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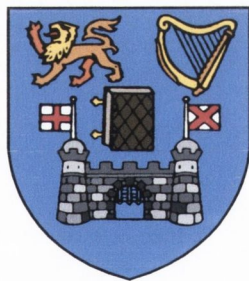
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# Organic Light-Emitting Diodes and Photovoltaic Devices: *Incorporation of Carbon Nanotubes as Charge Transport Media*

by

Patrick Fournet

submitted for the degree of

Doctor of Philosophy

in the

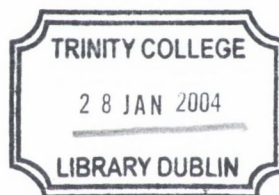
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August 2003





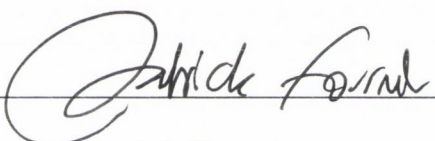
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Patrick Fournet

August 2003



*Pour Margaret, pour mes parents*

*Rose Mme A. Meilland – 'Peace', créée par Antoine  
Meilland, né à Chamboeuf (Loire, France) en 1884*



## ACKNOWLEDGEMENTS

I would like to express my thanks to a number of people, without whom this work would never have been possible. First and foremost, I would like to thank my supervisor Prof. Werner Blau for his help, confidence and support. I would like to acknowledge his warm welcome to his research group and the financial support during the course of the last four years. I am also very grateful to Dr. Jonathan Coleman and Dr. Diarmuid O'Brien, whose guidance and expertise helped me throughout this entire PhD.

I would like to express a special thank to Prof. Gordon Wallace for giving me the opportunity to work at the Intelligent Polymer Research Institute at the University of Wollongong, Australia from January to March 2002, and Dr. Paul Dastoor for welcoming me to the Department of Physics at the University of Newcastle, Australia from October to December 2001.

From members of staff in the Department of Physics, I would like to acknowledge the valued help of Jeanette Cummins, Tom Burke and John Kelly for administrative assistance, and Dave Grouse for technical aid.

Within the group, I would like to say a special thank to Anna Drury for provision of polymers but also constant happiness, Dr. Bernd Lahr for provision of multiwalled carbon nanotubes, and, for their technical and moral support to Dr. Margaret Brennan, Dr. Colin Belton, Dr. Stephen Lipson, Dr. Jean-Edouard Communal, Adam Strevens, Christopher McNeill, Brian Kilbride, Anthony Kelly and Marie-Aude Measson. There are of course a lot of other people in the group, past and present, who helped me make these last few years memorable ones: Robert Murphy, Kevin Ryan, Grace Jordan, Martin Cadek, David Blond, Christian Nitschke, Dr. Michael Kröll, Caitriona Creely, Keith Fortune, Sean O'Flaherty, Alexander Fleming, Dr. Takeyuki Kobayashi, Dr. Manuel Rüther, Dr. Valerie Barron, Dr. Stefanie Maier, Dr. Brendan McCarthy, Dr. Rebekah D'Arcy, Cathal Frizzell, Eimhin Ni Mhuircheartaigh, Emer Lahiff, Eveann Nolan, Dennis McCarthy, James Doyle, Rory Leahy, and Valeria Nicolosi, and I would like to express my thanks to all of them!

Finally, I would like to thank my parents, H       and R      , my brothers, Nicolas and Damien, and especially Margaret for their irreplaceable and continual support.



# ABSTRACT

The effects of incorporating multi-walled carbon nanotubes (MWNT) in two existing functional organic devices: organic light emitting diodes (OLEDs) and organic solar cells have been studied. Single layer OLEDs and organic photovoltaic devices were firstly prepared and characterised in order to understand the physics of conjugated polymers based organic devices without the use of MWNT. Careful analysis of the device's characteristics of a single layer OLED allowed us to determine the intrinsic electronic parameters (Fermi energy level, majority charge carriers' mobility, ...) of one the main conjugated polymers used throughout this Thesis: poly(2,5-dimethoxy-1,4-phenylenevinylene-2-methoxy-5(2'-ethylhexyloxy)-1,4-phenylenevinylene) (M3EH-PPV). As regards single layer polymer solar cells, we found that only a very thin layer was photo-active, resulting in power efficiency being greater for thinner polymer solar cells. Before using it in OLEDs and organic photovoltaic devices, a poly(m-phenylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PmPV) and MWNT composite (PmPV+MWNT) was prepared and characterised. Both DC and AC conductivities of the composite were measured. Percolation scaling laws were used to discuss the results, and conduction due to fluctuation induced tunnelling was indicated. Absorption and photoluminescence studies on M3EH-PPV and PmPV+MWNT bilayers revealed that energy transfer from M3EH-PPV to PmPV, followed by charge transfer from M3EH-PPV to MWNT is likely to occur. Using the PmPV+MWNT composite in M3EH-PPV based OLEDs, a potential barrier to both holes and electrons at the M3EH-PPV / composite interface was observed. However, at all nanotube to polymer mass ratios used for the composite, the relative efficiencies improved compared to the M3EH-PPV single layered devices. The optimum relative efficiency was obtained for a nanotube mass ratio of 1.2 %. As regards the use of MWNT in polymer solar cells, we measured the photovoltaic response of cells using the PmPV+MWNT composite and a thin MEH-PPV buffer layer in a sandwich structure with ITO as the anode and Al as the cathode. Moreover, an ITO / M3EH-PPV+MWNT /  $\text{I}^3\text{I}^-$  / Pt photoelectrochemical cell was prepared and characterised. The presence of MWNT widened the optical active layer and increased the power efficiency by an order of magnitude compared to a cell without MWNT, while increased short-circuit density in polytertiophene based photoelectrochemical cells with MWNT was observed. We concluded that the carbon nanotubes allowed electrons to be transferred and efficiently transported, via their continuous conductive network, to the collecting electrode.

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## I.1. Background and Motivation

Organic materials have displaced traditional materials such as natural polymers (*e.g.* wood), metals, ceramics and glass in many applications owing to the combination of their physical, mechanical properties and ease of processability. Over the last 30 years there has been increasing interest in exploiting these characteristics in combination with electrical properties over and above the purely insulating characteristics that one would expect from organic materials.

In 1977, A. J. Heeger, A. G. McDiarmid, and H. Shirakawa, who were awarded by the Nobel Prize of Chemistry in 2000, brought the unique properties of one class of organic materials: conjugated polymers to the fore when they discovered that chemical doping of these materials resulted in increases in electronic conductivity over several orders of magnitude.<sup>1</sup> Since then, electronically conducting materials have been applied in diverse applications such as organic light-emitting diodes (OLEDs) and organic solar cells.

Both technologies, which will be the main topic of this Thesis, will be introduced in the following Sections I.1.1 and I.1.2. A new class of organic materials: carbon nanotubes and the reasons why they could be potential candidates to improve the efficiency of the above mentioned organic displays will then be presented in Section I.1.3.

### I.1.1. Organic Light-Emitting Diodes (OLEDs)

While the current display market is many billions of dollars by any estimate, its technology of cathode ray tubes and expensive, slow liquid crystals can be considered primitive compared to computing technology. In order for the future display technology to become more compact and portable, vastly smaller, lighter, cheaper and more environmentally benign displays need to be developed.

Organic electroluminescence, a phenomenon first observed and extensively studied in the 1960s,<sup>2,3</sup> forms the basis for the most likely candidate to serve this role. Because crystalline order is not required, organic materials, both molecular and polymeric, can be deposited far more cheaply than the inorganic semiconductors used in conventional LEDs. Patterning is also easier, and may even be accomplished by techniques borrowed from the printing

industry. Displays can be prepared on flexible, transparent substrates. These characteristics form the basis for a display technology that can eventually even replace paper, providing the same resolution and reading comfort in a long-lived, fully reusable (and eventually recyclable) digital medium.

The transformation of this academic endeavour to a practical display technology traces its origins to C.W. Tang *et al.*, who introduced the double layer concept in 1987.<sup>4</sup> This was the first publication that combined modern thin film deposition techniques with suitable materials and structure to give a moderately low bias voltage, attractive efficiency, and encouraging device lifetimes. Their devices were made by subliming molecules of a triarylamine as hole transporter, followed by aluminum-tris-8-hydroxyquinolate (Alq<sub>3</sub>) for electron injection and emission, and using magnesium-silver alloy as the cathode.

In 1990, J. Burroughes *et al.* reported a similar single-layer device made with a conjugated polymeric medium: poly(phenylene vinylene) (PPV).<sup>5</sup> Conjugated polymers are carbon-based semiconductors whose properties are largely dominated by the formation of a partially delocalised  $\pi$ -orbital. Both charged and neutral excitations are mobile in these materials, allowing for both charge and energy transport. The physics of charge transport and light emission in these devices is very similar to that of Tang's, however significant practical differences arise when one begins to contemplate manufacturing issues.

### **I.1.2. Organic Solar Cells**

On a different note, as the energy needs of the planet are likely to double within the next 50 years, the stage is set for a major energy shortage, unless renewable energy can cover the substantial deficit left by fossil fuels. Public concern has been heightened by the disastrous environmental pollution arising from all-too-frequent oil spills and the frightening climatic consequences of the greenhouse effect caused by fossil fuel combustion. Fortunately the supply of energy from the Sun to the Earth is gigantic:  $3 \times 10^{24}$  J per year, or about 10,000 times more than the global population currently consumes. In other words, covering 0.1 % of the Earth's surface with solar cells with an efficiency of 10 % would satisfy our present needs. However enormous technical challenges need to be tackled in order to efficiently use this vast energy reservoir.

Photovoltaics takes advantage of the fact that photons falling on a semiconductor can create electron – hole pairs, and at a junction between two different materials, this effect



can set up an electric potential difference across the interface. So far, the science of solar cells has been dominated by devices in which the junction is between inorganic solid-state materials, usually doped forms of crystalline or amorphous silicon, and profiting from the experience and material availability resulting from the semiconductor industry. Recently, we have seen more use of devices made from compound semiconductors (III / V compounds for high-efficiency aerospace components and copper – indium – sulphide / selenide materials for thin-film, low-cost terrestrial cells). But the dominance of the field by inorganic solid-state junction devices faces new challenges in the coming years.

Indeed recent years have seen increasing awareness of the possible advantages of nanocrystalline and conducting polymer devices, since these are relatively cheap to fabricate, and can be used on flexible substrates, shaped or tinted to suit domestic devices or architectural or decorative styles. It is now even possible to depart completely from the classical solid-state junction device, by replacing the phase in contact with the semiconductor by an electrolyte (liquid, gel or organic solid), thereby forming a photoelectrochemical device. Another advantage in using organic materials lies in the choice of materials. This latter factor is practically unlimited, and specific parts of the solar spectrum can be selectively absorbed.

Although organic cells are still considerably less efficient than single-crystal gallium arsenide or silicon, progress has been impressive over the past few years. In particular, solar cells based on interpenetrating polymer networks,<sup>6</sup> polymer / fullerene blends,<sup>7</sup> and solid-state dye-sensitised devices<sup>8</sup> have shown surprisingly high solar conversion efficiencies, currently reaching values of 2 – 3 %.

### **I.1.3. Carbon Nanotubes: Introduction and Applications**

Until 1985 the only known crystalline forms of carbon were diamond and graphite. A new form of carbon was discovered in 1985 by Kroto, *et al.* when studying small clusters of carbon.<sup>9</sup> A notable stability of particular cluster sizes revealed the ball-like structures of which the football shaped C<sub>60</sub> is the best known example. The new molecules were named fullerenes and macroscopic quantities of pure fullerenes were not available until 1990, when the first successful chemical separation of C<sub>60</sub> was made.<sup>10</sup>

The next important discovery in fullerene science came in 1991, when Iijima discovered thin hollow carbon needles in the cathode deposit of a carbon arc discharge intended for

making fullerenes.<sup>11</sup> It was proven that the structures were not just a single rolled sheet of graphite but actually composed of several seamless cylinders and were later to be known as multi-walled carbon nanotubes (MWNT). Two years later nanotubes consisting of a single graphite layer, single-wall carbon nanotubes (SWNT), were produced.<sup>12,13</sup> High yields of such nanotubes were obtained in 1996,<sup>14</sup> igniting amongst a number of groups the line of research to which the present work belong.

Depending on their precise molecular symmetry, nanotubes can be either semiconducting or metallic. This behaviour, coupled with their nanoscale geometry, makes them ideal candidates for wires, interconnects and even devices for true molecular electronics.

The background for molecular electronics is found in current microelectronics. Indeed, the fabrication of microelectronic devices has gradually moved to feature sizes substantially below a micrometer over the past decade. In research laboratories, submicron electron beam lithography has allowed fabrication of artificial structures with high control of the geometrical design. However, the present exponential reduction of feature sizes with time cannot continue indefinitely using bulk materials and standard lithographic techniques. One possibility is to incorporate ready-made nanostructures such as molecules or self-assembled structures in electronic devices. In the case of molecules, this clearly poses demands to the individual components: the molecules must be stable, have well defined electrical properties and preferentially allow manipulation or have the ability to participate in self-organisation.

Nanotubes are interesting candidates as they are chemically stable and have superb electrical properties. In particular they can act as metallic wires and their strength and extended length makes it relatively straightforward to attach metallic electrodes to them.

This has enabled a number of recent studies of the transport properties of individual nanotubes and ropes (ordered bundles of nanotubes), yielding new information on the detailed behaviour of the electron system in the nanotubes. Progress over the past few years has revealed numerous interesting effects in these molecules: single-electron tunnelling,<sup>15,16</sup> field-effect transistor action,<sup>17</sup> proximity-induced superconductivity,<sup>18,19</sup> spin injection,<sup>20</sup> Aharonov-Bohm effect,<sup>21</sup> to mention a few. However, the road to real molecular electronics applications using nanotubes is not at all clear. Challenges lie in particular in assembling and integrating multiple active parts into functioning circuits.



At present, some of the most promising applications of nanotubes are field emitters in flat panel displays<sup>22</sup> and scanning probe tips.<sup>23</sup> As part of the work in this Thesis, the belief that carbon nanotubes could find another interesting application in improving the efficiency of existing organic displays, such as organic light-emitting diodes and organic solar cells, which have been introduced earlier, is explored. Indeed, while many conjugated polymers can be used as hole-transport materials, polymers that work effectively as electron-transport layers are not so common. Carbon nanotubes can therefore be thought to represent the ideal candidate to tackle this technical issue.

## I.2. Outline of the Thesis

In this Thesis we will present the work carried out in order to study the effect of using carbon nanotubes in two existing types of functional organic devices: organic light emitting diodes and organic solar cells.

Following this introductory Chapter, fundamental properties of conjugated polymers and carbon nanotubes will be reviewed in Chapter II. This will also include the electrical conduction mechanisms and photophysical processes that could occur in conjugated polymers, and the electronic, mechanical and other properties of carbon nanotubes.

Chapter III will outline the experimental procedures employed throughout this Thesis. Three distinct Sections will be attributed to sequentially present the preparation of each material, the preparation of each device and finally the different characterisation techniques used in this work.

Chapter IV will both introduce the basic physical and technical issues concerning organic light-emitting diodes (OLEDs), and show how careful analysis of the device's characteristics of a single layer OLED allowed us to determine the intrinsic electronic parameters one of the main conjugated polymers used throughout this Thesis: poly ( 2,5 – dimethoxy – 1,4 – phenylene – vinylene – 2 – methoxy – 5 ( 2' – ethylhexyloxy ) – 1,4 – phenylene-vinylene (M3EH-PPV).

This will be followed, in Chapter V, by the demonstration of the use of a composite fabricated from carbon nanotubes and poly ( m – phenylene – co – 2,5 – dioctyloxy – p – phenylenevinylene ) (PmPV) as an electron-transport layer in OLEDs. Conductivity of the



nanotube and polymer composite, and analysis of the characteristics of the OLEDs using the nanotube and polymer composite will be discussed.

Chapter VI will outline both physical and technical issues concerning the second type of organic device, which we focused on in this Thesis: organic photovoltaic devices. While we will mainly detail the principles of polymer solar cells, we will also present issues regarding photoelectrochemical cells. Optical filter effect in polymer solar cells and the choice of either electropolymerised or soluble polymers in photoelectrochemical cells will be included.

Chapter VII will show the effects of using nanotube and polymer composites in organic photovoltaic devices. After discussing the photophysical processes occurring in nanotube and polymer bilayers and blends, we will present the analysis of the characteristics of polymer solar cells and photoelectrochemical cells with the nanotube and polymer composite.

Finally, Chapter VIII will conclude this Thesis by reviewing the research presented in the previous Chapters. The implications of this research will also be addressed, and areas for future work will be considered.

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## II.1. Introduction

The fundamental properties of conjugated polymers and carbon nanotubes will be reviewed in this Chapter. While we will present the electrical conduction mechanisms and photophysical processes that could occur in conjugated polymers in Section II.2, we will describe the electronic, mechanical and other properties of carbon nanotubes in Section II.3.

## II.2. Conjugated Polymers

The geometric structure of several common polymers is sketched in Figure II.1, where their monomeric repeat units are indicated.

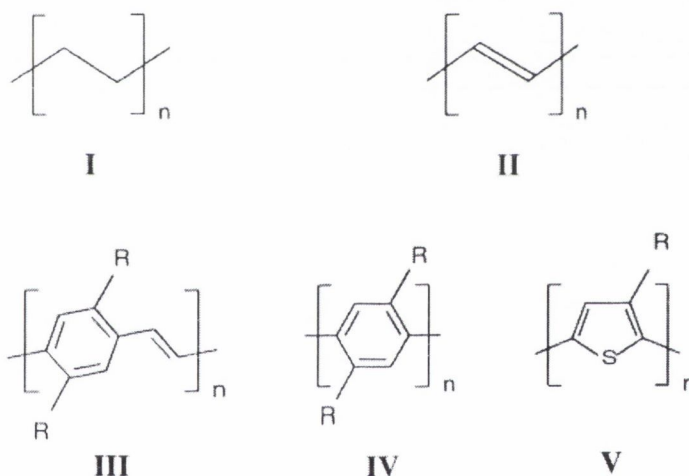


Figure II.1 Structural formulae of several common polymers chains are illustrated. (I) polyethylene, or PE; (II) *trans*-polyacetylene, or PA; (III) poly(*para*-phenylenevinylene), or PPV; (IV) poly(*para*-phenylene), or PPP; and (V) poly(thiophene), or PT. Note that the R groups may be hydrogen atoms, alkyl-chains, or even oxygen containing groups such as methoxy-, ethoxy- or decyloxy-groups.

Since carbon has the electronic structure  $1s^2 2s^2 2p^2$ , carbon atoms can form up to four nearest-neighbour bonds. In  $\sigma$ -bonded polymers, the carbon atoms are  $sp^3$  hybridised, as in polyethylene (PE), polymer I in Figure II.1, and each atom has four  $\sigma$ -bonds. In such non-conjugated polymers, the electronic structure of the chain of atoms which comprises the backbone of the macromolecule consists of only  $\sigma$ -bands (possibly with  $\pi$ -electronic levels localised on side groups as, for example, in polystyrene). The large electron energy band gaps in  $\sigma$ -bonded polymers,  $E_g(\sigma)$ , renders these polymer materials electrically insulating,



and generally non-absorbing to visible light. In polyethylene, for example, the optical band gap is on the order of 8 eV.

In conjugated polymers, however, there exists a continuous network, often a simple chain, of adjacent unsaturated carbon atoms, *i.e.* carbon atoms in the  $sp^2$  (or  $sp$ ) hybridised state. Each of these  $sp^2$  carbon atoms has three  $\sigma$ -bonds, and a remaining  $p_z$  atomic orbital which exhibits  $\pi$ -overlap with the  $p_z$  orbitals of the nearest  $sp^2$  hybridised neighbour. This chain of atoms with  $\pi$ -overlap of the atomic  $p_z$  orbitals leads to the formation of  $\pi$ -states delocalised along the polymer chain. In a system with one-dimensional periodicity, these  $\pi$ -states form the frontier electronic bands, with a  $\pi$ -band gap,  $E_g(\pi) < E_g(\sigma)$ , accounting for optical absorption at lower photon energies. The essential properties of the delocalised  $\pi$ -electron system, which differentiate a typical conjugated polymer from a conventional polymer with  $\sigma$ -bands, are as follows:

- the electronic band gap,  $E_g$ , is relatively small ( $\sim 1 - 4$  eV), leading to low-energy electronic excitations and semiconductor behaviour;
- the polymer chains can be rather easily oxidised or reduced, usually through charge transfer with molecular dopant species;
- carrier mobilities are large enough that high electrical conductivities are realised in the doped (chemically oxidised or reduced) state;
- charge carrying species are not free electrons or holes, but quasi-particles, which may move relatively freely through the material, or at least along uninterrupted polymer chains.

Some of these interesting properties will be discussed in more details in the following Sections.

### II.2.1. Ground State Electronic Structure

Electronic states of conjugated molecules are generally treated using the molecular orbital (MO) method in an approximate way: the Hückel model, the Pariser-Parr-Pople model, various semi-empirical methods, *ab-initio* Hartree-Fock methods, high-level methods including correlation effects, *etc.* On the other hand, in solid-state physics, electron-phonon and electron-electron interactions are important in modelling conjugated polymers. The pure electron-phonon interaction limit corresponds to the Peierls (Hückel) model, and the pure electron-electron interaction limit corresponds to the Hubbard (Pariser-Parr-Pople) model. The Peierls-Hubbard model incorporates both the electron-phonon and electron-electron interactions.<sup>1</sup> Su, Schrieffer, and Heeger<sup>2,3</sup> have used a tight-binding Hamiltonian

with an electron-phonon coupling term for interpreting the physical properties of *trans*-polyacetylene.

This Su-Schrieffer-Heeger model (SSH) corresponds to the Hückel MO method in which structural changes are effectively incorporated by expressing the resonance integrals as a function of bond length. The chains have been modelled as a series of carbon atoms joined by springs with an effective force constant  $k$ . Electron-phonon interactions were incorporated using a nearest neighbour overlap integral. For equally spaced carbon atoms this model predicts a half filled highest energy band. This is what we would expect from a one dimensional system with one unpaired electron per unit cell, *i.e.* a one dimensional metal. This is illustrated schematically in Figure II.2:

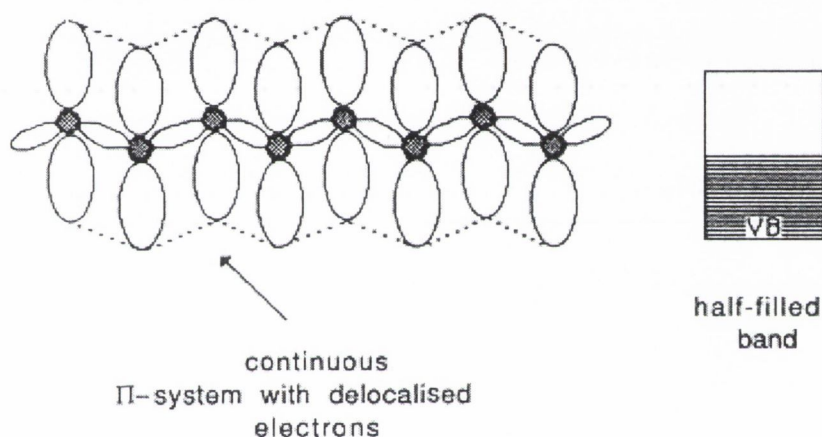


Figure II.2 Unsaturated backbone structure of polyacetylene. The carbon atoms form a zigzag chain with an angle of  $120^\circ$  through  $sp^2$  hybridisation. All  $\sigma$  bonds shown in the figure are in the plane, with one  $\pi$  orbital per carbon atom perpendicular to the plane. Complete delocalisation would result in a one-dimensional metal with a half filled conduction band.

This would in fact be the case if the electronic wavefunctions were completely delocalised along the chain and all carbon atoms equally spaced.

However Peierls model showed that such a one dimensional metal would be unstable. It turns out that for 1-D systems, the chain can lower its energy by introducing bond alternation or dimerisation as depicted in Figure II.3:

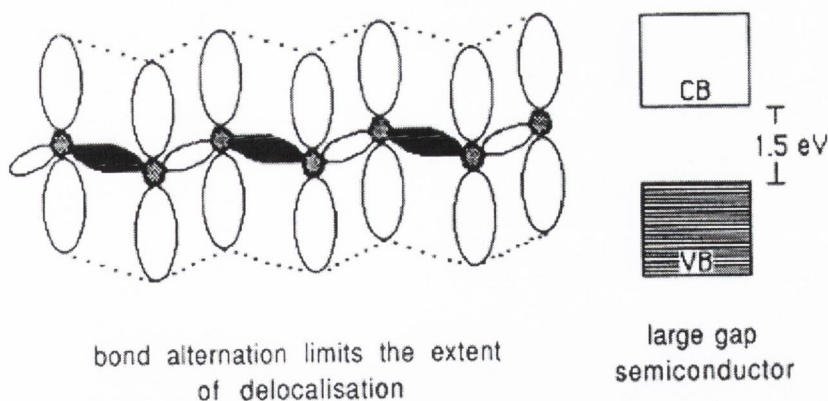


Figure II.3 Alternation of bond lengths along a conjugated polymer chain (estimated to be about 0.01 nm for polyacetylene) results in a material with the properties of a large gap semiconductor.

This alternation of single and double bonds limits the extent of electron delocalisation that can take place along the backbone. For most conjugated polymer chains the maximum extent of delocalisation is over about 15 – 20 multiple bonds.<sup>4,5</sup> Bond alternation is a direct consequence of the strong coupling which exists between the  $\pi$  electrons and the phonon modes of the chain. This is characteristic of many 1-D systems.<sup>6</sup> The driving force for bond alternation is the fact that the decrease in electronic energy is greater than the energy increase due to distortion.

The terms Valence Band (VB) and Conduction Band (CB) used with inorganic semiconductors are commonly replaced by Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO) respectively to best describe the MO character of the electronic structure of conjugated polymers.

Note in Figure II.1 that for polymer II, *trans*-polyacetylene, an interchange of the carbon single and double bonds reproduces the identical ground-state geometry. Thus, *trans*-polyacetylene is termed a degenerate ground-state system. This geometric symmetry has consequences for the nature of the self-localised charge bearing species in *trans*-polyacetylene, which are termed solitons, after the mathematics and wave equations which describe their behaviour.<sup>7,8</sup>

In the remainder of the conjugated polymers shown in the Figure II.1, polymers III, IV, and V, a simple interchange of the carbon single and double bonds does not reproduce the same ground-state geometric configuration, but produces higher-energy geometric configurations.<sup>9-11</sup> Thus, these polymer systems are termed non-degenerate ground-state



systems. This means that there are two ways of arranging the single and double bonds with different energies. In polymers such as polyphenylenevinylene (PPV) these variations are called benzenoid and quinoid and are shown in Figure II.4:

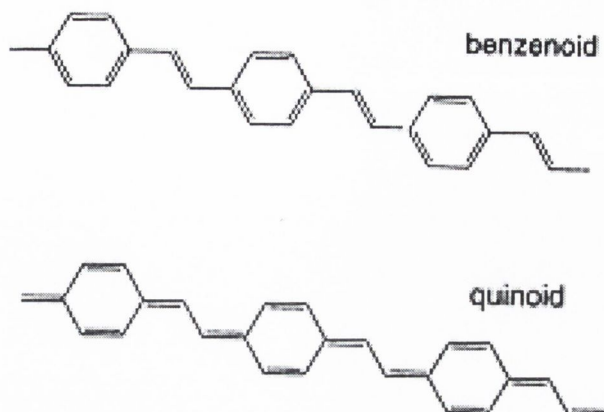


Figure II.4 Benzenoid and quinoid forms of PPV. The quinoid form is of higher energy and is therefore not stable over large lengths of polymer chain.

The aromatic region is lower in energy than the quinoid which will only form in the vicinity of a charge excitation. Unlike polyacetylene, these materials tend to have a relatively large bandgap, up to 3 eV. This is because the bandgap in these materials is not solely due to Peierls distortion. Non-degenerate ground state polymers have a component of dimerisation, independent of Peierls distortion, due to their asymmetry in chemical structure.

This symmetry also has consequences for the type of charge bearing species (and the type of optical excitations) which occur in these polymer chains and this will be discussed in the following Section.

### II.2.2. Excitation species

The intrinsic low-dimensional geometrical nature of polymer chains leads to the existence of unusual charge carrying species. The charge bearing species are not free electrons or holes, but may be any one of several different types of essentially well-defined quasi-particles, each consisting of a coupled charge-lattice deformation entity. The charge bearing species are self-localised, in the sense that the presence of electronic charge leads to local changes in the lattice, which, in turn, leads to localised changes in the electronic structure. These species are generated, for example, through optical absorption in the neutral system, or through charge transfer doping. Associated with these species are localised electronic states with energy levels within the otherwise forbidden electron

energy gap, the so-called gap states.

Electronic energy-level diagrams of self-localised excitations in conjugated polymers are shown in Figure II.5. For polarons, bipolarons, and excitons, two localised electronic levels are formed symmetrically at  $\pm\omega_0$  with respect to the gap centre (Figures II.5b – II.5g) because of electron-hole symmetry. The positions of the localised electronic levels, *i.e.*  $\pm\omega_0$ , depend on the extent of the structural changes associated with the excitations. On the other hand, for solitons one localised electronic level is formed at the gap centre (Figures II.5h – II.5j).

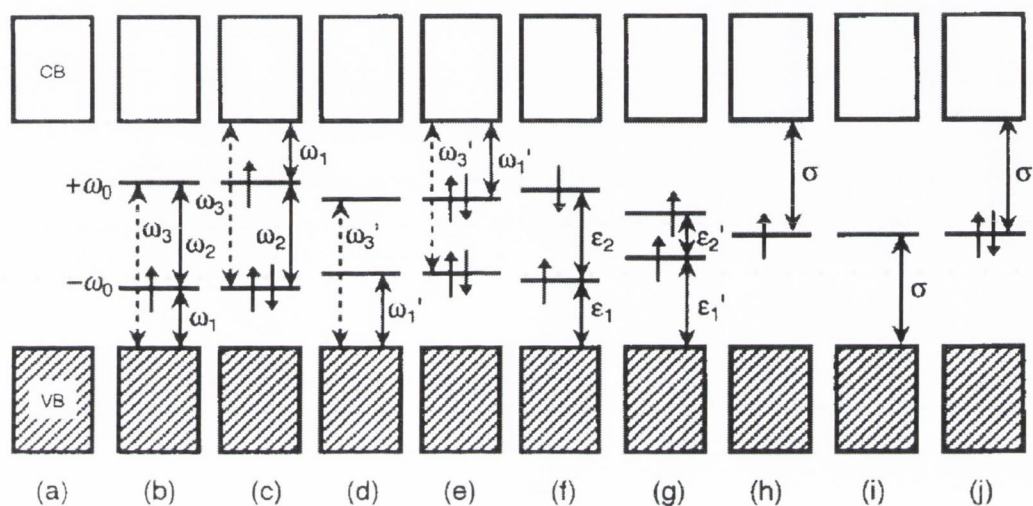


Figure II.5 Electronic energy-level diagrams of self-localised excitations: (a) neutral polymer; (b) positive polaron; (c) negative polaron; (d) positive bipolaron; (e) negative bipolaron; (f) singlet exciton; (g) triplet exciton; (h) neutral soliton; (i) positive soliton; (j) negative soliton.

### II.2.2.1. Polarons

The origin of the term polaron for charged quasi-particles can be found in classical polar crystals where the associated charge *e.g.* the electron repulses adjacent electrons while attracting the nuclei resulting in a polarisation of the lattice in its closer vicinity. Moreover, this accompanying cloud of polarisation causes an increasing effective mass decreasing the mobility of these quasi-particles.

Due to the dimerisation of the bonds, conjugated systems exhibit neither pure covalent nor pure polar bonds. In fact, they represent a separate class with regard to their bond nature exhibiting huge electron-lattice coupling compared to the inorganic solids. This strong electron-lattice coupling is responsible for the existence of the quasi-particles such as polarons and polaron excitons in conjugated systems. These quasi particles can be identified by the additional energy levels<sup>12</sup> associated with them which appear within the



semiconductor bandgap. For a positive polaron and a negative polaron, the two localised electronic levels lead to three intra-gap transitions ( $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  in Figures II.5b and II.5c).

### II.2.2.2. Bipolarons

A bipolaron is the coupling of two charges to the chain. It costs less elastic energy to form one bipolaron than two polarons so bipolarons dominate at high local polaron density. For a positive bipolaron and a negative bipolaron, the two localised electronic levels lead to two intra-gap transitions ( $\omega_1'$  and  $\omega_3'$  in Figures II.5d and II.5e).

### II.2.2.3. Solitons

In the case of *trans*-polyacetylene, it has been established that pairing up of polarons leads to spinless, singly charged solitons that represent the lowest energy eigenstates of the coupled electron (hole) – lattice systems, and are responsible for the unusual electrical, magnetic and linear as well as non-linear optical properties. For a neutral soliton, a positive soliton, and a negative soliton, one localised electronic level leads to a single intra-gap transition ( $\sigma$  in Figures II.5h, II.5i, and II.5j).

### II.2.2.4. Excitons

The polaron-exciton is equivalent to an oppositely charged polaron pair and can be formed by photoluminescence. They can also be formed in a light emitting diode by the recombination of an oppositely charged polaron pair. On recombination the energy is emitted as a photon of light.

The following gives a brief overview of the differences between excitons in inorganic systems as they are much better understood and the organic ones.

#### II.2.2.4.1. Excitons in Inorganic Semiconductors

The binding energy  $E_b$  of inorganic excitons is estimated to be around 16 meV which means that these excitons become important predominantly at lower temperatures (where  $k_B T$  becomes small compared to  $E_b$ ).<sup>13</sup> Unlike its constituent's particles, an inorganic exciton is a Boson rather than a Fermion, with its occupation statistics is determined by the Bose-Einstein equation. These excitons can reduce their energy further if they bind with impurities or defects. Since they are Bosons, all of them can occupy the lowest lying state (at once) giving sharp peaks in the light emitted at low temperatures due to radiative



recombination of the constituent electron and hole. At high densities and low temperatures, the free exciton gas can condense to give an electron-hole liquid phase with interesting properties.<sup>14</sup>

#### II.2.2.4.2. Excitons in Conjugated Polymers

The binding energy  $E_b$  of excitons in organic semiconductors, in particular for conjugated polymers like PPV and its derivatives, has been subject to intense debate over the past decade.  $E_b$  values ranging from very small<sup>15</sup> to intermediate values (around 0.4 eV)<sup>16-18</sup> to very high (up to 0.95 eV)<sup>19</sup> have been proposed. In the following we give a brief description of different types of excitons:

- Frenkel exciton: the electron hole pair is confined to not more than one molecular unit;<sup>20,21</sup>
- Mott-Wannier exciton: the distance between electron and hole is much greater than the spacing between unit cells.<sup>22,23</sup> Their energy levels can be described as hydrogen-like bound states, calculated using a reduced effective mass;
- Charge transfer exciton: the exciton extends over only a few adjacent molecular units.<sup>24</sup>
- Inter-chain exciton: this term is used for polymeric semiconductors to indicate that the constituent charges are located on different polymer chains. It can be regarded as a charge transfer exciton;
- Intra-chain exciton: this term also refers to polymeric semiconductors to indicate that the constituent charges are located on the same polymer chain. It is believed that intra-chain excitons represent the main species that is formed after photoexcitation in conjugated polymers.<sup>25-27</sup>

We note that there is another related excited species, the excimer, that can play an important role in organic semiconductors. An excimer can be understood as a dimer that is only stable in the excited state.<sup>24,28</sup> Hence, it is only weakly absorbing and shows little vibronic structure in its emission spectrum. It can be formed by interaction of an excited molecule with a molecule in its ground state. Both singlet and triplet excimers have been observed in organic molecules such as naphthalenes or perylenes.<sup>28,29</sup> An exciplex is an excimer consisting of two different molecules.

### II.2.3. Photophysical Processes

In this Section, we will describe both luminescence (fluorescence and phosphorescence) and deactivation processes (energy and charge transfer) occurring in conjugated polymers.

### II.2.3.1. Luminescence

#### II.2.3.1.1. Fluorescence

When a photon of light of the appropriate energy interacts with an electron in the ground state, the electron is promoted from the HOMO to the LUMO. This is known as a  $\pi$ - $\pi^*$  transition. The probability of transition between two states is proportional to the overlap of ground and excited state wavefunctions. The energy of an excited state is usually plotted as a function of configuration co-ordinate in a Franck-Condon diagram as shown in Figure II.6. The configuration co-ordinate is a measure of the spatial arrangement of the nuclei on the chain in the region of the excitation.

Under the conditions of excitation the equilibrium position of the nuclei is different from that in the ground state. In the ground state the lowest energy arrangement of the nuclei is the benzenoid while for the excited state it is the quinoid configuration. As electronic transitions occur about 100 times faster than vibrational excitations ( $10^{-15}$  s compared to  $10^{-13}$  s) the nuclei do not have time to change configuration over the time scale of the electronic transition. This is known as a vertical Franck-Condon transition.

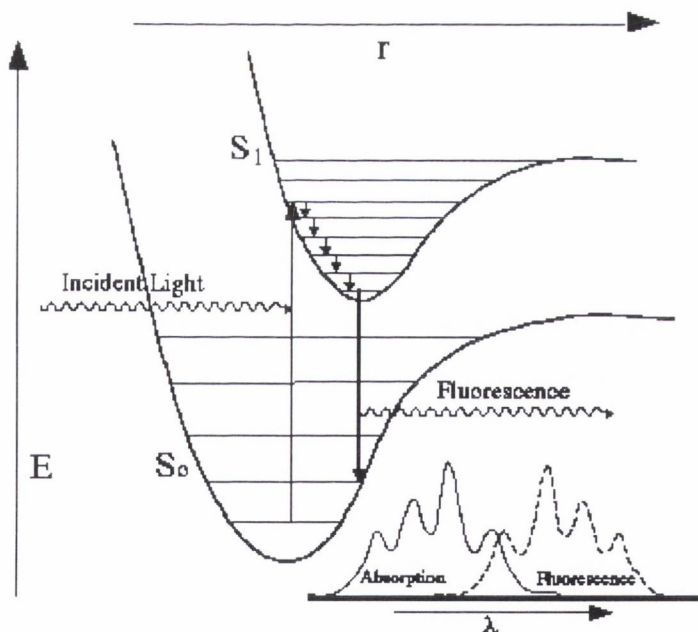


Figure II.6 Mechanism of fluorescence. The initial excitation takes place between states of same multiplicity (singlet states  $S_0$  and  $S_1$ ) and in accord with the Franck-Condon principle.

As the nuclei are now not in an equilibrium position they must vibrationally relax to their lowest energy state. This is possible because the lifetime of a singlet excitation is about 10

times longer than the timescale of vibrational relaxation. On relaxation of the excitation to the ground state the nuclei must once again move into the lowest vibrational state. Hence emission is at a lower energy than absorption. The energy difference is called the Stokes shift.

### II.2.3.1.2. Phosphorescence

Phosphorescence may be defined as the emission occurring due to the radiative transition between two states of different spin multiplicity, for example between  $T_1$  and  $S_0$ . It is generally delayed relative to the exciting radiation, and may persist for several seconds after the exciting source is removed. The mechanism of phosphorescence is shown in Figure II.7:

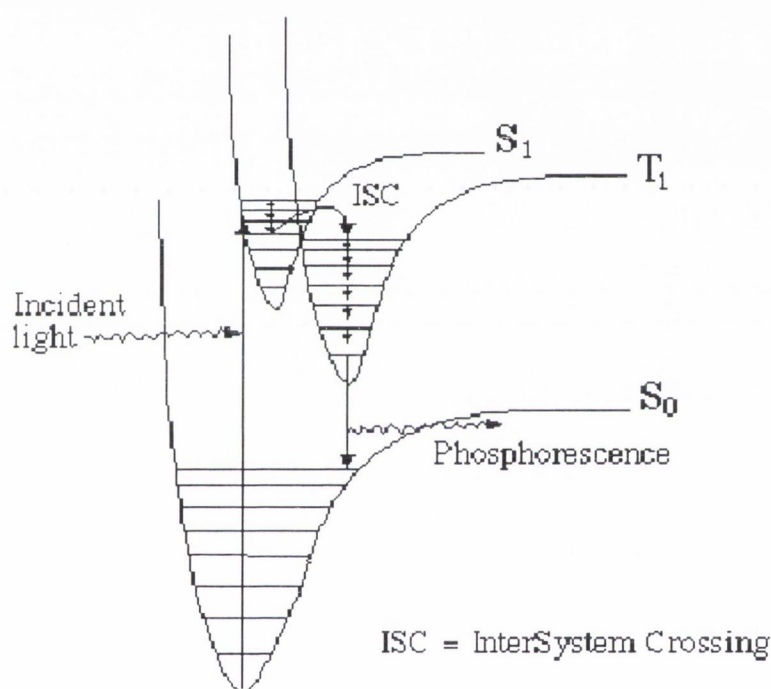


Figure II.7 Mechanism of phosphorescence. Absorption of light raises the molecule to its excited singlet state which intersystem crosses to the triplet state. Non-radiative vibrational relaxation continues to leave the molecule trapped in its lowest excited triplet state before a weak radiative transition returns it to the ground state singlet.

This shows how the incident radiation excites the molecule from the singlet ground state,  $S_0$ , to the excited singlet state,  $S_1$ , as in the initial stages of fluorescence. Radiationless decay occurs until at some point, if a triplet state of a suitable energy is nearby, the molecule may convert, under the influence of spin-orbit coupling, to that triplet state. Following the intersystem crossing process (ISC), radiationless decay continues, but now in the triplet state of the molecule. Once the lowest excited triplet state ( $T_1$ ) is reached the molecule becomes trapped. Continued deactivation now requires a triplet-singlet transition which is spin-forbidden by selection rules. However as the intersystem crossing occurred,



this shows that spin-orbit coupling is sufficient to partially break down the singlet-triplet selection rules, making the transition weakly allowed.

Because the T – S transition is only weakly allowed it becomes a ‘slow’ transition and can therefore persist for up to many seconds after the incident radiation has ceased. Several factors control the occurrence of this phosphorescence:

- it may occur if there is a suitable triplet state in the vicinity of the excited singlet states of the molecule and the spin orbit coupling is sufficient to induce the intersystem crossing;
- heavy atoms such as copper, tin, ruthenium, chlorine and fluorine can enhance intersystem crossing. However, they also increase the rate of non-radiative transitions (internal conversion).

### II.2.3.2. Deactivation Processes

Electronically excited states, once formed, can be deactivated by electronic energy transfer and electron transfer together with other processes including chemical reaction.

#### II.2.3.2.1. Energy transfer

Several different mechanisms of electronic energy transfer are believed to operate under different circumstances.

The first of which is known as the trivial or radiative energy transfer mechanism. It is represented by the process, in which the emission from the decay of the excited donor molecule ( $D^*$ ) to the non-excited donor molecule (D) is re-absorbed by the non-excited acceptor molecule (A) to give the excited acceptor molecule ( $A^*$ ). This process is able to operate over extremely large separation distances providing that the emission spectrum of  $D^*$  and the absorption spectrum of  $A^*$  overlap. The absorption of sunlight by chromophores on Earth is a classic example of radiative energy transfer.

The second mechanism of electronic energy transfer, that of non-radiative energy transfer, requires specific  $D^*$  and A interactions with the energy transfer step being thought to proceed by the formation of a ( $D^*/A$ ) encounter complex. This mechanism is subdivided into short range energy transfer arising from exchange interaction over intermolecular or inter atomic distances, and into long range energy transfer which may arise by sequential short range excitation of many species so that the excitation appears ultimately at a place

distant from the original location of excitation, or interactions between transition dipoles:

- Electron-exchange energy transfer (short range): this mechanism, which is also known as Dexter's mechanism requires a distance of less than 1 nm separation between  $D^*$  and A. During the energy transfer process the excited electron on  $D^*$  is transferred to the LUMO of A, and simultaneously an electron is transferred from the HOMO of A to the lower partially occupied molecular orbital of  $D^*$ . In this type of energy transfer, the donor and acceptor energy gaps must be equal, and the spin multiplicity of the complex, conserved (Wigners Rule). Hence singlet-triplet energy transfer may proceed by this mechanism.
- Coulombic energy transfer (long range): this mechanism, which is also known as the Förster mechanism can occur at intermolecular distances of up to 10 nm and involves the dipole-dipole interaction that can occur when  $D^*$  and A are in close proximity. For  $A^*$  to be formed, certain resonance conditions must be met. That is the energy difference  $\Delta E$  between the ground state donor (D) and the excited state donor ( $D^*$ ) must be equivalent to the energy gap between the acceptor ground state (A) and the acceptor excited state ( $A^*$ ):

$$\Delta E(D^* \rightarrow D) \approx \Delta E(A \rightarrow A^*) \quad \text{Equation II.1}$$

It is important to note that in this process, no change in the spin multiplicity of either of the components is allowed. Although the mechanism is common for singlet – singlet energy transfer where transition dipoles are relatively large, triplet – triplet energy transfer is forbidden by the dipole – dipole mechanism, since the respective transition moments are extremely small.

#### II.2.3.2.2. Electron Transfer

Electron transfer is also a short range process, occurring at similar distances to the short-range electron exchange energy transfer. This mechanism involves an electron 'jumping' from the HOMO of the donor ( $D^*$ ) to a molecular orbital of the acceptor (A), leading to the formation of a radical ion pair, or a charge transfer complex ( $D^+/A^-$ ):



The process of electron transfer is of interest in many different scientific disciplines such as molecular biology (photosynthesis, DNA damage / repair, redox enzymes), synthetic



photochemistry, physics (scanning tunnelling microscopy, semiconductors), supramolecular chemistry (rotaxanes, dendrimers), and display technology (light emitting devices).

### Thermodynamic Considerations

The Gibbs free energy ( $\Delta G_{D^+A^-}$ ) stored in the  $D^+/A^-$  radical ion pair state produced by one electron transfer from D to A can be expressed by Equation II.3:

$$\Delta G_{D^+A^-} = e(E_{ox}(D) - E_{red}(A)) - \frac{e^2}{4\pi\epsilon_0\epsilon_S R_{DA}} \quad \text{Equation II.3}$$

In this expression the first term contains the electrochemical one-electron oxidation potential of D and the reduction potential of A, and thereby gives the ion-pair energy at infinite separation. The last term corrects this for the Coulomb energy gained by bringing the ions together to their actual distance  $R_{DA}$ . Regrettably, this simple expression is often inadequate because reliable electrochemical data can only be obtained in polar solvents such as acetonitrile ( $\epsilon_S = 37.5$ ) while electron transfer reactions often also occur in quite non-polar environments. Weller has proposed<sup>30-32</sup> that corrections for the differences in ion-pair solvation upon transfer from acetonitrile to solvents with a relative dielectric permittivity  $\epsilon_S$ , can be obtained by application of Equation II.4:

$$\Delta G_{D^+A^-} = e(E_{ox}(D) - E_{red}(A)) - \frac{e^2}{4\pi\epsilon_0\epsilon_S R_{DA}} + \frac{e^2}{8\pi\epsilon_0} \left( \frac{1}{r_{D^+}} + \frac{1}{r_{A^-}} \right) \left( \frac{1}{\epsilon_S} - \frac{1}{37.5} \right) \quad \text{Equation II.4}$$

where  $r_{D^+}$  and  $r_{A^-}$  are the effective ionic radii of  $D^+$  and  $A^-$ .

In order for photoinduced charge separation to be thermodynamically feasible the energy of the excited state from which charge separation is intended to occur, must of course exceed  $\Delta G_{D^+A^-}$ . In some electron donor-acceptor compounds or complexes, the lowest energy vertical absorption band corresponds to direct charge transfer (CT-absorption). More commonly, excitation occurs primarily to a singlet excited state of D or A. In the condensed phase rapid internal conversion and vibrational relaxation then occur to populate the lowest vibrational level of the first singlet state ( $E_{S0}$ ) from which charge separation can take place if there is sufficient 'driving force' ( $-\Delta G_{CS}$ ) as can be estimated using Equation II.5:

$$\Delta G_{CS} = \Delta G_{D^+A^-} - E_{S0} \quad \text{Equation II.5}$$

It should be mentioned that in principle charge separation can occur from singlet states, but



also from excited states of D and A with higher multiplicities (in particular from triplet states) as long as  $E_{S0} > G_{D+A\cdot}$ . This is because there is no electron spin restriction to either conversion from a locally excited singlet to a singlet state of the radical ion pair, nor from a locally excited triplet to the radical ion pair triplet state.

### Kinetic Considerations (Marcus Model)

The rates of most electron transfer reactions,  $k$ , like other chemical reactions, can be expressed in terms of an Arrhenius expression<sup>33-36</sup> (Equation II.6) with a pre-exponential factor  $A$  and an exponential temperature dependence, the magnitude of which depends on an activation energy,  $E_a$ .

$$k = Ae^{\left(\frac{-E_a}{k_B T}\right)} \quad \text{Equation II.6}$$

For weak electronic interactions between D and A, it is usually assumed that electron transfer is non-adiabatic, which means that the probability of crossing over from the reactant energy surface to that of the product is limited by the magnitude of the electronic interaction. In that case another possible starting point for a rate expression is Fermi's golden rule<sup>37-39</sup> (Equation II.7), which treats electron transfer as a radiationless transition.

$$k_{ET} = \frac{4\pi^2}{h} V_{DA}^2 \text{FCWD} \quad \text{Equation II.7}$$

The electron transfer rate,  $k_{ET}$ , is given as the product of the electronic term  $V_{DA}$  and a factor depending on the nuclear coordinates, the Franck-Condon weighted density of states (FCWD).  $V_{DA}$  is approximately equal to the resonance energy  $\langle \Psi_{DA} | H | \Psi_{D+A\cdot} \rangle$ , the interaction energy between zero-order wavefunctions. To make a connection with Equation II.6,  $V_{DA}$  is contained in the pre-exponential factor  $A$ . The FCWD is the sum of the products of overlap integrals of the vibrational wavefunctions of the reactant with those of the product and weighted for the Boltzmann population of the vibrational levels. Especially the FCWD factor in Equation II.7 is not easily related to experimentally accessible parameters. We therefore use a theory based on Marcus's classical papers.<sup>40-44</sup> In Marcus's description an activation barrier for electron transfer ( $\Delta G_{ET}^\ddagger$ ) is derived by employing a model in which electron transfer occurs after reorganisation of nuclear coordinates (in reactants and solvent) to a transition state in which the energies of reactants (*i.e.* D / A) and products (*i.e.*  $D^+/A^\cdot$ ) are equal. The activation energy change ( $\Delta G_{ET}^\ddagger$ ) is a function of two main parameters: the free energy change ( $\Delta G_{ET}$ ), and the total nuclear reorganisation energy ( $\lambda$ ), required to accommodate the changing charge distribution. Assuming harmonic

nuclear reorganisation potentials the expression is then Equation II.8:

$$\Delta G^{\#}_{ET} = \frac{(\lambda + \Delta G_{ET})}{4\lambda} \quad \text{Equation II.8}$$

This leads to Equation II.9 for the rate of electron transfer which has a form similar to the Arrhenius equation:

$$k_{ET} = \frac{2}{h} \sqrt{\frac{\pi^3}{\lambda k_B T}} V_{DA}^2 e^{\left(-\frac{\Delta G^{\#}_{ET}}{k_B T}\right)} \quad \text{Equation II.9}$$

Here  $k_B$  is the Boltzmann constant,  $h$  is Planck constant and  $V_{DA}$  is the electronic coupling. This fundamental formula is probably the most important relationship in electron transfer rate theory.<sup>44</sup> In Equation II.8,  $\Delta G_{ET}$  is the Gibbs free energy change between reactants and products (such as  $\Delta G_{CS}$  in Equation II.5 for photoinduced charge separation) and  $\lambda$  is the total nuclear reorganisation energy. The latter may be written as a sum of an internal  $\lambda_i$  (related to nuclear coordinates of the reactants) and an external term  $\lambda_s$  (related to nuclear coordinates in the medium / solvent):

$$\lambda = \lambda_i + \lambda_s \quad \text{Equation II.10}$$

Marcus<sup>42</sup> and Hush<sup>45</sup> used the dielectric continuum description of the solvent and an ion-pair model of the charge separated state to estimate the solvent reorganisation energy  $\lambda_s$ :

$$\lambda_s (\text{eV}) = 14.4 \left( \frac{1}{2r_{D^+}} + \frac{1}{2r_{A^-}} - \frac{1}{R_{DA}} \right) \left( \frac{1}{n^2} - \frac{1}{\epsilon_s} \right) \quad \text{Equation II.11}$$

In Equation II.11,  $r_{D^+}$  and  $r_{A^-}$  are the radii (in Å) of the two ions.  $R_{DA}$  (in Å) is the centre to centre distance between them,  $n^2$  and  $\epsilon_s$  are the optical and static dielectric constants of the solvent, respectively. The consequence of Equation II.8 is that two free energy regions, denoted as 'normal' and 'inverted', respectively, can be distinguished depending on the relative magnitude of  $\Delta G_{ET}$  and  $\lambda$ . In Figure II.8 schematic potential energy curves are depicted for the reactant and the product states that can be involved in an electron transfer reaction such as the photoinduced charge separation  $D^* - A^* \rightarrow D^+ - A^-$ :

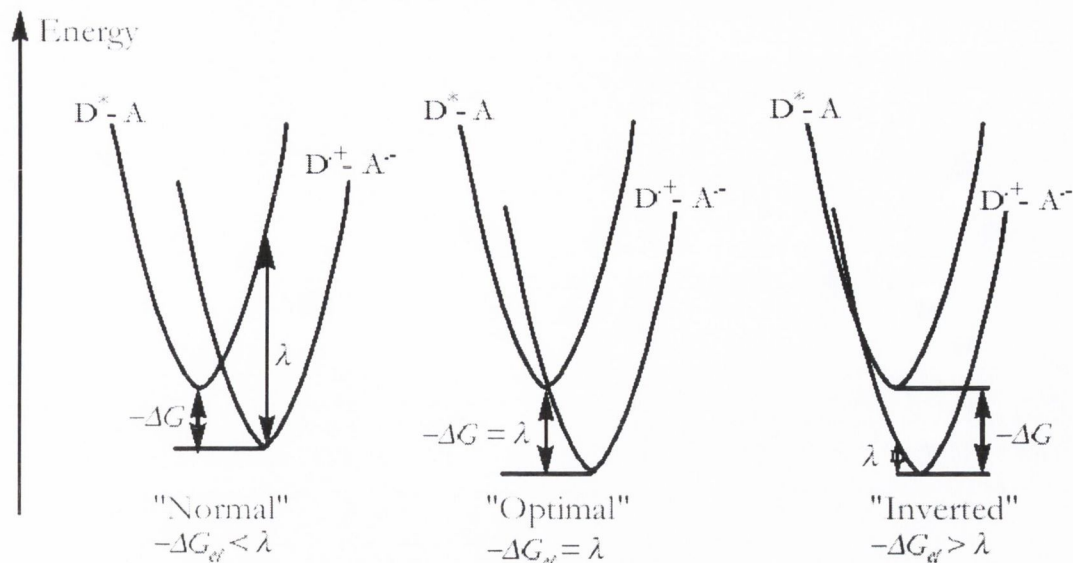


Figure II.8 Schematic, one-dimensional representation of free energy surfaces relevant in the normal region, the special optimal case where  $-\Delta G_{ET} = \lambda$ , and in the inverted region where the free energy change is even greater than the reorganisation energy.

In the 'normal' region the barrier decreases (at constant  $\lambda$ ) if the driving force  $-\Delta G_{ET}$  increases. In the 'optimal' region  $-\Delta G_{ET}$  is equal to  $\lambda$  and then  $\Delta G_{ET}^{\#} = 0$ . In the 'inverted' region  $-\Delta G_{ET}$  is larger than  $\lambda$  and Equation II.9 predicts that  $\Delta G_{ET}^{\#}$  increases as the driving force increases, implying that, contrary to intuition, electron transfer should slow down upon increasing the thermodynamic driving force.

## II.2.4. Electronic Conduction Mechanisms

The electronic conduction mechanisms (metallic – semiconductor transition, hopping, tunnelling processes, *etc.*) occurring in conjugated polymers will now be introduced.

### II.2.4.1. Highly Anisotropic Metallic Conduction

A key feature of polymer conductivity is that it is highly anisotropic, being much greater along the polymer chains. This quasi-1D nature leads to a mechanism that avoids the usual limitation on conductivity due to scattering of carriers by thermally excited lattice vibrations. The basic idea can be understood with reference to the idealised situation depicted in Figure II.9 where the charge carriers are taken to have wavevectors  $k_F$  or  $-k_F$  parallel to the direction of the polymer chains. To scatter these carriers and create resistance, phonons would need to have a wavevector  $2k_F$  spanning the Fermi surface.<sup>46</sup> However, the energy of these phonons is large, so very few are excited at ordinary temperatures and the resistivity is suppressed below that in conventional isotropic metals. In this way, it is expected that such quasi-1D metals could have conductivities much higher



than conventional metals, in which scattering of electrons by phonons limits conductivity to about  $0.6 \times 10^6 \text{ S.cm}^{-1}$  at room temperature even in the best metals such as copper and silver.

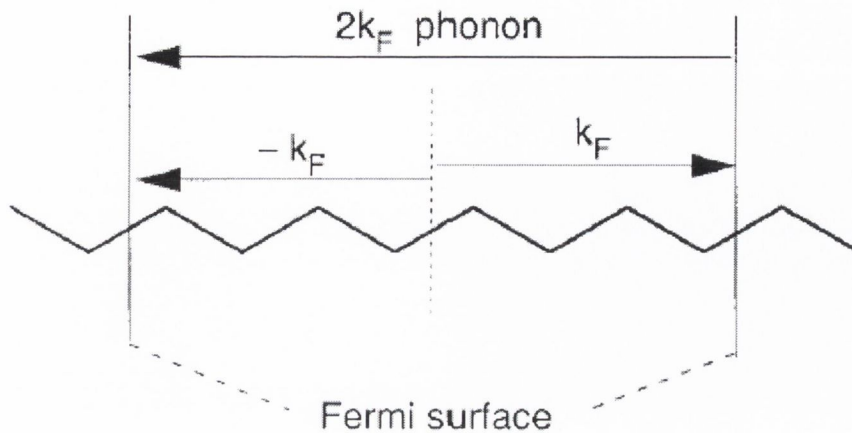


Figure II.9 Sketch showing backscattering along the polymer chain direction by phonons of wavevector  $2k_F$  in a highly anisotropic ('quasi-1D') polymeric metal in which the Fermi surface consists of sheets perpendicular to the chain direction ( $k_F$  is the electronic Fermi wavevector).

For temperatures  $T$  such that  $k_B T$  is much less than the energy  $\hbar\omega_b$  of the backscattering phonons, the resistivity would be expected<sup>46,47</sup> to vary as the number of these phonons thermally excited, *i.e.* the dominant term will be:

$$\rho(T) = \rho_m \exp\left(-\frac{\hbar\omega_b}{k_B T}\right) \quad \text{Equation II.12}$$

with  $\rho_m$  independent of temperature.

This quasi-1D metal resistivity is sketched in Figure II.10, showing its small magnitude at low temperatures and the sharp increase at higher temperatures. For comparison, Figure II.10 also shows the Bloch–Grüneisen resistivity of conventional crystalline metals arising from the scattering of the electrons by phonons: this resistivity increases as  $T^5$  at low temperatures, and linearly in  $T$  at higher temperatures as the number of phonons excited increases as  $T$ .<sup>48</sup> At high temperatures ( $k_B T \geq \hbar\omega_b$ ), this linear Bose excitation law would also apply for quasi-1D metal resistivity. Pietronero<sup>46</sup> suggested an energy of  $\hbar\omega_b \sim 0.2 \text{ eV}$  for the  $2k_F$  backscattering phonons in polyacetylene, leading to a predicted maximum conductivity of  $14 \times 10^6 \text{ S.cm}^{-1}$  at room temperature considering first-order scattering, while Kivelson and Heeger<sup>47</sup> in their treatment used the value  $\hbar\omega_b \sim 0.12 \text{ eV}$  (*i.e.* 1400 K) and obtained a maximum conductivity of  $2 \times 10^6 \text{ S.cm}^{-1}$ . These values are both substantially higher than the largest experimentally observed conductivity of any bulk material at room temperature.

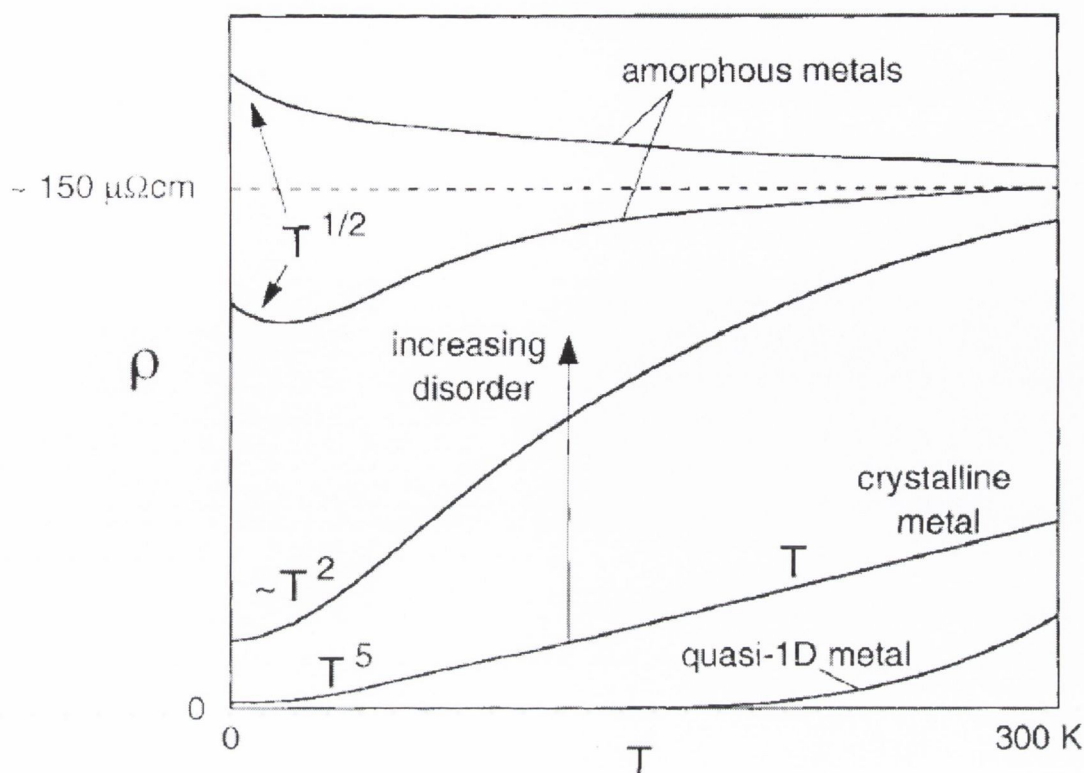


Figure II.10 Sketch of the metallic resistivity temperature dependence expected for highly anisotropic ('quasi-1D') metallic resistivity compared to that for typical crystalline metals (the behaviour of metallic resistivity as disorder increases is also shown).

#### II.2.4.2. Metal – Semiconductor Transition

The evolution of conventional metallic resistivity as disorder is increased is sketched in Figure II.10. As the resistivity increases, its temperature dependence tends to show a saturation effect at higher temperatures and a  $T^2$  power law at lower temperatures.<sup>49</sup> For very highly disordered (amorphous) metals, there is only a small temperature dependence of the resistivity since elastic structural scattering dominates. A striking feature of the resistivity  $\rho$  of amorphous metals is the Mooij correlation:<sup>50</sup>  $\rho$  usually shows a negative temperature coefficient (*i.e.*  $d\rho/dT < 0$ ) when the magnitude of the resistivity is greater than  $150 \mu\Omega\text{cm}$ , as sketched in Figure II.10 (this value applies only for conventional 3D metals with normal carrier densities). This decrease of resistivity as temperature increases arises largely from weak localisation, and signals the approach to a metal – semiconductor transition induced by increasing disorder (the Anderson transition). In addition, there is a characteristic  $T^{1/2}$  upturn in resistivity below about 15 K consistent with electron – electron interactions.<sup>51</sup> Note that samples with reversed temperature dependence but with resistivity extrapolating to finite values in the zero-temperature limit are still regarded as metallic: the transition to a semiconductor occurs where the zero-temperature conductivity becomes



zero, indicating that thermal excitation is needed to permit conduction. Prigodin and Efetov<sup>52</sup> have shown that a network of metallic wires will undergo an Anderson transition from insulator to metal as the localisation length of a single wire and the inter-wire coupling increase; such a model could be applicable to describe a metal – semiconductor transition in fibrillar conducting polymers.

#### II.2.4.3. Hopping in Disordered Semiconductors

For a large variety of disordered materials on the semiconductor side of a metal – semiconductor transition, the conductivity is well described by Mott's law for variable-range hopping.<sup>53</sup> In disordered semiconductors with localised states in the band gap, conduction occurs by hopping (*i.e.* phonon-assisted tunnelling between electronic localised states centred at different positions). As the thermal energy  $k_B T$  decreases with temperature, there are fewer nearby states with accessible energies, so the mean range of hopping increases. This leads to the following expression for the conductivity:<sup>54</sup>

$$\sigma(T) = \sigma_0 \exp\left(-\left(\frac{T_0}{T}\right)^\gamma\right) \quad \text{Equation II.13}$$

For hopping in three dimensions, the exponent has the value  $\gamma = 1/4$ . If the electronic wavefunctions decay with distance  $r$  as  $\exp(-r/L_{loc})$ , where  $L_{loc}$  is the localisation length, the constant  $T_0$  is given approximately by  $k_B T_0 \sim 16/(N(E_F)L_{loc}^3)$ , where  $N(E_F)$  is the density of localised states at the Fermi level. The prefactor  $\sigma_0$  is also temperature dependent, with different authors deriving different power laws,<sup>54</sup> but this temperature dependence is often neglected compared to the stronger temperature dependence of the exponential term. At temperatures sufficiently high such that the hopping is to nearest neighbours, the conductivity would instead show the simple activated form given by Equation II.13 with  $\gamma = 1$ . This form also applies for electron transport by thermal excitation into a conduction band of extended states in a crystalline semiconductor, since in this case the conductivity would be approximately proportional to the number of electrons excited across the semiconductor gap. For 2D hopping  $\gamma = 1/3$ , and for 1D hopping  $\gamma = 1/2$ , although this latter exponent could also arise for 3D hopping when account is taken of electron – electron interactions, according to Efros and Shlovskii.<sup>55</sup> It has been emphasised<sup>56,57</sup> that quasi-1D hopping could play a key role in conducting polymers where polymer chains traverse disordered regions to connect crystalline regions. Charge carriers would diffuse along such electrically isolated disordered chains as part of the conduction path, but would readily localise owing to the 1D nature of the chains. In such a case, quasi-



1D variable-range hopping along the disordered chains with  $\gamma = 1/2$  could dominate the overall resistance of the polymer.

#### II.2.4.4. Tunnelling Between Metallic Regions

According to calculations by Sheng and Klafter<sup>58</sup> and Sheng,<sup>59</sup> if conduction is by electronic tunnelling through non-conducting material separating mesoscopic metallic regions rather than between localised states, the expression for the tunnelling conductivity approximately follows the Equation II.13 with  $\gamma = 1/2$  (*i.e.* the same form as for 1D variable range hopping). Such a picture should be appropriate for a granular metal in which small metallic grains are surrounded by non-conducting shells. These calculations apply when the conductivity is limited by the electrostatic charging energy when an electron is transferred from one island to the next; the inhibition of tunnelling when the thermal energy  $k_B T$  is less than the charging energy is referred to as a Coulomb blockade.<sup>60</sup> If, however, the metallic regions are large enough that the electrostatic charging energy is much smaller than  $k_B T$  for accessible temperatures, tunnelling can occur between metallic states of the same energy on different sides of the barrier without thermal excitation, provided that the wavefunctions overlap. Fluctuations in the voltage across the tunnelling junction can greatly increase the tunnelling current as temperature increases, according to Sheng.<sup>59</sup> The conductivity due to this fluctuation-assisted tunnelling, for a simple parabolic barrier shape and making several assumptions can be written in the simple form:

$$\sigma(T) = \sigma_t(T) \exp\left(-\frac{T_t}{T + T_s}\right) \quad \text{Equation II.14}$$

where the parameter  $T_t$  represents the temperature at which the thermal voltage fluctuations become large enough to raise the energy of electronic states to the top of the barrier, and the ratio  $T_t / T_s$  determines the tunnelling in the absence of fluctuations and so the conductivity  $\sigma(0)$  in the low-temperature limit. The prefactor  $\sigma_t$  is approximated as independent of temperature.

#### II.2.4.5. Conduction in Heterogeneous Polymers

Crystallinity in polymers typically differs from that in low-molecular-weight compounds in that it is only partial: the polymer chains are not aligned with each other over their whole length, but only in small crystallite regions of typical dimensions 10 – 50 nm.<sup>61-63</sup>

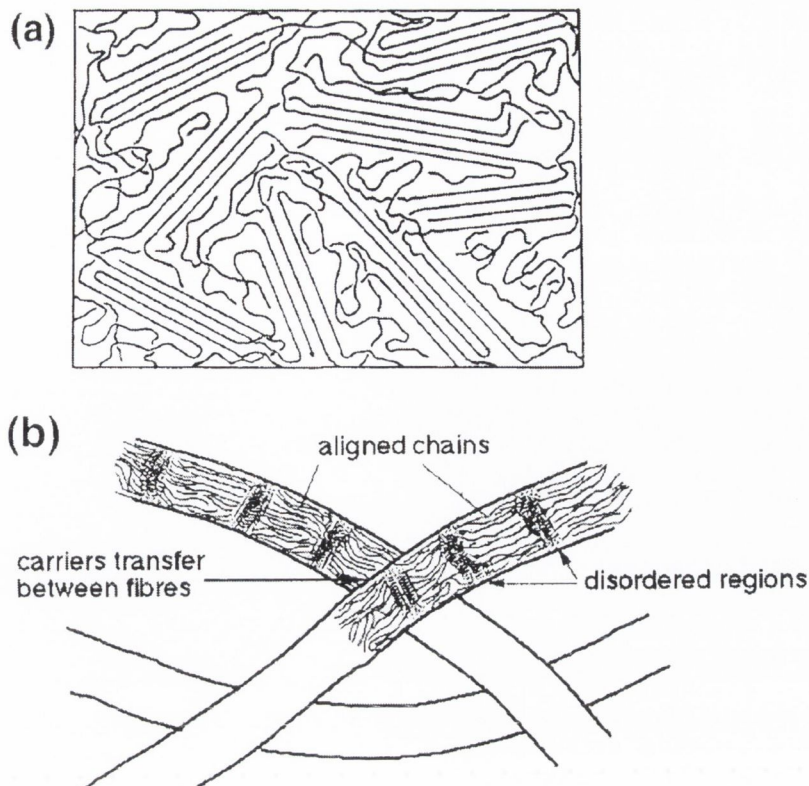


Figure II.11 a) The fringed crystallite model for the crystalline – amorphous structure of polymers  
 b) A sketch of the structure of highly doped fibrillar.

Particular polymer chains may extend through a number of crystallite regions, or they may be folded back on themselves within the crystallite regions; in either case the ordered crystallites are interconnected by amorphous regions, as illustrated in Figure II.11a.

In general, it might be expected that a similar heterogeneity plays a significant role in the conduction process for conducting polymers. If the conductivity of ordered crystalline regions is high, as discussed in Section II.2.4.1, the total resistance of the conducting polymer will be dominated by the disordered regions through which the current must pass. According to x-ray studies, organic conducting polymers also show at most only partial crystallinity.<sup>64</sup> The only exception appears to be polydiacetylene,<sup>65</sup> which can be made from a crystalline precursor material, but this polymer has only a relatively small conductivity. Evidence for the heterogeneous nature of conduction in organic conducting polymers was first pointed out by Park *et al.*<sup>66</sup> soon after their discovery, and further developed by Epstein *et al.*<sup>56</sup> and Travers *et al.*<sup>67</sup> The morphology proposed for fibrillar highly conducting polyacetylene<sup>68</sup> is shown in Figure II.11b. For conduction along fibres of similar type, the expression for the total resistivity  $\rho(T)$  in a heterogeneous model with higher- and lower-conductivity sections in series can be written as:<sup>69</sup>



$$\sigma(T)^{-1} = \rho(T) = \sum_i f_i \rho_i(T) \quad \text{Equation II.15}$$

where the geometric factors  $f_i$  are defined by:

$$f_i = \frac{L_i A}{L A_i} \quad \text{Equation II.16}$$

Here  $L$  and  $A$  are the total effective length and cross-sectional area of the sample,  $L_i$  is the length of the path consisting of material  $i$  with intrinsic resistivity  $\rho_i(T)$ , and  $A_i$  is the effective cross-sectional area for conduction in each region. For example, in the simplest model in which the conduction paths consist of ordered and disordered parts,  $i = 1$  would correspond to the metallic regions, and  $i = 2$  to barrier regions, and the temperature dependence of the geometric factors  $f_i$  can be neglected if the fibres have similar properties. For non-fibrillar polymers, a more complex model is needed for a full analysis, but the conduction for a material such as that in Figure II.11a would have a qualitatively similar temperature dependence to the series heterogeneous model, since the significant conduction paths would all consist of a series combination of higher- and lower-conductivity sections. Note that an effective-medium approximation, in which the heterogeneous material is considered as homogeneous with averaged properties, is not so useful for DC conductivity in the polymers where resistance may depend crucially on the morphology of thin barriers rather than their total volume. This is particularly true for quasi-1D conduction where the possibility of transverse transport to circumvent barriers is limited. A series model is clearly the most appropriate in this case.

For extended metallic regions separated by thin barriers, the overall conductivity is given by Equation II.15 as a combination of quasi-1D metallic conduction (Section II.2.4.1) and fluctuation-assisted tunnelling (Section II.2.4.4) with the appropriate geometric weighting factors  $f_i$ :<sup>70</sup>

$$\sigma(T)^{-1} = \rho(T) = f_1 \rho_m \exp\left(-\frac{T_m}{T}\right) + f_2 \rho_t \exp\left(\frac{T_t}{T + T_s}\right) \quad \text{Equation II.17}$$

Since the tunnelling conductivity increases with temperature while the metallic conductivity decreases, this expression gives rise to a peak in conductivity at a crossover temperature  $T^*$  where the temperature coefficient of the conductivity changes sign from non-metallic to metallic. For smaller metallic regions, we replace the fluctuation-induced tunnelling term by that for tunnelling between mesoscopic islands limited by their charging energies:<sup>71</sup>



$$\sigma(T)^{-1} = \rho(T) = f_1 \rho_m \exp\left(-\frac{T_m}{T}\right) + f_2 \rho_0 \exp\left(\left(\frac{T_0}{T}\right)^{1/2}\right) \quad \text{Equation II.18}$$

This expression is also applicable where conduction through the barrier region is by variable-range hopping, with the same exponent  $\gamma = 1/2$  in the barrier term for quasi-1D hopping, as discussed in Section II.2.5.3. It therefore represents the temperature dependence of the conductivity in the inhomogeneous disorder picture of Epstein *et al.*,<sup>56</sup> which involves quasi-1D hopping along polymer chains connecting crystalline 3D metallic islands, provided that the extent of the metallic regions does not change with temperature. If charges delocalise over larger regions as temperature increases,<sup>72</sup> the coefficients  $f_i$  in Equation II.18 would have a corresponding temperature dependence. The key difference from Equation II.17 is that the conductivity goes to zero in the low-temperature limit as for a disordered semiconductor. Where there are regions on the metallic side of the semiconductor – metal transition in parts of the barrier, a disordered metal term with finite conductivity at zero temperature is appropriate instead of a hopping term; this situation has been modelled by adding a disordered metal term in parallel with the hopping tunnelling term in Equation II.18.<sup>73</sup>

#### II.2.4.6. Electrode and Bulk Limited Conduction Mechanisms

If a semiconductor material is contacted to an electrode whose work function is similar to the HOMO or LUMO of the material itself, carriers can be easily injected from electrode to semiconductor. However, in many cases, conjugated polymers will have a HOMO or LUMO that doesn't match the work function of the electrode, creating a barrier at the semiconductor – metal interface. Moreover, charges in organic materials with low conductivity cannot be quickly dispersed away from the electrode and so a space charge region forms. This in turn modifies the conduction properties of the material and can be described as electrode and bulk limited conduction mechanisms. This will be studied in greater detail in Section IV.3.

### II.2.5. Frequency-dependent Conductivity

In this Section, models for the frequency-dependent conductivity of conjugated polymers will be presented.

#### II.2.5.1. Heterogeneous Model

The presence of low-conductivity barrier regions in the conduction path of heterogeneous

models such as those shown in Figure II.11 means that the AC conductivity will be greater than the DC conductivity, as in the DC case the carriers must travel through the barriers. A simple way to model the capacitive effect of the barriers for the frequency-dependent case is to add a capacitance in parallel with the barrier resistance to the DC heterogeneous model in Section II.2.4.5. Assuming similar barriers, this yields the following expression for the overall complex frequency-dependent conductivity:<sup>74,75</sup>

$$\sigma_c(\omega)^{-1} = f_1 [\sigma_{D1}(\omega)]^{-1} + \left[ \frac{\sigma_2}{f_2} + \frac{i\omega\epsilon}{f_3} \right]^{-1} \quad \text{Equation II.19}$$

where  $\epsilon$  is the permittivity of the capacitive material,  $f_i$  are geometric factors as defined for the DC case in Section II.2.4.5, and  $\sigma_{D1}(\omega)$  is the complex Drude conductivity of the highly conducting part of the polymer, given by the usual expression:<sup>76</sup>

$$\sigma_{D1}(\omega) = \frac{\sigma_1}{1 - i\omega\tau_1} \quad \text{Equation II.20}$$

Here  $\sigma_1$  is the DC conductivity and  $\tau_1$  the scattering time for the highly conducting region. The conductivity  $\sigma_2$  of the disordered barrier regions is taken as having a smaller frequency dependence which is neglected.

### II.2.5.2. Localisation-modified Drude Model

It is also possible to obtain a peak in the conductivity for a homogeneous material if it is very close to the metal – semiconductor transition.<sup>77</sup> In analogy with the weak-localisation expression for the DC case:

$$\frac{\Delta\sigma_1(T)}{\sigma_0} = -\frac{C}{(k_F\Lambda)^2} \left[ 1 - \left( \frac{3\tau}{\tau_{in}} \right)^{1/2} \right] \quad \text{Equation II.21}$$

where  $\Lambda$  and  $\tau$  are the elastic mean free path and relaxation time,  $\tau_{in}$  is the inelastic relaxation time, and  $C$  is a constant which is of order unity, there is a corresponding modification<sup>78</sup> to the frequency-dependent Drude conductivity:

$$\sigma(\omega) = \sigma_D(\omega) \left[ 1 - \frac{C}{(k_F\Lambda)^2} (1 - (3\omega\tau)^{1/2}) \right] \quad \text{Equation II.22}$$

This weak-localisation effect reduces the frequency-dependent conductivity at low frequencies compared to the Drude value  $\sigma_D(\omega)$ , owing to the constructive interference of backscattered waves. In this case, however, the reduction of conductivity is destroyed by the time variation of the applied field as frequency increases, rather than by the increase of inelastic scattering as temperature increases.

## II.3. Carbon Nanotubes

We will now focus on another class of organic materials: carbon nanotubes. We will introduce their structure, electronic and other properties.

### II.3.1. Introduction

Carbon is unique among the elements for the wide range of different structures and forms that it can assume. This variety is in part due to the fact that carbon is stable in  $sp^3$ ,  $sp^2$ , and  $sp$  hybridised forms and partly because it is the only group-four element that can form stable double bonds.

Diamond and graphite are the two well known forms of crystalline carbon. Diamond has four-coordinate  $sp^3$  carbon atoms forming an extended three-dimensional network, whose motif is the chair conformation of cyclohexane. Graphite has three-coordinate  $sp^2$  carbons forming planar sheets, whose motif is the flat six-membered benzene ring. The new carbon allotrope, fullerene, is a closed-cage carbon molecule with three coordinate carbon atoms tiling the spherical or nearly spherical surfaces, the best known example being  $C_{60}$  with a truncated icosahedral structure formed by twelve pentagonal rings and twenty hexagonal rings, as Figure II.12 shows:

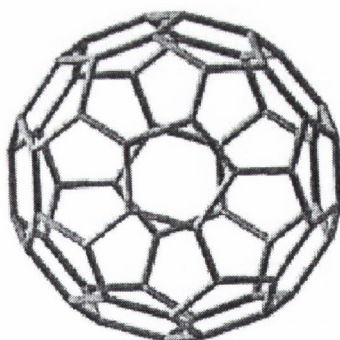


Figure II.12 Schematic image of  $C_{60}$ .

Fullerenes were discovered by Kroto *et al.*<sup>79</sup> in 1985 while investigating the nature of carbon present in interstellar space. The coordination at every carbon atom in fullerenes is not planar but rather slightly pyramidalised, with some  $sp^3$  character present in the essentially  $sp^2$  carbons. The key feature is the presence of five-membered rings which provide the curvature necessary for forming a closed-cage structure.

In 1990, Krätschmer *et al.*<sup>80</sup> found that the soot produced by arcing graphite electrodes



contained  $C_{60}$  and other fullerenes. It was the ability to generate fullerenes in gram-scale quantities in the laboratory, using a relatively simple apparatus that gave rise to intense research activity on these molecules and caused a renaissance in the study of carbon.

Iijima<sup>81</sup> observed in 1991 that nanotubes of graphite were deposited on the negative electrode during the direct-current arcing of graphite for the preparation of fullerenes. These nanotubes are concentric graphitic cylinders closed at either end due to the presence of five-membered rings. Nanotubes can be multi-walled (MWNT) with a central tubule of nanometric diameter surrounded by graphitic layers separated by  $\sim 3.4 \text{ \AA}$  and single-walled (SWNT) with only one tubule. The first transmission electron microscopic (TEM) image of MWNT<sup>81</sup> is shown in Figure II.13:

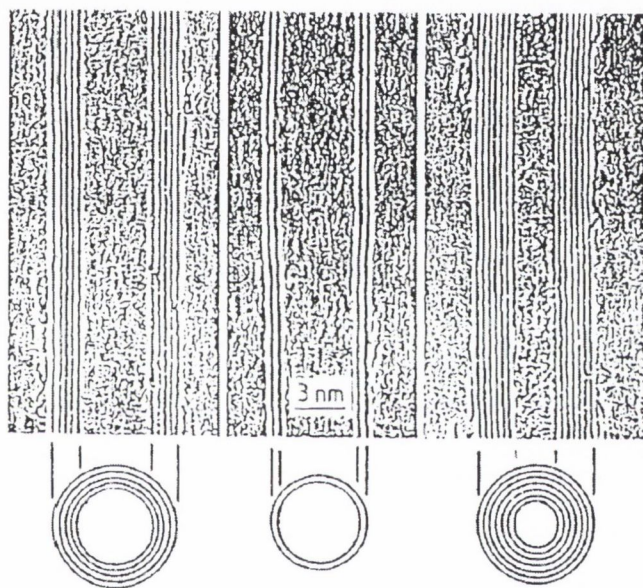


Figure II.13 First transmission micrograph images of carbon nanotubes. The diameter is 67, 55, and 65  $\text{\AA}$  from left to right.

### II.3.2. Structure

In essence carbon nanotubes are made of one or more two dimensional sheets of graphene wrapped around each other in concentric cylinders. In multi-walled nanotubes the walls are separated by a constant spacing of 0.34 nm, which is very close to the basal plane spacing in graphite (0.335 nm).<sup>82,83</sup> They tend to have outer diameters ranging from 2 – 40 nm and lengths up to 100  $\mu\text{m}$ . On the other hand single-walled nanotubes have a very narrow diameter distribution range, varying from 0.7 – 1.7 nm and lengths in excess of several micrometers.<sup>84,85</sup>

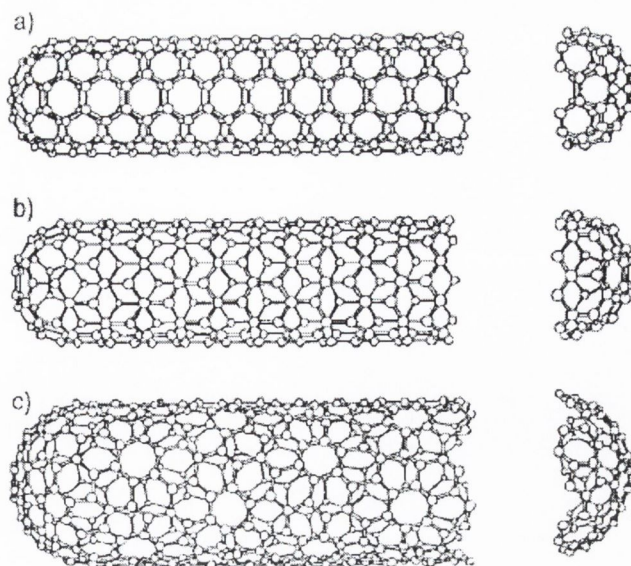


Figure II.14 Models of a) armchair, b) zigzag, and c) chiral nanotubes.

The simplest possible single-walled carbon nanotube can be visualised by cutting the  $C_{60}$  structure across the middle and adding a cylinder of graphite of the same diameter. If  $C_{60}$  is bisected normal to a five-fold axis, an armchair nanotube is formed, and if it is bisected normal to a threefold axis, a zigzag nanotube is formed. Armchair and zigzag nanotubes are achiral. In addition to these, a variety of chiral nanotubes can be formed with the screw axis along the axis of the nanotube. Figure II.14 shows the models of the three types of nanotubes formed by bisecting the  $C_{60}$  molecule and adding a cylinder of graphite.

Nanotubes can be defined by a chiral angle  $\theta$  and a chiral vector  $C_h$ , given by Equation II.23, where  $a_1$  and  $a_2$  are unit vectors in a 2D graphene lattice and  $n$  and  $m$  are integers:

$$\vec{C}_h = n \cdot \vec{a}_1 + m \cdot \vec{a}_2 \quad \text{Equation II.23}$$

The vector  $C_h$  connects two crystallographically equivalent sites on a 2D graphene sheet and the chiral angle is the angle it makes with respect to the zigzag direction, as shown in Figure II.15:



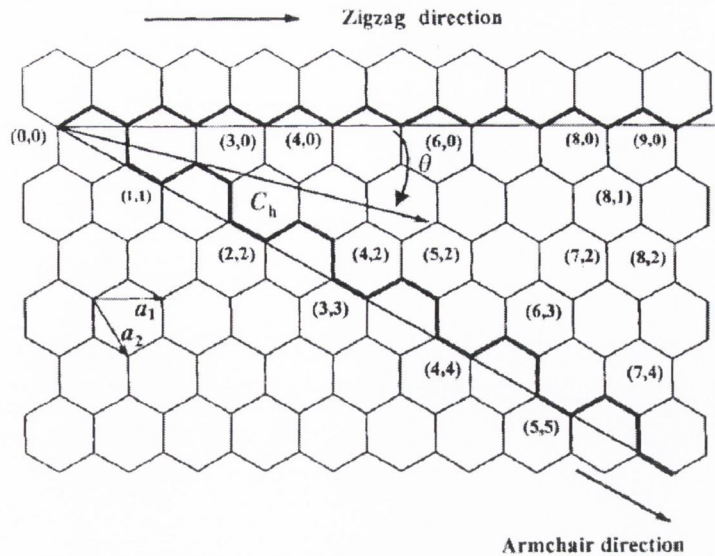


Figure II.15 2D graphene sheet showing chiral vector  $C_h$  and chiral angle  $\theta$ .

A nanotube is formed by rolling up the graphene sheet in such a way that the two points connected by the chiral vector coincide. A number of possible chiral vectors can be specified by Equation II.23 in terms of integer pairs  $(n, m)$ . Many such pairs are shown in Figure II.15 and each pair  $(n, m)$  defines a different way of rolling the graphene sheet to form a carbon nanotube of certain chirality. The limiting cases are  $n \neq 0, m = 0$  (zigzag nanotube), and  $n = m \neq 0$  (armchair nanotube). For a carbon nanotube defined by the index  $(n, m)$ , the diameter  $d$  and the chiral angle  $\theta$  are given by Equations II.24 and II.25 respectively:

$$d = \frac{a\sqrt{m^2 + mn + n^2}}{\pi} \quad \text{Equation II.24}$$

$$\theta = \arctan\left(\frac{-\sqrt{3}m}{2n + m}\right) \quad \text{Equation II.25}$$

where  $a$  is the distance between neighbouring carbon atoms in the flat sheet and  $0 \leq \theta \leq 30^\circ$ .

As mentioned earlier, multi-walled carbon nanotubes consist of capped concentric cylinders separated by  $3.4 \text{ \AA}$ , which is slightly larger than interlayer spacing in graphite. This is because the number of carbon atoms increases as we go from an inner cylinder to an outer cylinder and it is not possible to maintain perfect ABAB... stacking, as in graphite. Thus, an interlayer spacing close to that in turbostratic graphite is observed in MWNT. In addition to pentagons and hexagons, carbon nanotubes can also have heptagons. Pentagons impart a positive curvature whereas heptagons give rise to a negative curvature, to the otherwise flat graphene sheet made of hexagons. Thus, nanotubes with pentagons and



heptagons will have unusual curvatures and shapes. Bent nanotubes arising from the presence of pentagons and heptagons on opposite side of the nanotube have been observed.<sup>86</sup>

### II.3.3. Properties

#### II.3.3.1. Electronic Properties

The electronic structure of carbon nanotubes, in relation to that of graphite and graphitic fibres, is an important aspect. As with the fullerenes, the curvature of the graphitic sheets in the nanotubes would be expected to influence the electronic structure. Calculations show that nanotubes may conduct as well as copper, although a combination of the degree of helicity and the number of six-membered rings per turn around the nanotube can tune the electronic properties into the metal – semiconductor range.<sup>87-89</sup>

The unique properties of carbon nanotubes are primarily due to their quasi-one dimensional nature. This leads to the quantum confinement of electrons normal to the nanotube axis. In the radial direction electrons are confined by the monolayer thickness of the graphene sheet. This leads to periodic boundary conditions around the nanotube circumference. These are known as Born-von Karmen boundary conditions and restrict the allowed electronic states to those that satisfy  $k.C_h = 2\pi q$ , where  $q$  is an integer.

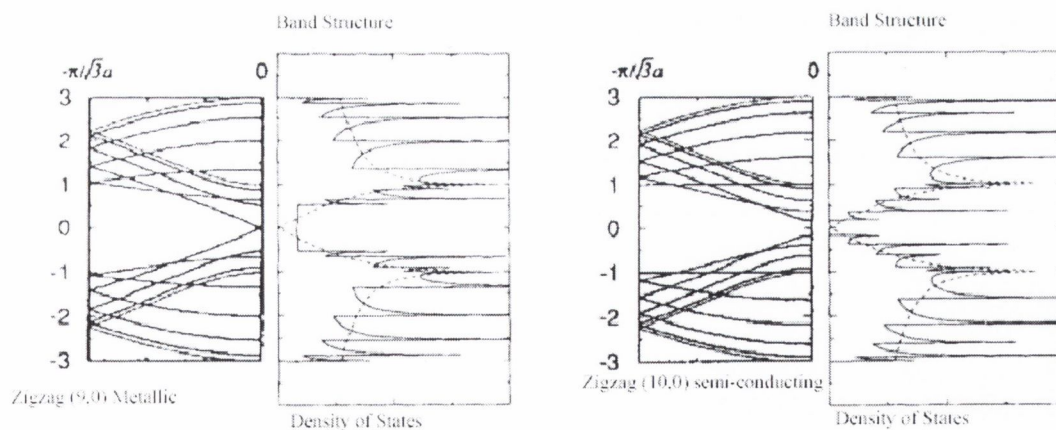


Figure II.16 Band structure and density of state calculations for a metallic nanotube and a semiconducting nanotube with zero bandgap.

Due to quantum confinement, electrons can only propagate along the nanotube axis and so their wavevectors point in that direction. The effective density of states in the one dimensional bands is therefore related to the standing waves which can exist around the

circumference of the nanotube. This is obviously related to the diameter of the nanotube and hence its chirality. These ideas were used by Hamada and Saito<sup>90</sup> to calculate dispersion relations for small diameter single-walled nanotubes. This is shown in Figure II.16.

It shows, as previously noted, that the chirality and diameter strongly influence the band structure and hence the electronic properties. In general an (n,m) nanotube will be metallic if  $n - m = 3p$ , where p is an integer.<sup>91</sup>

Hence all armchair nanotubes are metallic as are one third of zigzag nanotubes. In strict terms only armchair nanotubes (n, n), *i.e.* those with  $p = 0$  in the above equation, are truly metallic, in that they have bands crossing at the Fermi level. For those zigzag nanotubes that satisfy the above equation an infinitesimally small bandgap is induced by the curvature of the hexagonal lattice. As this is much smaller than  $k_B T$  electrons can be excited thermally and these nanotubes act like metals. For nanotubes where  $n - m \neq 3p$  lattice curvature induces a bandgap and so these nanotubes are semiconductors. As this gap is lattice strain induced, it decreases as the diameter, d, increases as the nanotube gets more graphene like. This is described by the Equation II.26:

$$E_{\text{gap}} = \frac{2a\gamma_0}{d} \quad \text{Equation II.26}$$

where  $\gamma_0$  is the C-C tight binding overlap energy.

This has been measured by scanning tunnelling spectroscopy (STS)<sup>92</sup> which gives a value of  $\gamma_0 = 2.7$  eV in good agreement with 2.5 eV for a single graphene sheet.<sup>93</sup>

The density of electronic states (DOS) as a function of energy has been calculated by many groups and shown in Figure II.16. While for a conventional 3-D metal we would expect a smooth density of states here we see a number of singularities. These are known as van Hove singularities and correspond to individual quantum sub-bands. These reflect the one dimensional nature of the nanotube, in that semiconductor theory predicts a DOS at the band edge of the form:  $N(E) \propto 1/E$ , where  $N(E)$  is the density of states. Given that, depending on the diameter, there may be many quantum sub-bands in a given single-walled nanotube we would expect there to be more than one set of singularities in the density of states in that nanotube. This has been seen by various researchers.<sup>94,95</sup> As shown by experiment however, the peaks tend to be of finite height and are broadened<sup>93</sup> relative to



the theoretical prediction.<sup>96</sup> This is attributed to hybridisation between the wavefunctions of the nanotube and the substrate although it may be due to coupling between the quantum sub-bands.

However it must be noted that the electronic properties of multi-walled nanotubes should vary significantly from those of single-walled nanotubes. This is because MWNT are typically composed of both metallic and semiconducting shells so the overall electronic behaviour will depend on how these shells interact. Lambin *et al.*<sup>97</sup> have shown that this interaction depends not only on the various types of nanotubes involved but the relative orientation of one inside the other. Hence we cannot expect the density of states in MWNT to resemble those calculated for pristine SWNT.

Employing ultraviolet photoelectron spectroscopy, Ago *et al.*<sup>98</sup> have obtained the work function of multi-walled nanotubes. While pure MWNT show a lower work function (4.3 eV), the acid-oxidised nanotubes show a higher work function (4.8 eV) due to the disruption of  $\pi$ -conjugation and the introduction of surface dipole moments.

Frank *et al.*<sup>99</sup> have studied quantum transport in the MWNT by attaching the nanotubes with a nanotube fibre and contacting them onto liquid metal to establish electrical contact. A conductance of 77.5  $\mu\text{S}$  ( $= 2e^2/h$ ), which is simply one unit of conductance quantum, was obtained for the MWNT. The charge transport is ballistic even at room temperatures.

One problem with contacting individual nanotubes is the presence of a large contact potential. This gives a contact resistance generally in the region of 1 M $\Omega$ . As shown by Bachtold *et al.*<sup>100</sup> this can be reduced by irradiating the contact area with an electron beam. However whatever the conduction process, for composite applications, contact potential and charging may be important. In composite transport the rate limiting step is probably injection from polymer to nanotube. It is probable that similar barriers exist at the polymer nanotube interface as do at a metal nanotube interface.

### II.3.3.2. Mechanical Properties

Calculations suggest that nanotubes would be exceptionally stiff and strong along their length.<sup>101,102</sup> The aspect ratio of the MWNT prepared by the usual methods is around 50 – 100:1 or even larger and MWNT can therefore be used as reinforcers in composite materials. Surfactant-assisted processing of carbon nanotube polymer composites has been



recently reported.<sup>103</sup> Newer methods, such as plasma-enhanced chemical vapor deposition<sup>104,105</sup> and argon ion irradiation,<sup>106</sup> are being developed that may serve to increase the aspect ratio. SWNT with aspect ratios of the order of 1000:1 or more can be used as reinforcers.

Treacy *et al.*<sup>107</sup> estimated the Young's modulus of individual multi-walled nanotubes to be in the range of a TPa by measuring the amplitude of their intrinsic thermal vibrations in a TEM. Nanoindentation was also used to estimate the Young's modulus of MWNT composites.<sup>108</sup> Falvo *et al.*<sup>109</sup> have used an AFM tip to bend nanotubes to study their strength and flexibility. Since SWNT are made of single-rolled graphene sheets, they would be ideal graphite fibres in terms of elastic properties. The Young's modulus of SWNT has been estimated on the basis of the frequency shifts of stress-sensitive Raman bands.<sup>110</sup> A theoretical estimate for the Young's modulus of closed SWNT is greater than 1 TPa.<sup>111</sup> It must be recalled that even pressures up to 30 GPa do not destroy the basic structure of the nanotubes, as revealed in the Raman spectroscopy studies.<sup>112,113</sup> Krishnan *et al.*<sup>114</sup> estimate the Young's modulus of SWNT to be 1.25 TPa. Zhang and Iijima<sup>115</sup> subjected SWNT bundles to visible light and observed their elastic response in terms of macroscopic movements of the bundles. Mechanical deflections are induced electrically in cantilevered MWNT in a TEM,<sup>116</sup> to resonantly excite the nanotubes to the fundamental frequency or higher harmonics. From the measurement of the elastic bending modulus, the nanotubes were used to calibrate masses of tiny particles, of the order of femtograms, attached to the nanotubes.

### II.3.3.3. Other Properties

Mizel *et al.*<sup>117</sup> studied the low-temperature specific heat of MWNT and SWNT. The specific heat of MWNT agrees well with that of graphite, whereas for the SWNT ropes it exceeds the value for graphite. Using molecular dynamics simulations with accurate carbon potentials, Berber *et al.*<sup>118</sup> predict an unusually high value for the thermal conductivity ( $\lambda = 6600 \text{ W.m}^{-1}\text{.K}^{-1}$ ) of an armchair SWNT. Such high values of  $\lambda$  are associated with large phonon mean free paths, which are otherwise reduced significantly due to interlayer coupling, as in graphite or MWNT.

The third-order optical nonlinear properties of the doped nanotubes have been investigated theoretically by Xie,<sup>119</sup> and the doping-induced change in hyper-polarisability suggest the possible use of doped nanotubes as photonic materials.<sup>120-124</sup> Optical limiting properties of

the carbon nanotubes are considered important for applications involving high power lasers. Optical limiting behaviour of visible nanosecond laser pulses in the SWNT suspensions occurs mainly due to nonlinear scattering.<sup>125</sup>

Nanotube composites with conducting polymers seem to possess novel electrical and optical properties. Yoshino *et al.*<sup>126</sup> observed increased conductivity at relatively low nanotube concentrations in the composites and an enhancement of photoconductivity, to imply possible uses in optoelectronic devices. SWNT-coated molybdenum electrodes appear to be alternatives for gas discharge tubes in advanced telecommunication networks, due to their lower direct-current breakdown voltage and higher reliability.<sup>127</sup>

Electromechanical actuators based on SWNT sheets appear to generate stresses higher than natural muscles and higher strains than the ferroelectric counterparts.<sup>128</sup> This behaviour of nanotubes may be useful in the direct conversion of electrical energy to mechanical energy, relevant to applications in robotics. Wood and Wagner<sup>129</sup> observe a significant shift of the peaks in the Raman spectrum of SWNT upon immersion in liquids; this allows the use of nanotubes as molecular sensors.

Kong *et al.*<sup>130</sup> have measured the sensitivity of the electron transport properties of SWNT to gaseous molecules, such as NO<sub>2</sub> or NH<sub>3</sub>. The nanotubes exhibit faster response and a higher sensitivity than the available solid-state sensors at room temperature. There is also good sensor reversibility.

## II.4. Conclusions

An introduction to the fundamental properties of conjugated polymers and carbon nanotubes was presented in this Chapter. Concepts such as electron transfer or hopping conduction in conjugated polymers and the metallic nature of multi-walled carbon nanotubes were discussed and will be of great importance in the following Chapters.

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### III.1. Introduction

This Chapter will outline the experimental procedures employed throughout this Thesis. In Section III.2, the preparation of each material used in this work will be presented. This will be followed by the description of the devices' preparation in Section III.3. Finally, the different devices' characterisation techniques will be presented in Section III.4.

### III.2. Materials

In this Section, we will present the preparation of both classes of organic materials used in this work: conjugated polymers (PmPV, M3EH-PPV, PVK and polyterthiophene) and multi-walled carbon nanotubes (MWNT).

#### III.2.1. Conjugated Polymers

##### III.2.1.1. PmPV

One of the two main conjugated polymers used in this work is poly(m-phenylene-co-2,5-diethoxy-p-phenylenevinylene) (PmPV). PmPV is a derivative of polyphenylenevinylene and was synthesised in our laboratory. Figure III.1 shows its repeat unit:

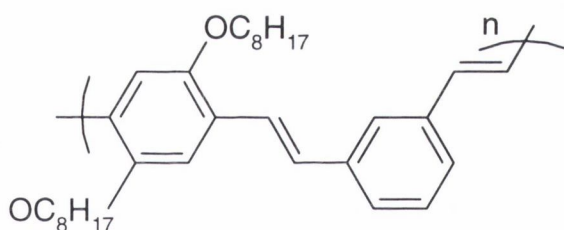


Figure III.1 Repeat unit of poly(m-phenylene-co-2,5-diethoxy- p-phenylenevinylene) (PmPV).

A Horner-Emmons poly-condensation reaction in dry DMF was used as the synthetic route.<sup>1</sup> The starting material is hydroquinone. This material is reacted with potassium hydroxide and bromooctane in a solution of dimethyl sulfoxide (DMSO) to form 1,4 diethoxybenzene. A methyl bromination is performed on 1,4 diethoxybenzene using KBr and *para*-formaldehyde in the presence of acetic and sulphuric acids to produce 1,4-bis (2,5-di-n-octoxy) bromomethyl benzene. This was then heated with triethyl phosphite to form the Horner ester, 1,4-bis (2,5-di-n-octoxy) phenyl diethyl phosphonate. This material is the immediate precursor of the polymer.

The conversion of the precursor to the polymer is done by the Horner-Eammons condensation reaction. The Horner ester is reacted in toluene solution with isophthalaldehyde. This molecule has two CHO groups in the *meta* position. This means that when it reacts with the Horner ester there is still a free CHO group to react with another ester molecule. This can continue until the reaction is quenched to produce a long chain polymer. It should be noted that if the precursor was reacted with *para*-phthalaldehyde the result would be all *para*-PPV.

The introduction of *meta* linkages introduces a steric effect. Energy minimisation calculations for a perfect PmPV chain in which all the vinylene double bonds are in the *trans* position have been carried out.<sup>2</sup> These show that a single PmPV strand tends to form a regular helix, while all *trans*-PPV is a linear molecule. This curvature has been shown to be one of the reasons why there is good interaction with a nanotube. In reality however, there is always some *cis* linkages but Horner PmPV has been characterised as having a very low *cis-trans* ratio.<sup>1</sup>

### III.2.1.2. M3EH-PPV

The second main conjugated polymer, poly(2,5-dimethoxy-1,4-phenylene-vinylene-2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene-vinylene (M3EH-PPV), was used as the emissive layer in OLEDs and active layer in solar cells. Synthesis of this polymer was carried out in Jena and is described elsewhere.<sup>3</sup> Figure III.2 shows its repeat unit:

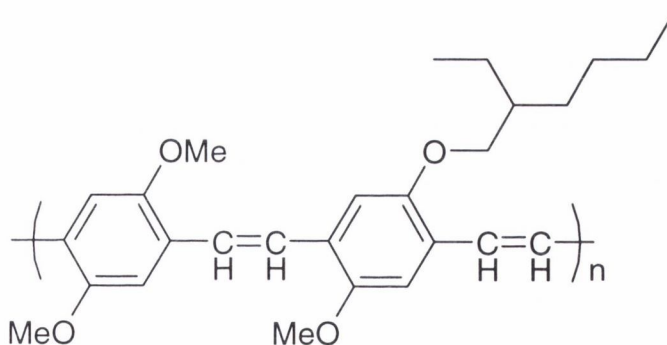


Figure III.2 Repeat unit of poly(2,5-dimethoxy-1,4-phenylene-vinylene-2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene-vinylene (M3EH-PPV).

This polymer, which is a close derivative of poly(2-methoxy,5-ethyl(2'-hexyloxy)-p-phenylene-vinylene) (MEH-PPV), was chosen because of its particularly good emissive properties.



MEH-PPV with a small band gap of around 2.1 eV has a low operating voltage for light emission and exhibits similar mobility properties for both holes and electrons.<sup>4,6</sup> Chlorobenzene was chosen as the solvent.

### III.2.1.3. PVK

In order to stabilise the injection of holes in organic light emitting diodes, poly(9-vinylcarbazole) (PVK) was used. PVK, which was obtained from Sigma Aldrich, was dissolved in dichloromethane. Its repeat unit is shown in Figure III.3:

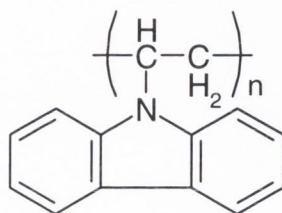


Figure III.3 Repeat unit of poly(9-vinylcarbazole) (PVK).

PVK represents a common hole-transport material because of its high hole mobility.<sup>4,7</sup> Moreover, PVK with a band gap of 3.6 eV is transparent to visible light.

### III.2.1.4. Polyterthiophene

Polyterthiophene, as shown in Figure III.4, was utilised as photoactive layer in photoelectrochemical cells. Such conjugated polymers have been shown to behave as p-type semiconductors in the reduced state, whereas n-type semiconductor behaviour was observed in their oxidised state.

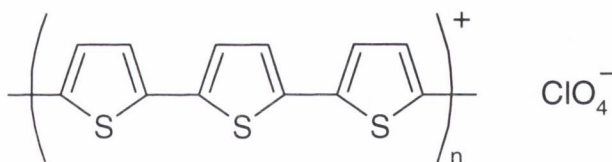


Figure III.4 Repeat unit of polyterthiophene in its reduced state with A<sup>+</sup> counter ion.

Polythiophenes are of particular interest to us as several polymer processing options are available, including simple electrodeposition to produce thin films.<sup>8</sup> In addition the monomer is readily modified by attaching a range of functional groups, including photoactive groups such as porphyrins.<sup>9-11</sup> We used polyterthiophene in photoelectrochemical cells and it was electrochemically grown from the monomer purchased from Sigma Aldrich.

## III.2.2. Multi-walled Carbon Nanotubes (MWNT)

### III.2.2.1. Methods of Preparation

Carbon nanotubes are readily prepared by striking an arc between graphite electrodes in 2 – 3 atm ( $\sim 500$  torr) of helium, considerably higher than the pressure of helium used in the production of fullerene soot. A current of 60 – 100 A across a potential drop of about 25 V gives high yields of carbon nanotubes. The arcing process can be optimised such that the major portion of the carbon anode is deposited on the cathode in the form of carbon nanotubes and graphitic nanoparticles.<sup>12</sup>

Carbon nanotubes have also been produced by using plasma arc jets<sup>13</sup> and, in large quantities, by optimising the quenching process in an arc between a graphite anode and a cooled copper electrode.<sup>14</sup> Studies with scanning tunnelling microscopy (STM) show that the deposition of carbon vapour on cooled substrates of highly oriented pyrolytic graphite gives rise to tube-like structures.<sup>15</sup> Carbon nanotubes are also produced by carrying out electrolysis in molten halide salts with carbon electrodes under an argon atmosphere.<sup>16</sup>

Besides these techniques, carbon nanotubes are produced by the decomposition of hydrocarbons, such as acetylene, under inert conditions around 700 °C over iron/graphite,<sup>17</sup> cobalt/graphite,<sup>18</sup> or iron/silica<sup>19</sup> catalysts. The presence of transition metal particles is essential for the formation of nanotubes by the pyrolysis process and the diameter of the nanotube is determined by the size of the metal particles.<sup>20</sup>

Sen *et al.*<sup>21</sup> prepared carbon nanotubes and metal-filled onion-like structures by the pyrolysis of ferrocene, cobaltocene, and nickelocene under reductive conditions, wherein the precursor acts as a source of the metal as well as carbon. They also showed that the pyrolysis of benzene in the presence of ferrocene or  $\text{Fe}(\text{CO})_5$  gives high yields of nanotubes; the wall thickness of the nanotubes depends on the proportion of the carbon source and the metal precursor.<sup>22</sup>

### III.2.2.2. Arc Discharge Method

The multi-walled carbon nanotubes used in this work were produced in our laboratory by the Krätschmer arc discharge method and used without further treatment.

It is this method that was first developed by Krätschmer *et al.* to produce fullerenes in relatively large quantities.<sup>23</sup> The Krätschmer generator consists of a cylindrical chamber in the region of 300 mm long and 100 mm in diameter. This chamber is water cooled, evacuated and filled with an inert gas. For MWNT this is usually helium but for single-walled nanotubes (SWNT) other gasses such as argon and nitrogen can be used. Enclosed in the chamber are two graphite electrodes, a stationary cathode made of 95 % pure graphite and a 99.99 % pure moveable anode. A high voltage power supply drives a current between the electrodes, which in turn causes a plasma to form. During this process the anode sublimates and the nanotubes are found in the deposit on the cathode.

The optimum conditions for production of pure MWNT differ from those for SWNT and fullerenes and depend on the stability of the plasma, current density, temperature, composition of ambient gas atmosphere, to name but a few of the relevant factors.<sup>12,24,25</sup> Results on optimisation of the technique at our laboratory have recently been published.<sup>26</sup>

The cathode deposit clearly shows two distinct microstructures: a hard outer shell consisting of an inseparable pyrolytic graphite mass and an inner core region which consists of loosely packed columns aligned in the axial direction of the deposit. These columns are made up of straight, stiff, multi-walled nanotubes, closed carbon nanoparticles and turbostratic graphite. These nanotubes tend to have a small inner cavity (1 – 2 nm) and up to one hundred shells, which tends to make them very stiff and straight. A good yield of nanotubes relative to starting material can be between 30 % and 60 %.

### **III.2.3. Carbon Nanotube and Polymer Composites**

#### **III.2.3.1. Introduction**

Carbon nanotubes are insoluble in all common solvents. While they can be dispersed by ultrasonic agitation in solvents such as toluene, ethanol or water they tend to precipitate over the course of a few hours.

Recent work at our laboratory has shown that efficient purification of carbon nanotubes can be achieved through the incorporation of the nanotubes into a polymer matrix to form a polymer nanotube composite. Mixing nanotube powder with a solution of the conjugated polymer, poly(m-phenylene-vinylene-co-2,5-dioctyloxy-p-phenylene-vinylene) (PmPV), results in the selective interaction of PmPV strands and nanotubes. These polymer-coated



nanotubes remain in solution while graphitic impurities sediment out. This impurity material can be removed by decantation yielding a composite solution containing up to 90 % nanotubes.<sup>27</sup>

### III.2.3.2. Preparation

PmPV was added to toluene to form a solution with a concentration of 20 g/l. This solution was placed in a sonic bath before adding the raw MWNT powder from the Krätschmer generator to the solution. This was then ultrasonically agitated using a high power sonic tip for one to two minutes. This tends to break up and disperse the large aggregates present in the nanotube powder. It must be noted that over exposure to high power ultrasound can break up MWNT and thus destroy the sample.

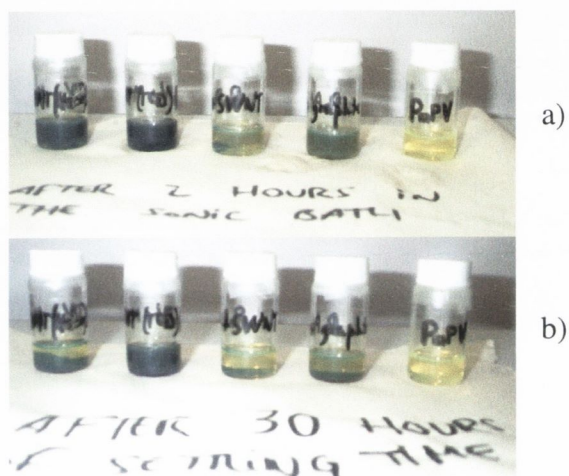


Figure III.5 Samples of composite solutions a) after 2 hours of sonication and b) after 30 hours of settling time. From left to right: catalytically grown MWNT and PmPV composite, arc-discharge MWNT and PmPV composite, arc-discharge SWNT and PmPV composite, graphite and PmPV composite, and PmPV.

For this reason the solution is then transferred to a low power sonic bath and sonicated for one to two hours to completely disperse the nanotubes and break up any smaller aggregates.

As the nanotube powder obtained from the generator contains nanoparticles and large turbostratic graphite flakes in addition to nanotubes it is necessary to allow the solution to settle after sonication. Although transmission electron microscopy shows that organic materials coat all the carbonic material, the large turbostratic flakes tend to fall to the bottom of the solution as a sediment, as shown in Figure III.5. This process occurs in a matter of minutes but in general the settling time was 48 hours to allow all large particles to precipitate.

After settling the top two thirds could be decanted off to yield a composite of organic material, a large amount of nanotubes and very little extraneous carbonic material. At this point the turbostratic flakes are left in the bottom of the original sample bottle.

An extensive number of publications from our group on the subject of composite preparation, characterisation and nanotube purification, which describe the above Section in greater detail, can be found.<sup>27-33</sup>

In order to produce a range of composites with different concentrations of nanotubes the following method was used. The organic material and nanotubes were weighed out in the relevant proportions for the highest nanotube concentration required. This was quantified by dividing the mass of nanotube powder by the mass of the organic powder, and was known as the mass fraction. An estimate of the true mass fraction was then determined using 15 % as the ratio of true mass of nanotubes in solution to mass of raw nanotube powder put in solution.<sup>27</sup> When this solution was fully prepared as described above it can be blended in the appropriate proportions with a solution of the same organic material, of the same molarity to provide given fractions of the original mass fraction. As we blend this with the 0 % solution in given ratios we know how the mass fractions of the range relate to each other.

### **III.3. Device Preparation**

We will now outline the different preparation techniques used to produce the organic light-emitting diodes (OLEDs), polymer solar cells and photoelectrochemical cells tested in this work.

#### **III.3.1. OLEDs and Polymer Solar Cells**

##### **III.3.1.1. Device Architecture**

The organic light emitting diodes (OLEDs) and polymer solar cells were fabricated by spin coating the different polymer solutions onto indium tin oxide (ITO) coated glass substrates and by thermally evaporating six aluminium (Al) electrodes onto the polymer layers. This device architecture is so-called sandwich architecture.

Figure III.6 shows an example of the device architecture of an OLED prepared for this work:

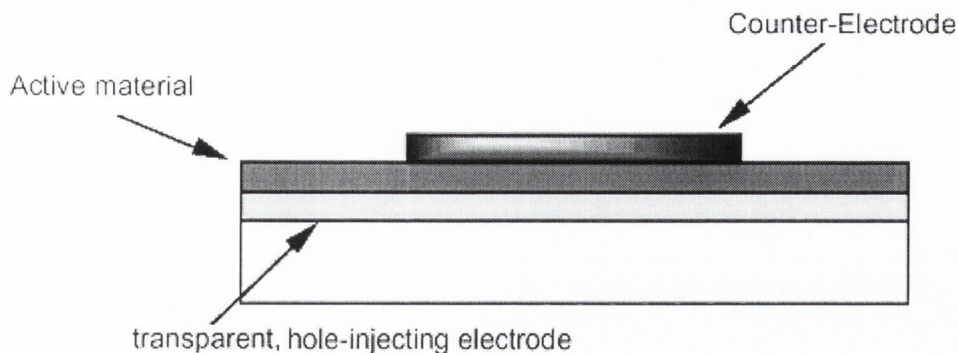


Figure III.6 Side view of the device architecture of the polymer LEDs and solar cells studied in this work.

### III.3.1.2. Indium Tin Oxide Anode

For both solar cells and OLEDs one contact has to be at least partly transparent. Semi transparency can be obtained if the sublimed metal *e.g.* Au is not much thicker than about 15 – 20 nm compared to about 50 – 100 nm which are typical values for non transparent contact. We note that the sheet resistance of such a thin layer can be considerably increased compared to a 50 to 100 nm thick layer and possibly add to the series resistor of the cell significantly. Also the optical properties change considerably in the thickness range from 10 – 20 nm so that devices with slightly different thickness may not be immediately comparable.

For these reasons so called conducting glasses are often used. Particularly Indium Tin Oxide (ITO) which is a degenerated semiconductor comprising a mixture of  $\text{In}_2\text{O}_3$  (90 %) and  $\text{SnO}_2$  (10 %) with a bandgap of 3.7 eV and a Fermi-level between 4.5 and 4.9 eV is widely used. The large bandgap allows no absorption of wavelengths longer than about 350 nm. The material can be highly conducting if there is excess of In due to a lack of oxygen – so that In acts as n-type dopant leading to very low sheet resistances for already only 100 nm thick layers of ITO.

ITO covered quartz substrates are commercially available since they are widely used as conducting glasses in the liquid crystal screen industry. The sheet resistance of these ITO substrates is lower, the thicker the ITO layer is. Typical thickness of ITO in our devices is 100 nm. Values smaller than  $5 \Omega/\square$  are available. The transmission properties of the thicker ITO substrates do not change much since the material does not absorb in the visible but interference effects cause significant spectral dependence of the transmission. Very thick



ITO layers (several 100 nm – microns) are problematic because of the increased absolute surface roughness which can cause shorts in the thin organic films. We note that ITO itself can be used as anti-reflection layer<sup>34</sup> and active semiconductor.<sup>35</sup> The surface can be modified via plasma etching<sup>36,37</sup> or the semiconducting molecules can even be chemically attached to it.<sup>38</sup>

Other conducting glasses are Tin oxide and Indium oxide. Alternatively, conjugated polymers with absorption in the whole visible range can be used if they are doped so that the allowed energy levels move deep into the bandgap and create an absorption minimum in the visible region. Example for such polymers are poly(3,4-ethlenedioxythiophene) (PEDOT)<sup>39,40</sup> and poly(isothianaphtenes) (PITN).<sup>41-43</sup> An additional advantage of PEDOT is that it can be processed from (water) solution and therefore easily be spin-coated. Moreover, other water-insoluble materials may be spun on top of it.

ITO coated glass substrates were used in this work. The 12 mm × 12 mm pieces of ITO coated glass substrate were cleaned in a surfactant, Decon 90, to remove any grease. They were then washed in deionised water and sonicated in acetone. After rinsing with acetone and isopropanol they were dried by blowing hot air across them. An etching procedure was then followed in order to obtain a strip of ITO onto the glass substrate. This was to isolate each of the six devices prepared on one glass substrate. Indeed, the overlap between the top metal electrode, which will be described below, and the ITO represented the active area of each device (approximately 0.06 cm<sup>2</sup>), as shown in Figure III.7:

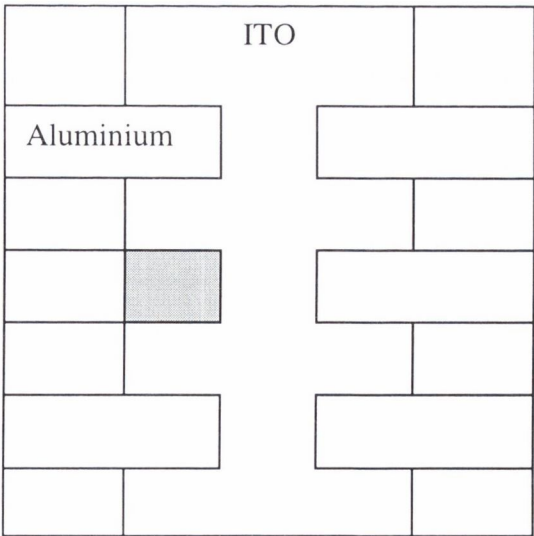


Figure III.7 Top view of the device architecture of the polymer LEDs and solar cells studied in this work. The grey area represents the device active area: 0.06 cm<sup>2</sup>.

### III.3.1.3. Organic Film Preparation

There are several methods for producing organic films: spin coating, drop casting, thermal evaporation, *etc.*

Spin coating tends to give the best results in terms of film homogeneity and was preferably used. The spin coater used was a Convac 1001. In order to ensure clean, particle free films all spin coating was performed in a laminar flow cabinet. The substrate is held in place on the chuck by a rotary vacuum, while a uniform film of solution is pipetted onto the whole of the substrate surface. The substrate can then be rotated at frequencies between 200 and 10,000 rpm depending on the required film thickness. The thickness can then be estimated from the following Equation III.1:<sup>44</sup>

$$t \propto f(C)\omega^{-a}$$

Equation III.1

where  $t$  is the film thickness,  $f(C)$  is a function of the concentration,  $\omega$  is the spin speed and  $a$  is a constant approximately equal to one half.

The film thicknesses were measured by Dektak surface profilometry. Figure III.8 shows the thickness of M3EH-PPV films at two different concentrations as a function of the spin speed.

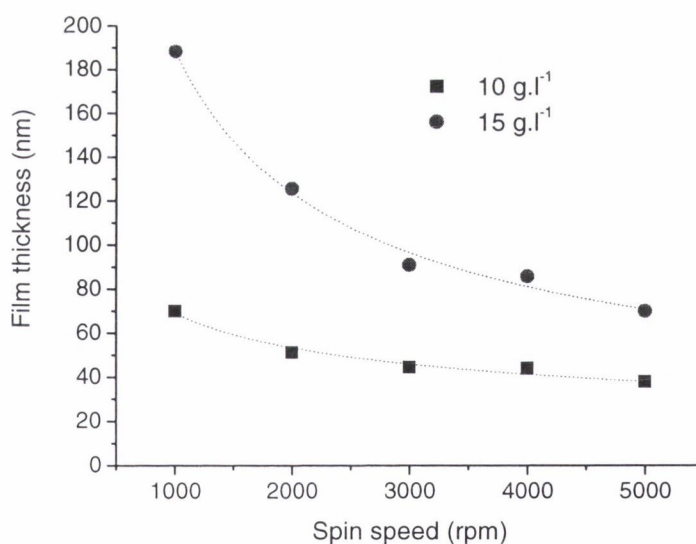


Figure III.8 M3EH-PPV film thickness as a function of spin coating speed for two different concentrations.

Note that, while solvent choice for the organic solutions was motivated by the desire to avoid film mixing at the interface between the different layers, this was not always possible.

In fact, although chlorobenzene was used to dissolve M3EH-PPV, PmPV and M3EH-PPV share a common solvent, toluene. Some mixing at this interface was therefore unavoidable when spin coating the nanotube and polymer composite film onto the M3EH-PPV layer, for example.

#### III.3.1.4. Aluminium Cathode Preparation

The top aluminium (Al) cathode was finally thermally evaporated onto the organic films. The electrode thickness was between 50 to 100 nm.

Thin (20 nm) semi-transparent Al electrodes were also prepared in order to perform device characterisations through this electrode.

#### III.3.2. Photoelectrochemical Cells

Photoelectrochemical cells, as shown in Figure III.9, consisted of a polyterthiophene polymer film electrochemically grown onto the ITO glass (as the anode) and a counter electrode of platinum (Pt) coated ITO coated glass with a liquid electrolyte containing an  $I^3/I^-$  redox couple sandwiched between them.

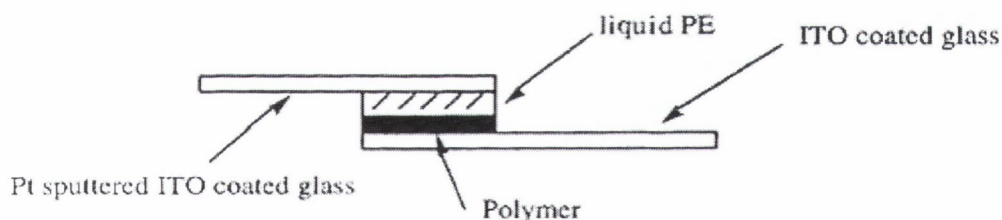


Figure III.9 Electrochemical cells tested in this work.

Cyclic Voltammetry growth of polythiophene was performed using a PAR 363 Potentiostat / Galvanostat connected to a Macintosh computer via a MacLab/400 (AD Instruments) with EChem v 1.3.2 software (AD Instruments).

Iodine (60 mM) and tetrapropylammonium iodide (500 mM) were dissolved in a 1:1 ratio by weight ratio mixture of propylene carbonate and ethylene carbonate in order to prepare the liquid electrolyte.

The platinum electrode was sputter coated onto the glass using a Dynavac Magnetron



Sputter Coater (model SC 100MS). The sputtering current was 50 mA under argon pressure of  $2 \times 10^{-3}$  mbar. The platinum layer deposited was 10 Å thick. To avoid short circuiting between the two electrodes and to retain the liquid electrolyte, thin strips of parafilm were placed around the edges of the copolymer to form a gasket. The device was assembled and held together by two clips, ensuring that there were no air bubbles trapped in the device.

### III.4. Characterisation Techniques

In this Section, the several devices' characterisation techniques (DC and AC conductivity, impedance and optical spectroscopy, I(V)s) will be presented.

#### III.4.1. Electrical Conductivity

##### III.4.1.1. DC Conductivity

To measure DC conductivities, a sandwich structure was adopted with one organic film sandwiched between two electrodes. This configuration was shown schematically in Figure III.6. Two main differences are to be noted however between the device configuration and the conductivity measurements. For conductivity measurements:

- Anode and cathode were metals of approximately same work function in order to investigate one charge carrier at a time: thermally evaporated Al electrodes for electrons, and ITO anode with a sputtered Pt cathode for holes;
- Only one organic film is deposited between the anode and the cathode.

The sample DC conductance ( $G_{DC}$ ) is related to the sample DC conductivity ( $\sigma_{DC}$ ) and the sample geometry by the equation:

$$G_{DC} = \frac{\sigma_{DC} A}{d} = \left( \frac{I_{DC}}{V_{DC}} \right)_0 \quad \text{Equation III.2}$$

where  $A$  is the electrode area,  $d$  is the film thickness.  $I_{DC}$  and  $V_{DC}$  are the measured DC current and applied DC voltage around 0 respectively.

The devices were tested in a vacuum chamber (using a rotary pump, pressure of  $10^{-1}$  mbar). Contact was made to the electrodes using pressure probes and conductive silver paint. Currents and voltages were measured using a Keithley Model 2400 sourcemeter, controlled by a Visual Basic program.

### III.4.1.2. AC Conductivity

#### III.4.1.2.1. Definitions

In AC measurements, the same device configuration as in DC measurements was used. A voltage that is a superposition of a DC voltage and an AC component  $v$  is applied to the sample:

$$V_{AC} = V_{DC} + v \cdot \sin(\omega t) \quad \text{Equation III.3}$$

The resulting current can also be decomposed in a DC and an AC part:

$$I_{AC} = I_{DC} + i \cdot \sin(\omega t + \phi) \quad \text{Equation III.4}$$

$I_{DC}$  is the current of the previous Section. The AC current,  $i$ , can easily be calculated if we assume that the AC voltage  $v$  is small. In that case, the current is proportional to the derivative of the DC current  $I(V)$  times the AC voltage.

The admittance ( $Y$ ) is defined as the ratio of AC current and AC voltage:

$$Y = \frac{i}{v} = \frac{\partial I_{AC}}{\partial V_{AC}} \quad \text{Equation III.5}$$

and therefore can be expressed by a complex number:

$$Y = \text{Re}(Y) + i \text{Im}(Y) \quad \text{Equation III.6}$$

The conductance of the sample is then defined as:

$$G_{AC} = \text{Re}(Y) \quad \text{Equation III.7}$$

In general  $G_{AC}$  depends on the applied bias ( $V_{DC}$ ) as well as the frequency ( $\omega$ ).

The AC conductivity of the sample is defined, as previously, as:

$$\sigma_{AC} = \frac{G_{AC} d}{A} \quad \text{Equation III.8}$$

In some cases the conductance is also expressed in terms of loss  $L_{AC}$ :

$$L_{AC} = \frac{G_{AC}}{\omega} \quad \text{Equation III.9}$$

The capacitance of the sample is defined as:

$$C_{AC} = \frac{\text{Im}(Y)}{\omega} \quad \text{Equation III.10}$$

We can also define the loss-tangent  $\tan \delta$ :

$$\tan \delta = \frac{G_{AC}}{\omega C_{AC}} \quad \text{Equation III.11}$$

The name loss-tangent stems from the fact that in a phase plot, the lossy current, comprised of  $\omega C_{AC}$  and  $G_{AC}$ , makes an angle  $\delta = \tan^{-1}(G_{AC}/\omega C_{AC})$  with the capacitance axis. For the simple model, the loss tangent shows no features in the spectra ( $\tan\delta$  vs. frequency) and is flat ( $\sim 1/\omega$ ). Deep states however can produce peaks in the spectra.

Finally, in some cases it is more convenient to deal with impedance ( $Z$ ) values, which can be defined as the inverse of the admittance:

$$Z = \frac{V}{I} = \frac{\partial V_{AC}}{\partial I_{AC}} \quad \text{Equation III.12}$$

and therefore:

$$Z = \text{Re}(Z) + i \text{Im}(Z) \quad \text{Equation III.13}$$

The complex modulus, defined as:

$$M = i\omega Z \quad \text{Equation III.14}$$

is then often used in impedance spectroscopy, since the  $\text{Im}(M)$  vs.  $\text{Re}(M)$  plots (so called Cole-Cole plots) show the number of regions present in the sample, as this will be described in the next Section for the admittance spectroscopy.

#### III.4.1.2.2. Admittance Spectroscopy

Values of the measured capacitance and conductance depend on the probing frequency. Very often, the data can be described very well with equivalent circuits. The advantage of them is that a lot of things can be described in this way, but the disadvantage is that the physical meaning of the found parameters is often difficult to interpret. One example of an equivalent circuit (Figure III.10) that is very illustrative and that still has a strong link with the actual physical structure of the device is the following:

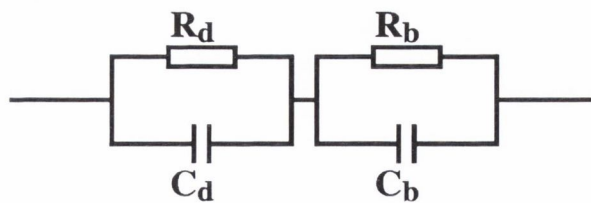


Figure III.10 Equivalent circuit of the device, consisting of a bulk part (denoted with b) with its capacitance and resistance placed in series with the interface part (denoted with d).

Such a model for both a bulk and a depleted region in a device seems a very reasonable assumption. Even in such a simple circuit, the measured capacitance and conductance follow complicated equations. Even if we take the elements in the circuit to be frequency



independent, the measured capacitance ( $C_{AC}$ ) and conductance ( $G_{AC}$ ) are not:

$$C_{AC} = \frac{R_d^2 C_d + R_b^2 C_b + \omega^2 R_d^2 R_b^2 C_d C_b (C_d + C_b)}{(R_d + R_b)^2 + \omega^2 R_d^2 R_b^2 (C_d + C_b)^2}$$

Equation III.15

$$G_{AC} = \frac{R_d + R_b + \omega^2 R_d R_b (R_d C_d^2 + R_b C_b^2)}{(R_d + R_b)^2 + \omega^2 R_d^2 R_b^2 (C_d + C_b)^2}$$

Equation III.16

Under the approximations  $R_b \ll R_d$  and  $\omega R_b R_d C_d^2 \gg 1$  the loss tangent reduces to:

$$\tan \delta = \frac{\omega C_d R_b}{1 + (\omega R_b)^2 (C_d + C_b) C_b}$$

Equation III.17

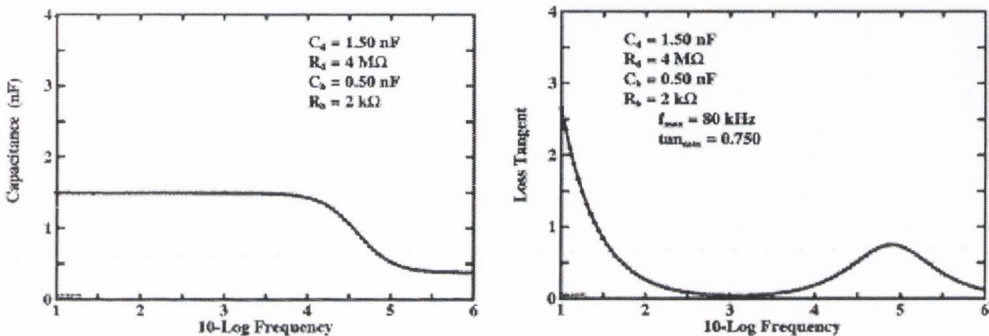


Figure III.11 Simulation of the capacitance (left) and loss tangent (right) as a function of the probing frequency  $f (= \omega/2\pi)$ .

Figure III.11 shows that for low frequencies the capacitance flattens out and saturates at the interface value  $C_d$  (assuming this is the larger of the two), while for higher frequencies it reaches the bulk value. This bulk value is in fact the so-called geometrical capacitance  $C_{geo}$  which is the capacitance of the parallel plates with area  $A$  at mutual distance  $d$  filled with a dielectric medium  $\epsilon$ .

Table III.1 Values of the capacitance ( $C_{AC}$ ), conductance ( $G_{AC}$ ) and loss tangent ( $\tan\delta$ ) at three important values of used frequency.

| Parameters   | $\omega = 0$         | $\omega \rightarrow \infty$ | $\omega = \omega_{max}$       |
|--------------|----------------------|-----------------------------|-------------------------------|
| $C_{AC}$     | $C_d$                | $C_b$                       | -                             |
| $G_{AC}$     | $G_d = 1/R_d$        | $G_b = 1/R_b$               | -                             |
| $\tan\delta$ | $1 / \omega R_d C_d$ | $1 / \omega R_b C_b$        | $C_d / 2(C_b(C_d+C_b))^{1/2}$ |

Admittance data are often presented in the form of so-called Cole-Cole plots. In that case the loss versus the capacitance is plotted as depicted in Figure III.12:

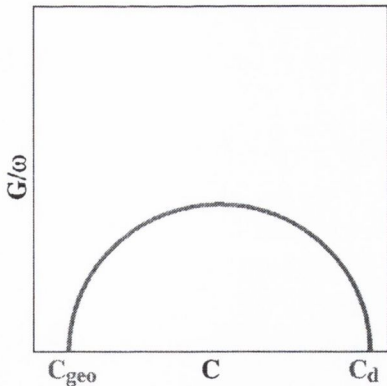


Figure III.12 Example of Cole-Cole plot of admittance data.

For systems as described above it can be shown that the Cole-Cole plot is a semicircle (with the centre on the horizontal axis) and meeting the horizontal axis at  $C = C_{\text{geo}}$  and  $C = C_d$ . If the dimensions of the device,  $A$  and  $d$ , are known, the relative permittivity  $\epsilon_r$  of the material can be calculated:

$$\epsilon_r = \frac{dC_{\text{geo}}}{\epsilon_0 A}$$

Equation III.18

In the figures of the loss-tangent we see a local maximum somewhere at a frequency:

$$\omega_{\text{max}} = \frac{1}{R_b} \sqrt{\frac{1}{C_b(C_d + C_b)}}$$

Equation III.19

The equivalent circuit can be expanded with other RC loops. For instance, an extra RC loop can be added to simulate that the material has two parts with different doping densities.<sup>45</sup> Every loop causes a peak in the loss-tangent and an extra semi-circle in the Cole-Cole plots. Therefore, if there are  $n$  loops, there will be  $(n - 1)$  semicircles in the Cole-Cole plots and  $(n - 1)$  peaks in the loss-tangent.

Also, loops can be added that do not directly have a link to the geometrical nature of the device. In principle any process that has a relaxation time  $\tau$  (from interface states for example) can be simulated with a loop, such that  $\tau = RC$ .

III.4.1.2.3. AC Measurements

AC measurements were performed using a Zahner IM6e impedance spectrometer over a frequency range 1 Hz -1 MHz with applied alternating voltage of 50 mV.

For both AC and DC testing, measurements were made on all six devices on each substrate and subsequently averaged.

### **III.4.2. Optical Spectroscopy**

Optical spectroscopy uses the interaction of radiation in a material to gather information on the electronic, chemical and physical structure of materials.

The two principal optical spectroscopic techniques used are the complementary techniques of absorption and fluorescence spectroscopy. These two techniques examine optical excitations and de-excitations of materials, and can give a great deal of information about the material and its local environment.

#### **III.4.2.1. Absorption**

Absorption spectroscopy involves passing a monochromatic beam of light through a sample and measuring the absorption of the material at this wavelength. This absorption is measured as a function of wavelength over a range extending from the infrared to ultraviolet. The absorption is usually measured in reference to a blank sample in a double beam arrangement, to eliminate variations caused by the differences in lamp intensities at different frequencies. As the photons pass through a material, it is possible that photons of a suitable energy can interact with the material, resulting in an electron being excited to a higher energy state, and the photon being absorbed. By measuring the amount of light absorbed for a particular wavelength, it is possible to deduce information about the electronic structure of the material.

At room temperature molecules, which are in thermal equilibrium, generally reside in the lowest vibrational level of the ground state. The vast majority of the excitation transitions therefore occur from the  $S_0$  level in the ground state, as shown in Figure III.13. Since excitation occurs from only one level in the ground state to the vibrational levels in the excited state, an absorption spectrum yields information on the vibrational energy distribution of the first excited state. The linear absorption spectrum of a material hence yields information on the vibrational energy distribution of one photon excited states.



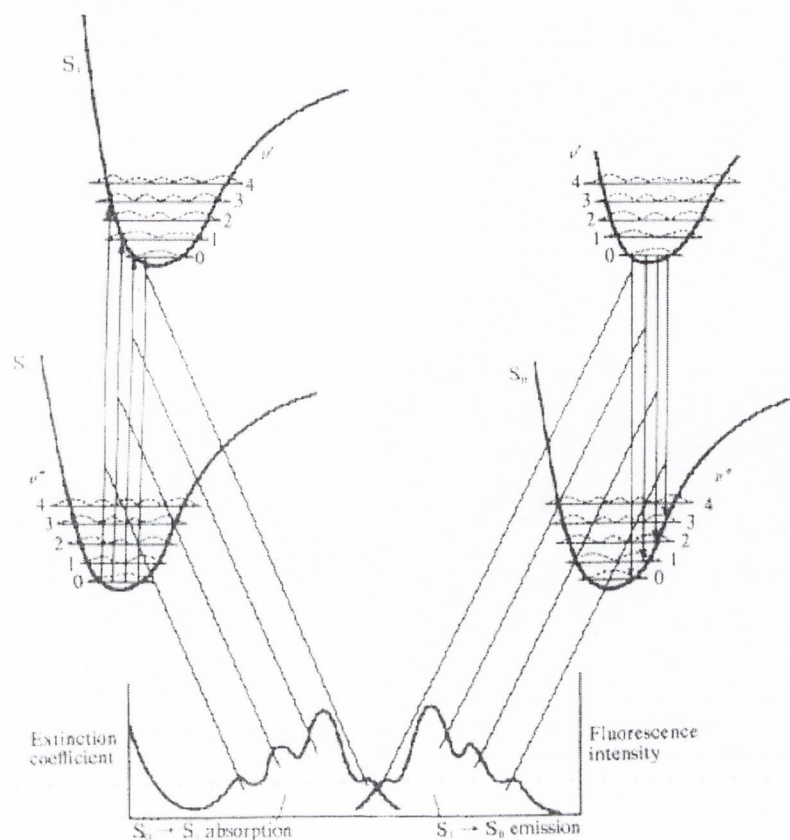


Figure III.13 Schematic diagram of absorption (left) and fluorescence (right) spectra.

Absorption measurements were performed using a Shimadzu UV-Vis spectrometer.

#### III.4.2.2. Fluorescence

Fluorescence spectroscopy is a useful complementary technique to absorption spectroscopy. While absorption spectroscopy probes the energies of excitations to higher states, fluorescence spectroscopy probes the energies at which higher states relax radiatively back to the ground state. Usually a suitable fixed wavelength is used to excite the material, and the wavelength distribution of the emitted light is recorded.

On excitation, an electron is promoted to a vibronic level of the first excited state, and subsequently falls rapidly through the vibrational manifold to the lowest energy level of that excited state. The emission then proceeds from the lowest vibrational level in the first excited state to the vibrational levels of the ground state. Since relaxation occurs from only one level in the excited state to the vibrational levels in the ground state, a fluorescence spectrum yields information on the vibrational energy level distribution of the ground state.

Due to the thermal relaxation, which ensues after initial excitation, the molecule loses energy. This is manifested as a red shift in the emission spectrum compared to that of the

absorption spectrum and is termed Stokes shift as discussed in Section II.2.3.1.1.

Photoluminescence measurements were carried out by exciting the samples with a Roithner NSHU590E narrow band UV diode and recorded using an Andor B401-UV CCD detector connected to an Oriel 77400 spectrograph. Alternatively a Perkin-Elmer fluorometer was also used.

### **III.4.3. Device Characterisation**

#### **III.4.3.1. OLEDs**

A series of three characterisation techniques was performed for all OLEDs tested in this work:

- Current-voltage characteristics were recorded using a Keithley 2400 sourcemeter, which was controlled by a Visual Basic program. These were used to obtain the operating voltage of each device tested.
- Luminance characteristics were performed using this sourcemeter, a silicon photodiode and a Keithley 2001 multimeter. Arbitrary units of luminance were used in order to characterise the brightness of the samples.
- Finally, electroluminescence (EL) spectra were obtained using an Andor B401-UV CCD detector connected to an Oriel 77400 spectrograph. The light was collected by an Oriel 77863 optical fibre, which was placed directly in front of the devices. The CCD was controlled by a computer running Andor custom software.

Figure III.14 shows a diagram of the setup used to perform these measurements:

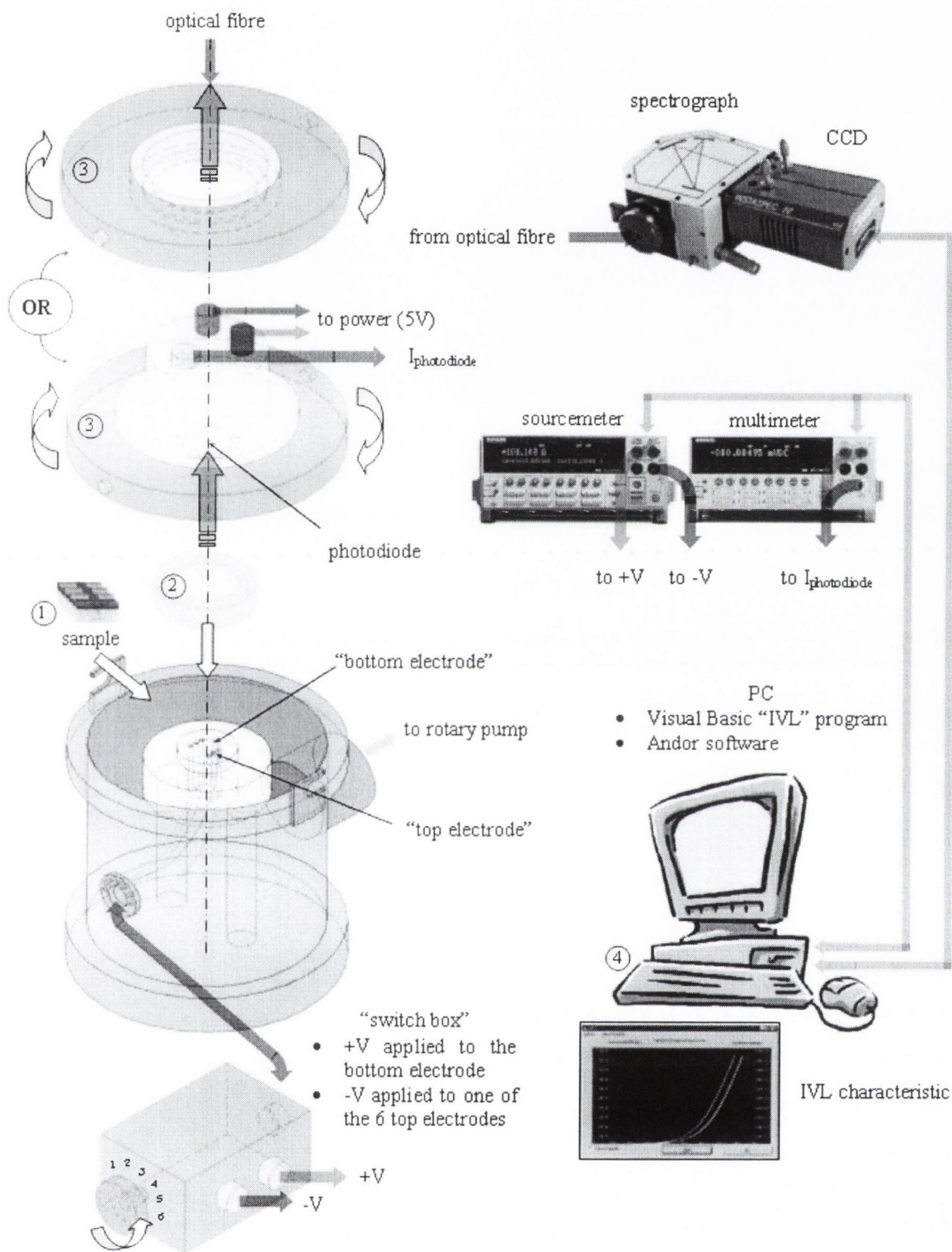


Figure III.14 OLED experimental setup.



III.4.3.2. Photovoltaic Cells

III.4.3.2.1. Parameters

Open-Circuit Voltage

Figure III.15 shows the equivalent circuit diagram (ECD) of a solar cell. It consists of the following ideal components: a current source  $I_L$  that considers the light-generated current, a diode ( $D$ ) that accounts for the nonlinear voltage dependence and a shunt ( $R_{sh}$ ) as well as a series resistor ( $R_s$ ).

Also shown is a load resistor  $R_L$  and its voltage drop ( $V$ ) and current ( $I$ ). The current arrows point into the direction the holes flow.

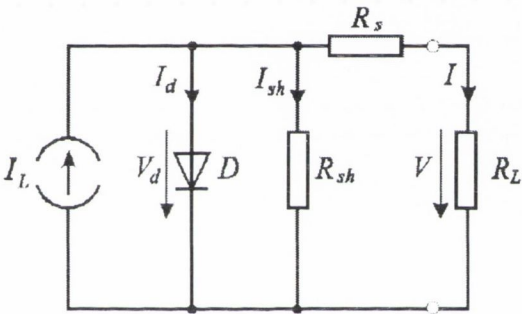


Figure III.15 Equivalent circuit diagram (ECD) of a solar cell.

The open-circuit voltage is defined as follows: the current  $I$  is negative if  $V > V_{oc}$  (open-circuit voltage) and it flows ‘into’ the device – otherwise it is positive.

Using the simple ECD and Kirchoff’s laws for current knots and voltage loops, we can formulate the following relation:

$$(I_L - I_d - I)R_{sh} = V + IR_s \tag{Equation III.20}$$

which can be transformed into:

$$I \left( \frac{R_s}{R_{sh}} + 1 \right) = I_L - I_d - \frac{V}{R_{sh}} \tag{Equation III.21}$$

If we now assume that the Shockley diode equation describes the voltage dependence of the current  $I_d$  through the ideal diode  $D$ :

$$I_d = I_0 \left( \exp \left( \frac{V - IR_s}{nkT/q} \right) - 1 \right) \quad \text{Equation III.22}$$

and replace  $I_d$  in Equation III.21 we obtain:

$$I = \left( I_L - \frac{V}{R_{sh}} \right) \frac{R_{sh}}{R_{sh} + R_s} - I_0 \frac{R_{sh}}{R_{sh} + R_s} \left( \exp \left( \frac{V - IR_s}{nkT/q} \right) - 1 \right) \quad \text{Equation III.23}$$

### Short-circuit Current

The current  $I_{sc}$  under short circuit condition ( $R_L = 0$ ) can be derived from Equation III.23 by setting  $V = 0$ . If we also consider the influence of the photoluminescence efficiency ( $\Phi_{PL}$ ) we can write:

$$I_{sc} = \frac{I_L}{1 + \frac{R_s}{R_{sh}}} - \frac{\frac{I_0}{\Phi_{PL}}}{1 + \frac{R_s}{R_{sh}}} \left( \exp \left( \frac{V - IR_s}{nkT/q} \right) - 1 \right) \quad \text{Equation III.24}$$

From the ECD in Figure III.15 can be seen that the short circuit current is simply the light current  $I_L$  (photogenerated charge carriers/s *i.e.* number of split excitons/s) reduced by the current through the shunt  $I_{sh}$  and the diode  $D$ ,  $I_d$ :

$$I_{sc} = I_L - I_{sh} - I_d \quad \text{Equation III.25}$$

$I_{sc}$  is the highest current that can be extracted from a solar cell. The light current increases linearly with the illumination intensity. In order to extract a quantity that describes how efficiently photons are converted into charges in the external circuit,  $I_{sc}$  has to be related to light intensity. This leads to the definition of the spectral response.

### Spectral Response

The definition of the spectral response is as follows:

$$SR(\lambda) = \frac{J_{sc}(\lambda)}{\Phi(\lambda)} \quad \text{Equation III.26}$$

with  $\Phi$  being the light intensity per illuminated area ( $W/m^2$ ) and  $J_{sc}$  representing the current density ( $A/m^2$ ) in short circuit mode.

The spectral response (SR) thus gives the current in the external circuit per watt incident light ( $A/W$ ).

For the characterisation of solar cells a quantity that considers the actual fraction of the

incident photons that can be converted into electrons in an external circuit is also used:  $\text{EQE} \equiv \text{number of electrons in external circuit divided by number of incident photons}$ .

EQE stands for external quantum efficiency and represents, together with the power conversion efficiency, the most interesting parameter of a solar cell. The EQE can be derived from the spectral response considering that the energy of a photon  $E_p = hc / \lambda$ , with  $h$  being Planck's constant,  $c$  the speed of light and  $q$  the elementary charge using the following formula:

$$\text{EQE}(\lambda) = \text{SR}(\lambda) \cdot \frac{hc}{q\lambda} \quad \text{Equation III.27}$$

Note that the EQE gives higher values for shorter wavelengths when compared with the SR spectrum. This is because the spectral response relates to the energy of photons whereas the EQE refers only to the number of particles. Since the output current is determined by the number of electrons that can be 'pumped' into the LUMO regardless of their energy, the EQE represents a true measure for the photon to current conversion efficiency in contrast to SR. The EQE can be converted into the internal quantum efficiency IQE if only the fraction of the actually absorbed photons are considered:

$$\text{IQE}(\lambda) = \frac{\text{EQE}(\lambda)}{1 - R(\lambda) - T(\lambda)} \quad \text{Equation III.28}$$

with  $R$  denoting the fraction of reflected light and  $T$  the fraction of the transmitted light.

The IQE is very helpful and frequently used in inorganic devices to investigate the physical processes in the semiconductor material. In contrast to inorganic solar cells where the complete bulk absorbs light and contributes to the photocurrent, organic devices have typically large regions that act only as optical filter. In addition, interference effects would have to be considered because of the very thin films compared to inorganic cells. This makes the interpretation of IQE spectra in organic cells only more speculative rather than simpler and therefore generally less useful at the present time. The EQE is therefore the preferred quantity in these devices.

However, since only an arbitrary value of  $\Phi(\lambda)$  was available to us, we will use an arbitrary value of the spectral response (SR) parameter in this Thesis.

### Fill Factor

Since a high load resistor reduces the current flux the charges need more time to get out of



the material. This means that recombination can take place increasingly and the extracted external current decreases. This behaviour can be seen in the fourth Quadrant of the I(V) characteristic in Figure III.16.

Thus considering the voltage dependence of the I(V) curve – the maximum power is the maximum product of I and V that can be found amongst the data points in the fourth quadrant. This maximum area is larger the more the I(V) curve resembles a rectangle with the area  $V_{oc} \times I_{sc}$ . The ratio between these two areas represents a measure of the quality of the shape of the I(V) characteristics:

$$FF = \frac{(IV)_{max}}{I_{sc} V_{oc}}$$

Equation III.29

thus:

$$P_{max} = (IV)_{max} = I_{sc} V_{oc} FF$$

Equation III.30

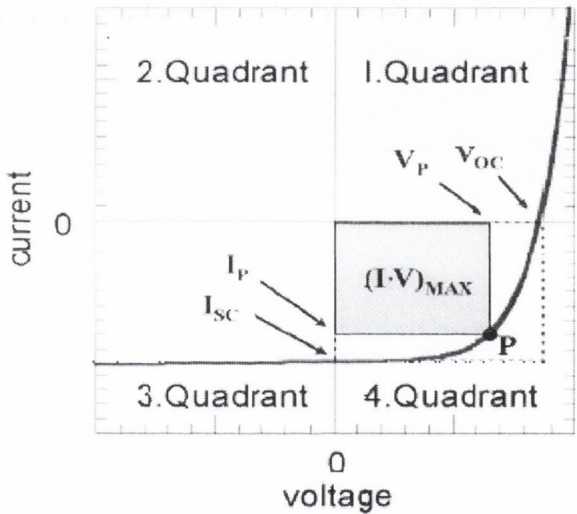


Figure III.16 Current-voltage characteristic of a solar cell under illumination.  $I_{sc}$  and  $I_p$  are the short-circuit and maximum current respectively.  $V_{oc}$  and  $V_p$  are the open-circuit and maximum voltage respectively.

The higher FF the more the I(V) characteristics resembles a constant current source with a maximum voltage and the higher is the electric power that can be extracted. The voltage / current ( $V_p$ ,  $I_p$ ) combination that gives the largest power rectangle is called the maximum power point. Thus, any appliance connected to a solar cell can utilise the maximum output power only if its supply voltage is around  $V_p$  or in other words: the load resistor  $R_L = V_p / I_p$ . Otherwise power would be wasted in heating the series resistor ( $V < V_p$ ) or via increased current losses through the ideal diode and shunt resistor ( $V > V_p$ ).

Even if an external voltage is applied, only the photosensitivity can be amplified – any current higher than  $I_{sc}$  current originates in the external voltage source.

**Power Conversion Efficiency**

In order to describe the power conversion efficiency  $\eta$  of a solar cell the maximum output power  $P_{max}$  has to be related to the power of the incident light  $P_{light}$ . Using Equation III.30 to express  $P_{max}$  considering the wavelength dependence of the parameters involved we can write:

$$\eta(\lambda) = \frac{I_{sc}(\lambda) \cdot V_{oc}(\lambda) \cdot FF(\lambda)}{P_{light}}$$

Equation III.31

Because of the wavelength and intensity dependence power conversion efficiencies are only meaningful for a given spectral distribution and intensity. This can be the solar spectrum or the spectrum of the artificial illumination for indoor applications (*e.g.* pocket calculators).

In order to compare efficiencies of solar cells, solar radiation standards have been defined in the past. The most common standard at present is the AM1.5 spectrum (Figure III.17), which can be approached by commercial solar simulators. It corresponds to the terrestrial solar irradiance.

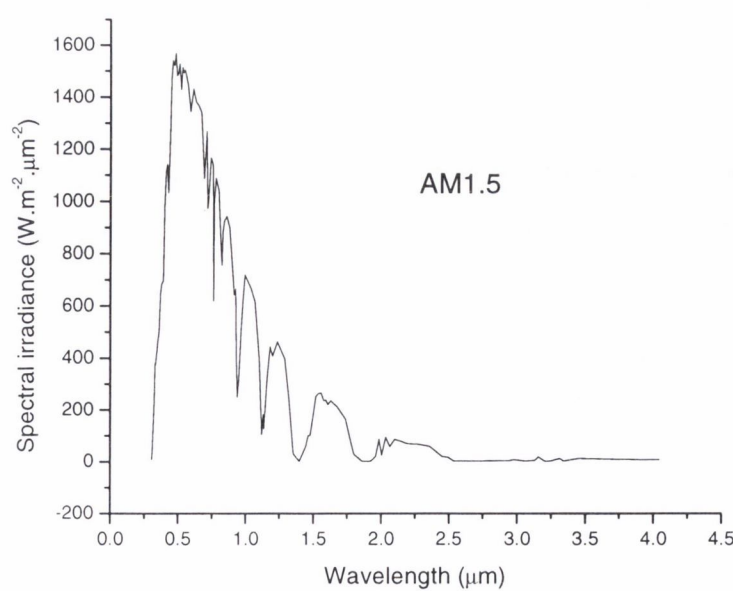


Figure III.17 AM1.5 solar spectral irradiance.

### III.4.3.2.2. Measurements Techniques

#### Polymer Solar Cells

Current-voltage characteristics and spectral responses under illumination both through the ITO electrode and the semi-transparent Al contact were performed for each polymer solar cell studied in this work.

The white source used was a Solux MR16 W-halogen lamp delivering  $80 \text{ mW/cm}^2$  when 12 V applied and placed at 30 cm from the devices. The  $I(V)$  characteristics were carried out using a home-made sourcemeter and plotter software.

The spectral responses were taken using an Oriel monochromator coupled to a Tektronic TDS 360 oscilloscope.

#### Photoelectrochemical Cells

The photoelectrochemical cells devices were tested immediately after fabrication in a black box containing a broad spectrum halogen lamp ( $500 \text{ W/m}^2$ ) (SOLUX, 4700 K). The polymer coated side was faced to the lamp.

A multimeter (HP 34401 A) was connected in parallel and a BAS CV27/MacLab/400 were connected to the device in a two-electrode configuration. EChem software was used to run linear sweep voltammetry (LSV) with a lower limit of  $-800 \text{ mV}$ , an upper limit of  $400 \text{ mV}$  and a scan rate of  $100 \text{ mV/s}$ . This potential range was scanned first in the dark then under illumination to record the change in current due to the absorption of light. The maximum voltage achieved under illumination for each device was then used as the upper limit to determine the current – voltage characteristics over a smaller range with the lower limit at  $0 \text{ mV}$ .

### III.5. Conclusions

Materials' preparation, as well as devices' preparation and characterisation techniques used in this work were presented in this Chapter.

While M3EH-PPV, MEH-PPV, PVK and terthiophene were synthesised either in laboratory with which we collaborated or in industry, PmPV was prepared in our laboratory.



The multi-walled carbon nanotubes were prepared by the arc discharge technique in our laboratory and used in a polymer composite form.

A sandwich device structure was used for each organic optoelectronic device tested in this work. For most of devices, an ITO anode and Al cathode were used as main injecting electrodes. While organic light-emitting diodes were tested and analysed with admittance spectroscopy and current-voltage characteristics, organic photovoltaic devices were characterised using current-voltage and spectral response studies.

Finally, most materials underwent spectroscopic studies using absorption and fluorescence techniques in order to study photophysical processes that could occur.

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### IV.1. Introduction

This Chapter will introduce the basic principles of organic light-emitting diodes (OLEDs). While the physical processes and device's architectures of these devices will be presented in Section IV.2, their electrical conduction models will be outlined in Section IV.3. Finally, the analysis of the device's characteristics of a single layer OLED will allow us to determine the intrinsic electronic parameters of one the main conjugated polymers used throughout this Thesis: M3EH-PPV. This will be shown in Section IV.4.

## IV.2. Basic Principles and Practical Issues

### IV.2.1. Physical Processes

#### IV.2.1.1. Organic Electroluminescence

Organic electroluminescence (EL) is obtained simply by placing a charge-transporting and light-emitting organic material between two electrodes (one of which is transparent) and applying a suitable bias, as shown in Figures IV.1 and IV.2:

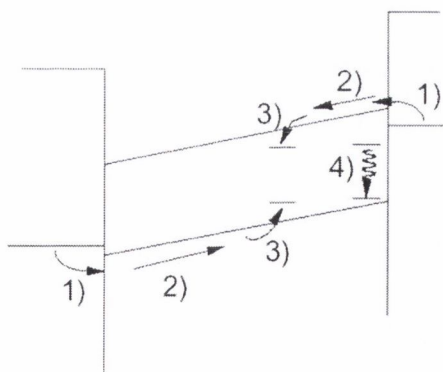


Figure IV.1 Organic electroluminescence mechanism with: 1) opposite sign carrier injection, 2) carrier transport, 3) exciton formation and 4) radiative recombination.

The organic material may be either a polymer, deposited by various solution processing techniques, or low molecular weight molecules, deposited by evaporation or sublimation in

vacuum. Total device thickness (excluding the substrate) is of the order of hundreds of nm. When biased, charge is injected into the highest occupied molecular orbital (HOMO) at the anode (positive), and the lowest unoccupied molecular orbital (LUMO) at the cathode (negative), and these injected charges migrate in the applied field until two charges of opposite polarity encounter each other, at which point they combine to produce a radiative state.

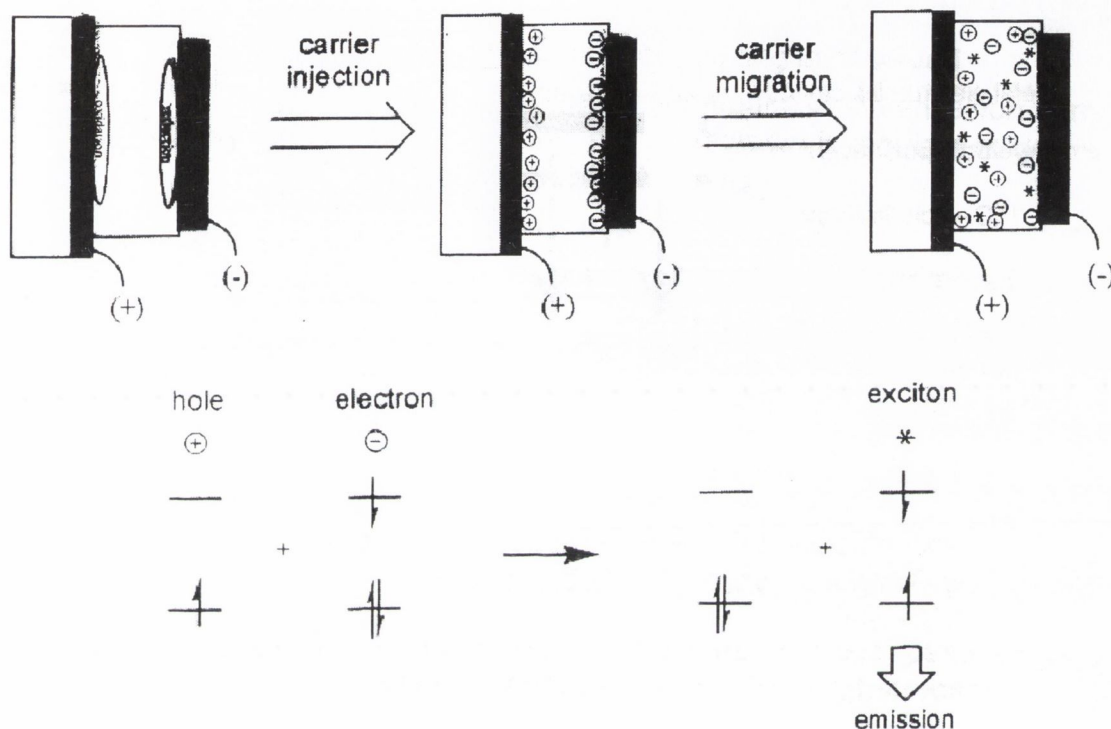


Figure IV.2 Device structure and electroluminescence processes in organic light-emitting diodes (OLEDs).

Although the luminescent states are typically singlets, exploitation of phosphorescence has been demonstrated recently in this type of devices for both molecule and polymeric conjugated systems.<sup>1,2</sup>

#### IV.2.1.2. Charge Injection

Theoretical modelling of charge injection has been attempted by several approaches. Excellent quantitative results have been obtained by P. Davids and D. Smith,<sup>3</sup> who assume injection to be a combination of thermionic emission and quantum mechanical tunnelling, but with the important feature of a thermionic backflow: if the mobility of carriers in the organic layer is small, the local concentration quickly increases and the probability of reverse hops increases. In this model, which has given good agreement with experiment for single layer devices both with unipolar and bipolar structure, the barrier height derived

from modelling is not, in general, what would be calculated from tabulated work functions for the metal electrodes, suggesting some chemical reaction between electrode metal and active material.

Recently J. Bharathan and Y. Yang showed that just 2 Å of calcium for the cathode followed by aluminium gives identical electrical characteristics to 2000 Å of calcium.<sup>4</sup> Their data are difficult to reconcile with any mechanism other than doping of the interface by reaction of calcium with the polymer, creating surface states that pin the surface energy levels in a manner somewhat analogous to the pinning of the Fermi level by surface states of an inorganic semiconductor.

Additional experiments by J. Sheats and co-workers using zirconium carbide cathodes were best explained by postulating that electrons, injected from a pristine metal into an undoped polymer, quickly become trapped, and these traps are effective luminescence quenching centres.<sup>5</sup> When some doping is present, the charge carriers remain mobile and device performance is correspondingly enhanced. These reactive surface states must be protected from oxygen and water, and complicate the electrode processing compared to liquid crystal display processes.

#### **IV.2.1.3. Charge Transport**

We have already seen that charge carriers can move by electron transfer reactions, or hopping between molecules or polymer segments; even along a polymer chain. Moreover, conformational disorder interrupts the idealised one-dimensional transport. Mobilities for electrons, which are believed to be more easily trapped (especially by sites containing oxygen), are generally lower than for holes; both are low compared to mobilities in inorganic semiconductors.

### **IV.2.2. Practical Device Issues**

#### **IV.2.2.1. Charge Injection Balance**

Single-layer devices tend to produce unbalanced charge injection (and transport) and consequently lower efficiency. To prevent this, a charge transport or injection layer (for either holes or electrons, or both) is used.

A proper choice of energy level offsets between the layers can block the transmission of



the majority carriers, creating a space charge that reduces its current and balances the charge transport. Transport layers can also lower the injection barriers at the electrodes.

Creating multiple layer structures is not without difficulties, however, since interlayer mixing is in general undesirable.

#### **IV.2.2.2. Light Extraction Efficiency**

In accordance with Snell's law, when light passes from a medium of high refractive index to one of lower index, there exists a critical angle of incidence (the angle between the light propagation direction and the perpendicular to the surface) beyond which the light is totally internally reflected; this is the basis for the nearly lossless transport of light over long distances in optical fibres. For the glass-air interface the angle is approximately 43 degrees, and polymers are similar.

Thus, a great deal of the light generated by an OLED is trapped inside the glass or plastic substrate and waveguided out to the sides; this is normally about 80% of the total.

Current research activity in inorganic LEDs (where the problem is even worse because the index of the inorganic materials is higher still) is directed toward various surface treatments that can greatly increase extraction efficiency. It is reasonable to expect that these losses may be cut at least in half by innovation in this area.

#### **IV.2.2.3. Power Efficiency**

The fundamental quantity important to the user is power efficiency, since this determines the size and durability of the battery required to power a portable device for example. Power efficiency is measured in lumens per watt.

Incandescent light bulbs used in the home range from about 10 – 15 lumens/watt; fluorescent bulbs can be as much as 80. Currently, the best OLEDs are achieving in excess of 20 lumens/watt (for green), although many devices are well below this (often only a few lumens/watt). Progress in improving this number has been rapid during the last few years and will doubtlessly continue; in fact, while it is a long range goal, the use of OLEDs for general illumination may prove feasible.

Power efficiency is affected not only by the quantum efficiency of the device (number of

photons out per electron in), but also by the voltage at which the device operates, since according to Ohm's law power is the product of current and voltage. Thus it is important to obtain low operating voltages. This is related to the charge injection barrier issue mentioned earlier. Low voltage is also desirable to avoid expensive voltage upconverters to provide compatibility with batteries. Voltages for the systems likely to see early application are around 3 – 6 V.

One of the most exciting results in the area of OLEDs is the exploitation of triplet emission, where, for example a molecular aluminium quinoline or polymeric host naphthalimide derivative is doped with a phosphorescent dye Pt-porphyrine, allowing for both singlet and triplet emission.<sup>1</sup> The energy transfer from the host to the guest takes place via a combination of Förster long-range and Dexter short-range mechanisms, and allows for EL efficiencies reaching up to 90 % of the emitter PL efficiency, defeating the so-called spin-statistics restraint, which had so far limited the EL efficiency to less than one-quarter of the PL efficiency.

Although the host PL efficiency is not exceptionally high in the reported cases, these experiments open the way to both very efficient devices and also to a powerful tool for gaining quantitative information on the energy and on the photophysics of triplets, which are hard to observe in the vast majority of conjugated polymers. Emission from these states is, in fact, a spin-forbidden process, unless inter-system crossing is enhanced, for example by means of increased spin-orbit coupling due to the presence of atoms with high atomic number.

#### IV.2.2.4. Colour Issues

Different colours are obtained in OLEDs from different materials; hence for a full colour (RGB) display, some patterning of the organic material must occur (in order to get all colours one must have red, green, and blue subpixels at each pixel of the display).

This has important ramifications for manufacturing, and while several solutions have been proposed and demonstrated at the laboratory level, it is not yet clear which will be preferred for production.

Organic molecules typically emit light in a band of wavelengths that is rather broad (of the order of 50 – 70 nm at an intensity level equal to half of the maximum). When three such



bands (which may individually appear red, green, and blue) are mixed to obtain an arbitrary colour, the results may not be as satisfactory as when three narrow-band ('saturated') colours are mixed. Various ways to address this include using well-known thin film interference effects to sharpen the emission bands.<sup>6</sup>

#### **IV.2.2.5. Lifetime and Environmental Sensitivity**

The operation of OLED devices generally leads to a more or less steady loss of efficiency. Two types of loss are often distinguished: the quantum efficiency decreases, and the voltage required to maintain constant current increases.

Lifetimes depend on the brightness at which the display is operated, and are typically quoted as the time to reach half of an initial brightness of 100 cd/m<sup>2</sup> (which is that of a typical desktop CRT).

In the best materials, polyfuorenes and dyes,<sup>7,8</sup> offered by several companies at the present (Kodak, Xerox, DuPont Displays, ...), the lifetime now exceeds 10,000 hours and in a few cases is greater than 50,000 hours. This parameter has also seen substantial and steady improvement in recent years, and can be expected to improve still further.

Every device has temperature and other environmental limits. OLEDs must be hermetically sealed from exposure to water and oxygen; while it has been a challenge to find a suitable flexible, transparent material with the required properties, this has been accomplished. Low temperature does not adversely affect OLEDs as it does LCDs (indeed they become more efficient), but devices must typically be kept below 60 °C for operation (their lifetime is substantially shortened when operated at such higher temperatures) and 80 °C for storage.

### **IV.3. Electrical Conduction Mechanisms**

#### **IV.3.1. Introduction**

With regard to electrical studies in any semiconductor material it is important to remember that we can rarely look at the material in isolation. In general we will always have to take into account the effects, if any, of the electrodes and external circuit on transport in the material under study. When two different materials come into intimate contact there is initially an energy difference between their Fermi levels. The system comes into equilibrium by carriers flowing from one material into the other until the Fermi energies



have equalised. This interfacial charge redistribution causes the bands to bend in the region of the interface. In general this will result in a barrier to charge injection into the material.

The size of this barrier is related to the band structure of the materials and specifically the size of the work function of the metal in relation to the ionisation potential or electron affinity of the semiconductor. If the electrode work function is within 0.5 eV of the ionisation potential the barrier to injection into the HOMO or valence band will be small.<sup>9</sup> Similarly if the electrode work function is within 0.5 eV of the electron affinity the barrier to injection into the LUMO or conduction band will be small. This is termed ohmic contact. We can assume that for applied voltages greater than a few volts the barriers at the electrodes are negligible. In this case the applied voltage is of negligible difference to the internal voltage.<sup>10-12</sup> For a semiconductor connected to ohmic electrodes the current flow, in principle, is controlled by bulk properties of the material and not properties of the electrodes. This is known as bulk limited current flow.

However if the work function of the electrodes is not close to either the ionisation potential or electron affinity, a large potential barrier may exist at the electrode-semiconductor interface. In this case we cannot neglect the effects of the barrier and the transport properties become electrode limited.

## **IV.3.2. Electrode Limited Conduction Mechanisms**

### **IV.3.2.1. Electrode – Semiconductor Interfaces**

#### **IV.3.2.1.1. Definitions**

The theory of contacts between doped semiconductors and metals was developed in 1938 by Mott and Schottky.<sup>13,14</sup> Since then charge injection from metallic contacts into semiconductors has been studied extensively and is explained in detail in the semiconductor literature.<sup>10,11,15,16</sup>

A Schottky barrier is created by the intimate contact of a metal and a semiconductor surface. Figure IV.3 shows the situation of a Schottky barrier of a metal and a p-type semiconductor:

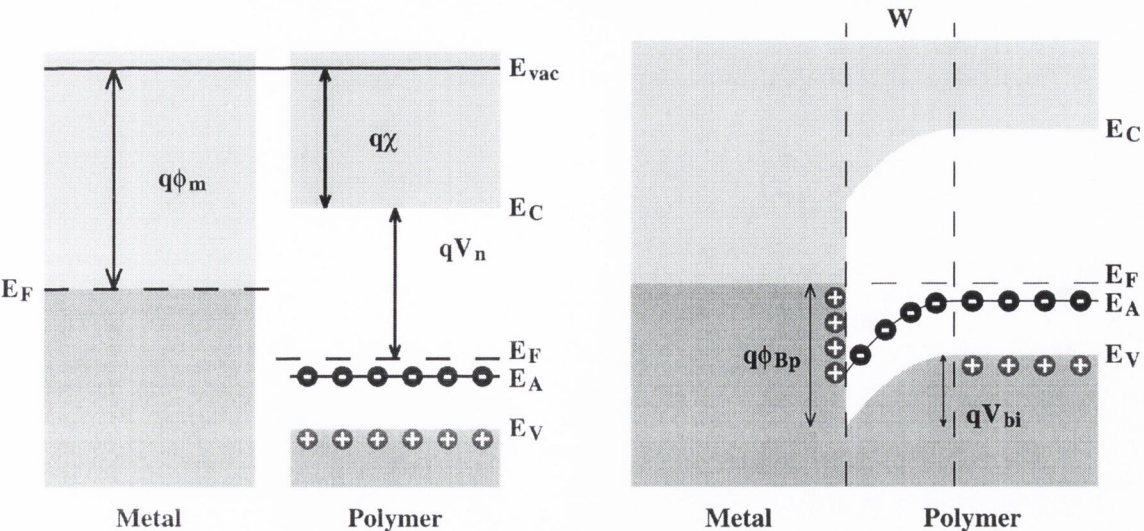


Figure IV.3 Schottky barrier between a metal and a p-type semiconductor. The left drawing shows the situation before contact and the right drawing the resulting Schottky barrier after contact.

At equilibrium, in the absence of externally applied voltages, the Fermi level must be constant throughout the sample, since otherwise a current would flow. In the metal the Fermi level is the top of the ‘electron sea’, while in the semiconductor, far from the interface, the Fermi level is determined (‘pinned’) by the impurity level. The Fermi level is matched in the following way: before equilibrium, the Fermi level is lower in the semiconductor (when the work function of the polymer,  $E_{vac} - E_F = \chi + V_n$ , is larger than that of the metal,  $\Phi_m$ ), therefore, electrons will flow from the metal to the polymer. This causes the build up of charges on both sides of the interface, resulting in an electric field and therefore a potential gradient according to Poisson's equation  $d^2V/dx^2 = \rho(x)$ . This is the so-called band bending. In this region, the electric field has caused the holes to move away from the interface; they drift to the top of the valence band. The result is that in this area, of width  $W$ , there is a surplus of negative charge caused by uncompensated charged acceptors, the ‘space charge region’ or ‘depletion region’, since there is an absence of majority carriers (holes in p-type semiconductors).

The parameters that describe the Schottky barrier are:

- $\Phi_{Bp}$ : barrier height, or the barrier as seen by (majority) carriers coming from the metal. It depends on the difference in electron affinity of the metal and the semiconductor, and (for p-type semiconductors) also depends on the energy gap  $E_g$ :  $\Phi_{Bp} = \chi + E_g - \Phi_m$ . It is independent of the position of the Fermi level in the semiconductor and thus on the presence of impurities, *etc.* It might be lowered by the so-called image-force-lowering effect which adds to the energy scheme the potential caused by the interaction of the

charge with its image (virtual) charge on the metal.

- $V_{bi}$ : built-in voltage or zero-bias band bending, or the barrier as seen by (majority) carriers going into the metal. This is determined by the difference in Fermi level before contact:  $V_{bi} = (E_{vac} - E_F)_{semicon.} - (E_{vac} - E_F)_{metal} = \chi + V_n - \Phi_m$ .
- $W$ : depletion width, or the width of the area devoid of (majority) carriers. The depletion width can be calculated when the doping profile is known (as will be shown in the next Section).

For a Schottky barrier the forward bias is when a positive voltage is applied to the (p-type) semiconductor and a negative voltage to the metal. This will compensate the band bending and diminish the barrier.

**IV.3.2.1.2. Depletion Width of a Schottky Barrier**

The depletion width of a Schottky barrier can be calculated from Poisson's equation  $d^2V/dx^2 = \rho(x)$ , with  $\rho(x)$  the space charge density at position  $x$ . In a first approximation we can assume a rectangular distribution of the space charge, as Figure IV.4 shows:

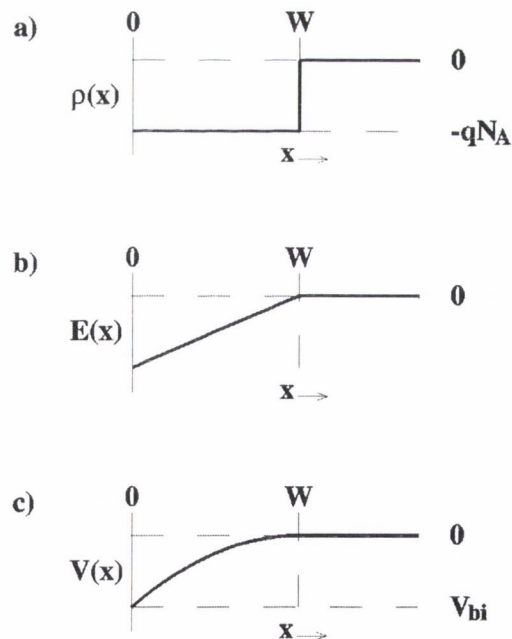


Figure IV.4 Space distribution of a) the charge density, b) the electric field and c) potential at a Schottky barrier.

This is valid when the acceptors are all ionised and the free charges have moved out of the interface region leaving behind the now uncompensated ionised acceptors exactly up to a



certain point  $W$ .  $N_A$  can be defined as the density of ionised acceptors (and impurities). In that case the electric field can be calculated by Poisson's equation:

$$E(x) = \frac{dV}{dx} = \frac{qN_A}{\epsilon} (x - W) \quad \text{Equation IV.1}$$

where the boundary condition  $E(W) = 0$  was used. The voltage can then be found by integrating this equation to give:

$$V(x) = \frac{qN_A}{2\epsilon} (x - W)^2 \quad \text{Equation IV.2}$$

(boundary condition  $V(W) = 0$ ).

At  $x = 0$  the voltage must be equal to the built-in voltage,  $V_{bi}$ , therefore:

$$V_{bi} = \frac{qN_A W^2}{2\epsilon}, \text{ and } W = \sqrt{\frac{2\epsilon V_{bi}}{qN_A}} \quad \text{Equation IV.3}$$

When bias is applied to the device the voltage at  $x = 0$  should be equal to  $V_{bi} - V$ , therefore:

$$W(V) = \sqrt{\frac{2\epsilon(V_{bi} - V)}{qN_A}} \quad \text{Equation IV.4}$$

#### IV.3.2.1.3. Capacitance of a Schottky Barrier

When the bias voltage on the device is changed, a new equilibrium state will be reached with a new amount of space charge as described above. The AC capacitance of a Schottky barrier can be defined as the incremental change of space charge  $Q$  in the depletion range upon an incremental change of voltage:  $C = dQ/dV$ . Note that this capacitance can depend on the applied voltage, in contrast to normal capacitor which have a constant  $C = Q/V$ .

It can be shown that a Schottky barrier behaves like a capacitor made of parallel plates with area  $A$ , spaced  $W$  and filled with a dielectric medium  $\epsilon$ . Substituting the calculated depletion width from Equation IV.4 therefore gives:

$$C(V) = \frac{\epsilon A}{W(V)} = A \sqrt{\frac{\epsilon q N_A}{2(V_{bi} - V)}} \quad \text{Equation IV.5}$$

This shows that a Mott-Schottky plot ( $C^{-2}$  vs.  $V$ ) is a straight line and the slope reveals the acceptor concentration,  $N_A$ :

$$N_A = -\frac{2}{\text{slope} \cdot A^2 \epsilon q} \quad \text{Equation IV.6}$$

In the same plot, extrapolating to  $C^{-2} = 0$  reveals the built-in voltage and hence the barrier height (if the shallow level depth is known). For normal shallow acceptor levels this is equal to the acceptor density, but for deeper levels it can be the case that they are only partially ionised. The capacitance (and depletion width) sees only the ionised defects. A capacitance transient for instance, monitors the change in density of these ionised defects.

#### IV.3.2.2. Shottky Barrier Electrical Conduction Mechanisms

Although it is not clear to what extent the developed models can be applied to organic semiconductors, we only describe the basic concepts as they are often used to understand and predict the behaviour of organic semiconductor / electrode interfaces.

There are two principal mechanisms for the charge carriers to overcome barriers: thermionic emission and quantum mechanical tunnelling (field emission).

##### IV.3.2.2.1. Thermionic Emission

For thermionic emission over a triangular barrier of height  $\Phi$  from a metal into a high-mobility semi-conductor, the current density (J) is given by:

$$J = A^* T^2 \exp\left(-\frac{\Phi}{kT}\right) \quad \text{Equation IV.7}$$

where  $A^*$  is the effective Richardson constant and T the absolute temperature.

If an electric field is applied across the barrier, the barrier height decreases by:

$$\Delta\Phi = \sqrt{\frac{q^3 E}{4\pi\epsilon_0}} \quad \text{Equation IV.8}$$

where E is the applied electric field, q the elementary charge and  $\epsilon_0$  the dielectric constant of vacuum.

In a semiconductor with a low mobility, it is necessary to take into account the diffusion of carriers within the barrier region back towards the contact. A full analysis is given by Kao and Hwang.<sup>11</sup>

##### IV.3.2.2.2. Quantum Mechanical Tunnelling

At sufficiently low temperatures, or for large barriers at high fields, emission due to quantum mechanical tunnelling through the barrier can become important. For a Schottky barrier the current is given by:

$$J \propto \frac{\Phi_b + qV}{\Phi} \exp\left(K \frac{\Phi^{3/2}}{(\Phi + qV)^{1/2}}\right) \quad \text{Equation IV.9}$$

where  $V$  is the applied voltage and  $K$  a material constant.

The essential characteristic of field emission is that the current is insensitive to temperature, but strongly dependent on the applied field (voltage). Since the tunnelling rate depends also strongly on the width of the barrier, thermal excitation can increase the tunnelling current. For a Schottky barrier the current can then be written as:

$$J = J_0 \exp\left(\frac{qV}{nkT}\right) \quad \text{Equation IV.10}$$

where  $J_0$  is essentially a constant for low doping levels and  $n \approx 1$  at high temperatures.<sup>17</sup>

### IV.3.3. Bulk Limited Conduction Mechanisms

The bulk properties of an organic material will dominate its electrical properties in the presence of a small barrier to charge injection. At low voltages, majority intrinsic carriers (positive polarons in most organic materials) will begin to drift with the field with an average velocity which is proportional to the applied field. This is governed by Ohm's law:

$$J = \sigma E \quad \text{Equation IV.11}$$

where  $J$  is the current density,  $\sigma$  is the conductivity and  $E$  is the electric field.

The conductivity is related to the mobility, carrier density and carrier charge by:

$$\sigma = pq\mu_p \quad \text{Equation IV.12}$$

where  $p$  is the free hole carrier density,  $q$  is the elementary charge and  $\mu_p$  is the carrier mobility.

However organic materials tend to have extremely low intrinsic carrier densities and cannot compensate for injected charge. The ability of a material to redistribute excess charge in order to maintain charge neutrality is governed by the dielectric relaxation time  $\tau_d$ . This is the time taken for a material to restore itself to charge neutrality after the injection of a small charge excess. This is described by Equation IV.13:

$$\tau_d = \frac{\epsilon}{pq\mu_p} \quad \text{Equation IV.13}$$

where  $\epsilon$  is the permittivity of the material.

However as the applied field is increased the carrier transit time  $\tau_t$  decreases because the average carrier velocity increases with field. When these two terms are equal the material



can no longer redistribute charge during the course of a carriers journey through the material. This is described by Equation IV.14:

$$\tau_d = \frac{\epsilon}{pq\mu_p} = \tau_t = \frac{d^2}{\mu_p V} \quad \text{Equation IV.14}$$

where  $d$  is the material thickness and  $V$  is the applied voltage.

This shows that above a certain voltage the charge injected into the material is that which can be stored in a similar capacitor. This occurs at a voltage  $V_\Omega$  given by:

$$V_\Omega = \frac{pqd^2}{\epsilon} \quad \text{Equation IV.15}$$

A more detailed analysis gives approximately the same result but includes a factor of 8/9:

$$V_\Omega = \frac{8pqd^2}{9\epsilon} \quad \text{Equation IV.16}$$

Above this applied voltage a space charge region builds up and the conduction is said to be space charge limited (SCL).

In the case of unipolar carrier injection (identical electrodes) this behaviour can be described using the single carrier SCL current model. This model is based on a number of assumptions. These are, that the intrinsic charge density is negligible compared to the injected charge, that the injecting contact is ohmic and that the material is trap free. Also the mobility is assumed to be field independent. As shown by Mott and Gurney<sup>18</sup> the solution works out to be:

$$J = \frac{9\epsilon\mu_p V^2}{8d^3} \quad \text{Equation IV.17}$$

This equation is the solid state analogue of Childs law for SCL current in a vacuum. In summary at low applied voltages the current will follow Ohms law but for voltages in excess of  $V_\Omega$  the current will be quadratic in voltage.

In the case of real materials however there will always be traps present. These dramatically alter the SCL current and hence the form of the  $I(V)$  characteristic. The simplest case is when the traps lie at a single discrete energy level. In this case a significant proportion of injected charge may remain untrapped. The total charge density can then considered to be:

$$\rho = \rho_f + \rho_t \quad \text{Equation IV.18}$$

where  $\rho_f$  is the free charge density and  $\rho_t$  is the trapped charge density.

Hence at low bias the traps simply reduce the number of injected carriers which are free to conduct. For a given voltage the current is reduced by a factor of  $\theta$ , the fraction of free charge:

$$\theta = \frac{\rho_f}{\rho_f + \rho_t} \quad \text{Equation IV.19}$$

Equation IV.18 then becomes:

$$J = \frac{9\epsilon\mu_p\theta V^2}{8d^3} \quad \text{Equation IV.20}$$

The current density is still quadratic in voltage but its magnitude is reduced sometimes by as much as  $10^8$ .<sup>10,11</sup> In addition to this the transition voltage  $V_\Omega$  is increased because the density of free injected charge is reduced.

As the applied field is increased a critical voltage, VTFL, is reached at which all traps are filled. Any increase will result in all injected charge being free to conduct. This voltage is known as the trap free limit (TFL). Above this critical bias the current increases sharply before reverting to the value described by Equation IV.20. The density of the traps filled at VTFL can be written as:

$$N_t = \frac{3\epsilon V_{TFL}}{2qd^2} \quad \text{Equation IV.21}$$

For many real organic systems the traps may be distributed over a range of energies in the gap. Mark and Helfrich considered a hole only system with an exponential distribution of traps of the form:<sup>19</sup>

$$N_t(E) \propto N_0 \exp\left(\frac{E_{HOMO} - E}{kT}\right) \quad \text{Equation IV.22}$$

This equation can then be used to calculate the current voltage behaviour:

$$J = N_{HOMO}\mu_p q^{1-m} \left(\frac{\epsilon m}{N_t(m+1)}\right)^m \left(\frac{2m+1}{m+1}\right)^{m+1} \frac{V^{m+1}}{d^{2m+1}} \quad \text{Equation IV.23}$$

where  $N_{HOMO}$  is the density of states in the HOMO,  $\mu_p$  is the hole mobility and  $m = E_t / k_B T$  ( $E_t$  is the characteristic trap energy).

It is also possible to calculate  $V_\Omega$  for a broad distribution of traps by setting Equation IV.23

equal to Ohms law for J. This yields:

$$V_{\Omega} = \frac{qd^2N_t}{\epsilon} \left( \frac{p}{N_{HOMO}} \right)^{1/m} \left( \frac{m+1}{m} \right) \left( \frac{m+1}{2m+1} \right)^{m+1/m}$$

Equation IV.24

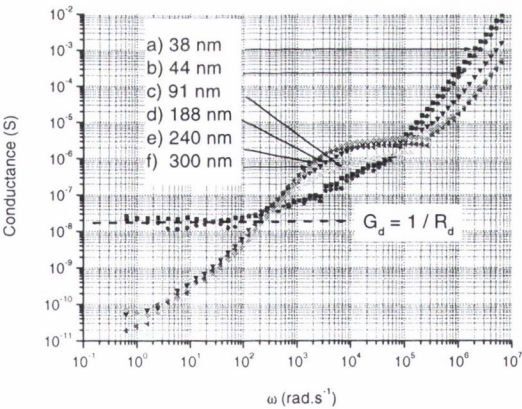
Thus SCL conduction is characterised by the current being related to the voltage by a power law  $J = KV^{m+1}$  where m is related to the depth of the traps.

**IV.4. Electrical Properties of Single Layer OLEDs**

In order to investigate the electrical properties of single layer OLEDs, several ITO / M3EH-PPV / Al devices were prepared with the thickness of the M3EH-PPV layer ranging from 38 to 300 nm. Admittance, C(V) and I(V) data were recorded and analysed.

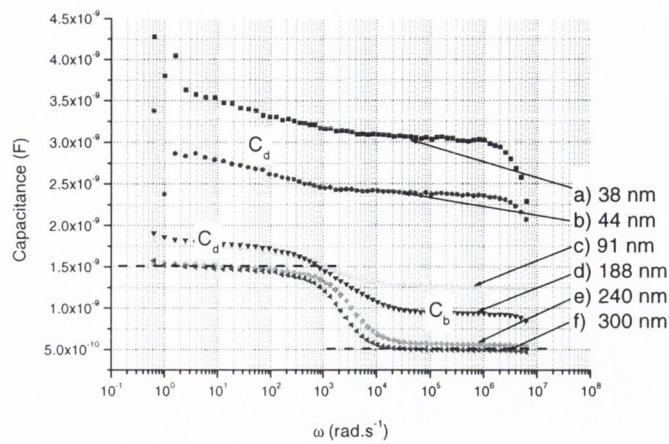
**IV.4.1. Electrical Model**

Admittance measurements of the ITO / M3EH-PPV / Al devices are shown in Figures IV.5a to IV.5d, with plots of their conductance ( $G_{AC}$ ), their capacitance ( $C_{AC}$ ), their loss-tangent ( $\tan\delta$ ), and the real part of their impedance ( $Re(Z)$ ) as a function of angular frequency respectively:

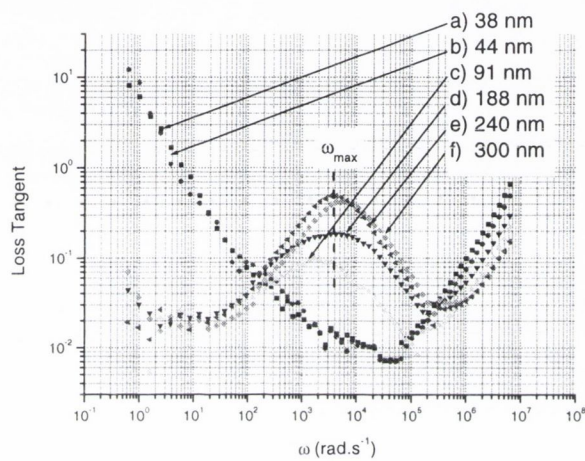


a)

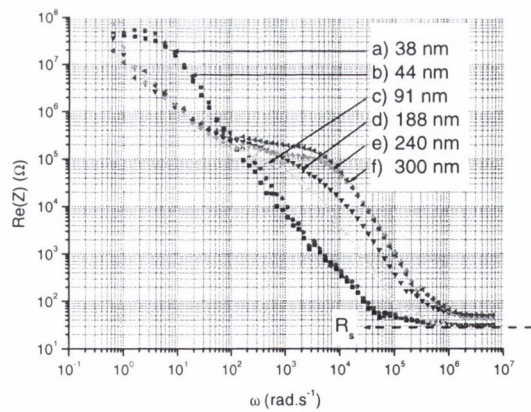




b)



c)



d)

Figure IV.5 a) Conductance, b) capacitance, c) loss-tangent, and d) real part of the impedance:  $Re(Z)$  as a function of angular frequency for each ITO / M3EH-PPV / Al device.

The series resistance:  $R_s$  can firstly be extracted from the high frequency regime ( $10^7 - 10^8$  rad.s $^{-1}$ ) of the real part of the impedance.  $R_s$  corresponds to the sum of contact resistances, *i.e.* between the electrodes and the external circuit. The average value calculated was 37  $\Omega$  and can be considered negligible. However, it is to be noted that this non-zero value affects

the shape of the loss-tangent's spectra at high frequency. With  $R_s = 0 \, \Omega$ , the loss-tangent should indeed decrease to 0 at high frequency, while in our case  $\tan\delta$  increases.

The loss-tangent, as described in Section III.4.1.2.1, is defined as the ratio between the real part and the imaginary part of the admittance:  $\tan\delta = \text{Re}(Y)/\text{Im}(Y) = G_{AC}/\omega C_{AC}$ . For the simple model, the loss tangent decreases as  $1/\omega$ . Interface barriers however can produce peaks in the spectra.

Figure IV.5c clearly shows no peak for the first two samples (38 and 44 nm), while there is one peak for the remaining devices (from 91 to 300 nm). Therefore, we can use a simple model (small resistor  $R_s$  in series with a capacitor and a resistor in parallel) for the first two samples (38 and 44 nm), and the remaining devices (from 91 to 300 nm) can be modelled by a resistor  $R_s$  in series with two capacitor – resistor loops, as shown in Figure IV.6:

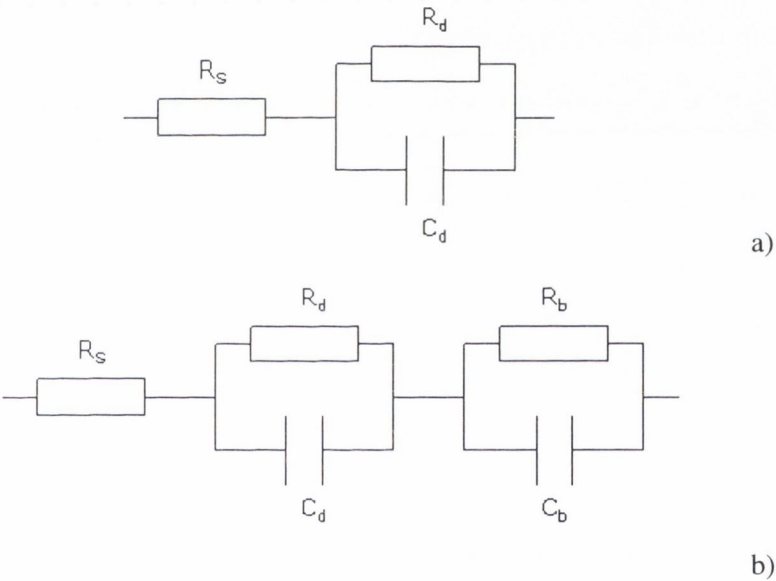


Figure IV.6 Resistor – capacitor model for a) the thin ITO / M3EH-PPV / Al devices and b) the thick ITO / M3EH-PPV / Al devices.  $R_s$  denotes the series resistor, while d and b represent the depleted and bulk parts of the model respectively.

$R_s$ ,  $R_d$ , and  $R_b$  correspond to the series, depleted and bulk resistors respectively, while  $C_d$  and  $C_b$  represent the depleted and bulk capacitors of the model.

In other words, our results show that two regions are present in the ‘thick’ samples: one depleted and one bulk region (therefore modelled by two capacitor – resistor loops), and that the ‘thin’ samples are fully depleted (therefore modelled by only one capacitor – resistor loop). The depleted region in either case can be considered as a Schottky barrier at

the interface between one of the metal electrodes (ITO and Al) and the polymer M3EH-PPV. Since ITO’s work function and M3EH-PPV’s HOMO level are very similar (4.8 and 4.9 respectively) it is unlikely that such a barrier will form at this interface. Therefore, we can conclude that the Schottky barrier is formed at the interface between M3EH-PPV and Al and that the ITO / M3EH-PPV contact remain ohmic.

As seen in Section III.4.1.2.2, it is possible to extract each of the parameters defined above with careful analysis of the conductance, capacitance and loss tangent spectra (Figures IV.5a to IV.5c).  $C_d$  and  $C_b$  can be obtained from the capacitance spectra at low and high frequency respectively, while  $R_d$  and  $R_b$  can be obtained from the conductance spectra at low and high frequency respectively.

Alternatively  $R_b$  can be calculated from the frequency at the peak of the loss tangent,  $\omega_{max}$ :

$$\omega_{max} = \frac{1}{R_b} \sqrt{\frac{1}{C_b(C_d + C_b)}}$$

Equation IV.25

therefore:

$$R_b = \frac{1}{\omega_{max}} \sqrt{\frac{1}{C_b(C_d + C_b)}}$$

Equation IV.26

Table IV.1 shows the summary of these results:

Table IV.1 Series resistance ( $R_s$ ), depleted resistance and capacitance ( $R_d$  and  $C_d$ ), and bulk resistance and capacitance ( $R_b$  and  $C_b$ ) of ITO / M3EH-PPV / Al devices as a function of the thickness of the M3EH-PPV film.

| Film thickness (nm)            | 38   | 44   | 91   | 188  | 240  | 300  |
|--------------------------------|------|------|------|------|------|------|
| $R_s$ ( $\Omega$ )             | 30   | 30   | 30   | 40   | 52   | 41   |
| $R_d$ ( $\times 10^8 \Omega$ ) | 5.46 | 5.80 | -    | -    | -    | -    |
| $C_d$ ( $\times 10^{-9}$ F)    | 3.10 | 2.50 | 1.70 | 1.16 | 1.59 | 1.81 |
| $R_b$ ( $\times 10^4 \Omega$ ) | -    | -    | 9.88 | 10.9 | 10.4 | 17.3 |
| $C_b$ ( $\times 10^{-10}$ F)   | -    | -    | 47.7 | 12.8 | 9.72 | 8.55 |

From these results, we can have an approximate value of  $\epsilon_{r,d}$ , relative permittivity of the depleted region of the polymer. Indeed, both samples with 38 nm and 44 nm are fully depleted. Therefore their thickness is the thickness of the depleted zone.



Considering the geometrical value of the capacitor  $C_d$ :

$$C_d = \frac{\epsilon_0 \epsilon_{r,d} A}{W_d} \quad \text{Equation IV.27}$$

we can write:

$$\epsilon_{r,d} = \frac{W_d C_d}{\epsilon_0 A} \text{ and } W_d = \frac{\epsilon_0 \epsilon_{r,d} A}{C_d} \quad \text{Equation IV.28}$$

With  $A = 6 \times 10^{-6} \text{ m}^2$ , we obtained  $\epsilon_{r,d} \approx 2.09$ . Using this value, we can now calculate the width of the depleted region ( $W_d$ ) in the remaining 'thick' samples (from 91 to 300 nm) using Equation IV.28. The width of the bulk region can also be estimated using:

$$W_b = W - W_d \quad \text{Equation IV.29}$$

with  $W$  the total thickness of the sample.

Figure IV.7 shows the width of each zone as a function of the device thickness for the 'thick' samples and clearly shows that the width of the depleted region remains constant at  $W_d \approx 65 \text{ nm}$ :

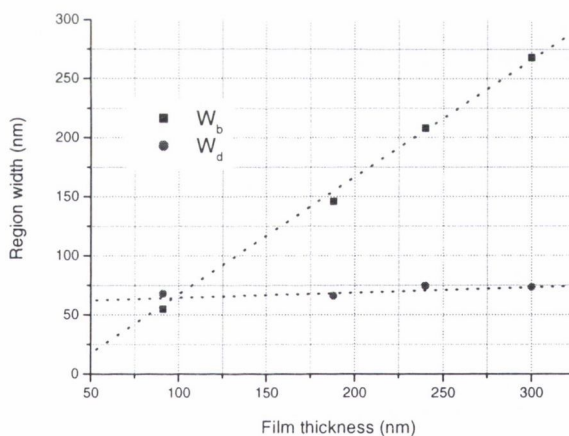


Figure IV.7 Width of the depleted and bulk regions as a function of the device thickness.

These results have clearly demonstrated that:

- a Schottky barrier is formed at the M3EH-PPV / Al interface;
- the width of this barrier is constant.

Figure IV.8 shows a schematic band diagram of the structure. The values of  $\Phi_{Al}$ ,  $\Phi_{ITO}$ ,  $HOMO_{M3EH-PPV}$ ,  $LUMO_{M3EH-PPV}$  are given in the literature.<sup>8</sup>

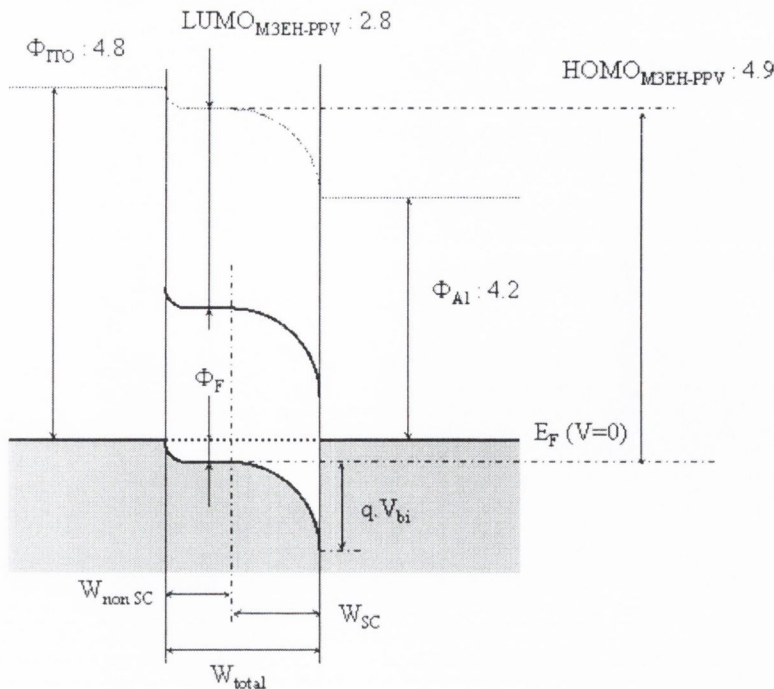


Figure IV.8 Schematic band diagram of the thick ITO / M3EH-PPV / Al devices.

IV.4.2. Relative Permittivity of M3EH-PPV

C(V) measurements were taken at 100 Hz for the ‘thick’ samples (91 to 300 nm) in order to measure the capacitance of the depleted region as a function of the applied DC bias. Results are shown in Figure IV.9:

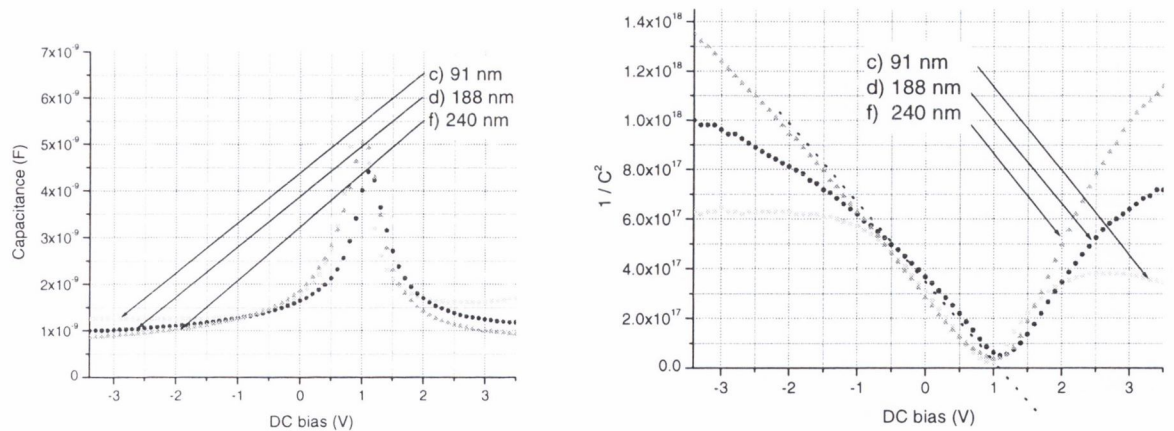


Figure IV.9 Capacitance-voltage C(V) measurements (left) and Mott-Schottky plots  $1/C^2(V)$  (right) for the of the thick ITO / M3EH-PPV / Al devices.

$1/C^2(V)$  Mott-Scottky plots are presented in Figure IV.9b and analysed as described in Section IV.3.2.1.3. The slope of the linear fit gives us the ‘doping concentration’ ( $N_A$ ), using  $\epsilon_{r,d} \approx 2.09$  from the previous section, and the built-in voltage ( $V_{bi}$ ) is given by the intercept with the origin.

The values of  $N_A$  and  $V_{bi}$ , are summarised in Table IV.2 for all samples:

Table IV.2 Doping concentration ( $N_A$ ) and built-in voltage ( $V_{bi}$ ) in ITO / M3EH-PPV / Al samples.

| Film thickness (nm)                        | 91   | 188  | 240  | 300  |
|--------------------------------------------|------|------|------|------|
| $N_A$ ( $\times 10^{16} \text{ cm}^{-3}$ ) | 6.10 | 3.37 | 5.62 | 7.09 |
| $V_{bi}$ (V)                               | 0.83 | 1.27 | 1.02 | 1.04 |

The average value for the doping concentration is  $N_A = (5.57 \pm 1.59) \times 10^{16} \text{ cm}^{-3}$ . Values of lower doping concentration, resulting in larger depleted region (over 100 nm) often as large as the sample, have been published.<sup>20</sup> Our relatively large doping concentration can be explained in terms of cleanliness of the raw material, which may present more impurities than the ones produced in industry.

Correlating  $C(V)$  and admittance data obtained in the previous section,  $\epsilon_{r,d}$  and  $\epsilon_{r,b}$ , relative permittivity of the bulk and the depleted regions respectively, can now be deduced. Indeed,  $\epsilon_{r,d}$  et  $\epsilon_{r,b}$  can be obtained with the slope of  $1/C_d$  vs.  $W_d$  and  $1/C_b$  vs.  $W_b = W - W_d$  respectively, as Equation IV.30 shows:

$$\frac{1}{C_d} = \frac{1}{\epsilon_0 \epsilon_{r,d} A} W_d \text{ and } \frac{1}{C_b} = \frac{1}{\epsilon_0 \epsilon_{r,b} A} W_b$$

Equation IV.30

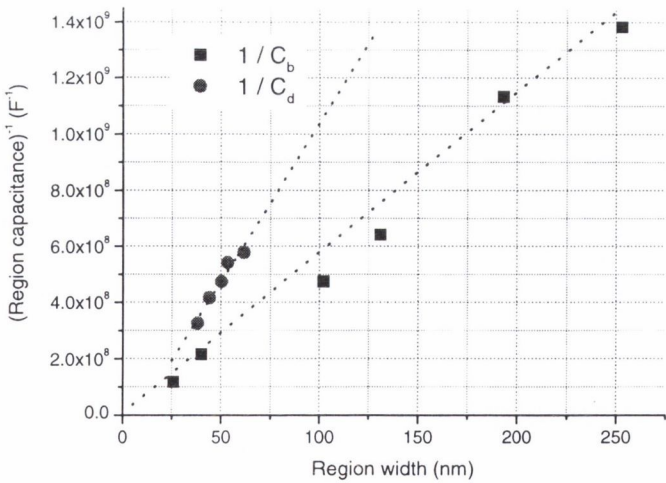


Figure IV.10  $1/C$  as a function of the width of either the depletion or bulk region.

$C_d$  and  $C_b$  are values obtained with admittance data (conductance), while  $W_d$  can be estimated, as presented in Section IV.3.2.1.2, with the  $C(V)$  data obtained above ( $N_A$ ,  $V_{bi}$ ):



$$W_d = \sqrt{\frac{2\epsilon_{r,d} V_{bi}}{qN_A}}$$

Equation IV.31

using  $\epsilon_{r,d} \approx 2.09$  as a first estimate.

The slope of both linear fits in Figure IV.10 gives us a value of both  $\epsilon_{r,b}$  et  $\epsilon_{r,d}$  using Equation IV.30. Interestingly, using the values found in re-calculating  $N_A$  (Equation IV.6) and then  $W_d$  (Equation IV.31), the same graphs can be re-plotted in order to obtain new values of  $\epsilon_{r,b}$  et  $\epsilon_{r,d}$ . This recurrence process can be used until we get stable values.

We finally found:

- $\epsilon_{r,b} = 3.65$
- $\epsilon_{r,d} = 2.19$

IV.4.3. Fermi Level in M3EH-PPV

To further investigate the intrinsic properties of M3EH-PPV, I(V) characteristics of the ITO / M3EH-PPV / Al devices were measured and are shown in Figure IV.11:

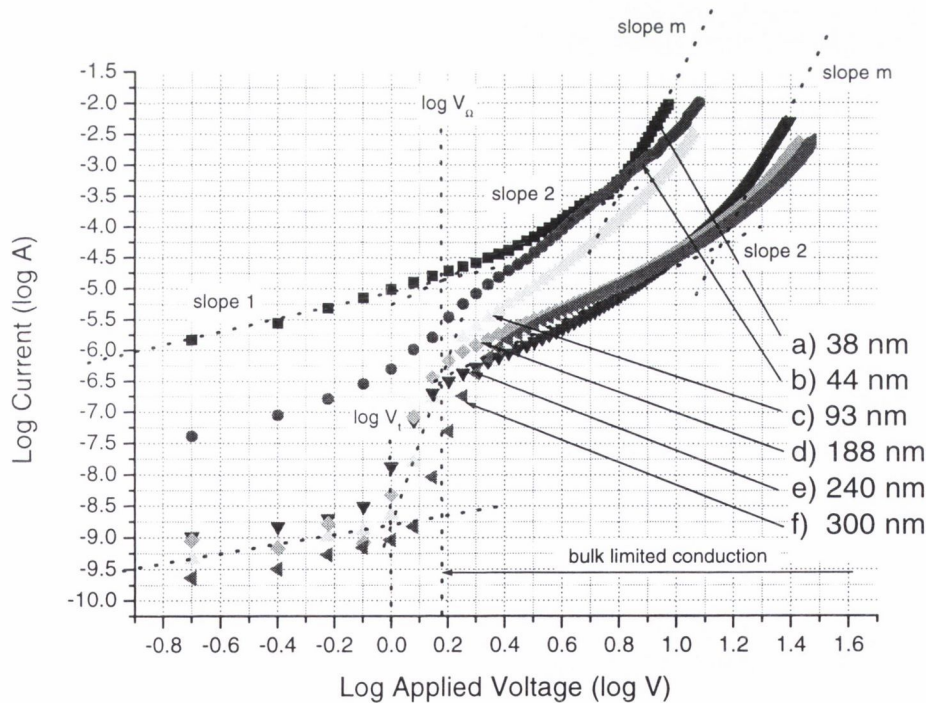


Figure IV.11 Current-voltage characteristics of each device tested in this Section.

Once again, on can clearly distinguish two groups of samples:

- ‘thin’ samples (38 nm and 44 nm) with a bulk limited conduction mechanism, and

- ‘thick’ samples (91 to 300 nm), with a transition to a bulk limited conduction mechanism above a particular voltage  $V_t$ .

The values of both  $V_{bi}$  from the previous Section and  $V_t$  are summarised in Table IV.3:

Table IV.3 Built-in voltage ( $V_{bi}$ ) and DC transition voltage ( $V_t$ ) in ITO / M3EH-PPV / Al devices.

| Film thickness (nm) | 91   | 188  | 240  | 300  |
|---------------------|------|------|------|------|
| $V_{bi}$ (V)        | 0.83 | 1.27 | 1.02 | 1.04 |
| $V_t$ (V)           | 0.74 | 0.93 | 0.89 | 0.63 |

Correlation between the voltage at which this transition occurs,  $V_t$ , and the built-in voltage,  $V_{bi}$ , measured by  $C(V)$  is obvious. Again  $V_t$  does not depend on the thickness of the film. However,  $V_t = (0.80 \pm 0.14)$  V is slightly lower than  $V_{bi} = (1.04 \pm 0.18)$  V.

In the light of Section IV.3.2.1.1 and the energy diagram shown in Figure IV.8, the Fermi level  $\Phi_F$ , intrinsic value of the polymer M3EH-PPV, can be obtained using the relation:

$$\Phi_F = \text{HOMO}_{\text{M3EH-PPV}} - \Phi_{\text{Al}} - qV_{bi}$$

Equation IV.32

The Fermi level value  $\Phi_F$  is relative to the HOMO level of M3EH-PPV and we found:

- using  $V_{bi}$ ,  $\Phi_F = (-0.38 \pm 0.18)$  eV,
- using  $V_t$ ,  $\Phi_F = (-0.06 \pm 0.14)$  eV.

In both cases the Fermi level lies in the HOMO and the semiconducting polymer can be considered as positively degenerated as described by Sze.<sup>16</sup> This result is consistent with the widely recognised mainly hole conduction in PPV derivatives, due to the fact that negative charges are trapped in much greater quantities within the device. We can therefore conclude that the majority carriers in M3EH-PPV are positive polarons.

**IV.4.4. Mobility of the Majority Carriers in M3EH-PPV**

From the  $I(V)$  characteristic of the thin 38 nm sample, the density and mobility of the majority carriers in M3EH-PPV can also be deduced. As found in the above Section, we can assume that the majority carriers in M3EH-PPV are positive polarons (or more commonly named holes).

The ohmic conduction region, as showed by Equation IV.11, can be described by:

$$\log I = M + N.\log V \quad \text{Equation IV.33}$$

with N being ideally equal to one.

The space-charge limited conduction (SCLC) region, as showed by Equation IV.17, can be described by:

$$\log I = O + P.\log V \quad \text{Equation IV.34}$$

with P being ideally equal to two.

We found:  $M = -5.10$ ,  $N = 1.06$ ,  $O = -5.20$ ,  $P = 2.10$ . Using these results we can now determine the transition voltage between the ohmic and the SCLC region:  $V_\Omega$ . Indeed, the transition current  $I_\Omega$  and voltage  $V_\Omega$  can be used in both Equation IV.33 and IV.34:

$$\log I_\Omega = M + N.\log V_\Omega = O + P.\log V_\Omega$$

As a result:

$$V_\Omega = 10^{\frac{M-O}{P-N}} \quad \text{Equation IV.35}$$

The voltage at which the transition from the ohmic region to the SCLC region therefore was in our sample:  $V_\Omega = 1.25$  V.

From Equation IV.16, we can easily write:

$$p = \frac{9.V_\Omega \epsilon}{8.qd^2} \quad \text{Equation IV.36}$$

and the estimated density of positive carriers is:  $p = 1.08 \times 10^{17} \text{ cm}^{-3}$ . This value is consistent with the C(V) data, which gave a doping concentration of  $6.20 \times 10^{16} \text{ cm}^{-3}$ .

The mobility of the majority carriers can now be calculated using the ohmic region, the SCLC region, as well as an estimate from the admittance data:

Firstly, the ohmic mobility can be calculated using Equations IV.11 and IV.12, which give:

$$I = \frac{qpA\mu_p}{d} V \quad \text{Equation IV.37}$$

Therefore:

$$\mu_p = \frac{10^M d}{qpA} \quad \text{Equation IV.38}$$

where M is from Equation IV.33.

Secondly, the SCLC mobility can be calculated using Equation IV.17, which gives:

$$I = \frac{9.\epsilon A \mu_p}{8.d^3} V \quad \text{Equation IV.39}$$



Therefore:

$$\mu_p = \frac{8.10^0 d^3}{9.\varepsilon A}$$

Equation IV.40

where O is from Equation IV.33.

Thirdly, the admittance mobility can be calculated using:

$$R_b = \frac{d}{\sigma A} = \frac{d}{qN_A\mu_p A}$$

Equation IV.41

Therefore:

$$\mu_p = \frac{d}{qAN_AR_b}$$

Equation IV.42

Table IV.4 summarises the results of the ohmic, SCLC, admittance mobility of the majority carriers in M3EH-PPV calculated from Equations IV.38, IV.40 and IV.42 respectively:

Table IV.4 Ohmic, SCLC and admittance mobility of majority carriers in M3EH-PPV.

|                     |                                             |
|---------------------|---------------------------------------------|
| ohmic mobility      | $2.91\times10^{-12} \text{ m}^2/\text{V.s}$ |
| SCLC mobility       | $2.88\times10^{-12} \text{ m}^2/\text{V.s}$ |
| admittance mobility | $6.59\times10^{-12} \text{ m}^2/\text{V.s}$ |

Theses values are all of the same order of magnitude and consistent with values published in the literature.<sup>8</sup> It reflects the low conductivity, yet greater than insulators, of un-doped organic semiconductors.

IV.5. Conclusions

Recent progress on organic light emitting diodes’ (OLEDs) basic principles, electrical conduction mechanisms and technical issues has been reviewed.

In particular, we presented the electrode limited injection model at a Schottky barrier interface between a polymer and a metal, and the space charge limited bulk conduction mechanism. OLEDs’ current-voltage characteristics can be analysed using either model in order to extract intrinsic parameters such as the polymer’s Fermi energy level, or majority charge carriers’ mobility.

We studied ITO / M3EH-PPV / Al devices and found that:

- a depleted zone appeared at the M3EH-PPV / Al interface consistent to a Schottky barrier;
- the width of the depleted region was constant:  $W = 65 \text{ nm}$ ;
- the doping concentration was:  $N_A = 6.20 \times 10^{16} \text{ cm}^{-3}$ ;
- the built in voltage was:  $V_{bi} = 1.08 \text{ V}$ ;
- the Fermi level lied near the HOMO band.

We concluded that M3EH-PPV is a semiconducting polymer, which exhibit a highly p-doped-like behaviour. This result is consistent to the well established fact that positive carriers are in majority in polymer semiconductors, since negative charges are trapped in greater numbers.

We were also able to determine both the bulk and depleted value of the relative permittivity of M3EH-PPV:

- $\epsilon_{r,b} = 3.65$ ;
- $\epsilon_{r,d} = 2.19$ ;

with  $\epsilon_{r,b}$  and  $\epsilon_{r,d}$  the bulk and depleted value of the relative permittivity respectively.

These values are the signature of the fact that the depleted region, which is empty of free carriers, has a larger value of resistance and therefore a smaller value of relative permittivity.

Finally, we estimated the majority carrier's mobility in M3EH-PPV using three different methods: from the ohmic and space charge limited conduction mechanisms in the  $I(V)$  characteristics and from the value of the bulk resistance obtained from admittance measurements. The three values were of the same order of magnitude ( $10^{-12} \text{ m}^2/\text{V.s}$ ), which indicated a good estimate of the real value, and were consistent with values obtained in the literature.

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### V.1. Introduction

As discussed in Chapter I, carbon nanotubes have so far reached few viable practical applications. We believe that the most accessible applications are those using nanotubes to improve the performance of existing functional organic devices. In this Chapter, we will show the effects of using a composite fabricated from carbon nanotubes and PmPV, as an electron-transport layer in organic light-emitting diodes. The conductivity and the electrode behaviour of the nanotube and polymer composite will be discussed in Section V.2 and Section V.3 respectively. Current-voltage-luminance and electroluminescent spectral measurements of double layer devices using the composite as an electron-transport layer, triple layer devices with a composite electron-transport layer and PVK as a hole-transport layer, as well as M3EH-PPV single layer devices will be presented and discussed in Section V.4.

### V.2. Conductivity of the Nanotube and Polymer Composite

In this Section, we will show the conductive nature of the nanotube and polymer composite used in this Thesis. We will discuss both DC and AC conductivity results in terms of percolation and will first introduce the theory of percolation.

#### V.2.1. Percolation Theory

##### V.2.1.1. Introduction

Percolation deals with the effects of varying the richness of interconnections present in a random system. The basic idea of percolation is the existence of a sharp transition at which the long-range connectivity of the system appears. This transition occurs abruptly when some generalised density in this system reaches a critical value: percolation threshold.

Due to the importance of percolation in application, many mathematical theories have been developed to describe percolation. Table V.1 lists some situations to which percolation ideas have been applied:

Table V.1 Applications of percolation theory.

| Phenomenon or System                               | Transition                   |
|----------------------------------------------------|------------------------------|
| Flow of liquid in a porous medium                  | Local / extended wetting     |
| Spread of disease in a population                  | Containment / epidemic       |
| Communication or resistor networks                 | Disconnected / connected     |
| Conductor-insulator composite materials            | Insulator / metal            |
| Discontinuous metal films                          | Insulator / metal            |
| Composite superconductor-metal oxides              | Normal / superconducting     |
| Stochastic star formation in spiral galaxies       | Nonpropagation / propagation |
| Quarks in nuclear matter                           | Confinement / nonconfinement |
| Thin helium films on surface                       | Normal / superfluid          |
| Metal-atom dispersion in insulators                | Insulator / metal            |
| Dilute magnets                                     | Para / ferromagnetic         |
| Polymer gelation, vulcanisation                    | Liquid / gel                 |
| The glass transition                               | Liquid / gel                 |
| Mobility edge in amorphous semiconductors          | Localised / extended states  |
| Variable-range hopping in amorphous semiconductors | Resistor network analogy     |

V.2.1.2. Bond Percolation and Site Percolation

Consider the passage of a fluid through a network of channels, with some of the channels randomly blocked. A sketch of such a bond-percolation situation, with the channel network idealised as a 2D honeycomb lattice, is shown in Figure V.1:

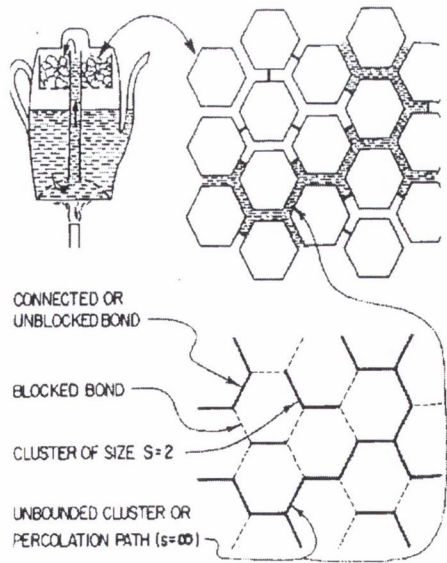


Figure V.1 Percolation of a fluid through a porous medium that is modelled as a network of interconnected channels (some of which are blocked at random) constitutes a bond-percolation process. The connectivity map shown in the lower part of the figure corresponds to the array of blockages shown in the upper diagram. In the latter, liquid is shown in the channels which belong to the percolation path.

There is a possible percolation path in this network, as labelled in the lower part of the figure. This kind of bond-percolation can thus be viewed in terms of the flow of some generalised fluid through a medium represented by interconnecting pipes, some of which are valved shut as shown in Figure V.2b.

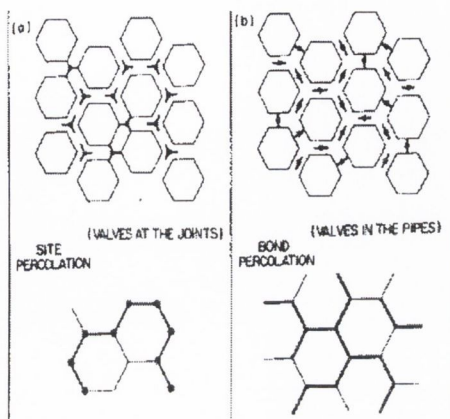


Figure V.2 Plumbing analogy for the distinction between site percolation and bond percolation.

Such a plumbing analogy can similarly be constructed for site-percolation, as indicated in Figure V.2a. Now the valves are placed at the joints (intersections), rather than in the pipes, of the plumbing network.

It is clear that a combined percolation process can be considered which corresponds to valves placed both in the pipes and on at the joints. It is called site-bond percolation.

### V.2.1.3. Characteristic Functions of Lattice Percolation

Figure V.3 portrays a portion of a square lattice upon which a site-percolation process has been superimposed. The three frames represent the same region of the lattice at three different concentrations: The fraction of filled sites ( $p$ ) grows from 0.25 to 0.50 to 0.75 in going from Figure V.3a to V.3b to V.3c. Nearest-neighbour filled sites (which are connected, *i.e.* belong to the same linked cluster) are shown joined by heavy lines, and several cluster sizes are indicated.

For  $p \ll 1$ , the low-concentration regime, nearly all of the filled sites occur as isolated singlets, clusters of size one. Choosing a site at random, the chance of it being a filled site is  $p$ . Since there are four nearest neighbours in the square lattice, and  $p \ll 1$ , the likelihood that it belongs to a cluster of size two is  $4p^2$ , which is negligible. By similarly counting the possibilities, the probability of a given filled site belonging to a cluster of size 3 is  $18p^3$  for the square lattice, which is even more negligible in the small- $p$  limit. In fact, at low



concentration the probability of encountering a cluster of size  $s$  is of the order of  $p^s$ . Thus the cluster-size distribution, in the  $p \rightarrow 0$  low-density limit, is sharply peaked at  $s = 1$  and falls off exponentially with increasing  $s$ .

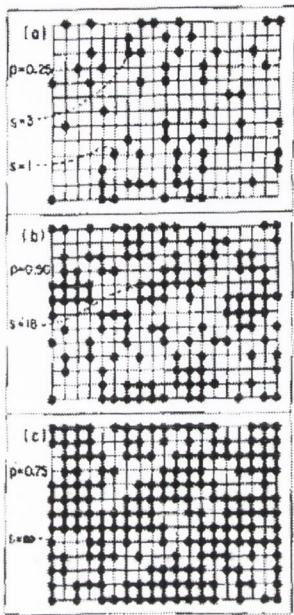


Figure V.3 Site percolation on the square lattice, illustrating various cluster sizes ( $s$ ) for three values of  $p$ , the fraction of filled sites. For  $p = 0.75$ , an unbounded cluster is present.

The cluster-size distribution is typically expressed as a discrete function  $n(s)$ , defined at  $s = 1, 2, 3, 4, \dots$ , where  $n(s)$  is the number of clusters of size  $s$  divided by the total number of sites in the huge system. Away from  $p \approx 0$ , it is not easy to specify  $n(s)$  analytically. For site percolation on the square lattice, we already knew that at  $p \rightarrow 0$ ,  $n(s) \sim p, 4p^2, 18p^3$ , for  $s = 1, 2, 3$ . We are interested in the qualitative change that takes place at the percolation threshold. As  $p$  increases, the proportion of filled sites belonging to  $s \geq 2$  clusters increases, since the probability of continuing a cluster, by finding an adjacent filled site, becomes larger. The mean cluster size, which we will denote as  $s_{av}$ , grows. Since the number of sites occurring in clusters of size  $s$  is proportional to  $s.n(s)$ , then the site-weighted average cluster size is given by:

$$s_{av} = \frac{\sum_{s=1}^{\infty} s^2 . n(s)}{\sum_{s=1}^{\infty} s . n(s)} \tag{Equation V.1}$$

$s_{av}$  starts out (for small  $p$ ) at unity, reflecting the total dominance of singlet clusters at low concentrations. As  $p$  increases,  $s_{av}$  increases very rapidly indeed, as indicated in Figure V.3. In Figure V.3c we observe a large cluster (spanning cluster) which extends across the

entire sample. For an ideal sample with infinite size, this infinitely extended or unbounded cluster is called the percolation cluster or percolation path.

The critical event in the connectivity has occurred between Figure V.3b and V.3c, *i.e.*, between  $p = 0.50$  and  $0.75$ . Actually the percolation path is first observed at  $p \approx 0.59$ , which is the percolation threshold  $p_c$  for site percolation on the 2D square lattice. It signals the point at which the system of interconnections has thickened sufficiently for a connected network to propagate infinitely. Above  $p_c$ , the percolation path exists; below  $p_c$ , it does not. From  $p = p_c$  to  $p = 1$ , the percolation path fleshes out until it fills the entire lattice. The growth in volume of the infinite cluster is shown as the heavy curve in Figure V.4. This curve describes the percolation probability  $P(p)$ , which is the fraction of the entire system that is taken up by the infinite percolation path. The percolation probability vanishes until the concentration of connections reaches  $p_c$ , and then it rises very steeply. Eventually  $P(p)$  approaches  $p$  as  $p$  approaches 1. It marks the qualitative change at  $p_c$  as the opportunity for long-range connectivity goes from nothing to something, and it provides the principal measure of the growth in volume of the extended network as the concentration increases beyond  $p$ . We also draw the curve of normalised conductivity  $\sigma/\sigma_0$  in Figure V.4, where  $\sigma_0$  is the conductivity of the net at  $p = p_c$ . Obviously it also vanishes below  $p_c$ .

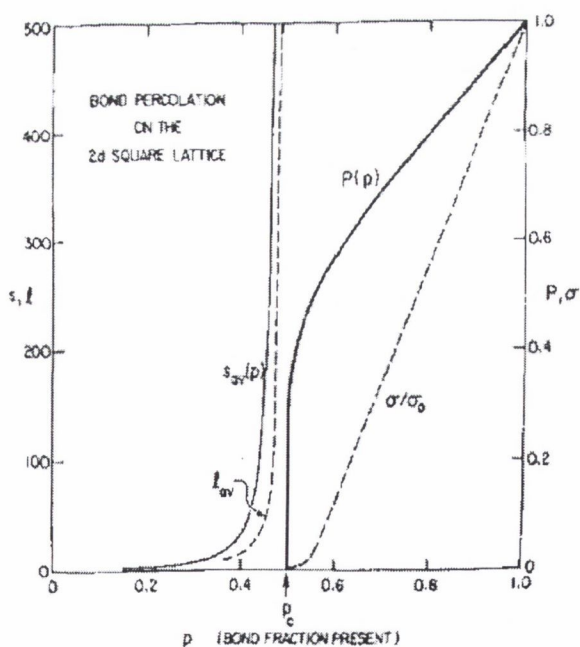


Figure V.4 Behaviour of key properties that characterise bond percolation on the square lattice in two dimensions, as a function of the fraction  $p$  of filled bonds.

Going back to the low-density regime  $0 < p < p_c$ , the functions  $P(p)$  and  $\sigma/\sigma_0$  give us no physical information about the percolation system.

The average cluster size  $s_{av}(p)$  defined by Equation V.1 diverges as the density draws near to  $p_c$ . The number of connected sites or bonds,  $s$ , provides the natural measure of the content or volume or mass of a given cluster, while  $l$  provides a measure of the cluster's characteristic linear dimension.  $l$  and  $s$  are separate and different attributes. Most notably, because of the subtlety and complexity of the question of cluster shape for the large clusters that occur close to threshold, we shall find that the conventionally expected relationship  $s \sim l^d$  does not hold as  $l, s \rightarrow \infty$  (Here  $d$  is the space dimensionality of the system). In other words, the effective dimensionality of the cluster is no longer the original one of the net.

It is simplest to take  $l$  to be the spanning length of the cluster, which is defined as the maximum separation of two sites (or bonds, for bond percolation) in the cluster:

$$l = \max |r_i - r_j|_{i, j \text{ in cluster}} \quad \text{Equation V.2}$$

For a given  $p$ , the characteristic length obtained by averaging  $l$  over all clusters is the mean spanning length  $l_{av}(p)$ . This quantity plays a part in analogous to that played by the correlation length  $\xi$  in phase transition. Both provide length scales which correspond to the graininess of the system. This graininess is very fine far away from the percolation threshold or phase transition, and coarsens dramatically as the transition is approached. This property is indicated by the divergence of  $l_{av}$  at  $p_c$ .

These four characteristic functions displayed in Figure V.4 suffice to illustrate the main features of the system. Two of them,  $s_{av}(p)$  and  $l_{av}(p)$ , describe geometric aspects of the growth of the clusters below the percolation threshold. These quantities are finite below  $p_c$  and infinite above. They may be regarded as being complementary to the quantities  $P(p)$  and  $\sigma(p)$ , which vanish below  $p_c$  and are finite above. Once the percolation path appears, our attention then shifts to  $P$  and  $\sigma$ , which describe the macroscopically extended (delocalised) cluster.

#### V.2.1.4. Critical Exponents of Characteristic Functions

In the regime very close to the percolation threshold, the critical region in which  $|p - p_c| \ll 1$ , the percolation functions are observed to obey power-law dependences on the deviation from threshold  $|p - p_c|$ . For the divergence of the average size and linear dimension of the clusters as  $p_c$  is approached from below:



$$(p - p_c) \rightarrow 0 : s_{av} \approx \frac{1}{(p_c - p)^\gamma}, l_{av} \approx \frac{1}{(p_c - p)^\nu} \quad \text{Equation V.3}$$

For the initial increase in the content and conductivity of the percolation path:

$$(p - p_c) \rightarrow 0 : P \approx (p - p_c)^\beta, \sigma \approx (p - p_c)^t \quad \text{Equation V.4}$$

In Equations V.3 and V.4, the critical exponents  $\gamma$ ,  $\nu$ ,  $\beta$  and  $t$  are found to be positive non-integers for lattices in two and three dimensions, as presented in Table V.2:

Table V.2 Critical exponents controlling the near-threshold scaling behaviour of key quantities in percolation.

| Functional Form close to $p = p_c$           | Exponent | Value of Exponent in d Dimension |       |       |
|----------------------------------------------|----------|----------------------------------|-------|-------|
|                                              |          | d = 2                            | d = 3 | d ≥ 6 |
| $P(p) \sim (p - p_c)^\beta$                  | $\beta$  | 0.14                             | 0.4   | 1     |
| $\sigma(p) \sim (p - p_c)^t$                 | $t$      | 1.1                              | 1.65  | 3     |
| $s_{av}(p) \sim (p_c - p)^{-\gamma}$         | $\gamma$ | 2.4                              | 1.7   | 1     |
| $l_{av}(p) \sim (p_c - p)^{-\nu}$            | $\nu$    | 1.35                             | 0.85  | 0.5   |
| $s \rightarrow \infty : n(s) \sim s^{-\tau}$ | $\tau$   | 2.06                             | 2.2   | 2.5   |
| $s \rightarrow \infty : l(s) \sim s^{(1/f)}$ | $f$      | 1.9                              | 2.6   | 4     |

The percolation threshold  $p_c$  is a quantity which varies greatly from lattice to lattice. For instance, the critical concentration for site percolation on the diamond lattice is more than double that for fcc lattice. It also depends on the type of percolation (site or bond). However, the critical exponents do not depend on the details of lattice geometry. They are the same for all lattices of the same dimensionality  $d$ . In a word, the critical exponents are dimensional invariants. Each exponent has a fixed value for a given dimensionality  $d$ , without regard to the specific nature of the short-range structure.

Instead of describing the asymptotic behaviour of some functions as  $|p - p_c| \rightarrow 0$ , the exponent  $\tau$  describes the behaviour, at  $p = p_c$ , of the cluster-size distribution in the asymptotic limit of large cluster size:

$$p = p_c, s \rightarrow \infty : n(s) \approx s^{-\tau} \quad \text{Equation V.5}$$

Experiments show that for large clusters, the relationship between the cluster size  $s$  and the spanning length  $l$  is well described by a power law:

$$p = p_c, s \rightarrow \infty : s \approx l^f$$

Equation V.6

This relation links a length dimension ( $l$ ) with a measure of content or volume ( $s$ ), and the exponent that normally appears in such a relation in the place of  $f$  is the space dimensionality  $d$ . But in percolation system,  $f$  does not coincide with  $d$  for large clusters. Instead, it is found to be smaller than  $d$ . The dimensionality deficit  $d - f$  (Hausdorff co-dimension) provides the best measure of insubstantialness of the percolation cluster. It vanishes for an ordinary, substantial body.

V.2.1.5.      **Scaling Laws of Critical Exponents**

There exist some important relations between these critical exponents:

$$f = \frac{d}{\tau - 1}$$

Equation V.7

$$d = f + \frac{\beta}{\nu}$$

Equation V.8

$$2\beta + \gamma = d\nu$$

Equation V.9

There are scaling laws in sufficient supply to ensure that only two of the six critical exponents can be independently set. These laws can be theoretically proved and are experimentally verified.

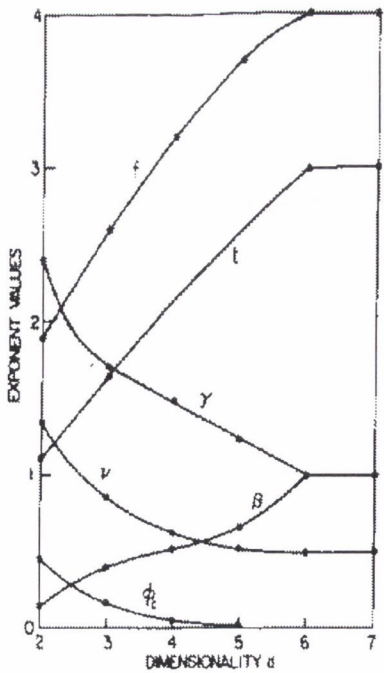


Figure V.5 Dimensionality dependences of the critical exponents for percolation.

In Figure V.5 these critical exponents are plotted as functions of the space dimension  $d$ . Their dimensional universality is clearly indicated. Another striking feature is the existence of marginal dimensionality  $d^* = 6$ , the critical exponents no longer change and keep their constant classical (mean field) values for  $d \geq d^*$ . For  $d \geq d^*$ , the coordination number  $z$  is so large that Mean Field Approximation can be reasonably applied on the system without making any essential mistake. Here the coordination number  $z$  is defined as the number of nearest neighbours for a given site.  $z$  goes up much more rapidly than space dimensionality  $d$ . For instance, for close-packed lattice  $z(d)$  is 2, 6, 12, 24, 40, 72, 126, 240 for  $d = 1$  through 8, respectively.

#### V.2.1.6. Continuum Percolation

We first introduce a basic geometric quantity in continuum percolation. For a given  $d$ -dimensional lattice  $j$ , we imagine there are equal-sized, touching, non-overlapping,  $d$ -dimensional spheres centred on the lattice sites. Packing factor  $v(j,d)$  of the lattice is defined as the fraction of space occupied by all of these spheres. If a fraction  $p$  of the spheres are made of metal, and the others are made of plastic, there is a definite site-percolation threshold  $p_c(j,d)$ , which denotes the fraction of number of metal spheres as the conductor-insulator transition occurs for the entire system. The critical fraction of space occupied by metal spheres is then given by:

$$\phi_c(j,d) = v(j,d)p_c(j,d) \quad \text{Equation V.10}$$

$v$  and  $p_c$  definitely depend on the specific lattice structure  $j$ . Interestingly, however,  $\Phi$  is found to be almost independent of the specific lattice structure  $j$ .  $\Phi_c(j,d)$  can be written as  $\Phi_c(d)$ . This conclusion can be drawn from Figure V.6 (For bond percolation, the packing factor  $v$  is replaced by lattice coordination number  $z$ ).

The critical volume fraction  $\Phi_c$  is an approximate dimensional invariant for the threshold in lattice percolation processes. Hence in continuum percolation, we can let the volume fraction  $\Phi$  play the same role as  $p$  plays in lattice percolation. Both of them provide a measure of the difficulty of percolation in systems.



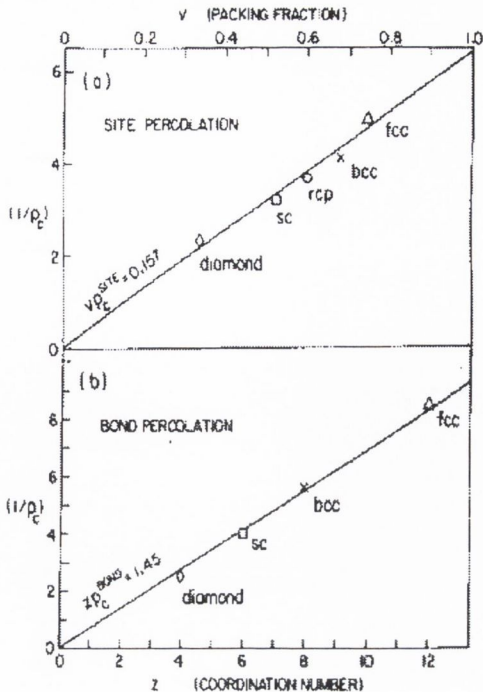


Figure V.6 Two empirical correlations between percolation threshold and lattice connectivity for various 3D structures. For site percolation, the correlation between the reciprocal of the percolation threshold and the lattice packing factor is shown in (a). For bond percolation, the correlation between the reciprocal of the threshold and the lattice coordination is shown in (b).

Figure V.7 shows a typical example of continuum percolation: stochastic-geometry conductor-insulator film photolithographically generated from laser speckle patterns. The black areas are metal. We can use the area fraction of metal film  $\Phi$  as the percolation criterion, because this concept dispenses with the need for a lattice.

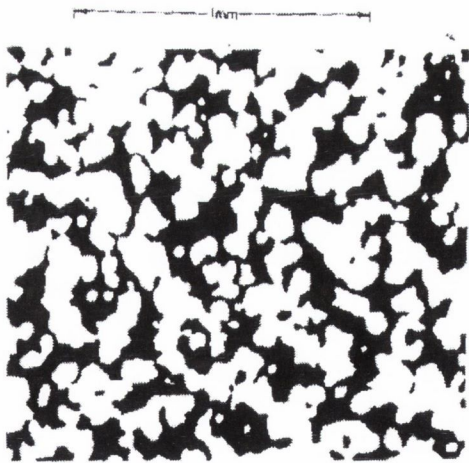


Figure V.7 Stochastic-geometry conductor-insulator films photolithographically generated from laser speckle patterns. The black areas are metal.

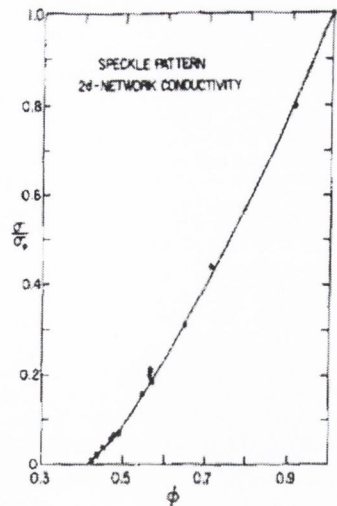


Figure V.8 Conductivity measurements on films of the type shown in Figure V.7, as a function of metal area fraction.

Figure V.8 shows the results of electrical measurements on a series of such films. The normalised conductivity  $\sigma/\sigma_0$  scales as:

$$\frac{\sigma}{\sigma_0} \approx (\phi - \phi_c)^t \tag{Equation V.11}$$

where  $t \approx 1.25$ , slightly different from the conductivity exponent  $t$  in 2D lattice percolation (see Table V.2).

**V.2.1.7. Critical Transport Properties of Percolation**

The Nodes-Links-Blobs (NLB) model provides a quantitative description of the percolation system. In this picture, the percolation system above the threshold is modelled as chain (links) with resistance:

$$r_{\text{link}} \approx r_{\text{bond}} (p - p_c)^{-\varphi} \tag{Equation V.12}$$

which join at nodes uniformly separated by a distance (correlation length):

$$\xi \approx (p - p_c)^{-\nu} \tag{Equation V.13}$$

The index  $\varphi$  depends on the way in which these bonds are arranged to form a link, *i.e.*, the twistedness of a typical chain. A conducting link consists of both singly connected bonds, which are responsible for the dc resistance and which, if cut, disconnect the two end nodes, as well as multiply connected segments, the blobs, as depicted in Figure V.9.

Nodes can only be removed away from the network by cutting more than two links. In an applied field  $E$ , the voltage drop across a chain is of the order  $\xi E$ , giving a current  $\xi E/r_{\text{link}}$  and current density  $J = (\xi E/r_{\text{link}})/\xi^{d-1}$  in  $d$  dimensions. Then, in the neighbourhood of the

threshold, the conductivity  $\sigma = J / E$  behaves like  $(p-p_c)^t$  with:

$$t = (d - 2)\nu + \varphi$$

Equation V.14

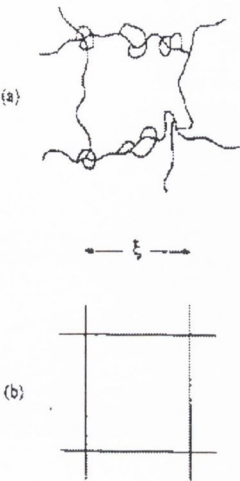


Figure V.9 a) Schematic picture of a section of the backbone containing four nodes. Upper and lower links contain blobs; left- and right-hand links do not. b) Analytically solvable model of the backbone, which replaces all of the different links with identical typical links.

Consider a  $d$ -dimensional composite material, a fraction  $p$  of which is conducting, with  $1-p$  being insulating. For the regime above percolation threshold, the material can carry a current. A high local current density can cause enhanced heat production and lead to a considerable rise in local temperature. When the temperature of a hot spot reaches the fusing point of the metallic isthmus, an irreversible geometrical change occurs as the isthmus is disconnected. As observed in experiments on 2D semi-continuous metal films, the breaking process is self-sustaining once the first spot is broken. The entire conducting network quickly breaks apart, and the film resistance jumps to a high level. Usually, the first fused isthmus is the weakest and narrowest one in the network. Now consider a hypercube with volume  $L^d$ , which has faces of area  $L^{d-1}$ . If a current is injected into one face and removed from the opposite, the critical current for the hypercube will be given by:

$$I_B = i_B \left( \frac{L}{\xi} \right)^{d-1} \approx \xi^{1-d} \approx (p - p_c)^{\nu(d-1)}$$

Equation V.15

where  $I_B$  is the breakdown current of a typical link.

Combined with Equation V.14, we find that the macroscopic breakdown current scales with the resistance  $R$  of the system as  $I_B \sim R^a$ , where:

$$a = \frac{\nu(d-1)}{\nu(d-2) + \varphi}$$

Equation V.16



## V.2.2. Results and Discussion

### V.2.2.1. Introduction

Al / PmPV+MWNT / Al devices were prepared and both DC and AC conductivity measurements were carried out. All DC current voltage  $I(V)$  characteristics were ohmic in the voltage range studied ( $-0.15 - 0.15$  V) and the conductivities  $\sigma_{DC}$  were calculated from the slope of the  $I(V)$  curves as seen in Section III.4.1.1.

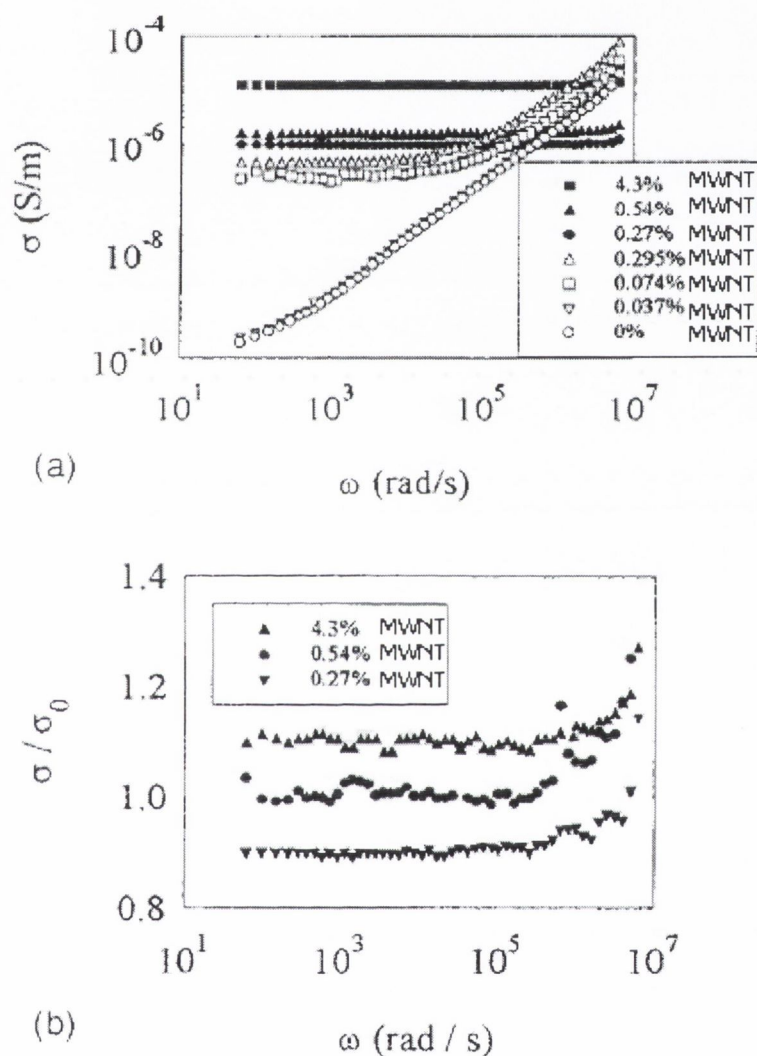


Figure V.10 a) Frequency dependent conductivity for some of the samples studied in this work. Filled symbols represent PmPV based composites while unfilled symbols represent PVA based composites. b) Frequency dependent conductivity results for three of the PmPV composites. The shift to frequency dependent conductivity can clearly be seen above  $10^5$  rad/s. In the interest of clarity these data have been normalised to the  $\sigma_0$  value and two of the curves shifted by 10%.

The real part of the AC conductivities ( $\sigma_{AC}$  as seen in Section III.4.1.2) for selected nanotube concentrations are presented in Figure V.10a as a function of angular frequency  $\omega$  for both PmPV and polyvinylalcohol (PVA) composites (PVA composites were prepared and tested by B. Kilbride<sup>1</sup> and are shown for comparison purposes). The

frequency dependent conductivity for the PmPV composites can be more clearly seen in Figure V.10b.

### V.2.2.2. Percolation Threshold

Two cases must be distinguished: those with low nanotube mass fraction ( $p < 0.037\%$ ) and those with higher mass fraction. In the former case conductivity is frequency dependent in the frequency range studied with a slope of unity on a log-log scale. This is in good agreement with the expression  $\sigma = \omega \epsilon_r'' \epsilon_0$ , valid for dielectric materials.<sup>2</sup> The higher mass fraction curves are characterised by a frequency independent conductivity  $\sigma_0$  up to a critical frequency  $\omega_0$ , followed by a region of increasing conductivity. This frequency independent conductivity is indicative of non zero DC conductivity, *i.e.* non-dielectric behaviour. Shown in Figure V.11a are the DC conductivity  $\sigma_{DC}$  and the frequency independent AC conductivity  $\sigma_0$  as a function of nanotube mass fraction  $p$  for both PmPV and higher mass fraction non-dielectric PVA composites. In general, good agreement is observed between the DC and AC data with the conductivities of both composite types appearing to fall on the same curve. As the mass fraction is increased, the conductivity increases from approximately  $10^{-12}$  S/m for the host material to over  $10^{-5}$  S/m for the 4.3 % PmPV sample, with most of the increase occurring below  $p = 0.5$  %. Extrapolation to  $p = 100$  % using the scaling law described in Equation V.4 gives an approximate conductivity of  $10^{-3}$  S/m, which is 6 orders of magnitude lower than the conductivity expected for a mat of multi-walled nanotubes.<sup>3</sup> This discrepancy may be partly due to the fact that as the film thickness ( $\sim 80$  nm) is much less than the length of the nanotubes (length  $\approx 1 - 2$  mm, diameter  $\approx 15 - 20$  nm), they are constrained to lie in the plane of the film, resulting in a larger effective film thickness.

However this explanation cannot explain a discrepancy of 6 orders of magnitude. Alternatively, previous studies have shown that individual nanotubes in PmPV based composites tend to be coated by a thick polymer layer.<sup>4</sup> This layer is thought to form in the solution phase and is responsible for the solubility of nanotubes in composite solutions. This is expected to result in poor electrical contact between individual nanotubes, resulting in lower effective conductivity. This is because the highest resistance sections in the electrical pathway, manifested by the inter-nanotube connections, dominate the macroscopic conductivity.

The second explanation seems more likely as further measurements of conductivity in the

plane of the film (not shown) were observed to be only marginally higher than these measurements perpendicular to the plane of the film. It should be pointed out that in plane conductivity measurements could only be carried out for high conductivity samples due to limited detection sensitivity.

According to classical percolation theory, introduced earlier, the conductivity of composite materials as conductive filler content is increased can be described by a scaling law as in Equation V.4. The exponent  $t$  is expected to depend on sample dimensionality with calculated values of  $t = 1.1$  and  $t = 1.65$  in two and three dimensions, respectively, as shown in Table V.2. It should be noted however that these values vary depending on the authors and the type of simulation used.<sup>5-7</sup> Both AC and DC conductivities for each host polymer have been plotted logarithmically and are shown in Figure V.11.

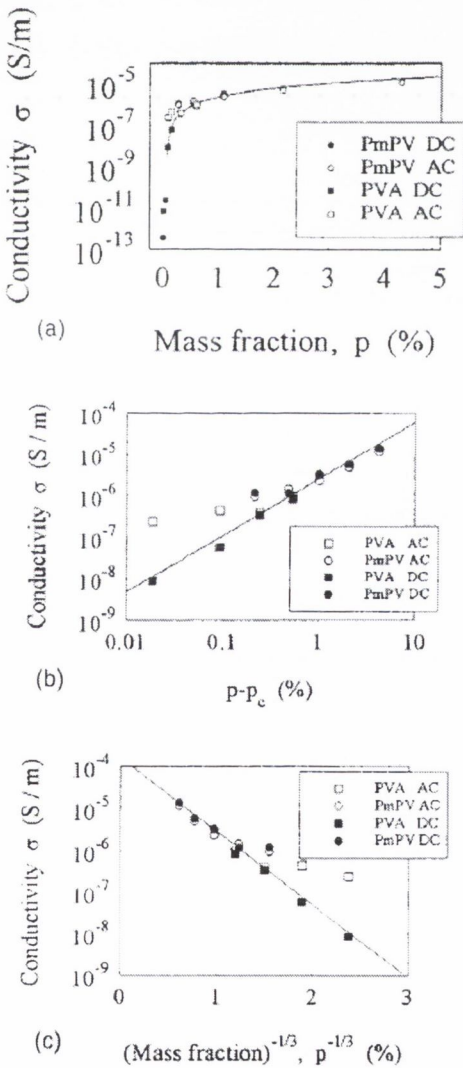


Figure V.11 a) DC and frequency independent AC conductivity for all samples studied in this work. b) Logarithmic plot of conductivity vs. reduced mass fraction. The solid line is a fit of the dc data to the percolation scaling law Equation V.4 giving  $p_c = 0.055\%$  and  $t = 1.36$ . c) Plot of the log of conductivity against  $p^{-1/3}$ .



The solid line is a fit of Equation V.4 to the DC data for both composites and gives  $p_c = 0.055 \pm 0.01$  % by mass ( $p_c = 0.029 \pm 0.01$  % by volume) and  $t = 1.36 \pm 0.13$ . This fit was found by incrementally varying  $p_c$  until the best linear fit to the equation was found.

This extremely low percolation threshold compares with values for fibular filler particles found in the literature of 0.035 % by volume for polyaniline – polyvinylalcohol composites<sup>8</sup> to 1.1 % by volume for polymer – carbon black composites.<sup>9</sup> It also compares well with previous values found for polymer – nanotube composites of 8 % by mass for low purity MWNT – polymer composites<sup>10</sup> and 1.1 % by mass for low purity single-walled nanotube–polymer composites.<sup>11</sup> This value is, however, rather low compared with percolation thresholds calculated by Munson – McGee for cylindrical conductors in a insulating matrix. In this study statistical analysis was used to show that a percolation threshold in the region of 1 % – 5 % is expected for a system of conductive fillers of aspect ratio between 50 and 130 (consistent with the nanotubes used in this study).<sup>12</sup> However, it should be pointed out that the value presented here may be artificially reduced by individual nanotubes shorting through the thin film in the sandwiched structure configuration.

### V.2.2.3. Dimensionality

While the low value of  $t = 1.36$  suggests charge transport through a two dimensional object this seems unlikely as the charge must flow through the film and not along any surface or interface. Values of  $t$  in the region of 1.3 have, in fact, been observed in a number of bulk systems. These include  $t = 1.33$  and  $t = 1.42$  in separate polyaniline-PMMA networks<sup>13,14</sup> and  $t = 1.3$  in polyethelene – carbon black composites.<sup>15</sup>

One possible explanation for this is that the charge must flow solely through the conductive network which itself may be a fractal object of fractal dimension in the region of 2. An alternative suggestion has been made by Reghu *et al.* in a study of percolation in polyaniline – PMMA networks.<sup>16</sup> They observed the critical exponent  $t = 1.99$  at 10 K indicating transport in three dimensions. However on return to room temperature the exponent decreased to  $t = 1.33$ . This was suggested to arise from thermally induced hopping transport between disconnected (or weakly connected) parts of the network. This latter description seems plausible and supports the suggestion that the nanotubes are separated by a thick polymer barrier.

While the data for the DC conductivity for all samples agrees well with Equation V.4, the AC data at low mass fraction diverges from the DC data and is approximately 1 order of magnitude higher for the 0.074 % mass fraction PVA sample. It is well known for hopping conduction that the DC conductivity is limited by the maximum of the range of activation energies<sup>17</sup> as a carrier hops through the sample. In contrast, AC conduction is limited by the highest barrier experienced as the carrier travels for one half period of the field, as we have seen in Section II.2.5.1. It is possible for low mass fraction, just above the percolation threshold, that AC transport in a small fraction of the network is more favourable than DC conduction through the entire incipient network as large energy barriers can be avoided. This may result in  $\sigma_{AC} > \sigma_{DC}$ .

As the mass fraction is increased, the number of inter-nanotube connections increases and many conductive paths become available. In this situation, substantial numbers of carriers travelling through the entire network follow paths which avoid the larger barriers and the DC conductivity approaches the AC conductivity. Alternatively at mass fractions just above the percolation threshold, relatively large networks may exist which are not connected to the main network linking the electrodes. These networks could contribute a significant component of the AC conductivity which would not appear in the DC conductivity, again resulting in  $\sigma_{AC} > \sigma_{DC}$ . Given that each nanotube is probably coated with polymer which acts as a potential barrier to inter-nanotube hopping, it is likely that electrical conductivity in this system is limited by tunnelling between conductive regions (*i.e.* nanotubes).

This behaviour is described by the fluctuation induced tunnelling model<sup>18</sup> which takes into account tunnelling through potential barriers of varying height due to local temperature fluctuations, predicting a conductivity described by, as introduced in Section II.2.5.4:

$$\sigma_{DC} \propto \exp\left(-\frac{T_1}{T + T_0}\right) \quad \text{Equation V.17}$$

where  $T_1 = WA\varepsilon^2/8\pi k_B$  and  $T_0 = 2T_1/\pi W\chi$ , with  $\chi = (2mV_0/h^2)^{1/2}$ ,  $\varepsilon = 4V_0/qW$ ,  $q$  and  $m$  the electron charge and mass,  $V_0$  the potential barrier height,  $W$  the internanotube gap width, and  $A$  the area of capacitance formed at the junction.

It can easily be seen that for constant temperature this equation can be written in the form<sup>6</sup>  $\ln(\sigma_{DC}) \propto -\omega$ . If we assume that the nanotube content in the polymer host is homogenous,



the composite conductivity at a given temperature can be described by the behaviour of a single tunnel junction where the gap width is  $\omega \propto p^{-1/3}$  due to spatial considerations. This suggests the DC conductivity should follow the following rule  $\ln(\sigma_{DC}) \propto -p^{-1/3}$ . In Figure V.11c, both the DC and AC conductivity data presented in Figure V.11b are shown on a semilogarithmic scale versus  $p^{-1/3}$ . The expected linear relationship is observed, with the solid line as a fit to the DC conductivity data.

This plot further supports the idea that the current is limited by potential barriers between nanotubes due to the polymer coating.

### V.3. MWNT and Polymer Composite Injecting Electrode

#### V.3.1. Introduction

While many organic materials can be used as hole-transport layers, materials that work effectively as electron-transport layers are not so common. There are various reasons for this, n-type undoped polymers are rare while electron mobilities tend to be low as a result of the efficient trapping of negative carriers by impurities, *etc.* One possible alternative to polymers or molecular materials as electron-transport layers would be to use a high mobility material such as carbon nanotubes.

In this Section, we will show how the conductive nanotube and polymer composite studied above can be in fact considered as an electron injecting electrode that can be used in organic based devices. The latter will be discussed in the next Section.

#### V.3.2. Impedance Measurements

Figure V.12 shows the complex modulus (as defined in Section III.4.1.2.1) Cole-Cole plot of three devices: Al / M3EH-PPV / Al, Al / M3EH-PPV / Pt and ITO / M3EH-PPV / PmPV+MWNT / Al. The layer of M3EH-PPV was 300 nm thick.

Since the M3EH-PPV layer is significantly thicker than 65 nm, we expect to observe a Schottky barrier at the interface between the polymer and Al, as seen in Section III.3.2.1. Indeed, the Cole-Cole plots show three regions in the Al / M3EH-PPV / Al sample, and two regions in the Al / M3EH-PPV / Pt, which indicate the presence of a barrier at the Al / M3EH-PPV only.



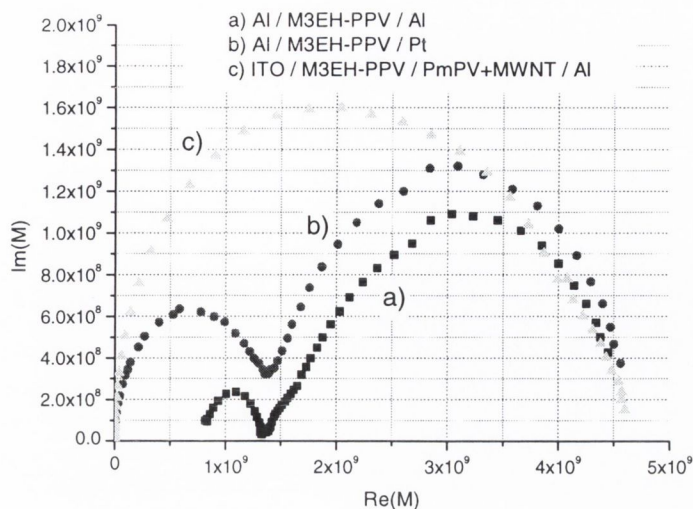


Figure V.12 Complex modulus Cole-Cole plots of Al / M3EH-PPV / Al, Al / M3EH-PPV / Pt, and ITO / M3EH-PPV / PmPV+MWNT / Al devices.

The ITO / M3EH-PPV / PmPV+MWNT / Al sample however appears to be modelled by only one capacitor – resistor system, which will correspond to the bulk of the polymer. This result indicates that the Schottky barrier originally present at the M3EH-PPV / Al interface vanishes following the introduction of the conductive PmPV+MWNT composite layer. This result strongly supports the idea of using the nanotube and polymer composite as an injecting electrode in organic light-emitting diodes for example.

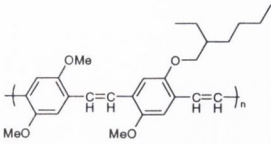
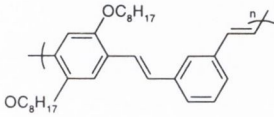
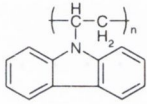
However, the Cole-Cole semi-circle of the ITO / M3EH-PPV / PmPV+MWNT / Al sample is not perfect and this could be explained by the presence of another capacitor – resistor system in the model. This would suggest that yet another barrier occurs at the interface between the polymer and most likely the composite layer. This will be investigated in the next Section.

## V.4. MWNT and Polymer Composite in OLEDs

### V.4.1. Introduction

A number of multilayer organic light-emitting diodes (OLEDs), incorporating electron- and hole-transport layers, in conjunction with an emissive layer, were fabricated. Table V.3 shows the different materials used for the different layers of the OLEDs tested in this Section.

Table V.3 Chemical structure, and film thickness for the different organic layers: ETL (electron-transport layer), EL (emissive layer) and HTL (hole-transport layer) used in this Section.

| Layer | Material    | Chemical structure                                                                            | Thickness |
|-------|-------------|-----------------------------------------------------------------------------------------------|-----------|
|       |             |                                                                                               | (nm)      |
| ETL   | PmPV + MWNT |  + nanotubes | 110       |
| EL    | M3EH-PPV    |              | 110       |
| HTL   | PVK         |              | 125       |

The devices studied in this work consisted of:

- a single M3EH-PPV layer (to be referred to as SL: ITO / M3EH-PPV / Al);
- a double layered device consisting of PVK as a hole-transport layer and M3EH-PPV as the emissive layer (to be referred to as DLH: ITO / PVK / M3EH-PPV / Al);
- six double layer devices with M3EH-PPV as the emissive layer and composite films of six various mass ratios as the electron-transport layer (to be referred to as DLE: ITO / M3EH-PPV / composite / Al);
- six triple layer devices with PVK as the hole-transport layer, M3EH-PPV as the emissive layer and composite films of six various mass ratios as the electron-transport layer (to be referred to as TL: ITO / PVK / M3EH-PPV / composite / Al) as depicted in Figure V.13:

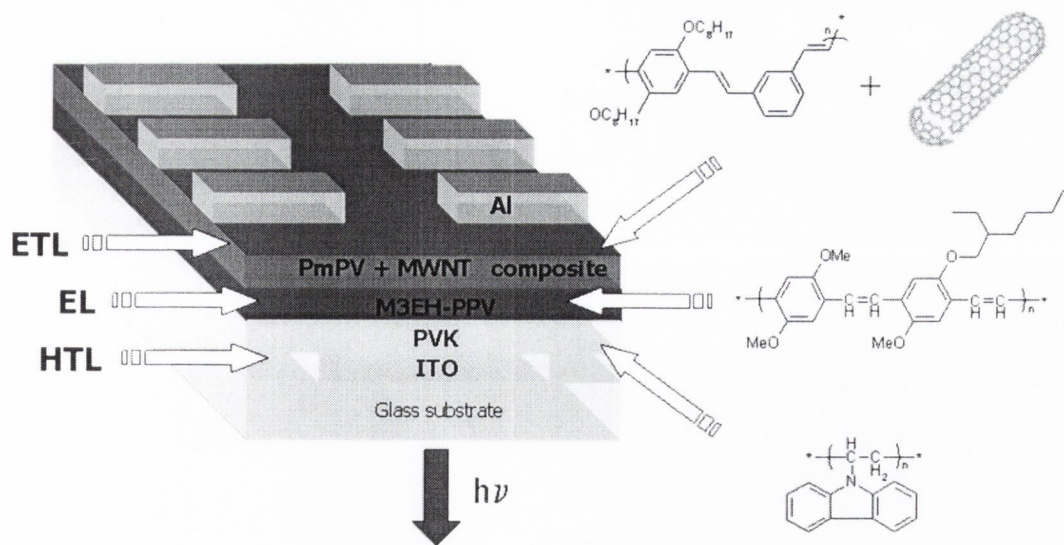


Figure V.13 Device architecture of the triple layer devices tested in this Section.

V.4.2. Results

Shown in Figure V.14 are typical current voltage characteristics for the four types of OLEDs (SL, DLH, DLE and TL) used in this study. In the case of the DLE and TL devices the composite mass ratio was 1.2 %.

It can clearly be seen that these curves tend to shift along the voltage axis from the SL to the TL device as device thickness increases. This can be characterised by an arbitrary voltage required to drive a current of 15 mA/cm<sup>2</sup> through each device.

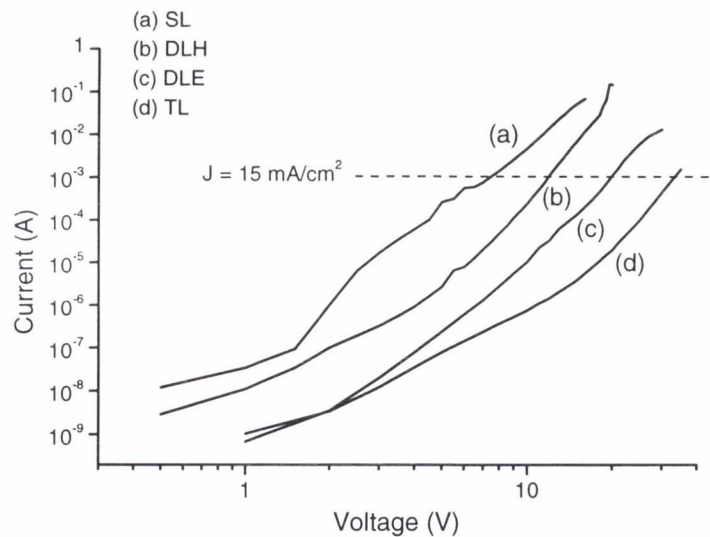


Figure V.14 Typical current-voltage characteristics for the main types of devices used in this work: SL (ITO / M3EH-PPV / Al), DLH (ITO / PVK / M3EH-PPV / Al), DLE (ITO / M3EH-PPV / composite / Al) and TL (ITO / PVK / M3EH-PPV / composite / Al).



This ‘operating voltage’ increases from 7.6 V in the SL to 13.2 V, 23.8 V and 30.6 V in the DLH, DLE and TL devices respectively.

Shown in Figure V.15 are luminance (in arbitrary units) versus current density plots for the four devices described in Figure V.14. These curves are linear in the low current density region as expected. These devices can be compared using the luminance at the arbitrary current density of  $15 \text{ mA/cm}^2$ . This ‘relative efficiency’ value (in arbitrary unit) increases from 3.4 for the SL device to 3.7, 15.8 and 19.0 for the DLH, DLE and TL respectively.

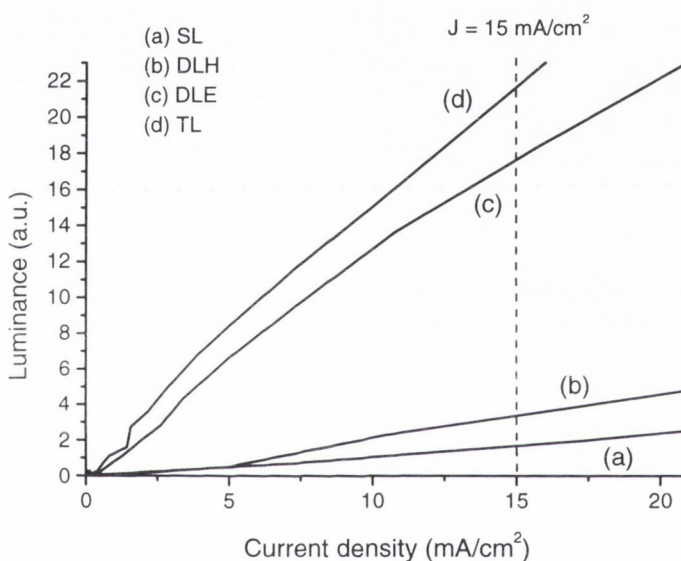


Figure V.15 Typical luminance-current relationships for the main types of devices: SL (ITO / M3EH-PPV / Al), DLH (ITO / PVK / M3EH-PPV / Al), DLE (ITO / M3EH-PPV / composite / Al) and TL (ITO / PVK / M3EH-PPV / composite / Al).

As mentioned previously, a range of nanotube mass ratios was used in the electron-transport layer for the DLE and TL devices. While only the results for the 1.2 % composite devices are reported in Figures V.14 and V.15, the operating voltage and relative efficiency for the whole range of electron-transport layers mass ratios are given in Table V.4.

Two broad trends are observed. In the DLE, as the nanotube mass ratio is increased from 0 to 4.8 % the operating voltage falls from 36.0 V to 17.6 V. Similarly in the case of the TL device this voltage falls from 39.5 V to 24.4 V. However these voltages are still in excess of the operating voltages observed in the absence of the composite layer. These values were 7.6 V and 13.2 V for the SL and DLH devices respectively.

Table V.4 Operating voltage (arbitrary voltage required to drive 15 mA/cm<sup>2</sup>) and relative efficiency (luminance at the arbitrary current density of 15 mA/cm<sup>2</sup>) for each device: SL (ITO / M3EH-PPV / Al), DLH (ITO / PVK / M3EH-PPV / Al), DLE (ITO / M3EH-PPV / composite / Al) and TL (ITO / PVK / M3EH-PPV / composite / Al).

| Device |                      |     | Operating voltage | Effective operating field | Relative efficiency |
|--------|----------------------|-----|-------------------|---------------------------|---------------------|
|        |                      |     | (V)               | (V/nm)                    | (a.u.)              |
| SL     |                      |     | 7.6               | 0.076                     | 3.4                 |
| DLH    |                      |     | 13.2              | 0.066                     | 3.7                 |
| DLE    | carbon nanotubes (%) | 0   | 36.0              | 0.360                     | 4.5                 |
|        |                      | 0.3 | 26.7              | 0.267                     | 6.5                 |
|        |                      | 0.6 | 26.1              | 0.261                     | 9.5                 |
|        |                      | 1.2 | 23.8              | 0.238                     | 15.8                |
|        |                      | 2.4 | 19.3              | 0.193                     | 5.7                 |
|        |                      | 4.8 | 17.6              | 0.176                     | 2.9                 |
| TL     | carbon nanotubes (%) | 0   | 39.5              | 0.198                     | 3.0                 |
|        |                      | 0.3 | 32.4              | 0.162                     | 8.8                 |
|        |                      | 0.6 | 31.8              | 0.159                     | 12.7                |
|        |                      | 1.2 | 30.6              | 0.153                     | 19.0                |
|        |                      | 2.4 | 25.1              | 0.126                     | 12.6                |
|        |                      | 4.8 | 24.4              | 0.122                     | 5.3                 |

For the SL and DLH devices the relative efficiencies were 3.4 and 3.7 (in arbitrary units) respectively. For both the DLE and TL devices as the nanotube mass ratio increased, the relative efficiency rose to a maximum of 15.8 and 19.0 respectively at a loading level of 1.2 %, before falling steadily to 2.9 and 5.3 at 4.8 %.

In addition, for the four devices described above electroluminescent spectra were measured and are presented in Figure V.16. For comparison purposes the EL spectrum for a single layer PmPV device is also shown. No significant spectral variations could be seen for any of the devices studied. For the four types of OLEDs used in this work, the spectra are

consistent with emission from M3EH-PPV. No emission was observed from the low wavelength spectral region associated with electroluminescence from PmPV.

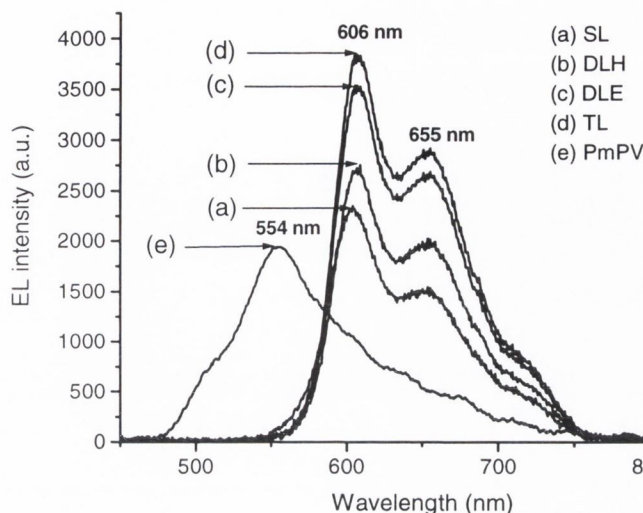


Figure V.16 Electroluminescence (EL) spectra for the SL, DLH, DLE and TL devices. For comparison a PmPV single layer device EL spectrum is plotted. The spectra of the four different types of devices are consistent with emission from M3EH-PPV.

### V.4.3. Discussion

As shown in Figure V.14 the current voltage curves for the four types of device seem to show a clear trend with the largest current for a given voltage flowing through the SL device and the smallest current flowing in the TL device. However this graph is slightly misleading as these devices vary in thickness from approximately 110 nm to 345 nm for the SL and TL devices respectively. Thus, the electric field is the more relevant parameter in this case. Consideration must also be given to the relative conductivities of the three individual layers.

The conductivity of M3EH-PPV as estimated from Figure V.14 is approximately  $5 \times 10^{-10}$  S/m, while PVK can be assumed to exhibit conductivity of similar magnitude. The conductivity of the 1.2 % composite layer however is  $2.83 \times 10^{-4}$  S/m. As this is five orders of magnitude higher than the other two materials we can assume that very little voltage is dropped across this layer. This suggests that virtually all of the applied voltage is dropped across the more resistive materials. Thus, we must use an effective thickness when calculating the effective field. This effective thickness is the combined thickness of the resistive layers in the device and does not include the thickness of the composite layer. Thus, the effective devices were 110 nm, 235 nm, 110 nm and 235 nm for the SL, DLH,



DLE and TL devices respectively. Plots of current versus effective fields calculated using these thicknesses are presented in Figure V.17.

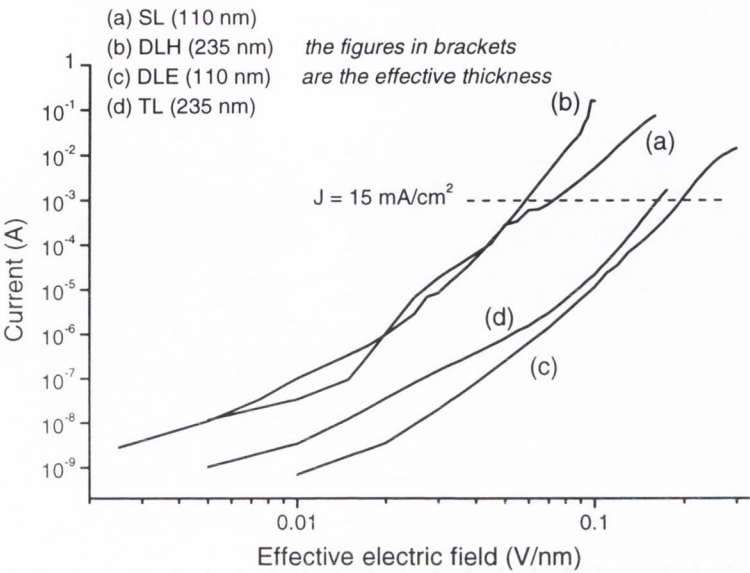


Figure V.17 Typical current-effective electric field characteristics for the main types of devices used in this work: SL, DLH, DLE and TL. For each device the effective electric field represents the applied voltage divided by the effective thickness defined as the device thickness without considering the polymer-nanotube composite layer. The composite exhibits conductivity  $10^5$  greater than PVK and M3EH-PPV so it could be assumed that almost no voltage would be dropped across the composite layer.

In this plot the four curves are clearly split into two groups of two. At lower field values are the SL and DLH current-effective field characteristics, while those for the DLE and TL devices are shifted up in field. The only difference between these groups is the presence of a composite electron-transport layer in the higher field curves. This data strongly suggests that for the materials used in this study the introduction of the electron-transport layer is accompanied by an increase in the potential barriers at the M3EH-PPV / composite interface, blocking the passage of holes into the composite layer, as it was suspected in Section V.3. Electron injection into the M3EH-PPV is probably also impeded at low nanotube doping level. This is most likely due to the complicated energy structure in the composite with states associated with the semiconducting polymer and both semiconducting and metallic nanotubes.

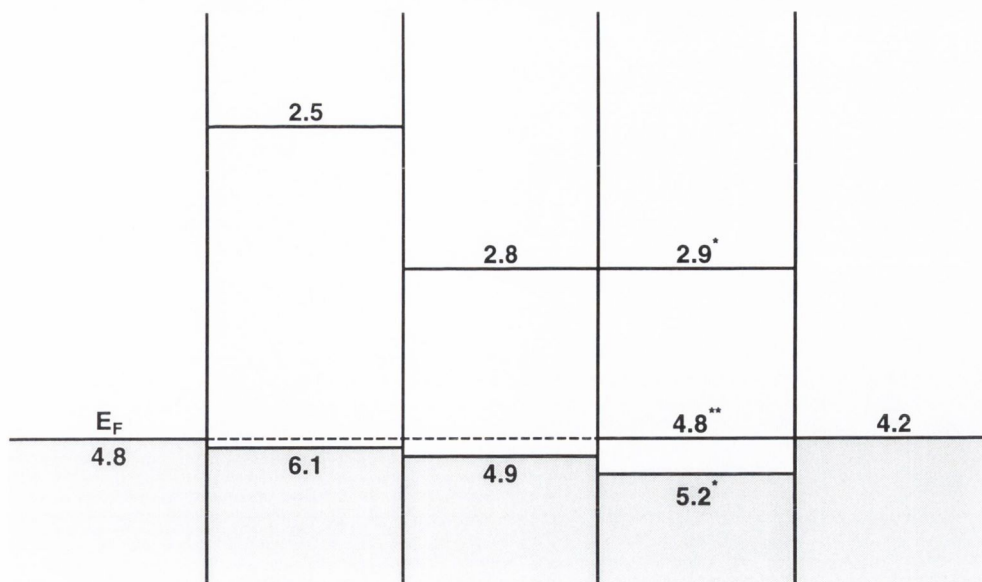


Figure V.18 Proposed schematic band diagram for a TL device (ITO / PVK / M3EH-PPV / composite / Al) after equalisation of Fermi energy levels. The HOMO and LUMO of the polymers (PVK, M3EH-PPV and PmPV) and work functions of electrodes (ITO, Al) and nanotubes are in eV. The stars on PmPV and MWNT refer to the HOMO/LUMO of PmPV and work function of the nanotubes respectively.

Shown in Figure V.18 is a proposed schematic diagram representing the band structure of a TL device, after equalisation of Fermi energy levels. As PVK and M3EH-PPV are organic semiconductors, their Fermi energy levels lie close to the Highest Occupied Molecular Orbits (HOMO) allowing efficient hole injection from the ITO anode. The situation is not so clear for the composite electron-transport layer. While aluminium has a work function of 4.2 eV, multi-walled carbon nanotubes have been experimentally shown to have a work function<sup>19</sup> in the region of 4.8 eV. This should suggest that the composite should act as a hole-injection layer.

However, electroluminescence is observed from the M3EH-PPV layer, so it is clear that electrons are injected from the cathode and through the composite layer. While it is probable that the difference between the nanotube work function and the M3EH-PPV Lowest Unoccupied Molecular Orbits (LUMO) (2.8 eV) is responsible for the potential barrier inferred from the current-effective electric field data, this is probably not a complete picture. Field enhancement due to curvature effect at nanotube tips probably plays a more important role in the injection of electron in the emissive layer.

The potential barrier however seems to be dependent on nanotube mass ratio. As the nanotube mass ratio is increased (not shown) the current flowing for a given voltage

increases. This can be clearly seen in Figure V.19b and Table V.5 where the operating voltage can be seen to fall as the mass ratio rises. This suggests that the potential barrier associated with the relative band energies of M3EH-PPV and the composite falls as more nanotubes are introduced into the system. This could possibly be explained by the formation of a new band as the nanotube concentration increases or curvature related field enhancement at the nanotube tips. However it should be noted that as the current in the DLE or TL devices never reaches the level observed in the SL, barrier effects are significant even at high nanotube mass ratios.

Another effect to be noted is that more current is observed in the TL device than in the DLE for a given voltage. The difference between these structures is the presence of a hole-transport layer in the TL device. This result shows that this PVK layer acts to improve band matching and hence hole injection at the ITO electrode in these devices.

The electroluminescence spectra presented in Figure V.16 showed no spectral variations for all different devices with an emission wavelength characteristic of M3EH-PPV. Therefore, we can assume that every singlet exciton's radiative decay occurs in the M3EH-PPV layer. This result is of great importance since it shows that no radiative recombination occurs within the composite layer and emphasises that the composite only acts to inject electrons into the emissive layer. Nevertheless this data doesn't exclude the formation of singlet excitons in the composite layer but shows that their decays are non radiative.

Shown in Figure V.19a is the electroluminescence at a given current as a function of nanotube mass ratio for the DLE and TL devices. This number is proportional to the relative efficiency of each device. For both DLE and TL devices this efficiency value increases to a maximum at approximately 1.2 % mass ratio before falling by ca. 80 % from the peak value. As both PVK and M3EH-PPV have good hole-transport properties it is probable that a significant number of holes travel from the ITO to the M3EH-PPV / composite interface where they are confined by the potential barrier caused by the difference in M3EH-PPV and composite band energies. Thus, it is probable that formation of singlet excitons is limited by the number of electrons entering the M3EH-PPV. Thus, as the nanotube mass ratio is increased and more electrons enter the M3EH-PPV, more excitons are formed and the luminescent intensity increases.



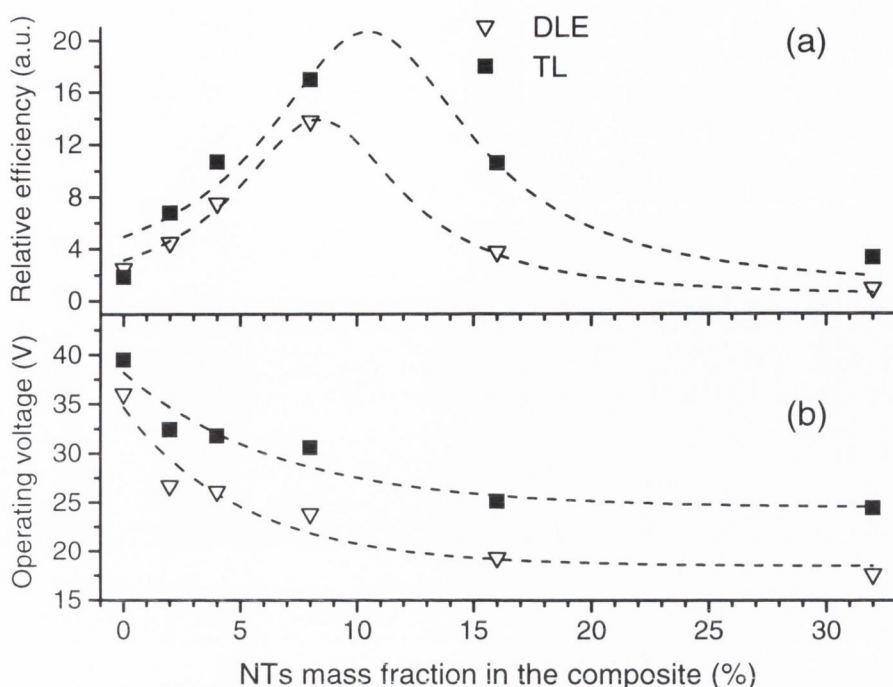


Figure V.19 a) Relative efficiency (luminance at the arbitrary current density of  $15 \text{ mA/cm}^2$ ), and b) operating voltage (arbitrary voltage required to drive  $15 \text{ mA/cm}^2$ ) as a function of nanotube to polymer mass ratio for the DLE (ITO / M3EH-PPV / composite / Al) and TL (ITO / PVK / M3EH-PPV / composite / Al) devices.

As electron injection into the M3EH-PPV increases with nanotube content, we would expect to see a plateau in the efficiency as the mass ratio is increased in the absence of any change in the hole current. However Figure V.19a shows that the efficiency reaches a maximum for the 1.2 % sample before dropping to close to the 0 % value by 4.8 % mass ratio. This shows that this picture is too simplistic and some other effects must occur. While PL shows that singlet excitons in PmPV formed by photoexcitation are quenched by the presence of nanotubes, this quenching is much less than expected. This will be discussed later in Section VII.2.1. The PL intensity for the 4.8 % sample was reduced by only 42 % relative to the pure PmPV. Thus, even if all excitons were formed in the M3EH-PPV, near the interface, quenching due to nanotubes cannot explain a fall in EL of approximately 80 % relative to the 1.2 % doping composite TL device. Other quenching processes such as singlet-singlet exciton annihilation are also unlikely in this case.

While it is likely that the barrier to electrons at the M3EH-PPV / composite interface falls as nanotube mass ratio increases, we have not considered changes in the barrier to holes travelling in the other direction. We have assumed that holes are confined in the M3EH-PPV by a potential barrier at the composite interface. Increased electron current then

allows the formation of more excitons by better current balance. However if the barrier to holes was also dependent on nanotube mass ratio, this confinement could be reduced resulting in the leakage of holes into the composite. As a result, even though we have more electrons in the recombination zone, we are losing holes faster due to leakage above 1.2 % nanotube mass ratio. As a result less singlet excitons are formed resulting in lower EL intensity.

While the luminance efficiency (photons/injected charges) appears to increase in the presence of the composite electron-transport layer, current density flowing through the devices actually falls. This means that the device power efficiency (photons/watt) is lowered upon the introduction of the carbon nanotubes. We have assumed that this is partly due to a barrier effect at the M3EH-PPV / composite interface. However, it must be noted that the composite layer was spin coated onto the M3EH-PPV layer. As toluene used for the composite is a common solvent for both materials, a degree of mixing can be expected at the interface. This is known to degrade carrier injection.<sup>20,21</sup>

In fact, an increase in current injection of up to six orders of magnitude has been observed<sup>22</sup> using the composite in heterojunctions with clean interfaces (Al / PMMA / composite / Al). This effect was not observed for devices where mixing had occurred (Al / PmPV / composite / Al). This suggests that electron injection from the composite could be substantially improved by careful choice, with regard to solvent, of the emissive layer or the use of host polymers, such as water-soluble polyvinylalcohol (PVA), in the composite material.

## V.5. Conclusions

In this Chapter, we studied and analysed the conductive nature of the nanotube and polymer composite and its use in organic light-emitting diodes.

As regards the conductivity of the nanotube and polymer composite, both DC and AC conductivities were measured for a series of composite thin films with varying nanotube mass fraction. In all cases DC  $I(V)$  characteristics were ohmic, while in general the AC conductivities displayed two regions: a low frequency region of constant conductivity and a high frequency region of increasing conductivity.

All DC conductivities followed the percolation scaling law with percolation threshold  $p_c =$

0.055 % by mass and exponent  $t = 1.36$ . While AC conductivities for higher mass fraction composites fell on the same curve as the DC measurements, those for the lower mass fraction samples exhibited significantly higher conductivity.

The extrapolated conductivity for a nanotube film was significantly lower than expected with  $\sigma_{NT} = 10^{-3}$  S/m. This was due to a thick coating of polymer, resulting in poor electrical connection between nanotubes, suggesting that conduction in this system is due to fluctuation induced tunnelling.

As regards the use of the composite in M3EH-PPV based OLEDs, introduction of the composite layer causes a potential barrier to both holes and electrons at the M3EH-PPV / composite interface. This barrier decreases with nanotube to polymer mass ratio leading to larger device currents. However, at all nanotube to polymer mass ratios used for the composite, the relative efficiencies for the devices using this material as an electron-transport layer have been improved compared to the M3EH-PPV single layered devices. In addition, for all devices studied, the electroluminescence spectra showed exciton recombination to occur in the M3EH-PPV layer.

The optimum in the relative efficiency was observed for a nanotube mass ratio of 1.2 % suggesting increased electron injection into the M3EH-PPV with increasing mass fraction coupled to increased hole leakage into the composite layer above 1.2 %.



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# **Chapter VI                      ORGANIC    PHOTOVOLTAIC DEVICES**

## **VI.1.    Introduction**

This Chapter will outline both physical and technical issues concerning the second type of organic devices, which we focused on in this Thesis: organic photovoltaic devices. It will be divided into two distinct sections. While Section VI.2 will discuss issues regarding polymer solar cells, Section VI.3 will focus on photoelectrochemical cells. Results and discussion on subjects such as the optical filter effect in polymer solar cells and the choice of either electropolymerised or soluble polymers in photoelectrochemical cells will be included in the respective Sections.

## **VI.2.    Polymer Solar Cells**

In this Section, fundamental properties of polymer solar cells will be outlined. In particular, results on the optical filter effect will be presented and discussed.

### **VI.2.1.    Basic Principles**

#### **VI.2.1.1.    Photovoltaic Effect**

The conversion of solar light into electric power requires the generation of both negative and positive charges as well as a driving force that can push these charges through an external electric circuit. When connected to the external electric circuit any electrical device may then utilise the converted solar energy.

In fact, a solar cell may be seen as a ‘solar-light driven electron pump’: the maximum height the electrons can be ‘pumped’ is equal to the highest voltage the solar cell can develop. The maximum current is determined by the ‘pump rate’.

#### **VI.2.1.2.    Photogeneration of Free Carriers**

In organic semiconductors, absorption of photons leads to the creation of bound excitons rather than free charges. These excitons carrying energy but no net charge may diffuse to dissociation sites where their charges can be separated. The separated charges then need to travel to the respective device electrodes, holes to the anode and electrons to the cathode to

provide voltage and be available for injection into an external circuit.

Given that photo excitation results in the formation of excitons with a binding energy considerably higher than  $k_B T$  (26 meV), photogeneration of charge is always assisted by an external factor such as the presence of traps, a donor / acceptor (D / A) interface or a metal which can also act as an electron or hole acceptor or simply provide an electric field that can split the exciton. Thus photogeneration of charge in these organic semiconductors can be regarded as extrinsic as opposed to inorganic semiconductors where separation occurs mainly together with photo excitation.

#### VI.2.1.2.1. Photogeneration due to Oxygen Traps

It is widely believed that oxygen atoms can act as traps for electrons in the LUMO of organic materials and thereby lead to a higher number of free holes in the HOMO. In this sense oxygen can act as a dopant that favours p-type conductivity. However, oxygen traps can also act as exciton dissociation sites and therefore generate free charge carriers in the presence of excitons. The proposed mechanism is the following: after a certain period, an electron in the oxygen trap may further decrease its energy by decaying to the HOMO where it recombines with either a free hole or the hole of an exciton. Thus three scenarios may be distinguished:

- The electron stems from a not yet dissociated exciton and it recombines with a hole that comes from a different exciton. Both excitons are dissociated – but only two charges (the hole of the first exciton and the electron of the other) are produced since the other two recombined;
- Only one recombination partner is associated with an exciton. This means its dissociation produces one free charge but still eliminates two;
- None of the recombination partners belongs to an exciton. Two charges are lost, none is generated.

Note that both electrons and holes can be produced with the same probability according to the above list. In any case, the electron in the oxygen trap still reduces predominantly the mobility of negative charges thus sustaining its p-dopant character. We note that basically any defect that leads to an allowed free energy level between the middle of the bandgap and the LUMO may have the same effect as the here discussed oxygen trap – although other effects may become more important. For example, photo-oxidised PPV is believed to contain a large amount of carbonyl-groups which can facilitate exciton splitting but may



also decrease both electron and hole as well as exciton transport properties.<sup>1</sup>

#### VI.2.1.2.2. Electron Transfer at a Donor / Acceptor Interface

We have seen that photogeneration of charge due to traps is not very efficient since there is always the recombination of two charge carriers involved. Here we describe a more efficient way to generate free charge carriers – the formation of an electron donor (D) / electron acceptor (A) interface. Although at first glance the concept may be reminiscent of the p/n junction in inorganic materials, the physical process is often very different.

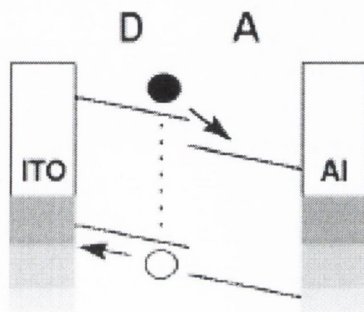


Figure VI.1 Schematic diagram of the energy levels at a donor / acceptor interface.

Figure VI.1 shows that the required transfer of charges can be realised at the interface between two materials if one material has a higher electron affinity (EA) whereas the other has a lower ionisation potential (IP). The one with the larger EA can accept an electron from the LUMO of the other and is therefore called electron acceptor. The material with the lower IP can accept the hole from the HOMO of the contacting semiconductor may therefore be termed hole acceptor or electron donor since it also donates the electron to the contacting acceptor.

We note that the onset of IP and EA needs to be large enough so that the resulting field (the potential gradient at the junction) can overcome the exciton binding energy which is typically around 0.4 eV. Otherwise charge transfer may occur but the excitons do not split into their constituent charges and recombine eventually at the D / A interface.

Confirmation of exciton dissociation can be obtained by comparing the spectral response (SR) of a blend solar cell with equivalent devices comprising only the pure components. If the SR of the blend cell is clearly higher over the entire spectrum, exciton splitting at the D / A interface is most likely. Extra confirmation may be obtained if the experimental and / or theoretical LUMO and HOMO data of the components also suggest a sufficient onset of the band edges to split the exciton. We note that the prediction of the onset of the band

edges actually requires the knowledge of the accurate position of the Fermi levels – since those have to equalise upon contact.

### Studies of MEH-PPV / C<sub>60</sub> Systems

Independently, Sariciftci *et al.* and Yoshino *et al.* reported studies on the photophysics of mixtures of semiconducting polymer (poly((2-methoxy-5-(2'-ethylhexoxy)-p-phenylene) vinylene) (MEH-PPV) and C<sub>60</sub>.<sup>2-11</sup> The observations clearly evidenced an ultrafast, reversible, metastable photo-induced electron transfer from conjugated polymers onto buckminsterfullerene in solid films. A schematic description of these systems is shown in Figure VI.2:

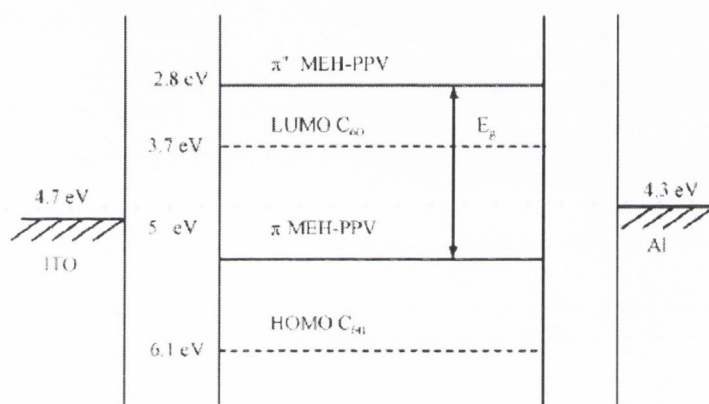


Figure VI.2 Energy levels of a MEH-PPV / C<sub>60</sub> system under flat band conditions.

The linear optical absorption spectrum of a MEH-PPV / C<sub>60</sub> film is a simple superposition of the two components without any indication of states below the  $\pi$ - $\pi^*$  gap of the conducting polymer as might arise from interaction between the two materials in the ground state.

The strong luminescence of MEH-PPV was, however, quenched by a factor in excess of  $10^3$ .<sup>2</sup> The luminescence decay time was reduced from  $\tau_0 = 550$  ps to  $\tau_{\text{rad}} \ll 60$  ps (the instrumental resolution) indicating the existence of a rapid quenching process; *e.g.* sub-picosecond electron transfer.<sup>3</sup> The strong quenching of the luminescence of another conjugated polymer, P3OT, reported by Morita *et al.*<sup>8</sup> was also consistent with efficient photo-induced electron transfer. Thus, the quenching of luminescence was observed in a number of conjugated polymers in composites with fullerenes, indicating this to be a general phenomenon for the non-degenerate ground state conjugated polymers.<sup>12</sup> This confirmed that photo-induced electron transfer occurs in a timescale sufficiently fast to quench the radiative relaxation of the conjugated polymer excited state.



Photo-induced absorption detected magnetic resonance (PIADMR) experiments were performed in conjugated polymer / C<sub>60</sub> composites giving evidence for a complete quenching of the MEH-PPV triplet – triplet absorption signal at 1.35 eV. Instead a strong spin = 1/2 signal dominated the PIADMR spectrum, indicating charged polarons as photoexcitations on the polymer donor.<sup>7</sup> This confirmed that the photo-induced electron transfer occurs on a time scale sufficiently fast to quench the intersystem crossing to the triplet state.

Very recently the forward transfer of the photoexcited electrons from conjugated polymer donors onto 1-(3-methoxycarbonyl)-propyl-1-1-phenyl-(6,6)C<sub>61</sub> (PCBM) acceptors was resolved by pump-probe experiments with an unprecedented time resolution of 10 fs.<sup>13</sup> In these studies, the relaxation of the photo-induced excitations on the polymer chain switched from radiative (intense stimulated emission in pristine polymer,  $\Delta T > 0$ ) to non-radiative (electron transfer in composites, PIA,  $\Delta T < 0$ ) upon mixing PCBM into the polymer matrix. This experimental setup allowed to time-resolve the photo-induced electron transfer time with  $\sim 40$  fs after an initial relaxation (Kasha relaxation). As a consequence of the resonant excitation of the conjugated polymer by a sub-10 fs laser pulse, the phonon modes which are strongly coupled to the  $\pi$ -electron excitations were directly observed as coherent oscillations within the pump probe experiment. By Fourier transforming the oscillatory decay of the time dependent signal the resonant / non-resonant Raman spectrum of the conjugated polymer was reproduced. Furthermore, by adding PCBM to the conjugated polymer matrix these vibrational oscillations were quenched nearly completely indicating a rapid depopulation of the excited state on the conjugated polymer due to the electron transfer. These results demonstrated a direct competition of photo-induced electron transfer with vibrational oscillations the conjugated polymer donor indicating a photo-induced electron transfer rate of  $>10^{13} \text{ s}^{-1}$  ( $\tau_{\text{et}} < 100 \text{ fs}$ ). As such this photo-induced electron transfer is indeed ultrafast, resulting in a quantum yield of photo-induced charge generation of 100 %.

The time-resolved transient photocurrent (PC) of MEH-PPV / C<sub>60</sub> composites with different C<sub>60</sub> content<sup>14</sup> shows an increase of initial photocurrent by an order of magnitude upon admixture of 1 % of C<sub>60</sub>. This increase of the photocarrier generation efficiency was accompanied by the successive increase in lifetime of the photocarriers upon adding more and more C<sub>60</sub>. Thus, the ultrafast photo-induced electron transfer from the semiconducting



polymer to  $C_{60}$  not only enhances the charge carrier generation in the host polymer but also serves to prevent recombination by separating the charges and stabilising them.<sup>14</sup>

### VI.2.1.3. Physical Processes

In the following we comment on the individual conversion steps with regard to the special situation in organic solar cells. Figure VI.3 shows the charge generation process in a single layer polymer solar cell:

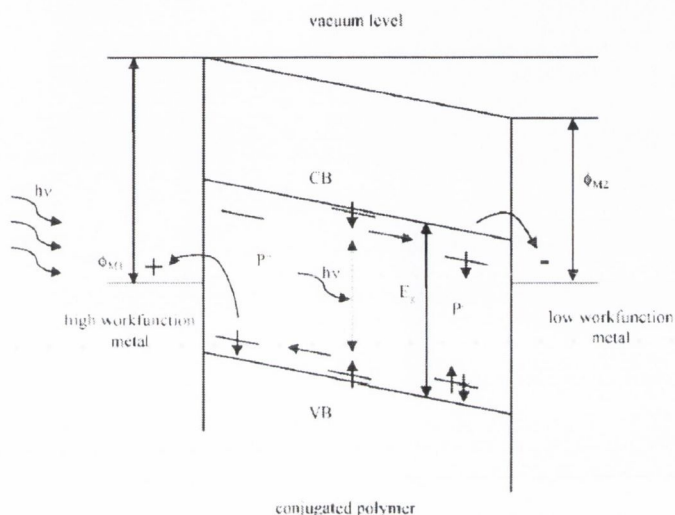


Figure VI.3 Charge generation process in a single layer conjugated polymer device under short circuit conditions.

#### VI.2.1.3.1. Absorption of Photons

In most organic device only a small portion of the incident light is absorbed for the following reasons:

- The semiconductor bandgap is too high. A polymer with bandgap of 1.1 eV absorbs only 77 % of the solar radiation on Earth. Semiconducting polymers have bandgaps higher than 2.0 eV, limiting the possible absorption to less than 30 %
- The organic layer is too thin. The typically low charge carrier and exciton mobilities require layer thickness in the order of 100 nm. Fortunately the absorption coefficient of organic materials is generally much higher than in *e.g.* Si so that only about 100 nm are necessary to absorb between 60 and 90 % if a reflective back contact is used;
- Reflection losses are probably significant but little investigated in these materials. Systematic measurements of photovoltaic materials are desired to provide knowledge of their impact on absorption losses. Anti-reflection coatings as used in inorganic devices may then prove useful once other losses such as recombination become less dominant.

### VI.2.1.3.2. Exciton Diffusion

Ideally, all photoexcited excitons should reach a dissociation site. Since such a site may be at the other end of the semi-conductor, their diffusion length should be at least equal the required layer thickness (for sufficient absorption) – otherwise they recombine and photons would be wasted. Exciton diffusion ranges in polymers and pigments are typically around 10 nm.<sup>15-18</sup> However, some pigments like perylenes are believed to have exciton diffusion lengths of several 100 nm.<sup>19</sup>

### VI.2.1.3.3. Charge Separation

As we have seen above, charge separation is known to occur at organic semiconductor / metal interfaces, impurities (*e.g.* oxygen) or between materials with sufficiently different electron affinities (EA) and ionisation potentials (IA). In the latter one material can then act as electron acceptor (A) while the other keeps the positive charge and is referred to as electron donor (D) – since it did actually donate the electron to A.

If the difference in IA and EA is not sufficient, the exciton may just hop onto the material with the lower bandgap without splitting up its charges. Eventually it will recombine without contributing charges to the photocurrent.

### VI.2.1.3.4. Charge Transport

The transport of charges is affected by recombination during the journey to the electrodes – particularly if the same material serves as transport medium for both electrons and holes. Also, interaction with atoms or other charges may slow down the travel speed and thereby limit the current – see also space charge limited current in Section IV.3.3.

### VI.2.1.3.5. Charge Collection

In order to enter an electrode material with a relatively low work function (*e.g.* Al, Ca) the charges often have to overcome the potential barrier of a thin oxide layer. In addition, the metal may have formed a blocking contact with the semiconductor so that they can not immediately reach the metal.

## VI.2.2. Device Architecture

In the following we give a brief summary including the strengths and weak points of the main four different architectures for polymer solar cells.

### VI.2.2.1. Single Layer Cells

The simplest and most widely used organic semiconductor device is a metal – insulator – metal (MIM) tunnel diode with metal electrodes of asymmetrical work function. Under forward bias, holes from the high work function metal and electrons from the low work function metal are injected into a thin film of a single-component organic semiconductor. Because of the asymmetry of the work function of the cathode and the anode, forward bias currents for a single carrier type material are orders of magnitude larger than reverse bias currents at low voltages. The rectifying diode characteristics can be accompanied by radiative recombination channels of the injected electrons and holes within the molecular solid.

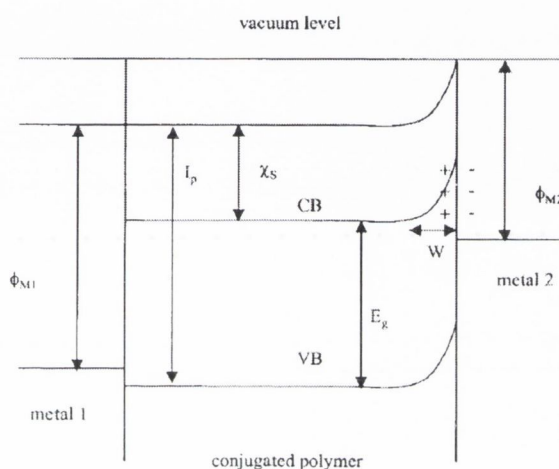


Figure VI.4 Energy diagram of a metal / semiconductor / metal Schottky barrier under open circuit conditions, when the metals have different work functions ( $\Phi_M$ : work function,  $\chi_s$ : electron affinity,  $I_p$ : ionisation potential,  $E_g$ : bandgap,  $W$ : depletion width).

In the photovoltaic mode, where no external voltage is applied and short circuit conditions exist, the potential difference available in the MIM device is caused by the difference between the workfunctions of the metal electrodes. In most of the cases (*e.g.* ITO and Al) the potential difference due to this workfunction difference is not high enough to give efficient photo-induced charge generation, limiting the operation of the PV cells. Some improvement was reported for photodiodes utilising a Schottky-type junction formed between the conjugated polymer and one of the metal electrodes as shown in Figure VI.4. However, the problem of inefficient charge generation in conjugated polymers was not overcome by this approach, since both positive and negative photoexcited charges travel through the same material.

To overcome this limitation of the photo-induced charge carrier generation, a donor / acceptor (dual molecule) approach, as described above, has been suggested<sup>2,20-22</sup> and used



in the following devices architectures.

### VI.2.2.2. Double Layer Cells

Double layer cell's structure, shown in Figure VI.5, benefits from the separated charge transport layers that ensure connectivity with the correct electrode and give the separated charge carriers only little chance to recombine with its counterpart. The drawback is the small interface that allows only excitons of a thin layer to reach it and get dissociated.

The findings for the different bilayer systems investigated so far can be summarised the following way: although the quantum efficiency for photo-induced charge separation is near unity for a D / A pair, the energy conversion efficiency in a bilayer heterojunction device is limited:

- Due to the molecular nature of the heterojunction, efficient charge separation occurs only close to the D / A interface, either within the exciton diffusion path or within the space charge region; thus, photoexcitations created far from the D / A junction recombine prior to diffusing to the heterojunction.
- Since charge separation is restricted to a rather small region of the photoactive device, the PV conversion efficiency is limited by the amount of photons absorbed within this region and materials with high molar absorption coefficients are required. Further increase of the layer thickness of the single components would reduce the efficiency by the increased series resistance.

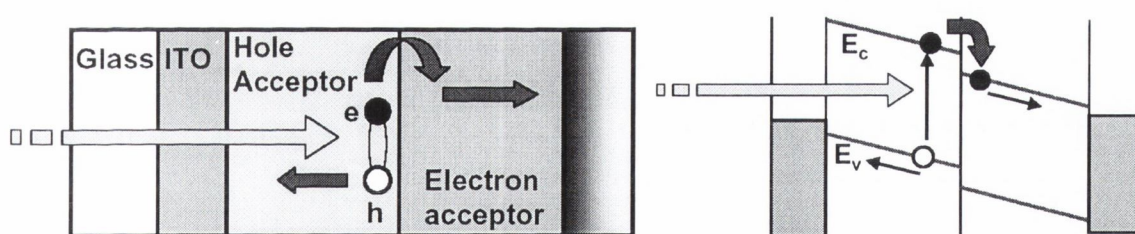


Figure VI.5 Schematic diagram of a double layer polymer solar cell.

### VI.2.2.3. Blend Cells

The strong point of blend cells is the large interface area if the molecular mixing occurs on a scale that allows good contact between alike molecules (charge percolation) and most excitons to reach the D / A interface.

Donor – acceptor heterojunctions, as depicted in Figure VI.6, are formed simply by blending the two organic materials serving as electron donor and electron acceptor. The

advantage of these structures over the flat-junction organic solar cells is the interpenetration of the two materials that conduct positive and negative charge carriers, reducing the size of the individual phase domains to the nanometre range. This overcomes one of the problems of the first generation of organic photovoltaic cells: the unfavourable ratio of exciton diffusion length to optical absorption length. Light is absorbed throughout the composite material, but in the composite, the distance the exciton has to travel before reaching the interface is at most a few nanometres, which is commensurate with its diffusion length. Hence photo-induced charge separation can occur very efficiently.

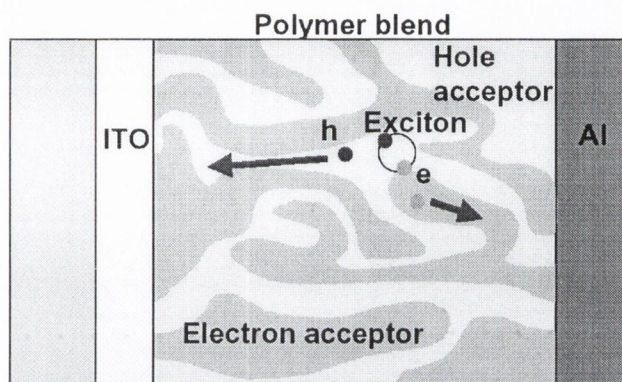


Figure VI.6 Schematic picture of a D / A blend cell.

One of the technological challenges, however, is to achieve good mixing between the donor and the acceptor molecules and good connectivity with the correct electrode.

#### VI.2.2.4. Laminated Devices

Laminated devices are relatively recent types, which represent the successful attempt to unify the advantages of the two structures above. Charge separation occurs in the blend layer in the middle that is obtained after laminating the two separate layers together and charge transport can only occur via the correct transport layer.

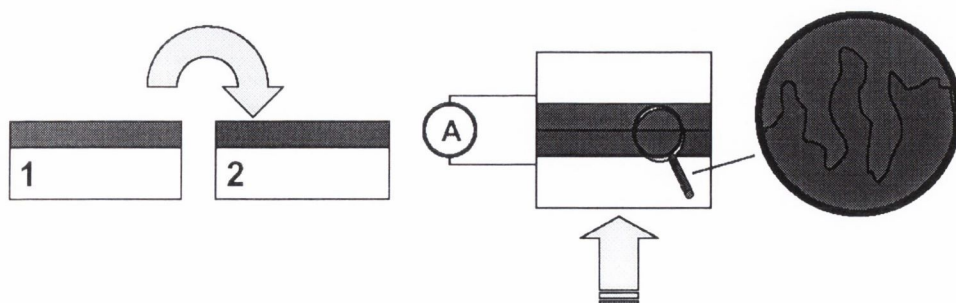


Figure VI.7 Device preparation of laminated polymer solar cell.

This structure, shown in Figure VI.7, also features the useful options to treat each layer



separately (*e.g.* doping, physical / chemical conversion) before forming the blend layer and instant encapsulation between the two substrates. The drawback is that certain mechanical properties of the organic semiconductors are required (low glass transition temperature) to form the intermixed layer.

### VI.2.3. Materials

#### VI.2.3.1. Introduction

For the design of D / A solar cells it is important to know whether a specific material combination is likely to lead to charge transfer. One way to find out is to build blend devices and look for PL quenching of both components and enhanced SR with respect to the single components – as discussed above.

In the following we provide some background knowledge that allows the prediction of not only the D / A properties but also some other relevant properties for organic photovoltaic materials.

#### VI.2.3.2. Donor / Acceptor Properties

Since a donor can act as an acceptor for an even stronger donor – these two terms can not really be used separately. There are certain functionalities that are likely to make a material an electron acceptor with respect to most other materials. Examples for functionalities that favour electron acceptor properties are: CN, CF<sub>3</sub>, F, keto-groups or diimides. These groups are known as electron withdrawing groups if they are attached to an unsaturated (*i.e.* conjugated) system. Note that their ability to enhance the electron affinity (EA) of the entire molecule is not purely connected to the electron withdrawing properties of these functionalities. It is essentially a result of both the inductive and the mesomeric effect. While the inductive effect is determined by the electronegativity of the substituents, the mesomeric effect takes into account the influence of free electron pairs. The latter considers that many conjugated structures can equally be drawn with a different double / single bond (*i.e.* electron) arrangement. The average of these possible electron locations can be regarded as the overall mesomeric effect of a specific molecular structure. Examples for electron acceptors are: CN-PPV, CF<sub>3</sub> substituted PPV and perylene diimides.<sup>19,23</sup> Most organic semiconductors behave more like electron donors, for example PPV, PT, PPP and phthalocyanines.



### VI.2.3.3. Bandgap

As a rule of thumb: the lower the bandgap, the larger the conjugated system. Examples for large systems are phthalocyanines,<sup>19,24-26</sup> naphthalocyanines<sup>27-29</sup> and perylenes.<sup>19,30,31</sup> Sulfur in a conjugated systems also tends to reduce  $E_g$ . The bandgap can also be small if a molecule consists of a donor and an electron acceptor that are connected via a conjugated structure to create a 'push / pull system' as in *e.g.* polymethines. Such structures can accomplish charge transfer sometimes already in the ground state (*e.g.* charge transfer salt) or only little extra photonic energy is required to complete it. Examples for charge transfer salts are PVK-TNF<sup>19</sup> and for polymethines: merocyanines.<sup>32-34</sup>

### VI.2.3.4. Solubility

Solubility is good if the planar parts of the conjugated – systems of the molecules cannot get too close to each other. Otherwise they would stick together, driven by their interaction, to form aggregates *i.e.* larger clusters, particles which do not contain solvent. Flexible and bulky side chains or atoms that stick out of the molecular plane can prevent molecules from getting too close. The general rule is: molecules dissolve in solvents with similar structure. Polar solvents like water, alcohol or isopropanol dissolve polar molecules while less polar solvents (*e.g.* toluene, xylene) dissolve non-polar molecules. As a rule of thumb, it can be said that a solvent containing other atoms than carbon and hydrogen has a good chance to be more polar – particularly if the structure is asymmetric.

### VI.2.3.5. Photoluminescence

Practice shows that PL is quenched if the molecules can aggregate. Consequently, molecules in solution fluoresce with greater efficiency. Materials with higher bandgaps tend to show stronger PL. Moreover, the presence of impurities or structural defects usually leads to energy levels within the bandgap. The energetic decay of an excited electron can occur faster and therefore more efficiently if smaller energy jumps are required. Also conjugated systems containing certain atoms like sulphur, which tend to lower the band gap,<sup>35</sup> give lower PL than conjugated structures containing only carbon and hydrogen.

## VI.2.4. Devices Performances

### VI.2.4.1. Single Layer Cells

Results on devices based on derivatives of polythiophene showed high photoresponse (80

% el/ph at  $-15$  V), competitive with ultraviolet sensitised Si photodiodes.<sup>36,37</sup> A photovoltaic response was observed under zero bias conditions. The charge carrier concentration in these undoped, pristine materials is sufficiently low in dark so that the semiconducting layer (several hundred nm) is fully depleted. Note, however, that the mobility of injected charge carriers is not symmetric. Upon photoinduced charge carrier generation, an additional effect may become representative. For low charge carrier density materials photodoping may be sufficient in these materials to lead to interface effects such as photo-induced band bending or photoinduced space charge regions. Such effects are typical for organic semiconductors.<sup>38,39</sup> The exact nature of this band bending and barrier creation at the interfaces under light illumination will be an important parameter for optimising the solar cell performance in these devices.

For photovoltaic cells made with pure conjugated polymers, energy conversion efficiencies are typically  $10^{-3} - 10^{-1}$  %.<sup>37,40,41</sup>

#### VI.2.4.2. Double Layer Cells

The use of organic bilayers with photo-induced electron transfer at the interface has been investigated heavily during the last couple of decades.<sup>20,42-45</sup> Tang demonstrated PV activity in small molecular bilayers which were vacuum deposited.<sup>43</sup> In this pioneering work Tang used a vacuum evaporated copper-phthalocyanine (250 Å) / perylene derivative (450 Å) system sandwiched between  $\text{In}_2\text{O}_3$  and silver electrodes, with a white light PV power conversion efficiency of around 1 %.

Extensive literature exists on the fabrication of solar cells based on small molecular dyes as well as donor – acceptor systems.<sup>46,47</sup> Inorganic oxide semiconductors also were used to facilitate electron transfer from organic dyes onto inorganic nanoparticles to achieve charge separation and PV conversion.<sup>48,49</sup> Yamashita and co-workers reported a bilayer photodiode based on the organic donor tetrathiafulvalene (TTF) and  $\text{C}_{60}$ .<sup>50</sup>

A recent approach to enhance the PV properties of organic solar cells by sensitisation with fullerenes was introduced by Meissner *et al.*<sup>51-54</sup> The performance of a zinc-phthalocyanine (ZnPc) / N,NM'-dimethylperylene-3,4,9,10-tetracarboxylic diimide (MPP) bilayer device was significantly enhanced by inserting a 30 nm thick  $\text{C}_{60}$  – ZnPc composite layer between the ZnPc (50 nm) and the MPP (20 nm).<sup>52</sup> These devices delivered a short circuit current of  $5.26 \text{ mA/cm}^2$  under  $860 \text{ W/m}^2$  AM 1.5 solar simulators, and an open circuit voltage of 0.39



V. Together with a fill factor of 0.45 the overall power efficiency was calculated as 1.05 %. For PV cells made with bilayers of conjugated polymer and C<sub>60</sub>, monochromatic energy efficiencies as high as 1% and incident photon to converted electron (IPCE) efficiencies as high as 15 % were measured.<sup>16,55</sup>

#### VI.2.4.3. Blend Cells

Conversion efficiency from incident photons to current of over 50 % has been achieved with a blend containing PPV and methanofullerene derivatives.<sup>56</sup> The overall conversion efficiency from solar to electric power under full sunlight achieved with this cell was 2.5 %.

Important progress has been made toward creating materials for blend cells.<sup>21,22,57,58</sup> Yu *et al.* used the bulk heterojunction formed in a solid-state composite of conjugated polymers and methanofullerene PCBM<sup>21</sup> with a short circuit current,  $I_{sc} = 0.5 \text{ mA/cm}^2$  under 20 mW/cm<sup>2</sup> monochromatic illumination, approximately two orders of magnitude higher than that of pure MEH-PPV tunnel diodes. Uniform films with even higher concentrations of the PCBM were cast from 1,2-dichlorobenzene solutions containing up to 1:4 weight ratio MEH-PPV / PCBM. The efficiencies of the devices are nearly independent of the incident illumination intensity.

The groups of Friend in Cambridge and Heeger in Santa Barbara also simultaneously made a PV bulk heterojunction using two different conjugated polymers.<sup>22,57,58</sup> Both approaches use MEH-PPV as donor conjugated polymer in composite with a cyano substituted MEH-PPV-type polymer. The cyano substitution was originally introduced into the light emitting device materials because of the lowered LUMO level of this derivative relative to unsubstituted one.<sup>59</sup> This lower LUMO of the high electron affinity material, on one side eases the electron injection from a medium workfunction metal such as aluminium.

#### VI.2.5. Optical Filter Effect in Single Layer Cells

In this Section, we will show one the main issues encountered when testing single layer (SL) polymer solar cells: the optical filter effect. We prepared and tested single layer ITO / M3EH-PPV / Al photovoltaic cells. The thickness of the M3EH-PPV layer was varied from 40 nm to 100 nm.



Figure VI.8 shows the  $I(V)$  characteristics of the SL polymer cells. The summary of the cell's photovoltaic parameters, as defined in Section III.4.3.2.1, is given in Table VI.1:

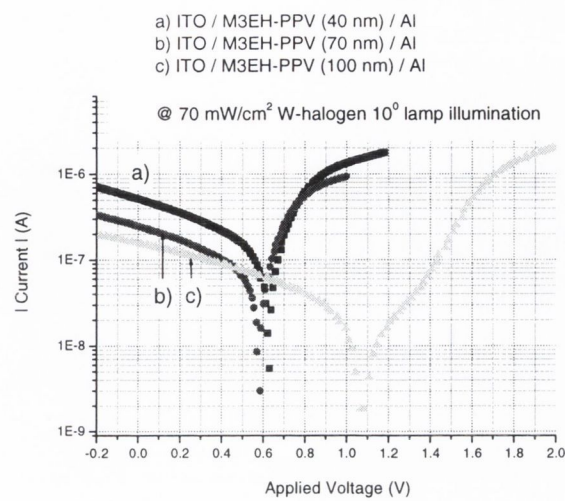


Figure VI.8 Current-voltage characteristics of the ITO / M3EH-PPV / Al cells tested in this Section.

Table VI.1 Short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), maximum power ( $P_{max}$ ), fill factor (FF) and power efficiency ( $\eta$ ) of ITO / M3EH-PPV / Al cells as a function of the thickness of the M3EH-PPV layer.

| Film Thickness<br>(nm) | $J_{sc}$<br>( $\times 10^{-2}$ A/m <sup>2</sup> ) | $V_{oc}$<br>(V) | $P_{max}$<br>( $\times 10^{-3}$ W/m <sup>2</sup> ) | FF<br>(%) | $\eta$<br>( $\times 10^{-3}$ %) |
|------------------------|---------------------------------------------------|-----------------|----------------------------------------------------|-----------|---------------------------------|
| 40                     | 8.58                                              | 0.63            | 14.92                                              | 27.6      | 2.13                            |
| 70                     | 4.12                                              | 0.59            | 6.97                                               | 28.7      | 0.996                           |
| 100                    | 2.63                                              | 1.07            | 6.45                                               | 22.9      | 0.921                           |

These results show that for a given material in a single layer device structure, the cell's short-circuit current density as well as its power efficiency increase as the thickness of the polymer layer decreases.

This can be seen in Figure VI.9, where the power efficiency is plotted as a function of the cell's thickness. Only three data points can be shown and the graph is somewhat misleading. Indeed one can expect the power efficiency of the cell not to exponentially increase to infinity but to plateau (or peak at an optimum thickness) as the device gets thinner.

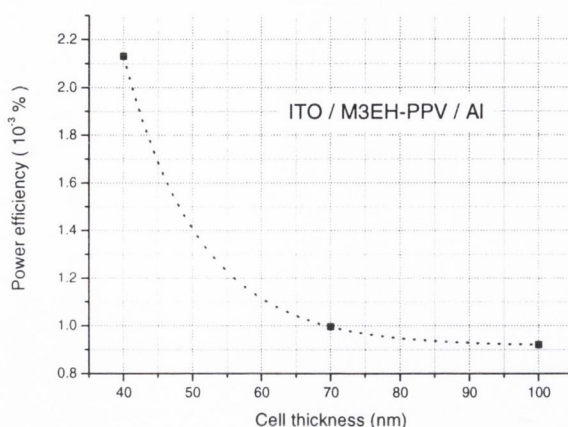


Figure VI.9 Power efficiency of the ITO / M3EH-PPV / Al single layer cells as a function of the M3EH-PPV layer's thickness.

This result however shows that part of the photogenerated current in thick single layer devices is lost, since only a thin active layer gives rise to the photocurrent. This phenomenon is often called the filter effect and is explained below.

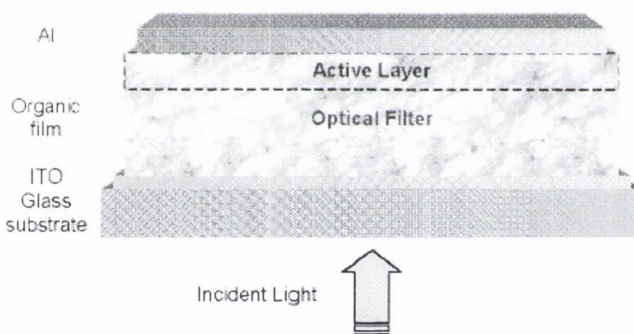


Figure VI.10 In organic devices very often only a thin layer (active layer) near back electrode is electronically active (contributes to the photocurrent). Depending on the thickness and absorption coefficient a significant fraction of photons can be absorbed in the semiconductor bulk (optical filter) before this region is reached.

The region in the semiconductor that allows photoexcited excitons to dissociate and the separated charges to reach their respective electrodes is often called the 'active region' – see Figure VI.10. Thus, only light absorbed in the active region can contribute to the photocurrent. The layer that absorbs light before it reaches the active region is the actual optical filter.

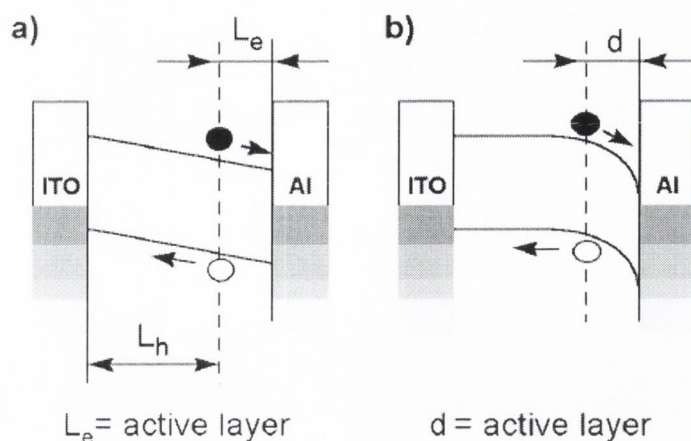


Figure VI.11 Two scenarios that can lead to the formation of an optical filter: a) exciton dissociation occurs throughout the entire bulk but one charge carrier (here the electron) can only travel a very short distance before it recombines. b) exciton dissociation occurs only near the (here negative, Al) electrode due to a local high field. Thus a small exciton diffusion length determines the width of the active layer – provided the charge carrier travelling distance is sufficiently high.

Figure VI.11 shows two scenarios for the formation of an active region smaller than the bulk which can lead to an optical filter effect:

- Exciton dissociation throughout the entire bulk but small mobility of one charge carrier. Often the mobility of the hole is considerably higher than the mobility of the electron. Thus, free electrons have to be generated close to the negative electrode for charge collection. Even if the excitons have large diffusion lengths, a considerable fraction of the photogenerated excitons would dissociate too far away from the negative electrode. Thus the width of the active layer is determined by the distance electrons can travel in the specific material *i.e.* the electron mobility – see Figure V.11a;
- Exciton dissociation occurs only near one electrode interface. If exciton splitting occurs due to a strong local field (band bending), excitons that are generated outside the band bending area have to diffuse into this region to supply charges. Although small hole and electron mobilities can still become limiting factors it is usually the exciton diffusion length that determines the width of the active layer in this case – see Figure VI.11b.

Only if the active region extends across the entire bulk *i.e.* the bulk is thin enough, most of the dissociated excitons can generate a photocurrent so that the spectral response (SR) essentially follows the absorption features, as shown in Figure VI.12 below:



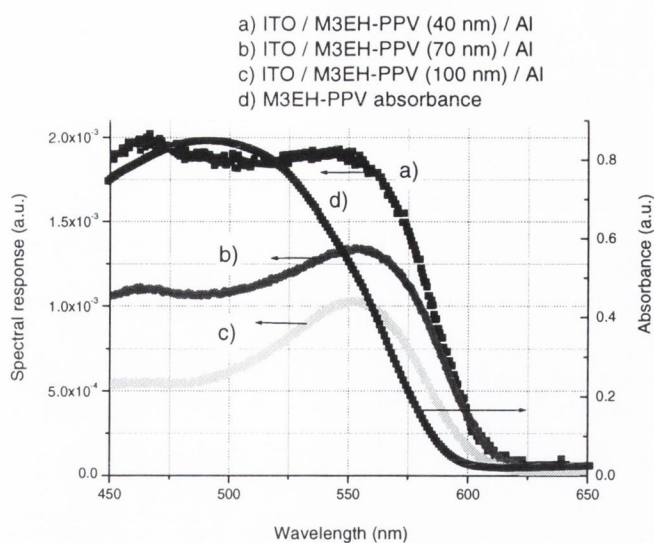


Figure VI.12 Spectral response of the ITO / M3EH-PPV / Al single layer cells with M3EH-PPV absorbance for comparison.

Due to short exciton diffusion lengths most organic cells have a bulk thickness that is considerably larger than the active layer (to avoid shorts). Thus these SR spectra show a strong filter effect resulting in SR maxima at wavelengths where the optical density (OD) is low and SR minima where the OD is too high to allow many photons to reach the active region. Such a spectrum is termed antibatic spectrum in contrast to the symbatic spectrum that shows no onset between absorption and SR features.<sup>60</sup> Note that a symbatic spectrum can be obtained if the device is illuminated through the other contact – if it is sufficiently transparent.

### VI.3. Photoelectrochemical Cells

We will now introduce the basic principles and devices architecture of photoelectrochemical cells, and present results on single layer devices using no MWNT.

#### VI.3.1. Semiconductor – Electrolyte Interface

When a semiconductor is placed in contact with an electrolyte, electric current initially flows across the junction until electronic equilibrium is reached, where the Fermi energy of the electrons in the solid ( $E_F$ ) is equal to the redox potential of the electrolyte ( $E_{\text{redox}}$ ), as shown in Figure VI.13 The transfer of electric charge produces a region on each side of the junction where the charge distribution differs from the bulk material, and this is known as the space-charge layer. On the electrolyte side, this corresponds to the familiar electrolytic double layer, that is, the compact (Helmholtz) layer followed by the diffuse (Gouy –

Chapman) layer. On the semiconductor side of the junction the nature of the band bending depends on the position of the Fermi level in the solid. If the Fermi level of the electrode is equal to the flat band potential, there is no excess charge on either side of the junction and the bands are flat. If electrons accumulate at the semiconductor side one obtains an accumulation layer. If, however, they deplete from the solid into the solution, a depletion layer is formed, leaving behind a positive excess charge formed by immobile ionised donor states. Finally, electron depletion can go so far that their concentration at the interface falls below the intrinsic level. As a consequence, the semiconductor is p-type at the surface and n-type in the bulk, corresponding to an inversion layer. The illustration in Figure VI.13 refers to n-type materials where electrons are the mobile charge carriers. For p-type semiconductors, analogous considerations apply. Positive holes are the mobile charge carriers and the immobile negatively charged states of the acceptor dopant form the excess space charge within the depletion layer.

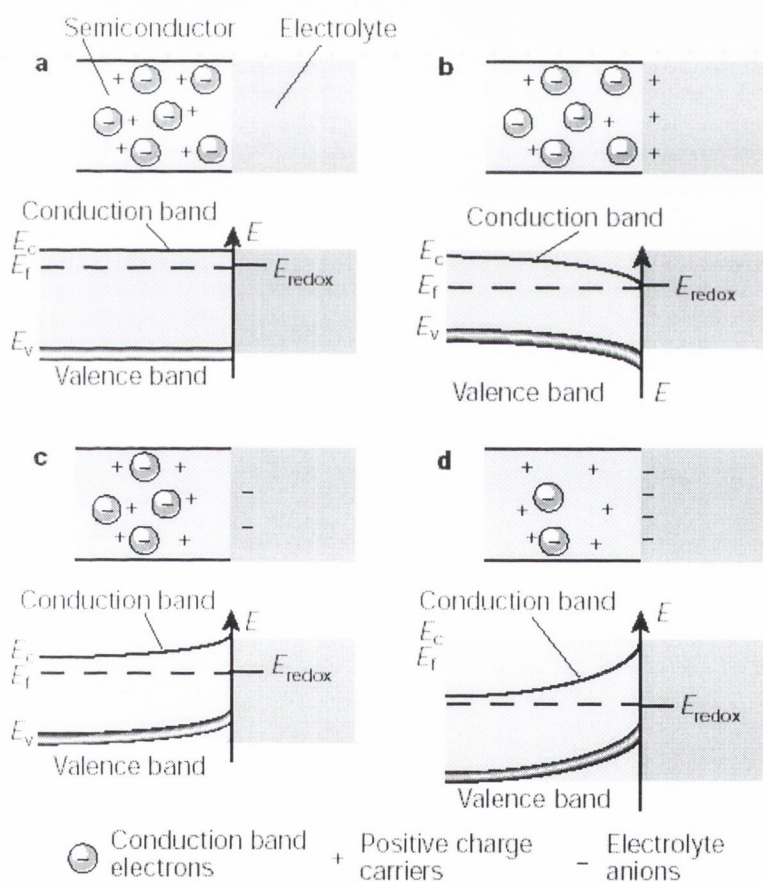


Figure VI.13 Schematic showing the electronic energy levels at the interface between an n-type semiconductor and an electrolyte containing a redox couple. The four cases indicated are: a) flat band potential, where no space-charge layer exists in the semiconductor; b) accumulation layer, where excess electrons have been injected into the solid producing a downward bending of the conduction and valence band towards the interface; c) depletion layer, where electrons have moved from the semiconductor to the electrolyte, producing an upward bending of the bands; and d) inversion layer where the electrons have been depleted below their intrinsic level, enhancing the upward band bending and rendering the semiconductor p-type at the surface.



The flat band potential is a very useful quantity in photoelectrochemistry as it facilitates location of the energetic position of the valence and conduction band edge of a given semiconductor material. It is obtained by measuring the capacity of the semiconductor – electrolyte junction. The semiconductor is subjected to reverse bias — that is, a voltage is applied to increase the potential step across the junction — and the differential capacity is determined as a function of the applied potential,  $V$ . The space charge capacity of the semiconductor ( $C_{sc}$ ) is in series with that of the Helmholtz layer ( $C_H$ ) present at the electrolyte side of the interface. In the depletion regime the condition  $C_H > C_{sc}$  applies, so the measured capacity is that of the space-charge layer. This depends on the applied bias voltage according to the Mott–Schottky equation:

$$\frac{1}{C_{sc}^2} = 2 \frac{\Delta\Phi_{sc} RT/F}{\epsilon^l N} \quad \text{Equation VI.1}$$

where  $\Delta\Phi_{sc} = V - V_{fb}$  is the voltage drop in the space-charge layer,  $R$  is the gas constant,  $F$  the Faraday number,  $\epsilon$  the dielectric constant of the semiconductor, and  $^lN$  the ionised donor dopant concentration.

A plot of the square of the reciprocal capacity against the applied voltage gives a straight line and this is extrapolated to  $C_{sc}^{-2} = 0$  to derive the flat band potential,  $V_{fb}$ .

## VI.3.2. Devices Architectures

### VI.3.2.1. Regenerative Cells

Research investigations on photoelectrochemical cells focused on two types of cells whose principle of operation is shown in Figure VI.14.

The first type is the regenerative cell, which converts light to electric power leaving no net chemical change behind. Photons of energy exceeding that of the band gap generate electron – hole pairs, which are separated by the electric field present in the space-charge layer. The negative charge carriers move through the bulk of the semiconductor to the current collector and the external circuit. The positive holes are driven to the surface where they are scavenged by the reduced form of the redox relay molecule ( $R$ ), oxidising it:



The oxidised form  $O$  is reduced back to  $R$  by the electrons that re-enter the cell from the



external circuit.

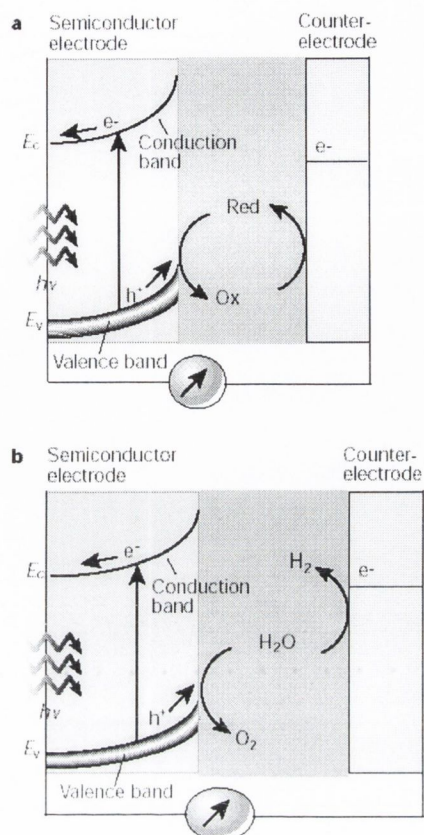


Figure VI.14 Principle of operation of photoelectrochemical cells based on n-type semiconductors. a) Regenerative-type cell producing electric current from sunlight; b) a cell that generates a chemical fuel, hydrogen, through the photo-cleavage of water.

Much of the work on regenerative cells has focused on electron-doped (n-type) II/VI or III/V semiconductors using electrolytes based on sulphide / polysulphide, vanadium(II) / vanadium(III) or  $I^2 / I^-$  redox couples. Conversion efficiencies of up to 19.6 % have been reported for multijunction regenerative cells.<sup>61</sup>

### VI.3.2.2. Photosynthetic Cells

The second type, photosynthetic cells, operate on a similar principle except that there are two redox systems: one reacting with the holes at the surface of the semiconductor electrode and the second reacting with the electrons entering the counter-electrode. In the example shown, water is oxidised to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. The overall reaction is the cleavage of water by sunlight.

Titanium dioxide ( $TiO_2$ ) has been the favoured semiconductor for these studies, following its use by Fujishima and Honda for water photolysis.<sup>62</sup> Unfortunately, because of its large band gap (3 – 3.2 eV),  $TiO_2$  absorbs only the ultraviolet part of the solar emission and so

has low conversion efficiencies. Numerous attempts to shift the spectral response of  $\text{TiO}_2$  into the visible, or to develop alternative oxides affording water cleavage by visible light, have so far had very little success.

### VI.3.2.3. Dye-sensitised Electrochemical Cells

#### VI.3.2.3.1. Introduction

In view of these prolonged efforts, disillusionment has grown about the prospects of photoelectrochemical cells being able to give rise to competitive photovoltaic devices, as those semiconductors with band gaps narrow enough for efficient absorption of visible light are unstable against photocorrosion.

The resolution of this dilemma came in the separation of the optical absorption and charge-generating functions, using an electron transfer sensitizer absorbing in the visible to inject charge carriers across the semiconductor–electrolyte junction into a substrate with a wide band gap, and therefore stable. Figure VI.15 shows the operational principle of such a device:

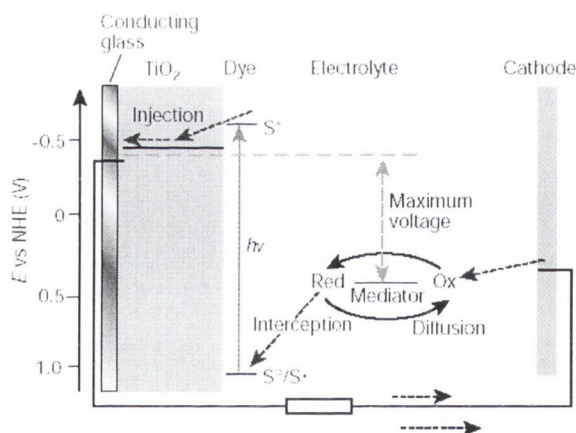


Figure VI.15 Schematic of operation of the dye-sensitized electrochemical photovoltaic cell. The photoanode, made of a mesoporous dye-sensitized semiconductor, receives electrons from the photo-excited dye which is thereby oxidised, and which in turn oxidises the mediator, a redox species dissolved in the electrolyte. The mediator is regenerated by reduction at the cathode by the electrons circulated through the external circuit.

In the conventional picture, the photovoltage of photoelectrochemical cells does not exceed the potential drop in the space-charge layer. But nanocrystalline cells can develop photovoltages close to 1 V even though the junction potential is in the millivolt range. It has been suggested that a built-in potential difference at the back contact of the

nanocrystalline film with the conducting glass is responsible for the observed photovoltage.<sup>63</sup> Other evidence<sup>64</sup> suggests that under illumination, electron injection from the sensitiser increases the electron concentration in the nanocrystalline electrode, raising the Fermi level of the oxide and thus shifting its potential.<sup>65</sup> From recent electrical impedance studies,<sup>66</sup> it seems that both changes — the potential drop across the back contact and the Fermi level shift of the TiO<sub>2</sub> nanoparticles — contribute to the photovoltage of dye-sensitised solar cells.

#### VI.3.2.3.2. Materials

The need for dye-sensitised solar cells to absorb far more of the incident light was the driving force for the development of mesoscopic semiconductor materials<sup>67</sup> — minutely structured materials with an enormous internal surface area — which have attracted great attention during recent years. Mesoporous oxide films are made up of arrays of tiny crystals measuring a few nanometres across. Oxides such as TiO<sub>2</sub>, ZnO, SnO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>, or chalcogenides such as CdSe, are the preferred compounds. These are interconnected to allow electronic conduction to take place.

Between the particles are mesoscopic pores filled with a semiconducting or a conducting medium, such as a p-type semiconductor, a polymer, a hole transmitter or an electrolyte. The net result is a junction of extremely large contact area between two interpenetrating, individually continuous networks. Particularly intriguing is the ease with which charge carriers percolate across the mesoscopic particle network, making the huge internal surface area electronically addressable. Charge transport in such mesoporous systems is under intense investigation today<sup>68,69</sup> and is best described by a random walk model.<sup>70</sup>

#### VI.3.2.3.3. Device Performances

Cells based on a spirobisfluorene-connected arylamine hole transmitter,<sup>49</sup> which fills the pores of a dye-sensitised nanocrystalline TiO<sub>2</sub> film, have reached a conversion efficiency of 2.56 % at full sunlight.<sup>71</sup> The high open-circuit voltage of these devices, exceeding 900 mV, is particularly noteworthy and promising for further substantial improvements in performance. In general, dye-sensitised heterojunction cells offer great flexibility because the light absorber and charge-transport material can be selected independently to obtain optimal solar energy harvesting and high photovoltaic output. The great advantage of such a configuration is that the charge carriers are generated by the dye precisely at the site of the junction where the electric field is greatest, enhancing charge separation.



Incident-photon-to-current conversion efficiency (IPCE) value obtained with a single-crystal electrode is only 0.13 % near 530 nm (where the sensitizer has an absorption maximum), whereas it reaches 88 % with the nanocrystalline electrode<sup>72</sup> — more than 600 times greater. The photocurrent in standard sunlight augments  $10^3 - 10^4$  times when passing from a single crystal to a nanocrystalline electrode. This striking improvement is due largely to the far better light harvesting of the dye-sensitized nanocrystalline film as compared with a flat single-crystal electrode, but is also due, at least in part, to the mesoscopic film texture favouring photogeneration and collection of charge carriers.<sup>73</sup>

Under full sunlight, short-circuit photocurrents ranging from 16 to 22 mA.cm<sup>-2</sup> are reached with state-of-the-art ruthenium sensitizers, while  $V_{oc}$  is 0.7 – 0.8 V and the fill factor values are 0.65 – 0.75. A certified overall power conversion efficiency of 10.4 % has been attained at the US National Renewable Energy Laboratory.<sup>74</sup>

Although this efficiency makes dye-sensitized cells fully competitive with the better amorphous silicon devices, an even more significant parameter is the dye lifetime achieved under working conditions. For credible system performance, a dye molecule must sustain at least  $10^8$  redox cycles of photo-excitation, electron injection and regeneration, to give a device service life of 20 years. The use of solvents such as valeronitrile, or *g*-butyrolactone, appropriately purified, in the electrolyte formulation provide a system able to pass the standard stability qualification tests for outdoor applications, including thermal stress for 1,000 h at 85 °C, and this has been verified independently.<sup>75</sup>

### VI.3.3. Single Layer Photoelectrochemical Cells

#### VI.3.3.1. Polyterthiophene Based Photoelectrochemical Cells

In this Section, we are now interested in studying the effect of the redox properties of polyterthiophene based photoelectrochemical cells on their power efficiency. Several terthiophene films were electropolymerised onto ITO glass substrates with different reduction bias and number of cycles, and fabricated into photovoltaic devices as described in Section III.3.2.

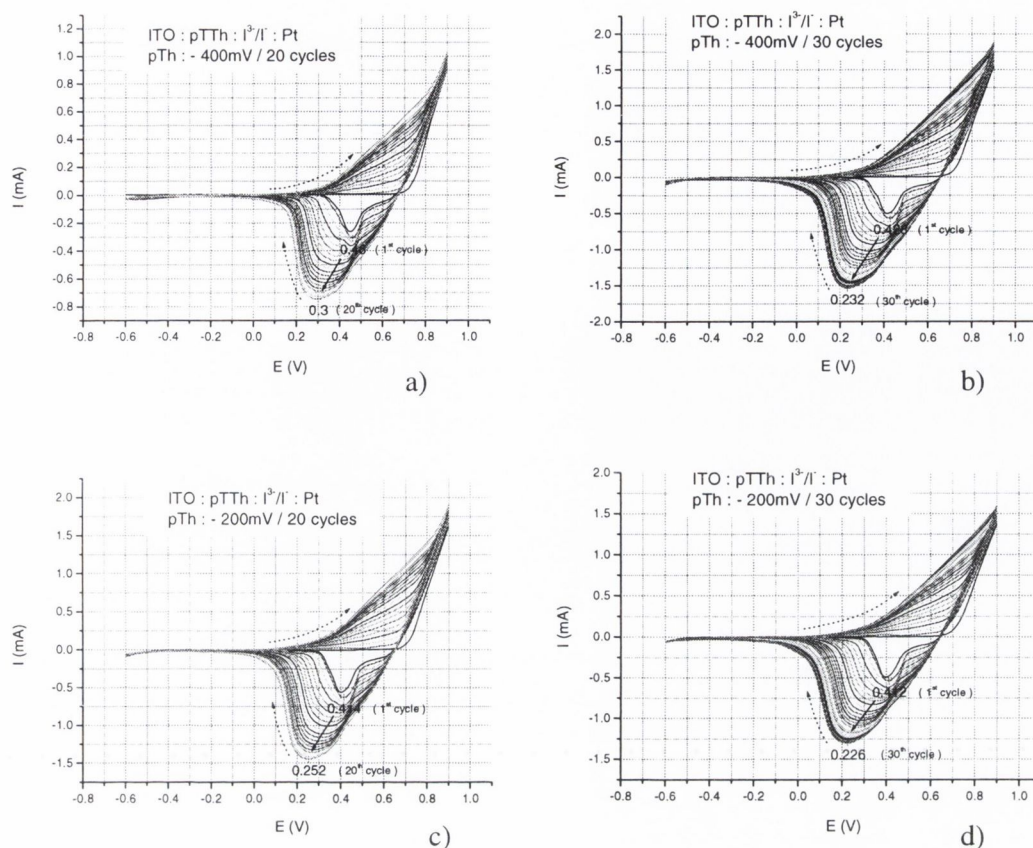


Figure VI.16 Cyclic voltammogram of the growth of polyterthiophene (pTTh) on ITO coated glass for a) – 400 mV final bias and 20 cycles, b) – 400 mV final bias and 30 cycles, c) – 200 mV final bias and 20 cycles and d) – 200 mV final bias and 30 cycles.

Cyclic voltammograms (CV) obtained for each of the polymer materials after growth are shown in Figure VI.16. In all cases, the polymer underwent reversible colour changes from blue (oxidised) to red/orange (reduced). As it is known for conducting polymers incorporated with small mobile counter anions, these redox processes can be represented by Figure VI.17:

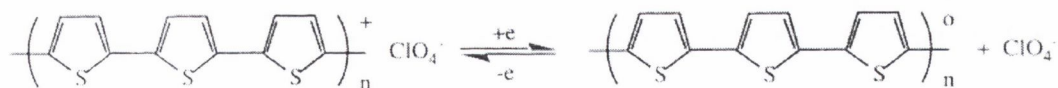


Figure VI.17 Redox process encountered by polyterthiophene.

where the counter anion ( $\text{ClO}_4^-$ ) is released into the electrolyte solution.

Figure VI.16 illustrates that at a given number of cycles of CV growth, the final reduction potential of the polymer films decreases as the reduction bias increases. Moreover one can see that the final reduction potential of the polymer films decreases as the number of cycles increases.

Figure VI.18 shows a typical I(V) characteristics of the photoelectrochemical cells tested in this Section. While it only shows the dark and illuminated I(V) characteristics of the polyterthiophene cell prepared with a – 200 mV reduction bias and 30 cycles, Table V.2 summarises the photovoltaic parameters of each of the cells.

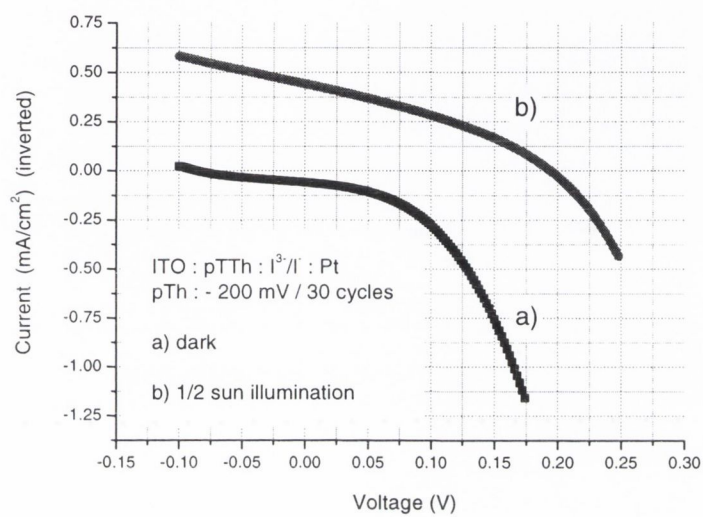


Figure VI.18 Current-voltage characteristics a) in the dark and b) under illumination of the polyterthiophene based photoelectrochemical cell.

Table VI.2 Short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and power efficiency ( $\eta$ ) of ITO / polyterthiophene /  $I^3/I^-$  / Pt cells as a function of the polymer reduction potential.

| Bias<br>(mV) | N° of<br>cycles | Reduction<br>potential<br>(mV) | $J_{sc}$<br>(mA/cm <sup>2</sup> ) | $V_{oc}$<br>(V) | FF<br>(%) | $\eta$<br>( $\times 10^{-2}$ %) |
|--------------|-----------------|--------------------------------|-----------------------------------|-----------------|-----------|---------------------------------|
| - 400        | 20              | 300                            | 0.322                             | 0.205           | 33.8      | 4.66                            |
|              | 30              | 232                            | 0.407                             | 0.213           | 32.5      | 5.64                            |
| - 200        | 20              | 252                            | 0.336                             | 0.209           | 33.8      | 4.82                            |
|              | 30              | 226                            | 0.442                             | 0.195           | 33.7      | 5.80                            |

Correlating the reduction potential of the polymer film and the power efficiency of its photoelectrochemical cell, an interesting trend appears. Indeed, as Figure VI.19 shows, the cell’s power efficiency decays exponentially as the reduction potential increases.



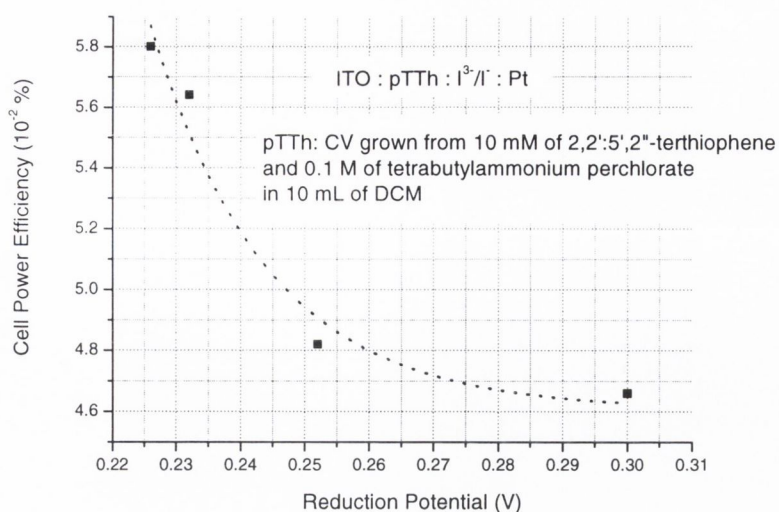


Figure VI.19 Power efficiency of the polyterthiophene based photoelectrochemical cell as a function of the reduction potential of the polyterthiophene film.

This result shows that the more oxydised the polymer is, the more efficient the photoelectrochemical cell is, which is consistent with results published in the literature.

### VI.3.3.2. Soluble Polymer Based Photoelectrochemical Cell

Soluble polymers have rarely been used in photoelectrochemical cells since their low conductivity makes them poor candidates for such cells. However, we tested an ITO / M3EH-PPV / I<sup>3-</sup>/I<sup>-</sup> / Pt cell in order to compare its efficiency to the more conventional electropolymerised based photoelectrochemical cells, as shown above.

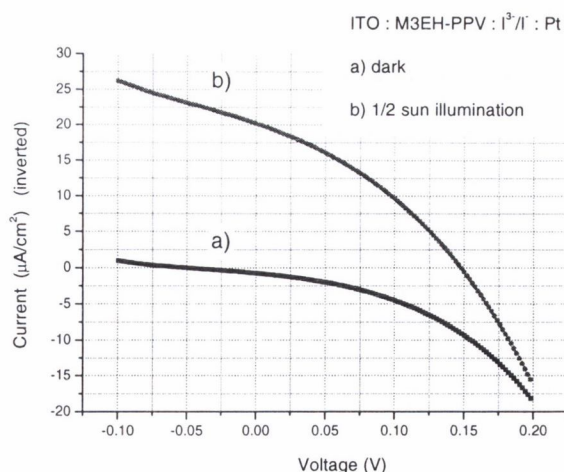


Figure VI.20 Current-voltage characteristics a) in the dark and b) under illumination of the M3EH-PPV based photoelectrochemical cell.

Figure VI.20 shows the results of the photovoltaic effect in the soluble polymer based photoelectrochemical cells tested in this Section. The photovoltaic parameters are summarised below:

- $J_{sc} = 20.2 \mu A/cm^2$
- $V_{oc} = 0.147$
- $FF = 34.0 \%$
- $\eta = 2.02 \times 10^{-3} \%$

We have therefore shown that such soluble polymer based photoelectrochemical cells can be prepared and be as efficient as single layer polymer cells. However, they are about an order of magnitude less efficient than electropolymerised based cells.

## VI.4. Conclusions

Many of up-to-date physical issues and developments on polymer solar cells and photoelectrochemical cells have been reviewed in this Chapter.

Photoinduced charge transfer from a donor acceptor molecule to an acceptor molecule represents one of the most used and efficient processes in polymer solar cells. This implies that bilayers, blends or laminated architectures using two materials with different and suitable ionisation potential, give the best power efficiency results.

In order to characterise the photovoltaic response of the main conjugated polymer used throughout this Thesis, a single M3EH-PPV layer polymer solar cell was prepared and studied in this Chapter, and discussed in terms of optical filter effect. We found that only a very thin layer was photo-active in single layer polymer solar cell, since primarily the exciton diffusion length in conjugated polymers remains small. This resulted in power efficiency being greater for thinner polymer solar cells.

As regards single layer photoelectrochemical cells, we found that, in the case of electropolymerised materials, the cell's power efficiency decayed exponentially as the reduction potential of the material increased. Soluble polymer based cells were also tested and found to have similar power efficiency to that of polymer solar cells. However, such cells were an order of magnitude less efficient than that of the electropolymerised based cells.

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# Chapter VII      ORGANIC    PHOTOVOLTAIC DEVICES USING MWNT

## VII.1. Introduction

As seen in Chapter VI, carbon nanotubes have been successfully used in organic light-emitting diodes. In this Chapter, we will now show the effects of using the same nanotube and polymer composite in organic photovoltaic devices. Section VII.2 will firstly discuss the photophysical processes occurring in nanotube and polymer bilayers and blends. Section VII.3 and Section VII.4 will then show the results and discussion on current-voltage characteristics and spectral responses under illumination both through the ITO electrode and the Al contact of polymer solar cells and photoelectrochemical cells respectively.

## VII.2. Photophysical Processes in MWNT Bilayers and Blends

### VII.2.1. Photoluminescence (PL) of the MWNT and Polymer Composite

We prepared several nanotube and polymer composite films with six various MWNT to PmPV mass ratios and measured their photoluminescence (PL).

Figures VII.1a and VII.1b show the wavelength dependence of the composites' PL intensity and the normalised PL intensity as a function of the MWNT to PmPV mass ratios respectively:

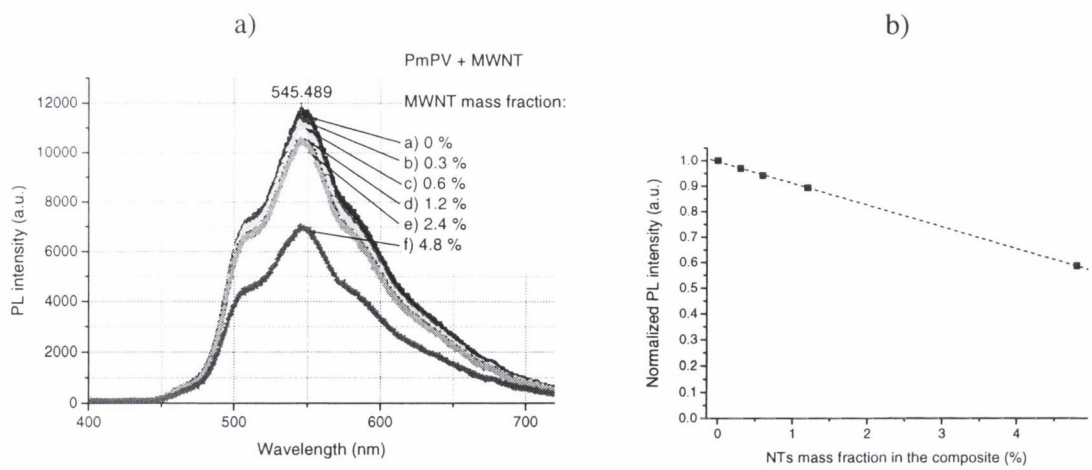


Figure VII.1 a) Photoluminescence (PL) intensity for polymer and nanotube composite films as a function wavelength and b) normalised PL intensity as a function of mass ratio.



Figure VII.1 shows that the photoluminescence intensity decreased linearly with the nanotube to polymer mass ratio. This decrease, however, was small. Indeed, in the case of the 4.8 % sample the photoluminescence intensity had fallen by only 42 % compared to the host polymer.

In addition, no spectral changes occurred in the composite film. As studied elsewhere, this result suggests that charge transfer from PPV to MWNT appear less efficient than a from a conjugated polymer to C<sub>60</sub> for example<sup>1-10</sup> and that only partial charge transfer and energy transfer is believed to occur in PPV and MWNT composites. Absorption and photoinduced-absorption (PIA) data from Ago *et al.* illustrated this point.<sup>11</sup> Neither data show features, such as polarons states in PIA, in the composite which indicate neither a ground state nor an excited interaction between PPV and MWNT.

In order to explain the decrease in PL intensity in the PmPV+MWNT composite, a model for the system has been recently developed by Ryan *et al.*<sup>12</sup> based on the assumption that the polymer strands adsorb in an ordered fashion onto the nanotube. A decrease in the alignment of the polymer chains will give a transition from a crystalline polymer layer at the nanotube surface to the amorphous structure of the bulk polymer. This will reduce the likelihood of low efficiency interchain species such as non-emissive excimers and exciplexes<sup>13</sup> forming far from the nanotube since it is the high level of crystallinity brought about by chain alignment which makes their formation possible.

A PL efficiency approaching that of the bulk polymer is therefore expected far from the nanotube while strong quenching in PL efficiency is anticipated at the nanotube surface due to greater interchain interactions.<sup>14</sup> Based on this argument the PL efficiency is assumed to fall off linearly from a maximum value at the amorphous-crystalline polymer boundary to a minimum at the crystalline polymer-nanotube interface.

### VII.2.2. Absorption and PL of MWNT Bilayers and Blends

In this Section, absorption and photoluminescence studies were performed on polymer bilayers and blends with MWNT, in order to elucidate the photophysical processes that could occur in the PmPV and MWNT composite and at the interface between the composite and other polymers.

VII.2.2.1. Introduction

Table VI.1 shows the summary of the samples prepared and tested in this Section.

Table VII.1 Thickness of the PmPV, M3EH-PPV and MWNT single layer, bilayers and blend samples prepared in this Section.

| Type          | Polymers                       | Thickness (nm) |
|---------------|--------------------------------|----------------|
| Single-layers | PmPV                           | 41             |
|               | M3EH-PPV                       | 95             |
| Bi-layers     | PmPV / M3EH-PPV                | 106            |
|               | M3EH-PPV / PmPV                | 136            |
|               | PmPV+1%MWNT / M3EH-PPV         | 78             |
|               | M3EH-PPV / PmPV+1%MWNT         | 290            |
| Blends        | M3EH-PPV 25% : PmPV 75%        | 54             |
|               | M3EH-PPV 50% : PmPV 50%        | 46             |
|               | M3EH-PPV 75% : PmPV 25%        | 83             |
|               | M3EH-PPV 25% : PmPV+1%MWNT 75% | 61             |
|               | M3EH-PPV 50% : PmPV+1%MWNT 50% | 63             |
|               | M3EH-PPV 75% : PmPV+1%MWNT 25% | 97             |

VII.2.2.2. Results and Discussion

VII.2.2.2.1. Absorption

In this Section, we are examining the ground state electronic interaction in the systems described above using UV-Vis absorption spectroscopy.

As discussed in Section III.4.2.1, absorption data reflect the vibrational energy distribution of the first excited state of a molecule or system of molecules either in solution or in solid state form. No shift in the absorption data of either blends or bilayers will indicate no ground state electronic interaction between the different macro-molecules involved. However, a red shift in the absorption data will not necessarily be the signature of ground

state interaction, but is often due to increased conjugation upon doping.

In the following Sections, the absorbance absolute values were divided by the thickness of the film in order to be able to compare the relative absorbance of each material or blend of materials. In each Figure below, the incident light was coming from the ‘right’ of the sample, *e.g.* for a PmPV / M3EH-PPV device from the M3EH-PPV side.

## Bilayers

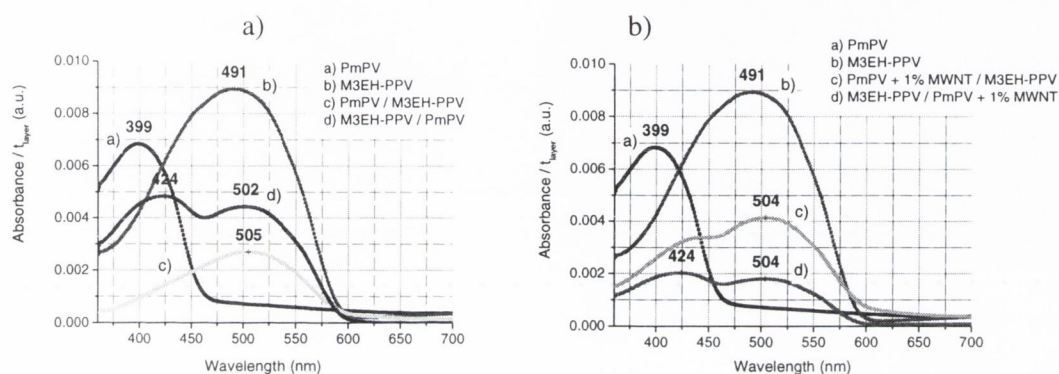


Figure VII.2 Relative absorbance of a) PmPV / M3EH-PPV and M3EH-PPV / PmPV bilayers, and b) PmPV+MWNT / M3EH-PPV and M3EH-PPV / PmPV+MWNT bilayers.

Figure VII.2a shows the relative absorbance of PmPV / M3EH-PPV and M3EH-PPV / PmPV bilayers, while Figure VII.2b shows the relative absorbance of PmPV+MWNT / M3EH-PPV and M3EH-PPV / PmPV+MWNT bilayers. The relative absorbance of PmPV and M3EH-PPV single layers is shown for comparison.

Although the absorbance should be independent of how the sample is oriented in the light path, a difference is observed between the PmPV / M3EH-PPV and M3EH-PPV / PmPV bilayers. This result could be explained by the difference in mixing at the interface and could be related to the result on blends, which will be presented in the following Section. No significant changes in terms of shift in wavelength however can be observed with the presence of MWNT in the system, which indicate there are no ground state interactions between MWNT and either PmPV or M3EH-PPV.

## Blends

Figure VII.3a shows the relative absorbance of M3EH-PPV 25 % : PmPV 75 %, M3EH-PPV 50 % : PmPV 50 %, M3EH-PPV 75 % : PmPV 25 % blends, and Figure VII.3b



shows the relative absorbance of M3EH-PPV 25 % : PmPV+MWNT 75 %, M3EH-PPV 50 % : PmPV+MWNT 50 %, M3EH-PPV 75 % : PmPV+MWNT 25 % blends, compared with the relative absorbance of PmPV and M3EH-PPV single layers.

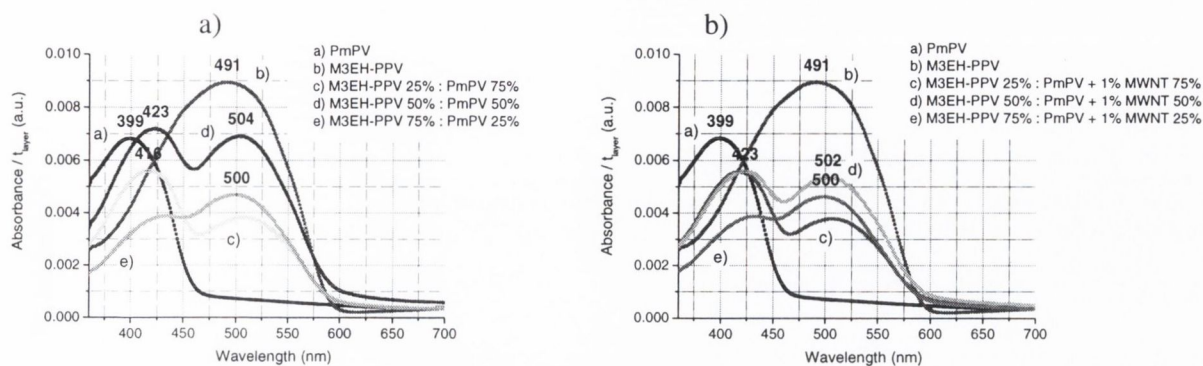


Figure VII.3 Relative absorbance of a) M3EH-PPV 25 % : PmPV 75 %, M3EH-PPV 50 % : PmPV 50 %, M3EH-PPV 75 % : PmPV 25 % blends, and b) M3EH-PPV 25 % : PmPV+MWNT 75 %, M3EH-PPV 50 % : PmPV+MWNT 50 %, M3EH-PPV 75 % : PmPV+MWNT 25 % blends.

This result interestingly shows that the M3EH-PPV to PmPV peak ratio scales with the blend concentration and that the relative absorbance of each of the blend samples is consistent with that of the bilayer samples.

Again one can see that MWNT show no ground state electronic interaction with the other materials, since no shift appear between the samples without and with MWNT.

#### VII.2.2.2.2. Photoluminescence

In this Section, we are now examining the excited state electronic interaction in the systems described above using photoluminescence (PL).

While PL reflects the vibrational energy distribution of the ground state as discussed in Section III.4.2.2, a decrease in PL is here of greater importance. Indeed processes such as charge transfer in bilayer or blend systems might compete with excitons radiative decay and therefore result in a PL decrease. Energy transfer on the other hand will result in the enhancement or generation of new peaks. Finally, the addition of two overlapping PL species might results in an apparent shift in the overall PL spectrum.

In the following Section, the PL absolute intensity of each sample was divided by the thickness of the film in order to be able to compare their relative PL intensity.

Single Layers

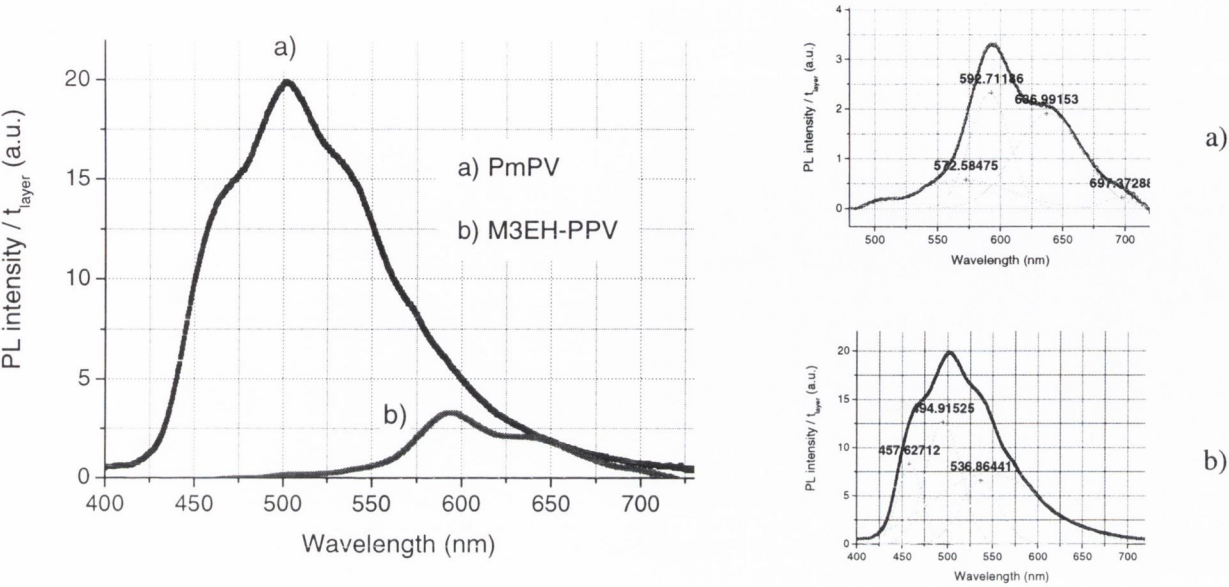


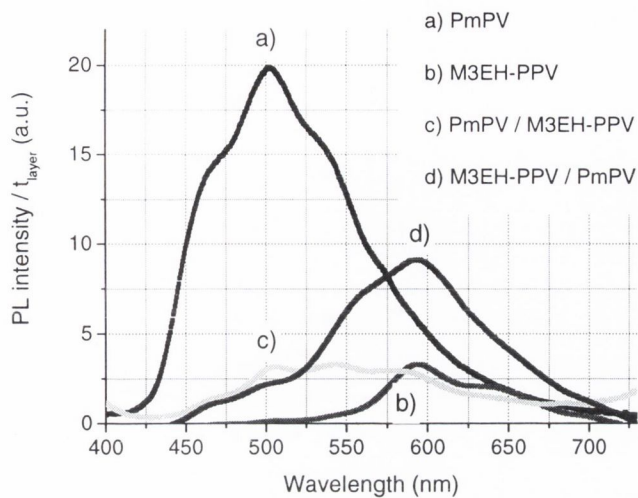
Figure VII.4 Relative PL intensity of a) PmPV and b) M3EH-PPV single layers.

Figure VII.4a and VII.4b show the relative PL intensity of PmPV and M3EH-PPV single layers respectively. Once can see that the PL efficiency of PmPV is greater than that of M3EH-PPV.

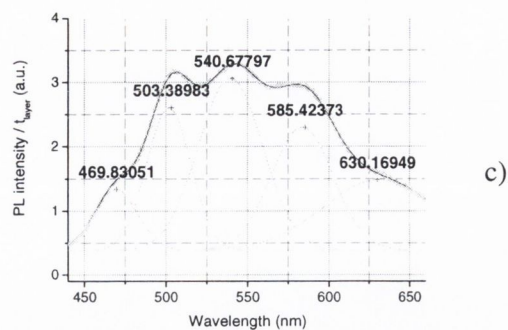
Bilayers

Figure VII.5 shows the relative PL intensity of PmPV / M3EH-PPV and M3EH-PPV / PmPV bilayers, compared with the relative PL intensity of PmPV and M3EH-PPV single layers.

When excited from the M3EH-PPV side, there is an addition of PL relative intensity in the PmPV / M3EH-PPV bilayer, as showed in FigureVII.5c. However, on excitation from the PmPV side, as seen in Figure VII.5d, one can see a clear M3EH-PPV dominance PL relative intensity. This result suggests that energy transfer is occurring from PmPV to M3EH-PPV.



Exciting from M3EH-PPV side



Exciting from PmPV side

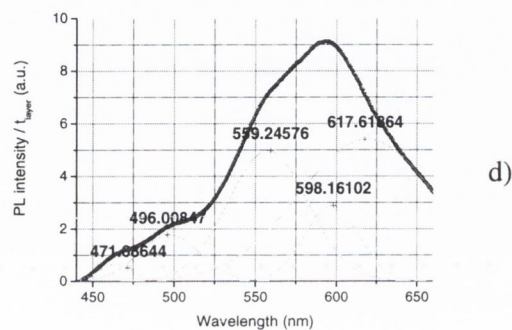
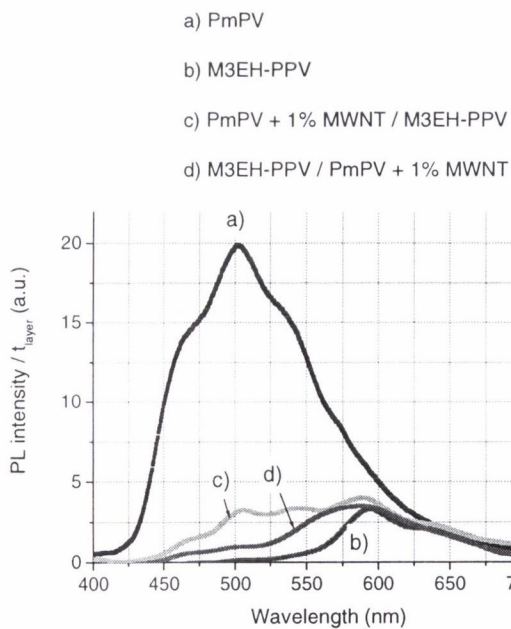
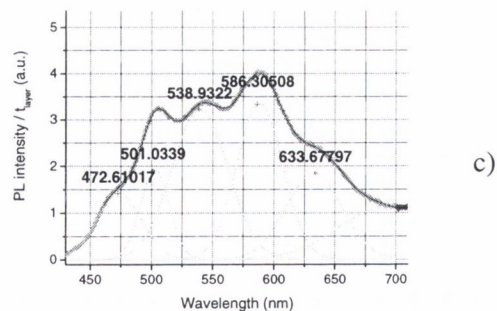


Figure VII.5 Relative PL intensity of c) PmPV / M3EH-PPV and d) M3EH-PPV / PmPV bilayers.



Exciting from M3EH-PPV side



Exciting from PmPV side

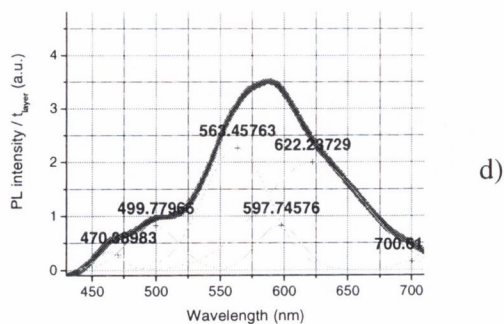


Figure VII.6 Relative PL intensity of c) PmPV+MWNT / M3EH-PPV and d) M3EH-PPV / PmPV+MWNT bilayers.



Figure VII.6 now shows the relative PL intensity of PmPV+MWNT / M3EH-PPV and M3EH-PPV / PmPV+MWNT bilayers, compared with the relative PL intensity of PmPV and M3EH-PPV single layers.

PL from the M3EH-PPV side shows a slight increase in the M3EH-PPV peak in the presence of MWNT, but the main result is that the PL of the M3EH-PPV / PmPV+MWNT bilayer (*i.e.* excited from the PmPV side) showed a decrease by more than half in relative intensity compared to the PL relative intensity of the same bilayer without MWNT.

This would suggest there a possible charge transfer from M3EH-PPV to MWNT.

## Blends

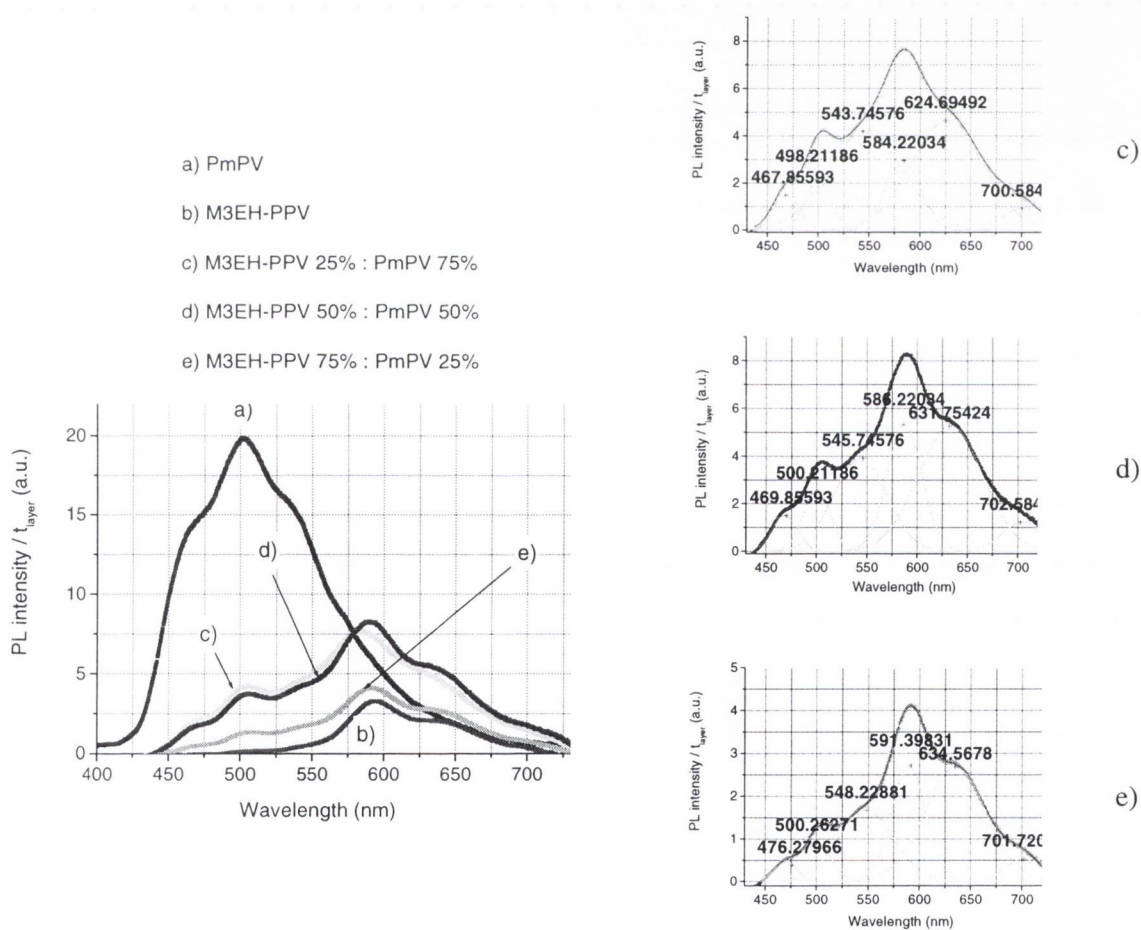


Figure VII.7 Relative PL intensity of c) M3EH-PPV 25 % : PmPV 75 %, d) M3EH-PPV 50 % : PmPV 50 %, and e) M3EH-PPV 75 % : PmPV 25 % blends.

Figure VII.7 shows the relative PL intensity of M3EH-PPV 25 % : PmPV 75 %, M3EH-PPV 50 % : PmPV 50 %, M3EH-PPV 75 % : PmPV 25 % blends, compared with the relative PL intensity of PmPV and M3EH-PPV single layers.

The M3EH-PPV PL is dominant in each blend samples, suggesting that, as in bilayer samples, energy transfer is occurring from PmPV to M3EH-PPV.

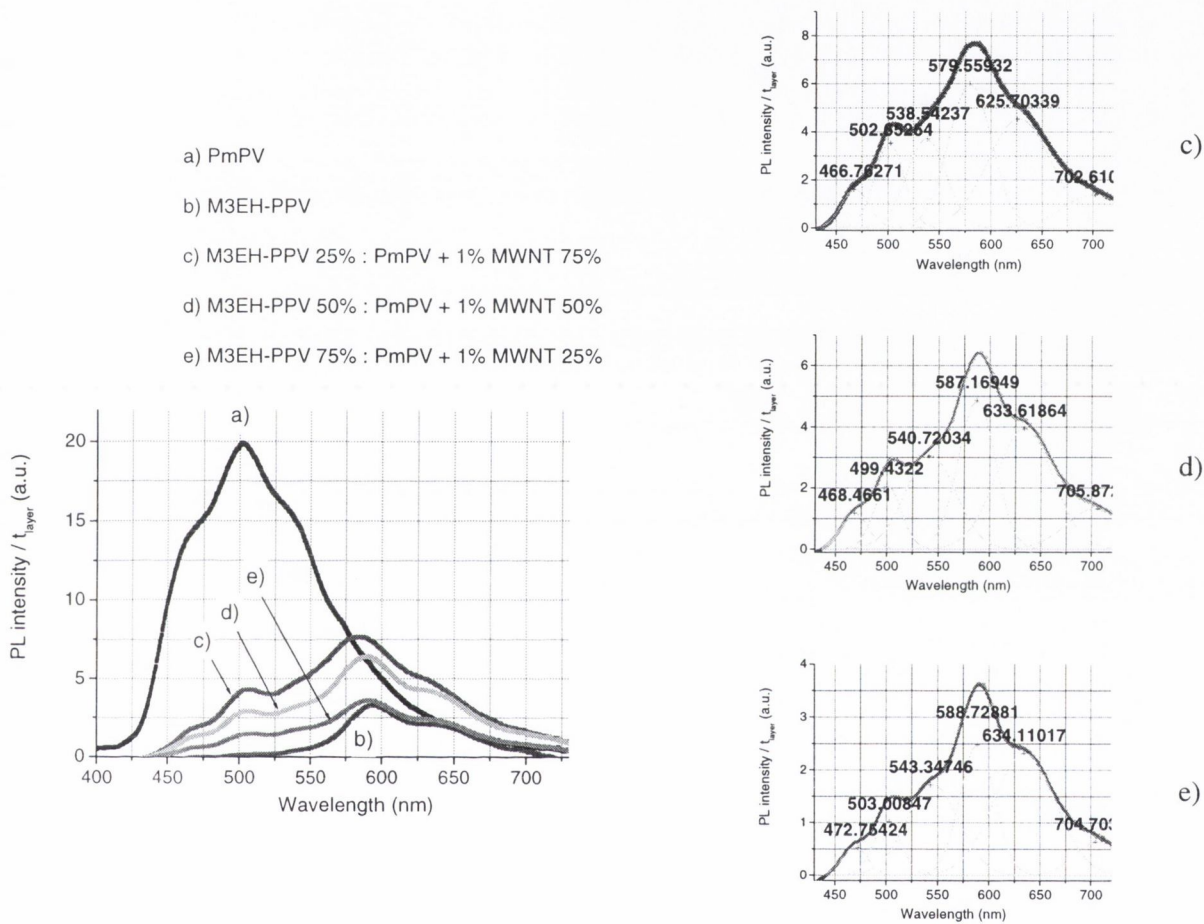


Figure VII.8 Relative PL intensity of c) M3EH-PPV 25 % : PmPV+MWNT 75 %, d) M3EH-PPV 50 % : PmPV+MWNT 50 %, and e) M3EH-PPV 75 % : PmPV+MWNT 25 % blends.

Figure VII.8 shows the relative PL intensity of M3EH-PPV 25 % : PmPV+MWNT 75 %, M3EH-PPV 50 % : PmPV+MWNT 50 %, M3EH-PPV 75 % : PmPV+MWNT 25 % blends, compared with the relative PL intensity of PmPV and M3EH-PPV single layers.

Again, the M3EH-PPV PL is dominant, suggesting energy transfer from PmPV to M3EH-PPV. But there is this time no evidence of charge transfer from M3EH-PPV to MWNT, since the presence of MWNT in the blend samples is not followed by a decrease in the PL relative intensity.

### VII.2.2.3. Summary

Absorption spectroscopy has showed that no electronic interaction is occurring between the different species present in the systems studies (bilayers and blends): M3EH-PPV, PmPV and MWNT.

On the other hand, PL studies have showed that in M3EH-PPV / PmPV, M3EH-PPV / PmPV bi-layers:

- excited from the M3EH-PPV side, there is an addition in the PL;
- excited from the PmPV side, M3EH-PPV PL is dominant;

suggesting energy transfer from PmPV to M3EH-PPV.

Moreover, comparing the relative PL intensity of M3EH-PPV / PmPV+MWNT to that of M3EH-PPV / PmPV, a definite quenching was observed, suggesting a possible charge transfer from M3EH-PPV to MWNT. However, this wasn't observed in the M3EH-PPV : PmPV+MWNT blend samples, suggesting that the physical interface is needed in order for the process to happen.

Nevertheless, the energy transfer from PmPV to M3EH-PPV, consistent with both M3EH-PPV and PmPV energy levels, was observed in the blends, as well as in the bilayers.

## VII.3. Polymer Solar Cells

### VII.3.1. Introduction

In this Section, we will show the use of the PmPV and MWNT composite as the active layer in a photovoltaic cell in order to investigate the role of carbon nanotubes in such a device. A buffer layer was used between an indium tin oxide (ITO) anode and the composite layer in order to avoid short-circuits, which could occur in single-layered composite cells due to the highly conductive nature of MWNT. The choice of M3EH-PPV as the thin buffer layer was motivated by both the need to isolate the composite layer and provide a good hole-transport medium. Therefore, the main solar cell studied in this work consisted of the following structure: ITO / M3EH-PPV / PmPV+MWNT / Al. In addition, PmPV and M3EH-PPV single-layered photovoltaic cells were fabricated, as well as a double-layered cell without MWNT, as shown in Figure VII.9:



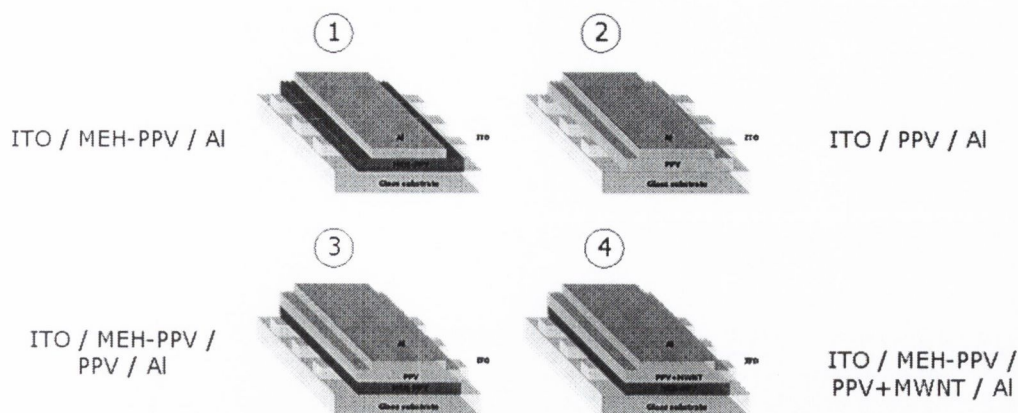


Figure VII.9 Polymer solar cells with MWNT tested in this Section.

## VII.3.2. Results and Discussion

### VII.3.2.1. Optical Filter Effect

Shown in Figures VII.10 and VII.11 are the current-voltage characteristics and spectral response of each photovoltaic device when illuminated through the ITO electrode respectively. The important electrical parameters associated with these devices are summarised in Table VII.2:

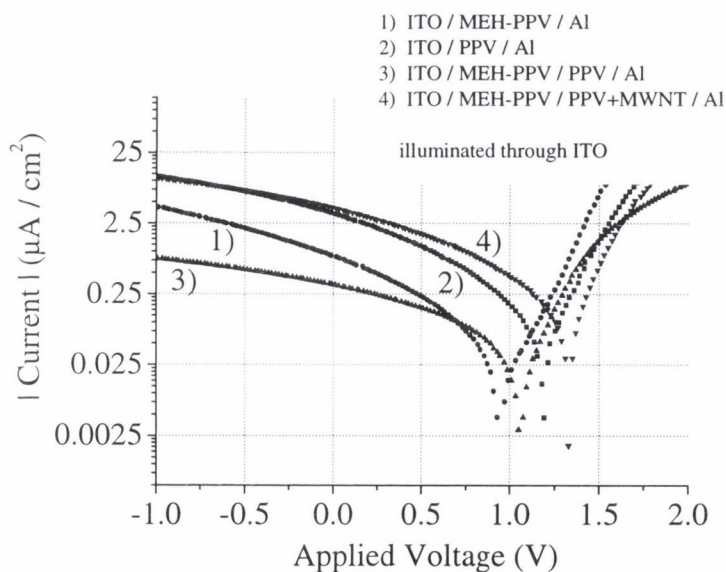


Figure VII.10 Current-voltage characteristics for each cell under 80 mW/cm<sup>2</sup> white illumination through ITO.

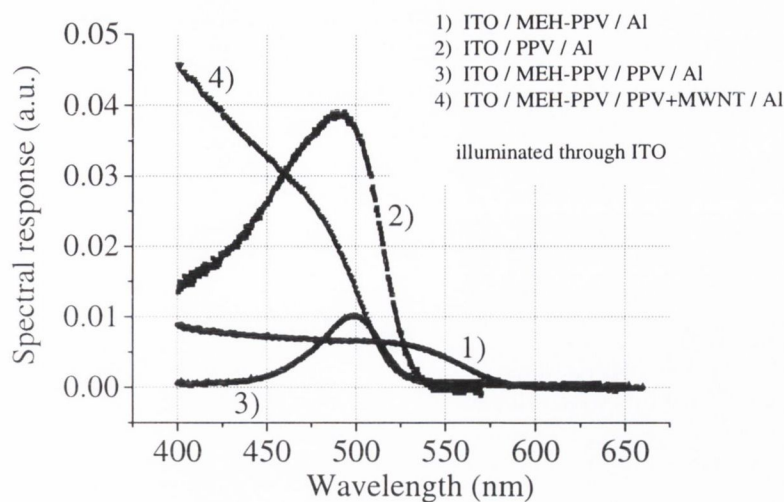


Figure VII.11 Spectral response for each cell under 80 mW/cm<sup>2</sup> white illumination through ITO.

The ‘MWNT’ cell (device n° 4) exhibited the highest open-circuit voltage ( $V_{oc}$ ) at 1.33 V, short-circuit current density ( $J_{sc}$ ) at 4.05 mA/cm<sup>2</sup> and indeed power conversion efficiency ( $\eta$ ) at  $11.2 \times 10^{-4} \%$ . The power conversion efficiency of the ‘MWNT’ cell was an order of magnitude greater than that of the cell ‘without MWNT’ (device n° 3) and even greater than that of the ‘PPV’ single-layered cell (device n° 2), despite the partial absorption of the incident light by the MEH-PPV buffer layer.

Table VII.2 Open-circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), fill factor (FF) and power conversion efficiency ( $\eta$ ) for each photovoltaic cell tested under 80 mW/cm<sup>2</sup> white illumination through ITO: ITO / MEH-PPV / Al (‘MEH-PPV’), ITO / PPV / Al (‘PPV’), ITO / MEH-PPV / PPV / Al (‘without MWNT’) and ITO / MEH-PPV / PPV+MWNT / Al (‘MWNT’).

| Name of cell   | n° | $V_{oc}$ (V) | $J_{sc}$ ( $\mu A/cm^2$ ) | FF (%) | $\eta$ ( $\times 10^{-4} \%$ ) |
|----------------|----|--------------|---------------------------|--------|--------------------------------|
| ‘MEH-PPV’      | 1  | 0.95         | 0.84                      | 16.4   | 1.63                           |
| ‘PPV’          | 2  | 1.18         | 3.40                      | 15.5   | 7.75                           |
| ‘without MWNT’ | 3  | 1.05         | 0.34                      | 22.9   | 1.01                           |
| ‘MWNT’         | 4  | 1.33         | 4.05                      | 16.7   | 11.2                           |

As regards their spectral response under illumination through ITO, the ‘MWNT’ cell exhibited a wide response, also referred as to ‘sympatic’ response, while the cell ‘without MWNT’ showed a narrow response, also referred as to ‘antibatic’ response. Similarly, the ‘PPV’ device showed a narrow spectral response. This result, referred as optical filter effect as discussed in Section VI.2.5, is a consequence of the poor electron mobility in

PPV. The only active region in this device is that which lies close to the Al contact, where excitons are split and collected. This 'filter-effect' decreases dramatically if the PPV thickness is reduced or if the cell is illuminated through the Al contact as shown in Figure VII.13.

Shown in Figure VII.12 are the current-voltage characteristics and spectral response of each photovoltaic device when illuminated through the Al electrode respectively. While it is to be noted that the ITO / PPV / Al, ITO / MEH-PPV / PPV / Al and ITO / MEH-PPV / PPV+MWNT / Al cells showed no difference in terms of either power conversion efficiency or spectral response despite the presence of MWNT, the spectral response of each cell clearly demonstrated no 'filter effect', as Figure VII.13 shows.

Under illumination through ITO however, we have shown that the addition of MWNT has significantly increased the short-circuit current of the device to a value slightly better than that of the original 'PPV' cell. Moreover, the shape of the spectral response has changed significantly. Indeed, this spectral response is almost identical to that of a device illuminated through a semi-transparent Al electrode. Thus, the 'filter effect' has been effectively eliminated in the presence of MWNT and thus the excitons that are contributing to the current have been created by photons that have not been absorbed by the PPV material.

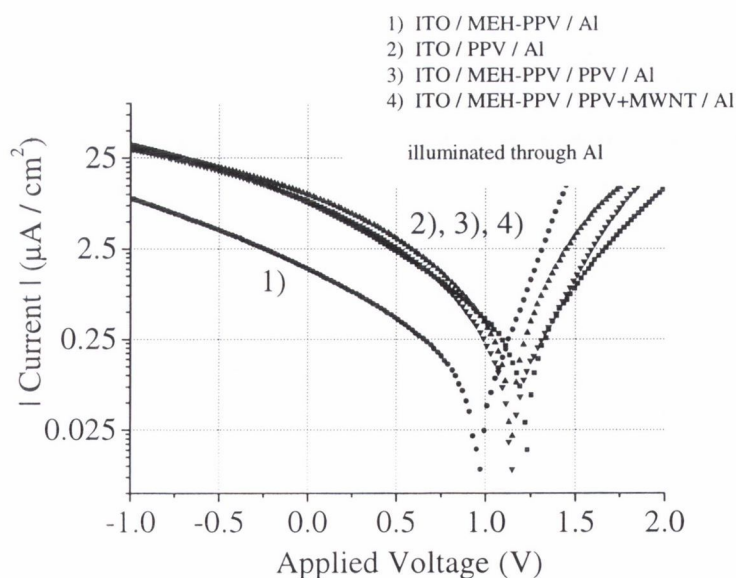


Figure VII.12 Current-voltage characteristics for each cell under  $80 \text{ mW/cm}^2$  white illumination through Al.



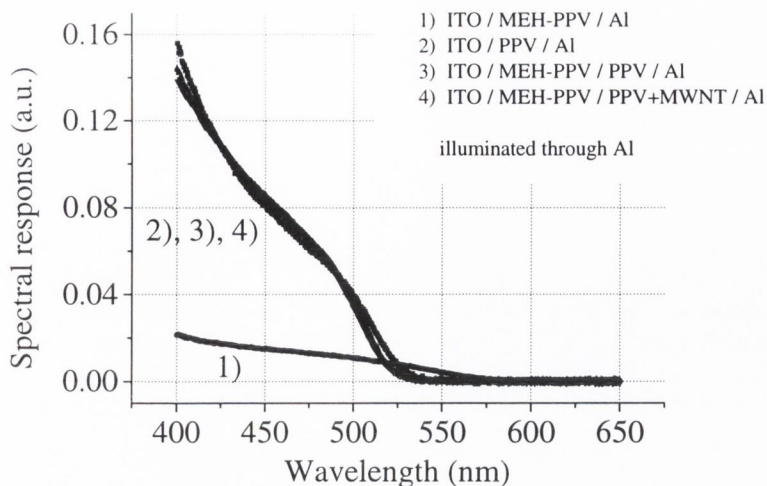


Figure VII.13 Spectral response for each cell under  $80 \text{ mW/cm}^2$  white illumination through Al.

### VII.3.2.2. Charge Dissociation

As shown in Figure VII.12, the ‘MWNT’ and ‘without MWNT’ devices behave identically when illuminated through Al. If there would be any additional charge transfer from PPV to MWNT, we would see an increase in the efficiency of the ITO / MEH-PPV / PPV+MWNT / Al cell over the ITO / MEH-PPV / PPV / Al cell. Therefore, these results clearly suggest that no or little additional charge transfer process occurs between PPV and MWNT, which confirm the results from the previous Section VII.2.1.

As a result, the improvements that we have seen under illumination through ITO, can only be explained by charge dissociation at the one extra planar interface, namely the MEH-PPV / PPV interface, involving hole transfer from PPV to MEH-PPV.

As we have demonstrated in Section VII.2.2, we believe that further to this electronic transfer, energy transfer from M3EH-PPV to MWNT is likely to occur at the M3EH-PPV / PmPV+MWNT interface.

Kymakis *et al.* attributed their two orders of magnitude increase in short-circuit current to an efficient charge transfer and transport through SWNT,<sup>15</sup> while Ago *et al.* explained their increase in external quantum efficiency by an energy transfer and partial hole transfer from PPV to MWNT together with scattering and absorption by MWNT.<sup>16</sup> This suggests that, although some form of charge and / or energy transfer is likely to occur in our ‘MWNT’

photovoltaic cell, we are not seeing the fruits of these processes and the efficient charge transport via the continuous conductive nanotube network the Al electrode, following charge dissociation at the MEH-PPV / PPV interface, is to play a more significant role.

VII.3.2.3. Charge Transport

Since the absorbance of the ‘MWNT’ device is comparable to that of the ‘without MWNT’ device, the change in spectral response under illumination through ITO, as seen in Figure VII.14, is not due to a reduction in the optical absorbance of the material. The only explanation, therefore, is that MWNT have allowed the optical active layer in the device to be larger. We have seen above that no charge transfer is occurring between PPV and MWNT in order to explain this increased active layer.

We therefore believe that efficient charge transport via the continuous conductive nanotube network to the Al electrode is to play a significant role. As we have seen no improvement in hole transport between the ‘MWNT’ and ‘without MWNT’ cells when illuminated through Al, enhanced electron transport can only explain the increased power conversion efficiency when illuminated through ITO. We believe that following light absorption near the MEH-PPV / PPV interface, electrons are transported through the MWNT phase to the Al electrode, as they cannot be transported through the PPV. Figure VII.14 summarises the different processes believed to take place in the ITO / MEH-PPV / PPV+MWNT / Al cell under short-circuit conditions when illuminated through ITO:

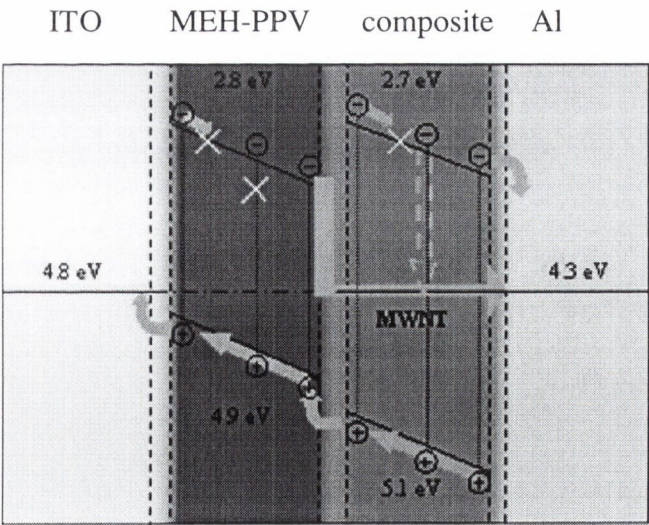


Figure VII.14 Proposed schematic band diagram for the ‘MWNT’ cell under short-circuit conditions and 80 mW/cm<sup>2</sup> white illumination through ITO. The crosses show excitons / charges that are not giving rise to the photocurrent.



#### VII.3.2.4. Open-circuit Voltage

The open-circuit voltage ( $V_{oc}$ ) of the 'MWNT' cell was 0.15 V greater than that of the 'PPV' cell and 0.32 V greater than that of the cell 'without MWNT' under illumination through ITO, while no difference in  $V_{oc}$  was observed when illuminated through Al. Interestingly, the presence of MWNT not only has increased the magnitude of the short-circuit current density but was also responsible for a change in the device open circuit voltage.

Although  $V_{oc}$  is to be set by the difference in work functions of the two electrodes, this model doesn't work as in our case it should be  $\sim 0.5$  V. However, models have proposed that in donor-acceptor organic solar cells this parameter depends on the energetic levels of the species involved in the process of dissociation of photo-generated excitons.<sup>14</sup> Interfacial layers at the electrode / polymer boundary (*e.g.* oxygen, aluminium-polymer complexes) is also known to play an important part.

Given the conducting nature of the MWNT, electrons would immediately decay to the Fermi energy, and thus there should be no potential difference maintained at the PPV / MWNT interface. Given also that the MWNT are in the layer adjacent to the Al electrode it is unlikely that the  $V_{oc}$  change is related to the ITO interface. Therefore, the change in the open-circuit voltage is likely to arise from differences in work functions and chemical reactions at the PPV+MWNT / Al interface.<sup>17,18</sup> While charges transferred to MWNT and then to Al may lose less energy than charges transferred from polymer to Al, it also plausible that MWNT, in contact with the Al electrode, may cause a difference in aluminium's oxidation state and thus change the open-circuit voltage of the device.

### VII.4. Photoelectrochemical Cells

#### VII.4.1. Introduction

In order to investigate the effect of MWNT in another type of organic photovoltaic device, we prepared and studied an ITO / M3EH-PPV+MWNT /  $I^3^-/I^-$  / Pt photoelectrochemical cell. An ITO / M3EH-PPV /  $I^3^-/I^-$  / Pt photoelectrochemical cell was also prepared for comparison and  $I(V)$  characteristics in the dark and under 50 mW/cm<sup>2</sup> (half sun) white illumination were analysed for both devices.



VII.4.2. Results and Discussion

Current-voltage characteristics of the devices listed above are shown in Figure VII.15, and the photovoltaic parameters of each cell are summarised in Table VII.3:

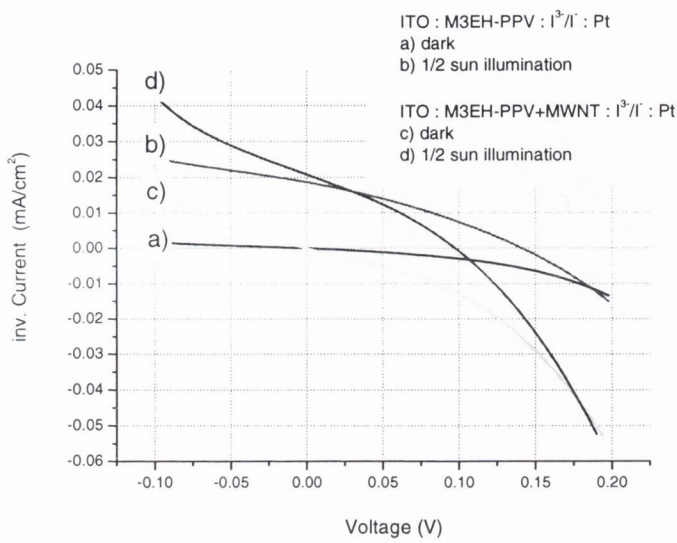


Figure VII.15 Dark current-voltage characteristics of a) the M3EH-PPV photoelectrochemical cell and b) the M3EH-PPV+MWNT photoelectrochemical cell, and I(V)s under illumination for c) the M3EH-PPV photoelectrochemical cell and d) the M3EH-PPV+MWNT photoelectrochemical cell.

The current intensity of the photoelectrochemical cell with MWNT both in the dark and under illumination is greater than that of the cell without MWNT, suggesting enhanced charge carrier transport in the polymer film with MWNT as seen before.

Table VII.3 Short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and power efficiency ( $\eta$ ) of ITO / M3EH-PPV /  $I^3^+/I^-$  / Pt and ITO / M3EH-PPV+MWNT /  $I^3^+/I^-$  / Pt cells.

| Film          | $J_{sc}$<br>( $\mu A/cm^2$ ) | $V_{oc}$<br>(mV) | FF<br>(%) | $\eta$<br>( $\times 10^{-3} \%$ ) |
|---------------|------------------------------|------------------|-----------|-----------------------------------|
| M3EH-PPV      | 18.63                        | 141              | 31.4      | 1.65                              |
| M3EH-PPV+MWNT | 20.78                        | 97               | 30.9      | 1.24                              |

This resulted in the short current density of the M3EH-PPV+MWNT cell to be greater than that of the M3EH-PPV cell. However, the open-circuit voltage of the cell with MWNT dropped by 40 mV. The power efficiency of the M3EH-PPV+MWNT photoelectrochemical cell therefore was overall slightly smaller than that of the M3EH-PPV cell.

## VII.5. Conclusions

In this Chapter, photophysical processes in bilayers and blends comprising carbon nanotubes and the use of nanotubes in organic photovoltaic devices were studied and analysed.

No electronic interaction in the ground state were found to occur between PmPV, M3EH-PPV and multi-walled carbon nanotubes, while a slight decrease in photoluminescence intensity in PmPV and MWNT composite wasn't believed to be attributed to charge transfer between PmPV and MWNT.

Absorption and photoluminescence studies on M3EH-PPV and PmPV+MWNT bilayers however revealed that energy transfer from M3EH-PPV to PmPV, followed by charge transfer from M3EH-PPV to MWNT is likely to occur.

As regards the use of nanotubes in polymer solar cells, we measured the photovoltaic response of cells using a nanotube and polymer composite and a thin MEH-PPV buffer layer in a sandwich structure with ITO as the anode and Al as the cathode. Moreover, an ITO / M3EH-PPV+MWNT /  $I^3-/I^-$  / Pt photoelectrochemical cell was prepared and characterised.

The ITO / MEH-PPV / PPV+MWNT / Al photovoltaic cell was found to have an operating voltage ( $V_{oc}$ ) of 1.33 V, a short-circuit current density ( $J_{sc}$ ) of 4.05 mA/cm<sup>2</sup> and a power conversion efficiency ( $\eta$ ) of  $11.2 \times 10^{-4}$  % under 80 mW/cm<sup>2</sup> white illumination through ITO. The presence of MWNT widened the optical active layer and increased the power conversion by an order of magnitude, compared to a cell without MWNT.

Increased short-circuit density in polytertiophene based photoelectrochemical cells with MWNT was also observed.

We have concluded that the carbon nanotubes have allowed electrons to be transferred and efficiently transported, via their continuous conductive network, to the Al electrode. In addition, we have seen that electrochemical changes at the composite / Al interface have lead to an increase in open-circuit voltage in polymer solar cells.

## VII.6. References

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# Chapter VIII CONCLUSIONS AND IDEAS FOR FUTURE WORK

## VIII.1. Conclusions

The discovery of carbon nanotubes has marked an important milestone in materials science and nanotechnology, due to the prospects for their use in future nano-scale applications. The work presented in this Thesis has clearly demonstrated that carbon nanotubes can be used as charge transport media in organic devices.

In order to understand the physics of conjugated polymers based organic devices without the use of carbon nanotubes, we firstly prepared and characterised single layer organic light-emitting diodes (OLEDs) and organic photovoltaic devices.

We presented the electrode limited injection model at a Schottky barrier interface between a polymer and a metal, and the space charge limited bulk conduction mechanism in conjugated polymers. Single layer OLEDs' current-voltage characteristics were analysed using both models in order to extract intrinsic parameters such as the polymer's Fermi energy level, or majority charge carriers' mobility.

As regards single layer photovoltaic devices, we discussed the results in terms of optical filter effect and found that only a very thin layer was photo-active in single layer polymer solar cell, resulting in power efficiency being greater for thinner polymer solar cells.

Research characterising polymer and carbon nanotube composites (PmPV+MWNT) determined that the nanotubes can be easily purified, processed and then used in existing all organic devices.

Both DC and AC conductivities of the nanotube and polymer composite were measured and percolation scaling laws were used to discuss the results. Percolation threshold  $p_c = 0.055$  % by mass and exponent  $t = 1.36$  were extracted from the experimental data. The extrapolated conductivity for a nanotube film was significantly lower than expected with  $\sigma_{NT} = 10^{-3}$  S/m. We suggested that this was due to a thick coating of polymer, resulting in poor electrical connection between nanotubes and concluded that conduction in this system

is due to fluctuation induced tunnelling.

Absorption and photoluminescence studies on PmPV+MWNT composites and M3EH-PPV and PmPV+MWNT bilayers were also carried out. No electronic interaction in the ground state was found to occur between PmPV, M3EH-PPV and multi-walled carbon nanotubes. Charge transfer between PmPV and MWNT was believed to be very unlikely, as photoluminescence intensity in PmPV+MWNT composites only decreased slightly as the MWNT content increased. However, absorption and photoluminescence studies on M3EH-PPV and PmPV+MWNT bilayers revealed that energy transfer from M3EH-PPV to PmPV, followed by charge transfer from M3EH-PPV to MWNT is likely to occur.

As regards the use of the PmPV+MWNT composite in M3EH-PPV based OLEDs, introduction of the composite layer causes a potential barrier to both holes and electrons at the M3EH-PPV / composite interface. This barrier decreased with nanotube to polymer mass ratio leading to larger device currents. However, at all nanotube to polymer mass ratios used for the composite, the relative efficiencies for the devices using this material as an electron-transport layer improved compared to the M3EH-PPV single layered devices. The optimum in the relative efficiency was observed for a nanotube mass ratio of 1.2 %.

Concerning the use of nanotubes in polymer solar cells, we measured the photovoltaic response of cells using a nanotube and polymer composite and a thin MEH-PPV buffer layer in a sandwich structure with ITO as the anode and Al as the cathode. Moreover, an ITO / M3EH-PPV+MWNT /  $I^3/I$  / Pt photoelectrochemical cell was prepared and characterised. The presence of MWNT widened the optical active layer and increased the power conversion by an order of magnitude, compared to a cell without MWNT, while increased short-circuit density in polytertiophene based photoelectrochemical cells with MWNT was observed. We concluded that the carbon nanotubes have allowed electrons to be transferred and efficiently transported, via their continuous conductive network, to the Al electrode.

## VIII.2. Future Work

While these results have shown that one particular class of organic materials: carbon nanotubes can be used as charge transport media to enhance the efficiency of existing organic devices, there are still improvements to be made.

As regards increasing the power efficiency of polymer solar cells with MWNT, work is ongoing to use MWNT in conjugated polymer and C<sub>60</sub> derivatives blend cells in order to both tackle charge transfer and charge transport in such organic devices. Another interesting subject to explore will be the use of photonic bandgap structures to extend the range of available low bandgap materials. Such photonic structures may even be realised in an highly ordered structure consisting of co-block polymers.

However, a common problem for all the applications of conjugated polymers will also remain: stability. Even though the expectation on the lifetimes of electronic devices is shrinking due to very short life / fashion cycles of such applications and even though industry may be interested in the cost of an item rather than in a very long durability of it, a shelf lifetime of several years as well as an operational lifetime of tens of thousands of hours are requested for all durable applications. Conjugated polymers have to be protected from air and humidity to achieve such lifetimes. These protection methods are being developed for light emitting diodes (LEDs) as well as PV elements. Their effectiveness is going to be crucial for the success of any applications using these materials. Recent reports from LED research indicate that the stability problem has been sufficiently overcome in order to enter into large scale applications, which in turn is a good sign for plastic solar cells.



# APPENDIX A      PUBLICATIONS ASSOCIATED WITH THIS THESIS

- 9      P. Fournet, M.-A. Measson, J. N. Coleman, and W. J. Blau, "*Impedance spectroscopy analysis of novel semiconducting polymers*".  
In preparation (2003).
- 8      P. Fournet, J. N. Coleman, C. R. McNeill, P. C. Dastoor, G. G. Wallace, H.-H. Hörhold, and W. J. Blau, "*Efficient charge transfer and transport using carbon nanotube composites in organic photovoltaic cells*".  
In preparation (2003).
- 7      P. Fournet, J. N. Coleman, D. F. O'Brien, B. Lahr, A. Drury, C. R. McNeill, P. C. Dastoor, G. G. Wallace, H.-H. Hörhold, and W. J. Blau, "*Carbon nanotube composites as efficient charge transport media in organic optoelectronic devices*".  
Proceedings of SPIE Vol. 4876, 338-350 (2003).
- 6      B. E. Kilbride, J. N. Coleman, J. Fraysse, P. Fournet, M. Cadek, A. Drury, S. Hutzler, S. Roth, W. J. Blau, "*Experimental observation of scaling laws for ac and dc conductivity in polymer-carbon nanotube composite thin film*".  
Journal of Applied Physics 92 (7), 4024-4030 (2002).
- 5      P. Fournet, T. Kobayashi, J. N. Coleman, D. F. O'Brien, B. Lahr, A. Drury, H.-H. Hörhold, W. J. Blau, "*A carbon nanotube composite as an electron-transport layer in organic light-emitting diodes*".  
CLEO 2001 Postconference Technical Digest, IEEE cat. no. 01CH37170, 34-35
- 4      P. Fournet, J. N. Coleman, D. F. O'Brien, B. Lahr, A. Drury, H.-H. Hörhold, W. J. Blau, "*Enhanced brightness in organic light-emitting diodes using a carbon nanotube composite as an electron-transport layer*".  
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