mu) \quad [2.2]$$

$$A = \left(1 - \frac{L_c}{L_b}\right) \quad [2.3]$$

This analysis relies on the assumption that excitation light scattered from the sphere contributes identically to PL spectrum, this was experimentally verified to $\pm 2\%$ by De Mello et al.

The integrated photon intensity of the emissive spectrum in (b) and (c) are defined as P_b and P_c . It clearly follows that in experiment (b) the total number of photons detected is $L_b + P_b$, and that in experiment (c) $(1-A)(L_b + P_b)$ photons are detected due to scattered light, with fractions of incident

light being reflected by the sample, transmitted and absorbed. Additionally the fraction due to direct absorption by the sample can be defined as $\eta L_a A$. This leads to [2.4].

$$L_c + P_c = (1 - A)(L_b + P_b) + \eta L_a A \quad [2.4]$$

Which by elimination of L_c and L_b leads to the equation for external PLQE [2.5].

$$\eta = \frac{P_c - (1 - A)P_b}{L_a A} \quad [2.5]$$

Where A can be determined from [2.3] for the sample and the other terms are easily found by experiment and integration. Reabsorption is a concern with this technique, so it should be mentioned that values of η found are likely to be slight overestimates. It is possible to scale the emission spectrum within the sphere to compensate for this effect, but this has not been done here.

In this work L_x was measured between 440 nm and 480 nm, with P_x emission above that.

2.3.4 Photoluminescence Lifetime (PL (τ))

Photoluminescence lifetime measurements were done at Imperial College, London. PL(τ) is used to determine radiative decay rate of a fluorescent sample, by measuring the excited state lifetime; the time dependence of PL emission. This leads to information about the possible decay paths in a material, with decay times increasing as more, faster, non-radiative decay paths become available.

Photoluminescence lifetime PL(τ) experiments, like standard PL, work using an excitation beam and measuring the fluorescent emission. However, instead of measuring the relative strengths of emission at different wavelengths PL(τ) is used to measure the time it takes for an exciton to decay and emit radiatively. A Hamatsu streak scope was used, with a laser excitation wavelength of 409 nm and 200 ps pulsewidth. Results were taken until $\sim 10^5$ counts were measured. Initial results were analysed in Igor Pro (16), later in Mathworks' MatLab 7 (17) with the assistance of Dr. Paul Stavrinou and Dr. Colin Belton.

The sample is illuminated with a short laser pulse, which also triggers the detector. After photoemission a streak camera is used to measure the emitted intensity with time. After passing through a spectrometer the emitted photons are incident on a photocathode, which converts them to electrons via the photoelectric effect. This setup is shown schematically below in *figure 15* (18). The electrons are then accelerated by an electrical field towards a CCD detector as well as by a time-varying field orthogonal to that, giving a time-varying deflection of electrons. This means the

position of the electrons on the detector can be used to measure the temporal profile of the emitted light. This 'streak-pattern' can then be de-convolved from the residual excitation pulse width, and a fluorescent decay time can be calculated.

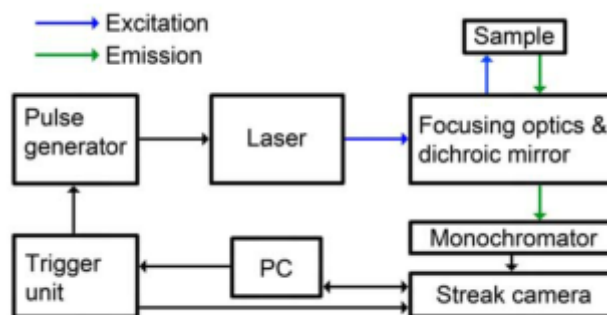


Figure 15 Schematic diagram of PL lifetime setup (18)

The PL emission intensity is recorded as both a function of wavelength and time $I_{pl}(\lambda, t)$, and by integrating over wavelength range intensity as a function of time is found $I_{pl}(t)$. Assuming an ideal case, there is a single emissive species in the sample which decays exponentially after instantaneous excitation. This is unlikely in reality, so instead, a characteristic decay time τ is extracted. The simplest analysis involves fitting an exponential decay to the decay period, the time after ~ 1 ns in *figure 16(a)*, and in some cases this is appropriate. A more complex analysis can involve a double-exponential fit, however this is rarely a valid approach as various values for fitting parameters can result in 'good' fits. The approach taken in this work (unless a single exponential is specifically mentioned) is to use a statistical approach as described in (19). This approach avoids the need for prior knowledge of the form of the decay, and through its consistency facilitates comparisons between systems.

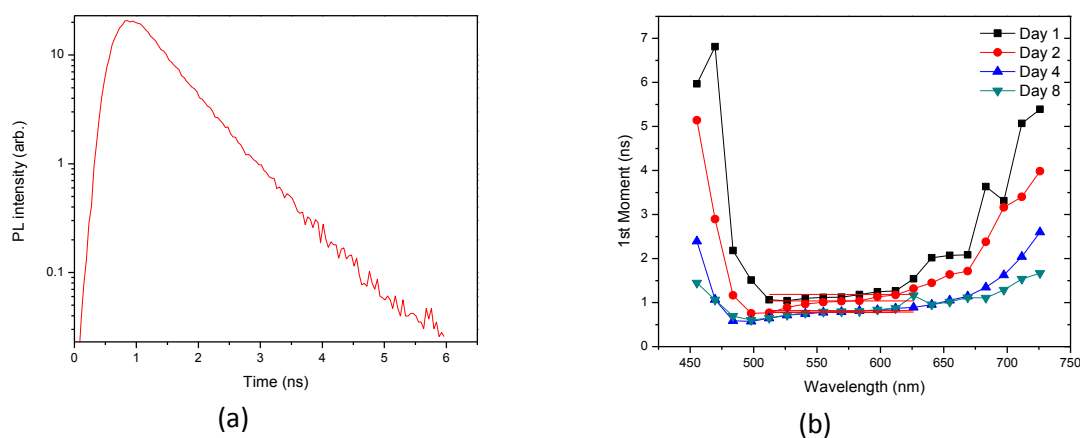


Figure 16 Example plots of (a) PL lifetime decay, (b) 1st moment by wavelength calculations of F8T2 in THF thin films described in Chapter 5

The 1st moment or expectation value of the lifetime $\langle \tau \rangle$ is defined as:

$$\langle \tau \rangle = \frac{\int_0^{\infty} t \cdot I_{pl}(t) dt}{\int_0^{\infty} I_{pl}(t) dt} \quad [2.6]$$

With $t = 0$ at the peak of the PL intensity decay curve, clearly if the decay is a single exponential such that $I_{pl}(t) = Ae^{-\frac{t}{\tau}}$, then $\langle \tau \rangle = \tau$, otherwise $\langle \tau \rangle$ deviates from the true value of τ . This calculation is undertaken in Matlab, with values of $\langle \tau \rangle$ determined for different wavelength regimes. An example of the output from this is shown in *figure 16(b)*, where a horizontal line of best fit is taken over the central range to determine a value for $\langle \tau \rangle$.

2.3.5 Photoluminescence with Temperature

The effects of heating on photoluminescence spectra were studied, to determine if phase transitions could be observed spectroscopically, as shown by Sims et al. (2) in PFO. F8T2 films were processed and placed onto a controllable hot-stage in an evacuated pyrostat. Films were heated in vacuum from 50° C to ~290° C at 1° /min (ideal), held for 2 hours and cooled back to 50° C at 1° /min, with photoluminescence spectra taken every 2° using a corrected Instaspec CCD and a shuttered excitation wavelength of 420 nm. Three thermal treatments were studied; plain spin-coated films, films quenched from 290° C and films cooled from 290° C.

2.4 Grazing Incident Wide-Angle X-Ray Scattering (GIWAXS)

GIWAXS and SAXS were undertaken using the Cornell High Energy Synchrotron Source, CHESS, at Cornell University, Ithaca, New York. Synchrotron X-ray radiation is obtained through the use of ‘wigglers’ on the Cornell Electron Storage Ring, CESR, an electron-positron collider with an energy range up to 12 GeV. The intensity of synchrotron based X-ray sources can easily be 10¹¹ times that of laboratory based sources (20). SAXS and GIWAXS experiments are undertaken on the D-line. The CHESS layout is shown in *figure 17*.

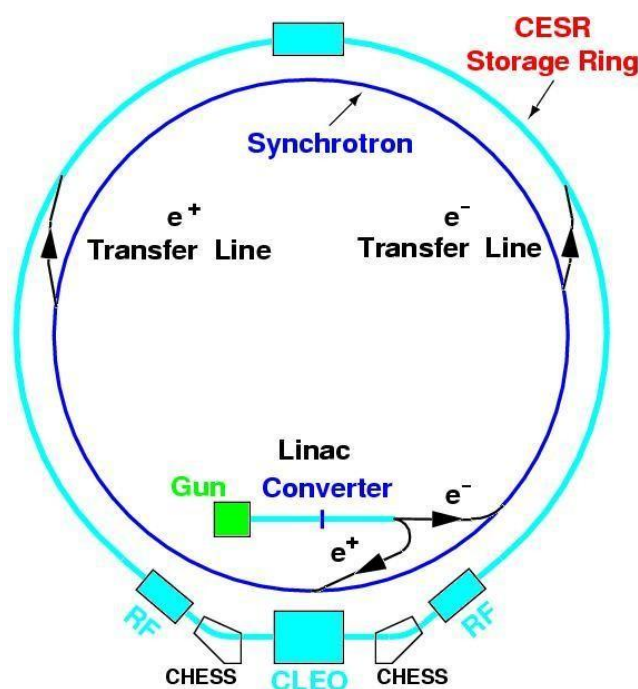


Figure 17 Layout of the CHESS facility at Cornell University

GIWAXS is a useful technique for establishing the structure and morphology of thin films. Samples were prepared in the Malliaras Laboratory for Organic Electronics at Cornell University, Ithaca, in a fume cupboard and following the procedures outlines in *Section 2.2.2* onto silicon substrates. When rubbed PI layers were used, as described in *Section 2.2.2.5*, polymer films were spin-coated and thermally annealed in nitrogen at $>310^{\circ}\text{C}$ to induce polymer ordering. Data processing and analysis was done using the Fit2d software from ESRF (21; 22). X-Ray radiation is incident onto the thin-film, with the intensity of the scattered radiation measured with a Medoptics CCD detector, with a $48 \times 48\text{ mm}$ active area made up from a 1024×1024 array of $46.9\text{ }\mu\text{m} \times 46.9\text{ }\mu\text{m}$ pixels. Incident wavelengths were $1.2288\text{ }\text{\AA}$ and $1.2524\text{ }\text{\AA}$. Exposure times were between 1 and 100s, chosen to maximise the signal without saturating the detector. Sample-detector distance was $\sim 10\text{ cm}$, then moved by a known distance of 30 mm , and by comparison of similar triangles outlined in *figure 19* the true sample-detector distance is obtained if precision $<1\%$ is required.

Incident angles are chosen to be between the critical angles of the substrate and polymer film, approximately 0.1° . The stage is rocked, and its reflectivity measured to find the critical angle of the film, this is then increased by $\sim 0.02^{\circ}$ and used as α_i , this is chosen to be above the critical angle of the polymer film, but below the critical angle of the silicon substrate or PI alignment layer, such that the dominant scattering material is the polymer, this real-space setup is shown in *figure 18* (23).

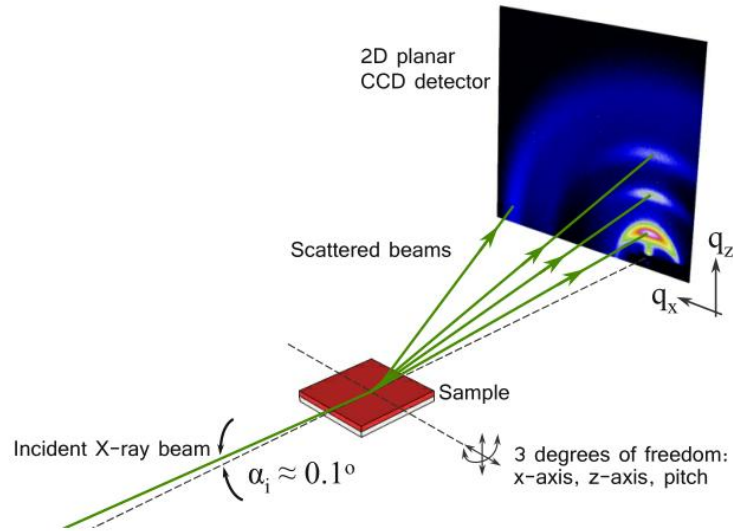


Figure 18 Real-space experimental setup for GIWAXS at d-line, CHESS (23)

The x-rays are scattered as they undergo diffraction. Bragg's law determines the scattering angle by the plane separation; this is further discussed in *Chapter 2* and *Chapter 6*.

By the use of similar triangles precise calculation of sample-detector distance can be achieved, as shown below, where Z_1 and Z_2 are heights to a known scattering point at on the detector plane and ΔL is a known distance, 30mm.

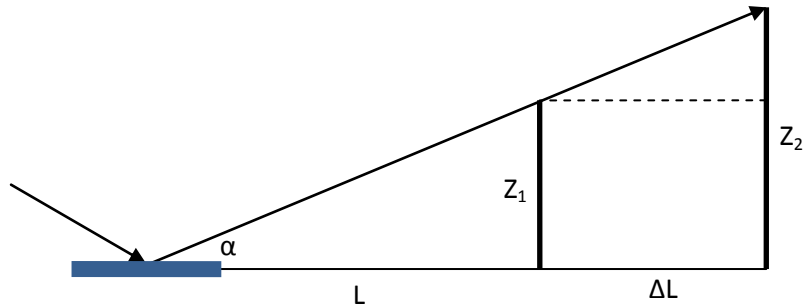


Figure 19 Determination of sample-detector distance by similar triangles

As $\tan \alpha$ is clearly [2.6], it follows that the sample-detector distance L , is:

$$\tan \alpha = \frac{Z_1}{L} = \frac{Z_2 - Z_1}{\Delta L} \quad [2.6]$$

$$L = \Delta L \left(\frac{Z_2}{Z_2 - Z_1} - 1 \right) \quad [2.7]$$

Further analytical details for GIWAXS are described in *Chapter 6*.

2.4.1 In Situ Vapour Annealing

For vapour annealing experiments a vapour cell designed by Dr Detlef Smilgies (24) as described by Dr Aram Amassian (25) was used, to take *in situ* GIWAXS measurements of thin films as they are exposed to solvent vapour. GIWAXS images are taken at a defined interval, with manual solvent injection into a sealed vapour cell with a Kapton®¹ window. Injection involved ~2 ml of solvent added to the vapour cell, which then pooled and caused a solvent rich atmosphere to develop in the cell. PFO was studied in this manner. Analysis is as with standard GIWAXS results with Fit2d. A cross section showing the vapour cell makeup is shown in *figure 20* (23). Giwaxs images were taken every 20 seconds, with an exposure time of 10 seconds.

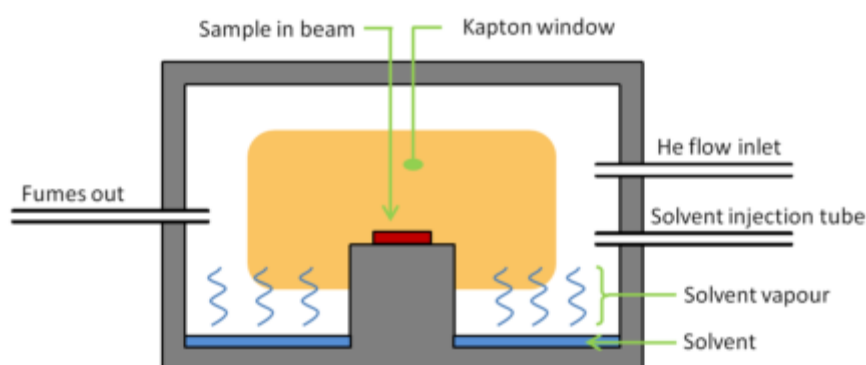


Figure 20 Cross-section of Solvent Flow-Cell for GIWAXS (23)

2.5 Small-Angle X-Ray Scattering (SAXS)

Solutions for SAXS were made in the Malliaras Laboratory for Organic Electronics at Cornell University, Ithaca, in a fume cupboard and following the procedures outlines in *Section 2.2.1*. F8T2 in THF and toluene solutions were studied at 10 and 30 mg/ml, as fresh and 24 hour aged samples. THF and toluene backgrounds were also taken.

Sample solutions (~10 μ L) were placed in 1.5 mm outer-diameter borosilicate glass tubes from Hilgenberg GmbH for measurements, held in a sample holder 100 mm from the detector. Due to the powerful nature of the X-rays and the possibility of sample degradation after collection runs of up to 2x100 s, after each collection the capillary was moved vertically, such that a new area of solution was irradiated. Exposure time was up to 100 seconds, for maximum signal to noise ratio without saturating the detector.

¹ A Polyimide film developed by DuPont™.

Monochromatic 10 keV ($\lambda = 1.23906$ nm) X-ray radiation passes through the sample, with scattering measured using a Medoptics CCD detector, with a 48 x 48 mm active area made up from a 1024 x 1024 array of 46.9 μm x 46.9 μm pixels. Data processing and analysis was done using the fit2d software from ESRF (21).

2.6 Small-Angle Neutron Scattering (SANS)

Neutron scattering experiments were undertaken at the LOQ instrument, using the ISIS neutron source at the Rutherford Appleton Laboratory, (RAL) at Chilton, UK. The ISIS source uses an 800MeV proton accelerator and a tungsten spallation source, with a typical neutron flux of $2 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ (ISIS TS1 at 40Hz, 160 μA 800 MeV proton beam, tantalum target), and typical beam size of 8 mm at the LOQ experiment. This allows LOQ to probe length scales of 1–100 nm.

A schematic of the LOQ beamline is shown in *figure 21* (26).

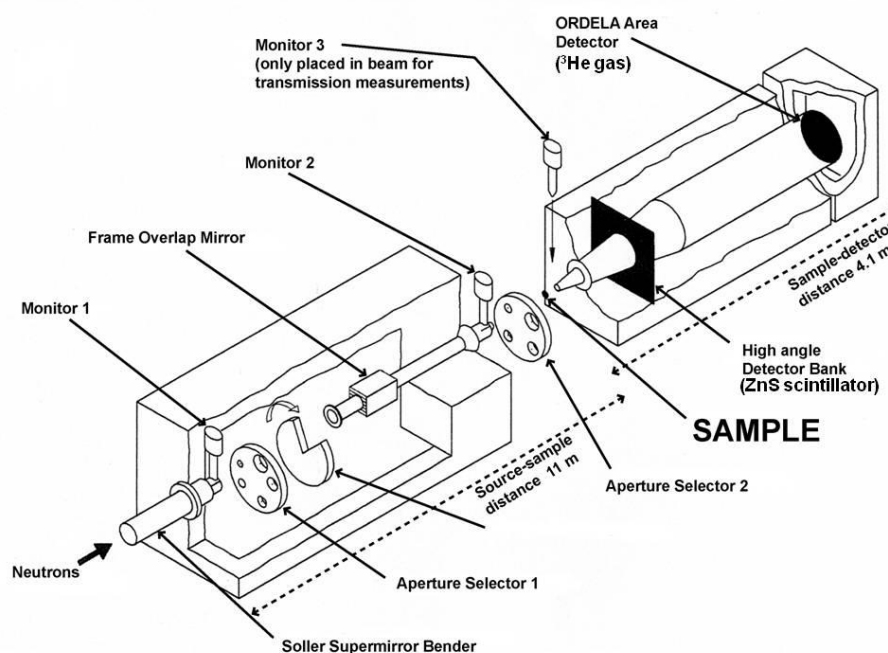


Figure 21 Schematic of the LOQ detector

Solutions were processed in fume cupboards at RAL, using HPLC grade deuterated solvents from Sigma-Aldrich, as described in *Section 2.1.4* above. Deuteration increases the contrast in organic polymer neutron scattering experiments by replacing the hydrogen in the solvent with deuterium atoms. Quartz cuvettes from Hellma with 10mm light-paths were used as sample vials. Solutions were made as described in *Section 2.2.1*.

Three solvents and polymers were used; F8T2, F8BT and PFO, each in d-THF, CDCl_3 , and d-toluene. Heat was applied at well below the boiling point of the polymer as needed, to aid dissolving. Data

was taken with at a standard concentration of 10 mg/ml, apart from in a single concentration dependence run of F8T2, where a range from 2–20 mg/ml was used. Polymer was measured by weight with an accuracy ± 0.1 mg and solvent added volumetrically to achieve the intended concentration. All experimental runs were taken at room temperature, apart from two temperature dependence experiments, where a range from room temperature to $\sim 50^\circ\text{C}$ was used. Solutions were used as freshly dissolved as possible, usually within 1 hour, unless age related properties were being studied, where ageing times of up to 24 hours were used.

The sealed sample vials were held in an automated sample holder in a temperature controllable fluid bath in the beam line.

These combinations are summarised in *table 5* below.

Polymer	Solvent(s)	Additional
F8T2	d-THF / CDCl_3 / d-tol	Ageing
F8T2	d-THF / CDCl_3	Temperature
F8T2	d-THF	Concentration
F8BT	d-tol/ CDCl_3	
PFO	d-tol/ CDCl_3	

Table 5 Summary of SANS experiments

Data was recorded for each sample to high experimental precision, which resulted in an in beam time of ~ 1 hour, increasing with lower concentration samples. Each raw scattering data set was then corrected for the detector efficiencies, sample transmission and background scattering and converted to scattering cross-section data ($\partial\Sigma/\partial\Omega$ vs Q) using the instrument-specific software, Collette (27; 28) by Dr Maximillian Skoda. Data was then placed on an absolute scale (cm^{-1}) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene) in accordance with established procedures (29). Further analytical specifics are discussed in *Chapter 3*.

2.7 Multi-Angle Light Scattering (MALS)

Multi-angle light scattering is a complex and effective, but underused technique in the field of semiconducting polymers. Light scattering measurements were made on very dilute polymer solutions, to determine z-average radius of gyration R_g , and weight average molecular weight, M_w . In a light scattering experiment laser light is scattered by Rayleigh Scattering from particles in solution, a range of detector angles and solution concentrations are used, from which a double-extrapolation can be made, as described by Zimm (30; 31), and R_g and M_w can be determined.

A Wyatt Technologies DAWN DSP was used for all light scattering measurements described. The DAWN has 18 in plane detectors, their angles to the incident beam are evenly spread between 22.5° and 149°, and uses 690 nm scattering laser. Detector angles are shown in *table 6* below. An incident wavelength of 690 nm ensures no absorption by the materials being studied.

Channel #	Θ , fixed detector angle (°)
1	22.5
2	28.0
3	32.0
4	38.0
5	44.0
6	50.0
7	57.0
8	64.0
9	72.0
10	81.0
11	90.0
12	99.0
13	108.0
14	117.0
15	126.0
16	134.0
17	141.0
18	147.0

Table 6 Detector angles in a Dawn EOS

Solutions for light scattering need to be scrupulously clean, 20 ml Scintillation Vials from Wheaton Scientific were cleaned as described above in *section 2.2.1* with IPA and acetone. Polymers were weighed out to $\pm 5 \times 10^{-3}$ mg precision, with solvents added volumetrically and then weighed to the same precision, giving a precise concentration value, using solvent densities defined in *table 2*. HPLC grade solvents were used from Sigma-Aldrich, and filtered through a 0.02 μm PTFE filter prior to use. Concentrations used were generally in the range 0.1 mg/ml to 0.6 mg/ml.

In addition to experimental solutions a calibration solution of ~5k polystyrene standard in THF was prepared in a cleanroom to be in the range 10-15 mg/ml; precise concentration is not vital as the

solution is used as an isotropic homogenous scatterer to normalise the detector responses. Normalisation was undertaken for each new batch of samples. A clean vial of pure toluene is also needed with a known Rayleigh ratio.

Wyatt Technology's Astra software (version 4.73.04) was used for data analysis. The DAWN EOS system was used in batch mode, with a 690nm scattering laser, which will not be absorbed by the polymers investigated. The Astra software uses a (proprietary) combination of techniques, based on those of Zimm (31) in 1948 and described in a review article Philip Wyatt (32) to automatically extract molecular weight and size data from the scattering levels. Low angle detectors were rarely used in analysis due to the strong effect of dust particles at low-angles.

2.7.1 Differential Refractometry

A key value needed for the analysis of a light-scattering experiment is the change of refractive index n , of solution with concentration c , dn/dc .

For dn/dc measurements a Brookhaven Industries Differential Refractometer, BI-DNDC was used. The refractometer sends 620 nm laser light through a diagonally split quartz cell, with pure solvent in one side and a solvent/polymer solution in the other. The deviation of the light path, measured by the asymmetry of the voltages in two detectors is proportional to difference in refractive index between the pure solvent and solution. A concentration series is then used to extrapolate n to zero concentration. It is assumed that the value of dn/dc obtained over the higher concentration range used in the DR is still valid at the lower concentration ranges used for light scattering. This is outlined below in *figure 22* (33). It is assumed that there is no significant change in dn/dc values over the range 620 nm used in the differential refractometer and 690 nm used for light scattering.

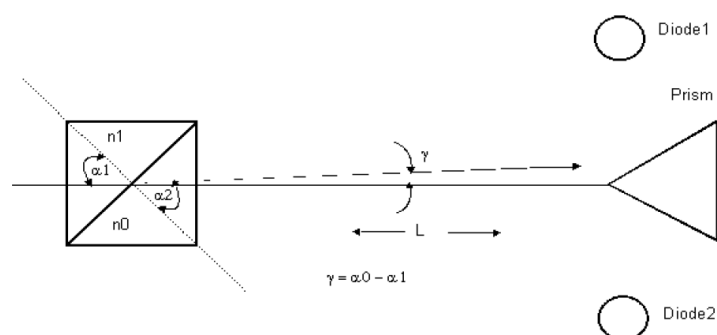


Figure 22 Internal schematic of Brookhave BI-DNDC flow cell and detectors (33)

Six solutions in the range 0.5-5.0 mg/ml are used for each polymer/solvent combination. Each made in the cleanroom with solvents and polymers measured to $\pm 5 \times 10^{-2}$ mg precision, and following the standard solution processing.

Prior to any dn/dc measurement the refractometer was calibrated(33), using 5 solutions of dried potassium-chloride dissolved in water in the range 0.5–5.0 mg/ml, with KCl being measured to $\pm 5 \times 10^{-2}$ mg, after it was dried in a vacuum oven for 1 hour to remove residual water. Solvent was added volumetrically with final concentrations calculated by mass. Calibrations were undertaken if the previous calibration was completed over 48 hours prior.

Concern must be taken when using volatile solvents and uncapped tubes, as due to the small amount of solution in the device ($< 300 \mu\text{l}$), evaporation can taint the result. Evaporation is usually very obvious, and would be seen as a gradient in the sample baselines and can easily be rectified by reinjecting. Temperature dependence can also be very important in these measurements, with both DR and MALS temperatures were set to 40°C , it is of particular importance that the pure solvent and solution are at the same temperature. The Brookhaven Industries differential refractometer keeps both sides of the cell within $\pm 0.01^\circ \text{C}$ of each other from $5-80^\circ \text{C}$ above ambient temperature.

Experimental solutions were made in a cleanroom environment with the same level of precision as calibration solutions. Values for dn/dc of F8T2 in THF, chloroform and toluene were obtained.

Values of dn/dc of PFO in THF solutions were obtained using a Viscotek Triple-Detector, which contains a differential refractometer as part of its detector array.

2.8 Field-Effect Transistors (FETs)

Organic Field-Effect Transistors (OFETs) were made in the Malliaras Laboratory for Organic Electronics at Cornell University, Ithaca, in a fume cupboard and following the procedures outlines in *Section 2.2.2* onto silicon substrates described there.

Transfer and output characteristics were measured Malliaras Laboratory for Organic Electronics under vacuum, following standard procedures as outlined by the IEEE (34). Separate electrodes measure source, drain and gate voltage and current values simultaneously. Output characteristics are initially studied to determine if the device exhibits FET like behaviour and channel conductance, where I_{drain} against V_{drain} at varied, constant values of V_{gate} are recorded. Transfer measurements study I_{drain} against V_{gate} at various values of V_{drain} , and on/off ratio, threshold voltage and field-effect mobility μ , can be determined.

Experimental variables were chosen to show the device switching on and off, with linear and saturation current regimes. Hysteresis measurements were included in the scans to determine any memory effects.

FETS were measured following the thermal annealing techniques described in *Section 2.2.2.7*, and after exposure to toluene vapour in a similar fashion to that described in *Section 2.4.1*.

2.9 Other Techniques

Other polymer characterisation experiments were done in the course of this work. They are now described below, with thanks those who either allowed their machines to be used, or gave up their time to help characterise my samples.

2.9.1 Atomic Force Microscopy (AFM)

Atomic force microscopy is used to view the topography of the surface of a film in the nanometre regime. In a tapping AFM scan there is no contact with the sample, a cantilever tip is driven at its resonant frequency and placed very close to the surface of the sample, as the distance from the surface changes the vibrational amplitude of the tip varies due to electrostatic Van der Waals interactions. The deviations of reflected laser light focused on the tip are used to detect the small amplitude changes, and through a feedback loop intended to keep the oscillation amplitude constant the surface profile can be extracted.

AFM measurements were made at the Cornell Centre for Materials Research with a Veeco Dimension 3100 atomic force microscope operated in tapping mode at Cornell University. All AFM images were analysed using the WSxM (35) software for scanning probe microscopy.

2.9.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry is a technique used to find the phase transitions of a solid sample, usually T_{melt} , and the glass transition temperature T_g , as well as any crystallisation or liquid-crystal transition temperatures.

Sample and reference pans are heated, with the temperatures kept identical by changing the heatflow into the sample pan. By measuring the change in energy needed to heat the sample pan at the same rate as the reference the energy needed to heat the polymer sample can be measured. The changes in energy needed for phase transitions can then be seen on a graph of heatflow against time and the transition temperatures can be determined.

DSC was undertaken by Natasha Shirshova at Imperial College. 30 mg of pristine, untreated F8T2 was heated from room temperature to 330° C at a heating rate of 7.5° per minute. The sample was heated and cooled over the full range twice.

2.9.3 Gel-Permeation Chromatography (GPC)

Gel Permeation Chromatography is an oft used technique to ascertain the molecular weight distribution of a polymer sample. A Viscotek Triple Detector was used for its GPC, refractive index and right angle light scattering parts. For a GPC measurement a solution is forced through a tube, known as a column, containing pathways through it of different sizes. As the solution is forced through, the particles being studied are spread out in time, with the largest arriving soonest, having travelled the shortest distance and the smallest arriving last. GPC is a very easy technique, but can be inaccurate due to M_w values being for polystyrene equivalent and not absolute. This can sometimes be problematic (36; 37) with finding accurate mass values for rigid rod polymers such as those discussed here. Solutions were prepared as described previously.

2.10 Bibliography

1. **Sigma-Aldrich.** 685070. *Product Catalogue*.
2. **M Sims, K Zheng, M Campoy Quiles, R Xia, P N Stavrinou, D D C Bradley and P Etchegoin.** On the use of optical probes to monitor the thermal transitions in spin-coated poly(9,9-dioctylfluorene) films. *J. Phys.: Condens. Matter*. 2005. Vol. 17, 41, pp. 6307-6318.
3. **M Grell, D D C Bradley, X Long, T Chamberlain, M Inbasekaran, E P Woo and M Soliman.** Chain geometry, solution aggregation and enhanced dichroism in the liquidcrystalline conjugated polymer poly(9,9-dioctylfluorene). *Acta Polymerica*. 1999. Vol. 49, 8, pp. 439–444.
4. **A J Cadby, P A Lane, H Mellor, S J Martin, M Grell, C Giebeler, D D C Bradley, M Wohlgenannt, C An, Z V Vardeny.** Film morphology and photophysics of polyfluorene. *Phys. Rev. B*. 2000. Vol. 62, 23, pp. 15604-15609.
5. **Sigma-Aldrich.** 571652.
6. **B K Yap, R Xia, M Campoy-Quiles, P N Stavrinou, and D D C Bradley.** Simultaneous optimization of charge-carrier mobility and optical gain in semiconducting polymer films. *Nature Materials*. 2008. Vol. 7, pp. 376-380 .
7. **Sigma-Aldrich.** 698687. *Product Catalogue*.
8. **Sigma Aldrich.** *Sigma Aldrich Datasheet*. 2011.
9. **L Kinder, J Kanicki, J Swensen and P Petroff.** Structural ordering in F8T2 polyfluorene thin-film transistors. *Proceedings of SPIE*. Bellingham, WA : SPIE, 2003. Vol. 5217.
10. **G Lieser, M Oda, T Miteva, A Meisel, H-G Nothofer, and U Scherf.** Ordering, Graphoepitaxial Orientation, and Conformation of a Polyfluorene Derivative of the “Hairy-Rod” Type on an Oriented Substrate of Polyimide. *Macromolecules*. 2000. Vol. 33, 12, pp. 4490–4495.
11. **M Grell, D D C Bradley, M Inbasekaran, E P Woo.** A glass-forming conjugated main-chain liquid crystal polymer for polarized electroluminescence applications. *Advanced Materials*. 1997. Vol. 9, 10, pp. 798–802.

12. **Jasco International Co., Limited.** Jasco V560 Spectrophotometer Datasheet.
13. **Horiba Scientific.** FluoroMax-4. *How to Select a Spectrofluorometer*. 2011.
<http://www.horiba.com/fileadmin/uploads/Scientific/Documents/Fluorescence/Fluoromax-4.pdf>.
14. **Hellma Analytics.** Materials and Technical Information. http://www.hellma-analytics.com/text/129/en/pg_id,40/cells.html. July 2012.
15. **J C de Mello, H F Wittmann, and R H Friend.** An Improved Experimental Determination Of External Photoluminescence Quantum Efficiency. *Adv. Mater.* 1997. Vol. 9, 3, pp. 230–232.
16. **WaveMetrics Inc.** Igor Pro. *Lake Oswego, OR, USA*.
17. **The MathWorks Inc.** Matlab 7.10.0. *Natick, Massachusetts*. 2010.
18. **Matthew Ng.** Coupling of excited molecules to surface plasmons. *Imperial College London*. 2010.
19. **J R Lakowicz.** *Principles of Fluorescence Spectroscopy*. New York : Kluwer Academic / Plenum Publishers, 1999.
20. **R Farchioni and G Grosso.** Organic Electronic Materials: Conjugated Polymers and Low Molecular Weight Organic Solids. *Springer*. 2001.
21. **A P Hammersley.** FIT2D: An Introduction and Overview. *ESRF Internal Report ESRF97HA02T*. 1997.
22. **A P Hammersley, S O Svensson, M Hanfland, A N Fitch, and D Häusermann.** Two-Dimensional Detector Software: From Real Detector to Idealised Image or Two-Theta Scan. *High Pressure Research*. 1996. Vol. 14, pp. 235-248.
23. **A Guite.** Microstructure, morphology and device physics of gravure printed and solution processed organic field-effect transistors. *Imperial College London*. 2011.

24. **D M Smilgies, R Li, Z Di, C Darko, C M Papadakis and D Posselt.** Probing the Self-Organization Kinetics in Block Copolymer Thin Films. *Symposium OO "GISAXS" : Mater. Res. Soc. Symp. Proc.* 2009.
25. **A Amassian, V A Pozdin, R Li , D-M. Smilgies and G G Malliaras.** Solvent vapor annealing of an insoluble molecular semiconductor. *J. Mater. Chem.* 2010. Vol. 20, pp. 2623-2629.
26. **LOQ.** The LOQ Beamline. *LOQ Technical Documentation.* <http://www.isis.stfc.ac.uk/>.
27. **S M King and R K Heenan.** Using COLETTE. *Rutherford Appleton Laboratory Report RAL-95-005.* 1995.
28. **R K Heenan, S M King, R Osborn and H B Stanley.** COLETTE Users Guide. *Rutherford Appleton Laboratory Report.* 1989.
29. **G D Wignall and F S Bates.** Absolute calibration of small-angle neutron scattering data. *J. Appl. Crystallog.* 1987. Vol. 20, pp. 28-40.
30. **B H Zimm.** Molecular Theory of the Scattering of Light in Fluids. *J. Chem. Phys.* 1945. Vol. 13, 4, pp. 141-145.
31. —. The Scattering of Light and the Radial Distribution Function of High Polymer Solutions. *J. Chem. Phys.* 1948. Vol. 16, 12, pp. 1093-1098.
32. **Philip J Wyatt.** Light Scattering and the absolute characterization of macromolecules. *Analytica Chimica Acta.* 1993. Vol. 272, 1, pp. 1–40.
33. **Brookhaven Instruments Corporation.** BI-DNDC Product Documentation.
34. **IEEE.** IEEE Standard Test Methods for the Characterization of Organic Transistors and Materials. *IEEE Std. 1620-2004.* 2004. Vol. 65.
35. **I Horcas, R Fernández, J M Gómez-Rodríguez, J Colchero, J Gómez-Herrero, and A M Barro.** WSXX: A software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* 2007. Vol. 78.
36. **G W Heffner and D S Pearson.** Molecular characterization of poly(3-hexylthiophene). *Macromolecules.* 1991. Vol. 24, 23, pp. 6295–6299.

37. **T Yamamoto, D Oguro and K Kubota.** Viscometric and Light Scattering Analyses of CHCl₃ Solutions of Poly(3-alkythiophene-2,5-diyl)s. *Macromolecules*. 1996. Vol. 29, 5, pp. 1833–1835.

Chapter 3

Small Angle Neutron Scattering

This chapter presents my work using the LOQ experimental setup at the ISIS neutron source at RAL, with special thanks to Steve Parnell and Max Skoda for their experimental and analytical assistance and Joachim Steinke.

This study is dedicated to investigating the time dependence solvation issues found in poly(9,9-dioctylfluorene-alt-bithiophene) in toluene, THF and chloroform. F8BT and PFO were also studied, freshly prepared in THF and chloroform. The polymer form in solution was elucidated, along with values for the molecular weight and persistence length estimates.

Additionally an overview of the physics of neutron scattering is given, and how that pertains to the analysis of neutron scattering data. A review of the literature of the field is also presented.

3.1 Introduction

Small angle neutron scattering is a useful technique to probe structural properties in the nanometer range. This is much smaller than the particle size of polyfluorenes in solution, so is used to probe the structure and persistence length at smaller scales. It is a well established technique, used to investigate and characterise the microstructure of many materials (1).

Neutrons are scattered by nuclei in the studied materials, or by the spins of unpaired electrons in magnetic samples. Their nuclear interactions are very short ranged, meaning they are very penetrating and do not heat up or destroy samples in the same way X-rays can.

The neutron scattering studies presented here tie in very well with the other scattering techniques used later in *Chapters 4* and *6*. The structure of polyfluorenes in solution was studied to determine without a priori knowledge, the physical morphology in solution. It has also shown that SANS is a powerful technique for use on polyfluorene copolymers.

3.2 Theory and Analytical Concerns

SANS uses elastic-scattering to determine properties of the material in solution, as do SAXS and light scattering experiments, outlined in *Chapter 4*. In a neutron scattering experiment a neutron beam is incident upon the probed material with the relevant neutron wavelength given by the De Broglie relationship (2).

$$\lambda = \frac{h}{mv} \quad [3.1]$$

Where h is Planck's constant, m the neutron mass and v its (group) velocity. For the SANS undertaken in this work neutron wavelengths from 1–10 Å (3) were available.

Neutrons are scattered by atomic nuclei and, as with light scattering, in the analysis here a dilute solution is assumed. Elastic neutron scattering is analysed in reciprocal space using the q vector as the prime variable. Using Bragg's law (4), radiation scattered from two planes, separated by distance d will be coherent when the following condition is met:

$$n\lambda = 2d \sin \theta \quad [3.2]$$

As shown in *figure 23*.

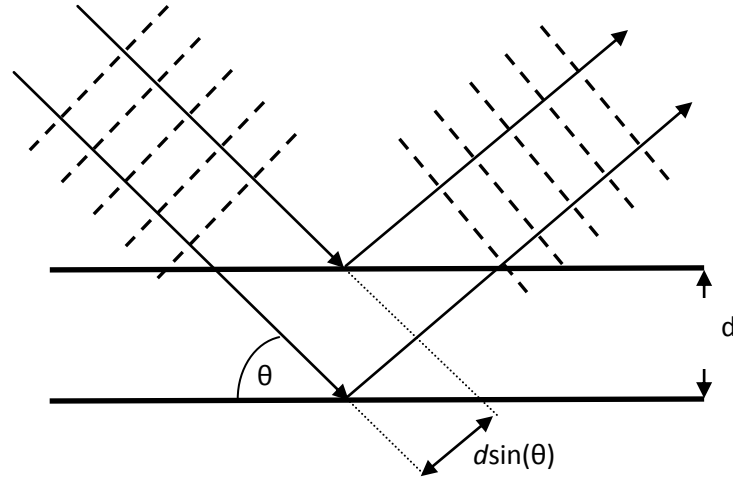


Figure 23 Coherent scattering from two planes separated by d

Additionally, when working in reciprocal space, taking k_i as the wavevector of the incident beam and k_f as that of the outgoing beam, and elastic scattering such that $|k_i| = |k_f|$, we can define q , the scattering vector as:

$$k_f - k_i = q \quad [3.3]$$

Introducing the reciprocal scattering vector G , defined by Laue (5) in 1912, as $2\pi/d$ and the scattering angle between incident and outward beam at 2θ , we obtain [3.4], which is analogous to Bragg's law.

$$q = \frac{4\pi \sin \theta}{\lambda} \quad [3.4]$$

Using [3.2] and [3.4] it follows that:

$$\sin \theta = \frac{\lambda}{2d} = \frac{\lambda q}{4\pi} \quad [3.5]$$

$$d = \frac{2\pi}{q} \quad [3.6]$$

When only the first order scattering plane, $n = 1$, is used it can clearly be seen from [3.6] that the relationship between d and q is inversely proportional, so as higher q values are probed, smaller features in real-space are being studied. Using [3.6] the real space domain which is probed by these studies is 2.2–70 nm, much smaller than the R_g established in *Chapter 4*, well within the Perod region described below.

The ability to deuterate solvents or parts of material being studied allows a very high contrast of materials under analysis, this allows a huge difference in coherent neutron scattering lengths F_N , coherent X-ray scattering lengths F_X and cross sections between H and D atoms, summarised below (6), with X-ray scattering lengths, and the values for carbon.

	H	D	C
Atomic Mass	1	2	12
N electrons	1	2	6
$F_N \cdot 10^{-12} \text{ cm}$	-0.374	0.667	0.665
$F_X \cdot 10^{-12} \text{ cm}$	0.282	0.282	1.69

Table 7 Scattering lengths of H, D and C atoms (6)

Deuteration is vital for getting good contrast between the sample, or parts of the sample, and the background medium. Shown below in *figure 24*, by deuterating the solvent, contrast is achieved between the polymer sample and the solvent background. In my work deuterated solvents were used, however in other fields parts of the studied material can be deuterated (7).

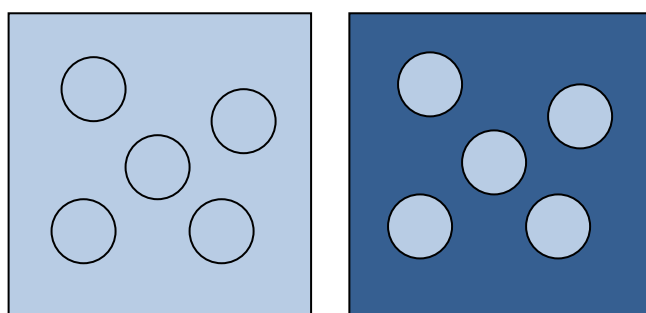


Figure 24 Example of contrast improvement through deuteration

As the key difference between MALS, SAXS and SANS is the incident scatterer, the same techniques and formalisms can be used in the process of analysis, notably those of Zimm , Gunier (10) and Debye (11). Neutron scattering is a useful technique as results can be obtained very quickly after data reduction, from standardised plotting techniques.

SANS is unlikely to have obvious scattering peaks as in NMR or diffraction experiments as crystals are not being studied, so more general analysis is undertaken. The vital plots used in SANS analysis are Guinier ($\ln[I(q)]$ vs q^2), which in its general form can yield information about the radius of gyration of scattering object, through:

$$I(q) = I_0 e^{-\left(\frac{q^2 R_g^2}{3}\right)} \quad [3.7]$$

Hence plotted as the natural logarithm, the gradient of the plot is:

$$-\frac{R_g^2}{3} \quad [3.8]$$

There is a modified version by Glatter and Kratky (12) in 1982, for low q analysis of cylinders, and flat objects. These analysis techniques are however outside the scope of this work, as they rely upon the sample being within the Guinier regime, which is where:

$$qR_g < \sqrt{3} \quad [3.9]$$

Using [3.9] and values of R_g from Chapter 4 the SANS analysis here is approximately an order of magnitude too large for analysis using Kratky's approach.

The Perod (13) law and plots however, corresponds to regions where the scattering object is larger than the scattered radiation and hence relates to the internal, local structure of objects. When $\text{Log}[I(q)]$ vs $\text{Log}(q)$ is plotted, the slope n , leads to information about the fractal dimension of the object, as from the Perod law:

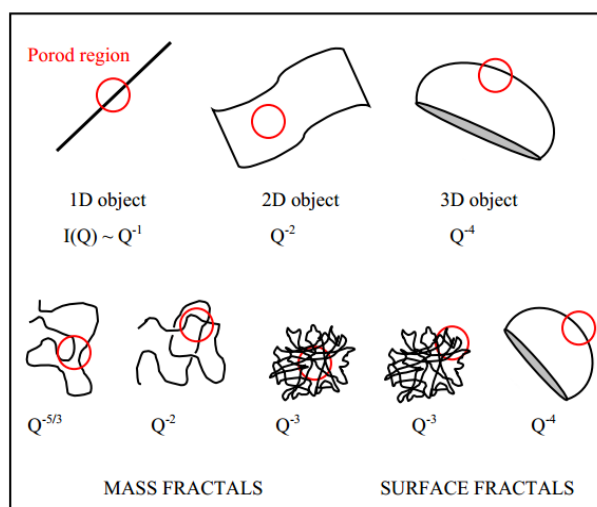
$$I(q) = Aq^{-n} + B \quad [3.10]$$

where B is a constant due mostly to the incoherent scattering background, and A is also a constant, related to the surface/volume ratio of the scatterer. Values of n and corresponding shapes are summarised in *tables 8* and *9* (14; 15) and in *figure 25* (14), extra details are included for polymer systems as n is related to the inverse of the excluded volume parameter by $n = 1/\nu$. For comparison with the equations above and these figures, $q^{-n} = Q^{-n}$.

n	General Characteristics
1	Rigid Rods
3 - 4	Rough surface, of fractal dimension D, with $D = 6 - n$
4	Smooth Surface

Table 8 Structural characteristics for Perod analysis

n	Polymer Characteristics
5/3	Fully swollen coils
2	Gaussian Chains in a dilute environment
2 - 3	Branched gels / networks
3	Collapsed polymer coils

Table 9 Structural characteristics for Perod anlysis with $1 < n < 3$ Figure 25 Different physical conformations for values of n in the Perod regime (14)

Throughout this work on neutron scattering Perod plots are used extensively and the Perod exponent is used to gain information about the makeup of the polymer sample. The measured scattering intensity is clearly a sum of particle, solvent and cuvette scattering effects, which are then corrected for solvent and cuvette effects. As neutrons are spin $\frac{1}{2}$ particles they interact with the magnetic field of objects and this is a constant incoherent term in the

scattering intensity. Data reduction was achieved and calibrated through the use of the COLETTE (16) software by Maximillian Skoda at RAL.

3.3 Previous Work

Small angle neutron scattering is a very well established technique in the field of polymer characterisation and in others (17; 18), notably biology (19). The quality of the ISIS source at RAL has meant it has been a well used resource since its inception (3).

Work on polyfluorene copolymers, PF2/6 and poly[9,9-di(3,7,11-trimethyldodecyl)fluorene] with varying fractions of randomly distributed fluorenone has been undertaken by Dias, Knaapia and Monkman (20) where they found the polymers to adopt a worm-like configuration in solution, to confirm that green emission in polyfluorenes is not due to excimer formation from a folded configuration and other complex photophysical behavior (21). Using dilute solutions of $\sim 10^{-3}$ mg/ml they studied fluorescence quenching, but also studied polyfluorene copolymers at 10 mg/ml concentrations in deuterated toluene at LOQ.

They, like others (22; 23) show a wormlike configuration, with persistence length of 7 nm, and that there is likely to be minimal if any interaction effects even increasing the concentration to that appropriate for neutron studies. The classic coiled polymer chain configuration is likely to be only found at higher concentrations (24) They suggest that this rod-like configuration is usual for polyfluorene copolymers in toluene, but not all pi-conjugated hairy-rod polymers, such as MEH-PPV (25).

In similar work Fytas et al (22) studied polyfluorene copolymers with SANS to determine wormlike chain properties of persistence length, and cross-sectional diameter, by probing in a difference q-regime where Kratky and Guinier analyses are valid.

Perhaps the largest body of work on SANS on polyfluorene and its copolymers in solution has been undertaken by Knaapila et al (26; 27; 28; 29) since 2006. They have comprehensively studied PFO in solutions, characterising the polymer structure in solution, particularly with varying side chain length (PF6-PF9) and solvent quality. They consistently found that PFO adopts a rod-like conformation of single polymer chains dissolved to molecular level. However PF2/6 a branched sidechaing copolymer of PFO in methylcyclohexane, was found to form sheets of two thicknesses, either single molecule meshes ~ 1 nm thick, or composed larger sheets composed of many layers, potentially described as early stages of PFO crystallization. Obviously, these changes between branched and linear side chain polymers in good and bad

solvents highlights the importance of structural knowledge and solvent choice for analysis. This work was built upon in 2008 (28) where side-chain lengths and branching can be used to control solution structure of polyfluorenes. They also studied (26) polyfluorene and copolymers with shorter sidechains in toluene solutions over timescales of up to 10 days, seeing very strong aggregation effects in PF6 solutions. When plotted on log-log Perod plots of $I(q)$ against q , a gradient of -1 is seen, as expected for rod-like polymers, however after a longer time period there is a sharp upturn for PF6, at $q = 0.06 \text{ \AA}^{-1}$, suggesting aggregation into sheets. Their summary of conclusions from these changes is reproduced below.

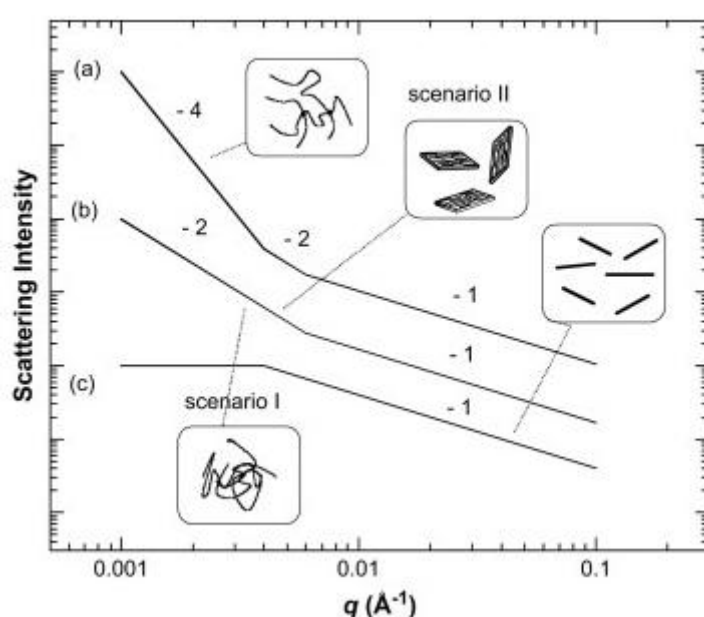


Figure 26 Schematic description of the scattering data and proposed structures of PFs in toluene: (a) a network-like structure with cross-linked nodes; (b) a structure of rodlike particles forming Gaussian coils (scenario I) or sheet-like aggregates (scenario II) in the longer length scales, and (c) a structure of fully dissolved rodlike particles (essentially single polymer chains) (26)

These results again highlight how the aggregation properties of polyfluorenes can be tuned by varying side-chain length and solvent quality. Interestingly larger sidechains promote dissolution down to single chain level as the shorter side-chain polymers were those found to form aggregate sheets. This analysis was further confirmed with NMR studies on the same solutions, with the longer sidechain groups of PF8 having mostly toluene-fluorene contact, and shorter PF6 being mostly fluorene-fluorene. Toluene-fluorene contact suggests good dissolution, whereas fluorene-fluorene contact, as coiling in rigid rods at this scale is highly unlikely, suggests sheet like aggregates.

They have also recently published (30) a further addition to their polyfluorene analysis, including beta-phase development in PFO containing co-polymers, in solutions of d-methylcyclohexane. They conclude that increasing proportions of PFO decrease the amount of free polymer in solution, and that sheet like structures are formed containing beta-phase material.

Although not directly a SANS study, Maçanita et al (31) have studied F8T2 in DCH solutions over a wide range of temperatures. They found substantial increases in chain ordering at low temperatures, however found similar spectroscopic changes such as improved vibrational resolution in absorption measurements in poorer solvents. They do however suggest that long coplanarisation of the chains cannot happen as the thiophene unit can only be coplanar with one of its neighbouring fluorene units.

Similar SANS and NMR analysis of PFO in toluene solution has been undertaken by Habibur Rahman et al (32) on concentration dependence of aggregation of PFO with similar conclusions.

F8T2, the largest focus of my SANS studies seems to be absent in the literature, although gellation and aggregation studies of other polymers has been completed (33; 34).

3.4 Results

All the polymers studied here are on the frontier between use of the Guinier and Perod equations for analysis. This is due to the overall size of the polymers in solution, as determined by light scattering with R_g 100-150 nm, except for F8BT in toluene of 22nm. The crossover between the Perod and Guinier regions q' , is shown by [3.11] (1) and is based on the established Guinier law generalised for elongated objects (12). The Perod region is defined as $q > q'$, and the Guinier for $q < q'$.

$$q' = \frac{1}{R_g} \sqrt{\frac{3n}{2}} \quad [3.11]$$

As the q' is dependent on R_g and the shape of the particles n (figure 25), and falls within the range studied both approaches are used. Perod analysis is used to understand the chain morphology as rods, coils or aggregates and results are plotted $I(q)$ vs q .

Using Guinier analysis $\ln[I(q)]$ vs q^2 is plotted with the slope being $-R_g^2/(3-n)$ taking n as 1 (equivalent to rods), a modified version of [3.8] (1). Clearly a radius of gyration R_g can be determined, although at the length scales probed this can clearly not be understood as the whole chain but a size within the chain. The physical meaning is not well understood, and absolute values should be treated with caution as $n = 1$ (rods) is not necessarily valid.

Molecular weight can be calculated from a concentration series following the procedures outlined in (35). This entails plotting $I(q)/c$ and extrapolating to $q = 0$, these are then plotted and the value of $I(0)$ at $c = 0$ can be used in [3.12] below.

$$M_w = \frac{N_A}{(\Delta b)^2} \left(\frac{I(0)}{c} \right)_{c=0} \quad [3.12]$$

where N_A is Avogadro's constant, Δb the scattering length density difference between the polymer and solvent, experimentally calculated by Max Skoda as $5.15 \times 10^{10} \text{ cm}^{-2}$.

3.4.1 F8T2

F8T2 solutions in THF were studied as a fresh sample immediately placed into the experimental equipment after dissolution and slight heating, and identically produced samples left sealed, at room temperature for 24.5 hours. These are here on referred to as 'fresh' and 'aged' samples respectively. Plotting the scattering intensity $I(q)$ against q in $\text{\AA}^{-1}$ on log/log scales, the magnitude of n can be found, where the gradient of slope is q^{-n} . No change in n between fresh and aged samples suggests no change in conformation between them. F8T2 in THF is well dissolved almost immediately and neither continues to dissolve over time nor aggregates over the timescales studied. This is an important result as it validates the use of F8T2 in THF solutions over a broad timescale. *Figure 27* shows $I(q)$ vs q for fresh and aged F8T2 in THF solution. The fitted powers of q , are shown below in *table 10*. Values of n below 1 are unusual but suggest a long, rod-like conformation over the q range studied ($\sim 2\text{-}70$ nm in real space). This agrees well with light scattering results discussed in *Chapter 4*.

Guinier plots were also studied, and fitting from $0.01\text{-}0.06 \text{ \AA}^{-2}$ leads to R_g values of 5.0 and $5.6 \pm 1 \text{ \AA}$ for fresh and aged solutions, again showing no change with time in THF solutions.

Values of n less than 1 in Perod plots are unusual, and I ascribe them to very well dissolved rod like polymers but with increased rotation along chain length. I believe these unusually low values come from polymer chains not being rod like, but hairy-rods and the effects of twisting

sidechains along the length of the polymer. Lower values would be expected in better solvents as this twisted conformation would allow a larger interface between polymer and solvent, hence better dissolution.

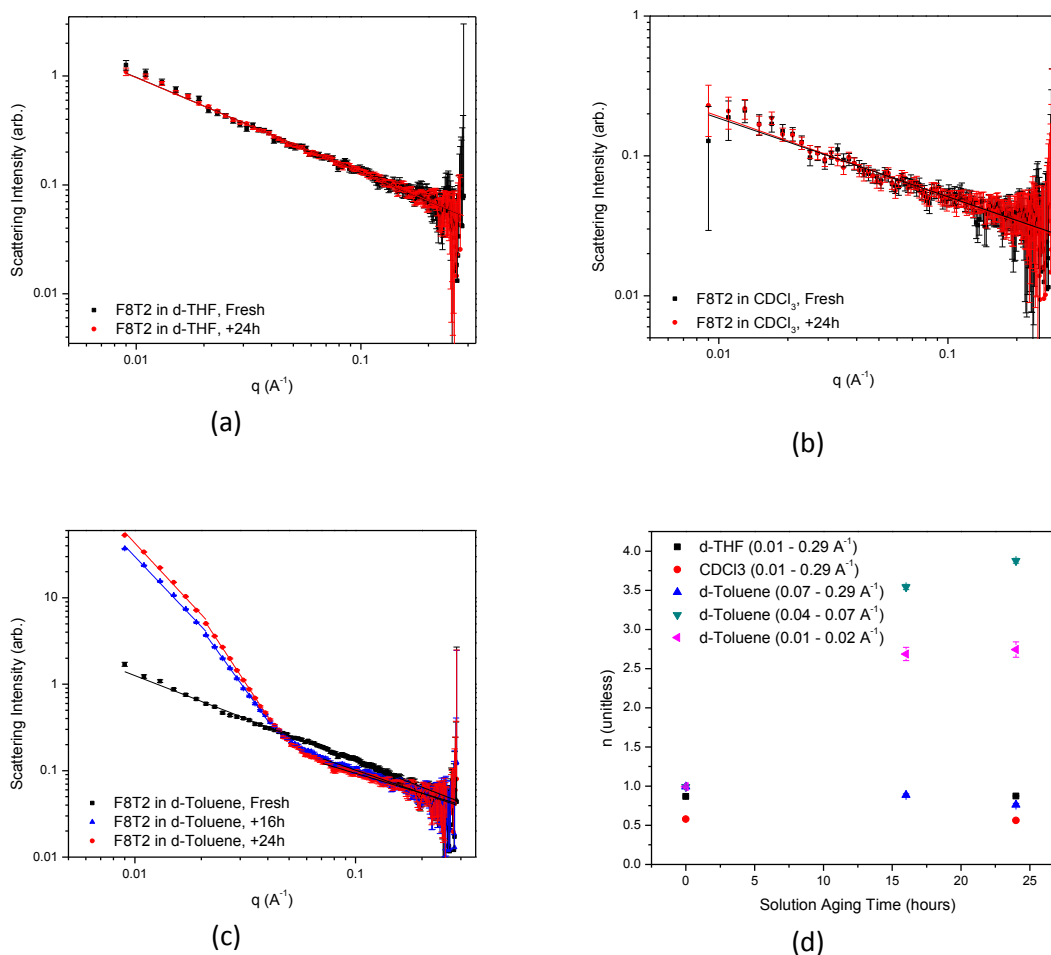


Figure 27 Neutron scattering intensities against q for F8T2 in (a) d-THF, (b) CDCl_3 , (c) d-Toluene. Variation in scattering with ageing solutions 24 hours is shown. Summary of magnitude of powers of q for each solvent is shown in (d).

Chloroform is a very good solvent for F8T2, again shown by the straightness of the plot over the q range studied. Showing a well dissolved, rod like polymer, with a gradient <1 . Unfortunately the results are noisier than with THF, but also appear to show no change between fresh and 26 hour old solutions, confirming that chloroform stays a good solvent for F8T2 over timescales of a day. From the Perod plots n values for F8T2 for cloroform are found to be even lower than those in THF, which is to be expected if n below 1 is understood to a measure how well dissolved the polymer is and of twistedness along the backbone and sidechains. Guinier analysis gives R_g values of 3.8 and 3.5 ± 1 $\text{\AA}$ for fresh and aged solutions

respectively which is slightly smaller than that of F8T2 in THF. I believe this to be a consequence of twisting along the length of the backbone. These lengths of 3-6 Å are comparable in scale to the unit cell size and rotation would be expected to decrease effective length.

Although THF and chloroform were found to be good solvents for F8T2 remaining stable and dissolved over time, toluene was found to not be. This was as expected, as F8T2 in toluene has been seen to have very obvious aggregation, *figure 27(c)*.

Freshly dissolved F8T2 in toluene shows a linear scattering intensity over the entire q -range, suggesting initially a well dissolved, rod like polymer. However, where the toluene samples split from the those in the 'good' solvents, is that after just 16 hours, a large gradient change is seen in the q range $< 0.055 \text{ Å}^{-1}$, or 11-70 nm in real space. This is explained as aggregation into larger 3D objects, with sheets being the most likely candidate by comparison to (26), as $n \approx 4$ and is likely to be noticable in toluene due to sidechain lengths of F8T2. Although aggregation is visible in toluene solutions, these results show that the aggregation happens within the first 16 hours, at 10mg/ml concentrations and although continues after that, further affects the solution minimally. It is also important to make sure toluene solutions of F8T2 are used quickly after dissolving. The Guinier analysis of F8T2 in toluene did not show the large changes seen in the Perod plots, when fitted from 0.01 to 0.6 Å^{-2} radius values were found to be $6.5 \pm 1 \text{ Å}$, $5.6 \pm 1 \text{ Å}$ and $5.3 \pm 1 \text{ Å}$ with increasing dissolution time. These values are higher than those in THF, with a small decrease suggesting at these very small scales there is still improving dissolution and chain twisting despite the large scale aggregation

As the only Perod plot with a sharp change in gradient, at 0.055 Å^{-1} persistence length can be calculated using [3.12] (36), giving a value of 35 Å .

$$l_p = \frac{6}{\pi q_{intercept}} \quad [3.12]$$

Three different regimes can be seen in the aged toluene data, q above 0.055 Å^{-1} , corresponding to values of 2-11 nm, a mid q value of 0.02 - 0.055 Å^{-1} corresponding to 11-31 nm and a low q range below 0.02 Å^{-1} , from 2-11 nm, the n values of these regimes are shown in *table 10*.

Time (hrs)	THF	CDCl ₃	Toluene high q	Toluene mid q	Toluene low q
2	0.87	0.58	0.99	0.99	0.99
16	-	-	0.88	3.54	2.69
24	0.87	0.56	0.76	3.88	2.74

Table 10 Values of n for F8T2 in each solvent over time

We can see from *table 10* that for the good solvents THF, chloroform and toluene (at high q) that n values are below 1, suggesting well dissolved yet potentially twisting polymers. At the middle values of q in toluene, clear aggregation effects are seen on a range 11-31 nm, these are ~ 3 -10 times the persistence length found and well below the R_g values found by light scattering in *Chapter 4* of 143 ± 12 nm, I interpret this as aggregation into loose sheets at those length scales.

F8T2 solutions in d-THF and d-chloroform were also studied for temperature dependence over the range ~ 25 -53° C. As before Period plots are used and n is calculated. The results are shown in *figure 28*. *Figure 28(c)* and *(d)* show n with temperature, where it can easily be seen that an inverse linear relationship holds. This suggests that as the solution is heated the polymer chains stretch and twist even further. The low contrast between the polymer and CDCl₃ and time constraints mean the data is still noisy, and the conclusions drawn not be overstated.

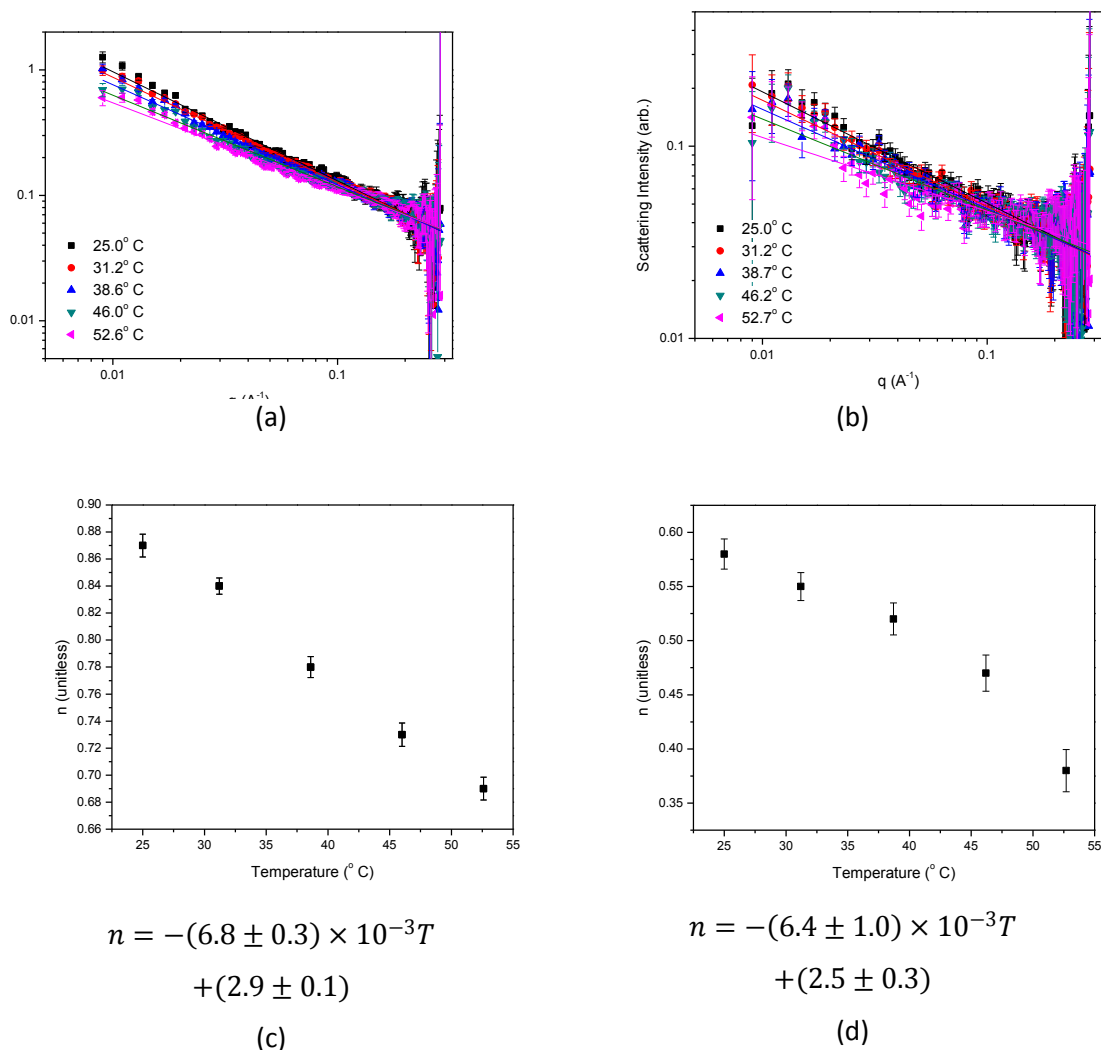


Figure 28 Neutron scattering intensities against q for F8T2 in (a) d-THF, (b) CDCl_3 . Variation in scattering with temperature of solutions is shown. The trend of the (mod) index n is shown for d-THF in (c) and CDCl_3 in (d), with formulae for n related to temperature T in Kelvin.

The results of the temperature dependence study of F8T2 in THF was graphed as an Arrhenius plot, with $\ln(n)$ against $1/T$ in Kelvin, to establish a conformational activation energy. From [3.13] it clearly follows that the gradient of this graph is $-E_A/k_B$, hence E_A can be calculated, where k is rate constant and A is a pre-exponential factor. It is assumed that n is temperature and structure dependent.

$$k = Ae^{\frac{-E_A}{k_B T}} \quad [3.13]$$

The plot is shown in *figure 29*, and E_A per molecule is calculated to be 72 ± 4 meV in THF and 116 ± 24 meV in CDCl_3 . These values compare very favourably with those of Macanita et al (31) for excited state conformational changes of F8T2 in DCH. They attribute these conformation changes to the bithiophene monomers able to be coplanar with only one of its neighbouring fluorene monomers. This is consistent with the results above, as the increase in available energy in chloroform solutions would allow more twisted conformations to be taken up by the dissolved polymer. They describe this twisted structure as analogous to the beta phase of PFO.

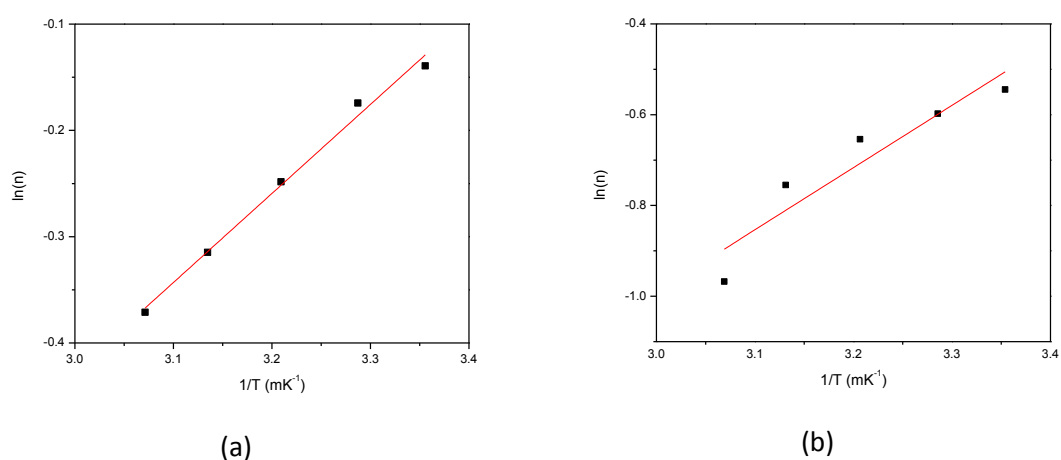


Figure 29 Arrhenius plots of 10 mg/ml F8T2 in (a) THF and (b) CDCl_3

The final neutron study done on F8T2 solutions was a measure of concentration dependence. This allows a calculation of molecular weight to be performed following the procedures outlined in (37). A Perod plot of the data is shown in *figure 30(a)* with values of n shown in *figure 30(b)*, these suggest that F8T2 in THF has a well dissolved rod like structure with $n \approx 1$ or below over an order of magnitude change in concentration.

The technique outlined in (37) relies on the extrapolation of $I(q)/c$ data to $q = 0$, which is then extrapolated to concentration $c = 0$ and used in [3.12]. This initial extrapolation has been a problem in this analysis as the data is expected to level off at low q values on a logarithmic ordinate axis, this was not seen in our data so extrapolation was completed on the lowest 9 points, a small number but leading to an underestimate rather than the large over estimate of taking fewer points due to the expectation that the data should level off. From these an M_w value of just 1100 ± 150 g/mol was found, between 1 and 2 orders of magnitude lower than that from light scattering. This extrapolation technique, although found to work well by Plestil et al is not valid at q values without a plateau at low q .

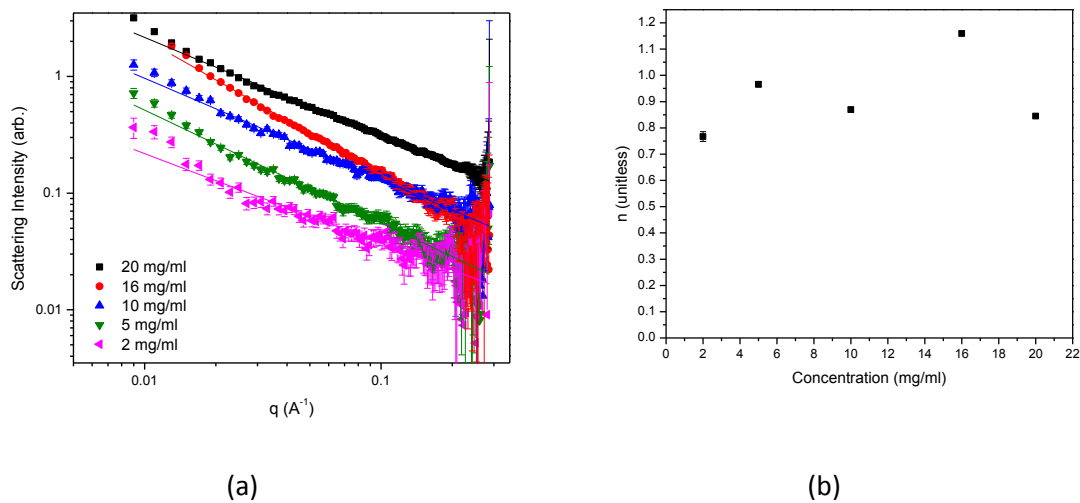


Figure 30 Scattering intensity variation of F8T2 in d-THF against concentration is shown in (a), (b) graphically shows the power n against concentration, having a mean value of 0.95 ± 0.07 .

3.4.2 F8BT and PFO

The polyfluorenes F8BT and PFO were also studied with SANS, in both d-toluene and d-chloroform solutions. The scattering intensities with respect to q are shown below in *figure 31*, along with the equivalent scattering intensities for F8T2 for comparison.

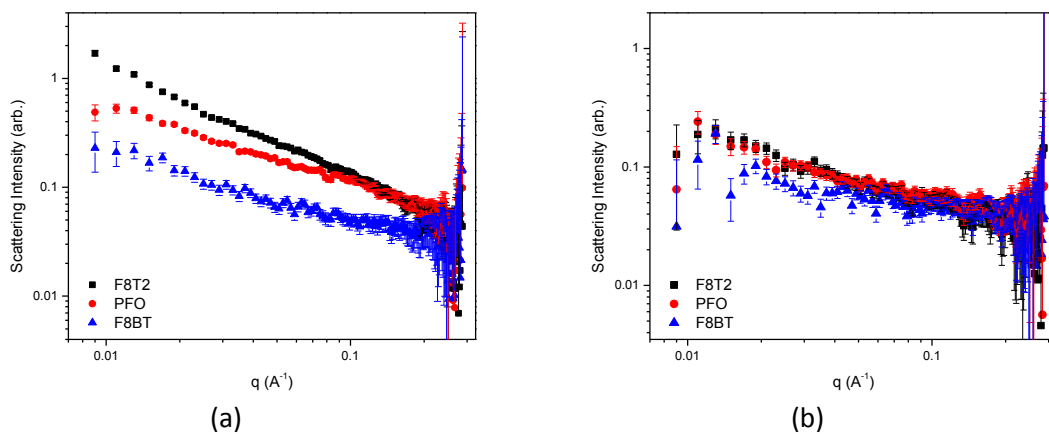


Figure 31 Neutron scattering intensity with q of 10mg/ml F8T2, PFO and F8BT in (a) d-toluene, (b) $CDCl_3$.

The values of n for all polymer and solvent combinations investigated are summarised in *table 11*.

Polymer	THF	Toluene	Chloroform
F8T2	0.87	0.99	0.58
PFO	-	0.70	0.47
F8BT	-	0.56	0.28

Table 11 Values of n for each polymer/solvent combination studied

Using the same analysis as with F8T2, F8BT clearly has much lower values of n in both toluene and chloroform. This is to be expected as they are both known as good solvents for F8BT. F8BT has a consistently high torsion angle along the backbone (38) in solution giving credence to this analysis.

PFO shows similar results in toluene and chloroform, consistently well dissolved with $n < 1$, and values between those of F8T2 and F8BT. This is not surprising as PFO is not as twisted as F8BT along the backbone, and clearly makes up only ~50% of copolymer chains, hence any twisting or reconfiguration of the sidechains would have a proportionally larger effect. Studies with temperature could help to understand where the twist and reconfiguration is likely to be on the polymer, by comparison with the work of Macanita et al (31).

3.5 Conclusions

This study has re-iterated that small-angle neutron scattering is a useful, non-damaging technique for the study of polyfluorene polymers in solution. However further modification and extension to the Guinier-Perod model used here would be useful. We have shown that all three polymers studied, F8T2, PFO and F8BT, have taken up very rigid rod like conformations in toluene and chloroform, and F8T2 in THF solution. Allowing time to pass and aggregation of the F8T2 solution in toluene over 16 hours suggests a sheet like aggregate structure, similar in scale to that found in PFO by Knaapila et al (26).

From Perod analysis values of n were interpreted as being indicative of increased torsion in the backbone of the polymers and hence improved dissolution, with Arrhenius plots to calculate activation energy in F8T2 comparable to those found by Macanita et al (31), where they find thermally induced conformation changes. As expected chloroform was the best solvent for all these polymers, showing the lowest n for each polymer.

SANS neutron scattering can be a very powerful technique in studying structural changes of polymers in solution.

The molecular weight of the F8T2 sample studied has also been calculated using the method described by Pleštil in (37), with the value of 1100 ± 150 g/mol being at least an order of magnitude lower than that calculated by the macromolecular technique of light scattering in *Chapter 4*, this is easily attributed to poor extrapolation without plateaus in $I(q)$ at low q values.

Studies over the range 2-20 g/ml of F8T2 in THF showed no change in the conformation or suggestions of aggregation of the polymer in solution, as n was consistently ~ 1 over that range.

Guinier analysis was used to calculate a radius of gyration for the samples in solution, however it is not clear the physical meaning of this, it was found to decrease slightly with the quality of solvent; ie. toluene $\rightarrow$ THF $\rightarrow$ chloroform.

SANS is a very useful technique, especially at high flux installations such as ISIS, from which a range of useful information can be recovered. Here the improved dissolution and conformational changes of the polyfluorene copolymers have been found and discussed.

3.6 Suggested Further Work

Further work in this domain should be focused on *in situ* measurements of dissolving dynamics, made possible by the high neutron flux of the ISIS source. What appear to be long term effects of polyfluorenes dissolving, seen in *Chapter 4*, could be studied in solutions where a high contrast ratio is available, such as THF and toluene.

Further work on PFO in THF would be useful, as aggregation effects seen in *Chapter 4* could be studied further.

A clear region for further study would also be model-fitting and more computational work in tandem with generating the excellent experimental data allowed by ISIS and LOQ. Computational models would allow more knowledge of the precise sizes of the rod-like structures these polymers take up in solution, this, in my view would impressively extend the analysis of these three polymers undertaken here. Being able to model the polymers as more complex than purely rods could help to understand the physical meaning of R_g found by Guinier analysis.

The Arrhenius analysis used to calculate activation energy of the conformational changes of F8T2 in THF should be repeated with more solvents, as THF and chloroform quite different results and with further polymers. This could help to understand if is twisting in the backbone being seen, or sidechain effects.

Perod analysis has been very useful in understanding the shape of these polymers in solution, increasing the q range to larger values of q would increase the regime in which this technique can be used. Extension to lower q values would hopefully allow a plateau to be seen and accurate determination of M_w values, for direct comparison with those established by light scattering and/or GPC.

A very general extension to this work would be an increased range of solvents, and different M_w values, and possibly extention of the time scales involved, to match the longer values used in *Chapter 4*.

3.7 Bibliography

1. **B Hammouda**. SANS from Polymers Tutorial. *NIST Center for Neutron Research*. 1995.
2. **L De Broglie**. *Recherches sur la théorie des quanta (Researches on the quantum theory)*. Paris : s.n., 1924.
3. **R K Heenan, J Penfold and S M King**. SANS at Pulsed Neutron Sources: Present and Future Prospects. *J. Appl. Cryst.* 1997. 30, pp. 1140-1147.
4. **W L Bragg**. The Diffraction of Short Electromagnetic Waves by a Crystal. *Proc. Cambridge Phil. Soc.* 1913. 17, pp. 43-57.
5. **M Laue**. Eine quantitative Prüfung der Theorie für die Interferenz-Erscheinungen bei Röntgenstrahlen. reprinted in *Ann. Phys.* : s.n., 1913. 41, pp. 989-1002.
6. **C T Chantler, K Olsen, R A Dragoset, J Chang, A R Kishore, S A Kotochigova, and D S Zucker**. *Detailed Tabulation of Atomic Form Factors, Photoelectric Absorption and Scattering Cross Section, and Mass Attenuation Coefficients for $Z = 1-92$ from $E = 1-10$ eV to $E = 0.4-1.0$ MeV*. s.l. : NIST, Physical Measurement Laboratory.
7. **ILL**. Deuteration Isotope Labelling Facility. *European Molecular Biology Laboratory*.
8. **B H Zimm**. Molecular Theory of the Scattering of Light in Fluids. *J. Chem. Phys.* 1945. Vol. 13, 4, pp. 141-145.
9. —. The Scattering of Light and the Radial Distribution Function of High Polymer Solutions. *J. Chem. Phys.* 1948. Vol. 16, 12, pp. 1093-1098.
10. **A Guinier**. *Small-angle scattering of X-rays*. 1955.
11. **P Debye**. Light Scattering in Solutions. *J. Appl. Phys.* 1944. Vol. 15, 4, pp. 338-342.
12. **O Kratky and O Glatter**. *Small-Angle X-Ray Scattering*. s.l. : Academic Press, 1982.
13. **Perod**. 1951.

14. **B Hammouda.** Probing Nanoscale Structures - The SANS Toolbox. *The Centre for Neutron Research, NIST*. Gaithersburg : s.n.
15. **P W Schmidt.** Some Fundamental Concepts and Techniques Useful in Small-Angle Scattering Studies of Disordered Solids. [book auth.] H Brumberger. *Modern Aspects of Small-Angle Scattering*. Dordrecht, The Netherlands : Kluwer Academic Publishers, 1995.
16. **S M King and R K Heenan.** Using COLETTE. *Rutherford Appleton Laboratory Report RAL-89-128*. s.l. : Rutherford Appleton Laboratory Report RAL-95-005, 1995.
17. **D I Svergun, S Richard, M H J Koch, Z Sayers, S Kuprin, and G Zaccai.** Protein hydration in solution: Experimental observation by x-ray and neutron scattering. *PNAS*. 1998. Vol. 95, 5, pp. 2267-2272.
18. **R Triolo, L J Magid, J S Johnson Jr and H R Child.** Small-angle neutron scattering from aqueous micellar solutions of a nonionic surfactant as a function of temperature. *J. Phys. Chem.* 1982. Vol. 86, 19, pp. 3689–3695.
19. **M V Petoukhov, D I Svergun.** Analysis of X-ray and neutron scattering from biomacromolecular solutions. *Current Opinion in Structural Biology*. 2007. Vol. 17, 5, pp. 562–571.
20. **F B Dias, M Knaapila, and A P Monkman.** Fast and Slow Time Regimes of Fluorescence Quenching in Conjugated Polyfluorene–Fluorenone Random Copolymers: The Role of Exciton Hopping and Dexter Transfer along the Polymer Backbone. *Macromolecules*. 2006. Vol. 39, 4, pp. 1598–1606.
21. **E Hennebicq, G Pourtois, G D Scholes, L M Herz, D M Russell, C Silva, S Setayesh, A C Grimsdale, K Müllen, J-L Brédas, and D Beljonne.** Exciton Migration in Rigid-Rod Conjugated Polymers: An Improved Förster Model. s.l. : J. Am. Chem. Soc., 2005. Vol. 127, 13, pp. 4744 - 4762.

22. **G Fytas, H G Nothofer, U Scherf, D Vlassopoulos, and G Meier.** Structure and Dynamics of Nondilute Polyfluorene Solutions. *Macromolecules*. 2002. Vol. 32, 2, pp. 481-488.
23. **M Knaapila, R Stepanyan, M Torkkeli, B P Lyons, T P Ikonen, L Almásy, J P Foreman, R Serimaa, R Güntner, U Scherf, and A P Monkman.** Influence of molecular weight on the phase behavior and structure formation of branched side-chain hairy-rod polyfluorene in bulk phase. *Phys. Rev. E*. 2005. Vol. 71, 4, p. 041802.
24. **A Y Grosberg and A R Khokhlov.** Statistical Physics of Macromolecules. *American Institute of Physics*. New York : American Institute of Physics, 1994.
25. **W-C Ou-Yang, C-S Chang, H-L Chen, C-S Tsao, K-Y Peng, S-A Chen and C C Han.** Micellelike aggregates in solutions of semirigid hairy-rod polymers. s.l. : Phys. Rev. E, 2005. Vol. 72, 3, p. 031802 .
26. **M Knaapila, L Almásy, V M Garamus, M L Ramos, L L G Justino, F Galbrecht, E Preis, U Scherfe, H D Burrows, and A P Monkman.** An effect of side chain length on the solution structure of poly(9,9-dialkylfluorene)s in toluene. *Polymer*. 2008. Vol. 49, 8, pp. 2033–2038.
27. **M Knaapila, V M Garamus, F B Dias, L Almásy, F Galbrecht, A Charas, J Morgado, H D Burrows, U Scherf and A P Monkman.** Influence of Solvent Quality on the Self-Organization of Archetypical Hairy Rods–Branched and Linear Side Chain Polyfluorenes: Rodlike Chains versus “Beta-Sheets” in Solution. *Macromolecules*. 2006. Vol. 39, 19, pp. 6505-6512.
28. **M Knaapila, R Stepanyan, M Torkkeli, V M Garamus, F Galbrecht, B S Nehls, E Preis, U Scherf, A P Monkman.** Control over phase behavior and solution structure of hairy-rod polyfluorene by means of side-chain length and branching. *Phys. Rev. E*. 2008. Vol. 77, 5, p. 051803.

29. **M Knaapila, V M Garamus, L Almásy, J S Pang, M Forster, A Gutacker, U Scherf and A P Monkman.** Fractal Aggregates of Polyfluorene–Polyaniline Triblock Copolymer in Solution State. *J. Phys. Chem. B.* 2008. Vol. 112, 51, pp. 16415–16421.
30. **M Knaapila, D W Bright, B S Nehls, V M Garamus, L Almásy, R Schweins, U Scherf, and A P Monkman.** Development of Intermolecular Structure and Beta-phase of Random Poly[9,9-bis(2-ethylhexyl)fluorene]-co-(9,9-dioctylfluorene) in Methylcyclohexane. s.l. : *Macromolecules*, 2011. Vol. 44, 16, pp. 6453–6460.
31. **R F Rodrigues, A Charas, J Morgado and A Macanita.** Self-Organization and Excited-State Dynamics of a Fluorene-Bithiophene Copolymer (F8T2) in Solution. *Macromolecules*. 2010. Vol. 43, pp. 765–771.
32. **M H Rahman, C-Y Chen, S-C Liao, H-L Chen, C-S Tsao, J-H Chen, J-L Liao, V A Ivanov and S-A Chen.** Segmental Alignment in the Aggregate Domains of Poly(9,9-dioctylfluorene) in Semidilute Solution. s.l. : *Macromolecules*, 2007. Vol. 40, 18, pp. 6572–6578.
33. **Y-C Li, K-B Chen, H-L Chen, C-S Hsu, C-S Tsao, J-H Chen and S-A Chen.** Fractal Aggregates of Conjugated Polymer in Solution State. *Langmuir*. 2006. Vol. 22, 26, pp. 11009–11015.
34. **C-Y Chen, C-S Chang, S-W Huang, J-J Chen, H-L Chen, C-I Su, and S-A Chen.** Phase-Separation-Induced Gelation of Poly(9,9-dioctylfluorene)/Methylcyclohexane Solution. *Macromolecules*. 2010. Vol. 43, 9, pp. 4346–4354.
35. **J Plestil, H Pospisil, Y M Ostanevich and G Degovics.** Molecular-Weight Determination from Small-Angle Scattering Without Absolute. *J. Appl. Cryst.* 1991. Vol. 24, pp. 659 -664.
36. **G Beaucage, S Rane, S Sukumaran, M M Satkowski L A Schechtman and Y Doi.** Persistence Length of Isotactic Poly(hydroxy butyrate). *Macromolecules*. 1997. Vol. 30, pp. 4158-4162.

37. **J Pleštil, H Pospíšil, Y M Ostanevich and G Degovics.** Molecular-weight determination from small-angle scattering without absolute intensities: advantages and limitations. *J. Appl. Cryst.* 1991. Vol. 24, pp. 659-664.
38. **C L Donley, J Zaumseil, J W Andreasen, M M Nielsen, H Sirringhaus, R H Friend, and J-S Kim.** Effects of Packing Structure on the Optoelectronic and Charge Transport Properties in Poly(9,9-di-n-octylfluorene-alt-benzothiadiazole). *J. Am. Chem. Soc.* 2005. Vol. 127, pp. 12890-12899.

Chapter 4

Multi-Angle Light Scattering and Small Angle X-ray Scattering

This chapter presents my work on static multi-angle light scattering undertaken at Imperial College London, with thanks to Joachim Steinke and Natasha Shirshova for use of their equipment and experimental and theoretical discussions. Initially the mechanics of Rayleigh scattering and its extension to scattering of particles in solutions is discussed, followed by a review of the use of light scattering techniques in the literature. Finally my results using light scattering as a technique to discover the molecular weight and radius of gyration of F8T2, PFO and F8BT in solutions of various solvents.

Additionally my work on small-angle x-ray scattering of F8T2 in THF and toluene solutions is discussed, with a description of the physical and analytical processes involved. Thanks go to Detlef Smilgies at the CHESS facility at Cornell for his assistance in this work and George Maliaras.

4.1 Introduction

Multi-angle light scattering is a powerful but underused technique, used to discern molar mass and the size of particles in solution with no a priori knowledge of those variables. It relies on the extension of Rayleigh scattering by Zimm and others, to extrapolate scattering intensities to those at zero scattering angle and zero concentration. It can be an impressive technique, but is very dependant on the quality and cleanliness of solution preparation.

Small Angle X-Ray Scattering SAXS, is an X-ray scattering technique, used to understand the internal structure of the polymers in solution as X-rays are scattered off the electron clouds rather than the large scale macromolecule as with light scattering, or the nucleons as with neutron scattering. My work on SAXS is presented here, but the conclusions drawn are minimal due to the poor scattering cross section of F8T2 in THF solutions.

4.2 Theory and Analytical Concerns

Most descriptions of scattering used in this work are based on elastic scattering of light in gasses as described by Lord Rayleigh in 1871 (1). This and its extensions for use in light scattering and X-ray scattering experiments are shown.

4.2.1 Rayleigh Scattering

For Rayleigh scattering to be valid, particle size must be small compared to incident EM wavelength. The scattering particle can be characterised for validity by

$$x = \frac{2\pi r}{\lambda} \quad [4.1]$$

Where r is the particle size, λ the wavelength of incident radiation, and $x \ll 1$. When an electromagnetic wave is incident on an atom or molecule the electrons oscillate around their equilibrium positions at the frequency of the incident radiation. This induces transient dipoles in the particle, which release the absorbed energy in all directions as light, this is realised as scattering.

Rayleigh showed that in gasses, the intensity of scattered light R_θ , at an angle θ to the incident beam is as follows (2), often referred to as the Rayleigh Ratio.

$$R_\theta = \left(\frac{2\pi^2}{N_A \lambda^4} \right) \left(\frac{dn}{dc} \right)^2 (1 + \cos^2 \theta) M_W c \quad [4.2]$$

The intensity of scattered light is a function of incident wavelength λ , the weight average molecular mass M_w , concentration c , and refractive index increment dn/dc , and N_A is Avagadro's constant.

4.2.2 Light Scattering

This analysis of scattering was extended in 1944 by Debye(3), thanks to the work of Einstein(4), Raman (5), Zimm (6; 7) and others (8) to include solutes dissolved in solution. Debye showed that Rayleigh ratio of a solute can be expressed as:

$$R_\theta(\text{solute}) = R_\theta(\text{solution}) - R_\theta(\text{solvent}) \quad [4.3]$$

Assuming that both the molecules of solute and solvent are small compared to the wavelength of incident light, the Rayleigh ratio of the solute is now related to M_w and a constant, A_2 the second virial coefficient from expansion: (2)

$$K' \frac{(1 + \cos^2 \theta)c}{R_\theta} = \frac{1}{M_w} + 2A_2c \quad [4.4]$$

Where:

$$K' = \frac{2\pi^2 n_0^2}{\lambda^4 N_A} \left(\frac{dn}{dc} \right)^2 \quad [4.5]$$

And n_0 is the refractive index of the solvent.

The polymers in solutions studied in this work are above the condition of being small ($< \lambda/20n_0$), compared to the incident laser light ($\lambda = 690 \text{ nm}$), so further modification is needed. In the large particle regime there can be multiple scattering sites on each particle, leading to modifications to account for particle shape. Due to multiple scattering sites on each particle, the scattered light is likely to now arrive out of phase, as such the angular attenuation of scattered intensity P_θ due to this effect can be defined as the ratio of the scattering intensity at an angle θ , to the scattering intensity without interference. P_θ can also be related to u , a shape dependent function which depends on the radius of gyration R_g and the shape of the scattering object (2). Using u for monodisperse, randomly coiling polymers:

$$P(\theta) = \left(\frac{2}{u^2}\right) (e^{-u} - (1 - u)) \quad [4.6]$$

Where:

$$u = \left(\frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)\right)^2 R_g^2 \quad [4.7]$$

Other functions of u can be used for other particle configurations in solution. For small values of θ the non-model specific expansion [4.7] can be used to estimate coil size, but in practice the small angles in light scattering are the least reliable.

$$P(\theta)^{-1} = 1 + \frac{u}{3} - \dots \quad [4.8]$$

The analysis techniques for large particles were laid out by Zimm in 1945 (7; 9) allowing determination of M_w and R_g . The analysis relies on a double extrapolation, but is based on the fact that the scattering at $\theta = 0$ is independent of particle size, so $P(0) = 1$. This is experimentally very hard to measure so Zimm proposed a modified form of [4.4] above for large particles, which after including the scattering factor leads to:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} + \frac{1}{M_w} \left[\left(\frac{16\pi^2 n_0}{3\lambda^2} \right) \sin^2\left(\frac{\theta}{2}\right) R_g^2 \right] + 2A_2c + \dots \quad [4.9]$$

A Zimm plot is constructed by plotting Kc/R_θ against $(\sin^2(\theta/2) + k'c)$ where k' is a constant chosen to give a convenient spread of data, for the range of scattering angles and concentrations chosen. A double extrapolation is carried out, to extrapolate to zero angle and zero concentration, leading to the (ideally) characteristic grid-like graph, shown in *figure 32*, with the extrapolation to zero angle shown as green, and zero concentration as red.

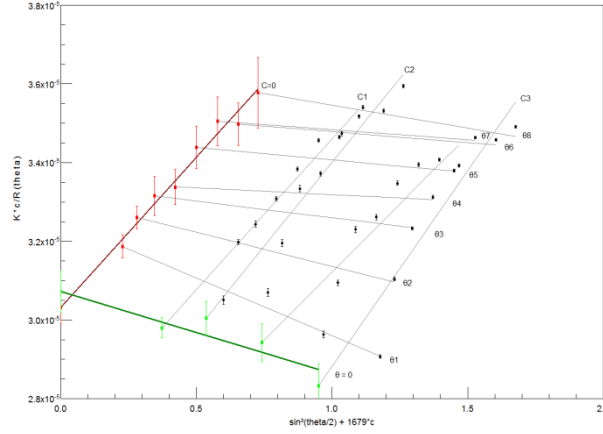


Figure 32 Example of grid-like structure in a Zimm Plot showing 4 concentrations (C1-C4) and 8 angular extrapolations (more horizontal lines) of F8T2 in THF. Red shows $c = 0$, green $\theta = 0$. Note x-axis = $\sin^2(\theta/2) + (1679 \cdot c)$ and y-axis = $K \cdot c / R_\theta$.

Ideally both extrapolations should meet at the same point, the intercept of which is M_W^{-1} , as expected from [4.9], the slope of $\theta = 0$ give A_2 and z-average R_g is given by the initial slope s , of the zero concentration, $c = 0$ line, following: (2)

$$R_g^2 = s M_W \left(\frac{3\lambda^2}{16\pi^2 n_0} \right) \quad [4.10]$$

In addition to Zimm's formulation, there are two further common ways of plotting light scattering data, that of Debye (10) and that of Berry (11). They use the same data, with the same abscissa $\sin^2(\theta/2)$, but vary in their ordinate axis. These variations and the effects on the initial slope and intercept are summarised below in *table 12* (12).

Method	Ordinate Axis	Intercept with y-axis	Initial Slope
Debye	$\frac{R_\theta}{Kc}$	M_W	$-M_W R_g^2 \left(\frac{16\pi^2 n_0}{3\lambda^2} \right)$
Zimm	$\frac{Kc}{R_\theta}$	$\frac{1}{M_W}$	$\frac{R_g^2}{M_W} \left(\frac{16\pi^2 n_0}{3\lambda^2} \right)$
Berry	$\sqrt{\frac{Kc}{R_\theta}}$	$\frac{1}{\sqrt{M_W}}$	$\frac{R_g^2}{\sqrt{M_W}} \left(\frac{8\pi^2 n_0}{3\lambda^2} \right)$

Table 12 Variations in slope and axis from different light scattering formulations (12)

Andersson et al (12) by comparison of real data to fitted models have established that for light scattering of random coils, or those with no a priori structural knowledge the Berry formulation is the most accurate and robust for the extrapolations needed. The Debye method is superior for spherical particles, and the Zimm formulation although traditional is the weakest of the three. However, for particle sizes <50 nm extrapolation errors are <1% with linear fits, for larger particle sizes higher order polynomial terms should be used, however care must be taken to use reliable data and not 'force fit' higher order terms to weak data. Additionally they suggest that the data from lowest reliable angles should be chosen preferentially, as higher angles do not improve the accuracy, however erroneous data points have a much larger effect at low angles. As such care must be taken to choose strong data before plotting for extrapolation.

4.2.3 Small Angle X-ray Scattering

Small angle x-ray scattering is discussed using the same formalism as that described for SANS in *Chapter 3*, based on the works of Guinier, Kratky and Perod. Whereas light scattering relies on the differences in refractive index and polarisation of electrons for contrast, X-ray scattering is reliant on the differences of electron densities, and neutron scattering from differences in atomic nuclei.

4.3 Previous Work

Light scattering is not regularly used in the field of organic electronics, perhaps due to its experimental and analytical complexity, but when used successfully can give some very useful, absolute information about a sample in solution. There is very little previous work on multi-angle light scattering of semi-conducting polymers, and even less on polyfluorene and its copolymers. Multi-angle light scattering for characterisation is however, regularly used in the fields of food science (13; 14) and bio-chemistry (15; 16).

Light scattering is often used with the other characterising methods, gel-permeation chromatography or size-exclusion chromatography (17; 18), with dynamic light scattering taking precedence over static multi-angle.

Light scattering is often used to determine effects of aggregation on solutions, and conformational changes with heat, time or solvent. Such as the work of Lim et al, (19) where the polydiacetylene polymer poly[5,7-dodecadiyn-1,12-diol-bis (n-butoxycarbonylmethyl urethane)], P(4BCMU), was studied in solution. Initially in a solution of chloroform, hexane a

non-solvent for the polymer was added, and the hydrodynamic radius sharply increases from a coil like structure solutions < 40% hexane to a rod-like structure in those of > 40% hexane. An example of the use of light scattering outside the field of conjugated polymers is the work of Manning et al (20), who study the aggregation of organic carbon humic acid in aqueous solution, allowing the preparation of a Zimm plot using the Berry formulation, giving molar mass and RMS radius values.

An impressive work of dn/dc value determination for polystyrene standard in different solvents was undertaken by Ghazy et al. (21), using a Mach-Zehnder interferometer to measure specific refractive index increments, a technique in this work undertaken by the Brookhaven Diffractometer.

Cametti (17) et al have studied stereoregular polyphenylacetylene (PPA), in THF, toluene and chloroform, using static and dynamic light scattering and compared the results with those of UV/Vis spectroscopy. They found, unexpectedly, that in THF the molecular weight increases with time, stays constant in toluene and decreases in chloroform, yet R_g stays constant in THF and decreases to a smaller, stable value in toluene and chloroform over 8–16 hours. They attribute these behaviours to different effects due to the solvents; polymer chain entanglement by THF leading to a higher apparent molecular weight, toluene promoting a narrow, helical rod form and chloroform leading to isomerisation and degradation.

Težak (22) et al studied the structure of colloids by light scattering, paying particular attention to solution dynamics and aggregate formation. Irregular Zimm plots were obtained, due to polydispersity, association and aggregation ability of particles, optical anisotropy as discussed in the literature (23; 24). They found that although regular Zimm plots are the norm, in polydisperse synthesised materials, molecular weight and size information can be obtained from polydisperse samples, with knowledge of aggregation and solution dynamics. They found aggregate sizes obtained by light scattering agreed with those obtained by electron microscopy.

Hefner et al. (25) made a similar study of solvent effects on P3HT, observing chain conformations in toluene and chloroform solutions. They also compared molecular weight measurements from GPC with static light scattering, as GPC results are calibrated against a polystyrene standard one would expect the technique to overestimate the weights of more rigid materials. They did not find this (25), with weights agreeing within 5%, however

Yamamoto et al. (26) found GPC weights of P3HT obtained by GPC to be approximately double those of light-scattering.

A good analysis using static, multi-angle light scattering on PMMA in acetone and methyl-ethyl-ketone was undertaken by Ghazy et al. (27) in 1999, developing a laser based multi-angle light scattering system, allowing a standard Zimm plot to be made and key features of the PMMA to be extracted.

Woo et al. (28) also used static light scattering to characterise a styrene-(ethylene-co-butylene)-styrene triblock copolymer (SEBS) and its sulfonated ionomers in THF, particularly noting the dissolution characteristics of the polymer and aggregate formation, as well as the effects of undissolvable species within the sample.

Although a large body of work exists on the characterisation of polyfluorenes (29; 30), light scattering investigations in to polyfluorene and its co-polymers appear to have been neglected, underlining the basis for this study.

4.4 Light Scattering Results

4.4.1 Differential Refractometry

Shown below are the results of the first differential refractometer (DR) measurements to determine dn/dc of F8T2 in THF. *Figure 33(a)* shows the absolute voltage changes from the DR due to the insertion of polymer solution into the flow cell described in *Chapter 2*. Each injection is bordered by spikes, with C1 beginning at 1.5 min. It can clearly be seen that the 5.0 mg/ml solution is beyond the upper limits of the device, at 14.5 min and can safely be removed from the analysis. Concentration five is just within limits, due to drift in the detector. In addition to the simple change in voltage measured at the photodetector, after the experiment the initial state is remeasured, and the voltage change for each concentration is recalculated from the line connecting the before and after measurements, ie pure solvent at <1.5 min and >15 min. This is to account from any drift in the device, and is strongly advised by Brookhaven.

The difference in refractive index with concentration compared the pure solvent is shown in *figure 33(b)*, with the gradient being the dn/dc value.

Using this technique, dn/dc for the batch of F8T2 used throughout this work, in THF solution at 30° C is given as 0.4328 ± 0.0009 mL/g. This is the value used throughout for dn/dc in light scattering measurements, and has been used for all different F8T2 batches used in these

investigations. A similar technique was used for PFO in THF using a Viscotek Triple Detector by Natasha Shirshova, the equivalent result is shown in *figure 33(c)* for completeness, and the complete range of dn/dc values used for each polymer/solvent combination is shown in *table 13*.

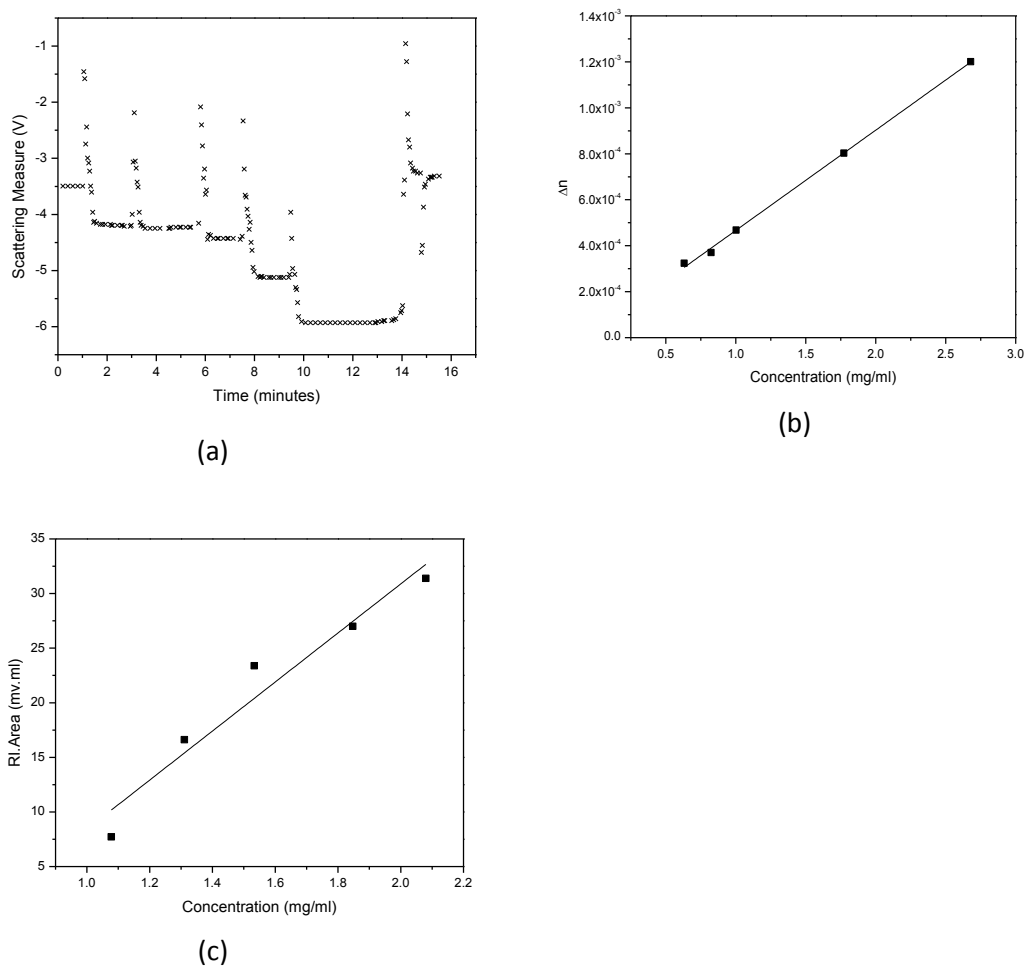


Figure 33 Differential Refractometry results at 620nm, (a) direct voltage of F8T2 in THF, with C0,1,2,3,4,5,0 shown (b) n vs c of F8T2 in THF, (c) RI Area vs c of PFO in THF

The Berry formulation is used throughout for plotting light scattering data as Zimm plots, as it has been found to be the superior extrapolation method (12) for random coils, or those with no a priori knowledge.

Polymer : Solvent	dn/dc (mL/g)
F8T2 : THF	0.4328 ± 0.0009
F8T2 : Toluene	0.02924 ± 0.0053
F8T2 : Chloroform	0.3656 ± 0.0084
PFO : THF	$0.3461 \pm 0.0306^*$
PFO : Toluene	0.110 ± 0.01

Table 13 dn/dc values of the polymer.solvent combinations used in this work. *Visotek result

4.4.2 Light Scattering

Most light scattering experiments presented here were done on F8T2 in THF, but F8T2 in toluene and in chloroform solutions were also completed. PFO and F8BT samples were studied in both chloroform and toluene, a sample of Dow's proprietary red emission copolymer Dow Red F was also attempted, but no dn/dc value is known, and experimentally had very poor results, possibly due to the low concentration range chosen (0.001 mg/ml to 1 mg/ml), and overlap with excitation laser wavelength.

Analysis was done using Wyatt's Astra software, developed for use with their light scattering equipment. A standard result chart is shown below in *figure 34*, scattered light intensity is shown against time (labelled as volume in software), with each 'peak' being a different concentration, weak spike-removal within the Astra software has been used. Here plain solvent is at each extreme, with increasing concentration of polymer in between. Detector number is shown in the top right. Detector 11, at 90° is shown, and a comparison with the noisy lower angle detector 8, at 64°. At lower angles at least one concentration saturates the detector. Pure solvent is recorded at the beginning and end, to set a baseline over the timescale of measurements, C1 to C6 are six concentrations to be studied, and PS is the isotropically scattering polystyrene standard to normalise the detector responses.

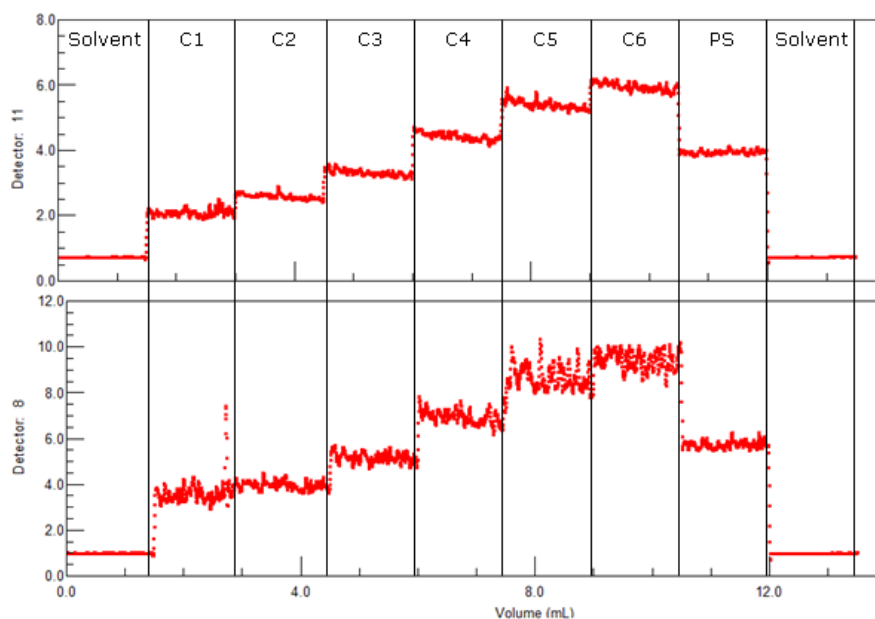


Figure 34 Wyatt Astra strip chart example showing pure THF (solvent), 6 increasing concentrations of F8T2 in THF (C2-C6), 4K polystyrene standard in THF (PS) and pure THF

When using Zimm plots, second order fits were used on the angles, as non-linearity in this is generally due to poly-dispersity (23) and can be justifiably be used with the samples. The Berry formulation was used, as this has been found to be most accurate (12) and seemed the most consistent throughout this analysis. Only first order fits were used in the concentration extrapolation as usually only 4 or 5 concentrations were used.

It is worth noting that although errors appear to be around the 10% level, they can change by up to 20% with the addition or subtraction of detectors or concentrations. Angles and concentrations were chosen to minimise errors shown in the Astra software and to maintain robustness between additions or subtractions. Concentrations are deemed to be too high when a large number of the centre angle detectors are overloaded, and so ignored. A standard range of detectors was from numbers 5 to 16 (44-130°). For solutions with an unknown dn/dc value, only R_g can be found.

Concentrations were also rejected from Zimm plots if they were found to be well away from the norm, suggesting errors in the preparation of the sample.

Radii of gyration and molecular weights are given in absolute units, and also as multiples of the repeat unit length L_{RU} for R_g and multiples of the monomer mass M_{RU} for M_w . The figures

used are shown below in *table 14*, F8BT and PFO values are from X-ray characterisation, F8T2 is estimated as a PFO monomer and two P3HT monomers.

Polymer	L_{RU} (Å)	M_{RU}
F8T2	16.7	552
F8BT	14.7	522
PFO	8.3	389

Table 14 Monomer size and weight of F8, F8T2 and F8BT used for light scattering (31) (32) (33)

4.4.3 Light Scattering of F8T2 in THF

F8T2 was most studied in solutions of THF. *Figure 35(a)* shows a Zimm plot using just 3 sample concentrations and 10 detector angles, this low value was used due to overloading the detectors with overly concentrated solutions. *Figure 35(b)* and *35(c)* show both show Zimm plots with a full range of concentrations and detector angles, these are, despite appearances, consistent with each other for both R_g and M_w of F8T2 in THF.

The three Zimm plots shown in *figure 35* are from different sets of solutions of F8T2 and, despite the technical difficulties of good solution preparation show the technique to be very robust. Giving an RMS radius of F8T2 dissolved in THF of 154 nm. M_w is less consistent, but gives a mean of $(1.3 \pm 0.3) \times 10^5$ g/mol for the F8T2 sample. Using the linear chemical formula of $C_{37}H_{44}S_2$ (34) giving a monomer mass of 552, this implies 236 ± 54 repeat units per F8T2 chain. As F8T2 has been shown to be a rigid rod (*Chapter 3*), the value of R_g is taken to be very close to the rod length. These initial results in THF, suggest a fairly well dissolved polymer but slight aggregation, by comparison of M_w / M_{RU} the total number of RUs in the scattering object and its size of 91 RUs, one would expect ~ 2.6 rods aggregating.

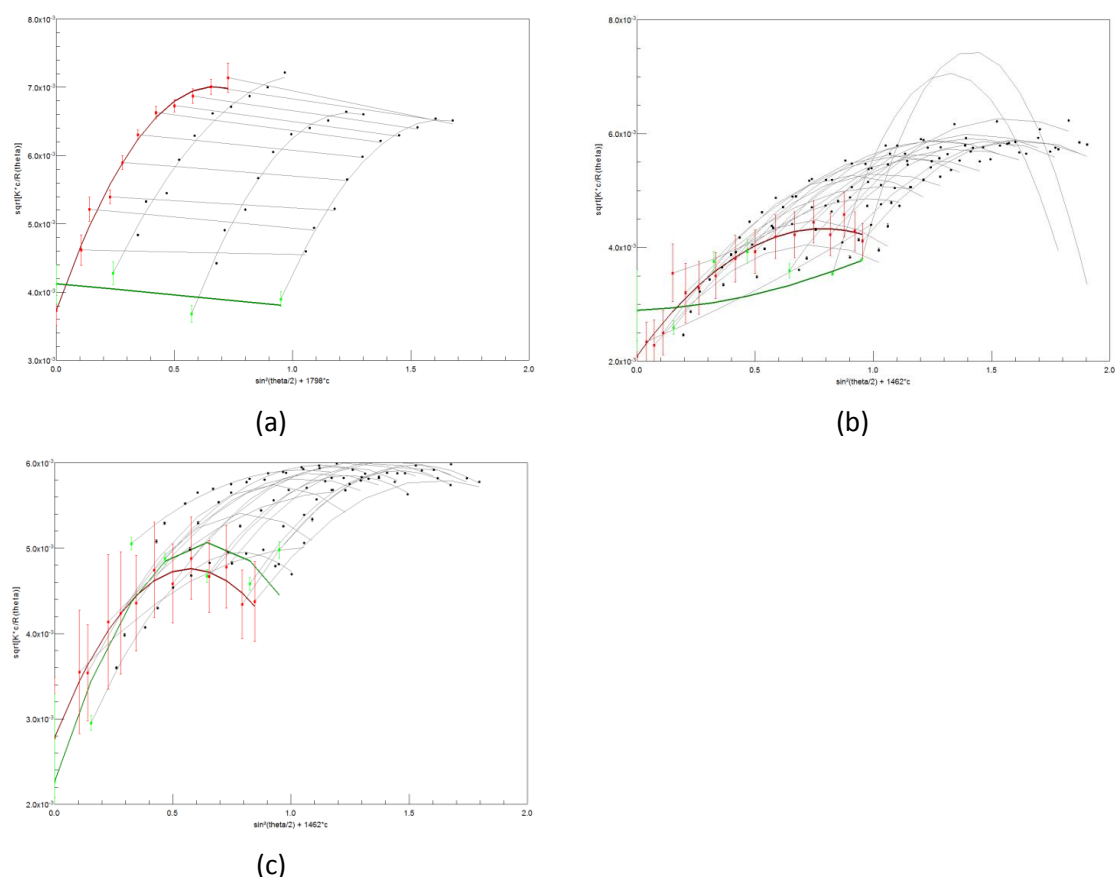


Figure 35 Initial Zimm plots of F8T2 in THF, showing robustness of R_g and M_w values despite what appear to be large changes in data and fit quality. Note x-axis = $\sin^2(\theta/2) + (\text{constant} \cdot c)$ and y-axis = $\sqrt{[K^*c/R_\theta]}$

Sample	R_g (nm)	R_g / L_{RU}	M_w (g/mol) $\times 10^4$	M_w / M_{RU}
(a)	155 ± 10	91 ± 6	(6.5 ± 6)	118 ± 109
(b)	158 ± 21	93 ± 12	(17 ± 4)	308 ± 72
(c)	151 ± 39	89 ± 23	(16 ± 9)	290 ± 163
mean	155 ± 15	91 ± 9	(13 ± 3)	236 ± 54

Table 15 Radius of Gyration and Molecular Weight results for 3 separate light scattering experiments on F8T2 in THF

After the initial tests to determine concentration ranges and understand the repeatability of the analysis, further experimentation on F8T2 in THF was undertaken. *Figure 36* shows Zimm plots from light scattering results at set times after initial solvation of F8T2 in THF. In this experiment the same solutions were studied over 6 days and the same concentrations and identical analysis with reliable, central detector angles were used to generate the Zimm plots.

The ‘high’ samples are from the same batch as those shown in *figure 36* and used throughout this work, ‘low’ are a second batch of assumed different M_w .

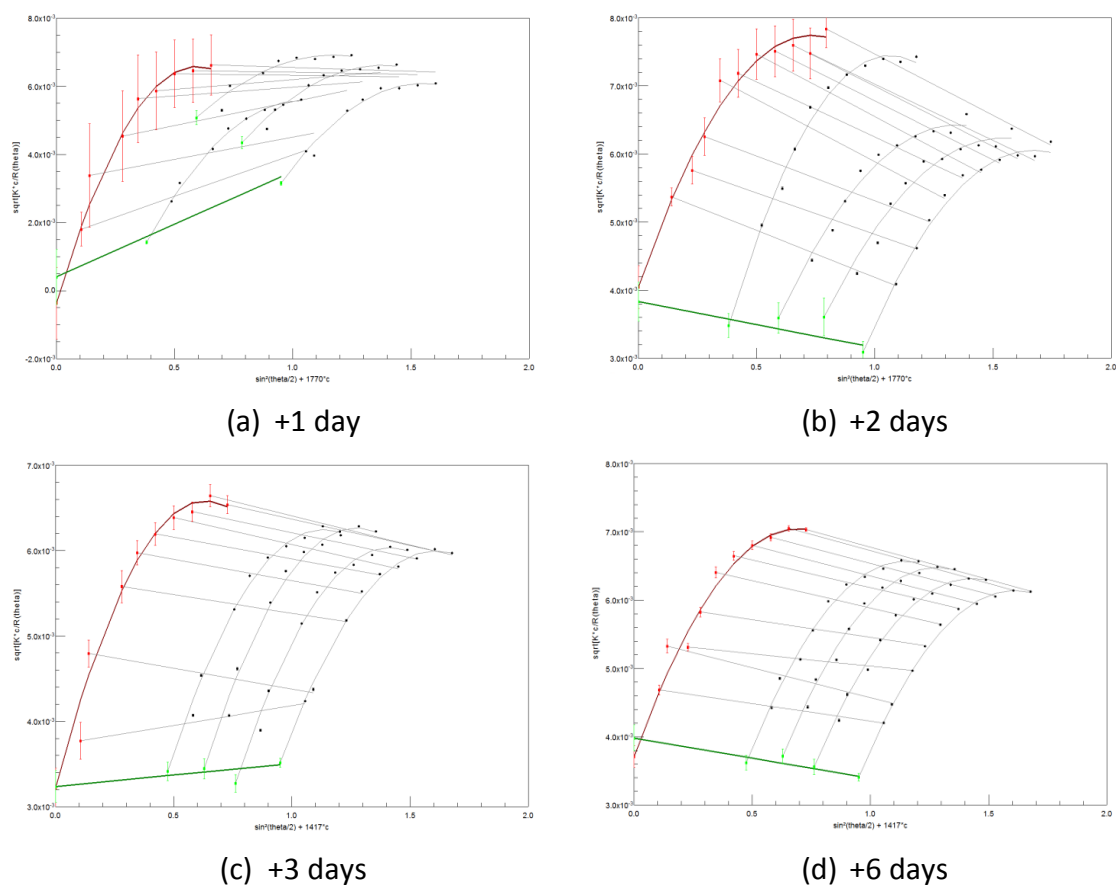


Figure 36 Zimm Plots of ‘high’ sample F8T2 in THF with time
 (a) +1 day, (b) +2 days, (c) +3days (d) +6 days. Note x-axis = $\sin^2(\theta/2) + (\text{constant} \cdot c)$ and y-axis = $\sqrt{K^*c/R_\theta}$

As before R_g and M_w are calculated in multiples of repeat units. The progression of R_g and M_w values suggest an improvement of dissolution of polymer with time, and although visibly dissolved within minutes, the polymer continues to dissolve for some days afterwards. A clear change between the first measurements after 0/1 days and the later values, suggests that there is a noticable length of time for the solution to stabilise.

Polymer Batch	Solution Age (days)	R_g (nm)	R_g / L_{RU}	M_w (g/mol) $\times 10^4$	M_w / M_{RU}
'High' F8T2	0 (~3 hrs)	763.8 ± 1096	449 ± 645	(670 ± 25)	12100 ± 453
'High' F8T2	2	151.4 ± 15.4	89 ± 9	(6.5 ± 0.7)	118 ± 13
'High' F8T2	3	174.0 ± 11.3	102 ± 6	(9.6 ± 0.9)	174 ± 16
'High' F8T2	6	154.5 ± 7.3	91 ± 4	(6.8 ± 0.4)	123 ± 7
'Low' F8T2	1	857.2 ± 1923.5	504 ± 1132	(1000 ± 90)	18100 ± 1600
'Low' F8T2	2	191.2 ± 17.1	112 ± 10	(7.4 ± 1.2)	134 ± 22
'Low' F8T2	3	163.5 ± 14.7	96 ± 9	(5.6 ± 1.0)	101 ± 18
'Low' F8T2	6	125.7 ± 25.7	74 ± 15	(3.4 ± 0.7)	62 ± 13

Table 16 RMS radius and molecular weight of polymer samples as they dissolve determined by light scattering

Taking a mean of days 3 and 6, the 'high' sample was found to have an R_g value 164 ± 9 nm, corresponding to 97 ± 5 repeat units, and a M_w value corresponding to 149 ± 12 RUs. I understand this to suggest by now the F8T2 is fully dissolved, perhaps with some twisting along the chain length, or some level of two-chain interactions to account for this increase in mass over that of a single chain.

The 'low' F8T2 sample was found to have an R_g value of 145 ± 20 nm, corresponding to 85 ± 12 RUs, with M_w being 82 ± 16 RUs. This suggests that the 'low' sample is very well dissolved after 3 days, occurring as single chains in solution. These two samples have the same length within errors; however M_w is smaller for the 'low' sample

It is of note that the M_w values for the high sample in *figure 36* are approximately 2-3 times larger, than those found in *figure 37*, I attribute this to the time passed before measurements. Prior to understanding the dissolution timescales needed for F8T2 in THF, the earlier test samples were measured some hours after solvent addition and with a short heating time. These factors would explain the M_w values being inbetween the immediately measured values and +2 days values in *table 16*. Interestingly it is only the molecular weight that is increased, suggesting that the particles in solution are aggregate stacks of the length of the polymer rod until fully dissolved in a good solvent.

4.4.4 Light Scattering of F8T2 in Chloroform

Light scattering was also undertaken on F8T2 in chloroform solutions, here only three concentrations were found to be reliable. The Zimm plots taken immediately after visibly dissolved and after 1 week in solution are shown below in *figure 37*, with the same solutions and processing parameters used in 7(a) and 7(b).

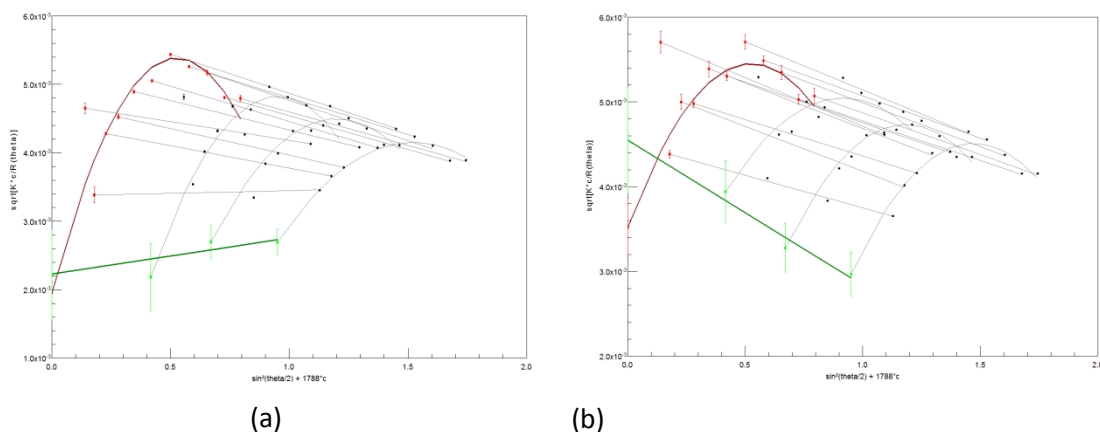


Figure 37 Zimm Plots of F8T2 in chloroform solution
(a) Freshly prepared, (b) +1 Week. Note x-axis = $\sin^2(\theta/2) + (\text{constant} \cdot c)$ and y-axis = $\nu(K \cdot c / R_\theta)$

Age	R_g (nm)	R_g / L_{RU}	M_w (g/mol) $\times 10^4$	M_w / M_{RU}
Fresh	241 ± 12	142 ± 7	(23 ± 6)	417 ± 109
+1 week	133 ± 18	78 ± 11	(6.5 ± 1)	118 ± 18

Table 17 Calculated values for F8T2 in CHCl₃

These results show R_g decreasing from 241 ± 12 nm to 133 ± 18 nm over a period of a week, comparable to F8T2 in THF after full dissolution. In a good solvent, with fully extended chains this is expected. Similarly molecular weight decreased from $(23 \pm 6) \times 10^4$ g/mol to $(6.5 \pm 1) \times 10^4$ g/mol. This is expected as SANS studies suggest that F8T2 dissolves well in chloroform with no change with time in the 2-70nm range, after one day in solution. These results are shown graphically in *figure 40* in *Section 4.4.5* below. The light scattering results further confirm chloroform dissolves F8T2 well, and dissolution improves with time, continuing to be stable over timescales up to a week.

4.4.5 Light Scattering of F8T2 in Toluene

Toluene is a harder solvent to use for light scattering, as aggregation is very obvious and even at the concentrations measured here would be expected to void the assumptions implicit in

the Zimm analysis, particularly when considering the polydispersity of solutes when aggregated and non-aggregated particles are seen, and the large scale of aggregates (easily visible to the naked eye). F8T2 in toluene was studied for comparison to the other solvents, and solutions were made the day before to allow dissolution. The Zimm plots shown in *figure 38* show data from the same experiment as an example of the remarkable robustness of the analysis procedure. The same data is used, and despite adding a fourth concentration, which appears to be well away from the expected position, very little difference in final values is found. Nonetheless, a mean of the two values is used.

Consistent with the previous solvents, F8T2 R_g in toluene is found to be 143 ± 12 nm in both analyses. Molecular weight is changed by the addition of a fourth concentration, increasing from $1.8 \pm 0.3 \times 10^7$ g/mol to $1.9 \pm 0.2 \times 10^7$ g/mol, although clearly the same within error bounds.

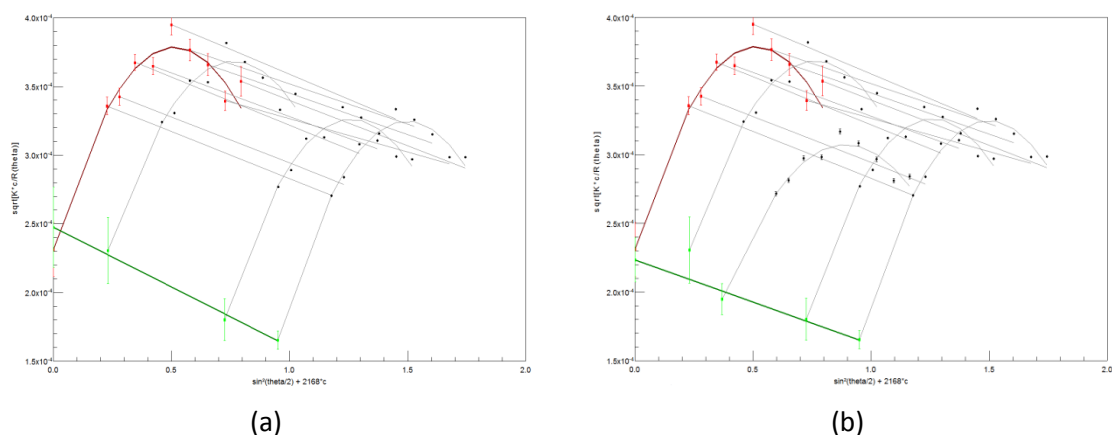


Figure 38 Zimm Plots of F8T2 in toluene solution, showing the robustness of the analysis to loss/gain of a concentration. Note x-axis = $\sin^2(\theta/2) + (\text{constant} \cdot c)$ and y-axis = $\sqrt{K \cdot c / R_\theta}$

F8T2 in toluene has approximately the same size as in the other solvents, but a mass well over an order of magnitude higher.

The same solution left to dissolve for one week are shown in *figure 39*, with and without the fourth concentration, with processing parameters as before.

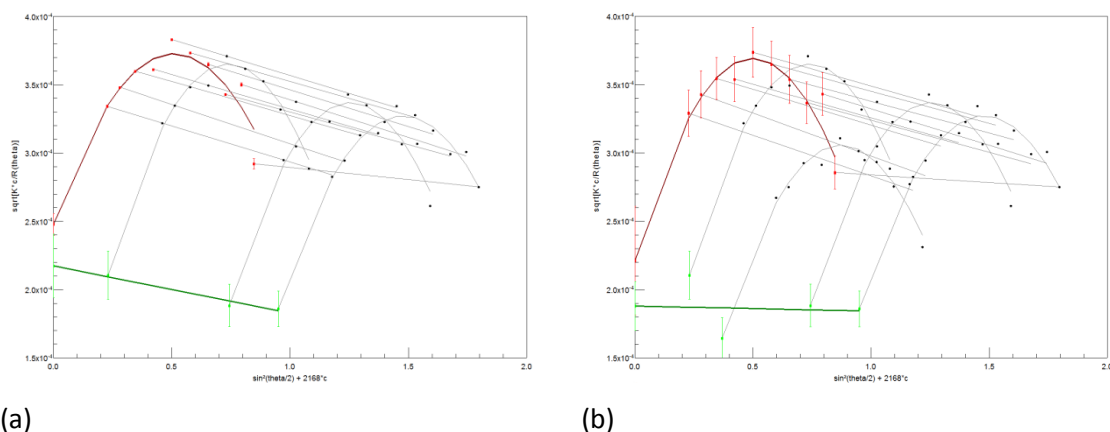


Figure 39 Zimm plots of F8T2 in toluene solution taken after 1 week. Analysed with (a) 3 concentrations, (b) 4 concentrations. Note x-axis = $\sin^2(\theta/2) + (\text{constant} \cdot c)$ and y-axis = $\sqrt{K \cdot c / R_\theta}$.

Age	Concentrations Used	R_g (nm)	R_g / L_{RU}	M_w (g/mol) $\times 10^7$	M_w / M_{RU} $\times 10^2$
Fresh	3	143 ± 7	84 ± 4	(1.8 ± 0.3)	326 ± 54
+1 week	3	127 ± 5	74 ± 7	(1.9 ± 0.2)	344 ± 36
Fresh	4	143 ± 12	84 ± 7	(1.9 ± 0.2)	344 ± 36
+1 week	4	148 ± 24	87 ± 14	(2.4 ± 0.5)	435 ± 91
Fresh	Mean	143 ± 10	84 ± 6	(1.9 ± 0.3)	335 ± 45
+1 week	Mean	138 ± 15	81 ± 11	(2.2 ± 0.4)	390 ± 64

Table 18 R_g and M_w results for F8T2 in toluene with age

The results shown in *table 18* again show no change in R_g , and consistent with the other solvents at 80-90 repeat units per chain. The effect of aggregation in a poor solvent can clearly be seen, with values for M_w being ~ 300 times larger than those seen in THF, suggesting large numbers of chains in each aggregate particle. However, due to the mass of the particles studied I would expect the particle size to be larger, although if aggregates are well stacked with a spacing of $\sim 4.4 \text{ \AA}$ (35), ~ 300 layers would lead to a height of $\sim 140 \text{ nm}$, and consistent with the aggregate sheets seen in *Chapter 3*. These dissolved configurations are summarised below in *figure 40*.

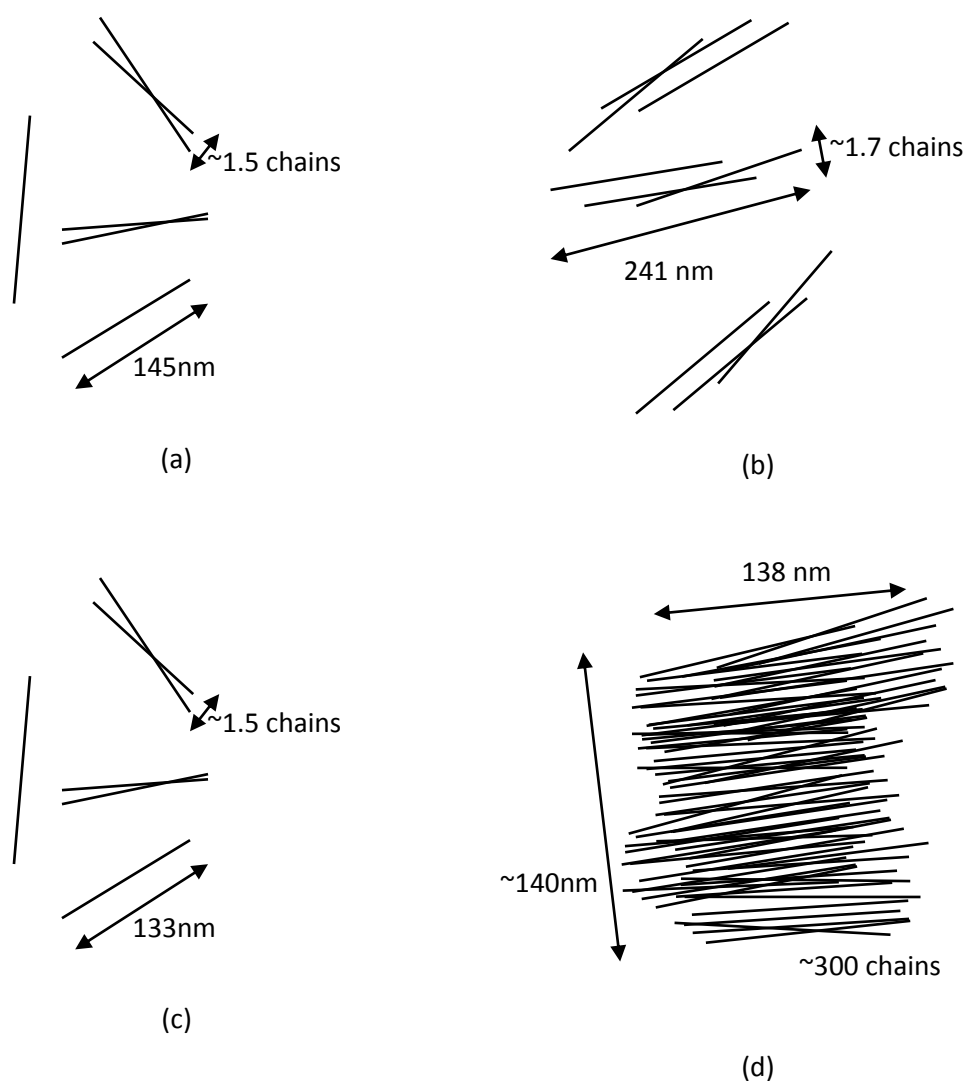


Figure 40 Schematic diagram of possible F8T2 configurations in (a) THF (b) fresh chloroform (c) 1 week old chloroform and (d) aggregated toluene solutions.

4.4.6 Light Scattering of PFO

PFO was studied in two solvents, THF and toluene, by multi-angle light scattering. The Zimm plots are shown below in *figure 41(a)* and *(b)* respectively. *Figure 41(a)* is unusual in this analysis as linear fits gave the most consistent values. PFO was found to be a difficult polymer to study with light scattering, this can be seen by the large relative errors on both R_g and M_w values.

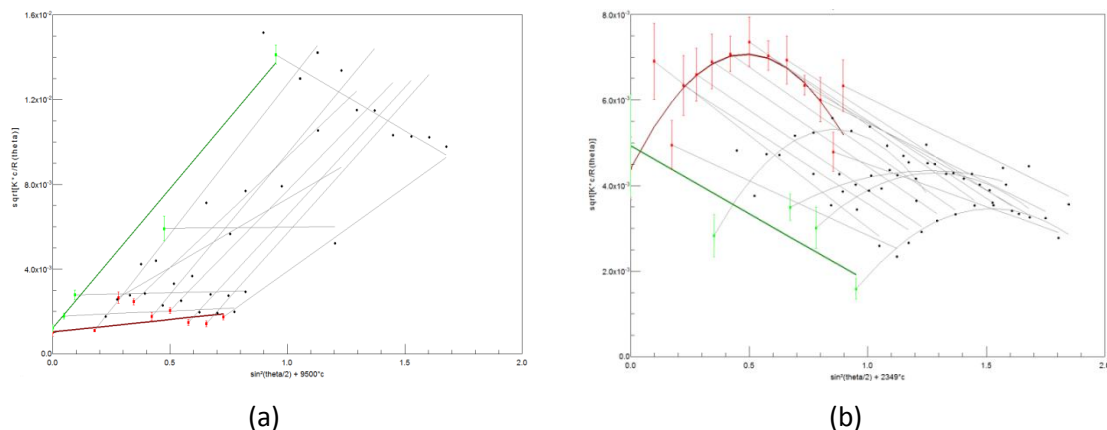


Figure 41 Zimm Plots of PFO in (a) THF and (b) toluene solutions.
Note x-axis = $\sin^2(\theta/2) + (\text{constant} \cdot c)$ and y-axis = $V(K \cdot c / R_\theta)$.

Solvent	R_g (nm)	R_g / L_{RU}	M_w (g/mol) $\times 10^4$	M_w / M_{RU}
THF	103 ± 22	124 ± 27	80 ± 19	2057 ± 463
Toluene	143 ± 22	172 ± 27	4.6 ± 1.3	118 ± 33

Table 19 R_g and M_w values expressed in RUs for PFO in THF and Toluene solutions

PFO was found to have R_g values of 103 ± 22 nm and 143 ± 22 nm in THF and toluene, equating to 124 ± 27 and 172 ± 27 repeat units per chain, large variation was found in the M_w values however. These were found to be $(8.0 \pm 1.9) \times 10^5$ g/mol and $(4.6 \pm 1.3) \times 10^4$ g/mol in THF and toluene respectively. These suggest that for PFO toluene is a better solvent than THF, as more aggregation can be seen, but as the polymer size does not appear to change I expect this aggregation to manifest as stacking as seen with F8T2 above and the similar rigid polymer P3HT(36). GPC results of the same polymer batch in THF are shown below in *table 20*.

Concentration (mg/ml)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
1.08	35,201	50,680	1.440
1.31	45,625	80,174	1.757
1.54	61,473	84,585	1.376
1.85	59,388	88,872	1.496
2.08	43,365	72,591	1.674

Table 20 GPC results of PFO in THF

Here, M_w values in THF are an order of magnitude smaller than those obtained by light scattering. Unexpectedly this is unlike the results found in (25) and (26) where GPC weights either agreed with those found by light scattering or were approximately double. This could be caused by the fact that GPC works under very high pressure, potentially forcing any aggregates apart during the measurement, which would explain this anomaly. The GPC values are very close to those seen with light scattering in toluene adding credence to this analysis. Using these values, each PFO chain in this batch is likely to contain ~ 140 RUs.

4.4.7 Light Scattering of F8BT

F8BT was studied only in toluene solutions, with freshly prepared results show in *figure 42(a)* and those from +24 hours in *12(b)*. Although the plots appear noisy, straight lines could be fitted and radii of gyration found to be 22 ± 11 nm in both. Clearly this high error is due to the noisiness of the measurements, and cannot and should not be improved by increasing the fit degree. M_w is also found to be constant in the two measurements with the fresh and +24 hour samples being $(6.4 \pm 0.5) \times 10^4$ g/mol and $(6.2 \pm 0.5) \times 10^4$ g/mol respectively.

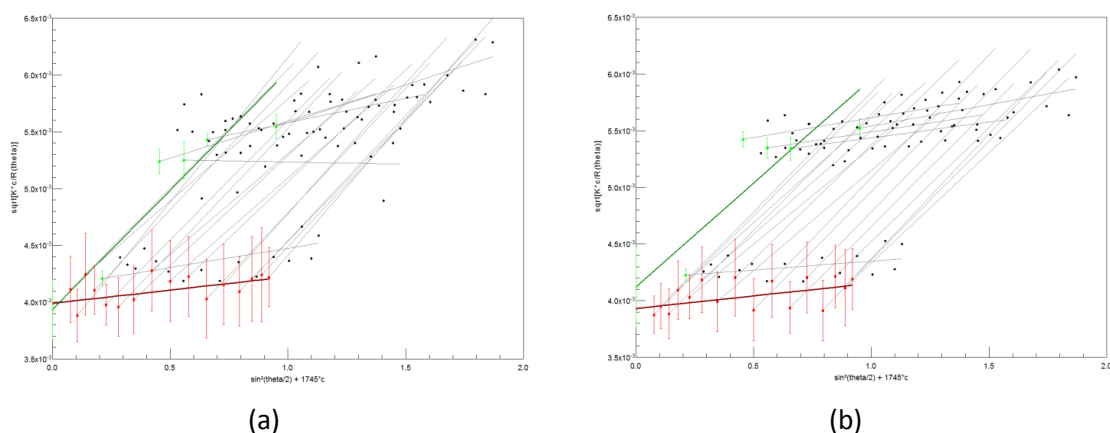


Figure 42 Zimm plots of F8BT in toluene (a) Freshly made, (b) +24 hours. Note x-axis = $\sin^2(\theta/2) + (\text{constant} \cdot c)$ and y-axis = $\sqrt{K \cdot c / R_\theta}$.

Age	R_g (nm)	R_g / L_{RU}	M_w (g/mol) $\times 10^4$	M_w / M_{RU}
Fresh	22 ± 11	15 ± 8	6.4 ± 0.5	123 ± 10
+1 week	22 ± 11	15 ± 8	6.2 ± 0.5	119 ± 10

Table 21 R_g and M_w values obtained by light scattering and in RUs, of F8BT in toluene over 1 week.

These results show what appears to be a massive but very tightly coiled polymer in solution, however one that is stable in than configuration over the range of a single day. This analysis is

not fully understood with the interpretation put forwards in *Chapter 3*, that F8BT is rigid but twisted in THF, unless aggregation stacking of approximately 8 chains of 15 RUs each per particle is considered. Further experiments in a range of solutions would allow this to be further understood.

4.5 SAXS Results

Small Angle X-Ray Scattering uses the same analytical techniques as SANS discussed in *Chapter 3*, namely the analysis of scattering intensity against scattering vector, q . As X-rays elastically scatter off of the electron cloud SAXS can be used to elicit information about the internal structure of the material. Here, SAXS was used to study the emergence of any structure in the aggregation of F8T2 in toluene solutions.

F8T2 was studied in toluene and THF solutions at two different concentrations to determine if SAXS could show the effects of time on solvation and aggregation. Absolute scattering intensity against q is shown below in *figure 43(a)*. F8T2 appears to be a very weak scatterer of X-rays, and this is shown in *figure 43(b)*, the background subtracted scattering with an example of recorded scattering intensities show in *43(c)* and *43(d)*. The integration range used is shown outlined in *figure 13(d)*, with the beam position marked at (950, 90).

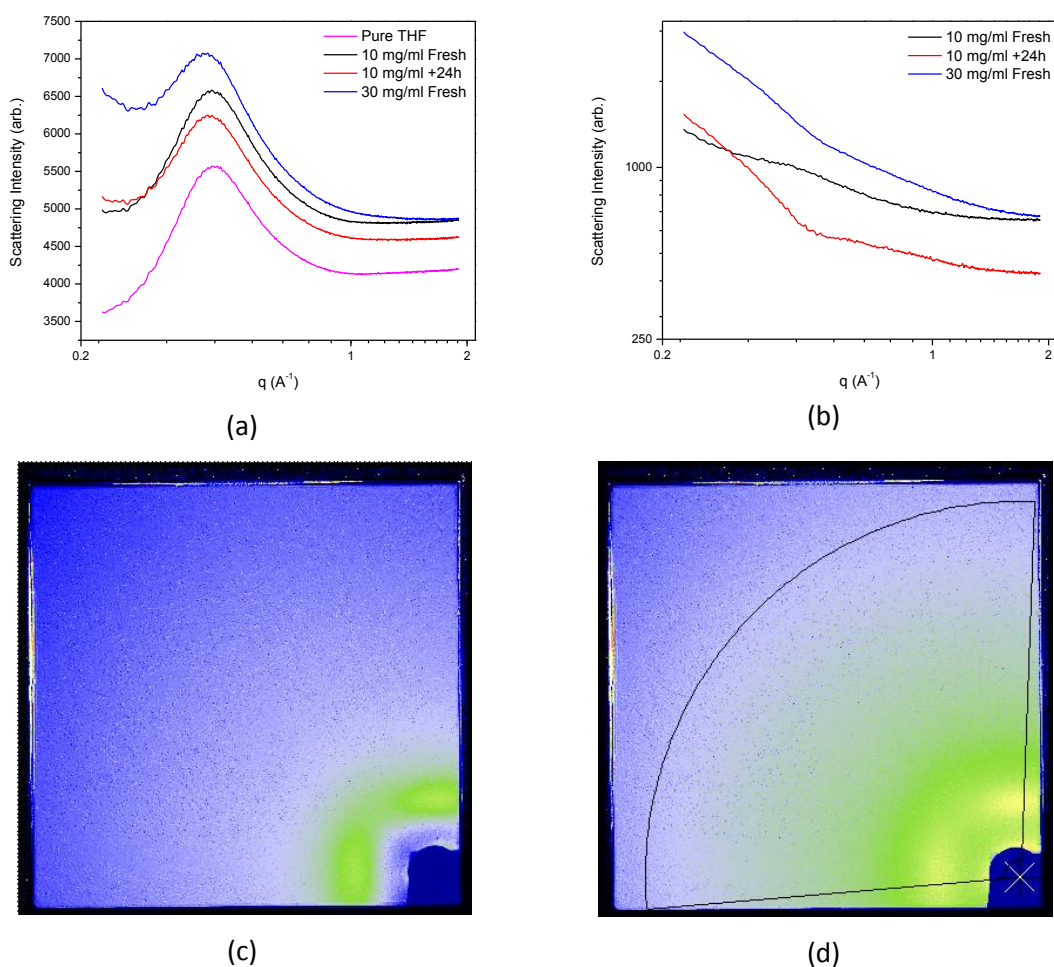


Figure 43 Scattering Intensities of F8T2 in THF.
 (a) absolute, (b) Background Subtracted (c) Pure THF scattering
 (d) F8T2 30 mg/ml scattering and integration range used

Slope values were computed, to find n , as outlined in *Chapter 3*, however these appear to be artifacts as the change in slope could be related to beam position accuracy and changes between background and sample images. The scattering intensity is greater than, but very similar to the pure solvent background, so without further experimental time I do not feel confident in these results. The peak position could also be complicated due to problems with finding the beam centre, and without definite knowledge of the direct beam position accurate analysis is impossible. Nonetheless scattering results for the potentially more interesting case of F8T2 in toluene are shown in *figure 44*. Problems occurred with the aged 30 mg/ml solution, no scattering from the material, vial or solvent could be seen in any of the recorded images. *Figure 44 (a)* shows the period plot of F8T2 in toluene, again very weak scattering curves are

observed, and very minor changes from background are observed. They are included for completeness in *table 22*, showing n values for all solutions studied, but with little confidence.

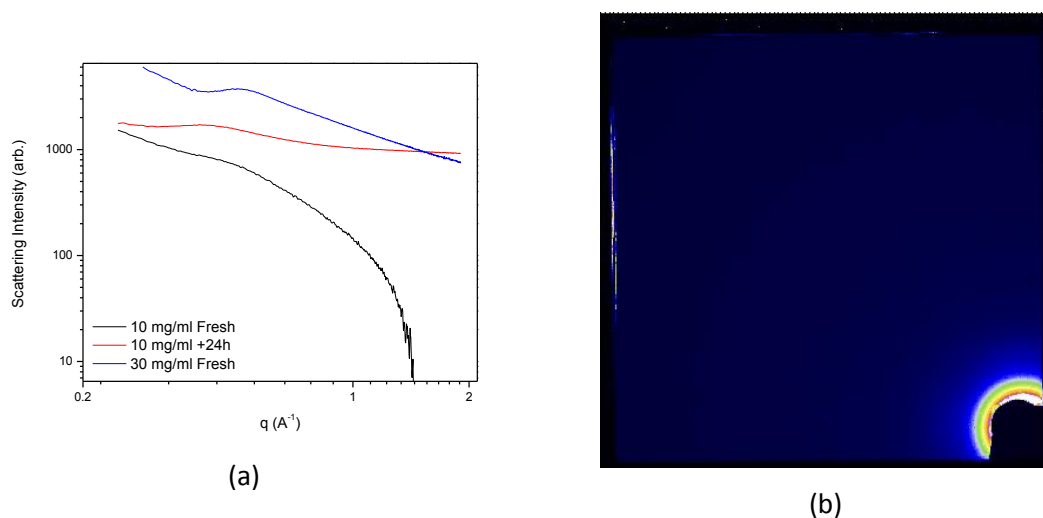


Figure 44 Scattering results for F8T2 in toluene
(a) Period plot (b) SAXS image of 30mg/ml problem

Solvent	Concentration (mg/ml)	Solution Age (+days)	Q Range ($\text{\AA}^{-1}$)	n
THF	10	0	< 0.55	0.42
THF	10	0	> 0.55	0.22
THF	10	1	< 0.55	1.23
THF	10	1	> 0.55	0.25
THF	30	0	< 0.55	1.08
THF	30	0	> 0.55	0.46
Toluene	10	0	< 0.70	1.16
Toluene	10	1	full	0.39
Toluene	30	0	full	1.0

Table 22 Values of n for all available SAXS measurements.

4.6 Conclusions

Overall the analysis of polyfluorene co-polymers in solution by multi-angle light scattering has been a very fruitful endeavour. F8T2 batches were successfully studied in THF, chloroform and toluene, with size ~ 140 nm, and molecular weights of $\sim 82 \pm 7$ kg/mol in THF after given time to dissolve fully. In chloroform and toluene polymer size was consistently very similar, allowing

me to determine that the F8T2 chains in these solvents are very rigid rods composed of approximately 80-90 repeat units. Molecular mass determinations have shown that, as with SANS, chloroform and THF are very good solvents, and chloroform shows continued stability over timescales of a week, much longer than that studied in *Chapter 3*. F8T2 in THF needs 2-3 days to dissolve fully without heating the solution, and each particle is composed of 1-2 polymer chains in both THF and chloroform. Aggregation in toluene was expected, and from molecular weight calculations shown to involve ~ 300 polymer chains but does not increase over a week. These results tie in with those found by neutron studies, regarding the quality of solvents, and the rod-like aspect of F8T2 in these solutions. R_g values from guinier analysis of SANS data are comparable with expected interchain distances, but I cannot say they do correspond.

PFO samples were also studied in THF and toluene, again with good results. This PFO batch was found to be composed of ~ 170 RUs per chain, and with noticeable aggregation in THF, and this is likely to explain the discrepancies between light scattering and GPC results. No such issues were found with the toluene samples.

F8BT was studied in toluene over two days. Again further studies of this polymer system could be undertaken, with errors on R_g of 50% on the 22 nm value and values of molecular weight of 60 kg/mol. These disproportionate size and mass values have been explained as stacking of ~ 8 chains, each of 15 repeat units in toluene solution. Further light scattering to improve comparisons with SANS results would be useful here. SANS results would still show long chains, as inter-stack layer distances are expected to be ~ 4.5 Å, meaning the length to height would still be in a ratio of 6:1.

SAXS results are very weak, and the key outcome is that F8T2 in solution is not a good candidate for further study with X-rays, although Angular-Resolved Near-Edge X-ray Absorption Fine Structure (NEXAFS) measurements have been completed by Werzer et al (35).

Multi-angle light scattering can be a very useful technique, and once processing complications are overcome should be used more often in the characterisation of polymers in solution.

4.7 Suggested Further Work

The obvious extension to this work is the development of more powerful light scattering processing software, able to use different structural factors in the analysis to improve

knowledge of the shape of the polymer in solution. However, plenty of information can be gained using the standard ASTRA software supplied by Wyatt.

Clearly multi-angle light scattering is a consistent and useful technique to aid in the characterisation of polymers in solution, once any processing issues have been dealt with.

With regards to F8T2 results, due to the short times needed to take a complete set of readings further *in situ* dissolution studies could be completed, particularly of F8T2 in toluene and the slight aggregation found in chloroform. These would be very helpful in understanding the dissolution dynamics, particularly when compared with SANS studies. Additionally further molecular weights could easily be studied and the range of solvents extended. Comparison with GPC values in different solvents would also be useful, as GPC is calibrated against polystyrene standards and this is unlikely to be a valid calibration sample for conjugated polymers.

PFO results could be repeated in chloroform, for comparison with SANS results, and variations in molecular weights could be studied to see if aggregation size scales with weight.

The F8BT sample used was very small compared to the other polymers, but also appears to aggregate in groups of ~ 8 chains. Studies in chloroform and other solvents would be useful for characterising this further.

In general, further work on comparing characteristics from SANS and light-scattering for rigid polymers should be completed, as a large amount of information about the particles in solution can be found from both.

SAXS has, unfortunately been far less successful than light scattering on F8T2. With some extra time much longer exposures of scattering could be taken, however unless the sample contrast could be improved I would not recommend this course. Other polyfluorenes are better at scattering X-rays, as shown in *Chapter 6* and these could be studied in solution with this technique, particularly F8BT for comparison with the work here and in *Chapter 3*.

4.8 Bibliography

1. **Lord Rayleigh (J. W. Strutt)**. On the light from the sky, its polarisation and colour. *Phil. Mag.* 1871. Vol. 41, pp. 107-120, 274-279.
2. **J M G Cowie**. Polymers: Chemistry and Physics of Modern Materials. *Chapman and Hall*, 2nd ed. 1991.
3. **P Debye**. Light Scattering in Solutions. *J. Appl. Phys.* 1944. Vol. 15, 4, pp. 338-342.
4. **A Einstein**. Theorie der Opaleszenz von homogenen Flüssigkeiten und Flüssigkeitsgemischen in der Nähe des kritischen Zustandes (The Theory of the Opalescence of Homogeneous Fluids and Liquid Mixtures near the Critical State). *Ann. der Phys.* 1910. Vol. 33, 4, pp. 1275–1298.
5. **C V Raman**. A New Radiation. *Indian J. Phys.* 1927. Vol. 2, p. 387.
6. **B H Zimm**. Molecular Theory of the Scattering of Light in Fluids. *J. Chem. Phys.* 1945. Vol. 13, 4, pp. 141-145.
7. —. Apparatus and methods for measurement and interpretation of the angular variation of light scattering; preliminary results on polystyrene solutions. *J. Chem. Phys.* 1948. Vol. 16, 12, pp. 1093-1099.
8. **A Guinier**. *Small-angle scattering of X-rays*. [ed.] G Fournet. Michigan : Wiley, 1955.
9. **P M Doty, B H Zimm and R S Stein, R. S.** Classical theory of light scattering from solutions—A review. *Polym. Bull.* 1945. Vol. 1, pp. 90-119.
10. **P Debye**. Molecular-weight Determination by Light Scattering. *J. Phys. Chem.* 1947. Vol. 51, 1, pp. 18-32.
11. **G C Berry**. Thermodynamic and Conformational Properties of Polystyrene, Light-Scattering Studies on Dilute Solutions of Linear Polystyrenes. *J. Chem Phys.* 1966. Vol. 44, pp. 4550-4564.

12. **M Andersson, B Wittgren and K G Wahlund.** Accuracy in multiangle light scattering measurements for molar mass and radius estimations. Model calculations and experiments. *Anal. Chem.* 2003. Vol. 75, 16, pp. 4279-4291.
13. **T Wang and J A Lucey.** Use of Multi-Angle Laser Light Scattering and Size-Exclusion Chromatography to Characterize the Molecular Weight and Types of Aggregates Present in Commercial Whey Protein Products. *Journal of Dairy Science.* 2003. Vol. 86, 10, pp. 3090-3101.
14. **S-H Yoo and J-I Jane.** Molecular weights and gyration radii of amylopectins determined by high-performance size-exclusion chromatography equipped with multi-angle laser-light scattering and refractive index detectors. *Carbohydrate Polymers.* 2002. Vol. 49, 3, pp. 307–314.
15. **K Jumel, I Fiebrig and S E Harding.** Rapid size distribution and purity analysis of gastric mucus glycoproteins by size exclusion chromatography/multi angle laser light scattering. *Int. J. of Bio. Mac.* 2996. Vol. 18, 1-2, pp. 133-139.
16. **J Luo, M Leeman, A Ballagi, A Elfwing, Z Su, J Janson and K Wahlund.** Size characterization of green fluorescent protein inclusion bodies in E. coli using asymmetrical flow field-flow fractionation–multi-angle light scattering. *J. of Chromatography. 29th International Symposium on High Performance Liquid Phase Separations and Related Techniques — Part II.* 2006. Vol. 1120, 1-2, pp. 158–164.
17. **C Cametti, P Codastefano, R D'Amato, A Furlani and M V Russo.** Static and dynamic light scattering measurements of polyphenylacetylene (PPA) in different organic solvents (tetrahydrofuran, toluene and chloroform). *Synthetic Metals.* 2000. Vol. 114, 2, pp. 173–179.
18. **S Girod, P Baldet-Dupy, H Maillols and J M Devoisselle.** On-line direct determination of the second virial coefficient of a natural polysaccharide using size-exclusion chromatography and multi-angle laser light scattering. *Journal of Chromatography A.* 2002. Vol. 943, 1, pp. 147-152.

19. **K C Lim, C R Fincher Jr. and A J Heeger.** Rod-to-Coil Transition of a Conjugated Polymer in Solution. *Phys. Rev. Lett.* 1983. Vol. 50, 24, pp. 1934-1937.
20. **T J Manning, T Bennett and D Milton.** Aggregation studies of humic acid using multiangle laser light scattering. *Science of The Total Environment.* 2000. Vol. 257, 2-3, pp. 171-176.
21. **B El-Baradie, R Ghazy, A El-Shaer, F El-Mekawey.** Optical selection of the preferred solvent of a standard polymer for laser light scattering phenomena investigations. *Physica B: Condensed Matter.* 2000. Vol. 292, 3-4, pp. 208–212.
22. **S Heimer and D Težak.** Structure of polydispersed colloids characterised by light scattering and electron microscopy. *Advances in Colloid and Interface Science.* 2002. Vol. 98, 1, pp. 1–23.
23. **M B Huglin.** *Light Scattering from Polymer Solution.* London : Academic Press, 1942.
24. **P C Hiemenz and R Rajagopalan.** *Principles of Colloid and Surface Chemistry, Revised and Expanded (3rd Ed.).* New York : Marcel Dekker Inc, 1997.
25. **G W Heffner and D S Pearson.** Molecular characterization of poly(3-hexylthiophene). *Macromolecules.* 1991. Vol. 24, 23, pp. 6295–6299.
26. **T Yamamoto, D Oguro and K Kubota.** Viscometric and Light Scattering Analyses of CHCl₃ Solutions of Poly(3-alkylthiophene-2,5-diyl)s. *Macromolecules.* 1996. Vol. 29, 5, pp. 1833–1835.
27. **R Ghazy, B El-Baradie, A El-Shaer and F El-Mekawey.** Static laser light scattering (SLLS) investigations of the scattering parameters of a synthetic polymer. *Optics & Laser Technology.* 1999. Vol. 31, 6, pp. 447–453.
28. **C Wu, K Woo and M Jiang.** Light-Scattering Studies of Styrene–(Ethylene-co-butylene)–Styrene Triblock Copolymer and Its Sulfonated Ionomers in Tetrahydrofuran. *Macromolecules.* 1996. Vol. 29, 16, pp. 5361-5367.

29. **M Grell, D D C Bradley, X Long, T Chamberlain, M Inbasekaran, E P Woo and M Soliman.** Chain geometry, solution aggregation and enhanced dichroism in the liquidcrystalline conjugated polymer poly(9,9-dioctylfluorene). *Acta Polymerica*. 1998. Vol. 49, 8, pp. 439–444.
30. **R Grisorio, P Mastrorilli, C F Nobile, G Romanazzi, G P Suranna, D Acierno and E Amendola.** New Spiro-Functionalized Polyfluorenes: Synthesis and Properties. *Macromolecular Chemistry and Physics*. 2005. Vol. 206, 4, pp. 448–455.
31. **M Brinkmann, N Charoenthai, R Traiphol, P Piyakulawat, J Wlosnewski, and U Asawapirom.** Structure and Morphology in Highly Oriented Films of Poly(9,9-bis(n-octyl)fluorene-2,7-diyl) and Poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) Grown on Friction Transferred Poly(tetrafluoroethylene). *Macromolecules*. 2009. Vol. 42, 21, pp. 8298–8306.
32. **C L Donley, J Zaumseil, J W Andreasen, M M Nielsen, H Sirringhaus, R H Friend, and J-S Kim.** Effects of Packing Structure on the Optoelectronic and Charge Transport Properties in Poly(9,9-di-n-octylfluorene-alt-benzothiadiazole). *J. Am. Chem. Soc.* 2005. Vol. 127, 37, pp. 12890-9.
33. **D H Kim, J T Han, Y D Park, Y Jang, J H Cho, M Hwang, and K Cho.** Single crystal polythiophene microwires grown by self-assembly. *Adv. Mater.* 2006. Vol. 18, pp. 719–723.
34. **Sigma-Aldrich.** Catalogue 685070.
35. **O Werzer, K Matoy, D M Smilgies, M M Rothmann, P Strohriegl, and R Resel.** Uniaxially aligned poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-bithiophene] thin films characterized by the X-ray diffraction pole figure technique. *Journal of Applied Polymer Science*. 2008. Vol. 107, 3, pp. 1817–1821.
36. **A Guite.** Microstructure, morphology and device physics of gravure printed and solution processed field-effect transistors. *Imperial College London*. 2011.

Chapter 5

Spectroscopy and Thin Films

This chapter presents my work using spectroscopic techniques, on F8T2 solutions and thin-films. Photoluminescence, absorption, PLQE and lifetime measurements are presented. Key studies have been in understanding the solvochromatic shifts of F8T2, both in solution and in spin-coated films, and the strong effects thermal treatments can have on thin-film morphology and characteristics. In addition, structural characterisation work on F8T2 thin-films and TFT results are also shown.

5.1 Introduction

Spectroscopy is one of the first measurements to be taken on new samples and is particularly important for electroluminescent and photovoltaic materials. Changing and tuning emission wavelengths is an important part of general organic semiconductor development. Spectroscopic measurements can give information about structural order, and more generally information about polymer chains in solutions and solid films. Thermal and vapour treatment of films is studied usually in the context of improving electrical device performance, and polarisation.

In this Chapter my spectroscopic results on F8T2 and other PFO copolymers is presented, with a wide range of experimental procedures covered; most notably the effect of solvent choice, solution concentration and solution ageing on PL and absorption. Whether spectroscopy can be used on F8T2 to ascertain transition temperatures, in comparison to DSC was also studied. Finally AFM images of thermally treated films spin coated from fresh and old solutions are shown, along with some OFET results.

5.2 Theory and analytical concerns

The techniques covered in this chapter are widely used and understood, and discussed in *Chapters 1* and *2*. There are no unusual or complex analytical procedures, however the absorption and photoluminescence will be discussed using the following processes and terminology. *Figure 45* shows the photoluminescence and absorption spectra of F8T2 in films and solutions using THF as the dissolving solvent. Discussion proceeds with reference to the labelled peaks. The most important feature is a distinct vibronic structure, with increased absorption and PL structure correlating with increased physical structure. Additionally the ratio of the 0-0 and 0-1 peaks is important, with a larger relative 0-0 correlating to increased order and for single chains a more planar backbone configuration. The Stokes Shift can also be seen, the offset between the absorption 0-0 and PL 0-0 peaks, showing the reorganisation energy between the ground and excited states. Finally, the overlap of the absorption and PL spectra is the spectral region where self-absorption can occur.

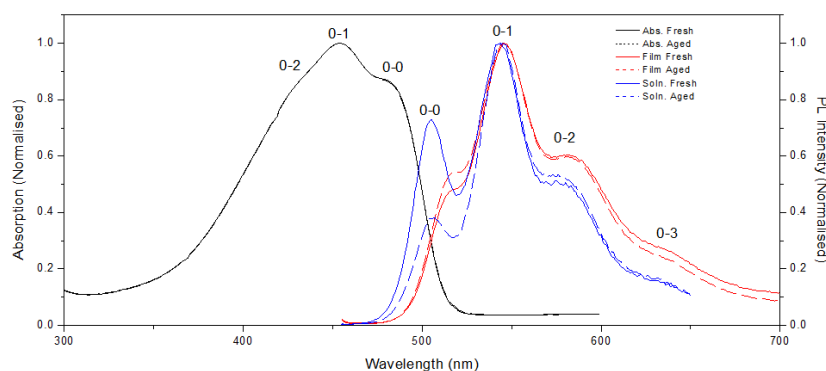


Figure 45 Overall absorption and PL spectra of F8T2 using THF as the solvent, showing labelled vibronic peaks

5.3 Previous Work

There are relatively large amount of previous data on F8T2, both spectroscopic (1) and electrical (2), with anisotropic absorption or emission tested spectroscopically.

Spectroscopy is one of the first studies undertaken on new polymers, large amounts of information can be gleamed from absorption and emission measurements and is the standard technique for noting changes in films.

A large body of work on polyfluorenes in solution has been done by Knappilia and colleagues (3; 4; 5; 6), previously discussed in *Chapter 4*, mostly to understand aggregation dynamics and self assembly. The literature is lacking a comprehensive solvatochromic study of polyfluorenes, which I feel is an oversight as some solvent effects can be seen in solution and can be held into the solid state. Although not studied here this is a clear issue for P3HT based films and devices (7). Very interesting experimental work by Clark et al. (8), based on the theoretical analysis of Spano (9; 10) has been shown to estimate the exciton bandwidth, a measure related to conjugation length and crystalline quality, as well as the fraction of a P3HT film composed of crystalline aggregates. Generally they found that percentage of a spun film in a crystalline aggregate phase was related to the boiling point of the solvent used. Interestingly in regards to this work they found that the relative intensity of the 0-0 peak in absorption spectra increases with the percentage of aggregate in the film. That this effect was not seen in F8T2 is not surprising, the effect in P3HT is reliant on a single molecule per unit cell and various symmetry arguments.

Thermal annealing to induce crystallinity on directional substrates to induce monodomain alignment (1) is a technique for the creating of polarised OLEDs(11; 12) from polyfluorene and copolymers; and alignment can give strong improvements to OFET characterisitcs(13; 2). F8BT and F8T2 were studied

by Grell et al (1) on rubbed substrates after annealing to induce liquid crystal alignment, following on from early work into EL in polyfluorenes by Grice (14) and from similar work by Wendorff et al. (15) although not on polyfluorenes. F8T2 is an interesting polymer for study as it can be used for efficient OLEDs (16) and OFETs (2).

Vapour treatment has been used Whitehead and colleagues (17) to induce β -phase effects in PFO OLEDs, and was studied by Guite (18) to improve self organisation in P3HT printed OFETs. This second use is followed in this thesis, with regards to F8T2 OFETs.

An interesting study later in this chapter follows in the footsteps of Sims et al. (19) who were able to determine the glass transition, onset of crystallisation and the liquid crystal melt in PFO films by spectroscopic means. By heating PFO films in vacuum and measuring PL and PL intensity strong changes were seen at these transitions. Changes in peak positions and relative peak heights were seen and their values agree with bulk DSC. PFO is particularly well suited to this type of analysis as clear spectroscopic and intensity changes can be seen. Sadly experiments of this type do not seem to have been repeated for other polymer materials.

5.4 Results

Many experimental results are covered in this chapter. Initially the effects of concentration on F8T2 photoluminescence emission in various solvents are discussed, followed by the effects of aggregation over time and solvatochromism. Lifetime and PLQE results are then discussed, on films made from F8T2 in a range of solvents and solution ageing times. Finally vapour and thermal treatments of films are covered, and the effects of these treatments on OFETs.

5.4.1 Concentration Dependences of F8T2

Initial spectroscopic results are presented on concentration dependent photoluminescence of F8T2 in solution, with regards to both spectral characteristics and overall intensity.

5.4.1.1 F8T2 in THF Solutions

Solutions of F8T2 in THF were studied, following the procedures outlined in *Chapter 2*, using a Fluoromax spectrophotometer with excitation wavelength of 450 nm. Solutions were measured immediately after heating and visibly appearing dissolved, in practice within 2 hours, which as suggested in *Chapter 3* and *4* would suggest fully or almost fully dissolved chains. *Figure 46* shows PL intensity with wavelength over a range of concentrations from 10^{-4} mg/ml to ~ 10 mg/ml, with an arbitrary but consistent ordinate axis scale.

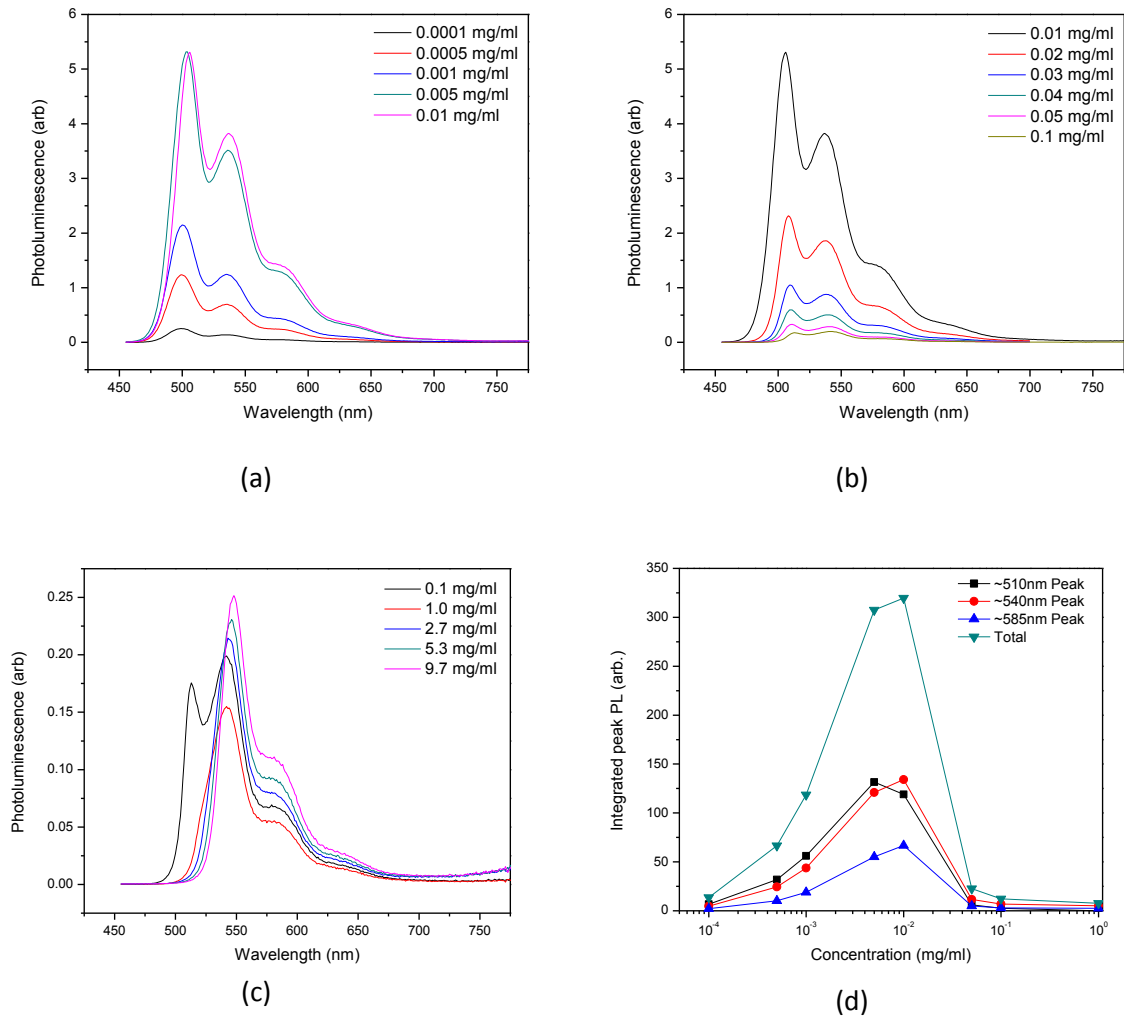


Figure 46 PL intensities of F8T2 in THF over 5 decades of concentrations (a) Low, (b) Mid, (c) High (d) Integrated PL intensity to gaussian fit of each peak

It is very interesting to note the large change in PL intensity with concentration and complete removal of the (0-0) peak at 500 nm at higher concentrations. PL intensity increases from 10^{-4} - 10^{-2} mg/ml by a factor of 21 when measured for as the 500 nm peak height, with a corresponding 22 fold increase in total PL intensity, and peak positional shift from 500nm to 505nm. These clearly show the PL spectrum of a solitary F8T2 chain in a good solvent. Assuming polymer chains are evenly spread throughout the solution, and using values for M_w calculated in *Chapter 4* an interchain distance L_c in nanometres can be calculated from [5.1], assuming each chain inhabits a cube with sides of length L_c .

$$L_c = \left(\frac{CN_A}{M_w} \cdot 10^3 \right)^{\frac{1}{3}} \cdot 10^9 \text{ nm} \quad [5.1]$$

Where C is the concentration in mg/ml, M_w molecular weight in g/mol (7.6×10^4 g/mol) and N_A Avagadro's number.

Over the range 10^{-4} mg/ml to 10^{-2} mg/ml L_c varies from ~ 1 μm to ~ 230 nm, to be compared with R_g value of 164 ± 9 nm for this F8T2 batch in THF measured by light scattering. As concentrations increase above 0.01 mg/ml to 0.1 mg/ml PL intensity measured at the peak drops to one 26^{th} of its value, with a further redshift of the peak from 505 nm to 512 nm and interchain spacing dropping to ~ 108 nm, well below the extended size of the polymer.

At concentrations above 0.1 mg/ml there is no longer any trace of a peak at 512 nm, and the now highest energy (0-1) peak appears to move from 542 to 548 nm as the average distance from chain to chain decreases to just 24 nm.

These large changes in both intensity and relative peak heights are attributed to two different physical processes. Initially PL intensity increases as concentration increases as more polymer is added to the solution, although not in a direct relationship with total dissolved mass. Around concentration levels of 0.01-0.05 mg/ml the interchain cube dimensions from [5.1] become comparable with the chain length, and interchain effects become more important quenching PL to much lower levels. SANS studies have ruled out aggregation in THF in the range 2-20 mg/ml, so this is likely to be from interaction of individual chains rather than non-radiative decay in large aggregate particles. This combination of self-absorption of the (0-0) peak and increasing interchain interactions open up new non-radiative PL quenching pathways, leading to a large loss of PL intensity.

Above ~ 1 mg/ml a PL spectrum corresponding to highly concentrated solution is observed, with increasing intensity due to increased dissolved mass and strong self absorption effects due to the large overlap of absorption and PL spectra from the onset of absorption around 520 nm.

Ignoring interchain and self-absorption effects three PL peaks can be defined for F8T2 in dilute THF solutions.

Peak	Peak Position (nm)	Peak Position (eV)
0-0	503 ± 4	2.47 ± 0.02
0-1	536 ± 2	2.31 ± 0.01
0-2	580 ± 10	2.14 ± 0.04

Table 23 Peak positions of 0-0, 0-1, and 0-2 fluorescent transitions of F8T2 in F8T2 in THF solutions

5.4.1.2 F8T2 Absorption and PL in THF Solutions and Thin Films

Absorption and PL spectra were taken of F8T2 in solution, and from films spin cast from each solution concentration. These can be seen below in *figure 47*.

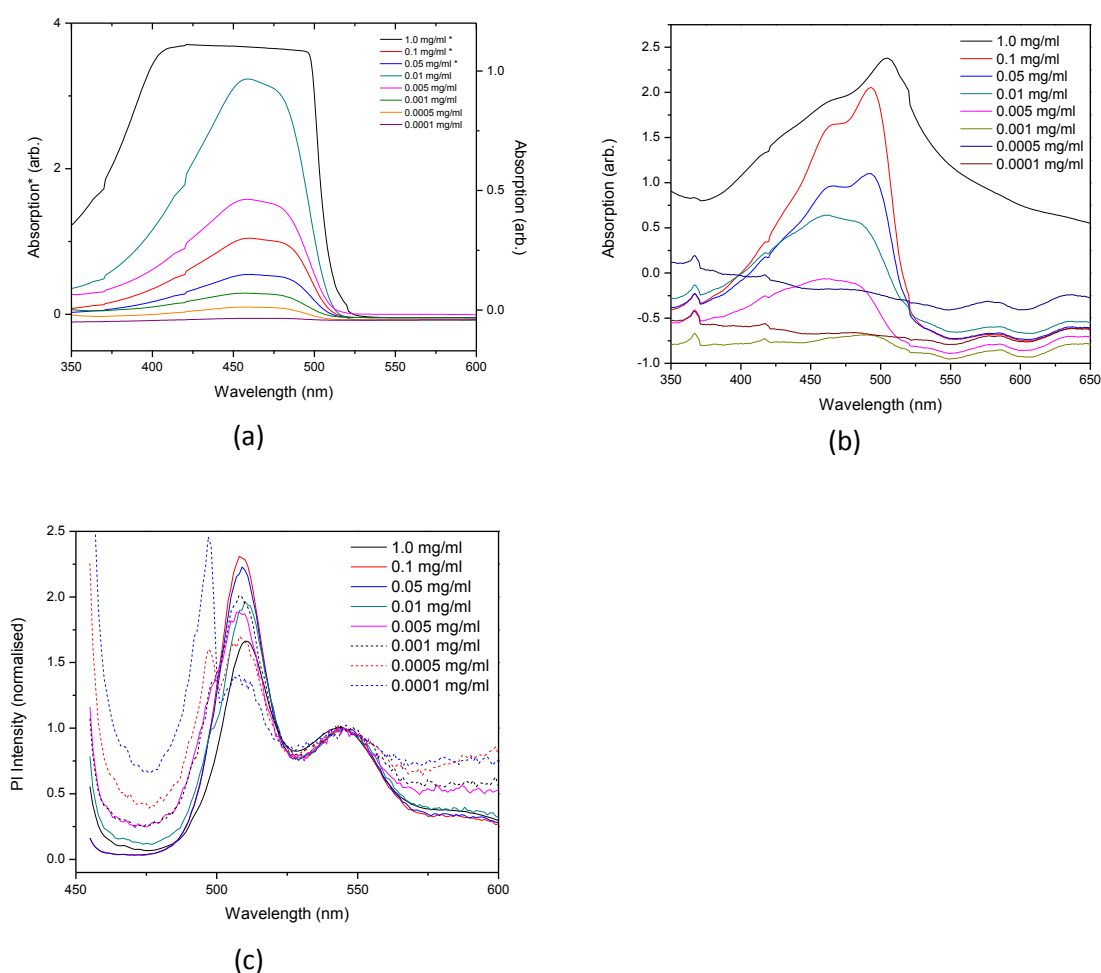


Figure 47 Absorption of F8T2 in THF (a) solution, note *scale to left for high concentrations with 1mm lightpath and (b) film by concentration (c) PL of films by concentration normalised to 0-1 peak

Figure 47(a) shows the absorption spectra of all concentrations of F8T2 in THF from 10^{-4} -1.0 mg/ml in solution, with a 10 mm light path for concentrations below 0.05 mg/ml and 1 mm for those above. Although no visible vibronic structure is usual in solution, the 0-0 and 0-1 absorption peaks can be defined from changes in slope, at 457 ± 3 nm and 480 ± 10 nm respectively.

Figure 47(b) shows absorption spectra from films spin cast from each of the solution concentrations. Very low concentrations were very close to background levels, and clear vibronic peaks can be seen in films spun from concentrations of 0.05 mg/ml and above. Concentrations below this show the same featureless absorption as the solutions, with the very slight vibronic peaks beginning to appear in the 0.01 mg/ml film. Increasing concentration redshifts the longer wavelength peak from 480 nm in solution to 505 nm in films spun from 1 mg/ml, equivalent to a decrease from 2.58 eV to 2.46 eV. At these higher concentrations the 0-0 peak is much stronger than the 0-1, with 0-0:0-1 peak height ratios of 1.6:1, compared to 0.9:1 for 0.1 mg/ml and 0.005 mg/ml respectively. This is due to a more planar backbone conformation and higher crystallinity in films spun from higher concentrations. As this is a clear concentration effect it is likely that the film order is improved by chain proximity in solution. When films are spun from low concentrations with little interaction between polymers in solution an amorphous solid film is formed, but at higher solution concentrations, when interchain distance is comparable to the chain length, interactions in solution are kept in the solid phase. This is in keeping with the results found in *Chapter 4* where F8T2 in THF at the low light scattering concentrations were found to be likely to be composed of 2-3 chains per scattering particle. This small-number proto-aggregation/order is likely to stay in films.

Figure 47(c) shows the PL spectra of the films discussed above, normalised to the 0-1 peak at 545 nm. In the solid state spectra are red-shifted such that the 0-0 peak is at 510 nm, and the 0-1 at 545 nm, due to the thinness of the films the 0-2 peak is not visible over the background noise, with the highest concentration studied 1.0 mg/ml the most red-shifted. The unusual peaks at 498 nm in the lowest concentration films are expected to be measurement issues with the Fluoromax. These films would be expected to mirror the absorption spectra, with the 0-0 dominating over the 0-1 and this is seen, even in the films from the lowest concentration solution. As in the absorption spectra there is improved planarity and order from more concentrated solutions, with the relative 0-0 peak heights increasing from 1.4:1 to 2.3:1 from 10^{-4} mg/ml to 0.1 mg/ml. The red-shift would also imply a more structured material than in solution, as expected. Clearly as these films are very thin, self-absorption is not the issue it is in solutions, and the 0-0 peak is clearly visible, although in the 1 mg/ml film it is decreasing noticeably with respect to the 0-1 peak. Films spun from a range of concentrations up to 1 mg/ml show the same PL spectrum of emission as low concentration solvents, suggesting the aggregation effects of a few chains seen around 0.01mg/ml do not significantly effect emission. The increased density would lead to expectations of strong self absorption, however due to visible emission being mostly seen from the top surface of the film rather than perpendicular to the excitation direction as in the solution work, this is not as strong an effect.

5.4.1.3 F8T2 in Toluene Solutions

The concentration dependent PL measurements were repeated for F8T2 in toluene solutions, over the range 10^{-4} to 1.0 mg/ml, heated to aid dissolution and then measured. Despite the changes in molecular weight in toluene found in *Chapter 4*, the same level of drop in PL intensity occurs between 0.01 and 0.05 mg/ml. Using M_w values of $\sim 2 \times 10^7$ g/mol, much higher than without aggregation in THF, this gives a cube side value of ~ 1.5 μm to 873 nm over that range. The intermolecular range here is clearly far larger than that seen in *Section 5.4.1.1* and used to explain this drop in PL. Here I think this shows the effect of solvent thermal treatments to aid dissolution, and hypothesise that in these solutions the F8T2 is well dissolved, and these intermolecular effects are happening at scales equivalent to R_g in THF ~ 140 nm, rather than the larger poorly dissolved, or aggregated sizes. Additional investigation with time could help understand these dissolution effects and chain interactions. Concentrations from 10^{-4} to 0.01 mg/ml all have 0-0 peak positions of 504 ± 2 nm and 0-1 at 540 ± 2 nm, the same as in THF again suggesting that chain conformations are similar if not the same. At higher concentrations, above 0.05 mg/ml self absorption is again observed, strongly reducing the peak at 504 nm until it is no longer visible at 1.0 mg/ml, and appearing to red-shift its position to 512 nm. Photoluminescence spectra of these solutions can be seen in *figure 48*. These all suggest that the same interactions effecting PL quenching in THF solutions are happening in toluene, but due to heating to induce good solvation the effects of aggregation seen in *Chapter 4* are not important to these solutions, and from the relative intensities of the 0-0 and 0-1 PL peaks, chains take up a similar planar conformation in solution, until at higher concentrations interchain interactions begin to dominate.

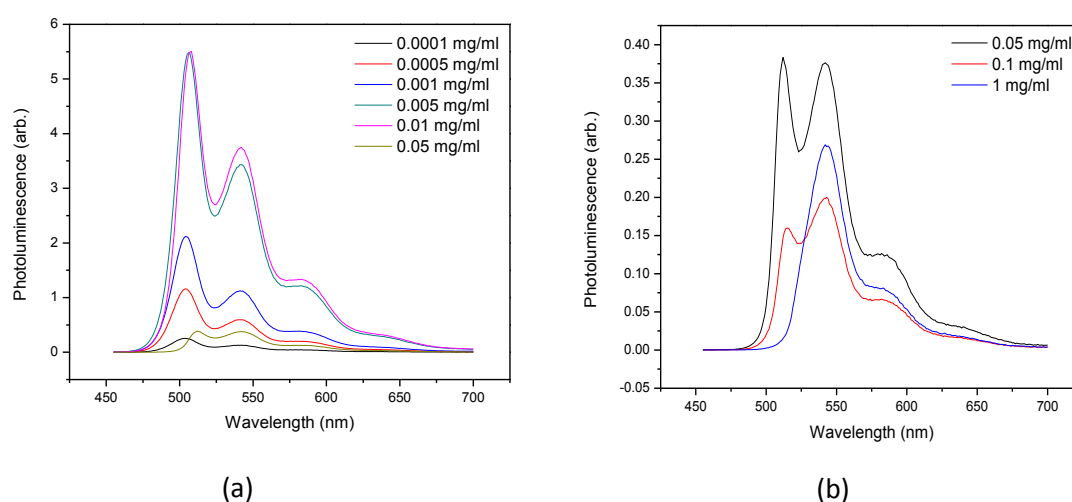


Figure 48 PL of F8T2 in toluene solution at concentrations from 0.0001 mg/ml to 1 mg/ml

In addition to concentration dependent PL quenching, toluene solutions were studied as aggregation is a clear issue in these solutions. The solutions above were remeasured for PL emission after ~ 2 weeks standing in the dark. The results of these experiments are shown in *figure 49*, where *49(a)* shows the lower concentrations and *49(b)* the higher with PL spectra of the aged solutions shown dashed.

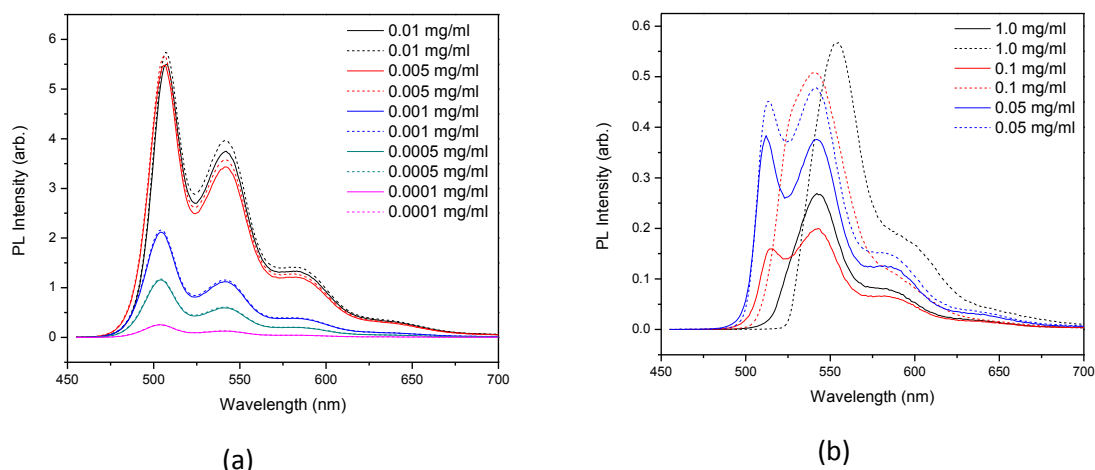


Figure 49 PL Spectra of aged (~ 2 weeks) F8T2 in toluene solutions at (a) high and (b) low concentrations dashed are aged spectra

At the lowest concentrations from 10^{-4} to 10^{-2} mg/ml no changes in shape or intensity are seen, suggesting at these concentrations aggregation is not seen on these timescales. Taking the M_w of F8T2 in THF as an estimate of well dissolved F8T2 in toluene, these chains would be separated by up to $1\ \mu\text{m}$ in solution, almost an order of magnitude larger than expected R_g values of $\sim 160\ \text{nm}$. At higher concentrations however, clear effects of aggregation are seen. The 0.05 mg/ml concentration has no change in spectral shape, but decreases in magnitude. 0-0 and 0-1 peak positions stay at 512 nm and 540 nm. At 0.1 mg/ml the low wavelength peak disappears almost completely, leaving just a weak shoulder at 526 nm. Most interestingly, at 1.0 mg/ml (and above, see *Section 5.4.1.4*) emission intensity increases and the peak undergoes a large red-shift to 554 nm. This large relative increase of the 0-1 peak compared to the 0-0 and the corresponding red-shift suggests a new aggregate phase, with more structure and a more twisted backbone in aged solutions but lower energy.

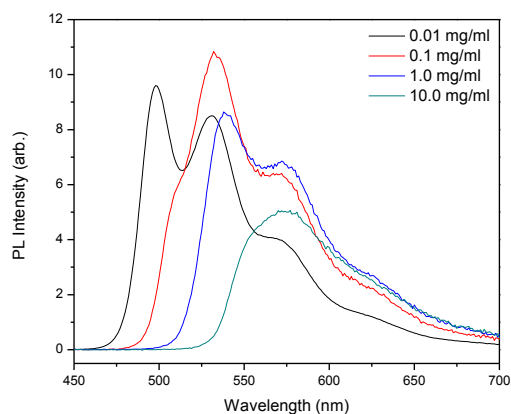
These results all combine to suggest that heating allows even relatively poor F8T2 solvents to dissolve the polymer well for a time, but aggregation occurs, leading to large particles in solution with lower energy emissive states. PL quenching in these well dissolved solutions happens at the same concentrations for the same reasons as described in *Section 5.4.1.1*.

5.4.1.4 F8T2 in Other Solvents

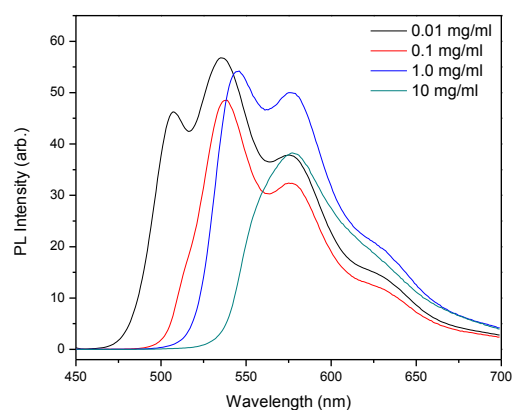
In addition to the detailed spectroscopic measurements with concentrations taken above, F8T2 was studied in three further solvents: xylene, chlorobenzene and chloroform, as well as results retaken in THF and toluene. Concentrations ranged from 0.01-10 mg/ml, the higher end of the concentration scale where spectroscopic changes were seen in the sections above. *Figure 50* shows the PL spectra of F8T2 in each of the five solvents being studied, for each of the four concentrations.

There are common trends for each concentration, mostly the complete loss of the peak around 500 nm by 0.1 mg/ml, and loss of the 540 nm peak by 10 mg/ml. As before, F8T2 is well dissolved in THF with a planar chain conformation at the low concentration. In the other solvents, the 0-1 peak dominates the 0-0 at 0.01 mg/ml, suggesting a more twisted backbone, which ties in well with the light scattering results in *Chapter 4*. It is worth noting the change in the toluene spectra in *figure 49* and *50*, which I anticipate to be caused by the 'better' thermal history of the solutions in the previous section, without enough heating F8T2 in toluene takes on a more twisted backbone configuration. As before, the loss of the 0-0 peak at higher concentrations is caused initially by interchain quenching, then self absorption at higher concentrations. Changes in the exact position of the PL intensity peak with concentration would need further study, and lower concentrations. However, clear solvatochromic shifts are seen for each concentration with solvent.

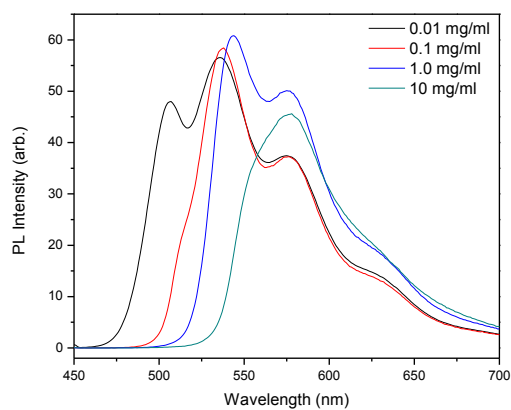
Absorption spectra of these solutions are shown in *figure 54* and discussed in *Section 5.4.2*.



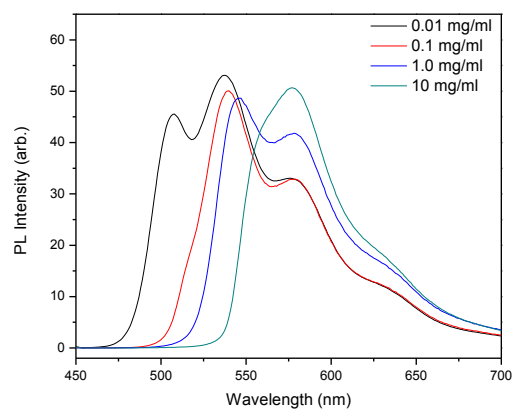
(a)**



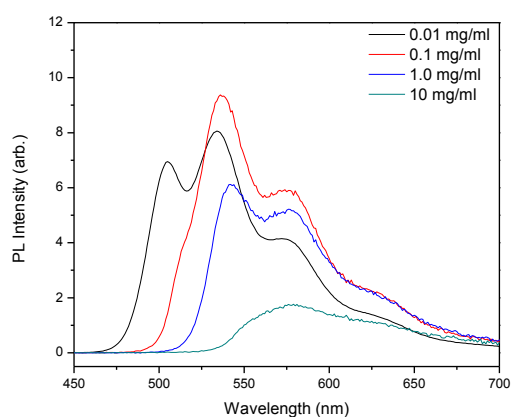
(b)*



(c)*



(d)*



(e)***

Figure 50 PL spectra with concentration of (a) THF (b) Toluene (c) Xylene (d) Chlorobenzene (e) Chloroform *0.01 mg/ml PL reduced by a factor of 15 **0.01 mg/ml PL reduced by a factor of 30 *0.01 mg/ml PL reduced by a factor of 15, 10 mg/ml reduced by a factor of 2**

5.4.2 Solvatochromic Shifts of F8T2

To study the effects of solvent choice on F8T2 solutions, seven solvents were studied; THF, toluene, xylene chlorbenzene, chloroform, hexane and acetone. All dissolved F8T2 with gentle heating, except hexane and acetone in which F8T2 appears insoluble and THF and chloroform which did not need heat. Images of these solutions freshly prepared and after 24 hours at room temperature are shown below in *figures 51 and 52*, at 10 mg/ml, 1 mg/ml and 0.1 mg/ml from left to right.

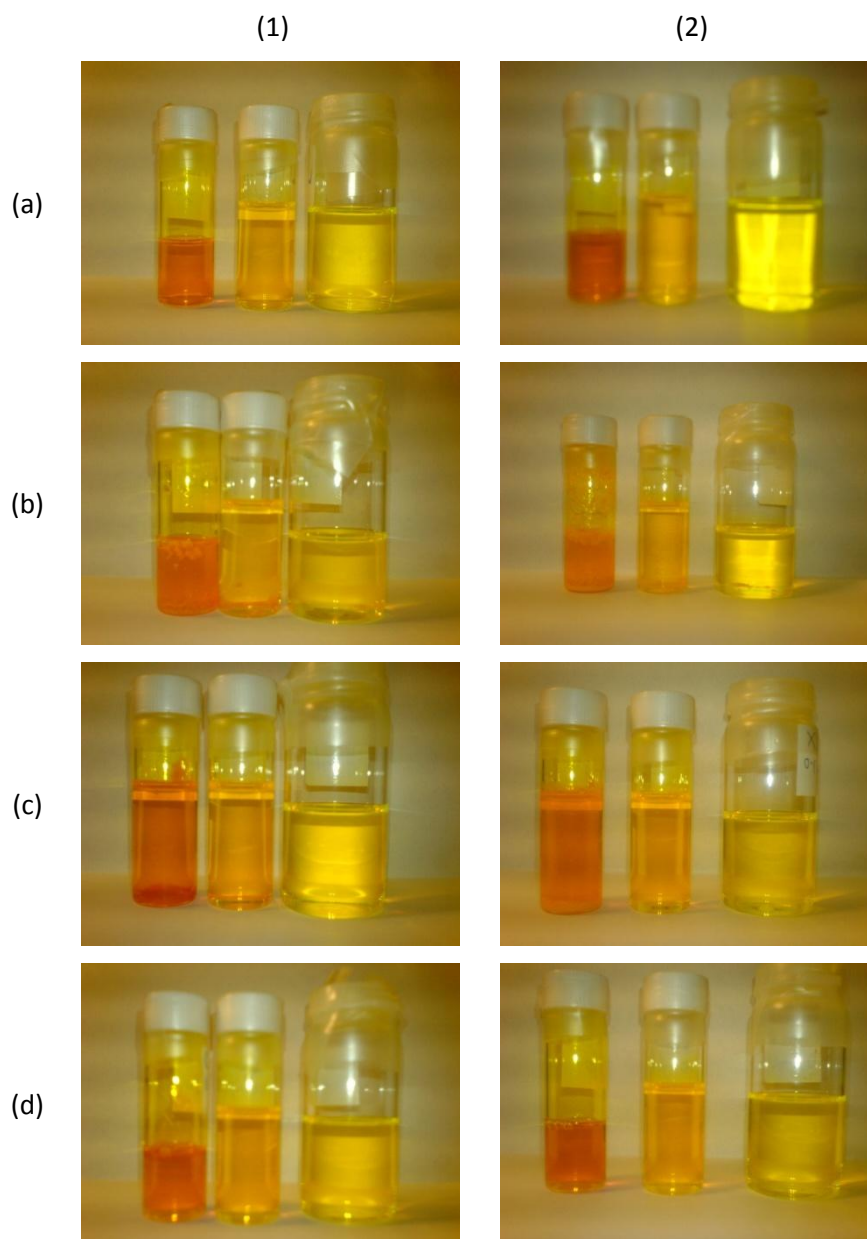


Figure 51 Vials of F8T2 at concentrations of 10, 1 and 0.1 mg/ml (1) Freshly made and (2) after ~24 hours in (a) THF (b) Toluene (c) Xylene (d) Chlorobenzene

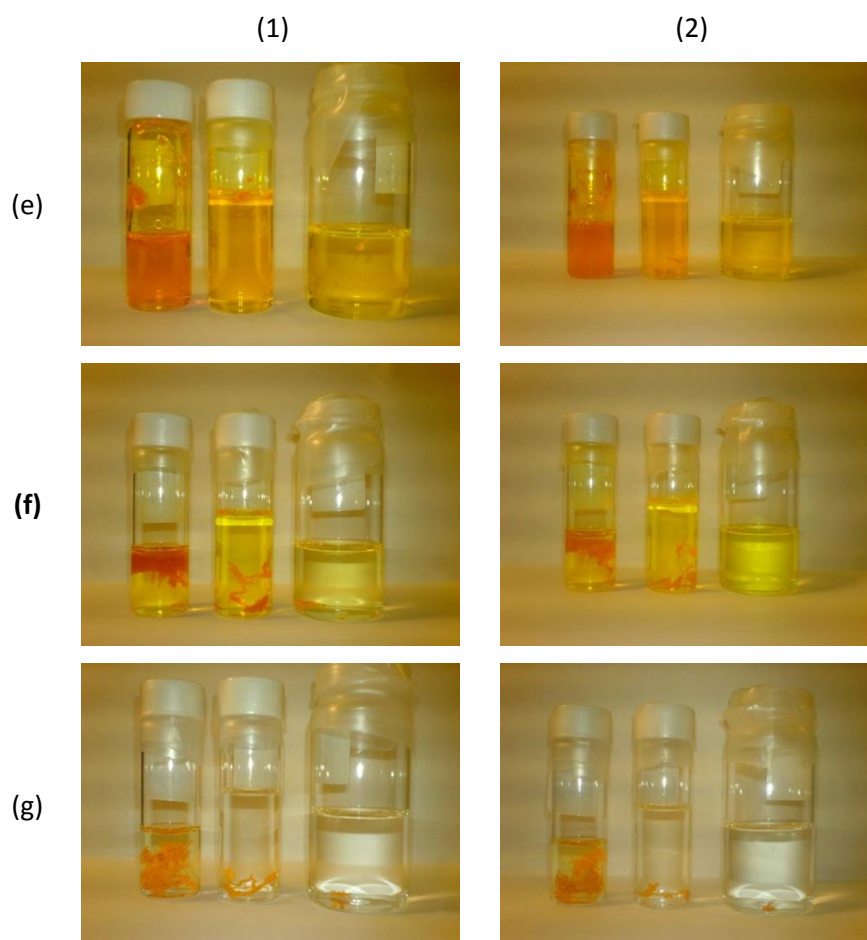


Figure 52 Vials of F8T2 at concentrations of 10, 1 and 0.1 mg/ml (1) Freshly made and (2) after ~24 hours in (e) Chloroform (f) Hexane (g) Acetone

F8T2 does not readily dissolve in hexane, and as one would expect not at all in acetone. F8T2 dissolved in toluene does not stay in solution, and the time before gelling or obvious aggregation is concentration dependant. At typical device concentrations of >10 mg/ml it is on the order of hours.

5.4.2.1 Solvatochromism in Solution with Concentration

Solutions of F8T2 in THF, toluene, xylene, chlorobenzene and chloroform at 0.01 mg/ml, 0.1 mg/ml, 1.0 mg/ml and 10 mg/ml were chosen for study. Changes in PL and absorption spectra in solution for each solvent at each concentration were studied, along with the effects of ageing in certain solvents, discussed in Section 5.4.2.2.

Figure 53 shown the PL spectra for F8T2 in each of the five solvents, at the four concentrations studied, normalised to the 0-1 peak for all but the highest concentration which is normalised to the remaining 0-2 peak.

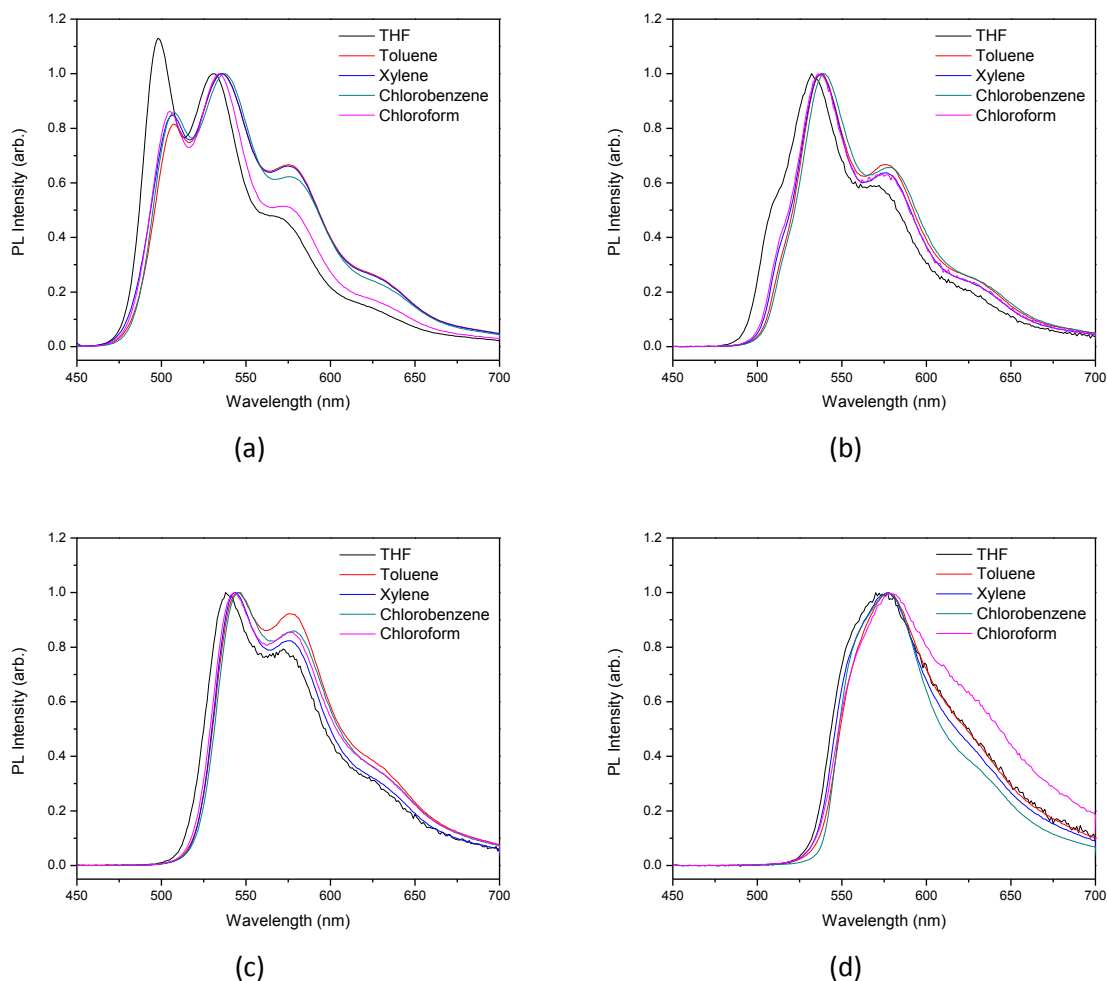


Figure 53 PL intensities of F8T2 in five solvents at concentrations of
(a) 0.01 mg/ml (b) 0.1 mg/ml (c) 1.0 mg/ml (d) 10 mg/ml

Most noticeable is the ~ 5 nm blue-shift in THF in the three lowest concentrations, and the clear increase in the 0-0 peak at the lowest concentration. Assuming solitary chains at 0.01 mg/ml, which seems likely as discussed in *Section 5.4.1.1*, this suggests that F8T2 in THF has the most planar backbone configuration, but that the more twisted conformation seen in the other solvents is lower energy due to the red-shift. This partially ties in with the results in *Chapters 3* and *4*, where F8T2 is expected to be a well dissolved, rigid but twisted rod in THF with little aggregation. However, chloroform and toluene do not show this blue-shift, but this may well be offset by some level of aggregation. The onset of chain interactions in all these solvents is likely to be around this concentration, a further study at lower and higher values would be beneficial to understand if the assumption of single chains in solution is valid.

At concentrations above 0.01 mg/ml there is no suggestion of a peak at 505 nm, as seen in *Section 5.4.1*. And by 10 mg/ml only the broad weak peak at 578 nm is seen. This appears to be the remnant of the 0-2 peak after all higher energy emission is strongly self-absorbed.

Clearly solvent choice, particularly the use of THF with its high dipole moment, changes the structure of F8T2 in solution, and THF should be avoided as despite its quality at dissolving F8T2, gives atypical spectra when compared to other good solvents.

Absorption spectra of the solutions were also taken and are shown below, organised by concentration in *figure 54*, clearly saturation occurs at 1.0 mg/ml but spectra are included for completeness.

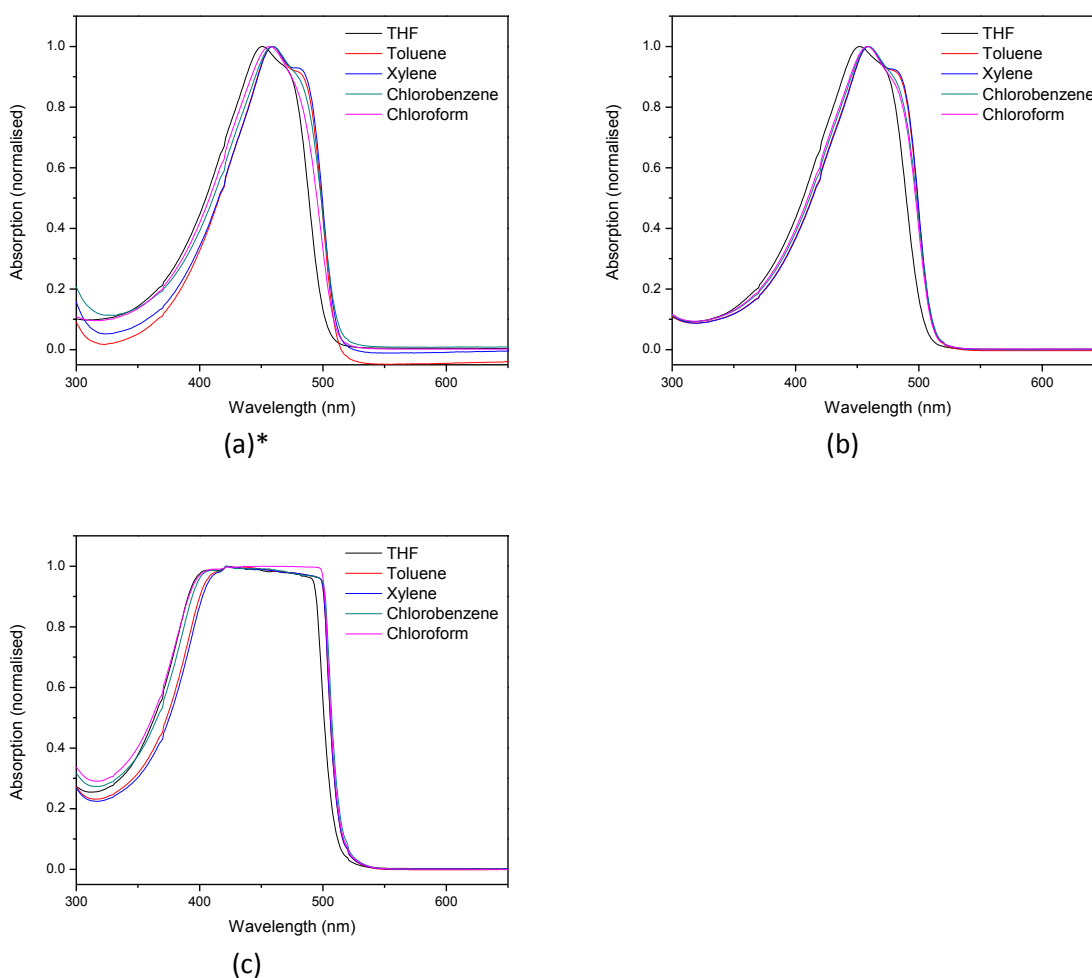


Figure 54 Absorption spectra of solutions of F8T2 in five solvents at (a) 0.01 mg/ml (b) 0.1 mg/ml (c) 1.0 mg/ml.

As expected the vibronic structure is less distinct in solution, and as in the PL spectra THF solutions, are blue-shifted with respect to the other solvents. In all solvents at the two lowest the 0-0 and 0-1 peaks are at 480 ± 1 nm and 460 ± 1 nm, except for THF where they are at 470 ± 1 nm and 450 ± 1 nm, corresponding with the results above that F8T2 in THF takes on a more planar conformation in solution.

The peaks are most pronounced in toluene and xylene, and this is not surprising as it has already been shown that F8T2 aggregates fairly quickly in toluene solutions, and I expect the same to happen in xylene. The 1.0 mg/ml solutions saturated the absorption measurements, but are included for completeness as the lower energy absorption edge of F8T2 in THF can clearly be seen.

Chloroform and chlorobenzene appear inbetween these two extremes, as good solvents, but without the clear vibronic structure seen in toluene and xylene.

5.4.2.2 Time Dependent Effects of F8T2 in Solution

In addition to studying spectral shift of F8T2 solutions with varying concentration and solvent, PL was used to study changes in aggregation after 92 hours in solution. *Figure 55* shows the offset PL spectra of F8T2 in the five solvents studied.

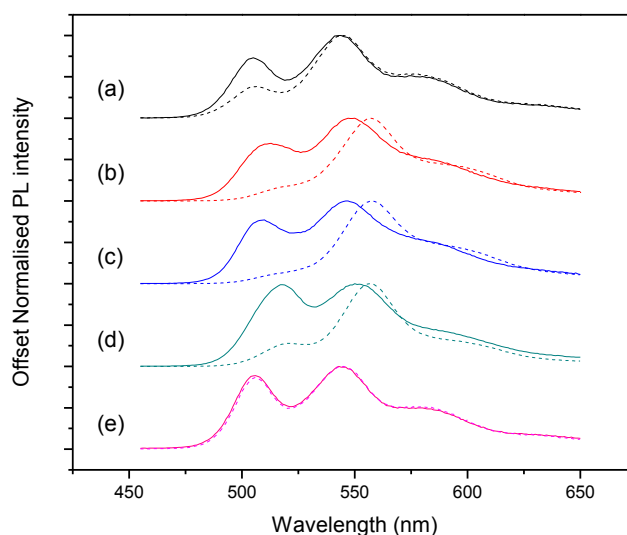


Figure 55 Offset PL of fresh (solid line) and old (dashed line) 1 mg/ml solutions of F8T2 in (a) THF (b) Toluene (c) Xylene (d) Chlorobenzene (e) Chloroform

Although THF appears to not suffer aggregation from light scattering and SANS studies, clear changes do occur over these timescales at higher concentrations, the relative loss in intensity of the low wavelength peak. This is probably due to very slight aggregation. Chloroform is at the other extreme and appears to have no change in how well F8T2 dissolves in it over even the longer timescales studied here. Toluene, xylene and chlorobenzene show clear aggregation effects of a loss of the low wavelength 0-0 peak and red-shift of the ~540 nm 0-1 peak, suggesting clearly that aggregation happens over these timescales and concentration, and that a lower energy aggregate phase is formed, with a more twisted conformation.

A more detailed spectroscopic picture of the aggregation dynamics was taken, by measurements of the PL spectra of 10 mg/ml F8T2 solutions in THF, toluene and xylene over a period of three days, these spectra are shown in *figure 56*.

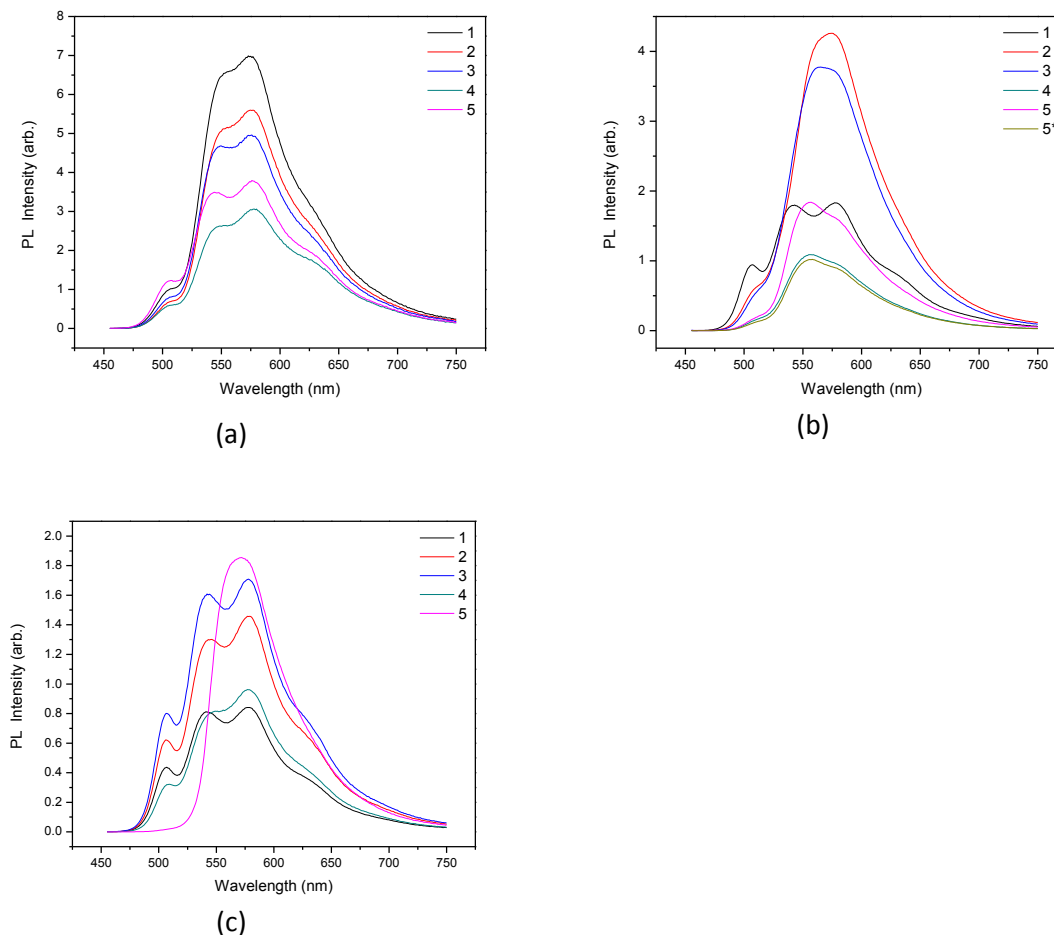


Figure 56 PL of 10mg/ml solutions of (a) THF (b) Toluene (c) Xylene after (1) +0hrs (2) +20hrs (3) +42hrs (4) +70hrs (5) +92hrs (5*) sediment

Of the three solvents, F8T2 in THF shows the simplest behaviour, as time passed PL intensity decreases, with no consistent shifts in peak position meaning there is no specific aggregate phase formed. This seems to be a consequence of very slow 'aggregation' between chains, slowly decreasing PL efficiency in the solution. An increase in interchain interactions would decrease PL efficiency via interchain quenching, and at 10 mg/ml, calculations in *Section 5.4.1.1* show very close single chains.

F8T2 in toluene and xylene show more complex behaviour, initially increasing PL intensity and then decreasing and eventually losing structure. This happens more quickly in toluene, the most non-polar solvent tested. Aggregation causes loss of the low wavelength peak as this aggregate phase

forms, as well as changing the PL efficiency making new non-radiative decay pathways available, and very clear spectral changes are seen.

Films were made of the solutions used in the PL experiments above, both freshly made, and after 92 hours in solution. Films were spin coated, or drop cast at room temperature and at 80° C for toluene and xylene and 40° C for THF solutions. PL intensity normalised to 580 nm and normalised absorption spectra are shown below in *figure 57*. The 0-0 transition appears to be no longer present, suggesting only the aggregate or more ordered phases are present. PL emission is also dependent on the deposition method, with the thick films formed by drop casting losing the 0-1 peak at 540 nm. This is most likely to be due to self absorption in these micron scale thick films, but could also indicate a more ordered phase with a more twisted backbone conformation than the aggregate phase. Absorption is only shown for spin cast films as drop cast films were too thick to allow light through, there also seems to be some issues with the THF films. It is clear that aggregation effects found in solution are held when spin or drop cast into films, and if the loss of the 0-1 peak is due to twisted backbone conformation rather than self absorption the film deposition can mimic these aggregation effects. It is clearly very important to control the thermal history, whether heat been used to dissolve polymers and at higher concentrations be aware of the time-scales between dissolution and spin casting, as aggregation effects can take place quickly and their influence is kept in thin films. Clear film/measurement problems are seen in *figure 57(d)* in THF and aged toluene samples, but they are left for completeness.

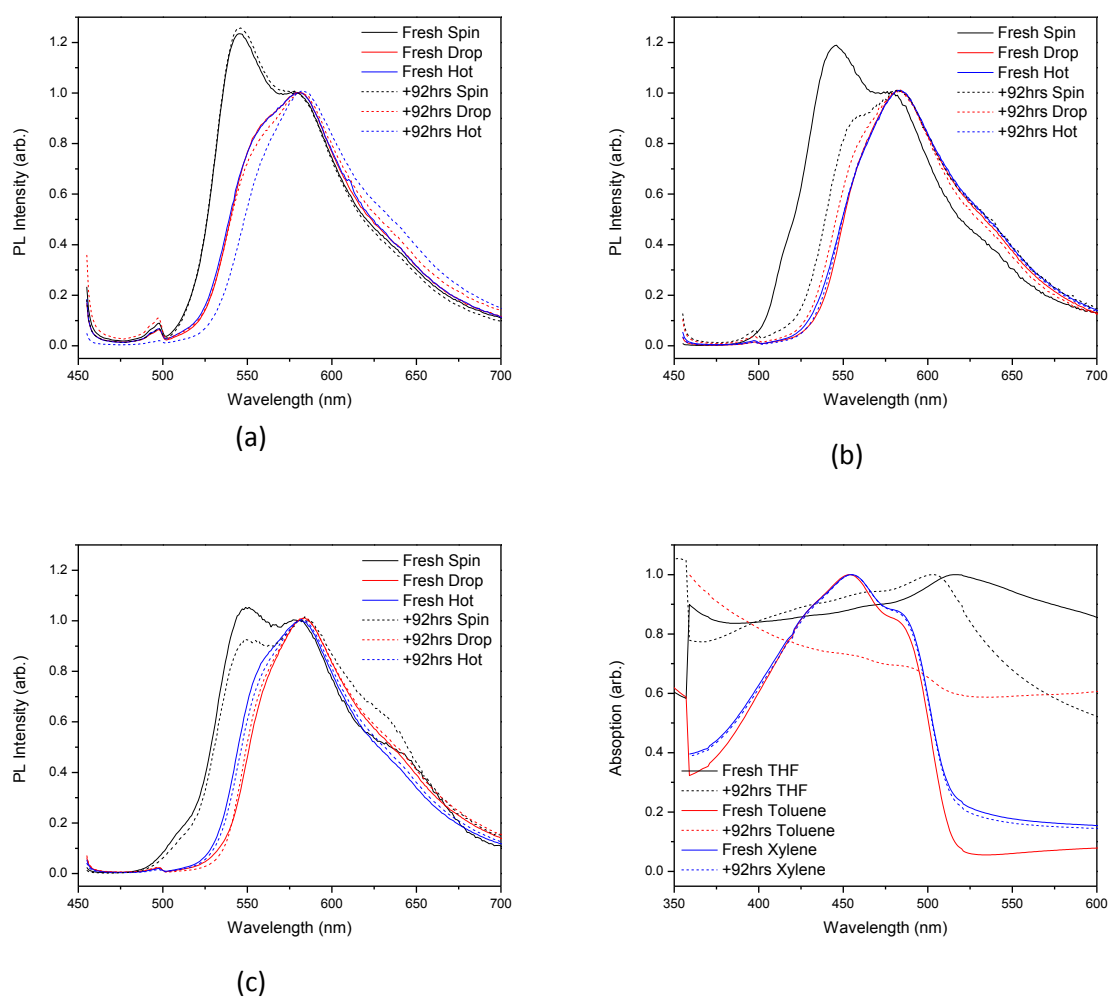


Figure 57 PL of films of (a) THF (b) Toluene (c) Xylene and (d) absorption of same films spin coated

Finally, feature size (aggregates kept in films) and film thicknesses of films used for these measurements and in Section 5.4.4 are shown below in *table 24*.

Solvent	Film Thickness from Fresh Solution (nm)	Film thickness from Old Solution (nm)
THF	100	95
Toluene	90	2-3 μ m features
		1-3 μ m features after 2hrs
Xylene	60-65	$\sim$ 1.5 μ m features
Chlorobenzene	50	45
Chloroform	100	100

Table 24 Film thicknesses and feature sizes of F8T2 films spin coated from various solvents, freshly prepared and after 92 hours.

Absorption spectra from these films are shown in *figure 58*, but very little change is seen between them.

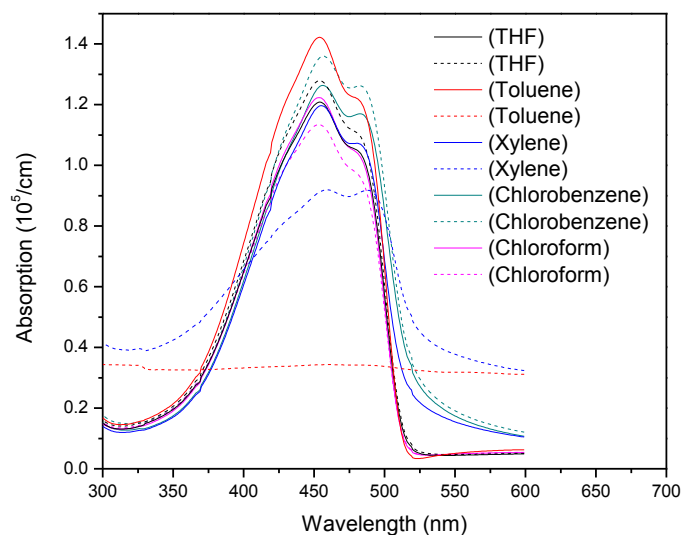


Figure 58 Absorption spectra of films made from fresh (full lines) and aged (dashed lines) F8T2 in solutions.

5.4.2.3 Spectral Results Summary and Conclusions

Combined PL and absorption spectra for F8T2 in all five solvents studied are shown in *Appendix A* at the end of this chapter. The results clearly show the differences in PL emission from fresh and aged solutions and from films spin-coated from those solutions. Most importantly they show that PL emission is often red-shifted as aggregation occurs, with a lower energy aggregate phase occurring with a more twisted backbone configuration. Importantly these changes seem to be kept in films as seen by the reduction in the 0-0 peak intensity. Also, THF seems to be an unusual solvent for F8T2. In THF which appears to be a good solvent, F8T2 does not form aggregates, but some level of interchain PL quenching is seen with time, and a more planar configuration in solution is seen.

The most common feature of all the PL spectra studied is the loss of the 0-0 peak. This is due to self absorption at higher concentrations, combined with the appearance of the aggregate phase, which can be seen to shift emission to the 0-1 peak, and red-shifts the entire spectrum.

5.4.3 Lifetime Measurements of F8T2

Various lifetime measurements were undertaken in the course of this work. Shown below in *table 25* are the calculated lifetime expectation values for F8T2 films spin coated from a range of solvents at 10 mg/ml, used in *Section 5.4.2* with calculation methods discussed in *Chapter 3*. It can clearly be seen that the lifetime of the emissive species when spun into films is not affected by the time spent

in solution, with the exception of the toluene sample. This is somewhat surprising as clear spectral changes have been seen previously, and PLQE changes can be seen in the following section. With additional time and polymer samples this could be further investigated, as this may be a consequence of the expectation value calculation, which is not accurate for multiple emissive species.

Solvent	Age	Lifetime
		Expectation Value (ns)
THF	Fresh	0.66±0.02
THF	4 days	0.68±0.02
Xylene	Fresh	0.64±0.02
Xylene	4 days	0.63±0.03
Chloroform	Fresh	0.66±0.02
Chloroform	4 days	0.64±0.02
Chlorobenzene	Fresh	0.64±0.02
Chlorobenzene	4 days	0.65±0.02
Toluene	Fresh	0.61±0.02
Toluene	4 days	0.71±0.03*

Table 25 Lifetime Expectation Values of F8T2 films spin coated from a range of solvents. *mean of 6 points, not 7.

Measurements were taken of 10 mg/ml F8T2 solutions in THF, toluene and xylene over a period of four days to constantly determine if any changes are visible in the lifetime values of the solution. These are shown below in *figure 59*.

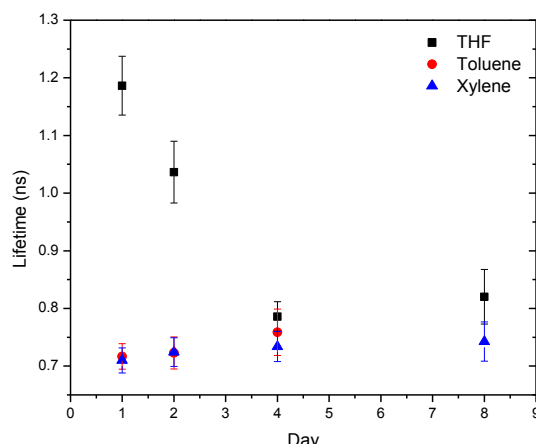


Figure S9 Lifetime Expectation Values with time of 10mg/ml F8T2 in THF, toluene and xylene solutions

Here change is visible, with the THF solution decreasing from 1.2 to 0.8 ns, suggesting improved dissolution and less interaction between chains, without thermally aided dissolution. Toluene which very clearly visibly aggregates appears to have lifetime increases from 0.72 to 0.76 ns, however these are both within the error bounds of each other, so further experimentation would be needed to draw definite conclusions. Xylene increases from 0.71 to 0.74 ns, again very close to errors. Clear aggregation effects on the PL spectra are seen in both toluene and xylene, but these are not shown in this analysis. As before, expectation value analysis may not be the correct analytical method, if multiple emissive species with very different lifetimes are being studied. This is possible if aggregation is occurring against the backdrop of unaggregated and well dissolved chains. The reduction in lifetimes in THF is likely to be due to improving dissolution of the solutions after initial dissolution was seen, as opposed to the very slight increase in interchain interaction and quenching seen previously. Again further study would be beneficial.

A final range of lifetime measurements were taken on F8T2 in THF solutions over the large range of concentrations discussed in *Section 5.4.1*. These are shown below in *figure 60*.

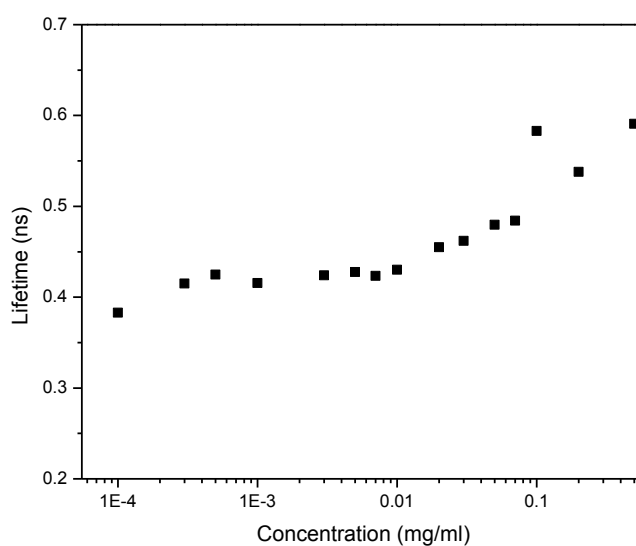


Figure 60 Single Exponential Decay Lifetimes of F8T2 in THF over a range of concentrations

The solutions measured in *figure 60* were measured quickly after dissolving with heat and a clear trend can be seen with concentration dependence. The increase of lifetime at higher concentrations may suggest that there is some interaction between multiple chromophores even in the still dilute solutions of ~ 1 mg/ml. This trend appears to coincide with the results in *figure 59* above for 10 mg/ml solutions, even though single exponential decays were fitted, a change in calculation technique. With careful further study of PL lifetimes of films and solutions I would expect an increase of lifetime as interchain interactions increase, as is seen in *figure 60*.

5.4.4 PLQE Measurements of F8T2 Films

PLQE measurements were taken on films of F8T2 spin coated from the five different solvents studied in *Section 5.4.2*, with films made immediately after dissolution and after some hours in solution. THF and chloroform were allowed to age longer, as they appeared to be the best solvents. The method used by de Mello et al. in (20) was followed, with the use of an integrating sphere and analysis followed in Matlab, using software written by Dr. Paul Stavrinou at Imperial College. An example of the three measured PL curves was shown in 2.3.3, and PLQE values calculated following equation [5.2] below.

$$\eta = \frac{P_c - (1 - A)P_b}{L_a A} \quad [5.2]$$

Table 26 shows the final values of the calculated absorption coefficient A with an excitation wavelength of 450 nm, and the external quantum efficiency η , as well as film thicknesses for each sample.

Solvent	Age	A	η	% change in η	Thickness (nm) *Feature size (μm)
THF	Fresh	0.61	0.316	0	100
THF	+72 hrs	0.71	0.258	-18	95
Xylene	Fresh	0.46	0.343	0	60-65
Xylene	+24 hrs	0.42	0.150	-56	1.5*
Chloroform	Fresh	0.62	0.193	0	100
Chloroform	+48 hrs	0.56	0.059	-70	100
Chlorobenzene	Fresh	0.20	0.634	0	50
Chlorobenzene	+24 hrs	0.40	0.155	-76	45
Toluene	Fresh	0.61	0.317	0	90
Toluene	+2 hrs	0.41	0.259	-18	1-3*
Toluene	+24 hrs	0.31	0.197	-38	2-3*

Table 26 PLQE values for all F8T2 and solvent combinations studied

PLQE decreases strongly with ageing of solutions, with the smallest decrease of 18% seen in the THF solutions even over 72 hours. F8T2 in chloroform solutions, which in *figure 55* show no spectroscopic changes over longer timescales, shows a large drop in PLQE of 70%. Surprisingly, despite toluene showing strong aggregation effects in solution these do not appear to affect the PLQE in thin films as much as in other solvents, perhaps here the large scale aggregates concentrate the loss of PL efficiency allowing the bulk to still emit efficiently, which is consistent with the decrease in absorption coefficient as large aggregates form. Thermal history and extent of polymer dissolution is important here, and further studies with more data points would expand the usefulness of this type of investigation. Any level of aggregate species in solution and films make new non-radiative decay pathways possible as they are kept in thin films, leading to this decrease in PLQE. This further shows the importance of well dissolved unaggregated polymer chains in the spin casting solution for efficient, consistent and comparable PL emission from thin films.

5.4.5 Thermal Treatment of F8T2 Films

F8T2 films were studied in a pyrostat to 265°C to test whether spectroscopic shifts in PL emission from films could be used to ascertain transition temperatures as previously completed by Sims et al. (19) on PFO films.

5.4.5.1 Photoluminescence

Only photoluminescence was studied with temperature in the pyrostat. Three films were studied, all spin coated F8T2 in THF at 5 mg/ml. Initially a pristine film was studied, followed by films heated to 290° C and held for 1 minute in a nitrogen atmosphere before being either quenched by placing on a room temperature metal table top, or slowly cooled back to room temperature at ~0.5° c/min. Slow cooling from above the melt would be expected to induce liquid crystal order as the film cools through the liquid crystal transition, whereas quenching would be expected to cause the film to keep the amorphous structure of the melt. Intensity maps of PL spectrum with film temperature are shown in *figure 61(a)-(c)* and total integrated PL is shown in *(d)*.

Large changes in PL can be seen as temperature increases, and clear spectral differences between the three films. From the integrated PL, we can see a plateau in the spin coated film at 130-150° C and a corresponding sharp upturn in the quenched film at 150° C which I attribute to the glass transition temperature, this is also shown in *figure 62*, where the maximum red-shift for a spin-coated film is at 190° C. Slow cooling from the anneal temperature leads to a more ordered phase, with strong PL emission over the entire temperature range studied. Quenching however, allows chains to enter a conformation which helps them to easily reorganise into a strongly emissive phase when reheated.

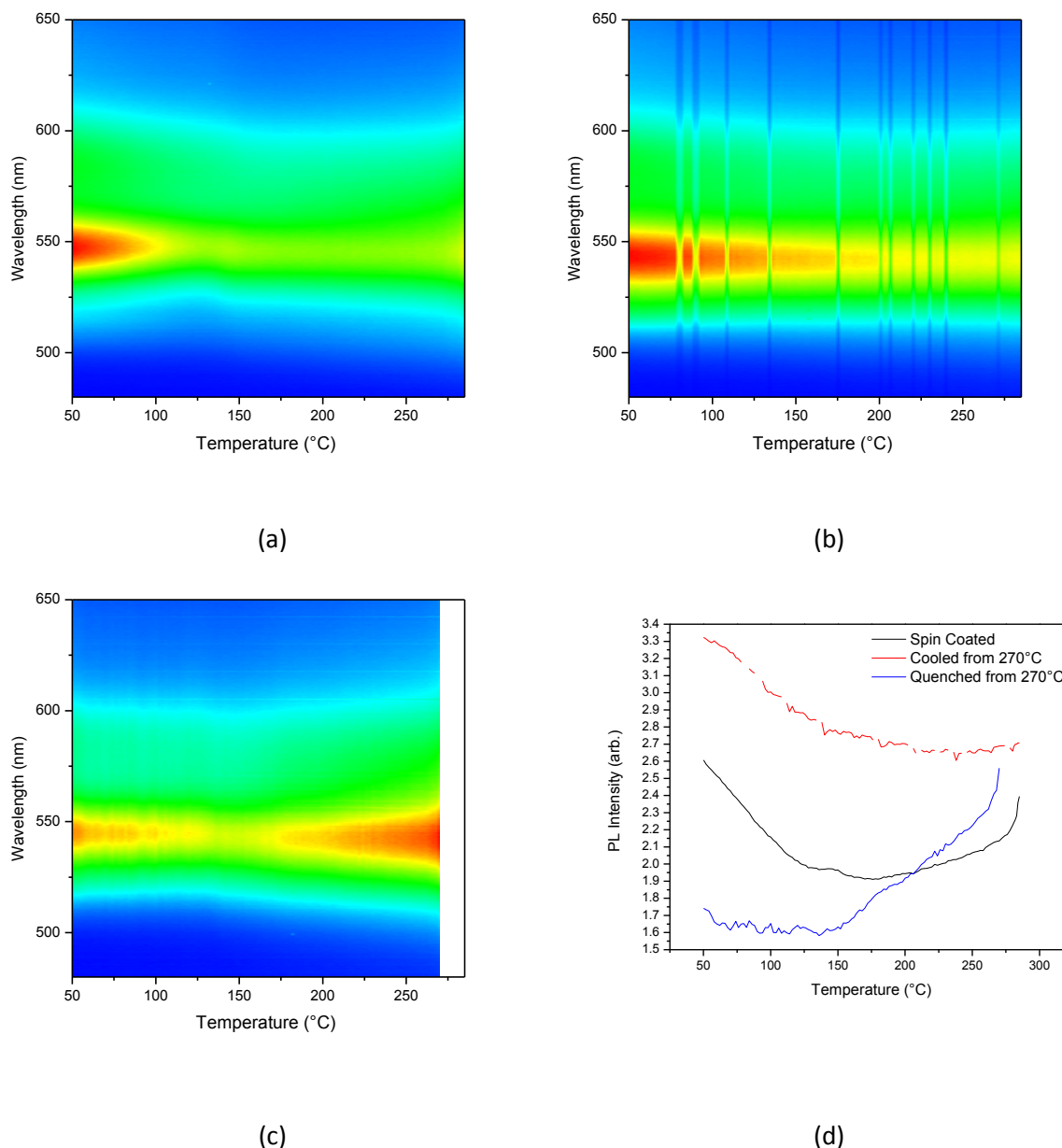


Figure 61 PL intensity maps against temperature of (a) Spin Coated (b) Cooled and (c) Quenched F8T2 films. (d) Integrated PL

Figure 62 shows PL spectra of freshly prepared, spin coated films heated and quenched to room temperature from various temperatures. These are expected to keep the polymer configuration at that temperature from various temperatures. These are expected to keep the polymer configuration at that temperature in the cooled solid film. Red-shift in the spectrum at T_g is expected, as at this temperature the polymer chains are more free to move around and take up lower energy configuration, here that is from a peak at 517 nm shifted to 523 nm. The 290° C PL spectrum in figure 62 has returned to a peak at 517 nm, and there is seen a sharp upturn in the integrated PL of the spin coated and quenched films in figure 61, I expect this to be caused by liquid crystallinity occurring in the film.

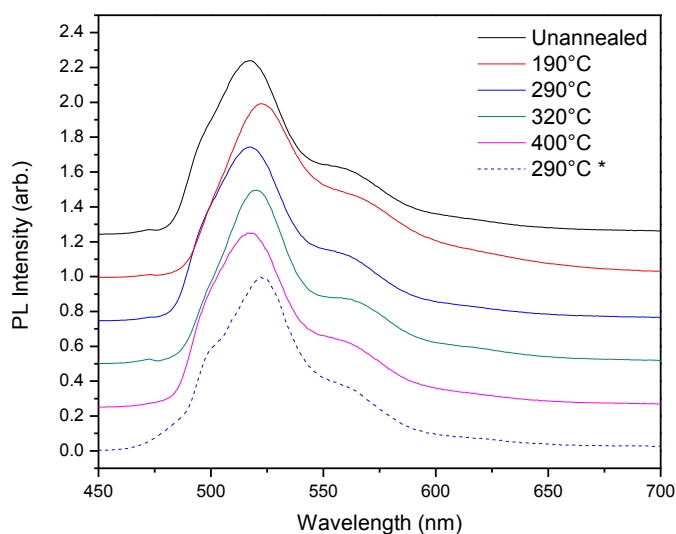


Figure 62 PL of films annealed and quenched, with the quenching temperature shown. The starred 290° C spectrum has been slowly cooled, and the unannealed is purely spin coated.

A slight redshift to a peak at 520 nm at 320° C is likely to be the beginning of the film melting, to be fully amorphous at 400° C, however this is a very high melt temperature for F8T2, when compared to the work of Kinder et al. below (2), so I anticipate this final blue-shift is likely to be due to some level of thermal damage to the polymer film despite heating in a nitrogen atmosphere. The film slowly cooled from 290° C shows more structure than any of the others, with a slight remnant of the 0-0 peak appearing, and red-shifted peak position with respect to the spin coated film suggesting slow cooling from this temperature is enough to induce lower energy structure in the form of nematic liquid crystallinity.

Returning to *figure 61*, ascertaining transition temperatures by optical methods seems possible for spin coated F8T2 films. The slow cooled film does not have any clear vertices of changes, just a general decline in total PL emission.

Further work on this technique could use aligned films and polarisers to more easily measure specific alignment. T_g appears to be easy to find in a spin coated film, as does the onset of the LC phase, a more powerful pyrostat would allow melt temperatures to be determined as well.

5.4.5.2 DSC

DSC was undertaken by Natasha Shirshova at Imperial College. It's a standard technique to find transition temperatures in the solid material, usually the melt and the glass transition, and the onset of crystallisation. The results of heating 30 mg of F8T2 from room temperature to 330° C at a rate of 7.5° per minute is shown below in *figure 63*.

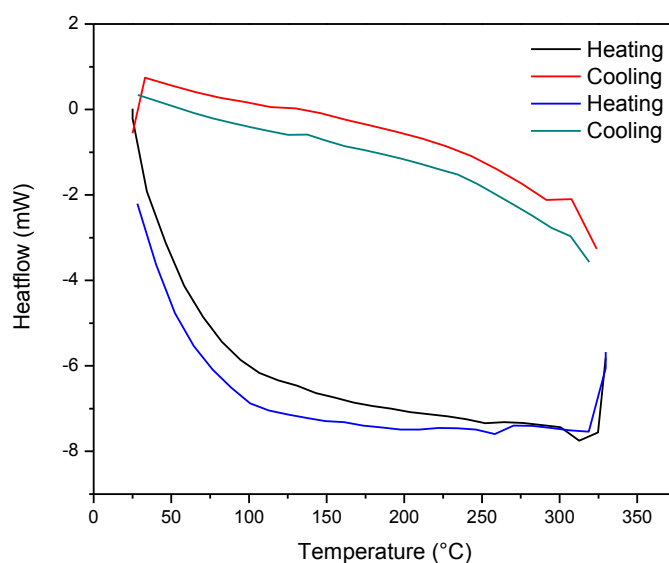


Figure 63 DSC results of F8T2, showing heating and cooling cycles

Unfortunately transitions are not very obvious in the data, yet structural changes from thermal annealing are seen in other parts of this work. This is likely to be due to the large amount of polymer used in the test, particularly when considered with the relatively high heating rate of 7.5° per minute. As the DSC results here are inconclusive, transition temperatures determined by Kinder et al. (13) are used as needed in this work, and reproduced here in *table 27*.

Copolymer	A	B	C
	151.5 kg/mol	39.3 kg/mol	31.3 kg/mol
Glass Transition, T_g (°C)	164	125	128
Liquid Crystal Transition, T_{XL-N} (°C)	252/275	216/252	221/259
Isotropic Transition, T_{N-I} (°C)	330	315	314

Table 27 Transition temperatures of 3 F8T2 samples, determined by Kinder et al(2).

By comparison with the data from Kinder et al. the data supports the use of their transition temperatures, with plateaus seen in the cooling data around 120° C, corresponding to T_g . A weak effect can be seen around the 250° C mark in the heating curves, likely to coincide with the liquid crystal transition, and a very steep rise around 325° C, likely to be the polymer melting. Light scattering results in *Chapter 4* suggest a comparable sample to their sample A, however GPC, as used by Kinder et al. and these DSC results would suggest closer to sample B and C.

5.4.5.3 AFM

AFM was done by Hon Hang Fong at Cornell University, USA, for which I am very grateful. Films spin coated from F8T2 in THF at 10mg/ml were imaged, to understand the effect of increased dissolution time/solution ageing and the effect of thermal treatments on film homogeneity and roughness. Pristine films and films cooled or quenched from 270° C, referred to as N, C and Q respectively, are scanned by AFM at two scales: 10x10 μm and 1x1 μm . RMS roughness and average film height are calculated. Images from these scans are shown below in *figure 64*. As the THF solutions were not heated to aid dissolving, and measured after a few hours to be visibly dissolved and after a day in solution, this study seems to show the effect of improved dissolution in THF rather than aggregation. Films in toluene were not studied as the large feature size of aggregate particles was above the safe limit for the AFM.

Images of films made from fresh solution show that heat treatment appears to decrease the RMS roughness of the film at the larger scale, but to increase the average height, see *table 28*. From the smaller 1x1 μm scans, roughness increases slightly after treatment. This suggests that the time spent at temperature is not long enough to fully homogenise the surface features. By visual inspection of the 1x1 μm both thermal treatments appear to increase the extent of each 'bump', and at 10x10 μm quenching also appears to increase the scale of the roughness. Slow cooling does not appear to improve the quality of the top surface but increases the height of the feature size. This is important if using alignment films or thermal treatments for OFET production, but the increased feature size may be a by-product of not fully dissolved F8T2 in solution when films were spun.

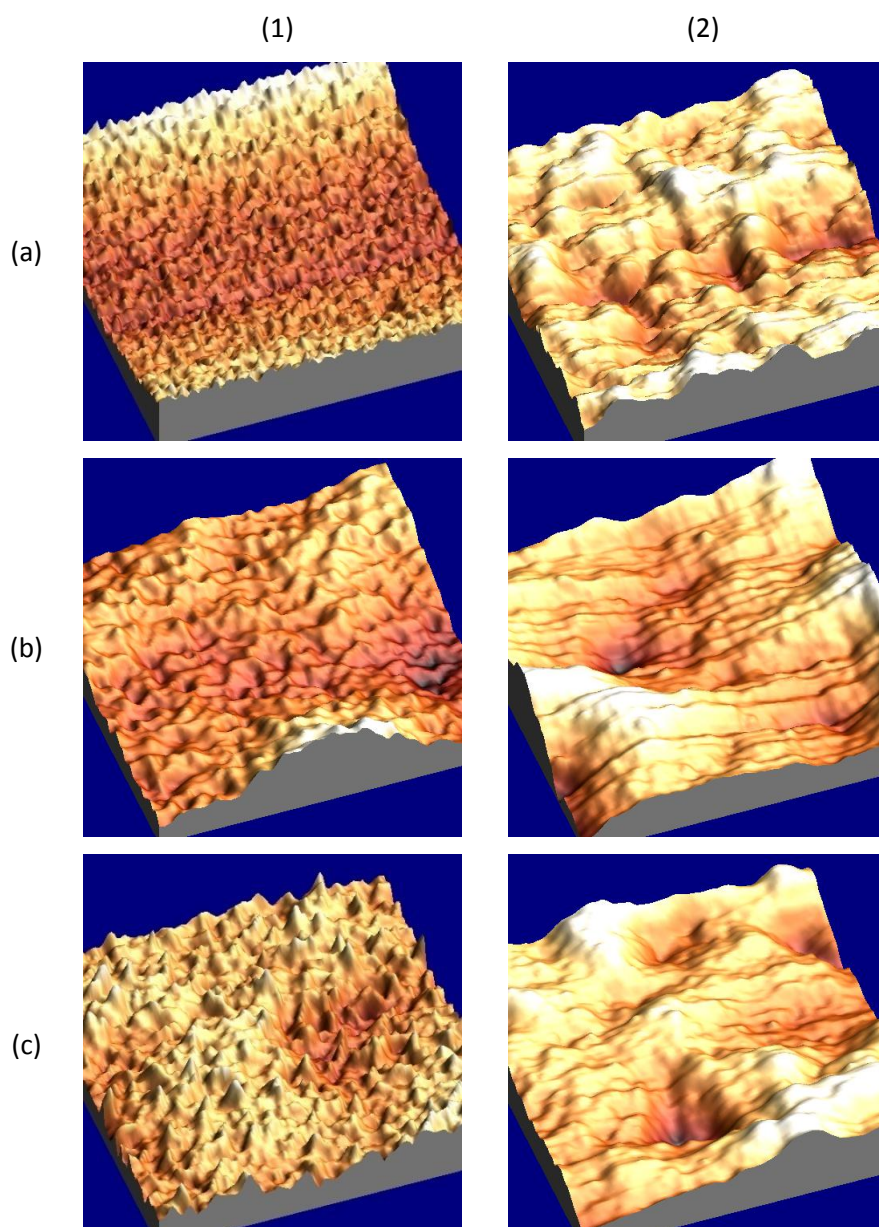


**Figure 64 AFM images of F8T2 films from fresh solutions
(1) 10x10 μm (2) 1x1 μm (a) Spin cast (b) Quenched (c) Cooled**

AFM images from films of F8T2 in THF spin coated +24 hours after solvent addition are shown below in *figure 65*. Again, 10x10 μm and 1x1 μm scans are presented, with the same three thermal treatments. Again at the smaller scale heating does increase the domain of each feature however does appear to have increased the average height and roughness. In 10x10 μm scans heating again increases the feature size, however films appear to be better, likely to due more fully dissolved F8T2.

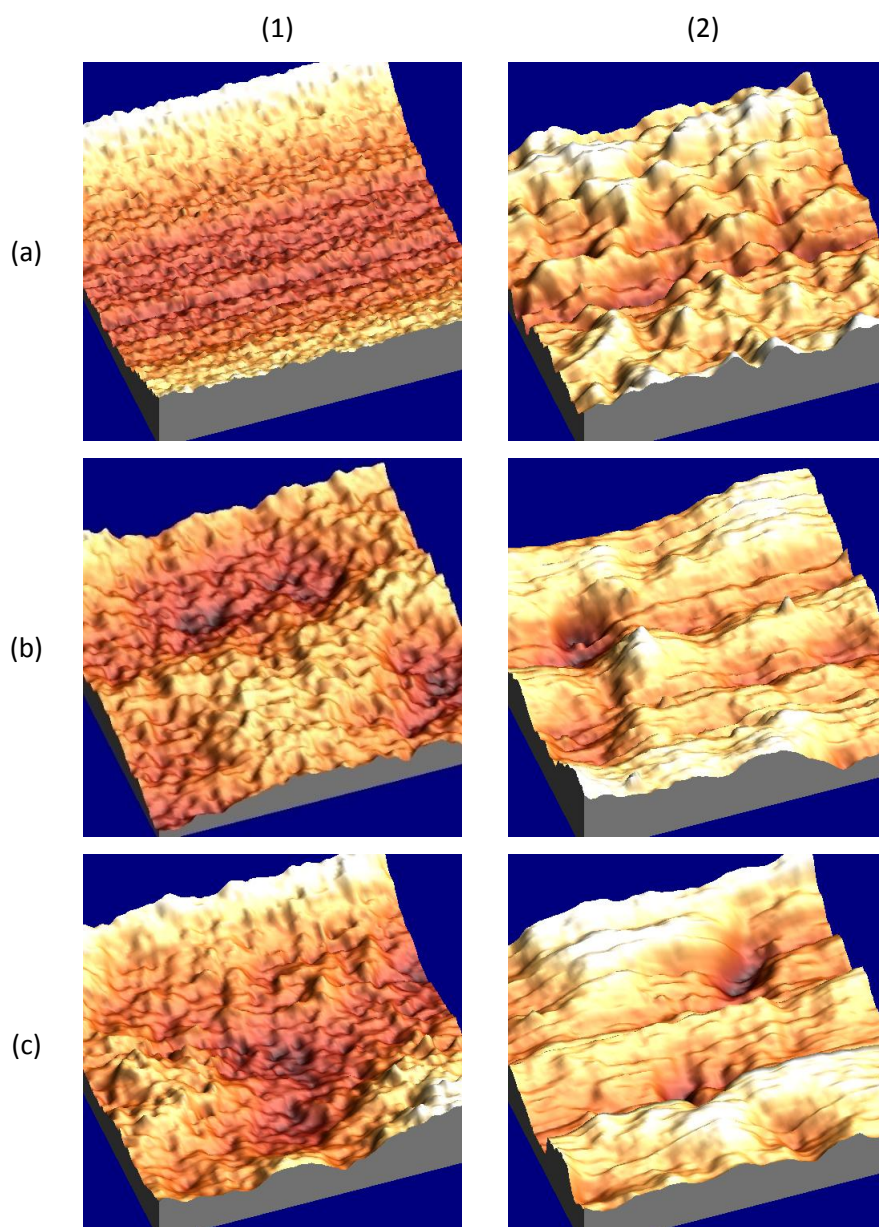


Figure 65 AFM images of F8T2 films from aged solutions
 (1) 10x10 μm (2) 1x1 μm
 (a) Spin cast (b) Quenched (c) Cooled

These AFM images clearly reiterate the importance of well dissolved solutions for quality films. Further studies could be used to understand the difference in solvent choice, as with spectroscopy in *Section 5.4.2*, with comparison to know particle sizes measured in *Chapter 4*. Thermal treatments have not homogenised the surface as much as anticipated, further studies could determine more ideal temperatures and annealing timescales, as although 1 minute anneals effect spectroscopic output, they do not appear to effect the macroscopic film surface to as large an extent as possible. For completeness *table 28* shows RMS roughnesses and average heights for all films studied by AFM.

Scan size (μm)	Fresh/Old Solutions	Heat N/Q/C	RMS Roughness (nm)	Average Height (nm)
10x10	Fresh	N	20.971	6.463
10x10	Fresh	Q	6.618	16.924
10x10	Fresh	C	5.161	21.194
1x1	Fresh	N	1.15	4.484
1x1	Fresh	Q	1.699	5.23
1x1	Fresh	C	2.887	10.283
10x10	Old	N	3.511	6.609
10x10	Old	Q	4.876	11.877
10x10	Old	C	8.324	17.221
1x1	Old	N	1.522	4.852
1x1	Old	Q	1.541	5.06
1x1	Old	C	2.003	6.148

Table 28 Table showing RMS roughness and average heights of AFM images shown in *figure 64* and *65*

5.4.6 Field-Effect Transistors

The initial investigation was to look at the effect of HMDS or OTS layers. The results of which are shown below in *figure 66* and *table 29*.

After confirmation of FET behaviour seen in the output characteristics, source-drain current vs voltage, transfer characteristics were used to calculate the saturation mobility μ_{sat} , on/off ratio (between -5 V and -55 V for consistency), and the turn-on voltage by extrapolation to crossing the x-axis.

From the output and transfer characteristics it can be seen that each device functioned as an OFET, however with varying degrees of success. Quantitative analysis is shown in *table 29*. Gradients were taken for both increasing and decreasing V_{GS} , and a mean value taken, for mobility calculations. Turn-on voltage was calculated by extending the linear fit of the transfer characteristics to zero current, for consistent discussion between sample devices. All output characteristics show significant leakage current prior to turn-on.

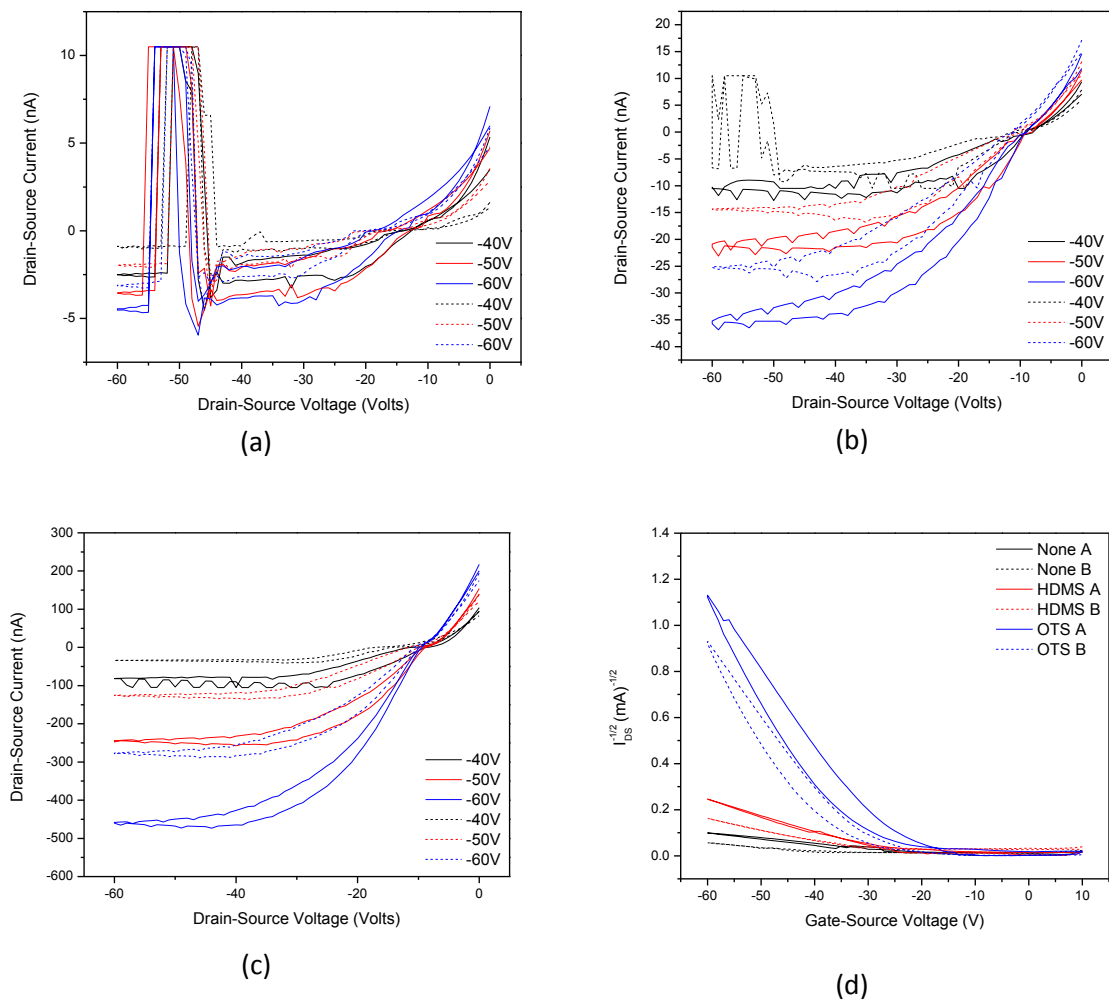


Figure 66 Output Characteristics of F8T2 OFETs with (a) no treatment, (b) HMDS (c) OTS and (d) Transfer characteristic. Solid and dashed lines indicated different devices

Pre-treatment	FET effects (Y/N)	Sat. mob. (cm^2/Vs) $\times 10^{-4}$	On/off ratio	Turn on (V)
None	Y	0.2	52, 3	-16, -22
HMDS	Y	1.6	2.1, 4.4	-23, -22
OTS	Y	49.7	251, 569	-24, -17

Table 29 Output characteristics for F8T2 films from 10mg/ml toluene solutions, for no treatments, HMDS and OTS

Although OTS was clearly the better treatment, with saturation mobilities of $49.7 \times 10^{-4} \text{ cm}^2/\text{Vs}$ compared to $1.67 \times 10^{-4} \text{ cm}^2/\text{Vs}$ for HMDS, it was found that creation of a good film to achieve these values was very difficult. OTS mobility values are approximately a quarter of some well aligned films (21), but as with no coating and HMDS devices, have very poor turn on voltages. OTS appeared to almost completely stop wetting of the polymer solution on a treated film, so HMDS was chosen for

all further devices, with comparable mobilities to literature values, however with poor turn on voltages (2). It improved transistors compared to an untreated film and was consistent in being easy to apply. Study with contact angle measurements could be useful in the future to find a good solvent to wet on OTS, as it clearly improves transistor functioning by a large factor.

5.4.6.1 Ageing and Thermal Treatments

Understanding the effects on transistor measurements of the thermal annealing processes described above, and the effect of aggregation in older solutions, seen in spectroscopic measurements is very important. To this end F8T2 was dissolved in THF a good solvent and toluene a poor solvent, to make OFETs on an HMDS layer as described above with evaporated gold contacts. In addition to the measuring the effects of solution ageing, it was tested whether thermal treatment could improve OFET qualities when made from poor solutions. Transfer characteristics of these devices are shown in *figure 67*, and numerical values given in *table 30*, where results for multiple devices are shown they are separated by a comma, to highlight the range of variation between devices. Solutions were heated for initial dissolution and then allowed to age for ~24 hours before a second set of devices were made.

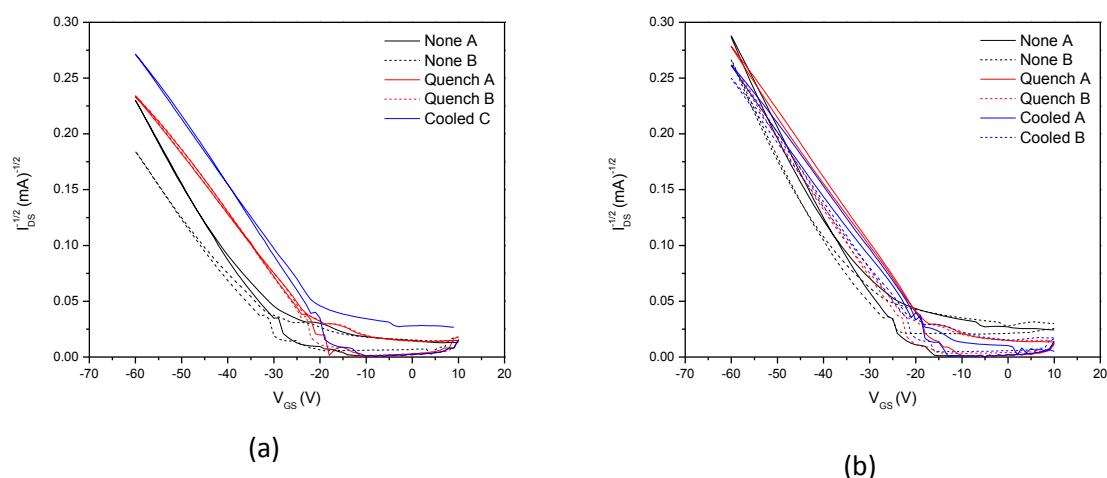


Figure 67 Transfer Characteristics for heat treated F8T2 toluene solutions, (a) fresh, (b) aged

Devices made from older solutions appear to generally be better in all measured properties, possibly due to further time allowed for dissolution, although initial heating has previously been found to negate this need. This is an intriguing effect, and with further time and improvement of OFET production methods could be well studied.

Solution Age	Thermal Treatment	FET effects	Sat mob. (cm^2/Vs) $\times 10^{-4}$	On/off ratio	Turn on (V)
Fresh	None	Y	2.0	10, 25	-25, -25
Fresh	Quenched	Y	1.7	143, 309	-17, -17
Fresh	Cooled	Y	2.0	134	-15
Old	None	Y	3.1	154, 11	-22, -23
Old	Quenched	Y	2.2	160, 620	-13, -19
Old	Cooled	Y	1.9	163, 45	-13, -17

Table 30 OFET characteristics for F8T2 in toluene films, from fresh and aged solutions.

5.4.6.2 Ageing and Vapour Treatments

Finally, the effects of vapour exposure on OFET devices were tested, again with fresh and old solutions made from F8T2 in toluene. The four channel lengths available on pre-patterned substrates were tested, however no 2.5 μm devices worked, and in general devices did not work well. An example of the improvement in output characteristics due to vapour treatment is shown in *figure 68(a)*, with corresponding output characteristics *figure 68(b)* for a 10 μm channel length device, but equally likely vapour treatment was found to inhibit transistor functioning. Output characteristics were taken at -40 V to ensure saturation. Due to polymer supply issues the smaller M_w batch of F8T2 was used for these experiments, described in *Chapter 4*.

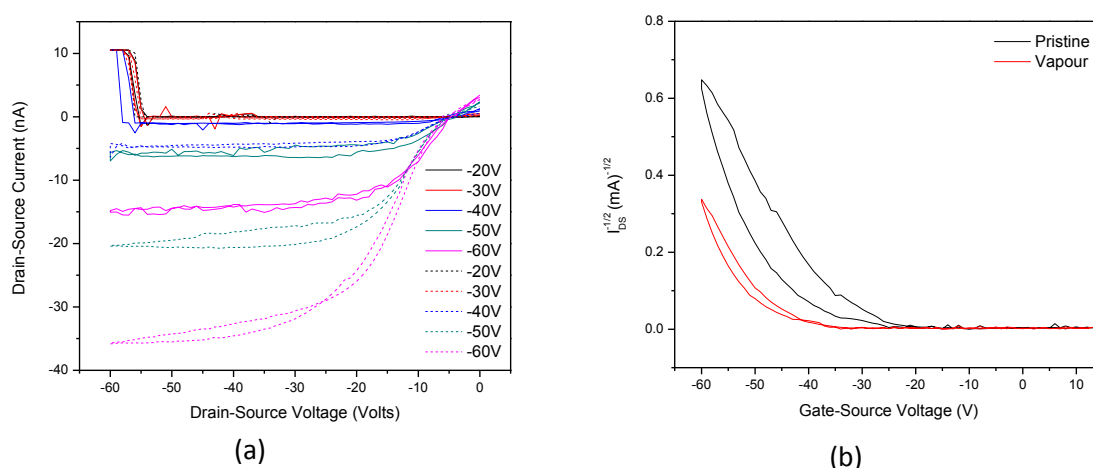


Figure 68 (a) output (dashed have had vapour) and (b) transfer characteristics for a 10 μm F8T2 OFET, made from freshly dissolved toluene solution

Results from working devices are shown in *table 32*, but are very much inconclusive. I would expect vapour treatment to improve device functioning by allowing polymer chains to relax to a lower energy state, in a similar fashion to that seen in P3HT (18) however as conduction occurs near the

silicon substrate rather than top of the film this may well not affect the device. Much further studies would be very useful on this effect, along with spectroscopic studies of vapour treatments which were not undertaken as part of this study.

In general my OFETs were poor devices, with very poor repeatability and consistency between devices, and further study is needed before strong conclusions can be drawn.

Solution Age	Channel Length (μm)	Vapour treatment	Saturation	On/off ratio	Turn on V (V)
			mob. (cm^2/Vs) $\times 10^{-4}$		
Fresh	10	N	7.2	306	-33
Fresh	10	Y	2.2	71	-39
Fresh	20	N	1.8	184	-29
Fresh	20	Y	3.2	213	-33
Old	10	N	3.3	192	-34
Old	10	Y	8.1	350	-36

Table 31 Results of working F8T2 OFETs, with films made from fresh and old solutions in toluene

5.5 Conclusions

Spectroscopic studies of F8T2 in solutions of THF and toluene have found strong PL quenching effects as solution concentration increases. These have been attributed to interchain interactions at concentrations around 0.01 mg/ml, where interchain spacing is becoming close to the chain size in solution. At higher concentrations, above ~ 0.1 mg/ml, self absorption from the large overlap of the PL and absorption spectra, leading to complete loss of 0-0 and 0-1 peaks at ~ 505 nm and 545 nm respectively. Self absorption effects were found in the solid phase, evident by strong-red shifts of the low wavelength peak, with vibronic structure still clearly visible.

F8T2 shows interesting solvatochromism and aggregation in the five solvents studied. Choice of solvent for solution based measurements is important, as is the importance of having well dissolved solutions. Spectroscopic effects due to solvent choice, aggregation and thermal dissolution histories can be seen in solid films. Most notably F8T2 cast from THF solutions are blue-shifted compared to the other solvent choices.

Lifetime measurements in films show little difference within errors for F8T2 in each different solvent solutions, which is unexpected when seen in context of the above, and these experiments should be

repeated, perhaps using a different analysis technique. Lifetime measurements are however seen to decrease as F8T2 improves its dissolution in THF, again showing the importance of knowing how dissolved the polymer is, and are seen to increase as interchain interactions become more important with concentration increases.

PLQE values of F8T2 films were found to strongly decrease with solution ageing, even in solutions which have previously shown improved dissolution with time.

Photoluminescence was studied as a way of determining transition temperature without the use of a DSC. This was partially successful, with reasonable estimates made of T_g and T_c from integrated PL values. Again, further study of this interesting technique would be useful.

Finally thermal and vapour treatments of F8T2 films and FETs were studied. AFM showed interesting results, but FET devices were very poor. The most useful result is the large improvement with OTS layers, but large wetting problems. Further tests with F8T2 spin coated from a range of solvents would be helpful in improving these, and it would be interesting to study if the solvent choice effects seen in film spectroscopy are kept in OFET devices.

5.6 Further Work

The most important aspects of much of this work are recognition and understanding of the complex dynamics of dissolution and aggregation of polymers being studied in a range of solvents. The importance of knowing if and when a solution contains a 'well dissolved' polymer cannot be understated. As such very systematic studies of F8T2 in solution and films with controlled heating and or unaided dissolution would be useful. Heating is generally advised and use of solutions as soon as possible after a confidently fully dissolved polymer is sensible. Due to the speed of most spectroscopic measurements, particularly with newer CCD based devices this could be studied at a very high rate. Similarly studies of aggregation could be undertaken.

Further measurements to optically determine transition temperatures would be interesting, particularly with a range of molecular masses and with a re-run DSC measurement for precise values for each mass.

Unknowns from poor a DSC run may have caused problems for thermal treatments, although definite spectroscopic changes were seen, further DSC measurements with less material and a slower heating rate may well show more detail. Thermal treatments for longer and at different temperatures would be usefully combined with AFM to see if homogenisation of the film is useful and easy, as with understanding the effects of vapour treatment. Spectroscopic measurements of

vapour exposure to films would be useful, especially combined with further GIWAXS measurements, seen in *Chapter 6*.

5.7 Appendix A

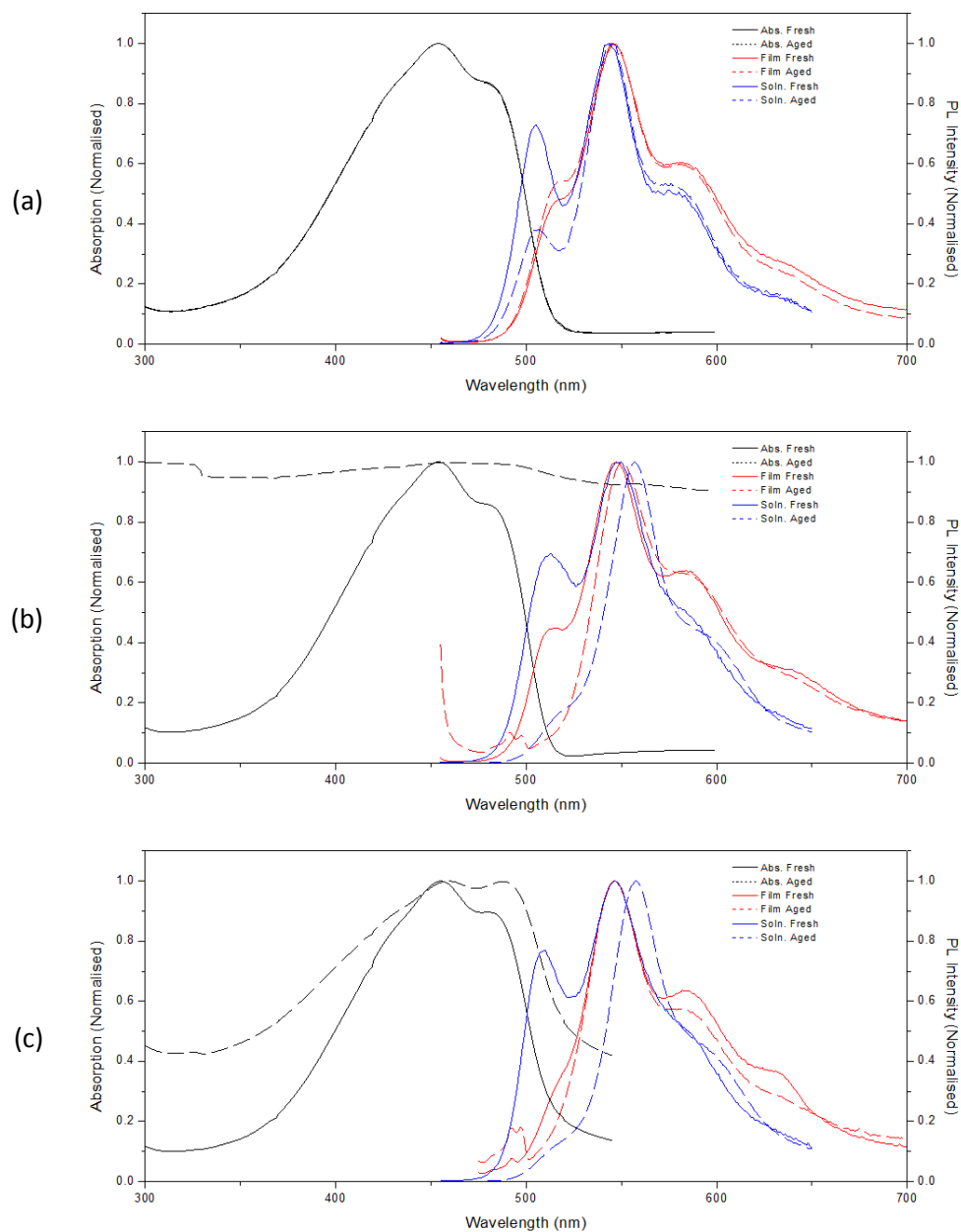


Figure 69 All spectra for (a) THF, (b) Toluene, (c) Xylene

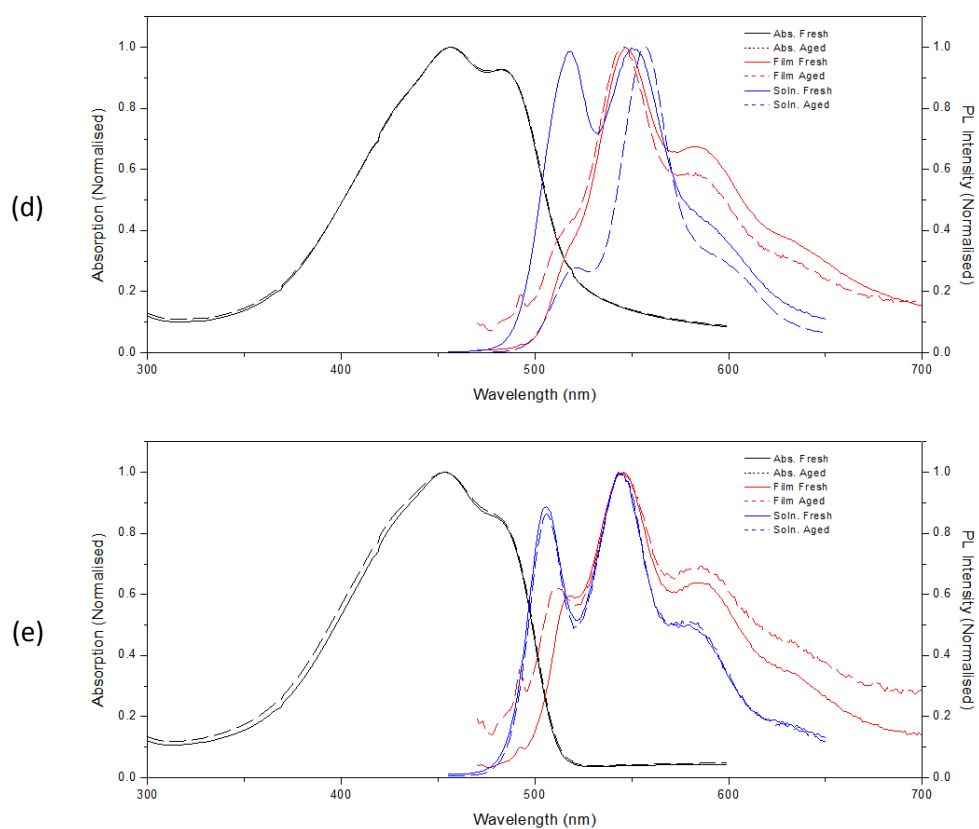


Figure 70 All spectra for (d) Chlorobenzene (e) Chloroform

5.8 Bibliography

1. **M Grell, M Redecker, K S Whitehead, D D C Bradley, M Inbasekaran, and E P Woo.** Monodomain alignment of thermotropic fluorene copolymers. *Liquid Crystals*. 1999. Vol. 26, 9, pp. 1403-1407.
2. **L Kinder, J Kanickia, and P Petrof.** Structural ordering and enhanced carrier mobility in organic polymer thin film transistors. *Synthetic Metals*. 2004. Vol. 146, pp. 181-185.
3. **F B Dias, M Knaapila, and A P Monkman.** Fast and Slow Time Regimes of Fluorescence Quenching in Conjugated Polyfluorene–Fluorenone Random Copolymers: The Role of Exciton Hopping and Dexter Transfer along the Polymer Backbone. *Macromolecules*. 2006. Vol. 39, 4, pp. 1598–1606.
4. **M Knaapila, R Stepanyan, M Torkkeli, B P Lyons, T P Ikonen, L Almásy, J P Foreman, R Serimaa, R Güntner, U Scherf, and A P Monkman.** Influence of molecular weight on the phase behavior and structure formation of branched side-chain hairy-rod polyfluorene in bulk phase. *Phys. Rev. E*. 2005. Vol. 71, 4, p. 041802.
5. **M Knaapila, R Stepanyan, M Torkkeli, V M Garamus, F Galbrecht, B S Nehls, E Preis, U Scherf, A P Monkman.** Control over phase behavior and solution structure of hairy-rod polyfluorene by means of side-chain length and branching. *Phys. Rev. E*. 2008. Vol. 77, 5, p. 051803.
6. **M Knaapila, L Almásy, V M Garamus, M L Ramos, L L G Justino, F Galbrecht, E Preis, U Scherfe, H D Burrows, and A P Monkman.** An effect of side chain length on the solution structure of poly(9,9-dialkylfluorene)s in toluene. *Polymer*. 2008. Vol. 49, 8, pp. 2033–2038.
7. **Z Bao, A Dodabalapur, and A J Lovinge.** Soluble and processable regioregular poly(3-hexylthiophene) for thin film field-effect transistor applications with high mobility. *Appl. Phys. Lett.* 1996. Vol. 69, 26, pp. 4108-4110.
8. **J Clark, J-F Chang, F C Spano, R H Friend and C Silva.** Determining exciton bandwidth and film microstructure in polythiophene films using linear absorption spectroscopy. *Appl. Phys. Lett.* 2009. Vol. 94, pp. 163306-08.

9. **F C Spano.** Absorption in regio-regular poly(3-hexyl)thiophene thin films: Fermi resonances, interband coupling and disorder. *Chem. Phys.* 2006. Vol. 325, 1, pp. 22-35.
10. —. Modeling disorder in polymer aggregates: The optical spectroscopy of regioregular poly(3-hexylthiophene) thin films. *J. Chem. Phys.* 2005. Vol. 122, pp. 234701-15.
11. **M Grell, D D C Bradley, M Inbasekaran, E P Woo.** A glass-forming conjugated main-chain liquid crystal polymer for polarized electroluminescence applications. *Advanced Materials.* 1997. Vol. 9, 10, pp. 798–802.
12. **M Grell, W Knoll, D Lupo, A Meisel, T Miteva, D Neher, H-G Nothofer, U Scherf, and A Yasuda.** Blue Polarized Electroluminescence from a Liquid Crystalline Polyfluorene. *Advanced Materials.* 1999. Vol. 11, 8, pp. 671–675.
13. **L Kinder, J Kanicki, J Swensen, P Petroff.** Structural ordering in F8T2 polyfluorene thin-film transistors. *Proceedings of SPIE Organic Field Effect Transistors II.* Bellingham, WA : s.n., 2003. Vol. 5217.
14. **A W Grice, D D C Bradley, M T Bernius, M Inbasekaran, W W Wu, and E P Woo.** High brightness and efficiency blue light-emitting polymer diodes. *Appl. Phys. Lett.* 1998. Vol. 73, 5, pp. 629-631 .
15. **J Oberski, R Festag, C Schmidt, G Luessem, J H Wendorff, A Greiner, M Hopmeier, F Motamedi.** Synthesis and Structure-Property Relationships of Processable Liquid Crystalline Polymers with Arylenevinylene Segments in the Main Chain for Light-Emitting Applications. *Macromolecules.* 1995. Vol. 28, 25, pp. 8676–8682.
16. **P A Levermore, R Jin, X Wang, J C de Mello, D D C Bradley.** Organic Light-Emitting Diodes Based on Poly(9,9-dioctylfluorene-co-bithiophene) (F8T2). *Advanced Functional Materials.* 2009. Vol. 19, 6, pp. 950–957.
17. **K S Whitehead, M Grell, D D C Bradley, M Inbasekaran, and E P Woo.** Polarized emission from liquid crystal polymers. *Synthetic Metals.* 2000 йил. Vols. 111-112, pp. 181–185.

-
18. **A Guite.** Microstructure, morphology and device physics of gravure printed and solutionprocessed organic field-effect transistors. *Imperial College London*. 2011.
19. **M Sims, K Zheng, M Campoy Quiles, R Xia, P N Stavrinou, D D C Bradley, and P Etchegoin.** On the use of optical probes to monitor the thermal transitions in spin-coated poly(9,9-dioctylfluorene) films. *J. Phys.: Condens. Matter*. 2005. Vol. 17, 41, p. 6307.
20. **J C de Mello, H F Wittmann, and R H Friend.** An Improved Experimental Determination Of External Photoluminescence Quantum Efficiency. *Adv. Mater.* 1997. Vol. 9, 3, pp. 230–232.
21. **H Sirringhaus, R J Wilson, R H Friend, M Inbasekaran, W Wu, E P Woo, M Grell, and D D C Bradley.** Mobility enhancement in conjugated polymer field-effect transistors through chain alignment in a liquid-crystalline phase. *Appl. Phys. Lett.* 200. Vol. 77, 3, pp. 406-408 .

Chapter 6

Grazing Incident Wide-Angle X-Ray Scattering (GIWAXS)

This chapter presents my work using the technique of GIWAXS on polyfluorene copolymer thin-films at the Cornell High Energy Synchrotron Source. Measurements were attempted upon thermally aligned and non-aligned films and the effects of solvent annealing with toluene vapour measured *in situ*.

Thanks to Detlef Smilgies, George Malliaras for use of their equipment and labs at Cornell as well as Hon Hang Fon, Ruipeng Li, and Aram Amassian for experimental help and very useful discussions about the work.

6.1 Introduction

Grazing Incident Wide Angle X-ray Scattering (GIWAXS) is a very useful technique for investigating the structure and morphology of thin-films of ordered materials. Here I have studied thin-films of four polymers, F8BT, PFO, F6T2 and SC005, on silicon and rubbed polyimide alignment substrates. I have also investigated the effect of *in situ* vapour exposure on PFO thin-films.

6.2 Theory and analytical concerns

Once data collection is completed, analysis proceeds by use of the Fit2D (1) software by ESRF. As in SAXS and SANS studies, the collected data is related to the scattering vector q , although here data is collected in two dimensions q_z and q_x . Where q_z is the real-space ordinate axis, and is due to scattering in the axis perpendicular to the plane of the substrate, and q_x being the detector abscissa with scattering parallel to the plane of the substrate. Converting from 2D graphical information to the more usable, scattering intensity against q or equivalent is done with Fit2D software. For data analysis, precise knowledge of the sample detector distance is needed. This is calculated from knowledge of the direct beam position and a known strong scattering peak as described in *Chapter 3*.

In amorphous, glassy films, GIWAXS will show broad rings indicative of the average repeat distance of scattering objects within the film. If a polycrystalline material with a single preferred crystallographic direction relative to the substrate is being studied, GIWAXS can produce a diffraction pattern similar to that of a single crystal, allowing determination not only of the preferred molecular orientation but also some of the unit cell parameters including angles. If the crystallites are randomly orientated relative to the substrate, the result will be more similar to a Debye-Scherrer powder diffraction pattern showing a series of rings, although again allowing unit cell parameters to be extracted. The spot (or ring) size can also be used to extract crystallite dimension information using the Scherrer method (2).

For analysis of semi-ordered polymer samples in which there may be a preferred molecular orientation relative to the plane of the substrate, integration across an arc either side of the z -axis and the x -axis in Fit2D can be used to quantify these differences. This is shown below in *figure 71*.

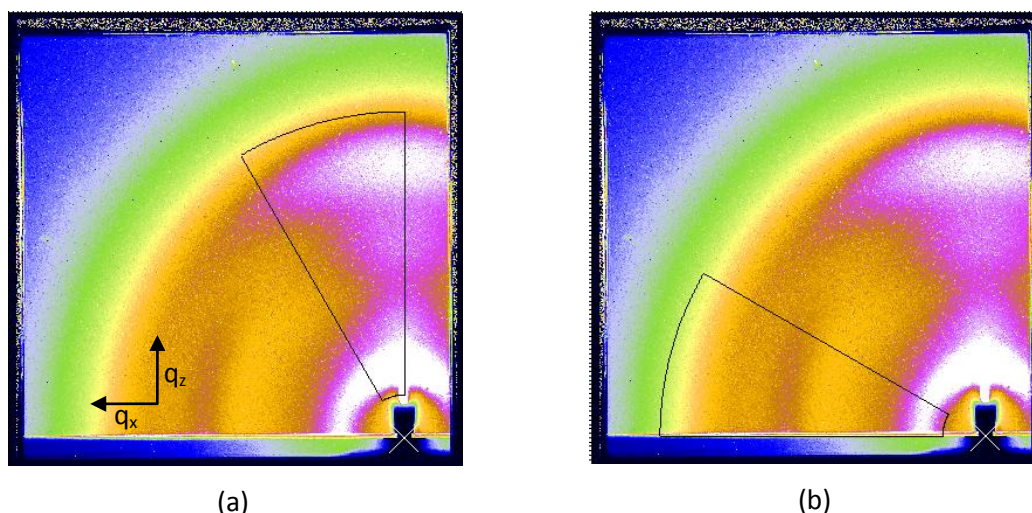


Figure 71 GIWAXS intensity plots of an annealed F8BT film on silicon. Showing (a) the vertical 90-120° integration region and (b) the in plane 150-180° region

These two results give information about the polymer backbone and sidechain orientation within the film.

6.3 Previous Work

There is large amount of GIWAXS previous work on F8BT and PFO films. However F8T2, as discussed in *Chapter 4*, does not appear to scatter X-rays well enough to study using these techniques.

F8BT has been studied using X-rays by various groups (3; 4), important results are discussed here, alignment is a regularly used technique (5) in OFET production (6) and polarized emission (7).

Donley et al. (3) experimentally studied a range of different molecular weights of F8BT, from 9 to 255 kg/mol, with a variety of techniques in both pristine and annealed films. Some of their most important results are that in pristine unannealed films there is a high torsion angle between the F8 and BT units, and that BT units on neighbouring chains align with each other and are close together. Annealing significantly reduces this torsion angle, and chains preferentially pack with F8 units aligned with the BT units in neighbouring chains. This restructuring however, significantly reduces electron mobilities in annealed films. Importantly, they found the polymer backbone orientation is parallel to the substrate, with stacking between the polymer chains perpendicular to the substrate, shown below in *figure 72(a)*, with other possible configurations in *figure 72(b)* and *(c)*.

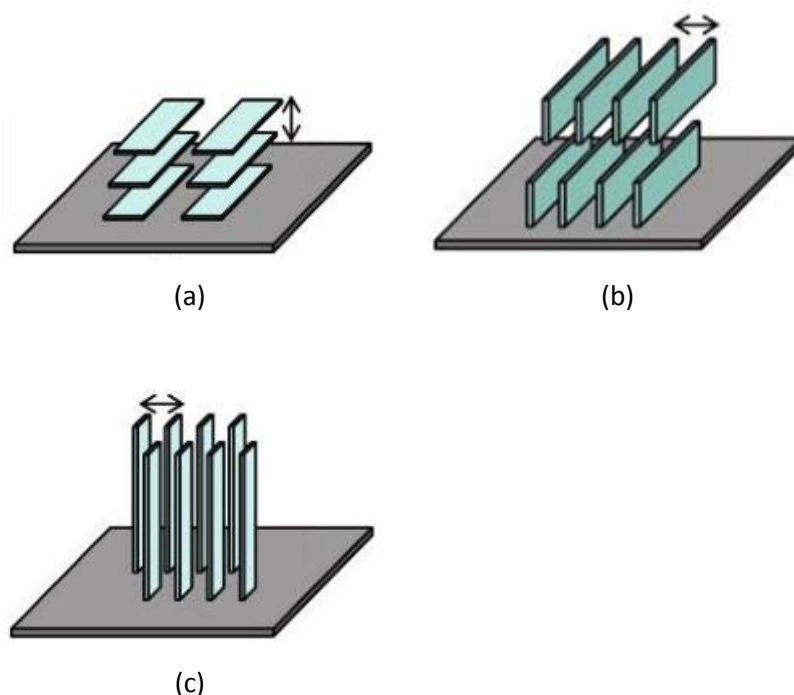


Figure 72 (a) Likely packing structure of F8BT in thin films. (b) and (c) shown alternatives (3)

This packing structure is shown below in *figure 73*, and was used in charge transport simulations done by Lagowski and Li (4). One of the most intense scattering spots would be expected to be the (0,0,1), with a d-spacing of 16.7 Å, with (0,0,4) also visible, in the q_z direction. The structure proposed by Donley et al is shown in *table 32*.

Distance	Corresponding to
$a = 14.65 \text{ Å}$	Along the backbone, monomer length
$b = 5.3 \text{ Å}$	Interchain Distance
$c = 16.7 \text{ Å}$	4 x pi stacking
$\alpha = 98^\circ$	c-axis with respect to the a-b plane

Table 32 F8BT unit cell dimensions from (3)

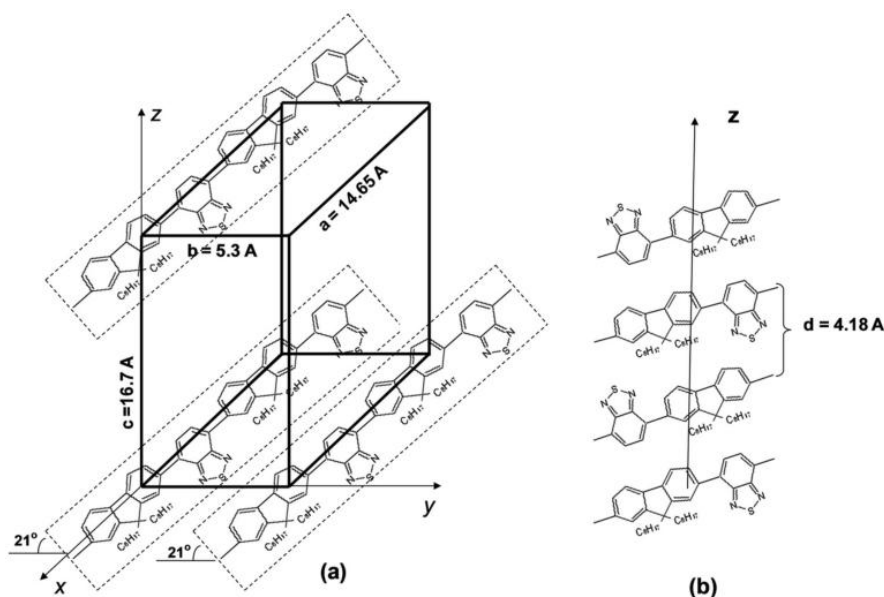


Figure 73 Unit cell dimension of F8T2 from (4)

Various X-ray studies of PFO films have been undertaken, using x-ray and electron diffraction techniques and GIWAXS, however the unit cell structure is much more complex. Two studies of note, by Chen (8) and Brinkmann (9) are key when discussing repeat unit cell size of PFO films. Both groups have determined a packing structure containing eight PFO chains. Chen et al do not account for ordering in the sidechains, likely to be an important factor, whereas Brinkmann et al assumed the crystallisation in the solid state is largely due to crystallisation and packing of the n-octyl sidechains. Other important factors are the high non-planarity between monomer units in polyfluorenes, and that the sidechains can follow a zig-zag like conformation, allowing good sidechain interdigitation (9). These two possible structures are shown below in *figure 74*, and the effective dimer configuration suggested by Brinkman.

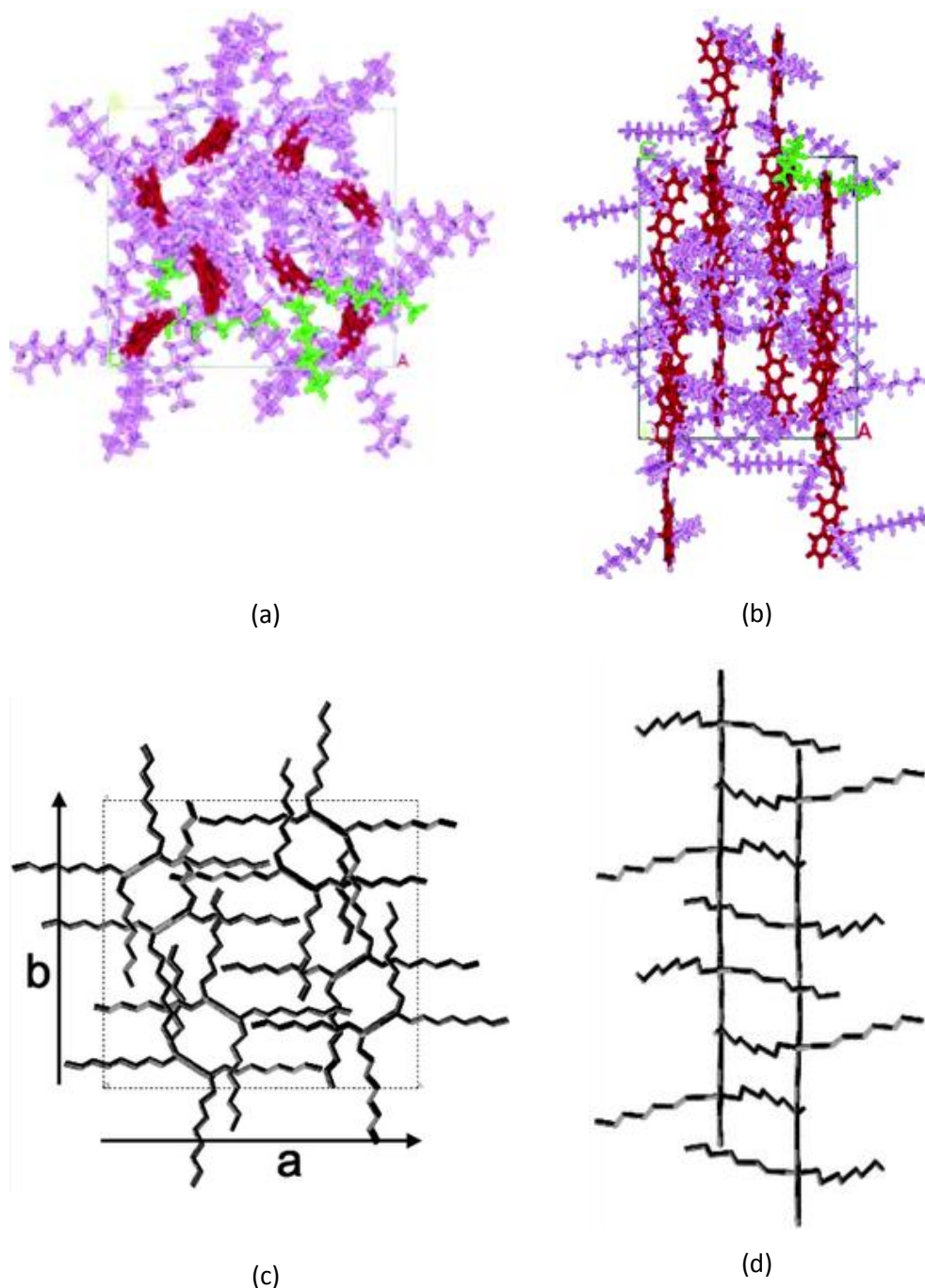


Figure 74 Suggested PFO repeat cell (a) along the backbone and (b) viewed from the b-axis from (8). PFO structure along the backbone with side chain crystallinity is shown in (d) and interdigitation in dimer structure (e) from (9).

The calculated unit cell dimensions for the structures proposed above are 3.32 nm along the c axis, which is the polymer backbone direction, and 2.56 and 2.34 nm for the a and b axis respectively. Additionally, when the alpha-beta phase of PFO (10) is discussed and aggregation is seen, it is suggested that one key structural difference is increased coplanarity along the polymer backbone (11) and the importance of sidechain packing (12). This will be important as vapour treatment is

likely to induce this structural behaviour (10). Various previously actertained structural parameters are shown below in *table 33*, with c being along the polymer axis.

Group	a (Å)	b (Å)	c* (Å)	Experiment Type	Note
Ueda(13)	11.7		33.5	TEM	
					½ repeat unit –
Kawana (14)	12.8		n x 4.5	X-Ray Diffraction	sidechain interdigitation
					using values
Misaki (15)	25.6	23.4	33.2	GIXD	from (8)
Brinkmann (9)	25.6	23.4	32.4	TEM and modelling	
Grell (10)	16	4.4	33.4	X-Ray fibre Diffraction	
Chen (8)	25.6	23.4	33.2	TEM and simulation	

Table 33 Repeat unit cell values of PFO, from various groups

F6T2 is analogous to F8T2, however the octyl sidechain groups are replaced with hexyl, and can be aligned into nano-crystalline domains (16), however at notable higher temperatures than F8T2 (17) (~320° C as opposed to 270°C), T_g was found to be around 135° C hence the two annealing temperatures used later are expected to be below and above the glass transition temperature. Unit cell parameters are notably lacking in the literature.

The final polymer studied in this fashion is known as SC005, a polyfluorene copolymer composed of 80% F5 and 20% F8, with F5 being a fluorene monomer with short pentylsidechains, found to have much improved mobility over PFO (18). DSC results found annealing (~16 hours) at 150° C induces ordered crystal structure.

6.4 Results

Having found in *Chapter 4* the poor quality of scattering of F8T2 samples, they were not used again. Instead, F6T2 along with PFO and F8BT were studied. Additionally the polyfluorene co-polymer SC005, as described by Bradley et al. (18) was investigated. Alignment using rubbed polyimide layers was inconsistent at best and non-applicable at worst, however changes between parallel and perpendicular alignments can occasionally be seen.

A sample of grooved PI was scanned with AFM by Jeremy Smith at Imperial College London, the results of which are shown below in *figure 75*, at $5 \times 5 \mu\text{m}$ and $2 \times 2 \mu\text{m}$ clear alignment grooves are seen. This suggests that the thermal treatment is not causing regular alignment rather than PI rubbing issues. I anticipate this is likely due to the annealing temperature not being hot enough or perhaps more likely, not held for sufficient time.

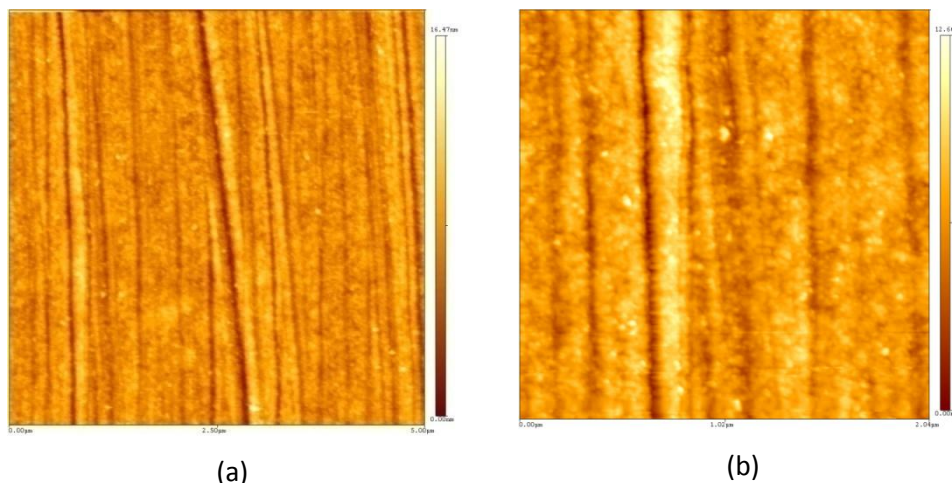


Figure 75 AFM images of rubbed alignment grooves on polyimide films (a) $5 \times 5 \mu\text{m}$, (b) $2 \times 2 \mu\text{m}$

As discussed in *Chapter 3*, the q_z direction strongly correlates with the physical z direction of the film, and the q_x direction is in the plane parallel to the substrate.

6.4.1 F8BT

F8BT was studied after annealing on silicon substrates and on PI alignment layers, with incident beam direction being parallel and perpendicular to the rubbing direction. F8BT alignment protocol followed that of Whitehead et al. (7), namely cooling from $265\text{--}235^\circ\text{C}$ at 1° per minute and quenching to room temperature.

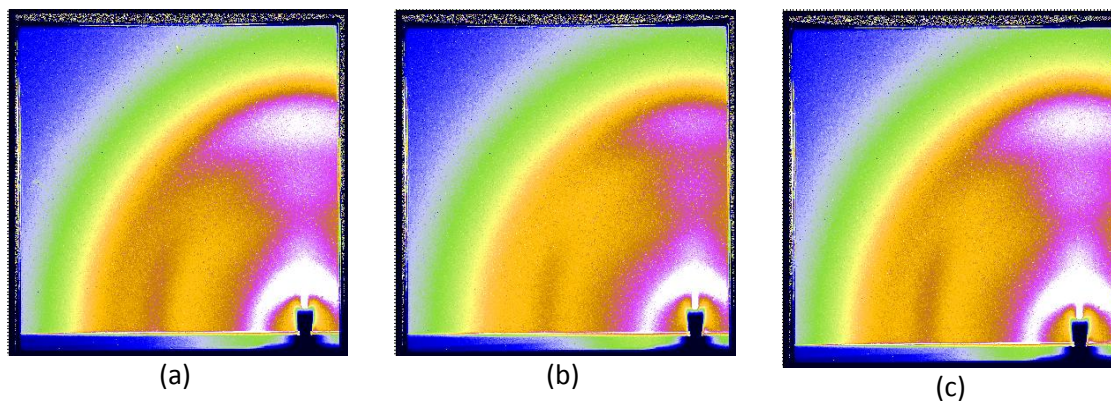


Figure 76 GIWAXS scattering intensities of F8BT thin films, on (a) silicon, (b) incident beam parallel to the rubbing direction, and (c) with the incident beam perpendicular to the rubbing direction

As no peak positional changes are seen in the three different samples in *figure 76* analysis continues with the most intense scattering of the anneal film on silicon. In the q_z direction, perpendicular to the substrate layer, three clear peaks can be seen, as well as two in the q_x direction. These are labelled below in *figure 77*, with d-spacings shown in *table 34*.

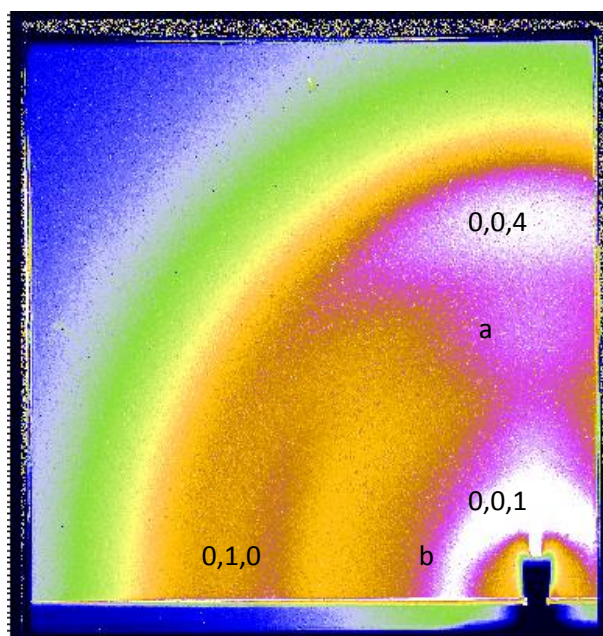


Figure 77 GIWAXS image of annealed F8BT film on silicon substrate, with peaks assigned where possible.

Peak	d-spacing (Å)
(0,0,4)	4.4
(0,1,0)	5.8
(0,0,1)	17.2
a	6.1
b	18.4

Table 34 Showing d-spacings for peaks in GIWAXS intensity of annealed F8BT

The (0,0,1) and (0,0,4) peaks in the vertical direction correspond to the four chains per cell vertical stacking seen previously in (3; 4), however with a slightly larger π - π spacing of 4.4 Å. By comparison to literature the peak at 5.8 Å is tentatively assigned as the (0,1,0), the sidechain packing distance, again slightly larger than the surprisingly low value of 5.3 Å seen previously. It is difficult to confidently assign the remaining peaks. The q_z peak at 6.1 Å is likely to also be due to the sidechain packing and tilted crystalites in the film, however could be the (0,0,3) although this would be

expected to be at $5.7 \text{ \AA}$ from the position of the (0,0,1). The peak labelled b is expected to be the (0,0,1) seen as a ring due to missaligned chains in the film.

Unfortunately full indexation of the scattering peaks were not possible with this sample, further study and practice of alignment and annealing techniques would allow much more detailed results to be obtained from F8BT samples. However, the assignments which could be made compare favourably with those in *Section 6.3*, with $b = 5.8 \text{ \AA}$ and $c = 17.2 \text{ \AA}$. The backbone repeat does not appear in these results.

Overall, these results imply that as expected F8BT aligns with backbone broadly parallel to the substrate, with some rotation either between chains or along the backbone allowing a chain to chain spacing of $5.8 \text{ \AA}$ due to interdigitation of sidechains, and π - π stacking of $4.4 \text{ \AA}$.

6.4.2 PFO

PFO was studied by GIWAXS, both as thin films and the more unusual case of *in situ* vapour exposure. Due to the lack of obvious changes between films on silicon substrates and rubbed polyimide layers, shown below in *figure 78*, preferential alignment appears to not have been induced, so analysis proceeds upon the film on a silicon substrate as it has the most intense scattering pattern.

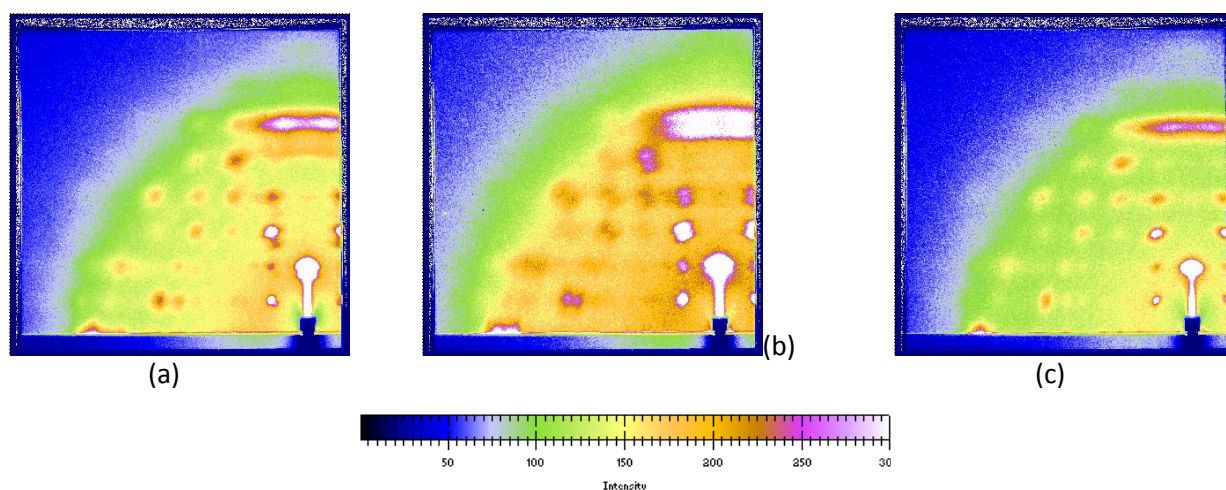


Figure 78 GIWAXS images of PFO annealed on (a) Silicon substrate, and with (b) Beam parallel to alignment and (c) perpendicular.

Figure 79 below shows annealed PFO on a silicon substrate, with the three crystallographic planes shown in (a), (b) and (c). The h plane in the z direction perpendicular to the substrate corresponds to the a axis of the repeat unit, whereas k and l correspond to the b and c repeat unit axis in the plane of the substrate respectively, with c being along the backbone. From *figure 10(a)* and (b) it appears clear that γ , the angle between the a and b axis is 90° , and similarly as l planes lie on h

planes in *figure 79 (a)* and *(c)*, β the angle between a and c is also 90° . The position of the planes is tabulated in *table 35*.

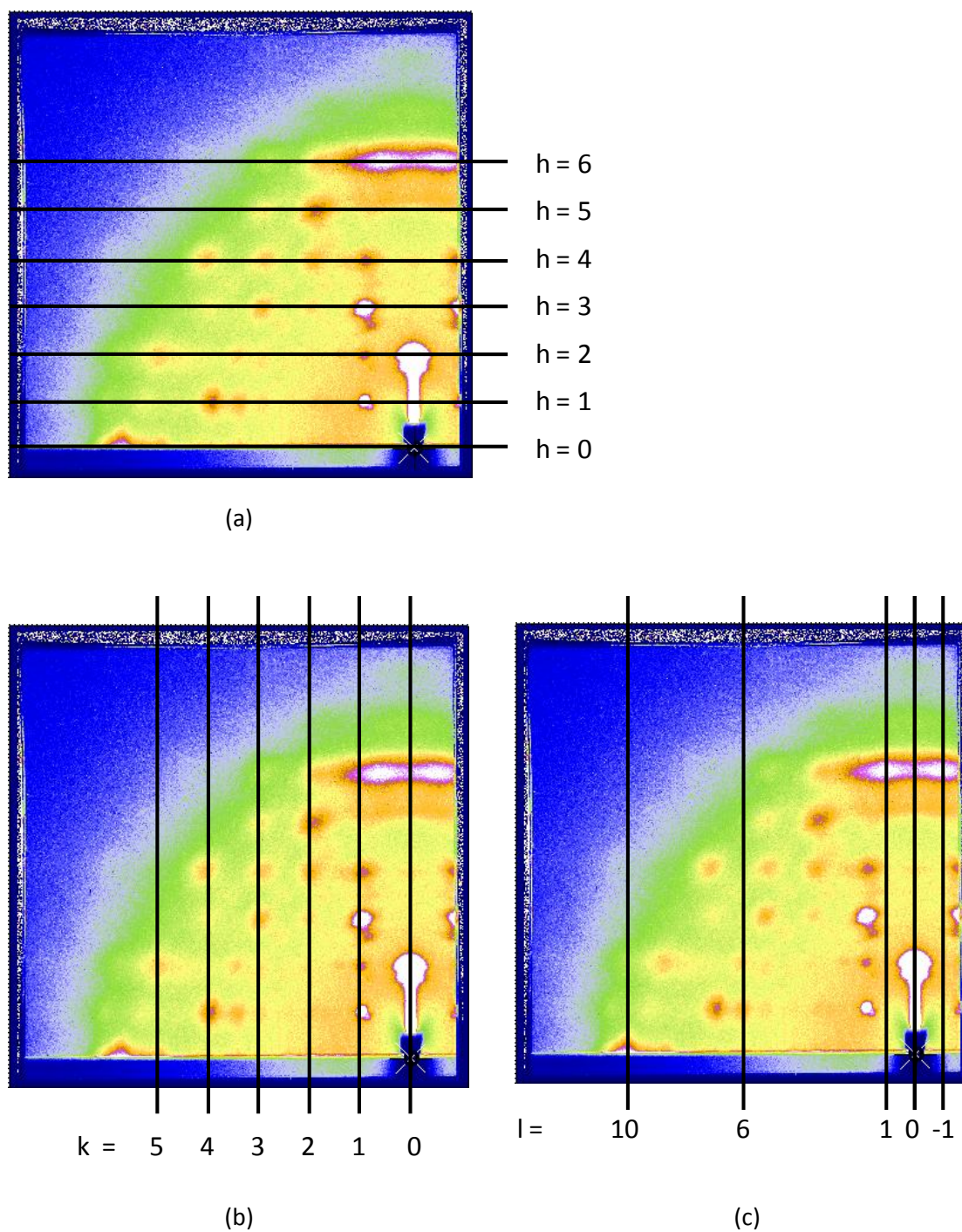


Figure 79 PFO crystal planes

The positions of the planes shown in *figure 79* are shown in *table 35*.

h	d-spacing (Å)	d-spacing (Å) from (8; 9)
1	26.4	25.6
2	13.1	12.8
3	8.5	8.6
4	6.5	6.4
5	5.1	5.1
6	4.4	4.3

(a)

k	d-spacing (Å)	d-spacing (Å) from (8; 9)
1	24.2	23.1
2	12.4	11.7
3	8.1	7.8
4	6.0	5.9
5	4.9	4.7

(b)

l	d-spacing (Å)	d-spacing (Å) from (8; 9)
-1	39	33.2
1	38	33.2
6	6.9	5.5
10	4.2	3.3

(c)

Table 35 Values for crystallographic planes, from experiment and for comparison with modelling (a) h, (b) k, (c) l.

Finally a fully indexed GIWAXS image of an annealed PFO film is shown in *figure 80*.

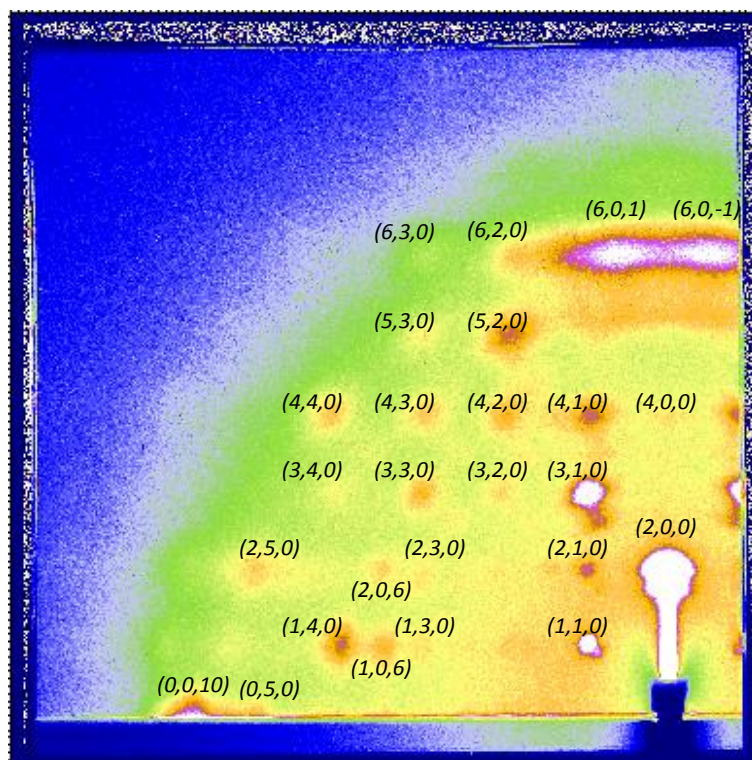


Figure 80 2D GIWAXS scattering intensity plot showing the indices of all peaks

From these, the unit cell in these films is $a = 26.4 \text{ \AA}$, $b = 24.2 \text{ \AA}$ and $c = 38.5 \text{ \AA}$, but there is not preferential alignment in the planes parallel to the substrate. Annealing PFO films, causes highly ordered crystallites with the backbone in the plane of the substrate along the c direction, and one axis perpendicular to the substrate plane. These results are very comparable to those obtained by Brinkmann (9) and Chen (8), confirming their results that PFO packs with eight chains per repeat unit cell.

6.4.2.1 In Situ Vapour Annealing

PFO thin films were studied, unaligned as determined above but annealed to induce a large level of crystalline order, in the vapour cell outlined by Aramissian et al. (19). Films are enclosed in low pressure flow cell, and solvent is added, to the effect of being exposed to a high solvent atmosphere. Here toluene was used, as a good solvent for PFO, on unaligned annealed PFO films on a silicon substrate. Images were recorded with 10 second exposure every 20 seconds.

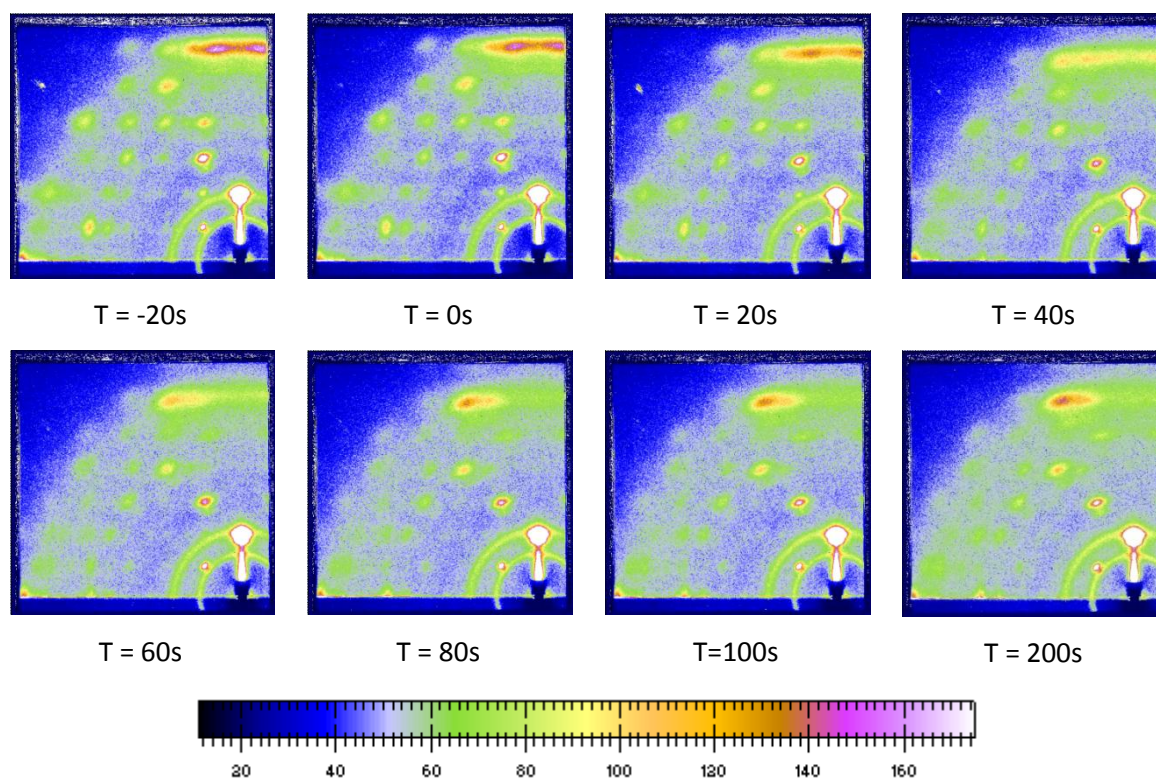
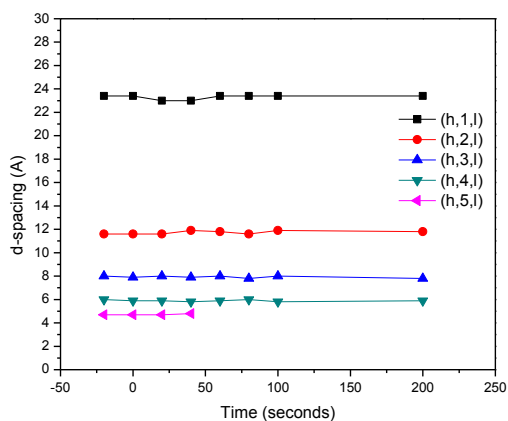
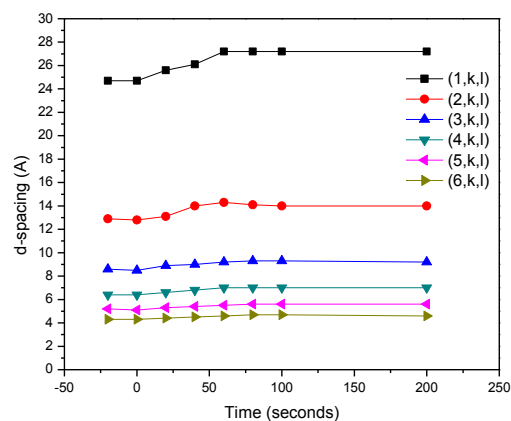


Figure 81 Scattering intensity images of annealed PFO film, with solvent added at $T = 0s$

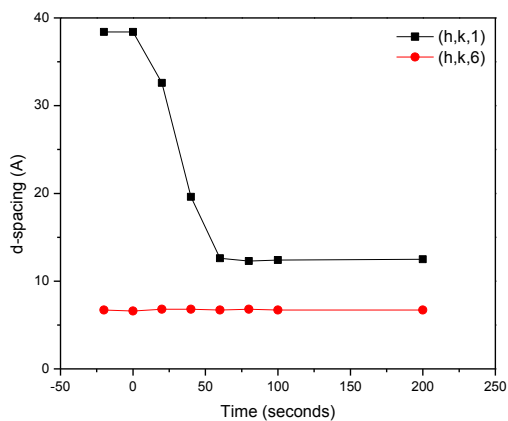
There are clear changes in a relatively short amount of time after vapour is added to the cell, the reference scheme shown in *figure 80* is used throughout to discuss specific spots. Using the indexing scheme above, changes in position were measured and plotted against time, with $T = 0$ being initial exposure to toluene vapour, these are shown in *figure 82*. From the images and graphs changes happen within the first 60 seconds, and then stabilise for the remainder of the experiment. Spacing in the b direction, of planes parallel to the substrate increases by $\sim 10\%$ in this time, suggesting a rapid uptake of solvent, in the sidechain direction. A similar increase of 11.3% has been seen by Ueda et al (20) however after 100 hours exposure to toluene vapour of friction transferred films. No change is seen in the a spacing direction, somewhat suprisingly meaning there is likely no change in the interchain backbone spacing. A very large change however is seen in the (6,0,1) peak, reducing spacing from $38.4 \text{ \AA}$ to $12.5 \text{ \AA}$, a drop of 67%. This is along the c axis, the backbone direction and is to do with a reduction in the number of backbone repeats in the unit cell dropping. This was not seen in the work of Ueda, but I believe the apparent reduction in chains per cell is likely to be due to increased rotation along the backbone, as suggested by Brinkman as PFO changes to a β -phase configuration. Unit cells along the c -axis are now likely to contain 1.5 monomer units, suggesting improved interdigitation facilitated by the solvent absorption of the sidechains.



(a)



(b)



(c)

Figure 82 Lattice spacing changes of annealed PFO films with time from exposure to toluene vapour for (a) h axis, (b) k axis, (c) l axis

In addition positional changes, clear changes in intensities are seen. Most obviously the changes of the (6,0,1) peak, but also the loss of the bright peaks at (1,4,0), (5,2,0) and (4,1,0). These changes can be seen in the larger scale images in *figure 83* below, showing $T = -10$ s and $T = 100$ s with key spots labelled, note the bright rings due to the Kapton window.

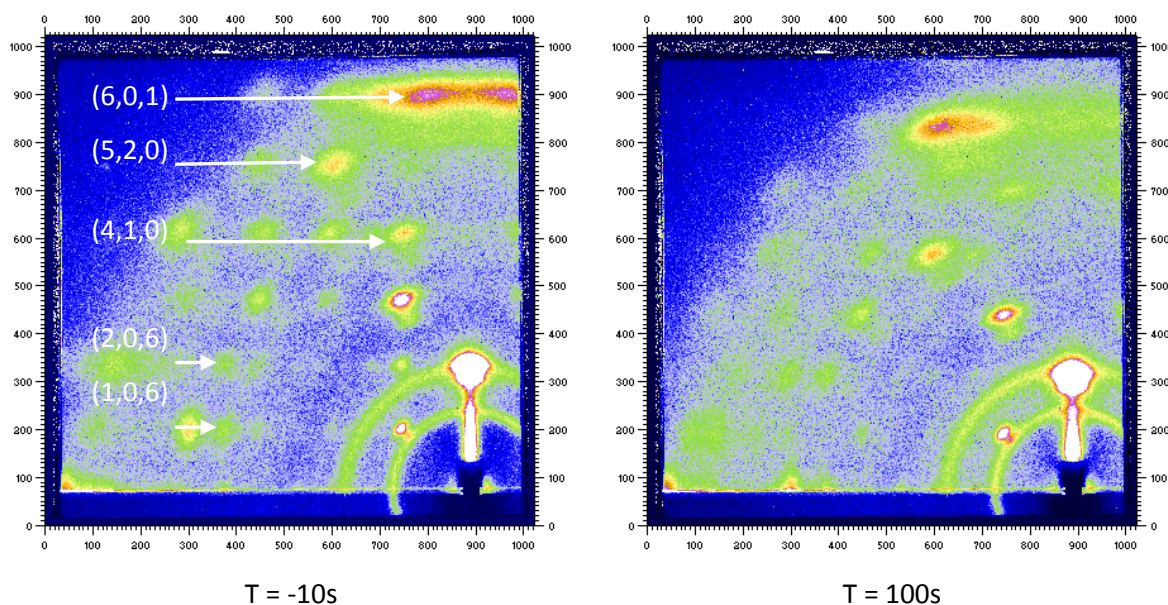


Figure 83 GIWAXS intensity images of annealed PFO films exposed to toluene vapour at $T = 0$ s.

The most obvious changes are the large loss of intensity of many spots, I expect this to be due to sidechains taking up the solvent vapour, and due to their importance in the crystallised structure (9), this loss of regularity in all directions contributes to a loss of scattering from them. The reduction in intensity, but not complete loss of the peaks at (2,0,6) and (1,0,6) agrees with the analysis above of changes in the backbone direction, but does suggest that only a proportion of the film is taking up the solvent. Similarly there is still an increase over background level of scattering at the initial position of the (6,0,1) peak, however it has dropped to 50%.

After exposure to solvent vapour, swelling in the sidechain direction is seen by of 10%, and a reduction from 38.4 Å to 12.5 Å is seen along the backbone repeat axis. This is likely to be due to a change to β -phase in the annealed film and gives swollen unit cell parameters of $a = 27.1$ Å, $b = 23.4$ Å and $c = 12.5$ Å. Vapour annealing of PFO films causes clear and strong structural changes in a very short amount of time (~ 1 minute), further *in situ* measurements would be useful to understand if these changes stay in the film.

It is worth noting that the decrease of intensity is not due to radiation damage, as multiple exposures were checked on other films and this decrease is not seen without vapour, and these changes with solvent exposure are not seen in unannealed films.

6.4.3 Other Polymers

6.4.3.1 F6T2

F6T2 is a copolymer of polyfluorene with shorter F6 sidechains and bithiophene units. F6T2 was studied here as it was found that F8T2 is a very poor X-ray scatterer in *Chapter 4*, and is somewhat

analogous, and scattering changes may only be due to sidechain packing differences. Due to time constraints and the use of the vapour cell as described in *Section 6.4.2* above, the F6T2 films were studied inside the cell, but without a flow of solvent. As such the background scattering of the cell window must be taken into account and ignored as a background reading.

F6T2 was studied on silicon substrates, unaligned, but annealed at 90° or 150° for 1 hour in a nitrogen atmosphere, chosen to be above and below T_g (16), however without DSC on this specific M_w this is only assumed. Scattering from the two annealing temperatures and integrated intensities from 90° to 140° are shown below in *figure 84*, along with the window measurement for comparison

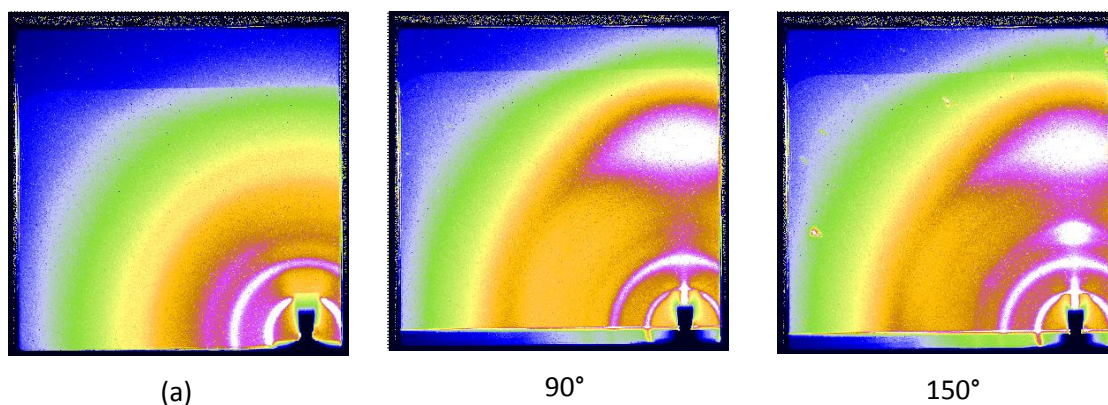


Figure 84 GIWAXS images of (a) the Kapton window background, (b) F6T2 film annealed at 90° and (c) 150°

Analysis is shown on the film annealed at 150° C, but positions are the same in both films, indexed peak positions are shown in *figure 85*.

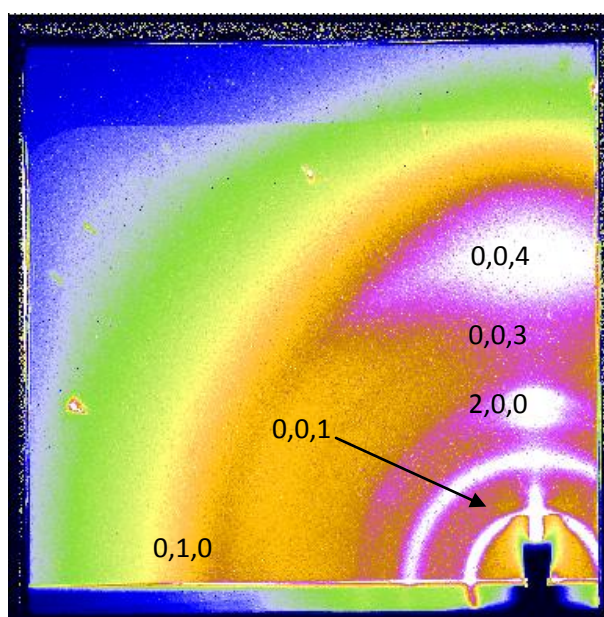


Figure 85 GIWAXS image of F6T2 film annealed at 150° C, with peak indices shown

The d-spacing of the indexed peaks are shown in *table 36*.

Peak	d-spacing (Å)
(0,0,4)	4.8
(0,0,3)	6.4
(0,0,1)	21.6
(0,1,0)	5.1
(2,0,0)	8.1

Table 36 d-spacing of indexed peaks of an annealed F6T2 film

As in the F8BT sample clear peaks in the q_z direction are the vertical packing between backbones, with four chains per cell. Here $c = 21.6$ Å, with stacking between the chains of 4.8 Å. The (0,1,0) peak at 5.1 Å can confidently be labelled the interchain packing distance in the plane of the sidechains, parallel to the substrate. It is less than the literature values for F8BT and the experimental values seen in *Section 6.4.1*, which is to be expected due to the shorter sidechains in F6T2. It is likely that F8T2 would have interdigitation of the sidechains leading to comparable packing distances in the b direction to F8BT. The peak labelled (2,0,0) is in fact a double peak at 8.1 Å and 9.2 Å, however the 9.2 Å peak is window background, which can be seen in the scattering image in *figure 84(a)*. The value of 8.1 Å has led to the tentative assignment of (2,0,0) due to being close to half the repeat unit distance along the backbone of F8T2 (21) of 16.7 Å.

Annealed F6T2, like F8BT stacks broadly parallel to the substrate, with interdigitation of the F6 sidechains, leading to a smaller packing in the plane of the substrate than equivalent F8 materials. The unit cell can tentatively be defined as $a^* = 16.2$ Å, $b = 5.1$ Å and $c = 21.6$ Å, with a being the backbone direction. As before, F6T2 is a good candidate for further X-ray studies, particularly if well aligned films can be reliably produced.

6.4.3.2 SC005

The final polyfluorene copolymer studied by GIWAXS is known as SC005, previously discussed by Bradley et al. (18) composed of Suzuki route 80% F8 / 20% F5 random copolymers. SC005 was spin coated from a toluene solution and annealed for 150°C for ~6 hours to attempt to ensure good alignment. As with F8BT, films were studied on silicon and rubbed PI substrates. GIWAXS intensity images of these films with three treatments are shown below in *figure 86*. *Figure 86(a)* suggest a polycrystalline sample with no preferential direction as expected on silicon, however (b) and (c) do show some preferential alignment.

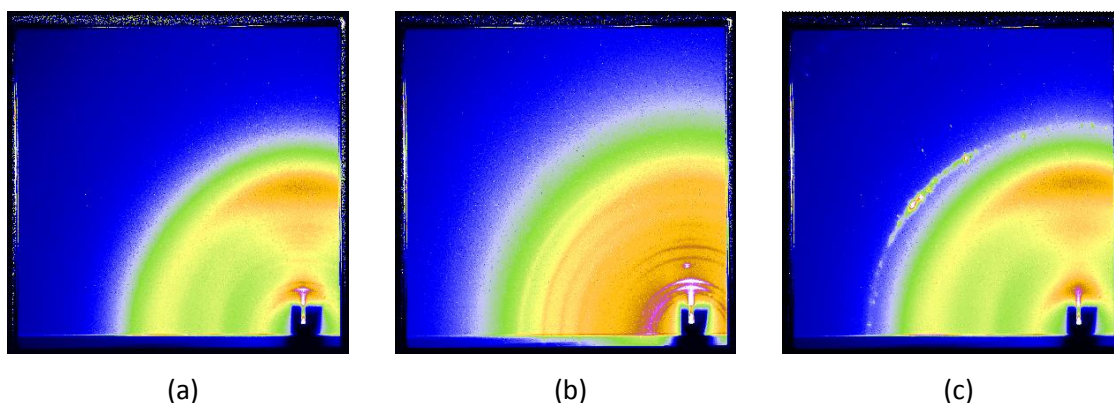


Figure 86 GIWAXS intensity images of SC005 annealed on (a) silicon substrate, and on grooved PI (b) parallel and (c) perpendicular to the incident beam direction

As there are clear differences between each film, each will be studied separately but with common features noted. In all the unaligned and perpendicular films there are three common scattering rings, clearly seen coming from the q_x axis in *figure 86(a)* and *(c)*, their positions are shown in *table 37*.

Ring	Silicon Anneal		Perpendicular to beam	
	d-spacing at q_z (Å)	d-spacing at q_x (Å)	d-spacing at q_z (Å)	d-spacing at q_x (Å)
(0,0,1)	19.0	20.1	21.0	19.9
(0,0,2)	-	9.1	-	9.4
(0,0,3)	6.1	6.4	6.1	6.1

Table 37 d-spacing positions seen in SC005 annealed on silicon substrates and perpendicular aligned

Peaks are also seen in the unaligned film in the q_z direction at 8.1 Å and 11.8 Å, as well as some other very weak arcs. The peak at 8.1 Å could be along the backbone of the polymer, by comparison with the PFO monomer length of 8.3 Å, this is seen in the silicon film at 8.4 Å and the perpendicularly aligned at 8.6 Å. The peak at 11.8 Å is very hard to index, along with the other weak arcs but if the repeat unit is large and involves many chains like pure F8 PFO they could well be the (0,1,0), (0,1,1) or (0,2,2), along the b axis. I believe this to be likely as the random distribution of F8 and F5 moieties are likely to lead to complex packing behaviour.

The scattering intensity of the film aligned parallel to the incident beam direction, shows many arcs. They are particularly hard to index, but if the double peaks are an experimental artifact due to film size in the beam direction, which is likely, some tentative assignments can be made. These are tabulated in *table 38*.

SC005 is likely to pack in a complex way, similar to PFO. Chains are preferentially aligned along the a axis, with multiple repeats per unit cell, but unlikely to be simply stacked like F6T2 and F8BT. The c spacing is 20 Å, comparable to the a and b axis in PFO above for multiple chains packing into each unit cell, but smaller, possibly due to the proportion of shorter sidechains. Annealing causes a polycrystalline sample, but the very strong directional ordering previously seen was not seen here. SC005 however is a very good candidate for further study by GIWAXS, due to its strong scattering.

d-spacing (Å)	Mean d-spacing (Å)	Possible Assignment
6.0	6.5	(0,0,3)
6.9		
8.0	8.7	Monomer repeat
9.3		
10.0	10.8	b axis?
11.5		
12.5	12.8	Bright spot, artifact
13.0		
16.2	17.5	Double monomer repeat?
18.7		
20.5	21.9	(0,0,1)
23.3		

Table 38 d-spacings seen in SC005 film aligned parallel to the incident beam and likely assignments

6.5 Conclusions

F8BT has been well studied, and is still not fully characterised but chain stacking of four chains parallel with the substrate appears to have occurred here as seen previously. Some of the scattering peaks were indexed, but unfortunately due to the lack of alignment d-spacing along the backbone was not seen, however in addition to a vertical interchain distance of 4.4 Å I also expect an interchain separation of 5.8 Å due to sidechains

F6T2 was found to likely stack in a similar fashion to F8BT, preferentially parallel the plane of the substrate. Peaks in the vertical direction were confidently indexed, with regular vertical separations of 4.8 Å and four chains per unit cell. Equally confidently interchain spacing in the sidechain direction was seen to be 5.1 Å smaller than the spacing found in F8 based polyfluorene copolymers.

SC005 was a good candidate for study with GIWAXS, and appears to have a more complex structure. Chains are preferentially orientated parallel to the substrate and some level of alignment was seen. Like PFO SC005 appears to pack in a complex, multichain per cell structure with one unit cell parameter of 20.0 Å, comparable to the a and b directions in PFO. SC005 is a very interesting polymer to study, and clearly benefits from long anneal times to induce alignment.

Annealed PFO films were studied, both as plain films and to understand the effects of solvent vapour annealing. The initial annealed film was well indexed, leading to unit parameters of $a = 26.4 \text{ Å}$, $b = 24.2 \text{ Å}$ and $c = 38.5 \text{ Å}$, in the polycrystalline sample, with c being the backbone direction. Extensive changes in the film were seen on exposure to toluene vapour. Within 60 seconds the b axis has increased by 10%, due to sidechains absorbing the solvent. In addition the c axis in the backbone direction reduces from 38.4 Å to 12.5 Å, suggesting an extensive reconfiguration of the unit cell packing structure leading to a shorter repeat unit, likely the formation of twisted β -phase structures.

6.6 Further Work

The GIWAXS experiments undertaken here were largely successful, but the obvious choice for further work would be improvement of alignment procedures and repeating both plain film and vapour exposure experiments for these polymers. Clearly batch specific DSC results to find transition temperatures and systematic understanding of alignment procedures are key to this. Due to the large effect toluene vapour was found to have on the PFO film, and the high data acquisition rate possible at CHESS further vapour exposure with different solvents would be very interesting, as would continuation to see if chains relax back after vapour is removed. Finally, despite choosing to not study F8T2 due to the poor scattering in SAXS measurements, a brief study as to whether well aligned crystalline films could be studied would be sensible.

6.7 Bibliography

1. **A P Hammersley.** FIT2D: An Introduction and Overview. *ESRF Internal Report: ESRF97HA02T*. 1997.
2. **P. Scherrer.** Bestimmung der Grösse und der innern Struktur von Kolloidteilchen mittels Röntgenstrahlen. *Nachr. Ges. Wiss. Göttingen*. 1918. Vol. 26, pp. 98-100.
3. **C L Donley, J Zaumseil, J W Andreasen, M M Nielsen, H Sirringhaus, R H Friend, and J-S Kim.** Effects of Packing Structure on the Optoelectronic and Charge Transport Properties in Poly(9,9-di-n-octylfluorene-alt-benzothiadiazole). *J. Am. Chem. Soc.* 2005. Vol. 127, 37, pp. 12890-9.
4. **J B Lagowski and Y Li.** A multi-step simulation of electron mobility in fluorene–benzothiadiazole conjugated polymer – Case study. *Computational and Theoretical Chemistry*. 2011. Vol. 997, 1-3, pp. 157–162.
5. **M Grell, M Redecker, K S Whitehead, D D C Bradley, M Inbasekaran, and E P Woo.** Monodomain alignment of thermotropic fluorene copolymers. *Liquid Crystals*. 1999. Vol. 26, 9, pp. 1403-1407.
6. **L Kinder, J Kanicki, J Swensen, and P Petroff.** Structural ordering in F8T2 polyfluorene thin-film transistors . *Proceedings of SPIE*. 2003. Vol. 5217.
7. **K S Whitehead, M Grell, D D C Bradley, M Inbasekaran, and E P Woo.** Polarized emission from liquid crystal polymers. *Synthetic Metals*. 2000. Vols. 111-112, pp. 181–185.
8. **S A Chen, A C Su, and S H Chen.** Molecular Packing in Crystalline Poly(9,9-di-n-octyl-2,7-fluorene). *Macromol.* 2004. Vol. 37, 18, pp. 6833-6838.
9. **M Brinkmann.** Directional Epitaxial Crystallization and Tentative Crystal Structure of Poly(9,9'-di-n-octyl-2,7-fluorene). *Macromolecules*. 2007. Vol. 40, 21, pp. 7532–7541.
10. **M. Grell, D D C Bradley, G Ungar, J Hill, and K S Whitehead.** Interplay of Physical Structure and Photophysics for a Liquid Crystalline Polyfluorene. *Macromolecules*. 1999. Vol. 32, 18, pp. 5810–5817.

11. **D Lu, L Huang, X Huang, G Sun, C Gu, and Y Ma.** Study of β phase and Chains Aggregation Degrees in Poly(9,9-dioctylfluorene) (PFO) Solution. *J. Phys. Chem. C*. 2012. Vol. 116, 14, pp. 7993–7999.
12. **D W Bright, F B Dia, F Galbrecht, U Scherf, and A P Monkman.** The Influence of Alkyl-Chain Length on Beta-Phase Formation in Polyfluorenes. *Advanced Functional Materials*. 2009 йил. Vol. 19, 1, pp. 67–73.
13. **M Misaki, Y Ueda, S Nagamatsu, Y Yoshida, N Tanigaki, and K Yase.** Formation of Single-Crystal-like Poly(9,9-dioctylfluorene) Thin Film by the Friction-Transfer Technique with Subsequent Thermal Treatments. *Macromolecules*. 2004. Vol. 37, 18, pp. 6926–6931.
14. **S Kawana, M Durrell, J Lu, J E Macdonald, M Grell, D D C Bradley, P C Jukes, R A L Jones, and S L Bennett.** X-ray diffraction study of the structure of thin polyfluorene films. *Polymer*. 2002. Vol. 43, 6, pp. 1907-1913.
15. **M Misaki, S Nagamatsu, M Chikamatsu, Y Yoshida, R Azumi, N Tanigaki, Y Ueda and K Yase.** Single-Crystal-like Structure of Poly(9,9-dioctylfluorene) Thin Films Evaluated by Synchrotron-Sourced Grazing-Incidence X-ray Diffraction. *Polymer Journal Japan*. 2007. Vol. 39, 12, pp. 1306 - 1311.
16. **W Tang, V Chellappan, M Liu, Z-K Chen and L Ke.** Hole Transport in Poly[2,7-(9,9-dihexylfluorene)-alt-bithiophene] and High-Efficiency Polymer Solar Cells from Its Blends with PCBM. *ACS Appl. Mater. Interfaces*,. 2009. Vol. 1, 7, pp. 1467–1473.
17. **E Lim, B-J Jung, J Lee, H-K Shim, J-I Lee, Y S Yang, and L-M Do.** Thin-Film Morphologies and Solution-Processable Field-Effect Transistor Behavior of a Fluorene–Thieno[3,2-b]thiophene-Based Conjugated Copolymer. *Macromolecules*. 2005. Vol. 38, 10, pp. 4531–4535.
18. **B K Yap, R Xia, M Campoy-Quiles, P N Stavrinou, and D D C Bradley.** Simultaneous optimization of charge-carrier mobility and optical gain in semiconducting polymer films. *Nature Materials*. 2008. Vol. 7, pp. 376-380 .
19. **A Amassian, V A Pozdin, R Li , D-M. Smilgies and G G Malliaras.** Solvent vapor annealing of an insoluble molecular semiconductor. *J. Mater. Chem*. 2010. Vol. 20, pp. 2623-2629.

20. **T Kawamura, M Misaki, Y Koshiba, S Horie and K Kinashi.** Crystalline thin films of β -phase poly(9,9-dioctylfluorene). *Thin Solid Films*. 2011. Vol. 519, 7, pp. 2247–2250.

21. **M Brinkmann, N Charoenthai, R Traiphol, P Piyakulawat, J Wlosnewski, and U Asawapirom.** Structure and Morphology in Highly Oriented Films of Poly(9,9-bis(n-octyl)fluorene-2,7-diyl) and Poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) Grown on Friction Transferred Poly(tetrafluoroethylene). *Macromolecules*. s.l. : 42, 2009. Vol. 21, pp. 8298–8306.

22. **M Knaapila, T P A Hase, M Torkkeli, R Stepanyan, L Bouchenoire, H-S Cheun, M J Winokur, and A P Monkman.** Meridional Orientation in Biaxially Aligned Thin Films of Hairy-Rod Polyfluorene. *Crystal Growth & Design*. 2007. Vol. 7, 9.

Chapter 7

Conclusions and Further Work

This chapter discusses my conclusions from the four experimental chapters in this thesis. Initially my work on Small Angle Neutron Scattering and Multi-Angle Light Scattering is considered, followed by the results of the large Spectroscopy and Thin Film chapter, and finally the Grazing Incident Wide Angle X-ray Scattering results from thin films.

Chapter 3: Small Angle Neutron Scattering

In Chapter 3 my work on Small Angle Neutron Scattering at the LOQ detector at the ISIS source at RAL was presented. The time dependence solvation issues found in poly(9,9-dioctylfluorene-alt-bithiophene) in toluene, THF and chloroform were studied. F8BT and PFO were also studied, freshly prepared in THF and chloroform. The polymer form in solution was elucidated, along with values for the molecular weight and persistence length

All three polymers were shown to take up rigid rod-like conformations in these solvents. With F8T2, aggregation in toluene over a 24 hour period was found to form sheet-like particulates.

From Perod analysis, values of n were interpreted as being indicative of increased torsion in the backbone of the polymers and hence improved dissolution, with Arrhenius plots used to calculate the activation energy in F8T2 of thermally induced conformation changes. As expected, chloroform was the best solvent for all these polymers, showing the lowest n values for each polymer.

Concentration dependent SANS showed no conformation changes of F8T2 in THF over the range 2 to 20 mg/ml. Concentration dependence was also used to elucidate molecular weight of the F8T2 sample, but by comparison to light scattering the extrapolation method used was poor.

SANS is a very useful technique, especially at high flux installations such as ISIS, from which a range of useful information can be recovered. Here the improved dissolution and conformational changes of the polyfluorene copolymers have been found and discussed.

Further Work

Further work in this domain should be focused on *in situ* measurements of dissolving dynamics, made possible by the high neutron flux of the ISIS source. What appear to be long term effects of polyfluorenes dissolving, seen in *Chapter 4*, could be studied in solutions where a high contrast ratio is available, such as THF and toluene, as well as further studies of other polymer species.

A clear region for further study would also be model-fitting and more computational work in tandem with generating the excellent experimental data allowed by ISIS and LOQ. Computational models would allow more knowledge of the precise sizes of the rod-like structures these polymers take up in solution. This, in my view, would impressively extend the analysis of these three polymers undertaken here. Being able to model the polymers as more complex than purely rods could help to understand the physical meaning of R_g found by Guinier analysis. Perod analysis has been very useful in understanding the shape of these polymers in solution but increasing the q range to larger values of q would increase the regime in which this technique can be used. Extension to lower q values

would hopefully allow a plateau to be seen and accurate determination of M_w values, for direct comparison with those established by light scattering and/or GPC.

In general, in addition to the specific experimental conclusion above, SANS analysis is a very powerful technique and should be extended to further polymers and solvents as needed.

Chapter 4: Multi-Angle Light Scattering and Small Angle X-ray Scattering

Chapter 4 discusses my work undertaken using the technique of Multi Angle Light Scattering on F8T2 in toluene, THF and chloroform. Additionally light scattering results from PFO in THF and toluene are presented, and from F8BT in toluene over the period of a week.

Radius of gyration and molecular weight values were successfully ascertained for all three polymers allowing likely chain dimensions and particulate sizes to be determined for free chain and aggregate species. The importance of good polymer dissolution was found, and the physical effects of aggregation were seen in molecular weight values.

SAX results were weak and unfortunately no conclusions could be drawn apart from the fact that F8T2 is a poor candidate for this experimental technique. Clearly multi-angle light scattering is a consistent and useful technique to aid in the characterisation of polymers in solution, once any processing issues have been dealt with.

Further Work

The obvious extension to this work is the development of more powerful light scattering processing software, able to use different structural factors in the analysis to improve knowledge of the shape of the polymer in solution. However, plenty of information can be gained using the standard ASTRA software supplied by Wyatt.

With regards to F8T2 results, due to the short times needed to take a complete set of readings further *in situ* dissolution studies could be completed, particularly of F8T2 in toluene and the slight aggregation found in chloroform. These would be very helpful in understanding the dissolution dynamics, particularly when compared with SANS studies. Additionally further molecular weights could easily be studied and the range of solvents extended. Comparison with GPC values in different solvents would also be useful, as GPC seems to break apart any aggregation.

As with many of the techniques here, further experimentation in a larger range of solvents would be a useful result, particularly with respect to the conclusions drawn in *Chapter 5*, and light scattering is a good technique to use in tandem with SANS studies.

SAXS could be repeated, perhaps with more concentrated solution or extended to the GIWAXS studies discussed in *Chapter 6*.

Chapter 5: Spectroscopy and Thin Films

This extensive chapter covered my work using spectroscopic techniques on F8T2 in solutions and thin films, with absorption, photoluminescence, photoluminescence lifetime and photoluminescence quantum efficiency studies presented. Additionally, thermal and structural measurements are shown on F8T2 thin films, which were also tested in organic field effect transistors (OFETs).

Spectroscopic studies of F8T2 in solutions of THF and toluene showed strong PL quenching effects as solution concentration increases, which have been attributed to interchain interactions at concentrations around 0.01mg/ml, where interchain spacing is becoming close to the chain size in solution using values from *Chapter 4*. At higher concentrations, above ~0.1 mg/ml, self absorption from the large overlap of the PL and absorption spectra, leads to the complete loss of 0-0 and 0-1 peaks. Self-absorption effects were found in the solid phase, evident by strong-red shifts of the low wavelength peak, with vibronic structure still clearly visible.

F8T2 shows interesting solvatochromism and aggregation in the five solvents studied. Choice of solvent for solution based measurements is important, as is the importance of having well dissolved solutions. Aggregation and the red-shift of PL emission was observed with time in certain solvents, which can be related to solvent driven aggregation. Spectroscopic effects due to solvent choice, aggregation and thermal dissolution histories can also be seen in solid films. Most notably F8T2 cast from THF solutions are blue-shifted compared to the other solvent choices. PLQE values of F8T2 film were found to strongly decrease with solution ageing, except from THF films, again suggesting improved dissolution from that solvent, with some level of aggregation reducing PL efficiency in the others. Photoluminescence was studied as a way of determining transition temperature without the use of a DSC. This was partially successful, with reasonable estimates made of T_g and T_c from integrated PL values.

Finally thermal and vapour treatments of F8T2 films in OFETs were studied. AFM showed interesting results, but FET devices were very poor. The most useful result is the large improvement with OTS layers, but the large wetting problems. Further tests with F8T2 spin coated from a range of solvents would be helpful in improving these as would contact angle analysis.

Further Work

The obvious extension to this work, not only for F8T2 but for other polymers would be an extension of the solvatochromatic studies. Having a well dissolved polymer in spectroscopic measurements in

solution and thin films is vital, and understanding the polymer under study in solution is very important. Not least because of the ubiquitous nature of solution processing for these materials. Using newer CCD based spectrometers a very high data acquisition rate can be used, allowing even the fast aggregation of high concentration F8T2 in toluene to be dynamically studied.

The possibility of using optical methods to determine transition temperatures is intriguing and further study with larger F8T2 masses would be useful, as strong DSC peaks have been seen by other groups.

Chapter 6: Grazing Incident Wide Angle X-Ray Scattering

In the final experimental chapter Grazing Incident Wide Angle X-ray Scattering was used to study annealed F8T2, F8BT, SC005 and PFO thin films, with PFO additionally having *in situ* vapour exposure measurements taken.

Annealed but unaligned PFO films were fully indexed, with a very similar unit cell size to those found in the literature. Exposure to toluene vapour was found to affect the *b* and *c* axis unit cell dimensions very quickly, with striking changes occurring within 1 minute of vapour exposure. Some indexation was possible with the other polymers. F8BT was found, as in the literature, to pack preferentially with the backbone in the plane of the substrate, with four stacked chains per cell and regular sidechain spacing. F6T2, as an analogue of F8T2 was found to stack in a similar fashion to F8BT, but with smaller sidechain spacings. The new polymer SC005 was found to be a good candidate for GIWAXS measurements, and some level of directional alignment was found. It is likely to have a complex packing structure like PFO, but full indexation is not possible at this stage.

Further Work

GIWAXS is clearly a very powerful technique to use to understand the solid film structure of polyfluorene copolymers. Due to the disappointing alignment seen in these films, repeats with well aligned films would be an obvious extension, after further study to improve alignment. The high data acquisition rate available at CHESS due to its high flux means that *in situ* vapour measurements are a very interesting technique for further study. Obviously PFO exposure to different solvents would be interesting, as well as the timescales and unit cell changes due to different solvents. Finally, despite choosing to not study F8T2 due to the poor scattering in SAXS measurements, a brief study as to whether well aligned crystalline films could be investigated would be worthwhile.