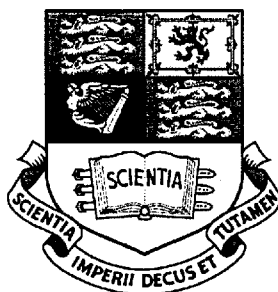


Role of Molecular Architecture and Interface Morphology on the Performance of Organic Solar Cells

A thesis submitted for the degree of
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ABSTRACT

Identifying and controlling the criteria which distinguish the most efficient organic solar cells plays a crucial role in their continuing development and forms the underlying theme of this research. In particular, this thesis sets out to refine the relationship between molecular architecture and photovoltaic behaviour and to clarify some of the key physical parameters that influence their performance.

Organic solar cells incorporating a vacuum codeposited donor-acceptor copper phthalocyanine (CuPc):C₆₀ mixed layer are described. Significant improvements in device performance are seen when mixed layers are used compared to discrete layers; these are rationalized by spectroscopic and morphological measurements. The discussion focuses on the mixed layer thickness, and, in particular, recognizes that there is a finite limit beyond which the benefits gained from enhanced exciton dissociation no longer outweigh the increased resistance to charge transport.

Post-fabrication heat treatments of CuPc:PhEt-PTC bulk heterojunctions are explored as a potential strategy for overcoming the mixed layer thickness limit, while annealing of the CuPc films in CuPc/C₆₀ discrete heterojunctions reveals the importance of controlling the molecular morphology and demonstrates how structural defects and rough D-A interfaces hinder device performance. On a fundamental physical level, the polymorphic transitions in CuPc and PhEt-PTC are elucidated.

Finally, bilayer solar cells comprising a novel self-assembling discotic liquid crystal complex are investigated. Optical studies confirm that uniform homeotropic alignment for the columnar tetragonal (Col_{tet,d}) mesophase of

(C₁₄O)₁₆TzCu is achievable not only between glass or quartz plates, but also when spin-coated onto ITO-coated glass substrates at room temperature. Nonetheless, the disordered arrangement of molecules within the columns ultimately limits device efficiency.

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LIST OF SYMBOLS, ABBREVIATIONS & COMPOUNDS

Symbols

E_F	Fermi level (eV)
η_p	power conversion efficiency (%)
FF	fill factor
J_{sc}	short-circuit current density (mA cm ⁻²)
l	exciton diffusion length (nm)
λ	wavelength (nm)
μ	mobility (cm ² V ⁻¹ s ⁻¹)
P_{inc}	incident light power intensity (mW cm ⁻²)
R_q	root-mean-square roughness (nm)
R_s	series resistance (Ω cm ⁻²)
R_{sh}	shunt resistance (Ω cm ⁻²)
V_{oc}	open circuit voltage (V)

Abbreviations

AM1.5	air mass 1.5
AFM	atomic force microscope
BHJ	bulk heterojunction
CT	charge-transfer
D-A	donor-acceptor
DHJ	discrete heterojunction
DLC	discotic liquid crystal
EBL	electron blocking layer

HOMO	highest occupied molecular orbital
IR	infra-red
J-V	current-voltage
K-cell	Knudsen effusion cell
LC	liquid crystal
LUMO	lowest unoccupied molecular orbital
OLED	organic light-emitting diode
OMBD	organic molecular beam deposition
PM-HJ	planar-mixed heterojunction
PV	photovoltaic
QCM	quartz crystal microbalance
UHV	ultra-high vacuum ($>10^{-9}$ Torr)
UV/Vis	ultra-violet/visible
XRD	X-ray diffraction

Compounds

Al	aluminium
BCP	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine)
(C ₁₄ O) ₁₆ TzCu	tetrakis (2,3,6,7-tetradodecyloxy) diazatriphenylenocyaninato
C ₆₀	fullerene
CuPc	copper phthalocyanine
H ₂ Pc	free base phthalocyanine
HBC	hexabenzocoronene
ITO	indium tin oxide
Me-PTC	N,N' dimethylperylene-3,4:9,10-bis-dicarboximide
MPc	metal phthalocyanine, where M=Cu, Zn etc.
Pc	phthalocyanine
PCBM	[6,6]-phenyl-C ₆₁ butyric acid methyl ester
PEDOT:PSS	poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate)

PhEt-PTC	N,N'-bis(phenylethyl)-perylene-3,4,9,10-bis(dicarboximide)
Por	porphyrin
PTCBI	3,4,9,10-perylene tetracarboxylic bis-benzimidazole
PTCDA	3,4,9,10-perylene tetracarboxylic dianhydride
PTCDI	3,4,9,10-perylene tetracarboxylic diimide

1 INTRODUCTION

1.1 Organic semiconductors

Conjugated molecular materials that exhibit semiconducting behaviour are of considerable interest not only from a fundamental perspective but also because of their prospective application in the fields of chemical sensing (JANATA, 2003), photovoltaics (SHAHEEN *et al.*, 2005), digital circuitry (REESE *et al.*, 2004) and display technology (VAETH, 2003). The appeal of these materials lies primarily in their chemical diversity and processing characteristics, having the potential to be manufactured at low cost, over large areas and onto a wide range of cheap, flexible substrates. Their tuneable (opto)electronic properties, by means of synthetic chemistry and controlled morphological modification, allows for tailoring to suit individual device requirements (FORREST, 2004).

Indeed, solar cells employing thin films of 'small molecule' and polymeric material as their photoactive components have received much attention in recent years (see, for example, (FORREST, 2005), (JANSSEN *et al.*, 2005) and references therein). However, in contrast to conventional inorganic semiconductors, the dominant optical charge generating processes in organic films involve the formation of strongly-bound excitons that have insufficient energy to dissociate into free carriers in a pure bulk phase (GREGG, 2003). This inherent constraint, combined with a charge transport mechanism that involves hopping between localized states rather than transport within a band (NELSON, 2002), have been the principal obstacles in achieving commercially viable device efficiencies. Although significant progress has been realized in addressing these issues (SARICIFTCI, 2004), their continuing development will require the optimisation of existing device architectures and the preparation of novel organic materials.

The purpose of this introduction is to review the current state of organic photovoltaic technology (with particular emphasis on small molecule devices fabricated by vacuum sublimation), to present an overview of the photophysical processes arising in organic semiconductors, and to describe the electronic and optoelectronic properties of the molecular materials utilised in this study.

1.2 Organic photovoltaics – a selective history

A comprehensive review of the early history of organic solar cells can be found in (CHAMBERLAIN, 1983) and (SIMON & ANDRÉ, 1985). Briefly, these first molecular-based devices comprised a vacuum-evaporated porphyrin (Por) or phthalocyanine (Pc) thin film (typically no more than 100 nm thick) sandwiched between two dissimilar metal electrodes. Their rectifying behaviour (i.e., the asymmetric conduction) under an oxygenated atmosphere was attributed to the formation of a Schottky junction between the '*p*-type' organic semiconductor and the lower work function metal (HOPPE & SARICIFTCI, 2004). However, the potential gradient generated by the offset in electrode work functions is seldom high enough to dissociate the strongly-bound photogenerated excitons, limiting the photoactive region to a small area in the vicinity of the metal contact (HALLS & FRIEND, 2001). This, in addition to the necessity for bipolar charge transport, which results in high recombination losses, means that Schottky-type devices like these rarely display power conversion efficiencies above 0.01% (NELSON, 2002).

In his seminal publication, Tang (TANG, 1986) demonstrated that the interface between two organic semiconductors of contrasting ionisation potential and electron affinity could serve as a site for efficient exciton dissociation. The introduction of this donor-acceptor (D-A) heterojunction, fabricated by the sequential deposition of a perylene tetracarboxylic derivative (PTCBI) and

copper phthalocyanine (CuPc), resulted in a power conversion efficiency of 0.95%, an order of magnitude greater than previous values. The use of two distinct organic semiconducting layers provides separate and continuous electron and hole pathways, reducing the likelihood of recombination, in addition to distancing the exciton generating donor-layer from the cathode, thus minimising the non-radiative loss processes that can occur between excitonic states and metal electrodes (HALLS & FRIEND, 2001).

It was soon recognized that the short exciton diffusion lengths of organic semiconductors, with respect to the film thickness required for comprehensive optical absorption, was a fundamental limiting factor in achieving higher device efficiencies. Hiramoto and co-workers (HIRAMOTO *et al.*, 1990; HIRAMOTO *et al.*, 1991) employed novel device architectures in order to increase the effective thickness of the absorbent layers, demonstrating both the first ‘tandem’ and ‘bulk heterojunction’ devices. The former consisted of a stack of two similar phthalocyanine (H₂Pc) / perylene derivative (Me-PTC) discrete heterojunctions separated by a thin (~10 nm) semi-transparent layer of gold, which acted as a recombination zone for unpaired charge carriers generated in the device. Although the open circuit voltage (V_{oc}) of the tandem device was equal to twice that of the equivalent single heterojunction cell, the power conversion efficiency was considerably lower due to the absorption of light by the interstitial metal layer and an increased series resistance. The use of codeposition, however, proved more successful. The nanostructured D-A interface of an intermediate mixed layer (H₂Pc / H₂Pc:Me-PTC (1:1 ratio) / Me-PTC) ensured that excitons were photogenerated within diffusion range of a dissociation site and was the principal reason behind the twofold increase in the photocurrent. Despite these promising results, device efficiencies remained around the 1% mark.

Continued improvements in organic photovoltaic efficiencies can, to a great extent, be attributed to the discovery of C₆₀ (KROTO *et al.*, 1985), the invention of a method for its isolation in bulk quantities (KRÄTSCHMER *et al.*, 1990), and the

subsequent observation of fast charge transfer in conjugated polymer/C₆₀ composite systems (SARICIFTCI *et al.*, 1992). Its use has become increasingly ubiquitous, being either vacuum sublimed in conjunction with metal-phthalocyanines (ROSTALSKI & MEISSNER, 2000; SULLIVAN *et al.*, 2004), or spin-coated from solution (in its soluble form, PCBM) as part of a blend (BRABEC *et al.*, 2001). In polymeric systems, where the donor and acceptor materials phase separate during spin-coating and solvent evaporation, there are considerable efforts being directed at optimizing blend morphology and D-A percolation (SHAHEEN *et al.*, 2001; GEENS *et al.*, 2002; MARTENS *et al.*, 2003) while post-fabrication heat treatments in order to enhance crystallization of the polymer have also been investigated (PADINGER *et al.*, 2003). Peak efficiencies are currently at ~3.5% for large area polymeric devices (PADINGER *et al.*, 2003; WALDAUF *et al.*, 2004). Similarly, work on small molecule devices has focused mainly on optimizing film thicknesses (PEUMANS & FORREST, 2001) and composition ratios (GEBEYEHU *et al.*, 2003; HEUTZ *et al.*, 2004) in discrete and bulk heterojunctions respectively, with maximum power conversion efficiencies in the range of 3-6% for phthalocyanine-C₆₀ and pentacene-C₆₀ devices (PEUMANS & FORREST, 2001; XUE *et al.*, 2004; YOO *et al.*, 2004).

In contrast to polymer blends, the thermal annealing of molecular-based mixed systems, in order to achieve increased crystallinity or to induce phase segregation, has proven largely unsuccessful. This is mainly due to the increased film roughness and high pinhole density associated with annealing small molecule films at high temperatures (FORREST, 1997). Recent work by Peumans *et al.* (PEUMANS *et al.*, 2003), however, has demonstrated that a metal 'capping' layer can be utilized to confine a codeposited film (CuPc:PTCBI) to a fixed geometry during the annealing process, allowing the formation of an interpenetrating D-A network without the detrimental surface roughening effects. Corresponding efficiencies were observed to be 50% higher than that of a discrete CuPc/PTCBI cell.

Although the relatively fine-scale mixing in blends and codeposited films favors efficient photogeneration of charges, carriers must often travel through convoluted pathways or opposing domains in order to reach the relevant electrode, thereby increasing the chances of recombination (HALLS & FRIEND, 2001). Structural control over film morphology on the sub-micron scale therefore becomes desirable. Interdigitated structures achieved by thermal annealing (as described above), through compositional grading of molecular films (SULLIVAN *et al.*, 2004) or *via* lamination techniques (GRANSTRÖM *et al.*, 1998), have been shown to benefit both charge separation and charge collection but often require complex fabrication procedures. For that reason, the synthesis and application of solution-processible materials that exhibit supramolecular order *via* ‘self-assembly’ has become a highly topical field of research (recently reviewed by (SIMPSON *et al.*, 2004)). A promising example exploited a liquid crystalline hexabenzocoronene (HBC)-perylene diimide blend that vertically phase separated to a bilayer after spin-coating, while still retaining good percolation at the interface, to achieve a peak external quantum efficiency of 34% (SCHMIDT-MENDE *et al.*, 2001). Of the numerous materials available, discotic liquid crystals are particularly appropriate because of their long-range order, though there are comparatively few published reports on their photovoltaic application, primarily because achieving uniform homeotropic alignment (in which the columns are stacked perpendicular to the substrate) in suitable large-core discotic compounds has proven difficult (O’NEILL & KELLY, 2003). Consequently, device efficiencies have tended to be rather low (<0.1%) (YOO *et al.*, 2004), though additional improvements are envisaged through the optimization of these self-assembled systems.

1.3 Fundamental photophysical theory

The photoinduced generation of charge and its subsequent transfer between molecules or their subunits is the underlying mechanism of organic solar cell device operation (BÄSSLER, 1997), a process that depends not only upon the properties of the individual molecules but also on the structure of the molecular semiconductor as a whole (WRIGHT, 1995). The fundamental aspects relating to these processes and properties, beginning with the physics of optical transitions in monomers and dimers, and then expanded to encompass the formation, migration and dissociation of excited states in molecular crystals, are elucidated in the following sections.

1.3.1 *Molecular electronic structure*

The state of a molecule (structure, energetics and dynamics), and ultimately the macroscopic properties of molecular solids can, in principle, be determined from its corresponding quantum mechanical wavefunction, $\psi(\{r_j\}, \{R_n\})$, a combination of all the electronic $\{r_j\}$ and nuclear $\{R_n\}$ coordinates with respect to both space (orbital, position) and spin. This can be obtained by solving the Schrödinger equation of the complete many electron system. However, solving such an N -body problem empirically proves to be impossible. Consequently, much molecular physics relies on the use of the Born-Oppenheimer approximation, which states that the response of an electron relative to the displacement of the nuclei occurs almost instantaneously as a result of the large difference in mass ($m_{\text{nucleus}} \gg m_{\text{electron}}$) (POPE & SWENBERG, 1982). Accounting for nuclear and electronic interactions therefore becomes greatly simplified because nuclei are essentially fixed in position on the timescale of electronic motion, allowing for the molecular wavefunction to be factorised into independent

electronic and nuclear components. Solving the electronic Schrödinger equation for every set of nuclear coordinates gives rise to a molecular potential energy surface for each electronic state. The lowest energy solution provides the ground state surface while the other roots generate the excited state surfaces, although typically only the lowest of these, the first excited state, is of interest. Electronic transitions between potential energy surfaces, such as the promotion of an electron from the ground to the first excited state ($S_0 \rightarrow S_1$), are governed by the Franck-Condon principle (ATKINS & FRIEDMAN, 1997).

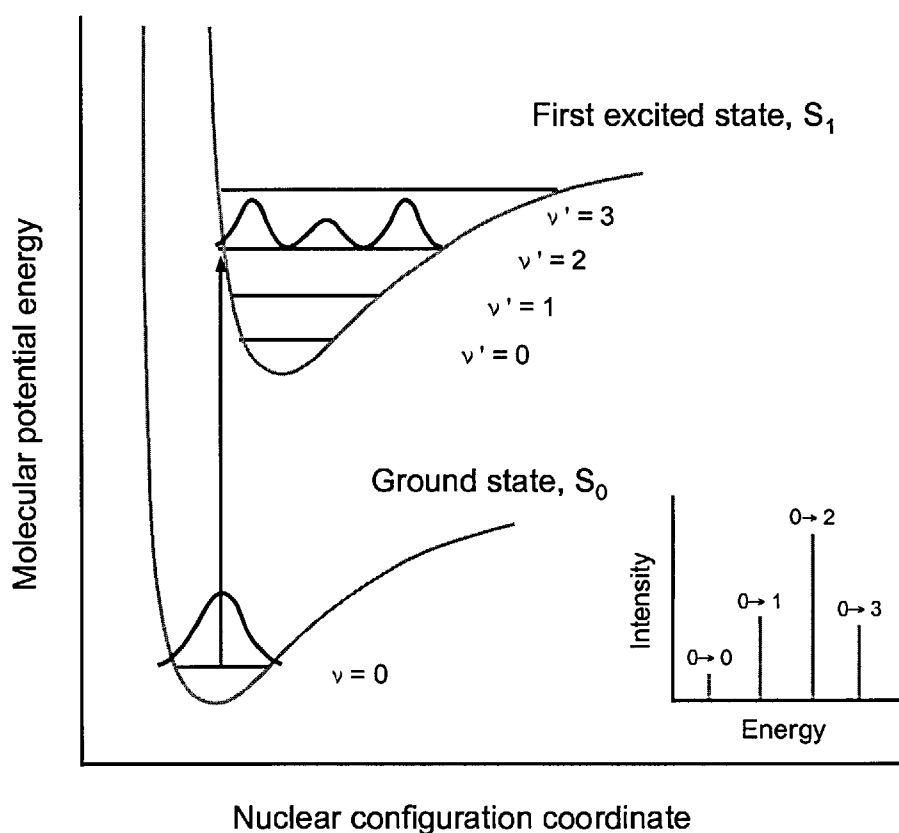


Figure 1.1 – The quantum mechanical interpretation of the Franck-Condon principle. The electronic transition between the lowest vibrational level of the ground state $v = 0$, and the $v' = 2$ vibrational level of the first excited state, for example, is represented by a vertical arrow. Transitions to adjacent vibrational levels can also take place but are less intense, as shown in the corresponding line absorption spectra (after TURRO, 1991).

Classically, the Franck–Condon principle is the approximation that the initial and final nuclear geometries of a molecule do not change during electronic transitions on the basis that these occur much more rapidly ($\sim 10^{-15}$ s) than vibrational motion ($\sim 10^{-13}$ s). The resulting state is called a Franck–Condon state, in which the transitions involved are vertical in nature (shown schematically in Fig. 1.1). The quantum mechanical formulation of this principle is embodied in a nuclear or vibrational wavefunction (χ) for which electronic transitions demand a net positive overlap of the nuclear wavefunctions in the initial (χ_i) and final (χ_f) states at the instant of transition. This is given by the Franck–Condon integral, $\langle \chi_i | \chi_f \rangle$, where the probability of any electronic transition is directly related to the square of the vibrational overlap integral, $\langle \chi_i | \chi_f \rangle^2$, and is referred to as the Franck–Condon factor. It is an indication of the relative intensities of vibrational bands in electronic absorption and emission spectra (TURRO, 1991).

Furthermore, selection rules for optical transitions dictate that some electronic transitions are ‘allowed’ while others are ‘forbidden’, though such transitions are generally forbidden ‘to first order’ only, which means they may occur in practice with low probabilities if the selection rule is relaxed by an appropriate perturbation (KLESSINGER & MICHL, 1995). The spin multiplicity rule ($\Delta S = 0$) demands that transitions must involve the promotion of electrons without a change in spin orientation. Therefore singlet-singlet and triplet-triplet transitions are allowed, while singlet-triplet and triplet-singlet transitions are forbidden. Relaxation of the spin selection rules through spin-orbit coupling, which is particularly significant in the presence of atoms of high atomic number (heavy atom effect), can give rise to weak spin forbidden bands. Thus, triplet states are usually formed by intersystem crossing from an excited singlet state rather than by direct excitation from the ground state. Decay of singlet and triplet excited states back to the ground state may be accompanied by fluorescence or phosphorescence, respectively (POPE & SWENBERG, 1982). For

centrosymmetric molecules, the Laporte selection rule ($\Delta l = \pm 1$) applies: the only allowed transitions are those that are accompanied by a change of parity. Thus, the $\pi \rightarrow \pi^*$ transition is symmetry allowed since the π orbital is *ungerade* (*u*) and the π^* is *gerade* (*g*), while a transition from σ (*g* symmetry) to π^* (also *g* symmetry) is parity forbidden. However, this selection rule can be lifted if the geometry of the orbitals involved becomes distorted due to vibronic coupling (TURRO, 1991).

1.3.2 Excited states in molecular aggregates

Though many of the spectral properties of molecular aggregates and crystals are directly traceable to properties of the individual molecules, the evident discrepancies in position, shape and intensity of their corresponding electronic absorption spectra arise from interactions between the electronic states of two or more molecules (POPE & SWENBERG, 1982; WRIGHT, 1995). For the simplest case of a dimer pair, the electronic coupling and subsequent energy level diagram is depicted in Fig. 1.2 below.

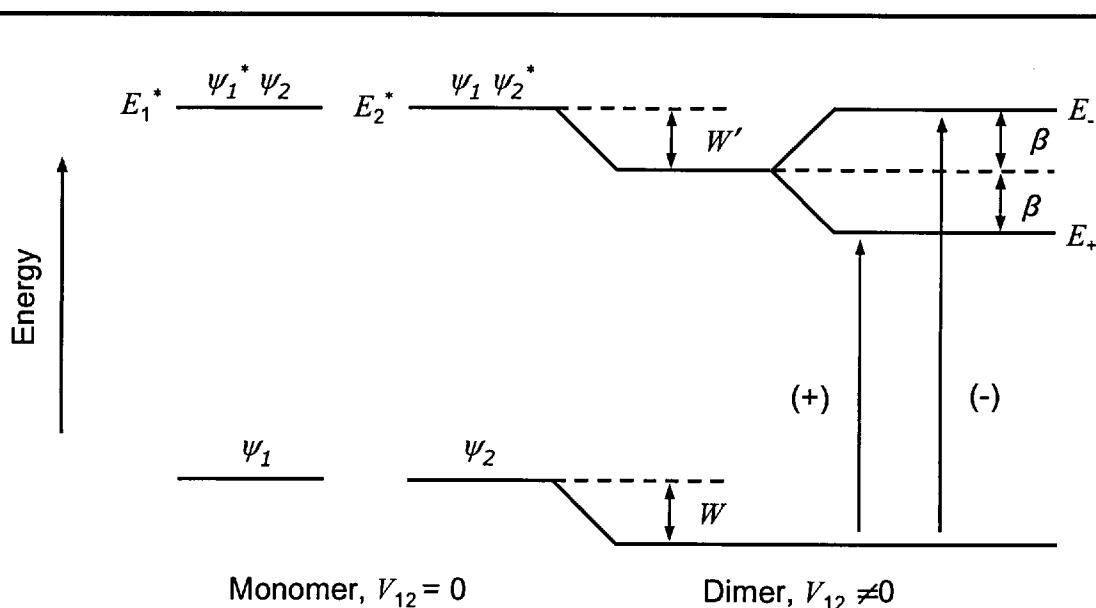


Figure 1.2 – A schematic showing the effect of physical dimer formation on the excited state energy levels and exciton band splitting. See text for definition of symbols (from POPE & SWENBERG, 1982).

The ground-state wavefunction (ψ_g) of this so-called orientated physical dimer, in which spatial coordination but no chemical union exists, can, if the vibrational and spin parts of the overall wavefunction are suppressed, be approximated to

$$\psi_g = \psi_1 \psi_2 \quad (1.1)$$

where ψ_1 and ψ_2 are the ground-state wavefunctions of molecules 1 and 2, respectively. Assuming that both molecules have equal probability of being excited, then the wavefunction of the singly excited state ($\psi_{e\pm}$) is given by

$$\psi_{e\pm} = \frac{1}{\sqrt{2}} (\psi_1 \psi_2^* \pm \psi_1^* \psi_2) \quad (1.2)$$

where ψ_1^* and ψ_2^* are the wavefunctions of the corresponding excited state molecules. Intermolecular interactions between the two identical molecules give rise to dimer energies that can be expressed as

$$E(\pm) = E_1^* + E_2 + W' \pm \beta \quad (1.3)$$

Equation 1.3 is defined in terms of the monomer ground and excitation energies (E_2 and E_1^*), the resonance interaction energy ($\beta = \langle \psi_1^* \psi_2 | V_{12} | \psi_1 \psi_2^* \rangle$) and the coulombic energy of interaction of the charge distribution of the excited state ($W' = \langle \psi_1^* \psi_2 | V_{12} | \psi_1^* \psi_2 \rangle$). The term V_{12} represents the intermolecular interaction energy operator. The magnitudes of the coulombic and resonance interaction energies, which depend on such factors as the polarity of the ground and excited state and the overlap of the relevant orbitals of the two molecules, determine the spectral shifts and band splitting of electronic absorption spectra. Some of these transitions may be forbidden as a result of the dimer orientations. For the ($\pm$) dimer states, the corresponding dimer transition moment can be expressed as

$$M_{(\pm)} = \frac{1}{\sqrt{2}} (M_1 \pm M_2) \quad (1.4)$$

where M_1 and M_2 are the transition dipole moments for the individual molecules 1 and 2 (WRIGHT, 1995). The relative orientation of the dipole moments for both molecules will therefore determine the intensity of the electronic transition, as depicted in Fig. 1.3. For cofacial dimers (Fig. 1.3(a)), transitions to the higher energy levels are allowed and the associated spectral band is shifted to shorter wavelengths relative to its position in the isolated molecular spectrum. This is known as a hypsochromic or blue shift. Conversely, for coplanar arrangements (Fig. 1.3(b)), the lower energy state has a larger transition dipole moment and the net effect is a bathochromic or red shift. A splitting of the band in the electronic or vibrational spectra (Fig. 1.3(c)), owing to the dipoles cancelling each other out neither in the higher nor in the lower energy configurations, is referred to as 'Davydov splitting' (MCKEOWN, 1998).

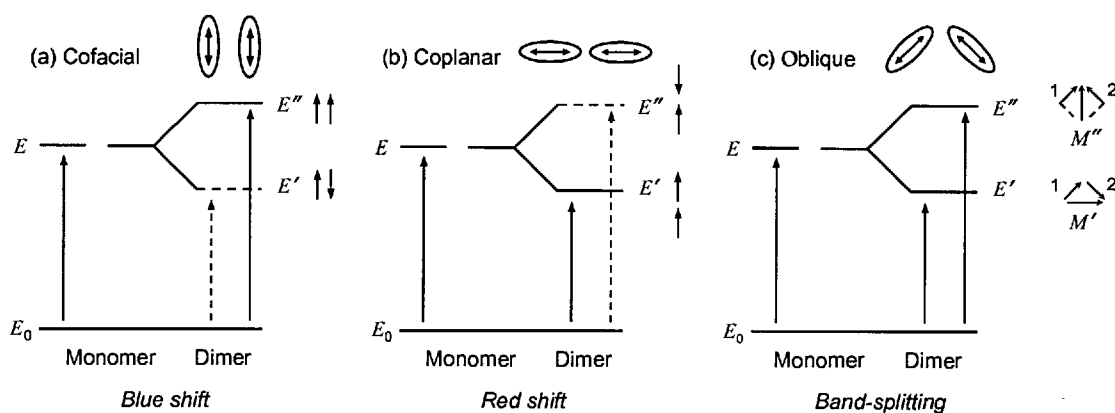


Figure 1.3 – Exciton splitting in dimers of different geometries. The long solid and dashed arrows represent dipole transitions (allowed and forbidden, respectively) while short arrows denote monomer transition dipoles. The characteristic shifts/splitting of absorption spectra are also given (from POPE & SWENBERG, 1982).

1.3.2.1 Excitons

Extending the physical dimer model to an 'infinite' array of identical molecules leads to the formation of a band of energy levels, whose width depends upon the intermolecular overlap. Typically these are relatively narrow (<0.1 eV) as a consequence of the weak coupling in molecular crystals. The corresponding electrically neutral excited states are referred to as 'excitons' and are defined more specifically by the extent of their delocalisation over the crystal lattice (WRIGHT, 1995). The highly localised yet mobile excited states common to amorphous semiconductors are known as Frenkel excitons, and have radii (i.e., mean electron-hole separation) on the order of the molecular size, generally <5 Å. This is in contrast to Wannier (or Wannier-Mott) excitons that are characteristic of conventional inorganic semiconductors, in which the radius is larger than the lattice spacing. Additionally, it is possible for excitons to occupy an intermediate spatial configuration such that the charge pairs are localized at the nearest, or next-nearest, molecules. Labelled Charge-Transfer (CT) excitons, these are generally treated as Wannier excitons for all but the lowest states, and are considered an important transitional state in the creation of free carriers in the photovoltaic process (POPE & SWENBERG, 1982).

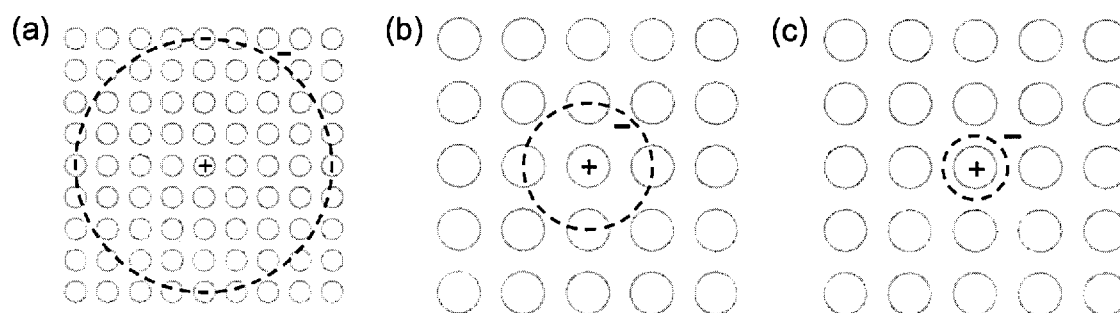


Figure 1.4 – Graphic representation of: (a) Wannier, (b) Charge-Transfer (CT), and (c) Frenkel excitons. Frenkel excitons in molecular semiconductors have binding energies of about 0.5-1.0 eV, compared to 25 meV for the Wannier excitons found in silicon, for example. Excitons in the latter can therefore spontaneously dissociate into charge pairs at room temperature ($kT = 26$ meV) (from WRIGHT, 1995).

1.3.2.2 Frenkel exciton migration and geminate pairs

Intermolecular interactions can lead to the transfer of electronic excitations from one molecule to another. In a perfect molecular crystal the exciton states can propagate in a coherent wave-like manner, but the presence of structural disorder (impurities and defects) and natural lattice vibrations introduce energy levels that become accessible to the exciton, limiting the time for which excitons remain coherent. Exciton migration consequently becomes incoherent, being described as a random hopping-like motion between nearest-neighbour sites.¹ The exciton diffusion length, l , or average displacement of an exciton from its point of origin, is given by the relationship $l = \sqrt{D\tau}$, where τ is the exciton lifetime and D the diffusion coefficient, though the total distance that an exciton may travel during its lifetime may be much greater than this (POPE & SWENBERG, 1982). Typically, l is in the region of 10-40 nm for polycrystalline molecular semiconductors (PEUMANS *et al.*, 2003).

Exciton diffusion can be limited by a variety of processes during its lifetime including trapping at defects or impurities, interactions with other excitons or with a photon, or by dissociation to yield charge-carriers (a necessary requirement for solar cell operation). Dissociation in monomolecular devices can usually only take place if there is charge transfer to an extrinsic state because the built-in electric field does not exert sufficient force to dissociate the excitons. However, this process can become energetically favourable at an

¹ It should be noted that along with exciton migration, excited state energy transfer may also proceed by other means. Pope and Swenberg (POPE & SWENBERG, 1982) make a distinction between energy transfer and energy migration in that the latter comprises the translational movement of an electronic excited state through a molecular solid. Energy transfer processes, on the other hand, proceed *via* radiative or non-radiative mechanisms that depend on the overlap between the fluorescence and absorption spectra of a single respective donor and acceptor molecule. Radiative transfer, often termed cascade or trivial energy transfer, is one of the simplest mechanisms and involves the emission of a photon from a donor molecule and subsequent absorption by an acceptor molecule. Consequently it is a process that can involve large distances (>100 Å). Resonance, or Förster, energy transfer is a long-range (~40-100 Å), non-radiative, dipole-dipole coupling of donor and acceptor molecules. It is restricted to allowed transitions and thus the transfer of singlet excitons, though expansion of the theory by Dexter accounts for short-range (<20 Å) triplet energy transfer *via* electron exchange.

interface between a donor material with a low ionization potential and an acceptor material with a high electron affinity. Exciton dissociation initially results in the formation of an interfacial ‘geminate charge-pair’, where the electron is localized in the LUMO of the acceptor with the correlated hole residing in the HOMO of the donor (ARKHIPOV & BÄSSLER, 2004). The probability of charge-pair separation subsequently depends on the competition between the attractive Coulomb force and the electric field at the D-A heterojunction that acts to separate the two carriers. Those charge-pairs that do not separate can recombine either in geminate recombination processes (referring to the recombination of a charge carrier with its parent countercharge) or alternatively with an unrelated electron/hole, decaying either radiatively, by the emission of light, or non-radiatively, by the production of heat. A number of models based on the Onsager treatment of field-induced exciton dissociation in the bulk of a disordered solid (in which the probability of geminate pair dissociation is discussed in terms of the distance, or thermalization radius (r_{th}), within which the two charges will spontaneously recombine (WRIGHT, 1995)), have recently been proposed to account for these processes in small molecule heterojunctions (PEUMANS & FORREST, 2004) and polymer blends (ARKHIPOV *et al.*, 2003; MORTEANI *et al.*, 2004). A schematic diagram detailing the former is shown in Fig. 1.5.

Once a metastable charge-separated state has been attained, the net electrochemical potential gradient generated across the D-A heterojunction acts as an effective driving force for carrier extraction. Its origins can be traced to the difference in electron and hole carrier concentration densities at either side of the interface and to the presence of a built-in electric field. The latter is provided, in undoped organic transport layers, by the difference in electrode work functions. The corresponding transport processes are referred to as the diffusion and drift currents (HOPPE & SARICIFTCI, 2004; GREGG, 2005).

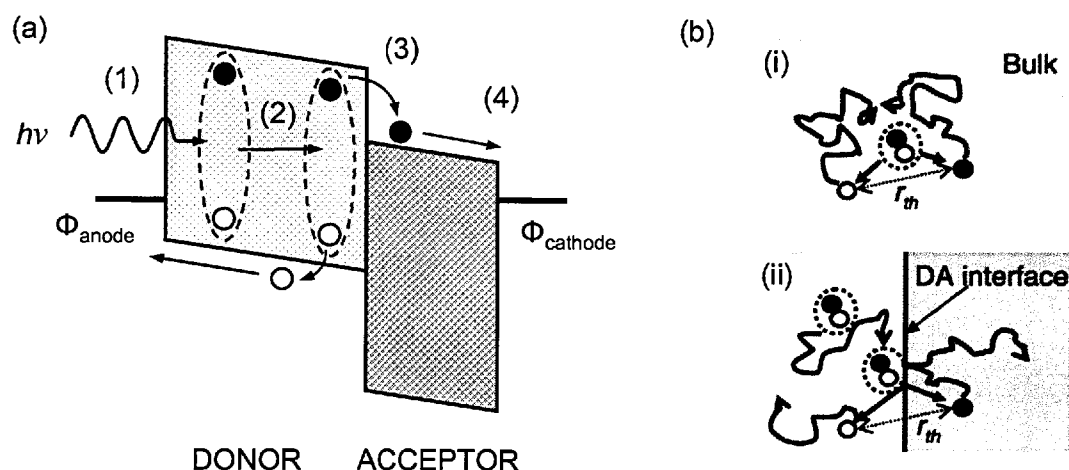


Figure 1.5 – (a) Schematic energy level diagram of a D-A heterojunction. Photocurrent generation entails the four successive steps of: (1) photoinduced exciton generation; (2) diffusion of the exciton to the D-A heterojunction; (3) interfacial dissociation of the exciton and geminate pair formation; and (4) transport of free-charge carriers to the electrodes. (b) (i) The Onsager theory of geminate-pair separation in the bulk of a disordered solid assumes that the exciton autoionizes immediately after photogeneration, resulting in a 'hot' carrier that can travel through the organic medium until it relaxes at a distance r_{th} away from the positively charged parent molecule; (ii) The model proposed by Peumans and Forrest (PEUMANS & FORREST, 2004) for molecular D-A heterojunctions assumes that the initial thermalization process is analogous to that in the bulk but also incorporates the influence of the spatial and energetic effects of the D-A interface (i.e., excess kinetic energy resulting from HOMO and LUMO offsets) (adapted from PEUMANS & FORREST, 2004).

1.3.3 Charge transport

Carrier mobility is largely determined by the intrinsic properties of the organic material such as the crystal symmetry and periodicity (WRIGHT, 1995). The absence of long-range order in polycrystalline organic semiconductors results in room-temperature values that are, in general, considerably less than the $0.1 - 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ that is often quoted as the 'band-to-hopping' transition boundary (DIMITRAKOPOULOS & MASCARO, 2001). Consequently, charge transport proceeds *via* a mechanism that involves thermally activated hopping between localized states. Even though temperature- and field-dependent conductivity measurements support this notion, the precise nature of the hopping mechanism still attracts considerable debate. The two most common explanations that quantify this behaviour relate to the inherent energetic and

static disorder of the molecular solid, and in many instances, the carrier's interaction with phonons, i.e. polaron formation (HALLS & FRIEND, 2001). The former, exemplified in the so-called 'Gaussian Disorder Model', was originally developed to describe the conductivity in molecularly doped polymers and depicts carrier hopping as a 'random walk' among dopant molecules with characteristic Gaussian-distributed transport states of an energetic width of about 0.1 eV (BÄSSLER, 1997). The polaron formalism, on the other hand, considers the self-trapping of charge carriers as a consequence of the strong interactions between carriers and molecular vibrations, resulting in a localized charge and lattice distortion. Polaron hopping requires the coincident transport of this molecular deformation (MIRCHIN & PELED, 2004). Despite considerable success in correlating theory and experiment, neither model can fully simulate the charge carrier mobility dependence on electric field strength and temperature in conjugated materials (HALLS & FRIEND, 2001).

1.4 Device Characterisation

The current-voltage ($J-V$) characteristics of a PV device provide a means of quantifying the useful work that it produces (shown schematically in Fig. 1.6). The short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) correspond to the conditions at which the maximum photogenerated current flows through the cell and to the point at which this current is balanced to zero, respectively. At a certain current/voltage within this regime, denoted by the subscripts 'm', their product will be maximised and the largest output power of the device obtained (NELSON, 2003; HOPPE & SARICIFTCI, 2004). The ratio of the two rectangular areas defined by $J_m V_m$ and $J_{sc} V_{oc}$ gives rise to the so-called fill factor (FF)

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (1.5)$$

As this ratio approaches 1, the curve becomes more 'square' and the device more efficient. The power conversion efficiency (η_p) can subsequently be determined by relating the specific $J-V$ parameters to the incident light power intensity (P_{inc}),

$$\eta_p = \frac{J_{sc} V_{oc} FF}{P_{inc}} \quad (1.6)$$

where P_{inc} is typically equal to 100 mW cm⁻² (AM1.5 spectrum). Clearly, increasing the J_{sc} and V_{oc} , while simultaneously retaining a high FF , are paramount in obtaining high device efficiencies, though these are often dependent on the intrinsically poor semiconducting properties of the organic thin films.

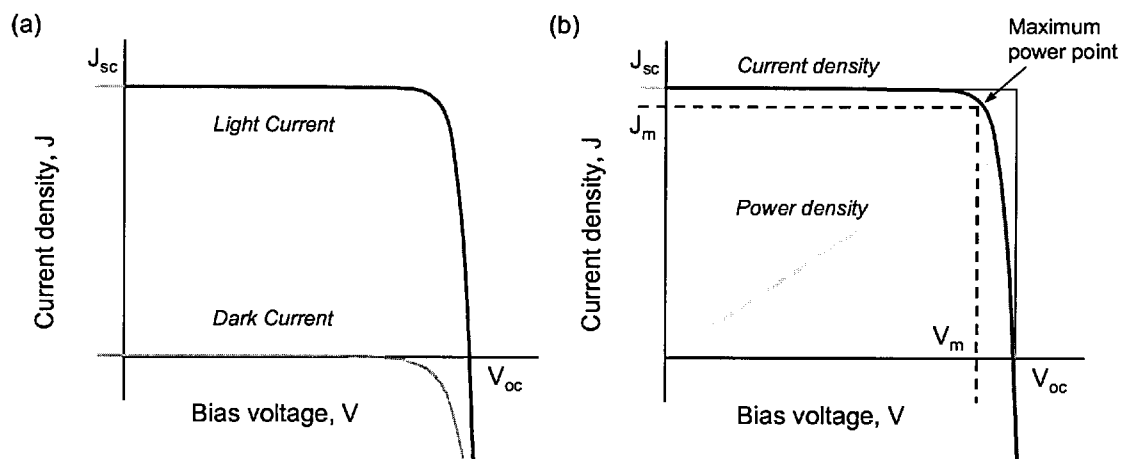


Figure 1.6 – (a) Current-voltage (J - V) characteristic of an ideal diode in the dark (grey line) and under illumination (black line). The sign convention is such that the short-circuit photocurrent is positive, though J - V curves are typically plotted in the opposing (negative photocurrent) quadrants; **(b)** Current-voltage (black) and corresponding power-voltage (light grey) curves of an ideal cell. The important parameters utilised in determining device efficiency, including the rectangles that establish the FF, are shown (from NELSON, 2003).

The short-circuit current, for example, is considerably lower in organic devices than that found in conventional inorganic devices. This is partly due to the mismatch between the solar spectrum and the optical absorption profile of the organic materials, but also due to low charge-carrier mobilities (MILHAILETCHI *et al.*, 2003). Improvements in J_{sc} have been realized by optimizing processing conditions and thin film morphologies (SHAHEEN *et al.*, 2001; HEUTZ *et al.*, 2004), by increasing polymer crystallinity (BRABEC, 2004) and by incorporating light-harvesting structures (PEUMANS *et al.*, 2000). Open-circuit voltages, on the other hand, display relatively high values and are sensitive to the work function difference between electrodes (MILHAILETCHI *et al.*, 2003), interfacial effects (RAMSDALE *et al.*, 2002) and to donor-acceptor energy levels (BRABEC *et al.*, 2001). Nevertheless, it has been suggested that the mismatch in HOMO-LUMO levels in polymer/fullerene devices accounts for a loss of ~ 0.4 - 0.8 eV in the electron transfer reaction (JANSSEN *et al.*, 2005). Furthermore, charge transport loss mechanisms, embodied in the equivalent electrical circuit as the shunt and series resistances (R_{sh} and R_s , respectively), may act to lower the FF and

adversely influence device performance. The latter accounts for the resistance to charge transfer in the bulk, across semiconductor/electrode interfaces and through resistive contacts, while the shunt, or parallel, resistance arises from leakage of current within the device (NELSON, 2003).

1.5 Molecular materials

The semiconducting properties of molecular materials arise from the delocalization of the π -electron system, and, in particular, due to the overlap of the p_z orbitals (HALLS & FRIEND, 2001). For planar π -electron conjugated systems, many of the bulk properties, such as the charge carrier transport, are dependent on the degree of intermolecular π -electron interaction and consequently on the stacking and organization of the material (POPE & SWENBERG, 1982). Thus an understanding of the molecular arrangement in thin films is required in order to assess the suitability of a material for its potential application in PV devices. The work comprising this thesis is based on four molecular materials (Fig. 1.7(a-d)), two electron donating materials in the form of copper phthalocyanine (CuPc) and its discotic liquid crystalline derivative (C₁₄O)₁₆TzCu, and two electron accepting materials in the form of fullerene (C₆₀) and the perylene diimide derivative PhEt-PTC.²

² In the context of organic semiconductor physics, the terms 'donor' and 'acceptor' refer to the relative positions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of two dissimilar organic materials, rather than referring to the types of dopants that may be used to create characteristic inorganic n- and p-type layers. Likewise, their denotation as being of the 'n-type' or 'p-type' indicate that the majority carriers are electrons and holes respectively, though this does not necessarily imply that the majority carriers have the higher carrier mobility (WÖRHLE *et al.*, 1996).

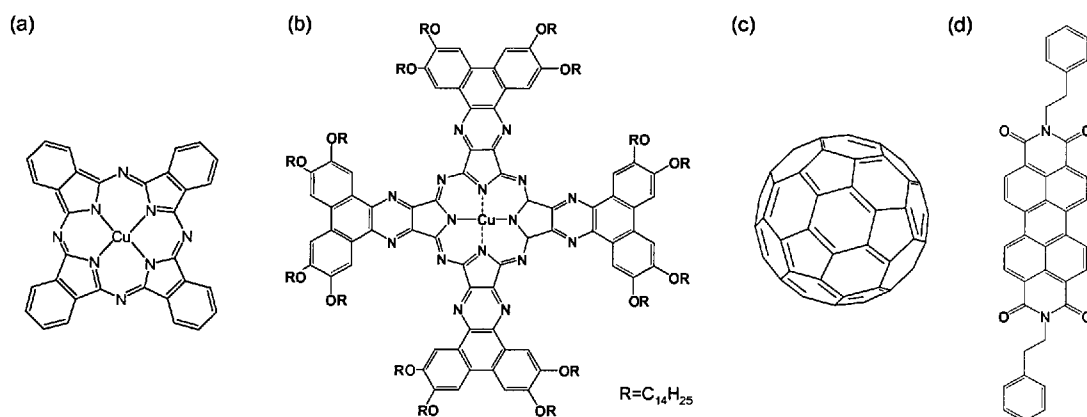


Figure 1.7 – Chemical structure of (a) copper phthalocyanine (CuPc) and (b) its discotic liquid crystal derivative, the tetrakis (2,3,6,7-tetradodecyloxy) diazatriphenylenocyaninato metal complex, $(C_{14}O)_{16}TzCu$; (c) fullerene (C_{60}) and (d) the perylene derivative N,N' -bis(phenylethyl)-perylene-3,4,9,10-bis(dicarboximide), (PhEt-PTC).

1.5.1 Copper phthalocyanine

Phthalocyanines (Pc) are a versatile class of material that have found extensive use in a wide range of electronic and optoelectronic applications (LEZNOFF & LEVER, 1989). About seventy elemental ions can be placed in the central cavity of the polyaromatic ring (MCKEOWN, 1998), giving rise to derivatives of which most notably CuPc (TANG, 1986; PEUMANS & FORREST, 2001), H_2Pc (HIRAMOTO *et al.*, 1991) and $ZnPc$ (ROSTALSKI & MEISSNER, 2000; MURGIA *et al.*, 2001) have been used in molecular solar cells. Structurally, the weak intermolecular interactions within phthalocyanine crystals enable different crystallographic ordering, with nine polymorphic forms known for CuPc depending on the preparation conditions (MATHER, 1999), though vacuum sublimed thin films crystallize predominantly as one of two polymorphs, α and β . The α -phase is obtained by growth onto weakly interacting substrates at room temperature (GOULD, 1996), while the so-called 'thermodynamically stable' β -phase results from deposition onto elevated (>200 °C) substrate temperatures or after thermal annealing of the as-deposited thin film (SNOW & BARGER, 1989; SHIHUB & GOULD, 1996).

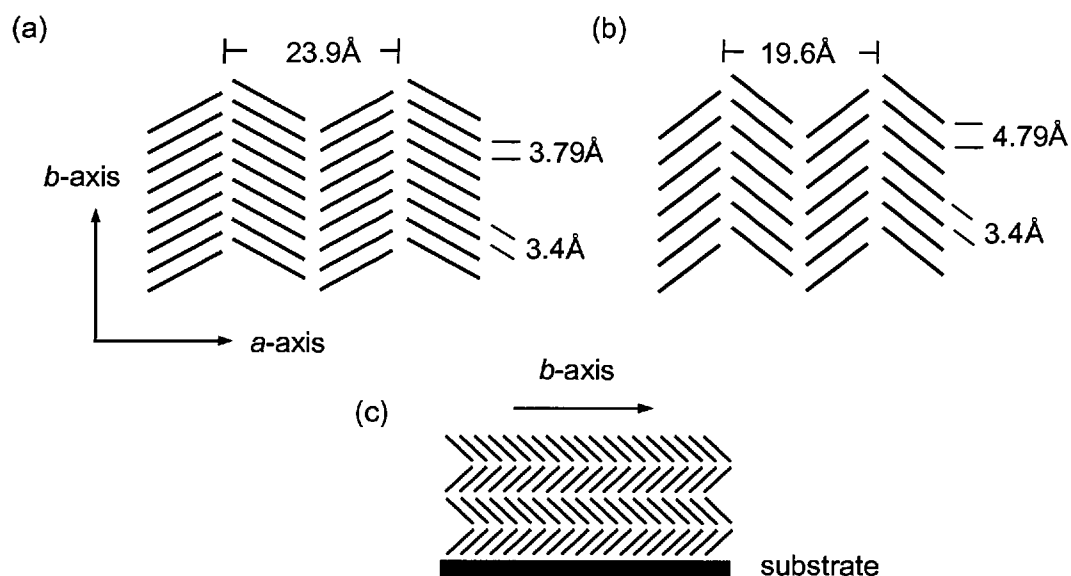


Figure 1.8 – The ‘herringbone-type’ molecular crystal structures of CuPc. The α form (a) has a monoclinic crystal structure in the $C2/c$ space group with four molecules per unit cell, while the β form (b) belongs to the $P2_1/a$ space group and is more closely packed. Typical cell parameters are also given. (c) On weakly interacting substrates (e.g., glass), the preferred molecular orientation is such that the b -axis runs parallel to the substrate surface (after MCKEOWN, 1998).

Both the α - and β - crystallites adopt a similar structure in which the molecules of adjacent stacks are alternately angled in a ‘herringbone’ array (Fig. 1.8), though the angle between the molecular plane and the b - stacking axis is different (26.5° for the α polymorph and 45.8° for β the polymorph) (GOULD, 1996). Furthermore, the molecular arrangement of CuPc thin films deposited onto ITO or quartz substrates is such that the b -axis (along which the greatest π - π orbital overlaps occur) is parallel to the substrate surface. Consequently, the largest charge carrier mobilities (in the range of $0.1\text{-}2.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) have been obtained along the lateral b - crystallographic direction with only limited conductivity in the vertical a - and c -axes (MCKEOWN, 1998). Notably, the conduction of α - and β - CuPc films measured under strictly intrinsic conditions are very similar (SIMON & ANDRÉ, 1985), with observed differences attributed to the increased oxygen adsorption at grain boundaries of the α - type films (MCKEOWN, 1998).

Planar phthalocyanines (D_{4h} point group) can be regarded as an extensively delocalized 18 π -electron system where the π -orbitals of the ligand form a conjugated system (STILLMAN & NYOKONG, 1989). The introduction of a transition metal ion, such as Cu^{2+} , results in the overlap of the metal 3d electronic states with nitrogen p_π orbitals within the molecule that produces a combination of both localized and delocalized states near the Fermi level (E_F). The uppermost energy levels of CuPc (shown in Fig. 1.9) consist of a half-filled b_{1g} orbital, a filled state of a_{1u} symmetry approximately 0.5 eV below that, and a manifold of states roughly 2.0 eV beneath E_F , marking the onset of the main valence band (DOWNES *et al.*, 2004).

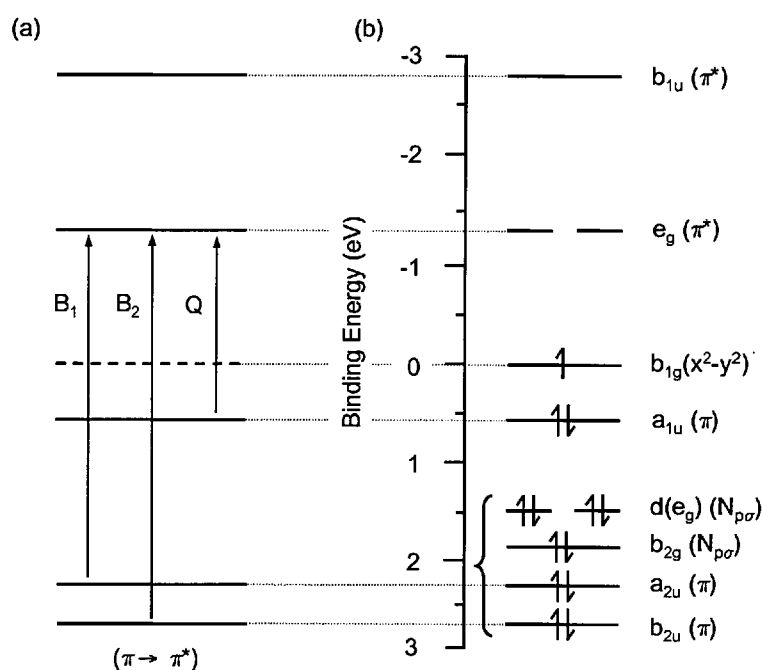


Figure 1.9 – (a) Conventional energy scheme of electronic transitions in phthalocyanines showing the origin of the Q- and B- absorption bands, and (b) corresponding electronic structure of CuPc, in which the metal b_{1g} state at E_F is set to zero and is positioned between the HOMO (π) and LUMO (π^*) orbitals of the Pc ligand. Electrons are depicted as small arrows (adapted from LEVER *et al.*, 1992 and DOWNES *et al.*, 2004)

Both semi-empirical results (SCHAFFER *et al.*, 1973) and theoretical calculations (CARNIATO *et al.*, 1994) suggest that for the higher MO (b_{1g} symmetry) the single electron is mainly localized on the central copper atom, with some anti-bonding character between the copper $3d_{x^2-y^2}$ and the nitrogen $2p$ molecular orbital of the nearest ligands. The LUMO, of e_g symmetry, is degenerate and mainly delocalized on the macrocycle, with a small amount of $3d_{xz,yz}$ character. Significantly, the ionization energy of the b_{1g} state is calculated to be 0.7 eV higher than that of the a_{1u} state, due to the large difference in the degree of localization of the two states (LIAO & SCHEINER, 2001). Consequently, ionization of the CuPc molecule first occurs from the ligand a_{1u} state rather than the lower binding energy ligand-metal shared b_{1g} state. The resulting solid state electronic absorption spectrum of copper phthalocyanine is therefore dominated by two strong absorption bands which have both been correlated to $\pi \rightarrow \pi^*$ transitions (Fig. 1.9(a)). The Q-band, centred at *ca.* 680 nm, is assigned to an $a_{1u} \rightarrow e_g^*$ transition, while the absorption band in the ultra-violet (UV) region at around 350 nm (denoted as the B-band or Soret band) is principally a result of an $a_{2u} \rightarrow e_g^*$ transition (SIMON & ANDRÉ, 1985; MCKEOWN, 1998).

1.5.2 Discotic liquid crystals

The discovery of discotic liquid crystals (DLCs) is generally attributed to Chandrasekhar (CHANDRASEKHAR *et al.*, 1977), although the concept that such disk-like molecules might form liquid crystalline phases had been anticipated prior to that by DeGennes (DEGENNES, 1974). The columnar arrangement of the molecules, in which the stacking distances of molecular cores are considerably shorter ($\sim 3\text{-}4$ Å) than the intercolumnar distances ($\sim 20\text{-}40$ Å), provides highly anisotropic and well-defined exciton and charge transport channels (BUSHBY & LOZMAN, 2002). Indeed, fast photoconduction (>0.1 cm² V⁻¹ s⁻¹) has already been demonstrated in a wide variety of DLCs including triphenylenes (ADAM *et al.*, 1994; VAN DE CRAATS *et al.*, 1996), hexabenzocoronenes (VAN DE CRAATS *et al.*, 1999) and phthalocyanines (OHTA *et al.*, 2003).

Phthalocyanine-based mesogens are especially suitable for PV applications as they combine the optoelectronic properties of their parent molecule (i.e., intense absorption between 300 and 800 nm and relatively small HOMO-LUMO gaps of ~1.5-2.0 eV) with the orientational control of conventional liquid-crystal systems (EICHHORN, 2000). However, achieving uniform homeotropic alignment (where the columnar axis, and thus the charge transport direction, is perpendicular to the substrate/electrode surface) in these large-core discotics is difficult because of their highly viscous nature, which tends to give rise to tilted columnar mesophases with polydomains and line defects. Both of these can suppress carrier transport (OHTA *et al.*, 2003).

Since the first discotic phthalocyanine derivative was reported by Piechocki and coworkers (PIECHOCKI *et al.*, 1982), many variants have been synthesized with the aim of exploring the influence of the central metal ion, side chain structure and linking group type on the phase behavior, thermal stability, and mobility in phthalocyanine mesogens ((CAMMIDGE & BUSHBY, 1998) and references therein). The central metal atom, for example, can play a role in determining the photophysical and mesomorphic properties, but conductivity measurements have suggested that it does not significantly influence the charge transport properties of discotic phthalocyanines. Charge migration therefore occurs primarily *via* interactions between neighbouring aromatic π - systems (WARMAN *et al.*, 2003). The same authors report that the structure of the hydrocarbon chains and nature of the chain-to-core coupling element can have a much stronger influence. This is a direct consequence of the morphological changes, such as the formation of tilted domains, which they can affect. Defects, including large amplitude displacements and positional variations of molecules within a column, traps (in the form of chemical impurities) as well as macrocyclic core sizes also play prominent roles (VAN DE CRAATS & WARMAN, 2001).

Recently, work by Hatsusaka *et al.* (HATSUSAKA *et al.*, 2000) has shown that uniform homeotropic alignment without domain boundaries or disclinations is achievable for octaphenoxy-substituted phthalocyaninato complexes (Fig. 1.10 (a)) at elevated temperatures (*ca.* 130-160 °C). The authors speculated that the lone pairs of the oxygen in the phenoxy group coordinated to the dangling bonds of the silicon atoms on the surface of the substrate, cause the first Pc disk to adhere to the surface and, in turn, trigger the stacking of the disks in a homeotropic fashion. Further structural modifications of these types of materials has resulted in the synthesis of (C₁₄O)₁₆TzCu (Fig. 1.10 (b)), which displays spontaneous homeotropic alignment at room temperature up to its decomposition temperature of 300 °C. This wider temperature range of homeotropic alignment is much more suitable for device applications. The columnar structure of the (C₁₄O)₁₆TzCu complex is characterised as having a two-dimensional tetragonal array in which the molecules are stacked in a disordered, cofacial arrangement (*Col_{tet,d}*) (ICHIHARA, 2005). The implications of orientation and degree of order within the column on photovoltaic device performance are discussed in Chapter 5.

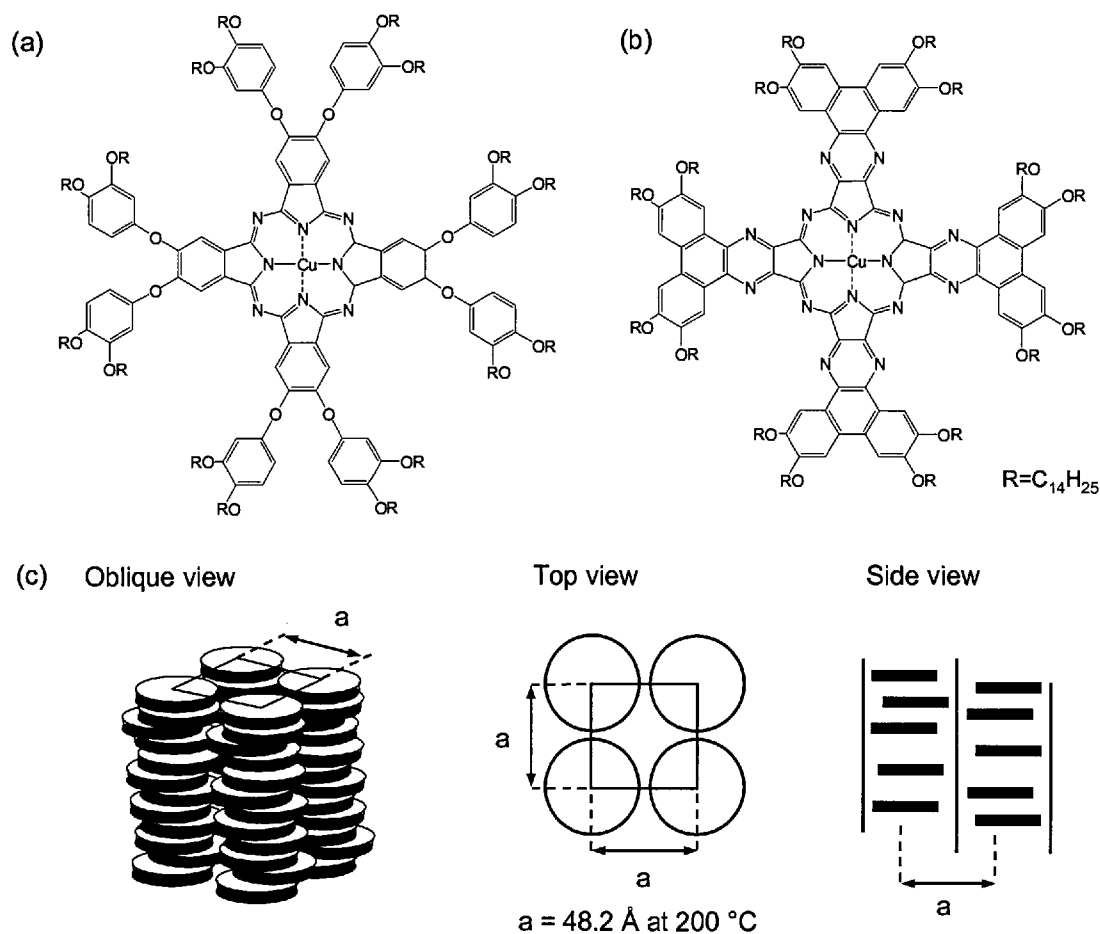


Figure 1.10 – Chemical structure of CuPc liquid crystal derivatives: (a) octaphenoxy-substituted phthalocyaninato and (b) tetrakis (2,3,6,7-tetradodecyloxy) diazatriphenylenocyaninato metal complex, $(C_{14}O)_{16}TzCu$; (c) A schematic representative of the mesomorphic structure of $(C_{14}O)_{16}TzCu$.

1.5.3 PhEt-PTC

Perylene derivatives, like phthalocyanines, are some of the most commonly used dyes in molecular PV devices (see for example the work of (TANG, 1986; HIRAMOTO *et al.*, 1991; GREGG, 2003). Their propensity to form well-ordered crystals with superior π -electron networks has made them archetypal organic semiconductors. Functionalisation of the perylene core, while having little influence on the electronic properties of isolated molecules, plays an influential

role in determining the crystal packing. This in turn strongly affects the solid-state optical properties (HÄDICKE & GRASER, 1986; KLEBE *et al.*, 1989). As a result, the extent of orbital overlap between adjacent molecules is governed by the type, size and shape of the functionalised end groups. The additional steric bulk due to the phenyl ring and ethylene bridge on each dicarboximide end group of PhEt-PTC, for example, gives rise to a number of polymorphs that have distinct optical and electronic properties (MIZUGUCHI, 1998).

Nominally, vacuum sublimed PhEt-PTC thin films are classified as belonging to one of two polymorphs ('amorphous' or 'crystalline', with the latter further subdivided into 'modification I' and 'modification II'), though they can exist in a broad range of morphologies and structures depending on the deposition and processing conditions (BARBARA *et al.*, 1999; FERGUSON, 2004). Thin films deposited at room temperature are often described as being amorphous in nature (despite the obvious appearance of elongated crystallites in some AFM images), while exposure to vapours such as acetone, thermal annealing above 100 °C, or growth at elevated substrate temperatures induces a transition to the 'crystalline' polymorph (DEBE *et al.*, 1988).³ Modification I was identified by Mizuguchi (MIZUGUCHI, 1998) as forming a monoclinic $C2/c$ structure with four molecules per unit cell. In this case, the phenyl groups do not lie in the same plane as the perylene cores but are twisted by about 19 degrees. The molecular stacks arrange themselves so that the long molecular axes of molecules in adjacent stacks lie parallel to each other. A second crystal phase was discovered when single crystals grown from the vapor phase were found to have crystallized in the monoclinic, $P2_1/c$ space group (modification II) (MIZUGUCHI & TOJO, 2002). Here the phenyl groups lie parallel to, but are not in the same plane as, the perylene core. The structures of the two 'crystalline' polymorphs are shown in Fig. 1.11.

³ Recent work by Ferguson (FERGUSON, 2004) suggests that 'crystalline' PhEt-PTC films (i.e., heat-treated films) consist of a mixture of modification I and II. However, since XRD data from annealed films in this study (see section 4.3.3) more closely resembles that of modification I, the 'crystalline' polymorph will simply be referred to as 'PhEt-PTC_{mod I}' or 'modification I.'

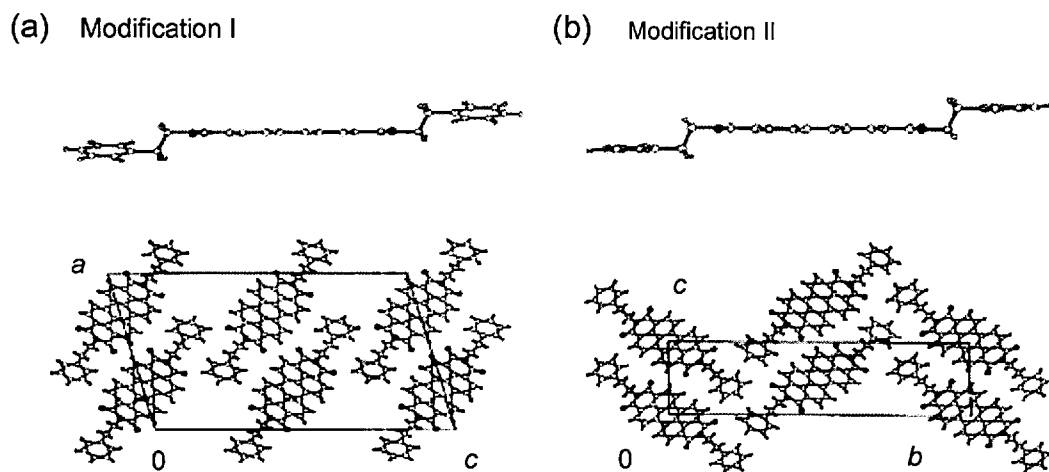


Figure 1.11 – Crystal structure of (a) 'modification I' and (b) 'modification II' of PhEt-PTC (from MIZUGUCHI, 2002).

The electronic absorption spectra of many perylene derivatives show well structured vibronic transitions to the S_1 state, where the 0-0 transition is located at ~ 530 nm. The splitting of the PhEt-PTC absorption band in the solid state into higher and lower energy components, after thermal- or vapour-annealing, is evidence of strong intermolecular interactions. Gregg (GREGG, 1996) has proposed a CT and Frenkel exciton absorption model based on that initially suggested by Bulovic *et al.* (BULOVIĆ *et al.*, 1996) for PTCDA, in which the high energy band is assigned as the transition to a so-called S_1 Frenkel-like state (i.e., the excitation is confined to the monomer) and the low energy band is allocated to a charge transfer (CT) excitonic state involving more than one perylene molecule (Fig. 1.12). Gregg points out that while the S_1 Frenkel state designation is a misnomer, since the CT band of the crystal is actually the lowest energy excited singlet state, it does correspond to S_1 of perylenes in solution, for which the CT is absent and the lowest excited state is a $\pi-\pi^*$ in-plane, long axis polarized transition.

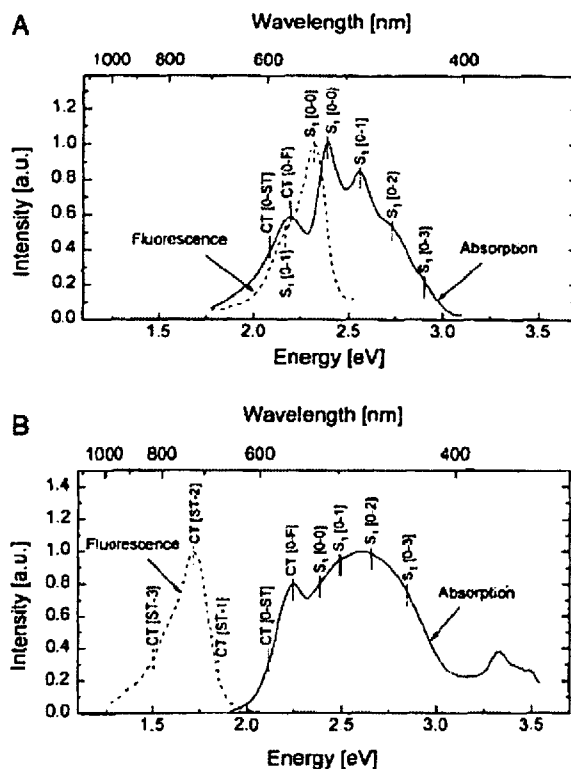


Figure 1.12 – Absorption (continuous line) and emission (dashed line) of PTCDA in a 2 μM DMSO solution (a) or as a thin film (b). The electronic transitions corresponding to the spectral features have been identified (from BULOVIĆ, 1996).

1.5.4 C_{60}

The fullerenes, along with their cylindrical off-shoot, the carbon nanotube, display a variety of remarkable electronic properties (DRESSELHAUS *et al.*, 1998). C_{60} , in particular, is noted for its extremely high electronegativity (electron affinity of 2.7 eV) and low reorganization energy⁴, and is exploited accordingly in photovoltaic devices (WRIGHT, 1995). The characteristic chemical reactivity is

⁴ The energy required for all the structural adjustments that are needed in order for donor and acceptor assume the necessary configuration for the transfer of electrons (McNAUGHT & WILKINSON, 1997). The low reorganization energy of the fullerene is directly associated with a high degree of charge delocalization within the 3-dimensional carbon framework (GULDI, 2002).

a direct consequence of its unique spherical geometry and, more specifically, due to the curvature-induced strain of the carbon bonding network that comprises twelve pentagonal and twenty hexagonal faces (HADDON, 1993). The ensuing hybridization of the s and p orbitals is therefore neither purely sp^2 (trigonal) nor entirely sp^3 (tetrahedral) in nature (WEAVER & POIRIER, 1994), but rather of an intermediate state with a ‘pyramidalization angle’ (θ_p), as defined by Haddon (HADDON, 1993), of 11.6 degrees (Fig. 1.13(a)). Since this geometry lies closer to the tetrahedral than the trigonal hybridization ($\theta_p = 19.47^\circ$ and 0° , respectively), chemical conversion of any trivalent carbon atom to a tetravalent carbon atom provides strain relief for the molecule, and reactions that serve to saturate the carbon atoms in C_{60} are strongly favoured (NIYOGA *et al.*, 2002).

The molecular orbital energy level diagram for C_{60} (Fig. 1.13(b)), consisting of a completely filled five-fold degenerate HOMO level (h_u symmetry) and a strongly bound triply degenerate LUMO level (t_{1u} symmetry), suggests that it might be expected to accept at least six electrons, and possibly up to twelve, under the right conditions (HADDON *et al.*, 1986; DRESSELHAUS & DRESSELHAUS, 1995).

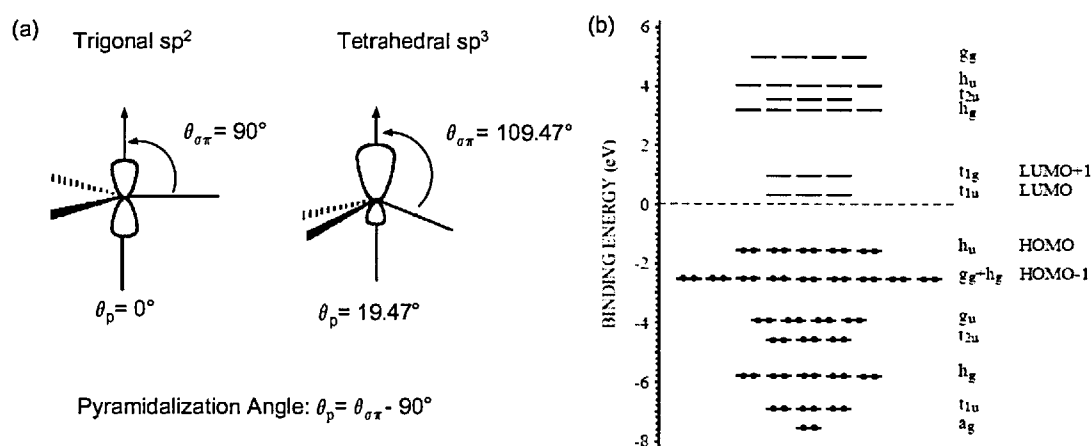


Figure 1.13 – (a) Pyramidalization angle for trigonal and tetrahedral carbon bonds, (b) Electronic structure of C_{60} (from HADDON, 1993 and HESPER, 2000)

Unlike many organic dyes, C₆₀ does not contribute significantly to the overall light harvesting capacity of a photovoltaic device. First measured by Krätschmer *et al.* (KRÄTSCHMER *et al.*, 1990), it is characterized by strong absorption features between 190 and 410 nm, assigned to the allowed $h_u \rightarrow t_{1g}$ and $h_g \rightarrow t_{1u}$ transitions, as well as by the forbidden $h_u \rightarrow t_{1u}$ singlet-singlet absorption in the visible part of the spectrum. These latter transitions, located between 410 and 620 nm, are responsible for the purple colour of C₆₀ (HIRSCH & BRETTREICH, 2005). Degradation of C₆₀ thin films under oxygen and light occurs rapidly and even at low temperatures (TAYLOR *et al.*, 1991), resulting in an irreversible reduction of conductivity (ASAKAWA *et al.*, 1995). Hamed (HAMED *et al.*, 1993), Katz (KATZ *et al.*, 1996) and coworkers have suggested that illumination of C₆₀ films under oxygen promotes a C-O reaction that results in the formation of dangling carbon bonds, generating defect states such as recombination centers. The long-term stability of PV devices incorporating C₆₀ will therefore require effective encapsulation technologies, a feature that is already being demonstrated for OLEDs (SARICIFTCI, 2004).

1.6 Thesis objectives and outline

The principal aim of this thesis is to examine the role of molecular architecture on the performance of organic solar cells. More specifically, the effects of codeposition and annealing on small-molecular-weight systems are explored, with a view to establishing the physical parameters (e.g., D-A interface morphology, film thickness, crystallinity) that determine the optimal device characteristics. Moreover, this work aims to evaluate the performance and limitations of photovoltaic cells fabricated from self-assembled organics, with particular emphasis placed on the relationship between molecular order, charge transport and device efficiency.

The thesis is ordered as follows. Experimental techniques and analytical methods are described in chapter 2. In chapter 3, the influence of codeposition on the photovoltaic, morphological and spectroscopic properties of CuPc-C₆₀ heterojunctions is presented. This theme is further developed in chapter 4, in which results pertaining to the thermal annealing of CuPc/C₆₀ discrete heterojunctions and CuPc:PhEt-PTC bulk heterojunction structures are discussed. Following this, chapter 5 elaborates on the photovoltaic properties of cells containing a novel CuPc-based discotic liquid crystal. Finally, chapter 6 provides a brief overview of the results as well as offering some concluding remarks concerning the prospective directions that molecular photovoltaic research may take in the near future.

2 EXPERIMENTAL

2.1 Material preparation and film growth

2.1.1 Purification

The fabrication of high-quality thin films and devices requires, as a first step, the systematic purification of the source material. Of the several techniques available, thermal gradient sublimation has become the most widely used method for purification of the powders employed by OMBD (FORREST, 1997). The apparatus, shown in Fig. 2.1, consists of a disposable inner quartz tube, into which the source material is loaded, and a reusable outer quartz tube, which can be attached directly to a turbomolecular pump. A wad of glass wool placed at the open end of the inner tube prevents any volatile impurities from contaminating the pump.

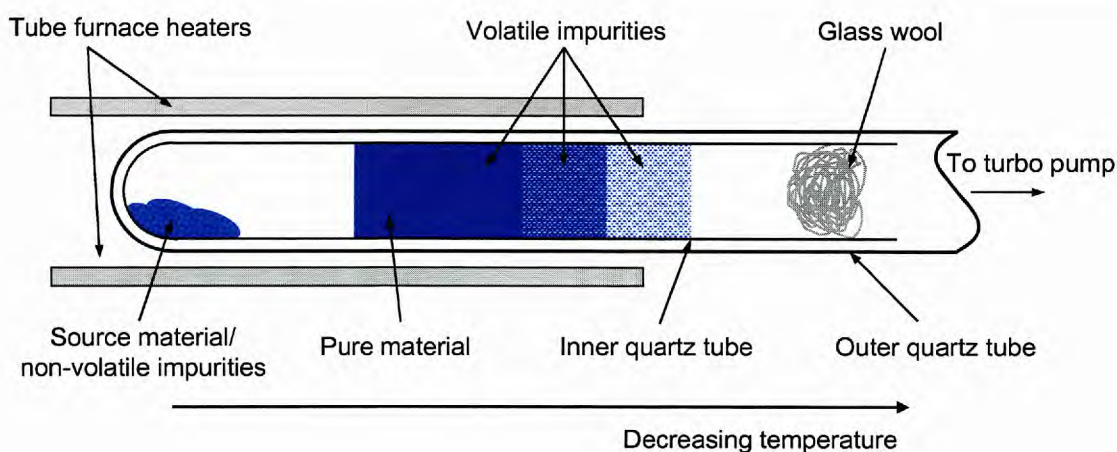


Figure 2.1 – Schematic of the gradient sublimation set-up used for material purification.

The tube is evacuated to about 10^{-6} Torr and the end containing the source material inserted into a tube furnace, the temperature of which is gradually increased ($<1\text{ }^{\circ}\text{C min}^{-1}$) until the sublimation point of the material is reached. Purified organic crystals grow along the interior of the quartz tube in the warm zone of the furnace, while more volatile impurities condense along cooler sections of the inner tube. Non-volatile impurities remain at the hottest (sealed) end of the inner tube. CuPc (Aldrich 97%), BCP (Aldrich 98%), C₆₀ (MER Corp. 99.5%) and PhEt-PTC (Sensient Imaging Technologies, SynTec Division) underwent at least two successive cycles of thermal gradient sublimation prior to being loaded into the vacuum growth chambers. Once under vacuum, the materials were outgassed thoroughly, which reduces the likelihood of ambients, including oxygen, being present in the films.

2.1.2 Organic molecular beam deposition

Although significantly more complicated than spin-coating or dipping techniques, organic molecular beam deposition (OMBD) allows the reproducible growth of complex heterostructures with a defined film thickness ranging from molecular monolayers to hundreds of nanometers (SCHREIBER, 2004). Two vacuum chambers were utilised for this work. Codeposition experiments and device fabrication were carried out on a Kurt J. Lesker Spectros high vacuum system, while annealing experiments were performed on a custom-built ultra-high vacuum (UHV) system.

The substrate holder in the Spectros system (shown schematically in Fig. 2.2) comprises a tiered platen that is capable of rotating about its centre and supporting an array of samples and masks on either two 10 x 10 cm or two 5 x 5 cm holders, which can be manipulated while under vacuum. The entire chamber is pumped by a 1500 Ls⁻¹ cryopump (base pressure of 8×10^{-8} Torr) with roughing and regeneration provided by a vane pump. The chamber has four organic evaporation sources, operating at low temperature (up to 500 °C). In addition, there are two evaporation boat sources that reach temperatures

commonly required for metal deposition (up to 1500 °C). All six sources have separate power supplies, quartz crystal microbalances (QCMs) and pneumatically operated shutters. Loading or removal of samples/source material requires venting of the entire chamber.

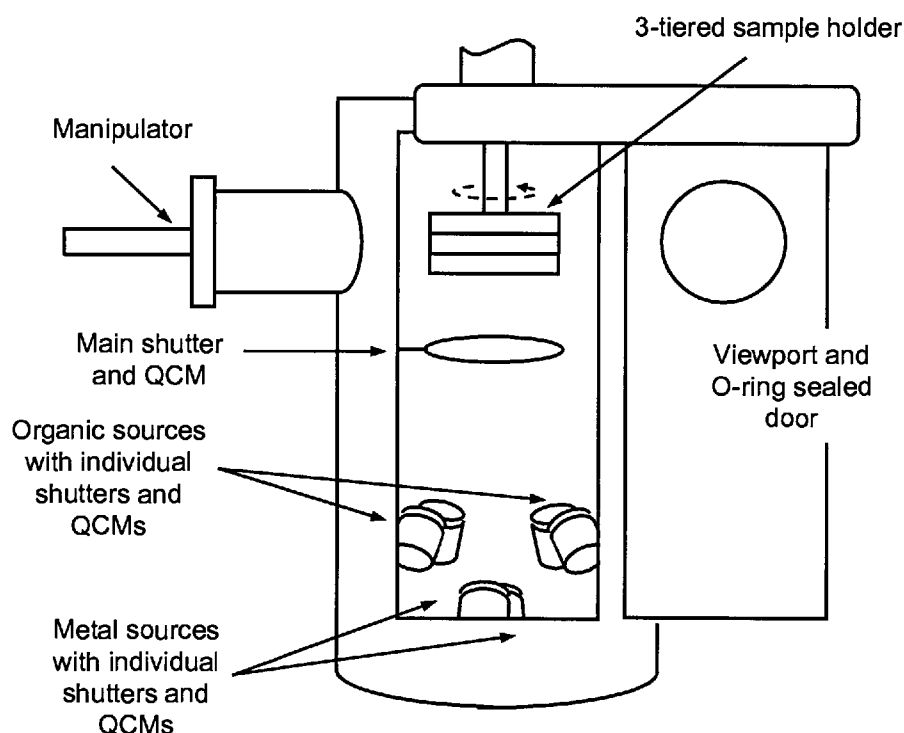


Figure 2.2 – Cross-sectional view of the Spectros molecular beam deposition chamber used for codeposition experiments.

The second system (for which only the growth chamber is shown in Fig. 2.3), on the other hand, is permanently maintained under UHV conditions by a pair of ion pumps (base pressure 10^{-11} Torr), with samples being introduced to, and removed from, the growth chamber *via* a load lock, gate valve and transfer arm arrangement. Up to two Knudsen evaporation cells simultaneously (i.e., codeposition) can be used to provide a flux of molecules at the substrate surface, which is held about 20 cm away from the source at an approximately perpendicular angle to the molecular beam by a manipulator equipped with x, y, z translation, as well as primary and azimuthal rotation. The manipulator

also allows resistive sample heating and deposition at elevated substrate temperatures. The growth of thin films relies on the sublimation of a compound from a resistively heated boat, crucible or Knudsen cell (K-cell). Since transport through vacuum is almost instantaneous, the deposition rate (typically in the range of $1\text{--}10 \text{ \AA s}^{-1}$) is set by the rate at which molecules escape the K-cell and is therefore controlled by the source temperature. The growth rate is measured using a single QCM and it should be noted that the deposition of metals was not possible on this system.

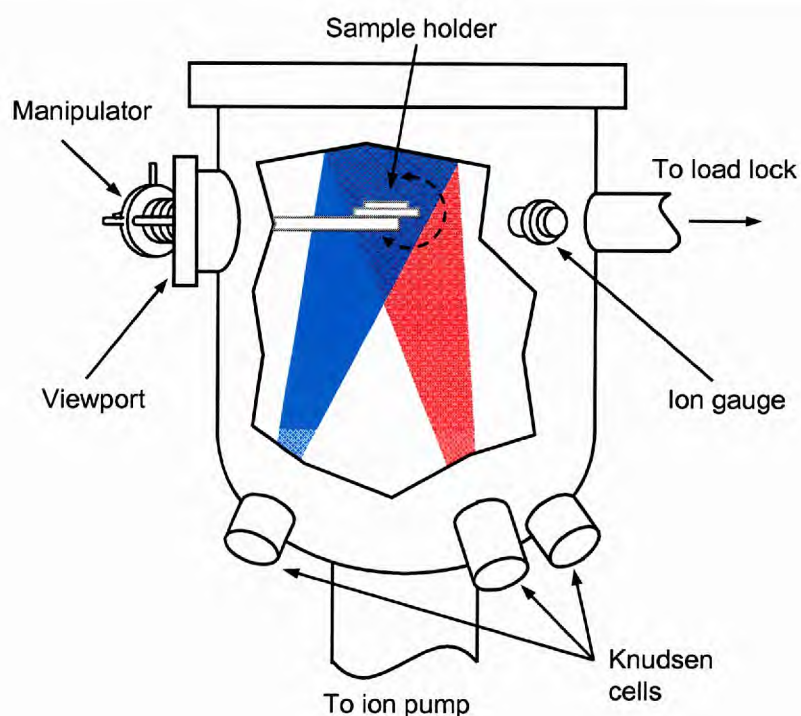


Figure 2.3 – Cross-sectional view of the organic molecular beam deposition chamber used for post-growth annealing experiments.

It is common in vacuum technology to subdivide its overall pressure range (somewhat arbitrarily) into smaller individual regimes. These are generally defined as follows:

- Rough vacuum (RV) 1-10⁻³ Torr
- Medium vacuum (MV) 10⁻³-10⁻⁵ Torr
- High vacuum (HV) 10⁻⁶-10⁻⁸ Torr
- Ultrahigh vacuum (UHV) <10⁻⁹ Torr

This is of importance, in so far as the reproducible growth of thin films and devices is concerned, in that the background pressure is a determining factor in how long a surface can be maintained clean and contaminant-free (or, alternatively, how long it takes to build-up a certain surface concentration of adsorbed species). To ensure that significant contamination by ambient gases does not occur, the background pressure must be such that the time required for contaminant build-up is substantially greater than that required for film growth. For a given set of conditions (pressure, temperature, etc.) the flux is readily calculated using a combination of statistical physics, the ideal gas equation and the Maxwell-Boltzmann gas velocity distribution (BIRD, 1994). In short, if ζ is the average sticking coefficient of an impurity in the chamber and m its molecular mass, the time required for a monolayer of N_s impurity molecules per unit area is

$$\tau_{ML} = \frac{N_s \sqrt{2\pi m k T}}{\zeta P} \quad (2.1)$$

where k is Boltzmann's constant, P is the partial pressure of the impurity and T is the temperature of the gas. Assuming that the gas in the chamber has a composition identical to that of air and that O₂ forms an impurity in the film with $\zeta = 1$, then at a background pressure of $P = 10^{-6}$ Torr, $\tau_{ML} = 1.4$ seconds for $N_s = 10^{14}$ cm⁻². For $P = 10^{-11}$ Torr, $\tau_{ML} = 3.9$ hours. Clearly, in order to avoid contamination UHV conditions are necessary.

2.1.3 Spin-coating

The spin-coating process involves depositing a fluid solution onto a substrate and then spinning the substrate at high speed (typically around 3000 rpm). Centripetal acceleration will cause the fluid to spread across, and eventually off, the substrate leaving a thin film of material on the surface. The final film thickness will depend on the nature of the fluid (viscosity, drying rate, percent solids, surface tension, *etc.*) and the parameters chosen for the spin process. Factors such as final rotational speed, acceleration, and fume exhaust contribute to how the morphology of coated films is defined.

The Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) aqueous dispersion (PEDOT:PSS, BaytronP, for which the chemical structure is shown in Fig. 2.4) thin films utilised for the discotic liquid crystal solar cells were fabricated using the procedure of Huang *et al.* (HUANG *et al.*, 2003) and Ravirajan *et al.* (RAVIRAJAN *et al.*, 2005).

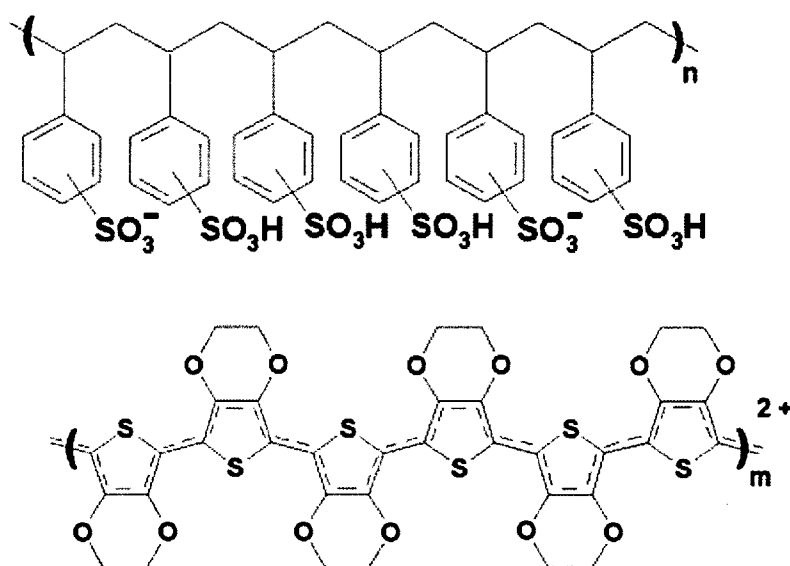


Figure 2.4 – Chemical structure of Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) aqueous dispersion (PEDOT:PSS).

The PEDOT:PSS solution was first ultrasonicated for 15 minutes and then heated for 15 minutes at 90 °C. Subsequently, the solution was filtered with a 0.45 µm filter and spin-coated onto the ITO substrate in a water-free environment. The substrate was then annealed at 100 °C for 5 minutes under N₂ gas. High quality thin films of (C₁₄O)₁₆TzCu were spin-coated from a chloroform solution that was similarly sonicated, heated and filtered in order to remove aggregates. Thicknesses were calibrated using AFM step-edge measurements.

2.1.4 Substrate preparation

Thin films and devices were grown on pre-cut, commercially available quartz and indium tin oxide (ITO)-coated glass substrates (CRL Opto). Cleaning involved the immersion of the substrates in an ultrasonic bath (20 min in methanol) before drying with nitrogen. Samples subjected to thermal annealing were attached to a molybdenum sample holder using an indium-gallium eutectic mixture in order to provide good thermal contact. After cleaning, samples were transferred directly into the chamber.

2.2 Thin film and device characterisation

2.2.1 Atomic force microscopy

AFM has become an indispensable tool in the field of surface science and brings together aspects of scanning tunneling microscopy (STM) and stylus profiling instruments (BINNING *et al.*, 1986; ALBRECHT & QUATE, 1988). However, while both STM and AFM are based upon scanning an atomically sharp probe over a surface (typically at a distance of a few angstroms or nanometers), STM depends on achieving a tunneling current between a metallic tip and an electrically conducting sample, a restriction not imposed upon AFM. Instead, the AFM utilizes the various interatomic forces encountered when two objects are brought within close proximity (nanometers) of each other (COLTON, 1998).

In order to measure these forces, a probe tip is mounted on a cantilever-type spring. Briefly, the force interaction between the sample and the tip causes the cantilever to bend according to Hooke's Law

$$F_s = -k z \quad (2.2)$$

where k is the spring constant of the tip and z is the displacement. In practical terms, these forces are not measured directly, but calculated by measuring the deflection of the cantilever upon which the tip is mounted, given a specific stiffness. During the scan, a particular operating parameter is maintained at a constant level, and images are generated through a feedback loop between the optical detection system and the piezoelectric scanner (Fig. 2.5(a)). The forces experienced by the tip as it slowly approaches the sample surface are shown schematically in Fig. 2.5(b), and define the operating regime of the AFM.

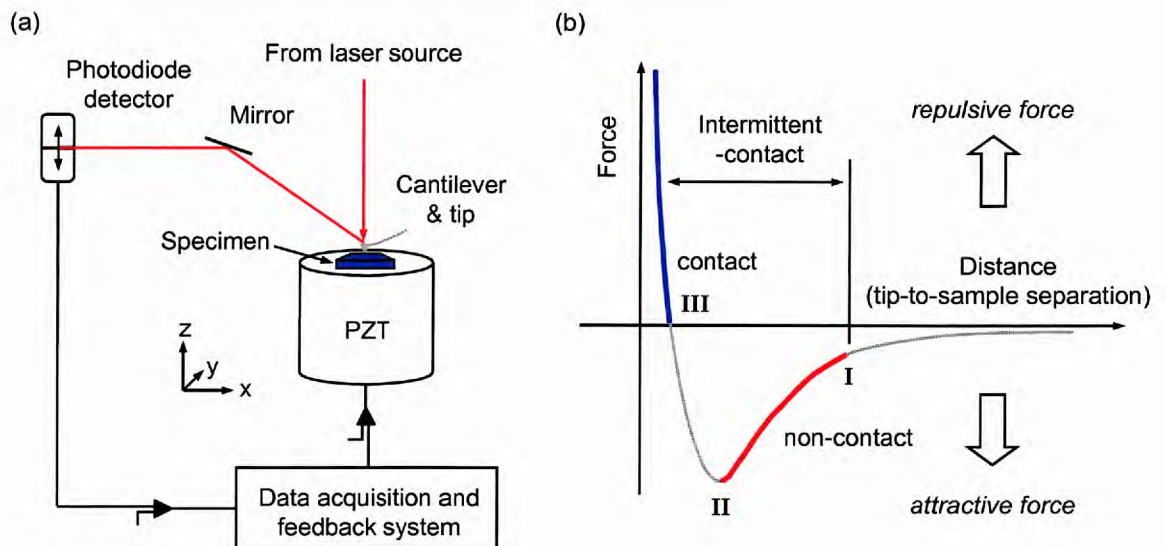


Figure 2.5 – (a) Schematic diagram of the AFM set-up. Cantilever displacements are detected using optical techniques, in which a laser beam is reflected off the top surface of the cantilever and onto a position-sensitive photodiode array; **(b)** force-distance plot showing the various tip-sample interactions. When two atoms that are separated by large distances are brought together they are, at first, weakly attracted to each other (point I). This attractive force gradually increases until the atoms are so close together that their electron clouds begin to repel each other electrostatically (point II). If the interatomic separation continues to decrease, the electrostatic repulsion progressively weakens the attractive force until the two forces are balanced to zero, typically when the distance between the atoms reaches a couple of angstroms (point III). When the total van der Waals force becomes positive (repulsive), the atoms are in contact.

In contact mode, the AFM tip is pushed against the sample surface, inducing a repulsive tip-sample interaction. The spatial variations of the cantilever deflection as it is rastered across the sample correspond to the lateral position of the features on the surface (constant-height mode). Alternatively, the deflection of the cantilever can be used as input to a feedback circuit that moves a piezoelectric tube in the z-direction, responding to the topography by keeping the cantilever deflection constant. In this way, the total force applied by the cantilever to the sample is kept constant (constant-force mode). However, problems associated with contact mode operation include: (i) excessive tracking forces between the probe to the sample, which can cause significant deformation to 'soft' samples such as small-molecule and polymeric thin films and, (ii) attractive electrostatic and/or surface tension forces due to adsorbed gas layers, which pull the scanning tip toward the surface and can damage the sample, dull the cantilever probe and distort image data.

To reduce or eliminate the frictional and adhesive forces associated with contact mode operation, the cantilever can be oscillated near its resonant frequency as it is scanned above the surface in either non-contact or intermittent contact (tapping) mode. These modes utilise the attractive van der Waals force acting between the tip and the sample; topographic data can be obtained by relating the changes in the resonant frequency (or amplitude) of the cantilever to changes in tip-sample distances and thus to feature height. Unfortunately, the relatively weak force values in the non-contact regime and the greater stiffness of the cantilevers (a necessary requirement to reduce the tendency for the tip to be pulled down to the surface) are both factors that make the non-contact AFM signal small, and therefore difficult to measure.

Tapping mode overcomes the problems associated with the friction, adhesion and electrostatic forces of contact mode AFM, as well as the weak van der Waals interactions encountered by the non-contact AFM method, by intermittently contacting the surface with the cantilever during each oscillation

cycle, thereby achieving high resolution while simultaneously preventing the tip from dragging across the surface. During tapping mode operation, the feedback system seeks to maintain a constant amplitude of tip oscillation by comparing a voltage signal generated at the photodiode detector with a user selected set-point voltage. The piezoelectric transducer rasters across the sample at a typical scan rate setting of 0.5 to 2 Hz (compared to 1 to 4 Hz for contact mode) while adjusting the vertical position as required to maintain a constant tip amplitude, thereby generating topographical images. By changing the set-point voltage, the amount of force exerted on the sample during each 'tap' can be adjusted. The large, linear operating range makes such a vertical feedback system highly stable, allowing routine, reproducible sample measurements.

AFM images were obtained using a Burleigh Metris-2000 microscope operated in non-contact (tapping) mode. The laser beam was adjusted on the tip end using an optical microscope. The piezoelectric heads correspond to a 70 μm or a 5 μm maximum scan range. Commercially available tips were used; the tip was attached to a ~ 200 μm cantilever with a resonant frequency of about 160 kHz. Subsequent to data acquisition, two filters were applied to all of the raw images in order to accentuate the contrast. The 'line removal' filter normalises horizontal scan lines (fast scan direction) to a fixed height and tilt, while the 'plane removal' filter normalises the image to a flat plane, removing tilt and tip-drift effects.

A description of a surface may be made on several levels. A single parameter may be sufficient to characterise a surface for some purposes; in other cases a much greater degree of description is required. The rms roughness (R_q) is perhaps the most widely used parameter for specification of the roughness of optical surfaces (i.e., manufactured to an accuracy comparable with the wavelength of light). It is defined as the root mean square of the deviations of the surface profile from the mean line (STACHOWIAK & BATCHELOR, 1993). If

Z_{avg} is the average height of the surface and Z_i the height of the N each individual points forming the surface, R_q is defined by the equation

$$R_q = \sqrt{\frac{1}{N} \sum_i^N (Z_i - Z_{avg})^2} \quad (2.3)$$

2.2.2 X-ray diffraction

Vacuum evaporated thin films can exhibit varying degrees of anisotropy. The information pertaining to the preferred crystallite orientation (or texture) can be quantified and evaluated using X-ray diffraction (XRD) techniques.

Diffraction occurs when electromagnetic radiation interacts with a periodic structure whose repeat distance is on the order of the wavelength of the radiation. This phenomenon is relatively common, and occurs across a broad range of scales. Since the wavelength of X-rays is comparable to the typical interatomic distances in crystalline solids (angstroms), they are ideally suited for probing the structural arrangement of atoms and molecules (WOOLFSON, 1997).

When certain geometric requirements are met, diffracted waves from different atoms can interfere with each other in such a manner that the resultant intensity distribution is strongly modulated. This condition is described by Bragg's Law, which states that diffraction from a series of planes with Miller Indices (hkl) and interplanar distance d_{hkl} will only occur if the path-length difference ($ab + bc$) between the beams striking two different planes of the same indices is equal to a multiple of λ . As shown in Fig. 2.6(b), $ab + bc$ can be expressed as a function of the incident (or glancing) angle (θ) and the interplanar spacing (d_{hkl}) using

$$ab + bc = 2d_{hkl} \sin \theta \quad (2.4)$$

Since constructive diffraction is only observed when $ab + bc = n\lambda$, where n is an integer (i.e., 1,2,3,...), equation (2.4) can be written as

$$2d \sin \theta = n\lambda \quad (2.5)$$

The characteristic set of d -spacings generated in a typical X-ray scan provides a unique "fingerprint" of the material and provides a means of phase identification.

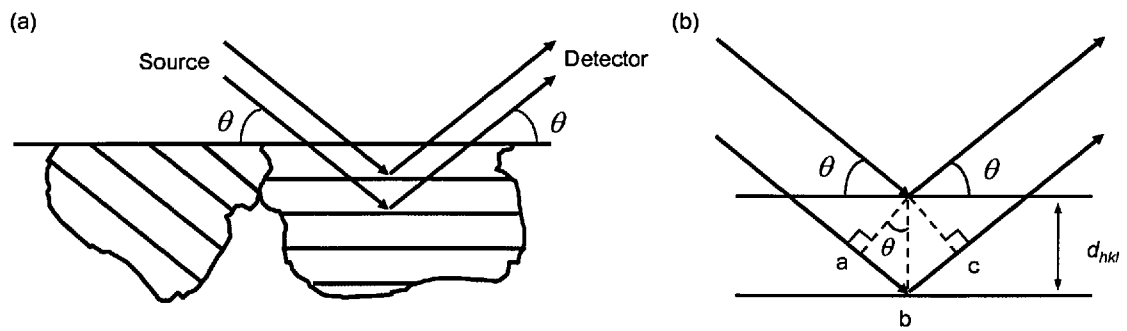


Figure 2.6 – (a) Principle of powder XRD. Samples typically consist of randomly oriented crystallites, and a fraction of these crystallites will possess diffraction planes, with separation d_{hkl} , in a suitable position for diffraction at the corresponding angle, θ . Variation of the angle between the substrate surface and incident x-ray beam will give rise to diffraction from other crystallites that possess suitably spaced diffraction planes parallel to the sample surface; **(b)** diffraction from two planes to demonstrate Bragg's Law.

Powder XRD is the most widely used x-ray diffraction technique for characterizing bulk or thin film materials in which the crystalline domains are randomly oriented in the sample, a proportion of which will have their planes in a position suitable for diffraction at a certain angle or wavelength. This $\theta - 2\theta$ diffraction technique, so-called because any rotation of the source by an angle of θ is accompanied by a rotation of the detector by 2θ , is shown in Figure 2.6(a). Experimental acquisition of powder patterns is often accomplished using the Debye-Scherrer method, in which the whole diffraction pattern, for a given angle, is recorded simultaneously. The concentric rings of scattering peaks acquired using this technique corresponds to the various d -

spacings in the crystal lattice. The positions of the peaks are used for identifying the underlying structure (or phase) of the material, while the intensities of the diffracted beams are proportional to the crystalline sample volume irradiated by the beam.

Quantitatively, the average dimension of the crystals that compose a crystalline powder can be established from the widths of the diffraction peak using the Debye-Scherrer equation

$$D_{hkl} = \frac{0.9\lambda}{B \cos \theta} \quad (2.6)$$

where λ is the radiation wavelength ($\text{CuK}\alpha = 1.54 \text{ \AA}$), θ is the Bragg angle and B is the broadening of the diffraction line measured at half of its maximum intensity (FWHM) and calculated in radians.

2.2.3 *Electronic absorption spectroscopy*

Electronic absorption processes involve strong coupling of molecules with UV or visible light (BIRKS, 1970). When radiation of fixed intensity (I_0) impinges onto the sample, it causes a reorganization of electron configurations before exiting the sample with an attenuated intensity (I). In practice, the sample is scanned over a range of wavelengths, for which the transmitted intensity is recorded accordingly (SKOOG & LEARY, 1992). The attenuation of the light is quantified by the absorbance (A) and described by the Beer-Lambert Law

$$A = \log \frac{I_0}{I} = \epsilon bc \quad (2.7)$$

where b is the path length, ϵ is the molar absorption coefficient, which is constant for a particular compound at a given wavelength, and c is the concentration. For solids the concentration can be obtained by multiplication of

the relative molecular mass by the density; the terms due to the molar absorption coefficient and concentration are amalgamated into a term known as the absorptivity (α) of the material. This leads to the modified form of the Beer-Lambert Law

$$A = \log \frac{I_0}{I} = \alpha L \quad (2.8)$$

where L is the film thickness. Hence it is possible to estimate the thickness of a film by calculating b since the integrated absorption is proportional to the amount of absorbing material. However, solid state samples were calibrated using an AFM scan of the 'step-edge' between the material and the bare substrate, thus relating the electronic absorption intensity to film thickness.

All absorption spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer, interfaced to an IBM compatible computer running the Perkin-Elmer software (PECSS401). Data was recorded at a resolution of 1 nm and a scan speed of 60 nm min⁻¹. Solution state samples were measured in quartz cuvettes, while thin film samples were measured using an adapted sample holder, which maintained the sample in an identical perpendicular position to the incident beam, thereby allowing quantitative comparison between samples. All solution and solid state spectra were corrected for solvent, cuvette and substrate absorption, respectively.

2.2.4 Solar simulation

PV devices are characterized by the efficiency with which they can convert incident solar power to useful electric power. For quantitative evaluations to be valid, these solar intensities are commonly normalized with respect to full sun solar radiation at sea level with average humidity and aerosol particulate concentration - atmospheric conditions commonly referred to as "air mass 1.5" (AM1.5). The solar radiation at AM1.5 is approximately 100 mW cm⁻²,

significantly less than the 135 mW cm^{-2} of radiant energy bathing the earth at AM0 (on the outer edge of the earth's atmosphere) – see Fig. 2.7(a).

The solar simulator (Fig. 2.7(b)) comprises a high power air cooled Xenon lamp that provides uniform illumination over a large area ($15 \text{ cm} \times 15 \text{ cm}$) coupled with an AM1.5 solar filter. Calibration was performed with a Centronic silicon photodiode (1 cm^2). Device measurements were carried out in air and immediately after device fabrication. Quoted efficiencies are an average of three 0.16 cm^2 Al contact readings (unless otherwise stated) and at least two repeat samples.

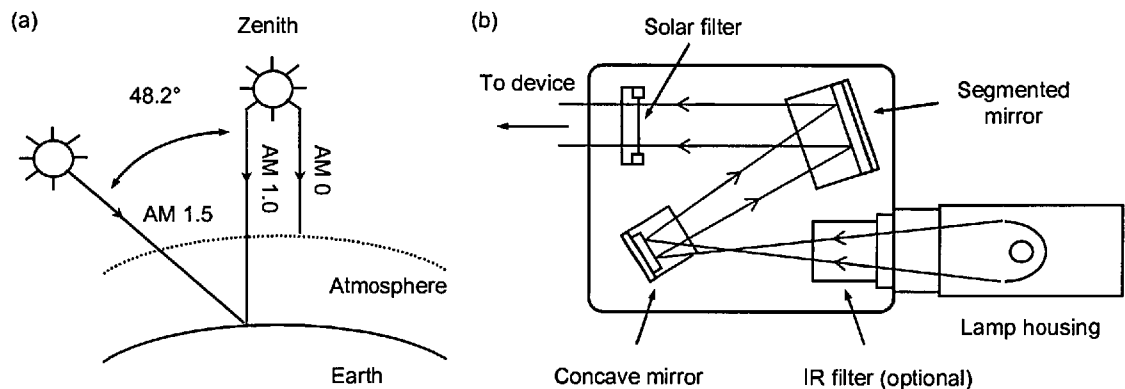


Figure 2.7 – (a) Schematic explanation of the different AM sun light spectra (from ROSTALSKI, 2000); (b) Experimental set-up of the solar simulator.

It has previously been shown that differences in spatial uniformity (PV cell positioning), poorly collimated light and changes of light intensity over time can introduce errors of up to 3% (EMERY *et al.* 1987). However, these are minimised due to fact that device areas are significantly smaller than the incident beam uniformity, and as a consequence of using a set-up that ensures the geometric arrangement of the solar simulator and device remains consistent. Nevertheless, differences between the spectral irradiance under AM1.5 conditions and the spectral irradiance of the solar simulator will introduce an error, known as the spectral mismatch. This is particularly significant for

phthalocyanine-based devices, for which the incident spectral irradiance of the solar simulator in the 600-700 nm range (the region of maximum absorption) deviates by approximately 7% from that of the standard AM1.5 spectrum (see Fig. 2.8). It should be noted that the effects of spectral variations have not been taken into account for the devices described herein.

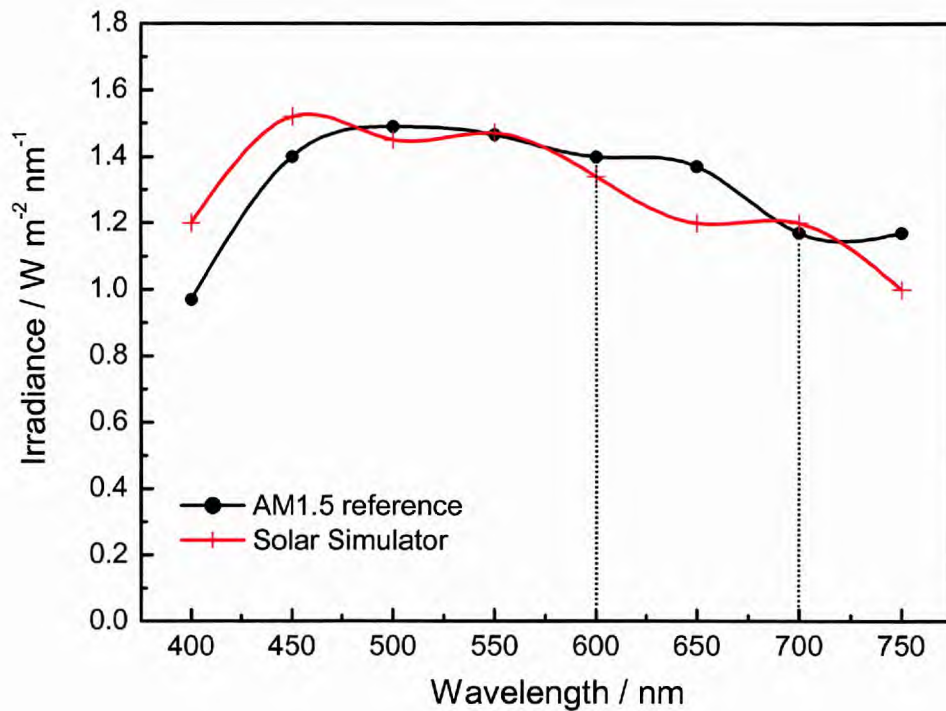


Figure 2.8 – Comparison between the spectral irradiance under AM1.5 conditions and the spectral irradiance of the laboratory-based solar simulator.

3 CuPc-C₆₀ HETEROJUNCTIONS

3.1 Introduction

The use of codeposition as a means of minimising the average distance between photoexcitation sites and D/A interfaces and, in so doing, significantly improving the efficiency of small molecule photovoltaic devices has already been established in the literature (HIRAMOTO *et al.*, 1991; WÖHRLE *et al.*, 1996; MEISSNER & ROSTALSKI, 2000). Parallel studies have elucidated some of the more fundamental aspects of mixing phthalocyanines with fullerenes. Spectroscopic analyses of ZnPc-C₆₀ mixed systems, for example, have ascertained the existence of a weak charge-transfer (CT) complex involving neighbouring Pc and C₆₀ molecules, which serves as an efficient precursor to free charge carrier formation (RUANI *et al.*, 2002). Furthermore, these authors credit Pc/C₆₀ phase segregation and concomitant microdomain formation to 'spinodal decomposition', a term usually associated with the phase-separation mechanism of binary fluids (MCNAUGHT & WILKINSON, 1997). Xue and co-workers (XUE *et al.*, 2005), on the other hand, cite the spherical shape of the C₆₀ molecules as the most prevalent factor influencing domain formation, in that it does not disrupt the orderly stacking (aggregation) of the phthalocyanine molecules to the same extent as another planar molecule would.

Despite these noteworthy developments, surprisingly little is known about the physical parameters (e.g., thin film thickness, morphology) that control device performance. In this chapter, the photophysical and photovoltaic properties of three CuPc/C₆₀-based devices are assessed in terms of their architectures and the efficiencies correlated to the morphological and spectroscopic properties of their constituent thin films.

3.2 Device architectures

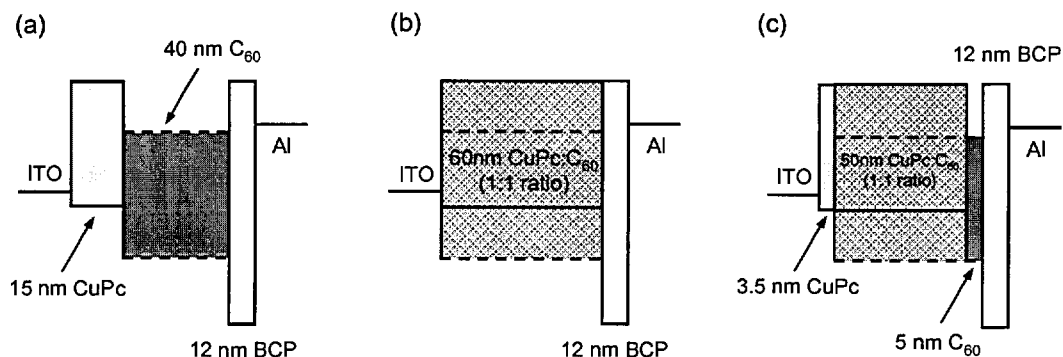


Figure 3.1 – A schematic energy diagram of the photovoltaic device architectures investigated: (a) a discrete CuPc/C₆₀ heterojunction; (b) a fully mixed CuPc:C₆₀ bulk heterojunction; and (c) a planar-mixed structure. The solid and dashed horizontal lines represent the HOMO/LUMO energy levels of CuPc and C₆₀, respectively.

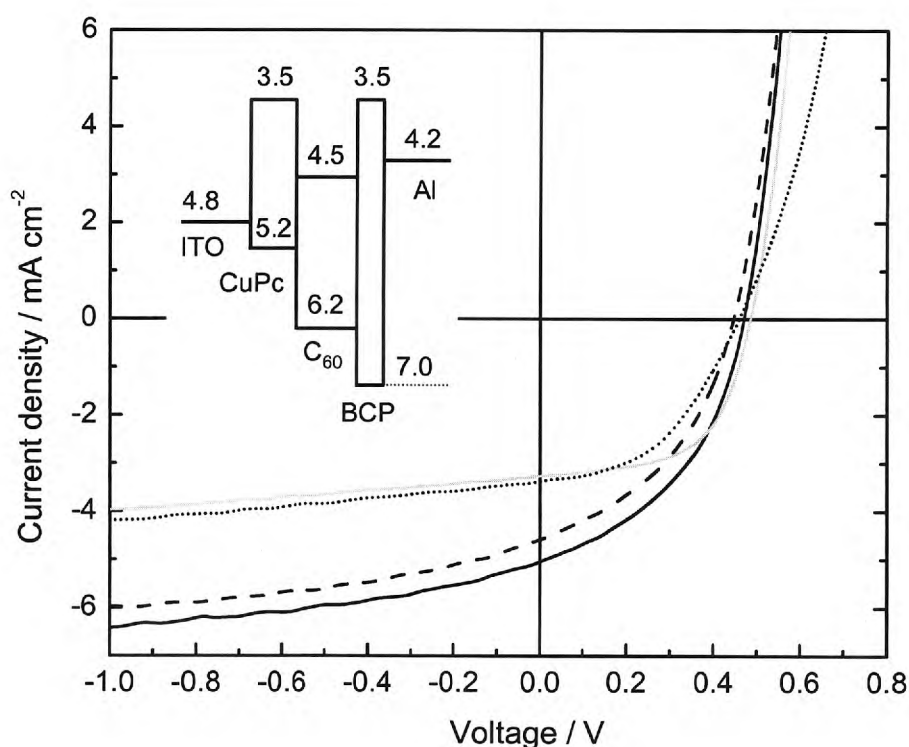
The device structures examined in this chapter are shown schematically in Fig. 3.1 and encompass: (a) a discrete heterojunction analogous to that demonstrated by Peumans and Forrest (PEUMANS & FORREST, 2001) (though without the optimizing ITO surface treatments), which achieved a power conversion efficiency of 3.6% by utilising thin film thicknesses that were of a similar magnitude to the material exciton diffusion lengths ($l_{\text{CuPc}} \approx 10$ nm and $l_{\text{C}_{60}} \approx 40$ nm) (PEUMANS *et al.*, 2003)⁵; (b) a 60 nm single-layer CuPc:C₆₀ (1:1 ratio) bulk heterojunction (BHJ); and, (c) a planar-mixed heterojunction (PM-HJ) structure comprising a 50 nm CuPc:C₆₀ mixed layer (1:1 ratio) sandwiched between two thin continuous layers of pure organic material. All devices incorporate a transparent 12 nm thick BCP ‘exciton blocking layer’ (EBL) between the photoactive region and the Al cathode, which prevents parasitic quenching of

⁵ Exciton diffusion lengths determined by fitting experimental external quantum efficiency (η_{EQE}) data (obtained from ITO/CuPc/C₆₀/Al bilayer devices) to model predications. A general limitation to this approach, however, is that it is experimentally difficult to distinguish between possible contributions due to exciton diffusion and those due to optical interference effects, for example.

the photogenerated excitons at the organic/electrode interface (PEUMANS *et al.*, 2003), and also protects the fragile organic layers from damage during the high-temperature metal deposition (HEUTZ *et al.*, 2004). Electron transport across the large energy gap at the C₆₀/BCP interface occurs mainly through defect states below the BCP LUMO that are introduced during the deposition of the cathode, for which the density of states is sufficient to extract carriers at a rate exceeding photocarrier generation (HIROSE *et al.*, 1996). The trade-off between defect state density, which decreases exponentially as a function of BCP thickness, and depth of film damage, yields an optimal BCP layer thickness of between 10 and 15 nm (PEUMANS *et al.*, 2003).

3.3 J-V characteristics

3.3.1 Device architecture comparison



Device architecture	J_{sc} / mA cm ⁻²	V_{oc} / V	FF	η_p / %
Discrete heterojunction, 15 nm CuPc (.....)	3.41	0.47	0.47	0.75
Discrete heterojunction, 30 nm CuPc (——)	3.25	0.50	0.58	0.94
Bulk heterojunction (---)	4.57	0.45	0.43	0.87
Planar-mixed heterojunction (—)	5.06	0.47	0.44	1.05

Figure 3.2 – Typical J-V characteristics of discrete heterojunctions incorporating 15 nm CuPc (dotted line) and 40 nm CuPc (solid grey line), a bulk heterojunction (dashed line), and a planar-mixed architecture (solid black line). The inset shows the HOMO-LUMO energy levels of the materials with respect to the vacuum level, while the table provides a summary of the characteristic device parameters. All devices were measured under AM1.5 simulated solar illumination at 100 mW cm⁻² (1 sun) with Al contact areas of 0.16 cm².

The effects of incorporating a codeposited CuPc:C₆₀ (1:1 ratio) layer into PV device architectures are clearly evident from J - V measurements under illumination (Fig. 3.2). The short-circuit current density (J_{sc}) of a fully mixed structure (4.57 mA cm⁻²) is significantly enhanced compared to that of the 15 nm CuPc bilayer device (3.41 mA cm⁻²) and is indicative of a higher degree of free-charge generation and collection. These results correspond well with the premise that for discrete heterojunctions only excitons generated within the vicinity of the planar D/A interface contribute to the photocurrent (in this case further limited to the thin CuPc component since C₆₀ exhibits negligible absorption in the visible and IR region of the spectrum), whereas in the bulk heterojunction device the dispersed CuPc-C₆₀ microstructure ensures optical absorption and exciton dissociation throughout the entire device structure. As a result, device efficiencies improve from 0.75 to 0.87%. This is at odds with more recent findings reported by Taima, Uchida and co-workers (TAIMA *et al.*, 2004; UCHIDA *et al.*, 2004) though, in which similar Pc-C₆₀ (1:1 ratio) BHJ devices exhibit power conversion efficiencies that approach, but not exceed, those of the corresponding bilayer systems. This apparent discrepancy is primarily a result of the higher dark conductivity of the device under consideration, which reduces both the V_{oc} and the FF . Doubling of the CuPc thickness to 30 nm raises both the FF and η_p considerably (to 0.58 and 0.94%, respectively), and although the origin of this effect is not clear, it may be an indication that thicker films provide better coverage of the ITO surface and prevent the formation of pinholes and short-circuit pathways that might otherwise arise in thinner films. Indeed, several studies have highlighted the importance of interface modifiers, such as plasma-etching processes and conducting polymer films, including PEDOT:PSS, on the chemical and morphological compatibility of ITO/organic interfaces (PEUMANS & FORREST, 2001; ARMSTRONG *et al.*, 2003). Of note is that compared to this DHJ architecture, the greater optical depth and increased exciton dissociation of the BHJ do not compensate for the increased recombination and trapping losses incurred during carrier extraction through such an intimately blended structure, deduced from the lower FF and η_p values.

In contrast to planar p/n-junctions, in which a large concentration gradient of separated charge pairs exists at a single heterointerface, carrier generation in bulk heterojunctions extends across the whole device thickness such that the driving force for charge separation is reduced. Taking advantage of the improved D-A interfacial area while at the same time avoiding this drop in the internal electric field (inferred from the slightly lower open-circuit voltage value of the BHJ) can be achieved by introducing thin continuous layers of CuPc and C₆₀ at the appropriate organic/electrode interface. As a result, these planar-mixed structures exhibit an open-circuit voltage that almost matches that of the discrete heterojunctions, and combined with a further increase in the short-circuit current density ($\sim 0.5 \text{ mA cm}^{-2}$) yields a power conversion efficiency of 1.05%.

3.3.2 *Light-intensity dependent measurements*

Light-intensity dependent measurements provide an indirect approach to unravelling some of the major loss mechanisms in PV device operation. The *J-V* curves over a range of intensities are shown in Fig. 3.3(a) and Fig. 3.4(a) for discrete and planar-mixed heterojunction devices, respectively, with the characteristic cell parameters plotted as a function of incident optical power in the corresponding lower panels. It should be noted that the PM-HJ structure described hereafter (ITO/20 nm CuPc/40nm CuPc:C₆₀ (1:1 ratio)/20 nm C₆₀/12 nm BCP/Al) differs to that described in the previous section (ITO/3.5 nm CuPc/50 nm CuPc:C₆₀ (1:1 ratio)/5 nm C₆₀/12 nm BCP/Al).

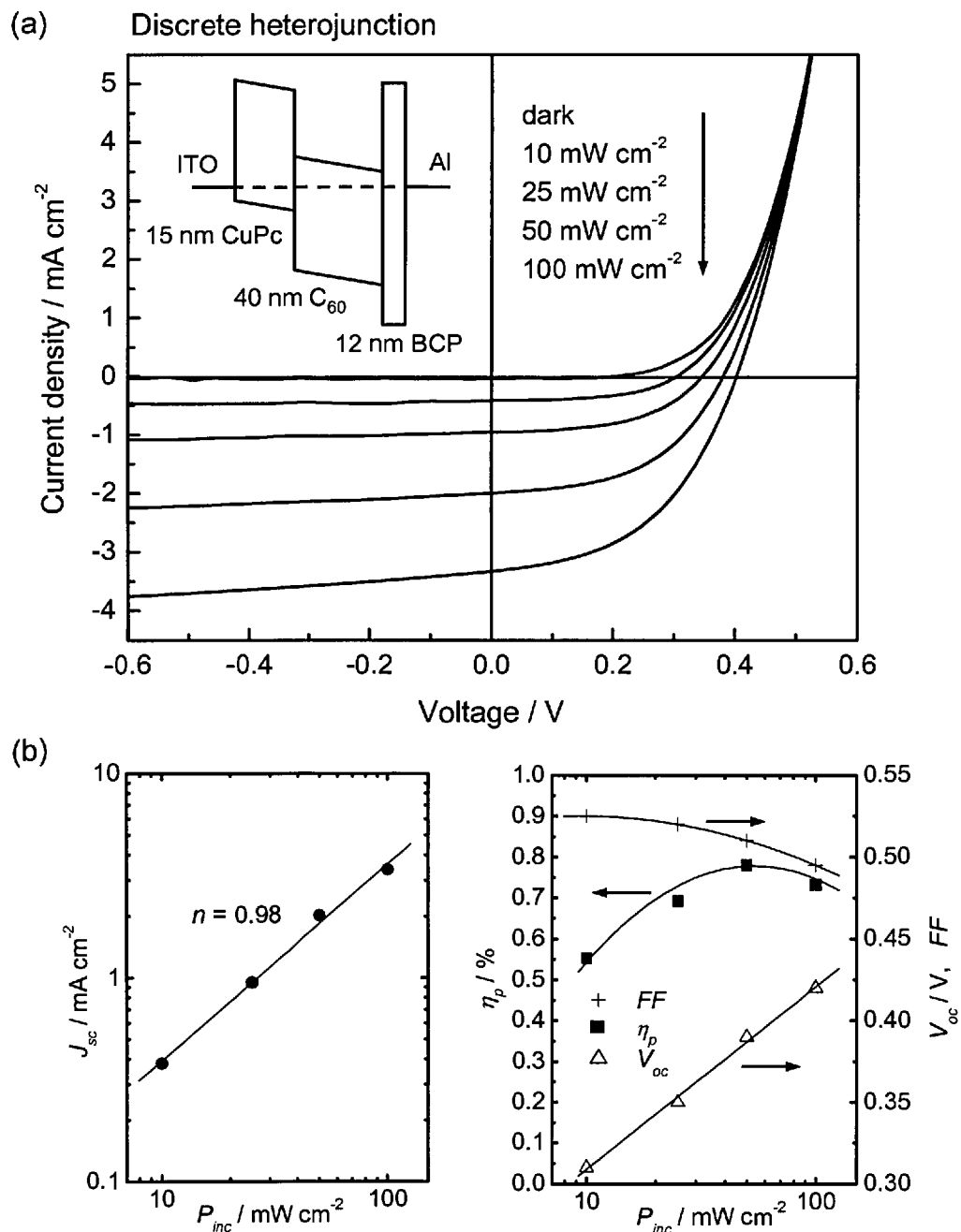


Figure 3.3 – (a) *J-V* curves for an ITO / 15 nm CuPc / 40 nm C₆₀ / 12 nm BCP / Al discrete heterojunction at various illumination intensities, and (b) the corresponding device parameters plotted as a function of incident optical power; **left panel**: short-circuit current density (closed circles); **right panel**: fill factor (crosses), open-circuit voltage (open triangles), and power conversion efficiency (closed squares). The solid lines through the experimental data points are a guide to the eye. The schematic band diagram under short-circuit conditions is also shown.

For both architectures, the short-circuit current density (J_{sc}) increases linearly with the log of illumination intensity, signifying that the cell is governed by a power-law dependence (i.e., $J_{sc} \propto P_{inc}^n$). The exponent n gives some indication as to the relative exciton generation and annihilation kinetics. A square-root dependence ($n = 0.5$) implies bimolecular recombination between non-related 'distant-pairs', while a linear behaviour ($n = 1$) points toward recombination that is predominantly monomolecular in nature (i.e., geminate-pair recombination) and that charge carrier losses are localized on defects or impurities. The scaling exponent of the DHJ short-circuit current density line fit (Fig. 3.3(b)), as expected from a structure that utilises two well-defined transporting layers in which the electrons and holes are effectively separated from each other, is close to unity ($n = 0.98$) and suggests that bimolecular recombination is not significant, even at the highest illumination intensities/carrier concentrations. The intimately mixed phase structure of a PM-HJ, on the other hand, results in an increased recombination probability within the codeposited bulk and a greater deviation from the more uniform regime ($n = 0.84$) (Fig. 3.4(b)). Indeed, linear proportionality between J_{sc} and P_{inc} (with a slope of unity) has previously also been observed for similarly configured CuPc/C₆₀ ($n = 1.01$) (XUE *et al.*, 2004) and pentacene/C₆₀ ($n = 0.998$) (YOO *et al.*, 2005) devices, while the exponent obtained for the PM-HJ falls within the large range of values reported for PPV:PCBM ($n = 0.85 - 0.92$) (GEBEYEHU *et al.*, 2001; DYAKONOV, 2004), P3HT:PCBM ($n = 0.81$) (KIM *et al.*, 2005) and ZnPc:C₆₀ ($n = 0.62$) (GEBEYEHU *et al.*, 2003) BHJs. The extensive diversity of BHJ-related scaling exponents is presumably material and morphology dependent. That is to say, it is determined by the carrier mobility in the pristine materials and the phase separation and aggregation of the two components inside the interpenetrating mixture, both of which can vary considerably from one system to the next.

The increased recombination, as well as the low mobility and higher dark conductivity associated with an interpenetrating CuPc:C₆₀-containing structure, contributes towards the significantly lower *FF*s of the planar-mixed device, and is noticeable in particular as the density of carriers builds up under intense solar illumination (Fig. 3.4(b)). In contrast, the *FF* of the discrete heterojunction device remains relatively constant, decreasing only marginally from 0.52 at 10 mW cm⁻² to just below 0.5 at 100 mW cm⁻² (Fig. 3.3(b)). Consequently, the power conversion efficiency (η_p) of the PM-HJ device decreases monotonically, and almost linearly, with increasing log of irradiation intensity (from 0.56 to 0.42% between 10 and 100 mW cm⁻², respectively), while that of the DHJ device steadily increases up to its maximum value of 0.75% at 50 mW cm⁻² before rolling off at the highest intensity. This behaviour is again comparable with that described in the literature: ITO/pentacene (45 nm)/C₆₀ (50 nm)/BCP (10 nm)/Al structures, for example, exhibit a moderate increase in the V_{oc} (from 0.33 to 0.36 V), a slight decrease in the *FF* (from 0.54 to 0.50) and, consequently, a relatively stable η_p (~2.7%) as a function of illumination (P_{inc} varied between 27 and 100 mW cm⁻²) (YOO *et al.*, 2005). However, as with the $J_{sc} \propto P_{inc}^n$ dependence, variations in the *FF* and η_p of BHJ and PM-HJ structures depend, to a great extent, on the choice of materials and, in particular, on the film thicknesses and composition ratios, making generalizations much more difficult. Nevertheless, the introduction of a mixed layer typically results in a considerable reduction of the *FF* and η_p with increasing light intensity (MEISSNER & ROSTALSKI, 2000; UCHIDA *et al.*, 2004).

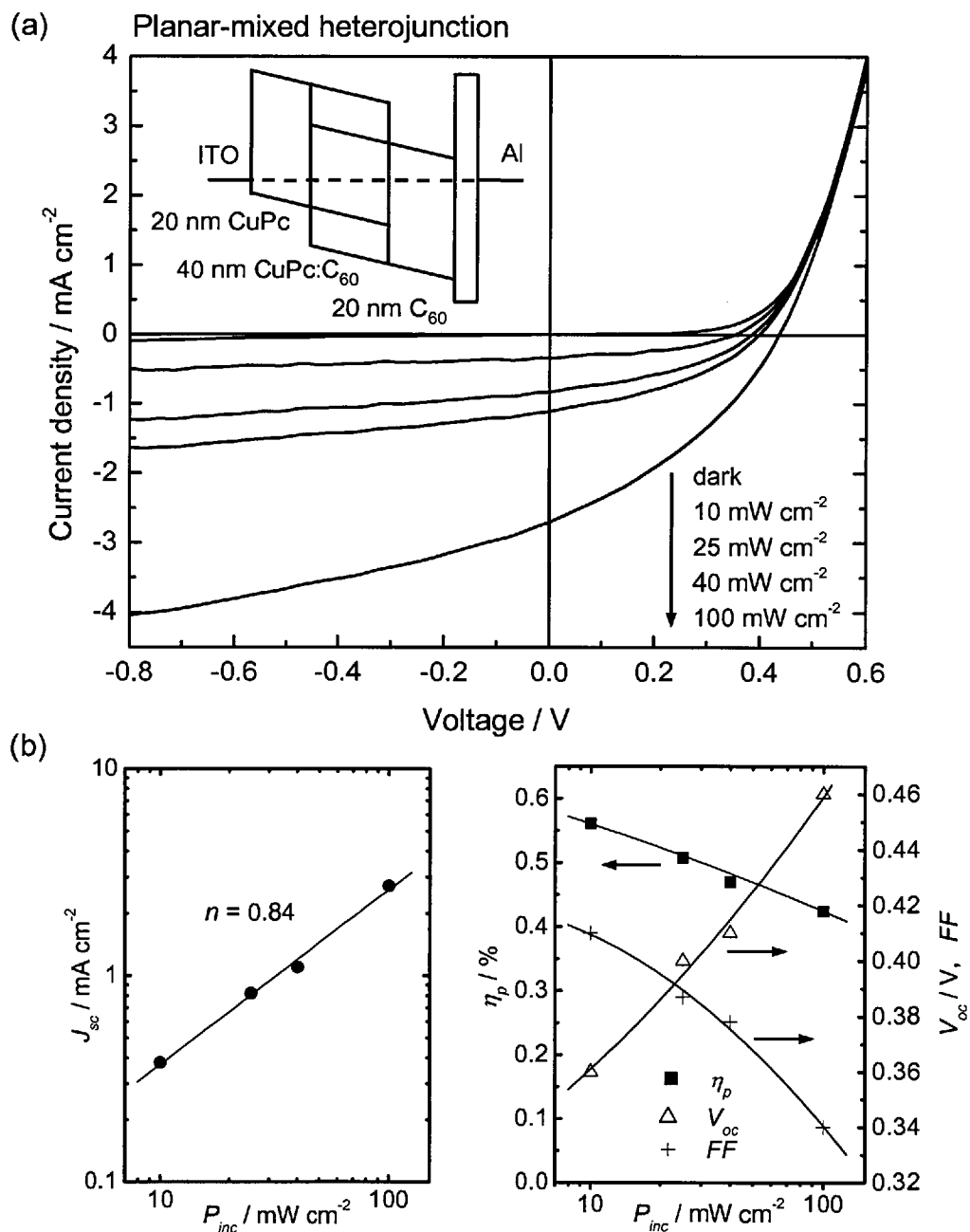


Figure 3.4 – (a) *J-V* plots for an ITO/20 nm CuPc/40nm CuPc:C₆₀/20 nm C₆₀/12 nm BCP/Al planar-mixed heterojunction at various illumination intensities, and (b) the corresponding device parameters plotted as a function of incident optical power; **left panel**: short-circuit current density (closed circles); **right panel**: fill factor (crosses), open-circuit voltage (open triangles), and power conversion efficiency (closed squares). The solid lines through the experimental data points are a guide to the eye. The schematic band diagram under short-circuit conditions is also shown.

3.3.3 Normalised light-intensity characteristics

The overlap of the normalised light-intensity dependent J - V curves⁶ (Fig. 3.5 and Fig. 3.6) at $V < 0.2$ V and $V < 0.3$ V for the DHJ and PM-HJ devices, respectively, implies that the dark current within this regime is negligible and that the quantum efficiency is independent of the incident optical power. At higher irradiation levels and forward bias ($V > 0.4$ V) the increasing contribution of the dark conductivity, as well as the concomitant reduction in FF , become apparent, and are especially pronounced for structures incorporating a mixed layer. The net effect on the PM-HJ, as elucidated in section 3.2.2, is the continuous reduction in device performance. In contrast, the increased dark current and diminished FF do not outweigh the increase in J_{sc} of the DHJ until a light intensity of approximately 50 mW cm^{-2} is reached, at which point the power conversion efficiency starts to drop.

The maximum power that a PV cell generates occurs when the product of current and voltage is greatest, a point situated between the J_{sc} and V_{oc} along the J - V curve. This point represents the maximum efficiency of the solar device in converting sunlight into electricity. Shown in the inset of Fig. 3.5 and 3.6, respectively, are the power-voltage (P - V) curves of the DHJ and PM-HJ device. The discrete heterojunction device delivers 0.73 mW at a maximum power point (P_m) of 0.28 V under solar irradiation of 100 mW cm^{-2} , significantly higher than the 0.42 mW that the planar-mixed device generates at a P_m of 0.26 V . The power output decreases nearly linearly with incident solar power and at lower intensities the power curves display a relatively broad plateau, thus operating close to their maximum power over a greater range.

⁶ J - V curves arbitrarily normalised to their short-circuit current values.

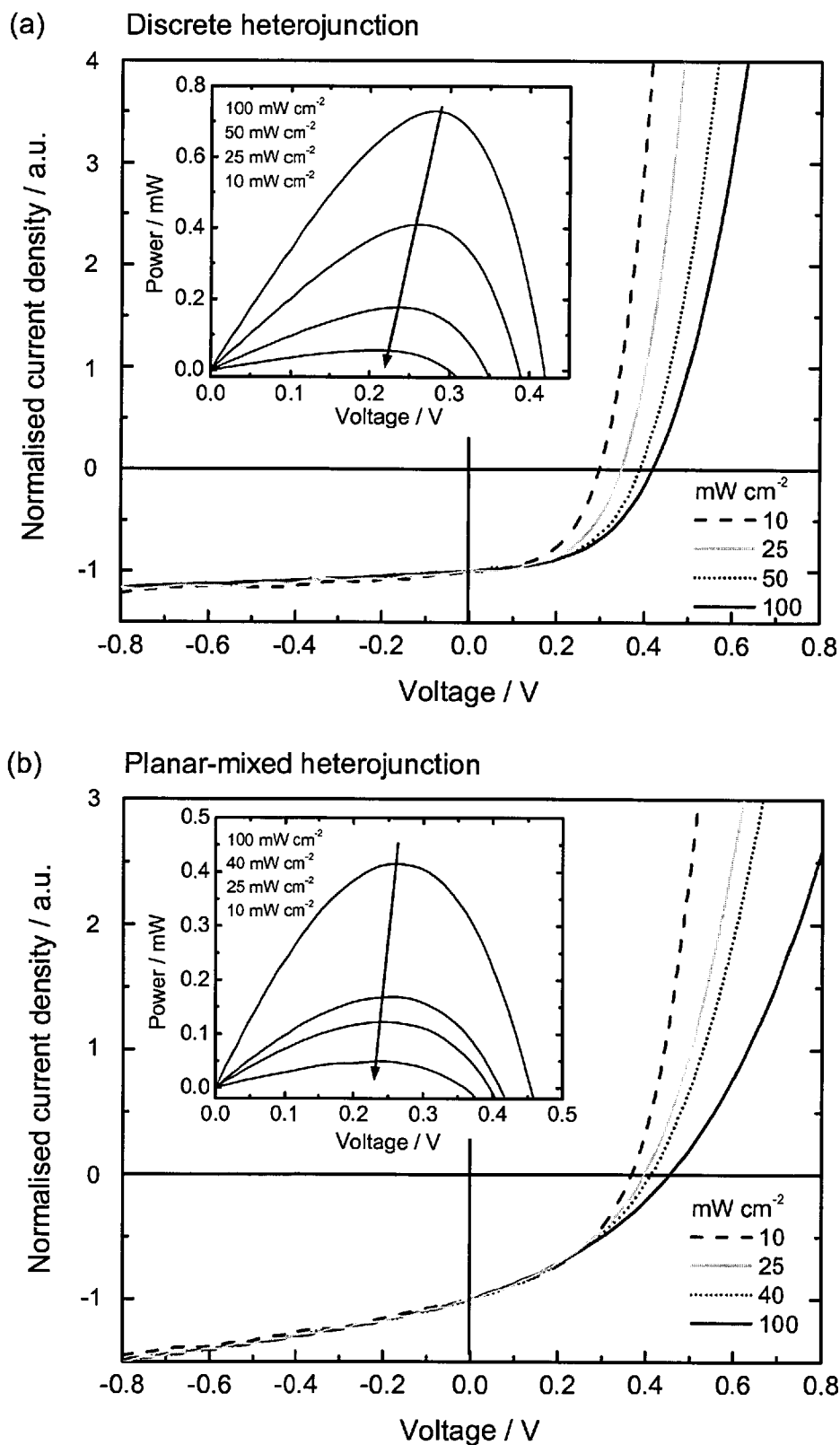


Figure 3.5 – Normalised J-V curves of (a) ITO/15 nm CuPc/40 nm C₆₀/12 nm BCP/Al devices, and (b) ITO/20 nm CuPc/40 nm CuPc:C₆₀/20 nm C₆₀/12 nm BCP/Al devices, as a function of incident optical light intensity. The inset shows the corresponding P-V curves.

3.4 Morphology and spectroscopy

Figure 3.6 shows AFM images of single-, double- and mixed-layer surface morphologies. CuPc films deposited at room temperature (Fig. 3.6(a)) adopt small spherical crystallites of the α -polymorphic phase with a root-mean square roughness, R_q , of between 1 and 4 nm depending on film thickness. C₆₀ thin films (Fig. 3.6(b)) feature a similar topography (typically $R_q = 0.6$ nm), though with much finer grains. Codeposition produces substantial changes in the morphology compared to the sequentially evaporated double layer, with films containing 50% CuPc (Fig. 3.6(c)) assuming a smooth amorphous morphology that is notable for the absence of any crystallites. The homogeneity of the corresponding phase image (Fig. 3.6(d)) suggests that microdomain formation (if present) is on a length scale that is less than the resolution of the AFM (~10 nm). The smooth morphology of codeposited films is retained within a narrow range of mixing ratios (approximately 50-75% CuPc), below which the topography features large island-like structures about 40-60 nm in diameter (HEUTZ *et al.*, 2004), and above which the topography is characteristic of monomolecular CuPc thin films (Fig. 3.6(e)).

The electronic absorption spectrum of CuPc in solution displays sharp monomer absorption at 679 nm with vibronic progression at lower wavelengths (solid grey line, Fig. 3.7). In the solid state, CuPc thin films generally adopt the α -polymorphic structure (see section 1.5.1, p. 21); the crystals can be reduced to tilted dimers where the molecular transitions are split into two components due to Davydov splitting (LEZNOFF & LEVER, 1989). This leads to two broad peaks centered at 625 and 694 nm (solid black line), the latter being less intense in the pure phase. For mixed layers, the relative peak heights vary with CuPc:C₆₀ mixing ratio, with the higher wavelength peak beginning to dominate as the CuPc content decreases from 75 to 50% (dashed and dotted lines, respectively). Since C₆₀ absorbs mainly at lower wavelengths (<500 nm), the evolution of the

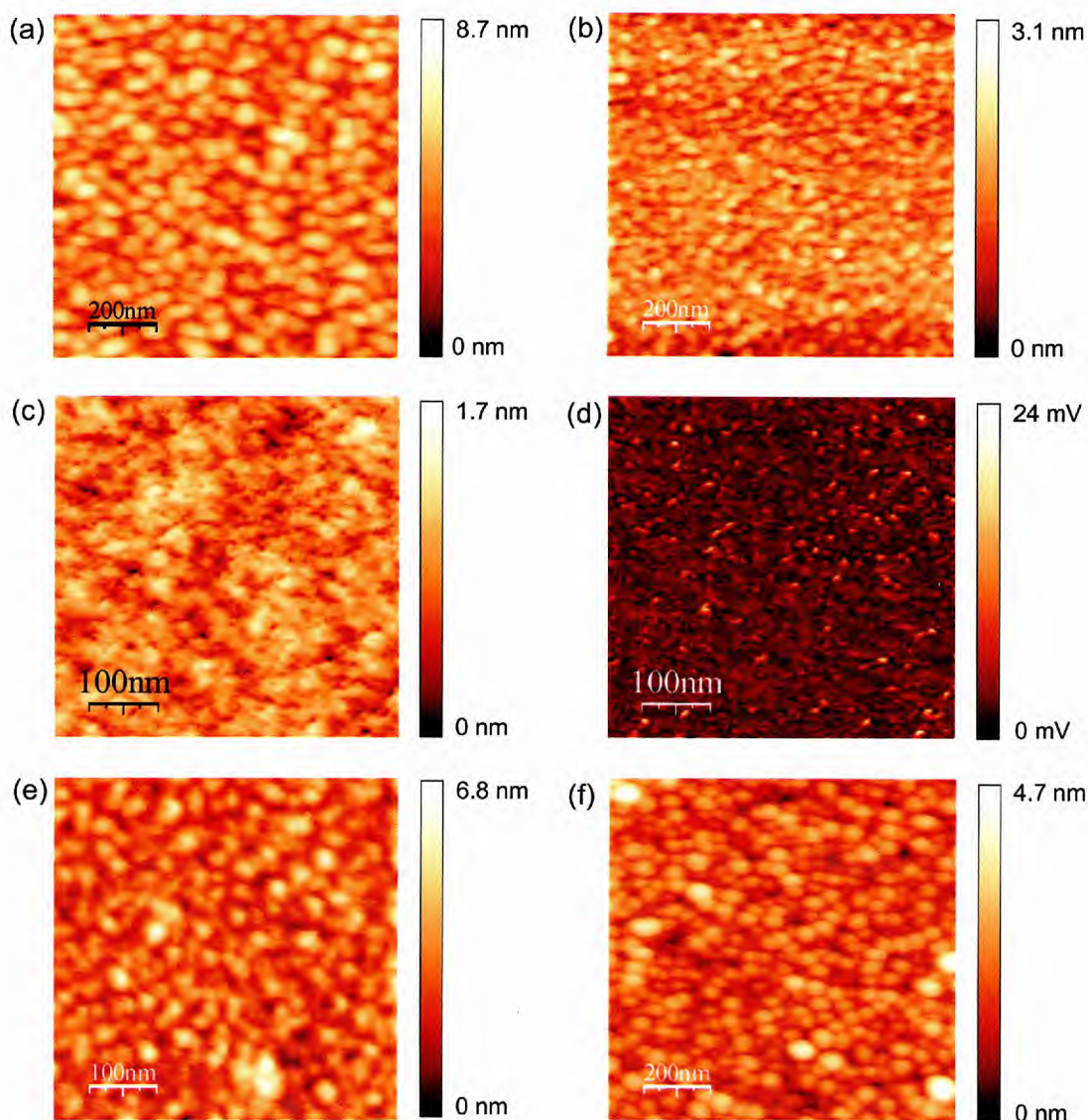


Figure 3.6 – AFM images of (a) 40 nm CuPc ($R_q=1.52$ nm); (b) 75 nm C₆₀ ($R_q = 0.6$ nm); (c,d) 40 nm CuPc:C₆₀ (1:1 ratio), topographical ($R_q = 0.39$ nm) and phase image, respectively; (e) 40 nm CuPc:C₆₀ (9:1 ratio) mixed film ($R_q = 0.84$ nm); (f) 20 nm CuPc/40 nm C₆₀ double layer ($R_q = 1.6$ nm). All films grown on quartz substrates.

694 nm peak cannot be rationalized in terms of additional C₆₀ content. As the enhanced intensity occurs in the region of monomer absorption, and since in the solid state the sharp monomer peak observed at 679 nm in solution is broadened due to molecular aggregation, it can be concluded that these changes are due to an increasing contribution from non-interacting CuPc monomer species.

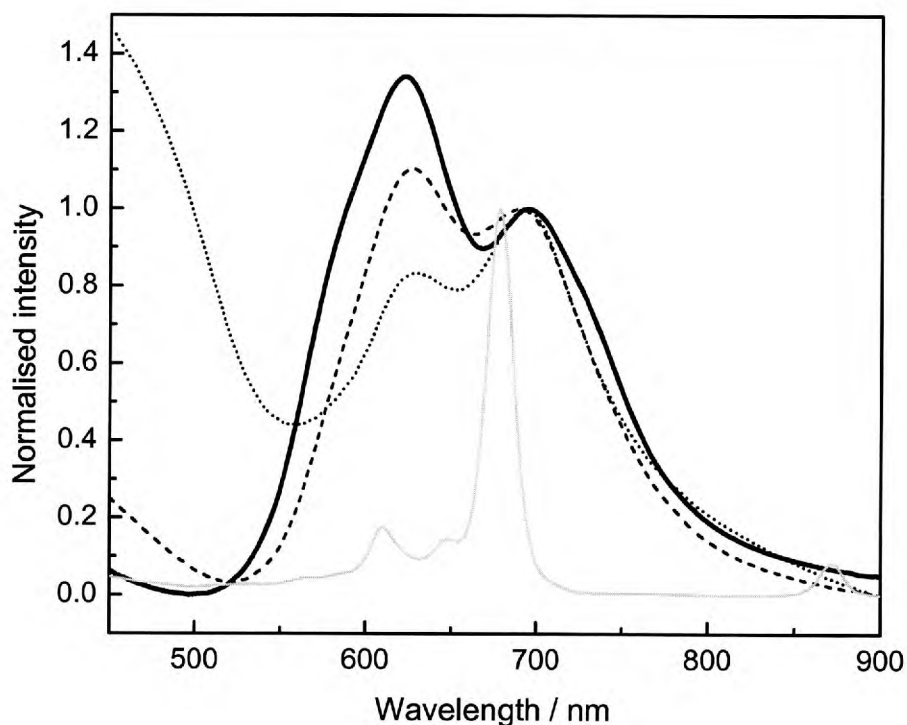


Figure 3.7 – Electronic absorption spectra for solution phase CuPc (solid grey line), a single layer CuPc film (solid black line), a CuPc:C₆₀ mixed layer containing 75% CuPc (dashed line) and a CuPc:C₆₀ mixed layer containing 50% CuPc (dotted line). All thin-film spectra are normalized to the maximum between 650 and 750 nm. C₆₀ (not shown) absorbs below 500 nm.

3.5 Conclusions

This chapter has demonstrated some of the potential benefits (and shortcomings) associated with the use of codeposited films in organic PV devices. A comparative device and performance analysis of a 15 nm CuPc/40 nm C₆₀ discrete heterojunction, a 30 nm CuPc/40 nm C₆₀ discrete heterojunction, a 60 nm CuPc:C₆₀ (1:1 ratio) bulk heterojunction and a 3.5 nm CuPc/50 nm CuPc:C₆₀ (1:1 ratio)/5 nm C₆₀ planar-mixed heterojunction has been performed. While the incorporation of CuPc:C₆₀ (1:1 ratio) mixed layers enhances photocarrier generation, losses incurred by trapping and recombination in such intimately mixed films dictate device performance. This is reflected in the cell

characteristics: the device comprising a fully mixed layer exhibited a superior short-circuit current density (4.57 mA cm^{-2}) compared to both discrete heterojunction architectures (3.41 and 3.25 mA cm^{-2} for the 15 nm and 30 nm CuPc-containing devices, respectively), but a diminished fill factor and open-circuit voltage (values of 0.43 and 0.45 V for the BHJ compared to 0.47 and 0.47 V for the 15 nm CuPc-containing DHJ and 0.58 and 0.50 V for the 30 nm CuPc-containing DHJ). The corresponding device efficiencies are therefore 0.87% for the 60 nm CuPc:C₆₀ BHJ, 0.75% for the 15 nm CuPc/ 40 nm C₆₀ DHJ and 0.94% for the 30 nm CuPc/ 40 nm C₆₀ DHJ.

Taking advantage of the improved D-A interfacial area while at the same time avoiding the drop in internal electric field can be achieved by adding thin continuous layers of CuPc and C₆₀ at the appropriate organic/electrode interface. The high J_{sc} (5.06 mA cm^{-2}) and V_{oc} (0.47 V) are offset by a low FF (0.44) and consequently improvements in η_p are only marginal (1.05%). However, it is known that the characteristic device parameters are dependent on the mixing ratio, and that optimization of the structure can lead to further improvements (HEUTZ *et al.*, 2004; SULLIVAN *et al.*, 2004).

Light-intensity dependent measurements on a 15 nm CuPc/ 40 nm C₆₀ DHJ device and a 20 nm CuPc/ 40 nm CuPc:C₆₀ ($1:1$ ratio)/ 20 nm C₆₀ PM-HJ device have elucidated some of the loss mechanisms occurring in molecular PV devices. For both architectures the J_{sc} was observed to increase linearly with the log of illumination intensity signifying that the cells are governed by a power-law dependence. Differences in the scaling exponent ($n = 0.98$ for the DHJ and $n = 0.84$ for the PM-HJ) arise from the increased recombination probability within the codeposited bulk, as expected. Increasing the light intensity from 10 to 100 mW cm^{-2} was found to have a particularly strong and detrimental effect on the FF and η_p of the PM-HJ device, attributed to the increased resistance to charge transport within the CuPc:C₆₀ bulk.

Morphological and spectroscopic results highlighted the intimately mixed nature of CuPc:C₆₀ (1:1 ratio) codeposited structures. Compared to the spherical crystallites obtained for CuPc thin films ($R_q = 1 - 4$ nm), the codeposited film assumes a smooth, amorphous morphology ($R_q = 0.39$ nm) with microdomains that, if present, are less than 10 nm in size. These findings support the electronic absorption data from such mixed films, which showed an increased contribution from non-interacting CuPc monomer species (i.e., a decrease in the relative intensity of the CuPc peak at 625 nm).

4 INFLUENCE OF ANNEALING

4.1 Introduction

Although the photoactive region in bulk heterojunctions is greatly enlarged compared to that of the corresponding planar architecture, studies on molecular-based solar cells have demonstrated that there is an optimal mixed layer thickness (~30-50 nm) beyond which the advantages gained by greater exciton dissociation no longer outweigh the increasing resistance to charge transport (MEISSNER & ROSTALSKI, 2000; DRECHSEL *et al.*, 2004; TAIMA *et al.*, 2004). Indeed, it has recently been calculated that the respective electron and hole mobilities are reduced by approximately one and a half orders of magnitude when intermixing C₆₀ and CuPc at a ratio of 1:1 by weight (XUE *et al.*, 2005), a consequence of the excessively small D/A domain sizes. As the electric current that a PV cell delivers is not only contingent upon the fraction of electron-hole pairs that are dissociated but also upon the fraction of charges that reach the electrodes, controlling the scale of phase separation becomes paramount. Codeposition at elevated substrate temperatures and, in particular, post-growth thermal annealing may provide a means of achieving that aim (see, for example, (PEUMANS *et al.*, 2003) and (SUEMORI *et al.*, 2005)).

This chapter explores some of the fundamental issues associated with high-temperature heat treatments, such as increases in film roughness and changes in polymorphic form, and examines their impact on CuPc/C₆₀ discrete heterojunction device performance. Furthermore, the phase segregation in CuPc:PhEt-PTC composite structures subjected to post-fabrication thermal annealing is elucidated by means of electronic absorption, AFM and XRD.

4.2 Thermal annealing of CuPc in discrete heterojunctions

4.2.1 Structural and spectroscopic characterisation

As pointed out in the introduction (section 1.5.1, p. 21), vacuum evaporated CuPc films generally adopt one of two polymorphic forms, α or β . As-deposited thin films, and those subsequently annealed for up to an hour at 325 °C, display the optical and morphological features of the α -phase; that is, a broad electronic absorption profile in the visible region with maxima at 625 and 694 nm (solid black line, Fig. 4.1(a)) and a surface morphology composed of small, spherical crystallites (Fig. 4.2(a) and (b)). Only a modest variation in the relative peak intensities and positions are observed during this time period (6% increase in the 694 nm peak and a 5 nm red-shift, respectively), though the gradual increase in surface roughness (from 1.5 to 4.1 nm) as well as the nucleation of progressively larger crystallites suggests a reorganisation of the underlying structure. This is confirmed by the powder XRD scans of half-hour and hour-long annealed films (dashed and dashed-dotted lines in Fig. 4.1(b), respectively), which exhibit neither intense reflection from the (200) lattice plane of the α -phase at $2\theta = 6.9^\circ$ nor the well-defined (001) diffraction peak at $2\theta = 7.1^\circ$ that is characteristic of the β -polymorph.⁷ The diffractogram of the latter, in particular, is notable for the absence of any distinct features. The structural inhomogeneity of this intermediate state is attributed to the distortion of the CuPc unit cell during the $\alpha \rightarrow \beta$ transition.

⁷ It should be noted that diffraction from the β -CuPc (001) peak, even for thin films annealed for longer than the two hours necessary for complete transformation, was generally observed to be less intense than that of the less crystalline α -phase, possibly due to partial desorption of material, especially as the annealing process takes place close to the thermal sublimation temperature of CuPc (~360-370 °C).

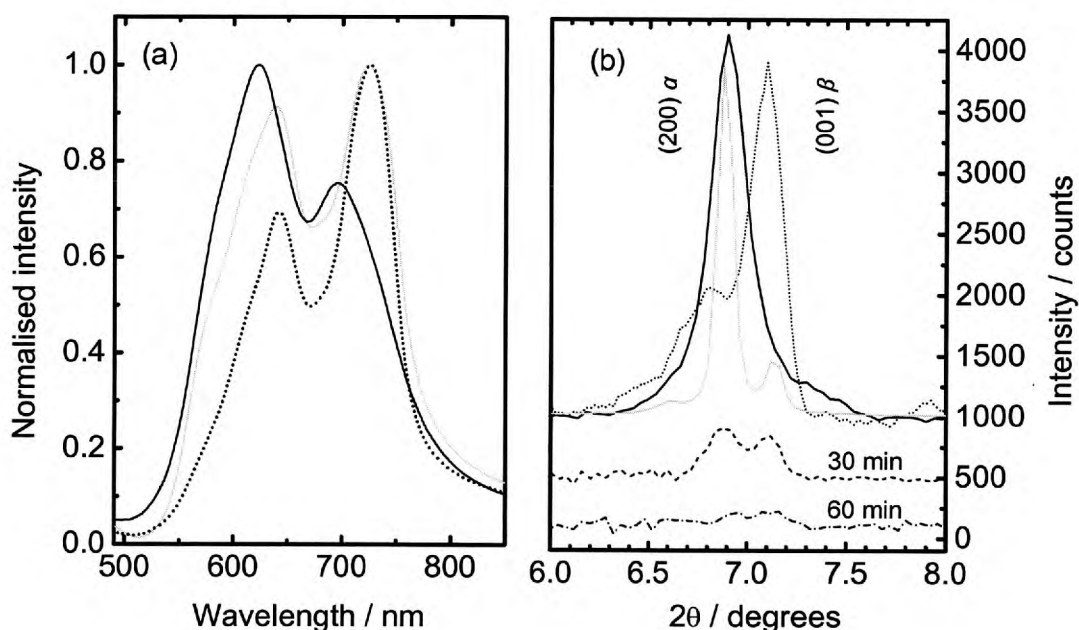


Figure 4.1 – Normalised electronic absorption spectra (a) and corresponding powder XRD scans (b) of a CuPc thin film: grown at room temperature, α -polymorph (solid black line); subjected to a post-growth anneal of 325 °C for two hours, β -polymorph (dotted line); deposited at an elevated substrate temperature of 325 °C (solid grey line). Also shown in (b) is the x-ray diffractogram of CuPc films grown at room temperature and then annealed at 325 °C for half-an-hour (dashed line) and one hour (dashed-dotted line). The diffraction peaks at $2\theta = 6.9^\circ$ and $2\theta = 7.1^\circ$ correspond to a value of d , the interplanar spacing, of 12.83 Å and 12.44 Å, respectively. The XRD data from the α -CuPc (solid black line) and elevated substrate temperature (solid grey line) samples have been scaled down by a factor of 2 and 50 respectively.

Pronounced morphological changes, in the form of elongated β -crystallites, become apparent after at least an hour of thermal annealing (Fig. 4.2(c)). These are directionally aligned over small domains, although across larger surface areas there is no preferential orientation. Complete coverage ensues after an annealing period of two hours at 325 °C (Fig. 4.2(d)). The corresponding electronic absorption spectra of these films feature a transposition of the peak maxima relative to the α -CuPc polymorph in addition to a spectral red-shift of approximately 20 nm, observations that have previously been correlated to the increase in crystallite size (LOUTFY & HSIAO, 1981). Prolonged periods of annealing (>2 hours) do not lead to any appreciable change in either the morphological or the optical properties.

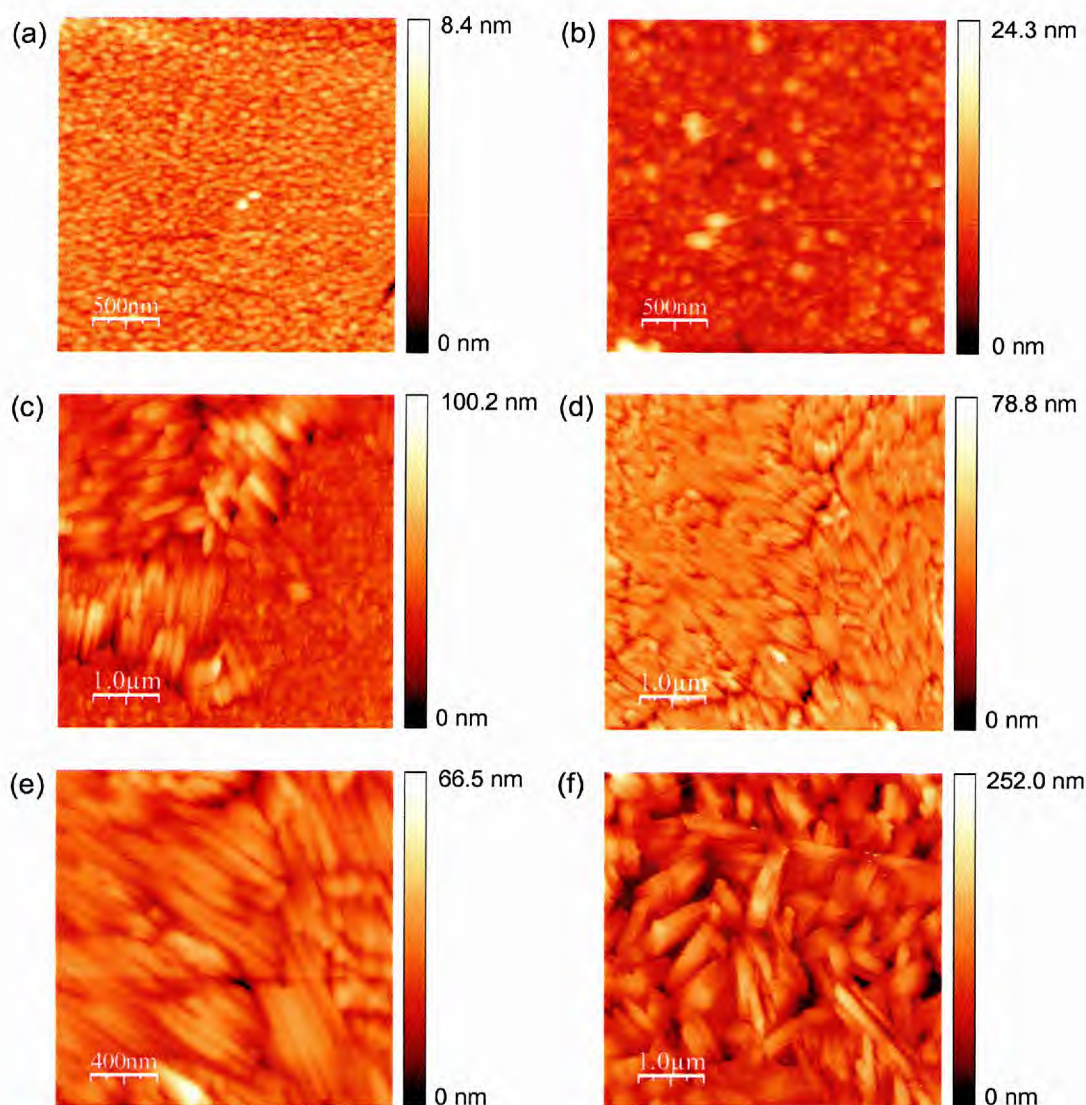


Figure 4.2 – AFM images of (a) an as-deposited 40 nm thick α -CuPc film; (b-d) 40 nm α -CuPc films subjected to a post-growth heat treatment of 325 °C for 60, 75 and 120 minutes, respectively; (e) detail of the 120 minute annealed, fully-transformed, β -CuPc film; (f) a CuPc film deposited at $T_s = 325$ °C. The typical R_q values are (a) 1.5 nm, (b) 4.1 nm, (c) 8.9 nm, (d) 6.2 nm, (e) 5.5 nm, and (f) 28.6 nm.

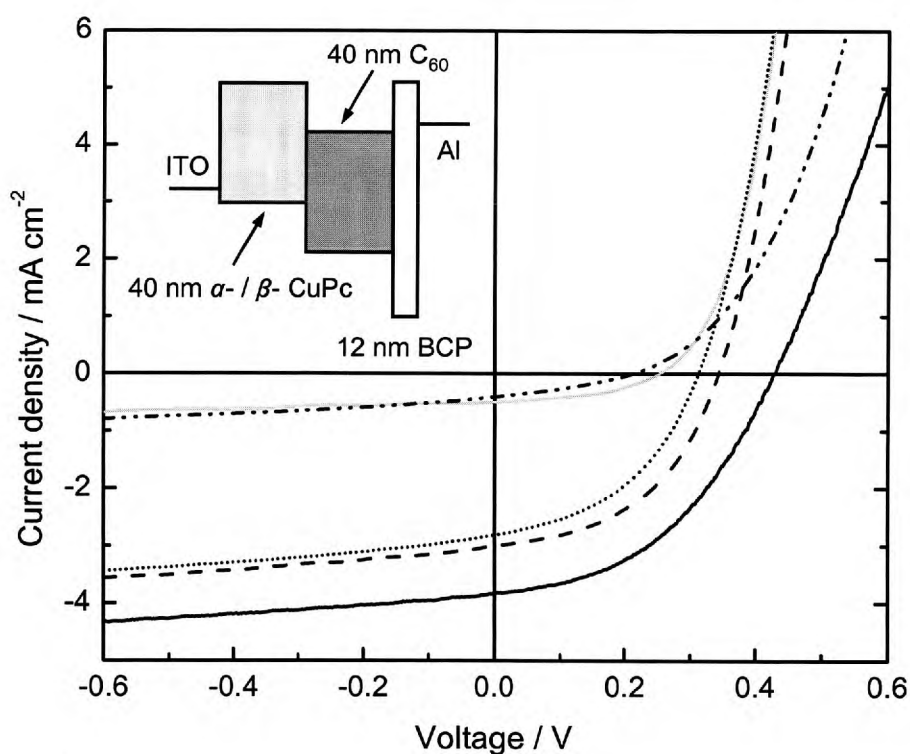
Films produced by sublimation onto quartz or ITO substrates maintained at elevated substrate temperatures ($T_s = 325$ °C) feature a coarse, granular morphology with randomly orientated crystallites that share the same shape, but are almost twice the size, as those obtained by thermal annealing (Fig. 4.2(f)). Both electronic absorption and XRD measurements (grey lines in Fig.

4.1(a) and (b), respectively) reveal that these highly crystalline films are composed of a mixture of α -phase material and β -crystallites.

4.2.2 Device characterisation

The importance of thin film morphology and structural order in molecular solar cells is evident from the J - V characteristics of devices incorporating thermally annealed CuPc layers, shown in figure 4.3. Discrete heterojunctions, in which the CuPc films are annealed for shorter time periods (30 and 60 minutes), demonstrate power conversion efficiencies that are over an order of magnitude less than that of the as-deposited device. This is primarily due to the diminished short-circuit current densities, and correlates well with the previous observation of a disordered phthalocyanine film in which the molecules undergo a structural reorganisation (i.e., the absence of any distinct peaks in the corresponding X-ray diffraction spectra). This general lack of long-range order presumably inhibits exciton diffusion and dominates carrier mobility.

Devices containing 90 and 120 minute annealed CuPc layers exhibit a similar, though less severe, reduction in efficiency compared to the α -CuPc/C₆₀ device. As the transition from the α - to the β -phase is almost or fully complete at this stage of the annealing process (as indicated by the electronic absorption spectra and XRD scans) this decrease cannot simply be ascribed to structural deformities. Two possible explanations are therefore considered: first, the interface morphology of the β -CuPc/C₆₀ double layers, and second, the ostensibly inferior conductive properties of the β -CuPc polymorph.



CuPc anneal time at 325 °C / mins	$J_{sc} / \text{mA cm}^{-2}$	V_{oc} / V	FF	$\eta_p / \%$
30 (—)	0.49	0.26	0.46	0.06
60 (— · ·)	0.41	0.22	0.32	0.03
90 (· · · · ·)	2.81	0.29	0.45	0.36
120 (— — —)	3.02	0.31	0.48	0.46
No anneal [†] (—)	3.84	0.43	0.44	0.73
No anneal [‡] (not shown)	4.03	0.45	0.49	0.87

Figure 4.3 – J-V characteristics (under AM1.5 simulated solar illumination at 100 mW cm^{-2}) of CuPc/ C_{60} discrete heterojunction devices, in which the CuPc thin films were annealed for variable time periods prior to the deposition of C_{60} , BCP and Al. The inset shows a schematic energy level diagram while the table provides a summary of the characteristic device parameters. Al contact areas for all cells are 0.16 cm^2 . [†]'Control' sample, in which the device was exposed to air subsequent to CuPc deposition. [‡]'Control' sample grown without venting chamber. Note that there is very little difference between the two control samples with or without exposure to air. See text for details.

AFM images of as-deposited and annealed bilayers (Fig. 4.4(b-d)) reveal that the heat-treated structure features a substantial increase in surface roughness (from 1.2 to 8.1 nm). The marked morphological templating, whereby the C_{60} layer adopts the topography of the underlying β -CuPc film, is a consequence of the ‘shadowing’ effects that are inherent in molecular-beam growth systems; the ballistic trajectory of the sublimed C_{60} source material prevents it from adequately filling the voids that arise during the phthalocyanine transformation process (HEUTZ, 2002). This reduces the effective contact area at both the β -CuPc/ C_{60} heterointerface and the organic/metal interface and, in turn, diminishes the probability of exciton separation and charge collection. This effect is particularly problematic for devices incorporating CuPc grown at elevated substrate temperatures, where the high density of ‘pin-holes’ leads to short-circuited devices.

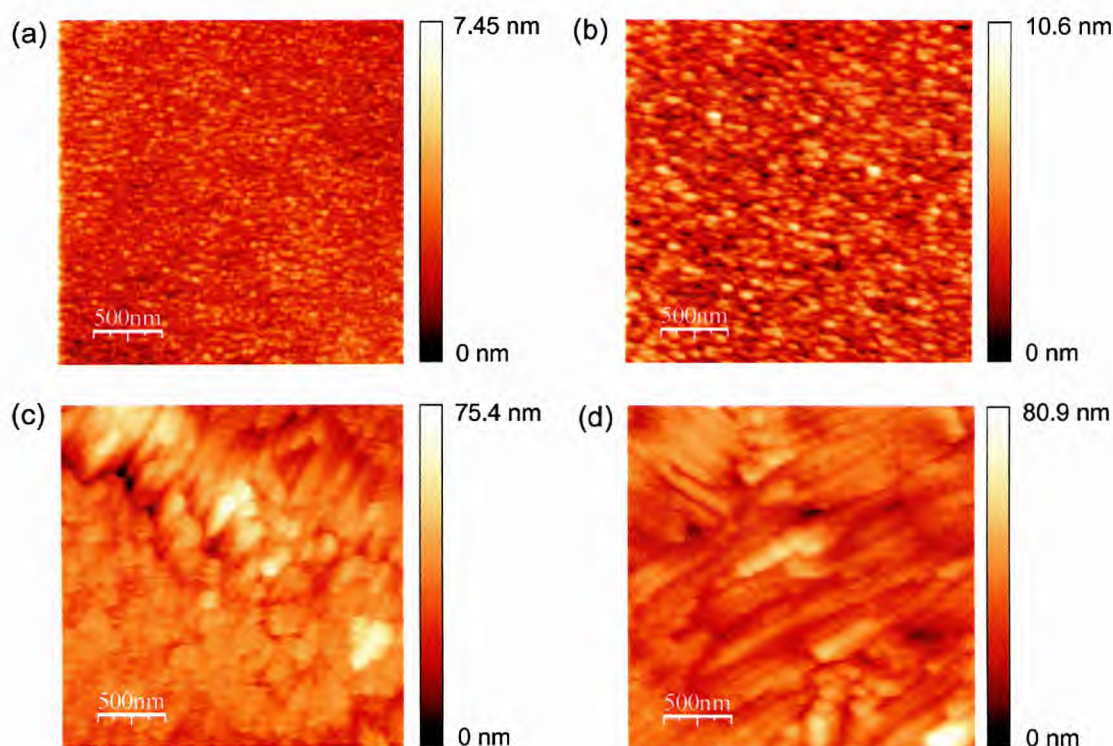


Figure 4.4 – AFM images of (a) a 40 nm C_{60} film; and 40 nm CuPc/40 nm C_{60} structures containing CuPc films annealed for (b) no anneal (α -CuPc); (c) 75 minutes (partial transformation); (d) 120 minutes (fully transformed β -CuPc film). The measured R_q values are (a) 0.66 nm, (b) 1.21 nm, (c) 8.13 nm, (d) 8.10 nm.

The structural form of the CuPc film (α or β) is of importance, in so far as it relates to conductivity, in that the α form exhibits a greater ability to bind oxygen than the β form (SHIHUB & GOULD, 1996). McKeown (MCKEOWN, 1998) discounts the commonly held assumption that it is the larger $\pi-\pi$ orbital overlap of the α -CuPc polymorph which make it a superior conductor to the β -type, on the basis that contaminants and dopants, especially the inclusion of absorbed gases such as oxygen, dominate the electrical properties of phthalocyanines. Indeed, under strictly intrinsic conditions their conductivities prove to be very similar (SIMON & ANDRÉ, 1985). The introduction of oxygen generates acceptor levels within the bandgap of CuPc which can lower the thermal activation energy for conduction, and the presence of even minute amounts of adsorbates on the surfaces of thin films can have a strong influence on their electrical properties (HASSAN & GOULD, 1989). This effect is particularly noticeable in thin films because of their high surface-to-volume ratio. While advantageously removing residual contaminants and impurities, annealing of the α -CuPc (a prerequisite for achieving the phase transition) drives out the oxygen, thus lowering the conductivity (GOULD, 1996).

It should be noted that since thin film annealing and metal deposition could not be performed in the same vacuum chamber (see *Experimental*, section 2.1.2), annealed ITO/(α/β)-CuPc samples were transferred (in air) to a second vacuum chamber for the final device fabrication steps (deposition of C₆₀/BCP/Al). Such experimental conditions invariably make it difficult to determine whether the differences observed in the performance of the as-deposited α -CuPc/C₆₀ device and the fully transformed β -CuPc/C₆₀ cell are primarily morphological or oxygen permeation dependent. Certainly, the effects of oxygen cannot be excluded. However, an ITO/ α -CuPc/C₆₀/BCP/Al 'control' sample, for which the vacuum chamber was vented after deposition of the CuPc, exhibits characteristic J - V parameters (solid black line, Fig. 4.3; $J_{sc} = 3.84 \text{ mA cm}^{-2}$, $V_{oc} = 0.47 \text{ V}$, $FF = 0.42$, $\eta_p = 0.75\%$) that fall within the range of

values obtained for a second CuPc/C₆₀ ‘control’ device grown without curtailing the vacuum ($J_{sc} = 4.03 \text{ mA cm}^{-2}$, $V_{oc} = 0.45 \text{ V}$, $FF = 0.49$, $\eta_p = 0.87\%$). This suggests that morphological templating rather than exposure to air plays the decisive role in the inferior performance of β -CuPc/C₆₀ cells.

4.3 Thermal annealing of CuPc:PhEt-PTC mixed layers

4.3.1 Morphological and spectroscopic characterisation of PhEt-PTC

The microstructure of a 30 nm PhEt-PTC film deposited onto an ITO-coated glass substrate at room temperature consists of randomly orientated, elongated crystal aggregates approximately 250 nm in length, surrounded by an amorphous bulk (Fig. 4.5 (a)). Although previous work has suggested that the as-grown film is uniformly amorphous (MIZUGUCHI, 1998), the annealing process has been reported to begin just above room temperature (DEBE *et al.*, 1988). The 10 °C rise in substrate temperature observed during deposition may have been sufficient to initiate crystallization of the PhEt-PTC film and could account for the apparent discrepancy.

The polymorphic transition (from the so-called ‘amorphous’ to the crystalline ‘modification I’ form – see section 1.5.3, p. 27, for details) induced by an hour-long, post-deposition heat treatment at 280 °C, generates a film topography of leaf-like crystal aggregates, each averaging about 500 nm in size (Fig. 4.5(b)). In contrast, the morphological features observed after extended exposure to methylene chloride vapor (Fig. 4.5(c)) consist of individual, micron-sized PhEt-PTC crystals scattered across an amorphous underlayer (BARBARA *et al.*, 1999). These differences have been rationalized on the basis of the annealing mechanism. The vapour driven process, by its very nature, is primarily limited to the exposed surface and produces a gradient of crystal sizes toward the substrate from micron size to amorphous. The thermally activated transformation process, on the other hand, is a ‘bulk mechanism’ that affects the entire structure (ADAMS *et al.*, 1997).

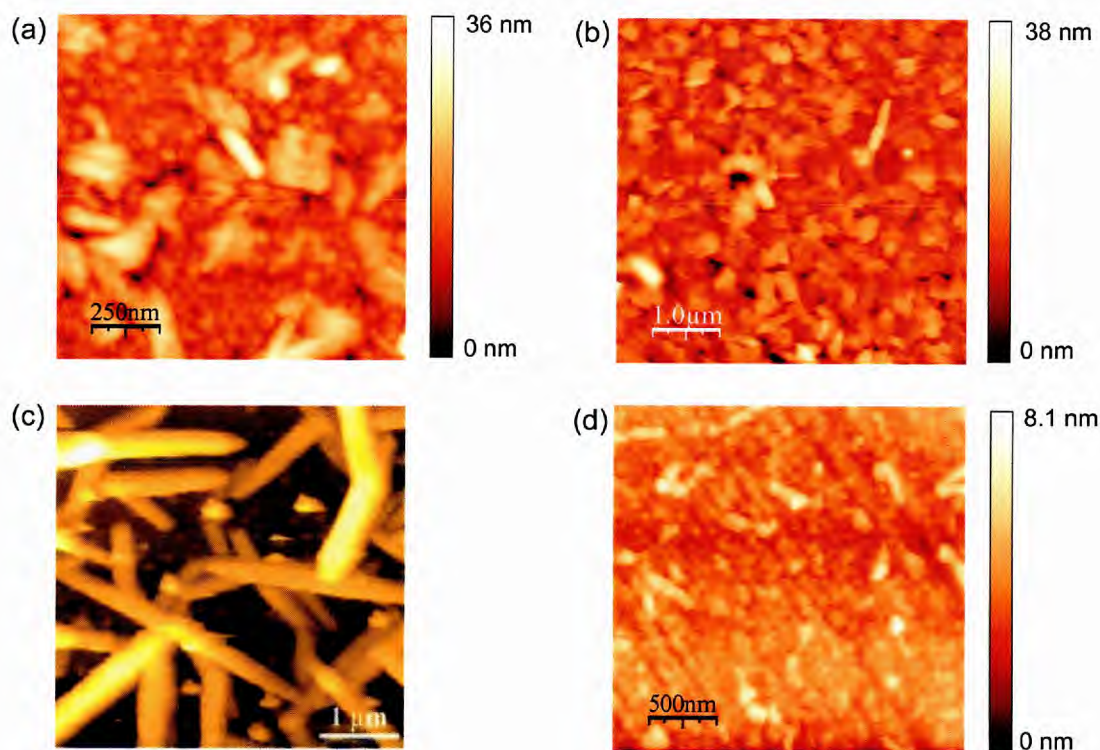


Figure 4.5 – AFM data of (a) a 30 nm PhEt-PTC film deposited at room temperature, $R_q = 8.6$ nm; (b) a 30 nm PhEt-PTC film annealed at 280 °C for an hour, $R_q = 8.8$ nm; (c) a PhEt-PTC film subjected to solvent annealing (methylene chloride) and imaged by near-field scanning optical microscopy (NSOM), from (BARBARA, 1999); (d) a 60 nm CuPc:PhEt-PTC (1:1 ratio) mixed film at room temperature, $R_q = 1.5$ nm.

Polymorphic changes attendant upon thermal annealing are also discernible by spectroscopic analyses. The electronic absorption measurements, given in Fig. 4.6, show that the room temperature solid state PhEt-PTC absorption profile is analogous to the well-structured vibronic bands characteristic of the solution spectrum (dashed-dotted-dotted lines in upper and lower panels, respectively), but broadened and split into higher and lower energy components due to molecular aggregation. The transition to modification I coincides with an enhancement of the shoulder at 610 nm and a relative decrease in intensity of the features at 475, 500 and 550 nm (solid grey line, upper panel), changes that are almost identical to those observed during vapour-annealing (*cf.* (GREGG, 1996)).

4.3.2 Morphological and spectroscopic properties of annealed CuPc:PhEt-PTC

In view of the tendency of perylene-based molecules to form crystal aggregates, and on the basis of previously published work (DITTMER *et al.*, 2000; PEUMANS *et al.*, 2003) in which phase segregation and crystal network formation in perylene derivative-containing systems was achieved by post-growth thermal annealing techniques, it is of interest to explore domain size, distribution and polymorphism in CuPc:PhEt-PTC composite systems.

The absorption spectrum of CuPc/PhEt-PTC bilayer structures (solid black line, Fig. 4.6, upper panel) can simply be interpreted on the basis of the two constituent solid state components, whereas the spectral shape and peak positions of CuPc:PhEt-PTC mixed films (solid black line, Fig. 4.6, lower panel) are remarkably similar to the individual monomer solution spectra. Indeed, AFM analysis strongly suggests that PhEt-PTC aggregation is greatly, though not entirely, suppressed by the addition of CuPc on a 1:1 molar ratio (Fig. 4.5(d)). The topography, consisting of elongated clusters on an amorphous background, is similar to that described by Rudiono *et al.* (RUDIONO *et al.*, 1999) for CuPc:perylene mixed films.

The spectral evolution of CuPc:PhEt-PTC thin films as a function of annealing temperature (Fig. 4.7, lower panel) provides a qualitative measure of phase segregation. The similarities between as-deposited mixed films and those annealed for up to an hour at 260 °C (dotted line and solid grey line, respectively) suggest that there is relatively little change in the microstructure. At intermediate temperatures (260-290 °C), a significant broadening of the PhEt-PTC-related shoulder at 450 nm, as well as a sizeable increase in the intensity of the 625 nm band, is observed. On account of the well-defined peaks at 500 and 540 nm, it is likely that these changes are due to increased intermolecular interactions from phase segregated CuPc rather than from a PhEt-PTC_{mod I} (620 nm) component, notwithstanding that this temperature regime is well above

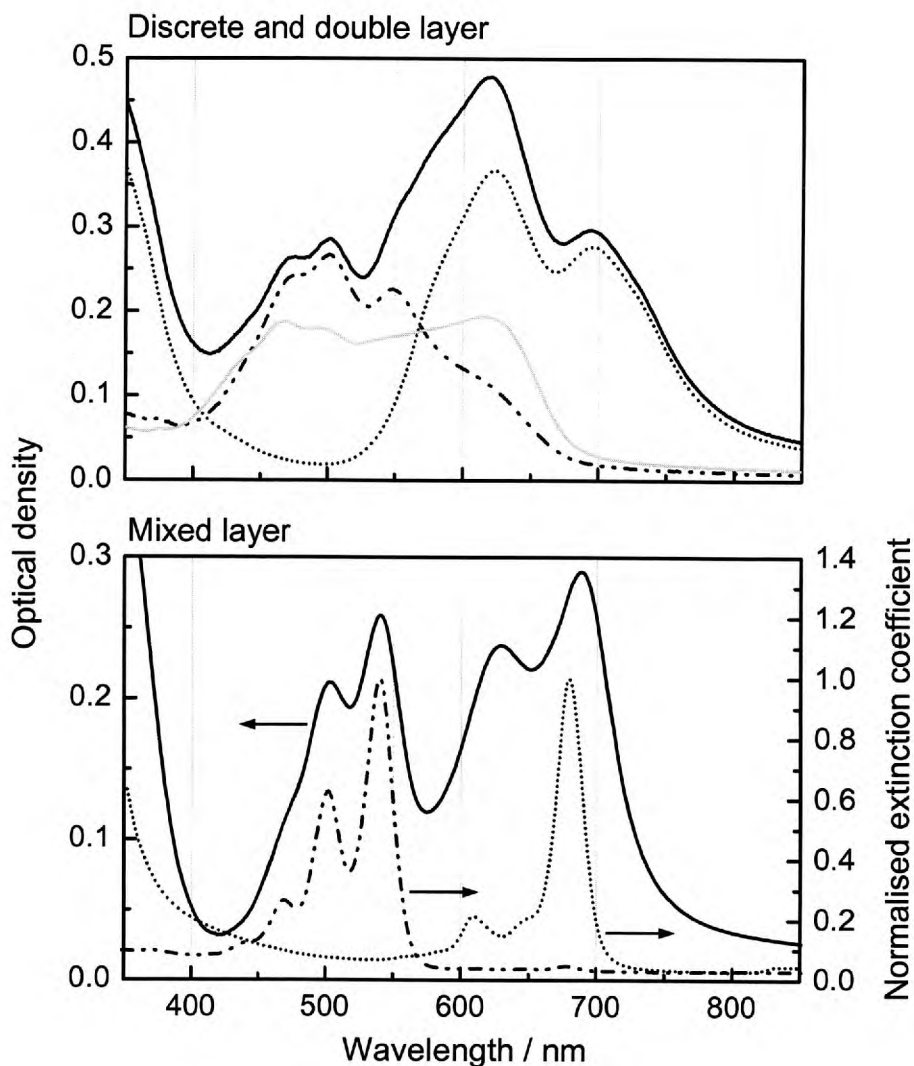


Figure 4.6 – Upper panel: electronic absorption spectra of a 30 nm PhEt-PTC film grown at room temperature (dashed-dotted-dotted line), a 30 nm PhEt-PTC film subjected to a post-growth heat treatment of 280 °C for 1 hour (solid grey line), a 30 nm α -CuPc film (dotted line) and, a 30 nm CuPc / 30 nm PhEt-PTC ('amorphous') double layer (solid black line); **lower panel:** solution spectra of PhEt-PTC (dashed-dotted-dotted line) and CuPc (dotted line) as well as a CuPc:PhEt-PTC (1:1 ratio) mixed film.

that necessary for its phase transformation. Evidence of phase segregation from such optical measurements is consistent with AFM data, which shows the formation of large crystalline aggregates on a polycrystalline background (Fig. 4.8(a)). The exact chemical composition of either morphological feature, however, is unclear.

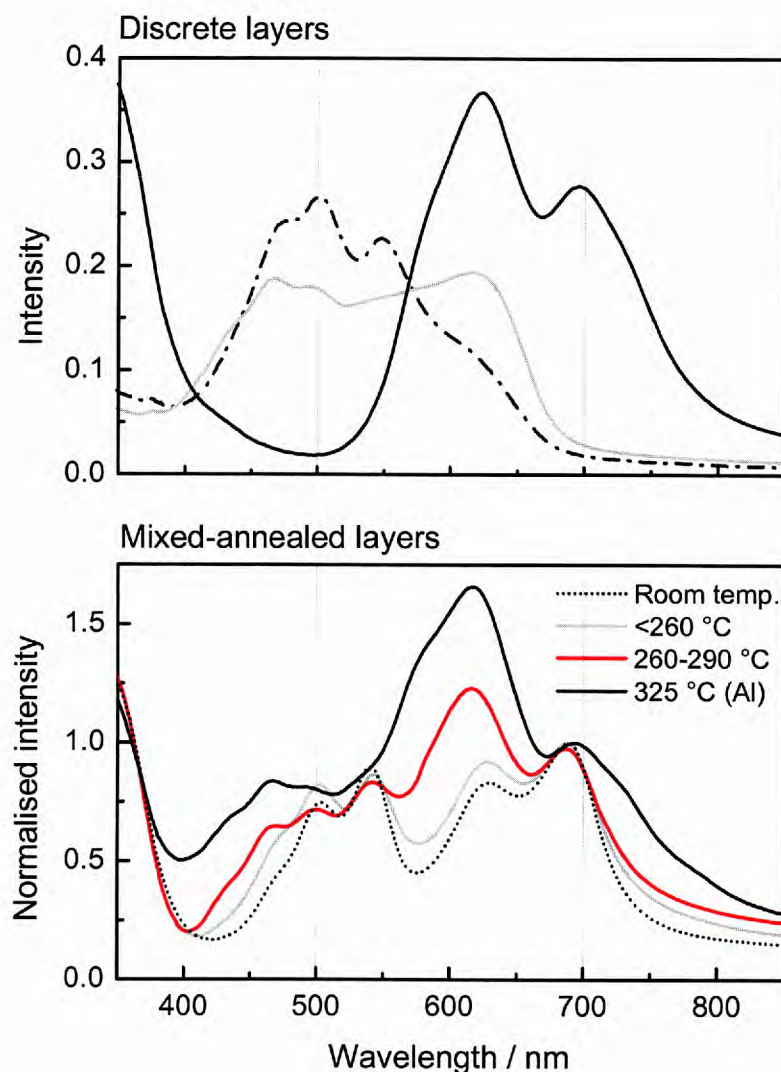


Figure 4.7 – Upper panel: electronic absorption profiles of a 30 nm α -CuPc film (solid black line), a 30 nm PhEt-PTC ('amorphous') film (dashed-dotted line) and a 30 nm PhEt-PTC ('crystalline') film (solid grey line); **lower panel:** normalised spectra of 60 nm CuPc:PhEt-PTC (1:1 molar ratio) mixed films subjected to a thermal anneal of (i) no anneal (room temperature) (dotted line), (ii) <260 °C for 1 hr (solid grey line), (iii) 260-290 °C for 1 hr (solid red line) and, (iv) 325 °C for 2 hrs (with 100 nm Al 'capping' layer). Spectra are normalised to the peak at 695 nm.

Films become progressively more phase segregated at higher annealing temperatures (325 °C), reflected by the increasingly pronounced changes in the electronic absorption spectrum (solid black line, lower panel). Since such temperatures exceed the sublimation point of PhEt-PTC (310-320 °C), these films required a 'capping' layer (in this case a 100 nm Al layer) to prevent loss

of material. Fortuitously, such a layer also serves the secondary purpose of confining the film to a fixed geometry, thereby avoiding the formation of coarse morphologies. However, its addition necessitates longer annealing periods (~2 hours) in order for significant structural changes to occur. As the 620 nm peak associated with the PhEt-PTC_{mod I} phase is hidden beneath the CuPc spectrum, it is difficult to determine from these measurements whether a polymorphic transition has occurred. The corresponding topography (Fig. 4.8(b)) subsequent to removal of the Al layer is, as expected, smooth and featureless, although the presence of pin-holes, most likely caused by conformational changes (e.g., lattice distortion and strain relief during the annealing process), is visible.

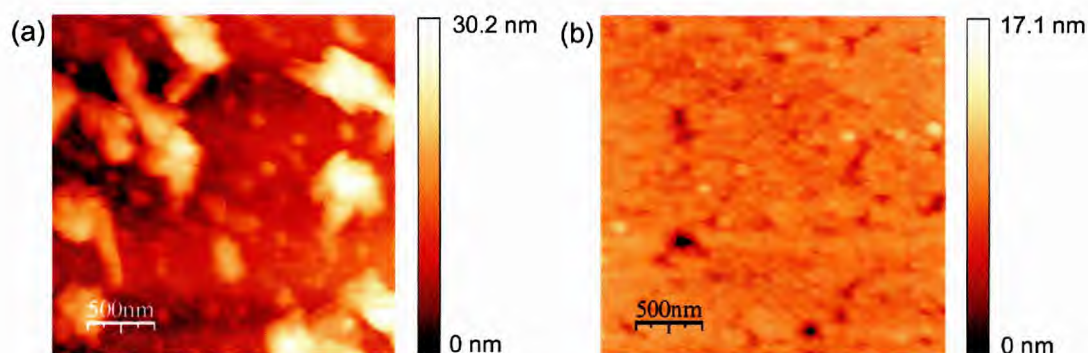


Figure 4.8 – AFM images of CuPc:PhEt-PTC mixed films annealed (a) at 275 °C for 1 hour without an Al capping layer and, (b) at 325 °C for 2 hours with an Al capping layer, subsequent to its removal. The root-mean-square roughness values are 7.1 and 1.2 nm, respectively.

4.3.3 Structural characterisation of annealed CuPc:PhEt-PTC

The XRD trace of the pure PhEt-PTC thin film (not shown) displays no obvious peaks, indicative of its amorphous nature. Upon annealing (280 °C), a prominent peak centered at approximately $2\theta = 5.7^\circ$, corresponding to an interplanar spacing of $d = 15.39 \text{ \AA}$, emerges (Fig. 4.9). There are considerable discrepancies within the published literature as to the origin of this peak, though it is generally assigned to the (020) reflection of the PhEt-PTC_{mod I} phase (see section 1.5.3, p. 27, for a discussion of the crystal structure).

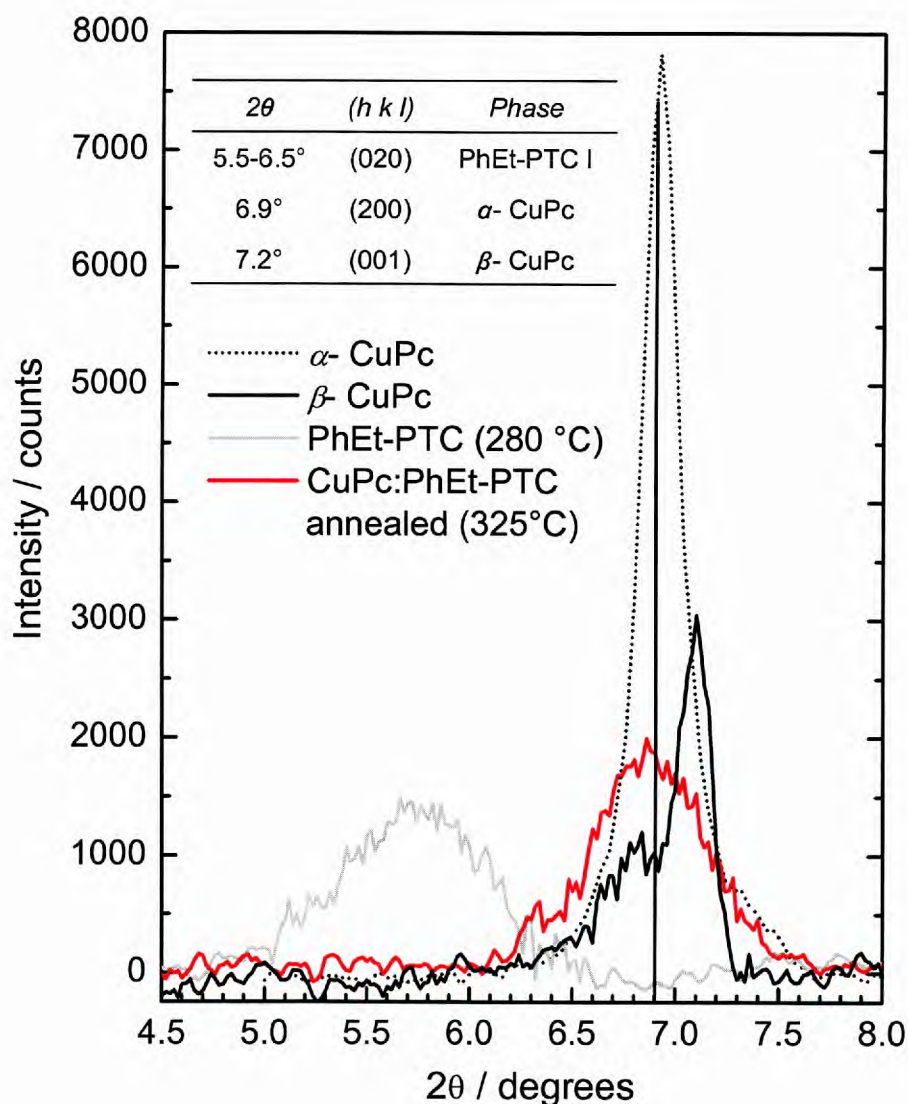


Figure 4.9 – X-ray diffractograms of films grown on ITO using the Cu-K α line including α -CuPc (dotted line), β -CuPc (solid black line), ‘crystalline’ PhEt-PTC_{mod I} (solid grey line) and, annealed CuPc:PhEt-PTC incorporating an Al ‘capping’ layer (solid red line). Inset: Miller indices and 2θ values.

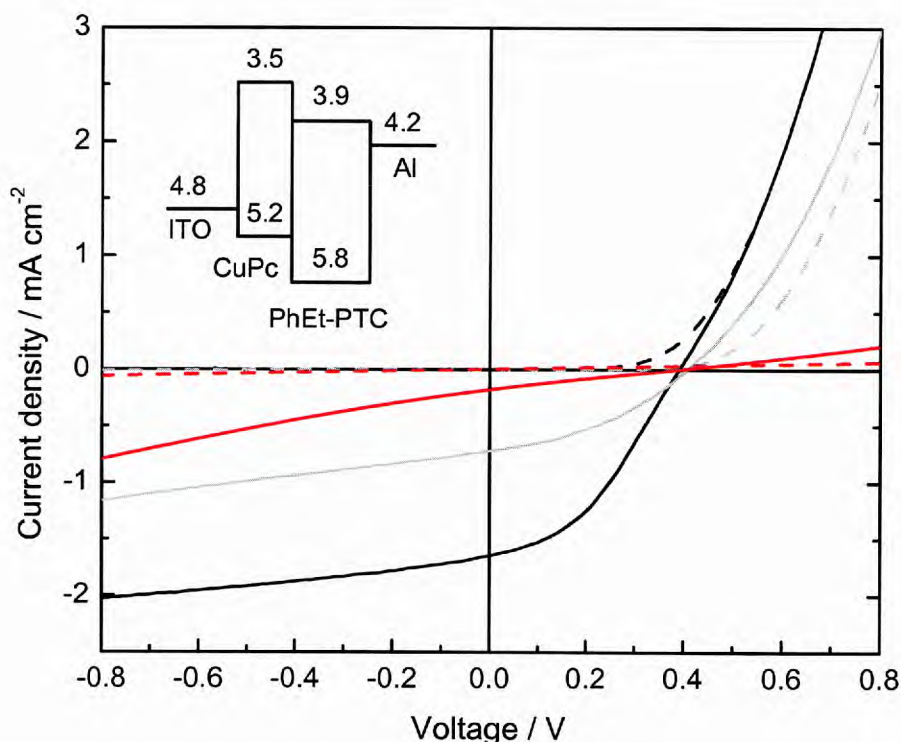
As expected, no peaks are detectable over the entire range ($2\theta = 3.0$ - 30°) of the as-deposited CuPc:PhEt-PTC spectrum (not shown), consistent with the optical absorption and morphological studies in suggesting that crystallization is suppressed during codeposition. Interestingly, the XRD pattern of the thermally annealed (325°C) ITO/60 nm CuPc:PhEt-PTC/100 nm Al structure offers no

evidence of either β -CuPc or PhEt-PTC_{mod 1} formation, only a lone α -CuPc peak at $2\theta = 6.9^\circ$. Quantitatively, the average crystalline domain size, estimated using the Debye-Scherrer broadening formula, (see *Experimental*, section 2.2.2), is about 23 nm. However, crystallite size determination is complicated by, among other factors, 'micro-strain' effects (dislocations, vacancies and similar defects), instrumental errors (sample misalignment), and molecular doping (of the CuPc-rich phase with PhEt-PTC), all of which could contribute to peak broadening. This value therefore represents a lower limit to the domain size. Taken together with the optical absorption data these results confirm that while phase segregation takes place over a range of temperatures, no polymorphic changes occur, even above transition temperatures.

4.3.4 Device characterisation

Shown in Fig. 4.10 are the dark and illuminated J - V characteristics (dashed and solid lines, respectively) of an ITO/20 nm CuPc/40 nm PhEt-PTC/100 nm Al DHJ (black lines), an as-deposited ITO/60 nm CuPc:PhEt-PTC (1:1 ratio)/100 nm Al BHJ (grey lines), and an ITO/60 nm CuPc:PhEt-PTC (1:1 ratio)/100 nm Al BHJ that was subjected to a 2 hour post-fabrication heat treatment at 325 °C (red lines). In the latter device, the Al layer acts as both the 'capping' layer during the heat treatment as well as the cell electrode. Since the sublimation temperature and the melting point of BCP are substantially lower (120 °C and 280 °C, respectively) than the annealing temperature and in order to achieve a valid comparison between cell architectures, it was not incorporated into any of the devices. The HOMO and LUMO levels of PhEt-PTC are taken from the literature (HIRAMOTO *et al.*, 1998).

While the reduction in power conversion efficiency accompanying the change from a DHJ architecture to a BHJ architecture (0.26% and 0.11%, respectively) is, perhaps, not unexpected, the decrease in the J_{sc} by over half, from 1.64 to 0.72 mA cm⁻², is rather surprising. These findings are not only at variance with the



Device architecture	$J_{sc} / \text{mA cm}^{-2}$	V_{oc} / V	FF	$\eta_p / \%$
Discrete heterojunction (—)	1.64	0.39	0.43	0.26
Bulk heterojunction (—)	0.72	0.41	0.39	0.11
Annealed bulk heterojunction (—)	0.13	0.36	0.23	0.01

Figure 4.10 – J-V characteristics of an ITO/20 nm CuPc/40 nm PhEt-PTC/Al DHJ (solid black line), an ITO/60 nm CuPc:PhEt-PTC (1:1 ratio)/Al BHJ (solid grey line) and an annealed (325 °C for 2 hours) ITO/60 nm CuPc:PhEt-PTC (1:1 ratio)/Al BHJ (solid red line). The table provides a summary of the characteristic device parameters. All devices measured under AM1.5 simulated solar illumination (solid lines) at 100 mW cm⁻² (1 sun) or in the dark (corresponding dashed lines).

results obtained for CuPc:C₆₀ BHJs (chapter 3), but are also at odds with numerous examples of phthalocyanine-perylene systems that exhibit a significant increase in the J_{sc} upon mixing (*cf.* (HIRAMOTO *et al.*, 1992) and (WÖHRLE *et al.*, 1996)). Nevertheless, such behaviour has recently been attributed to the lack of percolating pathways across codeposited films that incorporate two planar molecules (XUE *et al.*, 2005), though it may also reflect the

excessively thick nature of the mixed layer in this case (60 nm). As with most other molecular-based BHJs described in the literature, the FF of the CuPc:PhEt-PTC structure (0.39) is slightly lower than that of its planar counterpart (0.43) due to the resistance to charge transport across the mixed film.

‘Thermodynamically driven’ phase segregation methods have previously been utilized to enhance the power conversion efficiency of BHJ devices comprising similar materials (CuPc and PTCBI) (PEUMANS *et al.*, 2003). Although a greater increase in domain size is observed in the structure under consideration (23.3 nm compared to 12 ± 1 nm), the J - V characteristics of the thermally annealed CuPc:PhEt-PTC BHJ (red line) are clearly inferior to both the CuPc/PhEt-PTC DHJ and the as-deposited CuPc:PhEt-PTC BHJ. However, unlike the heat-treated devices fabricated by Peumans *et al.*, no polymorphic transition (neither of the CuPc nor of the PhEt-PTC) is observed. This suggests that the structure of the constituent materials is analogous to that within the annealed CuPc/C₆₀ bilayers described in section 4.2.2, in that the CuPc and PhEt-PTC, having not fully undergone a polymorphic transition, form structurally disordered aggregates through which charge transport is limited. Indeed, the XRD profile of the annealed (325 °C) ITO/60 nm CuPc:PhEt-PTC/Al device is only slightly more intense (and much broader) than the 30 minute annealed (325 °C) CuPc thin film (Fig. 4.1(b)), suggesting a similar lack of crystallinity. Longer anneal times may be necessary to complete the phase transition.

4.4 Conclusions

This chapter has demonstrated the importance of thin film morphology and structure in molecular PV device performance. In-situ annealing of α -CuPc films at suitably elevated temperatures leads to a polymorphic transformation to the β -phase, which is characterized by long, needle-like crystallites and an increased film roughness (from 1.5 to 5.5 nm). This is accompanied by an increase in the relative intensity of the 694 nm peak in the electronic absorption spectrum as well as the emergence of a new peak at $2\theta = 7.1^\circ$ in the powder XRD pattern, corresponding to the (001) spacing. Films annealed for intermediate time periods (<2 hours) are distinguished by their morphologies and, in particular, by their XRD profiles, which point toward inhomogeneous structures. Such changes were observed to impact detrimentally on device efficiency. CuPc/C₆₀ discrete heterojunction cells incorporating a fully transformed β -CuPc layer were found to exhibit diminished *J-V* characteristics ($J_{sc} = 3.02 \text{ mA cm}^{-2}$, $V_{oc} = 0.31 \text{ V}$, $FF = 0.48$, $\eta_p = 0.46\%$) compared to the corresponding as-deposited structure ($J_{sc} = 3.84 \text{ mA cm}^{-2}$, $V_{oc} = 0.43 \text{ V}$, $FF = 0.44$, $\eta_p = 0.73\%$), which can be attributed to morphological templating of the C₆₀ layer and discontinuities at the organic/metal interface. These reduce the likelihood of exciton separation and charge collection. Discrete heterojunctions in which the CuPc films were annealed for shorter time periods demonstrated power conversion efficiencies that were over an order of magnitude less than that of the as-deposited device ($\eta_p = 0.06$ and 0.03% for the 30 and 60 minute annealed devices, respectively). This was ascribed to the lack of long-range order within the partially transformed CuPc films.

The PhEt-PTC ‘amorphous’ $\rightarrow$ ‘modification I’ polymorphic transition has been investigated. The morphological features observed after an hour-long heat treatment (280 °C) consist of leaf-like crystal aggregates approximately 500 nm

in size. This coincides with an enhancement of the shoulder at 610 nm and a decrease in intensity of the features at 475, 500 and 550 nm in the UV/Vis spectrum, in addition to the appearance of a broad, low-intensity XRD band centered at $2\theta = 5.7^\circ$. Results compare well with the published literature.

Furthermore, it has been shown that thermal annealing of CuPc:PhEt-PTC composite systems provides a route for increasing the phase segregation within intimately mixed nanostructures. CuPc:PhEt-PTC films deposited at room temperature are best described as a 'solid solution' of molecules or small aggregates: the spectral shape and peak positions of the mixed film are remarkably similar to the individual monomer solution spectra. Post-growth heat treatments at increasingly higher temperatures (260 $\rightarrow$ 325 $^\circ\text{C}$) produce a gradual change in the electronic absorption spectrum that tends toward the individual solid state spectra. Evidence of phase segregation from the optical measurements was consistent with AFM data, which showed large crystalline aggregates on a polycrystalline background ($R_q = 7.1$ nm). The utilisation of an Al 'capping' layer prevents material desorption at the highest temperatures and minimises the resultant film roughness ($R_q = 1.2$ nm). The maximum average domain size was of the order of 23 nm, although, on the basis of optical and structural measurements, it is established that no polymorphic changes occur. Finally, a comparative analysis between a 20 nm CuPc/40nm PhEt-PTC DHJ, a 60 nm CuPc:PhEt-PTC (1:1) BHJ and an annealed 60 nm CuPc:PhEt-PTC (1:1) BHJ was presented. Significantly, the performance of the DHJ was not enhanced through codeposition ($\eta_p = 0.26$ and 0.11%, respectively), nor through the subsequent annealing of the BHJ structure ($\eta_p = 0.01\%$). It was concluded that this was due to the excessive thickness of and structural disorder within the mixed film.

5 PHTHALOCYANINE-BASED DISCOTIC LIQUID CRYSTALS

5.1 Introduction

The tendency towards employing ever-more complicated device architectures, such as the mixed-annealed structures reported by Peumans *et al.* (PEUMANS *et al.*, 2003), or the asymmetric PM-HJ tandem cells demonstrated by Männing, Xue and co-workers (MÄNNIG *et al.*, 2004; XUE *et al.*, 2004), necessitates an increasing number of potentially impractical and costly processing steps. Chemical self-assembly offers an inexpensive alternative for device fabrication, and several authors have shown that the ease of processing afforded by such a method can be exploited to good effect in photovoltaic devices (SCHMIDT-MENDE *et al.*, 2001; SAGER *et al.*, 2004).

Phthalocyanine-based discotic liquid crystals constitute a class of molecular semiconductor that combine the solid state optoelectronic properties of the vacuum evaporated parent molecule with the solution-processible characteristics and self-organising propensity of conventional liquid-crystal mesogens, making thin film fabrication *via* spin-coating or ink-jet printing methods relatively straightforward (MCKEOWN, 1998; SIMPSON *et al.*, 2004). Nevertheless, the difficulty of reliably achieving uniform homeotropic alignment remains a major issue in their application to this field.

In this chapter, the thin film optical and physical characteristics of the copper-phthalocyanine liquid crystal complex $(C_{14}O)_{16}TzCu$ are investigated and its utility as a hole transporting medium in DHJ solar cells is evaluated. Issues relating to charge transport within columnar mesophases are also discussed.

5.2 Thin film characterisation

5.2.1 Homeotropic alignment

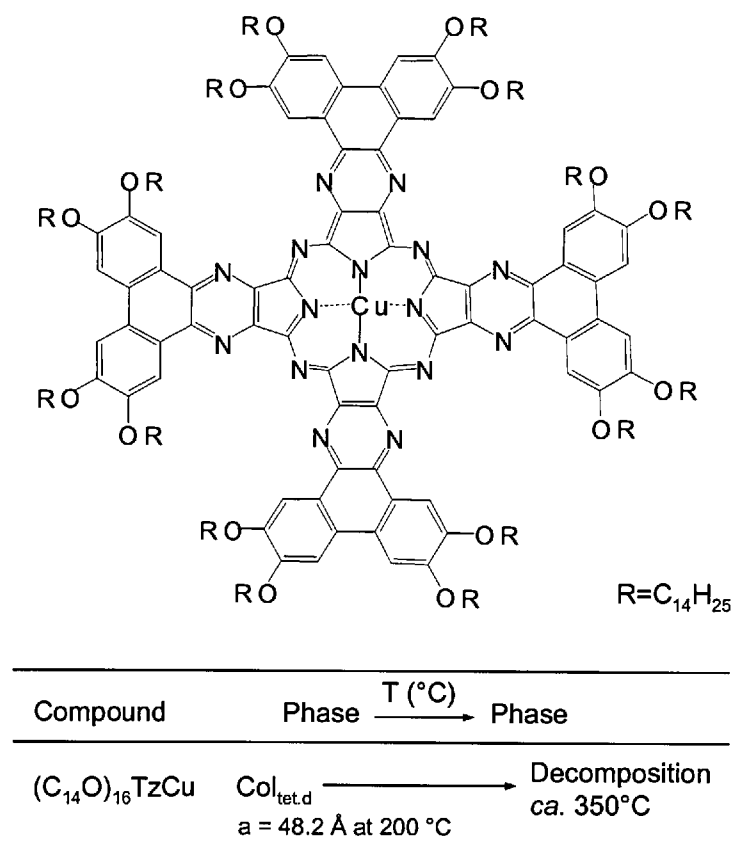


Figure 5.1 – Chemical structure and phase transition behavior of the tetrakis (2,3,6,7-tetradecyloxy) diazatriphenylenocyaninato metal complex, $(C_{14}O)_{16}TzCu$. The intercolumnar spacing, a , at $200^{\circ}C$ is also given.

The chemical structure and phase behaviour of $(C_{14}O)_{16}TzCu$ (summarized in Fig. 5.1) were established from microscopic observations, differential scanning calorimetry measurements and temperature-dependent X-ray diffraction studies that, in addition to the synthetic route, can be found in Ichihara *et al.* (ICHIHARA, 2005). Although homeotropic alignment for a wide variety of columnar phase-forming materials has been demonstrated, it is usually

attainable at a single surface only after cooling sufficiently thin films from the melt (JUNG *et al.*, 2002; TERASAWA *et al.*, 2003) or after prolonged heating (HATSUSAKA *et al.*, 2001; HATSUSAKA *et al.*, 2003). Remarkably, uniform homeotropic alignment for the columnar tetragonal ($\text{Col}_{\text{tet.d}}$) mesophase of $(\text{C}_{14}\text{O})_{16}\text{TzCu}$ is achievable not only between glass or quartz plates, but also when spin-coated onto ITO-coated glass substrates at room temperature. When viewed between crossed polarizers, $(\text{C}_{14}\text{O})_{16}\text{TzCu}$ thin films exhibit a uniformly dark background that is notable for its lack of birefringent defects (Fig. 5.2(a)), features associated with domain boundaries and disclinations that manifest themselves as bright stripes (*cf.* Fig. 5.2(c)). Scratching the film surface confirms that the optical extinction is due to the homeotropic alignment: ‘peeled’ sections become bright, indicative of tilted columns, while the undisturbed areas remain dark (Fig. 5.2(b)).⁸

⁸ Polarising optical microscopy (POM) enables the identification of liquid crystal phases and defects from the distinct optical textures that are generated (COLLINGS, 1997). In the ‘crossed polarizer’ configuration, the polarizer and analyzer are positioned at right angles to each other, with no light passing through the system and a dark field of view present in the eyepieces. Since the molecules that constitute the phase structure in homeotropically aligned discotic liquid crystals are orientated such that their long axis (and more importantly their optic axis) is perpendicular to the substrate plane, polarised light is unaffected as it passes through the material. Consequently, the field of view remains completely black. However, when light enters a non-equivalent axis (as is the case for tilted phases), it is refracted into two rays each polarized with the vibration directions oriented at right angles to one another, and travelling at different velocities. This phenomenon is termed ‘birefringence’ and results in the transmission of light.

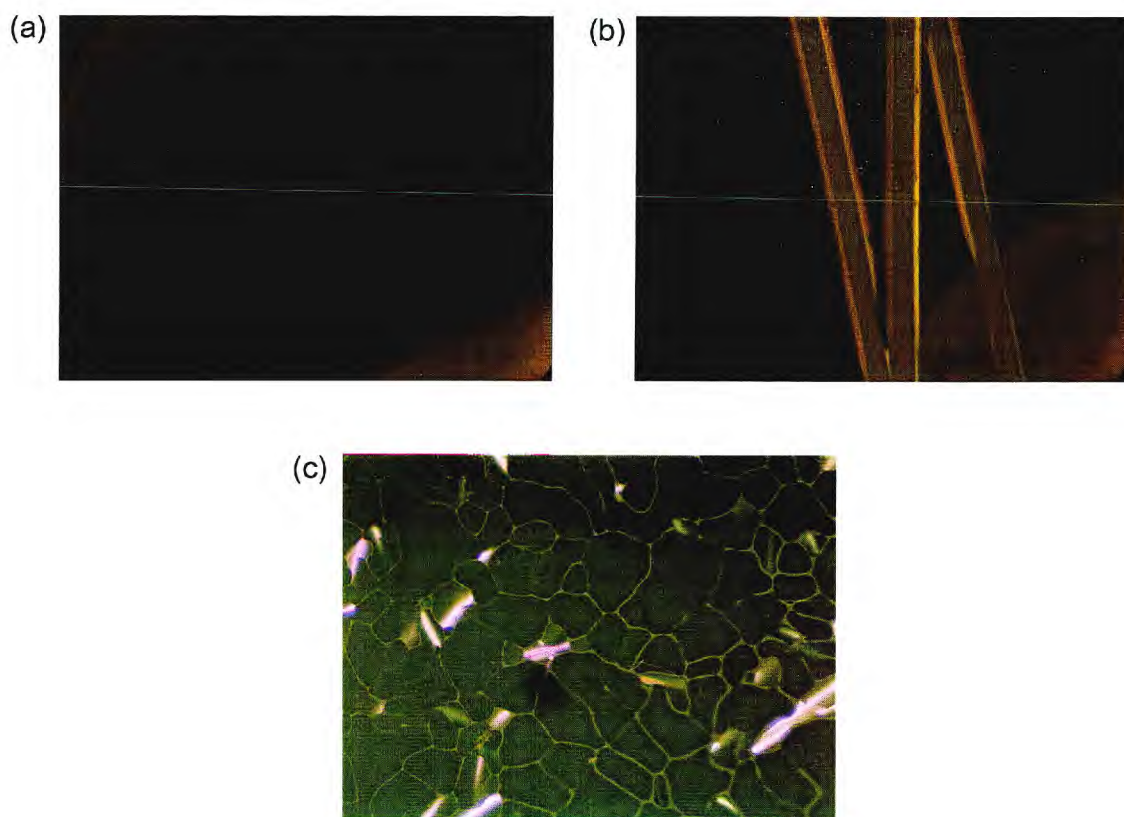


Figure 5.2 – Polarizing optical micrographs of a 50 nm spin-coated $(C_{14}O)_{16}TzCu$ thin film viewed between crossed polarizers before (a) and after (b) scratching of the film with a needle; (c) example of defective homeotropic alignment in a phthalocyanine-based mesogen, from (VAN DE CRAATS, 1997).

5.2.2 Electronic absorption spectroscopy

In solution ($CHCl_3$), the electronic absorption spectrum of $(C_{14}O)_{16}TzCu$ is characterised by a narrow, well-resolved absorption band with $\lambda_{max} = 730$ nm, consistent with solvated phthalocyanine monomers (LEZNOFF & LEVER, 1989). Subsequent to spin-coating the profile becomes broadened and red-shifted, with a peak centred at 755 nm and a shoulder at 680 nm (Fig. 5.3). Such spectral modifications are generally interpreted on the basis of the exciton coupling theory developed by Kasha *et al.* (KASHA *et al.*, 1965), in which the relative

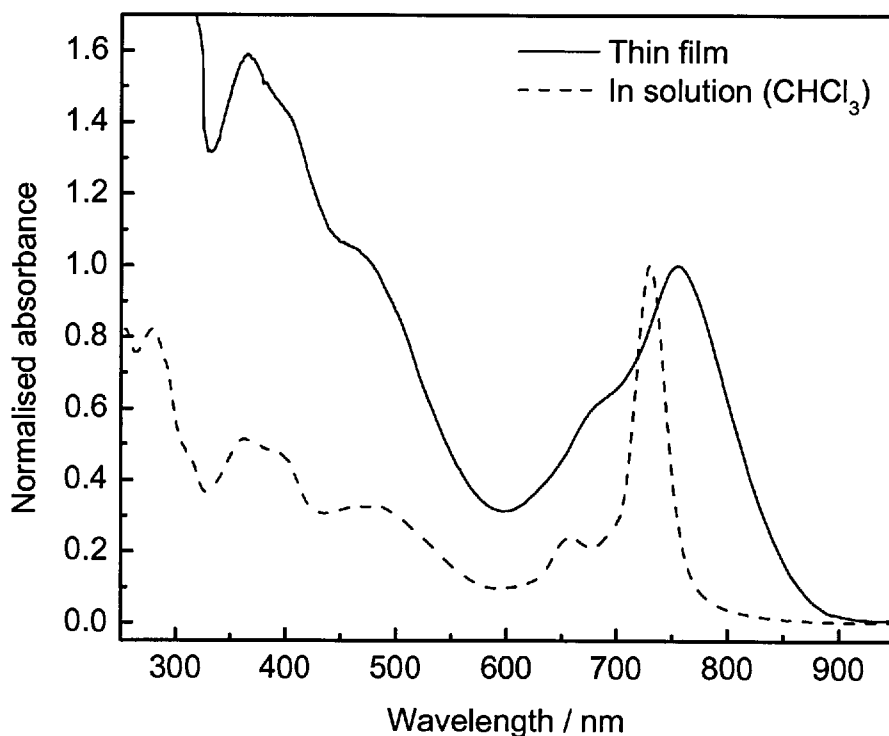


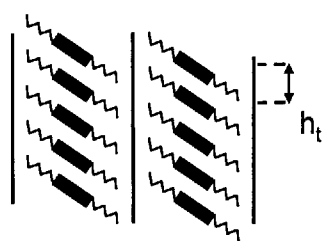
Figure 5.3 – Normalised electronic absorption spectra of $(C_{14}O)_{16}TzCu$ in $CHCl_3$ (dotted line) and after spin-coating (solid black line).

orientation of the dipole moments of interacting molecules determine the intensity of the electronic transitions. The appearance of a blue-shifted band is indicative of excitonic effects within a cofacial columnar structure, while a red-shift of the Q-band can be expected for an assembly of phthalocyanine molecules in which the adjacent rings within a columnar structure are offset, i.e., the molecules are not fully aligned cofacially (COOK, 1993). Chromophore misalignment can be in the form of local rotations or lateral displacements, though the latter, also referred to as the 'slipped-stack' orientation (shown schematically in Fig. 5.4), is unlikely in this case since such molecular arrangements typically give rise to tilted columns and the concomitant formation of domains and line defects (OHTA *et al.*, 2003), neither of which were observed under the polarizing microscope. Thus, the bathochromic shift is in all

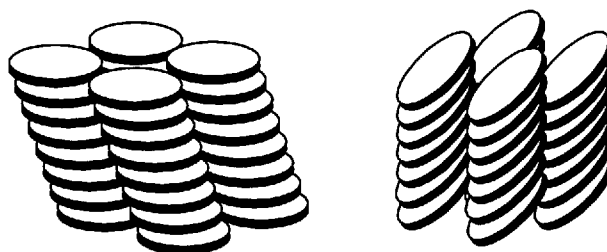
probability the consequence of a lowering in the molecular symmetry due to rotational motion, which relaxes the selection rules such that the lower energy, orbitally forbidden excitonic transition becomes allowed (KASHA, 1976). While rotations around the director axis do not necessarily perturb homeotropic alignment (there are numerous examples of triphenylene-based columnar discotics that form homeotropic phases which exhibit an ordered helical geometry (BUSHBY & LOZMAN, 2002)), it is known that orientational disorder adversely affects charge transport (*vide post*). It should be noted that ‘in-line’ dimer formation (edge-to-edge exciton interactions) can be excluded for discotic mesophases that feature long insulating side chains in their molecular structure.

(a) Slipped-stack disks

Side view

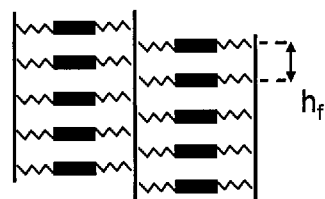


Oblique view

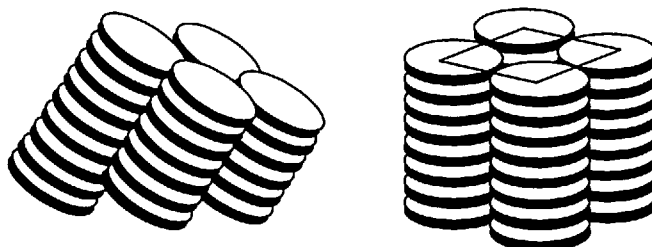


(b) Cofacial disks

Side view



Oblique view



Tilted homeotropic

Homeotropic

Figure 5.4 – Idealised stacking structures of ordered discotic (columnar) mesophases comprising (a) slipped-stack and (b) cofacial orientations. Slipped-stack and tilted homeotropic arrangements usually give rise to multiple domains with tilt disclinations. In the ‘side view’, the solid bars represent the core moiety, while the zig-zagged lines represent the side-chains. Adapted from (OHTA, 2003).

In addition to symmetry considerations, it is also well-documented that the absorption and emission spectra of many columnar liquid crystals in solution depend on the local electric fields generated by the surrounding solvent molecules (see, for example, (LEVITSKY *et al.*, 2000; NGUYEN *et al.*, 2004) and references therein). This so-called ‘solvatochromic effect’ is a result of intermolecular solute-solvent interaction forces (dielectric interactions such as dipole-dipole or dipole-induced dipole). These tend to stretch molecular bonds and shift charge distribution on molecules, altering the energy difference between the ground and excited states of the solute (chromophore) and resulting in a spectral shift (KÖHLER & RECHTHALER, 1993; REICHARDT, 1994). However, while it is possible that the changes in the solid-state and solution absorption spectra of (C₁₄O)₁₆TzCu arise from differences in specific molecule-solvent interactions and/or the difference between their dielectric constants, polarity-dependent measurements (Fig. 5.5(a)) suggest that the red-shift associated with the spin-coated film is actually due to chromophore-chromophore interactions. In polar solvents such as CHCl₃ (large dipole moment and high dielectric constant), for example, the absorption spectrum is slightly blue-shifted ($\lambda_{\text{max}} = 736$ nm) and substantially narrower compared to that in highly apolar *n*-hexane ($\lambda_{\text{max}} = 750$ nm). The profile of the latter is almost identical to that of the spin-coated thin film ($\lambda_{\text{max}} = 755$ nm), suggesting a progressive increase in the presence of aggregated dye molecules with decreasing polarity rather than the enhancement in the local fields (i.e., decreasing the solvent polarity induces aggregation by non-specific interactions such as solvophobic effects).

Moreover, temperature-dependent measurements (Fig. 5.5(b)) reveal that the Q-band is shifted to shorter wavelengths upon heating ($\lambda_{\text{max}} = 736$ nm at 220 °C compared to 755 nm at room temperature), which may be indicative of molecular rotations within the columnar stacks and increased cofacial coupling. Thus these orientations, while being thermodynamically unfavourable at room temperature, can be induced at elevated temperatures.

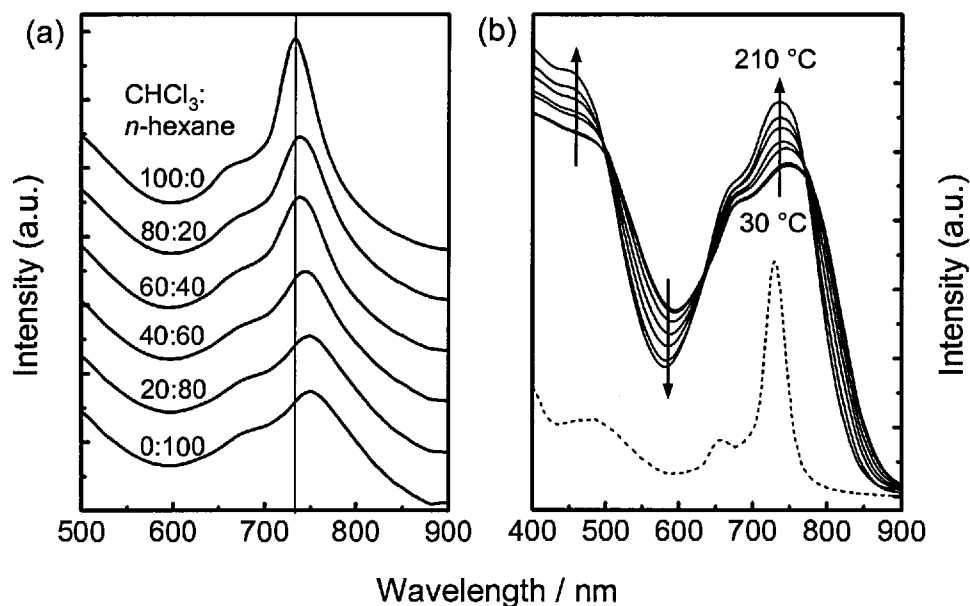


Figure 5.5 – Electronic absorption spectra of $(C_{14}O)_{16}TzCu$ as a function of (a) solvent polarity and (b) temperature.

5.2.3 Atomic force microscopy

Although homeotropic alignment for $(C_{14}O)_{16}TzCu$ is achievable by spin-coating onto bare ITO substrates, AFM analysis reveals that the rough surface profile of such substrates causes significant pin-hole formation within the organic film (Fig. 5.6 (a)), thus necessitating the prior deposition of a 30 nm PEDOT:PSS layer. The morphology of the ITO/PEDOT:PSS/ $(C_{14}O)_{16}TzCu$ structure (Fig. 5.6 (b)) is relatively featureless and smooth, with a root-mean-square roughness, R_q , of 0.56 nm. Vacuum deposited thin films of C_{60} (Fig. 5.6 (c)) feature small spherical crystallites approximately 30-40 nm in size with an R_q value of 0.62 nm, while subsequent deposition onto ITO/PEDOT:PSS/ $(C_{14}O)_{16}TzCu$ only marginally increases the roughness (Fig. 5.6 (d)). The relatively planar topography of the bilayer structure suggests that there is good

interfacial contact between the two organic layers, an important feature for device performance.

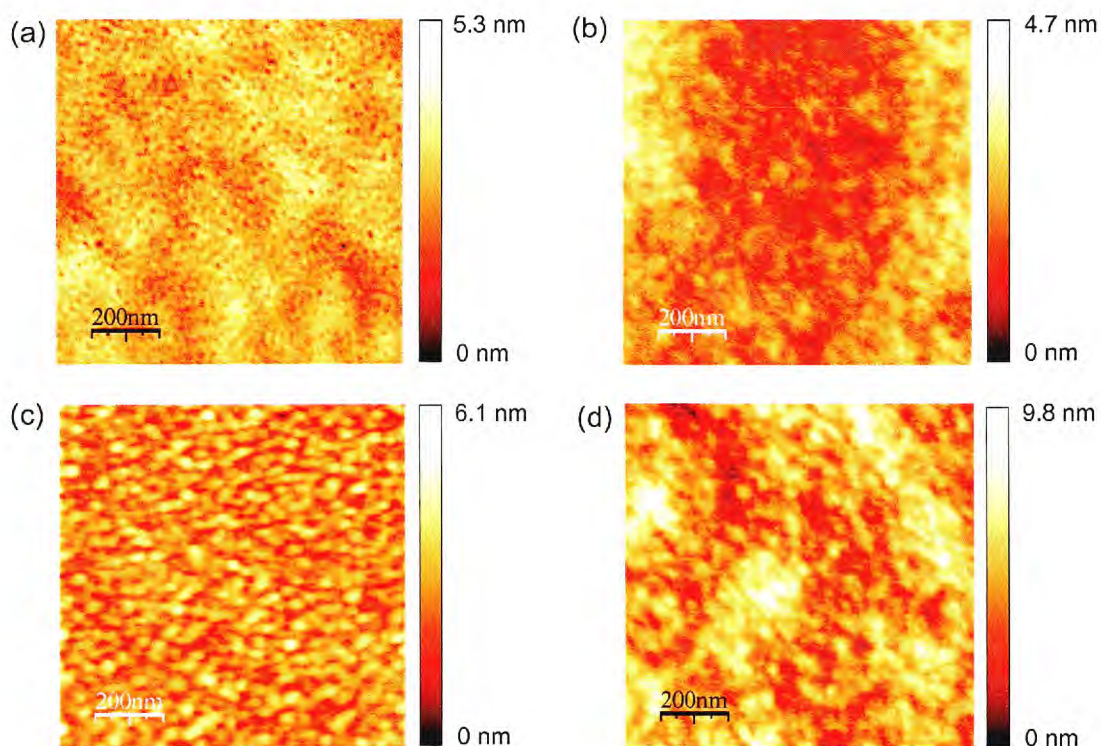


Figure 5.6 – AFM images of (a) ITO / $(C_{14}O)_{16}TzCu$ and (b) ITO / PEDOT:PSS / $(C_{14}O)_{16}TzCu$; (c) a C_{60} thin film, and (d) an ITO/PEDOT:PSS/ $(C_{14}O)_{16}TzCu/C_{60}$ structure.

5.3 Device characterisation

5.3.1 $(C_{14}O)_{16}TzCu$ band gap

Organic solar cell operation is driven by charge generation *via* the interfacial dissociation of strongly bound excitons (HALLS *et al.*, 1995; YU *et al.*, 1995) and, as such, knowledge of the energy level offset between donor and acceptor species is essential. Electrochemical measurements, in the form of cyclic voltammetry (CV), allow an empirical estimation of the relative positions of the HOMO/LUMO levels. The ionization potential (IP), equivalent to the HOMO level, can be estimated from the onset potential of oxidation, while the electron affinity (EA), corresponding to the LUMO level, is determined from the onset potential of reduction. Figure 5.7 shows the cyclic voltammogram obtained from a $(C_{14}O)_{16}TzCu$ film spin-coated directly onto the working electrode (ITO) and measured in an acetonitrile solution of tetrabutylammonium perchlorate (TBAP) (0.1 M) at a scan rate of 25 mV s⁻¹. Assuming an average standard hydrogen potential value of -4.6 eV on the zero vacuum-level scale (BOCKRIS & KHAN, 1983), and correcting for the Ag/AgCl reference electrode (+0.2 eV) (MICARONI *et al.*, 2002), the onset potentials of oxidation ($E'_{ox} = 0.85$ V) and reduction ($E'_{red} = -0.20$ V) correspond to a HOMO and LUMO level ($E_{HOMO/LUMO} = [-E_{ox/red}] - 4.4$) of -5.25 and -4.2 eV, respectively. Consequently, the band gap is estimated as being approximately 1.05 eV, slightly smaller than the optical gap determined from the absorption edge of the UV/Vis spectrum, $\lambda' \approx 920$ nm (1.35 eV). Thus, in combination with fullerene (HOMO of 6.2 eV and LUMO of 4.5 eV (PEUMANS & FORREST, 2001)), a $(C_{14}O)_{16}TzCu/C_{60}$ heterojunction can be expected to promote efficient exciton dissociation and charge transfer.

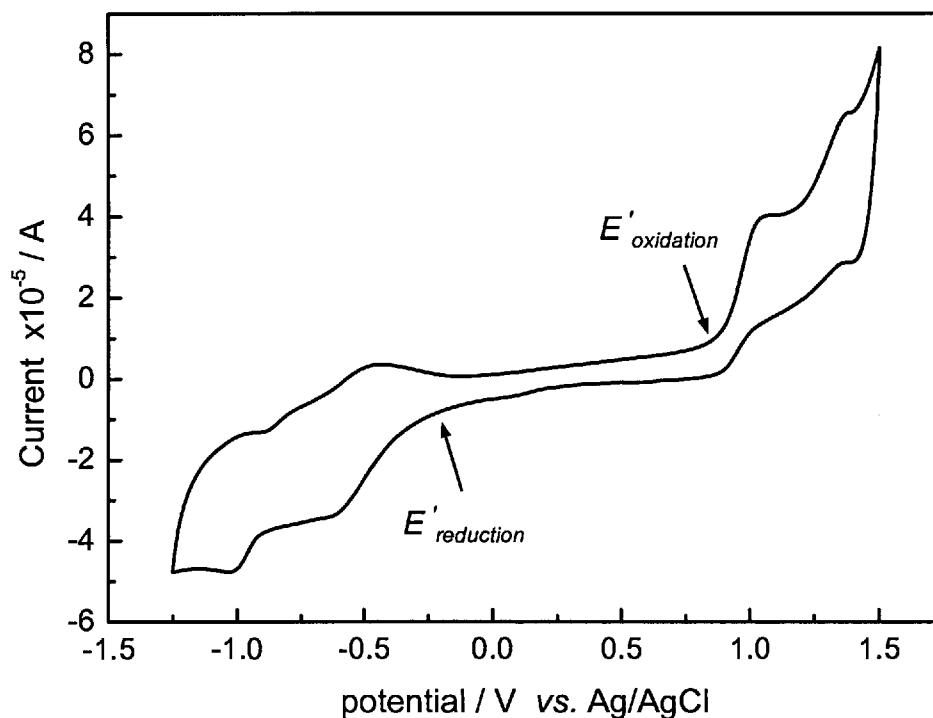


Figure 5.7 – Cyclic voltammogram of a thin film of $(C_{14}O)_{16}TzCu$ in CH_3CN with TBAP (0.1 M), $v=25\text{ mV s}^{-1}$.

5.3.2 Device performance

The J - V characteristics of a bilayer heterojunction photovoltaic device employing $(C_{14}O)_{16}TzCu$ (20 nm) and C_{60} (40 nm) as the hole- and electron-transporting materials, respectively, are shown in Fig. 5.8. Devices are analogous to those described in chapter 3 with the exception of the inclusion of the thin (30 nm) PEDOT:PSS layer. Under white-light illumination (100 mW cm^{-2}) the device exhibits a short-circuit current of $J_{sc} = 0.57\text{ mA cm}^{-2}$, an open-circuit voltage of $V_{oc} = 0.33\text{ V}$, and a fill factor of $FF = 0.38$. This yields a power conversion efficiency of $\eta_p = 0.07\%$ and is of a similar magnitude to those reported in the literature for other discotic liquid crystalline materials (YOO *et al.*, 2004). The photocurrent is characterised by a steeply increasing slope in forward

bias and an approximately linear rise with voltage under reverse bias. The origin of the increased current at $V > 0.4$ V is uncertain.

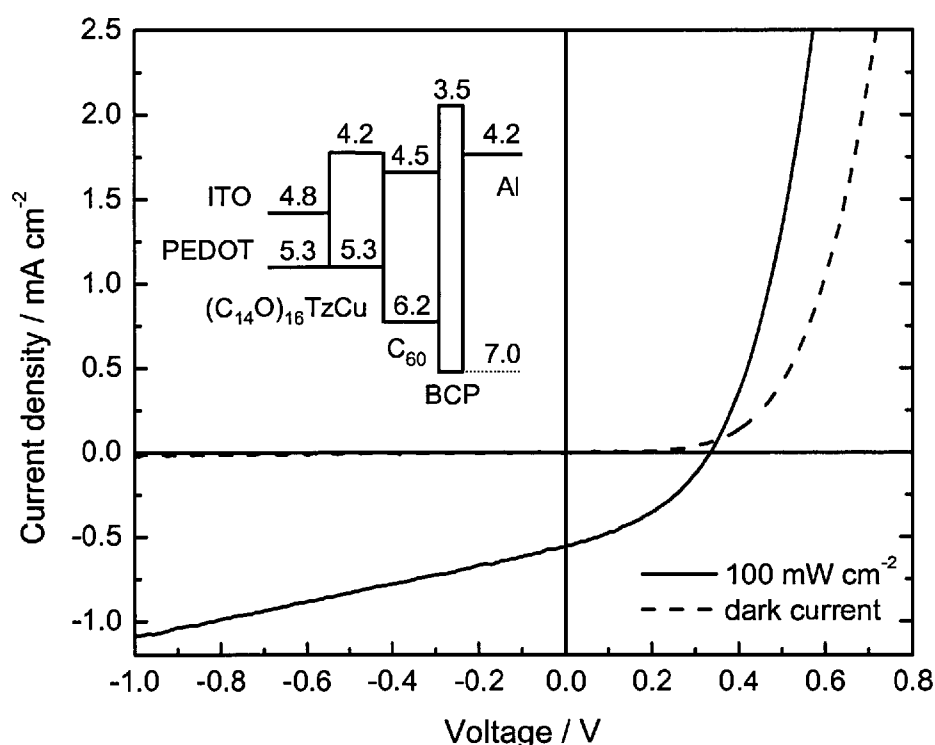


Figure 5.8 – J-V characteristics of an ITO/30 nm PEDOT:PSS/20 nm (C₁₄O)₁₆TzCu/40 nm C₆₀/12 nm BCP/Al device. The inset shows the HOMO-LUMO energy levels of the constituent materials with respect to the vacuum level. Devices were measured under AM1.5 simulated solar illumination at 100 mW cm⁻² (1 sun) with Al contact areas of 0.16 cm².

Large-area orientational order is undoubtedly a prerequisite for discotic liquid crystalline-based solar cells. Liu and co-workers (LIU *et al.*, 2003), for example, have demonstrated that the short-circuit conductivities associated with the homeotropic regions of ITO/HBC-C_{4/16}/ITO cells are about five times greater than those of poorly orientated regions. However, in addition to homeotropic alignment, long-range molecular periodicity is also a necessity for highly efficient PV devices. The modest power conversion efficiency is therefore attributed to the relatively low degree of intermolecular order within the Col_{tet,d} mesophase and, in particular, to the detrimental effect that this has on the charge transport properties.

Charge transport in self-organizing columnar phases has variously been interpreted on the basis of hopping models that invoke the static/dynamic disorder present in the system (VAN DE CRAATS *et al.*, 1998; BLEYL *et al.*, 1999)⁹, the Holstein small polaron in the nonadiabatic limit (KREOUZIS *et al.*, 2001)¹⁰ and, more recently, the semiclassical Marcus theory (LEMAUR *et al.*, 2004).¹¹ While the precise methodology may differ, the relative positions of the molecules within the columns (i.e., intermolecular distances and/or rotations of the disks around the stacking axis) feature prominently in all of these theoretical analyses. In particular, deviations from a fully cofacial geometry (often encountered due to short-range steric repulsions) as well as large lateral displacements of the molecular cores are viewed as being detrimental to carrier mobility. Indeed, this

⁹ Structural disorder is approximated by potential energy profiles with wells of random energy depths and/or barriers with random energy heights, with carriers that are temporarily localized either in one of these wells or between adjacent barriers. The motion of a charge carrier is subsequently described in terms of the energy required to transit between nearest-neighbour sites in one-dimension. Variations in the shape of the potential energy profile and/or the particular transport mechanism (e.g., thermally activated over-the-barrier jumps or tunnelling-assisted hopping) depend on the precise nature of the theoretical model used (see (VAN DE CRAATS, 1998) and references therein).

¹⁰ The ‘small polaron’ approach employs the transport mechanism developed by Holstein (HOLSTEIN, 1959) for 1-D charge transport in molecular crystals, in which carriers are considered to be strongly localized on the molecules, causing a distortion of the molecular configuration. The transport of a localized polaron depends on the magnitude of the intermolecular transfer integral (J) between two hopping sites, which characterizes the strength of the electronic coupling. In the case of the nonadiabatic transfer (i.e., involving the transfer of heat), J is small compared to the activation energy for polaron hopping ($\Delta E \approx E_p/2$, where E_p is the polaron binding energy), such that the mobility (μ) varies with temperature (T) according to

$$\mu = \frac{ea^2}{kT} \frac{1}{\hbar} \left(\frac{\pi}{2E_p kT} \right)^{1/2} J^2 \exp\left(\frac{-E_p}{2kT}\right)$$

where e is the electronic charge, a is the intermolecular separation along the stack, $\hbar$ is Planck’s constant and k is Boltzmann’s constant. This model appears to be a good candidate for explaining the almost temperature-independent mobility of numerous triphenylene compounds (KREOUZIS, 2001).

¹¹ The formalism utilised by Lemaury *et al.* (LEMAUR, 2004) to model charge transport depends, in addition to the magnitude of J , on the reorganization energy (λ) of the system. This reflects the geometric changes in the molecules when going from the neutral to the ionized state (or vice versa) and the changes in electronic polarization of the surrounding molecules as well as their possible reorientations around the charge carrier. High transfer rates, and hence high charge mobilities, require large values for J and small values for λ .

is reflected in experimental results. For example, the highly ordered columnar hexagonal plastic phase (Col_{hp}) of the triphenylene based HAT3 and HAT4 compounds (where the integers 3 and 4 define the alkyl chain length, $\text{C}_n\text{H}_{2n+1}$) exhibit hole mobilities ($1.2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) that are an order of magnitude greater than the less ordered columnar hexagonal mesophase (Col_{h}) of the related HAT5 molecule ($1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and two orders of magnitude greater than that of HAT11 ($1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (BUSHBY & LOZMAN, 2002). This is attributable to the increase in order, and thus molecular orbital overlap, within the Col_{h} phase as the side chains become shorter. Likewise, the alkylthio-substituted phthalocyanine complex $(\text{C}_{12}\text{S})_8\text{PcH}_2$, in which the alkyl chains are coupled to the Pc core *via* bulky sulphur atoms, exhibits an absolute one-dimensional intracolumnar mobility¹² of $0.28 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the Col_{h} phase, close to an order of magnitude greater than that of the similarly structured alkoxy-substituted $(\text{C}_{12}\text{O})_8\text{PcH}_2$ derivative ($0.051 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (OHTA *et al.*, 2003). The larger size of the sulphur atom (compared to the oxygen) hinders lateral and rotational motion of the macrocycles within the columnar stacks of $(\text{C}_{12}\text{S})_8\text{PcH}_2$, thereby increasing the structural order and electronic coupling (BAN *et al.*, 2001). While the mobility values of $(\text{C}_{14}\text{O})_{16}\text{TzCu}$ are not known, it is clear that the degree of intracolumnar order plays a critical role in the rate of charge migration.

¹² Carrier mobilities are often measured using pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) methods. In short, the PR-TRMC technique involves the irradiation of a material with high energy electrons, giving rise to the transient formation of charge carriers (holes and electrons). By monitoring the change in the power levels of propagating microwaves, it is possible to extract absolute charge carrier mobilities (i.e., it is not possible to distinguish hole and electron mobilities). Also of importance is that because of the nanosecond timescale of the observations and the ultra-high frequency of the probing microwaves, the mobilities determined by PR-TRMC are the intrinsic, trap-free values associated with organized domains within the material. They therefore represent close to the maximum mobility that might be achievable and are often, though not always, orders of magnitude greater than those obtained by time-of-flight (TOF) methods (SCHOUTEN *et al.*, 1994; WARMAN *et al.*, 2003).

5.4 Conclusions

This chapter has elucidated the physical and photovoltaic properties of a novel discotic liquid crystalline material. Polarizing optical microscopy established that the copper phthalocyanine complex $(C_{14}O)_{16}TzCu$ exhibits uniform homeotropic alignment when deposited at room temperature onto a single surface: when viewed between crossed polarizers, spin-coated samples displayed no birefringent domains or liquid crystalline textures. The Q-band electronic absorption spectrum of $(C_{14}O)_{16}TzCu$ thin films is characterised by a single, well-resolved peak centred at 755 nm, a red-shift of approximately 25 nm with respect to that for $(C_{14}O)_{16}TzCu$ in solution ($CHCl_3$). In conjunction with polarity-dependent electronic absorption measurements, which demonstrated that the solvated ($CHCl_3$) spectrum becomes progressively broadened and red-shifted (~ 20 nm) with increasing concentrations of *n*-hexane, and based on the optical evidence, it was concluded that the spectral changes attendant upon spin-coating were due to local rotations rather than lateral displacements of adjacent chromophores.

Morphological and electrochemical measurements have been performed. It was noted that films spin-coated directly onto bare ITO substrates contained a significant number of pin-holes, an avoidable hindrance to device performance if a thin, planarizing PEDOT:PSS layer is utilised. The resulting morphology is smooth ($R_q = 0.56$ nm) and featureless. Cyclic voltammetry experiments indicated a HOMO level of 5.25 eV and a LUMO level of 4.2 eV (from the onset potentials of oxidation (0.85 V) and reduction (-0.20 V), respectively), energy levels that provide efficient exciton dissociation and charge transfer when utilised in conjunction with fullerene.

Devices incorporating $(C_{14}O)_{16}TzCu$ as a hole-transporting layer display characteristic *J-V* parameters of $J_{sc} = 0.57$ mA cm⁻², $V_{oc} = 0.33$ V, $FF = 0.38$ and

consequently a power conversion efficiency of 0.07%. It was speculated that the device performance is ultimately limited by the large degree of geometric fluctuations within the columns, which are detrimental to charge transport. Further enhancements in the conductivity, through tailoring of the molecular structure, may lead to improvements in device performance.

6 CONCLUSION

Elucidating the physical parameters that govern the photovoltaic behaviour of molecular-based solar cells plays a vital role in their continuing development and has been the central aim of this thesis. More specifically, the experimental results described herein have addressed the following points:

1. To assess the influence of codeposition on CuPc-C₆₀ heterojunctions, to determine the dominant loss mechanism(s) and to explore the implications of these findings;
2. To investigate the effects of annealing on the interface morphology of CuPc/C₆₀ bilayers and to provide an insight into the phase segregation in binary composites comprising CuPc and PhEt-PTC;
3. To report on the thin film properties of a novel discotic liquid crystal phthalocyanine and to exploit its self-assembling properties for device application.

CuPc-C₆₀ heterojunctions

A comparative study of the morphological, spectroscopic and photovoltaic properties of vacuum deposited CuPc-C₆₀ heterojunctions has been presented (chapter 3). Analysis of the J - V curves revealed that the J_{sc} was significantly improved when varying the device architecture from an ITO/15 nm CuPc/40 nm C₆₀/12 nm BCP/Al discrete heterojunction to an ITO/60 nm CuPc:C₆₀ (1:1)/12 nm BCP/Al bulk heterojunction. Additional enhancements were obtained when utilising a combinatorial planar-mixed structure (ITO/3.5 nm

CuPc/50 nm CuPc:C₆₀ (1:1)/5 nm CuPc/12 nm BCP/Al). This was attributed to increased exciton dissociation within the intimately mixed D-A layers. However, although the corresponding η_p values improve in parallel, the increasing resistance to charge transport becomes apparent: the *FF* of devices containing mixed layers is substantially lower than architectures that comprise two well-defined D/A layers. This ultimately limits the mixed layer thickness.

Light-intensity dependent measurements demonstrated that the exciton annihilation kinetics in CuPc/C₆₀ DHJs were predominantly monomolecular in nature and that, as expected, this value tends to be lower for mixed heterojunctions, due to increased geminate-pair recombination. Experimental values correlated well with recently reported findings. The lower mobility and higher series resistance associated with an interpenetrating CuPc:C₆₀-containing structure becomes particularly noticeable at the highest illumination intensities, for which the *FF* decreased dramatically. In contrast, the *FF* of the DHJ remained relatively constant over all irradiation levels. Normalised *J-V* curves showed that the internal electric field due to the concentration gradient of charge carriers across the heterointerface varies according to the device architecture, while the corresponding *P-V* curves established that, although generating less power than its DHJ counterpart, the PM-HJ operated close to its maximum power point over a greater voltage range.

Morphological and spectroscopic results corroborate the findings of the PV device investigations. AFM analysis showed that codeposition produces substantial changes in the morphology compared to sequentially evaporated double layers; the mixed layer is smooth and amorphous with the absence of any large crystallites suggesting that phase segregation (if present) is on a length scale that is less than the resolution of the AFM (~10 nm). This is consistent with electronic absorption measurements, in which an increased contribution from non-interacting monomer species was observed.

Influence of annealing

A semi-quantitative evaluation of annealed CuPc/C₆₀ bilayer solar cells suggests that there is a strong correlation between the interface morphology/structural homogeneity of molecular thin films and the device performance (chapter 4).

CuPc thin films annealed at 325 °C for 2 hours undergo a phase change from the α - to the β - form. Salient characteristics of this transition are: (i) the appearance of a new peak at $2\theta = 7.1^\circ$ in the powder XRD scan, corresponding to a narrowing of the interplanar spacing from 12.83 Å to 12.44 Å; (ii) a change in the surface morphology from small spherical to large needle-like crystallites, with an attendant increase in the RMS roughness from 1.5 to 5.5 nm; and (iii) a crossover in the relative Q-band peak intensities, in conjunction with a slight bathochromic shift.

The performance of PV devices incorporating heat-treated CuPc films were, without exception, significantly less efficient than the as-grown cells. This was attributed to structural reorganizations in the CuPc film and to morphological modifications of the C₆₀ layer, rather than the varying effects of oxygen doping on the electronic conduction processes in different CuPc polymorphs. However, it is acknowledged that, in this instance, this cannot be verified with certainty due to experimental limitations.

In the second half of chapter 4, experiments conducted on CuPc:PhEt-PTC BHJs provided further insights into the 'thermodynamically driven' phase segregation reported by Peumans *et al.* (PEUMANS *et al.*, 2003). Similar to CuPc, a phase transition in PhEt-PTC (from 'amorphous' to the crystalline 'modification I') can be induced through thermal annealing. Apart from a minor discrepancy in the onset of annealing temperature, the obtained results were very similar to

those published previously in the literature. Mixing CuPc with PhEt-PTC produced spectroscopic and morphological results that were indicative of a 'solid solution', while successive heat treatments at elevated temperatures (up to 325 °C when utilising a metal 'capping' layer) resulted in the progressive phase segregation of material. The average domain size, established from the (200) α - CuPc diffraction peak, was approximately 23 nm, though this was taken to be the lower limit. As with the annealed CuPc/C₆₀ discrete heterojunctions, the efficiency of heat-treated CuPc:PhEt-PTC devices was found to depend strongly on the structural form of the CuPc.

Phthalocyanine-based discotic liquid crystals

The physical and photovoltaic properties of a novel discotic liquid crystalline material based on copper phthalocyanine have been established (chapter 5). (C₁₄O)₁₆TzCu thin films were characterised by polarizing optical and atomic force microscopy, polarity- and temperature- dependent absorption spectroscopy, as well as electrochemical measurements.

Molecules assemble into a columnar tetragonal disordered mesophase that displays uniform homeotropic alignment from room temperature up to its decomposition temperature (*ca.* 350 °C). Within columns, chromophore orientation is characterised by small, symmetry lowering rotations around the stacking axis, as evidenced by the bathochromic shift in the solid state absorption spectrum and confirmed by the polarity-dependent solution measurements. Decreasing the solvent polarity (through an increasing concentration of *n*-hexane) results in a red-shifted, broadened absorption profile, suggestive of increased aggregation.

The planar topography of (C₁₄O)₁₆TzCu/C₆₀ bilayer structures indicates that there is good interfacial contact, while CV experiments suggest that the energy

level offsets at this heterojunction is well-suited to exciton dissociation and charge transfer. Nevertheless, devices incorporating $(\text{C}_{14}\text{O})_{16}\text{TzCu}$ as a hole-transporting layer display power conversion efficiencies of $<0.1\%$, ultimately limited by the large degree of geometric fluctuations within the columns. Further enhancements in the conductivity, through tailoring of the molecular structure, may lead to improvements in device performance.

Outlook

Despite some impressive advances in the field of organic photovoltaics in recent years, the inferior charge transport properties of molecular semiconductors remains a major obstacle in their commercial viability. As far back as the 1970s, researchers envisaged the synthesis of 'excitonic superconductors', metallo-organic complexes that form one-dimensional 'metallic chains' *via* the overlap of d_z platinum orbitals (LITTLE, 1975). In practice, such compounds not only proved difficult to prepare but also lacked the orientational control necessary to achieve the required stacking (SIMON & ANDRÉ, 1985). It is, of course, exactly for this reason why molecular self-assembly and discotic liquid crystals have become such a highly topical and promising field of research. Even so, achieving the desired combination of molecular alignment and ordering will require further work. Nevertheless, the accurate and controlled application of intermolecular forces, including hydrogen bonding, ionic bonding (electrostatic interactions), hydrophobic interactions and van der Waals interactions among others, could lead to one-dimensional semiconductors of comparably high mobility as well as new and previously unachievable nanostructures that could benefit organic photovoltaic performance.

BIBLIOGRAPHY

- Adam, D., Schuhmacher, P., Simmerer, J., Haussling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., and Haarer, D. (1994). **Fast photoconduction in the highly ordered columnar phase of a discotic liquid-crystal.** *Nature*, **371**, 141-143.
- Adams, D. M., Kerimo, J., Olson, E. J. C., Zaban, A., Gregg, B. A., and Barbara, P. F. (1997). **Spatially-resolving nanoscopic structure and excitonic-charge-transfer quenching in molecular semiconductor heterojunctions.** *Journal of the American Chemical Society*, **119** (44), 10608-10619.
- Albrecht, T. R. and Quate, C. F. (1988). **Atomic resolution with atomic force microscope on conductors and non-conductors.** *Journal of Vacuum Science and Technology A*, **6** (2), 271-274.
- Arkhipov, V., Heremans, P., and Bäessler, H. (2003). **Why is exciton dissociation so efficient at the interface between a conjugated polymer and an electron acceptor?** *Applied Physics Letters*, **82** (25), 4605-4608.
- Arkhipov, V. and Bäessler, H. (2004). **Exciton dissociation and charge photogeneration in pristine and doped conjugated polymers.** *Physica Status Solidi A*, **201** (6), 1152-1187.
- Armstrong, N. R., Carter, C., Donley, C., Simmonds, A., Lee, P., Brumbach, M., Kippelen, B., Domercq, B., and Yoo, S. (2003). **Interface modification of ITO thin films: organic photovoltaic cells.** *Thin Solid Films*, **445**, 342-352.
- Asakawa, T., Sasaki, M., Shirashi, T., and Koinuma, H. (1995). **Dark and photoconductivity behaviors of amorphous and crystalline C₆₀ films.** *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers*, **34**, 1958.
- Atkins, P. W. and Friedman, R. S. (1997). *Molecular Quantum Mechanics*, New York: Oxford University Press.
- Barbara, P. F., Adams, D. M., and O'Conner, D. B. (1999). **Characterization of organic thin film materials with near-field scanning optical microscopy (NSOM).** *Annual Review of Materials Science*, **29**, 433-469.
- Bäessler, H. (1997). Semiconducting and Photoconducting Organic Solids. In *Organic Molecular Solids. Properties and Applications.*, W. Jones, p. 267-308, Boca Raton: CRC Press, Inc.
- Binnig, G., Quate, C. F., and Gerber, C. (1986). **Atomic force microscope.** *Physical Review Letters*, **67** (9), 930-933.

- Bird, G. A. (1994). *Molecular gas dynamics and the direct simulation of gas flows*, Oxford: Clarendon Press.
- Birks, J. B. (1970). *Photophysics of Aromatic Molecules*, New York: Wiley-Interscience.
- Bleyl, I., Erdelen, C., Schmidt, H.-W., and Haarer, D. (1999). **One-dimensional hopping transport in a columnar discotic liquid-crystalline glass.** *Philosophical Magazine B*, **79**, 463.
- Bockris, J. O. M. and Khan, S. U. M. (1983). *Surface electrochemistry - a molecular level approach*, New York: Plenum Press.
- Brabec, C., Cravino, A., Meissner, D., Sariciftci, N. S., Fromherz, T., Rispen, M. T., Sanchez, L., and Hummelen, J. C. (2001). **Origin of the open circuit voltage of plastic solar cells.** *Advanced Functional Materials*, **11**, 374.
- Brabec, C. (2004). **Organic photovoltaics: technology and market.** *Solar Energy Materials and Solar Cells*, **83**, 273-292.
- Brabec, C. J., Sariciftci, N. S., and Hummelen, J. C. (2001). **Plastic solar cells.** *Advanced Functional Materials*, **11** (1), 15-26.
- Bulovic, V., Burrows, P. E., Forrest, S. R., Cronin, J. A., and Thompson, M. E. (1996). **Study of localized and extended excitons in 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) .1. Spectroscopic properties of thin films and solutions.** *Chemical Physics*, **210** (1-2), 1-12.
- Bushby, R. J. and Lozman, O. R. (2002). **Photoconducting liquid crystals.** *Current Opinion in Solid State & Materials Science*, **6** (6), 569-578.
- Cambridge, A. N. and Bushby, R. J. (1998). Synthesis and Structural Features. In *Handbook of Liquid Crystals. Low Molecular Weight Liquid Crystals, Vol. 2B*, Ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, p. 693-748, Weinheim: Wiley-VCH.
- Carniato, S., Dufour, G., Rochet, F., Roulet, H., Chaquin, P., and Geissner-Prettre, C. (1994). **Theory assisted interpretation of copper phthalocyanine core levels XPS spectra.** *Journal of Electron Spectroscopy and Related Phenomena*, **67** (1), 189-209.
- Chamberlain, G. A. (1983). **Organic solar cells: a review.** *Solar Cells*, **8**, 47.
- Chandrasekhar, S., Shadashiva, B. K., and Suresh, K. A. (1977). **Liquid crystals of disc-like molecules.** *Pramana*, **9** (5), 471-480.
- Collings, P. J. and Hird, M. (1997). *Introduction to Liquid Crystals - Chemistry and Physics*, London: Taylor & Francis.
- Colton, R. J. (1998). *Procedures in Scanning Probe Microscopies*, Chichester: John Wiley & Sons.

- Cook, M. J. (1993). Optical and infrared spectroscopy of phthalocyanine molecular assemblies. In *Spectroscopy of New Materials - Advances in Spectroscopy*, R. E. Hester and C. R. J. H., p. 87-150, New York: Wiley.
- Debe, M. K., Kam, K. K., Liu, J. C., and Poirer, R. J. (1988). **Vacuum vapor-deposited thin-films of a perylene dicarboximide derivative - microstructure versus deposition parameters.** *Journal of Vacuum Science and Technology A*, **6** (3), 1907-1911.
- DeGennes, P. G. (1974). *The Physics of Liquid Crystals*, Oxford: Oxford University Press.
- Dimitrakopoulos, C. D. and Mascaro, D. J. (2001). **Organic thin-film transistors: a review of recent advances.** *IBM Journal of Research and Development*, **45** (1), 11-27.
- Dittmer, J. J., Lazzaroni, R., Leclere, P., Moretti, P., Granstrom, M., Petritsch, K., Marseglia, E. A., Friend, R. H., Bredas, J. L., Rost, H., and Holmes, A. B. (2000). **Crystal network formation in organic solar cells.** *Solar Energy Materials and Solar Cells*, **61** (1), 53-61.
- Downes, J. E., McGuinness, C., Glans, P.-A., Learmonth, T., Fu, D., Sheridan, P., and Smith, K. E. (2004). **Electronic structure near the Fermi level of the organic semiconductor copper phthalocyanine.** *Chemical Physics Letters*, **390**, 203-207.
- Drechsel, J., Männig, B., Gebeyehu, D., Pfeiffer, M., Leo, K., and Hoppe, H. (2004). **MIP-type organic solar cells incorporating phthalocyanine/fullerene mixed layers and doped wide-gap transport layers.** *Organic Electronics*, **5**, 175-186.
- Dresselhaus, M. S. and Dresselhaus, G. (1995). **Fullerenes and fullerene-derived solids as electronic materials.** *Annual Review of Materials Science*, **25**, 487-523.
- Dresselhaus, M. S., Dresselhaus, G., Eklund, P. C., and Saito, R. (1998). **Carbon nanotubes.** *Physics World*, **11** (1), 33-38.
- Dyakonov, V. (2004). **Mechanisms controlling the efficiency of polymer solar cells.** *Applied Physics A - Materials Science & Processing*, **79**, 21-25.
- Eichhorn, H. (2000). **Mesomorphic phthalocyanines, tetraazaporphyrins, porphyrins and triphenylenes as charge-transporting materials.** *Journal of Porphyrins and Phthalocyanines*, **4** (1), 88-102.
- Emery, K. A., Osterwald, C. R. and Wells, C. V. (1987). **Uncertainty analysis of photovoltaic efficiency measurements.** *Proceedings of the Nineteenth IEEE Photovoltaic Specialists Conference*, New Orleans, USA, 153-159.
- Ferguson, A. J., Thesis, Imperial College London, 2004.

- Forrest, S. R. (1997). **Ultrathin organic films grown by organic molecular beam deposition and related techniques.** *Chemical Reviews*, **97** (6), 1793-1896.
- Forrest, S. R. (2004). **The path to ubiquitous and low-cost organic electronic appliances on plastic.** *Nature*, **428**, 911-918.
- Forrest, S. R. (2005). **The limits to organic photovoltaic cell efficiency.** *MRS Bulletin*, **30** (1), 28-32.
- Gebeyehu, D., Brabec, C. J., Padinger, F., Fromherz, T., Hummelen, J. C., Badt, D., Schindler, H., and Sariciftci, N. S. (2001). **The interplay of efficiency and morphology in photovoltaic devices based on interpenetrating networks of conjugated polymers with fullerenes.** *Synthetic Metals*, **118** (1-3), 1-9.
- Gebeyehu, D., Männig, B., Drechsel, J., Leo, K., and Pfeiffer, M. (2003). **Bulk-heterojunction photovoltaic devices based on donor- acceptor organic small molecule blends.** *Solar Energy Materials and Solar Cells*, **79** (1), 81-92.
- Geens, W., Shaheen, S. E., Wessling, B., Brabec, C. J., Poortmans, J., and Sariciftci, N. S. (2002). **Dependence of field-effect hole mobility of PPV-based polymer films on the spin-casting solvent.** *Organic Electronics*, **3** (3-4), 105-110.
- Gould, R. D. (1996). **Structure and electrical conduction properties of phthalocyanine thin films.** *Coordination Chemistry Reviews*, **156**, 237-274.
- Granström, M., Petritsch, K., Arias, A. C., Lux, A., Andersson, M. R., and Friend, R. H. (1998). **Laminated fabrication of polymeric photovoltaic diodes.** *Nature*, **395** (6699), 257-260.
- Gregg, B. A. (1996). **Evolution of photophysical properties of perylene bis(phenethylimide) films upon solvent vapor annealing.** *Journal of Physical Chemistry*, **100**, 3365.
- Gregg, B. A. (2003). **Excitonic solar cells: The physics and chemistry of organic- based photovoltaics.** In *Molecules as Components of Electronic Devices*, Vol. 844, Ed. 243-257,
- Gregg, B. A. (2005). **The photoconversion mechanism of excitonic solar cells.** *MRS Bulletin*, **30** (1), 20-22.
- Guldi, D. M. (2002). **Fullerene-porphyrin architectures; photosynthetic antenna and reaction center models.** *Chemical Society Reviews*, **31** (1), 22-36.
- Haddon, R. C., Brus, L. E., and Raghavachari, K. (1986). **Electronic-structure and bonding in icosahedral C₆₀.** *Chemical Physics Letters*, **125** (5-6), 459-464.
- Haddon, R. C. (1993). **Chemistry of fullerenes: the manifestation of strain in a class of continuous aromatic molecules.** *Science*, **261**, 1545-1550.

- Hädicke, E. and Graser, F. (1986). **Structures of 11 perylene 3-4-9,10-bis(dicarboximide) pigments.** *Acta Crystallographica Section C-Crystal Structure Communications*, **42**, 189.
- Halls, J. J. M., Walsh, C. A., Greenham, N. C., Marseglia, E. A., Friend, R. H., Moratti, S. C., and Holmes, A. B. (1995). **Efficient photodiodes from interpenetrating polymer networks.** *Nature*, **376** (6540), 498-500.
- Halls, J. J. M. and Friend, R. H. (2001). Organic Photovoltaic Devices. In *Clean Energy from Photovoltaics*, M. A. Archer and R. Hill, p. London: Imperial College Press.
- Hamed, A., Sun, Y. Y., Tao, Y. K., Meng, R. L., and Hor, P. H. (1993). **Effects of oxygen and illumination on the *in situ* conductivity of C₆₀ thin-films.** *Physical Review B*, **47** (16), 10873-10880.
- Hassan, A. K. and Gould, R. D. (1989). **The effects of exposure to oxygen and annealing on the conductivity of copper phthalocyanine thin films.** *Journal of Physics: Condensed Matter*, **1** (37), 6679-6684.
- Hatsusaka, K., Ohta, K., Yamamoto, I., and Shirai, H. (2000). **Discotic liquid crystals of transition metal complexes.** *Journal of Materials Chemistry*, **11**, 423-433.
- Hatsusaka, K., Ohta, K., Yamamoto, I., and Shirai, H. (2001). **Discotic liquid crystals of transition metal complexes, part 30: spontaneous uniform homeotropic alignment of octakis(dialkoxyphenoxy) phthalocyaninatocopper(II) complexes.** *Journal of Materials Chemistry*, **11**, 423-433.
- Hatsusaka, K., Kimuar, M., and Ohta, K. (2003). **Discotic liquid crystals of transition metal complexes 33: spontaneous uniform homeotropic alignment and unique mesophase transition behavior of bis[2,3,9,10,16,17,23,24-octakis (3,4-dialkoxyphenoxy)-phthalocyaninato] lutetium(III) complexes.** *Bulletin of the Chemical Society of Japan*, **76**, 781-787.
- Hesper, R., Thesis, Rijksuniversiteit Groningen, 2000.
- Heutz, S., Thesis, Imperial College, 2002.
- Heutz, S., Sullivan, P., Sanderson, B. M., Schultes, S. M., and Jones, T. S. (2004). **Influence of molecular architecture and intermixing on the photovoltaic, morphological and spectroscopic properties of CuPc-C₆₀ heterojunctions.** *Solar Energy Materials and Solar Cells*, **83**, 229-245.
- Hiramoto, M., Suezaki, M., and Yokoyama, M. (1990). **Effect of thin gold interstitial-layer on the photovoltaic properties of tandem organic solar-cell.** *Chemistry Letters*, (3), 327-330.
- Hiramoto, M., Fujiwara, H., and Yokoyama, M. (1991). **3-layered organic solar-cell with a photoactive interlayer of codeposited pigments.** *Applied Physics Letters*, **58** (10), 1062-1064.

- Hiramoto, M., Fujiwara, H., and Yokoyama, M. (1992). **P-I-N like behavior in 3-layered organic solar-cells having a co-deposited interlayer of pigments.** *Journal of Applied Physics*, **72** (8), 3781-3787.
- Hiramoto, M., Nakayama, K., Sato, I., Kumaoka, H., and Yokoyama, M. (1998). **Photocurrent multiplication phenomena at organic/metal and organic/organic interfaces.** *Thin Solid Films*, **331** (1-2), 71-75.
- Hirose, Y., Kahn, A., Aristov, Y., Soukiassian, P., Bulovic, V., and Forrest, S. R. (1996). **Chemistry and electronic properties of metal-organic semiconductor interfaces: Al, Ti, In, Sn, Ag, and Au on PTCDA.** *Physical Review B*, **54** (19), 13748.
- Hirsch, A. and Brettreich, M. (2005). *Fullerenes: Chemistry and Reactions*, Weinheim: WILEY-VCH Verlag GmbH & Co.
- Holstein, T. (1959). *Annalen der Physik (N.Y.)*, **8**, 325.
- Holstein, T. (1959). *Annalen der Physik (N.Y.)*, **8**, 343.
- Hoppe, H. and Sariciftci, N. S. (2004). **Organic solar cells: an overview.** *Journal of Materials Research*, **19** (7), 1924-1945.
- Huang, J., Miller, P. F., de Mello, J. C., de Mello, A. J., and Bradley, D. D. C. (2003). **Influence of thermal treatment on the conductivity and morphology of PEDOT/PSS films.** *Synthetic Metals*, **139** (3), 569-572.
- Ichihara, M. (2005) in preparation.
- Janata, J. (2003). **Organic semiconductors in molecular electronics.** *Physical Chemistry Chemical Physics*, **5** (23), 5155-5158.
- Janssen, R. A. J., Hummelen, J. C., and Sariciftci, N. S. (2005). **Polymer-fullerene bulk heterojunctions solar cells.** *MRS Bulletin*, **30** (1), 33-36.
- Jung, H.-T., Kim, S. O., Ko, Y. K., and Yoon, D. K. (2002). **Surface order in thin films of self-assembled columnar liquid crystals.** *Macromolecules*, **35** (9), 3717-3721.
- Kasha, M., Rawls, H. R., and El-Bayoumi, M. A. (1965). **The exciton model in molecular spectroscopy.** *Pure and Applied Chemistry*, **11**, 371.
- Kasha, M. (1976). The Spectroscopy of the Excited State. In *NATO Advanced Study Institutes Series*, B. Di Bartolo, p. 337 NewYork: Plenum Press.
- Katz, E. A., Lyubin, V. M., Faiman, D., Shtutina, S., Shames, A., and Goren, S. (1996). **Persistent photoelectric phenomena in oxygenated C₆₀ thin films.** *Solid State Communications*, **100** (11), 781-784.

- Kim, Y., Choulis, S. A., Nelson, J., Bradley, D. D. C., Cook, S., and Durrant, J. R. (2005). **Device annealing effect in organic solar cells with blends of regioregular poly(3-hexylthiophene) and soluble fullerene.** *Applied Physics Letters*, **86**, 063502.
- Klebe, G., Graser, F., Hadicke, E., and Berndt, J. (1989). **Crystallochromy as a solid-state effect - correlation of molecular-conformation, crystal packing and color in perylene- 3,4-9,10-bis(dicarboximide) pigments.** *Acta Crystallographica Section B-Structural Science*, **45**, 69.
- Klessinger, M. and Michl, J. (1995). *Excited States and Photochemistry of Organic Molecules*, New York: VCH Publishers Inc.
- Köhler, G. and Rechthaler, K. (1993). **Solvent effects in excited state relaxation phenomena.** *Pure & Applied Chemistry*, **65** (8), 1647-1652.
- Krätschmer, W., Lamb, L. D., Fostiropoulos, K., and Huffman, D. R. (1990). **Solid C₆₀ - a new form of carbon.** *Nature*, **347**, 354-358.
- Kreouzis, T., Donovan, K., Boden, N., Bushby, R. J., Lozman, O. R., and Liu, Q. (2001). **Temperature-independent hole mobility in discotic liquid crystals.** *Journal of Chemical Physics*, **114** (4), 1797-1802.
- Kroto, H., Heath, J. R., O'Brien, S. C., Curl, R. F., and Smalley, R. E. (1985). **C₆₀: buckminsterfullerene.** *Nature*, **318**, 162-163.
- Lemaur, V., Da Silva Filho, D. A., Coropceanu, V., Lehmann, M., Geerts, Y., Piris, J., Debije, M. G., Van de Craats, A. M., Senthilkumar, K., Siebbeles, L. D. A., Warman, J. M., Bredas, J. L., and Cornil, J. (2004). **Charge transport properties in discotic liquid crystals: a quantum-chemical insight into structure-property relationships.** *Journal of the American Chemical Society*, **126** (10), 3271-3279.
- Levitsky, I. A., Kishikawa, K., Eichhorn, S. H., and Swager, T. M. (2000). **Exciton coupling and dipolar correlations in a columnar liquid crystal: photophysics of a bent-rod hexacatenar mesogen.** *Journal of the American Chemical Society*, **122** (11), 2474-2479.
- Leznoff, C. C. and Lever, A. B. P. (1989). *Phthalocyanines - Properties and Applications*, New York: VCH.
- Liao, M.-S. and Scheiner, S. (2001). **Electronic structure and bonding in metal phthalocyanines, Metal=Fe, Co, Ni, Cu, Zn, Mg.** *Journal of Chemical Physics*, **114** (22), 9780-9791.
- Little, W. A. (1975). *Low Dimensional Cooperative Phenomena*, New York: Plenum Press.

- Liu, J. C., Fechtenkötter, A., Watson, M. D., Müllen, K., and Bard, A. J. (2003). **Room temperature discotic liquid crystalline thin films of hexa-peri-hexabenzocoronene: synthesis and optoelectronic properties.** *Chemistry of Materials*, **15** (1), 124-130.
- Loutfy, R. O. and Hsiao, C. K. (1981). **Effect of temperature on organic Schottky-barrier cells.** *Canadian Journal of Physics*, **59** (6), 727-732.
- Männig, B., Drechsel, J., Gebeyehu, D., Simon, P., Kozłowski, F., Werner, A., Li, F., Grundmann, S., Sonntag, S., Koch, M., Leo, K., Pfeiffer, M., Hoppe, H., Meissner, D., Sarıciǧci, N. S., Riedel, I., Dyakonov, V., and Parisi, J. (2004). **Organic p-i-n solar cells.** *Applied Physics A - Materials Science & Processing*, **79**, 1-14.
- Martens, T., D'Haen, J., Munters, T., Beelen, Z., Goris, L., Manca, J., D'Olieslaeger, M., Vanderzande, D., De Schepper, L., and Andriessen, R. (2003). **Disclosure of the nanostructure of MDMO-PPV:PCBM bulk heterojunction organic solar cells by a combination of SPM and TEM.** *Synthetic Metals*, **138** (1-2), 243-247.
- Mather, R. P. (1999). **The effect of crystal properties on the manufacture and application performance of copper phthalocyanine pigments.** *Journal of Porphyrins and Phthalocyanines*, **3**, 643-646.
- McKeown, N. B. (1998). *Phthalocyanine materials: synthesis, structure and function.*, Cambridge University Press.
- McNaught, A. D. and Wilkinson, A. (1997). *IUPAC Compendium of Chemical Terminology*, Oxford: Blackwell Science.
- Meissner, D. and Rostalski, J., in *Highly Efficient Molecular Organic Solar Cells*, Glasgow, 2000.
- Micaroni, L., Nart, F. C., and Hümmelgen, I. A. (2002). **Considerations about the electrochemical estimation of the ionization potential of conducting polymers.** *Journal of Solid State Electrochemistry*, **7**, 55-59.
- Milhailetchi, V. D., Blom, P. W. M., Hummelen, J. C., and Rispen, M. T. (2003). **Cathode dependence of the open-circuit voltage of polymer:fullerene bulk heterojunction solar cells.** *Journal of Applied Physics*, **94** (10), 6849-6854.
- Mirchin, N. R. and Peled, A. (2004). **Modeling of electronic transport in molecular doped polymers by the time-of-flight method.** *HAIT Journal of Science and Engineering*, **1** (4), 782-810.
- Mizuguchi, J. (1998). **Electronic characterization of N,N'-bis(2-phenylethyl) perylene-3,4:9,10-bis(dicarboximide) and its application to optical disks.** *Journal of Applied Physics*, **84**, 4479.

- Mizuguchi, J. and Tojo, K. (2002). **Electronic structure of perylene pigments as viewed from the crystal structure and excitonic interactions.** *Journal of Physical Chemistry B*, **106**, 767.
- Morteani, A. C., Sreearunothai, P., Herz, L. M., Friend, R. H., and Silva, C. (2004). **Exciton regeneration at polymeric semiconductor heterojunctions.** *Physical Review Letters*, **92** (24), 247402.
- Murgia, M., Biscarini, F., Cavallini, M., Taliani, C., and Ruani, G. (2001). **Intedigitated p-n junction: a route to improve the efficiency in organic photovoltaic cells.** *Synthetic Metals*, **121** (1-3), 1533-1534.
- Nelson, J. (2002). **Organic photovoltaic films.** *Current Opinion in Solid State & Materials Science*, **6** (1), 87-95.
- Nelson, J. (2003). *The Physics of Solar Cells*, Imperial College Press.
- Nguyen, T.-Q., Martel, R., Avouris, P., Bushey, M. L., Brus, L. E., and Nuckolls, C. (2004). **Molecular interactions in one-dimensional organic nanostructures.** *Journal of the American Chemical Society*, **126** (16), 5234-5242.
- Niyoga, S., Hamon, M. A., Hu, H., Zhao, B., Bhowmik, P., Sen, R., Itkis, M. E., and Haddon, R. C. (2002). **Chemistry of single-walled carbon nanotubes.** *Accounts of Chemical Research*, **35** (12), 1105-1113.
- Ohta, K., Hatsusaka, K., Sugibayashi, M., Ariyoshi, M., Ban, K., Maeda, F., Naito, R., Nishizawa, K., van de Craats, A. M., and Warman, J. M. (2003). **Discotic liquid crystalline semiconductors.** *Molecular Crystals and Liquid Crystals*, **397**, 325-345.
- O'Neill, M. and Kelly, S. M. (2003). **Liquid crystals for charge transport, luminescence, and photonics.** *Advanced Materials*, **15** (14), 1135-1146.
- Padinger, F., Rittberger, R. S., and Sariciftci, N. S. (2003). **Effects of postproduction treatment on plastic solar cells.** *Advanced Functional Materials*, **13** (1), 85-88.
- Peumans, P., Bulovic, V., and Forrest, S. R. (2000). **Efficient photon harvesting at high optical intensities in ultrathin organic double-heterostructure photovoltaic diodes.** *Applied Physics Letters*, **76** (19), 2650-2652.
- Peumans, P. and Forrest, S. R. (2001). **Very-high-efficiency double-heterostructure copper phthalocyanine/C₆₀ photovoltaic cells.** *Applied Physics Letters*, **79** (1), 126-128.
- Peumans, P., Uchida, S., and Forrest, S. R. (2003). **Efficient bulk heterojunction photovoltaic cells using small- molecular-weight organic thin films.** *Nature*, **425** (6954), 158-162.

- Peumans, P., Yakimov, A., and Forrest, S. R. (2003). **Small molecular weight organic thin-film photodetectors and solar cells.** *Journal of Applied Physics*, **93** (7), 3693-3723.
- Peumans, P. and Forrest, S. R. (2004). **Separation of geminate charge-pairs at donor-acceptor interfaces in disordered solids.** *Chemical Physics Letters*, **398**, 27-31.
- Piechocki, C., Simon, J., Skoulis, A., Guillon, D., and Weber, P. J. (1982). **Discotic mesophases obtained from substituted metallophthalocyanines - crystalline one-dimensional conductors.** *Journal of the American Chemical Society*, **104** (19), 5245-5247.
- Pope, M. and Swenberg, C. E. (1982). *Electronic Processes in Organic Crystals*, Oxford: Clarendon Press.
- Ramsdale, C. M., A., B. J., Arias, A. C., MacKenzie, J. D., Friend, R. H., and Greenham, N. C. (2002). **The origin of the open-circuit voltage in polyfluorene-based photovoltaic devices.** *Journal of Applied Physics*, **92** (8), 4266-4270.
- Ravirajan, P., Haque, S. A., Durrant, J. R., Bradley, D. D. C., and Nelson, J. (2005). **The effect of polymer optoelectronic properties on the performance of multilayer hybrid polymer/TiO₂ solar cells.** *Advanced Functional Materials*, **15** (4), 609-618.
- Reese, C., Roberts, M., Ling, M.-M., and Bao, Z. (2004). **Organic thin film transistors.** *Materials Today*, **7** (9), 20-27.
- Reichardt, C. (1994). **Solvatochromic dyes as solvent polarity indicators.** *Chemical Reviews*, **94**, 2319-2358.
- Rostalski, J. and Meissner, D. (2000). **Photocurrent spectroscopy for the investigation of charge carrier generation and transport mechanisms in organic p/n- junction solar cells.** *Solar Energy Materials and Solar Cells*, **63** (1), 37-47.
- Rostalski, J. and Meissner, D. (2000). **Monochromatic versus solar efficiencies of organic solar cells.** *Solar Energy Materials and Solar Cells*, **61** (1), 87-95.
- Ruani, G., Fontanini, C., Murgia, M., and Taliani, C. (2002). **Weak intrinsic charge transfer complexes: a new route for developing wide spectrum organic photovoltaic cells.** *Journal of Chemical Physics*, **116** (4), 1713-1719.
- Rudiono, Kaneko, F., and Takeuchi, M. (1999). **Morphological characteristics of perylene-doped phthalocyanine thin films and their photovoltaic effect.** *Applied Surface Science*, **142** (1-4), 598-602.
- Sager, B. M., Roscheisen, M. R., Petritsch, K., Pichler, K., Fidanza, J., Yu, D. (2004) **Photovoltaic devices fabricated by growth from porous template.** *Chemical Abstracts*, **140**, 426122.

- Sariciftci, N. S., Smilowitz, L., Heeger, A. J., and Wudl, F. (1992). **Photoinduced electron transfer from a conducting polymer to buckminsterfullerene.** *Science*, **258**, 1474-1476.
- Sariciftci, N. S. (2004). **Plastic photovoltaic devices.** *Materials Today*, September, 36-40.
- Schaffer, A. M., Gouterman, M., and Davidson, E. R. (1973). **Extended Hückel calculations on metal phthalocyanines and tetraporphins.** *Theoretica Chimica Acta*, **30**, 9.
- Schmidt-Mende, L., Fechtenkötter, A., Müllen, K., Moons, E., Friend, R. H., and MacKenzie, J. D. (2001). **Self-organized discotic liquid crystals for high-efficiency organic photovoltaics.** *Science*, **293** (5532), 1119-1122.
- Schouten, P. G., Warman, J. M., Mattheijs, P., de Haas, M. P., van Nostrum, C. F., Gelinck, G. H., Nolte, R. J. M., Copyn, M. J., Zwikker, J. W., Engel, M. K., Hanack, M., Chang, Y. H., and Ford, W. T. (1994). **The effect of structural modifications on charge migration in mesomorphic phthalocyanines.** *Journal of the American Chemical Society*, **116** (15), 6880 - 6894.
- Schreiber, F. (2004). **Organic molecular beam deposition: growth studies beyond the first monolayer.** *Physical Status Solidi A*, **201** (6), 1037-1054.
- Shaheen, S. E., Brabec, C. J., Sariciftci, N. S., Padinger, F., Fromherz, T., and Hummelen, J. C. (2001). **2.5% efficient organic plastic solar cells.** *Applied Physics Letters*, **78** (6), 841-843.
- Shaheen, S. E., Ginley, D. S., and Jabbour, G. E. (2005). **Organic-based photovoltaics.** *MRS Bulletin*, **30** (1), 10-19.
- Shihub, S. I. and Gould, R. D. (1996). **Studies of phase transformations in some metal phthalocyanine thin films using measurements of current as a function of temperature.** *Thin Solid Films*, **291**, 390-394.
- Simon, J. and André, J.-J. (1985). *Molecular Semiconductors*, Berlin: Springer-Verlag.
- Simpson, C. D., Wu, J. S., Watson, M. D., and Müllen, K. (2004). **From graphite molecules to columnar superstructures - an exercise in nanoscience.** *Journal of Materials Chemistry*, **14** (4), 494-504.
- Skoog, D. A. and Leary, J. J. (1992). *Principles of Instrumental Analysis*, Fort Worth: Saunders College Publishing.
- Snow, W. and Barger, W. R. (1989). Phthalocyanine Films in Chemical Sensors. In *Phthalocyanines. Properties and Applications, Vol. 1*, Ed. C. C. Leznoff and A. B. P. Lever, p. 341, Cambridge: VCH.
- Stachowiak, G. W. and Batchelor, A. W. (1993). *Engineering Tribology*, Amsterdam: Elsevier Science Publishers B.V.

- Stillman, M. J. and Nyokong, T. (1989). Absorption and Magnetic Circular Dichroism Spectral Properties of Phthalocyanines Part 1: Complexes of the Dianion, $\text{Pc}(-2)$. In *Phthalocyanine: properties and applications, Vol. 1*, Ed. C. C. Leznoff and A. B. P. Lever, p. 133-289, New York: VCH.
- Suemori, K., Miyata, T., Yokoyama, M., and Hiramoto, M. (2005). **Three-layered organic solar cells incorporating nanostructure-optimized phthalocyanine:fullerene codeposited interlayer.** *Applied Physics Letters*, **86**, 063509.
- Sullivan, P., Heutz, S., Schultes, S. M., and Jones, T. S. (2004). **Influence of codeposition on the performance of CuPc-C_{60} heterojunction photovoltaic devices.** *Applied Physics Letters*, **84** (7), 1210-1212.
- Taima, T., Chikamatsu, M., Yoshida, Y., Saito, K., and Yase, K. (2004). **Effects of intrinsic layer thickness on solar cell parameters of organic *p-i-n* heterojunction photovoltaic cells.** *Applied Physics Letters*, **85** (26), 6412-6415.
- Tang, C. W. (1986). **2-Layer organic photovoltaic cell.** *Applied Physics Letters*, **48** (2), 183-185.
- Taylor, R., Parsons, J. P., Avent, A. G., Rannard, S. P., Dennis, J. T., Hare, J. P., Kroto, H. W., and Walton, D. R. (1991). **Degradation of C_{60} by light.** *Nature*, **351**, 271.
- Terasawa, N., Monobe, H., Kiyohara, K., and Shimizu, Y. (2003). **Strong tendency towards homeotropic alignment in a hexagonal columnar mesophase of fluoroalkylated triphenylenes.** *Chemical Communications*, **14**, 1678-1679.
- Turro, N. J. (1991). *Modern Molecular Photochemistry*, Sausalito: University Science Books.
- Uchida, S., Xue, J. G., Rand, B. P., and Forrest, S. R. (2004). **Organic small molecule solar cells with a homogeneously mixed copper phthalocyanine: C_{60} active layer.** *Applied Physics Letters*, **84** (21), 4218-4220.
- Vaeth, K. M. (2003). **OLED-display technology.** *Information Display*, **19**, 12-17.
- van de Craats, A. M., Warman, J. M., de Haas, M. P., Adam, D., Simmerer, J., Haarer, D., and Schuhmacher, P. (1996). **The mobility of charge carriers in all four phases of the columnar discotic material hexakis(hexylthio)-triphenylene: combined TOF and PR-TRMC results.** *Advanced Materials*, **8**, 823.
- van de Craats, A. M., Siebbeles, L. D. A., Bleyl, I., Haarer, D., Berlin, Y. A., Zharikov, A. A., and Warman, J. M. (1998). **Mechanism of charge transport along columnar stacks of a triphenylene dimer.** *Journal of Physical Chemistry B*, **102**, 9625-9634.

- van de Craats, A. M., Warman, J. M., Fechtenkötter, A., Brand, J. D., Harbison, M. A., and Müllen, K. (1999). **Record charge carrier mobility in a room-temperature discotic liquid-crystalline derivative of hexabenzocoronene.** *Advanced Materials*, **11** (17), 1469-1472.
- van de Craats, A. M. and Warman, J. M. (2001). **The core-size effect on the mobility of charge in discotic liquid crystalline materials.** *Advanced Materials*, **13** (2), 130-133.
- Waldauf, C., Schilinsky, P., Hauch, J., and Brabec, C. (2004). **Material and device concepts for organic photovoltaics: towards competitive efficiencies.** *Thin Solid Films*, **451**, 503-507.
- Warman, J. M., Kroeze, J. E., Schouten, P. G., and van de Craats, A. M. (2003). **Charge mobility in discotic liquid crystalline porphyrins and phthalocyanines measured by PR-TRMC.** *Journal of Porphyrins and Phthalocyanines*, **7** (4-5), 342-350.
- Warman, J. M. and Van de Craats, A. M. (2003). **Charge mobility in discotic materials studied by PR-TRMC.** *Molecular Crystals and Liquid Crystals*, **396**, 41-72.
- Weaver, J. H. and Poirier, D. M. (1994). Solid state properties of Fullerenes and Fullerene-based materials. In *Solid State Physics: Fullerenes*, H. Ehrenreich and F. Spaepen, p. 1-107, Boston: Academic Press Inc.
- Wöhrle, D., Kreienhoop, L., and Schlettwein, D. (1996). Phthalocyanines and Related Macrocycles in Organic Photovoltaic Junctions. In *Phthalocyanine: properties and applications, Vol. 4*, Ed. C. C. Leznoff and A. B. P. Lever, p. 219-284, New York: VCH.
- Woolfson, M. M. (1997). *An Introduction to X-Ray Crystallography*, Cambridge: Cambridge University Press.
- Wright, J. D. (1995). *Molecular crystals*, Trowbridge: Cambridge University Press.
- Xue, J. G., Uchida, M., Rand, B. P., and Forrest, S. R. (2004). **Asymmetric tandem organic photovoltaic cells with hybrid planar-mixed molecular heterojunctions.** *Applied Physics Letters*, **85** (23), 5757-5759.
- Xue, J. G., Uchida, M., Rand, B. P., and Forrest, S. R. (2004). **4.2% efficient organic photovoltaic cells with low series resistances.** *Applied Physics Letters*, **84** (16), 3013-3015.
- Xue, J. G., Rand, B. P., Uchida, M., and Forrest, S. R. (2005). **A hybrid planar-mixed molecular heterojunction photovoltaic cell.** *Advanced Materials*, **17** (1), 66-71.

- Yoo, S., Domercq, B., Donley, C., Carter, C., Xia, W., Minch, B. A., O'Brien, D. F., Armstrong, N. R., and Kippelen, B. (2004). **Organic Photovoltaic cells containing discotic liquid crystalline phthalocyanines.** *Proceedings of SPIE*, **5215**, 71-78.
- Yoo, S., Domercq, B., and Kippelen, B. (2004). **Efficient thin-film organic solar cells based of pentacene/C₆₀ heterojunctions.** *Applied Physics Letters*, **85** (22), 5427-5430.
- Yoo, S., Domercq, B., and Kippelen, B. (2005). **Intensity-dependent equivalent circuit parameters of organic solar cells based on pentacene and C₆₀.** *Journal of Applied Physics*, **97**, 103706.
- Yu, G., Gao, J., Hummelen, J. C., Wudl, F., and Heeger, A. J. (1995). **Polymer photovoltaic cells - enhanced efficiencies via a network of internal donor-acceptor heterojunctions.** *Science*, **270** (5243), 1789-1791.