# Fabrication of organic field effect transistors using photosensitive active materials

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# LIST OF ABBREVIATIONS

5,14-MPn	5,14-dihydro-5,14-methanopentacene-15-one
6,13-Epn	6,13-dihydro-6,13-ethanopentacene-15,16-dione
6,13-MPn	6,13-dihydro-6,13-methanopentacene-15-one
ADT	Anthradithiophene
AFM	Atomic force microscopy
AR	Analytical reagent
BBBT	Benzo[1,2-b:4,5-b']bis[b]benzothiophene
BJT	Bipolar junction transistor
BTBT	Benzothieno[3,2-b]benzothiophene
C6-DTBDT	Dihexyl-dithieno[2,3-d;2',3'-d']benzo[1,2-b;4,5-b']dithiophene
C8-PTCDI	N,N'-dioctyl-perylene-3,4,9,10-tetracarboxylic acid diimide
C8-BTBT	Dioctyl-[1]benzothieno[3,2-b]benzothiophene
C10-DNTT	2,9-decyl-dinaptho[2,3-b:2',3'-f]thieno[3,2-b]thiophene
C12-BTBT	Dodecyl-[1]benzothieno[3,2-b]benzothiophene
CSA	Camphorsulfonic acid
CV	Capacitance-voltage
DAcTTs	Diacene-fused thienothiophenes
DAST	4(4-dimethylaminostyryl)-1-methylpyridinium tosylate
DATT	Dianthra[2,3-b:2',3'-f]thieno[3,2-b]thiophene
DC	Direct current
DFT	Density functional theory
DIC	Differential interference contrast
DiF-TES-ADT	2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene
DMSO	Dimethyl sulfoxide
DNTT	Dinaptho[2,3-b:2',3'-f]thieno[3,2-b]thiophene

DOS	Density of states
DPh-BTBT	2,7-diphenyl[1]benzothieno[3,2-b][1]benzothiophene
DPh-NDT	Diphenyl-naptho[2,3-b:6,7-b']dithiophene
DPh-PTCDI	N,N'-diphenyl-perylene-3,4,9,10-tetracarboxylic acid diimide
EDOT	3,4-ethylenedioxythiophene
EHO-OPPE	Poly[2,5-dioctyloxy-1,4-diethynylphenylene-fl/f-2,5-bis(2'- ethylhexyloxy)-1,4- phenylene]
E-MOSFET	Enhancement metal oxide semiconductor field effect transistor
FET	Field-effect transistor
FWHM	Full width at half maximum
HMDS	Hexamethyldisilazane
НОМО	Highest occupied molecular orbital
INDO/S	Intermediate neglect of differential overlap/screened
IR	Infrared
ITO	Indium tin oxide
IV	Current-voltage
LED	Light-emitting diode
LINAC	Linear accelerator
LLDPE	Linear low density polyethylene
LUMO	Lowest unoccupied molecular orbital
LVF-HL	Linear variable filter – high low
LVF-UV-HH	Linear variable filter – ultraviolet – high high
LVF-UV-HL	Linear variable filter – ultraviolet – high low
МО	Molecular orbital
MOSFET	Metal-oxide-semiconductor field effect transistor
MSQ	Methyl silsesquioxane
MTR	Multiple trap and release
NDT	Napthodithiophene

NEXAFS	Near edge x-ray absorption fine structure spectroscopy
NLO	Nonlinear optical
OFET	Organic field effect transistor
OLED	Organic light emitting diode
OPV	Organic photovoltaic
OTS8	Octyltrichlorosilane
РЗНТ	Poly(3-hexylthiophene)
PAG	Photoacid generator
PANI	Polyaniline
РСВМ	Phenyl-C61-butyric acid methyl ester
PDOS	Partial density of states
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PFBT	Pentafluorobenzenethiol
PID	Proportional-integral-derivative
Poly-4BCME	Poly[5,7-dodecadiyn-1,12-diol-bis(n-butoxycarbonyl-methyl-urethane)]
РОРОР	1,4-bis(5-phenyl-2-oxazolyl)benzene
PPV	Poly(p-phenylene vinylene)
PTCDA	Perylene-3,4,9,10-tetracarboxylic dianhydride
PTHPET	Poly(3-(2-(tetrahydropyran-2-yloxy)ethyl)thiophene
РХТ	Poly(p-xylene tetrahydrothiophenium chloride)
RF	Radio frequency
RFID	Radio frequency identification tag
RMS	Root mean square
SAXS	Small angle x-ray scattering
SXES	Soft x-ray emission spectroscopy
TIPS-Pn	6,13-bis(triisopropylsilylethynyl)pentacene
TED-ADT	Triethylsilylethynyl anthradithiophene

THF	Tetrahydrofuran
UHMW-PE	Ultra-high molecular weight polyethylene
UV	Ultraviolet
WAXS	Wide angle x-ray scattering
XPS	X-ray photoelectron spectroscopy
YSZ	Yttrium stabilised zirconium oxide
ZINDO	Zerner's intermediate neglect of differential overlap

#### ABSTRACT

The research described in this thesis was conducted with the aim of finding a versatile group of organic semiconducting and conducting materials that could be used in a practical manner for the production of organic field effect transistors (OFETs) via a direct photopatterning process. It was established that a suitable class of materials – photosensitive Diels-Alder bridged pentacene precursors – already existed, but had not been fully exploited for this purpose.

Calculations of synthetic UV-visible, infrared and partial density of states spectra, based on models of single molecules with geometries optimised using density functional theory, proved to be useful in understanding the photochemical properties of existing semiconductor materials and precursors. The viability of these calculations was tested by comparing them with the UV-visible spectra and synchrotron based x-ray photoelectron, x-ray emission and near-edge x-ray absorption fine structure spectra of a series of robust n-type organic semiconductors with shared perylene core structures.

Narrowband UV exposures of 6,13-dihydro-6,13-methanopentacene-15one (6,13-MPn) and 5,14-dihydro-5,14-methanopentacene-15-one (5,14-MPn) were carried out. It was found that they were sensitive to light with wavelengths < 325 nm and < 315 nm, respectively. The difference in the photosensitivity of the two pentacene precursors was utilised in a study of the means to independently pattern multiple layers of electronically active materials. It was also found that patterns could be transferred to films of the organic conductor PEDOT:PSS by photobleaching and that the resistance of the films changed in a predictable manner. Following this, the performance of OFETs produced using 6,13-MPn and 5,14-MPn as precursors for the active semiconductor layers was studied. A measureable increase in conductivity through the source-drain channel of 6,13-MPn and 5,14-MPn based transistors resulted when they were illuminated with broadband light and simultaneously annealed at 95 °C and 90 °C, respectively. Exposing the 6,13-MPn precursor to filtered light in the range from 270-340 nm once again resulted in conversion to a semiconductor with gate voltage enhanced mobility. In the case of the 5,14-MPn transistor, the output curves appeared to be affected by carrier trapping.

Following the studies on the precursors of pentacene, a new range of photoprecursors for semiconductors containing thiophene rings was proposed. The photolysis wavelengths of these materials were predicted by investigating the synthetic UV-visible absorption spectra of the materials.

## DECLARATION

This thesis contains an updated analysis of the soft x-ray emission spectrum and synthetic partial density of states of the material 3,4,9,10-perylenetetracarboxylic dianhydride that was included in my Honours thesis which was undertaken at Macquarie University in 2008, entitled "Photobleaching of organic semiconductor thin films". Other than the above stipulated case, this thesis entitled "Fabrication of organic field effect transistors using photosensitive active materials" contains no material which has previously been submitted or accepted for a higher degree, as part of the requirements for a degree, or for a diploma to Macquarie University or to any other institution. To the best of my knowledge, this thesis contains no material previously published or written by another person except where due acknowledgement has been made in the text. Further, I certify that this thesis is an original piece of research written by myself, and any help I have received for this research and in preparing this thesis has been appropriately acknowledged.

Christopher McMahon

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## PUBLICATIONS AND PRESENTATIONS

#### Publications resulting from work related to this thesis

 J. E. Downes and C. J. McMahon, (2014). Wavelength-Selective Patterning of Multi-Layered Electronic Devices. Australian provisional patent number 2014900201. Australian Patent Office.

# Additional journal articles and conference proceedings from this author

- C.G. Baldwin, J.E. Downes, C.J. McMahon, C. Bradac, and R.P. Mildren, Nanostructuring and oxidation of diamond by two-photon ultraviolet surface excitation: An XPS and NEXAFS study. Physical Review B, 89, 195422 (2014).
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# CHAPTERIntroductionONE

The use of organic materials in electronic devices is a concept that was first proposed a century ago, although many years passed before these materials could be handled easily and used in commercial applications. In 1911, McCoy and Moore published a paper on organic salts that appeared to display metallic properties [1]. Much later, in the early 1960s, around the time that the first metal-oxide-semiconductor integrated circuits became commercially available [2], electroluminescence from a solid state organic material was observed when an electric field was applied to flakes of anthracene by Pope at al. [3] and Helfrich and Schneider [4]. This observation went largely unnoticed during the concurrent expansion in silicon based electronics research that continued through the latter half of the 20<sup>th</sup> century. The problem was that it remained comparatively difficult to grow and then process organic crystals for use in devices and the effort was not considered worthwhile given the poor performance of such devices. However,

more success came during 1987 with the work of Tang and Van Slyke, two researchers with the Kodak company. They reliably produced organic light emitting diodes (OLEDs) by vacuum subliming thin layers of small organic molecules that were then sandwiched between pairs of electrodes [5]. Organic field effect transistors (OFETs) made from semiconducting polymer films were also described at this time [6]. In the 25 years since, the market for OLED display technologies has reached an annual turnover of several billion dollars, with further growth expected to come [7, 8]. Similar growth is expected to occur in the OLED lighting industry over the next few years [9].

While there is expected to be a greater number and variety of organic devices commercialised in the coming years, there is no indication that organic electronics will supersede inorganic electronics in many applications. Rather, organic electronics will be implemented where inorganic devices would be impractical or simply too expensive. Such applications include flexible displays, RFID tags, electronic textiles, chemical sensors, electronic skin, photovoltaics and disposable electronics [10-15]. The commercial success of these applications depends on the ability to deposit organic materials onto flexible substrates by a solution deposition process, such as spraying or inkjet printing. Flexible substrates allow for roll-to-roll processing of electronics, a rapid throughput manufacturing technique that decreases the cost of device production [16]. End applications such as roll-away display screens (see Figure 1.1 [17]), touch screens, or electronic skins require that the device can be bent to small radii and then relaxed repeatedly without degrading electronic performance. This is difficult to achieve with inorganic materials, as they tend to form as crystals with strong covalent bonding, meaning that they are brittle when bending forces are applied. The weaker van der



**Figure 1.1** The Philips Fluid concept smart phone can be rolled up and worn as a wristband due to the use of a flexible OLED display screen [17].

Waals bonding of molecules in organic thin films means that organic devices can be bent repeatedly without causing permanent damage [18].

One of the main advantages of working with organic electronic materials instead of inorganics is that inkjet printing methods for film deposition and patterning can be used [19, 20]. Solutions may be printed onto arbitrary substrates, with structures defined by the position of the nozzle head relative to the substrate. Ultra high vacuum environments, which are required for the deposition of inorganic materials, add time and costs to the manufacturing of conventional electronics. On the other hand, printing can be performed in ambient atmosphere. It is also an additive process, where different functional layers are built up over each other, without removing any material that is already in place. Photolithography, which is the standard technique for defining structures in conventional electronics using a photosensitive resist, is a subtractive process, meaning that materials are deposited on a substrate and then removed again in a later step by dissolving the patterned resist layer [21]. Multiple subtractive steps are typically carried out, meaning that there is considerable wastage of materials. Photolithography does not tend to be compatible with manufacturing organic electronic devices that have multiple organic layers, because the developer and lift-off solvents tend to degrade the active organic materials. It follows that the major theme uniting organic electronics research over the last decade and a half has been the push to develop printable insulating, semiconducting and conducting materials for use as the electrodes and other active layers in devices [22].

A great deal of research has focused on finding methods for solubilising pentacene, a linear oligoacene that held the record for the highest performance OFETs during much of the 1990s and 2000s [23]. Pentacene is typically deposited directly as a thin film using vacuum sublimation, because of its low solubility in most common solvents. Pentacene can be deposited from solution in specific cases where high temperature solutions are deposited on high temperature substrates [24]. However, these temperatures are unlikely to be compatible with all components of plastic electronics, which has inhibited progress towards commercialisation of devices made from pentacene. Many alternative materials have since been developed which demonstrate improved electronic performance and better environmental stability [25], but the research conducted on pentacene continues to inform the design of these new materials. One of the earliest approaches used to deposit pentacene from a room temperature solution was to form a Diels-Alder pentacene precursor, which could be dissolved, deposited onto a substrate and then converted into pentacene in a subsequent step. Measurements on OFETs made from the first such precursor, which had a tetrachlorobenzene group bridging the central pentacene ring, were presented in 1996. The bridging group was removed when the material was heated to 180 °C [26]. Other precursors were later produced, which could be converted to pentacene by exposure to light [27-29]. However, while these materials were being developed in the mid to late 2000s, other solubilisation routes such as alkylsilination of pentacene were also shown to produce good transistor performance [30]. Promising results were also reported for solution processed thienoacene transistors, which are more stable than pentacene in air [19, 25, 31, 32]. Few reports regarding the use of semiconductor precursors in OFETs have been released in the past few years and it appears that the precursor solubilisation route has been somewhat superseded by the technique of adding alkyl groups and other permanent substituents [19, 32-35].

Despite the recent relative lack of progress in precursor synthesis, there are some benefits to the use of photosensitive semiconductor precursors, as compared to otherwise photochemically inactive soluble semiconductors. These materials can be patterned by processes familiar from photolithography, where selected regions of a film are locally addressed by exposure to light through a photomask or by translating a point light source. The difference is that the insulating precursor is converted directly into a semiconducting material without the need for the multiple deposition and lift-off steps of photolithographic techniques. When defining patterns by inkjet printing, solution mechanics limits control over the size and position of droplets and must be thoroughly understood when working with critical feature sizes on the micron scale or lower. The resolution limitations in the direct photopatterning technique are influenced by other factors and there is still room to optimise OFET production by the precursor route in future organic semiconductor research.

Recognising the inherent benefits of directly photopatterning semiconductor precursor films, a number of questions were posed for this research thesis:

5

- Is there anything that can be done to improve the performance of the pentacene precursors that have been examined in the past?
- Is it possible to directly photopattern other components of OFETs besides the semiconductor layer?
- Can these different photosensitive materials be deposited onto each other, or are there solvent compatibility problems?
- If different layers of an OFET are photosensitive, will patterning one layer inadvertently damage another?
- Is there any value in synthesising precursors for semiconductors besides pentacene and is it possible to predict the illumination conditions under which they can be patterned?
- Which new semiconductor materials are good candidates for functionalisation as Diels-Alder type precursors?

The first three questions are addressed in Chapter Six, which describes experiments that were performed in an attempt to enhance the performance of OFETs made from pentacene precursors, by testing the illumination and annealing treatments for the transistors. Attempts to independently pattern stacked layers of different pentacene precursors are outlined, as are studies of the photosensitivity of the organic conductor, PEDOT:PSS. Given that roll-to-roll manufacturing enables the rapid production of many identical devices on a large substrate, such as that shown in Figure 1.2, experiments were carried out with spray deposited organic solutions, as this is a roll-to-roll compatible deposition strategy.



**Figure 1.2** *Multiple OLED displays can be printed onto a flexible film and then separated into individual pieces after processing* [36].

The question as to whether multilayers can be independently photopatterned is examined theoretically and experimentally in Chapter Five. Synthetic UV-visible absorption spectra that were developed using computations based upon density functional theory are compared with experimental analogues, as a means of evaluating the accuracy of the calculations. Transitions between particular molecular orbitals in the synthetic spectra are related to the real absorption features in the experimental spectra. The value of this is that it enables the identification of the molecular orbital transitions responsible for the removal of the solubilising moieties from the semiconductor precursors. This work follows on from related calculations that are presented in Chapter Four. This chapter examines how well the soft x-ray spectra of a number of stable semiconductors, based on perylene, match with the synthetic spectra generated from models of single molecules.

The aim of Chapter Seven was to examine precursor materials that should be synthesised in future research, with the aim of improving upon the stability and performance deficiencies of pentacene devices. A thorough examination is made of the synthetic absorption spectra of proposed thienoacene photoprecursors. The photolysis wavelengths are predicted and those materials which appear to be the best candidates for synthesis are presented. Before discussing these results, an overview of the relevant literature is provided in Chapter Two, prior to a description in Chapter Three of the experimental apparatus used in this research.

# CHAPTER TWO

A review of the application of photopatterning in the production of organic electronic devices

As outlined in the introduction, the aim of this thesis was to examine materials that could be used to directly photopattern the functional architectures of organic field-effect transistors (OFETs). A review of the relevant literature is provided here, describing what organic conductors and semiconductors are and how these materials are used in OFETs. Various methods for patterning OFET features (photolithography, ink jet printing, etc.) are then discussed and contrasted with previous demonstrations of direct photopatterning in the production of organic electronic devices. A class of compounds which are particularly useful for this work, known as *bridged pentacene photoprecursors* (the Diels-Alder precursors mentioned in Chapter One) are then reviewed. Finally, an overview of *spray deposition* is provided. This is a novel method for depositing the soluble organic materials in OFETs and is reviewed with a particular focus on OFET and organic

solar cell applications. This will provide the grounding in the literature necessary to evaluate my contributions in the area of OFET patterning techniques.

#### 2.1 ORGANIC ELECTRONIC MATERIALS: MOLECULAR STRUCTURES AND CHARGE TRANSPORT

The following sections on organic semiconductors and conductors describe the characteristics of their respective molecular structures and the influence of the overlap between adjacent molecules on the resultant performance of devices.

#### 2.1.1 Organic semiconductors

Organic semiconductors can be classified as small-molecular-weight, polymer or biological materials. The term *small-molecular-weight material* refers to compounds with a defined molecular weight, as opposed to polymers which consist of repeated monomer units in long chains of variable length. A structural distinction exists between the two classes, however the bulk electronic and optical properties are similar. Some research has also been conducted into the exploitation of the optical and electronic properties of biological structures, but by far most materials research in organic electronics has centred on the first two classes [15].

The structures of small molecule and polymer semiconductor materials are characterised by highly conjugated  $\pi$ -electron systems. Conjugated systems are formed by the side-on-overlap of atomic p-orbitals, predominantly between the carbon atoms that comprise the molecular structure. This overlap results in the extended  $\pi$ -orbitals above and below the plane of the perylene-3,4,9,10tetracarboxylic dianhydride (PTCDA) molecule shown in Figure 2.1(a). This molecule is shown here because it is the subject of further studies using x-ray spectroscopic techniques, which are described in Chapter 4. The blue and green lobes represent the positive and negative phases of the molecular orbital (MO) wavefunction. The end-to-end overlap of trigonal planar carbon sp<sup>2</sup>-hybridised orbitals, results in the  $\sigma$ -bonds that compose the backbone of the molecule or polymer, as seen in Figure 2.1(b). The  $\pi$ -bonds, which lie outside of the carbon-carbon internuclear plane, are weaker than the in-plane  $\sigma$ -bonds. As such, the lowest energy electronic excitations in organic semiconductors are typically the  $\pi$ - $\pi$ \* transitions; an electron can move from the highest filled  $\pi$  MO to the



**Figure 2.1** The PTCDA molecule is shown in (a) and (b) with carbon atoms in grey, hydrogen atoms in white and oxygen atoms in red. (a) A  $\pi$ -bonding molecular orbital and (b) a  $\sigma$ bonding molecular orbital are shown above the molecular plane and in the molecular plane, respectively. The positive and negative phases of the orbitals are shown in blue and green. (c) The structure of the high performance semiconductor, pentacene. (d) The ab-plane of the pentacene unit cells shows an end-on view of the molecules as they stack in a herringbone structure (adapted from [37]). The directions of orbital overlap integrals, t, are shown. Calculations reveal that the orbital overlap is strong for  $t_a$ ,  $t_{(a+b)/2}$  and  $t_{(a-b)/2}$ , but is poor for  $t_b$ , which explains the observed charge mobility anisotropy in crystalline pentacene.
lowest unfilled  $\pi^*$  MO when the molecule absorbs a photon with an energy equivalent to the energy difference between the two orbitals. Typical energy gaps range from 1.5-3 eV, meaning that photonic absorption and emission often occurs in the visible part of the electromagnetic spectrum [38].

The carrier mobility of organic semiconductor materials is much higher than that of most organic materials because the overlap of successive p-orbitals leads to *intramolecular* electron delocalisation. Electrons are not confined to the space around their parent atoms because the MOs are spread out over much of the molecule [39]. In the case of well-ordered *inorganic* semiconducting materials, the delocalisation of electron wavefunctions over equivalent lattice sites leads to band-type charge transport. This delocalisation occurs over length scales that are much longer than the lattice constant of the material [40]. While delocalisation of electrons also occurs within conjugated molecules, the electron wavefunctions remain localised to single molecules in the solid state, meaning that the band states remain very narrow. The carrier mobility in amorphous organic solids is therefore thought to follow a charge-hopping mechanism between the discrete electronic states of individual molecules [41].

High mobility band-like transport, originating from the strong coupling of  $\pi$ -orbitals on adjacent molecules, is observed in purified, ordered organic single crystals [42]. This is distinguishable from true band-type transport, because the delocalisation of charge carriers only extends over a few neighbouring molecules and the mobility decreases with increasing temperature [40]. The semiconductor pentacene displays this behaviour and is the subject of most of the research in this thesis. The structure of pentacene and its highest occupied molecular orbital (HOMO) level are shown in Figure 2.1(c) [38] and Figure 2.1(d) shows the unit

cell of a pentacene crystal [37]. Wide valence and conduction bands develop due to overlap of the HOMOs and lowest unoccupied molecular orbitals (LUMOs) on neighbouring molecules. The anisotropic nature of crystal structures means that the charge transport properties of organic solids often become anisotropic as the macroscopic order increases. In Figure 2.1(d), there is little overlap between molecules along the b-axis, so the transfer integral, t, is small. There is more orbital overlap between molecules along the a-axis and with the molecule in the centre of the unit cell, thus t is large in these directions. This anisotropy means that the orientation of molecules in thin films must be controlled to produce high performance OFETs.

The type of charge carrier in organic semiconductors (electron or hole) is affected by the impurities in bulk materials and also by the presence of electronegative atoms in the molecular structure [43]. Organic semiconductor materials exhibit a form of inherent doping, where intrinsic p-type or n-type conductivity is observed due to the different effective masses of charge carriers, different carrier concentrations and discrepancies in the depths of electron and hole traps [44]. In addition, some materials have been shown to exhibit an ambipolar character (both p-type and n- type conduction) [41].

## 2.1.2 Organic conductors

The Nobel Prize in Chemistry was awarded in the year 2000 to Alan Heeger, Alan MacDiarmid and Hideki Shirakawa, for the discovery of the method by which a doped conducting polymer, polyacetylene, could be produced [45]. Organic conducting polymers have the electronic, magnetic and optical properties of a metal, yet retain the mechanical properties of conventional polymer materials.



**Figure 2.2** The structure of the organic conductor poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). (a) PEDOT is conjugated and carries positive charges, while the sulfonyl groups in PSS (b) are deprotonated and carry a negative charge [7].

They are sometimes referred to as synthetic metals or as intrinsically conducting polymers, where the intrinsic properties are those of the polymer itself. In the pure state the polymer materials are either insulators or semiconductors, with minimal conductivities in the range of  $10^{-10}$  to  $10^{-5}$  S cm<sup>-1</sup>. The polymers may be doped by the addition of non-stoichiometric quantities of basic or acidic species [46]. Doped polymers with conductivities in the metallic regime (from 1 to  $10^4$  S cm<sup>-1</sup>) have been synthesised. The conductivities of these materials can be varied from the fully insulating to the fully metallic state by adjusting the concentration of the Poly(3,4-ethylenedioxythiophene) dopants [47]. poly(styrenesulfonate) (PEDOT:PSS) is one example of a high performance conducting polymer blend. PEDOT is conjugated and carries positive charges, while the sulfonyl groups in PSS are deprotonated and carry a negative charge (see Figure 2.2). In the native state the blend has a conductivity of 1 S cm<sup>-1</sup>. However, when it is doped with dimethyl sulfoxide (DMSO), conductivities of up to 1000 S cm<sup>-1</sup> can be achieved [7, 48].

# 2.2 THE PHYSICS OF ORGANIC FIELD EFFECT TRANSISTORS

Transistors are semiconductor devices that can be used as switches or for the amplification of electrical signals. They usually have three terminals, where the current between two terminals is controlled by the current or voltage at a third terminal [49]. OFETs and inorganic metal-oxide semiconductor enhancement FETs (E-MOSFETs) are closely related and familiarity with the construction and operation of E-MOSFETs is helpful in understanding how OFETs work [50-53]. However, this thesis is focused on the construction of OFETs and the particular materials selection challenges that are faced in this task. Some background information on the architecture of E-MOSFETs is provided in Appendix One for reference, but the rest of this chapter focuses on the physics of OFETs.

## 2.2.1 OFET geometries

The most common geometries used for the construction of OFETs are called the *top-contact bottom-gate* and *bottom-contact bottom-gate* configurations [54]. In the top-contact structure an insulating material is formed over a gated substrate. An organic semiconductor film is deposited on the insulator and two electrodes, the *source* and the *drain*, are then attached. A diagram of this architecture is shown in Figure 2.3. In the bottom-contact structure the source and drain are deposited on the insulator and are then coated with the semiconductor. In OFET research the gate commonly consists of a highly doped semiconductor wafer or a metal film, on top of which lies an insulating oxide layer that is a few hundred nanometres thick. In roll-to-roll printed electronics the insulator may be a flexible



**Figure 2.3** A top-contact bottom-gate OFET structure. The source electrode is usually connected to ground, while the drain and gate voltages are manipulated. The channel width, *W*, is defined as the length of the source and drain electrodes, while the channel length, *L*, is defined as the distance between them. Adapted from [54].

plastic film that doubles as the substrate; the gate electrode and other layers can be deposited onto either side.

The organic semiconductor film is deposited either from the vapour phase or from a solution and is typically much thinner than the other layers (about 30-50 nm). Surface treatments are sometimes applied to the insulating layer before depositing the organic layer and have been observed to vastly improve both the crystalline order of the semiconductor and its electrical characteristics. Metals are often evaporated through a shadow mask or patterned photolithographically to produce the source and drain electrodes, although conductive inks can also be printed on the semiconductor to form the electrodes. The channel lengths, L, usually range between 10  $\mu$ m to 100  $\mu$ m, while the widths, W, are between 100  $\mu$ m and 1 mm. By convention, the channel length is defined as the distance between the source and drain electrodes [54].

#### 2.2.2 p-type and n-type functionality in OFETs

The illustration in Figure 2.3 shows how the semiconductor and gate electrode are capacitively coupled by the insulating layer, such that when a negative gate bias  $V_G$  is applied, positive charge carriers collect at the semiconductor-insulator interface. Application of a negative drain voltage,  $V_D$ , attracts holes from the source towards the drain. In this example, the transistor displays 'p-type' operation, because the charge carriers in the semiconductor are positively charged holes. The type of charge carrier is an intrinsic property of the semiconductor and electrode materials, which means that dopants are not required to confer p-type or n-type character to the semiconductor [54].

The term field effect refers to the gate-voltage-induced charging of the semiconductor/insulator interface. The mechanism at work here is that of Faraday shielding, where mobile charges rearrange in the semiconductor under the influence of the applied electric field so as to nullify the field. Figure 2.4 demonstrates how a mobile charge carrier channel forms in an OFET. The positions of the HOMO and LUMO levels of the semiconductor material are drawn with respect to the Fermi levels of the source and drain electrodes (the black lines at the top of the yellow rectangles). The yellow rectangles represent the electrode valence bands and the white rectangles are the conduction bands. Figure 2.4(a) shows that the semiconductor energy levels are misaligned with the Fermi levels of the electrodes when no voltages are applied. Even if a nonzero  $V_D$  were applied to the drain electrode there would be no conduction because of a lack of mobile charges in the channel. If a positive  $V_G$  is applied, the situation in Figure 2.4(b) arises. The applied electric field causes a downward shift in the semiconductor HOMO and LUMO levels, relative to the electrode Fermi levels.



**Figure 2.4** (a) The energy level diagram of an OFET with no voltages applied at the electrodes. The electrode valence bands are shown in yellow. The Fermi levels of the contacts lie between the HOMO and LUMO levels of the organic semiconductor. (b) Electron accumulation in the semiconductor LUMO and (c) hole accumulation in the HOMO occur when a positive or a negative gate voltage are applied, respectively. (d) Electron transport and (e) hole transport occur under the influence of a positive and a negative drain voltage, respectively. Adapted from [54].

The Fermi levels of the contacts do not shift because they are fixed by externally set voltages. Electrons flow from the contacts into the LUMO when it is matched with the electrode Fermi level. If a positive  $V_D$  is then applied the electrons flow through the LUMO level into the drain electrode (Figure 2.4(d)). Thus, the transistor acts as if it has an n-type channel. If instead a negative  $V_G$  is applied to

the transistor, the HOMO and LUMO would rise with respect to the contact Fermi level, bringing the HOMO into resonance. Electrons would flow from the semiconductor into the contacts, leaving positive holes behind, as shown in Figure 2.4(c). If a negative  $V_D$  is applied, as in Figure 2.4(e),

then the mobile holes are free to flow into the drain electrode.

The model described above gives the impression that all organic semiconductor materials can be used in ambipolar transistors, simply by manipulating the applied gate voltage so that the semiconductor HOMO or LUMO match the Fermi levels of the electrode material. In practice this is not always possible, meaning that semiconductors are classified as n-type and p-type [54]. The concept most commonly used to assign the carrier types to specific semiconductors takes account of the work functions of the limited range of materials that are suitable as electrodes [55]. Calcium and aluminium, for example, have Fermi levels that lie near the LUMO for many common organic semiconductors. The problem is that these metals tend to oxidise easily, which shifts the Fermi level, meaning that they are not suitable reference materials. Semiconductor classifications are therefore made with respect to stable electrode materials like gold. Hence, the energy levels of the semiconductor do come into play – materials with low ionisation potential (HOMOs close to the vacuum level) are p-type, while those with high electron affinity (deep LUMOs, far from the vacuum level) are n-type. Some semiconductors, such as pentacene, have both low ionisation potential and high electron affinity and can be used in complementary electronics, where p-type and n-type behaviour is achieved in a single layer [55].

## 2.2.3 Current flow in an OFET

The source-drain current in an OFET is directly controlled by the relative magnitudes of  $V_G$  and  $V_D$ . Firstly, the gate voltage must exceed a certain *threshold voltage*,  $V_T$ , before a charge carrier channel forms at the insulator interface. OFETs can operate in one of three separate current regimes: the *linear regime*, the *pinch-off point* and the *saturation regime*. The linear operation regime is shown in Figure 2.5(a). Assuming that the source is connected to ground, if the difference between  $V_G$  and  $V_T$  is much more positive than  $V_D$ , the thickness of the charge carrier channel is uniform between the source and drain electrodes. In this regime the drain current scales linearly with the drain voltage. When the difference between  $V_G$  and  $V_T$  is equal to  $V_D$ , as shown in Figure 2.5(b), the gate voltage is effectively zero at the drain electrode. Hence, there are no charges present at this point of the semiconductor-insulator interface. The channel is said to have *pinched off* and the drain current no longer increases with further increases in  $V_D$ .



**Figure 2.5** A schematic representation of the charge carrier concentration in the sourcedrain channel, in three voltage regimes. (a) Linear regime. (b) Pinch-off point. (c) Saturation regime. Adapted from [54].

lies somewhere between the source and drain electrodes (see Figure 2.5(c)). The transistor is in the saturation regime and the drain current ideally remains constant even with further increases in  $V_D$ .

The source-drain current can be predicted based upon the electrode geometry and materials properties. The derivation of the OFET current-voltage relationships closely follows the procedure for E-MOSFETs and is available in many textbooks and journal articles [50, 52, 54]. It is fully outlined in Appendix Two, but the two major results for operation in the linear and saturation regimes, respectively, are presented here. In the linear regime:

$$I_{D,lin} = \frac{W}{L} C_{dlc} \mu \left( (V_G - V_T) V_D - \frac{V_D^2}{2} \right)$$
(2.1)

where W is the channel width, L is the channel length,  $C_{dlc}$  is the capacitance of the dielectric layer and  $\mu$  is the semiconductor mobility [54]. At low values of V<sub>D</sub> the squared term is negligible, thus the drain current scales linearly with V<sub>D</sub>. In the saturation regime, the current is equal to its value reached at the pinch off point. In this case, V<sub>D</sub> is equal to V<sub>G</sub> – V<sub>T</sub>. It follows that:

$$I_{D,sat} = \frac{W}{2L} C_{dlc} \mu_{sat} (V_G - V_T)^2$$
(2.2)

and it is clear that the drain current is independent of  $V_D$ . The saturation mobility,  $\mu_{sat}$ , is found from the slope of a plot of  $I_{D,sat}^{1/2}$  against  $V_G$ , while the threshold voltage can be easily determined by calculating the value of the intercept with the current axis. Transistor parameters are commonly reported in the saturation regime.

### 2.2.4 The characteristic curves of a transistor: output and transfer

The characteristic curves in Figure 2.6 demonstrate how well (2.1) and (2.2) model the behaviour of real transistors and can therefore be used for parameter extraction. The curves were recorded for an N,N'-dioctyl-perylene-3,4,9,10-tetracarboxylic acid diimide (C8-PTCDI) OFET [54]. The set of *output curves* in Figure 2.6(a) were produced by setting a constant  $V_G$  and then varying  $V_D$  from 0 to 100 V. The *transfer curves* in Figure 2.6(b) were made by setting  $V_D$  and sweeping  $V_G$  across a wide range of voltages. In the output curves, it is clear to see that (2.1) holds at drain voltages which are a small fraction of the gate voltage, that is  $I_D$  scales linearly with  $V_D$ . At higher voltages the quadratic term becomes significant and there is an increased curvature in the plot. A saturation region (constant  $I_D$ ) is observed when the drain voltage is comparable to the value of the gate voltage, in accordance with (2.2).

The transfer curves show that I<sub>D</sub> varies linearly with V<sub>G</sub> when V<sub>G</sub> – V<sub>T</sub> >> V<sub>D</sub>. In the saturation regime, when these voltages are comparable, I<sub>D</sub> varies quadratically with the gate voltage. The square root of I<sub>D</sub> plotted against V<sub>G</sub> has a linear segment, the slope of which can be used to determine  $\mu_{sat}$ . V<sub>T</sub> is found by



**Figure 2.6** (a)  $I_D - V_D$  output curves for an n-type PTCDI-C8 OFET at four values of  $V_G$ . (b)  $I_D - V_G$  transfer curves for the same transistor, at three values of  $V_D$ . The  $I_D^{1/2}$  vs  $V_G$  curve is linear where  $V_D >> V_G - V_T$ . Taken from [54].

extrapolating this line to the intersection with the horizontal axis, where  $I_D$  is zero and  $V_G$  must equal  $V_T$ .

## 2.2.5 Important design considerations for OFET architectures

There are a number of choices and tradeoffs to be made in the areas of materials selection and device geometry when seeking to optimise the performance of OFETs. These factors are reviewed extensively in a number of papers [54, 55] although a few of the most important ones are briefly mentioned here.

- Morphology of the semiconductor at the dielectric interface: The Mott-Gurney charge distribution analysis suggests that the thickness of the gate voltage enhanced channel is usually only a fraction of the thickness of the semiconductor layer [55]. The morphology of the bulk of the semiconductor layer has less influence on the device performance than the molecular packing and orientation at the insulator surface.
- **Contact resistance**: Contact resistance arises at the metal-semiconductor junction and is usually greater than the resistance across the channel in high mobility semiconductors. According to the Schottky-Mott model, good ohmic contacts are formed when the Fermi level of the electrodes and the HOMO or LUMO of the semiconductor are aligned [55]. Reducing the resistance should be a matter of choosing materials with matching energy levels, but this is usually complicated by the formation of an interface dipole barrier (see Figure 2.7). The electron density of isolated metals tails off from the surface into the surrounding vacuum, but



**Figure 2.7** Photoelectron spectroscopy measurements of an Au-pentacene interface show that a dipole barrier of 1.05 eV exists between the two. With no dipole the pentacene HOMO would be 0.2 eV higher than the Au Fermi level. With the dipole it is 0.85 eV lower [55].

adsorbed molecules push the electrons back into the surface, lowering the metal work function and leading to the formation of a dipole barrier. The differences between the microstructure of the semiconductor on the electrodes and on the dielectric layer also diminish performance in bottom-contact OFETs, while access resistances through the film can hamper top-contact devices.

Good film forming properties: Vapour-deposited small-molecule organic semiconductors typically form granular polycrystalline films. Grain orientation strongly affects charge mobility; when the long axis of the grains is oriented along the source-drain channel, a higher apparent mobility is observed because the charges cross fewer grain boundaries. Evaporation rates and substrate temperatures can be varied to influence the level of grain connectivity and ordering. Solution processed films do not normally exhibit a level of crystallinity comparable to that achieved in

vapour deposited films, so bulky substituents are sometimes added to small molecules or polymers to effect a preferred crystalline packing after evaporation of the solvent [54].

- Chemical purity and device stability: Hysteresis is often observed in organic transistor transfer and characteristic curves. Over time, charges fill deep trap states at the dielectric/semiconductor boundary. The trapped charges change the threshold voltage required for channel formation. The trapping is affected by chemical purity and the structure of the organic film. Impurities can act as dopants, which leads to high off-currents, current leakage through the ungated portions of the device and increased power usage [54]. Achieving high device stability is a major problem, particularly for n-type transistors. In section 2.2.2 it was shown that the electron affinity (EA) of n-type materials must be large enough to allow electron injection from typical electrode materials into the semiconductor LUMO. At a minimum the EA needs to be about 3.0 eV, but the maximum practical electron affinity is considered to be around 4.0 eV because if a molecule is too electrophilic it is susceptible to doping by atmospheric moisture. Molecular anions form under positive gate bias and readily reduce the oxygen and water molecules that diffuse into thin organic films. Encapsulation of the transistor can help to slow this process, but adds cost and rarely acts as a perfect barrier to contaminants [54].
- Low-capacitance versus high-capacitance dielectrics: From (2.1) and (2.2) it can be seen that a large insulator capacitance should be an

advantage in OFETs, because it leads to a higher drain current given a certain applied voltage. Inorganic insulators often have high  $C_{dlc}$  values, but are mechanically inflexible. Organic insulators on the other hand usually have low  $C_{dlc}$  values, but they are easier to deposit. The insulator choice is complicated by the transport model suggested by Veres et al., which implies that charges hop in a Gaussian distribution of states [56]. This distribution is broadened by dipolar disorder at the insulator interface, disorder which scales as a function of  $C_{dlc}$ . Thus, low- $C_{dlc}$  dielectrics may actually lead to better transistor performance than high- $C_{dlc}$  dielectrics despite the capacitance of the insulator layer being lower.

# 2.3 FABRICATION OF OFETS: CONVENTIONAL APPROACHES FOR PATTERNING THE SEMICONDUCTOR LAYER AND CONTACTS

While the development of materials with ever higher charge-carrier mobility is required for the commercialisation of OFETs, this alone is not adequate for the production of high-performance OFET arrays. Transistor matrices, relevant to applications such as OLED display backplanes, must have minimal parasitic leakage currents to avoid cross-talk between neighbouring circuit elements [57]. A low off-current is also essential to ensure that there is an appreciable visual contrast ratio in LED pixels addressed by different transistors [58]. To satisfy both of these requirements the organic semiconductor should be patterned to restrict the flow of charge carriers to only the transistor channel, yet patterning is the most time and capital intensive part of the transistor fabrication process [59]. A diverse range of processing schemes that are compatible with both organic and traditional solid-state materials have been devised. The advantages and failings of some of these techniques will be briefly discussed here, so as to place the major topic of this thesis, *direct photopatterning*, into context [60].

# 2.3.1 Photolithography

Photolithography has been used for several decades to pattern transistor source and drain electrodes in inorganic electronics processing [61]. These processes act on whole wafers with many individual circuit elements, so that if a material is not required in certain regions it must be etched away or lifted-off by dissolving an underlying photoresist. In photolithographic patterning, a *photomask* defines areas where a light sensitive film, the *photoresist*, is exposed. The photoresist is developed after exposure and serves as a temporary mask for the following deposition steps [62]. Organic materials such as polyisoprene and phenolformaldehyde resin are commonly used as photoresists.

Photolithography can deliver the high-resolution required for electronics, but requires the application and removal of several photoresist layers. Exposure to solvents commonly used in photolithographic processing, even those in which certain organics are nominally insoluble, has been shown in some instances to degrade OFET performance by delaminating the semiconductor film or changing the film morphology [63, 64]. There have been some successful demonstrations of organic device patterning via photolithography using *orthogonal solvents*; photoresist solvents that do not dissolve the organic semiconductor and other layers [65]. Most organic materials are oleophilic or hydrophilic, that is they dissolve in either non-polar organic solvents or polar solvents that contain hydroxyl groups (solvents which are typical of most traditional photoresist systems). By using photoresists that are composed of fluorinated compounds that dissolve in fluorous solvents, it is possible to pattern and remove photoresist layers without damaging underlying layers of materials. Orthogonal solvent processing allows the large knowledge base and existing infrastructure for photolithography to be used for organic electronics. However, photolithography also has a high cost per unit area and is mainly suitable for the production of high performance devices such as computer processors. The advantage of organic electronics is the prospect of a much lower price-point than is possible for silicon electronics and this is more likely to be achieved with lower cost processes than photolithography.

### 2.3.2 Inkjet printing

Methods such as *inkjet printing* are a viable path to achieving cost savings in the production of organic displays and transistors [61]. Droplets of an organic solution are ejected from the nozzle of a modified inkjet printer to form the electrodes of a transistor, or to deposit the semiconductor layer [15]. Feature sizes of approximately  $25 \,\mu\text{m}$  can be routinely achieved [63]. However, by prepatterning the substrate surface with hydrophobic polymer walls that act to contain the droplets, transistor channel lengths as short as 200 nm have been demonstrated [15, 63]. The main shortfall of this technique is that high-resolution, rapid printing of the surface dewetting pattern must be perfected and this means returning to slow, expensive techniques such as photolithography [57].

An alternative to surface patterning is the self-aligned printing technique, where surfactants are added to the ink or an intermediate surface treatment step is performed between printing certain device structures [66]. In one example of this process, a strip of the conducting polymer PEDOT:PSS was printed on a glass substrate. The surface was then given a carbon tetrafluoride (CF<sub>4</sub>) post-deposition plasma treatment, creating a low-energy fluorinated surface on the PEDOT:PSS while increasing the surface energy of the glass. A second, overlapping PEDOT:PSS strip was printed on the first one, which flowed off the low-energy surface onto the glass and conformed to the edge-shape of the first strip. Sub-100 nm channel lengths were achieved [66].

# 2.3.3 Nanoimprinting

The *nanoimprinting* technique uses a hard mould with extended surface features to print a pattern into a comparatively soft organic film [67]. Silicon moulds are commonly patterned by conventional lithographic techniques. Imprinting is performed above the glass transition temperature of the organic layer, so that when the mould is pressed into the film, the fluid flows into the mold channels. OFETs are routinely produced with channel lengths between 500 – 1000 nm [68]. The main drawback of nanoimprinting has so far been the errors produced in complex, large-area patterns, due to deformation of the stamp [57]. Replacement stamps must be fabricated by costly optical lithography techniques [69]. Additionally, the patterning resolution is limited by the uncontrolled flow of liquid at high temperatures and by intermixing of molten materials [67].

## 2.3.4 Roll-to-roll printing

*Roll-to-roll* printing methods use a substrate in the form of a very long, mechanically flexible sheet (see Figure 1.2). In an optimised fabrication process, the bare substrate is unwound from one roll, enters the printing system and

emerges as a completed device that can be wound onto another roll. Printing of the semiconductor, dielectric or electrode inks are only a few of the steps that occur in this fabrication mechanism; heating, drying and UV curing treatments must also take place in sequence. Due to the typically order of magnitude differences in spraying, drying, annealing and patterning times, the printing process actually occurs in discrete steps, where the substrate is rolled up and unrolled multiple times. Several methods are available for patterning the deposited solutions. *Slot-die coating*, which feeds ink out of a nozzle, can be used to produce thin lines that can be both perpendicular and parallel to the direction of substrate movement. Alternatively, gravure rolling allows for two dimensional film patterning on a moving substrate. It typically involves a two roller system, where one of the rollers has a pattern engraved on the surface, both around the diameter and along the length of the cylinder. A mist of solution is formed in spray-coating, by forcing the printing ink through a fine nozzle. Carrier gases and electrostatic charging may be employed to direct the aerosol towards the substrate and to influence the drying time of the solution. Roll-to-roll printing is widely seen as the most efficient way of producing affordable organic electronics [16].

# 2.4 THE APPLICATION OF DIRECT PHOTOPATTERNING IN THE PRODUCTION OF ORGANIC ELECTRONIC DEVICES

The electronic components of an OFET should ideally be fabricated by simple, reliable techniques. In the context of device patterning, selective *photobleaching* or *photostructuring* refers to a spatially resolved manipulation of the chemical structure in the active materials of a device, by irradiation through a mask or by the translation of a light source [70]. In principal this appears to be a simple

approach, overcoming some of the drawbacks of the techniques in section 2.3, but to be truly successful it requires the design of materials with excellent solubility, photosensitivity and charge mobility. The fact that OFETs require precise patterning of active materials into structures with feature sizes on the scale of 100 nm to 100  $\mu$ m presents a considerable challenge [70]. The following section of this review examines procedures that have been used to locally photopattern structures in organic materials. The research that is discussed does not necessarily pertain directly to the construction of OFETs. Rather, the lessons learned from these independent streams of research may be brought together to inform the task of engineering OFETs by the selective photobleaching of organic materials.

# 2.4.1 Manipulating the photoluminescence of OLEDs

Kocher et al. examined the technique of spatially resolved photobleaching by producing 'chessboard' patterns in an electroluminescent polymer blend [70]. Films of EHO-OPPE/UHMW-PE and POPOP/LLDPE were irradiated through a mask with white light from a Xe UV lamp. The quartz photomask was coated with metal squares having lateral dimensions of 200 µm. The two photobleached films were then stacked in a bilayer fashion, so that the photobleached regions of one film overlapped with the pristine regions of the other. The array is shown under excitation by 365 nm light in Figure 2.8(a). The EHO-OPPE/UHME-PE film fluoresces with a green colour, while POPOP/LLDPE fluoresces blue. The polymer chains in the films happen to be aligned and therefore emit polarised light. Figure 2.8(b) and (c) are pictures of the bilayer array taken through a polariser with the optical axis parallel to the drawing direction of the blue POPOP and the green EHE-OPPE blends, respectively. Photoluminescence only occurs



**Figure 2.8** (a) A bilayer stack of two oriented, photostructured polymer blend films, shown under excitation at 365 nm. Green corresponds to EHO-OPPE/UHMW-PE and blue corresponds to POPOP/LLDPE films. Pictures are taken through a polariser with optical axis parallel to the drawing direction of the POPOP film (b) and parallel to the EHO-OPPE film (c). Image from [70].

from the pristine parts of the films.

# 2.4.2 Fabricating waveguides in polymer materials

Selective photobleaching has been used to pattern micron scale optical waveguide structures, by driving refractive index changes in organic thin films exposed to light tuned to the absorption band of the target material. Rochford et al. produced waveguides using the fact that poly[5,7-dodecadiyn-1,12-diol-bis(nbutoxycarbonyl-methyl-urethane)] (poly-4BCME) films become transparent when irradiated with UV or visible light in air [71]. A similar process of waveguide fabrication by photobleaching was demonstrated with the organic ionic crystal 4-(4-dimethylaminostyryl)-1-methylpyridinium tosylate (DAST) [72-75]. DAST is organic nonlinear optical (NLO) crystal and is of interest in the an telecommunications industry because of its low dielectric constant and large NLO coefficient. The chemical structure is shown in Figure 2.9(a). The salt consists of a positively charged stilbazolium cation and a negatively charged tosylate anion [72]. Photolithography is not a suitable technique for patterning DAST as the



**Figure 2.9** (a) The chemical structure of DAST and (b) a waveguide produced by photobleaching a DAST film. The minimum channel width is  $40 \mu m$  [73, 74].

material readily dissolves in water and standard organic solvents [74]. Photobleaching is a very attractive technique for creating a refractive index difference between the core of the waveguide and the cladding as it decreases the refractive index of DAST only in the UV exposed areas, thereby laterally confining light in the waveguides [72, 74].

The multimode optical waveguide in Figure 2.9(b) was fabricated by setting a photomask along the b-axis of a thin DAST crystal and exposing it to 0.24 W/cm<sup>2</sup> radiation from a Xe lamp for 65 hours [73]. The minimum channel width achieved was approximately 40  $\mu$ m. The depth of the refractive index change caused by photobleaching was estimated to be about 7-8  $\mu$ m, as determined by calculation of the diffraction efficiency of a fabricated refractive index grating [73, 74]. Infrared spectra of a DAST crystal showed that laser irradiation at 532 nm, at a power of 0.52 W/cm<sup>2</sup> for seven hours caused a reduction in the absorption peaks corresponding to the C=N, C-N and C=C vibrations. It is clear that decomposition of the molecules in the DAST crystal leads to the refractive index changes, by both scission of the C=C bonds of the

styryl moiety and decomposition of the pyridinium ring [74]. Bleaching did not occur in an  $N_2$  atmosphere, but proceeded quickly in an  $O_2$  environment, confirming that the photobleaching was actually a photo-oxidation process [72].

## 2.4.3 Electrical isolation of OFETs

Post deposition patterning of a solution deposited organic semiconductor, triethylsilylethylnyl anthradithiophene (TES-ADT), was investigated as a means of reducing parasitic leakage between OFETs and for improving the on/off current ratio [58]. The channel area of the thin-film transistor was isolated by exposing the non-channel regions of the film to 365 nm UV light at 540 mW/cm<sup>2</sup> for 1-2 minutes, in the presence of 1,2-dichloroethane solvent vapours. The result was that the TES-ADT dewetted the substrate in the exposed regions. The thermal energy provided by the UV light in the irradiated regions allowed the TES-ADT, which was sufficiently mobile due to the presence of the dichloroethane solvent vapours, to migrate from the substrate surface to the nearby, unirradiated TES-ADT surface. Figure 2.10(a) shows the gold source and drain electrodes covered in a polycrystalline film of TES-ADT, prior to treatment. The channel area was isolated after UV exposure, resulting in a square region of TES-ADT with the boundaries highlighted by the black dotted lines in Figure 2.10(c). The corresponding output curves for each of the transistors are shown in Figures 2.10(b) and (d) respectively. The charge carrier mobilities are comparable, but the parasitic leakage currents that are present in the unpatterned transistor at small source-drain currents are absent in the patterned transistor. The off current in the patterned transistor was an order of magnitude lower than the unpatterned transistor [58]. The UV-visible near-infrared spectra of the TES-ADT films were



**Figure 2.10** (a) Optical micrograph and (b) current-voltage characteristics of an unpatterned TES-ADT thin-film transistor. (c) Optical micrograph and (d) current-voltage characteristics of a TES-ADT transistor patterned by UV light in the presence of a solvent. The channel width is 500  $\mu$ m, the length is 100  $\mu$ m [58].

identical before and after illumination, demonstrating that there was no chemical decomposition as a result of the light exposure. However, the same results may have been achieved if the material in the illuminated region underwent a chemical change from a semiconductor into an insulator [58].

In another demonstration of device isolation by photobleaching, a film of poly(3-hexylthiophene) (P3HT) was exposed to pulses from a KrF excimer laser operating at 248 nm [57]. A test pattern, shown in Figure 2.11, was examined to determine the correct UV dose required to reduce the conductivity of the film without ablating it. P3HT OFETs were subsequently exposed to a fluence of 50 mJ/cm<sup>2</sup> per pulse. The mobilities of the pristine OFETs initially ranged from  $1.8 \times 10^{-3}$  to  $4.4 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. After one pulse the mobility fell to  $3.4 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. After sixteen pulses the mobility decreased further to  $7 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. It appears that by limiting radiation exposure to the regions of



**Figure 2.11** Photograph of a test pattern designed to determine the laser fluence and number of pulses required to photobleach P3HT without ablating the film. The light source was a 248 nm KrF excimer laser. The colour of the squares give a visual indication of the extent of photobleaching [57].

a P3HT film outside of the active semiconductor channel, the chain length of the polymer can be reduced by a photochemical reaction. This then reduces the charge carrier mobility and isolates the OFET from adjacent devices [57].

# 2.4.4 Photopatterning of conjugated polymers doped with a photoacid generator

Organic conductors may serve as the electrodes and interconnects in OFETs and other organic electronic devices. As discussed in section 2.1.2, conjugated polymers are normally combined with a dopant to enhance their conductivities when used as synthetic metals. For example, polyaniline (PANI) becomes a conductor when doped with camphorsulfonic acid (CSA). If the dopant is photosensitive, then the local conductivity of a film can be controlled by exposing selected regions to light. If a PANI solution is combined with a photoinitiator, 1hydroxycyclohexylphenylketone, UV exposure produces free radicals that cleave the CSA group from PANI. This converts PANI into a nonconductive form, with a sheet resistance of  $10^{14} \Omega$ /square compared to  $10^3 \Omega$ /square for the unexposed film [22]. Other polymers such as the polythiophene derivative, poly(3-(2-(tetrahydropyran-2-yloxy)ethyl)thiophene) (PTHPET), can also be photopatterned by combination with a photoacid generator. Acid cleaves the terahydropyran group from the PTHPET, producing a new polymer with a short side chain and reduced polarity. The reduction in polarity leads to the polymer becoming insoluble. Washing with a solvent removes the original PTHPET, leaving patterned features. Feature sizes of 15 µm in films with conductivities of 1-4 S/cm have been achieved by this method [22].

Cross-linking of polymers usually has an effect on their solubility. This fact was used to photopattern P3HT. UV exposure of the polymer in the presence of metal salts results in chain scission and the production of free radicals. These radicals remove hydrogen atoms from hydrocarbons and also result in the formation of hydroperoxide when the UV exposure is carried out in an oxygen environment. Continued illumination cleaves the peroxide and forms ether linkages between neighbouring polymer chains. The unexposed region is washed away, leaving a pattern of the photo cross-linked polymer. Exposure to nitrosonium tetrafluoroborate improves the conductivity of the remaining cross-linked P3HT. Line widths as short as 1 µm have been reported [22].

# 2.4.5 Photopatterning conjugated polymers from precursor films

Poly(p-phenylene vinylene) (PPV) is an electroluminescent conjugated polymer, the derivatives of which have been studied extensively and used as the active



**Figure 2.12** (a) The precursor material PXT in converted to the electroluminescent polymer PPV via thermal or optical exposure. (b) A tapping made AFM scan of an image produced in a PPV film by scanning near-field optical lithography using a 50 nm diameter probe aperture with a 325 nm light source. The pattern consists of approximately 65 000 overlapping pixels. (c) Tapping mode AFM scans highlighting the features shown in the white square in (b). The cross sections show that the smallest feature size achieved was in the range from 60 – 75 nm. Images are taken from [76].

material in OLEDs and organic photovoltaics. PPV films can be optically patterned on the sub-micron scale using a process called *scanning near-field optical lithography* [76]. This approach involves the optical or thermal conversion of a precursor compound, poly(p-xylene tetrahydrothiophenium chloride) (PXT), to insoluble PPV by means of a leaving group reaction (see Figure 2.12 (a)). The patterned film can be rinsed with methanol to remove any remaining PXT. A postrinse vacuum bake at 200 °C converts any remaining PXT to PPV [77].

The advantage of scanning near-field optical lithography and optical scanning probe techniques in general is that high resolution patterns can be written without the need for photomasks, which potentially reduces costs and allows for rapid prototyping of new devices. The image of a patterned PPV film in Figure 2.12 (b) was produced using a scanning near-field optical microscope as a near-field light source. The PXT precursor film was exposed to 325 nm laser light through a sharpened, gold coated optical fibre probe with a 50 nm aperture at the apex. The structure covers an area of 20  $\mu$ m × 20  $\mu$ m and was generated from 65 000 overlapping pixels. A range of feature sizes were produced, from a few microns to tens of nanometers. Tapping mode atomic force microscopy (AFM) scans of the smallest features are shown in Figure 2.12 (c). The cross sections of the developed PPV features are around 60 – 75 nm wide, demonstrating the high resolution patterning capabilities of this technique.

## 2.4.6 The argument for direct photopatterning

The demonstrations of photopatterning outlined above give strong support to the concept of fabricating organic electronics using photosensitive active materials. The features of the chessboard pattern produced by photobleaching electroluminescent polymers had lateral dimensions larger than would be desired for high performance OFETs, but this was simply due to the use of a rather crudely patterned mask. The fundamental physical and chemical limitations governing the resolution of patterned features should be the same as conventional photolithographic processes [70]. The study of DAST waveguides also showed that oxidative photobleaching could produce features around 10  $\mu$ m wide. It is easy to imagine using a similar technique to pattern such high resolution features for the electrodes of an OFET, or to isolate a semiconductor channel by photobleaching around it, as demonstrated in the TES-ADT transistor. The problem is to find materials that undergo rapid, facile chemical changes when

exposed to light, so as to maximise manufacturing throughput. The solutions to this problem are examined in the remainder of this chapter.

# 2.5 THE PRECURSOR ROUTE TO THE DEPOSITION OF ORGANIC SEMICONDUCTORS

Most research on organic small molecule semiconductors has proceeded using thin film transistors as the test bed, given that they have an architecture that is amenable to a variety of applications. Figure 2.13 shows the rise in the reported semiconductor mobilities for solution processed and vacuum deposited polymers and small molecules, between 1984 and 2010. The performance of all classes has improved at a similar rate over this time, with the high mobility of pentacene long



**Figure 2.13** The highest mobilites for the six major classes of organic semiconductors, reported between 1984 and 2010 [78].

being the stand-out performer against which new materials and processes were evaluated [78]. A great deal of research was conducted over the past two decades in an effort to optimise the performance of pentacene OFETs, specifically.

### 2.5.1 Pentacene OFETs: The state of the art

From the mid-1990s until the mid-2000s, the highest reported organic semiconductor mobilities consistently came from pentacene devices. Through continual optimisation of processing conditions, transistor geometry, dielectric selection and surface treatments, the highest reported *thin-film* pentacene OFET mobility rose from  $0.62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in 1996 to  $7.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in 2005 [23]. Carrier mobilities for many other materials are now routinely reported to exceed the benchmark of 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> that is achieved with amorphous Si FETs. The highest reported mobility for a transistor with a *single crystal* pentacene layer is almost 60 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [79]. Despite recently losing its place as the highest performance thin film organic semiconductor to new classes of materials, pentacene remains useful for testing device design concepts in organic electronics research because of the vast body of research on its behaviour [23].

Since pentacene is insoluble in most organic solvents a great deal of research has been conducted with the aim of imparting solubility, whilst maintaining the high performance resulting from the regular close-packing that occurs in vacuum deposited films [79]. Several approaches have been used, including end-substitution of pentacene with electron withdrawing groups, functionalisation at the central ring with bulky substituents and substitution of heteroatoms such as sulfur into the pentacene carbocyclic rings. The most interesting modification to pentacene, when concerned with photopatterning of thin films, was the development of *reversible functionalisation*. The pentacene molecule is bridged across one of its aromatic rings with a solubilising moiety. In this case the ring acts as a diene in retro Diels-Alder reactions. As mentioned in Chapter 1, the first such derivative to be demonstrated had a thermally labile tetrachlorobenzene group attached to the 6,13 carbons of the central ring. Heating the precursor at 180 °C for only 5 s produced pentacene films with mobilities of  $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and on/off current ratios of  $10^6$  [79]. A number of related derivatives that undergo a conversion to pentacene by exposure to light instead of heat have also been synthesised and are discussed next.

# 2.5.2 Reversibly functionalised pentacene: Retro-cycloaddition

Reversible functionalisation of pentacene precursors is a powerful strategy for both solubilising pentacene and for patterning active layers in devices. As discussed, several precursors have been synthesised, but it is the few that are photochemically modifiable that are of most interest in this thesis. Figure 2.14 shows the structures of three photosensitive pentacene precursors: (a) N-sulfinyl*tert*-butylcarbamate pentacene, (b) 6,13-dihydro-6,13-methanopentacene-15-one and (c) 6,13-dihydro-6,13-ethanopentacene-15,16-dione. The photochemistry of these materials and their application to devices is discussed in this section. The mechanisms that govern thermally and photochemically allowed Diels-Alder reactions are found in many standard organic chemistry textbooks and primers [81, 82], but a brief outline is provided in Appendix Three for ease of reference. The reaction that occurs when N-sulfinyl-tert-butylcarbamate pentacene and 6,13dihydro-6,13-ethanopentacene-15,16-dione are exposed to light is a standard *ene*-

diene retro-cycloaddition reaction. An example of such a reaction is shown in



**Figure 2.14** (a) N-sulfinyl-tert-butylcarbamate pentacene [27] (b) 6,13-dihydro-6,13methanopentacene-15-one [28] and (c) 6,13-dihydro-6,13-ethanopentacene-15,16-dione [80].

Figure 2.15(a) [82]. In this reaction anthracene and diazene are formed from the adduct of the two molecules. The reaction is thermodynamically favourable because the formation of the aromatic ring in anthracene means that the product is more stable than the starting material. The arrows show the movement of electron pairs around the bonds of the bridging moiety and the central ring. An electron pair moves from the  $\sigma$ -bond connecting the bridge to the ring, towards the bond connecting the two nitrogen atoms on the bridge. This then becomes a double bond. The other two arrows show how the electrons move to generate the aromaticity of the ring. The reaction that occurs when 6,13-dihydro-6,13-methanopentacene-15-one is exposed to light is a special case of a retro-cycloaddition known as a *chelotropic* reaction. In this case two bonds are broken at a single atom and that atom accepts an electron pair. The movement of electrons in two different reactions is shown in Figure 2.15(b), where in both cases a single atom accepts a pair of electrons and leaves the molecule [82]. A nitrogen molecule and a carbon monoxide molecule are easily generated from



**Figure 2.15** (a) A retro-cycloaddition reaction, with the arrows showing the movement of electron pairs between the bonds on the bridging group and the central ring. Bond breaking occurs to produce a diene (anthracene) and an ene (diazene) from the adduct of the two molecules. The generation of an aromatic ring in anthracene means that the reaction is thermodynamically favourable. (b) Bond making occurs at a single atom in a chelotropic cycloaddition; two  $\sigma$ -bonds are made to the same atom. In the chelotropic retro-cycloadditions shown above, two  $\sigma$ -bonds are broken at a single atom. Adapted from [82].

their respective parent compounds in the example above.

A comprehensive overview of the literature regarding these photosensitive pentacene precursors is provided here because all of the research in Chapters Five, Six and Seven relates to the spectroscopic analysis of this class of materials and testing of these materials in OFETs. Particular attention is given to the material 6,13-dihydro-6,13-ethanopentacene-15,16-dione, because it has been the subject of the most thorough research into the preparation of OFETs by the photopatterning of a semiconductor precursor. The literature regarding the materials 6,13-dihydro-6,13-methanopentacene-15-one and 5,14-dihydro-5,14-methanopentacene-15-one is also discussed in detail because these two materials were used in the OFET research that is presented in Chapter Six.

#### 2.5.3 N-sulfinyl-tert-butylcarbamate pentacene OFETs

N-sulfinyl-*tert*-butylcarbamate pentacene can undergo a conversion to pentacene when heated at 150 °C [27]. Figure 2.16 shows the IR and UV-visible spectra of



**Figure 2.16** Infrared and UV-vis spectra of the N-sulfinyl-tert-butylcarbamate pentacene precursor before heating and its conversion to pentacene after heating. The heated precursor material leaves a residue that shares an infrared spectrum with pure pentacene. The UV-vis spectrum of the heated material is also similar to that of pure pentacene [27].

the material on a silicon wafer and a quartz disk, respectively. Pentacene spectra are also shown for comparison. After heating, the spectra of the precursor film clearly show that a conversion to pentacene has taken place. N-sulfinyl*tert*-butylcarbamate pentacene is not strictly a photosensitive material, although films have been photopatterned using the technique sometimes applied for patterning organic conductors. That is, films of this precursor are combined with a photo acid generator (PAG) and the acid labile bridging group is removed by heating the areas of the film that were exposed to light.

Figure 2.17 shows an optical microscope image of a pentacene pattern on a silicon wafer, that was produced by exposing the precursor and a PAG to UV light through a chrome/quartz mask for 1 min and then heating at 130 °C for 5 mins [27]. After the post exposure bake, the areas illuminated by UV became



**Figure 2.17** The UV exposed N-sulfinyl-tert-butylcarbamate pentacene precursor on silicon. 40  $\mu$ m wide pentacene channels were patterned through a chrome photomask and appeared after heating at 130 °C [27].

dark purple in colour (the same colour as pentacene). The acid catalysed the conversion of UV exposed regions to pentacene, at a lower temperature than required in the shadowed regions. The unconverted precursor was then removed by rinsing in methanol. Features on the scale of 40  $\mu$ m were photopatterned. An OFET was also produced in the same study, having a channel length of 15  $\mu$ m and a width of 1 mm. The mobility and on/off ratios in the linear regime were 0.13 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 3 × 10<sup>5</sup>, respectively. In the saturation regime, the values were 0.25 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 8 × 10<sup>4</sup>.

# 2.5.4 6,13-dihydro-6,13-methanopentacene-15-one OFETs

A bottom contact OFET using 6,13-dihydro-6,13-methanopentacene-15-one (6,13-MPn) as the semiconductor precursor was fabricated by Chen et al. via a heat driven process [28]. An n-doped Si wafer was used as the substrate and gate. The insulator was a 200 nm thick thermally grown  $SiO_2$  layer. Interdigitated, 30 nm-thick gold electrodes were lithographically patterned on top of the  $SiO_2$ 



**Figure 2.18** (a) The output curves for a pentacene transistor thermally converted from 6,13-MPn [28]. (b) The absorption spectrum of 6,13-MPn in a degassed THF solution changes as it is irradiated with 310 nm light. Strong pentacene absorption peaks develop in the range from 450-600 nm, while 6,13-MPn peaks below 350 nm disappear [83].

layer, producing a channel width of 20 cm and channel length of 10  $\mu$ m. 6,13-MPn was then spin-coated over the structure and thermally converted to pentacene at 150 °C. An on/off current ratio of  $1.2 \times 10^5$  was measured and the apparent  $\mu_{sat}$  was  $8.8 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The output curves for this transistor are shown in Figure 2.18(a) [28]. The reported mobility is far lower than what is typically observed in vacuum deposited pentacene OFETs, however the low solubility of the precursor probably meant that the source-drain channel was not completely covered. The authors suggested that changing solvents, performing surface modifications on the dielectric and further thermal annealing could all aid in improving the device performance [28].

Chuang et al. found that irradiating 6,13-MPn in a degassed tetrahydrofuran (THF) solution at room temperature, with 310 nm UV light, changed the appearance of the compound from colourless to purple [83]. A series of absorption bands appeared between 450-600 nm, matching the vibronic progression observed in solutions of pentacene (Figure 2.18(b)). As happens when 6,13-MPn is heated, carbon monoxide is released from the molecule during


**Figure 2.19** When pentacene absorbs light it first transitions into a singlet excited state, then it may decay to a triplet state through intersystem crossing. Triplet excited pentacene in the presence of ground state triplet oxygen can transfer energy to the oxygen molecule, producing singlet oxygen and ground state pentacene. Singlet oxygen and ground state pentacene then react to produce the Diels-Alder adduct, pentacene endoperoxide. Pentacenequinone is produced by continued oxidation [86].

photolysis. Conversion of the precursor to pure pentacene only occurred in deoxygenated solutions [83]. When photolysis took place in aerated solutions, secondary reactions occurred between the pentacene product and oxygen molecules, following the reaction scheme shown in Figure 2.19 [29, 83-88]. Decay from the first excited state of pentacene sensitises singlet oxygen. Singlet oxygen then attacks ground-state pentacene in a Diels-Alder addition reaction, forming a peroxide bridge across one of the aromatic rings.

Chuang et al. also fabricated an OFET with a similar architecture to that used by Chen et al., except that an alternative precursor known as 5,14-dihydro-5,14-methanopentacene-15-one (5,14-MPn) was also used [83]. This had the carbonyl moiety bridged over the second pentacene ring, rather than the middle ring. An equimolar solution of the two precursors was deposited as the active layer. Photolysis of the film, at ambient temperature in a drybox, yielded a device with an on/off current ratio of  $3.96 \times 10^4$  and a field effect mobility of  $2.4 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The specific wavelength range used for the solid-state photolysis was not reported [83]. The experiment did show that photolysis of the precursor in the solid state is a viable means of producing OFETs, however difficulty in obtaining completely contiguous films of the precursor was suggested to be the main reason for the low apparent mobility and on/off ratio.

### 2.5.5 6,13-dihydro-6,13-ethanopentacene-15,16-dione OFETs

The highest performance OFETs produced by the photolysis of pentacene precursors have been made using the diketone bridged precursor, 6,13-dihydro-6,13-ethanopentacene-15,16-dione (6,13-EPn), shown in Figure 2.14(c). In a study by Matsumoto et al., 6,13-EPn in a chloroform/acetone solution was spun over an OFET bottom contact architecture. By combining mild heat treatment (not actually hot enough to directly decompose the precursor), simultaneous irradiation with light and treatment of the insulator surface with methyl silsesquioxane (MSQ), a carrier mobility of 0.34 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an on/off ratio of  $2.0 \times 10^6$  were measured for the transistor [80]. In Matsumoto et al.'s experiments, the thin film transistors were exposed to UV and visible light from a 250 W, PCS-UMX250 metal-halide lamp, with a filter to remove light below 300 nm. 6,13-EPn converts to pentacene when its broad absorption feature, centred at 460 nm, absorbs light. 6,13-EPn is thermally stable up to temperatures exceeding 300 °C and annealing it at moderate temperatures does not produce pentacene.

Table 2.1 shows how the mobilities and on/off ratios of the transistors depend on the illumination time and annealing temperatures [80]. The UV-visible

spectra of films on quartz plates (Figure 2.20), which are exposed under the same conditions as OFET samples A-C, show that after 5 mins of illumination the precursor absorption is still seen at 460 nm and in the UV region. With further illumination, the pentacene peaks between 500-700 nm continue to rise and the precursor peaks diminish. Despite the stronger pentacene absorption, the transistor performance decreased with longer exposure times as holes formed in the film due to sublimation of the pentacene. This also occurred as annealing temperatures were elevated. Sample D, which was heated to 197 °C, had a better mobility and on/off ratio than sample B except that sublimation led to irreproducible performance across a set of devices. Thus, it was concluded by Matsumoto et al. that a moderate substrate temperature of around 150 °C and exposure periods of at most 15 mins were optimal for the reliable production of OFETs [80].

In Table 2.1 it can be seen that sample E exhibited improved performance over samples A-D. This may have been due to a better balance between the speed of photocleavage of the diketone bridge and rearrangement of the molecules at the more moderate annealing temperature (120 °C). In crystals, 6,13-EPn packs so as to minimise the dipole-dipole repulsion of diketone groups on adjacent



**Figure 2.20** The absorption spectra of 6,13-EPn films on quartz, treated under the conditions shown in Table 2.1. Dashed line: sample A, solid line: sample B, bold line: sample C. Taken from [80].

Sample	Irradiation	Dielectric	Mobility	On/off ratio	V <sub>T</sub>
	conditions	surface coupling	(cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )		(V)
		reagent			
А	150 °C, 5 mins	None	0.00081	$7.8 \times 10^{3}$	_
В	150 °C, 15 mins	None	0.0014	$8.5 \times 10^{2}$	_
С	150 °C, 30 mins	None	0.00018	$3.8 \times 10^{2}$	-
D	197 °C, 5 mins	None	0.0024	$4.2 \times 10^{4}$	-
E	120 °C, 5 mins	None	0.098	$1.1 \times 10^{4}$	_
F	Room temperature,	MSQ	-	-	_
	15 mins				
G	15 mins exposure	MSQ	0.00034	$5.0 \times 10^{2}$	-33
	at room				
	temperature, 15				
	mins annealing post				
	exposure at 120 °C				
н	110 °C, 10 mins	MSQ	0.11	$4.4 \times 10^{5}$	-25
I	120 °C, 5 mins	MSQ	0.34	$2.0 \times 10^{6}$	-16
J	130 °C, 5 mins	MSQ	0.19	$1.8 \times 10^{4}$	-7
К	120 °C, 5 mins	HMDS	0.14	$2.9 \times 10^{4}$	-27

**Table 2.1** The performances of 6,13-EPn top-contact OFETs under various exposure periods and annealing temperatures. The effects of MSQ and HMDS surface treatments were also examined. Adapted from [80].

molecules. The molecules make centrosymmetric pairs and assemble in a nearly perpendicular manner. In spin-coated films, the precursor adopts an amorphous structure, but the diketone group may still influence the film structure. The solvent used for sample E was a 10:1 v/v combination of chloroform with acetone. The greater dipole moment of acetone compared to chloroform may also have affected the microstructure of the precursor, by its interaction with the diketone dipole.

The authors proposed that this led to a crystalline structure upon photoconversion that more closely resembled the herringbone packing of pentacene [80].

Two alkylating agents, hexamethyldisilazane (HMDS) and methylsilsesquioxane (MSQ), were used to modify the surface energy of the insulator interface. The effect that this modification had on the self-assembly of the converted pentacene in sample F to K was examined. This time, FET mobility was observed even for films illuminated at room temperature, then post-annealed at 120 °C for 15 mins. However, by comparing the mobilities of samples G and I, it is clear that better performance is obtained when heating and illumination occur simultaneously. Comparison of the performance of samples I , K and E show that the HMDS treated films performed better than the untreated FETs, but the MSQ treated FETs had an appreciable increase in mobility and on/off ratio [80].

Figure 2.21 shows SEM images of the pentacene crystals in samples E, I and K. Crystals were not observed in sample G. The images show that the grain size in sample I was larger than in the other films, explaining why the performance of the sample I OFET was superior to the others. In all cases, however, it appeared that the pentacene films were non-contiguous. Improving the film coverage may increase the observed FET mobilities.



**Figure 2.21** SEM images (30 000x magnification) of pentacene converted from 6,13-EPn, for samples E, I and K (see Table 2.1). Taken from [80].

### 2.5.6 Photoconversion conditions for known photopatternable semiconductor precursors

A variety of linear acene precursors (see Table 2.2) have been synthesised to incorporate the photodecarbonylation of  $\alpha$ -diketones as a route to deposition. Some are used as semiconductor precursors. Others are used as precursors for materials that are too air sensitive to prepare and study directly without the protective bridging group [89]. This is commonly referred to as a Strating-Zwanenburg decarbonylation after the formative work on these materials during the late 1960s [90]. Heating or exposure to light results in the removal of two CO molecules from the bridging moiety of the precursor. This reaction occurs so rapidly that experiments have not shown conclusively whether the removal of the bridge occurs in a concerted or step-wise manner [91]. The performances of very few of these materials have been tested in OFETs, but the conditions appropriate for photodecarbonylation have been described. While there are many different chemical structures in the table, it can be seen that the photolysis conditions are quite similar for most of them. Typically, irradiation of the n- $\pi^*$  absorption feature at 460 nm in each material leads to removal of two units of carbon monoxide. The HOMO-LUMO peak wavelength and the absorption edge are listed in Table 2.2 for comparison.

Figure 2.22 shows the HOMO and LUMO orbitals calculated for the  $\alpha$ -diketone 9,10-dihydro-9,10-ethanoanthracene-11,12-dione [91]. The shape of the orbitals on the bridging moiety is typical for  $\alpha$ -diketone precursors. The HOMO has  $\sigma$ -type bonds between the carbonyl bridge and the anthracene ring carbons, while the bond between the two carbonyl carbons is a  $\pi$ -type bond. Computations show that in the excited state the  $\sigma$ -bonds stretch while the  $\pi$ -bond

Material	HOMO-LUMO	Experimental	Best OFET	Refs
	peak	photoconversion	mobility /	
		setup	cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>	
7,16-dihydro-7,16-	Centre at 466 nm	LED array	NA	[88]
ethanoheptacene-19,20-dione	(in toluene)	) (205 - 25)		
	Absorption odgo	$Aex = (395 \pm 25) \text{ nm}$		
	Absorption edge			
	onset at 510 mm			
9,10-dihydro-9,10-	461 nm (in	LED array	NA	[88]
ethanoanthracene-11,12-dione	toluene)			
0		λex = (395 ± 25) nm		
0, /				
6,13-dihydro-6,13-	463 nm (in	Hg lamp, filtered so	0.34	[29, 80,
ethanopentacene-15,16-dione	chloroform)	that λex > 390 nm,		86]
		performed in toluene		
0, #	n- $\pi^*$ feature from	solution		
Y.	415 <i>–</i> 510 nm			
Disustal 2.2 Jactors 2.2 diana	454 pm	125 M/madium	NIA	[02]
D	454 1111	125 W medium	NA	[92]
o l <sup>i</sup>	n-π* feature from	with a 436 nm Schott		
- T	400 nm – 490 nm	interference filter		
	400 mm 490 mm			
6,13-dihydro-6,13-ethano-	465 nm	$\lambda ex = 395 \text{ nm or}$	NA	[93]
2,3,9,10-tetrabromopentacene-	Absention of a	λex > 450 nm		
15,16-dione 0	Absorption edge			
	onset at 510 nm			
Br				
Br				
Br				
2,9- and 2,10-dibromo-6,13-	465 nm	Hg lamp, filtered so	NA	[86]
dihydro-6,13-		that λex > 390 nm,		
ethanopentacene-15,16-dione	$n-\pi^*$ feature from	performed in toluene		
	410 - 510 nm	solution		
° 1				
Br - Br				

**Table 2.2** Semiconductor precursors with photolabile  $\alpha$ -diketone bridging groups.

6 10 17 21 Tetrabydro	108 nm	Irradiation with	NA	[00]
6 21·10 17-	470 1111	$\lambda_{\text{AV}} > 260 \text{ pm}$	INA	[69]
bisethanononasono	n #* footuro from			
22.24.25.26 totraketers		removes one		
23,24,25,26-letraketone	350 nm – 500 nm	bridging dione unit.		
		Irradiation with		
		Aex = 305 - 320  nm		
		removes the		
		remaining dione		
		bridge		
5,14-dihydro-5,14-	464 nm (in	460 W metal halide	NA	[94]
ethanopentacene-15,16-dione	toluene)	lamp through a blue		
0		filter in a glove box		
ο <i>μ</i> Ϊ	n- $\pi^*$ feature from			
A	440 – 510 nm,			
	slightly			
	overlapping with			
	absorption at			
	386 nm			
2,3-(2-methylphenyl)-6,13-	465 nm	395 nm light from an	NA	[84]
dihydro-6,13-		LED, or continuous		
ethanopentacene-15,15-dione	n- $\pi^*$ feature from	wavelength light		
0	410 – 510 nm	λex > 450 nm		
°.//				
R				
R				
R =				
H <sub>3</sub> C <sup>′</sup>				
2,3-(4-tert-butylphenyl)-6,13-	466 nm	395 nm light from an	NA	[84]
dihydro-6,13-		LED, or continuous		
ethanopentacene-15,15-dione	$n-\pi^*$ feature from	wavelength light		
0	410 – 510 nm	λex > 450 nm		
° (				
R				
R CH-				
R =				
CH3				
2,3,9,10-(2-methylphenyl)-	466 nm	395 nm light from an	NA	[84]
6,13-dihydro-6,13-		LED, or continuous		
ethanopentacene-15.15-dione	n- $\pi^*$ feature from	wavelength light		
9	410 – 510 nm	$\lambda ex > 450 \text{ nm}$		
° 1	-10 J10 IIII			
R				
R R				
H <sub>3</sub> C				

6,13-dihydro-6,13- ethanopentacene-15,15-dione $n-\pi^*$ feature from 410-510 nm LED, or continuous wavelength light $\lambda ex > 450$ nm R = -(-) + (-) +	
ethanopentacene-15,15-dione $n-\pi^*$ feature from 410 - 510  nm wavelength light $\lambda ex > 450 \text{ nm}$ $R = - (-) + (-CH_3) + (-CH$	
$410 - 510 \text{ nm} \qquad \lambda \text{ex} > 450 \text{ nm}$ $R = - \left( - \int_{CH_3}^{CH_3} - \int_{CH_3}^{C$	
$R = - \underbrace{CH_3}_{CH_3}$	
$R = - CH_3 \\ CH_3 \\ CH_3$	
R = - + + + + + + + + + + + + + + + + + +	
CH <sub>3</sub>	
9,10-dihydro -9,10-ethano-2,6- 466 nm (in 380 W metal halide $4.7 \times 10^{-2}$ [95, 96]	]
bis-2-thienyl-anthracene-11,12- solution), 470 nm lamp, with blue filter	
dione (in the solid state) and IR filter,	
λex > 390 nm, in	
toluene solution	
n #* footure from	
s 420 510 nm,	
$300 \text{ mW cm}^2 \text{ LED}$	
area lamp for OFETs	
Hexyl-substituted 9 10-dibydro $470 \text{ nm}$ (in the $470 \text{ nm}$ $2.6 \times 10^{-4}$ [96]	
-9.10-ethano-2.6-his-2-thienvl- solid state) 300 mW cm-2 I ED	
anthracene-11 12-dione area lamp for OFFTs	
$n-\pi^*$ feature from	
$^{C_6H_{13}}$ 420 – 510 nm	
Š	
$H_{13}C_{6}$	
H2P-DK Q bands appear Monochromatic light NA [97]	
at 509, 546, 574 from a Xe arc lamp,	
and 628 nm, but	
$n-Bu$ an $\alpha$ -diketone $\Lambda ex = 410$ him	
$n-\pi^*$ feature	
appears at	
$\rightarrow N$ $\rightarrow Et$ 407 nm.	
Et	
6 12 dibudro 6 12 othano 460 nm Plus LED NA [95]	
0,15-01119010-0,15-etilalio- 400 IIIII Blue LED NA [85]	
1 4 8 11-	
1,4,8,11- tetraphenylpentacene-15,16- $n-\pi^*$ feature from	



### **Table 2.3** Semiconductor precursors with a photolabile monoketone bridging group.

Material	HOMO-LUMO peak	Experimental photoconversion setup	Best OFET mobility / cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>	Refs
5,14-dihydro-5,14-	387 nm in THF	λex = 366 nm, in THF	$1.3 \times 10^{-3}$	[83]
methanopentacene-15-one		solution		
0 N	Ranging between			
	375 – 390 nm			
6,13-dihydro-6,13-	325 nm in THF	λex = 310 nm, in THF	8.8 × 10 <sup>-3</sup>	[28, 83]
methanopentacene-15-one				
	Ranging between 320 – 330 nm			
(6R,11S)-6,11-dihydro-6,11-	340 nm and, 357	1.25 mW cm <sup>-2</sup> UV	$3 \times 10^{-4}$	[98]
methanotetraceno[3,2-	nm in THF	lamp in $O_2$ free	(when	
b]thiophene-14-one		conditions	exposed to	
o N	Broad absorption		UV light in	
	features from		the solid	
	300 – 370 nm		state)	

Material	HOMO-LUMO	Experimental nhotoconversion	Best OFET mobility /	Refs
	peak	setup	$cm^2 V^{-1} s^{-1}$	
6,13-dihydro-6,13-	280 nm	λex = 254 nm from a	0.1	[99]
epithiomethanopentacene-16-		UV lamp, AS ONE		
one	Absorption edge	SLUV-4 with 614		
o s	at 300 nm	μW/cm²		
Pentacene-N-sulfinyl-tert-	252 nm	λex = 254 nm or 185	0.25	[27]
butylcarbamate adduct in the		nm, then heating to		
presence of a PAG	Absorption edge	130 °C in a dry		
	at 300 nm	nitrogen environment		

**Table 2.4** Alternative bridging groups for photopatternable semiconductor precursors.

between the carbonyl atoms shrinks, implying that the first step in the expulsion of CO involves bond breaking between the carbonyl bridge and the ring carbons of the anthracene molecule [91].



**Figure 2.22** Calculations of the HOMO and LUMO of the  $\alpha$ -diketone 9,10-dihydro-9,10ethanoanthracene-11,12-dione. The HOMO is of the  $\sigma$ -type at the bond between the carbonyl bridge and the carbon atoms of the anthracene backbone. The LUMO is a  $\pi$ -type orbital on the bond between the two carbon atoms of the bridge. Taken from [91].

Some other photopatternable semiconductor precursors are shown in Table 2.3, but unlike those in Table 2.2, the photolabile bridging group is a single carbon monoxide molecule. Because of the presence of other chromophores in the molecule, such as anthracene in the structure of 5,14-dihydro-5,14-methanopentacene-15-one, excitation of the HOMO-LUMO absorption does not necessarily drive the removal of the carbon monoxide group.

Table 2.4 shows the photoconversion conditions and OFET mobilities of molecules that have alternative bridging groups. Since the HOMO-LUMO absorption peaks exist at shorter wavelengths than the molecules in Tables 2.2 and 2.3, alternative light sources are required to drive the production of pentacene. Also, as outlined in section 2.5.3, the N-sulfinyl-tert-butylcarbamate precursor is not strictly photosensitive. A PAG is required to pattern the material.

### 2.6 FUNCTIONAL ALL-ORGANIC FETS AND INTEGRATED CIRCUITS

It has been recognised for some time that the production of organic field-effect transistors must proceed via low-cost techniques, otherwise the case for moving away from conventional microelectronics will be less convincing. One way to take full advantage of the low cost of organic processing is by using all-organic layers for the electrodes, interconnects and other parts of the device architecture [100]. Ideally, this would involve the use of photosensitive active materials.

In one investigation of such a fabrication method, all-organic transistors were fabricated on 50  $\mu$ m thick polyimide foils [100]. The electrodes and interconnects were patterned by UV exposure of doped PANI films (as discussed in section 2.4.4). PANI was doped with CSA and dissolved in m-cresol. The photoinitiator

1-hydroxycyclohexylphenylketone, was added to the solution and 200 nm thick films were spun over the polyimide foil. The films were exposed through a mask to deep UV radiation, in a nitrogen environment. The conducting PANI was reduced to an insulating form, leucoemeraldine, wherever it was exposed to light. The sheet resistance increased from  $10^3$  to  $10^{14} \Omega$ /square [101]. A 300 nm thick layer of SC100 photoresist was spin-coated on the patterned PANI gate electrode, forming both the gate dielectric for the transistors and the insulator for the interconnect pathways. Vias for connections between contacts on neighbouring transistors were patterned using another mask. PANI was deposited again and the source, drain, and top of the interconnects were patterned in this layer using a third mask. The resulting PANI-insulator-PANI structure is shown in the DIC micrograph in Figure 2.23(a). The channel length between the interdigitated source-drain electrodes is 5 µm, and the vias have a square dimension of  $5 \times 5 \,\mu$ m. The bottom-contact construction allows for variability in the deposition method for the semiconductor. In this experiment, devices were made with pentacene, poly(3-hexylthiophene) and polythienylenevinylene semiconductors.



**Figure 2.23** (a) A top-view DIC image of a bottom-gate PANI-insulator-PANI structure on a polyimide film. (b) The plot on the right shows the gain of several pentacene inverters (see inset) made from the all-organic transistors. The channel lengths were 1  $\mu$ m (triangles), 2  $\mu$ m (diamonds) and 10  $\mu$ m (squares). The conductors were photopatterned and pentacene was thermally converted from a tetrachlorobenzene precursor [100].

The pentacene was converted from a tetrachlorobenzene precursor, at a temperature of 180 °C. It gave the best performance of all of the semiconductors, with a linear-regime mobility of  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, at a source-drain voltage of -2 V and gate bias of -10 V [100].

To demonstrate how this process could be used to connect solitary devices and construct more complex integrated circuits, a simple logic gate test structure was produced, in the form of a pentacene inverter. A pair of transistors was connected, as in the inset of Figure 2.23(b). The maximum value of  $dV_{out}/dV_{in}$ was recorded during a voltage sweep, and plotted as a function of the supply voltage, V<sub>dd</sub>. Transistors with channel lengths 1 µm, 2 µm and 10 µm were tested. The switching frequency, controlled by the RC time constant of the load transistor, was 60 Hz for 5 µm devices and 2 kHz for 1 µm devices. A useful circuit element was produced because a gain of greater than one was obtained with a supply voltage of only 5 V for each of the inverters.

### **2.7 SPRAY DEPOSITION OF ORGANIC THIN FILMS**

Spray deposition is a relatively new technique for depositing soluble organic materials. It appears to be an attractive way to cover large areas, rapidly, with minimal use of materials. Researchers with an interest in depositing thin films for organic photovoltaics have employed airbrushes that are conventionally used for spray painting and have also developed ultrasonic-atomisation deposition systems [20, 102-110]. The main appeal of spray deposition is that it is possible to optimise the spray parameters so that multiple layers of organic materials can be deposited over each other. Variables in spray coating include the nozzle to substrate distance, solvent viscosity, droplet size, spray direction and spray

velocity. It could also prove to be a viable technique for the deposition of sparingly soluble organic materials, such as the pentacene precursors 6,13-MPn and 5,14-MPn. One of the problems encountered in making transistors using this material was that it was difficult to form contiguous films by spin coating [28, 83]. Spray deposition may provide a means to more completely cover substrates and thereby raise the performance of OFETs produced using semiconductor precursors, hence it is the main technique used for the spectroscopy work discussed in Chapter Five and the studies on OFET performance discussed in Chapter Six. Most of the research carried out so far into the use of spray deposition in organic electronics has involved organic solar cells, so this discussion of thin film formation begins with materials used in organic photovoltaics. An outline of the application of spray deposition in the production of OFETs follows.

### 2.7.1 Spray deposition systems

Some success has been attained in forming the active layers of organic solar cell devices using hand held airbrushes [102, 111]. These systems are inexpensive and provide control over the spraying parameters via appropriate selection of solvents and by variation of carrier gas flow rate. A more sophisticated ultrasonic spray deposition system was employed by Steirer et al. in the production of P3HT:PCBM solar cells [104]. The advantage that ultrasonic atomisation has over spray deposition using a conventional airbrush is seen as the ability to achieve more uniform coverage of very thin films over large substrate areas, deposition of multiple components using ganged spray heads and the generation of smaller droplet sizes. The megahertz resonator frequency allows the size of the spray



**Figure 2.24** (a) Schematic of the ultrasonic spray system [104]. (b) The spray from a Sonotek ultrasonic spray nozzle [112]. (c) The PEDOT:PSS layers of organic solar cells were spin coated, while the P3HT:PCBM active layers were spray deposited [104].

droplets to be tuned down to picolitre volumes, smaller than the microlitre droplets produced by air guns. The size of the spray droplet is one parameter that determines how rapidly the sprayed films dry and smaller droplets should also lead to smoother films.

A schematic of the spraying system used by Steirer et al. to deposit the P3HT:PCBM layer is shown in Figure 2.24(a) [104]. The ultrasonicating surface in the spray head is fed with a controlled volume of the semiconductor solution by a tri-phase flow pump. An inert carrier gas was used to direct the spray from the Sonotek ultrasonic spray nozzle #8700-120 towards the substrate, as shown in Figure 2.24(b) [112]. An Omega Engineering mass flow regulator was used to control the carrier gas flow rate. This system produced droplets with sizes close to those emanating from inkjet printer nozzles. The separate layers of the solar cell are shown in Figure 2.24(c).

### 2.7.2 Film formation regimes

By varying parameters such as the spraying distance, the solvent boiling point, the carrier gas velocity and the volume of solution pumped per second, films can be deposited in three distinct regimes: *wet, intermediate* and *dry*. These regimes are defined here according to the descriptions given by Abdellah et al. [113]. In the *wet* regime the nozzle-to-substrate distance is short, leading to a thick, wet solution layer on the substrate. This often leads to inhomogeneous film morphology with no control over thickness. In the *dry* regime the nozzle-to-substrate distance is long and the solvent evaporates before reaching the substrate, leading to covering the substrate with a poorly adhering powder of the solute. In the third regime, *intermediate*, the droplets reach the substrate then evaporate quickly. Homogeneous layers can be formed and multiple passes of the substrate allow for control over the film thickness. The small solvent droplets evaporate without redissolving the underlying material.

#### 2.7.3 Spraying in the intermediate regime

Figure 2.25(a) shows the relationship between absorbance versus deposition time for four P3HT:PCBM films. They were sprayed in a chlorobenzene solution using an airbrush [102]. The plots show the value of the absorbance at 510 nm, averaged across the edges and centres of three samples. The absorbances were monitored for deposition times of 5, 15, 30 and 45 seconds. A linear relationship was found to exist between the spray time and the average film thickness when the spray parameters were optimised. The inset to Figure 2.25(a) shows that the film absorbance for a non-optimised deposition did not change linearly with the deposition time. The polymer flooded the substrate as a thick solution in the *wet* 



**Figure 2.25** (a) The absorbance at 510 nm for the sprayed films varies linearly with deposition time. The nozzle to substrate distance has been optimised for intermediate deposition. The inset shows the relationship for deposition in the wet regime. (b) The surface profile of the sprayed film. Figure taken from [102].

regime because the spray nozzle was placed too close to the substrate. The linear relationship corresponded to the *intermediate* spraying regime, showing that an optimised spray does not redissolve or distort the underlying film at a macroscopic level. It is therefore reasonable to think that this process could be applied more widely to making multilayer or gradient composition films. The P3HT:PCBM film corresponding to the surface profile in Figure 2.25(b) had an rms roughness of 52 nm, which is large considering the maximum thickness of the film was only 300 nm.

### 2.7.4 Effects of solvent properties

When producing P3HT:PCBM solar cells using an airbrush, Vak et al. found that large substrate areas could be coated more practically when a high boiling point



**Figure 2.26** Optical micrographs of P3HT:PCBM films spray deposited in (a) chloroform (b) toluene (c) chlorobenzene and (d) p-xylene solutions [103].

solvent such as chlorobenzene (b.p. 131 °C) was used [102]. When dichloromethane was used instead (b.p. 39.6 °C), the nozzle was too close to the substrate in the intermediate deposition regime to be able to cover more than a few square centimetres at a time. Leading on from this, Green et al. examined the effects of solvent choice and annealing temperature on the performance of spray-deposited solar cells [103]. They produced solar cells using the same active layer and architecture as Vak et al. but trialled a number of solvents. All solutions were prepared by dissolving P3HT:PCBM in a particular solvent for 90 minutes at 60 °C, to obtain a 2 mg/mL solution. Figure 2.26 shows optical micrographs of films prepared from (a) chloroform (b) toluene (c) chlorobenzene and (d) p-xylene. Other higher boiling point solvents (1,2,4-trichlorobenzene and o-dichlorobenzene) were trialled as well, however they yielded films that dewetted from the substrate. Of the four films shown, three had isolated features with dimensions ranging from 10-100  $\mu$ m, while the chlorobenzene solution produced a highly uniform film.

Devices produced using p-xylene and chlorobenzene solvents displayed performance parameters (open circuit voltage, short circuit current, fill factor and power conversion efficiency) that were superior to those of the chloroform and toluene devices. The best p-xylene devices had the highest power conversion efficiencies, but there was a greater variation in performance across multiple devices compared to those deposited from chlorobenzene, which were exceptionally uniform. A ten-fold increase in short-circuit current density and power conversion efficiency was also achieved in devices sprayed from chlorobenzene when they were annealed at 110 °C. This was probably because of reordering in the active layer after annealing [103].

### 2.7.5 Spraying multiple organic layers: transport layers and heterojunctions in organic solar cells

So far, the use of ultrasonic and conventional spray deposition has only been discussed with reference to the processing of active semiconductor layers. However, some demonstrations of sprayed, conducting, organic contacts have also been made. Steirer et al. carried out experiments on organic solar cells with an ultrasonically sprayed conductor, PEDOT:PSS [20]. PEDOT:PSS is typically used in photovoltaics as a hole transport layer on transparent conducting oxides. Films were deposited on an indium tin oxide (ITO) film and the surface roughness was measured by tapping mode atomic force microscopy (AFM). The ITO substrate had an rms roughness of 3.2 nm, while the roughness of PEDOT:PSS films deposited by spin-coating, ultrasonic spray deposition and inkjet printing were, respectively: 1.2 nm, 1.3 nm and 1.5 nm. P3HT:PCBM active layers were then spun over the top, resulting in devices with power conversion efficiencies of 3.63%, 3.53% and 3.31% respectively. The performance of the sprayed device

was only slightly lower than the spin-coated equivalent and the shunt and series resistances were both slightly higher. The short circuit current density was lower, but the fill factor was similar. The high shunt resistance meant that the coverage of the ITO was good and there were very few current leakage paths through the PEDOT:PSS. The series resistance was higher because the greater roughness of the sprayed film leads to larger surface areas. The reason why the greater surface area increases the resistance is that the PEDOT:PSS layer mainly consists of insulating PSS at the surface. Thus, increasing the roughness increases the series resistance through the layer [20].

Following on from these studies showing that the active layers and the hole transporting electrode of an OPV could be spray deposited, it was natural to examine whether both of these steps could be carried out in a single device. Na et al. sought to produce sprayed devices without the usual ITO electrode, because ITO is prepared at high temperatures in vacuum and is not very flexible [105]. PEDOT:PSS layers were sprayed, using a conventional airbrush, on to glass substrates and ITO covered substrates so that a back-to-back performance comparison could be made between the two types of devices [114]. The aqueous PEDOT:PSS solution was combined with 5% DMSO and sprayed to form an anode with a conductivity near 500 S/cm. A P3HT:PCBM layer was then sprayed from a chlorobenzene solution. The transmission through the PEDOT:PSS layer was lower than the ITO layer, because a thicker layer of PEDOT:PSS is required to obtain an equivalent sheet resistance. When the right balance was reached between the transmittance and sheet resistance of the anode, a cell with a power conversion efficiency of 2.17% was fabricated. This compares to 2.86% for the ITO reference cell. Thus, highly cost effective, multiple-layer, solution sprayed solar cells were fabricated without expensive and inflexible ITO, with only a 25% decrease in performance [114]. This is a further demonstration of the fact that multiple organic layers can be sprayed on top of each other from different solvents and result in devices with competitive performance parameters.

### **2.8 SPRAY DEPOSITION OF TRANSISTORS**

Producing organic transistors by spray deposition is a novel concept [105, 113, 115, 116]. While sprayed solar cell research began around half a decade ago, the first spray deposited polymer OFETs were demonstrated as recently as 2010 [113, 115]. The first report on the fabrication of a small-molecule organic semiconductor OFET using a conventional airbrush followed later in 2010 [105]. Another related paper describes the fabrication of ZnO inorganic transistors by thermolysis of an ultrasonically spray-deposited precursor [117]. The move to spray coating and away from successful laboratory based fabrication techniques, such as spin coating and drop casting, stems from the need to investigate the applicability of materials to large-scale industrial electronics manufacturing. Spray deposition is compatible with rapid roll-to-roll manufacturing of electronics; unpatterned films of active materials can be applied quickly across a large substrate area with minimal materials loss. Also, when spraying atomised droplets in the intermediate regime, multilayer films can be deposited without redissolving underlying layers. This lends support to the concept of producing multilayer all-organic transistors with good performance, using soluble semiconductors and precursors in a simple process that conserves the stock material. This is clearly a new field of studies within organic electronics that will

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garner more attention over the coming years as materials systems are optimised for this deposition technique.

### 2.8.1 Sprayed polymer OFETs

Spray deposited polymer transistors were reported by Chan et al., who used an Iwata Kustom TH airbrush kit in the setup shown in Figure 2.27 [115]. P3HT was sprayed as a 2 mg/mL solution in 6:1 chlorobenzene:1,2,3,4-tetrahydronapthalene, in twenty sweeps across the substrate. The sweep rate was 10 cm/s, with a 10 s pause between each sweep.

Optical and AFM images of the top surface of the sprayed P3HT film, in Figures 2.27(a) and (b) respectively, reveal how rough the film is. Round features can be seen, with a diameter of approximately of 20  $\mu$ m. Other effects that can be observed in these images are the merging of adjacent droplets, the superposition



Figure 2.27 The spray deposition setup for fabrication of P3HT thin film transistors [115].

of droplets at a point of overlap, coffee stain effects (where most of the solute is driven towards the boundary of the droplet and evaporates [118]), spherical solidification and planar film formation (at the centre of a droplet). The AFM image inset in the bottom right of Figure 2.28(b) shows a single P3HT droplet in which the high-walled coffee stain mode of deposition is apparent. The white line through the middle of this droplet corresponds to the AFM line scan in Figure 2.28(c). The 12  $\mu$ m wide droplet has a perimeter height of 60 nm and a flat interior region that is 7 nm high across the central 5  $\mu$ m section. As more droplets coalesced and superimposed in thicker films, these effects led to the formation of inhomogeneous films with high surface roughness. The rms roughness of the thick P3HT films in this case was around 100 nm, however the roughness of the interior of the rings remained comparably low, at less than 20 nm.

To test the performance of sprayed OFETs, batches of 50 transistors were fabricated with channel widths of 1 mm and channel lengths of 10, 20, 25, 50, 80 and 100  $\mu$ m. The plot in Figure 2.28(d) shows that at all channel lengths, spray coated transistors had higher mobilities than spin coated transistors. Unfortunately, the mobility variance was much greater than for the spin coated transistors. Annealing at 85 °C in a vacuum oven for 12 hrs did not improve the performance of the devices. The variability in the mobilities of the sprayed films may have been related to the inhomogeneity of the films. Alternatively it may have been due to processing the sprayed films in air, while the spin-coated films were processed under Ar. The increase in mobility with the decrease in channel length observed for both types of transistor may be due to a field-enhanced transport mechanism, or due to a reduction in the number of grain boundaries in the channel. That is, as the channel length decreased to less than the average droplet diameter (25-50  $\mu$ m) there were fewer droplet boundaries in the path of the charge [115].



**Figure 2.28** (a) Optical microscopy (150  $\mu$ m x 250  $\mu$ m) and (b) AFM (30  $\mu$ m x 50  $\mu$ m) images of the top surface of the spray-deposited P3HT film. Features include: (i) merging of droplets (ii) superposition of droplets (iii) coffee stain effects (iv) spherical solidification and (v) planar film formation. (c) AFM line profile corresponding to the white line across the single P3HT droplet on OTS8/SiO2, inset in (b). (d) Average mobilities with standard deviations (error bars) of spray and spin coated P3HT transistors, plotted according to source-drain electrode separation [115].

The surprisingly good performance of the airbrushed transistors was further investigated by near-edge x-ray absorption fine structure (NEXAFS) spectroscopy (see Appendix Four for a discussion on the theory underpinning NEXAFS) [115]. NEXAFS spectroscopy is performed using synchrotron radiation, which is almost totally linearly polarised. NEXAFS K-shell spectra show resonances that originate from transitions between the 1s core level of atoms in a molecule and the empty  $\pi^*$  and  $\sigma^*$  molecular orbitals [119]. The intensity of NEXAFS absorption features depends on the filling of molecular orbitals in a sample and also on the angle between the electric field vector of the x-rays and the direction of the unoccupied orbitals. Orbitals with  $\pi$  symmetry, like the orbital shown in the PTCDA molecule in Figure 2.1(a), lie above and below the plane of the molecule. If the electric field vector of an x-ray were to be perpendicular to the molecular plane of PTCDA, electrons could move from the 1s core level (Kshell) to the unoccupied  $\pi^*$  orbital. This transition would not occur if the field vector was oriented in the plane of the molecule. This technique was used to compare the orientation of P3HT chains at the dielectric surface in sprayed and spin-coated transistors. P3HT layers were removed from the devices using a parylene adhesive, to expose the polymer at the gate interface. The orientation of the  $\pi$ -conjugated polymer backbone is determined from the *dichroic ratio*, which varies between -1 and 0.7 for chains which are perpendicular and parallel to the surface, respectively. The ratio was 0.21 for the sprayed films and 0.22 for the spin-coated P3HT. This means that the chain orientation for the two types of P3HT films was nearly identical at the dielectric surface. Given that only the first few nanometres of the semiconductor layer near the dielectric surface are important for charge transport, it is not surprising that the sprayed transistors perform well, despite the disorder in the bulk of the films.

A paper by Abdellah et al. [113] also describes the spray fabrication of P3HT transistors. A commercially available atomising spray gun was used, from Krautzberger GmbH, Germany. The polymer was deposited on prefabricated transistor architectures, with and without substrate heating. Transistors with an on/off ratio of 5.8 x  $10^1$  and field effect mobility of  $1.02 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  were made when depositing in the wet regime on a heated substrate. When depositing in the same regime on a room temperature substrate, the on/off ratio was  $5.8 \times 10^2$  and the field effect mobility was  $1.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The poor performance when the substrate was heated could be attributed to the fast drying of the

droplets, leading to disorder at the substrate interface. By flooding the surface with droplets and allowing the solvent to evaporate more slowly, there is more time for reorganisation of the polymer chains *at the surface* and the overall inhomogeneity of the film doesn't appear to be important. The slow layer formation makes this approach comparable to drop casting and dip coating. Clearly, some materials may perform better when deposited in the wet regime, while others respond better to intermediate regime deposition.

### 2.8.2 Sprayed small molecule OFETs

The advantages of spray deposition in small molecule transistor fabrication were highlighted for the first time by Azarova et al. [105]. They made transistors by depositing 2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (diF-TES-ADT) in chlorobenene, using an Iwata Kustom TH K9200 airbrush, with pressurised Ar carrier gas. Charge mobilities near 6 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> have been reported for diF-TES-ADT vapour grown single-crystal OFETs, although solution processed devices have lower mobilities. In drop cast films, mobilities of 1.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> were achieved, which compares well to 0.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for spin coated films on pentafluorobenzenethiol (PFBT) coated gold contacts. This value for spin coated films increased to 0.4 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> when a HMDS treated gate dielectric was used. The group's spray deposited transistors had mobilities as high as 0.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for PFBT coated contacts and on/off ratios of 10<sup>7</sup>, matching the performance of similar spin coated films.

The concentration of the diF-TES ADT solutions was found to be a critical parameter in controlling the film coverage. Optical micrographs of films in three source-drain channels are shown in Figure 2.29, corresponding to solution



**Figure 2.29** Top: optical micrographs of sprayed film coverage at three different concentrations, showing distinct microstructure. The coverage in the channel is particularly poor at c = 0.01 %. Bottom: variation of mobility with concentration of diF-TES-ADT in chlorobenzene [105].

concentrations of 0.01%, 0.05% and 0.1%. The mobility increases in step with the concentration because the film coverage improves. The small decrease in mobility beyond the optimal concentration of 0.1% may be due to mobility anisotropy or a non-uniform structural profile through the film. A structural phase transition for diF-TES-ADT has been reported to occur at room temperature, leading to two polymorphs with differing layer spacings and inherent electrical properties.

Figure 2.30(a) shows the mobility of the transistors as a function of the channel length, for both spin- and spray-coated films. The mobilities are similar at short channel lengths but diverge for channel lengths exceeding 25  $\mu$ m. Figures 2.29(b) and 2.29(c) show optical micrographs of both types of films. In the spray-deposited transistors the mobility varies monotonically with channel length, which implies that the film microstructure is relatively uniform in the channel for all of the transistors. This is consistent with Figure 2.30(b), which shows that the channel and the contacts are covered with a coating of plate-like crystals. Under optimised conditions, the spray droplets reach the substrate then combine to form



**Figure 2.30** (a) The measured saturation mobility of spin coated and sprayed diF-TES-ADT transistors as a function of the transistor channel length. The mobility reduced more rapidly with channel length for the spun films. (b) Optical micrograph of the sprayed device and (c) the spin coated device [105].

large crystals around nucleation sites. In spin-coated devices (Figure 2.30(c)), the solvent evaporates very quickly and the interactions at the electrodes lead to two distinct crystalline regions in the channel. Plate-like crystals grow on the contacts and then extend out through the channel, which is predominantly covered with small crystals. The large crystals can bridge the channel in short channel devices, leading to high mobilities, but as the channel length increases the mobility diminishes due to the poorly ordered film in the channel. It appears that spray deposition is better than spin coating as it allows the film growth to be tuned to produce large crystallites that bridge both long and short source-drain channels.

### **2.9 CONCLUSIONS**

In sections 2.1 and 2.2 of this review, the characteristic properties of organic electronic materials and the fundamentals of OFET design and materials requirements were described. In section 2.3 some of the common methods used to pattern OFET architectures were reviewed and then in section 2.4 some examples

of direct photopatterning were examined. The research showed that properties of materials such as the photoluminescence efficiency, the refractive index and charge carrier mobility can be dramatically altered by exposing organic thin films to light. Some of the patterning techniques applied to these photosensitive materials have already been extended to the photochemically modifiable Diels-Alder precursors of the high performance semiconductor, pentacene, as discussed in section 2.5. Photopatterning of a complicated all-organic integrated circuit structure was discussed in section 2.6. The insulating and conducting materials were fabricated by a direct photopatterning method, however the semiconductor layer was deposited as a bulk thin film layer. Ideally this layer should also be photopatterned, to prevent leakage currents diminishing the performance of individual transistors and to stop cross-talk from affecting integrated devices.

The production of fully solution-processed all-organic transistors with all features defined by direct photopatterning would represent a major step towards the rapid, cost-effective, roll-to-roll-compatible manufacturing of organic electronics. This will require multilayers of photosensitive materials, which are all solvent- and wavelength-compatible. It will be necessary to have a catalogue of materials that undergo changes in bulk electrical properties at different wavelengths, so that they can be individually addressed at different stages during manufacturing. Solution compatibility across multilayers stands as a major challenge; a fortuitous combination of materials may be found, but it is more likely that novel deposition methods will need to be exploited. Spray deposition of aerosolised solutions, as described in 2.7 and 2.8, may be one of these useful deposition strategies, particularly because of the ability to tune the deposition

from the wet regime, through the intermediate to dry. Solar cell researchers have already demonstrated that the spray deposition of different active layers on top of other organic materials results in functional devices with acceptable performance figures.

The remainder of this thesis describes experiments that were conceived to further investigate the use of photosensitive active materials in the fabrication of OFETs, by examining their decomposition wavelengths and the parameters required for good thin-film formation via spray deposition. Comparisons are made between experimental spectra of organic semiconductors, obtained using multiple complementary techniques, and synthetic spectra calculated using density functional theory software (DFT). DFT is introduced in Chapter 4 and the suitability of DFT software for examining the photophysics of organic semiconductor molecules and their precursors is evaluated. As outlined in this review, there are many factors that need to be carefully designed and optimised if the production of high performance OFETs is to be achieved. Molecules in the semiconductor active layer must be oriented so that charge flows readily between the contacts. The molecules must pack closely so that charge carriers are delocalised over neighbouring molecules. The contact resistance must also be minimised by careful selection of the semiconductor and contact materials. The main focus of this thesis is to identify and better understand materials that may be used to photopattern different components of OFETs. Most of the experiments that are described in this thesis focus primarily on the photophysical aspects of the materials and not the other important performance factors just mentioned. The optimisation of these performance parameters is a matter for additional study that is beyond the aims of this thesis.

# CHAPTER THREE

Instrumentation used to deposit, pattern and analyse OFET thin films

This chapter provides a general overview of the experimental techniques and equipment used when performing research for this thesis. The deposition, patterning and analysis of materials used in the production of OFETs are discussed.

## **3.1 DEPOSITING ELECTRODES AND SEMICONDUCTING LAYERS FOR OFETS**

Several materials were required for the fabrication of the OFETs examined in this thesis. Metals were deposited by sputtering and thermal evaporation, while organic semiconducting and conducting materials were deposited using a variety of processes including vacuum thermal evaporation, spin-coating and ultrasonic spray deposition. The equipment used for thin film deposition is described here.

### 3.1.1 Deposition of metals by sputtering and evaporation

Gold films were deposited during the production of OFETs to form the source and drain contacts. Gold electrodes were also deposited onto glass substrates to act as contact point in experiments examining the conductivity of PEDOT:PSS under various light sources. Chromium was deposited to act as an adhesion layer between the gold electrodes and glass substrates and was also used in the fabrication of photomasks. These films were deposited by sputtering, using a Dynavac dual head SC200HV/M2 magnetron sputter coater. A gold sputtered mask is shown in Figure 3.1(a). The sputtering targets, which can be seen in a reflection from the coated mask, are solid discs of gold and chromium and act as the cathodes in the sputter head circuit. This system utilises a rotatable substrate stage located underneath the two targets in top-down configuration. Electrodes were produced on the substrates by deposition over photolithographically patterned resists or glass shadow masks that were placed in contact with the top of the substrate. The shadow masks were produced by laser machining apertures through 150 µm thick glass coverslips.



DC magnetron sputtering is a simple process that can be applied to any

**Figure 3.1** (a) Gold is deposited through a glass shadow mask onto glass substrates in the Dynavac dual head SC200HV/M2 magnetron sputter coater. The sputter head is shown in the reflection from the mask. (b) Gold was also deposited by evaporation in a high vacuum system at 10<sup>-6</sup> Torr.

metallic target, including those for which evaporative deposition would be impractical. Sputtering occurs by transfer of kinetic energy from the ionised gas enveloping the target material. In the Dynavac system, the sample chamber is pumped down to  $10^{-5}$  Torr to remove reactive  $O_2$ . It is then filled to a pressure of  $10^{-3}$  Torr with high purity argon. A negative voltage is applied to the target, attracting positive argon ions to the surface. When the energy applied to a lattice site in the target exceeds the atomic binding energy, the atom may recoil from the surface. These neutral backscattered target atoms may head in the direction of the substrate and form a thin film. In addition to the ejection of neutral atoms from the source, electrons are also removed. A magnetic field is used to trap these secondary electrons in the plasma near the surface of the target. The electrons follow a helical path around the magnetic field lines and undergo collisions with the argon gas, enhancing ionisation of the gas. This leads to more ions bombarding the target surface and an increase in the sputtering rate [120].

Gold was evaporated onto silicon dioxide coated silicon substrates in an ultra-high vacuum system as part of the preparation of OFETs. The clean substrates were placed on a glass microscope slide and then a shadow mask was clipped into contact with the substrate. The set of substrates was then clipped to a stand, shown in Figure 3.1(b), located approximately 50 cm above an evaporation boat containing a piece of gold. The vacuum chamber was then typically pumped to less than  $5 \times 10^{-6}$  Torr before the evaporation boat was heated resistively.

## 3.1.2 Spray deposition of semiconductor precursors using a hand held airbrush

A spray deposition system was constructed so that thin films of active organic materials could be deposited in a controlled manner by the evaporation of microlitre sized droplets on heated substrates. The system was based upon the concepts presented in sections 2.7 and 2.8 [103, 105, 113-115]. The solvent spray was generated using a standard hand held airbrush, a Project Air model TA-MABK, that was fed from a bottle of high purity N<sub>2</sub> gas, typically at a pressure of 120 kPa which yielded a discharge rate of 4 mL/min. The airbrushing setup is shown in Figure 3.2.

Solutions of organic semiconductors, dielectric materials or conducting polymers were placed in the glass reservoir attached to the airbrush, then drawn through the nozzle and sprayed onto substrates. Brass shadow masks were placed over the substrates to define the patterns of features such as transistor electrodes. Both the mask and substrate were bolted to an aluminium heater block by



**Figure 3.2** The spray deposition system that was used to deposit organic layers for OFETs. A Project Air TA-MABK air-gun was used to produce the spray. The carrier gas was supplied by a high purity  $N_2$  gas bottle. Spraying was performed in a fume hood to avoid inhalation of the organic solvents. Substrates were placed on a heater block inside a plastic container so that the flow of the fume hood did not interfere with the trajectory of the spray. A PID controlled heater system was used to set the temperature of the substrate. An aluminium plate was bolted onto the heater block, to attach both the substrate and any masks used for patterning film features. A brass shim with an electrode pattern is shown attached to the block.

compression under a thin sheet of aluminium with a window cut out. Two 100 W Watlow heater strips were also bolted to the back face of the block, so as to cover the whole surface. Power was supplied to the heaters by a PID controller, with the temperature of the back face of the block monitored a K-type thermocouple wire. The temperature of the front of the block was monitored by a separate thermocouple, so that a constant temperature was maintained while substrates were sprayed multiple times (more details of the heater are provided in section 3.2.4). As a safety precaution, spraying was performed in a fume hood to avoid inhalation of the organic solvents. However, the flow inside the hood interferes with the trajectory of the spray, so the substrate block was placed inside a transparent container. A 15 cm wide slit was made in the front of the substrate.

The quality of the films produced using this equipment varied as a function of the substrate temperature, nozzle to substrate spraying distance, solvent boiling temperature and solution concentration. The nozzle of the air gun was translated at a rate of approximately 15 cm/s, however as this was simply performed by hand there was potential for some variance. Typically the substrate temperature was set to be a few degrees below the boiling point of the solvents, to help unite droplets on the substrate surface prior to evaporation. In results reported in Chapter Five, similar to those presented in Chapter Two, it was found that varying the nozzle-to-substrate distance had a measurable effect on the deposition conditions; whether films were deposited in the *wet* or *intermediate* regimes. It was found that when the spraying distance was optimised the absorbance of the films varied in a linear manner with respect to the number of times the spray was swept across the substrate. This was understood to mean that
the underlying material was not being dissolved and removed by the fresh solvent that was sprayed onto the surface [102]. When multiple organic layers were deposited on a single substrate, the spray distance was adjusted for each solvent to maintain linear deposition.

## 3.1.3 Semiconductor deposition in an ultra-high vacuum system

Vacuum thermal evaporation is the most common means of depositing uniform, ordered thin films of organic semiconducting materials [15]. Insoluble semiconducting compounds such as pentacene and PTCDA were deposited in the chamber shown in Figure 3.3(a). This ultra-high vacuum system was designed for the deposition of organic semiconductors by sublimation from powdered form in a contaminant-free environment. A system is classified as ultra-high vacuum if chamber pressures can be reduced to  $10^{-9}$  Torr ( $10^{-7}$  Pa). At higher pressures there is so much atmospheric oxygen and water in the chamber that any "clean" surface is contaminated within seconds. Achieving a low chamber pressure prior to deposition is essential because film ordering at the substrate surface is dependent on the surface energy, which is heavily modified by adsorbed water. The mean free path of evaporated molecules also increases with decreasing chamber pressure, so more of the molecules reach the substrate at lower pressures.

A series of pumps are used to achieve ultra-high vacuum conditions. No mechanical pump exists which can reduce the pressure all the way from atmospheric pressure to  $10^{-9}$  Torr [121]. Thus, turbomolecular pumps backed by rotary pumps were used to evacuate both the growth chamber and the load lock in the deposition system. The rotary vane pump itself can only reach a vacuum of  $10^{-3}$  Torr, so the turbomolecular pump is used to further reduce the pressure to

10<sup>-9</sup> Torr. Materials selection is a key factor in ensuring that ultra-high vacuum conditions can be reached in the chamber. It is necessary to use materials that do not outgas and surfaces must also be kept free of hydrocarbons. Low vapour pressure materials such as ceramics and stainless steel were used in the construction of all components within the chamber. Plastics and metals such as aluminium are unsuitable. Components were only welded together on one side to avoid forming vacancies in the welds which could trap gases and lead to virtual



**Figure 3.3** (a) The ultra-high vacuum system, showing the load lock, gate valve, growth chamber and pump. (b) The substrate holder is placed into the substrate stand within the growth chamber. (c) A close up view of the evaporator with the steel shroud removed shows the heater wire wound through machined ceramic rods. The ceramic crucible containing the organic powder is placed in the centre of the heater coil.

leaks in the chamber. Grooves were also machined along the shafts of bolts that were driven into blind holes, to allow pits of trapped gas to escape. The surface of the chamber and components were cleaned with acetone and ethanol to remove traces of dust and grease, while gloves were always worn when handling components to prevent outgassing from the skin oils in fingerprints. The chamber walls were also baked at greater than 200 °C after opening to promote the removal of adsorbed water and hydrocarbons.

When carrying out depositions, substrates with dimensions of up to  $75 \times 75$  mm are placed into the chamber by attaching them to the substrate holder, opening the load lock, then twisting the holder onto a bayonet piece at the end of the transfer arm. The load lock is pumped down to roughly match the pressure in the growth chamber. The gate valve is then opened and the sample is inserted into the substrate stand in the growth chamber, as shown in Figure 3.3(b). The substrate holder travels along some bevelled guides and is locked into place by a tantalum retainer clip, which compresses a flexible piece of molybdenum sheeting. The transfer bayonet is then rotated out of the substrate holder and is withdrawn from the chamber, which is once again sealed from the load lock. The evaporator cylinder can be seen at the base of the chamber, through the substrate holder. A close up of the evaporator with the shroud removed is shown in Figure 3.3(c). An alumina crucible holding roughly 2  $\text{cm}^3$  of the material to be evaporated sits in the centre of the evaporator on a thin tantalum stand. A thermocouple is attached to the stand. The heater wire that surrounds the crucible is fed through a number of holes drilled along the length of six machineable glass ceramic (MACOR<sup>®</sup>) rods. These supports prevent the wire from shorting out or collapsing and touching the crucible during heating. The crucible is uniformly heated by radiation, rather than by heat conduction. This prevents the formation of hot spots in the material, which eject solid clumps of powder from the crucible and lead to non-uniform films. Power is supplied to the heater wire by copper wires connected to an electrical feedthrough at the base of the chamber. The long throw distance of ~40 cm between the substrate and evaporators assists in the deposition of uniform films.

## **3.2 EQUIPMENT AND PROCESSES FOR THIN FILM PATTERNING**

The production of OFETs requires patterning of the electrodes and the semiconducting layer. Large scale features like metal electrodes can be patterned during deposition by simply evaporating or sputtering material through a shadow mask. It is important to also pattern the semiconducting layer, in order to prevent cross-talk between neighbouring devices and also to reduce materials usage. The equipment and techniques used to pattern thin films are described here.

## 3.2.1 Patterning gold films for OFET electrodes

As discussed in section 3.1.1, gold source and drain electrodes were deposited onto OFET test structures by thermal evaporation in an ultra-high vacuum system. A shadow masking technique was used for simplicity. The material used for the shadow masks was a 50  $\mu$ m thick nickel sheet. The substrate can be sandwiched between a magnet and the ferromagnetic mask so that the mask can be pulled into close contact with the substrate surface, however with the long throw distance in the evaporation chamber it was found that the mask outlines transferred well without the magnet. Apertures were cut out of a 30 mm  $\times$  20 mm section of nickel

sheet mask by laser machining. A typical mask is shown in Figure 3.4(a). The outside border of the square apertures was 4 mm  $\times$  4 mm, however a thin strip of nickel was left in the centre of the aperture to shadow the channel area. Figure 3.4(b) shows that this bridge was typically 30 µm wide, with some waviness at the edges. Figure 3.4(c) shows the separate source and drain electrodes on a substrate after the evaporation of a 30 nm thick layer of gold. Figure 3.4(d) shows a magnified image of the channel area and indicates that the outline of the nickel bridge has been transferred to the substrate without a significant change in the dimensions. Although these 30 µm channels are much longer than can be achieved by photolithographic techniques, the challenge of completely removing photoresist from the surfaces was avoided.



**Figure 3.4** (a) Patterned Au source-drain electrodes (yellow) on top of a layer of YSZ, over an Au gate electrode (orange). The 28  $\mu$ m source-drain channel is etched through a patterned photoresist. (b) The resist was patterned by exposure through a 9  $\mu$ m wide aperture in a chrome mask. The aperture was machined using a femtosecond laser.

## 3.2.2 Xe arc lamp light sources

Considering only standard laboratory light sources, arc lamps emit light with a brightness second only to that produced by lasers. The advantage of these lamps over lasers is that the light is produced in a broad spectrum, with intensity in the UV-vis-IR region of the electromagnetic spectrum. Arc lamps were therefore the ideal light source for the photochemistry experiments that were performed in this thesis. The bulb for an arc lamp is constructed by sealing an anode and a cathode in a quartz envelope. They are usually filled with high pressure Hg or Xe gas at 5-20 bar. If pure quartz is used to encapsulate the gas then wavelengths below 200 nm are transmitted. It can also be doped to prevent ozone formation by the reaction of sub-260 nm light with atmospheric oxygen [122].

A 150 W Xe arc lamp, model number 6255 from Oriel Instruments, was used for the majority of the photolysis experiments. The irradiance spectrum of



**Figure 3.5** The output spectrum of a range of Xe arc lamps from Oriel. The inset shows the irradiance of the lamps in the UV-visible range. The irradiance is approximately constant across the range, but decreases at about 275 nm. Ozone free lamp 6255 was primarily used in this thesis [123].

the lamp is shown in Figure 3.5, along with the spectra of other similar Xe bulbs. A research arc lamp housing with fused silica collimating optics was used to power the lamp and focus the output on the samples. Xe arc lamps are superior to Hg arc lamps when it is necessary to have a consistent output across a range of wavelengths. The Hg lamps have intense line outputs in the UV and are suitable for applications where UV line irradiance is required. Uniform irradiance across a range of UV and visible wavelengths was required to examine the photosensitivity of organic materials, so a Xe light source was ideal. The Xe lamp irradiates like a 5500-6000 K blackbody, with Xe emission lines superimposed. The emission lines are mainly in the IR spectrum, between 750-1000 nm, meaning that the UV-vis range is predominantly featureless.

## **3.2.3 Optical filters**

Linear variable filters figured as the key part of the illumination system that was used for photolysis studies, providing a practical means of tuning the source wavelength over a range of several hundred nanometres. These filters, produced by Ocean Optics, Inc., were used to spectrally shape the output from broadband light sources, such as the Oriel Xe arc lamps. Restricting the wavelength of light incident on a sample during these photochemistry experiments enabled the determination of the specific photon energies required to drive molecular scissions and rearrangements in active organic electronic materials.

The filters consist of 57 x 10 mm quartz substrates, with a variety of interference coatings applied along the length of the window [124]. Variable high-pass and low-pass filters can be produced in this way, but when these two types of filters are sandwiched together, variable band-pass filters are produced.

The back-to-back high-pass and low-pass filters can be translated with respect to each other to vary the bandwidth around the central transmitted wavelength. This eliminates the need for multiple single bandpass filters, and provides useful wavelength selectability. Figure 3.6(a) shows the output when a section of the bandpass filter is illuminated.



**Figure 3.6** (a) The light output of the Ocean-Optics LVF-UV-HL bandpass filter is projected onto a screen when broadly illuminated with a Xe arc lamp. (b) The transmission spectrum of the LVF-HL filter (taken from [124]), showing that a broad band at 550 nm accompanies the 300 nm window.

The two filters that were used in this work were the LVF-UV-HH double high-pass filter and the LVF-UV-HL bandpass filter. The first filter consisted of two high-pass filters sandwiched together to give 80% transmission of IR radiation, while blocking 99.96% of the intensity of shorter wavelengths. The second filter had a bandwidth minimum of approximately 20 nm at the FWHM and was used to shape the spectrum of the Xe arc lamp in the range between 230-500 nm. At band wavelengths lower than 350 nm, the filter transmits infrared as well as UV light. The spectral output for an Ocean Optics LVF-HL filter is shown in Figure 3.6(b). Narrow bands are produced in the range from 350 - 650 nm, but light is transmitted in two bands when shorter wavelengths are passed (a broad peak at 550 nm accompanies the 300 nm window) [124].

### 3.2.4 Setup of a nitrogen atmosphere glove box for UV exposures

As discussed in section 2.5.4, organic materials may undergo photo-oxidation when exposed to short wavelength radiation in the presence of oxygen and water vapour. Pentacene is particularly liable to oxidation across the central ring, even when sitting in dark conditions in atmosphere. In order to process materials such as the Diels-Alder precursors of pentacene by UV exposure without these unwanted side reactions, a controlled atmosphere glove box was constructed. Inert gases such as dry  $N_2$  or Ar can be pumped into the box so that over time the air inside it is displaced and OFET active layers can be reliably processed. The box, shown in Figure 3.7(a) is constructed out of clear Perspex and has an optical table array machined into the base so that optical elements can be held firmly in position. Items can be transferred into the box through a twist sealable access port at one end and can be manipulated whilst inside the box using the butyl rubber



**Figure 3.7** (a) The Perspex glove box constructed for inert environment photolysis experiments is shown on the right of a PID controller and transformer which supply power to the heater block inside the box. (b) The UV transparent window transmitting filtered green light onto a substrate. (c) The Al heater block and Watlow heater pads used when annealing samples during UV exposures.

gloves. These gloves are impermeable to water, but do leak oxygen. Swagelok bulkhead union adaptors are located diagonally across the top and bottom of the box ends. These are fitted with taps to control the flow rate of  $N_2$  into and out of the box. A safety outlet is located at the top of the box, which prevents build up of excessive pressure inside. Electrical and thermocouple feedthroughs are located on the end of the box. The power feedthrough consists of a pair of Weidmuller 6-way BK6/E terminal blocks, which are located both inside and outside of the box. The thermocouple feedthrough is composed of K-type barrier terminal strips, with connections for six thermocouple wires. The wires run between the inner and outer terminal strips via a hole above the arrays that is sealed with silicone filler. The most important component of the box, considering its use for UV exposure experiments, is the UV transparent window at the front. The 2 inch diameter CVI PW-2025-UV window is made of UV grade synthetic fused silica and is transparent at wavelengths of 180 nm and above. It fits into the recess of a metal flange with a rubber o-ring and is bolted to the front of the box, as shown in Figure 3.7(b).

Exposure experiments are typically conducted after bleeding dry  $N_2$  from the boil off of a liquid nitrogen tank into the box for a period of 15 minutes. The output of the light source is aimed at the UV transparent window, while optical elements such as filters and apertures can either be placed inside or outside the box. Samples can be exposed and then manipulated using the inbuilt gloves without needing to open the box to the atmosphere.

A heater stage was also constructed from a block of aluminium with Watlow 100 W heater strips bolted to the back (Figure 3.7(c)). A sample film can be held in a bracket attached to the front of the block so that the film can be annealed while simultaneously being exposed to UV light in the inert environment. A thin steel shield can also be attached to the block to reduce surface temperature fluctuations on the sample films, resulting from the flow of gas into the box. The two heater pads are rated for 120 V and are connected in parallel to the output of a 115 V transformer. The temperature of the heater block is set using a PID controller, shown on the bench in Figure 3.7(a), which adjusts the power supplied to the transformer so that a preset temperature is reached. The PID monitors the temperature of the back of the heater block via a thermocouple wire. The temperature of parts of the front surface of the substrate can be monitored using separate thermocouple meters.

## **3.3 ANALYTICAL INSTRUMENTATION AND SPECTROSCOPIC TECHNIQUES**

The aim of this thesis was to analyse applications of a number of photosensitive materials in the fabrication of OFETs. Evaluation of the materials can draw upon several figures of merit, but ultimately the most important are bulk electrical parameters such as the field effect mobility and the threshold voltage. These parameters can be extracted using a transistor parameter analyser; the setup used in this thesis is described in this section. The spectroscopic techniques used to study changes in the materials are also discussed.

#### 3.3.1 Setup of a transistor parameter analyser

A Tektronix PWS4721 Programmable DC Power Supply 0-72 V, 1.2 A was used in combination with a Keithley 617 programmable electrometer to build a transistor parameter analyser. The Tektronix power supply was used to set the gate voltage of the test transistors to any value from 0 - 72 V. A Keithley 705 scanner was used to switch the polarity of the gate voltage so that both positive and negative voltages could be applied for testing n-type and p-type transistors, respectively. The Keithley 617 was used to set the source-drain voltage. The source electrode was grounded while the drain electrode voltage was varied through a maximum range of -102.35 V to 102.35 V, with a maximum output current limited to 2 mA [125]. A labview program was coded to control the voltages applied to the terminals of the transistors. The electrometer was interfaced with LabVIEW software using a Prologix GPIB-USB controller. Transistor output curves were measured by setting a gate voltage range and increment and then recording  $I_D$  while varying  $V_{DS}$  at a specific gate voltage. The parameter analyser work station is shown in Figure 3.8(a).

Transistors were tested on a Wentworth Laboratories probe station, fitted with three probes for the source, drain and gate connections. "Pogo sticks" were connected to the source and drain electrodes to avoid damaging the delicate gold films, while a needle probe was connected to the gate electrode to make good contact with the silicon wafer. A typical connection to the transistor is shown in Figure 3.8(b). The gate electrode on the transistors was formed by removing an area of the SiO<sub>2</sub> layer using a diamond tipped scribe to expose the doped silicon underneath.

Organic transistor mobilities are usually reported for operation in the saturation regime. This practice originates from the development of Schottky barriers at the source-drain contacts. The integrated resistance of the channel is higher in the saturation regime than in the linear regime, which tends to mask the influence of the contact resistance. Thus, the saturation mobility,  $\mu_{sat}$ , is often



**Figure 3.8** (a) Parameter analyser workstation. (b) Probe connections to the gold source and drain electrodes and silicon gate electrode of a bottom-contact bottom-gate OFET.

found to be higher than the linear mobility,  $\mu_{lin}$ . The transistor geometry may also have an influence; access resistances in top-contact devices may be higher in the portion of the semiconductor that lies beyond the extents of the gate electrode. Thus, unless the contact resistances are known,  $\mu_{sat}$  should be quoted for a material as opposed to  $\mu_{lin}$  [54].

### 3.3.2 UV-vis absorption spectroscopy

As the premise of this thesis was to alter the bulk electrical properties of active thin films by photochemically driving changes in the electronic levels of the materials, UV-visible absorption spectroscopy proved to be an ideal way to track the susceptibility of sample materials to change. This technique provides information about the separation between occupied and unoccupied electronic levels in the films by monitoring the reduction in light transmitted through a film at the energies corresponding to the difference between the states. All UV-vis absorption spectra were recorded using a Cary 5000 spectrophotometer. For all thin film spectra in Chapters Four, Five and Six, films were deposited on UV-grade quartz coverslips. Spectra were recorded by measuring the transmission through a blank coverslip, then measuring the transmission through a coverslip coated with the film. The solution spectra for 5,14-MPn and 6,13-MPn that are presented in Chapter 5 were both recorded in 10 mm long quartz cuvettes, using 100% ethanol as the solvent.

#### 3.3.3 IR spectroscopy

IR spectroscopy also aided in monitoring the presence of specific functional groups within the molecules composing the thin films. Changes in these

vibrational spectra were monitored to assess the progress of photochemical reactions. The instrument used to perform measurements by IR spectroscopy was a Thermo Scientific Nicolet iS10 FT-IR spectrometer. Samples were prepared by grinding approximately 1 mg of the organic material with 100 mg of KBr grains in a mortar and pestle. When a homogeneous mixture was obtained, the powder was compressed into a disc using a hydraulic press. The disc was then inserted into a sample holder and placed into an analysis compartment that was flushed with N<sub>2</sub>. Since N<sub>2</sub> is a homonuclear diatomic molecule, it does not have an IR spectrum. It is used to displace atmospheric CO<sub>2</sub>, CO and H<sub>2</sub>O out of the system, overcoming the effects of fluctuations in the background concentrations. For the experiments regarding the photo-oxidation of pentacene that was produced via the decomposition of 5,14-MPn, a KBr matrix was not used. The photo-oxidised material was placed directly on a sample stage and compressed under a reflective surface.

## 3.3.4 Equipment used for soft x-ray spectroscopy

The suitability of materials for use in OFETs was also examined by x-ray spectroscopic techniques, which probe the energies of the occupied and unoccupied molecular orbitals independently. This provides complementary information to UV-visible spectroscopy which only reveals the energy *separation* of the orbitals, not the actual energies of the orbitals. Thus, information is provided directly on those orbitals that are active in the charge transport mechanism. In turn, artificial versions of these spectra can in some cases be created using software based on density functional theory (DFT). This software is

useful for making predictions about the electronic properties of materials prior to carrying out the more challenging task of chemical synthesis.

Soft x-ray spectroscopy was performed on different at separate times on three different synchrotron light sources. These included: beamline I511-3 at the MAX II synchrotron in Lund, Sweden, beamline X1B at the National Synchrotron Light Source, Long Island, New York and the soft x-ray beamline of the Australian Synchrotron, Melbourne. X-ray absorption and emission spectroscopy were performed on beamline I511-3, x-ray emission was performed at X1B and absorption and XPS measurements were made at the Australian Synchrotron. The exact beamlines used for the measurement of the spectra of certain materials are discussed in the experimental sections within Chapter Four. This section provides an overview of how experiments were performed on beamline I511-3, with similar procedures being followed at the other facilities. In addition to this description, a review of the background theory pertaining to soft x-ray spectroscopy and synchrotron light sources is provided in Appendix Four.

Beamline I511-3 is an experimental station on the MAX II synchrotron that is equipped for performing x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) measurements on bulk samples. A schematic overview of the beamline optical system is given in Figure 3.9. The beamline produces a small focus photon spot on the sample, while optimising the photon flux; essential for x-ray fluorescence spectroscopy.

The light source for the beamline is a hybrid undulator, which is an insertion device consisting of a periodic magnetic structure installed in a straight section of the synchrotron electron-storage ring [126]. A vertical magnetic field varies sinusoidally along the axis of the undulator, resulting in a sinusoidal



**Figure 3.9** *MAX-lab beamline I511-3 optical system and inset showing the geometry of the optical instruments within the XES-350 spectrometer.* 

oscillation of the electron beam in a perpendicular plane. Broadband synchrotron radiation is emitted by the accelerating electrons, in a direction parallel to the electron beam. The light is linearly polarised with E-vector in the horizontal plane of the beamline [127]. The I511 undulator has 49 magnetic periods of length 52 mm, with a  $K_{max}$  value of 2.7 [128]. K is a dimensionless parameter that is proportional to the deflection of the electron beam. Variation of the undulator gap between 23 mm and 250 mm gives rise to a useable broadband energy range from 50 eV to 1500 eV [128].

The optical system provides great flexibility in controlling photon flux, resolving power and the suppression of higher order diffraction modes [128]. The essential optical component of the 25 m long beamline is a modified Zeiss SX-700 monochromator, which disperses the broadband undulator radiation. The monochromator contains two exchangeable gratings; a gold coated one with 1220 lines/mm and another nickel coated one with 250 lines/mm. A spherical mirror focuses the undulator radiation onto a plane mirror, which redirects light onto the monochromator grating [129]. Light diffracted by the grating is directed by a

spherical mirror to the beamline exit slit. A series of beam waist monitors are placed between the grating and a moveable exit slit, which selects a range of wavelengths from the dispersed monochromator light. The refocusing optics for the beamline output are mounted in a Kirkpatrick-Baez configuration (the first mirror focuses in the vertical plane, the second in the horizontal) and consist of gold coated plane-elliptical mirrors [128, 129]. The available energy resolution E/dE varies from  $5 \times 10^3$  to  $2 \times 10^4$  when the 1220 lines/mm monochromator grating is used. With the same grating, the photon flux on the sample varies between  $10^{11}$  to  $10^{13}$  photons s<sup>-1</sup> [128]. The beam spot size at the sample is approximately 20 µm × 30 µm [127].

Rotation of a flip-mirror placed in the beam path immediately after the exit slit switches beam supply between two endstations. The two endstations supplied by the beamline are named I511-1 and I511-3. Surface science experiments are conducted with the first as it is equipped with an electron analyser for x-ray photoelectron spectroscopy (XPS) and an electron yield detector for XAS. Endstation I511-3 is used to perform bulk XES and XAS measurements on gas phase and solid phase systems [128]. As such, the latter was chosen as the instrument for NEXAFS and SXES experiments on PTCDA films (see section 4.2.1).

NEXAFS measurements are conducted by mounting a sample in the analysis chamber, in the path of the x-ray beam. All NEXAFS spectra in this thesis were recorded using the fluorescence detection mode for the system. The detection system for the fluorescent signal consists of a multichannel plate detector within the analysis chamber, with no additional optics [128]. The channel plate is negatively biased so as to exclude Auger electrons emitted by the sample.

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An additional mesh in front of the channel plate is positively biased so as to reject ions from inside the chamber, which would otherwise interfere with the signal [127]. A grid placed further down the beamline, prior to the analysis chamber is used to measure the total photon flux that is incident on the sample. The photon flux varies as the x-ray beam energy is scanned across a range of values (280 – 295 eV for carbon NEXAFS) appropriate for the absorption spectrum. The fluorescence signal is then divided by this grid signal to obtain the NEXAFS spectrum. In most beamlines an additional normalisation step first takes place. Due to carbon contamination on the optics of the beamline, a NEXAFS scan must be recorded with no sample in the endstation at the range of energies used for any carbon K-edge spectra. Any signal detected must be normalised out of sample NEXAFS scans [130].

SXES measurements are made with a Scienta XES-350 x-ray emission spectrometer [128]. The emission signal is focussed by placing the source, detector and spherical grating on a Rowland circle; a circle with half the radius of the spherical grating. The inset to Fig. 4.1 is an illustration of the spectrometer optical geometry. Three gratings are located on Rowland circles of different radii. They are mounted at varying angles of incidence with respect to the entrance slit and are optimised for different energy ranges. Two gratings have a radius of 5 m, the other has a radius of 3 m. They are holographically produced on glass, with a gold coated photoresist. They have a density of 400, 800 and 1200 lines/mm. The detection system, consisting of a stack of five multichannel plates of 40 mm diameter, measures the emission signal at grazing incidence. The detector is two dimensional, sampled with 32 virtual data slices perpendicular to the dispersion direction. The slices of the

single spectra are shifted in the dispersion direction (accounting for the imaging of the straight entrance slit as a curved line on the detector) to produce a one dimensional spectrum with 1024 channels representing the energy scale [127].

Beam damage of the organic materials studied is a problem, due to the high flux of incident x-rays. When x-ray emission studies were performed, the flux of photons emitted from the sample was so low that the maximum incident flux was used. To avoid measuring the spectrum of photodamaged material, the samples were constantly translated in front of the x-ray beam (see Figure 3.10) [131]. Translation is not possible in the case of the NEXAFS measurements, because this technique is sensitive to the local film morphology. Instead, the incident photon flux was minimised by reducing the gap in the exit slits ahead of the endstation and by setting the substrate at a grazing incidence with respect to the beam so as to spread the flux over as large an area as possible.



**Figure 3.10** *Translating a sample in the x-ray beam when conducting SXES measurements reduces the influence of beam damaged sample material in the spectrum [131].* 

## **3.4 MATERIALS ANALYSED**

A number of organic semiconducting and conducting materials, as well as organic semiconductor precursors are studied in this thesis. Three n-type semiconductors

**Table 3.1** Semiconductors and precursors studied in this thesis.

Material	Structure	Supplier	Product
			Number
5,14-dihydro-5,14-	0	Luminescence	LT-S971
methanopentacene-15-	Ĩ,	Technology	
one (5,14-MPn)		Corp, Hsin-	
		Chu, Taiwan	
6,13-dihydro-6,13-		Sigma-Aldrich	688045
methanopentacene-15-	0	Pty Ltd,	
one (6,13-MPn)	A	Australia	
Pentacene		Sigma-Aldrich	P1802
		Pty Ltd,	
		Australia	
perylene-3,4,9,10-		Sigma-Aldrich	P11255
tetracarboxylic	°	Pty Ltd,	
dianhydride (PTCDA)		Australia	
N,N'-diphenyl-perylene-		Sigma-Aldrich	663905
3,4,9,10-tetracarboxylic		Pty Ltd,	
acid diimide (DPh-PTCDI)		Australia	
N,N'-dioctyl-perylene-		Sigma-Aldrich	663913
3,4,9,10-tetracarboxylic		Pty Ltd,	
acid diimide (C8-PTCDI)	H <sub>17</sub> C <sub>8</sub> -N N-C <sub>8</sub> H <sub>17</sub>	Australia	
poly(3,4-		Ossila Limited,	M122
ethylenedioxythiophen		Sheffield, UK	
e)			
poly(styrenesulfonate)			
(PEDOT:PSS_PH1000)	s		
	s [		

with perylene cores are studied in Chapter Four. The UV-vis absorption spectra of pentacene and two precursor materials are studied in Chapter Five and Six. These are all small molecule materials. An aqueous dispersion of a polymer conductor, PEDOT:PSS is also studied in Chapter Six. The structures, suppliers and product numbers of each of the materials used are supplied in Table 3.1.

## **3.5 CONCLUSIONS**

The instrumentation and techniques used to deposit, pattern and analyse the materials used in the production of OFETs have been outlined in this chapter. The experimental procedures for the spectroscopic techniques that were used have been described. These techniques are in common use, but for ease of reference an additional overview of the background theory relating to UV-visible, IR and x-ray spectroscopy is provided in Appendix Four. The remaining chapters of this thesis now focus on the results of experiments that were carried out to test the performance of photopatternable materials in OFETs. In the following chapter the UV-visible absorption spectra and x-ray spectra of a family of semiconductors based on perylene are compared to synthetic spectra produced via computational techniques. This provides for an enhanced understanding of how molecular structure and geometry affect the electronic properties of organic materials.

# CHAPTER FOUR

Using density functional theory to model the electronic properties of small molecule organic semiconductor thin films

Density functional theory (DFT) is a computational tool that is used to model the geometry and the electronic structure of organic molecules. Additional calculations can be performed on the optimised electronic structures of the model molecules, yielding synthetic UV-vis, IR and density of states (DOS) spectra. Solvated molecules and even single crystals can be modelled, however the computational time scales faster than any increase in the total number of electrons in the system. This restricts the size of the molecules and limits the number of repeated units in crystals that can be practically analysed using limited computational resources. By performing calculations on single molecules the properties of a greater number of chemical species can be examined in a given time, although potentially at the cost of accuracy. It is, however, the best starting point when examining the properties of new materials.

The value of DFT is that it provides a means to design molecules and gain some understanding of their properties without having to do any actual chemical synthesis. For instance, if one was interested in modifying the colour of a chemical dye, the effects of adding new functional groups or other substituents can be predicted by calculating the UV-vis spectrum of the proposed structure. This type of information also proves to be useful for studying the photochemistry of organic semiconductor precursors. If the synthetic UV-vis spectra accurately mimic the spectra that are observed experimentally for thin films, then real absorption features can be confidently attributed to particular MO transitions from the calculation. Various forms of DFT software commonly allow the initial and final state MOs of an absorption feature to be visualised. This means that after the absorption of a photon, the movement of charge from one part of the molecular structure to another distinct region can be traced. This optically driven charge rearrangement is exactly what happens in the breakdown of the Diels-Alder pentacene precursors that were discussed earlier in section 2.5. The synthetic UV-vis spectra of these precursors will be examined in Chapter Five, but this chapter focuses on testing the accuracy of DFT calculations for a family of n-type semiconducting materials which all share a perylene core. Unlike the pentacene precursors, these materials are stable enough to allow x-ray absorption and emission spectra to be measured and compared against synthetic DOS spectra. Experimental x-ray absorption and emission spectra could not be obtained for the precursors of pentacene, which degrade rapidly under exposure to x-rays. This is why this chapter examines the spectra of the more robust perylene based materials.

## 4.1 MODELING THE ELECTRONIC STRUCTURE OF ORGANIC MOLECULES USING DFT

DFT is a quantum mechanical computation technique that is used to investigate the ground state energy of systems containing multiple interacting bodies. The central feature of DFT is the proof by Pierre Hohenberg and Walter Kohn that the ground state electronic energy of a system is determined completely by the electron density [132]. DFT is used to determine the electron density distribution  $\rho(r)$  as an alternative to calculating the electron wave functions of a molecule directly [133]. The advantage is that all calculations have the same number of dimensional variables, independent of the number of electrons in a system. This contrasts with the wave function calculations for an N-electron system which includes 3N coordinates; a total of three for each electron [132].

The general DFT energy expression is composed of a sum of density functionals and is given by:

$$E_{DFT}[\rho] = T_s[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho]$$
(4.1)

which represents the energy corresponding to an approximate electron density,  $\rho$ . The term  $T_s$  represents the kinetic energy of non-interacting electrons,  $E_{ne}$  represents the attraction between electrons and nuclei and J represents the Coulomb part of the electron-electron interaction.  $E_{xc}$  accounts for the exchange-correlation effects of interacting electrons. The usefulness of DFT depends upon finding suitably accurate and computationally efficient approximations for the functional  $E_{xc}[\rho]$ . If this term is neglected, (4.1) reduces to the simpler, but less accurate Hartree-Fock theory. DFT methods improve on this by the inclusion of the correlation energy (the computationally difficult aspect of wave mechanics) in a calculation requiring a similar demand for computational resources as the uncorrelated Hartree-Fock theory [132]. It is therefore ideal for computational chemistry work involving the multi-atom small molecules encountered in organic electronics.

The software used in this thesis for all DFT calculations was *Parallel DGauss under Ab Initio CAChe*, from Fujitsu Limited [134]. Models of the molecules of interest were drawn in the Cache workspace and then the molecular geometries were optimised using a generalised gradient approximation (GGA) and the B88-PW91 exchange-correlation energy functional. A triple-zeta valence potential orbital basis set was used, with zero pseudopotentials.

## 4.1.1 The synthetic partial density of states (PDOS) of a molecule as calculated using the DGauss software

After first optimising the geometry of the single molecule model of an organic semiconductor, the energy and spatial extent of the individual molecular orbitals were determined in a separate calculation. Following this, a calculation of the molecular DOS was made. The DOS represents the distribution of electronic states in a molecule; it is a count of the number of eigenstates per unit energy in the neighbourhood of a particular value of the electronic energy, *E*. The *partial* density of states (PDOS) of a molecule is simply a measure of all the eigenstates in a molecule that have the same orbital angular momentum quantum number. Soft x-ray emission spectroscopy (SXES) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy provide a direct means of obtaining this information because, as outlined in Appendix Four, the intensities of the transition resonances are a function of the molecular PDOS. They provide a measure of the occupied and unoccupied PDOS, respectively.

Molecules are finite systems, so the energy eigenvalues are discrete rather than continuous. In crystals, which are infinite systems, the DOS varies smoothly because electronic states are continuously distributed (as a result of the Pauli Exclusion Principle). The experimentally measured DOS of a certain molecular crystal may be compared with the calculated DOS of a single molecule by convolving the discrete eigenstates with a normalised Gaussian function, to simulate the influence of broadening effects. One source of broadening in condensed matter is *lifetime broadening*, which eventuates when a transition occurs between two quantum states. For a system that changes over time it is impossible to specify the energies of the upper and lower states exactly [39]. This lifetime broadening has a Lorentzian profile. However, the experimental broadening due to limited instrument resolution has a Gaussian nature and this effect tends to dominate the lifetime broadening. It is most appropriate to convolve the calculated discrete DOS with a Gaussian profile. This procedure has been carried out in a number of instances to study the relationship between the measured electronic structure of organic semiconductor thin films and the electronic properties of the corresponding single-molecule models [135, 136].

The PDOS of a molecule is calculated in DGauss by a process called Mulliken orbital population analysis. The PDOS with *p*-orbital character due to the atom *M* within a molecule is represented by  $D_{Mp}(E)$ . This term is evaluated using:

$$D_{M_p}(E) = \frac{1}{\Delta\sqrt{\pi}} \sum_{i} A_i \left(M_p\right) exp\left(-\left(\frac{E-\varepsilon_i}{\Delta}\right)^2\right)$$
(4.2)

where  $A_i(M_p)$  is the p-orbital population of the i<sup>th</sup> molecular orbital within the atom M.  $\Delta$  is the width of the broadening Gaussian and is typically taken to be

some fraction of an electron volt. Values of 0.3 eV were used in the PDOS calculations in this chapter. *E* simply represents energy and  $\varepsilon_i$  represents the energy eigenvalue of the i<sup>th</sup> molecular orbital [134].

## 4.1.2 Synthetic UV-visible spectra of molecules as calculated using the DGauss software

*DGauss under ab initio CAChe* was used to calculate and display molecular UV-vis spectra. Individual spectral absorption peaks may be viewed using the software, alongside the density isosurfaces of the two molecular orbitals involved in a given transition. These isosurfaces are superimposed over the physical molecular structure, showing which parts of the molecule make the strongest contribution to the transition probability – those areas of the molecule where the orbitals overlap. This also allows for the identification of excited states that are likely to be involved in structure altering photochemical reactions [137].

The UV-vis spectra of small-molecule organic semiconductors typically contain dozens of electronic transitions. The amplitude of an electronic excitation from a ground state 0 to an excited state *i* is approximated by the expression:

$$t_{0i} = \int \Psi_i^* \boldsymbol{r} \Psi_0 \tag{4.3}$$

which is the integral over all space of the dipole vector  $\mathbf{r} = (\mathbf{x}, \mathbf{y}, \mathbf{z})$  with the wavefunctions  $\Psi_0$  and  $\Psi_i^*$  of the ground state and excited state respectively [137]. This is called the *dipole approximation* and is accurate to the first order. Thus, to the first order, the absorption intensity depends on the overlap of the initial and final state orbitals. When there is little overlap between the orbitals the transition has little intensity.

All of the synthetic UV-vis spectra presented in this chapter were calculated in *CAChe* by a ZINDO (Zerner's Intermediate Neglect of Differential Overlap) configuration interaction using INDO/S parameters. The configuration interaction accounts for the fact that simply taking the HOMO-LUMO gap of a ground state molecule overestimates the transition energy [138]. The transition of an electron from the ground state to an excited state instantly perturbs the position of all of the orbitals, relaxing the unoccupied ground state orbitals to lower energies. It may seem counterintuitive, but this correction due to the configuration interaction is sometimes so large that the transition between the HOMO and LUMO orbitals of the *ground state* is not actually the lowest energy transition that occurs in a molecule.

There are some drawbacks to the ZINDO calculation which do complicate the task of assigning the absorption features in an experimental UV-vis spectrum to the transitions in the synthetic spectrum. Firstly, ZINDO only determines the energy difference between occupied and unoccupied electronic states; it does not account for excitation to different vibrational levels in the final state [138]. The other problem is that ZINDO predictions of the HOMO-LUMO transition wavelength appear to be systematically too short and a scaling factor should be applied to make the comparison easier. In practice this means that if the software is used to make predictions about the colour of dyes, for example, a series of synthetic spectra and experimental spectra should be compared so that an effective wavelength calibration can be made [139]. The experimental HOMO-LUMO peaks are often red-shifted for two main reasons. Where there is strong overlap of the frontier orbitals between neighbouring molecules, charge transfer or exciton states can exist, with charge carriers delocalised over neighbouring molecules. These states have lower energies than the HOMO-LUMO transition of the single molecule and of course in calculations of single molecules these states cannot be accounted for. A second source of error is the fact that the exchangecorrelation potentials typically used in DFT calculations lead to what is known as the "self-interaction error" because they do not show the correct 1/r asymptotic behaviour [140]. When strongly interacting semiconducting molecules are studied, these errors should be evident. In the case of true insulating van der Waals solids, where interactions with nearest neighbours are relatively weak, the single-molecule DFT absorption spectrum calculations should match the experimental spectra relatively well.

## 4.2 A COMPARISON OF THE SYNTHETIC AND EXPERIMENTAL PDOS AND UV-VISIBLE SPECTRA OF PERYLENE BASED ORGANIC SEMICONDUCTORS

To begin this investigation of the accuracy of the DFT calculations, three related molecules with a demonstrated semiconducting behaviour are examined. They are perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), N,N'-diphenyl-perylene-3,4,9,10-tetracarboxylic acid diimide (DPh-PTCDI) and N,N'-dioctyl-perylene-3,4,9,10-tetracarboxylic acid diimide (C8-PTCDI). The structures are shown in Figure 4.1. These three derivatives all have a perylene core (Figure 4.1(a)); a polyaromatic hydrocarbon consisting of five fused benzene rings that behaves as a p-type semiconductor. The introduction of highly electronegative oxygen and nitrogen atoms into the structure stabilises the molecule, so that these three perylene derivatives actually behave as n-type semiconductors. The smallest derivative in this group is PTCDA, which has two anhydride substituents at each



**Figure 4.1** Structures of the p-type semiconductor perylene (a) and the n-type semiconductors, perylene tetracarboxylic dianhydride (PTCDA) (b), N,N'-diphenyl-perylene-3,4,9,10-tetracarboxylic acid diimide (DPh-PTCDI) (c), and N,N'-dioctyl-perylene-3,4,9,10-tetracarboxylic acid diimide (C8-PTCDI) (d).

end of the perylene core. Its HOMO level lies at -7.00 eV and the LUMO is at -4.66 eV with respect to the vacuum level [141]. Since the LUMO is close to the Fermi level of gold, n-type organic thin film transistors have been produced via vapour deposition of PTCDA, yielding field effect mobilities of  $10^{-5} - 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [142].

Substitution of the oxygen atom in the centre of the PTCDA anhydride groups with nitrogen atoms allows for derivatisation of the ends of the molecule using a wide variety of substituents, such as aryl or alkyl groups. The substitution slightly modifies the HOMO and LUMO levels of the molecule, but the desired effect is to alter both the solubility of the molecule and the molecular packing orientation in the solid-state. There is minimal improvement in the performance of DPh-PTCDI transistors, for which a field effect mobility of only  $5 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> has been measured [143]. More successfully, the addition of long alkyl chains to the diimide group leads to much improved  $\pi$ -orbital interaction between neighbouring molecules. In the case of C8-PTCDI, a field effect mobility of 1.7 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an on/off current ratio of 10<sup>7</sup> have been observed [144].

Highly-conjugated small molecules that have very low charge mobilities in thin films (less than  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) generally do so because of poor  $\pi$ -orbital overlap between adjacent molecules or because the packing orientation does not allow for charge hopping along the length of the source-drain channel. Conversely, materials with high mobilities have extensive  $\pi$ -orbital overlap in the solid state and a packing orientation that promotes the flow of charges between the electrodes. Extensive overlap of frontier orbitals should lead to a modification of the HOMO and LUMO orbital energies. This is typically observed as a strong red-shift in the HOMO-LUMO peak of the thin film UV-vis spectrum relative to the synthetic spectrum. There should be noticeable differences in the case of the high mobility C8-PTCDI because the mobility implies that there is strong overlap of the  $\pi$ -orbitals on adjacent molecules in the solid state. This hypothesis is also tested in this chapter by comparing how well the NEXAFS and SXES spectra for thin films of the perylene derivatives match with the DFT calculations of the single-molecule partial density of states (PDOS), which neglect any overlap of adjacent  $\pi$ -orbitals. This is a procedure that is used frequently to check the accuracy of DFT calculations and ensure that the predictions made regarding the photophysics of materials are reliable [131, 145-147]. Single molecule DFT calculations tend to be useful for understanding thin film spectra where true van der Waals bonded materials are involved [147]. In this chapter the materials have widely varying charge mobilities which are possibly due to variations in the strength of bonding. It is therefore of interest to examine the differences in the match between the synthetic and thin film spectra in each case. The chapter concludes with a study of the angular dependence of NEXAFS spectra which reveals further information about the thin film packing order.

#### 4.2.1 PTCDA spectra

PTCDA was obtained from Sigma-Aldrich (product P11255) and used as received. The UV-vis absorption spectrum was measured for a thin film deposited onto a sapphire substrate by vapour deposition at 10<sup>-6</sup> Torr. The spectrum was measured using a Cary 5000 spectrophotometer. NEXAFS and XPS spectroscopy were performed on the Australian Synchrotron soft x-ray beamline, while SXES spectra were recorded on beamline I511 at the MAXlab synchrotron in Lund, Sweden. PTCDA was evaporated in-situ at the Australian synchrotron onto an n-doped silicon wafer. A growth rate of 0.5 nm/min was maintained at a temperature of 365 °C, yielding a film that was 45 nm thick. A PTCDA film could not be grown in-situ at MAXlab. Instead, a film was deposited onto a segment of n-doped silicon wafer in the vacuum system at Macquarie University and then transported to the beamline.

#### 4.2.1.1 PTCDA UV-visible spectra

The synthetic and thin film UV-vis absorption spectra of PTCDA are compared in Figure 4.2. They are shown at the bottom and the top, respectively. Four individual MO transitions are highlighted by the dashed lines in the synthetic



**Figure 4.2** The thin film (top) and synthetic (bottom) UV-vis absorption spectra of PTCDA. Individual transitions corresponding to the MO pairs in Figure 4.3 are highlighted by the dashed lines in the synthetic spectrum. The HOMO – LUMO peak of the thin film is red-shifted by 50 nm with respect to the peak in the synthetic spectrum. There is also an exciton peak in the thin film spectrum at 551 nm that does not appear in the synthetic spectrum.

spectrum. These features correspond to the pairs of occupied and unoccupied ground state PTCDA MOs illustrated in Figure 4.3. The central wavelengths of the Gaussians composing each absorption feature are also listed. The HOMO – LUMO transition occurs at the longest wavelength and it may be expected that the HOMO-1 to LUMO or HOMO to LUMO+1 transition would appear next, at a shorter wavelength. Instead, it is the HOMO-2 to LUMO transition that appears. This means that there is either no mutual overlap between the HOMO-1 and the LUMO, or the correction due to the configuration interaction means that the HOMO-2 orbital rather than the HOMO-1 is closer in energy to the LUMO.

The impression at first glance is that the spectra in Figure 4.2, while not



**Figure 4.3** The MO transitions shown above correspond to the synthetic absorption spectrum features that are highlighted by the coloured, dashed lines, in Figure 4.2. The location and amplitude of the ground state occupied and unoccupied orbitals are shown on the molecules. The lobes of the occupied orbitals are shown in solid blue and green, while the lobes of the unoccupied orbitals are shown in transparent red and yellow. The blue and green (or red and yellow) lobes simply represent the positive and negative phases of the MO wavefunctions.

identical, are reasonably similar. The features in the deep UV, below 300 nm, appear to correlate well, although the peak and shoulder at 250 nm and 275 nm in the synthetic spectrum appear as a single peak in the thin film spectrum. The weak HOMO-2 to LUMO absorption feature at 325-350 nm in the synthetic spectrum appears more strongly in the thin film spectrum, from 350-375 nm. The peak at 551 nm in the thin film spectrum is the commonly observed exciton peak. A number of complementary experiments which analysed the peak absorption, fluorescence energy, radiative lifetime and electroabsorption of PTCDA all concluded that this peak is a spatially extended exciton and is not a part of the

vibronic structure of the HOMO-LUMO absorption [148]. This feature isn't modelled by the single-molecule DFT calculation as it is a phenomenon that only occurs in the aggregated state. The exciton corresponds to an excited state of a molecule within the thin film, where an electron and hole are separated but remain locally positioned and therefore are attracted by Coulomb forces. Optically induced excitons appear just below the bandgap in semiconducting materials. The broad feature with a peak at 478 nm does correspond to the HOMO - LUMO transition in the synthetic spectrum at 445 nm. However, although it is somewhat disguised by broadening, it appears that there is a vibrational progression in the spectrum. The  $0 \rightarrow 0$  vibrational transition in the thin film HOMO-LUMO absorption appears to be present at ~495 nm, while the  $0 \rightarrow 1$  vibrational transition occurs near 478 nm. Since the ZINDO UV-vis calculation does not account for vibrational levels in the electronic spectra, it is really the 495 nm peak in the thin film spectrum that is comparable with the 445 nm peak in the synthetic spectrum. Considering all of these features, the correlation of the synthetic and experimental UV-vis spectra is strong enough for peaks in the thin film spectrum to be accurately assigned to the molecular orbitals shown in Figure 4.3. The presence of the exciton peak and the red-shifting of the HOMO-LUMO transition do show that there is some interaction between orbitals on adjacent molecules in the solid state, although the electronic properties of the single molecule are largely preserved.

## 4.2.1.2 PTCDA partial density of states spectra

X-ray absorption spectroscopy is sensitive to the multiple chemical environments of the carbon atoms within PTCDA. In systems with multiple aromatic rings, such


**Figure 4.4** The carbon 1s XPS spectra of a 45 nm thick PTCDA film recorded at an excitation energy of 800 eV.

as PTCDA, the separation in the energies of the carbon core levels tend to be small, ranging from 0 - 1 eV. However, the presence of highly electronegative atoms heavily shifts the position of the core electron level within adjacent carbon atoms. The large chemical shift is due to the fact that in the initial state, the bonded, highly electronegative oxygen atom withdraws the electrons from the carbon atom. This reduces the electron density around the carbon atom, thus increasing the core level binding energy due to the reduction in electron screening. There may also be a difference in the dynamic response of the different carbon groups to the formation of a core hole [149]. The size of the chemical shift can be measured directly by analysing the x-ray photoelectron spectrum (XPS) of a material. This is demonstrated in Figure 4.4, which shows the XPS spectrum of a PTCDA film that was recorded at the Australian Synchrotron, using an excitation energy of 800 eV. Four Voigt functions have been fitted to the major peak from 284 – 286.5 eV, while a single peak is fitted at 288.9 eV. The peak areas were set to a ratio of 8:4:4:4:4, to matching the number of carbon atoms in each environment. The signal for the major peak spanning lower binding energies is attributed to electrons ejected from the 20 carbon atoms of the perylene core within PTCDA. The smaller peak at 288.9 eV corresponds to the ejection from the heavily shifted core levels of the 4 carbons that are directly bonded to the oxygen atoms of the anhydride groups. The ratio of the areas of these peaks ideally corresponds to the ratio of carbon atoms in the two environments. The additional peaks either side of those highlighted are shake-up peaks, and arise due to the removal of a photoelectron from a molecule accompanied by a simultaneous MO transition.

Calculations of the MO energies for DFT optimized PTCDA molecules show that there are several carbon environments within PTCDA. These are labelled in the inset to Figure 4.4. According to the literature, the core levels of the four carbonyl carbon atoms (labelled environment C5 in Figure 4.4) are shifted 4.05 eV towards a higher binding energy, with respect to the lowest binding energy carbons in the perylene rings [149]. The largest chemical shift measured here was found to be 4.12 eV, which is close to the literature value. Taking C1 as the reference point, the chemical shifts are 0.38, 0.64, 0.72 and 4.12 eV for C2, C3, C4 and C5, respectively.

The carbon p-type PDOS for a single molecule of PTCDA was calculated across a range from 20 eV below the Fermi level to 20 eV above, and then convolved with a 0.3 eV FWHM Gaussian to account for instrumentation broadening. The synthetic occupied and unoccupied PDOS is shown as the red line in Figure 4.5. Some manipulation of the synthetic PDOS is required before it



**Figure 4.5** The synthetic carbon p-orbital PDOS for PTCDA. The PDOS of C2-C5 are shifted up by 0.19, 0.23, 0.23 and 1.4 eV with respect to environment C1. Additional shifting was required because the differences between the core level energies calculated for the different carbon environments did not match the separation of peaks fitted to the XPS spectrum.

can be compared to NEXAFS and XES spectra. The MO calculation does determine that there is a difference in the core level energies of the different carbon environments, however these energies and their separations do not match the fits to the XPS spectrum. The shifts between environments C2, C3, C4 and C5, with respect to C1, were calculated as 0.19, 0.41, 0.49 and 2.72 eV, respectively. To account for the additional chemical shifting observed in the XPS spectrum, the PDOS due to each of these environments was shifted up the energy scale by 0.19, 0.23, 0.23 and 1.4 eV, respectively. This was done to ensure that the chemical shifts between the carbon environments in the calculation would match the chemical shifts measured in the XPS spectrum from Figure 4.4. Figure 4.5 shows the sum of these individual carbon environments, taking account



**Figure 4.6** The synthetic (red) and experimental (blue) unoccupied carbon p-orbital PDOS for PTCDA. The carbon 1s NEXAFS spectrum was recorded with the sample oriented at 70° with respect to the direction of the beam. The calculated PDOS for the individual carbon environments are shown as dashed lines. The Fermi level of the synthetic spectrum has been shifted to 284 eV.

of these additional shifts.

The NEXAFS and SXES spectra of PTCDA are compared against the synthetic PDOS (for the sum of all carbon environments) in Figures 4.6 and 4.7, respectively. In Figure 4.6 the energy axis of the synthetic PDOS was shifted up by 284 eV. This value was chosen with reference to the lowest binding energy observed in the XPS spectrum and manipulated so that the experimental and synthetic spectra match as closely as possible.

The calculated unoccupied PDOS in Figure 4.6 corresponds to the actual PDOS relatively well, taking into account that the relative amplitudes of features are different. The amplitudes are not as significant as the relative positions of peaks on the energy scale when it comes to comparing the two spectra. This is

because the amplitudes of the NEXAFS peaks in the 10 eV range above the absorption edge vary with changes in the angle of the substrate (this is explained further in section 4.2.4). Also, there is a background signal in the NEXAFS spectrum that appears roughly 5 eV above the absorption edge, which is due to population of continuum states above the vacuum level during x-ray absorption. The calculation also only presents PDOS information on states associated with molecular orbitals, not the continuum or Rydberg states. The high resolution NEXAFS scan shows some vibrational states within the electronic levels of the unoccupied MOs, particularly those peaks in the range from 287.5 to 289.5 eV. Modern synchrotron sources offer such high energy resolution that fine structure which in the past was unobservable can now be measured. Previous NEXAFS studies on PTCDA have definitively assigned the fine structure to coupling between electronic transitions and individual vibronic states [150].

Examining the sum of environments in the range from 283.5 to 286 eV, it is observed that there is no contribution from the chemically shifted carbonyl group core levels, only from the carbons of the perylene rings. There are two major sets of peaks in the NEXAFS spectrum from 283.4 – 285 eV and from 285 eV to 286.5 eV. These are split into sharper peaks which are separated by energies consistent with the chemical shifts between different carbon ring environments, as determined from the XPS spectrum. The synthetic PDOS also has amplitude in these energy ranges, although splitting is not evident in the sum of peaks. Despite this, it is clear from inspection of the individual contributions of C1, C2 and C4 that there is a difference in the energies of the PDOS maxima for these environments. The shape of the synthetic PDOS from 286.5 – 290 eV appears to be similar to the NEXAFS scan from 287.5 – 290 eV. However, there

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appears to be an approximately 1 eV mismatch between the spectra.

In the case of the SXES spectrum shown in Figure 4.7, once again there is a relatively good correlation between the peaks in the synthetic and experimental spectra. The Fermi level was set to 281.5 eV to improve the match between the spectra. The peaks in the XES scan are strongly broadened due to the instrumentation, meaning that the spectrum is not as detailed as the artificially broadened PDOS spectrum. Taking this into account, it appears that the spectra match very well from 269 to 279 eV because the peaks and shoulders in the XES spectrum can be directly matched to distinct peaks in the synthetic PDOS spectrum. The main difference between the spectra is that the strong peak in the synthetic spectrum at 280.5 eV does not appear as distinctly in the XES spectrum, although there is spectral weight at that energy.



**Figure 4.7** The synthetic occupied carbon p-orbital PDOS (red) and SXES spectrum (blue) for PTCDA. The Fermi level of the synthetic spectrum has been set to 281.5 eV.

Clearly there is a good match between synthetic and experimental spectra for both the occupied and unoccupied PDOS, although there is a slight variation in the features near the Fermi level in both Figure 4.6 and 4.7. The effects of the discrepancies in the calculated and measured PDOS near the Fermi level are borne out in the UV-vis spectra; variations in the energies of the occupied and unoccupied frontier orbitals lead to the shift in the energies of the synthetic and thin-film HOMO-LUMO transitions. However, on balance it remains that the single-molecule DFT calculation did yield a good approximation of the electronic structure of PTCDA molecules in the thin film.

### 4.2.2 DPh-PTCDI spectra

DPh-PTCDI was obtained from Sigma-Aldrich (product 663975) and used as received. UV-vis spectra were measured for an 85 nm thick film deposited onto a UV transparent quartz coverslip. NEXAFS spectroscopy was performed at the Australian Synchrotron soft x-ray beamline and SXES spectra were measured at beamline X1B of the National Synchrotron Light Source, Brookhaven National Laboratory, New York. DPh-PTCDI was evaporated in-situ at the Australian synchrotron onto an n-doped silicon wafer. A growth rate of 0.5 nm/min was maintained at a temperature of 387 °C, yielding a film that was approximately 40 nm thick. The sample for the SXES measurement was grown in the X1B endstation on an n-type silicon wafer. In this case the thickness was not controlled but was considered to be greater than 100 nm, judging from the strength of the SXES signal.

### 4.2.2.1 DPh-PTCDI UV-visible spectra

The synthetic UV-vis absorption spectrum of DPh-PTCDI in Figure 4.8 resembles that of PTCDA (bottom of Figure 4.2), with a broad HOMO-LUMO absorption near 450 nm, a weak transition feature near 350 nm, and a complicated set of stronger peaks below 300 nm. Comparing the synthetic and thin film absorption spectra in Figure 4.8, it appears that the features of the HOMO-LUMO transition are very similar to those seen in PTCDA. This is to be expected because the HOMO-LUMO orbitals (see Figure 4.3 for PTCDA and Figure 4.9 for DPh-PTCDI) have virtually the same distribution across the perylene core and little intensity on the functional groups that differentiate the molecules. The



**Figure 4.8** The thin film (top) and synthetic (bottom) UV-vis absorption spectra of DPh-PTCDI. Individual transitions corresponding to the MO pairs in Figure 4.9 are highlighted by the dashed lines in the synthetic spectrum. The HOMO – LUMO peak of the thin film is red-shifted by 46 nm with respect to the peak in the synthetic spectrum. The exciton peak is centred at 447 nm.

exciton peak, familiar from PTCDA, is present at 547 nm. Two peaks in the vibronic progression of the HOMO-LUMO transition are located at 501 nm and 473 nm. The peak of the HOMO-LUMO transition in the synthetic spectrum occurs at 455 nm, meaning that there is a 46 nm red shift from the synthetic spectrum to the thin film spectrum. This is slightly less than the shift in PTCDA.

The weak absorption from 350 to 400 nm in the thin film spectrum has a different shape to the equivalent feature in the PTCDA spectrum. The calculations for the DPh-PTCDI synthetic spectrum show that there are actually two adjacent peaks at 333 nm and 340 nm that contribute to this feature, rather than the single transition at 341 nm in the PTCDA spectrum. The absorption features below 300 nm in each of the plots in Figure 4.8 are different to those seen in PTCDA



**Figure 4.9** The DPh-PTCDI MO transitions shown above correspond to the features in the synthetic absorption spectrum that are highlighted by the coloured, dashed lines, at the bottom of Figure 4.8. The HOMO and LUMO wavefunctions are the same as those found in PTCDA (see Figure 4.3) and are restricted to the perylene rings. This explains why the HOMO-LUMO absorption features in the thin film spectra of PTCDA and DPh-PTCDI are so similar.

because the MOs involved in the transitions have some intensity on the distinctive amide group and phenyl substituents at the ends of the molecules. It remains that despite the failure to account for vibrational effects and some other discrepancies in the amplitudes of the absorption features, the synthetic spectrum once again closely reflects the features observed in the thin film spectrum.

# 4.2.2.2 DPh-PTCDI partial density of states spectra

The XPS spectrum of DPh-PTCDI is shown in Figure 4.10. In this molecule there are five distinct carbon chemical environments, as indicated in the inset. According to the MO calculations, the 10 carbons of the phenyl substituents, labelled C1, have the smallest core level binding energy. Once again the carbonyl carbons, labelled C5, have the greatest binding energy. The two carbons of the phenyl substituents next to the nitrogen atoms, C4, have a similar binding energy to carbon atoms in the perylene core. Five Voigt functions were fitted to the XPS spectrum, with area ratios of 10:8:8:6:4 for the five carbon environments. Taking C1 as the reference point, the chemical shifts for C2, C3, C4 and C5 were 0.49, 0.85, 1.02 and 3.75 eV, respectively. The splits between these environments in the DFT calculation were 1.00, 1.25, 1.60 and 3.61 eV, respectively. To ensure that the different environments in the synthetic PDOS spectra (Figure 4.11) would have the separations measured in the XPS spectrum, they were shifted by the difference between the calculated shifts and the XPS shifts, that is: -0.51, -0.40, -0.58 and 0.14 eV.

The thin film NEXAFS and SXES spectra are compared with the synthetic carbon p-orbital PDOS in Figures 4.12 and 4.13, respectively. The Fermi level of the synthetic spectrum was chosen to be 283 eV in both cases. In Figure 4.12, the PDOS features (sum of environments) from 283.5 to 287 eV appear to

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**Figure 4.10** The carbon 1s XPS spectra of a 40 nm thick DPh-PTCDI film recorded at an excitation energy of 800 eV.



**Figure 4.11** The synthetic PDOS of DPh-PTCDI. The PDOS of C2-C5 are shifted up by -0.51, -0.40, -0.58 and 0.14 eV with respect to C1.



**Figure 4.12** The synthetic (red) and experimental (blue) unoccupied carbon p-orbital PDOS for DPh-PTCDI. The carbon 1s NEXAFS spectrum was recorded with the sample oriented at 70° with respect to the direction of the x-ray beam. The contribution from carbons C1-C5, shown in Figure 4.10, are indicated by the dashed lines. The Fermi level of the synthetic spectrum has been shifted to 283 eV.

coincide with peaks in the NEXAFS spectrum, although once again the contributions from the separate core levels are more apparent in the NEXAFS spectrum than in the broadened synthetic spectrum. From 287 - 291 eV, there are four distinct peaks in the NEXAFS spectrum. There appears to be a matching peak in the synthetic spectrum at 287.7 eV, but the correspondence between the spectra above 288 eV is poor. Vibrational peaks, which are not modelled in the synthetic PDOS, are also observed in the NEXAFS spectrum from 286 - 286.5 eV and from 287.7 - 288.5 eV.

The NEXAFS spectrum and the synthetic PDOS appeared to correlate reasonably well in the 4 eV range above the absorption edge, but poorly beyond that. The correlation of the occupied PDOS and the SXES spectrum appears to be much better across the full measurement range. The peaks can generally be



**Figure 4.13** The synthetic occupied carbon p-orbital PDOS (red) and SXES spectrum (blue) for DPh-PTCDI. The Fermi level of the synthetic spectrum was set to 283 eV.

matched in each spectrum, although it appears that the experimental spectrum is broadened more than is accounted for in the calculation. The troughs at 280.5 and 281.9 eV in the calculation are somewhat obscured by broadening in the experimental spectrum. However, the strong peak at 282.5 eV in the calculation is clearly seen at 282 eV in the SXES spectrum, unlike the similar case for PTCDA (Figure 4.7). From both Figure 4.12 and Figure 4.13, it can be concluded that the synthetic PDOS spectrum for DPh-PTCDI is a good approximation to the actual unoccupied and occupied PDOS that is observed.

# 4.2.3 C8-PTCDI spectra

C8-PTCDI was obtained from Sigma-Aldrich (product 663913) and used as received. UV-vis spectra were measured for a 50 nm thick film deposited onto a UV transparent quartz coverslip. NEXAFS and XPS spectroscopy were performed

at the Australian Synchrotron soft x-ray beamline and SXES spectra were measured at beamline X1B of the National Synchrotron Light Source, Brookhaven National Laboratory, New York. DPh-PTCDI was evaporated in-situ at the Australian synchrotron onto an n-doped silicon wafer. A growth rate of 1 nm/min was maintained at a temperature of 309 °C, yielding a film that was approximately 65 nm thick. The sample for the SXES measurement was grown in the X1B endstation on an n-type silicon wafer. As with DPh-PTCDI, the growth was uncontrolled, but the film was estimated to be more than 100 nm thick by judging from the magnitude of the SXES signal.

# 4.2.3.1 C8-PTCDI UV-visible spectra

Figure 4.14 shows the synthetic and experimental UV-vis spectra for a 50 nm thick film of C8-PTCDI. The synthetic spectrum is similar to the two other perylene derivatives and once again consists of a broad HOMO-LUMO feature near 450 nm, weaker transition features near 350 nm and a complicated set of stronger peaks below 300 nm. The first two MO transitions shown in Figure 4.15, at 451 nm and 344 nm, have the same distribution across the perylene rings as the corresponding transitions in PTCDA and DPh-PTCDI (at 445 nm and 341 nm in Figure 4.3 and 455 nm and 340 nm in Figure 4.9). This explains why the synthetic spectra of the three perylene derivatives have the same general shape.

When the synthetic and experimental spectra are compared in Figure 4.14, it is observed that there are some new features that are not observed in PTCDA and DPh-PTCDI. The HOMO-2 to LUMO transition at 344 nm in the synthetic spectrum appears weakly from 350 to 375 nm in the thin film spectrum, as it did in PTCDA. In the thin film spectrum there is an absorption feature, stronger than



**Figure 4.14** The thin film (top) and synthetic (bottom) UV-vis absorption spectra of C8-PTCDI. Individual transitions corresponding to the MO pairs in Figure 4.15 are highlighted by the dashed lines in the synthetic spectrum. The HOMO – LUMO maximum in the thin film is red-shifted by 38 nm with respect to the peak in the synthetic spectrum. The two peaks at 527 and 571 nm do not seem to correspond directly to peaks in the PTCDA and DPh-PTCDI spectra. The excitonic peak centred at 571 nm is red-shifted by ~20 nm with the equivalent peak in the other two derivatives.

previously observed, with a peak at 325 nm. This appears to correspond to the HOMO-6 to LUMO transition at 298 nm in the synthetic spectrum. The HOMO-6 wavefunction is located on the carbonyl groups and the nitrogen atoms of the molecule, which explains why a similar absorption feature is not seen in the PTCDA spectrum.

The most significant difference between C8-PTCDI and the spectra of the other two derivatives occurs near the HOMO-LUMO absorption. There are four discernible peaks in this region, at 470, 489, 527, and 571 nm (PTCDA has three peaks at 478, 495 and 551 nm; DPh-PTCDI has three peaks at 473, 501 and 547 nm). The red-shift in the exciton peak and the presence of another strong



**Figure 4.15** The C8-PTCDI MO transitions shown above correspond to the synthetic absorption spectrum features that are highlighted by the coloured, dashed lines, at the bottom of Figure 4.14. The HOMO, HOMO-2 and LUMO orbital wavefunctions are the same as those found in PTCDA (see Figure 4.3) and DPh-PTCDI (see Figure 4.9).

peak at 527 nm appear to be significant. The long alkyl chains play no part in the energy or shape of the HOMO or LUMO wavefunctions, however they do influence how the molecules pack in thin films. There could be multiple environments in the film, where in some cases there is little overlap of frontier orbitals between molecules, but in other directions within the film there is stronger overlap. Where there is weak overlap, the molecules would undergo the familiar HOMO-LUMO transition, producing the peaks at 470 and 489 nm, which are similar to the observed wavelengths in PTCDA and DPh-PTCDI. However, the 527 and 571 nm peaks may indicate that the strong overlap of frontier orbitals has reduced the energy of the HOMO-LUMO transition. The individual

peculiarities of the thin film spectrum may be related to the comparatively high performance of n-type C8-PTCDI devices, which is dependent on the flow of electrons in the solid state through the overlapping molecular LUMOs [54]. The change in energy of the LUMO that occurs in the condensed state may move the LUMO to an energy level in which efficient charge transfer occurs between the contacts and the semiconductor in OFETs [144]. The different alignment of C8-PTCDI molecules on a substrate, compared with PTCDA, also influences the charge mobility. The contrasting molecular orientations are examined in section 4.2.4.

# 4.2.3.2 C8-PTCDI partial density of states spectra

The molecular orbital calculation for C8-PTCDI predicts that there should be four different carbon environments with similar core level energies. There are 14 carbons on the octyl chains which have the lowest binding energies. There are a further 16 carbons in the perylene rings which have slightly higher binding energies. Another 6 carbons have even higher binding energies. These are the two on each octyl chain adjacent to nitrogen and another four on the central aromatic ring. As expected, the 4 carbonyl carbons that are adjacent to nitrogen and oxygen have the greatest binding energy. Considering this, four peaks were fitted to the XPS spectrum, shown in Figure 4.16, with the aim of preserving the area ratio of 14:16:6:4 expected from the number of carbon atoms in each environment. The shifts of environments C2-C4 relative to C1 were calculated as 1.42, 1.79 and 3.72 eV, respectively. The equivalent shifts from the fits to the XPS spectrum were 0.5, 1.02 and 3.56 eV. Thus, the synthetic PDOS of these environments was shifted by -0.92, -0.77 and -0.16 eV in Figure 4.17.



**Figure 4.16** The carbon 1s XPS spectra of a 65 nm thick C8-PTCDI film, recorded at an excitation energy of 800 eV.



**Figure 4.17** The synthetic PDOS of C8-PTCDI. The PDOS of the carbonyl carbons is shifted up by 3.9 eV with respect to the aromatic ring carbons and the carbons next to nitrogen are shifted up by 2.0 eV. Other perylene ring carbons and the alkyl carbons have not been shifted, but are shown separately.

As was the case for the NEXAFS spectra of PTCDA and DPh-PTCDI, it appears that most of the PDOS intensity near the absorption edge is due to excitation from carbon environments in the perylene core (C2 and C3). There is no influence below 291 eV, apparent in Figure 4.18, from the alkyl carbons of environment C1. The carbonyl carbons (C4) only make a weak contribution at 284.7 eV and above 286 eV. The gap between the peaks at 284.1 and 284.5 eV in the NEXAFS spectrum matches the splitting of the C2 and C3 peaks in the XPS spectrum. The dashed blue and purple lines in Figure 4.18 would suggest that the first peak does correspond to C2 and the second to C3. The troughs at 285 eV in the NEXAFS and synthetic spectra appear to match, as does the large peak at 285.7 eV, however the correlation at higher energies is less convincing.

As with PTCDA and DPh-PTCDI, the SXES spectrum and the synthetic PDOS appear to match more closely than do the NEXAFS and unoccupied PDOS spectra. The experimental spectrum is heavily broadened, however the peaks can be matched with confidence. The shoulders at 272, 275 and 278 eV match in each spectrum. The strong SXES peak at 279 eV matches strong peaks at the same energy in the synthetic spectrum. Like PTCDA and in contrast to DPh-PTCDI, the strongest feature in the PDOS spectrum at 281.2 eV does not appear to be well resolved in the SXES spectrum. There is, however, a discernible shoulder at 282 eV, which probably corresponds to this. Thus, it appears that the synthetic occupied PDOS spectrum provides a good approximation to the PDOS measured in the SXES spectrum of the thin film.



**Figure 4.18** The synthetic (red) unoccupied PDOS and NEXAFS spectrum (blue) for C8-PTCDI. The Fermi level of the synthetic spectrum has been set to 283.5 eV.



**Figure 4.19** The synthetic occupied carbon p-orbital PDOS (red) and SXES spectrum (blue) for C8-PTCDI. The Fermi level of the synthetic spectrum was set to 283.5 eV.

# 4.2.4 The relationship between the polarisation direction of the synchrotron radiation and the relative angle of the organic thin films in NEXAFS spectroscopy

The carbon 1s NEXAFS spectra in Figures 4.6, 4.12 and 4.18 reveal information about the p-orbital PDOS for the three perylene derivatives at energies above the carbon absorption edge of the molecules. The absorption features correspond to energies at which electrons are removed from the spherically symmetric 1s core levels of carbon and the unoccupied states, like the LUMO and LUMO+1, are populated. Strong coupling of the initial and final states occurs when the electric field vector aligns with the direction of the transition dipole moment between the occupied and unoccupied molecular orbitals. Given that in NEXAFS spectroscopy the initial state is the spherically symmetric atomic K-shell, the direction of the maximum amplitude in the final state wavefunction determines the direction of the dipole moment. As can be seen in the LUMO orbital of PTCDA in Figure 4.3, the  $\pi^*$ -type orbital has maximum amplitude perpendicular to the plane of the molecule and it has zero amplitude in the two dimensional plane of the molecule. Thus, by rotating a thin film with respect to the x-ray beam, it is possible to observe changes in the magnitude of the NEXAFS absorption features. This reveals whether the unoccupied final states have the directional  $\pi^*$ -type symmetry or the more spherical  $\sigma^*$ -type symmetry. It also shows whether there is a regular packing order for the molecules in the thin film.

Figures 4.20(a-c) show the NEXAFS spectra of PTCDA, DPh-PTCDI and C8-PTCDI, respectively. The figures reveal how the spectra change as the substrates are rotated from being situated along the normal to the beam, to an angle of  $70^{\circ}$  with respect to the beam (grazing incidence). The electric field vector (E-vector) of the x-ray beam was horizontally polarised, so that it was in the two



**Figure 4.20** (*a-c*) The angle dependent NEXAFS spectra of PTCDA, DPh-PTCDI and C8-PTCDI, respectively. The intensities of the near-edge features increase as the sample is rotated from normal to the beam, through to 70° with respect to the beam direction. The relative change in intensity is greatest for the PTCDA film. (*d-f*) The polarisation dependent NEXAFS spectra of the perylene-based materials. The beam polarisation was switched from horizontal to vertical and the sample was again rotated from the normal to 70° with respect to the beam direction. A significant change in intensity only occurred for the PTCDA sample at 70°.

dimensional plane of the thin film when the sample was at normal incidence to the beam. The E-vector had a near perpendicular orientation with respect to the thin film when the substrate was at  $70^{\circ}$  with respect to the path of the x-ray beam. In each of Figures 4.20(a-c), the NEXAFS absorption is strongest when the x-ray E-vector is perpendicular to the surface of the sample. This contrast between the normal incidence and grazing incidence spectra is the greatest for the PTCDA film. At normal incidence the absorption features from 283 – 291 eV are very weak and the tail from 292 eV onwards is relatively strong, but when the sample was rotated to 70°, the magnitude of the near-edge peaks increased greatly. The tail beyond 292 eV did not increase by the same proportion. The angular dependence implies that the peaks from 283 - 291 eV have  $\pi^*$  symmetry, which was expected from the PTCDA LUMO and LUMO+2 (see Figure 4.3). The relative absorbance intensities at the different angles suggest that the PTCDA molecules in the thin film stacked uniformly, with the molecular plane flat on the silicon substrates. The smaller contrast in the intensities with the change in angle of the DPh-PTCDI and C8-PTCDI spectra means that the molecules in these thin films do not stack with the perylene core perfectly flat on the substrate plane.

Additional insight into the molecular packing can be gained by altering not only the angle of the substrate with respect to the x-ray beam, but by changing the polarisation of the beam as well. The APPLE-II undulator at the Australian Synchrotron (Appendix Four, section A4.3) can be tuned so that the linear polarisation of the beam can be converted from the horizontal plane to the vertical (and any angle in between). The response of the NEXAFS spectra to changing both the sample orientation and the polarisation of the beam is shown in Figures 4.20(d-f). In the spectrum for PTCDA (Figure 4.20(d)) the  $\pi^*$  absorptions only



**Figure 4.21** When the PTCDA thin film was rotated in the horizontally polarised x-ray beam, the E-vector was only aligned with the maximum of the LUMO orbital when the sample was at 70° with respect to the beam (b). When the thin film was normal to the beam, the E-vector was directed in the plane of the molecule and could not couple the initial and final states (a). The situation was the same when the E-vector was vertically oriented (c), (d).

have a large intensity when the sample is at 70° with respect to the x-ray beam and the E-vector is horizontally polarised. In the other orientations, these features are weak while the tail beyond 292 eV remains strong. The reason for behaviour this is made clearer by Figures 4.21(a-d). The only case in which the initial and final states are strongly coupled is in Figure 4.21(b), when the E-vector is perpendicular to the substrate surface. With the PTCDA molecules lying flat on the substrate, the E-vector is oriented along the direction in which the lobes of the LUMO wavefunction have the most magnitude. In the other three orientations, the E-vector is in the two dimensional plane of the molecule and can't couple an electron from the initial C 1s state into the  $\pi^*$  final state. In Figures 4.20(e) and (f) it is clear that changing the angle of the substrate affects the amplitude of the near-edge absorption features, but changing the polarization angle does not seem to have a great effect on them. This confirms that the DPh-PTCDI and C8-PTCDI molecules do not pack as regularly in thin films as PTCDA molecules do, at least in the direction normal to the substrate surface.

# **4.3 CONCLUSIONS**

The preceding studies have demonstrated that DFT modelling of the electronic structure of molecules and the additional calculations that can be performed to generate synthetic spectra are useful for interpreting results from experimental spectroscopy. Even though the synthetic UV-vis and PDOS spectra do not take phenomena such as the population of vibrational levels or the excitonic states in thin films into account, careful analysis of the experimental spectra and the calculations does provide useful insights. In particular, visualisation of the MOs involved in the absorption features of the synthetic UV-vis spectra helped identify why there were certain common features in the spectra of the perylene derivatives and alternatively, why there were certain points of distinction. In particular, the exciton peaks at the red end of the spectra were easily identified because there were no similar MO transitions in the synthetic spectra. Analysis of the fine splitting on the peaks of the NEXAFS spectra and the attribution of these features to excitation from different core levels was supported by examining the peaks in the synthetic PDOS due to the different carbon environments. Although several discrepancies between the synthetic and experimental PDOS spectra were identified, the synthetic PDOS revealed detailed information that informed and improved the analysis of the experimental spectra. While it is difficult in many cases to find a direct match between the synthetic PDOS of single molecules and the NEXAFS spectra of thin films, the worst alignment occurred in the case of C8-PTCDI [131, 135, 151]. This is a strong indication that this material is not simply bonding as a van der Waals solid. Instead, it is likely that there is more significant overlap and distribution of frontier orbitals over neighbouring molecules, hence the poor alignment with the synthetic PDOS features. This modification of the frontier orbitals is consistent with the greater mobility of electrons in C8-PTCDI and in PTCDA and DPh-PTCDI.

A comparison of the synthetic UV-vis spectra for PTCDA, DPh-PTCDI and C8-PTCDI would suggest that there should not be any significant differences in the HOMO-LUMO absorption features in the thin films. However, the thin-film spectra of PTCDA and DPh-PTCDI were quite different to C8-PTCDI, which had an additional peak compared to the other two spectra and a heavily red-shifted exciton peak. This revealed that the modification to the MOs of the perylene derivatives that occurs in the solid state was uniquely strong for C8-PTCDI, which is known to have an electron mobility far superior to the other two materials. Additional information was provided by the angle and polarisation dependent NEXAFS studies. These showed that PTCDA molecules packed in highly ordered vertical layers in the thin film, along the substrate normal, unlike the DPh-PTCDI and C8-PTCDI molecules. The packing of the PTCDA molecules is not conducive to high carrier transport in conventional planar transistor structures, which is one reason why low mobility may be observed. The angular dependent NEXAFS spectra indicated that C8-PTCDI packed with more orbital overlap parallel to the substrate. This observation, together with the strong interactions evident in the UV-vis spectra, may have some connection to the superior charge mobility of this material compared to the other perylene derivatives.

The ability to visualize the amplitudes and spatial distribution of the MO wavefunctions using DFT calculations proved to be very useful in interpreting the experimental spectra presented in this chapter. This process is followed again in Chapter Five, where the UV-vis spectra of a set of pentacene photoprecursors are examined in detail. Once again, the DFT calculations of single molecules provide a useful means of understanding the features that are present in the experimental spectra. Results from solid state photolysis experiments on these Diels-Alder type precursors are examined with reference to the distribution of MOs on certain functional groups within the molecules. The DFT calculations are proven to be valuable tools for examining the photosensitivities of the pentacene precursors and the new set of proposed precursor compounds that are later described in Chapter Seven.

# CHAPTER FIVE

Synthetic and experimental spectra of pentacene and its precursors

In Chapter Four the x-ray and UV-vis spectra of three n-type organic semiconductor compounds, PTCDA, DPh-PTCDI and C8-PTCDI, were presented. The structures of these compounds are all derived from the p-type semiconductor, perylene, to which different functional groups are substituted so as to modify the solubilities and HOMO/LUMO energies of the semiconductors. By comparing the experimental measured spectra against the synthetic spectra of single molecules with geometries optimised using DFT, a deeper understanding of the electronic properties of the semiconductors was obtained. The synthetic spectra indicated that the HOMOs and LUMOs in the three materials had wavefunctions with an identical distribution over the perylene cores. It followed that the absorption spectra predicted for the materials were very similar at visible wavelengths. The subtle differences that existed in the experimental spectra were therefore recognised and given physical meaning. Once again, the powerful interpretive tools provided by DFT calculations are utilised in this chapter for the purposes of analysing the photochemical properties of pentacene photoprecursors.

Figure 5.1 shows films of 6,13-dihydro-6,13-methanopentacene-15-one (6,13-MPn) on silicon substrates. The films were placed in the ultra high vacuum endstation of beamline X1B, NSLS, New York, and raster scanned in front of the x-ray beam. The beamspot profile was approximately 30  $\mu$ m high by 100  $\mu$ m wide and raster scanning left the patterned stripes that are discernible in the image [148]. The parts of the films exposed to the beam have the purple colour of pentacene, while those areas that were avoided remain the white colour of pristine 6,13-MPn. This technique of using a focused light source to define patterns in the semiconductor film could prove to be useful for the production of electronic devices.



**Figure 5.1** Films of 6,13-MPn on silicon substrates were raster scanned in the beam spot of the soft x-ray beamline, X1B, at the NSLS, New York. NEXAFS and SXES spectra of the precursor could not be recorded because of its rapid conversion to pentacene in the beam. The circular sample plate has a diameter of 25 mm.

The conversion of 6,13-MPn to pentacene does not actually require x-ray photons; UV light is sufficient for the process. The range of wavelengths capable of driving the photoconversion can be determined by exposing a sample to monochromatic light and then monitoring changes in the UV-vis spectrum at wavelengths corresponding to the main absorption features of pentacene (see sections 2.5.3 and 2.5.4). It would be useful to be able to predict the photoconversion wavelengths by a theoretical method so that the optical properties of new materials could be optimised before synthesis. The ZINDO calculations of UV-vis absorption spectra that are performed on DFT optimised single molecules are one such method of doing this. This chapter shows how these synthetic spectra are analysed to make this photolysis wavelength determination for pentacene precursors. Direct comparisons are also made with the results of photolysis experiments to evaluate the validity of the predictions.

# 5.1 A COMPARISON OF THE SYNTHETIC AND EXPERIMENTAL SPECTRA OF A SERIES OF PENTACENE PRECURSORS

The structures of pentacene and the six photoprecursors that are discussed in this chapter are shown in Figure 5.2. The precursors in Figures 5.2 (b), (c), (d), (e) and (f) have all been synthesized and reported in the literature. The remaining one, Figures 5.2 (g), is an asymmetrical isomer of the equivalent symmetrical precursor. They are studied here as a means of determining the implications of shifting the position of the bridging moiety. Some of the properties of these materials were presented in Tables 2.2, 2.3 and 2.4. Specifically, the reported photoconversion conditions for the precursors were described. In the remainder



**Figure 5.2** (*a*) Pentacene and (*b*-*g*) its photopatternable precursors. (*b*) 6,13-dihydro-6,13methanopentacene-15-one (6,13-MPn), (*c*) 5,14-dihydro-5,14-methanopentacene-15-one (5,14-MPn), (*d*) 6,13-dihydro-6,13-ethanopentacene-15,16-dione (6,13-EPIMPn), (*e*) 5,14dihydro-5,14-ethanopentacene-15,16-dione (5,14-EPIMPn), (*f*) 6,13-dihydro-6,13epithiomethanopentacene-16-one (6,13-EPn), and (*g*) 5,14-dihydro-5,14epithiomethanopentacene-16-one (5,14-EPn).

of this section, the artificial UV-vis spectra of the five materials that have been synthesised are compared against experimental spectra and specific MOs are assigned to the absorption features of the experimental spectra.

# 5.1.1 Pentacene

To begin the examination of the accuracy of the ZINDO absorption spectrum calculations, the experimental and synthetic spectra of pentacene are compared.



Figure 5.3 The HOMO and LUMO of pentacene.

Figure 5.3 shows the HOMO and LUMO orbitals of pentacene. Both wavefunctions have greatest magnitude on the carbon atoms at the centre of the molecule, with weaker intensities at the ends; the expected result for linear acenes [31]. The ZINDO calculation predicts that the absorption spectrum should have a peak centred at 482 nm, corresponding to a transition between these orbitals. This peak is highlighted by a dashed red line in the black spectrum at the bottom of Figure 5.4. This figure also shows the absorption of pentacene in a solution (middle) and in a thin film (top). The synthetic spectrum has two large peaks below 350 nm, which also appear in the thin film spectrum, although there is a shift of ~25 nm between the peaks. The HOMO-LUMO feature is comparatively weak compared to the 350 nm peaks in all three spectra. It is also red-shifted in the solution and thin film spectra with respect to the synthetic spectrum.

In the thin film there are two peaks at 630 nm and 670 nm which do not appear in the solution spectrum and only arise when pentacene is in an aggregated state [152]. This Davydov doublet results from the splitting of the HOMO-LUMO absorption that occurs due to varying overlap of the frontier orbitals between adjacent molecules in the unit cell [153]. The vibronic progression from 450 - 600 nm in the thin film spectrum is mirrored in the solution spectrum,



**Figure 5.4** Absorption spectra of pentacene in different environments. (Top) UV-visible spectrum of a 70 nm thin film and (middle) a solution spectrum [154]. (Bottom) Synthetic spectrum based on DFT. Transitions between the HOMO and LUMO orbitals (Figure 5.3) correspond to the feature in the synthetic spectrum at 482 nm.

although the peaks are less affected by broadening. Having identified that the peaks at 630 nm and 670 nm in the thin film spectrum result from modification of the HOMO and LUMO energies in the solid state, it is clear that the peak at 580 - 590 nm corresponds to the 482 nm peak in the synthetic spectrum. The size of the red shift in the experimental spectrum is significant, but not unexpected. Red-shifting of the HOMO-LUMO feature compared to the synthetic spectrum is observed for most semiconductor materials and was also seen in the perylene derivatives of Chapter Four. As discussed at the beginning of Chapter 4, the DFT calculation of the UV-vis absorption spectrum does not account for vibrational states. The exchange-correlation potentials used also have a self-interaction error that partially accounts for the blue-shift of the HOMO-LUMO of the synthetic spectrum with respect to the experimental spectra [140]. The Davydov doublet in

the thin film is also a multi-molecule phenomenon which is obviously not included in single-molecule calculations.

# 5.1.2 6,13-dihydro-6,13-methanopentacene-15-one

The first of the pentacene precursors to be examined here is 6,13-dihydro-6,13methanopentacene-15-one (6,13-MPn). A pair of MO transitions is shown in Figure 5.5, followed by the thin film, solution and synthetic spectra in Figure 5.6. The synthetic spectrum has a large, broad peak at 250 nm, composed of many transitions. There is a less intense shoulder at 270 - 300 nm and then a pair of very weak features at 327 nm and 331 nm, which correspond to the MOs shown in Figure 5.5. The synthetic spectrum appears to accurately predict the solution spectrum, in which there is a strong peak at ~245 nm, a series of less intense peaks from 260 – 300 nm and a separate and quite distinct peak at 325 nm, which makes the assignment of the MOs from Figure 5.5 a simple process. While the



**Figure 5.5** The HOMO-2, HOMO-4, LUMO and LUMO+4 of 6,13-MPn. The HOMO-2 and LUMO have most intensity on the naphthalene chromophores. The HOMO-4 and LUMO+4 primarily overlap on the carbonyl bridging group at the centre of the molecule.



**Figure 5.6** (Top) The UV-visible absorption of 6,13-MPn, spray deposited from a dichloromethane solution. (Middle) The same material in an ethanol solution. (Bottom) The synthetic spectrum. MO transitions located on the carbonyl group correspond to a very weak absorption feature at 331 nm.

peaks in the thin film spectrum are naturally broader and there are additional vibrational features, once again the correlation with the synthetic spectrum is good. Chuang et al. reported that photolysis of 6,13-MPn in a THF solution and the subsequent production of pentacene via the removal of carbon monoxide, took place with an excitation wavelength of 310 nm [83]. As will be shown in section 5.3.2, the conversion wavelength in thin-films is slightly longer. This may correspond to excitation of the HOMO-4 to LUMO+4 transition from Figure 5.5, which clearly involves a movement of electrons from the  $\sigma$ -bonds of the carbonyl bridge to the p-orbitals of the carbon and oxygen atoms. This would be in keeping with the electron rearrangement in a chelotropic pericyclic reaction, leading to the

removal of the bridging group and the recovery of the aromatic ring in the centre of pentacene (see Figure 2.15).

# 5.1.3 5,14-dihydro-5,14-methanopentacene-15-one

Following 6,13-MPn is the related compound, 5,14-dihydro-5,14methanopentacene-15-one (5,14-MPn). It is an isomeric form in which the carbonyl group has been shifted one position over from the central ring, to the second ring from the end of the pentacene backbone. As a result of this shift, the MOs shown in Figure 5.7 are quite different from those in Figure 5.5. The new transition that occurs at 345 nm has most HOMO and LUMO wavefunction amplitude on the anthracene group (three benzene rings). The HOMO-5 to LUMO+2 transition that occurs at 328 nm is quite similar to the HOMO-4 to LUMO+4 transition in 6,13-MPn. The wavefunctions overlap primarily on the carbonyl bridge and once again it appears that there is a transfer of charge during this transition, from the  $\sigma$ -bonds of the carbonyl bridge to the p-orbitals of the carbon and oxygen atom.



Figure 5.7 The HOMO-5, HOMO, LUMO and LUMO+2 of 5,14-MPn.
The synthetic spectrum in Figure 5.8 has a strong peak at 265 nm and a weaker one centred at 345 nm. This is quite similar to the solution spectrum, which has a peak at ~270 nm and a vibronic progression from 325 – 390 nm. In the thin film spectrum this vibronic progression can be seen more clearly, having peaks at 340, 360, 382 and 406 nm. Considering the distributions of the HOMO and LUMO wavefunctions in Figure 5.7 and the UV-vis spectrum of anthracene, it is clear that this vibronic progression is associated with the anthracene chromophore [155]. The absorption peak of the HOMO-5 to LUMO+2 transition, expected at 328 nm, may be obscured by the anthracene chromophore. However, it could also correspond to the 310 nm absorption peak in the thin film spectrum.



**Figure 5.8** (Top) The UV-visible absorption spectrum of the asymmetrical monoketone pentacene precursor, 5,14-dihydro-5,14-methanopentacene-15-one (5,14-MPn)in the solid state. (Middle) The same material in an ethanol solution. (Bottom) The synthetic spectrum of a single molecule, with geometry optimised via DFT is shown as a black line. The transition involving orbitals located on the carbonyl group is weak and occurs at 328 nm, while the stronger peak centred at 345 nm corresponds to excitation of the anthracene chromophore.

A shift of ~20 nm compared to the synthetic spectrum is within the typical error range of the ZINDO calculations.

In the first publication on the photolysis of 5,14-MPn, the precursor was reported to undergo conversion to pentacene in a THF solution when exposed to 366 nm light [83]. This would correspond to excitation of the HOMO-LUMO transition to the first vibrational level. Light with this wavelength would not be sufficiently energetic to drive the HOMO-5 to LUMO+2 transition on the carbonyl bridge, although the nature of the UV light source and any filtering system used was not described in any detail. However, it was also reported that pentacene was produced when a solution of the precursor was irradiated with a 10 mW/cm<sup>2</sup>, 385 nm Nd:YAG pumped Ti<sup>3+</sup>:Sapphire laser, which again corresponds to excitation of the anthracene chromophore. Of note here is that the HOMO-5 to LUMO+2 transition in Figure 5.7 which has a wavelength of 328 nm is predicted to cause the decomposition of 5,14-MPn. Noting that the anthracene chromophore is red-shifted in the experimental spectra, the nearest feature observed is a small peak at 296 nm in the ethanol solution and at 310 nm in the thin film. Experiments described in section 5.3.3 unequivacolly show that this peak is related to the decomposition of 5,14-MPn.

#### 5.1.4 6,13-dihydro-6,13-epithiomethanopentacene-16-one

The pentacene precursor 6,13-dihydro-6,13-epithiomethanopentacene-16-one (6,13-EPIMPn) is different to the preceding precursors because the bridging group consists of a carbonyl group with a single bond to a sulfur atom. It is also known to be photosensitive, just like the solitary carbonyl bridge. It has been reported that pentacene was generated when 6,13-EPIMPn was irradiated with 254 nm



Figure 5.9 The HOMO-4, HOMO-1, LUMO and LUMO+1 of 6,13-EPIMPn.



**Figure 5.10** (Top) UV-visible absorption of the pentacene precursor, 6,13-dihydro-6,13epithiomethanopentacene-16-one (6,13-EPIMPn) in acetonitrile [99]. (Bottom) The equivalent single molecule synthetic spectrum. The transition between orbitals located on the epithiomethano bridging group occurs weakly at 351 nm.

light in an acetonitrile solution [99].

The MO transitions shown in Figure 5.9 correspond to the two longest wavelength transitions that are predicted in the synthetic spectrum of Figure 5.10. The synthetic and solution spectra are remarkably similar for 6,13-EPIMPn [99]. There is a moderate absorption from 270 – 300 nm in the solution spectrum that matches the HOMO-1 to LUMO transition in the synthetic spectrum. There is another common peak at 247 nm in both spectra. A third peak, appearing at 230 nm in the solution spectrum, most likely corresponds to the feature at 215 nm in the synthetic spectrum. The HOMO-4 to LUMO+1 feature in the synthetic spectrum, however it is difficult to determine given the scale. While the 254 nm incident light would not excite the HOMO-4 to LUMO+1 transition directly, perhaps the LUMO+1 orbital is populated after decay from a higher energy state, leading to the observed generation of pentacene.

#### 5.1.5 6,13-dihydro-6,13-ethanopentacene-15,16-dione

6,13-dihydro-6,13-ethanopentacene-15,16-dione (6,13-EPn) is an  $\alpha$ -diketone pentacene precursor. The structure is similar to 6,13-MPn except there are two carbonyl groups on the bridge, instead of only one. Figure 5.11 shows the two longest wavelength MO transitions from the synthetic spectrum that is displayed in Figure 5.12. The transition at 324 nm corresponds to absorption by the two naphthalene chromophores of the molecule. This is shifted slightly from the similar transition at 327 nm in 6,13-MPn (Figure 5.5). The HOMO-4 to LUMO absorption that has a peak at 408 nm in the synthetic spectrum is characterized by the familiar overlap of MOs solely on the carbonyl bridge. In repetition of the



Figure 5.11 The HOMO-4, HOMO-2, LUMO and LUMO+1 of 6,13-EPn.



**Figure 5.12** (Top) The UV-vis spectrum of the pentacene precursor, 6,13-dihydro-6,13ethanopentacene-15,16-dione (6,13-EPn) in acetonitrile [86]. The synthetic spectrum of a 6,13-EPn single molecule, with geometry optimised via DFT. Transitions between the HOMO-4 and LUMO, which have most magnitude on the carbonyl groups, correspond to the peak at 408 nm in the synthetic spectrum.

pattern seen in the prior three precursors, the HOMO-4 orbital has large intensity on the  $\sigma$ -bonds of the carbonyl bridge and the LUMO has most intensity on the p-orbitals of the carbon and oxygen atoms. A transition between these MOs should lead to a charge rearrangement typical of retro Diels-Alder reactions. The result would be the removal of two carbon monoxide molecules from the precursor. The feature in the solution spectrum that is equivalent to the HOMO-4 to LUMO transition is red shifted slightly and has a peak at ~460 nm, but covers a similarly broad wavelength range from 410 – 500 nm. As listed in Table 2.2, most molecules with an  $\alpha$ -diketone bridge have an absorption feature of this nature. All of these materials are observed to undergo a removal of the bridging group when exposed to blue light at wavelengths above 400 nm.

#### 5.1.6 5,14-dihydro-5,14-ethanopentacene-15,16-dione

5,14-dihydro-5,14-ethanopentacene-15,16-dione (5,14-EPn) is an  $\alpha$ -diketone pentacene precursor that is the asymmetrical isomer of 6,13-MPn. Figure 5.13 shows the two longest wavelength MO transitions from the synthetic spectrum that is displayed in Figure 5.14. The transition at 359 nm corresponds to absorption by the anthracene chromophores of the molecule. This is red-shifted by 35 nm from the naphthacene chromophore peak in 6,13-EPn (Figure 5.11). The HOMO-5 to LUMO absorption has a peak at 413 nm in the synthetic spectrum and is red-shifted by 5 nm from the same bridging group transition in 6,13-MPn. The spectrum of 5,14-MPn in toluene is shown in Figure 5.14 [94]. As with 6,13-EPn, the peak of the n- $\pi$ \* transistion is red shifted when compared with the synthetic spectrum and appears at 468 nm. The peaks at 333, 349 and 367 nm in the solution spectrum are anthracene-like. However, there is also another absorption at 386 nm that overlaps slightly with the n- $\pi$ \* absorption and the



Figure 5.13 The HOMO-5, HOMO and LUMO of 5,14-EPn.



**Figure 5.14** (Top) The UV-vis spectrum of the pentacene precursor, 5,15-dihydro-5,14ethanopentacene-15,16-dione (5,14-EPn) in toluene [94]. The synthetic spectrum of a 5,14-EPn single molecule, with geometry optimised via DFT. Transitions between the HOMO-5 and LUMO, which have most magnitude on the carbonyl groups, correspond to the peak at 413 nm in the synthetic spectrum.

anthracene peaks. It is proposed that this particular transition is an intramolecular charge transfer between the anthacene group and the diketone bridging group that doesn't appear in 6,13-MPn because in that material the energy separation between the napthacene HOMO and the diketone LUMO is too large [94].

### 5.2 IDENTIFICATION OF THE PHOTOLYSIS WAVELENGTH FOR PENTACENE PRECURSORS BY INSPECTION OF THE SYNTHETIC SPECTRA

The synthetic UV-vis absorption spectra of the six pentacene precursors from Figure 5.2 are shown in Figure 5.15. The spectra of the symmetrical and asymmetrical  $\alpha$ -diketone precursors are shown at the top of the figure. Both spectra contain absorption features that extend into the blue end of the visible spectrum. The remaining four spectra, corresponding to the symmetrical and asymmetrical monoketone and epithiomethano pentacene precursors, are all quite similar. They all have a low, broad feature, extending between 310 nm and 380 nm, with additional complexes of more intense features at deeper UV wavelengths. The six spectra have been listed according to the wavelengths of certain absorption features, which are shown in Figure 5.16 for each molecule. These particular occupied and unoccupied molecular orbitals have been highlighted because of their relationship to the Diels-Alder retro-cylcoaddition mechanism. In section 2.5.2 (and again in Appendix Three) the mechanism by which molecules undergo a photochemically sensitised retro Diels-Alder reaction was discussed. In summary, following the absorption of a photon, three pairs of electrons are redistributed in a concerted fashion between the bonds of the bridging group and the remaining bonds of the connected aromatic ring.

Specifically, one of the electron pairs is transferred from a  $\sigma$ -bond linking the bridging groups to the 'benzene' ring, towards the  $\pi$ -orbitals of the bridging moiety. Thus, those MOs that allow for this mechanism to take place; the transfer of an electron from a bridging group  $\sigma$ -bond in the occupied orbital, to a  $\pi^*$ -type orbital in the excited state, are selectively displayed in Figure 5.16. It is proposed that these absorption features have physical significance; the removal of the bridging groups from the pentacene precursors by photolysis can only proceed when electrons are promoted into the unoccupied orbitals that are displayed.

There are a few interesting properties relevant to the photolysis of these molecules that can be observed given the relative positions of the synthetic spectra. Firstly, it appears that there are certain wavelength *windows* where a given material can undergo a photochemical reaction, while another precursor



**Figure 5.15** The synthetic absorption spectra of the six pentacene precursors (b-g in Figure 5.2) showing the absorption peaks corresponding to the MOs in Figure 5.14.



**Figure 5.16** The peak wavelengths at which the MO transitions in the synthetic absorption spectra of the pentacene precursors involve an electron transfer on the bridging moiety. (a) 5,14-EPn (b) 6,13-EPn (c) 6,13-EPIMPn (d) 6,13-MPn (e) 5,14-MPn and (f) 5,14-EPIMPn.

may be unaffected by the light source. For instance, the HOMO-5 to LUMO transition in 5,14-EPn could be sensitised by light in the wavelength range from

375 - 470 nm, while the HOMO-5 to LUMO+2 transition of 5,14-MPn would be driven by light in the wavelength range from 306 - 353 nm. Thus, if both precursors were placed in a solution and exposed to light with wavelengths above 360 nm, the 5,14-EPn precursor would decompose to yield pentacene, but the 5,14-MPn would not. It may also be possible to expose the solution to light within the 306 - 353 nm range to decompose the 5,14-MPn without decomposing the 5,14-EPn, however intersystem crossing from other excited states within 5,14-EPn into the LUMO orbital may still lead to photoconversion. This would need to be tested experimentally but has not been investigated in this thesis.

The next point of interest coming from inspection of Figure 5.15 is that the wavelengths of the photolysis transitions appear to effectively be tuneable. Pentacene is produced from all of the precursors at different photolysis wavelengths by altering the chemical structures of the precursors. The peaks of the six transitions are all different and are affected by the structure of the solubilising moiety and its position on the pentacene backbone. This provides a means of designing molecules that have desirable photochemical properties, such as wavelength compatibility with other materials in a given electronic device. Finally, it is useful to note that the photolysis transitions are not strictly the lowest energy transitions that occur within the molecules. In 5,14-MPn and 5,14-EPIMPn there are other transitions that occur within the anthracene chromophores that are sensitised by wavelengths longer than those required to drive the absorptions on the bridging groups. Any assumption that exposure of the experimentally observed 'HOMO-LUMO' transition to light necessarily causes photoconversion is not strictly true.

The remainder of this chapter discusses the photolysis experiments that were carried out on two monoketone precursors, 6,13-MPn and 5,14-MPn, in the solid state. The purpose of these experiments was to determine the wavelength ranges at which the materials were sensitive to light and would produce pentacene via a chelotropic decarbonylation reaction. This provided a means of assessing the photolysis predictions made from synthetic absorption spectra discussed above. In particular, a determination was made as to whether excitation of the anthracene chromophore in the spectrum of 5,14-MPn could produce pentacene.

# **5.3 PHOTOLYSIS EXPERIMENTS ON 6,13-MPN AND 5,14-MPN THIN FILMS**

The photolysis conditions of the pentacene precursors were initially studied by monitoring the evolution of the absorption spectra under the influence of broadband light. The period of time required to observe the generation of pentacene was recorded, because in any industrial application of these materials the speed of photolysis is an important parameter. It was also necessary to establish whether the precursors could be processed in air, or whether photooxidation of pentacene occurs at a rate comparable to the decarbonylation of the precursor. With this information at hand, the dynamics of the precursor decarbonylation in the presence of narrowband light was examined, so as to define the wavelengths at which photolysis occurs most efficiently.

#### 5.3.1 Photolysis of 6,13-MPn with a broadband light source

Figure 5.17 shows a series of absorption spectra recorded over time, corresponding to a single segment of a 6,13-MPn film that was drop cast on a

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**Figure 5.17** Absorption spectra for a 6,13-MPn film exposed to the broadband output from a *Xe* arc lamp in air. Characteristic pentacene peaks developed at 511, 553 and 599 nm after only 1 s of exposure and continued to grow over the next 10 s. After 1-2 minutes the two peaks at 631 nm and 662 nm, which reveal the presence of aggregated pentacene, reached a maximum. With further exposure the pentacene peaks disappeared again due to photo-oxidation. The red lines are a guide for to the position of the pentacene peaks.

glass microscope slide. The sample was attached to an aperture plate that could be slid into the beam path of a Cary 5000 UV-vis spectrophotometer, analysed, then returned to its position in the output of a Xe arc lamp. The circular aperture allowed for the analysis of a 2 mm diameter portion of the sample. The sample was prepared and held in ambient atmosphere at all times, however the arc lamp was ozone filtered and the emission wavelengths were all greater than 260 nm. The UV-vis spectrum was measured between periods of exposure, which ranged from 1 s up to a total of 30 minutes.

After 1s of exposure to the Xe lamp, three peaks that are characteristic of pentacene are observed at 511, 553 and 599 nm in the spectrum of the sample. These correspond to the peaks observed at the same wavelengths in the spectrum of pentacene in a solution, shown in Figure 5.4. However, the doublet at 631 nm and 662 nm is not present. This pair gradually developed over the next 10 s and reached maximum strength after 1-2 minutes. These features correspond to pentacene in aggregate form and are an indication that sufficient quantities of the precursor was converted to pentacene to result in the overlap of individual molecules with nearest neighbours. After two minutes of exposure there appears to be a reversal in the trend of the peaks – they start to diminish. After a total of 30 minutes exposure to broadband light in air, there was no longer any evidence for the presence of pentacene in the sample. This is consistent with complete oxidation of the film. The sample spot was also observed to change to a light yellow colour, distinct from both the colours of the precursor and pentacene.

To examine whether this truly was a photo-oxidation process or an alternative degradation mechanism such as bond scission, a second sample was prepared and exposed to the same light source, but in a nitrogen glove box. The sample was spray deposited and was somewhat thinner than the first sample, as can be seen by the relative absorbances in Figures 5.17 and 5.18. Between absorption scans the sample was placed in the glove box, which was flushed with dry  $N_2$  from the bleed off of a liquid nitrogen tank for a period of 15 minutes prior to each exposure. The sample was exposed to light for the periods indicated next

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**Figure 5.18** Absorption spectra for a 6,13-MPn film exposed to the broadband output from a Xe arc lamp in an  $N_2$  glovebox. Characteristic pentacene peaks developed after only 10 s of exposure and continued to develop over the next minute. Unlike in the case of the photolysis in air, there is no further change in the spectrum of the sample. That is, the pentacene is protected from photo-oxidation. The red lines are located at the positions of the 510, 553 and 600 nm peaks in the 10 s spectrum and the 627 and 663 nm aggregate pentacene peaks in the 1 min spectrum.

to the spectra in Figure 5.18. The absorption peaks in these spectra are similar to those present in the first 1-2 minutes for the sample illuminated in air. Initially the spectrum was featureless from 400-750 nm, but the three familiar pentacene peaks later developed at 510, 553 and 600 nm. After further exposure the two pentacene

Davydov peaks appeared at 627 and 663 nm. From this point, the evolution of the absorption spectrum was different compared to exposure in air. Even after 30 minutes of exposure, these Davydov peaks remain strong. There is evidence of only a marginal decrease in absorbance, which appears to confirm that an  $N_2$  environment protects pentacene from photodegradation.

An effort was made to test whether the same changes could be observed in the spectrum of a vacuum deposited thin film of pentacene exposed to broadband UV light in air and in an N<sub>2</sub> environment. It was expected that the same changes would be observed in the oxygen environment and that no change would be observed in the N<sub>2</sub> atmosphere. In fact, no substantial change was observed in either film even after several hours of exposure. Similar results were found by Maliakal et al. in a study of the stability of evaporated pentacene and solution deposited TIPS-Pn films [156]. While pentacene is very reactive with dissolved oxygen in solutions, it appears that it is more stable in condensed films. The oxidation of the 5,14-MPn film may be explained by oxygen diffusion pathways available through the side chains, that aren't available in the herringbone packed evaporated pentacene. An alternative explanation is that in evaporated films, the singlet excited-state lifetime of pentacene is significantly shorter, thus the rate of photo-oxidation is significantly reduced [156]. Further studies with thinner films of pentacene and more intense UV sources would be ideal to check whether any photo-oxidation can be observed.

#### 5.3.2 Photolysis of 6,13-MPn using a narrowband light source

During the photolysis of 6,13-MPn using a broadband light source it was established that samples must be processed in  $N_2$  to avoid photo-oxidation. The

exact wavelengths to monitor for the evolution of pentacene absorption features were also determined. Studies of the photolysis of 6,13-MPn were continued by exposing it to narrowband radiation. New samples were prepared by spray deposition of 1 mg/mL dichloromethane solutions onto a glass microscope slide using an airbush. These films were exposed to the output of the Xe arc lamp again, except the light was filtered using an Ocean Optics LVF-UV-HL bandpass filter, as described in section 3.2.3, which had a nominal bandwidth of 20 nm around a peak UV wavelength. The exposures took place in a glove box for a period of 10 minutes, after earlier flushing the box with N<sub>2</sub> for 15 minutes. The spectra of the exposed spots were compared with the spectra of the pristine sample to check whether any change had occurred. The peak wavelength of the filtered light was then progressively reduced and a fresh part of the sample was irradiated. Peak wavelengths were ranged from 340 nm to 300 nm.

The left hand side of Figure 5.19 shows the absorption features in the 6,13-MPn spectrum that were exposed to the filtered light. The thick red line is aligned with the peak wavelength of the incident light, while the thinner black lines indicate where the intensity was equivalent to 10% of the peak value. The spectra on the right show the wavelength range in which pentacene is expected to be observed. It is clear that pentacene is generated when the sample is exposed to the light filtered with a peak wavelength of 330 nm. Shorter wavelengths also have the same effect. Upon closer inspection of the absorption spectra, and considering the bandwidths of the filtered light, it appears that in all cases where pentacene was generated the absorption features below 325 nm were exposed. The weak absorption peak from 320 - 330 nm in the 6,13-MPn spectrum is clearly associated with photodecomposition of the material. This is consistent with the



**Figure 5.19** The UV-vis absorption spectra of 6,13-MPn are shown. The spectra on the left show the absorption features that are sensitised by the incident filtered light. The peak wavelength of the light is indicated by the thick red lines, while the wavelengths at which the light intensity is 10% of the maximum are marked by the thin black lines. The spectra on the right show the wavelength range in which pentacene is expected to be observed. Pentacene absorption features developed when the sample was exposed to light with peak wavelengths below 330 nm. It appears that excitation of the absorption feature from 320 – 330 nm is a part of the degradation pathway for 6,13-MPn.

decomposition wavelength of 331 nm expected from the DFT calculations (see the HOMO-4 to LUMO+4 transition shown in Figures 5.15 and 5.16). This wavelength compares with the 310 nm photolysis wavelength that was reported by Chuang et al. for 6,13-MPn in a THF solution [83].

#### 5.3.3 Photolysis of 5,14-MPn using a narrowband light source

The precursor 5,14-MPn has been reported to decompose to pentacene when exposed to UV light, following by the same decarbonylation reaction that occurs for 6,13-MPn. As discussed in section 5.1.3, Chuang et al. reported that the reaction occurred in solution when the material was exposed to ~366 nm light (although the light source was not specified) or illuminated using a 385 nm laser. However, from the DFT calculations (see Figure 5.7 and 5.8) it is clear that these wavelengths correspond to absorption features associated with the anthracene chromophore. It is hypothesized from the wavefunction distribution over the carbonyl bridge in the HOMO-5 and LUMO+2 that the transition that is predicted to have a maximum at 328 nm is the one that leads to photodegradation. The inconsistency between the literature and this hypothesis was tested using a narrowband exposure procedure similar to that undertaken with the 6,13-MPn samples.

Figure 5.20 shows the spectra of 5,14-MPn samples exposed at peak wavelengths ranging from 340 – 406 nm; the part of the spectrum where the vibronic progression of the anthracene chromophore appears. The spectra on the right once again show the wavelength range in which pentacene peaks are expected to appear. However, none of the features that developed when 6,13-MPn was exposed to sufficiently energetic UV light are observed in this case. The spectra all resemble the pristine, unexposed 5,14-MPn. Changes in the spectra only occur when shorter wavelengths are used, as demonstrated in Figure 5.21.



**Figure 5.20** The UV-vis absorption spectra of 5,14-MPn are shown. The vibronic progression of the anthracene chromophore is visible from 340 – 420 nm in the spectra on the left. Exposing these peaks to narrowband radiation did not result in the production of pentacene, as can be seen by the lack of features in the spectra shown on the right.

When the sample was exposed to light with a peak at 325 nm, some characteristic pentacene peaks began to appear. These features were most intense when the precursor was exposed to light with a peak wavelength of 311 - 321 nm. Taking into account the bandwidths of the filtered light, this would seem to indicate that the weak absorption feature at 305-315 nm is actually responsible for photoconversion of 5,14-MPn to pentacene. This is slightly shorter than the



**Figure 5.21** The UV-vis absorption spectra of 5,14-MPn are shown again, but the peaks of the filtered light are at shorter wavelengths than in Figure 5.18. Characteristic pentacene peaks develop when the samples are exposed to 325 nm light, but the peaks are best defined when the sample is exposed to light with maximum intensity from 311 – 321 nm. Considering the bandwidths of the light sources, it appears that the feature in the 5,14-MPn spectrum from 305 – 315 nm is related to the photodecarbonylation mechanism.

wavelength predicted from the synthetic UV-vis spectrum (328 nm), but it is consistent with the hypothesis that sensitising the HOMO-LUMO transition in 5,14-MPn does not drive the decarbonylation reaction.

The discrepancy between my observations and the results reported in the literature may be explained in a number of ways. It may be that Chuang et al. used a Hg lamp with a dominant output wavelength of 366 nm, but the lamp also had a

sufficient output at shorter wavelengths to enable the photoconversion [157]. Also, the generation of pentacene by irradiation of a solution using a 385 nm laser may have been due to localized heating or some other process influenced by the high intensity of the laser. Whether these explanations are correct or not, it remains that I only observed the production of pentacene following the photolysis of 5,14-MPn in the solid state at wavelengths less than 315 nm.

## 5.3.4 Irradiation of 6,13-MPn and 5,14-MPn using a wide bandpass filter

6,13-MPn and 5,14-MPn were also exposed to light passed through a wide bandgap filter, in this case a Schott BG39. The short wavelength cutoff for this filter is nominally 320 nm and the long wavelength cutoff is 710 nm [158]. Similar films of 6,13-MPn and 5,14-MPn were prepared on UV transparent coverslips by spray deposition from a 1 mg/mL dichloromethane solution. The absorption spectra of the pristine samples were then recorded, before being exposed to the filtered light in the N<sub>2</sub> glovebox for a period of 15 minutes. The box had been flushed with N<sub>2</sub>, once again, for 15 minutes prior to exposure.

Figure 5.22 shows the spectra of 6,13-MPn before and after exposure. It is clear that post-exposure, the sub-325 nm peaks have diminished slightly and the pentacene peaks have appeared from 500 – 670 nm. This was expected because in the narrowband experiments, light with wavelengths shorter than 330 nm caused photoconversion of 6,13-MPn to pentacene. In the case of 5,14-MPn, shown in Figure 5.23, the changes in the absorption spectra were more subtle. There was only a weak change in the intensities of the sub-425 nm features. There is some evidence of the generation of pentacene peaks between 500 - 600 nm, but these are very weak. Also, there are no features between 600 - 700 nm that would



**Figure 5.22** Absorption spectra of a 6,13-MPn film exposed to Schott BG39 filtered light from a Xe arc lamp, in an  $N_2$  environment, for 15 minutes. Strong pentacene absorption peaks appeared from 500 - 670 nm.



**Figure 5.23** Absorption spectra of a 5,14-MPn film exposed to Schott BG39 filtered light from a Xe arc lamp, in an  $N_2$  environment, for 15 minutes. Pentacene absorption peaks appeared only weakly from 500 – 600 nm.

indicate the aggregation of pentacene, thus very little photoconversion occurred. This result once again confirms that the anthracene absorption features play no role in efficiently converting 5,14-MPn to pentacene. The generation of the weak pentacene peaks in 5,14-MPn can be explained by the fact that the nominal cutoff for the filter is 320 nm, but a very small percentage ~0.01% is transmitted at 310 nm, while 4% is transmitted at 320 nm [159].

#### **5.3.5 Conclusions**

These photolysis experiments on 6,13-MPn and 5,14-MPn have confirmed that these materials are sensitive to incident light with wavelengths below 330 nm and 315 nm, respectively. These sensitization wavelengths are very similar to those predicted from the synthetic UV-vis absorption spectra (331 nm and 328 nm). In the case of 6,13-MPn, excitation of the experimental HOMO-LUMO transition causes decomposition of the molecule. However, for 5,14-MPn, absorption of light by the experimental HOMO-LUMO transition does not lead to removal of the bridging carbonyl group from the molecule. Clearly, calculation of the synthetic UV-vis spectrum of a DFT optimized single molecule does allow for interpretation of the actual physical properties of these precursor materials. It was expected that shifting the position of the carbonyl bridging group on the pentacene backbone in 5,14-MPn would not only change the absorption spectrum, but more importantly it would change the photolysis wavelength for the material. A shift in the peak photolysis wavelength compared to 6,13-MPn was observed and was only displaced from the prediction of the ZINDO calculation by 15 – 20 nm.

### 5.4 MONITORING THE REMOVAL OF CARBONYL BRIDGING GROUPS USING IR SPECTROSCOPY

In the previous section the photolysis of the two pentacene precursors was studied using UV-vis spectroscopy, where the absorption features that were examined correspond to transitions between different electronic levels. It was observed that when both precursors were exposed to broadband UV radiation in an  $N_2$ environment, the peaks due to absorption by pentacene reached their maximum intensities within two minutes. With further irradiation of the films in the presence of O<sub>2</sub>, the pentacene peaks gradually diminished until they were no longer observed after 30 minutes. The samples converted from the initially white precursor, to the distinctive purple colour of pentacene, through to a yellow colour after 30 minutes of exposure. The yellow material is an oxidation product of pentacene. As described in section 2.5.4, the oxidation of pentacene is expected to occur through a two-step process via the initial formation of a transannular peroxide, then with further oxidation pentacenequinone is formed [86]. The exact nature of the product was confirmed here by measurement of the vibrational spectrum, which identifies the presence of certain functional groups within molecules by the absorption of IR radiation at wavelengths distinctive to particular interatomic vibrational modes. The vibrational modes due to the carbonyl groups of 6,13-pentacenequinone are very strong and distinct from the weak vibrational modes of 6,13-pentaceneendoperoxide. Thus, identification of the nature of the final photolysis product is a straightforward process.

Calculations based on single molecules with geometries optimised using DFT once again proved to be useful in the analysis of the experimental IR spectra. Synthetic transmission spectra of the precursor materials, pentacene, and the two



**Figure 5.24** *IR transmission spectra of 6,13-MPn in a KBr disc, exposed to broadband light from a Xe arc lamp. The synthetic spectra of 6,13-MPn and pentacene are shown at the top and bottom of the figure, respectively. After 20 minutes of exposure to light, the carbonyl peaks of 6,13-MPn at 1774 cm<sup>-1</sup> and 1790 cm<sup>-1</sup> are almost completely absent.* 

possible degradation products, 6,13-pentaceneendoperoxide and 6,13-pentacenequinone, were all calculated using DGauss. The IR vibrational transitions were calculated using a B88-PW91 GGA energy functional with double zeta valence potential basis sets at the optimised geometry. The individual vibrational modes that absorb the IR light can be visualized once again. For example, it is clear that the large absorption feature at 1820 cm<sup>-1</sup> in the synthetic

spectrum of 6,13-MPn is due to stretching of the C=O bond of the bridging carbonyl group because all ketones absorb IR radiation at a similar wavenumber. This same strong absorption feature appears in the experimental absorption spectrum. It is split into two peaks at 1774 and 1790 cm<sup>-1</sup>, shown in the 0 s spectrum of Figure 5.24, although these peaks are not as broad as in the synthetic spectrum.

The conversion of 6,13-MPn into pentacene was traced by grinding a few milligrams of the material with approximately 100 mg of KBr grains. The homogenised powder was compressed into a disc and then the transmission of the 6,13-MPn sample was measured. The top of Figure 5.24 shows the synthetic spectrum of 6,13-MPn, while the bottom shows the synthetic spectrum of pentacene for comparison. An experimental IR spectrum for pentacene is also shown in Figure 2.16 [27]. The major difference in the spectra is the absence in pentacene of the broad carbonyl peak that appears at 1820 cm<sup>-1</sup> in 6,13-MPn. It is also expected from the synthetic spectra that exposing 6,13-MPn to UV light should also result in a change in the intensities of the two peaks that range from  $900 - 700 \text{ cm}^{-1}$ .

After recording the spectrum of the KBr disc containing the pentacene precursor, the disc was exposed to the broadband output from a Xe arc lamp for a total of 20 minutes, over a series of smaller intervals. All exposures were carried out in air. After the first exposure, the KBr disc appeared to take on a faded purple colour, and with successive exposures the colour continued to deepen. It can be seen in the series of vibrational spectra shown in Figure 5.24 that over time the carbonyl peaks at 1774 cm<sup>-1</sup> and 1790 cm<sup>-1</sup> slowly diminish. Another peak at 754 cm<sup>-1</sup> also disappears, while new peaks at 906 cm<sup>-1</sup> and 731 cm<sup>-1</sup> increase in

strength. These changes are entirely consistent with the expectations from the synthetic spectra of 6,13-MPn and pentacene. The sample did not take on the yellow colour of the oxygen degradation product, but remained purple. It is clear that the compressed KBr matrix prevented oxygen from diffusing readily into the environment of the pentacene molecules. Despite the energy being available to drive the photo-oxidation reaction, it could not proceed due to the exclusion of oxygen. The photo-oxidation product had to be identified through a modified experimental method, although this first experiment proved that the carbonyl group was removed from 6,13-MPn by exposure to UV light.

When only two species are present in an IR or UV-vis absorption spectrum, the concentration of each species can be determined by a simple method. The spectra need to be inspected for two wavenumbers at which the absorbance changes significantly with the changing concentration of both species [160]. Figure 5.25 (a) shows the absorbance of the significant peaks in the IR spectra from Figure 5.24. The absorbance at 1774 and 1790 cm<sup>-1</sup> increases as pentacene is produced and the absorbance at 731 and 906 cm<sup>-1</sup> decreases as 6,13-MPn is photoconverted. From Beer's Law, given that the thickness of the KBr disk is constant, the absorbance at a given wavenumber is:

$$A_i = k_{i,1}C_1 + k_{i,2}C_2 \tag{5.1}$$

Where *i* is the wavenumber,  $C_1$  and  $C_2$  are the concentrations of the two materials and  $k_{i,1}$  and  $k_{i,2}$  are proportionality constants. These constants can be determined by solving the equation for the initial absorbance and the absorbance after all of the precursor material has converted to pentacene. For this data, that was at 0 s and 1800 s, respectively. Two equations were determined from the



**Figure 5.25** Absorbance of peaks in IR spectra from Figure 5.24 over time. The percentage concentrations of 6,13-MPn and pentacene are determined over the total period of exposure by solving equation 5.1 for the absorption of the peaks at 1774 and 906 cm<sup>-1</sup>.

absorbance data for the peaks at 1774 and 906 cm<sup>-1</sup>, then solved simultaneously to obtain the concentration of the 6,13-MPn and pentacene during the period of UV exposure. The concentration plots are shown in Figure 5.25 (b). The plot indicates that 50% of the 6,13-MPn was converted to pentacene within 60 s and 95% had

converted after a total of 10 minutes. This indicates that the amount of time required for complete conversion of the precursor to pentacene is at least 10 minutes in the KBr matrix.

To study the photo-oxidation of pentacene produced from a precursor, a sample of the yellow coloured oxygen degradation product was prepared by initially drop casting a thick film of the asymmetrical pentacene precursor, 5,14-MPn, onto a glass microscope slide. The slide was then placed in the output of the Xe lamp source, in air, for a number of hours. The slide was also illuminated from the backside, to ensure that as much of the precursor as was possible was converted to the oxidation product. The yellow material was then scraped off the slide and the IR transmission spectrum was analysed. The spectrum is compared against the synthetic spectra of 5,14-MPn, 6,13-pentaceneendoperoxide and 6,13-pentacenequinone in Figure 5.26. The experimental spectrum contained too much instrumentation noise below 750 cm<sup>-1</sup> to be able to make a comparison with the synthetic spectra. However, above this range it appears that the experimental spectrum most resembles 6,13-pentacenequinone, primarily due to the similarity with the synthetic spectrum in the wavenumber range from 1750 to 1000  $cm^{-1}$ . In particular, there are similar peaks at 1260 cm<sup>-1</sup>, 1430 cm<sup>-1</sup>, 1588 cm<sup>-1</sup>, and 1711 cm<sup>-1</sup>. There are also some other peaks in the spectrum at 1780 cm<sup>-1</sup> and 905 cm<sup>-1</sup>. The first peak corresponds to the carbonyl group of unconverted 5,14-MPn remaining in the sample and the second appears in the spectrum of pentacene (see Figure 5.24). Because the drop casted film was relatively thick, parts of the sample were obviously shielded from the UV light, even after several hours of illumination. However, from the overall shape of the spectrum at the bottom of Figure 5.26, it is clear that 6,13-pentacenequinone is the product eventually generated when these pentacene precursors are exposed to UV light in air for an extended period.



**Figure 5.26** The top three spectra correspond to the synthetic transmission spectra of 5,14-MPn, 6,13-pentaceneendoperoxide and 6,13-pentacenequinone. The experimental IR transmission spectrum of 5,14-MPn that has been exposed to UV light in air for several hours is shown at the bottom. The spectrum most resembles the synthetic 6,13-pentacenequinone spectrum, with a strong absorption at 1260 cm<sup>-1</sup>, 1430 cm<sup>-1</sup>, 1588 cm<sup>-1</sup>, and 1711 cm<sup>-1</sup>. It also appears that there is some portion of the precursor and pentacene still present, as indicated by the strong carbonyl peak at 1780 cm<sup>-1</sup> and strong pentacene peak at 905 cm<sup>-1</sup>.

#### **5.5 CONCLUSION**

In this chapter the relationship between the synthetic and experimental UV-vis absorption and IR transmission spectra of a set of pentacene precursors has been extensively examined. It was found that, as with the case of the pervlene based semiconductors in Chapter Four, the single molecule synthetic spectra and the experimental spectra of thin films can be easily compared. The correlations between the spectra are close enough to enable assignments to be made between particular MO transitions in the synthetic spectra and equivalent absorption features in the experimental spectra. This is despite the common red-shifts observed in the HOMO-LUMO absorptions in the experimental spectra when compared to the synthetic spectra. As described in section 4.1.2, these red-shifts are related to multi-molecule effects such as nearest neighbour overlap of frontier orbitals; behaviour that is not accounted for in single-molecule DFT calculations. An additional source of wavelength variation that was not analysed in this chapter is the magnitude of the red-shift due to the nature of the casting solvent. Polar solvents are more likely than non-polar solvents to cause shifts in the absorption peaks of materials in solutions [161]. It is also known that the polarity of the solvent used to deposit an organic material and the rotation speed in spin coating can affect the film morphology, due to different rates of drying [162]. Changes in morphology can lead to changes in the absorption spectra. Solution annealing also has an effect, but in both cases the magnitude of variation tends to in the order of a few tens of nanometers. This is a smaller shift than is produced by the inadequacies of the single-molecule DFT calculation, but would be worth quantifying in future experiments.

The prediction from the DFT calculations that the photolysis wavelength of the pentacene precursors change when the type and position of the bridging group is changed was confirmed through the narrowband exposure experiments that were performed. Additionally, a thorough investigation of the nature of the light source required to drive the conversion of the 5,14-MPn and 6,13-MPn pentacene precursors in thin films was made, something that has not been conducted previously. The wavelength below which decomposition of 6,13-MPn films occurs in thin films was found to be 325 nm, as distinct from 310 nm in solution [83]. In 5,14-MPn films it was conclusively shown that wavelengths below 310 - 315 nm result in the production of pentacene. Previous reports of photoconversion happening by excitation of the anthracene chromophore are not correct [83]. This new information is consistent with the interpretation of the synthetic spectra from the DFT calculations, which confirms the value of this tool for making predictions about the photophysics of new precursor materials.

When the pentacene precursor materials were exposed to UV light in air, the pentacene that was produced underwent an undesired photoreaction with atmospheric oxygen, as was expected. This was observed via the diminishing pentacene peaks in the UV-vis absorption spectra. The yellow product was identified as a pentacenequinone by examination of the vibrational spectrum. Identification of the appropriate photolysis conditions and the use of an inert atmospheric environment for converting the precursors to pentacene while avoiding side reactions did prove to be useful when attempting to examine the performance of precursor based pentacene OFETs. These experiments are described next in Chapter Six. Moreover, the photoconversion of semiconductor precursors in a controlled way, using narrowband radiation instead of broadband

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radiation, represents a new way of thinking about processing of active materials in organic electronic devices that doesn't appear to be widely considered in the literature. A new method for the production of organic electronics that is based on this concept and is called *orthogonal wavelength processing* is presented in the next chapter [163].

# CHAPTER SIX

Spray deposition and photopatterning of thin films for OFETs

As discussed in the preceding chapters, the use of organic electronics in low-cost devices will be achieved by the optimisation of rapid throughput production techniques for both depositing and patterning active materials in the device architectures. Ideally the substrate and the insulating, semiconducting and conducting components of these devices should be composed of organic materials, so as to take full advantage of the mechanical flexibility and processing options available with organic electronic materials. In the previous chapter the photosensitivities of two semiconductor precursors, 5,14-MPn and 6,13-MPn, were examined under the influence of broadband and narrowband light sources. This chapter examines how these sparingly soluble materials can be efficiently deposited and patterned in OFETs. The patterning concept examined in this chapter entails local manipulation of the bulk electronic properties of materials in

OFET devices, by direct photolysis through a photomask or by translation of a coated substrate in the field of view of a point light source [101]. This approach builds on the technologies developed for photolithographic patterning of conventional microelectronics, but has certain advantages. The method potentially reduces materials usage by allowing recovery of unconverted materials and it reduces the number of steps required to pattern structures by avoiding multiple etch and lift-off processes.

This chapter is presented in four sections, the first of which outlines how thin films of semiconductor precursors and conducting polymers are formed by spray coating. Methods for optimising the spraying conditions for single and multiple layers of films are discussed. In the following section, experiments regarding photopatterning of single and multilayer precursor films using shadow masks are described. This section also includes a study of the photo-oxidation of the conducting polymer dispersion, PEDOT:PSS. In particular, it shows how the depth of photobleaching can be determined by measuring the change in resistance of a UV exposed film. After this, the focus of the chapter moves towards the performance of 5,14-MPn and 6,13-MPn pentacene precursors in OFETs. The chapter then concludes with a discussion of the application of spray deposited photopatternable materials in the manufacturing of all-organic, flexible transistors.

#### **6.1 THIN FILM FORMATION BY SPRAY DEPOSITION**

Spray deposition, which was used to produce thin films for the UV-visible absorption spectra of 5,14-MPn and 6,13-MPn in Chapter Five, is also used in section 6.3 for the production of OFETs. The reason why spray deposition was initially investigated was that the two precursors are sparingly soluble in common
organic solvents, which makes it challenging to increase the thickness and uniformity of spin coated films. In previous publications regarding the two materials, the low performance of the pentacene precursors (see Table 2.3) was attributed to incomplete coverage of the source-drain channels in the OFET architectures [28, 83]. Spray deposition of small solution droplets onto substrates, which then quickly evaporate, allows the gradual build up of films without redissolving underlying materials. This should result in more complete coverage of substrate surfaces than spin coating or drop casting. This section examines the optimisation of spray conditions for these precursors and for PEDOT:PSS dispersions. This leads into further studies on the photochemistry of these materials in the later parts of this chapter.

# 6.1.1 Depositing semiconductor precursors in the wet and intermediate regimes

Figure 6.1 shows the absorption spectra of three 5,14-MPn films that were sprayed onto  $25 \times 25$  mm microscope slides using a conventional airbrush. The setup used was described in section 3.1.2. Slides were placed next to each other on a substrate and heated to 37 °C, just below the boiling point of the dichloromethane solvent (39.6 °C). The 1 mg/mL 5,14-MPn solution was sprayed using a sweeping motion at a nozzle-substrate distance of 20 cm. After ten sweeps of the airbrush, one substrate was removed. After a further ten, one of the remaining substrates was removed, and then the last substrate was sprayed another ten times. The absorbance of the films, which is proportional to the effective film thicknesses, increases with the number of sweeps. The absorbance was measured in three sections of each sample; at two corners and at the centre of the substrate. The vibronic progression of the anthracene chromophore in 5,14-MPn is visible in



**Figure 6.1** Absorbance spectra of 5,14-MPn films sprayed from a dichloromethane solution onto a glass substrate at a distance of 20 cm. The absorbance of the material was measured in three positions on the substrate to examine the variance in thickness. The spray conditions were optimised so that deposition occurred in the intermediate (linear) regime.

the range from 350 – 425 nm in Figure 6.1. The variance in absorbance across the films decreased as the thickness of the films increased. By averaging the absorbance of the scans at 407 nm and taking the uncertainty to be the greatest difference from the average absorbance, the analogue of the film thickness was plotted with respect to the number of sweeps of the airbrush. Three data sets are displayed in Figure 6.2, corresponding to spraying at nozzle-substrate distances of 10 cm, 15 cm and 20 cm. As the distance to the substrates was reduced, the average thicknesses of the films increased. However, the variance in film thickness increased significantly, indicating that the film deposition transitioned to a non-linear regime. A throw distance of 20 cm appeared to be optimal for achieving predictable, linear deposition of the pentacene precursor. Comparing the result with Figure 2.25(a) [102], it appears that this is consistent with



**Figure 6.2** The absorbance of 5,14-MPn films at the anthracene chromophore peak. The films were sprayed over different distances, with a variation in the number of sweeps of the nozzle. Absorbance varied linearly with the number of sweeps when the spraying distance was optimised.

deposition in the intermediate regime, where the solution evaporates rapidly upon striking the substrate, depositing the solute without redissolving the existing film.

To further test the process of intermediate regime deposition, a bilayer film was produced by spray depositing a 0.8 mg/mL solution of 6,13-MPn onto a UV transparent substrate and then overcoating it with a 1 mg/mL solution of 5,14-MPn (both in dichloromethane). Single layer films of each material were sprayed simultaneously. The absorbance spectrum of the bilayer film is shown in Figure 6.3 (black line) along with the sum of the single layer films of the two precursors (red line). The absorbance of the bilayer film is higher than the sum of the individual spectra across most of the wavelength range. From Figure 6.1 it is known that there is roughly a 5% variation in the absorbance of the films sprayed in the intermediate regime, which accounts for the offset between the spectra. Otherwise, the features of the spectra are very similar; no new features have



**Figure 6.3** The black line corresponds to the spectrum of a bilayer precursor film of 5,14-MPn sprayed over a film of 6,13-MPn. The red line corresponds to the addition of the spectra of two individual films of each precursor that were sprayed under the same conditions.

appeared due to major interactions between the two types of molecules. The bilayer film does appear to be a simple addition of the spectra of the two separate individual films.

# 6.1.2 Depositing PEDOT:PSS by spray coating: The effect of the substrate temperature and the sweeping motion of the spray on the resultant quality of the film

The high conductivity of PEDOT:PSS films was utilised as another means of examining the quality of film formation by spray deposition. The dichloromethane solvent used with the pentacene precursors has a very low boiling point of 39.6 C, so it evaporates rapidly when it strikes a substrate held near room temperature. PEDOT:PSS, on the other hand, is obtained as an aqueous dispersion. The higher boiling point of water means that there is a greater tendency for droplets to

coalesce on the substrate and to dry slowly. This leads to highly non-uniform films that are of little use for electronics. This behaviour is illustrated by Figure 6.4(a), which shows a PEDOT:PSS solution sprayed onto a glass substrate with a set of gold electrodes that were spaced 6 mm apart. A Clevios 1000 PEDOT:PSS solution was diluted to 25% v/v with deionised water, so as to avoid clogging the airbursh nozzle, and sprayed onto the room temperature substrate at a distance of 25 cm without sweeping the airbrush across the face of the substrate. After 10 s of spraying the substrate was placed on a 130 °C hot plate and dried for 5 minutes. The resistance between the electrodes was measured and then another layer of the solution was sprayed for 10 s. After spraying for a total of 60 s, a mottled, non-uniform film was produced, as shown in Figure 6.4(a).

The resistance of the film changed in an unpredictable manner between the depositions. The resistance was initially so high that it could not be measured, because there was no continuity in the film between the electrodes. Gradually, the resistance decreased as the vacancies in the PEDOT:PSS layer were filled in (see Table 6.1). After a total of 60 s of spraying, the resistance between the three pairs of electrodes ranged from 31 - 36 ohms, but until this point the variance was quite large.



**Figure 6.4** (a) A PEDOT:PSS film sprayed over a substrate at room temperature and without translation of the air gun appears has highly non-uniform coverage. (b) A similar substrate coated at a surface temperature of 120 °C with translation of the air gun nozzle in front of the substrate.

Total spraying time / s	Resistance / kΩ				
	Electrode Pair	Electrode Pair	Electrode Pair		
	1 and 2	2 and 3	3 and 4		
10	Unmeasurable	Unmeasurable	Unmeasurable		
20	106.6	216	16800		
30	0.682	0.98	4.98		
40	0.146	0.92	0.25		
50	0.066	0.057	0.115		
60	0.036	0.031	0.036		

**Table 6.1** Resistance of a PEDOT:PSS film as a function of spraying time with a room temperature substrate and no translation.

The resistance of the PEDOT:PSS film was far more uniform when the substrate was heated during the deposition and the airbrush was simultaneously swept across the surface of the substrate. Figure 6.4(b) shows a film produced after ninety side to side sweeps at a distance of 20 cm and a substrate temperature of 120 °C. It is far more uniform than the film in Figure 6.4(a), although at a higher magnification it can be seen that the film does consist of the addition of many individual, overlapping droplets. Table 6.2 shows how the resistance between the three pairs of gold electrodes changed with the number of sweeps. After sixty sweeps the resistance varied from 323 to 395 ohms. After 30 more sweeps the resistance varied between 152 and 163 ohms. It can be seen that sweeping the airbrush and heating the substrate resulted in a far more reliable mode of film formation, with lower resistance variance than in the case of the stationary nozzle.

**Table 6.2** *Resistance of a PEDOT:PSS film as a function of number of sweeps of the spray gun. The substrate temperature was 120 °C.* 

Total number of sweeps / s	Resistance / kΩ				
	Electrode Pair	Electrode Pair	Electrode Pair		
	1 and 2	2 and 3	3 and 4		
60	0.395	0.355	0.323		
90	0.163	0.152	0.152		

#### **6.2 PHOTOPATTERNED ORGANIC THIN FILMS**

Having established that spray deposition using an airbrush is a reliable method for depositing multiple layers of organic semiconductor precursors, photopatterning of those layers into useful structures for electronics is the primary concern. This section examines pattern formation in these materials by exposure to light through photomasks and suggests a means of making devices by utilising the differences in wavelength photosensitivities that exist between the materials.

# 6.2.1 Image formation using photosensitive semiconductor precursors

The advantage of using photopatternable materials like 5,14-MPn to produce pentacene organic electronics is that patterning of the active semiconducting layer can be achieved in a simple manner using conventional photomasking technology. An example is shown in Figure 6.5, where a thick film of the pentacene precursor 5,14-MPn was drop cast onto a glass microscope slide. A brass mask with a cross shaped aperture was placed over the white precursor, then exposed to UV light from a Xe arc lamp for 10 s. A region of purple pentacene is defined within the



**Figure 6.5** Images of a thick film of 5,14-MPn that was drop cast onto a glass microscope slide. A cross shaped aperture was placed over the film, which was then illuminated with the output of a Xe lamp. The white precursor converted to the purple pentacene where it was exposed.

shadowed precursor, which remained white. This is relevant to the production of highly integrated devices. On the micron or sub-micron scale, the avoidance of current leakage paths between adjacent devices is critical to maintaining predictable operating performance. Isolation can be achieved if the unconverted precursor material is an insulator, or, if not, the remaining precursor can be redissolved, leaving the insoluble active material behind [27]. As long as the solvent wash does not diminish the solid-state order of the converted semiconductor material, this would allow the recovery of otherwise redundant material and a reduction in manufacturing costs.

Figure 6.6 shows a polarised optical microscopy image of a photopatterned 6,13-MPn film. A chrome mask was placed in contact with the film and the area was illuminated with filtered light from a Xe arc lamp for 30



**Figure 6.6** (a and b) Chrome patterns on a photomask. (c and d) A photopattened 6,13-MPn film with a 10  $\mu$ m wide strip. The film was exposed to UV light from a Xe arc lamp, filtered with a Schott BG39 filter to restrict the photolysis wavelengths to 320-710 nm.

minutes. A Schott BG39 bandpass filter was used to restrict the photolysis wavelengths to the range between 320 and 710 nm. In this image the exposed region was photooxidised, but back reflections from the substrate converted the regions covered by the chrome areas to the purple colour, indicative of pentacene. A feature width of 10  $\mu$ m was achieved, which is on the scale of the transistor source-drain channel widths used in microelectronics. The location of pentacene on the substrate is clearly definable by a simple photomasking process, demonstrating that it would be possible to confine the active semiconducting material of this photosensitive compound to the channel of a transistor by this direct photopatterning approach.

## 6.2.2 A method for the production of OFETs using multiple layers of photosensitive active materials

If an organic semiconductor precursor lies above an organic conducting layer in a multilayer film, the electrodes of a transistor could be patterned by exposing the conductor to light that is sufficiently energetic to drive an oxidation reaction, but which also leaves the semiconductor precursor in its native insulating state. The semiconductor precursor could then be patterned by changing the light source to a wavelength that does not affect the organic conductor, but does convert the semiconductor precursor into a semiconductor material. By this means a semiconducting channel could be formed above the conducting electrodes in an organic transistor without the need for standard lithographic steps in between. This novel approach for patterning devices takes advantage of a previously underutilised property of organic electronic materials: the variation in photosensitivities of multiple materials within a stacked structure. A scheme for making OFETs using this principle is outlined in Figures 6.7 and 6.8.





Step 3



Step 4



**Figure 6.7** Steps 1-5 for one approach to producing an OFET using photosensitive active layers. Step 1: A conducting film is spread over a substrate. Step 2: The conductor is exposed to light at wavelength  $\lambda_1$ , causing it to degrade to an insulator where exposed. Step 3: A dielectric material is spread over the conductor. Step 4: A second conducting layer is deposited. Step 5: A new photomask is used to define the source and drain electrodes in the top conducting layer. The underlying conductor is unaffected because the dielectric blocks  $\lambda_1$ .



Step 8

Encapsulation						
Precursor		Semiconductor				
	Source				Drain	
Insulator						
Oxidised conductor			Gate			
			Substrate			

**Figure 6.8** Steps 6-8 for one approach to producing an OFET using photosensitive active layers. Step 6: Coat the conducting layer with a semiconductor precursor. Step 7: Pattern a semiconducting channel by converting the precursor to a semiconductor by exposing it to light with wavelength  $\lambda_2$ , which does not affect the underlying conducting material. Step 8: Encapsulate the stack with a thin polymer film that blocks light and protects the organic layers from the atmosphere.

In Figure 6.7, step 1, a blue conducting polymer is spread over a substrate. In step 2, this layer is patterned at a wavelength,  $\lambda_1$ , converting it to a white coloured insulator where exposed to light. This leaves a conducting gate electrode in the centre of the film. An insulating layer (shown in yellow) that also blocks  $\lambda_1$ is then deposited on the stack in step 3. The insulator is followed by deposition of another layer of the conducting polymer in step 4. In step 5, this layer is once again patterned through a photomask to form separate source and drain electrodes. In Figure 6.8, step 6, a semiconductor precursor layer (coloured green) is deposited over the patterned source and drain electrodes. In step 7 the precursor is converted to a semiconductor (shown in red) that bridges the source and drain electrodes. It is photopatterned at a wavelength  $\lambda_2$ , which does not affect the underlying conducting polymer layer. Finally, in step 8, an encapsulation layer is deposited over the top of the semiconductor, to protect the organic layers from water vapour, oxygen and light exposure.

The structure resulting from the *orthogonal wavelength photopatterning* of organic multilayers (patterning one layer in a stack at a wavelength that does not affect other layers) described above, is an OFET [163]. The features of the transistor are patterned at high resolution without needing to remove the unreacted materials that remain in the different layers. All of the high-resolution patterning processes were carried out by using photomasks, rather than by physically printing solutions in defined patterns. This process combines the resolution advantages and well developed technology associated with photomasking with the low cost, high throughput manufacturing of organic thin films by solution deposition. Many other direct photopatterning fabrication schemes are conceivable and the steps can be varied slightly depending on the wavelength sensitivities of the materials that are used.

#### 6.2.3 Orthogonal wavelength patterning of organic multilayers

The wavelength selectivity of the 6,13-MPn and 5,14-MPn photoconversion that was described in sections 5.3.2 and 5.3.3 offers some other opportunities for patterning more complex devices, with multiple precursor layers. 6,13-MPn was found to convert to pentacene when exposed to light at wavelengths below

325 nm. Similarly, 5,14-MPn was sensitive to light below 315 nm. Yamada et al. also reported that the photodecarbonylation of the  $\alpha$ -diketone precursor, 6,13-EPn, occurred with an excitation wavelength around 470 nm [86], which is red-shifted by ~150 nm from the wavelengths required for the monoketone precursors. Using this difference in wavelength sensitivities, it may be possible to pattern the precursor layers independently, by careful selection of the light source bandwidth. This pattern formation concept is outlined in Figure 6.9, where a substrate is initially coated with a layer of precursor 1, then overcoated with precursor 2. It is



Step 1

**Figure 6.9** Steps 1-3 for patterning a bilayer of two organic semiconductor precursors. Step 1: Deposit precursor 1 onto a substrate, then overcoat with precursor 2. Step 2: Expose the stack to light with wavelength  $\lambda_1$  through a photomask. This converts precursor 1 to a semiconductor, but does not affect precursor 2. Step 3: Expose the stack to light with wavelength  $\lambda_2$  through a photomask. This converts precursor 2 to a semiconductor, but does not affect precursor 1.

then patterned through a mask using the narrowband light source,  $\lambda_1$ . This converts the underlying precursor 1 to a semiconductor, but does not affect precursor 2 on top. Changing the mask and light source to  $\lambda_2$ , the upper layer is patterned, leaving the underlying layer unaffected.

The bilayer patterning process outlined above was tested experimentally using a layer of 5,14-MPn coated over 6,13-MPn on a UV transparent coverslip. The bilayer stack and some single layer films of each material were produced by the method described in section 6.1.1. Each film was exposed to narrowband light with a peak at 330 nm (10% of maximum intensity at 320 nm and 345 nm, as shown in Figure 5.19) and the UV-vis absorption spectra were measured. The exposures took place in an N<sub>2</sub> glovebox, for a period of 15 minutes. Figure 6.10 shows the absorption spectra of the 6,13-MPn and 5,14-MPn single layers as well as the bilayer film, after exposure to filtered light. The weak pentacene peaks that developed are emphasised in Figure 6.11. The spectra show the absorbance of the films prior to exposure (black) and after exposure (red). The formation of the pentacene vibronic progression from 450 – 600 nm in the 6,13-MPn single layer and in the bilayer stack, but not in the 5,14-MPn single layer, demonstrates that the 6,13-MPn film was photopatterned through the 5,14-MPn film, without affecting the upper layer.

The individual layers of the bilayer stack could not be truly independently photopatterned, in accordance with the scheme outlined in Figure 6. Exposing the stack to sub-315 nm light to convert 5,14-MPn to pentacene would also affect the 6,13-MPn layer. Ideally, independent patterning should be tested with materials that have a greater separation in the sensitisation wavelengths, such as 6,13-MPn and 6,13-EPn, but the latter material could not be obtained at the time of writing.



**Figure 6.10** Absorbance spectra (after UV exposure) of a 6,13-MPn film, a 5,14-MPn film and a bilayer film of 5,14-MPn on 6,13-MPn that were sprayed onto UV transparent substrates. Samples were exposed to narrowband light (330 nm peak) for a period of 15 mins in an  $N_2$  filled glovebox.



**Figure 6.11** The spectra from Figure 6.10 repeated with an emphasis on the characteristic vibronic progression of pentacene. The spectra show the absorbance of the films prior to exposure (black) and after exposure (red). Formation of the pentacene vibronic progression from 450 – 600 nm occurs in 6,13-MPn and in the bilayer stack, but not the 5,14-MPn film. This shows that the 6,13-MPn film was photopatterned through the 5,14-MPn film without affecting the upper layer.

#### 6.2.4 Photodecomposition of the organic conducting polymer PEDOT:PSS and the formation of an insulating product

In previous chapters and in the preceding section, the photolysis of semiconductor precursors has been discussed. But if the multilayer patterning scheme described in section 6.2.2 is to be realised, photopatternable organic conducting materials will also be needed. Patterning of organic conductors containing PAGs was discussed in section 2.4.4, but an alternative to the incorporation of a PAG is to selectively pattern the conducting polymer via a photo-oxidation process. If the oxidised polymer has a conductivity that is several orders of magnitude lower than the pristine material, conducting paths could be defined in a simple manner.

The conducting of organic polymer dispersion poly(3,4ethylenedioxythiophene) and poly(styrenesulfonic acid), known as PEDOT:PSS, is widely used in organic electronic devices. It is used as a hole injection layer in OLEDs and OPVs, as well as other applications such as anti-static coatings and capacitors [7]. Pure PEDOT:PSS films have a conductivity of only 1 S cm<sup>-1</sup> which is too low to be useful for most electronic applications. By adding high boiling point solvents to PEDOT:PSS solutions, the mean size of the PEDOT:PSS particles is reduced [164]. With an increase in contact area between the PEDOT:PSS particles, the conductivity may increase to 1000 S cm<sup>-1</sup>, which is comparable with the conductivity of indium tin oxide films. PEDOT:PSS is more environmentally stable than many other organic conducting materials, because the 3 and 4 positions of the thiophene rings in the PEDOT backbone are occupied by an ether bridge. This prevents further facile oxidation at these positions. Despite this comparative stability, PEDOT:PSS films remain sensitive to degradation at high temperatures in the presence of oxygen and water vapour. Degradation is also enhanced when the films are irradiated with light. This light sensitivity presents challenges in controlling the long-term device stability through packaging and encapsulation methods, but it does present the possibility of illuminating PEDOT:PSS films for the purposes of photopatterning circuit elements.

# 6.2.4.1 Changes in the conductivity of spin-coated films exposed to light

Experiments have previously been carried out by Andreas Elschner to investigate the spectral sensitivity of PEDOT:PSS conductivity [48]. In his studies, a number of PEDOT:PSS dispersions (under the trade name *Clevios PH500*, with 5 wt% DMSO) were either doctor-bladed or spin-coated over quartz substrates, then baked in air at 120-130 °C after deposition, for a period of ten minutes. The sheet resistances of the films were measured by evaporating parallel, 120 nm thick gold contacts onto the films through a shadow mask. The film resistance was measured using a Keithley 614 Ohmeter. To test the effects of exposure to air, the sheet resistance of samples was monitored over time as they were exposed to the output of a Xe arc lamp, with a glass filter that cutoff wavelengths shorter than 320 nm. Over a period of 20 days, the sheet resistance of a control sample stored in the dark, in air, rose by approximately 10%. On the other hand, the samples exposed to light in air underwent an increase in resistance of several orders of magnitude, while encapsulated samples exposed to light over the same time underwent a resistance increase that was only slightly higher than the control sample. Clearly, the resistivity of PEDOT:PSS films increases when irradiated in air.

Elschner also irradiated films in air, at room temperature, with monochromatic light, to examine the spectral sensitivity of the observed conductivity change [48]. 150 nm thick layers of the commercial formulation,



**Figure 6.12** A 150 nm thick layer of PEDOT:PSS (Clevios P) was irradiated in air using monochromatic light. (a) The change in resistivity above that of the control, according to radiation dose. (b) The change in resistivity as a function of wavelength [48].

*Clevios P*, were used in this case. The irradiance was roughly  $1.2 - 2.4 \text{ W/m}^2$  at each wavelength. The experiment was carried out over 550 hours, after which the

sheet resistance of a control sample stored in the dark had increased from 440 k $\Omega$ /sq to 860 k $\Omega$ /sq. Figure 6.12(a), shows the change in the sheet resistance of the PEDOT:PSS films (with the temporal change in resistance of the control film substracted) in response to the radiation dose provided over wavelengths ranging from 290 – 417 nm [48]. The resistance change is also plotted against wavelength for a constant exposure dose of 600 Wh/m<sup>2</sup> in Figure 6.12(b). Elschner concluded from his experiments that UV-B light (280-320 nm) is effective in changing the sheet resistance of films, while UV-A light (320-390 nm) has less influence. Also, for a given radiation dose, shorter wavelengths more effectively increase the sheet resistance of PEDOT:PSS.

Studies of the spectral sensitivity of PEDOT:PSS dispersions were continued by exposing films of Clevios F 010 and Clevios FET (commercially available dispersions which respectively exclude and include oxidation stabilisers), to the output of a 450 W Xe arc lamp [48]. Additional cut-off filters were placed in the beam path to measure the relative efficacy of UV-A, UV-B and UV-C light in driving changes in the film conductivity. A plot of resistance against exposure time is shown in Figure 6.13. The resistance of the stabilized film does not change significantly, while the resistance of the unstabilised film changes rapidly with UV exposure. The resistance increases more gradually when wavelengths shorter than 280 nm are blocked, however the increase is still appreciable. The resistance increase in the non-stabilised film when it is exposed exclusively to wavelengths longer than 305 nm is not much greater than in the stabilised film exposed to broadband radiation.

The UV-vis absorption spectrum of PEDOT:PSS (Clevios 520 + 5% DMSO), shown in Figure 6.14, has a low, broad absorption in the visible and

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**Figure 6.13** Films of PEDOT:PSS were exposed to broadband radiation from a 450 W Xe arc lamp and the resistance was monitored over time. The films consisted of an oxidation stabilised Clevios FET dispersion and a non-stablised Clevios F 010 dispersion. The rate of degradation was reduced by the introduction of high-pass filters (280 nm and 305 nm) into the beam path [48].



**Figure 6.14** The absorption spectrum of a 43 nm thick layer of PEDOT:PSS (Clevios 520 + 5% DMSO) changes after irradiation with the broadband output of a Hg lamp for 900 s. The irradiance was 20 mW/cm<sup>2</sup>, assumed to be primarily accounted for by the Hg spectral line at 253 nm. The inset shows the absorption of a solution of 3,4-ethylenedioxythiophene (EDOT) [48].

infrared, which is attributed to the presence of free charge carriers or to the excitation of polaronic or bipolaronic midgap states [48]. A shoulder at 260 nm is similar to one that appears in solutions of 3,4-ethylenedioxythiophene (EDOT). Strong absorptions at 193 and 225 nm are due to absorption by the benzene rings in the structure of PSS. Clearly, the strong, short wavelength absorption features are due to excitations within monomer units, in particular, it is the EDOT segment that is first excited as the illumination wavelength is stepped down from the visible towards the deep UV. Strong peaks disappear and a broad smooth absorption band appears after exposure to the output of a Hg arc lamp. It may be inferred that several new photoproducts result from the exposure. Elschner suggests that photooxidative degradation occurs within the EDOT units at the sulfur atom of the thiophene ring or at the terminal carbon of a PEDOT chain [48]. The suggested reaction scheme is shown in Figure 6.15. Oxidation of the sulfur atom in the thiophene ring shortens the conjugation length of PEDOT segments and reduces the concentration of charge transfer sites, which in turn diminishes the bulk conductivity of the exposed PEDOT:PSS thin film.



**Figure 6.15** Reaction schemes for oxidation of PEDOT at the thiophene ring. Above: Formation of sulphone groups by oxidation at the thiophene sulfur atom. Below: Formation of carbonyl groups by oxidation of the terminating carbon of a PEDOT chain [48].

#### 6.2.4.2 Exposure of Clevios PH1000 to light

Following Elschner's experimental methods for the photo-oxidation of PEDOT:PSS, the photo-oxidation susceptibility of a new formulation, *Clevios PH1000*, was studied. Samples were prepared by spin-coating a thin layer of the dispersion over a set of gold electrodes, so that changes in the conductivity of the films could be measured. The electrodes were deposited through a shadow mask onto a glass microscope slide. An adhesion layer of chromium was sputtered first, followed by the gold contacts. The contact patches were 5 mm wide and 3 mm apart (see Figure 6.16). The PEDOT:PSS formulation was pipetted into a glass dropper bottle, while DMSO was combined to make a 5 wt% solution. The bottle was sealed and then sonicated for 10 minutes. The solution was then spun over the glass substrates. Films with thicknesses ranging from 60 - 100 nm were produced by spinning the slides at 1000 rpm for 30 seconds. 25 - 35 nm thick films were produced by rotation at 4000 rpm for 40 seconds. The thickness measurements were made using a Tencor Alphastep 500 stylus profilometer. After spinning, the slides were immediately baked in air on a hotplate for 10 minutes at 130 °C.



**Figure 6.16** *PEDOT:PSS films were spin-coated on a set of gold electrodes, sputtered through a shadow mask onto a glass microscope slide. A strip of the blue coloured organic conductor was patterned between the contact patches by simply wiping excess material away with a wet cotton bud.* 

Excess material was wiped from the slide using a cotton bud dipped in deionised water, leaving a 5 mm wide strip of PEDOT:PSS across the contact patches of four gold electrodes. This faint strip is highlighted by the dashed lines in Figure 6.16.

Exposures were carried out in air using both broadband and filtered light from a Thermo Oriel Xe arc lamp, type 6255. Samples were placed in a filter holder with the film section located centrally in the output of the lamp. The resistance of the films between the gold contacts was measured intermittently during the exposures using a Keithley 614 electrometer. Figure 6.17 shows how the resistance of the Clevios 1000 films exposed to the output of the Xe arc lamp in air changed with respect to the period of exposure. A range of film thicknesses were illuminated. The 30 nm thick film initially had a resistance of approximately  $1 \text{ k}\Omega$ , compared to 0.15 k $\Omega$  for the 90 nm thick film. The resistance of each film



**Figure 6.17** Change in resistance of a set of PEDOT:PSS films of various thicknesses with respect to exposure time. The films were exposed to the broadband output of a Thermo Oriel Xe 6255 arc lamp in air.

steadily increased with the exposure period, growing by over five orders of magnitude within a few hours of exposure. The resistances of the thinner films increased more rapidly than the thicker films.

Another pair of films was exposed to the output of the Xe lamp, which was initially filtered using a Schott BG39 band-pass filter. This limits the light throughput to 320 - 710 nm. Figure 6.18 shows that over the three hours of exposure to filtered light, the film resistance remained steady. When the filter was removed and the exposure continued, there was a clear and immediate increase in the resistances. This result mirrors Elschner's conclusions that illumination with wavelengths above 305 nm (see Figure 6.13) has minimal impact on the resistance of PEDOT:PSS films [48].

Plots of the natural logarithm of resistance against time convincingly indicate that the resistances of PEDOT:PSS films change as an exponential



**Figure 6.18** *Resistance of PEDOT:PSS exposed to the broadband and filtered light from a Thermo Oriel Xe 6255 arc lamp. The filter was a Schott BG39 bandpass filter (320 – 710 nm).* 

function of the period of light exposure. Figure 6.19 shows an analysis of the resistance data for an 80 nm thick film directly exposed to the Xe lamp in air. The  $R^2$  value of 0.9986 confirms that the linear fit is highly accurate, proving that the relationship between resistance and exposure time is of the form,

$$R = R_0 e^{kt} \tag{6.1}$$

where *R* is the resistance,  $R_0$  is the resistance of the pristine film, *t* represents time in seconds and *k* is some constant with units of s<sup>-1</sup>. Figure 6.17 showed that the resistance increases more rapidly during the exposure of thinner films, so the film thickness must be a factor in the exponent. A modified form of the resistance relationship is,

$$R = R_0 e^{\frac{Dt}{H_0}} \tag{6.2}$$



where  $H_0$  is the thickness of the film in m, and D is some constant with units of

**Figure 6.19** Natural logarithm of resistance against time for an 80 nm thick PEDOT:PSS film.

m s<sup>-1</sup>. The slope of the regression line fitted to the plot of ln(R) against t is then equivalent to,

$$slope = \frac{D}{H_0} \tag{6.3}$$

which enables the extraction of the constant, *D*. The value of *D* should be dependent on the spectral irradiance of the light source, the molar absorptivity of PEDOT:PSS and the rate of diffusion of oxygen into the PEDOT:PSS film. Table 6.3 shows the values of *D* calculated from the thicknesses of films and the slope of the linear regression lines. The average value of *D* was found to be  $(2.7 \pm 0.5)$  m s<sup>-1</sup> when the films were illuminated with the broadband output of the Xe lamp.

Beer's Law implies that the incident light is absorbed throughout the entire thickness of the film, with most light being absorbed at the top surface [39]. Oxygen must be available for decomposition of the PEDOT:PSS to occur, as shown in the reaction scheme in Figure 6.15 [48]. With the high film absorbance and the limited oxygen diffusion rate, most oxidation will occur at the surface of the film and progress through to the base. The resistivity of the heavily oxidised upper PEDOT:PSS layer is much higher than the parallel, underlying layer of material. Thus, as photo-oxidation proceeds, current flows primarily in the continually narrowing underlying conducting layer. A simple, empirical model for this behaviour is presented here. It assumes that the film consists of a completely oxidised upper layer and a pristine lower layer that narrows as UV exposure proceeds. Taking the average value for the parameter D, shown in Table 6.3, the time required for a PEDOT:PSS film of a given thickness to fully photo-oxidise can be estimated.

Figure 6.20 illustrates how the film is composed of a pristine conducting layer in contact with the gold electrodes and an oxidised layer on top. The resistance of the conducting layer is related to the film geometry, according to,

Sample	Electrode	Film	Light	Slope of	R <sup>2</sup> value	D
	Pair	Thickness	source	regression line		/ m s <sup>-1</sup>
		/ nm		/ s <sup>-1</sup>		
1	1,2	70 ± 10	Xe 6255	$3.79908 \times 10^{-4}$	0.99738	$(2.7 \pm 0.4) \times 10^{-11}$
1	2,3	90 ± 10	Xe 6255	$2.74658 \times 10^{-4}$	0.99852	$(2.5 \pm 0.3) \times 10^{-11}$
1	3,4	80 ± 10	Xe 6255	$3.57303 \times 10^{-4}$	0.9986	$(2.9 \pm 0.4) \times 10^{-11}$
3	1,2	30 ± 5	Xe 6255	$6.78251 \times 10^{-4}$	0.98997	$(2.6 \pm 0.6) \times 10^{-11}$
3	2,3	33 ± 5	Xe 6255	7.11312 × 10 <sup>-4</sup>	0.98616	$(2.8 \pm 0.6) \times 10^{-11}$
					Average	$(2.7 \pm 0.5) \times 10^{-11}$

**Table 6.3** Calculations of the parameter D for PEDOT: PSS films of various thicknesses.



**Figure 6.20** The resistivity of the oxidised PEDOT:PSS layer (green) is higher than the parallel pristine conducting layer (blue), meaning that current primarily flows through the pristine layer. The change in the bulk resistance between the gold contacts is inversely proportional to the height of the pristine PEDOT:PSS layer, H.

$$R = \frac{\sigma L}{HW} \tag{6.4}$$

where the length of the current path, *L*, width of the current path, *W*, and resistivity of the PEDOT:PSS layer,  $\sigma$ , are constants. The height, *H*, changes as the top of the PEDOT:PSS film is photooxidised. Substituting (6.4) into (6.2) gives,

$$\frac{\sigma L}{HW} = \frac{\sigma L}{H_0 W} e^{\frac{Dt}{H_0}}$$
(6.5)

and the relationship between the height of the pristine PEDOT:PSS layer and the photo-oxidation time simplifies to,

$$H = H_0 e^{-\frac{Dt}{H_0}}$$
(6.6)

This means that the depth of the photo-oxidised layer, H<sub>photo-ox</sub>, is given by,

$$H_{photo-ox} = H_0 - H = H_0 - H_0 e^{-\frac{Dt}{H_0}} = H_0 \left(1 - e^{-\frac{Dt}{H_0}}\right)$$
(6.7)

which allows the time required to completely oxidise a film of a given thickness to be estimated.

#### 6.2.4.3 Patterning PEDOT:PSS by UV exposure

A study of the transfer of a simple pattern from a photomask onto a PEDOT:PSS film was carried out using a film prepared in the same manner as in the resistance studies. The brass mask in Figure 6.21(a) was laser machined with four 60  $\mu$ m wide slots in the centre. It was pressed into contact with the PEDOT:PSS film on a glass substrate and then placed in the output of a xenon arc lamp. The slots were illuminated for 2.5 hours at room temperature and in air. At the conclusion, faint

lines in the PEDOT:PSS film were visible to the naked eye. Figure 6.21(b) shows a dark field microscope image of one of the lines. Figure 6.21(c) shows a magnified image of the slot in the mask next to an image of the film at the same magnification in Figure 6.21(d). The contrast in this image has been enhanced to clearly show the photobleached area of the PEDOT:PSS film. This thin strip of photomodified material is approximately 60  $\mu$ m wide, matching the pattern on the photomask.

#### 6.2.4.4 Conclusions

From the studies by Elschner and the experiments on the photo-oxidation of Clevios PH1000 described above, PEDOT:PSS is clearly a photosensitive material. It undergoes oxidation at the sulfur atom of the thiophene ring or at the terminating carbon of a polymer chain when exposed to light at wavelengths shorter than approximately 300 nm, in the presence of air. As shown by the experiments examining the photo-oxidation of films in the broadband output of a Xe arc lamp, the resistance changes by several orders of magnitude after illumination for a few hours (the time required changes with the thickness of the film). By using light sources with greater irradiance it is likely that this period could be further reduced and the thickness of the PEDOT:PSS layer could be optimised so as to balance the requirements of low resistance in the conducting paths and a minimised photo-oxidation period for the exposed areas. However, it does appear that this photo-oxidation process is too slow for practically patterning commercial devices, a reaction speed closer to that for the photolysis of the pentacene precursors would be ideal. Regardless of this limitation, it remains that there is a sufficient contrast in the conductivity of pristine and photooxidised PEDOT:PSS to allow photopatterning of PEDOT:PSS circuit elements within an



**Figure 6.21** (a) The shadow mask used to photopattern a PEDOT:PSS film. The four slots in the mask were cut by laser machining and were 30 mm long and 60  $\mu$ m wide. (b) After 2.5 hours of exposure to broadband UV light, a faint line was observed in the dark field microscope image of the film. (c) A magnified view of the 60  $\mu$ m wide slot in the mask. (d) A view of the film at the same magnification with contrast enhancement of the image. The feature in the film appears to be approximately 60  $\mu$ m wide, matching the dimension of the photomask slot.

all-organic electronic device.

Additionally, it was demonstrated that the resistance of 70 nm and 90 nm thick PEDOT:PSS films barely changed over several hours of exposure through a Schott BG39 filter (Figure 6.18). In Figure 5.22, it was shown that the semiconductor precursor, 6,13-MPn, does convert to pentacene when exposed to the same light source. Clearly, if a layer of 6,13-MPn was deposited on a PEDOT:PSS film, it would be possible to convert the 6,13-MPn to pentacene by exposing it to wavelengths greater than 320 nm without changing the conductivity of the underlying PEDOT:PSS. Thus, these two materials could be tested for use

as the conductor and semiconductor precursor in an OFET produced via orthogonal wavelength photopatterning.

#### 6.3 A COMPARISON OF 5,14-MPN AND 6,13-MPN OFETS UNDER DIFFERENT ILLUMINATION CONDITIONS

In section 2.5.5 the surface treatment, annealing temperatures and UV exposure conditions applied in the testing of 6,13-EPn OFETs were reviewed [80]. A range of annealing temperatures and illumination periods were tested by the authors in an effort to maximise the mobilities and on/off ratios of the transistors. Moderate substrate annealing temperatures of 150 °C and UV illumination periods of 15 minutes or less were found to produce to best results. Surface treatments on the dielectric such as MSQ and HMDS were also found to boost the observed mobilities. These procedures informed the OFET research that is described here regarding the two monoketone bridged pentacene precursors, 5,14-MPn and 6,13-MPn.

The aim of these studies was to compare the mobilities and on off ratios of the OFETs prepared by converting the precursor either with heat, broadband UV light or narrowband UV light. The basic OFET fabrication scheme is shown in Figure 6.22. The substrate was a boron doped p-type silicon wafer with a thermally grown 285 nm thick SiO<sub>2</sub> layer on the surface. Wafers were diced into 30 mm  $\times$  20 mm rectangles to match the dimensions of the electrode shadow masks. It was important to avoid damage to the oxide layer, so the individual substrates were produced by first making a 2-3 mm long score at the edge of the blank wafer using a diamond tipped scribe. The point of a pair of needle nosed tweezers was place under this mark and then gentle pressure was applied to either Step 1



**Figure 6.22** The steps involved in making OFETs using photosensitive semiconductor precursors. Step 1: The basic OFET architecture is shown, with a glass substrate, a YSZ dielectric layer and gold gate, source and drain electrodes. Step 2: The semiconductor precursor is deposited. Step 3: Excess precursor is wiped away to separate the adjacent FETs and the precursor is converted to the semiconductor by exposure to light and heat. Step 4: The unconverted precursor can be redissolved and the effect of solvents on the performance of pentacene can be examined.

side to crack the wafer along the lattice plane. This generated very little debris. The wafers were then rinsed in ethanol and acetone, dried with an N<sub>2</sub> gun and then soaked in a 100% ethanol bath for 20 minutes. After a second drying step, a shadow mask was clipped to the substrates and then gold source and drain electrodes were deposited on the SiO<sub>2</sub> layer in the ultra-high vacuum system, as discussed in section 3.2.1. The substrates were removed, and then placed in a 0.5% (v/v) solution of HMDS in chloroform, which was then covered for 18 hours. The substrates were then removed from the bath and dried by spinning at



Figure 6.23 An OFET test structure with a 6,13-MPn film converted to pentacene by heating. 2000 rpm for 60 s, then placed on a hot plate at 110 °C for 5 mins. Next, the substrates were sprayed with a 1 mg/mL solution of either 5,14-MPn or 6,13-MPn in toluene with the setup shown in section 3.1.2. The films weren't of uniform thickness, but were sprayed under the same conditions. The N<sub>2</sub> bottle pressure was set to 120 kPa and the paintgun was set to a discharge rate of 4 mL/min. Each room temperature substrate was swept side-to-side a total of 40 times at a distance of 20 cm. The excess precursor material lying between adjacent electrode sets was wiped away using an ethanol soaked cotton bud. An area of the oxide layer was scratched away with a diamond scribe to allow access to the silicon gate. The substrate was held down using a credit card covered with Teflon tape to shield the FET contacts from any of the debris generated. The substrate was then taped to an aluminium heater block inside the glovebox shown in section 3.2.4. Dry N<sub>2</sub> was passed through the box for 15 minutes before the heater block was then brought

up to temperature. Figure 6.23 shows a completed OFET test structure after conversion of the precursor to pentacene.

The performance of these OFET structures was first tested using a semiconductor which has previously been demonstrated to have a high mobilitity. 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn) is a solution processable material. A 10 mg/mL solution in toluene was syringed onto the source and drain electrodes of a test structure. A credit card with Teflon tape covering one end was used to draw the solution across the electodes, in a direction parallel to the channel length and perpendicular to the channel width. The TIPS-Pn layer was then dried on a 90 °C hotplate for 2 minutes, following the procedure of Payne et al. [165].

The transistors did not perform to the level expected from the literature. Payne et al. used a similar substrate with a slightly thicker, 370 nm oxide layer and a source-drain channel that was 22  $\mu$ m long and 340  $\mu$ m wide [165]. With this structure, the drain current reached -5  $\mu$ A with -40 V set as both the drain and gate voltage. In the research carried out here, the channels were longer, but also wider. The output curves of an OFET with a 100  $\mu$ m long and 4 mm wide channel are shown in Figure 6.24(a). A current of -60 nA was obtained at the voltages equivalent to Payne et al.'s device; a figure several orders of magnitude worse. When the channel length was reduced to 30  $\mu$ m, the current reached -0.8  $\mu$ A at a drain voltage of -100 V and gate voltage of -30 V, still well below the current observed in the slightly shorter and much narrower OFET from the literature. Clearly the OFET structure used here needs to be optimised. Also it was observed that the 100  $\mu$ m transistor output curves appeared to have the typical shape expected for a FET, but the curves for the 30  $\mu$ m channel did not. There appeared

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**Figure 6.24** Output curves for TIPS-Pn transistors. (a) A 100  $\mu$ m long channel, 4 mm wide. (b) 30  $\mu$ m long channel. (c) 30  $\mu$ m long channel with the V<sub>G</sub> = -5 V current measurement subtracted from each of the others.

to be an additional background signal. When the lowest gate voltage measurement was subtracted from all of the others, as shown in Figure 6.24(c), the output curves were slightly closer to what was expected. This was also observed to be the case when the transistors were prepared from 5,14-MPn and 6,13-MPn.

Figure 6.25 (a-c) show the output curves of three transistors produced from the 6,13-MPn pentacene precursor. In the first case, the precursor was converted only by heating for 15 minutes at an indicated substrate temperature of 140 °C (decarbonylation of 6,13-MPn occurs at 150 °C [28], so the thermocouple reading for the heater block may have been 10-15 °C below the actual temperature). The second FET was produced by annealing the substrate to a temperature of 90-95 °C while simultaneously exposing the precursor film to the broadband output of a Xe arc lamp for 15 minutes. The third OFET was made by exposing the precursor film to a narrow set of wavelengths, ranging from 270 -



**Figure 6.25** Output curves of OFETs produced by converting 6,13-MPn into pentacene. All channels are 30  $\mu$ m long and 4 mm wide. (a) Pentacene generated by heating for 15 minutes at 140 °C. (b) Annealed at 90-95 °C and exposed to the broadband output of a Xe arc lamp for 15 minutes. (c) Exposed to filtered light (270 – 340 nm) for 60 minutes at a substrate temperature of 95 °C. (d-f) The curves in (a-c) with the current measurement at the smallest V<sub>G</sub> subtracted from all other curves.
340 nm for 60 minutes at a substrate temperature of 95 °C. In each case it can be seen that the drain current magnitude did increase in response to an increase in the magnitude of the gate voltage. However, it appeared that there was an almost linear background signal in each of the scans that resulted in an unusual shape in each of the output curves. This was probably due to the ohmic conductance through the semiconductor as a result of the source-drain voltage. This signal probably affected these output curves so significantly because of the poor mobility of the semiconductor. Repeating the procedure applied in Figure 6.24(c), the lowest gate voltage signal was removed from each of the other signals to give the output curves shown in Figure 6.25 (d-f). These curves more closely resemble typical OFET output curves. This shows that in each case, the product of the 6,13-MPn conversion did act as a semiconductor, albeit one with a poor performance consistent with the small drain currents that were only a few hundred picoamps in magnitude.

The transistor output curves shown in Figure 6.26(a-c) correspond to the precursor 5,14-MPn. The first OFET was produced by heating the sample to 130 °C for 15 minutes. The second was exposed to broadband light from the Xe lamp for 15 minutes at a temperature of 90 °C. The third OFET was produced by exposure to light at 260 - 330 nm for 60 minutes at an annealing temperature of 80 °C. The same light sources were used as for the 6,13-MPn based transistors, but the annealing temperatures were reduced because of the lower conversion temperature for this material (128 °C, as opposed to the 150 °C required for 6,13-MPn [28, 83]). The output curves are similar to the curves for 6,13-MPn in that the gate voltage does affect the magnitudes of the drain currents and there is also a linear background. When this was substracted, the curves shown in Figure 6.26(d-



**Figure 6.26** Output curves of OFETs produced by converting 5,14-MPn into pentacene. All channels are 30  $\mu$ m long and 4 mm wide. (a) Pentacene generated by heating for 15 minutes at 130 °C. (b) Annealed at 90 °C and exposed to the broadband output of a Xe arc lamp for 15 minutes. (c) Exposed to filtered light (270 – 340 nm) for 60 minutes at a substrate temperature of 80 °C. (d-f) The curves in (a-c) with the current measurement at the smallest V<sub>G</sub> subtracted from all other curves.

f) resulted. In this case the curves for the purely heat converted OFET and the broadband illuminated OFET look reasonable. However, the curves for the the narrowband illuminated OFET do not resemble normal output curves. In this case,



**Figure 6.27** Output curves for an OFET with (a) only a HMDS treatment in the channel and (b) an unconverted 6,13-MPn film, annealed at 95 °C. (c) Film exposed to 470 nm peaked filtered light from Figure 6.28, for 60 minutes at 95 °C. (d) Film exposed to filtered light with 310 nm peak (see Figure 6.28) for 60 minutes at 95 °C. (e) The  $V_G$  = -20 V signal subtracted from each of the other curves.

the drain current moves towards more positive values as the gate voltage becomes more negative. This is an unexpected trend and perhaps means that the conversion to pentacene was unsuccessful in this material or that this particular FET was subject to large trapping influences.

After the unsuccessful attempt to produce an OFET by narrowband exposure of the 5,14-MPn, further inspection of the process for 6,13-MPn was required, to confirm the result observed in Figure 6.25(f). Figure 6.27(a) shows the output curves for an OFET structure before spraying of the precursor, essentially a test of the conductance of the HMDS layer. Figure 6.27(b) shows the output curves of the pristine semiconductor after annealing to 95 °C. In both cases, it appears that there is little influence from the gate voltage and in general the drain current is less than a picoamp. In 6.27(c) and (d) the transistor was successively exposed to filtered light in the two ranges shown in Figure 6.28. After exposure to narrowband light with a peak at 470 nm for 80 minutes, there was no general increase in the drain current. After the wavelength range of the



**Figure 6.28** The spectra of the filtered light source used to study the effects of narrowband radiation on the performance of pentacene OFETs derived from the 6,13-MPn precursor.

light was altered to 270-340 nm, with a peak at 310 nm, the output curves in 6.27(d) were measured. There was clearly an increase in the drain current from a base level of roughly one tenth of a picoamp to several picoamps at higher drain and gate voltages. Once the low gate voltage signal was removed, the output curves in (e) were produced. While they are noisy, the maximum value is still in the picoamp range and the current does increase with the greater magnitude of the gate voltage.

As stated in the literature by Chen et al., the problem with these monoketone bridged pentacene precursors appears to be that because of their sparing solubility it is hard to form contiguous films [28]. Even so, they managed to measure currents in the milliamp range for a device prepared by heating a 6,13-MPn film that was spin coated over a channel with a length of 10 µm and a width of 20 cm. Given that the channels used in this study were 30 µm long and 4 mm wide, it was expected that the currents observed would be lower, but not by seven orders of magnitude. Inspection of the film coverage over the OFET channels reveals that even with spray deposition instead of spin coating, the channel is only patially covered in the precursor. This explains why the apparent mobility of the transistors was much lower than expected. Figures 6.29(a) and (b) show a OFET substrate covered in unconverted 6,13-MPn. The coverage is patchy and the material appears to be transparent. Some approximately 100 µm long crystals appear to be present, but mostly the coverage is amorphous and crystallites are shorter. Now, in Figure 6.29(c) and (d) it is observed that for a different OFET where 6,13-MPn was converted to pentacene by heating to 140 °C, the surface is covered in many crystallites. These are much darker and it seems that the amorphous film has shrunk. Coverage of the channel is sparse, but



**Figure 6.29** *Microscope images of the channels for OFETs produced from 6,13-MPn that is (a and b) pristine, (c and d) heated to 140 °C, (e and f) heated to 95 °C and exposed to a Xe arc lamp, and (g and h) exposed to 270 – 340 nm filtered light at 95 °C* 

some 100 µm long crystals do bridge the channel. The small currents in the nanoamp range are explained by the large number of grain boundaries and the low percentage areal coverage of the channel. This situation is repeated in the case of the broadband UV exposed sample, with a low fractional coverage of the channel. The narrowband exposed sample looks slightly different. The crystallites are present once again, but they don't appear as dark as in the prior cases. Perhaps this means that the conversion to pentacene is only partially complete and a longer period of time or higher flux is required to drive the complete degradation of the precursor. Or it could suggest that an even wider range of wavelengths is necessary. Regardless, it appears that further optimisation of the spray coating parameters is necessary to improve the coverage of the OFET channels by the pentacene precursors.

## **6.4 SPRAY DEPOSITION OF AN ALL-ORGANIC TRANSISTOR**

The future application of these techniques may be the following type of device. While much more work is required to prove the viability of photopatterning both the conducting and semiconducting layers of a flexible, all-organic transistor, this approach may enable rapid and low-cost production of OFETs. Due to the long period required to pattern the PEDOT:PSS films and the lower than expected drain currents observed in the OFETs tested using the 5,14-MPn and 6,13-MPn pentacene precursors, a working device was not actually developed. But as a demonstration, the structure shown in Figures 6.30(a-d) was made. The substrate was a polyethylene terephthalate sheet (an overhead slide). It is heat stabilised so that it does not change shape below 160 °C. A PEDOT:PSS layer was spray

deposited on the surface through a mask, then a layer of an organic insulating material, PMMA, was coated over the top. Next, another layer of PEDOT:PSS was spray-deposited. Using a mask like that in Figure 6.21(a), the channel region of the electrodes could be converted from a conductor to an insulator, thereby separating the source and drain electrodes. In figure (d), a thin layer of 6,13-MPn was sprayed over the top, which could be illuminated and converted to a semiconductor without affecting the conducting layer.



**Figure 6.30** Images of the layers that make up an all-organic transistor. The substrate was a flexible photocopier transparency film. All layers were deposited onto the heated substrate using an air gun. (a) PEDOT:PSS electrodes sprayed through a brass shadow mask. (b) A PMMA film sprayed over the gate electrodes, appearing as dull white rectangle over the reflective substrate. (c) Source-drain electrodes sprayed over the PMMA film, aligned over the underlying gate electrodes. (d) White coloured 5,14-MPn pentacene precursor was sprayed over the PEDOT:PSS source-drain electrodes.

## **6.5 CONCLUSIONS**

This chapter was presented in four sections, the first of which outlined how thin films of semiconductor precursors and conducting polymers could be formed by spray coating. The methods for optimising the spraying conditions for single and multiple layers of films were discussed. It was found that the precursor materials 5,14-MPn and 6,13-MPn could be deposited in the linear regime on room temperature substrates with a thickness variation of approximately 5%. The conducting material PEDOT:PSS had to be deposited on a high temperature substrate because of the higher boiling point of the aqueous solvent. Nevertheless, the appropriate conditions for depositing both materials reliably were described. In the following section, experiments regarding photopatterning of single and multilayer precursor films using shadow masks were described. In particular, it was shown that structures on a scale appropriate for transistor devices could be patterned in films of 5,14-MPn and 6,13-MPn using simple photomasks. A means of photopatterning all layers of an OFET device using photomasks and different light sources was then explained.

Orthogonal wavelength processing involves the independent patterning of multilayers of semiconductors and conductors when they are exposed to different, narrowband wavelength sources that only affect the mobility of one material at a time [163]. Appropriate conducting and semiconducting materials for which the charge mobilities can be controlled by exposure to separate narrowband wavelength ranges had to be found to be able to test this concept. Studies were presented on the photo-oxidation of the conducting polymer dispersion, PEDOT:PSS. It was shown conclusively that the conductivity of the film is controlled by the time of exposure to UV light with wavelengths below 300 nm. Light with wavelengths from 320 - 710 nm does not affect the conductivity of PEDOT:PSS. An empirical model was presented that can be used to predict the time required for total oxidation of films of thicknesses in the sub-100 nm range. In tests of transitors made by the conversion of 6,13-MPn to pentacene in the active semiconductor layer, it was shown that exposure to narrowband light in the range from 270 - 340 nm was effective at converting the precursor to pentacene and increasing the mobility of the active layer. This is a new way of thinking about processing semiconductor precursors, because this had previously been achieved in a less controlled manner using broadband light sources [83].

Although much work needs to be done to optimise the transistor fabrication and testing facilities, the results presented in this chapter are promising. They prove that a transistor can be fabricated from precursors exposed to narrowband and not broadband radiation and that this light would not necessarily affect an underlying layer of a conductor such as PEDOT:PSS. These materials could therefore be utilised in an all-organic, orthogonal wavelength patterned transistor of the type presented in section 6.4 and described in Figures 6.7 and 6.8 [163]. Although no device was actually produced, this chapter presents a roadmap for further research into orthogonal wavelength processing.

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# CHAPTER SEVEN

New photopatternable precursors for thienoacene semiconductors

Experiments with the pentacene precursors and the conducting polymer, PEDOT:PSS, which were described in the last two chapters, have shown that it should be possible to photopattern the architecture of an OFET using only solution processed materials for the electrodes and semiconducting layer. The appeal of patterning transistors using light is quite clear; it is compatible with high throughput production processes such as roll-to-roll printing and yields high resolution features. However, pentacene precursors like 6,13-MPn will not be used in the manufacturing of commercial transistors, since pentacene is simply not sufficiently stable for consumer electronics. The natural extension of the work on 6,13-MPn and related pentacene precursors must be towards using the photopatterning strategy with air-stable molecules. Over the past five years extraordinary progress has been made in the synthesis of such air-stable semiconductors for high performance organic electronics [25, 31]. The particular compounds used are the thienoacenes – small molecules consisting of fused benzene and thiophene rings. The question remains as to whether the precursor patterning strategy used with pentacene will work for the thienoacenes. The benefits would be substantial because carrying out the precursor photolysis without eliminating oxygen from the environment around the processing equipment would substantially simplify manufacturing. In examining this question some new thienoacene precursors were conceived, the structures of which are presented in this chapter. An analysis of the photochemical properties of these molecules is once again made through the use of density functional theory (DFT) calculations, but first an overview of some of the characteristics and structural forms of the thienoacenes is provided.

## 7.1 PROPERTIES OF SMALL MOLECULE ORGANIC SEMICONDUCTORS WITH FUSED THIOPHENE RINGS

In this section the different classes of thienoacenes are discussed and compared in terms of the threshold voltage and mobilities observed in transistors. An explanation of the air-stability of these materials is provided based upon a comparison with the structures of linear and kinked aromatic hydrocarbons.

## 7.1.1 The four classes of fused thiophene semiconductors

A vast array of thiophene containing molecular structures have been synthesised for use as organic semiconductors. These molecules contain one or more thiophene rings and fit into four main classes: the [n]thienoacenes, the benzenethiophene alternating molecules, the acenedithiophenes and the diacene-fused



**Figure 7.1** HOMO and LUMO orbitals, energy gaps and reorganisation energies  $(\lambda_h)$  of four representative thienoacenes (calculated using DFT at the B3LYP/6-31g(d) level) [25]. Carrier mobilities in bulk materials tend to be higher for materials with low reorganisation energies. **1** is an [n]thienoacene and **2** is the benzene-thiophene alternating molecule, benzo[1,2-b:4,5-b']bis[b]benzothiophene. **3** is the acenedithiophene, anthra[2,3-b:6,7-b']dithiophene. **4** is the diacene-fused thienothiophene, dinaptho[2,3-b:2',3'-f]thieno[3,2-b]thiophene.



**Figure 7.2** The thienoacene molecules **1-4**, (from Figure 7.1) are shown on the left and the polyaromatic hydrocarbons that they are isoelectronic with are shown on the right. The sulfur atoms provide an electron pair in the five-membered ring and thereby produce an aromatic sextet. An equivalent sextet is produced by substituting a pair of sp<sup>2</sup> hybridised carbons in place of the sulfur atom. Image from [25].

thienothiophenes [25]. Simple, representative molecules for these four classes are shown in Figure 7.1, along with calculations of the HOMO and LUMO orbital energies, orbital surfaces, and the molecular reorganisation energies (from [25]). The corresponding isoelectronic hydrocarbons are shown in Figure 7.2. These are visualised by substituting a pair of  $sp^2$  hybridised carbons in place of the sulfur atom in the five membered thiophene ring. The equivalent structures show that thienoacenes 1, 2, and 4 actually have *phene* type electronic structures; that is they are like acenes with one or more kinks somewhere in the structure. Only the isoelectronic hydrocarbon of 3 has the structure of a linear acene (pentacene). The significance with regards to the air-stability of thienoacenes is discussed shortly.

The stand-out performers from these four materials classes are the diacene-fused thienothiophenes (DAcTTs). The DAcTTs have excellent charge transport properties because they typically pack into herringbone structures in both thin films and single crystals. In most hydrocarbon semiconductors, there is strong edge-to-face packing but weaker edge-to-edge interactions between molecules in the solid-state. In the DAcTTs the coefficients of the HOMO orbitals are particularly large on the sulfur atoms of the thienothiophene groups. These orbitals, located in the centre of the molecules, interact strongly with other sulfur atoms on neighbouring molecules. Thus, the large overlap between HOMO orbitals leads to the high p-type FET mobilities observed for the DAcTT devices, such as those based on BTBT, DNTT and DATT (see Table 7.1) [25].

The performance figures for devices made using thienoacenes are shown in Table 7.1. We see that for BBBT, a strictly benzene-thiophene alternating molecule, the mobility is quite poor and the magnitude of the threshold voltage is rather high. However, with alkylation and a pair of fused thiophene rings around **Table 7.1** *FET* performances for a range of thienoacene based OFETs. Parameters were extracted from devices in the saturation regime. The molecules were deposited on Si/SiO2 substrates with gold contacts, unless noted otherwise. Adapted from Takimiya et al. [25].

Compound	Substrate Temperature	μ / cm² V <sup>-1</sup>	V <sub>th</sub> / V	I <sub>on</sub> /I <sub>off</sub>	Details of architecture	Ref.
	/ °C	s⁻¹				
Benzo[1,2-b:4,5- b']bis[b]benzothiophene (BBBT)	-	1.0 × 10 <sup>-2</sup>	-29	10 <sup>5</sup>	Drop casting, annealed at 100 °C, bottom contact, phenyltriethoxysilane	[166]
Dihexyl-Dithieno[2,3-d;2',3'- d']benzo[1,2-b;4,5-b']dithiophene <b>(C6-DTBDT)</b>	-	1.7	-56	10 <sup>7</sup>	Dip coating, top contact	[167]
H <sub>13</sub> C <sub>6</sub>	13					
Diphenyl-naptho[2,3-b:6,7- b']dithiophene <b>(DPh-NDT)</b>	100	1.5	-5	10 <sup>7</sup>	Vapour deposited, top contact, octyltrichlorosilane SAM	[33]
Ph-						
Anthradithiophene (ADT)	85	0.09	NA	NA	Vapour deposited, bottom contact	[168]
S S S S S S S S S S S S S S S S S S S						
Dodecyl-[1]benzothieno[3,2- b]benzothiophene (C12-BTBT)	Room temperature	3.9	NA	10 <sup>6</sup> -10 <sup>8</sup>	Vapour deposited, top contact, octadecyltrichlorosilane SAM	[169]
H <sub>25</sub> C <sub>12</sub> H <sub>25</sub> C <sub>12</sub>	5					
Dioctyl-[1]benzothieno[3,2- b]benzothiophene (C8-BTBT)	-	5	NA	10 <sup>6</sup>	Drop cast, decyltriethoxysilane	[170]
H <sub>17</sub> C <sub>8</sub> S						
Dioctyl-[1]benzothieno[3,2- b]benzothiophene (C8-BTBT)	-	9.1	-18.9	10 <sup>7</sup>	Spin coating, single crystal formation through solvent	[34]

H <sub>17</sub> C <sub>8</sub>					vapour annealing, PMMA dielectric	
Dioctyl-[1]benzothieno[3,2- b]benzothiophene (C8-BTBT) $\downarrow \downarrow $	-	31	-10	10 <sup>5</sup> -10 <sup>7</sup>	Single crystal, double-shot inkjet printing	[19]
Dinaptho[2,3-b:2',3'-f]thieno[3,2- b]thiophene (DNTT)	60	3.0	-11	10 <sup>7</sup>	Vapour deposited, top contact, octyltrichlorosilane	[171]
2,9-decyl-Dinaptho[2,3-b:2',3'- f]thieno[3,2-b]thiophene (C10-DNTT) $H_{21}C_{10}$	60	1 – 7.9	-8 – 13	10 <sup>8</sup>	Vapour deposited, top contact, octadecyltrichlorosilane	[172]
2,9-decyl-Dinaptho[2,3-b:2',3'- f]thieno[3,2-b]thiophene (C10-DNTT)	-	12	NA	10 <sup>5</sup> -10 <sup>6</sup>	Drop cast onto an N,N- dimethyl-10- aminodecyltriethoxysilane- SAM	[32]
Dianthra[2,3-b:2',3'-f]thieno[3,2- b]thiophene (DATT)	100	3.0	10	10 <sup>6</sup>	Vapour deposited, top contact, octadecyltrichlorosilane	[173]

the benzene core, the solution processed C6-DTBDT has a good hole mobility and on/off current ratio, although the threshold voltage of this device is even higher. This demonstrates that minor changes to the sulfur content in the molecular core and manipulation of the solid state packing through alkylation has a huge influence on the semiconductor performance. Unfortunately the high threshold voltage in these devices is a problem that may prove a challenge to easily overcome. The HOMO levels of benzene-thiophene alternating molecules (Figure 7.1) are much deeper than the Fermi level of gold, giving rise to nonohmic contact effects in such devices. This naturally requires a high applied gate voltage to achieve band alignment with gold, although the behaviour of the non-ohmic contacts may not be so severe if an electrode material other than gold is substituted. The acene dithiophene, DPh-NDT, which has a HOMO level that is closer to gold also has a much lower threshold voltage. The introduction of a substituent to the napthodithiophene (NDT) core again has a beneficial impact on the carrier mobility, as it compares favourably to the non-alkylated anthradithiophene (ADT). However, the alkylated DAcTT devices show another step up in performance again, satisfactorily reaching much higher mobilities while maintaining low threshold voltages.

#### 7.1.2 Why thienoacenes are ideal for air stable organic electronics

As discussed in Chapter Two, molecules with extensively distrubuted  $\pi$ -orbital systems are ideal for use in organic electronic applications. The intramolecular electron delocalisation is high because discrete molecular orbital (MO) wavefunctions tend to spread over most of the molecule. In concert with the high degree of  $\pi$ -orbital overlap in the solid state of many such materials, this leads to the appreciable bulk electron transport that is observed. The oligoacenes, such as pentacene, still provide a useful performance benchmark for thin-film transistor field-effect mobility. The best performing pentacene thin film OFETs had a hole mobility of 7.0 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [23]. Pentacene performs well as a p-type semiconductor for a number of reasons: the HOMO level is close to the work function of Au, there is a high degree of intermolecular orbital overlap and the molecules stack in a two dimensional herringbone arrangement, which leads to highly isotropic conductivity in thin films.

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While high performances have been demonstrated for oligoacene devices in the controlled environments of research laboratories, these materials are not ideal for practical applications. Short oligoacenes such as naphthalene and anthracene do not stack close enough and with an orientation that is conducive to devices with a high charge mobility. While the higher oligoacenes such as tetracene and pentacene have a suitable solid-state structure, they have enhanced electron density at the central rings which means that these molecules are susceptible to oxidation at these positions in ambient conditions [171]. The frontier orbital calculations in Figure 7.3 show the trend in the relative energies of the oligoacene HOMO levels: they increase in step with the number of aromatic rings [31]. Longer oligoacenes are less stable in their ground states than shorter oligoacenes due to the reduced ionisation energies. Additionally, the HOMO-



**Figure 7.3** The energies with respect to the vacuum level for the HOMO and LUMO orbitals of some oligoacenes: naphthalene, anthracene, napthacene (tetracene) and pentacene. When the number of aromatic rings increases the energy of the HOMO level increases (the ionisation energy reduces) and the HOMO-LUMO gap narrows. Calculations were performed on molecules with geometries optimised using DFT-MO analysis at the B3LYP/6-31G(d) level. Image taken from [31].

LUMO gaps contract as the molecular length increases. This is a behaviour that is familiar from quantum theory, where the separation of energy levels for a one-dimensional particle in a box reduces with an extension in the length of the box. A reduction in the HOMO-LUMO gap tends to reduce the photostability of a molecule in ambient light. Pentacene, with a HOMO-LUMO gap of 2.17 eV (equivalent to 571 nm), is therefore sensitive to photo-oxidation even when exposed to red light. Oxidation of the shorter molecule, anthracene, requires UV light.

As mentioned earlier, most thienoacene molecules have a kinked, phene-type structure, which leads to better stability for long molecules. To demonstrate why this is the case, the structures and frontier orbitals of the three-ringed and four-ringed phenes, phenanthrene and chrysene respectively, are shown in Figure 7.4 [31]. A major point of difference with the oligoacenes is apparent in the relative positions of the HOMO levels; as the number of aromatic rings increases, the HOMO level energy rises more slowly than for the oligoacenes with the same number of rings. The LUMO also stabilises more slowly as the number of rings increases. By comparing Figure 7.3 and Figure 7.4 it is clear that the energies of the frontier orbitals for the four-ringed phene, chrysene, resemble the three-ringed oligoacene, anthracene. In fact, the HOMO-LUMO bandgap is slightly greater and the HOMO level is slightly lower. Similarly, the energies of the phenanthrene and naphthalene HOMOs and LUMOs are comparable. Given that the HOMO energies remain low and that the bandgaps only reduce gradually with an increase in the number of fused rings, compounds with the phene structure are useful as air-stable semiconductors [31].

The thienoacene BTBT is isoelectronic with chrysene. The air stability of



**Figure 7.4** The energies with respect to the vacuum level for the HOMO and LUMO orbitals of two phenes: phenanthrene and chrysene. The HOMO levels are lower and the badgaps are larger than in oligoacenes with the same number of fused aromatic rings. Image from [31].

a transistor constructed with the BTBT derivative, 2,7diphenyl[1]benzothieno[3,2-b]benzothiophene (DPh-BTBT), was tested by Takimiya et al. over a period of 250 days [31]. The transistor initially had a  $\mu_{\text{FET}}$ of 2.0  $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and this value remained little changed after the long term test. This is a clear demonstration that the stabilising effect of the lowered HOMO level in the kinked aromatic structure does lead to OFETs with stable, predictable performances. This is further evidence that the thienoacenes are the materials of choice for current and future OFET research.

## 7.2 PHOTOPATTERNABLE PRECURSORS FOR THIENOACENE BASED SEMICONDUCTORS

As discussed in Chapters Two, Four and Five, the precursors of pentacene and other polyaromatic hydrocarbons with photolabile, solubilising moieties, bridged across one or more aromatic rings, can be converted to the semiconducting product molecule by simply exposing them to light. These materials are ideal for spatially selective direct photopatterning of organic electronic devices, although there are difficulties in processing these precursors in air. Population of the LUMO of the converted pentacene takes place during processing and photooxidation readily occurs as part of the decay process from this level. It may be worthwhile to synthesise photoprecursors of the thienoacene materials as a means of avoiding photo-oxidation of the product. With their wide HOMO-LUMO gaps, the thinenoacene precursors composed of only three or four rings may be processed by light exposure without then exciting an electron to the LUMO of the product.

In the remainder of this chapter, a range of thienoacene semiconductor precursors are proposed. The products are exclusively materials for which high OFET performances have been demonstrated, or materials which have large HOMO-LUMO gaps. Synthetic UV-visible absorption spectra and the MOs associated with the photochemically relevant transitions are displayed. All molecular geometries were optimised using *Parallel DGauss under ab initio CAChe* software from Fujitsu Limited. However, prior to discussion of these new molecules, a pair of previously synthesised thienoacene photoprecursors are examined as a means of evaluating the efficacy of this fabrication strategy.

### 7.2.1 Previous demonstrations of photopatternable thienoacenes

The overarching point of this chapter is to suggest that there is a case for synthesising a new set of molecules, with the aim of producing air-stable, photopatternable semiconductor precursors. In 2011, Watanabe et al. synthesised a precursor for a molecule similar to pentacene but with a single fused thiophene



**Figure 7.5** The semiconductor precursor (6R,11S)-6,11-dihydro-6,11-methanotetraceno[3,2b]thiophen-14-one decomposes to give tetraceno[2,3-b]thiophene when exposed to light.

ring. The aim was to produce tetraceno[2,3-b]thiophene by photolysis of its photoprecursor (6R,11S)-6,11-dihydro-6,11-methanotetraceno[3,2-b]thiophen-14one, which is shown in Figure 7.5. An OFET made from the semiconductor by vapour deposition had a mobility of 0.31 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (see Table 2.3 for further details) [142]. The presence of a fused thiophene ring increases the ionisation potential of the molecule by 0.12 eV compared to pentacene (that is, the HOMO is 0.12 eV further below the vacuum level). When a THF solution of the precursor was irradiated with a UV lamp in oxygen free conditions, the absorbance of the precursor peaks at 340 and 355 nm diminished. This is indicated by the downward pointing arrows in Figure 7.6(a). New absorption bands appeared from 420-550 nm. While the photoconversion process was successful, it was still found that all testing and photolysis of devices made from this compound had to be carried out in oxygen free conditions. In a direct comparison of the stability of this material against pentacene, it was found that it oxidised six times slower than pentacene did during the photolysis of equivalent solutions under the same conditions. This material is clearly more photostable than pentacene, although it is not completely immune to photo-oxidation.

Remembering that the synthetic UV-vis spectra derived from DFT optimised molecules do not take into account vibrational structure, it is seen in Figure 7.6(b) that the spectrum of the tetraceno[2,3-b]thiophene precursor is



**Figure 7.6** (a) The absorption spectrum shows the development of tetraceno[2,3b]thiophene as a THF solution of (6R,11S)-6,11-dihydro-6,11-methanotetraceno[3,2b]thiophen-14-one is exposed to a UV lamp. The inset plots the reducing concentration of the precursor over the 40 s exposure period and also shows the increasing absorbance of the product at 531 nm during the exposure. Spectra taken from [98]. (b) The synthetic spectrum of the precursor (red) is similar to the solution spectrum in (a). The synthetic spectrum of the product (black) has a HOMO-LUMO transition at similar wavelengths to the spectrum in (a), except there are no vibrational peaks.



**Figure 7.7** (a) The three MO transitions that contribute to the absorption peak of the (6R,11S)-6,11-dihydro-6,11-methanotetraceno[3,2-b]thiophen-14-one synthetic spectrum from 280 – 380 nm. The transition feature centred at 328 nm likely drives the decarbonylation as the occupied and unoccupied MOs overlap on the carbonyl group. (b) The transition on the carbonyl bridge is weak compared to the other transitions.

calculated with a good degree of accuracy. There is a strong peak in the synthetic spectrum at 260 nm and another weak one around 300 nm. In Figure 7.7(a) and (b) it can be seen that the weaker, longer wavelength feature, is dominated by the HOMO-LUMO transition at 303.7 nm. In the solid state, this transition is likely to be slightly red-shifted and have vibrational structure, which would match the features in the spectrum of Figure 7.5(a). Looking at Figure 7.6 again, the MO transition centred at 328 nm has large components of the HOMO-5 and LUMO+6 orbitals located on the bridging carbonyl group. As this leads to a rearrangement of charge on the bridge, it is likely that this is the transition that leads to removal of carbon monoxide from the molecule through a retrocyclic chelotropic decarbonylation reaction. The other weak transition at 348.2 nm only involves the three ringed chromophore and plays no role in the removal of the carbon monoxide bridge. The large change in energies of the orbitals that occurs in the configuration interaction can be seen from the fact that the transition on the carbon monoxide bridge occurs between the HOMO-5 and LUMO+6 orbitals of the ground state. The other transitions involve the frontier orbitals, which is more in line with expectations.

An example of the successful synthesis of a semiconductor precursor that was demonstrated to be air-stable in the operation of an OFET was reported by Yamada et al. during 2006. This was around the time when very high performance thienoacenes such as BTBT and DNTT were originally tested in OFETs [95]. The precursor, 9,10-ethano-9,10-dihydro-2,6-bis-2-thienyl-anthracene-11,12-dione, shown in Figure 7.8(a) (and Table 2.2), has an  $\alpha$ -diketone bridge across the central aromatic ring. Photolysis of the precursor on an OFET produced a bis-2thienyl-2,6-anthracene layer. The reason why the semiconductor is stable when



**Figure 7.8** (a) The photopatternable precursor molecule 9,10-ethano-9,10-dihydro-2,6-bis-2-thienyl-anthracene-11,12-dione converts to bis-2-thienyl-2,6-anthracene when exposed to UV light. (b) Anthracene-like peaks develop near 400 nm as the precursor is irradiated with a metal-halide lamp in a toluene solution, converting the precursor to bis-2-thienyl-2,6anthracene. The inset traces the absorbance at 467 nm (closed circles) and 395 nm (open circles) during the exposure [95].

processed in oxygen is that the anthracene core has a wider bandgap and lower HOMO level than pentacene. Also, the absorption band of the precursor lies between 400-500 nm, while the absorption band of the anthracene product lies below 400 nm [96].

The OFET had a field-effect mobility of 0.047 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an on/off ratio of  $7.4 \times 10^4$  [96]. This compared well with the equivalent values of  $0.063 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and an on/off ratio of  $8.76 \times 10^5$  when bis-2-thienyl-2,6-anthracene was deposited directly by vacuum sublimation [95]. A hexyl-substituted version of the precursor has also been tested, but the measured

mobility was far lower (see Table 2.2). X-ray diffraction measurements showed that this semiconductor had a mixture of edge-on and face-on alignments with the substrate, while only edge-on alignment was observed for bis-2-thienyl-2,6-anthracene [96].

Changes in the absorption spectra of the precursor compound in a toluene solution were observed during irradiation with a xenon lamp, using a UV and IR filter, so that the excitation wavelength was 467 nm. The diketone precursor in Figure 7.8(b) has the typical n- $\pi$ \* transition peak at 466 nm, while the product compound has absorption peaks at shorter wavelengths (418, 395 and 375 nm), which are distinct features of the anthracene core. The advantage that this material has over pentacene precursors is that the shorter wavelength absorption peaks of the photoproduct do not inhibit absorption of light by the precursor. The closed circles in the inset to the spectra show how the n- $\pi$ \* absorbance of the diketone bridge decreases over time and the open circles follow the increase in the absorbance of the product peaks. The same photoreaction occurred in an aerated solution, so the procedure is clearly photostable. When the same process was carried out with a diketone precursor of pentacene only, oxygen adducts of pentacene were obtained, because pentacene absorbs the 460 nm light that is necessary to excite the diketone n- $\pi$ \* transition [95].

When the photolysis of 9,10-ethano-9,10-dihydro-2,6-bis-2-thienylanthracene-11,12-dione was performed in films in the presence of air, no oxidation products were formed. In the solid state, the anthracene peaks were broadened and red-shifted, resulting in some overlap in the absorption spectrum of the product and the precursor, but surprisingly this did not lead to photo-oxidation [95]. This is very promising for the production of air-stable OFETs.

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**Figure 7.9** (a) The HOMO-1 to LUMO transition in 9,10-ethano-9,10-dihydro-2,6-bis-2thienyl-anthracene-11,12-dione and the HOMO-LUMO transition in bis-2-thienyl anthracene. (b) A single-molecule UV-vis spectrum calculated for the precursor, showing the strength of the HOMO-1 to LUMO transition. There is no overlap of the orbitals on the diketone bridge, so this transition does not lead to removal of the bridge.

The synthetic UV-vis spectrum of the precursor, shown in Figure 7.9 modelled the real spectrum reasonably well between 300 - 400 nm, although there is no weight in the spectrum from 400 - 500 nm. The transition at 354.9 nm does not resemble the typical diketone  $n-\pi^*$  absorption that is familiar from  $\alpha$ -diketone precursors of pentacene (see HOMO-4 to LUMO transition in Figure 5.11). There is no overlap of the occupied and unoccupied orbitals on the bridge itself, such as occurs in the HOMO-5 to LUMO+6 transition of Figure 7.7(a). This means that there is no obvious reason why this molecule would decompose under UV exposure, in contradiction to the experimental observations. In this case, the calculation has either failed to accurately model the absorption spectrum of the precursor or the transition between occupied and unoccupied orbitals on the bridge is so weak that it doesn't appear in the synthetic spectrum.

## 7.2.2 Synthetic UV-vis spectra of potentially photopatternable thienoacene precursors

The bridged photoprecursors of the thienooacenes discussed in the rest of this chapter have the same photolabile moieties as the pentacene precursors studied in Chapter 5; the single carbonyl group, a double carbonyl group and the epithiomethano group. The molecules with these groups are referred to as monoketone, diketone and epithiomethano precursors, respectively. Where the structure of the semiconductor molecule allows for it, both symmetrical and asymmetrical derivatives are investigated. Methods for the chemical synthesis of these materials are not provided as this would be the subject for a substantial chemistry research project that is beyond the capabilities of this researcher. The aim for this chapter was simply to perform some calculations with a view to learning about the electronic structure of these materials and then suggest which

would be the best candidates for chemical synthesis. The point of interest here is whether the observations pertaining to the decomposition of pentacene precursors generally carry over to the thienoacenes.

There are two main chemical traits that make for an air-stable and easily processed small molecule semiconductor precursor:

- It should be possible to tune the sensitisation wavelength of the precursor by changing the bridging location and type of photolabile moiety on the molecule. This will allow for multilayer, orthogonal wavelength processing of the family of precursors and production of complicated device structures.
- The sensitisation wavelength of the precursor should be greater than the longest absorption wavelength of the product, to prevent screening of the photolysis light source as the decomposition reaction proceeds. This means that a precursor film could be rapidly and completely converted to the product semiconductor. This also prevents population of the LUMO level of the product, which is the starting point of various degradation pathways.

In determining which MO transitions lead to decomposition of the precursor molecules, each set of occupied and unoccupied MO wavefunctions responsible for the features of the synthetic UV-vis spectrum were examined to see whether they had some intensity on the bridging moieties. The decomposition pathway was attributed to the transitions where there were occupied orbitals on the  $\sigma$ -bonds linking the bridge to the ring and unoccupied orbitals on the carbonyl groups of the bridging moiety itself. The justification is that this particular MO

transition leads to a distinct change in electron density around the bonds of the photolabile moiety.

## 7.2.2.1 ADT precursors

The first set of heteroacene precursors investigated here is based on ADT. ADT fits into the acenedithiophene class and is isoelectronic with pentacene. Figure 7.10 shows the structure of ADT and six proposed photopatternable precursors.



**Figure 7.10** The structures of (a) anthradithiophene (ADT) and (b-g) the range of precursor molecules for which synthetic UV-vis spectra are calculated. The molecules b, d and f are the symmetrical forms of the monoketone, diketone and epithiomethano bridged precursors respectively. Molecules c, e and g are the asymmetrical equivalents.

The corresponding synthetic single-molecule UV-vis spectra are shown in Figure 7.11 and the MOs suspected of being involved in the removal of the bridging groups are also shown explicitly in Figure 7.12. The contributions that these transitions make to the absorption spectra have been isolated and the intensities have been normalised, to assist with comparison and to check for overlap on the wavelength axis. These absorption features are shown at the bottom of Figure 7.11. The realative order of the wavelength peaks mirrors the case seen for the precursors of pentacene (see Figure 5.13), with the sensitisation wavelength of the symmetrical diketone precursor at the longest wavelength, while the decomposition wavelengths for the other precursors are shorter by 75-100 nm.



**Figure 7.11** A close up view of the long wavelength absorption features for the ADT precursors b-g in Figure 7.10, except the asymmetrical monoketone precursor for which no obvious decomposition feature was calculated. The diketone precursor has a broad feature, typical of the diketone bridging moiety, centred at 432.9 nm. The decomposition absorption of the monoketone precursor appears at 324.2 nm as a shoulder on a larger peak. Features for the other precursors appear at intermediate wavelengths.



**Figure 7.12** The occupied and unoccupied MOs for the ADT precursor degradation features highlighted in Figure 7.11.

The decomposition of epithiomethano precursors occurs at intermediate wavelengths. The only difference is that there is no obvious decomposition wavelength for the asymmetrical monoketone precursor shown in Figure 7.10(c).

Since the structures and synthetic UV-vis spectra of these ADT compounds are so similar to pentacene, these appear to be viable precursor materials. However, the drawback is that a  $\mu_{\text{FET}}$  of only 0.09 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> has been demonstrated for ADT (Table 7.1). Also, the HOMO level is very similar to pentacene – calculated to be 4.80 eV below vacuum (according to Figure 7.1) [25] – meaning that the stability of this material in ambient conditions is not likely to be any better than that of pentacene. Given that the HOMO-LUMO gap is small and the central benzene ring is open to Diels-Alder reactions, just like pentacene, ADT is unlikely to satisfy the requirements of high mobility and long-term operating stability in ambient conditions. The synthetic absorption spectrum of ADT which is at the top of Figure 7.11 extensively overlaps the precursor absorptions below 440 nm. Despite the wide spread in the sensitisation wavelengths of the precursors, the product is likely to remain susceptible to photo-oxidation, in a manner consistent with the structurally similar tetraceno[2,3-b]thiophene. However, if the materials were converted to ADT in an oxygen free environment, this problem could be avoided. Looking at the isolated decomposition transitions shown at the bottom of Figure 7.11, it is clear that a bilayer of the diketone precursor and the asymmetrical epithiomethano or the monoketone precursor could be independently photopatterned. There appears to be no overlap in the wavelength range of these transitions. Additionally, it appears that parts of the absorption features for the monoketone and asymmetrical epithiomethano precursors are aligned with a low-absorbance window in the ADT spectrum. Thus, it may be possible to pattern either of these precursors in air whithout photo-oxidising the ADT product, although this needs to be evaluated via experimentation.

### 7.2.2.2 DNTT precursors

DNTT, shown in Figure 7.13(a) is a very promising organic semiconducting material from the diacene-fused thienothiophene class. A high  $\mu_{FET}$  of  $3.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  has been demonstrated for vapour deposited DNTT while a  $\mu_{FET}$  of up to 7.9 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> has been measured in a device using a didecyl end-substituted derivative as the active semiconductor [171, 172]. The large HOMO-LUMO gap and low lying HOMO of DNTT (Figure 7.1) afford good operating stability.

The proposed symmetrical and asymmetrical DNTT precursors are shown in Figure 7.13, while their synthetic UV-vis spectra are shown in Figure 7.14. The obvious first impression is that there is not much of a difference between the spectra. There is a slight shift in the position of the largest absorption peak between those molecules functionalised at the inner benzene ring and those functionalised at the end benzene ring. This is because there is a four ring chromophore in the first set and a five ring chromophore in the second set. The absorption features that are proposed to lead to photodegradation of the precursors are presented as the dashed lines in Figure 7.15. The corresponding occupied to unoccupied MO transitions are also shown in Figure 7.16 (there were no obvious bond breaking transitions in the spectra of the epithiomethano and monoketone DNTT molecules bridged at the inner benzene ring). Once again, each of these transitions occurs from an occupied orbital with some magnitude on the  $\sigma$ -bonds



**Figure 7.13** The structures of (a) DNTT and (b-g) the range of precursor molecules for which synthetic UV-vis spectra are calculated. The molecules b, d and f are the monoketone, diketone and epithiomethano bridged precursors respectively. Molecules c, e and g are equivalent molecules except that the photolabile moiety is bridged across the terminating ring.

of the bridging group and finishes in the  $\pi^*$ -type unoccupied orbital located on the carbonyl groups of the bridge. Looking at the individual decomposition transitions highlighted in the spectra of Figure 7.15, it is seen that there is no overlap of the decomposition transitions in the diketone precursor and the end functionalised


**Figure 7.14** The synthetic UV-vis spectra for DNTT precursor molecules b-g from Figure 7.13. There is little to distinguish the spectra of the monoketone, diketone and epithiomethano bridged molecules from each other. There is a shift in the largest peak of the spectra due to symmetrical or asymmetrical placement of the bridge, but little shift due to the type of bridging group.



**Figure 7.15** Photodegradation absorption features (dashed lines) for the DNTT precursors, corresponding to the MO transitions shown in Figure 7.16. The synthetic UV-vis spectra are shown in red. There was no overlap of occupied and unoccupied MOs on the bridging groups of the molecules in Figures 7.13(b) and (f), so no decomposition transition was assigned. The dashed lines of the diketone and end monoketone molecules do not overlap at any wavelength, so these molecules could be orthogonally patterned.



**Figure 7.16** Proposed decomposition transitions for (a) diketone DNTT, (b) end diketone DNTT, (c) end epithiomethano DNTT and (d) end monoketone DNTT. Each of these transitions occur from an occupied orbital with some magnitude on the sigma bonds of the bridging group and end in the unoccupied orbital located on the carbonyl groups of the bridge.

monoketone precursor. Thus, it appears that it would be possible to orthogonally process these DNTT precursors since the transitions involving the bridging groups appear at different wavelengths. However, light that is used to decompose the precursors would also be absorbed by the molecules in alternative, non-destructive transitions, which would slow the conversion process in a thick sample of the material. Despite this and the fact that it seems only four molecules could be photoprocessed, the high performance and air-stability of DNTT devices warrants further research into precursor derivatisation.

### 7.2.2.3 BDT precursors

BDT is an acenedithiophene, consisting of three linearly fused aromatic rings. It is isoelectronic with anthracene, thus the HOMO level is lower than pentacene and the HOMO-LUMO gap is wider. This material is more stable under operation in ambient conditions than pentacene or its isoelectronic thienoacene, ADT, and is therefore a good candidate for the attempted synthesis of a photosensitive precursor. Figure 7.17 shows BDT and its proposed diketone precursor. Figure 7.18 also shows some of the MOs for the major transitions within the molecules while Figure 7.19 shows the corresponding synthetic absorption spectra. The HOMO-LUMO absorption band of the  $\alpha$ -diketone precursor spans 410-500 nm in the synthetic spectrum, as is typical for this bridging group. The carbonyl bridge absorption band for this precursor is centred at 453.6 nm, red-shifted by 100 nm with respect to the absorption edge of the synthetic BDT molecule. The HOMO-LUMO absorption bands in thin films tend to be red-shifted with respect to the synthetic spectra, which would potentially increase the overlap in the spectra of BDT and the diketone precursor. However, even with a sizeable red-shift of



Figure 7.17 (a) Benzenedithiophene (BDT) and (b) the diketone bridged BDT precursor.



**Figure 7.18** Frontier orbital transitions in (a) BDT and in (b) the diketone bridged precursor. The HOMO-2 to LUMO orbitals overlap on the diketone bridge.



**Figure 7.19** The synthetic UV-vis spectra for BDT and its diketone bridged precursor. The usual diketone absorption (dashed green line) occurs with a peak at 453.6 nm, which is heavily red-shifted from the peak of the BDT HOMO-LUMO+1 absorption at 320.4 nm.

80 nm, most of the sensitisation wavelengths for the precursor would lie above the HOMO-LUMO absorption for BDT. Thus, this material could be photopatterned in air, producing BDT, without risk of photooxidising the product through excitation of an electron to an unoccupied level.

The diketone precursor of BDT offers the possibility of photopatterning a semiconductor with not only good operational stability in air due to its stable HOMO, but also the ability to carry out the photolysis of the precursor in air. This would be ideal for roll-to-roll processing as there would be no need to carry out the photolysis step of the fabrication procedure in a controlled, inert atmosphere. The main problem is that the  $\mu_{FET}$  for BDT and its derivatives is poor compared with many other materials. The best  $\mu_{FET}$  for a solution-processed derivative, 0.081 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for diphenyl-BDT [25], is far lower than has been observed in

other solution-deposited materials. Since this is roughly two orders of magnitude below what can be routinely produced with some other soluble materials, BDT is unlikely to be a competitive semiconductor. Additionally, given that the decomposition transitions for epithiomethano and monoketone bridged precursors appears at wavelengths in the range from 320 – 350 nm, there is likely to be strong overlap of these transitions with the HOMO-LUMO and HOMO-LUMO+1 transitions of the BDT product. These transitions don't lie within a low absorption window of the product, unlike what is predicted for the thienoacene ADT.

#### 7.2.2.4 BTBT precursors

BTBT is an organic semiconducting material, from the DAcTT class, consisting of two fused thiophene rings at the centre of the molecule and a single benzene ring at each end (Figure 7.20(a)). Alkylated derivatives of the molecule are highly soluble and can be deposited from solutions to produce devices with exceptional performances. C8-BTBT devices, produced by drop casting, have displayed mobilities of  $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and an on/off current ratio of  $10^6$  [170]. Better



**Figure 7.20** (a) Benzothieno[3,2-b]benzothiophene (BTBT) (b) the diketone bridged BTBT precursor and (c) the monoketone precursor.

performances were obtained by spin-coating of single crystals, with a mobility of  $9.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and an on/off current ratio of  $10^7$  [34]. Most impressively, the record mobility for a solution processed organic semiconductor was obtained with C8-BTBT as the active material, which was produced by double-shot inkjet printing of single crystals. An average mobility of  $16.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was obtained for a set of OFETs, with a peak mobility of  $31 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and an on/off current ratio ranging from  $10^5$ - $10^7$  [19].

The synthetic absorption spectrum for the diketone precursor, shown in Figure 7.21, does have a weak feature from 390 – 460 nm, centred at 411.9 nm.



**Figure 7.21** The synthetic spectra of BTBT and its derivatives from Figure 7.20. The spectrum of BTBT in ethanol is provided to compare the single-molecule synthetic spectra with a real BTBT solution spectrum [174]. The major peaks of the two bridged molecules overlap quite accurately. Looking at Figure 7.22 (b) and (d), it can be seen that the molecular orbitals involved in the transitions are almost identical. They are similar to the HOMO-LUMO orbitals in BTBT, see Figure 7.22 (a), which explains why all three peaks are so similar. The diketone decomposition transition, from Figure 7.22 (c) appears at 411.9 nm. The monoketone decomposition transition, from Figure 7.22 (e) appears at the much shorter wavelength of 297.8 nm.



**Figure 7.22** (a) The HOMO-LUMO transition of BTBT. (b) The HOMO-LUMO orbitals for BTBT and (c) the proposed decarbonylation transition orbitals for the diketone bridged BTBT. (d) The HOMO-LUMO orbitals of the monoketone precursor. (e) The decarbonylation transition orbitals for the monoketone bridged BTBT. The HOMO-LUMO transition wavelengths of the two precursors are almost the same because the three ringed chromophore is identical in each molecule.

The corresponding MOs are, as predicted, located on the diketone bridging group, as shown in Figure 7.22(c). This peak occurs at a wavelength that is 20 nm shorter than for the equivalent transition in the diketone precursor of ADT,

demonstrating how much the environment surrounding the bridging group affects the energy separation of the occupied and unoccupied orbitals. The next strong absorption with a peak at 340.6 nm corresponds to orbitals on the three-ringed chromophore, highlighted in Figure 7.22(b). The orbitals are spread out over the two thiophene rings and the unbridged benzene ring. The corresponding chromophore in the monoketone precursor, appears at 345.7 nm. In fact the MOs in Figures 7.22 (a), (b) and (d) are all similar, explaining why the corresponding absorption features are located in the same regions of the three absorption spectra, with peaks from from 320 - 340 nm. The decomposition transition for the monoketone precursor is located at 298 nm (Figure 7.22(e)), 115 nm lower than the diketone equivalent. This is the same as was calculated for the DNTT precursors, so it is likely that these BTBT precursors should also be orthogonally patternable. The spectrum of BTBT in ethanol is provided to evaluate the accuracy of the calculation [174]. The HOMO-LUMO transitions of the solution spectrum and the synthetic spectrum are offset by only 10 nm, meaning that the ZINDO synthetic spectrum calculation of the BTBT molecule is quite accurate.

Given the low-lying HOMO levels in BTBT and its wide energy gap, BTBT appears to be ideal for photoprocessing. Good mobilities have previously been demonstrated for solution processed derivatives and the large shift between the peak photodegradation wavelengths for the two precursors should provide significant contrast for orthogonal wavelength patterning. In the case of the diketone precursor in particular, the product BTBT would not absorb the light used for the precursor photolysis. With the numerous options available for alkylation, the solid state order of the precursor could be tailored to enhance the mobility of the product.

#### 7.2.2.5 DTBDT precursors

A high mobility of 1.7 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> has been demonstrated in a dip-coated C6-DTBDT OFET [167]. The material is a benzene-thiophene alternating molecule and consists of five fused rings (Figure 7.23(a)). Only the central benzene ring is open to functionalisation with a bridging group. Inspection of Figure 7.24 reveals that the separated HOMO-2 to LUMO+2 transition of the synthetic diketone precursor, with large coefficients for both the occupied and unoccupied orbitals located on the bridging group, is the most likely to lead to photodecomposition. This molecule should be photopatternable, although the central benzene ring of DTBDT is open for oxidative attack. Also, the broad HOMO to LUMO+2 transition of the DTBDT product partially overlaps with the HOMO-2 to LUMO+2 feature of the precursor. Given that the absorption spectra of semiconductors and the diketone precursors tend to be red-shifted in the solid-state compared with the synthetic spectra, it is likely that there would still be a strong overlap of these features in a thin film. There is a risk that this may lead to photo-oxidation of the product if the photolysis environment were not carefully controlled, but it would be worth testing experimentally. There also appears to be a wide window of little absorption in the DTBDT spectrum in the range from 280 -310 nm. Depending on how large the red-shift is in the solid state, this window



Figure 7.23 (a) DTBDT and (b) the diketone bridged DTBDT precursor.

may overlap with the decomposition transition of a monoketone precursor. This would be ideal for photoprocessing a layer of such a precursor without the product material absorbing most of the sensitising light.



**Figure 7.24** The molecular orbitals involved in the main peaks of the synthetic spectra for DTBDT and its diketone bridged precursor. The usual peak due to absorption by the diketone bridge appears at 415.3 nm.



**Figure 7.25** The synthetic spectra of DTBDT and its diketone bridged precursor. The usual weak, broad absorption feature due to orbital overlap on the diketone bridge appears to be centred at 415.3 nm in this molecule.

## 7.3 CONCLUSIONS

In earlier chapters the case for using photopatternable small molecule semiconductor precursors for the manufacturing of OFETs and other organic electronic devices was examined. The original aim of producing precursors of pentacene with tetrachlorobenzene, N-sulfinylacetamide or carbonyl bridging moieties was to enable pentacene to be solution-processed [26, 27, 29]. The removal of the solubilising group through heating or light exposure was simply performed to regain the semiconductor, but as extensively explored already, the removal of a photolabile group is also an appealing device patterning strategy. With the well known operational stability problems inherent in devices with oligoacene active materials, the thienoacenes have become the material class of choice for state-of-the-art research devices and stable commercial products.

Most of the thienoacenes discussed in this chapter are more robust during device operation than pentacene, as proven by long-term device stability tests in ambient conditions. Efforts to make these materials solution processable and to influence the solid-state patterning have focused primarily on alkylation of terminal carbons on the thienoacene cores. The introduction of a photolabile bridging group, with the option of additional alkyl groups elsewhere (although it is noted that in some cases the presence of long substituents decreases performance [96]), would enable the orthogonal wavelength photopatterning strategy to be extended to devices using these materials. The calculations presented here reveal that out of the wide range of known thienoacene semiconductors, the functionalisation of molecules with BTBT cores in particular would be an advisable starting point since excellent performances have been demonstrated for solution processed C8-BTBT. Also, because of the large bandgap of the BTBT molecule, it is an ideal candidate for photoprocessing of multiple precursors via the orthogonal wavelength technique (section 6.2.2), because the precursors can be decomposed without driving oxidation-causing electron transitions into the unoccupied orbitals of the product molecules (Figure 7.21). BTBT precursor films sprayed over large-area, flexible substrates could be rapidly patterned, in air, producing very high performance devices that remain stable throughout long operation lifetimes due to their low-lying HOMO levels. This could be just one of the materials required to make roll-to-roll patterning of OFETs commercially viable.

Looking beyond BTBT alone, it would also be useful to produce

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precursors of DNTT and DTBDT, because high performances have been observed in previous studies of these semiconductors. The calculations presented in this chapter have shown that a number of different bridging groups could be introduced into these air-stable molecules. The bandgap of DNTT is narrower than the photon energy required to decompose the precursor molecules, meaning that there may be photo-oxidation of DNTT or at least self-absorption of light by the product during photolysis of thin films. The main drawback with the precursors of DTBDT is that the OFET performances have not been nearly as high as DNTT and BTBT devices. Despite the deficiencies of some of these materials, it would be advisable to attempt synthesis of at least a few of the precursors suggested here, so that the performance and stability of photoprocessed materials could be examined experimentally, in the manner performed in Chapter 5. It would be useful to confirm the accuracy of the ZINDO synthetic UV-vis spectra calculations and to determine how stable these materials are when exposed to light in air over an extended period of time. This will require setting up a future research collaboration with a group of synthetic chemists, as the synthesis of a number of new thienoacene precursors was beyond the expertise and capabilities of this researcher.

## CHAPTER <sup>Conclusion</sup> EIGHT

The aim of this thesis was to examine whether OFETs and related devices could be manufactured using the inherent photosensitivity of organic materials. Many of these materials are sensitive to attack by oxygen and water in the presence of light, which explains the need to encapsulate devices and protect them from the atmosphere, but this also means that photopatterning is possible. The photoprecursors of pentacene, developed over the last decade, are ideal for this type of manufacturing approach. They rapidly yield a high mobility material after periods of UV light exposure ranging from seconds to minutes. Despite the unique behavior of these materials, it appears that they have not been exploited in a serious way due to the number of alternative patterning and deposition methods available for OFET production and the low solubility of some of the precursors developed so far. Most of the experiments conducted for this thesis involved re-examining these materials to see whether they possessed any inherent advantages that would be useful for processing complicated multilayer devices. Photolysis experiments and ZINDO calculations for the precursors showed that simply by changing the type and position of the Diels-Alder bridging groups, the materials become sensitive to different wavelengths of light. Using the variable wavelength sensitivities of the structural isomers of certain precursors or by using precursors with different bridging groups, it appears that multilayer structures of thin films can be manipulated, independently, by photochemical processes. That is to say, two or more layers of photosensitive materials could be deposited in a stack, then each layer in the stack could be independently converted from a precursor to a semiconductor in a pattern defined by a photomask. A layer at the bottom of the stack could be converted using a narrow band of wavelengths that passes through a wavelength 'window' in which the layers above are not sensitive.

The photolysis experiments with 5,14-MPn and 6,13-MPn showed that the long wavelength cutoffs for conversion to pentacene were 315 nm and 325 nm, respectively. This wavelength separation is probably not great enough to independently convert multiple layers of the materials to pentacene in a manner effective enough for each layer to operate well in an OFET. This is due to the fact that in the experiments described in Chapter 6, when a 6,13-MPn OFET was exposed to a 25 nm wide window of light with a peak at 320 nm, transistor behaviour was not observed. However, with a wider band ranging from 270-340 nm, gate voltage enhanced conductivity in the source-drain channel was observed. The performance of the OFET test structures measured in this thesis was unfortunately too low to conclusively analyse the efficacy of the narrower

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wavelength range, but with the results so far it appears that a 60-70 nm wide source of light is required for 6,13-MPn conversion. However, by using layers of materials with *different* bridging groups, such as a monoketone precursor over an  $\alpha$ -diketone precursor, multilayers of OFETs probably could be independently photopatterned due to the shifts in the wavelength sensitivity ranges. The ability to pattern individual layers of organic electronic materials in a stack after the deposition of all layers represents one of the major advantages of photopatterning compared to other more common and mature patterning methods.

The multilayer independent photopatterning technique applies not only to semiconductor precursors and if it is to be truly useful for manufacturing devices then it must be extended to other materials. The photopatterning experiments with PEDOT:PSS demonstrated that structures could be defined in thin films of this conducting material. The resistance studies showed that simply by illuminating PEDOT:PSS for a long enough period of time, the resistance could increase by as much as 5 to 6 orders of magnitude. It is known that only wavelengths less than 320 nm are effective in causing this change in PEDOT:PSS. Now, given that the time required to significantly change the resistance of PEDOT:PSS was several hours, this material wouldn't be suitable for making devices this way. With a serious research effort focussing on developing a highly photosensitive conducting organic material with a tailored wavelength sensitivity, multilayer electronic devices could be photopatterned from a predeposited stack of semiconductor and conductor precursors. This probably requires the use of a photoacid generator or perhaps the extension of the Diels-Alder bridging group concept to a conducting polymer.

Not only must work be carried out to develop a rapidly photopatternable

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organic conducting materials if multiayer organic devices are to be produced using orthogonal wavelength light sources, but the synthesis of photopatternable thienoacenes is also a priority. Air-stable semiconducting materials are essential for obtaining the product lifetimes required for consumer electronics. Some good candidates for synthesis, such as precursors of BTBT and DTBDT, were proposed in Chapter Seven. These materials represent a good starting point for further synthetic chemistry research, however these materials alone are not enough. As identified by the images in Chapter Six of the source-drain channels of OFETs derived from the 6,13-MPn precursor, improving the solubility of the precursors is essential. A maximum solubility of 1 mg/mL is too low to obtain contiguous films of the precursor and hence the product semiconductor. Optimising the spray deposition procedure by finding an ideal solvent or by using ultrasonic deposition and substrate heating to form layers slowly, may provide part of the answer. However, it is likely that some additional substituents may be required on the cores of the BTBT and DTBDT precursors to improve the solubility.

This thesis has identified some of the properties of photosensitive semiconductor precursors and conductors and has investigated the tools that can be used in the design of new materials. As it stands, the production of simple OFET structures using photosensitive materials appears to be unnecessary. Many other techniques can be used to produce the same architectures and deliver high performance. However, if an appropriate range of photosensitive organic conducting and semiconducting materials can be developed and combined in a preformed multilayer stack that can later be individually patterned by a user to their own design, then there may still be some applications where photosensitive precursors have distinct advantages over traditional OFET materials.

# APPENDIXThe architecture of<br/>inorganic enhancementONEThe architecture of<br/>inorganic enhancementONEmetal-oxide semiconductor<br/>field effect transistors

Transistors are semiconductor devices that can be used as switches or for the amplification of electrical signals. They usually have three terminals, where the current between two terminals is controlled by the current or voltage at a third terminal [49]. The bipolar junction transistor (BJT) is an example of a current-controlled device, while the field-effect transistor (FET) is an example of a voltage-controlled device [49]. Organic field-effect transistors (OFETs) are typically produced with architectures that mirror a common inorganic transistor: the metal-oxide semiconductor enhancement FET (E-MOSFET). However, charge transport in inorganic semiconductors occurs by a different mechanism to that in organic semiconductors. The physics of the E-MOSFET is described here, following a discussion of the differences between charge transport in organic and inorganic materials.

The electronic properties of organic semiconducting materials were discussed at the beginning of Chapter Two. Although there is still some debate as to the carrier transport mechanism in organic semiconductors, the multiple trap and release (MTR) model appears to be consistent with observations [175]. There is a high degree of intramolecular electron delocalisation within the highly conjugated organic semiconductor molecules. The molecules are only weakly bonded in the solid state via van der Waals or dispersion forces. Charge carriers are localised on a molecule within the solid, but occasionally hop to an adjacent molecule through overlapping  $\pi$ -orbitals.

In the case of intrinsic inorganic semiconductors such as silicon and germanium, atoms pack into a tetrahedral crystal structure in the solid state. The atomic valence electrons are shared with neighbouring atoms in the form of four covalent bonds, which is a much stronger form of bonding than occurs between adjacent organic molecules [51]. This accounts for the comparative brittleness of inorganic materials and their inability to be applied to flexible substrates. However, it remains that only 1.1 eV is required to promote an electron from the valence band into the conduction band in solid Si, while 0.7 eV is required to do the same to an electron in Ge. These energies are small enough that some electrons can be thermally excited into the otherwise empty conduction band at room temperature, leaving a positively charged vacancy (a hole) in the region of the broken covalent bond. In this situation, both holes and electrons contribute to conduction, with holes moving in the valence band and electrons flowing in the conduction band. Current flows when a uniform electric field of E V/m is applied to the conductor. The randomly moving electrons attain a component of velocity in the direction of -E, while holes move in the opposite direction. The electrons

gain a drift velocity,  $u_n$ , that is directly proportional to E,

$$u_n = -\mu_n E \tag{A1.1}$$

where  $\mu_n$  is the electron mobility, which has units of m<sup>2</sup>/Vs [51]. If there are *n* free electrons per cubic metre, flowing at a velocity  $u_n$  with a charge -e, and *p* free holes with a charge *e* and a velocity of  $u_p$ , then the current density *J* A/m<sup>2</sup> is:

$$J = n(-e)u_n + p(e)u_p \tag{A1.2}$$

Substituting (A1.1) gives:

$$J = n(-e)(-\mu_n E) + pe\mu_p E \tag{A1.3}$$

which simplifies to:

$$J = ne\mu_n E + pe\mu_p E = \sigma E \tag{A1.4}$$

where:

$$\sigma = (n\mu_n + p\mu_p)e \tag{A1.5}$$

and (A1.5) represents the conductivity of the semiconductor,  $\sigma$ , in S/m (Siemens per meter). The conductivity of a semiconductor can be increased in a controlled manner by a process called *doping*, which is simply the addition of an impurity element to a pure semiconductor. This creates an excess of free negative carriers (n-type doping) or free positive carriers (p-type doping), although the material remains electrically neutral overall. Thus, the conductivity of inorganic semiconductors can be carefully tuned across a wide range by doping.

When a p-type material is brought into contact with an n-type material a *p-n junction* is formed. Due to the carrier concentration gradient at the junction, holes diffuse from the p-type material to the n-type material and electrons move



**Figure A1.1** An expanded view of the concentration of charges at the interface of p-type and n-type materials in a p-n junction diode. The imbalance in the concentration of holes and electrons at the boundary leads to diffusion of the majority charge carriers across the boundary, forming a depletion layer. The n-type material takes on a localised positive charge and the p-type material takes on a negative charge. An electric field builds up at the junction due to the uncovered donor and acceptor ions. The diffusion of charges is balanced by the thermal generation of electron-hole pairs in the materials, which act as minority charge carriers and flow under the influence of the electric field. (Adapted from Figure 5.9 in [51]).

from the n-type side to the p-type side. Figure A1.1 shows this transfer of carriers across the p-n junction. Diffusion of *majority* charge carriers (holes in the p-type material and electrons in the n-type) leads to the formation of a *depletion region* at the junction. An internal electric field, *E*, arises due to the nuclear charge of the immobile lattice sites, which have lost either an electron or a hole. Under the influence of this field, *minority* charge carriers, electrons in the p-type material and holes in the n-type material then drift across the junction. When the junction is *forward biased* (application of a positive external voltage to the p-type material, negative voltage to the n-type) the junction potential is reduced and the width of the depletion region decreases. Majority charge carriers can then flow across the junction more easily. Under *reverse biasing* (application of a negative external voltage to the p-type material, positive voltage to the n-type) it becomes less likely that majority charge carriers will flow across the boundary. Current will only flow across a junction diode in a single direction; under forward biasing.

Given that the mechanism for carrier flow in inorganic devices is so different to organic devices, it is surprising that the architectures of OFETs and E-MOSFETs are so similar. The structure of an E-MOSFET is illustrated in Figure A1.2 under the effect of different gate biases. It can be seen that pn-junctions play an important role in the electronic behaviour of the devices. The E-MOSFET has no structural channel, rather the channel is induced by the applied gate voltage [49]. The transistor is normally operated with the substrate connected to the source. If the gate is at the same potential as the source, there is no potential difference between the gate and the substrate. In this situation there is a reverse biased p-n junction either at the drain or the source, hence current flow between the source and the drain is blocked [176]. In an n-channel device, the p-type



**Figure A1.2** An enhancement MOSFET under various levels of gate bias. (a) The white area around the source and drain electrodes between the n-type and p-type materials represents the depletion region at the two p-n-junctions. Irrespective of the voltages at the source and drain, one junction will be under reverse bias, so charge will not flow between the electrodes. (b) As the gate bias is made positive, holes in the p-type material are driven away from the semiconductor/insulator boundary, forming a depletion layer. Charge flow is still impeded between the source and drain electrodes. (c) As the gate bias is increased further, beyond the threshold voltage, electrons from the source electrode are drawn into the channel, forming an n-type enhancement region. Since there is an n-type channel linking the n-type electrodes, charge can flow between the electrodes. Adapted from Figure 6.3 in [51].

substrate actually extends all the way to the SiO<sub>2</sub> layer when there is no applied gate voltage, as shown in Figure A1.2(a) [49]. A small positive V<sub>G</sub> repels holes in the p-type material and forms a depletion layer, shown as the white region at the insulator interface in Figure A1.2(b). When the potential is increased beyond a point called the threshold voltage, V<sub>T</sub>, free electrons are drawn towards the gate by diffusion from the source, forming an inversion layer of mobile electrons at the insulator interface. This effect is shown in Figure A1.2(c) [176]. The inversion occurs because the density of electrons increases to account for the reduction in the hole density [51]. The E-MOSFET only operates when a positive V<sub>G</sub> (above some threshold) is applied to an n-channel device, and vice-versa for a p-channel device [49]. If a source-drain voltage is applied without an inversion layer at one of the gates, then there will be a reverse biased p-n junction at one of the contacts, preventing the flow of charge carriers. The value of the threshold voltage is typically between 2-4 V for devices but it varies upon the electrical properties of the oxide and the substrate [176].

## TWO

APPENDIX Derivation of the drain current equations for field effect transistors

Equations for the drain current in the linear and saturation regimes of field effect transistors are available in many textbooks and journal articles [50, 52, 54]. The derivations of these equations are provided here. Following through them helps with understanding how the characteristic parameters of the different materials in a transistor, such as charge carrier mobility in the semiconductor layer, affect the overall performance. If certain performance parameters are required for an application, one can better understand how to vary, for example, the capacitance of the dielectric layer or the geometry of the electrodes, by analysing these drain current equations. The derivation of the equations that is included here closely follows that of Newman et al.'s paper in the journal Chemistry of Materials [54].

Figure A2.1 (which is repeated here from Chapter Two) shows how the carrier concentration at the semiconductor-dielectric interface changes when a



**Figure A2.1** A schematic representation of the charge carrier concentration in the sourcedrain channel, in three voltage regimes. (a) Linear regime. (b) Pinch-off point. (c) Saturation regime. Adapted from [54].

transistor is operated in the linear regime, at the pinch-off point and in the saturation regime. It is useful to refer to this figure throughout the following derivations. Firstly, looking at Figure A2.1(a), assume that the device is an n-type transistor and that a positive gate voltage,  $V_G$ , is applied. Positive charges are induced at the gate/dielectric interface and these are balanced by negative charges which are induced at the semiconductor/dielectric interface. These negative charges are supplied equally by the source and drain contacts. The induced charge density in the semiconductor, shown in blue, is uniform across the channel because no source-drain voltage is applied. When the positive gate voltage is changed, the quantity of charge induced at the boundary also varies. Imagine now that the potential of the drain electrode,  $V_D$ , is positive, so that the voltage difference across the dielectric at the drain electrode is  $V_G - V_D$ . At any other point in the channel, denoted by *x*, the voltage difference is  $V_G - V(x)$ . The induced areal charge density at each point,  $q_{ind}(x)$ , which has units of C/m<sup>2</sup>, is proportional to this voltage difference. It follows that:

$$q_{ind}(x) = n(x)et = C_{dlc}(V_G - V(x))$$
(A2.1)

where n(x) is the number density of charges in the channel, e is the fundamental unit of charge, t is the thickness of the charged layer in the channel (not the whole semiconductor layer).  $C_{dlc}$  is the areal capacitance of the dielectric and V(x) is the position dependent voltage in the channel.

In practice, mobile charge carriers do not tend to form in the channel as soon as V<sub>G</sub> switches from zero to some positive value. Misalignment, in any direction, of the electrode Fermi level and the semiconductor LUMO (HOMO for p-type transistors) causes a transfer of charge between the metal and the organic material. A dipole then forms, resulting in band bending in the semiconductor material. This means that either a positive or negative voltage must be applied before the bands align and mobile charges can populate the channel. Deep electron traps may exist at the dielectric interface, which must be filled before electrons are available for conduction. This necessitates the application of a positive gate voltage of some magnitude before the transistor switches on. Alternatively, the semiconductor may be doped with impurities that donate negative charge carriers. In this situation, the channel will be conductive even when  $V_G$  is zero; a negative gate voltage must be applied to shut the transistor off. Instead of accounting for all of these effects individually in the equations for the drain current, a term called the *threshold gate voltage* is introduced to deal with all of them. Modifying (A2.1) to account for this new correction term gives:

$$q_{ind}(x) = n(x)et = C_{dlc}(V_G - V_T - V(x))$$
 (A2.2)

where  $V_T$  is the threshold voltage.

In Figure A2.1(a) V(x) is zero since there is no applied  $V_D$ . The charge

density is identical everywhere in the source-drain channel. When  $V_D$  is positive and less than  $V_G - V_T$ , V(x) varies along the whole length of the channel. V(x)equals  $V_D$  at the drain electrode and is zero at the grounded source electrode. This results in a linear variation in the channel charge density, which is implied by the wedge in Figure A2.1(b). The charge density at the source electrode is greater than at the drain electrode because V(x) is effectively lower. Figure A2.1(b) actually shows a special case where  $V_D$  is approximately equal to  $V_G - V_T$ , meaning that there is no charge density at the drain electrode. This is termed the *pinch-off point*. Generally, when  $V_D$  is much less than  $V_G - V_T$ , the calculations of the drain current equations are simplified by using the average value of  $q_{ind}(x)$  in the channel, which is given by:

$$q_{ind,avg} = n_{ind,avg}et = C_{dlc}\left(V_G - V_T - \frac{V_D}{2}\right)$$
(A2.3)

This is the induced areal charge density at the middle of the channel, where V(x) is equal to  $V_D/2$ .

Having now determined the charge density in the channel in terms of quantities such as the capacitance of the dielectric layer and the voltages at the contacts, the IV relationship of the transistor is found from Ohm's law:

$$J = \sigma E \tag{A2.4}$$

where J is the current density,  $\sigma$  is the channel conductivity and E is the electric field across the channel. The current density is equal to the drain current divided by the cross sectional area of the semiconductor channel (thickness of the charged layer, *t*, multiplied by the width of the channel, *W*) and the electric field is simply the voltage between the two terminals divided by the channel length, L. Substituting into (A2.4) gives:

$$\frac{I_D}{tW} = \sigma \frac{V_D}{L} \tag{A2.5}$$

and noting that:

$$\sigma = n_{ind,avg} e\mu \tag{A2.6}$$

where  $\mu$  is the mobility of charge carriers in the semiconductor, it follows that:

$$I_D = \frac{W}{L} n_{ind,avg} e \mu t V_D \tag{A2.7}$$

which is an equation for the source-drain current. This still contains terms which are not easy to measure in practice, but substituting (A2.3) gives:

$$I_D = \frac{W}{L} q_{ind,avg} \mu V_D \tag{A2.8}$$

This is equivalent to:

$$I_D = \frac{W}{L} C_{dlc} \mu V_D \left( V_G - V_T - \frac{V_D}{2} \right)$$
(A2.9)

which only contains terms which are based on the transistor geometry, material properties and the applied voltages. This equation is more commonly expressed as:

$$I_D = \frac{W}{L} C_{dlc} \mu \left( (V_G - V_T) V_D - \frac{V_D^2}{2} \right)$$
(A2.10)

by multiplying  $V_D$  through the parentheses. From (A2.10) it can be seen that the current scales linearly with  $V_G$  and quadratically with  $V_D$ . However, when  $V_D \ll V_G - V_T$ , the squared term is negligible, thus the drain current also varies in

proportion to the drain voltage. This is the reason why the transistor is said to operate in the *linear regime*. In this situation, the mobility of the semiconductor is usually expressed as  $\mu_{lin}$ .

To calculate the field effect mobility of the transistor (one of the most important performance indicators for the device) two derivatives can be calculated. They are:

$$g_m = \left. \frac{\partial I_D}{\partial V_G} \right|_{V_D} = \frac{W}{L} C_{dlc} \mu_{lin} V_D \tag{A2.11}$$

and

$$g_d = \left. \frac{\partial I_D}{\partial V_D} \right|_{V_G} \sim \frac{W}{L} C_{dlc} \mu_{lin} (V_G - V_T) \tag{A2.12}$$

for the case where  $V_D \ll V_G - V_T$ . The derivatives  $g_m$  and  $g_d$  are known respectively as the *transconductance* and the *conductance*. The linear regime mobility,  $\mu_{lin}$ , can be calculated from either of these given that  $V_D$ ,  $V_G$  and  $V_T$  are quantified.

As already mentioned, when the drain voltage is high enough that  $V_D = V_G - V_T$ , the charge carrier channel pinches off and there is no charge density at the drain electrode. As  $V_D$  increases, the pinch-off point moves along the channel towards the source electrode, as indicated by the shorter wedge in Figure A2.1(c). Further increases in  $V_D$  no longer increase the current flow because there is no change in the integrated charge density across the length of the channel. Current still flows between the source and drain electrodes because charge carriers are driven across the short space-charge region (between the pinch-off point and the drain electrode) by the high electric field. Thus, the

current saturates at the value reached when  $V_D = V_G - V_T$ . Substituting this voltage into (A2.10) gives:

$$I_{D,sat} = \frac{W}{2L} C_{dlc} \mu_{sat} (V_G - V_T)^2$$
(A2.13)

If  $I_{D,sat}^{1/2}$  is plotted with respect to  $V_G$ ,  $\mu_{sat}$  can be extracted from the gradient of the resulting line.  $V_T$  can also be found from the intercept with the current axis.

## APPENDIX Molecular orbital THREE

Much of the research presented in this thesis regards the patterning of organic semiconductor precursors by selective exposure to light. In each case, a cyclic structure in the precursor molecule fragmented into two components when exposed to light, forming the organic semiconductor and a volatile small molecule. These retro-cycloaddition reactions are a special kind of ring opening process that occur in organic chemistry when a molecule is exposed to light or heat. This process fall into a broad class of reactions called *pericyclic reactions*, which are distinct from the polar and radical type of interactions which frequently take place in organic chemistry. Pericyclic reactions follow an organic reaction mechanism in which all bonding changes at the same time, in a single step, through a cyclic transistion state [81]. The movement of electrons is described as concerted, which refers to the fact that new bonds are made between atoms while other bonds are simultaneously broken elsewhere in the molecule. There are four sub-classes which fit into the category of pericyclic reactions: *cycloaddition reactions*, *electrocyclic reactions*, *sigmatropic rearrangements* and *group transfer reactions*. The signifying feature of cycloadditions is that there is an interaction between the ends of two components, resulting in the formation of two new  $\sigma$ -bonds and the production of a ring structure. Electrons that are bound in  $\pi$ -bonds in the separate parts rearrange to form the new  $\sigma$ -bonds. Through this mechanism, cycloaddition reactions bring about a reduction in the lengths of the conjugated orbitals in each component. Retro-cycloaddition reactions therefore lead to two components with increased conjugation, thus this type of chemistry is useful for the generation of organic semiconductors from cyclic precursors like those discussed throughout this thesis [82].

Cycloaddition reactions can be separated further into a number of classes depending on whether new  $\sigma$ -bonds are formed at a single atom or at two atoms. The first case is called a *cheletropic* reaction and the second is known as a *Diels-Alder* reaction [82]. In its most basic form, the Diels-Alder reaction combines a butadiene molecule and an ethene molecule to form cyclohexene. The butadiene molecule is known as the *diene* because four electrons in two  $\pi$ -bonds rearrange in the cycloaddition reaction. The ethene molecule is called the *dienophile* because it "seeks" to react with the diene molecule. Two electrons in the double bond of the ethene molecule rearrange in the reaction with the diene. In total the reaction involves the movement of six electrons in three pairs. Substituents on the two molecules are not directly involved in the mechanism of the reaction, however they do affect the reaction rate. The direction of the reaction is governed by thermodynamic principles; cycloadditions usually taking place to form a ring, because two  $\pi$ -bonds in the reactants convert to two  $\sigma$ -bonds in the products. Since  $\sigma$ -bonds are more stable than  $\pi$ -bonds, the ring structure is more stable overall than the separate components. Retro-cycloaddition reactions are thermodynamically allowed in the case of the organic semiconductor precursors because the diene that is produced is an aromatic ring, which is particularly stable because of the delocalisation of electrons in the extended  $\pi$ -orbitals.

As mentioned earlier, pericyclic reactions are driven by exposure to heat or light. A useful approach for determining whether a particular cycloaddition reaction is allowed is called the *frontier orbital method* [82]. Electrons must be transferred from the occupied molecular orbital of one molecule into the unoccupied orbital of the other molecule. By examining the phases of the HOMO and LUMO wavefunctions it is possible to determine whether the separate molecules attract or repel each other in the ground or excited state and thus whether the reaction is thermally of photochemically allowed. The application of the method is illustrated for two reactions in Figure A3.1. The reaction in Figure A3.1(a) is known as a [2+2] cycloaddition because two electrons from each of the ethene molecules are involved in the reaction. The reaction in Figure A3.1(b) is called a [4+2] cycloaddition because four electrons from the butadiene molecule and two electrons from the ethene molecule undergo a rearrangement. In the ground state of the [2+2] reaction, the HOMO of one ethene molecule must react with the LUMO of the remaining ethene molecule. The p-orbital lobes of the C-2 and C-2' atoms have the same phase and can bond together. However, the reaction is actually disallowed in the ground state because the lobes of the wavefunction at the C-1 and C-1' atoms are opposite in sign and therefore repel each other in an antibonding interaction. If the upper lobes of both



Excited state photochemical interaction



**Figure A3.1** The frontier orbital method is demonstrated here for a reaction between two ethene molecules in (a) and (c) and for a reaction between ethene and butadiene in (b) and (d). Positive lobes in molecular orbitals are white, negative lobes are shaded. (a) The [2+2] cycloaddition does not proceed in the thermal reaction because the signs of the frontier orbitals do not match at both ends. (b) The [4+2] cycloaddition does proceed because the signs of the approaching orbitals match. (c) In the excited state interaction, the signs of the orbital lobes do match in the [2+2] cycloaddition, but (d) do not match in the [4+2] addition. Adapted from [82].

C-1 and C-1' atoms could interact then bonding would occur. The problem is that in this short, inflexible molecule, there is no way for the twisting motion to occur and for the orbitals to meet while maintaining the sign match between the C-2 and C-2' orbitals. The ground state [4+2] reaction of Figure A3.1(b) is thermally allowed because the interacting lobes of the ethene and butadiene molecules have matching signs irrespective of which way the HOMO of LUMO orbitals are drawn.
The frontier orbital method also successfully explains why the tendency of molecules to undergo cycloaddition reactions changes so significantly when the system is exposed to light instead of heat. In such reactions, an electron is promoted from the HOMO of one molecule into its LUMO. The excited state molecule can then react with the ground state molecule, through either its HOMO or LUMO, because both are partially occupied [82]. In the [2+2] reaction shown in Figure A3.1(c), the LUMO of the ground state molecule can react with the orbital that was originally the LUMO of the excited molecule, denoted as the LUMO\* to account for its partial occupation. Likewise the HOMO of the ground state molecule can react with what was initially the HOMO of the excited state molecule, denoted as the HOMO\* to show that is partially, rather than completely, filled. The molecules can bond whether it is the HOMOs or the LUMOs that interact, because the signs of the orbital lobes match in each case. When the molecules interact they form an intermediate known as an *exciplex*, which must lose energy somehow to give the ground state of the final product. The interactions that occur in the photochemical [4+2] reaction in Figure A3.1(d) are antibonding for at least one pair of atoms, thus this reaction cannot occur in a concerted fashion.

Picturing the interacting MOs using the frontier orbital method has helped to demonstrate how different pairs of molecules can react in a concerted fashion to form a cyclic structure, either through exposure to heat or light. In turn, retro-cycloadditions are also sensitive to either heat or light. That is why it is possible to design organic semiconductor precursors that can decompose to form a semiconductor molecule by exposure to either source of energy.

# FOUR

APPENDIX Overview of spectroscopic techniques for the study of organic thin films

This appendix provides a detailed description of the spectroscopic techniques used to carry out studies on organic thin films for this thesis. The commonly used techniques of UV-visible absorption spectroscopy and IR spectroscopy are discussed. A basic introduction to x-ray spectroscopy, in particular the use of soft x-ray synchrotron radiation for x-ray absorption and emission spectroscopy, is also provided here.

# A4.1 UV-VISIBLE ABSORPTION SPECTROSCOPY

UV-vis spectroscopy is useful for the study of organic semiconductors as it provides specific information on the nature of conjugated  $\pi$ -electron systems. Electromagnetic radiation is absorbed or transmitted by an organic molecule, depending on whether the energy of the radiation corresponds to the energetic difference between occupied and unoccupied molecular orbitals. UV and visible photons are typically energetic enough to excite these transitions in organic materials. In organic semiconductor molecules, which are composed primarily of a network of conjugated carbon atoms, the lowest energy transitions are typically between  $\pi$ -bonding orbitals and  $\pi$ \*-antibonding orbitals. The minimum energy absorption for a single molecule occurs during the HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) transition, as illustrated in Figure A4.1 for the benzene molecule. As the excitation energy increases, transitions may occur from lower energy occupied orbitals (the HOMO-1) and end in higher energy unoccupied final states (the LUMO+1).

The red and blue ovals in Figure A4.1 represent the sign of the p-orbital wavefunction on an atom. Where adjacent lobes have the same sign, the wavefunctions combine constructively and where they have opposite sign, a node forms between them. The molecular orbital energy increases with the number of nodes [81]. Calculations of MOs for conjugated organic molecules show that the HOMO-LUMO energy gap decreases as the extent of conjugation increases. That



**Figure A4.1** The MOs of benzene corresponding to the lowest energy transitions observed for the molecule in UV-vis spectroscopy [81]. Positive lobes of the MO wavefunctions are shown in blue, negative lobes are coloured red. The MOs with a greater number of nodes between the lobes are less stable.

is, as the degree of p-orbital overlap between adjacent atoms within a molecule increases, the bandgap of the semiconductor decreases [39]. The wavelengths of the HOMO-LUMO peaks for the first seven members of the acene series are plotted in Figure A4.2 [152, 155]. The longer molecules with a greater number of aromatic rings have successively longer HOMO-LUMO peak wavelengths (normally referred to as a bathochromic shift). Molecules such as tetracene and pentacene are so highly conjugated that visible light is absorbed in the HOMO-LUMO transition, which means that they appear to have colour [81].

When UV-vis spectroscopy is performed on a molecule in the gas phase, individual molecules are far enough apart to vibrate and rotate freely. Fine structure can be observed in the electronic transitions, corresponding to excitations between the quantised vibrational and rotational states in individual



**Figure A4.2** *A plot of the HOMO-LUMO absorption wavelength for the seven members of the acene series. The wavelengths of benzene, naphthalene, anthracene and tetracene (black squares) were measured in an ethanol solution at room temperature [155]. The wavelengths of pentacene, hexacene and heptacene (red circles) were measured in an Ar matrix at 10 K due to their greater reactivity to oxygen [152].* 



**Figure A4.3** UV-vis absorption spectra of 1,2,4,5-tetrazine in (a) the gas phase (b) a hexane solution and (c) an aqueous solution. Fine structure is visible in (a), but not in (b). Electronic transitions are broadened and overlap in (c). Adapted from [177].

electronic manifolds. In solutions and in the solid state, molecules generally cannot rotate freely and consequently no rotational fine structure is observed. Additionally, frequent collisions between molecules strongly modify the vibrational and electronic energy levels. This occurs to such a degree that UV-vis spectra of solid state samples consist of broad absorption features, where several individual electronic transition peaks are broadened to the point of overlapping. The dependence of the UV-vis spectrum on the environment of the sample is shown in Figure A4.3 for the molecule 1,2,4,5-tetrazine [177]. In some cases vibrational structure can be observed in solid state UV-vis spectra as a *vibrational progression*. These are recognised by narrow peaks spaced at gradually narrowing intervals. They usually correspond to electronic transitions from the lowest vibrational level of the ground electronic state to successive vibrational levels of the excited electronic state [178].

In practice, UV-vis spectroscopy is performed by illuminating a sample and monitoring the intensity of transmitted light. The light source is ordinarily a black body emitter, but monochromatic light is output by a diffraction grating. The sample is scanned over all wavelengths in an interval of the UV-vis light spectrum, by progressively changing the angle of the grating with respect to an exit slit. A Varian Cary 5000 UV-vis-NIR Spectrophotometer was used for all UV-vis measurements in this thesis.

## A4.2 INFRARED SPECTROSCOPY

All organic molecules have energy distributed over their structures which causes the constituent atoms to vibrate relative to each other. Bonds stretch back and forth, symmetrically and antisymmetrically, and they bend as well, both in-plane and out-of-plane. These vibrations are quantised; bonds within a molecule only stretch and bend at discrete frequencies. A molecule only absorbs infrared (IR) radiation when the frequency of the incident light matches the vibrational frequency of a bond. The absorbed radiation simply increases the amplitude of the vibrations. Large organic molecules have multiple bond stretching modes, leading to complex IR spectra. Interpretation of the spectra is relatively straightforward if one only wants to identify the functional groups present in the molecule, because the vibrational frequency of specific functional groups does not tend to change greatly between molecules. For example, N-H and O-H bonds tend to absorb in the 3300-3600 cm<sup>-1</sup> range. C-C triple bond stretching occurs in the range from 1500-2000 cm<sup>-1</sup> [81]. The removal of a carbonyl group from a molecule, such as occurs in the exposure of 6,13-MPn to UV light, can be monitored simply by examining the IR spectra of the reactant and product materials in this narrow absorption range.

# A4.3 X-RAY SPECTROSCOPY USING SYNCHROTRON RADIATION

X-ray spectroscopy is used to probe the electronic and crystalline structure of materials. The crystalline orientations in the bulk and surface phases of materials are probed by various scattering techniques such as small- and wide-angle x-ray scattering (SAXS, WAXS) and through diffraction measurements. The electronic structure of a sample is examined through absorption and emission spectroscopies, where the highly energetic incident x-rays actually remove the core electrons from specific elements in a material. The electrons ejected in this process are detected and correlated with the incident x-ray energy to produce absorption and emission spectra. X-rays for laboratory based spectroscopy can be generated by firing high kinetic energy electrons (several keV) at a metallic target. Bremmstrahlung radiation from the deceleration of the electrons and characteristic radiation arising from transitions between discrete energy levels provide the source of x-rays. These sources have a low intensity and it therefore takes a long time to collect an x-ray spectrum. Bright synchrotron radiation is therefore used in all modern x-ray spectroscopy experiments and has the additional benefit of being tuneable across wide energy ranges.

Synchrotrons are roughly circular particle accelerators, which produce synchrotron radiation by manipulating a stored beam of electrons that travels

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through evacuated tubes at relativistic velocities. The floorplan of a synchrotron is shown in Figure A4.4 [179]. Electrons are initially accelerated in a linear accelerator (LINAC) and are then fed into a booster ring where the velocity is increased further. Finally, the electrons are fed into a main storage ring, where electric fields continue to accelerate the electron packets and magnetic fields are used to control the direction and shape of the beam. Synchrotron radiation is emitted as the electron beam changes direction. This radiation can be controlled and inserted into a beamline, where it is further manipulated by the beamline optics into a form suitable for experiments at the beamline endstation. The three types of insertion devices commonly used at synchrotrons are bending magnets, wigglers and undulators.

Undulators acted as the insertion devices for the soft-x-ray spectroscopy work conducted in this thesis. Undulators and wigglers are similar devices, working in different regimes. These insertion devices consist of a periodic array



**Figure A4.4** A schematic overview of the design of the Australian Synchrotron. (1) An electron gun inserts electrons into the linear accelerator (LINAC) (2) where they are accelerated to 99.9997% of the speed of light. (3) The electron beam is further accelerated in the booster ring. (4) The electron beam is transferred to the storage ring where its velocity is maintained. (5) Light is inserted into beamlines. (6) The synchrotron radiation interacts with samples at the beamline endstations [179].



**Figure A4.5** The insertion device of the soft x-ray beamline at the Australian synchrotron is an APPLE II undulator. As the electrons pass through the undulator gap, the variation in the magnetic field oscillates the electrons, which release dipole radiation. Shifting the banks of permanent magnets at fractions of the magnetic field period can change the polarisation of the x-ray beam. The geometries shown above lead to a beam with (a)horizontal linear polarisation (b) circular polarisation and (c) vertical linear polarisation [40].

of dipole magnets which are separated by a gap through which the electron beam passes (see Figure A4.5). The static magnetic field alternates along the undulator with a wavelength equal to  $\lambda_u$ . As the electrons pass through the undulator, the electron bunches oscillate along a path in a plane perpendicular to the directions of the magnetic fields, emitting electromagnetic radiation in the process. The operating regime of the insertion device is related to the dimensionless parameter K, where:

$$K = \frac{eB\lambda_u}{2\pi\beta m_e c} \tag{A4.1}$$

and *e* is the charge of the electron, *B* is the magnetic field,  $m_e$  is the electron rest mass, *c* is the velocity of light and  $\beta$  is equal to v/c. Where K << 1, the oscillation magnitude is small. The emitted radiation interferes and produces narrow energy bands. Where K >> 1, the oscillation is much larger and the radiation from the field periods sum up independently to produce a broad spectrum. The insertion device acts as an undulator in the first case and a wiggler in the second. The flux of undulator sources can be much higher than bending magnets of a similar size. The radiation intensity increases by a factor of N due to constructive interference across N periods. The emission angle of the radiation harmonics decreases as 1/N, thus leading to the comparatively higher radiation intensity.

Surface science problems deal with a low abundance of species, often with a lack of periodicity, which means that x-ray diffraction is not applicable to these studies. However, the orientations of specific molecular bonds on the surface or in the bulk of a solid can be measured with x-ray spectroscopic techniques, such as near edge x-ray absorption fine structure (NEXAFS) spectroscopy [180]. It is particularly applicable to low-Z molecules, those containing atoms with a low atomic number such as hydrogen, carbon, oxygen, nitrogen and fluorine. NEXAFS selects specific atomic species through their K-edge absorptions and probes the nature of bonds to intra-molecular neighbouring atoms. Soft x-ray emission spectroscopy (SXES) is a closely related technique, but does not give structural information on crystalline orientations. A property of synchrotron radiation sources is that they are generally linearly polarised, which means that polarisation-dependent studies are feasible [180]. The insertion device at the Australian Synchrotron soft x-ray beamline is an APPLE II undulator, as shown in Figure A4.5 [40]. The linear polarisation of the x-ray beam can be tuned from vertical to horizontal and any angle in between by shifting the separate banks of permanent magnets.

K-edge absorption is a phenomenon whereby an x-ray photon is absorbed by an electron in the innermost shell of an atom, generating a photoelectron and core hole. The process is shown in Figure A4.6(a). The hole is metastable and is filled by an electron from a higher shell; Figure A4.6(b) and (b) show an electron transition from the valence band to the inner core level. Energy is released in the decay by either a radiative process in which a fluorescent photon is emitted, or a nonradiative event resulting in the emission of Auger electrons. The transition of an electron between levels is governed by *Fermi's Golden Rule*, equation (A4.2). The rule provides the probability per unit time for an initial state  $|i\rangle$  to final state  $|f\rangle$  transition under the influence of a harmonic time-dependent perturbation, V(t) $= \overline{V}e^{-itot}$ . The probability of the transition is given by:



**Figure A4.6** (a) The formation of a core hole and photoelectron by absorption of an x-ray photon. The hole is filled by the transition of an electron from the valence level to the core level. The transition occurs radiatively by emission of (b) a fluorescent photon or nonradiatively by (c) emission of Auger electrons [180].

$$P_{if} = \frac{2\pi}{\hbar} |\langle f|\bar{V}|i\rangle|^2 \varrho_f(E)$$
(A4.2)

where  $\rho_f(E)$  is the energy density of final states. In a K-shell excitation,  $P_{if}$  gives the rate of transitions per unit time from the atomic core shell to a bound or continuum final state [180].

The quantum numbers for the core hole produced by x-ray absorption are simply the negative of those quantifying the electron that was removed. Thus, the selection rules for x-ray spectra are the same as those for a single electron atom. The selection rules are:  $\Delta n$  is unrestricted,  $\Delta l = \pm 1$ ,  $\Delta s = 0$ ,  $\Delta j = 0$  or  $\pm 1$ ,  $\Delta m_j = 0$ or  $\pm 1$ , except  $\Delta m_j = 0$  if  $\Delta j = 0$ . These represent the principal, orbital angular momentum, spin, total angular momentum and magnetic quantum numbers respectively. X-ray spectroscopy also has a unique notation which is associated with the location of the core hole. Spectra resulting from a hole in the n = 1, 2, 3 and 4 shells are denoted by K, L, M, and N respectively [126].

Extra-molecular interactions such as chemical or van der Waals bonds can change the ionisation potential of an atom and affect the positions of resonances in absorption and emission spectra. The environmental disturbances to the state of an atom are designated as the *chemical shift*, a feature which has two contributions. The first, called an *initial-state-bonding shift*, changes the bonding interaction of an atom in its ground state. This is usually due to electrostatic effects, such as the substitution of an electronegative oxygen atom for a hydrogen atom in a bond with carbon, which can shift the carbon K-shell binding energy. The second factor is called the *final-state-relaxation shift*, in which the charge polarisation of external ligands leads to different shielding or screening effects for a core hole [180].

#### A4.4 X-RAY ABSORPTION SPECTROSCOPY

As outlined, NEXAFS spectroscopy entails the excitation of core electrons in a solid state sample to unoccupied conduction band final states. The short bond lengths of organic samples and their variance with hybridisation of atomic orbitals creates K-shell absorption spectra with pronounced, structure-sensitive features in the range approximately 30 eV above the K-edge. This detailed structure is why *near-edge* absorption spectroscopy is useful. A valuable feature of this analytical tool is that polarised synchrotron radiation interacts with the bonds in organic molecules to yield polarisation dependent K-shell spectra for oriented molecules. Given that the initial state (1s level) is spherically symmetric, the spectra reveal the orientation of molecules via the magnitude of coupling with the final states.

The number of photons absorbed when a sample is exposed to a beam of soft x-rays is quantified by the expression:

$$N_{abs} = I_0 A_0 \left( 1 - e^{-\sigma_x(hv)\rho} \right) \cong I_0 A_0 \sigma_x(hv) \tag{A4.3}$$

where  $I_0$  is the incident photon flux density in photons/(s cm<sup>2</sup>),  $A_0$  is the area exposed to the beam in cm<sup>2</sup> and  $\rho$  is the atomic area density in atoms/cm<sup>2</sup>. The x-ray absorption cross section  $\sigma_x(hv)$  has units of  $10^{-18}$  cm<sup>2</sup>/atom. The absorption cross section is defined as the number of electrons excited per unit time divided by the number of incident photons per unit time per unit area. This is simply the transition probability per unit time (calculated from *Fermi's Golden Rule*, equation (A4.2), divided by the incident photon flux [180].

Equation (A4.3) shows that the number of absorbed photons in x-ray absorption spectroscopy is proportional to the absorption cross section.

Consequently, so are the number of core holes and photoelectrons. It is not possible to measure the absorption spectrum from the photoelectrons because states below the ionisation potential cannot be detected (the photoelectron would be located in a bound state). Thus, the fluorescent photons or Auger electrons resulting from core hole annihilation are measured because they directly quantify the probability that the core hole exists.

The absorption fine structure spectrum gives a measurement of the density of states (DOS) of all normally unoccupied final states, accessible by the excited core electron under appropriate conservation conditions. As the incident photon energies are scanned above the K absorption edge, a core electron is excited to empty final states with different binding energies. If the DOS of the unoccupied level is high, then there is a high probability of core hole formation. The highly probable core hole formation leads to multiple core hole annihilations, when valence electrons decay to fill the hole. This results in the emission of a large number of Auger electrons and fluorescent photons. Thus, the strength of the signals from this secondary decay process provides a measure of the density of unoccupied states.

In an absorption process to a bound state, the excited electron has a long enough final state lifetime to shield the localised core hole. Overall, the molecule remains neutral. A feature of the final state relaxation effect is that there is an identical shift in the energies of all molecular orbitals and also a change in ionisation potential, but no absolute shift in resonance energies between initial and final states. Final state effects must be considered when analysing absorption spectra [180].

## A4.5 X-RAY EMISSION SPECTROSCOPY

Soft x-ray emission spectroscopy (SXES) is closely related to NEXAFS, in that a core hole is created on an atom within a sample molecule. Emission spectra are produced when electrons make radiative transitions into an unoccupied core hole from an occupied valence state at a higher energy. Transitions from the valence level to the core hole produce spectra that are a measure of the electronic DOS of the valence bands of the material. The higher the DOS, the higher the probability of a transition to a core hole from the initial energy level. SXES spectra are also selective for chemical species, because core levels are localised to particular atoms and have distinct binding energies. Emission spectra are sensitive to the angular momentum state, because dipole selection rules are followed in optical transitions. Emission spectra therefore provide a measure of the local partial density of valence states for a solid, which is selective for a chemical species.

The *final state rule* is applied broadly as a guide to interpreting x-ray spectra and holds that the DOS should be calculated for the final state of an electronic process. In the case of absorption spectra, the DOS should be calculated for a core excited atom, while for an emission spectrum the DOS should be calculated for an atom with a filled core and a hole in the valence level. The final state of an absorption transition contains a localised core hole, meaning that variations in the core binding energy due to chemical shifts strongly affect the spectrum since there is a disturbance to the shielding of the hole by outer electrons. In the emission spectra this hole is delocalised and does not strongly affect the spectrum [126].

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