Improvements to Organic Light Emitting Devices with Carbon Nanotubes and Fluoropolymer

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Abstract

This thesis describes research on the effects of using carbon nanotubes (CNTs) and fluoropolymer based interlayers on the performance of organic devices. Photoelectron spectroscopy showed that the insertion of acid oxidised CNTs can improve the work function of indium-tin-oxide transparent electrodes. No significant changes of the HOMO level of triphenylidiamine (TPD) indicated that the equilibrium condition was met at the interfaces. Device I-V characteristic indicated that high density of trap levels had been introduced throughout the triphenylidiamine layer. This hypothesis is supported by Atomic Force Microscopy (AFM) and by high contrast current mapping using conductive AFM measurements. The broadening and featureless spectrum for the modified triphenylidiamine provides further confirmation. The high density of traps in TPD results in a high current density with lower luminance in the organic light-emitting diode (OLED) device due to the imbalance of charge injection from positive and negative electrodes. The insertion of CNTs into polymer LEDs shows that the direct contact between the nanotube with the electroluminescencing polymer could induce significant quenching effect of the photoluminescence at the interface. However, the insertion of a hole-transport interlayer which also acts as an electron-blocking layer between the CNT and the polymer can reduce the quenching effect by shifting the recombination zone away from the anode/CNT interface.

The effects of insertion of a polytetrafluoroethylene (PTFE) interlayer deposited via thermal evaporation in OLED and organic photovoltaic (OPV) devices are studied. The PTFE interlayer can improve the work function of PEDOT:PSS and reducing the electrochemical process in-between the PEDOT:PSS/polyfluorene. A remarkable improvement on the device lifetime and colour purity are found by incorporating PTFE to prevent the de-doping of the PEDOT:PSS. In the OPV devices, the PTFE and ultraviolet (UV) treated PTFE buffer layers at the anode/organic interface can improve the short-circuit current, open-circuit voltage and power conversion efficiency due to the reduction of the hole extraction barrier.
Declaration

This thesis is submitted for the degree of Doctor of Philosophy at the University of Surrey. Except where referenced, this work is original. No part of this thesis has been or is currently being submitted for any other degrees, diploma or other qualifications.

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CHAPTER 1

Introduction to Organic Light Emitting Diodes

This chapter gives an overview to the progress made in using organic material in electrical devices. The aim is to establish a context for the thesis that follows and at the same time demonstrate the unique properties and capabilities of molecular and polymeric materials. The recent progress in organic electronic devices has been tremendous. However there are many aspects of device physics that remain controversial at present and need further study.

1.1 Development of the inorganic electroluminescence device

Electroluminescence (EL), an optical and electrical phenomenon in which a material emits light in response to electrical current, was first discovered in 1907 by H.J. Round in a piece of carbon lamp crystal (SiC)\(^1\). At the beginning of 1962, when Nick Holonyak Jr. created the first practical inorganic light emitting diode (LED), it began a tremendous effort on commercial research in LEDs\(^2\). It lead to, in 1968, the first commercial mass production of 655nm red LEDs based on gallium arsenide phosphide (GaAs\(_{1-x}\)P\(_x\)) by Hewlett-Packard and Monsanto\(^4\).

The fast progress on the inorganic LED development has led to devices of various colours, ranging across the ultraviolet, visible and infrared, and with high brightness. In terms of lighting application, LEDs present many advantages over traditional light sources including lower energy consumption, longer lifetime, smaller size and faster switching. However, they are still relatively expensive and need precise current and heat management.

1.2 Organic light emitting diodes (OLEDs)

In the 1950s, Beraanose first observed the electroluminescence phenomena in organic material by applying a high voltage alternating current (AC) field to an acridine orange and quinacrine crystalline thin films\(^5\). A decade later, the direct current (DC) driven EL cell using single crystals of anthracene was demonstrated by Pope and co-workers\(^9\). In 1975, the first organic electroluminescence cell made from a polymer called polyvinylcarbazole (PVK) was demonstrated and an US patent was filed\(^10\).
At the onset of the development of organic EL devices, the driving voltage was of the order of 100V or above in order to achieve a suitable light output\textsuperscript{11,12}. By using the thermal evaporation method for the preparation of thin films of anthracene, Vincett et al. successfully reduced the operating voltage below 30V\textsuperscript{13}. A significant breakthrough in organic electronics came with the publication by C.W. Tang and Van Slyke SA on organic solar cells\textsuperscript{14} and light emitting devices\textsuperscript{15} fabricated from thin amorphous polycrystalline organic layers by vacuum thermal evaporation. Even though the disordered films possess lower charge transport properties, the devices still fulfill the requirement of being exceptionally thin, smooth, with no pinholes, electrically conducting and requiring low driving voltage. Nowadays, small molecule organic light-emitting diodes (SMOLEDs) made by means of thermal evaporation are widely used in industry for commercial display products.

Another type of organic semiconductor is conjugated polymers which were discovered in 1977 by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa\textsuperscript{16}. In the early development of conducting polymer, researchers focused on the novel physical and chemical properties of intrinsic (undoped state) and heavily doped materials\textsuperscript{17,18} in these materials. Even though a significant photosensitivity was demonstrated, the EL properties of the conductive polymer were intrinsically weak due to its electronic structure. In the early and mid-1980s, intensive research has been focused on searching and developing new materials with the aim of improving solution processibility. In the early 1990s, the first demonstration of a polymer light emitting diode (PLED) was made using unsubstituted poly(p-phenylene vinylene) (PPV) by R.H. Friend's group at the University of Cambridge\textsuperscript{19}. Consequently, a high efficiency PLED was made using the solution processable polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) by Heeger's group at the University of California, Santa Barbara\textsuperscript{20}.

1.3 Device structure and device physics

A basic OLED device consists of a transparent conducting anode, such as indium tin oxide (ITO) deposited on transparent glass or a polymer substrate, an organic semiconducting layer which allows the transport of electrons and holes, and a metal cathode such as aluminium (Al), calcium (Ca), barium (Ba). In a single layer OLED device, charge carriers are injected from the top and bottom electrodes into opposite sides of the sandwiched organic emissive layer, as shown in the energy diagram in Figure 1.1. Hole injection takes place from the anode Fermi level into the highest occupied molecular orbital (HOMO) of
the organic layer, overcoming the energy barrier $\phi_n$. The same applies to electrons for which the injection takes place from the Fermi level of the cathode into the lowest unoccupied molecular orbital (LUMO) of the organic layer by overcoming the energy barrier $\phi_n$. In most of the organic materials, either n- or p-conduction dominates inherently. Therefore, materials for n- and p-type conduction are chosen in order to sustain sufficient mobility to transport a balanced charge carrier population on either side of the recombination zone to the side chosen for recombination. During the recombination process, the recombination zone is where the wavefunction of electrons and holes overlap and the recombination process results a complex which is called Frenkel-exciton. Due to the spin multiplicity, the excited state singlet and triplet states occur with the ratio of one to three\textsuperscript{21}. After the recombination, the excitation energy can be transfer to neighbouring molecules with lower excitation energy by either dipole-dipole coupled (Förster) energy transfer or electron exchange energy transfer\textsuperscript{22,23}.

**Figure 1.1: Scheme of a single layer OLED**

Luminescence in OLEDs occurs via the radiative decay of the singlet excitons while the triplet excitons decays non-radiatively, which could occur at traps/impurities or contacts. To minimize the contact quenching, the excitons created in the emissive layer can be confined by introducing multilayers in the organic light emitting diodes.

To achieve a high efficiency device, choosing materials with the appropriate electronic and optical properties is as important as the design of the device architecture. The single layer OLED device in Figure 1.1 is not an optimum design since the carriers can reach the opposite contacts and there are no precautions taken to avoid contact quenching.
Figure 1.2 shows an example of a multilayers OLED where hole (HIL) and electron injection layers (EIL) are introduced to lower the energy barrier between the contact and organic interface. Separate hole (HTL) and electron transport layers (ETL) are present to improve the transport of charge carriers from the contacts to the emissive layer, and at the same time reducing the contact quenching by introducing a sufficiently large distance or barrier to the metal contact. To further improve the device efficiency, a large band gap material is introduced between the emissive layer and electron transport layer as the hole blocking layer (HBL) in order to confine the hole carriers in the recombination zone while the electron can be easily transport through the HBL. By using a well designed multilayer OLED architecture, the driving voltage, brightness, colour purity and device efficiency can be further improved\textsuperscript{24,25}.

![Energy level diagram of a multilayers OLED.](image)

1.4 Aims of thesis

As OLEDs develop, so has our understanding of the nature and importance of the interfaces formed between the metal/organic materials and organic/organic materials in these devices. The development of carbon nanotube (CNT) and fluorocarbon based materials as the interlayer for OLEDs are still at a very early stage. Therefore, this thesis focuses primarily on the effect of the insertion of solution processable acid oxidised single walled and multiwalled carbon nanotubes and fluorocarbon based material, polytetrafluoroethylene (PTFE), as the interlayer in SMOLED and PLED. Our main objective is to understand the
interfacial, injection, optical properties and the device physics obtained by inserting these interlayers in the structure. This means that rather than concentrating on optimising device performance by using various organic semiconductors or sample preparation techniques, we have chosen well-established SMOLED and PLED devices structures based on triphenyldiamine/aluminium quinoline (TPD/Alq3) and poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate)/polyfluorene (PEDOT:PSS/PFO) to work with. Water soluble acid oxidised multiwalled CNTs (o-MWCNTs) and single walled CNTs (o-SWCNTs) prepared in-house, are used as the interlayer between the anode and the organic material. First, the work function and the interface between the electrode, o-SWCNTs and TPD are systematically investigated. The effect of o-SWCNTs on the injection property and device physics is studied in OLED and PLED devices. The physical changes of the TPD deposited on top of o-SWCNTs are characterised using conductive atomic force microscopy (AFM), Raman spectroscopy and optical polarization microscopy. Device performance is characterized and correlated with the photoluminescence quenching effect at the o-SWCNT/PFO interface. The study of the changes to the physical properties and the work function of PEDOT:PSS/PTFE is carried out in detail. The effect of the PTFE layer thickness is further illustrated by studying the PLED device performance in term of external quantum efficiency, brightness and lifetime stability. Overall, it is expected to provide a detailed understanding on the effect of inserting CNTs and fluorocarbon interlayers in the fabrication of high efficiency and stability OLED devices.

1.5 Thesis layout

Following the introduction of using organic materials in electroluminescence devices in Chapter One, the basic material properties used in such devices are discussed in the literature review in Chapter Two followed by the description of experimental and characterisation techniques in Chapter Three.

In Chapter Four, we investigate the physical properties of acid-functionalised single-walled carbon nanotubes, the effect of o-SWCNT deposited on transparent indium-tin-oxide (ITO) and the interfacial properties between o-SWCNT and TPD. This study will be augmented with data obtained using ultraviolet photoemission spectroscopy (UPS).

In Chapter Five, the issues of the effects of inserting o-SWCNT in SMOLED in terms of injection properties and device physics are explored. The changes of diode characteristics in hole-only devices will be discussed. The discussion is focused on the changes in physical and optical properties of TPD upon the insertion of o-SWCNTs. The effects of using o-
SWCNTs interlayer in small molecule OLEDs (SMOLEDs) are discussed. For the polymer based LEDs (PLEDs) section, we explore the effect of photoluminescence quenching between o-SWCNTs with polyfluorene and how it impacts the device efficiency. The discussion is mainly focused on how to improve the system by inserting an interlayer between o-SWCNTs and the emissive material in order to avoid quenching.

In Chapter Six, we turn to investigate a new interlayer material, PTFE, in terms of the effect of its thickness on the physical properties and the work function of the material as well as its effect on the device physics and stability of PLED structures.

Chapter Seven provides the conclusion of the research conducted in this thesis by highlighting the key findings prior to suggesting avenues for future research.
CHAPTER 2

Literature Review

2.1 Introduction

This chapter will focus on the material properties of organic semiconductors, carbon nanotubes and fluorocarbons followed by a literature review of organic/metal interfaces, charge transport properties of organic semiconductor materials, and the usage of carbon nanotubes and fluorocarbon materials in organic light-emitting diodes and organic photovoltaics.

2.2 Organic semiconductors

The electronic properties of organic materials, in particular the polymeric and small molecular materials, were only investigated since 1963 when Weiss and his co-workers reported the passive high conductivity in iodine-"doped" oxidized polypyrrole. In 1977, Shirakawa et al. reported a high conductivity iodine-doped polyacetylene which enabled a major breakthrough in organic semiconductor studies. The awarding of Nobel Prizes in 2000 in Chemistry by Shirakawa, Heeger and MacDiarmid further proved the impact and the future potential of this material.

The basic element of an organic semiconductor compound is carbon (C), an element in Group IV of the periodic table. The special electron shell configuration of the C atom, \(1s^2 2s^2 2p^2\), providing four valence electrons for covalent bonding via its outer electronic orbitals, creating unique diversity of organic compounds. In the presence of other atoms such as C, nitrogen (N), hydrogen (H) or oxygen (O), these levels may hybridize either into \(sp\), \(sp^2\) or \(sp^3\) orbitals, each possessing their unique spatial character. In the case of \(sp^2\) hybridization, three electrons of each carbon atom form sigma (\(\sigma\)) bonds with other atoms, while the remaining one non-hybridized \(p_z\) orbital is oriented perpendicular to the three \(sp^2\) orbitals, which are coplanar with angles of 120° between each other (Figure 2.1). In the case of an identically hybridized neighbour C atom with similar orientation, these \(p_z\) orbitals will overlap and form a molecular \(\pi\)-bond. Together with the \(s\) bond between the
two C atoms (created by two hybridized $sp^2$ orbitals) this results in a double bond. Given a row of neighbouring $sp^3$ hybridized C atoms, all with their $p_z$ orbitals parallel, this then results in an alternating single bond, double bond structure (Figure 2.2). By maintaining this alternating sequence (conjugation structure), these bonds are located arbitrarily, i.e. the positions of the double and single bonds may be exchanged with small or no energy difference. The $p$-electrons in a conjugated structure are thus delocalized over the entire molecule. A simple example is the benzene molecule with two delocalized electron clouds on both sides of the carbon ring structure. Another example is polyacetylene chain like structure as shown in Figure 2.2.

![Figure 2.1: A top view and side view representative of sp2 hybridization of a carbon atom](image)

(a)

![Figure 2.2: (a) Basic unit of molecular orbital for sp2 hybridization C-C bonding (b) A segment of trans-polyacetylene](image)
The dominance of the $p$-electrons in the transport properties originates from the fact that they form the proximity of the orbitals when different molecules combine and form longer chain or larger molecules size that induces a splitting of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which are the electronic levels that determine the semiconducting properties of these materials in optical excitations and charge transport. In order to obtain charge transport on a macroscopic length scale there are two alternative routes one can pursue: growing a lattice of (smaller) molecules or casting films of molecules with high-molecular-weight from solution. Regardless of one's choice, charge transport is strongly determined by the interaction between molecules. The first method offers an opportunity to study these interactions due to the high level of symmetry in location and orientation of the molecules. In the latter technique the transport is dictated by a variety of phenomena that is generally accounted for by the disorder. This term includes the dispersion in the molecular structure, conjugation length, defects, impurities, morphology etc. Consequently, on a microscopic level each film is different. However, by variation of synthesis route, molecular structure, solvent and spin casting conditions a handle is obtained in controlling this disorder and consequently, the macroscopic transport properties in these films. Driven by a technological interest, attention has focused on the option of casting out from solution. The electronic properties of the conjugated material thus depend on microscopic variables that may also be expressed in energy parameters: electron-lattice interaction, electron-electron (electron-hole) interaction, bandwidth and the random disorder potential. The relative strength of the electron-hole interaction (exciton binding energy) in fact determines whether to view this material as a molecular solid or as a one-dimensional semiconductor. The hopping transport seems more representative to the organic transport mechanism compare to band type transport. The random disorder potential leads to (un)correlated hopping transport (as opposed to band transport) and gives rise to a field dependent mobility, the so-called Poole-Frenkel behaviour. There is discussion about its energetic or structural origin is beyond the scope of this thesis. However, the field dependence of the conduction has been recognized as charge density dependent.

2.3 Carbon nanotubes

Carbon nanotubes (CNTs) are arguably one of the most studied nanoscale materials. The main reason for this sustained interest and great research activities in this area is the wide variety of unique electronic and mechanical properties available to CNTs. For example,
single walled carbon nanotubes (SWCNTs) are the only material that can be either semiconductor or metallic depending on its conformation (or chirality). However, the credit for the discovery of carbon nanotube is still arguable\textsuperscript{33}.

In the early 90s, Iijima\textsuperscript{34} investigated the carbon soot which had been discarded as waste during the production of C\textsubscript{60} buckyballs by an arc discharge of graphite rods process. The physical appearance of this material looks like an hollow tube which closed at each end with the caps of six pentagonal rings\textsuperscript{34} that is now commonly known as carbon nanotube.

CNTs can be divided into two categories: SWCNTs and multi-walled carbon nanotubes (MWCNTs). A SWCNT is defined by a graphene sheet rolled into a cylinder with diameter within about 0.7-10.0 nm, though most of the observed single-wall nanotubes have diameter less than 2 nm\textsuperscript{35}. MWCNTs are formed by additional graphene sheets wrapped around the SWCNT which can be imagined as multilayer concentric graphene sheets as shown in Figure 2.3. The end cap of the tube structure is derived from fullerene such as C\textsubscript{60} as shown in Figure 2.4. With the high aspect ratio of the CNT (length/diameter can be as large as 10\textsuperscript{4}-10\textsuperscript{5}), these nanotube can be considered as one-dimensional nanostructures\textsuperscript{35}.

![Diagram of SWCNT, MWCNT, and C\textsubscript{60} buckyball](image)

**Figure 2.3: Diagram of (a) SWCNT, (b) MWCNT and (c) C\textsubscript{60} buckyball**

### 2.4 Structure and properties of carbon nanotubes

In general, SWCNTs can be seen as the mixture of two components with different physical and chemical properties. The first component is the side wall of the tube while the other component is the cap of the tube (Figure 2.4). The end cap structure of the CNT is formed of pentagonal and hexagonal carbon atom structures\textsuperscript{36}. The combination of six pentagons and a number of hexagons results in the carbon caps which resembles half fullerenes\textsuperscript{37}. As suggested from the literature, the structure and energetics of the cap is the key for chirality selective growth of SWCNT\textsuperscript{38}.
The other component of the CNT is the side wall of the CNT (most often the outer wall) which can be described as the two-dimensional graphene sheet rolled to form a cylinder. As the graphene sheet of a certain size can be rolled in a number of orientations, this is the key component which determines the property of the CNT. Therefore, the electronic properties of the CNT always correlated with its chirality, diameter and quality of the CNT structure. In this case, SWCNT can be either semi-conducting or metallic, while MWCNT are typically always metallic in nature.

Figure 2.4: SWCNTs with different chiralities. Difference structure of SWCNT is easily shown in open end of the tubes (top) armchair structure (middle) zigzag structure (bottom) chiral structure.

The chirality of the CNT is defined as the relationship between the tube axis and the helicity of the hexagonal lattice walls of the graphene sheet. To form a cylinder, a graphene sheet (Figure 2.5) must be connected by joining the carbon atoms at two joining edges. The joining edge can occur in a variety of ways and can be defined by the chiral vector \( C_h \). This vector is defined as:

\[
C_h = n \mathbf{a}_1 + m \mathbf{a}_2
\]

where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the graphene lattice vectors and \( n \) and \( m \) are integers. With the chiral integer, this leads to three classes of CNT: (i) armchair where \( n = m \); (ii) zigzag where \( m = 0 \) and (iii) chiral tubes where \( n \neq m \).
Figure 2.5: Vector OA is called the chiral vector. It can be defined by the vector $C_h = na_1 + ma_2$ and the chiral angle $\theta$ with the zigzag axis. Vector $a_1$ and $a_2$ are the lattice vectors.

CNTs have been shown to have excellent electrical, mechanical and thermal properties, which potentially can be applied to a wide range of fields from nano-electronics to biomedical applications\textsuperscript{39-41}. The superior properties of carbon nanotubes are summarised in Table 2.1. Further to the outstanding properties shown in Table 2-1, CNTs are also relatively chemically inert and display nonlinear optical properties\textsuperscript{40}. However, CNTs have not been used widely in many practical applications due to the difficulties in processing them due to their insolubility and infusible and inhomogeneous nature\textsuperscript{39}.

Table 2.1: Shortlist of Carbon Nanotubes' properties\textsuperscript{42-46}

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Assessment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity: $\sim 6000 \text{Wm}^{-2}\text{K}^{-1}$</td>
<td>$&gt; \text{diamond (900-2320 Wm}^{-2}\text{K}^{-1})$</td>
<td>42</td>
</tr>
<tr>
<td>Young's modulus: $\sim 1 \text{TPa}$</td>
<td>Stiffest material</td>
<td>43</td>
</tr>
<tr>
<td>Tensile strength: 150GPa</td>
<td>$\sim 100$ times the strength of steel</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>($\sim 1.8 \text{GPa}$)</td>
<td></td>
</tr>
<tr>
<td>Maximal supported electrical current density: $&gt; 10^8 \text{A/cm}^2$</td>
<td>$\sim 100$ times greater than copper wires ($10^6 \text{A/cm}^2$)</td>
<td>45</td>
</tr>
<tr>
<td>Carrier mobility: $\sim 10^5 \text{cm}^2/\text{V s}$</td>
<td>$&gt; \text{Hole mobility in Si (} \sim 450 \text{cm}^2/\text{V s})$</td>
<td>46</td>
</tr>
</tbody>
</table>

A detailed review of the functionalisation methods for CNT is beyond the scope of this report, and the interested reader is invited to read numerous reviews focused on this
subject\cite{47,48}. Instead, a brief review of the utilisation of CNT as electrodes in the field of organic electronic applications is introduced.

CNTs have been widely studied for the last 10 years as electrodes for various applications in large area electronic devices such as field emission\cite{49}, OLEDs\cite{50} and photovoltaic cells\cite{51}. The superior properties of SWCNTs and MWCNTs as electron field emitters were first reported by Saito and co-workers in 1997\cite{52,53}. At the same time, Liu et al. developed a purification and chemical functionalisation method to convert SWCNTs from long and highly tangled ropes into short and open ended fullerene pipes that can be suspended in a stable colloidal system\cite{54}. These suspensions permit a variety of manipulation and further processing of SWCNTs in a thin film form. In 2004, transparent and conductive carbon nanotube films were first reported by Wu\cite{55}. These highly transparent SWCNT films not only exhibited similar transmittance and conductivity compared to ITO thin films in the visible spectrum (400-1100nm), but also superior transmittance in the 2-5µm infrared spectral range\cite{55}. This indicates that the SWCNT films have broader applications for electrical coupling in photonic devices.

In OLEDs, ITO has been the most commonly used transparent electrode. However, it is expensive to produce and contains indium, an element whose mass availability for long term production is questionable. Moreover, indium migration from the ITO surface has often lead to premature device failure\cite{56}. Furthermore, adhesion issues between ITO and flexible substrates, leading to cracks and delamination of ITO after repeated bending have retarded the application of ITO in flexible OLED based displays.

The conducting polymer blend polyethylene dioxythiophene (PEDOT) doped with polystyrenesulfonate (PSS) is one of the most common hole conducting layers used in polymer based OLEDs. This is facilitated by the high ionization potential (~5.1 eV) of PEDOT. However, PEDOT:PSS is also a problematic material as an electrode in OLEDs because of its intrinsic acidity.

A possible alternative to ITO and PEDOT:PSS are SWCNT films since these films show high conductivities combined with high optical transmission and are solution processable. Furthermore, the intrinsic work function of SWCNT (4.5-5.1eV)\cite{57,58} is comparable to the work function of ITO (4.4-4.9eV)\cite{59} and the CNTs can be tailored through n-type or p-type doping\cite{60}. In the work reported by Wu et al.\cite{55}, transparent conductive carbon nanotube films were used as an electrical field-activated optical modulator, which constitutes an optical
analog to the nanotube-based field effect transistor (NFET). The superior transmittance of this film in the 2-5μm infrared spectral band may find applications in spacecraft thermal control, for example.

SWCNT films have been shown to be a good candidate as an anode for flexible OLEDs and OPVs\textsuperscript{61,62} due to their comparable work function. Excellent adhesion between SWCNT films and plastic substrates (eg. polyethylene terephalate (PET) and poly(methylmethacrylate) (PMMA) was found through the “scotch tape” test. The nanoporous structure of SWCNTs offers good hole injection potential which is very important in OLED applications. Moreover, the SWCNT film fabrication process is a room-temperature process and is relatively simple compared to ITO that requires vacuum and elaborate process equipment.

2.5 Application of carbon nanotubes for organic based electronic devices

In order to improve the processibility of CNTs, one needs to modify them chemically. Different methods have been developed for this purpose. For example, generation and functionalization of defect sites at the tube ends and side walls by oxidation and subsequent conversion into derivatives (Fig 2.6a); covalent side wall functionalisation by oxidation and subsequent nucleophilic substitution as additional reactions (Figure 2.6b); non-covalent exohedral functionalisation with surfactant-type molecules (Fig. 2.6c); and noncovalent exohedral functionalisation with polymers (Figure 2.6d) and endohedral functionalisation with C\textsubscript{60} (Figure 2.6e).

![Figure 2.6: Functionalisation possibilities for SWCNTs](image-url)

Figure 2.6: Functionalisation possibilities for SWCNTs\textsuperscript{47}
2.6 Interfacial study of CNTs with metals and organic materials

One of the most important considerations on designing OLED and OPV devices are the charge carrier injection and the interfaces energetics. The interfacial energetics such as the relative molecular energy level across the metal/organic interface ultimately determines the turn-on voltage and the balance of charge carriers (hole and electron) injection in OLEDs as well as the open circuit voltage in OPVs. Since most of the organic based devices are based on thin film architectures (< 200nm), the interfaces between each layer only involves a few nanometer thick material and has considerable influence on the overall stability, performance and integrity of the devices.

The important issue for the organic molecular device designer is to identify the band structure at the metal/organic interface including the vacuum level shift and band bending at the interface. Among the work covered in this topic, Ishii et al. reported detailed analyses of the band structures and the appearance of the shift in the vacuum level (VL) for various combination of molecules and metals using UPS and Kelvin probe (KP). Abrupt interfacial vacuum level shifts may originate as a result of numerous effects including; charge transfer between metal and organic materials, image effects or the modification of the surface dipoles at the metal surface by redistribution of the electron cloud, chemical interaction between the organic and metal layers, and other types of rearrangement of electronic charge.

In 1999, Ago et al. reported the first study on the work function of MWCNTs and its correlation with the surface functional groups attached on the CNTs using UPS and XPS. In this publication, acid oxidised MWCNTs exhibit higher work functions compared to pure MWCNT. Two mechanisms have been proposed to explain the increase in work function: (i) a reduction of \(\pi\)-conjugation which reduced the \(\pi\)-derived DOS and (ii) an enhancement of the surface dipoles pointing inward with the presence of oxygen functional groups. After that, Blanchard et al. published a convincing results on using cation exchange to tune the work function of oxidised MWCNTs. Most of the research has been conducted on MWCNT, but only little has been done for SWCNTs.

The research has not only been focused on CNT work function studies but some have been published on CNT/organic interface. In 2008, Lozzi et al. published results on copper phthloocyanine (CuPc)/MWCNT interfaces using XRD, XPS and soft x-ray spectroscopy. They found that the CuPc (18nm thick) formed nanocrystals on the MWCNTs but no strong
interaction occurred between these two compounds with only small effects on the spectra observed.

Another important literature report was found in 2009 where Liu et al. showed that OLEDs made from inserting CNT in between the cathode metal and organic layer have better electron injection as the CNT can induced geometry enhanced electric field effects which help to improve the electron injection into the organic layer.

Based on the current understanding about the interface properties on organic/metal and organic/organic interface, a few models were reviewed to explain various observations that are found in different materials interfaces and systems.

2.6.1 Standard model

The typical metal/organic interface properties are shown in Figure 2.8. The work function (Φ) of the material corresponds to the minimum amount of the energy needed to remove an electron from the material. For a metal, the valence band is filled with electrons up to the Fermi energy (E_F). Therefore, the energy difference between the Fermi energy and the vacuum energy level (E_vac) is called the work function. For semiconducting materials, the valence bands (i.e. HOMO) and conduction bands (i.e. LUMO) are separated by the band gap (E_g). In semiconductors, the energy difference between E_vac and the HOMO and LUMO level are defined as the ionization energy (IE) and electron affinity (EA), respectively. For a semiconductor with moderate doping, the Fermi level is located within the band gap and the Φ is different from the ionization potential. In this case, the Fermi level distribution is a statistical function that gives the probability to find an electron in a given electronic state.

In Figure 2.8, the vacuum level shift between the interfaces of two materials is defined as Δ. The injection barriers for a hole and electron through the interface are Φ_p and Φ_n, respectively. Based on the standard metal-semiconductor interface discussed in the literatures, simplified equations for an electron injection barrier can be presented below:

\[ \Phi_n = S(\Phi_m - EA) + (1 - S)E_{CNR} \]  \[ 2.1 \]

where \[ S = \frac{1}{1 + 4\pi^2 D_p \delta} \]  \[ 2.2 \]
Most of the parameters showed in the equations above have been defined, while \( \delta \) is the thickness of the interface layer, \( D_{is} \) is the interface-trap density in the unit states/cm\(^2\)-eV and \( E_{CNL} \) is the charge neutrality level at the interface states. If the interface \( E_F \) is above (below) \( E_{CNL} \), the net charge in the interface states is negative (positive) and a dipole formation, \( \Delta \) with the corresponding sign developed across the interface\(^{23}\).

One of the important aspects of the interface studies is the correlation between the carrier injection barriers with the nature and work function of the electrode where the density of interface states (\( D_{is} \)) is a crucial factor to define the injection barrier. In the section that follows, we reviewed different types of \( D_{is} \), such as interface free gap state and interfaces dominated by the gap states\(^{73}\) and their influence on the heterostructure properties.

### 2.6.2 Schottky-Mott model

Based on the assumption made by the Schottky-Mott (S-M) model, the metal and the semiconductor are considered as not interacting when they are close to each other. Since this is a non-interactive interface, the small density interface states, \( D_{is} \) can be ruled out in the discussion. Figure 2.9 shows the typical schematic diagram of metal-semiconducting interface based on the Schottky-Mott model where there is no vacuum level shift (\( \Delta = 0 \)) and the electron and hole injection barriers are shown in equation 2.3 and 2.4.

\[
\Phi_n = \Phi_m - EA \tag{2.3}
\]
\[ \Phi_p = IE - \Phi_m \]  

Based on the Schottky-Mott Model, the correlation between the injection barrier and the electrode work function is described by the interface parameter \( S \) where

\[ S = \frac{d\phi_n}{d\phi_M} \]  

The limitation of the Schottky-Mott model is that \( S \) is assumed to be equal to unity\textsuperscript{71,72} when the Fermi level of the metal overlaps with the band gap of the semiconductor, \( EA<\Phi_m<IE \). Furthermore, charge transfer in-between metal and organic material usually occurs when both materials are deposited next to each other\textsuperscript{73}.

![Typical band diagram of metal/organic interface based on Schottky-Mott model](image)

**Figure 2.9:** Typical band diagram of metal/organic interface based on Schottky-Mott model where \( E_{\text{vac}} \) is aligned at the same level between these two materials

### 2.6.3 Reorganization of surface metal electronic structure: the ‘pillow effect’ or ‘mirror force’

The deposition of an atom or molecule on a metal may result in a Coulomb repulsion between the electronic density of the organic molecule and the electrons on the metal surface. For that reason, the surface electrons suppressed locally the tail of the electron that spill into the vacuum\textsuperscript{65,73}. Therefore, an effectively positive charging surface on the vacuum side is formed and leads to the lowering of the metal work function. This phenomenon is commonly known as ‘pillow effect’ or ‘mirror force’ which has been studied extensively, and especially for noble gases on a series of metals\textsuperscript{74}. 

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2.6.4 **Interfaces dominated by interface states** $D_{is}$

The origin of the interface states $D_{is}$ can be quite diverse. The chemical bonding and the defect induced by the deposition of metal-on-organic or organic-on-metal could exhibit filled or empty electronic states at the interface that overlap with the original gap of the semiconductor. One of the pronounced examples is the evaporation of aluminium and magnesium on Alq3, which lead to the formation of gap states that pin the Fermi level of the Alq3 gap.

In inorganic semiconductor interfaces, the metal-induced gap states (MIGS) or induced density of interface states (IDIS) have been well studied. MIGS or IDIS is referring to the phenomenon involved with the penetration of the metal electron wave function tail state into the semiconductor band gap.

During the formation of metal-organic interfaces, electrons redistribute across the surface and induce the metal work function change relative to $E_{CNL}$. For metal work functions which are relatively smaller than $E_{CNL}$, electrons transfer from metal to IDIS, which will induce an upward dipole layer at the metal-organic interface. This dipole layer narrows the energy difference between $E_F$ and $E_{CNL}$. The IDIS and $E_{CNL}$ concepts are only applicable to weakly interacting organic-metal interfaces.

2.7 **Work function of carbon nanotubes**

Carbon nanotubes with the indices $(n, m)$ can be either metallic or semiconducting depending on whether $n-m$ is a multiple of three. The absolute potential of the Fermi level (work function) is one of the important and critical physical parameter for various applications such as field emission. For chemical sensors and organic electronic device applications, the CNT work function could also dictate the direction of the charge transfer and influence the molecule selectivity. It also affects the band lineup at the CNT/metal contact and has a considerable impact on the device performance. An understanding of the electronic structure, the work function of CNTs and the interaction of CNTs with different types of materials, including metals and organic molecules, is crucial for designing various structures for different device applications.

The work function of the MWCNTs with different oxidised functional group was first discussed by Ago et al. in 1999. The pure MWCNTs with a work function around $4.3\text{eV}$
can be further modified by introducing carboxylic groups at the surface and increase its work function to 5eV. Whilst it is possible to process pristine CNTs into thin films, it is often desirable to chemically functionalise the outer surface to impart enhanced functionality. For example, we have recently shown that partially oxidised single-wall and multi-wall carbon nanotubes (o-SWCNTs and o-MWCNTs respectively) can be used as high work function, hole-extracting electrodes in bulk-heterojunction OPVs. At the same time oxidized graphene flakes have also attracted interest as an electrode material for electronic applications.

The pristine SWCNT work function is around 4.8eV. However to the author's knowledge, no work has been published on oxidised SWCNT work function and its interaction with organic molecules.

2.8 Charge transport mechanisms in organic semiconductors

Although many concepts used in organic semiconductors are derived from those previously used in inorganic semiconductor theories, most of the polymeric and small molecular materials used in OLEDs are of disordered amorphous film morphologies. The charge transport in organic films is usually not a coherent motion, but rather a stochastic process of hopping due to the lack of extended delocalized states. In addition, many organic materials are wide band gap materials, typically 2-3eV or more. Thus, the intrinsic concentration of thermally generated free carriers is negligible. Even though amorphous organic materials have no well-defined structures, for simplicity, the molecular energy levels are usually drawn as a band-like diagram (Figures 2.3 and 2.4). However, the disordered nature of the organic materials have to be taken into account in order to get a better understanding with regard to injection processes from metals to organic materials.

When a voltage bias is applied to an organic diode, charge carriers are injected into the organic material and travel towards the counter electrode. Due to the disordered nature of the organic film, the charge carrier transport is based on a hopping process. In organic semiconductor materials, the charges are highly localized on individual molecules. The charges have to tunnel (hop) from one molecule to another since there is no continuous extended band in organic semiconducting materials. This is the main reason for the low charge carrier mobility in organic films that has a typical range from $10^{-3}$-$10^{-7}$cm$^2$V$^{-1}$s$^{-1}$ at room temperature.
An example of molecular conformation that can affect the charge mobility is shown in Figure 2.10. 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) is one of the organic materials that could have different types of molecular packing when produced by different deposition techniques. When the molecules are arranged in a stacking direction (Figure 2.3b), the mobility can reach up to 0.1 cm² V⁻¹ s⁻¹ due to the large π–π orbital overlap with short inter-molecular distance⁸⁵. In many cases, the carrier mobility is strongly dependent on the temperature and the magnitude of the applied field⁸⁶.

In order to lower the operating voltage and improve luminous efficiency, the heterojunction between the electrode/organic layers has to be designed in such a way as to facilitate either hole or electron injection in order to balance the charge injection. Since minimizing the operating voltage will increase the power efficiency of the device, it is necessary to have ohmic contacts. With effective charge-injection contacts and optimum charge transport of both charge carriers, it would be ideal for the device to operate at an optimum voltage which is close to its turn-on voltage. Turn-on voltage is conventionally defined as the voltage for an OLED to obtain a luminance of 100 cd/m².⁸⁷ This may be achieved if both anode and cathode are ohmic contacts so that the injected current is space charge limited. However, in reality, the normal green emission OLED emits light of about 100 cd/m² at two to four times the turn-on voltage. The main reasons are (1) the Schottky barrier between the contact and organic interface, (2) low mobility of organic materials and (3) Space charge limited (SCL) bulk properties of ETL (such as existing traps in ETL).
SCL and injection charge limited (ICL) are two limiting regimes for an operating device. In order for space charge limited current (SCLC) to occur, it is required that at least one side of the contact must have good injection properties to provide an unlimited carrier reservoir to the device. In contrast, injection limitation occurs if the injection barrier is so large that the injection current is not able to deliver the SCLC in the material

Carrier injection into a classical semiconductor is usually explained in terms of Fowler-Nordheim (FN) tunnelling or Richardson-Schottky (RS) thermionic emission\(^7\). Both concepts are appropriate to describe the charge injection into semiconductors under certain conditions. However, we cannot expect that they hold true at organic semiconductor/metal contact because the mean free path for organic materials is based on the order of the molecular distance. The disordered structure of organic material poses an additional obstacle to be overcome by the injected carriers. In bulk organic materials, carriers need to overcome the random energy barrier caused by disorder. This may lead to a backflow of injected carriers into the electrode. This types of injection process from a metal to a disordered hopping system have been well studied analytically\(^8\) and by Monte-Carlo simulation\(^9,10\).

In the case of a perfect dielectric without any intrinsic carriers or traps, and for a charge carrier mobility independent of the electric field, the SCLC obeys the Mott-Gurney equation\(^91\),

\[ J_{SCLC} = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{d^3} \tag{2.6} \]

where \(\mu\) is the free carrier mobility, \(\varepsilon\) the dielectric constant of the material, \(V\) the applied voltage and \(d\) is the distance between the electrodes. This equation is derived by neglecting diffusion and with the boundary condition that the electric field at the injection contact is vanishingly small, which leads to an infinitely high carrier density at the contact\(^8\). The significant concept given by SCLC is that there exists a maximum possible unipolar current a sample can sustain at a given applied voltage. A current exceeding this value will only be possible in the case of bipolar injection currents where charges of the opposite sign are mutually able to compensate part of the space charge.

For amorphous molecular materials, molecularly doped polymers and for most conjugated polymers, Poole-Frenkel (PF) field dependence of the mobility,
$\mu(F) = \mu_0 \exp(\beta \sqrt{F}) \quad [2.7]$  

is always observed, where $\mu_0$ is the mobility of the material at zero electric field, $\beta$ is the PF coefficient, and $F$ refers to the applied field (voltage/thickness in $V/cm$, $V/d$). The current density in this case is approximately the trap free SCLC multiplied with the PF mobility$^{92}$,

$$j_{\text{SCLC}}^{(PF)} \approx \frac{9}{8} \epsilon_0 \epsilon \mu_0 \frac{V^2}{d^3} \theta \exp \left( \frac{0.891 e^2 V}{kT \sqrt{\pi \epsilon \epsilon_0 d}} \right) \quad [2.8]$$

where $e$ is the electron charge and $\theta$ is the ratio of free carriers, $n$, to the total number of carriers $(n + n_t)$, where $n_t$ is referred to as the total number of trap as shown in Equation 2.9.

$$\theta = \frac{n}{(n + n_t)} \quad [2.9]$$

In this thesis, the experiment results which were obtained from single-carrier devices are analyzed using approximate analytical equations or the simple transport equation (Equation [2.6]) discussed above, neglecting diffusion but including field-dependent carrier mobility. TPD is reported to be trap-free and so the contribution of the trap-charge limited conduction has not been discussed in detail. However, from the current dependence on the electric field, there are three possible situations that can be described$^{84}$:

a) for purely injection limited behaviour (regardless of the actual mechanism) where the current at constant field has no explicit thickness dependence

$$j = j(F) \quad [2.10]$$

b) for trap-free space charge limited conduction with (or without) a field-dependent mobility, the current at constant field scales with $d^{-1}$

$$j = \frac{j(F)}{d} \quad [2.11]$$

c) for trap-charge limited conduction (TCLC) with an exponential trap distribution and a field-independent mobility, the current at constant field


scales with \(d^l\) with \(l>1\). In this case, the parameter \(l\) is derived from trap distribution given in the literature\(^9\).

\[
j = \frac{j(F)}{d^l}
\]  

[2.12]

### 2.9 Charge balancing in OLEDs

In Chapter 1, the basic operations of OLEDs were discussed. The light emitting process in OLEDs involves the injection of the oppositely charged carriers. Under the influence of the electric field, the carriers hop towards each other. If both charges arrive on a molecule, an electron-hole pair would be created in an unbound manner. Under the correct conditions, new quantum states called excitons can form, with the electron and hole bound to each other (Figure 2.11).

![Figure 2.11: Schematic diagram of electroluminescence (EL) process in OLED](image)

In Figure 2.11, \(\gamma\) is the number of electron-hole pairs (excitons) generated per unit volume per unit time divided by number of charge carriers injected into that unit volume at that particular time. In this case, the minority carrier will be the factor that affects \(\gamma\).

In this study, acid oxidised carbon nanotubes were studied as a hole injection layer even though the minority carrier for the organic devices were electrons. The rationale behind this study is to understand the hole injection properties of CNTs with organic materials since carbon nanotubes based films have been reported as a potential electrode to replace ITO as
anode for organic electronic devices. More details about the current literature review of using CNTs as electrode contact are discussed in Section 2.4.

\( \eta \) represents the luminous efficiency of the exciton. Not all the excitons can efficiently decay and emit light. For spin-symmetric excitons with a total spin of \( S = 1 \), the multiplicity of states is 3 and these are known as triplets. The spin-anti-symmetric excitons \( (S=0) \) have a multiplicity of one and are known as singlets\(^9\). During the electrical excitation, approximately one singlet exciton is created for every three triplet excitons. Therefore, about 75% of electron-hole pairs are expected to be triplet excitons, which do not decay radiatively with high efficiency. The emission of a photon conserves spin, so only singlet excitons can emit light in a fast and efficient process called fluorescence (Figure 2.12).

---

**Figure 2.12: The relaxation of singlet and triplets excitons. In fluorescent OLEDs, the probability of the creation of a singlet excitation state is around 25\%\(^9\).**

The luminescence from triplet excitons \( (S=1) \) is generally low and almost all their energy is lost to nonradiative processes. Although radiation from triplet state is rare, the process can be quite efficient in some materials. If the excited singlet and triplet states are mixed such that the triplet gains some of the singlet character, the decay from the triplet state is partially allowed. Even though the emission of the light in this case is slower than fluorescence light, if the decay rate is faster than nonradiative rate, the luminescence is still efficient and is called phosphorescence. If the molecule is excited electrically, it is known
as "electrophosphorescence". The phosphorescence OLEDs (PHOLEDs) have been extensively studied by Forrest group from Princeton University.

\[ \eta_2 \] is defined as the fraction of radiative transition from the singlet excitons while \( \eta_3 \) represents the fraction of light emitted at the surface of the device relative to the light produced in the emissive layer (bulk) of the OLED. The factors that can affect \( \eta_3 \) are mainly the device structure, the refractive indices (n) of the layers in the device and the internal reflections at the interfaces within the OLED. The internal quantum efficiency is described as \( \eta_{\text{in}} = \eta \eta_1 \eta_2 \), while the external quantum efficiency of OLED is defined as \( \eta_{\text{ext}} = \eta \eta_1 \eta_2 \eta_3 \). More details about measuring the efficiency of organic light-emitting devices can be found in reference 97.

### 2.9.1 OLEDs based on dopant emitter system

In 1987, C. W. Tang and S.A. VanSlyke reported the first OLED based on aluminum tria(8-hydroxyquinoline) (Alq3) as the ETL. Two years later in 1989, C.W. Tang and his co-workers again discovered high efficiency OLED based on a guest-host emitter system. In this guest-host doped emitter system, a single host material with optimized transport and luminescent properties can be used with different types of highly fluorescent guest dopants leading to the desired electroluminescence (in terms of wavelength of emitted light) with high efficiencies. The doped emitter system can also enhance the operating stability of the OLED by transferring the electrogenerated exciton to the highly emissive, stable dopant and subsequently minimizing the possibility for non-radiative decay. The doping principle has been extended to highly phosphorescent materials leading to nearly 100% internal EL efficiency by researchers at Princeton University.

### 2.9.2 High efficiency OLEDs with electron-hole balance

The balance of hole and electron injection is one of the most important factors to improve the efficiency of the OLED devices. To achieve efficient radiative recombination of an electron-hole pair, the charge recombination zones have to be confined and not be close to an injection contact in order to produce the exciton. J.C. Scott has introduced a useful diagram in order to understand the charge balance factor \( \gamma \) as illustrated in Figure 2.13.

In Figure 2.13, the bottom left and right corners of the triangle represent "hole-only" and "electron-only" devices, respectively. The factor \( \gamma \) will remain 0 if all the injected holes and
electrons escape to the respective electrodes without recombination, even when equal numbers of electrons and holes are injected. Therefore, the bottom line of the triangle represents $\gamma = 0$. For the cases of $\gamma = 0.5$, it occurs when there is an excess of one type of charge that cannot fully recombine due to the limited amount of opposite charge. However, it can happen for the devices with same amount of injected charges from both sides of the electrodes, but only half of the charges are recombined in the emissive layer. For the case when equal numbers of holes and electrons are injected from the respective electrodes and recombine inside the OLED device, the charge balance factor $\gamma$ is 1.0, which is shown at the apex of the triangle. To increase the charge balance factor, the injection of holes and electrons from both electrodes has to be balance and confine within the emissive region. By introducing charge blocking layers in multilayer OLED structure, the charge balance factor and subsequently the efficiency of the OLED device can be improved.

Figure 2.13: This diagram illustrating the charge balance factor $\gamma$ for different types of hypothetical OLED structures.
2.11 Polytetrafluoroethylene (PTFE)

Since the discovery of PTFE by Plunkett in 1931\textsuperscript{101}, fluorocarbon based polymers have been used in various applications that required chemical inertness, thermal and mechanical resistance, chemical inertness with low adhesion\textsuperscript{102}. For example, fluorocarbon based materials are widely used in chemical, biotechnology, space science and semiconducting industries to seal and isolate materials especially under harsh conditions such as coal-burning power plant and space craft\textsuperscript{103,104}.

The polymer formulation of PTFE is $-[\text{CF}_2]_m$. The C-F bond is essentially the origin of its peculiar characteristics where the fluorine atom, being the most electronegative element, displaces substantially the electronic charge distribution in its surrounding and the bond has ionic character in which the F atoms are held very tightly. Figure 2.7 show a schematic diagram of a PTFE chain which adopts a slowly twisting helix that comprises thirteen CF\textsubscript{2} groups every 180\textdegree\ turn, such that every main chain bond is rotated 20\textdegree\ from the next CF\textsubscript{2} group. Thermodynamically, this is a favourable configuration because of the mutual repulsion of the adjacent fluorine atoms. The helical twisting of PTFE molecules results the molecules packing like parallel rods where each rod is comprised of an outer sheath of fluorine atoms enveloping a carbon-based core. Since the early 1940s, a lot of developments have been carried out to improve the processability and the properties of the PTFE in term of mechanical, thermal, optical, chemical resistance and gas permeability\textsuperscript{105,106}.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{ptfe_molecular_helix.png}
\caption{Schematic of the PTFE molecular helix. The molecules consist of outer sheath fluorine atoms over the central core atoms of carbon.}
\end{figure}
In organic based electronic applications, it has been shown that when relatively thin (~1nm thickness) amorphous PTFE film (sputtered or thermally evaporated) is incorporated in OLEDs between ITO and the active layer, an enhancement of the hole injection is observed when the rugged surface of the insulator film induces localized hole-injection that leads to current channels in the organic semiconductor\(^7\). When the PTFE interlayer is thicker, then insulating properties prevail, reducing the hole injection. The major limiting factor for using PTFE in LEDs is its insulating nature (resistivity in the order of \(\sim 10^6\Omega\)·cm) and its poor wetting properties. But, its chemical inertness is an extremely attractive property in the context of organic electronics in which devices are often subject to praecox degradation due to electrochemical interaction between different materials.

PTFE is insoluble in common solvents and inert to the usual chemical reagents. For these reasons, alternative methods to solution processing are preferred for PTFE coating as for example, friction-transfer technique\(^7\) or thermal evaporation\(^8,9\) or e-beam evaporation. We recently employed ITO/PTFE cathodes in poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) OPV devices that revealed a 200mV increase of the open-circuit voltage when compared to ITO, suggesting the formation of an interfacial dipole\(^10,11\).

In 2001, the first result on using fluorocarbon material, CF\(_x\), in OLEDs was published by L.S. Hung et al.\(^12\). In this publication, CF\(_x\) was used to provide a good interface between ITO and NPB such that it impedes indium diffusion and inhibits water vapor absorption. In particular, conducting CF\(_x\) with a resistivity of \(\sim 10^7\)–\(10^8\) \(\Omega\)·cm was reported to enhance the stability of OLEDs\(^12\). A year later, in 2002, a buffer layer of Teflon on top of ITO has been used to improve the hole injection at an ITO/organic polymer interface\(^12\).

The primary function of the CF\(_x\) layer is to improve the adhesion and the hole injection properties. In the study of metal/CF\(_x\)/organic interface using UPS, XPS and high resolution electron energy loss spectroscopy (HREELS), a surface induced dipole layer was found on the CF\(_x\) plasma treated metal surface with the negative poles pointing outward toward the vacuum\(^13\). The UPS results suggested that the existence of the dipole layer on the CF\(_x\) plasma treatment reduced the hole injection from metal to organic layer\(^13\). This study also suggested that a thin layer of CF\(_x\) could improve the stability of the device as their result show that no surface state changes was observed following treatment with CF\(_x\) after 24hours of air exposure in ambient conditions.
The model of charge tunnelling through a barrier into an organic semiconducting material was presented by Parker et al.\textsuperscript{115} followed by Kim's proposal on the principle of carrier tunnelling through a thin layer of insulator from an electrode to an organic semiconductor\textsuperscript{116}. In the case of Teflon, Wu et al. developed a theoretical model which agreed well with their experimental result where they showed that the morphology of Teflon is a critical factor for enhancing the hole injection in OLEDs, leading to a further understanding of the physical process of charge injection in OLEDs\textsuperscript{117}. 
CHAPTER 3
Experimental Tools and Techniques

The first section of this chapter focuses on the chemical process that is used to modify CNT and the techniques that we used to characterise the chemically modified CNT. Subsequently, the preparation details for PTFE film will be described. The second section will describe in detail the fabrication of OLED devices, followed by the techniques that were used for device characterisation.

3.1 Material preparation

3.1.1 Preparation of water soluble SWCNT and MWCNT

SWCNTs and MWCNTs grown using chemical vapour deposition were purchased from Nanocyl. The preparation of water soluble MWCNTs was performed following a method in the literature. The o-MWCNTs were prepared by ultrasonically dispersing the MWCNT in a 3:1 (volume) mixture of sulphuric acid (98%) and nitric acid (70%) for 10min. The mixture was refluxed for 60min at 130°C and was subsequently diluted in High-performance liquid chromatography (HPLC) grade deionised water (Figure 3.1). The resulting dispersion was centrifuged for 20min before decanting the supernatant. The remaining solid was repeatedly washed and filtered with deionised water over a 50nm polycarbonate (PC) filter until the washings were pH6-7. The entire filter paper coated with MWCNT was then submerged in a small quantity of deionised water whereupon the o-MWCNTs spontaneously dispersed to form the water based o-MWCNT solution. A known volume of o-MWCNT solution was dried in an oven to determine the concentration of MWCNT in the solution.

The preparation method of o-SWCNTs is almost the same as the preparation for o-MWCNTs, but the refluxing time was reduced to avoid excessive scission of the tubes. After the evaluation of the concentration of CNTs in water, 2mg/ml solutions of acid oxidised CNTs were prepared.
Figure 3.1: Schematic showing the chemical reaction involved in preparation for o-SWCNTs

### 3.1.2 Preparation of CNT thin films

The thin films of acid oxidised CNT with a concentration of 2mg/ml were deposited on the indium-tin-oxide (ITO) coated glass as the supportive, transparent conducting substrate for the device fabrication or thin film characterisation process. The ITO coated glass was obtained from Lumtech, Taiwan. In its fabrication, ITO is uniformly coated on polished soda-lime glass (thickness: 0.7mm provided by Central Glass Corporation, Japan) utilising a 20nm silicon dioxide barrier layer to prevent the diffusion of sodium ions from the glass to the ITO. The thickness of ITO is ~ 120-160nm with the arithmetic mean surface roughness of less than 6nm and the transparency higher than 84% at 550nm. The ITO has a nominal sheet resistance of 9-15Ω/square.

To prevent contamination, the substrates were pre-cleaned with acetone and iso-propanol in ultrasonic bath for 10min, before blowing dry by nitrogen air stream. Substrates were then cleaned by oxygen plasma treatment for 5min at 80W. This serves as an extremely efficient method for cleaning the surface of the substrate by removing the organic residuel, which accumulates during the storage and cleaning process. In doing so, the surface of the substrate becomes hydrophilic and facilitates the deposition of aqueous based solutions such as acid oxidised CNT.
The acid oxidised CNT solution were spin coated on the pre-cleaned ITO glass using the spin coater provided by Laurell Model WS-400-6NPP-LITE at the spin rate of 2000 revolutions per min (rpm) for one minute. Subsequently, the substrate was dried on the pre-heated hotplate for 5 min at 100°C to remove the water vapour residue.

3.2 Material characterisation

3.2.1 Atomic force microscopy (AFM)

AFM is a very high resolution type of scanning probe microscope (SPM) which enables surface topography to be examined at the nanometer scale. AFM is capable of producing three-dimensional images of a sample by operating the system in air or vacuum.

The AFM consists of a micro-scale cantilever with a sharp tip mounted perpendicular to one end of the cantilever that is used to scan the surface of the sample. At the other end, the cantilever is connected to the tip holder of the AFM head. When the tip is brought close to the surface of a sample, forces between the tip and the sample deflect the cantilever. Piezoelectric components are used to control the height of the imaging tips. The deflection is measured using a laser spot which is reflected from the top of the cantilever onto an array of photodiodes. A simple schematic diagram of an AFM is showed in Figure 3.2.

There are mainly two operating modes in an AFM: contact mode and non-contact mode. The contact mode is the first AFM technique to be developed where a constant deflection is applied to maintain the force between the tip and the surface constant during the scanning process. The changes in the cantilever’s height are measured and used to produce the images. In this mode, the tip deflections are caused by ionic repulsive forces and the static tip deflection is used as a feedback signal. This technique enables one to produce atomic resolution images. However, it is also found to damage or alter the surface of sensitive samples. In non-contact mode, van der Waals, capillary forces, magnetic forces and electrostatic forces are responsible for the deflections. In this mode, the cantilever is vibrated close to its resonant frequency. The attractive forces from the sample are substantially weaker than the forces used by contact mode. Therefore the tip must be given a small oscillation so that AC detection methods can be used to detect the small forces between the tip and the sample by measuring the change in amplitude, phase, or frequency of the oscillating cantilever in response to force gradients from the sample.
In this project, a Veeco, Dimension 3100 AFM, operating in tapping mode, is used for the surface morphology characterization of o-SWCNTs, PEDOT:PSS, ITO and PTFE layers. During the scanning operation, the Nanoscope IV controller is used to control the AFM head and communicates data to the computer. A Dimension 3100 controller is used to monitor secondary functions such as the optical microscope and sample stage. In the normal operating condition, this instrument can scan areas between 500×500nm² and 60×60μm² in the XY plane and detects features between 1 and 500nm in the Z plane. The typical resolution in XY plane and Z plane are 20 and 0.1nm, respectively. The n-type Si tip provided by Nano Sensors with a resonance frequency of 210-490kHz and a force constant of 12-110N/m is used for non-contact/tapping mode AFM for the morphology scanning.

3.2.2 Conductive atomic force microscopy (c-AFM)

Conductive Atomic Force Microscopy (c-AFM) is a secondary imaging mode derived from contact AFM that characterises conductivity variations across medium- to low-conducting and semiconducting materials. During the operation of c-AFM, a DC bias is applied to the conductive probe tip and the sample is held at ground potential (Figure 4.3). When the z feedback signal is used to generate a normal contact AFM topography image, the current passing between the tip and sample is measured to generate the c-AFM image. The c-AFM has a typical current range of 2pA to 1μA and the applied voltage range is between -12 to 12V. In this project, Si cantilevers with a Pt/Ir coated tip supplied by Nano World are used.
for the contact mode c-AFM measurement. This tip has a typical resonance frequency of 13kHz and 0.2N/m force constant.

3.2.3 Scanning electron microscope

Scanning electron microscopy (SEM) is a quick and easy method of imaging the surface of the material by utilising the electromagnetic lenses to focus the electron beam generated from the source to strike on the surface of the sample in a high vacuum (HV) environment. Based on the signal generated from secondary electrons and backscattered electrons, the topographical information can be found. There are also specialist types of SEM such as environmental SEM (ESEM) which is designed to work under a variety atmospheres and pressures for less conductive or biological samples. SEM can also be integrated with other techniques such as scanning tunnelling microscopy (STM) and SPM to make the combined SEM/SPM and SEM/SPM for use in multi-technique analysis for sample characterisation. The SEM used for the work completed in this thesis was an FEI Quanta 2000.

3.2.4 Transmission electron microscope

The working principle of the transmission electron microscope (TEM) is similar to the slide projector where the TEM utilise the wave properties of electrons to focus a beam of electrons on a specimen and creating an enlarged image that can be viewed on a phosphor screen and captured by camera or computer. The electron beam is produced by thermionic discharge of electrons and is focused to a small, thin, coherent beam by the use of condenser lenses. The beam wavelength is tunable by controlling the accelerating electric fields. For the TEM to work the specimen should be relatively thin to enable the electrons
to penetrate through and allowing the details of the specimen to be captured. By selecting
the apertures to collect the un-scattered electron, high contrast image is feasible.

The sample preparation involves depositing a dilute dispersion of o-SWCNT in ethanol
onto a copper grid, which acts as a support material. The sample was left to dry for an
hour before transferred to TEM chamber. A Philips cm-200 TEM is used to analyse some
of the samples reported in this thesis.

3.2.5 Ultraviolet-visible absorption and transmission spectroscopy

Molecular spectroscopy based on ultraviolet (UV), visible (VIS) and infrared (IR) radiation
is widely used for the identification and determination of many inorganic, organic and
biochemical species. In general, absorption of UV/VIS radiation by molecules occurs is
associated with the electronic transition of the molecules from the ground state to the
excited electronic energy state. The wavelength which the molecule absorbs depends on
how tightly the electrons are bound.

According to the absorption law, also known as Beer-Lambert’s law, the amount of light
passing through a material attenuates exponentially and depends on the concentration of the
absorbing molecules and the path length of the absorbing solution. A simple example in
Figure 3.4 showed that when monochromatic radiation passes through an absorbing
solution with the thickness $b$ cm and concentration $c$ moles per litre, the radiant power
dery from $P_0$ to $P$. The transmittance $T$ of the solution is the fraction of the incident
radiation transmitted by the solution as shown in equation 3.1. Transmittance is often
express as a percentage called percentage transmittance. The absorbance $A$ of a specimen
is related to the transmittance in a logarithmic manner as shown in equation 3.2. As the
absorbance of a solution increases, the transmittance decreases. In this project, a Varian
Cary 5000 UV-VIS spectrometer is used to measure the spectral absorption and
transmission of a material in UV/VIS wavelengths.

$$T = \frac{P}{P_0} \quad (3.1)$$

$$A = -\log T = \log \frac{P_0}{P} \quad (3.2)$$
3.2.6 Photoluminescence quantum yield

Quantitative measurement of the photoluminescence (PL) quantum yield for organic samples, such as polymeric semiconductors, is always challenging and important as it determine the limit to the efficiency of electroluminescent diodes. PL efficiency of the solution is relatively simple because it is appropriate to make an assumption that the emission is isotropically distributed. However for thin film organic semiconductor materials, the PL measurement is not a straightforward process as the angular distribution of the emitted light is highly sensitive to the refractive index of the material and the anisotropy distribution of chromophores leads to an anisotropy in the emission, reflectivity and absorbance.

A standard technique for measuring thin-film photoluminescence quantum efficiencies involves the use of an integrating sphere. An integrating sphere is a hollow sphere with the inner surface coated with diffusely reflecting material (typically barium sulphate). When a light source is placed in an ideal sphere, the light is distributed isotropically over the sphere interior surface regardless of the angular dependence of the emission.

The basic setup for the PL measurement is shown in Figure 3.5. There is an optical fibre which leads from the wall of the integrating sphere to a grating spectrometer with a charge coupled device (CCD). To prevent the direct illumination of the optical fibre, a barium sulphate coated baffle is used in front of the optical fibre. A pulse diode laser with FWHM=100ps and with an appropriate wavelength is directed into the sphere through a small hole. In this project, F8BT and F8 samples were excited by 380nm laser excitation energy.
Three measurements are made using the sphere. For the 'NO' measurement, the empty sphere is used and only the laser light is detected by the spectrometer as shown in Figure 3.5a. For the 'OFF' measurement, the sample is placed inside the sphere and the laser is directed to the sphere wall (Figure 3.5b). For the 'ON' measurement (Figure 3.5c), the measurement setup is similar to the second measurement except the collimated laser beam is now directed to the sample. In this case, the sample is aligned such that the reflected laser light from the sample surface is not back through the entrance hole but directed onto the sphere wall.

![Diagram](a) CCD spectrometer (b) Fibre optic (c) Laser beam

Figure 3.5: Attenuation of a beam of radiation by an absorbing solution where the path length is b and the concentration is c. 

The procedure that we used in this project to determine the PL efficiency, $\eta$, has been demonstrated by J.C. de Mello in 1997 and illustrated with the measurement on F8 thin film. Experimental spectra of F8 are illustrated in Figure 3.6. The value in y-axis is proportional to the number of photons within the given wavelength interval. In this measurement, the sharp peak with the highest intensity at around 373nm corresponding to the detection of the laser excitation, while the wider profile at around 500 to 700nm corresponds to the emission of F8. For the measurement 'NO' (whereby no sample is inside the sphere), the area under the laser profile is proportional to the unabsorbed light while for
measurement ‘OFF’ and ‘ON’, the areas under the emission profile are proportional to the emitted light, $P$.

![Graph showing emission profiles](image)

**Figure 3.6:** The spectra for the measurement of F8 thin film. For clarity, the spectra is represented into two parts since the intensity of PL for F8 is much lower than the laser intensity. Left: Laser excitation wavelength at around 373nm; and Right: F8 emission detected from 500nm to 700nm.

Basically, there are two different sources of light that can strike on the sample and contribute to the emission. The first source is the incident beam from the laser beam which directly strikes the sample. The second source is the diffusive light which has scattered around the wall of the sphere and subsequently strikes on the sample surface. During the measurement OFF, we make an assumption that there is a fraction $N$ of the laser light scattered in the sphere which absorbed by the sample. For measurement ON, there is a fraction of the incident light absorbed by the sample, $A$ and the fraction of light that is transmitted or reflected is called $(1-A)$. The transmitted and reflected light will be scattered around that sphere and a fraction of this scattered light $\mu$ is reabsorb by the sample. $L_{\text{off}}$, $L_{\text{on}}$, and $L_{\text{c}}$ in equation (3.3) and (3.4) is referred to the value of $L$ for measurement of OFF and ON respectively.

\[
L_{\text{on}} = L_{\text{off}}(1 - \mu) \tag{3.3}
\]

\[
L_{\text{c}} = L_{\text{on}}(1 - A)(1 - \mu) \tag{3.4}
\]

\[
A = (1 - \frac{L_{\text{c}}}{L_{\text{on}}}) \tag{3.5}
\]
For measurement OFF, the number of photons detected by the detector is given by $L_0 + P_b$. For the measurement ON, there is a portion of light that has been reflected, another fraction of light is transmitted and the remaining fraction is absorbed, $A$. By making the assumption that laser light scattered from different locations on the sphere interior identically contributes to the measured spectrum, therefore the contribution of scattered light to the measured spectrum is $(1-A)(L_0 + P_b)$. The light emitted due to the contribution from the absorption of collimated light ($\eta L_\infty A$) also contributes to the profile measured in measurement (c). Thus the total intensity over the spectrum in measurement (c) is given by equation (3.6). By rearranging Eq. (3.5) and (3.6), PL efficiency $\eta$ can be obtained Eq. (3.7).

$$I_c + P_c = (1-A)(L_0 + P_b) + \eta L_\infty A$$

(3.6)

$$\eta = \frac{P_c - (1-A)P_b}{L_0 A}$$

(3.7)

In this PL efficiency measurement, a pulsed diode laser (FWHM: 100ps), an integrating sphere and an Andor Shamrock spectrograph coupled with CCD were used with the technical support from Dr Gianluca Latini.

### 3.2.7 PL lifetime measurement

The PL lifetime was measured using the time-correlated single photon counting (TCSPC) fluorescence technique\(^2\). This technique relies on the measurement of the time difference between each excitation light pulse and the detection of a single photon. During the experiment, a sample is excited by a pulsed laser, resulting in a waveform as shown at the top of the Figure 3.7. When many fluorophores are excited numerous photons are observed, but for TCSPC, the condition is adjusted such that no more than one photon is detected per pulse. The typical detector rate is 1 photon per 100 excitation pulses on average. The time between the excitation pulse ($t=0$) and the observed photon is measured and then stored in a histogram (Figure 3.7) which, after many photons are recorded, will give the emission lifetime decay\(^2\).

In this lifetime measurement, the setup consists of a ps-pulsed diode laser at 375nm (Edinburgh EPL-375) and a F-900 TCSPC unit with a temporal resolution ~150ps, with a
photomultiplier tube coupled to a monochromator. All the measurements were conducted with technical support from Dr Gianluca Latini.

3.3 Surface study

3.3.1 Ultraviolet photoemission spectroscopy (UPS)

Photoemission spectroscopy (PES) is a surface sensitive technique that has been used to probe the valence and the core electron states of a material with the principle of measuring the kinetic energy of photoelectrons emitted as a consequence of high energy photon absorption. The binding energy of the electron in the certain energy levels can be obtained from equation 3.12, where $E_b$ and $KE$ are referring to the binding energy and the kinetic energy, respectively. Primarily there are two commonly used photoelectron spectroscopic techniques which are based on X-ray or UV range incident photons energies. For ultraviolet photoemission spectroscopy (UPS), UV light of 21.2eV, is used as the incident light source in this project.

$$E_b = h\nu - KE$$

(3.8)
In this study, the work functions of ITO, acid oxidized thin films of CNT and 4,4'-bis(m-tolyphenylamino) biphenyl (TPD) thin films prepared by evaporation were studied using UPS. UPS has the advantage of directly providing the work function of the materials under study in ultrahigh vacuum (UHV). UPS was carried out at room temperature using a He discharge lamp (He I: $h\nu = 21.2$ eV) and an angle-integrated-type electron energy analyser. The sample was biased at -3V during the work function measurements to accelerate the low energy secondary electrons. The position of the Fermi level was calibrated using the Fermi edge of a clean gold (Au) film. In order to gain accuracy in the UPS measurement, each sample has been scanned with different slit sizes and steps for more than 10 times.

### 3.3.2 Kelvin probe

The Kelvin probe consists of a mesh electrode positioned in front of the sample surface being studied and driven by solenoid or piezoceramics electromagnetically. Basically, it works like a parallel plate capacitor where the gap between the plates can be varied in a periodic manner as shown in Figure 3.8. This vibration gives rise to an oscillating current:

$$i = \frac{dC}{dt}(e\Delta \phi - V^{\text{COMP}})$$

(3.9)

where $V^{\text{COMP}}$ is the external compensation voltage. $\Delta \phi$ arises from the contact potential difference that exists between the two conducting plates and is equal to the difference between the work function of the sample surface ($\phi^S$) and that of the reference probe ($\phi^R$). $V^{\text{COMP}}$ can be adjusted to null the current, and that particular value of the compensation voltage represents the difference in the work function of the two conducting plates (Eq. 3.10):

$$eV^{\text{COMP}} = \phi^S - \phi^R$$

(3.10)

The Kelvin Probe measurements can give a high intrinsic accuracy of ~20mV. However, the precision of the absolute value of the surface’s work function relies on the precise knowledge of the reference’s work function. This technique is a quick and easy way to measure the chemical potential difference. The instrument used in this project consisted of a Besocke Delta Phi Kelvin probe with a mesh electrode made of gold. Freshly cleaved highly ordered pyrolytic graphite (HOPG) with the work function of 4.475eV is used as the
reference sample before and after the measurement of the sample to determine measurement consistency.

Figure 3.8: Schematic diagram of Kelvin probe

3.3.3 Raman spectroscopy

Raman scattering is an optical process that involves simultaneous emission or absorption of a phonon associated with the scattering of a photon. Due to scattering with phonons of the solid, the scattered photons will have a shift in frequency, basically re-emitting with a lower (Stokes) or higher (Anti-Stokes) frequency as illustrated in Figure 3.9. In contrast to Rayleigh scattered light, the Raman scattered light is not coherent with the light of the primary beam. The frequency shifts are independent of the frequency of the primary light. It is just a function of the scattering due to the solid. As seen above, the resulting frequencies can be obtained \( \nu = \nu_o - \nu_m \) for the Stokes lines and \( \nu = \nu_o + \nu_m \) for the Anti-Stokes lines with the primary light frequency \( \nu_q \).

During the Stokes scattering, the solid absorbs energy from the photon whereas during the anti-Stokes scattering the solid delivers energy to the photon. The intensity ratio between Stokes and anti-Stokes lines are given by the occupation probability \( n \) of the initial states which are calculated with the Boltzmann equation. With decreasing temperature the Anti-Stokes lines become weaker.

At the instrument level, the measurement setup is based on what is known as micro-Raman spectroscopy. Basically a laser is focused onto a spot of the sample with diameter on the order of micrometers using an optical microscope. The scattered light is then collected by the microscope's objective lens and deflected to a spectrometer. The Raman spectra are recorded in backscattering configuration.
3.3.4 Polarized optical microscope

A polarised optical microscope is a microscope that utilizes polarised light to form a highly magnified image of an object. It plays an important role in crystallography, microchemistry, biology and geology as it has the advantage of being relatively non-destructive and could be safely used with living cells. The polarised microscope not only can provide information on absorption colour and boundaries between materials with different refractive indices, it can also distinguish between isotropic and anisotropic materials. Isotropic materials are the materials that demonstrate the same optical properties in all direction such as gases, liquids, unstressed glass and cubic crystals. They have only one refractive index and there is no restriction on the optical polarisation of light passing through them. Anisotropic materials in contrast have optical properties that vary with the orientation of the propagation and polarisation directions of the light with respect to crystallographic axes.
3.4 OLED and PLED device fabrication

3.4.1 Materials

SWCNT (>90wt.%) and MWCNT (>90wt%) grown by chemical vapour deposition (CVD) were obtained commercially from Nanocyl and used as received. For the PTFE, this bulk material with a density of 2.17±0.02g/cm³ was cut into a cubic size (1×2×1)cm³, pre-cleaned with propan-1-ol (IPA) and blow dried with N₂ before it was put on the tungsten evaporation boat for thermal evaporation. For the OLED fabrication, sublimation grade of triphenylamine (TPD) and aluminium quinoline (Alq₃), with the chemical structure showing in Figure 3.10, from LUMTECH is used as received. For the PLED device fabrication, the hole injection polymer, PEDOT:PS (Baytron P Al 4083) is used as received. For the light emitting polymer, poly(9,9-dioctylfluorene), F8 (ADS129BE, molecular weight Mₙ=48,800) and poly(9,9-dioctylfluorene-alt-benzothiadiazole), F8BT (ADS133YE, Mₙ=28,000) and poly(2,7-(9,9-di-n-octylfluorene)-alt-(1,4-phenylene-((4-sec-butylphenyl)imino)-1,4-phenylene)) (TFB) are dissolved separately in p-xylene with the concentration of 20 mg/ml and stirred for at least 24 hours before being used for PLED devices.

Figure 3.10: Chemical structure of materials used in this thesis
3.4.2 Device fabrication

o-SWCNTs based hole-only and OLEDs devices were prepared with respective device structure of ITO/o-SWCNTs/TPD/Al and ITO/o-SWCNTs/TPD/Alq3/LiF/Al. The ITO coated glass substrates (Merck) with >80% transmission, sheet resistance of 20Ω/cm and a surface roughness of ~2nm were ultrasonically cleaned in toluene, an aqueous solution of Decon-90, acetone, IPA and finally with acetone vapour before blown drying with N2 gas flow. Substrates were then treated with oxygen plasma at 50W for 5min before spin coating the aqueous solution of 0.2%wt o-SWCNTs at 2000rpm for 60sec and dried for 10min at 100°C. Subsequently, the sample has placed in the modified Edwards multi-crucible evaporator for small molecule thin film and metal deposition. All the depositions were performed at a pressure less than 5 × 10^-6 mbar. TPD and Alq3 were evaporated in the rate of 0.1-0.3nm/s. For the case of the electron injection material such as lithium fluoride (LiF), the typical deposition rate is less than 0.1nm/s as the total thickness needed is approximately 1nm or less. For cathode material such as aluminium (Al), the deposition rate is in between 0.3-0.5nm/s. For all the thermal evaporation processes, a quartz crystal thickness monitor is used to measure the deposition rate and the film thickness, based on the settings entered by the operator and the changes in the resonant frequency of the crystal.

For the o-SWCNTs based PLED devices with the structure of ITO/o-SWCNTs/TFB/F8BT/Ca/Al, the preparation method for o-SWCNTs layer is the same as above. After the ITO/o-SWCNTs sample was dried outside the glove box, then the sample was transferred into the glove box for spin coating the polymer layers. For the formation of a TFB/F8BT bilayers structure, 2%wt TFB dissolved in p-xylene solution was spin coated on ITO/o-SWCNTs substrate followed by annealing at 140°C for 5 min. After that, the top part of TFB layer was washed away by rinsing with p-xylene and spin dried. With this method, a thin layer (~ a few nanometers) of TFB layer, which was not washed or dissolved by the solvent, would stay on top of the substrate. Subsequently, the F8BT solution was spin coated on top of TFB to form the bilayer polymers structure. For the single layer PLED device (ITO/o-SWCNTs/F8/Ca/Al), 2wt% concentration of F8 dissolved in p-xylene was spun on top of the ITO/o-SWCNTs at 5000 rpm for 1min. No annealing treatment is applied to the F8 films. Subsequently, the sample was transfer to a vacuum chamber for calcium and aluminium cathode deposition with the thickness of 30 and 150nm, respectively.
For the PLEDs with the structure of ITO/PEDOT:PSS/PTFE/F8/Ca/Al, the devices were fabricated using ITO substrates that were first solvent cleaned (10 min ultrasonic bath in acetone and isopropanol) and then treated with oxygen-plasma. Thin films (60-80 nm) of PEDOT:PSS (Baytron P A1 4083) were deposited in air by spin coating and then annealed at 120°C in nitrogen. PEDOT:PSS films were then transferred in air to an evaporation chamber where PTFE was thermally evaporated at 10⁻⁴ mbar (evaporation rate=0.1 nm/s), and transferred (in air) to a glove box where F8 films (thickness ~110 nm) were deposited in nitrogen by spin coating p-xylene solutions (2% by weight). No annealing treatment was applied to the F8 films. Calcium(30 nm)/aluminum(150 nm) electrodes were thermally evaporated at 10⁻⁵ mbar on the polymer films. The thickness of the polymer films was measured using a Dektak profilometer. Non-encapsulated devices were characterized in low vacuum (ca. 10⁻¹-10⁻² mbar) after being transferred, under nitrogen, from the glove-box used for the cathode deposition.

3.5 Device characterisation

3.5.1 Current-luminance-voltage

For the current-luminance-voltage (I-L-V) characteristic of the OLED devices, the measurements are made using the setup shown in Figure 3.11. The diode is placed at the center of a chamber where the device is electrically connected with a Keithley Model 2400 source meter and the operating current is measured by a multimeter Keithley K195. The chamber is normally kept under vacuum with pressure below 10⁻² mbar when the measurement is conducted. A photodiode is placed in front of the device outside the chamber during the measurement.

\[\text{Voltage Source}\]

*Figure 3.11: Schematic diagram of the experimental set-up to measure current-voltage and light output characteristics of OLEDs*
Electroluminescence (EL) measures the luminescence given out by an LED operating under a given set of conditions. In a typical EL experiment, we measure a current $I$ flowing through the LED at a given voltage $V$ and the optical detector’s output voltage $V_{pd}$. Incorporating the following parameters: 1) photodiode’s responsivity, 2) eye’s response curve and 3) geometric dimensions of the optical enclosure, the LED’s EL responses, namely luminous efficiency and external quantum efficiency, can be derived$^{122}$.

Figure 3.11 above shows the schematic of the experimental setup for electroluminescence (EL) measurements. During the device operation, the optical detection is performed by a photo-amplifier. This photo-amplifier consisted of an amplifier circuitry that measures the current of the photodiode detector through a 1MΩ resistor. The resultant output is recorded by a Keithley 2000 multimeter. Finally, the optical enclosure’s atmosphere is pumped down to $10^{-3}$mbar by a mechanical pump.

In our optical enclosure, the measured light from the LED subtends a solid angle of $\Omega = 0.098$ steradian. Given the photodiode’s response $Q(\lambda)$, from the manufacturer’s datasheet, and the measured LED’s emission spectrum $S(\lambda)$, an emission weighted quantum efficiency of the photodiode, $C$ is calculated as below:

$$C = \frac{\int Q(\lambda)S(\lambda)d\lambda}{\int S(\lambda)d\lambda}$$  \hspace{1cm} (3.11)

Knowing the optical detector’s output $V_{pd}$, the incident optical flux is:

$$\Phi = \frac{A \times V_{pd}}{C} \text{ photons/sec}$$  \hspace{1cm} (3.12)

LED’s luminous intensity is given by $L$:

$$L = \frac{AK}{C \Omega} \times V_{pd} \text{ candela (cd)}$$  \hspace{1cm} (3.13)

where $K$ is the conversion factor that incorporates the eye’s response $P(\lambda)$ as follow:
\[ K = \frac{\int P(\lambda)S(\lambda)d\lambda}{h \lambda} \text{lm per (photon s)} \]  

where \( h \) is Planck's constant, \( c \) is speed of light.

Luminous intensity for the forward direction is:

\[ L = \frac{AK}{C\Omega} V_{pl} \text{ candela (cd)} \]  

(3.16)

After obtaining the above, to obtain the luminous output intensity over all the viewing angles, we make the assumption that the lambertian emission is observed leading to the following that the optical flux over a semi sphere in the forward direction, \( \Phi_{\text{flux}} \) is calculated to be:

\[ \Phi_{\text{flux}} = \frac{L d\Omega}{K} = \frac{2\pi L}{K} = \frac{\pi A}{C\Omega} V_{pl} \]  

(3.17)

With all the above equations, we can finally derive the following two efficiency calculations:

Luminous efficiency:

\[ \eta_{\text{Lum}} = \frac{\Phi_{\text{flux}}}{VI} \]  

(3.18)

External quantum efficiency:

\[ \eta_{\text{ext}} = \frac{\Phi_{\text{flux}}}{I} \]  

(3.19)

In order to estimate internal quantum efficiency, \( \eta_{\text{int}} \), we have to consider the output coupling efficiency in the presence of reflections and interference within the device structure.

From published literature\(^{129}\), one can consider the following relation to approximate the output coupling efficiency:

\[ \zeta = \frac{B}{n^2} \]  

(3.20)
where $\beta$ is a constant $\sim 0.75$ to 1.2 based on the device under consideration, and $n$ is refractive index. Thus internal quantum efficiency is

$$\eta_{\text{int}} = \frac{\eta_{\text{ext}}}{\zeta}$$

(3.21)

3.5.2 Lifetime measurements

In the lifetime measurement for OLEDs, the device is driven in a constant current under similar conditions to the $I$-$L$-$V$ measurement. At the same time, the applied voltage needed to maintain the constant current and the luminance of the device are recorded continuously for every interval of time that vary from a second to a minute in scale using a lab-view program.

3.6 Organic photovoltaic fabrication and characterisation

For OPV devices, the device consists of ITO-coated glass substrate, PTFE layer, poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) and Al cathode. ITO glass is pre-cleaned followed by an oxygen plasma treatment for 3 min prior to use for device fabrication. Polythiophene, P3HT (Rieke Metals, used as received) was dissolved in 1,2-dichlorobenzene (DCB) to make a 17mg/ml solution, followed by blending with PCBM (Nano-C, used as received) in 1:1 weight ratio. The blend was stirred for ~14 hours in a glove box, before being spin-coated on top of the ITO/PTFE surface. The typical film thickness of P3HT:PCBM is about 210-230nm. Five types of OPVs are prepared with a PTFE layer varied between 0.5 to 5.0nm. Both PTFE and Al films are deposited at a base pressure of $2 \times 10^{-5}$Torr. All the measurements are carried out in ambient atmosphere at room temperature. To study the consistency of the device performance, a minimum of 5 samples for each individual structure of the devices are tested.

For the double heterostructure OPV cells, the same pre-cleaning process was used before putting the substrate into the evaporator for further fabrication. Films were grown at room temperature with a base pressure of $2 \times 10^{-5}$Torr in the following sequence: thermal evaporation of PTFE layer varied between 0.3, 0.5 and 1.0nm; 20nm thick film of the donor-like copper phthalocyanine (CuPc); followed by a 40nm thick film of the acceptor-like buckyball $C_{60}$. A 12nm thick large band-gap material, bathocuproine (BCP) was
deposited as an exciton-blocking layer (EBL) because a previous report has found that BCP can be used to transport electrons to the cathode from the adjoining acceptor layer through the cathode-induced defect states in EBL energy gap, at the same time as effectively blocking excitons in the lower-energy-gap acceptor layer from recombining at the cathode. Subsequently, 100nm thick Al cathode was deposited by thermal evaporation through a shadow mask. A Honle UV America Inc. UV light source SOL500 was used, with a stabilization period of at least 10 min prior to UV exposure on PTFE films. The work function of ITO/PTFE layers before and after UV exposure were determined by examining the contact potential difference (CDP) of the sample using a Kelvin probe arrangement (SKP5050, KP Technologies). All the current-voltage (I-V) measurements were made with a Keithley 2400 source meter in air ambient, in dark and under $82\text{mW/cm}^2$ solar irradiance (Oriel light source). The active area for all the devices was in excess of $0.1\text{cm}^2$ for this study. The consistency of the device performance was obtained by measuring a minimum of 5 samples for each individual device structure.
CHAPTER 4

Physical and Interfacial Study of Acid Oxidised SWCNT

The peculiar electronic and morphological properties of carbon nanotubes have attracted a lot of attention to them as a versatile electrode material for electrochromic, OLED and OPV applications, most notably as a viable alternative to costly and problematic indium-tin oxide (ITO) coated glass. As such, it has already drawn the attention of investors and carbon nanotubes based electrode films are being produced. Whilst it is possible to process pristine CNTs into thin films it is often desirable to chemically functionalise the outer surface and ends to impart enhanced functionality. For example, we have recently shown that o-SWCNTs and o-MWCNTs respectively can be used as high work function, hole-extracting electrodes in bulk-heterojunction OPVs. However, as CNTs are used more widely as electrode materials in OPVs and OLEDs, understanding the interfacial interaction between CNT and organic materials is progressively becoming more important.

This Chapter investigates the effects of acid oxidation on pristine SWCNTs and MWCNTs in terms of their physical and surface properties. The composition of the sample after the acid oxidation process will also be discussed. In addition, we study the work function of CNT before and after the acid oxidation process as well as the interfacial energy level alignment between o-SWCNTs and o-MWCNTs respectively, and the archetypal triphenylamine hole transport material TPD.

4.1 Acid oxidation of single walled carbon nanotubes

Treatment of CNTs using nitric or hydrochloric acid under relatively mild conditions is an established method for removing metal catalyst particles without altering the CNTs’ physical dimensions. Conversely, sulphuric acid is known to shorten CNTs via scission of the sidewalls and ends and so is not normally used as part of a purification procedure. Both of these treatments introduce oxygen containing groups at pre-existing or new defect sites on CNTs, groups which stabilise the defective $sp^2$ carbon network and crucially for the present application – help to increase the solubility of the material in water. When nitric and sulphuric acids are used together at elevated temperature (70-130°C), oxidation and chopping proceed rapidly, decorating the CNT ends and sidewalls with a
high proportion of oxygen containing groups\textsuperscript{57} which render the CNTs highly soluble in water and alcohols. In this work the oxidation procedure has been optimised to strike a balance between achieving stable concentrated dispersions of CNTs via surface oxidation and the requirement to maintain the electronic integrity of the tubular structure.

Our group has previously reported a detailed XPS and high-resolution transmission electron microscope (HRTEM) study of the effect of acid oxidation on MWCNTs, which are more resistant to oxidation than SWCNTs owing to their large radius of curvature and multiple layer structure\textsuperscript{57}. Under the conditions described therein, only the outer 2-3 layers of the CVD MWCNTs that are appreciably modified. Fitting of the C1s core level spectra obtained using XPS revealed that carboxylic acid moieties are the most abundant surface group followed by hydroxyl moieties. The density of the carboxylic acid functionality was estimated to be as high as 12nm\textsuperscript{-2}. The work function measured using UPS was \textasciitilde 5.0eV upon acid oxidation, which is \textasciitilde 0.6eV higher than that of untreated MWCNTs and graphite\textsuperscript{66}. This large increase is believed to result from the modification of the CNT surface potential and has important implications for the electronic functionality in the current context\textsuperscript{66,67}.

Owing to their higher radius of curvature and single layer structure SWCNTs exhibit greatly increased susceptibility to oxidation. As a result, the oxidation time was reduced from 60min for MWCNTs to 25min for SWCNTs. To probe the effect of acid oxidation on the SWCNTs, HRTEM (Figure 4.1) was employed in conjunction with AFM (Figure 4.2).

Figure 4.1 shows the TEM images of MWCNTs and SWCNTs after the acid oxidation process. From these images, it can be seen that the o-MWCNTs surfaces are decorated by amorphous carbon due to the acidic attack. For o-SWCNTs, on the other hand, the surfaces are relatively clean and less damaged. Some of the SWNTs bundles show an intact surface but others display buckling, an effect that can be attributed to the acid oxidation process and the introduction of oxygen moieties such as carboxylic acid (COOH) groups on the side of the tubes. Furthermore, some of the o-SWCNTs bundles are still covered by amorphous carbon (Figure 4.1c). In addition, the length for a lot of o-SWCNTs bundles was found to be shortened by the scissoring and cutting effect of the acid oxidation process (Figure 4.1d). Therefore the ratio for tube length over tube diameter is significantly reduced after the acid oxidation process and the functional group at the end of the tubes play a significant role in determining the properties of the o-SWCNTs. All the TEM images for o-SWCNTs show no
significant amount of metal catalyst in these samples, indicating that the acid oxidation process can remove these impurities.

The AFM images of o-SWCNTs and o-MWCNTs in Figure 4.2 show significant differences in term of length and physical characteristics of the two types of tubes. For o-SWCNTs, the tubes length are significantly shorter, from a few hundreds of nm to 1μm, which is agreement with a previous report, while the o-MWCNTs remained long (> 2μm) and close packed.

*Figure 4.1: TEM images for (a) o-MWCNTs and (b-d) o-SWCNTs*
Figure 4.2: AFM images for o-SWCNTs (left) and o-MWCNTs (right) on ITO glass substrate

This can be explained by a different mechanism in the acid attack of the two types of tubes. For the oxidation of the SWCNTs, the chopping proceeds rapidly starting from the defect sites along the circumference of the tube and therefore the o-SWCNTs are shorter and straight; for o-MWCNTs, the oxygen moieties get mainly attached to the side wall of the outer tube during the oxidation process while the inner tube remains intact. Consequently the o-MWCNTs look long and worm-like.

Figure 4.3: XRD data of pristine SWCNTs, o-SWCNTs and o-SWCNTs after annealed at 850°C for 10 min.
To qualitatively analyse the composition of acid oxidised SWCNTs, the pristine SWCNTs, o-SWCNTs and o-SWCNTs residue after annealing at 850°C for 20min were further studied by X-Ray Diffraction (XRD) and the data is shown in Figure 4.3. The XRD patterns of pristine SWCNTs contains some sharp peak superimposed to the weak broad peak at around 18-30°. The sharp peak reflection at around 26° matches the one of hexagonal graphite (002) (JCPDS 26-1079) while the broad peak could come from fullerene-like nano-particle (FNP), onions and small amount of MWCNT which exist as the by-product of the purchased SWCNTs. After the acid treatment, the broad peak which superimposed to the graphite (002) reflection has slightly shifted but remains strong. For pristine SWCNTs, cubic Ni (c-Ni) (111) and (200) (JCPDS 04-0850) broad peaks are observed at 44° and 51° which originate from the remnant Ni catalyst nano-particles. The broadening observed is due to the nanoscale dimensions of the Ni particles. The c-Ni peaks are almost absent after the acid oxidation process, indicating that the oxidation process has removed large amounts of metal catalyst from the SWCNTs. After the annealing at 850°C, the broad graphite reflection still exists and a strong peak at 26° is observed. It is likely that the FNP remain in the sample after the annealing process. The peaks near 45° and 52° which are attributed to c-Ni (111) and c-Ni (200) appeared as sharp peaks after the annealing. The possible reason is the annealing process agglomerates the remaining Ni nanoparticle form larger clusters which display sharper XRD peaks.

The XRD data shows that the pristine SWCNTs contain a high proportion of impurities. Even after the acid treatment, some impurities such as fullerene-like nanoparticle, carbon nanoring/onion and some c-Ni catalyst remain in the sample.

### 4.2 Work function of o-SWCNTs

We report the UPS spectra corresponding to the valence band density of state (DOS) of ITO, pristine SWCNTs and o-SWCNTs in Figure 4.4 (top). For the pristine SWCNTs, a peak at around 3eV originates from the π hybridised p electrons while the peaks around 8eV stems from σ hybridised p electrons. For the o-SWCNTs, the acid oxidation process results in a significant change in the spectrum. The π derived DOS has almost disappeared and the σ derived DOS also changed drastically which indicates that the electronic properties of the nanotubes have changed after the acid oxidation process. Compared to the ITO work function determined in this study (21.2-17.0=4.2eV), the work function of both pristine SWCNTs and o-SWCNTs are higher, at 4.8 and 4.62eV, respectively (Figure 4.4 bottom). It has been reported by Ago that the acid oxidation process increases the work
function of MWCNT from 4.3eV to 5.0eV. Conversely, the UPS study of o-SWCNTs indicated that the work function is lower after the acid oxidation process, which could be correlated with the purity and degree of oxidation of the tubes.

By comparing the TEM results with the UPS work function study, we found that the walls for some of the o-SWCNTs bundles were still covered by amorphous carbon (Figure 4.2c). For the cleaned o-SWCNTs bundles showed in Figure 4.2b, some parts of the bundles’ surface look intact but others show a swelling effect on the tubes which could be attributed to the acid oxidation process where the oxygen moieties such as carboxylic acid (COOH) group were introducing defect in the tubes. Furthermore, the scissoring and cutting effects during the acid oxidation process shorten the length of the SWCNTs while transforming some of the o-SWCNTs to small graphite like structures or amorphous carbon material. The work function of graphite is approximately 4.4eV. Despite the variation of work function between pristine SWCNTs and o-SWCNTs, the important fact is that both CNT samples have higher work function when compared with ITO.

![Graph](image)

*Figure 4.4: (Top) UPS spectra of the high binding energy cut-off for ITO glass, pristine SWCNTs and o-SWCNTs; (Bottom) Secondary electron edge cut-off for the individual samples*
4.3 Interfacial study in ITO/o-SWCNTs/TPD and ITO/o-MWCNTs/TPD layered structures

UPS was used to probe the electronic structure of the contacts formed by vacuum deposition of TPD onto o-SWCNT and o-MWCNT films by measuring the interfacial energetics for the TPD layer thicknesses of 0, 1 and 5nm (Figure 4.5). From the UPS spectrum it is possible to deduce the work function from the difference between the incident photon energy (21.22eV) and the high binding energy cut-off (Figure 4.6). Both the work function and the HOMO position are determined directly from the UPS spectra by fitting straight lines to their low and high kinetic energy cut-off, respectively, and determining the intersect with the baseline of the spectra.

In this measurement of ITO, o-SWCNT and o-MWCNT, $E_f$ measured by UPS are 4.3, 4.6 and 5.00eV, respectively. The higher binding energy cut-off corresponds to the vacuum energy level, $E_{\text{vac}}$ (Figure 4.6) and so any change in the high binding energy cut-off upon deposition of a TPD overlayer can be interpreted as a change in $E_{\text{vac}}$, so called vacuum level shift ($\Delta E_{\text{vac}}$).

![Figure 4.5: UPS spectra of o-SWCNTs, o-SWCNT/TPD(5nm), o-SWCNT/TPD(1nm), o-MWCNTs, o-MWCNT/TPD(5nm) and o-MWCNT/TPD(1nm) supported on ITO glass substrates](image)
Figure 4.6: The high binding energy cut-off in the UPS spectra from which the vacuum level shifts ($\Delta E_{\text{vac}}$) are determined for the o-SWCNTs/TPD and o-MWCNTs/TPD interfaces.

For a TPD overlayer thickness of 1nm on o-SWCNTs, $\Delta E_{\text{vac}}$ is $\sim$ -0.4eV with no further change upon increasing the TPD layer thickness to 5nm. When a thin film of an organic semiconductor is deposited onto a conducting substrate, Fermi level alignment across the interface cannot be assumed. Seki et al. have previously proposed a criterion for judging the establishment of Fermi level alignment in such cases; namely that the work function of the organic overlayer should be independent of the work function of the underlying electrode.$^{140}$ Figure 4.5 shows that the work function of a 5nm TPD layer on o-MWCNTs is, within experimental error, the same as that of a 1nm (and 5nm) TPD overlayer on o-SWCNTs ($\sim$4.2eV) despite a $+0.4eV$ difference in work function between o-MWCNTs and o-SWCNTs. This result is compelling evidence that Fermi level alignment is achieved across both interfaces. Furthermore, the ionisation potentials of the TPD overlayers deduced from the UPS spectra are 5.0 ± 0.1eV and 5.1± 0.1eV for 5nm of TPD on o-SWCNT and o-MWCNT respectively (Figure 4.7). This is in good agreement with that reported by Seki et al.$^{64}$ and is further evidence that the TPD overlayer is in thermal equilibrium with the underlying carbon nanotubes in both cases.
In the case of the o-MWCNT/TPD interface, 90% of $\Delta E_{\text{vac}}$ occurs within the first 1 nm and its magnitude is more than twice that at the TPD/o-SWCNT interface. Such an abrupt shift in $E_{\text{vac}}$ has only previously been observed to occur at the interface with metals$^{65,73}$ and is believed to result from the pushing back of the electron cloud that spills into the vacuum. In metals the intrinsic surface dipole that results from the spilling out of the electron cloud into the vacuum makes a large contribution to the work function and so surface adsorbates often induce large changes in $E_{\text{vac}}$. Conversely, it is clear from Figure 4.5 that the density of electron states close to the Fermi level in carbon nanotube is small and so it is unlikely that that the same mechanism is operative in the current context. Crucially the magnitude and direction of the change in $E_{\text{vac}}$ observed coincides with that required to align the Fermi level across the interface.

Whilst the transition from molecular to bulk behaviour is ill-defined in molecular solids and the applicability of band theory to films of only a few molecules is questionable, the concept of the Fermi level remains valid because electrons fill the available states according to Fermi-Dirac statistics$^{141}$. In this case the samples were briefly exposed to air prior to loading into the ultra-high vacuum system for UPS measurement and so it plausible that the TPD overlayer was unintentionally doped with oxygen. The abruptness of the vacuum level
shift in both cases is however inconsistent with band bending at an interface with a doped organic semiconductor. Taken together these results are therefore consistent with Fermi level alignment across both interfaces accommodated by abrupt interfacial vacuum level shifts whose magnitude and direction correlates with the difference in work function between the carbon nanotube substrate and bulk TPD.

For device applications the energy offset between the electrode Fermi level and the relevant frontier molecular orbital in the adjacent organic semiconductor is the dominant factor determining the efficiency of charge carrier injection/extraction. In this instance the offsets between the HOMO of TPD and the Fermi levels of o-SWCNTs and o-MWCNTs are comparable (0.8-0.9eV) despite the large difference in the work function of these electrode materials. The shift of the vacuum level (~0.39eV) in both ITO/o-SWCNTs and ITO/o-MWCNTs may imply the formation of an electric double layer (dipole layer) at the interface.

In both cases, the large hole injection barrier height of 0.7-0.8eV may not be able to overcome by thermal activation energy effect, kT (where at 25°C, kT ~ 0.025eV). Therefore, an ohmic contact is not expected to form between these acid oxidised CNT layer and TPD. However, this result is not taking into account the geometrical field enhancement effect of CNTs on improving the charge injection, effect which has been reported to play an important role in improving the injection\textsuperscript{134,142}.
Figure 4.8: Schematic interfacial energy diagrams of the ITO/o-SWCNTs/TPD (4a and 4b) and ITO/o-MWCNTs/TPD(4c and 4d) contacts: (a & c) assuming no interfacial vacuum level shifts; (c & d) based on the UPS measurements reported herein.

4.4 Summary

In term of physical properties, the acid oxidation process has quite a different effect on the SWCNTs and MWCNTs where the o-SWCNTs looks shorter while o-MWCNTs remain long and curvy as the oxygen moieties mainly decorated the outer walls of o-MWCNTs while the inner walls remain intact.
Photoelectron spectroscopy analysis showed that the insertion of o-SWCNTs or o-MWCNTs can improve the work function of transparent electrode, ITO. Based on the UPS measurement, the vacuum level of CNT displayed a downward shift of 0.3-0.4eV after deposition TPD (<1nm) indicating that the possibility of dipole formation between CNT/TPD interfaces that encounter the VL shift. The HOMO level of oSWCNTs/TPD 1 and 5nm determined from the UPS spectra are in the similar energy level indicated that equilibrium condition have been achieved in o-SWCNTs/TPD and o-MWCNTs/TPD interface.
CHAPTER 5

Current Injection from o-SWCNTs in TPD/Alq3 based OLED

5.1 Introduction

Much attention has been drawn to the field of OLEDs since Tang and Van Slyke announced their first OLEDs\(^{15}\). Their report is concentrated on a bilayer device in which the hole transport layer (HTL), is TPD, and the electron transport layer (ETL), is Alq3. Alq3 in this case also functions as the emissive layer. Since then, considerable progress has been made to further improve the device efficiency and the stability of the device\(^{99,143}\).

CNTs have recently emerged as versatile material for optoelectronic applications\(^{55,144}\) including OLEDs\(^{50,61}\) and OPVs\(^{51,145}\). This is due to their remarkable properties, including high electrical conductivity, mechanical strength,\(^{61}\) excellent chemical stability\(^{146}\) and high, tuneable work function (4.5-5.1 eV)\(^{47,147}\). Because of these attractive properties and the fact that semiconducting SWCNTs behave as p-type semiconductors\(^{148}\), thin films of SWCNTs have been identified as a possible replacement for ITO as the hole conducting electrode in OLEDs and OPVs\(^{149,150}\). Therefore, understanding the basic transport mechanisms between o-SWCNTs and organic semiconductors is not only of fundamental academic interest, but also provides technical relevance that may help to improve device efficiency.

In this work, we show that the electrical and optical properties of evaporated films of the molecular semiconductor TPD are modified when a low density of o-SWCNTs are present at the ITO surface prior to TPD deposition. c-AFM images of the surface of ITO/o-SWCNTs/TPD show large variations of the current and strong correlation with the topography mapping. This observation is a further indication of the inhomogeneous transport properties of the o-SWCNTs/TPD system.

5.2 Hole-only device

In order to gain information into the hole-injection efficiency, the current-voltage characteristics of unipolar devices, ITO/TPD(150nm)/Al (reference device) and ITO/o-
SWCNT/TPD(150nm)/Al, were measured. For the reference, the barrier to electron injection in low field is prohibitively high as the barrier of Al ($\Phi_{AI} \sim 4.2eV$) and TPD (LUMO$_{TPD} \sim 3eV$) is approximately 1.2eV, so hole injection from the anode is the only contributor to the measured current.

The semilogarithmic current versus voltage (I-V) characteristic of ITO/TPD/Al devices with and without o-SWCNTs at the ITO/TPD interface is shown in Figure 5.1. TPD is an extensively studied hole-transport material and is known to be effectively trap free\textsuperscript{151}. The I-V characteristic of ITO/TPD/Al reference device exhibits a typical diode behavior, with a large barrier to carrier injection under reverse bias. Over the range of applied voltages, 0-5 V, the injected current in the reference device is expected to be hole-only as a consequence of the relatively large energy barrier at the cathode\textsuperscript{152,153}. Looking at the forward bias, one first notices that the steep increase of the current does not begin at 0V but a turn-on voltage of about 1V. This voltage can be identified with the built-in voltage $V_{bi}$ that is necessary to overcome the contact potential difference between the two electrodes\textsuperscript{84}. In this device, the strong dependence of the current on voltage under forward bias $>1V$, is consistent with a moderate barrier to hole-injection in agreement with previous reports\textsuperscript{154,155}. This barrier could partly arise from the presence of charge layers near the electrodes and their effect on the potential distribution in the organic layer\textsuperscript{156}.

I-V characteristics of devices incorporating o-SWCNTs at the ITO/TPD interface are rather different to those without o-SWCNT, especially in reverse bias and low voltage region as the devices exhibit current flow in this voltage range. At the low voltage regime $-2V<V<2V$, the measured current is symmetrical under forward and reverse bias indicating that there is no injection barrier from anode to organic or vice versa. During the forward bias, the current increases exponentially like the reference device at around 2-3V. We believe that in this device architecture, there are two distinct parts that contribute to the I-V characteristic of this device\textsuperscript{(Figure 5.1)}. Part A is defined as a high-current regime characterized by a strong dependence upon the applied voltage analogous to that in devices without o-SWCNTs. Part B, it is a low-current regime that is specific to devices incorporating o-SWCNTs (Figure 5.1). In this case, Part A is mainly contributing to the current for the applied voltage higher than 1V as indicated by the green dotted line (Figure 5.1). So it means that at high voltage regime ($>3V$), the current is the superposition of the contribution from Part A and B (Figure 5.1).
Figure 5.1: I-V characteristic of ITO/TPD/Al hole only device with (black square) and without (red circle) o-SWCNTs in between ITO and TPD layers. Part B and A represent the charge transport characteristic of the regions with and without trap states.

To understand further the injection properties of the device incorporated with o-SWCNT, the I-V characteristics for the reference and the o-SWCNT device in log-log scale are plotted in Figure 5.2. For the reference device, the low current in between 0.1-1 V indicates that the reference device has extremely low leakage current or diffusion limited current. Above the $V_{th}$, the current increases quasi-exponentially over many orders of magnitude in between 1-3 V and then continues to grow with a reduced slope which has been well studied by several groups and is considered to be injection limited.

For the device with o-SWCNTs, the I-V characteristic is quite different. By fitting the Part B to the power law dependence, the exponent of the power law dependence ($V^{m+1}$) under forward bias is $m+1=2.3$, which rules out the presence of filamentary short circuits across the TPD layer as the short circuit current is normally $I \propto V$. Since $m > 1$ the transport regime is best described by trap-charge bulk limited conduction.

Another compelling corroborating evidence for the existence of a high density of trap states throughout the TPD layer is the symmetry of the I-V characteristic at low voltage where $m = 1.8$, in reverse bias (not showing here), and $m = 1.3$ in forward bias (regime B in Figure 5.1).
Figure 5.2: Double logarithmic representation of the I-V characteristic of the hole only devices where the ITO/o-SWCNT/TPD/Al device fits to the power laws $J \sim V^{2.3}$

The surface morphology of ITO/o-SWCNT, ITO/o-SWCNT/TPD and ITO/TPD substrates were measured with AFM (Figure 5.3). Figure 5.3a shows well dispersed, short o-SWCNTs. The cross-sectional height of these features was found to be 5-8nm (Figure 5.3a). It is therefore concluded that they are o-SWCNT bundles rather than individual SWCNTs, since the latter would be expected to have a cross-sectional height of ~2nm. The acid oxidation process has improved the solubility of o-SWCNT and eases the thin film processing. Notably the o-SWCNT coating is discontinuous, such that only a small portion of the underlying ITO substrate is covered by o-SWCNTs as shown in Figure 5.3a and b where the polycrystalline ITO substrate is clearly visible in the regions not covered with o-SWCNTs.

While the topography of ITO/TPD (Figure 5.3c), characterized by ~200nm sized grains, exhibits an amorphous surface that is quite different compared to ITO/o-SWCNT/TPD (Figure 5.3e) and some differences emerge when the phase images are compared (Figure 5.3d and f). The AFM images for ITO/TPD film show a dense, small and ordered surface texture (Figure 5.3c) and the phase image of ITO/TPD (Figure 5.3d) display essentially ITO’s polycrystalline structures. Conversely, the AFM images for ITO/o-SWCNTs/TPD present variations of stiffness/phase that are strongly correlated to the topographical features (Figure 5.3e and f). The surfaces also consist of many randomly oriented crystals.
with fairly wide gaps about a few tenths of a nanometer in between the crystal (Figure 5.3f). Quantitative comparison of these two films in terms of surface roughness, reveals that the TPD film deposited on the ITO/o-SWCNT substrate (2-3nm) is rougher than on ITO alone (~1nm). The roughness of the TPD overlayer on ITO/o-SWCNTs is also significantly lower than that of the ITO/o-SWCNT substrate: ~5nm. Evidently the TPD layer is modified by the presence of underlying o-SWCNTs, which may correlate with changes observed in the transport properties when low voltages are applied to the devices. The increase in roughness of TPD is consistent with a difference in the structure of the TPD film when deposited onto ITO/o-SWCNT as compared to that deposited onto virgin ITO glass.

The change of morphology on small scale together with the slightly larger contrast in the phase images for ITO/o-SWCNTs/TPD indicate that the morphology of the TPD layer is modified by the presence of underlying o-SWCNTs, which may correlate with changes observed in the transport properties when low voltages are applied to the devices. The increase in roughness of TPD is consistent with a difference in the structure of the TPD film when deposited onto ITO/o-SWCNT as compared to that deposited onto virgin ITO glass.
Figure 5.3: AFM topographic and phase images of ITO/α-SWCNTs (a, b), ITO/TPD(c, d) and ITO/α-SWCNTs/TPD(e, f). The inset in (a) shows the cross-sectional analysis for the height of α-SWCNTs.
Conductive AFM (c-AFM) is a current sensing technique for characterizing conductivity variations with nanometer resolution. It allows current measurements in the range of hundreds of fA to nearly a μA. c-AFM is conventionally performed measuring simultaneously the topography and current flowing between the AFM tip and the sample. Figure 5.4 shows the topography and current distribution of ITO/o-SWCNT/TPD through the c-AFM measurement system conducted in contact mode with the tip bias at 0 and -11V. At V = 0, the sample shows a zero current throughout the sample surface. However, the current mapping for the sample under -11V bias on the tip shows very different features. Most notably, there are very significant correlations between the spatial variations in conductivity observed in the c-AFM image (Figure 5.4d) and the topography (Figure 5.4c): The highest topographic features are the least conductive, whilst the surrounding flatter regions are much more conductive.

The spatial variations in current cannot be attributed to variations in film thickness since the variation in TPD film thickness is < 12%. These variations of current might be correlated to the presence of the two different regimes with different TPD characteristics as observed in the I-V devices characteristics as discussed above. We believe the highest topographic features are referring to the ITO/o-SWCNT/TPD Type II while the flatter region is the
ITO/TPD Type I. One has to realize that the -11V bias on the c-AFM tip is equivalent to the 11V of forward bias in the device. In the earlier discussion, we explained that the current for V>3V is attributed to the current from Part A and B. In this case, we believe that the higher topographic with less conductive region promote the I-V characteristic similar to Part B. Meanwhile the flatter region has the current injection and transport properties similar to region contribute to Part A (Figure 5.1).

![Graph of UV/VIS absorption spectrum](image)

**Figure 5.5: UV/VIS absorption spectrum of o-SWCNTs (blue), TPD (black) and o-SWCNTs/TPD (red) on top of glass/ITO substrate.**

Furthermore, the difference in the structure of the TPD layer in the presence of o-SWCNTs is indicated by the observation of significant differences in the UV/VIS optical absorption spectra of the TPD films deposited on ITO and ITO/o-SWCNTs (Figure 5.5). The absorption spectrum of TPD on virgin ITO displays peaks at 315 and 354nm which are assigned to $\pi\rightarrow\pi_{\text{phenyl}}$ and $\pi\rightarrow\pi_{\text{peripheral}}$ transitions. These bands are not resolved in the spectrum of a o-SWCNT/TPD bi-layer which is broader and featureless and the superposition of the TPD and o-SWCNT spectra does not match with the spectrum of o-SWCNT/TPD. A broad featureless absorption spectrum is characteristic of a semiconductor having a high density of trap states in the band gap, which, in the absence of extrinsic impurities, can result from structural defects occuring on grain boundaries in polycrystalline layers.
Raman spectroscopy is a sensitive technique to verify the existence of o-SWCNTs underneath the TPD layer. The Raman spectroscopy coupled with polarized optical microscopy is used in this study. An ITO substrate is partly covered with o-SWCNTs before a 50nm thick TPD deposited on top of the substrate via thermal evaporation (Figure 5.6). The sample was monitored for 48hours after the TPD deposition in order to verify the correlation between crystalline TPD and the existence of o-SWCNTs.

**Figure 5.6: Schematic diagram for the ITO/o-SWCNTs/TPD sample prepared for Raman spectroscopy measurement coupled with polarized optical microscope**

Figure 5.7 shows the polarized images of TPD crystallites observed 24hours after the TPD deposition. The TPD crystals can only found in the edge of the o-SWCNTs patch. The Raman spectra for the TPD crystals, the o-SWCNTs and TPD are shown in Figure 5.8. For the TPD and o-SWCNTs, both materials show a strong signal in around 1590cm\(^{-1}\) which is associated to the stretch of phenyl ring associated with C—N stretch\(^{162}\). For TPD, the background noise is higher due to the amorphous nature and strong fluorescence of the TPD. The main difference between the o-SWCNTs and TPD are that the o-SWCNTs have a peak at around 2700cm\(^{-1}\) which corresponds to a second order Raman peak of CNT (G' band). TPD has a group of broad peaks at around 1300cm\(^{-1}\) which is related to C—N stretch with phenyl ring, but this peak is not observed in o-SWCNTs. The Raman spectra for the TPD crystal show a superposition of the Raman spectra for TPD and o-SWCNTs. This result may imply that TPD crystal growth is assisted by the o-SWCNTs underneath the TPD layer due to the edge effect created from the eveness of o-SWCNTs distribution.
Figure 5.7: Optical images of ITO/o-SWCNTs/TPD and ITO/TPD surfaces with TPD crystals observed at the centre and edge of o-SWCNTs pad. The images are taken under (a) unpolarised and (b, c) polarised light, respectively.

Figure 5.8: Left panel: Raman spectra of o-SWCNTs, TPD and TPD crystal found on o-SWCNTs pad. Right panel: Raman spectra of the TPD crystal in between 1000-1500cm⁻¹ with the optical images of the crystal taken under polarised light (red arrow).
By observing electrical properties of the hole only device, we propose a model to explain the different charge transport properties that we found in reference and o-SWCNTs devices as shown in Figure 5.1. Figure 5.9(top) proposes a schematic diagram for the reference device where the TPD deposited on top of ITO (TPD Type I) has mainly contributed to the current injection of Part A(Figure 5.1). For the device with o-SWCNTs, apart from the existing TPD Type I in the device, there is another region TPD Type II (Figure 5.9 bottom). This Type II region refers to the TPD deposited on top of o-SWCNTs which dominated with current injection and transport characteristic of Part B.

Reference Device:

\[
\text{ITO/TPD/Al} \quad \text{Al} \\
\text{TPD} \\
\text{ITO} \\
\text{ITO/o-SWCNT/TPD/Al} \quad \text{Al} \\
\text{TPD Type I} \\
\text{TPD Type II} \\
\text{o-SWCNTs}
\]

Figure 5.9: (Top) Schematic diagram of proposed model for reference device consisted of TPD Type I. (Bottom) Hole only device architecture with o-SWCNTs as the interlayer where TPD Type I and II co-existed in the device.

The energy levels on the hole only device with o-SWCNTs as the interlayer are given in Figure 5.10. We illustrate trap states existing throughout the TPD bulk material since there is no barrier observed based on the I-V characteristic of this device. One of the possible explanations for the existence of the trap states is due to the o-SWCNTs.

In this device architecture, the o-SWCNTs are confined to the ITO/TPD interface and so we postulate that these trap states result from a difference in the structure of the TPD induced by the presence of the o-SWCNTs. It is known that when TPD is deposited onto ITO glass it adopts a glassy state, as is well documented. Conversely, in the presence of o-SWCNTs it is possible that the TPD is partially crystallized as a result of seeding by the graphitic wall of the o-SWCNTs. Indeed, hydrogen bonding interactions between the first layer of TPD and the oxygen containing moieties (e.g. COOH and OH) at defect sites on the o-SWCNTs.
may also play a role in the seeding process\textsuperscript{163}. Seeding of crystallization by SWCNTs has previously been reported by Liu \textit{et al.}, who deposited sexithiophene and pentacene\textsuperscript{164} onto SWCNTs using the gradient sublimation approach. SWCNTs are also known to seed the crystallization of polymers\textsuperscript{165}. In polycrystalline materials trap states exist at the interface between crystallites and can form pathways for charge transport within the band gap\textsuperscript{164}. The results presented herein suggest that the presence of the discontinuous o-SWCNT interlayer dramatically alters the TPD layer structure, inducing the formation of a high density of trap states throughout the TPD layer (Figure 5.10).

Based on the changes in I-V characteristics, surface morphology, current mapping using c-AFM and the optical absorption measurement, certainly there are two current regimes that have been observed in the device result from the superposition of the contribution from the CNT-covered regions (TPD Type II), responsible for the regime B, and the uncovered region (TPD Type I) which is responsible for regime A as proposed in the Figure 5.1.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure5.10.png}
\caption{Schematic diagram proposed for the energy level of the contacts and trap states (O) and filled trap state (+) existing throughout the TPD layer}
\end{figure}

\section{5.3 TPD/Alq\textsubscript{3} based SMOLED with o-SWCNTs}

Following the previous discussion about the effect of inserting o-SWCNT in hole-only device, it is interesting to study the effect of o-SWCNTs in TPD/Alq\textsubscript{3} based OLED devices. Both devices are driven by sweeping the voltage from 0 to 10 V. The first measurement of the continuous current-voltage ($I$-$V$) [luminance-voltage ($L$-$V$)] characteristics for the
freshly prepared reference device is shown by filled black square [Figure 5.11(top)]. The current density and the luminance of the reference device for the first scan or so-called “conditioning” scan, and the subsequent measurements of the same device are almost the identical where the light output is linearly proportional to the input current in the current range from $10^2$ to $10^3$ mA/cm$^2$. The device starts to turn-on at around 2.5V and produces the light output of $10^5$ cd/m$^2$ at around 5.9V with a current density $3.0$ mA/cm$^2$. The device can be driven to produce high brightness ($\sim 4000$ cd/m$^2$) at around 10V.

For the OLED device consist of o-SWCNTs as the interlayer in between ITO and TPD, the I-V characteristic of this device across the voltage from 0 to 10V is shown in Figure 5.11 (bottom). During the first, “conditioning” scan for this device, the I-V characteristic is identical to the reference device with the turn-on voltage $\sim 2.5V$ and produces a similar light output, $10^5$ cd/m$^2$ at 5.9V with a higher current density $3.7$ mA/cm$^2$. In the subsequent measurements, the higher current was measured at the lower voltage (0-2.5V), where similar characteristic is observed in the hole-only device (with o-SWCNTs) as discussed in the previous section. The high current level observed at low voltages in the second and third sweep may indicate that the existence traps levels in TPD were filled during the conditioning scan. Therefore, the higher current was observed after the first swept.

![Figure 5.11a: Current density and luminance versus voltage characteristic for OLEDs with o-SWCNTs interlayer under multiple voltage sweeps from 0 to 10V](image-url)
To further study the effect of o-SWCNTs on OLEDs, the current density, luminance and luminance efficiency for both devices at 2, 6 and 9V respectively are plotted in Figure 5.12. For the reference device, the current density, luminance and efficiency are rather unchanged and stable throughout the measurements. However for OLED with o-SWCNTs interlayer, for the device which operates at 2V showed a current density increase of three order of magnitude in the second sweep compared to the conditioning scan. At the operating voltage of 9V, the o-SWCNTs device shows a decrease in current density along the three current-voltage sweep process which may indicate a reliability and stability issue in this device. For all the operating voltages, the current in OLED with o-SWCNTs is higher than reference device, but the light output intensity is similar for both devices.

In the previous section, we mentioned that o-SWCNTs may induced a lot of traps filled with hole carriers throughout the TPD layer. The existence of the high density of holes in the TPD layer may induce higher electric field at the interface between TPD and Alq3 which improves the injection of electrons from cathode to the ETL which then recombine with the holes. Therefore, the device consisting of o-SWCNTs interlayers show a slightly higher luminance intensity compared to the reference device at 6 and 9V (Figure 5.12). However the large quantity of holes injected from anode are flowing out from the device.
with recombine with the electron due to imbalance charge between hole and electron. Therefore a lot of current pass through the device without being exposed to any recombination process to produce light. As a result the reference device shows better efficiency.

Figure 5.13 shows the luminance efficiency of both devices with the operating voltage from 2 to 10V. The reference device is likely to be more efficient than the device with o-SWCNTs even though the injection current density is higher in device with o-SWCNTs. The high current density and low luminance efficiency for the device with o-SWCNTs should be connected to the evolution of TPD from Type I to Type II with the existence of o-SWCNTs, where the incurred high density of traps level via \( \pi \)-stacking of TPD on the wall of o-SWCNTs. As a consequence an excess of current flows without any radiative recombination to produce more light.
Figure 5.12: Current density, luminance and luminance efficiency of OLEDs with and without o-SWCNTs interlayer at 2, 6 and 9 V
5.4 Effect of acid oxidised carbon nanotubes in polymer light emitting diodes (PLEDs)

In this section, the discussion is mainly focused on the effect of using acid oxidised carbon nanotube (o-SWCNTs and o-MWCNTs) as the interlayer in between the ITO anode, the polymer based electroluminescence layer(EL) and hole transport layer(HTL).

Many questions still need to be answered regarding the interaction between the CNTs film and the material deposited on top of it (top material). In the case of OLEDs, this top material could be referring to the hole-transport/electron-blocking (EBL) or EL material. In addition to this, the effects of photoluminescence, PL, quenching is another important parameter in examine the effect of CNT interlayer toward the device properties, particularly considering CNTs as efficient electron acceptors.
In the first part of this chapter, detailed discussion has been focused on small molecule based OLEDs devices. Unlike the case of small molecules deposited by thermal evaporation, conjugated polymers are spin coated on the CNT layer from an organic solution. The processes governing the adsorption of spin coated polymers are expected to be less affected by seeding effect.

5.4.1 Single layer PLEDs

The current-density-luminance-voltage (I-L-V) and external quantum efficiency (EQE) of the single layer PLED devices fabricated on ITO, ITO/o-SWCNTs and ITO/o-MWCNTs are compared in Figure 5.14. In term of current-density-luminance-voltage (I-L-V) characteristics shown in Figure 5.14(a & b), the reference device showed the higher current injection at lower driving voltage where the maximum current density of ~350 mA/cm² is achieved at around 7.5 V. While for device with o-SWCNTs or o-MWCNTs interlayer, the similar current density only being achieved at higher voltage at around 9-10 V. The light output for these devices are also lower compare to the reference device. Meanwhile, the reference device also shows the highest EQE compare to the devices consist of CNTs, with EQE close to 0.009% at around 8 V.
5.4.2 Double-layers PLEDs

A significant change was observed in the device performances when a thin layer of TFB was inserted in between the anode and F8BT layer. The performance of the devices is obviously better than the single layer devices especially for the devices with CNT interlayers. In term of light output, all the double layers devices achieved similar luminance upto 9500cd/m² at around 13V with the current density at around 700 to 1000mA/cm² (Figure 5.2). By increasing the operating voltage higher than 13V, the I-L-V characteristics showed that the devices were over stressing to their limit with the performance drop after 14V of driving voltage. Comparing the reference and PLED with oxidised CNTs interlayers, similar current density were observed for these three different devices but a slightly higher luminance where observed on the devices with CNTs when the operating voltage is in between 8 to 13V.
The EQE for the heterostructure PLEDs also showed the significant improvement compared to single layer PLEDs in the previous section. For the devices consist of o-SWCNTs and o-MWCNTs interlayers, the EQE increase by a factor of ~50 and ~100, respectively where the optimum EQE that could be achieved by using acid oxidised CNTs are around 0.1 to 0.2 at 13-14V (Figure 5.14). With the insertion of the TFB layer (~70nm), the total thicknesses of the devices increase up to 40%. Therefore, it is not surprising to see the optimum EQE occurred at higher voltage region (~13-14V).

To ensure the device characteristics were representative, all the devices structure mentioned in section 5.4.1 and 5.4.2 were repeated and tested three times. The EQE and $V_{\text{on-off}}$ results were summarised in Table 5.1.
Table 5.1: Single and double layer PLEDs performances with and without using acid oxidised CNTs as the interlayer

<table>
<thead>
<tr>
<th>Device structure</th>
<th>EQE (%)</th>
<th>$I_{\text{max}}$ (cd/m²)</th>
<th>$V_{\text{on}}$ (V)</th>
<th>$\eta_{\text{eff}}$ (Cd/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IT0/F8BT/Ca/Al</td>
<td>0.011 (±0.0005)</td>
<td>73 (±10)</td>
<td>3.3 (±0.3)</td>
<td>0.028 (±0.001)</td>
</tr>
<tr>
<td>ITO/o-SWCNTs/F8BT/Ca/Al</td>
<td>0.004 (±0.0005)</td>
<td>24 (±6)</td>
<td>4.8 (±0.6)</td>
<td>0.009 (±0.001)</td>
</tr>
<tr>
<td>ITO/o-MWCNTs/F8BT/Ca/Al</td>
<td>0.003 (±0.001)</td>
<td>26 (±9)</td>
<td>4.1 (±0.4)</td>
<td>0.01 (±0.001)</td>
</tr>
<tr>
<td>ITO/TFB/F8BT/Ca/Al</td>
<td>0.257 (±0.005)</td>
<td>6940 (±620)</td>
<td>6.1 (±0.4)</td>
<td>0.8 (±0.1)</td>
</tr>
<tr>
<td>ITO/o-SWCNTs/TFB/F8BT/Ca/Al</td>
<td>0.18 (±0.01)</td>
<td>6021 (±350)</td>
<td>5.6 (±0.4)</td>
<td>0.56 (±0.04)</td>
</tr>
<tr>
<td>ITO/o-MWCNTs/TFB/F8BT/Ca/Al</td>
<td>0.28 (±0.01)</td>
<td>8792 (±1080)</td>
<td>5.6 (±0.2)</td>
<td>0.79 (±0.01)</td>
</tr>
</tbody>
</table>

5.4.3 Photoluminescence efficiency and exciton lifetime study

The interaction between the acid oxidised carbon and the emissive layer F8BT were further studied by measuring the photoluminescence quantum efficiency and the exciton lifetime using time correlated single photon counting (TCSPC). In this study, we carried out a direct investigation of the influence of the substrate on the PL quantum efficiency ($\Phi$) of F8BT either time resolved and in steady state as summarized in Figure 5.16. We observe quenching of the PL for F8BT deposited on ITO substrate ($\Phi_{\text{PL_{ITO}}}=0.25$). The CNTs, when deposited on ITO, quench further the PL efficiency.
Figure 5.16: PL efficiency ($\Phi_{pl}$), exciton lifetime and the non-radiative decay rate of the exciton measured on F8BT thin solid film deposited on ITO, ITO/o-SWCNTs and ITO/o-MWCNTs substrate.

When these data are combined with the measure of the radiative singlet lifetime, $\tau_0$, by time-resolved PL the non-radiative decay rate ($k_{nr}$) is extrapolated (Figure 5.16 bottom) and the higher value of $k_{nr}$ for CNTs testify the presence of a non radiative channel in this system.

$$
\begin{align*}
  k_r &= \frac{1}{\tau_r} = \frac{\Phi}{\tau_0} \\
  k_{nr} &= \frac{1-\Phi}{\tau_0}
\end{align*}
$$

5.4.4 Discussion

Unlike the case of small molecules deposited by thermal evaporation, conjugated polymers are spin coated on the CNT layer from an organic solution. Since the polymeric material that use in this study is an amorphous polymer, therefore the processes governing the adsorption of spin coated polymers is expected to be less affected by the seeding effects which were discussed in Section 5.1-5.3.
In section 5.4.1 and 5.4.2, the results clearly showed that the heterostructure PLEDs exhibited higher performance than the single layer PLEDs. In most of cases, holes are considerably more mobile and have higher mobility in polymer based semiconductor materials such as poly(phenylene vinylene). However, Chua et al. had shown that electron mobility in polyfluorene based materials is higher than the hole mobility based on the field effect transistor measurements. In our case, F8BT is an ambipolar polymer where the typical electron and hole mobilities are in between $10^{-4}$ to $10^{-3}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. However based on the band schematic diagrams in Figure 5.17, the deep HOMO level of F8BT at around 5.9eV results in a high hole injection barrier ($\sim 0.9\text{eV}$). Conversely, there is almost no barrier for the electron to inject into LUMO of F8BT since the work function of Ca is pinning the LUMO of F8BT. Since the electroluminescence process in PLEDs involve with electron-hole recombination and exciton formation, it is necessary that the electron and hole injected into F8BT can be recombine effectively in a confinement zone which is far from both side of the electrodes. The low luminance and EQE couple with high current density shown in single layer PLEDs clearly indicated that most of the charge carriers injected into the device are not captured and do not recombine to generate light. There is a high possibility that the recombination zone is closer to the anode/F8BT interface simply because the hole injection barrier is higher than the electron barrier.

Another important observation is that the oxidised CNTs act as a quencher which further reduces the light emission from the PLEDs. The PL measurement results also support this argument where the PL efficiency of F8BT was reduced from 40% on ITO to 35% or 33% for ITO/o-SWCNTs and ITO/o-MWCNTs substrates. By observing the lower PL efficiency of F8BT deposited on ITO/o-SWCNTs and ITO/o-MWCNTs coupling with high non radiative decay rate of the exciton, it is reasonably to explain that the low luminance and EQE of single layer PLEDs are mainly due to the high quenching of exciton by acid oxidised CNTs. In fact this is not a surprising results as the CNT have been widely used in fluorescence-based bioassay due to their ability to quench organic dyes or quantum dots. In the early 2001, Fournet et al. had also shown that inserting CNT in the poly(m-phenylene-vinylene-co-2,5-dioctyloxy-p-phenylene-vinylene) (PmPV) based OLED reduces the PL intensity of the EL layer but the CNT also help to improve the carrier transport and subsequently the EL intensity of the OLEDs. Most important is to understand the effect of CNT on organic materials and subsequently to make some modifications in order to improve the device performance.
The use of two or multilayers structure to control the injection rate of electrons and holes by introducing barrier charge transport at the heterojunction between the semiconductors has been well established in SMOLEDs and PLEDs. The multilayer structure is also an efficient way to improve the device performance by stacking interlayers with proper energetics to form a stepped electronic energy profile. Multilayer deposition, a sublimation process which is commonly used in SMOLED, is difficult to achieve by solution processing because of the issue of intermixing between the polymer layers during solution-coating of light emitting polymer (LEP) on top of the polymer interlayer which are complicating the charge transport, emission and subsequently lowering the emission efficiency. However, the fabrication of a ‘distributed heterojunction’ structure by de-mixing two polymers was demonstrated by Mortearini as an alternative solution to improve PLEDs efficiency.

In this study, TFB used as the interlayer in between anode and F8BT emission layer in order to confine the recombination zone such that it is away from the anode contact. In this case, TFB is a particularly suitable material as the HOMO level of TFB is around 5.4eV, which can reduce the hole injection barrier between the anode and HOMO\textsubscript{F8BT} (Figure 5.17: Band diagram of single layer and double layers PLEDs based on TFB and F8BT).
5.17). Furthermore, the LUMO level of TFB at around 2.5eV can also function as electron blocking layer since the LUMO_{F8BT} is around 3.3eV. The interlayer insertion has substantially improved the devices performance especially for the devices fabricated on ITO/o-SWCNTs and ITO/o-MWCNTs substrates because the quenching effect of CNT on excitons have been reduced or diminished as the recombination zone is moving away from the CNTs/F8BT interface to TFB/F8BT interface. In term of device performance, the current injection and luminance versus voltage showed similar results for the heterojunction PLEDs fabricated on ITO, ITO/o-SWCNTs and ITO/o-MWCNTs. Unlike the case of small molecules deposited by thermal evaporation, conjugated polymers are spin coated on the CNT layer from an organic solution. Since the polymeric material that use in this study is an amorphous polymer (within the processing temperature), therefore the processes governing the adsorption of spin coated polymers is expected to be less affected by seeding effect.

5.5 Summary

The changes in I-V characteristics for the hole only device indicates that the insertion of o-SWCNTs as an interlayer between the ITO and TPD has modified the TPD properties. As a result, a high density of trap levels has been introduced throughout the TPD layer (TPD Type II). This may be due to the \( \pi-\pi \) stacking of TPD molecules on the o-SWCNTs' wall. This argument is further supported by the changes of morphology observed through AFM and the high contrast of current mapping in o-SWCNTs device via c-AFM measurement. In addition, the broadening and featureless spectrum for modified TPD is further support for our interpretations. As a consequence, the high density of trap in TPD leading to a high current density of OLED with lower luminance in the o-SWCNTs OLED device due to the imbalance of charge injection from both sides of the electrodes. For the PLEDs devices, we show that thin layers of spin coated CNT on ITO improve significantly the only-ITO based devices provided a careful control of the radiative efficiency quenching arising from the exciton dissociation that occurs at the CNT/ emissive polymer interface. Such a control is obtained by the insertion of a hole-transport interlayer which also acts as electron-blocking layer (EBL) between the CNT and the polymer shifting the recombination zone away from the anode.
CHAPTER 6

Fluoropolymer Interlayers for Polymer Light Emitting Diodes

Polyfluorene (PF) is one of the widely used blue emitting polymers for PLEDs. However, the stability, lifetime and colour purity of these compounds in PLED applications is still a major issue. When the device is under operation, blue diodes made from PF material tend to degrade and produce undesirable low energy bands (such as green band or g-band). The spectral location of the g-band is usually found peaking at about 535nm. However an additional spectral feature has often been found, especially in electroluminescence, at shorter wavelength (i.e., between 475 and 510nm). Although such emission occurs very closely to the excimer emission peak of solid fluorenones films (520nm), it has been identified as not related to fluorenones, but rather to the formation of insoluble (cross-linked) species as a consequence of an electrochemical reaction induced by electron injection. Both the emission at 535nm and the one at higher energy have been found to be correlated with the presence of calcium electrodes that catalyze oxidative processes. These studies also suggest that such green emission originates mainly from the region in the vicinity of the cathode.

In this Chapter, a thin Teflon (PTFE) layer is used as the interlayer in between PEDOT:PSS and polyfluorene. Optical and electrical measurements of the device containing a PTFE interlayer show a better performance in term of quantum efficiency and long term stability.

6.1 Surface Morphology Study of PEDOT:PSS/PTFE Interlayer

The morphology of the $500 \times 500\text{nm}^2$ of PEDOT:PSS and PEDOT:PSS/PTFE (thermally evaporated) samples within the thicknesses of 1, 3 and 15nm are shown as measured by AFM in Figure 6.1. The morphology of PEDOT:PSS consists of a smooth topography with 200-300nm-sized domains that are ascribed to the lateral phase separation of PEDOT and PSS. The surface of teflon deposited on PEDOT:PSS is not perfectly flat but somewhat rough. The PTFE covers continuously the PEDOT:PSS substrate for the thinnest PTFE film in this study, 1nm, forming islands with a lateral size of about 10–30nm and height of approximately 2nm. For thicker PTFE films, such as 3nm thick films, islands of PTFE start...
to grow and coalescence of PTFE islands occurs, forming elongated structures with lateral size comparable with the diameter of the islands observed for the 1nm-thick film. When the PTFE thickness is further increased, the lateral size of the features increases progressively, reaching 50nm for 15nm-thick films, showing features similar to the ones of ITO/PTFE 15nm in a previous publication\textsuperscript{117}. The root-mean-square roughness, $R_{\text{rms}}$, of the films is 1.36±0.02nm for PEDOT:PSS and progressively increases as a function of the deposited PTFE thickness until it reaches a constant value of ~3.5nm for 12-15nm thick PTFE films (Figure 6.1).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\linewidth]{figure6.1}
\caption{Left: AFM height images of ITO/PEDOT:PSS and ITO/PEDOT:PSS/PTFE(xnm) films where x=1,3 and 15nm; the vertical color scale bar corresponds to 9, 10, 13 and 17nm respectively. Right: RMS roughness of the samples as a function of the PTFE thickness measured over 4 images representing 500x500nm$^2$ areas.}
\end{figure}

\section{6.2 Work function study of PEDOT:PSS/PTFE using Kelvin Probe}

It is interesting to study the effect of the PTFE interlayer and its thickness on the work function of the anode, in this case PTFE covered ITO/PEDOT:PSS. Figure 6.2 shows the effective work function of the anode, as a function of the PTFE thickness ranging from 0 to 15nm determined by Kelvin probe measurement. The work function for PEDOT:PSS was found to be 4.95±0.04eV, in agreement with earlier reports\textsuperscript{176}. When PTFE is deposited on top of PEDOT:PSS the work function increases with thickness and reaches a maximum of 5.05±0.02eV for PEDOT:PSS/PTFE(7nm). For thicker PTFE films the work function decreases towards values comparable with that of PEDOT:PSS.
Figure 6.2: Work Function measured with Kelvin Probe of PEDOT:PSS/PTFE as a function of the PTFE thicknesses. The error bars are the standard deviation across 3 samples fabricated in different evaporation badges. The measurements for each sample were repeated in order to monitor the reproducibility of the measurements.

Figure 6.3 illustrates the proposed mechanism for the changes in work function of the anode with the increase in Teflon thicknesses. At the beginning of the 1nm Teflon evaporation, the Teflon carbon back bone is believed to stay closer to the PSS’ surface while fluorine atoms stay away from PSS’ since fluorine is relatively more electronegative when compared to carbon (Figure 6.3). As the thickness of Teflon increases, the size of the Teflon island increases and covers more of the PEDOT:PSS surface (Figure 6.3). At this stage, a highly F rich negatively charged surface is formed and contributes to the high work function measured with KP. As the thickness of the Teflon increase further, the work function is reduced again, due to the fact that the fluorinated surface island screening effect disappears as a complete thin film of Teflon on PEDOT:PSS surface is formed. For that reason, the 12nm Teflon covered sample shows a work function comparable with the one of PEDOT:PSS. A continuous increase of the thickness of PTFE will further decrease the work function of the sample as the high resistance bulk properties of Teflon will get more pronounced.
6.3 Current-Luminance-Voltage Characteristics of PLEDs with a Fluoropolymer Interlayer

The structure of the ITO/PEDOT:PSS/PTFE/PFO/Ca/Al device, and a representative I-L-V characteristic, are shown in Figure 6.4. PEDOT:PSS is a highly conductive synthetic metal with a work function of \( \sim 5eV \). Bulk PTFE is a large bandgap material \( (E_{gap}=9.7eV) \) with HOMO and LUMO level of \( \sim 10.6eV \) and \( 0.9eV \), respectively. However, thin films of PTFE may not exhibit the same properties as the bulk. Without the PTFE interlayer, the mismatch between the PEDOT:PSS and the HOMO level of the blue emitting polymer, PFO, is \( \sim 0.9eV \). Therefore, it is expected that the hole current for this device is injection limited due to the presence of a large hole injection barrier between the anode and HOMO of PFO. Meanwhile, the contact between PFO and calcium is ohmic with an electron injection barrier of \( \sim 0.1eV \), calculated from the work function of calcium \( (\phi_{Ca}=2.8eV) \) and the LUMO level of PFO \( (LUMO_{PFO}=2.9eV) \).

In term of I-L-V characteristics, all the devices show similar trends. We can distinguish basically three regimes that represent three different states during the operation of the devices. The first regime (1) is the low voltage regime where the hole current is negligible and the current is carried by electrons; the current is in this case is almost linearly
proportional to the applied voltage \((J-V, \alpha=1.1)\). The absence of light output also indicates that the current in this regime is unipolar\(^{177}\). In the second regime (2), which we refer to as the turn-on regime, the device starts to turn-on at around \(5 \sim 5.5\) V and a sudden transition of the current density, increasing sharply by several orders of magnitude, is observed. In this regime, output light emitted from the device is detected. For the third regime (3), the device is in the operational regime and stays in this on-state.

By analyzing the I-L-V characteristics, we found that all the devices in this study show similar voltage dependence. A space-charge-limited current model with a field-dependent mobility\(^{178}\) can be invoked to describe the transport, which after switching, is bulk limited\(^{177}\) for the devices with PTFE layers of thickness up to 10nm. Above these values, the model fails to describe the devices' characteristics.

![Figure 6.4](image)

**Figure 6.4:** (Left) Energy-level diagram for isolated materials of the OLED. The HOMO and LUMO of PFO, PTFE and the work function of the electrodes are shown. The chemical structures of the polymeric materials are also shown. (Right) Representative current-luminescence vs. voltage characteristics of a device incorporating a 7nm PTFE interlayer. Three transport regimes are distinguished in the device characteristic. (Inset) External quantum efficiency as a function of the voltage bias.

The initial current detected at low voltage (Regime 1) is dominated by the electron current injected from the calcium to PFO since there is an ohmic contact between the Ca and PFO (Figure 6.4). Similar characteristics have been reported and discussed in a paper by Woundenbergh et al.\(^{177}\) where different anode and cathode materials were used to make electron and hole-only devices; it was confirmed that electrons are responsible the major part of the current in this regime. Therefore, in this regime, electron serves as the majority carrier in our devices. The accumulation of electrons at the PEDOT:PSS/polyfluorene
interface causes an increased field for hole injection enhancement. Therefore, performance of the PLEDs based on polyfluorene derivative is higher for double carrier device compared to single carrier (hole-only) device has been reported by Murata et al. in year 2001\textsuperscript{179}.

In the regime 2, the large amount of electrons injected from the cathode creates a strong accumulation of electrons at the interface between PFO and the hole injection layer and therefore forms a space-charged layer that could assist the hole injection and reduce the turn-on voltage. This statement has been confirmed in a study on the same system by analyzing the I-V characteristic of the devices and studying the charge accumulation at the interface by impedance spectroscopy measurement\textsuperscript{177}. After the device turn-on, high mobility of holes soon balances the amount of electrons and then holes become the majority carriers as can be deduced from the sharp increase in the EQE and the subsequent decrease (inset in the right panel of Figure 6.4). Charge transport in PFO is hole dominated as the high hole mobility values measured by time-of-flight measurements attest\textsuperscript{180}.

In regime 3 the device is operating in a more stable manner: the changes of both the current density and the luminance intensity are less pronounced and the device is fully turned-on. In this state, hole injection is reported as space charge limited current observed by Woundenbergh\textsuperscript{181} using transient electroluminescence measurements. For the operating voltage around 6V in regime 3, the device operation benefits from an improved balance of the hole and electron populations\textsuperscript{182}. Therefore, the EQE stays at around 1% in 6 and 7V bias. However, when the bias voltage is further increased, the EQE decreases continuously, which could reflect a poor charge balance (as the amount of holes exceeds the amount of electrons). Another possible reason for this drop in EQE is the current-induced radiative emission quenching\textsuperscript{181}.

Comparing the devices with and without a PTFE interlayer, the turn-on voltages ($V_{on}$) do not show a significant change with the PTFE thicknesses in the range 0-10nm. However, the $V_{on}$ is increased by 0.2-0.3V when the PTFE thicknesses is larger than 10nm. We believe this is mainly due to the high resistance of PTFE that requires a higher applied electric field to overcome the barrier for the carriers to tunnel through.

The effect of the PTFE interlayer thickness on the overall device performance is analyzed in term of EQE, current density ($J$), luminance intensity ($L$) and the PL quantum efficiency ($PLQE$) as shown in Figure 6.5. To study the charge balance of the devices, we compare the EQE of the devices at the same current density (Figure 6.5a). Here, we selected $J=\text{1 mA/cm}^2$ (for which the device has just turned-on) and $J=\text{10 mA/cm}^2$. At 1 mA/cm$^2$ the devices work efficiently, but the light output is quite low. For the devices operating at $J=\text{10 mA/cm}^2$, the
luminance is much higher and the devices are more stable. We observe that for both current density regimes, the EQE presents analogous trends: the EQE increases with the increase of PTFE thickness from 3 to 7nm. In the case of \(J=1\, \text{mA/cm}^2\), there is an enhancement by a factor 1.5 (from \(-0.8\%\) to \(-1.2\%)\), while for higher \(J\) the efficiency is approximately doubled (from \(-0.4\%\) to \(-0.8\%)\) by inserting the PTFE interlayer.

![Figure 6.5: a) External Quantum Efficiency as measured for current density \(J=1\, \text{mA/cm}^2\) (squares) and \(10\, \text{mA/cm}^2\) (circles); b) Current Density below (\(V_{\text{bias}}=3V\)) and above (\(V_{\text{bias}}=3V\)) the turn-on voltage; c) Luminance as measured at 6V, d) Values of the photoluminescence quantum efficiency of PFO when deposited on ITO/PEDOT:PSS, ITO/PEDOT:PSS/PTFE and spectrosil substrate). Open squares represent the data obtained exciting the PFO from the ITO/PEDOT:PSS/PTFE side (backward, BW) while the circles represent the data in the case the PFO is excited directly.](image)

The devices incorporating a PTFE interlayer thicker than 7nm display a progressive reduction of the EQE with PTFE thickness. The EQE is lowest for the thickest film (15nm): \(-0.35\%\) and \(-0.15\%\) for \(J=1\, \text{mA/cm}^2\) and \(10\, \text{mA/cm}^2\) respectively, which corresponds to a reduction of a factor \(-2.3\) and \(-2.7\) when compared with the reference device where no PTFE interlayer is used.

In the earlier discussion, we showed that the current below \(V_{\text{on}}\) is electron-dominated, while above the \(V_{\text{on}}\) the device is essentially bipolar with holes as the majority carriers. For that reason, we analyzed the current density for a series of devices for \(V_{\text{bias}}\) below \(V_{\text{on}}\) (3V) and above \(V_{\text{on}}\) (6V) (Figure 6.5b). The insertion of PTFE reduces the current density which
decreases progressively with the thicker PTFE interlayers. This result is in contrast with what has been observed in ITO/PTFE/emissive layer/cathode devices as reported by Qiu et al.\textsuperscript{108,117} where they showed, based on their theoretical simulation and experiment, that the insertion of PTFE between ITO and the emissive layer can improve the current injection dramatically due to the geometry assisted tunneling effect. For our case, no current injection enhancement is observed, even for the thinnest PTFE interlayer (1nm) studied here. Either at 3 or 6V, the current density decreases sharply with the insertion of PTFE films of thickness above 3nm. For thicker films, the dependence is much weaker as the lines show in Figure 6.5b. However, in the case of electron current for $V_{\text{bias}}=3$V, the current density decreases approximately by two decades with the insertion of a PTFE interlayer which may indicate that PTFE serves as a excellent electron blocking layer in this device. For current at $V_{\text{bias}}=6$V, only one order of magnitude decrease is observed and the population of holes and electrons are pretty balanced in this stage. The reduction in current is mainly caused by the reduction in the majority carrier (holes) and such a reduction is beneficial to the EQE of the device. By observing the luminance intensity for the operational device at $V_{\text{bias}}=6$V, as reported in Figure 6.5c, the trend reflects the product of $J$ and EQE with the decreasing of $J$ and the increasing of EQE when the interlayer thicknesses varies between 3-7nm. It is worth noting that in this range of thicknesses the luminance is comparable with the reference device that does not incorporate the PTFE interlayer. This strong indication can refer to the role of PTFE on reducing the majority carrier (holes) and subsequently improve the charge balancing of the electron and hole in the recombination and emissive region.

This is consistent with our interpretation that PTFE reduces the concentration of the majority carriers (holes) thereby improving the charge balancing, but leaving the recombination rate unchanged.

### 6.4 Photoluminescence (PL) and electroluminescence (EL) characteristics

In order to decouple the effect of the PTFE insertion on the charge balance from the PL enhancement that is expected with the insertion of an interlayer between PEDOT:PSS and the emissive layer\textsuperscript{183,184}, the PLQE is measured with an integrating sphere. Glass/ITO/PEDOT:PSS/PTFE(xnm)/PFO samples were excited with a laser beam at incidence angle of 45° from the glass side (backward excitation, BW) and PFO side (forward excitation, FW). The results (including the result measured from the spectroil/PFO sample) are shown in Figure 6.5d.
At the incidence angle of 45°, considering the absorption coefficient for PFO at the excitation energy (3.3 eV), namely $\sim 2.3 \times 10^4$ cm$^{-1}$, nearly 50% of light is absorbed in the first 20 nm of the polymer film. Therefore the measurement of the PLQE is sensitive to which side the PFO film is excited from. For the FW-excitation measurements, the PLQE is weakly dependent upon PTFE thickness. For the backward-excitation measurements, this experiment is mainly probing the PEDOT:PSS(PTFE)/PFO interface and the PL efficiency is very sensitive to different interface with the PLQE varying from 27% to 44% depending on the PTFE thickness. The lower PLQE measured on the PEDOT:PSS/PFO interface gives a strong indication that the PL quenching effect occurs at this interface. Nonetheless, the insertion of the PTFE interlayer in between these two layers reduced the PL quenching. Indeed, the measurements show a monotonic increase of the PLQE for both configurations and the efficiency asymptotically reaches the value measured for PFO deposited on an insulating substrate (spectrosil) at $\sim 44\%$.

The PL spectra of PFO directly deposited on PEDOT:PSS, PEDOT:PSS/PTFE and spectrosil respectively are shown in Figure 6.6a. The PL spectra consist of a vibronically structured spectrum in which the 0—0 band appears to be sensitive to the substrate. More specifically, the 0—0 replica is more intense for the samples deposited on PEDOT:PSS or PEDOT:PSS/PTFE. No significant differences were observed in the spectra with varying the PTFE thickness.

Figure 6.6b shows the study on the evolution of the EL spectra (solid lines) as a function of the device operating time. The EL spectra were recorded every minute while driving the devices at constant current density of 50 mA/cm$^2$. The EL spectra display analogous vibronic structure to the PL, however, they differ at longer wavelength (in the green spectral region) where a broad component, referred to in literature as “green band” (g-band), is present in the EL spectra. The latter becomes more intense with the device operating time and it is associated with the degradation of the device.

Some differences between EL and PL are also present in the short-wavelength region where the relative intensity of the 0—0 band to the 0—1, $E_{00}/E_{01}$, is higher when compared to the PL. By closely observing the intensity of the g-band at $t=0$ min, the g-band intensity does not significantly depend on the PTFE thickness. However, the changes of the g-band intensity are more dramatic with time for devices with thinner PTFE interlayer. By comparing the initial spectra with the ones collected after 15 min, there is a clear dependence of the g-band intensity on the PTFE thickness (Figure 6.6).
Figure 6.6: a) Photoluminescence spectra of PFO deposited on PEDOT:PSS, PEDOT:PSS/PTFE(5nm) and spectrosil. The spectra are normalized with respect to the 0-1 vibronic replica. b) Electroluminescence spectra normalized to the 0-0 peak (solid lines) of ITO/PEDOT:PSS/PTFE(xnm)/PFO/Ca/Al driven at constant current (50 mA/cm²). Spectra were recorded after driving the devices for 0 (bottom) and 15min (top) where x=0 (squares), 1 (circles), 3 (triangles) and 5nm (diamonds).

6.5 Lifetime of PLEDs with and without PTFE

The lifetime study of the non encapsulated devices as a function of the PTFE interlayer thickness driven at constant current density (100mA/cm²) in low vacuum (10⁻¹-10⁻² mbar) is reported in Figure 6.7a. In this study, the lifetime is defined as the time at which the EL intensity is equal to 10% of its initial value. The results show a remarkable increase of the device lifetime by the insertion of PTFE, which clearly correlated with PTFE layer thickness. For the most efficient devices, 7nm for example, we register an increase of a factor 5 of the device lifetime when compared to reference device (Figure 6.7b). Since the experiment was carried out at constant current density, the value of the luminance intensity directly reflects the EQE and, in corroboration with the observations above, the device with the PTFE interlayer is brighter as an OLED and more efficient. We observe that the EL intensity for the device with PTFE, decreases progressively with time. On the other hand, for the reference device (without PTFE), the reduction of the EL, is followed, after a certain operating time, by an increase of the EL intensity, although this value is still below the
values obtained for the OLED operating with a PTFE interlayer. The applied voltage, which change in order to sustain a constant current, increase with the longer operating time and displays a linear trend (Figure 6.7c). The insertion of the insulating PTFE layer requires an initial higher applied voltage, however, the slope with which the voltage increases with time is much less sharp for the devices incorporating the PTFE layer.

Figure 6.7: Longevity study of non-encapsulated ITO/PEDOT:PSS/PTFE/PFO/Ca/Al devices carried out at constant current density (100mA/cm²) in low vacuum (10⁻⁴-10⁻¹ mbar). A) Lifetime of the devices as a function of the PTFE interlayer thickness. B) Electroluminescence intensity and c) voltage bias as function of time of the devices with 7nm PTFE interlayer and without.

6.6 Discussion

When PTFE is deposited by thermal evaporation, it tends to form well defined islands that coalesce for higher nominal thicknesses. In previous work, it was reported that PTFE on ITO forms relatively rough surfaces with well isolated islands in morphology. We observe that the PTFE deposited on PEDOT:PSS forms islands which begin to coalesce at a thicknesses around 3nm and that the roughness of the PTFE surface increases with its thicknesses. However, the trend is significantly more gradual when compared to the ITO/PTFE samples for which a sharp increase of the roughness was observed even with sub-nm thick PTFE films when it is deposited on ITO. These observations lead to the point
that the effect of PTFE on ITO and PEDOT:PSS is different. Here we have been observing
that the PTFE wets the PEDOT:PSS relatively better than ITO. For that reason, no sharp
points are formed which could improve the hole injection in the PEDOT:PSS/PTFE system,
as has been observed by Wu\textsuperscript{108,117} in the ITO/PTFE anode system. In their publication, a
model is proposed where the improvement in hole injection can only be observed in the
presence of isolated rough PTFE islands.

The increase of roughness with thickness could also be linked to the work function changes
as a result of superficial dipoles. The Kelvin probe technique is sensitive to dipoles
formation at the sample surface. The changes in the effective work function suggest the
presence of a dipole layers induced by the fluorine and carbon backbone as suggested in
Figure 6.3 where the KP results show an increment of work function of PEDOT:PSS after
inserting the PTFE layer. Another argument in favour of this surface dipole effect is that it
would agree with the presence of superficial dipoles as expected for fluoropolymers as a
consequence of the negatively charge fluorine atoms\textsuperscript{185}.

The trend for the changes in work function of PEDOT:PSS/PTFE with PTFE thickness
(Figure 6.2) shows a close correlation with the EQE of the devices (Figure 6.4a). We
postulate that the PTFE in this case acts efficiently as an electron blocking layer, especially
for the interlayer thicknesses in between 3-7nm. For thicknesses of less than 3nm, the PTFE
layer may not cover the PEDOT:PSS completely, therefore, no significant improvement is
observed. The holes experience a large energy barrier at the PTFE/PFO interface
\((\text{HOMO}_{\text{PTFE}}=10.6\text{eV})\textsuperscript{187}\) and hole injection is expected to be strongly reduced by the
insertion of the PTFE layer. The modified charge balance of the device is confirmed by the
measured increasing external quantum efficiency for the devices with a PTFE interlayer (3-
7nm). Even though the result from the PLQE measurement also display some
improvements on reduction of PL quenching effect with the insertion of PTFE layer, this
may not be the main reason for the improvement in EQE since the PLQE displays a
monotonic trend as a function of the thickness of PTFE, while the EQE shows a well
defined maximum that correlates with the WF measurements. For PTFE layer thicker than
7nm, the high resistance of this interlayer may restrict the number of charge carriers that
can be transported at certain voltage. For all these reasons, a PTFE interlayer with a
thickness in between 5-7nm is considered as the optimum thickness to achieve the highest
efficiency.

When PTFE is incorporated in the OLEDs between the emitting polymer and anode, the
created dipoles play a role similar to the PSS-rich layer in PEDOT:PSS without altering the
device operation. So, the device still presents the three regimes in which an electron-only regime is followed by a sharp transition where the holes start to be injected and the device turns-on. When increasing the PTFE thickness, we observe a reduction of the current density in the on-state, but values of the luminance are preserved for the most efficient devices (3-7nm PTFE thick layer). Indeed, luminance is governed by the minority carriers so this agrees with the hypothesis in which the electrons (minority carriers) are efficiently kept confined in the PFO layer.

The direct correlation between the increase in lifetime of the devices and the insertion of a PTFE layer (Figure 6.7) indicates that the PTFE interlayer is able to stop, or at least slow down, the degradation processes that are related to the PEDOT:PSS/PFO interface. Kim et al. have identified one of the mechanisms that lead to a more resistive character of the PEDOT:PSS/ emissive polymer interface, namely due to local de-doping of the PEDOT:PSS that occurs due to the appearance in correspondence of pin holes at the cathode. This degradation mechanism is clearly visible for the reference device where the applied voltage has to be increased over time in order to maintain a constant current as a consequence of the increasing resistance of PEDOT:PSS due to the de-doping process. By incorporating PTFE as the interlayer on PEDOT:PSS, the de-doping process is reduced tremendously. Therefore, the applied voltage is apparently constant over time which improves the overall lifetime of the device. The slower evolution of the resistivity for the devices incorporating the PTFE (Figure 6.7c) suggests that the PTFE layer acts as a barrier and prevents the PEDOT:PSS de-doping process.

The PL g-band is, in our study, much less intense when compared to the g-band in the EL spectra. It occurs at shorter wavelength than 535nm, which we attribute to interfacial defects rather than from fluorenone. From the result of I-L-V characteristic for the devices incorporating of PTFE interlayer, the insertion of the PTFE interlayer is found to be able to increase the charge balance during the device operation and shift the recombination zone closer to the anode rather than cathode. Therefore a less intense green emission is expected as the more defective region is closer to the Ca cathode according to the literature. The EL spectra of the device with PTFE shows a lower g-band intensity than the reference device indicating that more balancing of charge injection from the electrodes could effectively reduce the g-band emission from the interfacial defects and increase the purity of the light emitted.
6.7 PTFE interlayer for organic photovoltaic

A PTFE interlayer can not only improve the performance of PLED, but it can also be used to further improve the OPV performances. Figure 6.8 shows the energy levels of the single components of a photovoltaic cell with a simple schematic diagram of the ITO/PTFE interface. The fluorine component aligns on top of the ITO surface as shown in Figure 6.8, creating a dipole rich surface with the dipole moment directed inward towards ITO. This reduces the energy barrier between the ITO and organic interface.

Figure 6.8: Energy-level diagram shows the HOMO and LUMO of each material in the OPV device. Inset: Schematic diagram of the ITO/PTFE interface.

In Figure 6.9, the Jsc of the OPV devices are plotted as a function of the PTFE thicknesses. Compared to the device without the PTFE buffer layer, all the devices with PTFE buffer layer showed a significant improvement by showing higher Jsc. The high Jsc in OPV devices with the PTFE layer are mainly due to the reduction in the barrier height between ITO and organic matrix and subsequently improve the hole extraction process. In general, for organic electronic material systems (such as P3HT/PCBM), the hole mobility is a few magnitudes higher than the measured electron mobility. Hence, hole accumulation occurs in the device and the photocurrent is under space-charge limited conditions which result in non-uniformity in the applied field within the active area or bulk of the device structure.
By utilizing the PTFE buffer layer, efficient hole extraction can reduce the hole accumulation at the ITO/organic interface and as a result, the short circuit current $J_{sc}$ is further improved. Since PTFE is an insulating material, with an extremely high resistivity of $10^{18} \Omega/cm$ for its bulk properties, and a large value for its ionization potential of $9.8eV^{108}$, it is reasonable to expect that the short circuit current densities of OPVs decrease with increasing thickness of the PTFE layer.

As shown in Figure 6.9, the $V_{oc}$ of the devices are strongly dependent on the PTFE thicknesses. For the reference devices, with the structure of ITO/P3HT:PCBM/Al and ITO/PEDOT/P3HT:PCBM, the typical $V_{oc}$ were found to be 0.35 and 0.44V, respectively (Table 6.1). However, the $V_{oc}$ is found to be improved up to 0.55V for the device with 5nm of PTFE buffer layer. The work function of the ITO surface typically varies from 3.90 to 4.80eV depending on the surface treatment$^{192,193}$. After inserting the PTFE layer, the $V_{oc}$ is improved from 0.35 to 0.56V, because of the strong dipole layer created by the negatively charged fluorine rich PTFE layer that has modified the surface and increased the effective work function of the ITO. Another possible explanation is correlated with the phase separation of P3HT:PCBM on top of PTFE interlayer, where P3HT rich phase separation may preferably found closer to the PTFE layer. Therefore, the $J_{sc}$ is increased with the insertion of PTFE interlayer.
Figure 6.10: Power conversion efficiency (PCE) response plots of OPV devices with different PTFE thicknesses.

The improvement of $J_{sc}$ and $V_{oc}$ of the devices with the PTFE is observed in the improvement of the power conversion efficiency of the device shown in Figure 6.10 as a function of the PTFE film thickness. As show in Table 6.1, the devices with PTFE buffer layer exhibited at least a 40% increase in term of power conversion efficiency, compare to the reference devices. Among the device with PTFE, a device with a 2nm PTFE buffer layer exhibited the best performance with the PCE of 2.2%, which is attributed to the good coverage of 2nm PTFE on the ITO to modify the ITO surface without increase in the surface resistivity of ITO/PTFE anode.

**TABLE 6.1 List of device performance of OPV devices with and without different PTFE thicknesses.**

<table>
<thead>
<tr>
<th>Device structure</th>
<th>PTFE Thickness (nm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PTFE/P3HT:PCBM/Al</td>
<td>5.0</td>
<td>6.6</td>
<td>0.55</td>
<td>46.0</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>6.7</td>
<td>0.52</td>
<td>48.6</td>
<td>2.05</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>7.1</td>
<td>0.53</td>
<td>45.0</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>7.4</td>
<td>0.52</td>
<td>48.5</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>7.2</td>
<td>0.46</td>
<td>42.9</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>7.5</td>
<td>0.45</td>
<td>47.2</td>
<td>1.92</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/Al</td>
<td>-</td>
<td>4.6</td>
<td>0.44</td>
<td>52.3</td>
<td>1.28</td>
</tr>
<tr>
<td>ITO/P3HT:PCBM/Al</td>
<td>-</td>
<td>6.0</td>
<td>0.35</td>
<td>40.2</td>
<td>0.94</td>
</tr>
</tbody>
</table>
6.8 UV illuminated PTFE for OPVs applications

The improved results shown in the previous section are a consequence of the formation of an artificial dipole layer resulting from the negatively charged fluorine that facilitates the hole extraction process. The UV illumination process further enhances the effect of this artificial dipole layer and subsequently reduces the barrier height between the ITO/copper phthalocyanine interface, which is shown as a result of measurement of the work function on UV illuminated ITO/PTFE samples using Kelvin probe and the device performance of small molecule based OPVs.

In Figure 6.11, the $J_{sc}$ of the devices are plotted as a function of the PTFE thicknesses for the ITO/PTFE/CuPc/C60/BCP/Al OPV devices. It is clear that the device with 0.5nm of PTFE as the buffer layer has better performances in term of $J_{sc}$, $V_{oc}$, and FF compared to reference devices with and without PEDOT:PSS. By inserting a 0.3nm of PTFE, the $J_{sc}$ increase 75% from 1.6 to 2.8mA/cm², while the $V_{oc}$ remained constant at 0.41V (Table 6.2). The $V_{oc}$ are significantly increased from 0.41 to 0.49V when the PTFE layer thickness increased to 1.0nm. However, the $J_{sc}$ is decreased when the PTFE thickness increases. Since PTFE is an insulating material, with an extremely high resistivity of $10^{18}$Ω/cm for its bulk properties, and a large value for its ionization potential of 9.8eV, it is reasonable to expect that the short circuit current densities of OPVs decrease with increasing thickness of the PTFE layer.

![Figure 6.11: I – V characteristics of OPV devices with and without PEDOT:PSS and with the different PTFE thicknesses.](image)

Figure 6.11: I – V characteristics of OPV devices with and without PEDOT:PSS and with the different PTFE thicknesses.
To study the effect of UV treatment on the ITO/PTFE layers, Kelvin probe measurements were conducted on ITO, ITO/PTFE(0.5nm) and ITO/PTFE(0.5nm) with different UV exposure times with the resultant the work functions listed in Table 6.2. The work function of the anode was shown to increase from 4.83eV (bare ITO) to 5.00eV after a 0.5nm PTFE layer was deposited on the ITO. For the UV illuminated ITO/PTFE samples, the work function increased approximately to ~ 5.17eV after 5 min of UV-illumination. However, further increase of the UV exposure time decreased the work function of ITO/UV illuminated PTFE layer as shown in Table 6.2.

### TABLE 6.2: Work function of ITO, ITO/PTFE and ITO/PTFE with different UV exposure time measured by Kelvin Probe.

<table>
<thead>
<tr>
<th>Sample</th>
<th>UV exposure time</th>
<th>Work function, eV (±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen plasma cleaned ITO</td>
<td>-</td>
<td>4.84</td>
</tr>
<tr>
<td>ITO/PTFE(0.5nm)</td>
<td>-</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>5.13</td>
</tr>
<tr>
<td></td>
<td>4 min</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>5.17</td>
</tr>
<tr>
<td></td>
<td>7 min</td>
<td>5.17</td>
</tr>
<tr>
<td></td>
<td>10 min</td>
<td>5.02</td>
</tr>
</tbody>
</table>

A similar treatment on the ITO buffer layer was used to make organic photovoltaic devices. The I-V characteristics of these OPV devices under solar simulator illumination are shown in Figure 6.12. The $J_{sc}$ and $V_{oc}$ of the devices improved in parallel with the increased UV illumination time for the initial 5 min. However, further increase of the UV illumination time beyond 5 min saw a decrease in the $J_{sc}$ and the $V_{oc}$. This observation is in agreement with the results from work function measurements where the work function increased for the first 5 min, with further increase in the illumination time reducing the work function of the ITO/PTFE anode.

The high $J_{sc}$ in OPV devices with PTFE layer is mainly due to the reduction in the barrier height between ITO and organic matrix and subsequently improved hole extraction processes. The improvement in current extraction from CuPc layer to anode is mainly due to the smaller barrier of charge extraction and, hence, an increased photo-generated current under forward bias which was observed with the increment in $J_{sc}$. As shown in Figure 6.10, the $V_{oc}$ of the devices is strongly dependent on the PTFE thicknesses. For the reference
devices, with the structure of ITO/CuPc/C_{60}/BCP/Al and ITO/PEDOT:PSS/CuPc/C_{60}/BCP/Al, the typical $V_{oc}$ were found to be 0.41 and 0.44V, respectively (Table 1). However, the $V_{oc}$ is found to be improved up to 0.55V for the device with 1nm of UV treated PTFE buffer layer (Figure 6.12). The work function of the ITO surface typically varies from 3.90 to 4.80eV depending on the surface treatment. After inserting the untreated PTFE layer and the UV treated PTFE layer, the $V_{oc}$ is improved from 0.41 to 0.49V, because of the strong dipole layer created by the negatively charged fluorine rich untreated PTFE layer and UV treated PTFE layer that has modified the surface and further increased the effective work function of the ITO. As show in Table 6.2, the devices with UV treated PTFE buffer layer exhibited at least a factor of 2 increases in term of power conversion efficiency, compared to the devices with untreated PTFE buffer layer. Among the device with PTFE, a device with a 0.5nm UV treated PTFE buffer layer exhibited the best performance with the PCE of 1.58%, which is attributed to the good coverage of 0.5nm UV treated PTFE on the ITO to modify the ITO surface without increase in the surface resistance of ITO/UV treated PTFE anode. It can be seen from Figure 6.12 that $J_{sc}$ of the structure ITO/UV treated PTFE(0.5nm)/CuPc/C_{60}/BCP/Al is the highest because of the smallest hole extraction barrier. Interestingly, UV treatment of PTFE buffer layer can significantly change the contact properties. These results show that while the pristine PTFE layer is useful for reducing the contact barrier, its effect is considerably enhanced by UV illumination.

![Figure 6.12: The I-V characteristics of OPV devices consisting of PTFE (0.5nm) as a buffer layer on ITO, which is exposed to different UV exposure times.](image_url)
Modification of polymers by exposure to UV irradiation has been reported previously\textsuperscript{105,106}. Radiation energy can be absorbed via ionization, phonon excitation and atomic displacement. This causes bond breaking, followed by scissoring and subsequent release of volatile fragments, which may result in the cross-linking through C-C bonding. In our case, clusters of sp\textsuperscript{2} bonding may also be formed, leading to an increased in conductivity\textsuperscript{194}. At present, there is no clear explanation with regard to the interaction of UV light with PTFE properties and PTFE is found to be highly resistant to UV exposure\textsuperscript{195}. However, UV illumination on a few atomic layers of PTFE may have a very different interactions compared to UV radiation and impact on bulk properties of PTFE. In 2004, Tong and his co-workers have shown that UV-illumination on fluorocarbon coatings CF\textsubscript{x} (the basic structure of PTFE), created the graphitic regions identified by X-ray photoelectron spectroscopy results. This leads to the higher conductivity of the CF\textsubscript{x} layer and further improved OLED performance\textsuperscript{194}. The same explanation may apply to the UV illuminated PTFE layer where the $J_{sc}$ of the OPV is improved due to the relatively higher conductivity of PTFE after UV illumination.

**6.8 Summary**

In this work, we have shown despite its strong hydrophobicity, when a nm-thick film of PTFE is deposited on PEDOT:PSS it still allows deposition of $p$-xylene solutions and fabricated solution-processed polymer-based OLEDs with PTFE as an interlayer between the PEDOT:PSS and PFO. We measure an increase of the effective work function of PEDOT:PSS/PTFE when compared to only PEDOT:PSS. The hypothesis of the formation of interfacial dipoles is confirmed by the study of the characteristics of ITO/PEDOT:PSS/PTFE/PFO/Ca/Al devices that show improved electron blocking properties for devices incorporating the PTFE interlayer. The analysis of current density, luminance and external electroluminescence quantum efficiency shows that the PTFE layer is capable of controlling the hole injection, which maximizes the efficiency of the OLED without altering the light output. Measurements of the photoluminescence efficiency at grazing angles confirm that insertion of PTFE is beneficial to prevent the PL quenching at the anode/polymer interface. However, a monotonic trend is observed for the PL efficiency as a function of the PTFE thickness, whereas the maximum of the EQE observed for 3-7 nm thick PTFE samples correlates well with work function measurement results. Therefore, although insertion of the PTFE interlayer could prevent the PL quenching, but here we ascribe the increased EQE are more prominent to the charge balancing instead. Stability of
the devices has also been investigated and a dramatic improvement on the device lifetime is found by incorporating PTFE to prevent the de-doping of the PEDOT:PSS and subsequently reduce the device stressing and ageing effect. We also observe a better colour purity for devices incorporating the PTFE interlayer where the typical green emission observed in polyfluorenes is strongly suppressed for long operating times. The improved efficiency and stability with the insertion of a few nm-thick chemically-inert PTFE layers at the PEDOT:PSS/polymer interface is a remarkable result considering that the film deposition method is still not optimized and that the mechanism of the dipole formation is still to be improved.

For OPVs devices, the insertion of PTFE buffer layer at the anode of ITO/organic interface can significantly improve the $J_{sc}$, $V_{oc}$ and PCE of bulk-heterojunction OPV. The performance improvement is attributed to the reduction in hole extraction barrier. This fluoro-material also offers a significant advantage in that the film can be simply prepared by thermal evaporation. Thus, it can be prepared at low substrate temperatures, which are compatible to flexible polymer substrates for OPV applications.

Furthermore, the insertion of UV treated PTFE buffer layer at the anode of ITO/organic interface can significantly improve the $J_{sc}$, $V_{oc}$ and PCE of bulk-heterojunction OPV. The improved performance in the UV treated PTFE-coated ITO contact are consistent with its small hole extraction barrier.
CHAPTER 7

Conclusion and Future Works

In multilayer structure devices, designing and inserting different types of interlayer involves careful investigation and understanding of the interaction between the layers. In this thesis, the effects of two different interlayer materials acid-oxidised carbon nanotubes and PTFE, are studied within OLED and OPV structures. Specifically, we investigate these effects in terms of transport properties, optical properties and device efficiencies.

7.1 Acid oxidised CNTs for organic light emitting diodes

We observed experimentally that o-SWCNTs modified the bulk properties of TPD (prepared by thermal evaporation) based on the changes observed in the I-V characteristics of ITO/o-SWCNTs/TPD/Al devices. This result is further supported by the changes of morphology observed through AFM and the high contrast of current mapping in o-SWCNTs device via c-AFM measurement. We note the broad and featureless spectrum for modified TPD as further support of our conjectures about the TPD changes and also the strong presence of traps in the TPD layer. As a consequence, the high density of traps in TPD resulted in a high current density combined with lower luminance in the o-SWCNTs based OLED device due to the imbalance charge injection from the positive and negative electrodes.

For the study of CNT interlayer in PLEDs, the amorphous light emitting polymers F8BT and TFB were used as the active layer to reduce the possibility of the morphology changes due to the processing condition. In this case, PL efficiency measurements show that the performance of ITO/CNTs based PLEDs can improve significantly provided we control the quenching of radiative efficiency arising from exciton dissociations that occurs at the interface of the CNT with the emissive polymer. Such control is obtained by the insertion of a hole transport layer which also acts as an electron-blocking layer (EBL) between the CNT and the polymer shifting the recombination zone away from the anode. Since CNTs are widely perceived as a viable replacement for ITO as the transparent conductive electrode, the results obtained from this thesis supplements the current literature on designing a multilayer PLEDs or OLEDs using CNTs as the electrode.
7.2 PTFE interlayer for PLEDs and OPVs

The marked improvements in PLED characteristics and lifetime using a PTFE interlayer revealed that fluoropolymers are potentially a good choice as an interlayer for organic-based electronic devices, despite their strong hydrophobicity. On the atomic scale (<10nm), PTFE interlayer does not exhibit as strong a hydrophobic and insulator characteristic as in its bulk form. The increase in the work function for PEDOT:PSS/PTFE and ITO/PTFE surfaces indicate a strong dipole due to the C and F elements in PTFE. For the PLED case, this strong dipole helps to block the electron injected from the Al cathode and confine the recombination zone at the proper distance from the electrodes. The analysis of current density, luminance and external EL quantum efficiency showed that the PTFE layer is capable of controlling hole injection, thereby maximizing the efficiency of the OLED without altering the light intensity output. Measurements of the photoluminescence efficiency at grazing angles confirmed that insertion of PTFE is beneficial to prevent any PL quenching at the anode/polymer interface. We do note that a monotonic trend is observed for the PL efficiency as a function of the PTFE thickness, whereas the maximum of the EQE observed for 3-7nm thick PTFE samples correlates well with work function measurement results. Therefore, although insertion of the PTFE interlayer can prevent PL quenching, we ascribe the increased EQE to the charge balancing instead.

Stability of the devices has also been investigated and a dramatic improvement of the device lifetime is found by incorporating a PTFE layer to prevent the de-doping of the PEDOT:PSS and subsequently reduce the device stressing and ageing effect. We also observed a better colour purity for devices incorporating the PTFE interlayer where the typical desired green emission observed in polyfluorenes is strongly suppressed for long operating times. The improved efficiency and stability with the insertion of nm-thick chemically-inert PTFE layers at the PEDOT:PSS/polymer interface is a remarkable result considering that the film deposition method is still not optimized and that the mechanism of the dipole formation is still to be improved.

For OPV devices, the insertion of a PTFE buffer layer at the anode of ITO/organic interface can significantly improve the $J_{sc}$, $V_{oc}$ and PCE of bulk-heterojunction OPV. The performance improvement is attributed to the reduction in the hole extraction barrier. This fluoro-material also offers a significant advantage in that the film can be easily prepared by thermal evaporation. Thus, it can be prepared at low substrate temperatures, which are compatible with flexible polymer substrates for OPV applications. Furthermore, the insertion of a UV treated PTFE buffer layer at the anode of ITO/organic interface can
significantly improve the $J_{sc}$, $V_{oc}$ and PCE of bulk-heterojunction OPV. The improved performance in the UV treated PTFE-coated ITO contact is consistent with its small hole extraction barrier.

Fluoro-based materials have been widely used as self assembled monolayers (SAMs) in organic and inorganic based devices by modifying the electrode in order to improve the charge injection (or extraction). However, issues concerning the stability of such structures are quite common as these materials are highly sensitive to the processing environment and storage conditions. Furthermore, the SAMs are designed such that only a specific surface is targeted for attachment. Therefore, the surface condition of the targeted material is very important and is critical to the success of the surface modification results. From the results of this thesis, fluoropolymer based materials (in this case PTFE) show potential as a useful interlayer material for various applications. The material itself is stable in air or vacuum. Furthermore, there is no requirement for special pre-treatment of the target surface and no solvent intermixing issue as only thermal evaporation process is used.

### 7.3 Future works

Based on the results in this thesis, a few interesting areas are proposed for the future work:

- In the present organic electronics (OE) field, highly crystalline semiconducting small molecules such as (TIPs-pentacene) show a high mobility in organic thin film transistors (o-TFTs) ~ 2cm²/Vs. The device performance is very sensitive to the crystal formation which is hugely affected by the formulation, process temperature and the electrode surface. Since the CNTs are a potential candidate for a solution processable flexible transparent electrode, it would be interesting to study how the carbon nanotube electrode will correlate with the crystal morphology of the organic semiconductor deposited on top of CNTs. This work can also be extended to the different deposition techniques such as inkjet printing, flexo printing and gravure printing process. In this case, fluoro based polymer or small molecules can also be used as the interlayer between CNTs and organic semiconductor to study the impact of this layer on the surface morphology and device performance.

- In this thesis, the surfaces of carbon nanotubes used for OLED and PLED are mainly decorated with hydroxyl (OH) and carboxylic acid (COOH) groups. There are two routes to extend this work. For the first route, different functional groups such as amine, fluorine, nitrate and sulfonate can be introduced on the CNTs surface and we can then study the interaction between these functional groups with
organic molecules or polymers in term of interfacial, optical and device performance. The second route is to compare the interaction of organic materials with a 1-D CNTs and a 2-D graphene layer, in terms of optical and electrical properties and device performance.

- PTFE is a fully fluorinated polymer while the partially fluorinated polymer can be used to increase the polarity of the resins. Therefore, different types of fluorinated polymers with different polarity can be used as the interlayer for OLED, OE and OPV in order to develop the understanding on how the polarity of the polymers affects the device performance.

- PTFE is a high molecular weight polymer. The concept of thermal evaporated polymeric material is very unusual as it is usually believed that a high molecular weight material would decompose during the thermal evaporation process. Therefore, it would be interesting to investigate the components that have been deposited on the substrate during the PTFE thermal evaporation process. In this study, X-ray photoemission study is a good experimental technique to employ as it can detect the composition of the layer accurately.
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Publications


Presentation List


