

Investigating electron transport layers in organic solar cells and the effects of doping, through electronic and spectroscopic characterisation techniques



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A thesis submitted for the degree of
Doctor of Philosophy
Summer vacation 2024

Abstract

Efficient extraction of charge carriers from a solar cell is essential to producing well-performing photovoltaic devices, with the aim of achieving current outputs upward of 20 mA/cm² and power conversion efficiencies competing with the best photovoltaic technologies available. Incorporation of thin interfacial films of selective electron and hole conductive materials, positioned either side of the photoactive layer and before the respective electrodes, can aid in this charge extraction. The energy levels of such thin films and their respective alignment within the stack can be measured using photoelectron spectroscopy techniques to ensure charge carriers can readily transport across the interfaces for improved transport to the electrodes. As such, the maximum power conversion efficiency that a photovoltaic device achieves heavily depends on its component materials, and these “charge transport” layers play a key role in achieving the best device efficiencies.

This thesis explores the physical and optoelectronic properties of an organic electron transport layer (ETL), deposited between the photoactive layer and the cathode, comprising the fullerene-derivative material phenyl-C61-butyric acid benzocyclobutene ester (PCBCB). Data from both neat films and device stacks are compared to data from those fabricated from the commonly used ETL material, zinc oxide (ZnO). This work aims to explore how this organic ETL could result in more stable devices than with metal oxide ETLs, by eliminating photocatalysis at material interfaces. The work dives into the processing of PCBCB films and its effects on film energetics, surface and bulk

morphology, and consequent effects on active layer morphology. The electronic tunability of PCBCB is further investigated by photoelectron spectroscopy, with particular focus on its work function and Fermi level position, via addition of organic n-type dopants, primarily 4-(2,3-Dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzenamine (N-DMBI) and its derivatives. Furthermore, enhanced device performance is exhibited with improved processing, and with the use of doped PCBCB layers. The design and integration of a new ultraviolet photoelectron spectroscopy tool in Oxford for spectroscopic analysis of thin film and material energetics is also detailed. Photoelectron spectroscopic characterisation of other materials to be used within the fields of both organic and perovskite optoelectronic devices are also explored as an example of other investigations conducted using these techniques. Ultimately, this work hopes to advance our understanding of how processing and optimisation of the ETL can have a significant impact on organic photovoltaic performance.

Declaration

This thesis and the work included within it is my own work, achieved over the course of my PhD from October 2020 - July 2024. Any ideas, data, images, or text resulting from the work of/with others (whether published or unpublished) have been explicitly noted and referenced, and any work to yet to be published has also been highlighted. Such work has been identified and attributed to the author(s) within the bibliography and/or text.

Department of Physics, University of Oxford, July 2024.

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Acknowledgements

First and foremost, I would like to thank my supervisors Prof. Moritz Riede and Prof. Henry Snaith for their incredible support and guidance throughout my DPhil. I also wish to express my gratitude to every member of both the Advance Functional Materials and Devices (AFMD) and Photovoltaic and Optoelectronic Devices (POD) groups for their support and friendships during my time in Oxford. I would specifically like to thank Moritz for his compassion and thoughtfulness towards the mental health of our group. Health is a vital consideration particularly for PhD students during stressful periods, and his positive approach towards this has not gone unnoticed! Not only this but his availability to talk and the support shown towards my project is much appreciated. I would also like to particularly thank Henry for finding me funding to pursue my DPhil in these wonderful groups and for sharing his encouraging enthusiasm and support for my research project, especially during times where I felt I was not achieving the results I desired—this truly helps students to be persistent and to hold onto hope when a project may feel like it’s losing its spark. I’m also thankful for the ever-flowing river of inspired ideas Henry provided to me throughout my DPhil, which proved especially helpful during my first year, in helping to formulate a project plan. I’d like to also thank Jin Yao for all his incredible work on the cluster lab and helping me navigate my way through setting up the UPS tool, it’s been tough, but his help has made it a lot easier and more fun than it would’ve been trying to tackle the task alone. Of course, thanks extend to all those in both research groups that have been by my side during my time in Oxford, particularly to all my B-Lab mentors, and my first year mentor

Alex. You have all been great people to not only collaborate with but also great friends to hang out with and you have helped make my time here enjoyable. Big shoutout to Jake and Mike for being awesome buddies these past few years!

From the University of Cologne, I'd like to firstly thank Dr. Selina Olthof for being a wonderful mentor into the world of photoelectron spectroscopy and all things UHV. Not only am I sincerely grateful for the valuable advice she imparted to me during my time with her group, but also for her extended kindness, offering me plentiful advice throughout the final two years of my DPhil. Thanks to her and also to Professor Klaus Meerholz for providing me with the opportunity to be a guest researcher at the University of Cologne and engage in collaborations with the wonderful Meerholz group. I'd also like to thank every member of the Meerholz group for helping me feel welcome and supporting me during my stay. Particular thanks go to the lovely Dilara Öz and to the top lad Max Reimer, for both helping me feel welcome during my stays in Cologne!

Finally, I would like to express my deepest thanks to my family, friends and all of the people that have supported me along the way during my DPhil and throughout my education. I won't name names as the list is long and I'd hate to miss someone out, but you know who you are! All your help and support has kept me persevering and encouraged me to succeed in reaching my academic goals and more. You have all played a role in helping me along the way and I truly appreciate all the support.

This work was supported by the Department of Physics Doctoral Training Programme studentship, as provided by the Engineering and Physical Sciences Research Council (EPSRC) of the UKRI.

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List of Abbreviations

PV	Photovoltaic
OPV	Organic photovoltaic(s)
PCE	Power conversion efficiency
UV	Ultraviolet
PCBCB	Phenyl-C61-butyric acid benzocyclobutene ester
ETL	Electron transport layer
PET	Polyethyleneterephthalat
TCO	Transparent conductive oxide
ITO	Indium tin oxide
PAL	Photoactive layer
CTL	Charge transport layer
HTL	Hole transport layer
HOMO	Highest occupied molecular orbital
WF	Work function
UPS	Ultraviolet photoelectron spectroscopy
SAM	Self-assembled monolayer
LUMO	Lowest unoccupied molecular orbital
IE	Ionisation energy
WF	Work function
EA	Electron affinity

D	Donor
A	Acceptor
CT	Charge transfer
CS	Charge separated
ISC	Inter-system crossing
IDIS	Induced density of interface states
PCBM	[6,6]-phenyl-C61-butyric acid methyl ester
PES	Photoelectron spectroscopy
FF	Fill factor
JV	Current density-voltage
N-DMBI	4-(2,3-Dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzenamine
SOMO	Singly occupied molecular orbital
XRR	X-ray reflectivity
RMS	Root mean square
GIWAXS	Grazing incidence wide angle X-ray scattering
UPS	Ultraviolet photoelectron spectroscopy
DOS	Density of states
CCD	Charge-coupled device
UHV	Ultra-high vacuum
HBEC	High binding energy cutoff
IPES	Inverse photoemission spectroscopy
XPS	X-ray photoelectron spectroscopy

FWHM	Full-width half-maximum
EPSRC	Engineering & Physical Sciences Research Council
NTCF	National Thin-film Cluster Facility
DLD	Double delayline
FRET	Förster Resonance Energy Transfer

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Chapter 1

Introduction

1.1. Wider Context

As climate change and the consequences of it becomes an ever more pressing threat to humanity and challenge to address, one of the key changes that needs to be made on a global scale is to drastically reduce our fossil fuel consumption and our reliance on such fuels to live. Through this, not only can we guarantee a reduce in global carbon emissions, but as a result we can expect to see decreases in the rate of rising temperatures across the planet and in the number of extreme weather events ensuing—resulting in more pleasant and hospitable environments for life to inhabit, reduce the number of pollutants in the air and decrease strain on healthcare systems, thus cutting costs associated with health problems from fossil fuel combustion [1-5]. As a result of all this, we can also hope to see improvements in Quality of Life [6-10] across the planet.

Photovoltaic (PV) devices can be one of the cornerstones of renewable energy production for the future. Silicon solar cells have demonstrated to be a viable source of green energy since their development 70 years ago [11], having first been

commercialized into 10% efficiency cells, by Hoffman Electronics in 1959 [12]. Emerging photovoltaic technologies include organic photovoltaics (OPV), comprised of predominantly organic materials (of which an extensive database can be found here [13]), i.e. carbon-based compounds, and perovskite photovoltaics, comprising a crystal structure of ABX_3 of both inorganic and organic-inorganic hybrid varieties, where the A site is typically a larger rare earth metal cation or an organic cation, the B site a smaller transition metal cation and the X site made up of three, often halogen, anions [14-19]. Scaled-up commercialisation of these technologies could prove crucial in the mission towards mass scale-up of efficient and stable solar cells. The organic photovoltaic industry is continually on the rise, with the global market volume for organic solar cells expecting to rise from 97 million U.S. dollars to in 2020, to 807 million by 2031 [20]. This technology has the potential to tackle mass urbanisation with a flexible, lightweight and customisable solar cell product; reducing the physical space needed for installation as compared to the heavy and rigid silicon modules. This is thanks to the ability to produce thin films ($< 1 \mu\text{m}$ thickness) on flexible substrates, either printed via ink formulations [21,22], or through thermal evaporation of organic materials [23-25], which is currently the leading technology in production of commercial OPV [26]. This technology can then bend freely and can be integrated directly into construction materials and thus buildings at low cost, in this case reducing the requirements for a central power grid and power distribution lines. This is just one application of such devices, with the ability to also use OPV for large scale solar farms, with a source to output grid setup. Not only this, but OPV allows for huge freedom of design, with the potential to customise shape, colour and level of transparency, providing a lot of choice to customers and giving an aesthetic advantage over other solar energy alternatives [27-29].

A lot has improved in the field of OPV in the last 40 years, since C. W. Tang documented a 1% efficient solar cell device using the first two-layer active layer in an organic photovoltaic [30]. This design concept, albeit now adapted and enhanced, has in many ways remained a keystone of current OPV architecture, with two-component bulk heterojunctions founded from this design, and ternary heterojunctions now evolving from this as an exciting prospect for OPV [31,32]. In conjunction with this, the latest investigations into solution processable non-fullerene acceptor materials [33-39] have resulted in record OPV device efficiencies, with the NREL certified highest PCE device now standing at 19.2% with a ternary active layer of the molecules more commonly known as PM6, D18 and L8:BO [40]. In terms of scale-up, OPV has seen the development of large-scale manufacturing methods of solution-based modules over the last 10-15 years, notably with the development of roll-to-roll fabrication [41-43]. Commercially produced solution processed modules are typically still produced with $PCE < \sim 10\%$ and on flexible substrates, often with customised designs. Investigating and improving the long-term stability of these devices is of real interest for large-scale commercialisation and global conversion to solar power.

When considering the current state of PV, it should be discussed that in addition to OPV, perovskite solar technology has similar customisable properties, with the ability to be produced on flexible substrates in many a design. Similarly, these materials provide some capability to tune the energy of the bandgap, in turn controlling the absorption spectrum of a solar cell device. Though the initial use of perovskite materials within the field of photovoltaic technology was by the group of Tsutomu Miyasaka [44-46] around 30 years later than the development of the first organic photovoltaic [30, 47-49], this soon led to the works of Grätzel and Park on perovskite sensitised all-solid-state solar cells [50] and that of Professor Henry Snaith proving halide perovskites to

themselves be capable of generating and transporting electrons to the electrodes [51,52]. Since then, these materials have proven to be extremely efficient and are now challenging gallium-arsenide devices for the number one spot in terms of power conversion efficiencies (PCE). Organic photovoltaics (OPV) and hybrid-organic perovskite photovoltaics are now beginning to compete as two of the leading PV technologies, with OPV technologies currently able to reach power conversion efficiencies (PCE) up to 19.2%, while perovskite is now pushing towards rivalling the power conversion efficiencies of silicon single junction cells, currently reaching 26.1% when in a single junction, 24.4% when in a perovskite/organic tandem [53], 29.1% when in an all-perovskite tandem and 33.9% when in perovskite/silicon tandem architecture [54,55]. From this, it is clear that emerging solar cell technologies can compete with silicon, and it is important that all technologies are worked on concurrently. While perovskite clearly is the front-runner in terms of device efficiency metrics, benefits of OPV include the abundance of materials that are notably of low toxicity, as well as the fact that the absorber materials we use in OPV come in a wide range of colours, allowing for great customisability when it comes to releasing a product to market. Furthermore, production of OPV proves to have considerably lower impact on the environment than the production of other second and third generation solar cells such as perovskite and particularly silicon-based photovoltaics, with production of these emitting significantly higher amounts of greenhouse gases [56-58]. Along with the already developed roll-to-roll techniques for large-scale production of OPV, this technology proves to still be one of real interest for the present and the future.

For some systems lifetime is no longer an issue, for example, Heliatek's commercial OPV product is a good example of those passing the required IEC tests [59], with other vacuum thermally deposited OPV reporting to maintain at least 80 percent of

their initial performance over extrapolated lifetimes (acquired through accelerated ageing as specified in the report) of 27,000 years outdoors [25]. However, questions over the stability of the most efficient (primarily solution processed) OPV devices remain to be fully resolved, with both technologies aiming to further improve in this department to facilitate a future push towards widespread generation of solar power. The limitations on stability can be tackled through further investigations into new materials and their charge generation and loss processes, understanding further the degradation mechanisms taking place in such systems, as well as by improving device stack design. Furthermore, research into the encapsulation of devices, providing a protective layer to the device from the elements (particularly oxygen and moisture), can add years to a device's lifetime if done correctly.

Not only this, the toxic solvents used primarily for solution processing of both technologies may also prove to be a hinderance to their upscaling. Finding a 'greener' alternative to these solvents is becoming much more of a prevalent research topic and a necessity to improve the positive environmental impact of PV even further. In addition to these considerations, devices should of course be able to perform with competing power conversion efficiencies. Therefore, materials must be investigated that can produce such properties whilst proving to have a stable lifetime, so device turnover is not too high, avoiding a strain on production and installation rates.

1.2. This Thesis

This thesis explores the physics of solution processible electron transport layer materials in organic solar cells. The work focuses on the implementation of an electron transport

layer comprising an organic fullerene-derivative, namely Phenyl-C61-butyric acid benzocyclobutene ester (PCBCB), and the use of dopant materials to tune the electronic and energetic properties of the thin film. In this work we aim to explore, understand, and for PCBCB optimise, both the physical and optoelectronic properties of electron transport layers that are key to efficient charge extraction and ultimately a well-performing PV device. To achieve this, we are comparing the use of metal oxide materials as the electron transport layer (ETL) in an OPV device stack to this organic alternative. This study is particularly interested in using photoelectronic spectroscopic characterisation to determine energetic values of ETL thin films, such as the position of the highest occupied molecular orbital (HOMO) onset and work function (WF), and the effects of introducing n-type dopant materials as an additive into the ETL on these values. With this we hope to deeply investigate and link the physical properties of PCBCB transport layer, such as surface roughness and film quality, crystallinity and other factors that change dependent on the exact fabrication steps involved in producing thin ETL, with the energetics of the ETL.

The thesis will now be segmented in the following way: Chapter 2 will delve deeper into the physics of OPV. Chapter 3 will explore electron transport layer materials, their functional characteristics, additive materials and chemical doping, while Chapter 4 will describe the techniques involved in photoelectron spectroscopy (UPS/IPES/XPS) and the energetic characterisation of thin films and materials. Chapter 5 investigates the relationship between the fabrication steps of fullerene-derivative thin films and the physical and electronic properties of the films. Chapter 6 focuses on the effects of doping on PCBCB energetics and the efficacy of a variety of dopants, determining the effectiveness of each on the conductivity of PCBCB thin films. The effects of the ETL and ETL doping on active layer energetics and morphology is also

explored. Chapter 7 is concerned with the characterisation of devices with varying transport layer materials, investigating the effect of doping on device performance with a PCBCB ETL, with the aim of trying to underpin which properties result in improved performance. A preliminary stability study is also detailed, with the aim of approaching a device stack in which the stability of devices comprising PCBCB results in a more consistent PCE (i.e. a less significant drop-off over time) than that in OPV devices comprising a typical ETL of zinc oxide.

Chapter 8 will focus on the implementation of a new Ultraviolet Photoelectron Spectroscopy (UPS) tool, here in the Department of Physics in the University of Oxford, specifically covering the design, integration, and setup of the tool. Chapter 9 studies the energetic characterisation using UPS of other materials investigated throughout the DPhil, such as novel materials with the potential to be used within perovskite technologies or OPV. Conclusively, chapter 10 aims to summarise the work and results discussed throughout this thesis, while also providing an outlook on the challenges ahead, in addition to the future projects to be investigated when continuing developments in this area of the field of solar cell physics.

Chapter 2

Background theory of Organic Photovoltaics

In this chapter we focus on the fundamental theory of OPV—this includes the stack configuration of devices, the roles of donors, acceptors and heterojunctions, band structure and energetics, charge generation, transport and interface interactions, morphology and device performance metrics (V_{OC} , J_{SC} , Fill Factor & PCE).

2.1. Organic Photovoltaics

Photovoltaic devices use semiconducting materials to convert solar radiation into direct current via the photovoltaic effect. This phenomenon occurs upon absorption of photons, causing excitation of electrons into higher energy states, resulting in free charge carrier generation and a current flow. There are different types of photovoltaic devices, from crystalline silicon photovoltaics to those using a perovskite-structured compound as the photon absorbing layer, in addition to organic solar cells which

primarily use organic (hydrocarbon-based) semiconductor materials [60]. These devices all comprise a sequential stack of different material layers deposited onto a substrate, each layer affecting the next in terms of energy level alignment at the interface, morphology of each successive layer and the charge carrier dynamics within the device. In this work, we are mainly concerned with the physics of solution processed organic solar cells, and specifically the impact of interfacial charge transport layers within the device stack.

Although a traditional crystalline silicon solar cell provides a combination of low production cost, high efficiency and long lifetime, these cells have an indirect bandgap, meaning the maximum energy state in the valence band and minimum energy state in the conduction band are not aligned in momentum space. The two energy states are each characterized by a crystal momentum or k-vector, which in the indirect bandgap case is different for each state respectively. While a typical photon may carry a small amount of momentum, for a photoexcited electron to transition from the valence band to the conduction band of an indirect bandgap semiconductor must also interact with a lattice vibration called a phonon, in order to significantly shift its momentum and k-vector to that of the conduction band minimum energy state, satisfying conservation of energy and momentum rules. This results in less frequent absorption of photons in the indirect bandgap than compared to direct bandgap. The direct bandgap of silicon is around 3.5 eV, which is too high to absorb the low-energy photons emitted from the sun. The indirect bandgap is around 1.1 eV at room temperature. This band structure originates from the crystalline ordering of the inorganic semiconductor lattice [61,62]. This low indirect bandgap allows for broad absorption of photons in the solar spectrum, and the high dielectric constant of silicon ($\epsilon = 11.7$) results in smaller electrostatic forces between photoexcited electrons from the valence band to the conduction band and their

counterpart, holes. These coulomb-bound charge carriers, known as excitons, are thus able to separate more easily due to the reduced exciton binding energy, which is lower than the thermal energy ($k_B T$) at operating temperatures. However, while silicon and similar inorganic materials such as germanium can absorb a broad range and generate free charges readily thanks to these properties, the reduced photonic absorption in such indirect bandgap materials due to the requirement for accompanying absorption of a phonon, requires that silicon solar cells must be at least tens of microns thick to allow for adequate light absorption. Most silicon cells are in fact typically on the scale of hundreds of microns thick, as this is more economically beneficial and mitigates handling incredibly delicate wafers.

On the other hand, organic semiconductors typically have energy levels that are closer to the ‘ideal’ bandgap of 1.4 eV, as demonstrated Shockley and Queisser in their work on Detailed Balance Limit of Efficiency of p-n Junction Solar Cells [63]. Organic semiconductor energy levels are formed again through interactions between the atoms making up the semiconductor material but are usually less band-like than in inorganic semiconductors and usually non-degenerate, due to the reduced crystallinity and less lattice-like structure of most organic systems [61]. The highest occupied energy state below the energy level gap, more commonly known as the highest occupied molecular orbital, is analogous to the valence band within an inorganic semiconductor. The lowest unoccupied molecular orbital (LUMO) is likewise comparable to the conduction band.

The dielectric constant of organic semiconductors is a lot lower, typically ranging from $\epsilon = 3$ -4. This results in a more significant exciton binding energy between excited electrons and their corresponding holes than in inorganic semiconductors, on the order of 0.5-1 eV [64,65]. This higher binding energy means that at room temperature, i.e. without additional energy for dissociation, free charges do not separate as readily as in

inorganic semiconductors, a problem that is typically overcome by taking two different light absorbing organic materials and placing them in contact with one another. The two materials will have an energy level offset that helps drive charges to the interface between the two and pull them apart to generate free charge carriers; this idea is explored in more detail in both 2.1.1 and 2.1.2. Depending on the stack, the material with the greater electron affinity and shallower LUMO band, known as the ‘acceptor’ material, accepts electrons from the one that has the lower electron affinity, known as the ‘donor’.

2.1.1 OPV structure

Organic solar cell devices are fabricated using hydrocarbon-based semiconducting materials. The basic device circuit of an ideal photovoltaic device, as shown by the schematic in Figure 2.1 [66], encompasses a current source, a diode, a total series resistance and a total shunt resistance. The total series resistance of a single cell device accounts for the resistance of each layer within the stack, while the shunt resistance represents alternate current paths that ultimately short the circuit, e.g. from protrusions, microtears or pinholes in these layers. The series resistance should be minimised and shunt resistance maximized, such that in an ideal device $R_{series} = 0$ and $R_{shunt} = \infty$. The ideal or Shockley-diode equation is given in section 2.1.5 where we discuss performance metrics of a solar cell device.

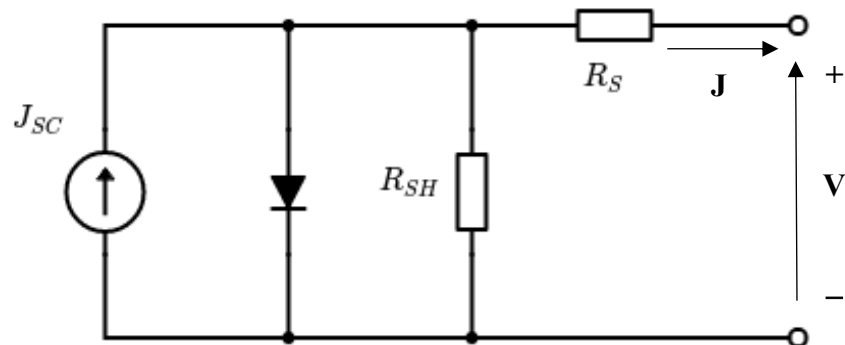


Figure 2.1 - Circuit model of a generic ideal photovoltaic device with a current source and sink, photodiode and a series and shunt resistance, R_S and R_{SH} – adapted from [66].

The OPV structure or stack starts with a substrate, usually either polyethylene terephthalate (PET) to warrant flexibility of the module and roll-to-roll production, or glass, often used in a smaller-scale research environment. The substrate is typically coated with a thin layer of a transparent conductive oxide (TCO), in this work indium tin oxide (ITO), which acts as the bottom electrode of the device. In a typical simple device structure, a photoactive layer (PAL) will be sandwiched between two charge transport layer (CTL), one a hole transport layer and the other an ETL. A final electrode is placed on top, frequently this is comprised of either aluminium, silver or gold. As the names suggest, the ETL aids electron transport towards the cathode and due to an energetic offset and deeper ionisation energy with that of the active layer components, helps suppress hole and exciton transport towards the cathode, whilst the HTL layers similarly supports hole transportation and reduces the respective electron and exciton transport to the anode, thus enhancing the diode behaviour of the device. Depending on the material used for each of the charge transport layers and how n-type or p-type it is determines whether it is the electron or hole transport layer. The stack architecture determines the energetic alignment throughout the stack and the direction of charge carrier transport. In OPV, a device comprising an ITO/HTL/PAL/ETL/Ag stack for example is commonly referred to as a conventional stack or when using doped CTLs ‘p-i-n’, meaning positive-intrinsic-negative, referring to the p- and n- doped layers sandwiching the nominally intrinsic photoactive layer in that order, from bottom (substrate side) to top. The alternative, in which the electrode polarity is reversed, e.g. ITO/ETL/PAL/HTL/Ag, is known as an inverted stack or ‘n-i-p’ stack. Figure 2.2 is a

schematic of these two types of device architecture, with the inverted stack depicted the one that is studied in this thesis.

The device architecture of bulk heterojunction OPV devices has a strong effect on the performance of devices comprising the same active layer material [67,68]. This is a product of many factors: vertical phase separation of the donor and acceptor material throughout the active layer [69-71] and with the use of different contact layer materials, varying built-in field or optical intensity distribution in the active layer, with imbalance between hole and electron mobilities in the active layer seemingly the main contributor to differing performance [72,73]. Recent literature suggests that solution processed OPV with the conventional stack architecture may have a small advantage when it comes to device current density – voltage performance [74]. The available open-circuit voltage (V_{oc}) is lower in the typical solution processed inverted device architecture stack due to a smaller difference in work function between the zinc oxide ETL and molybdenum oxide (MoO_3) HTL, than between the calcium (Ca) ETL and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) HTL in a typical conventional device stack. This same study by Murthy, Zhang & Hsu [74] also indicates that the largest short-circuit current densities (J_{sc}) can be produced in their conventional stack OPV, with this specifically proving to be dependent on the generation and how efficiently photogenerated holes can be collected. Here, hole collection has a stronger effect on performance than electron collection due to their lower mobility than electrons in these systems, meaning comparatively electrons can travel further distances. In these conventional devices, the holes can be collected more efficiently due to the peak generation position being closer to the anode [74]. This leads to a balancing of the charge carrier mobilities that results in less recombination and higher J_{sc} . This improvement in device performance with balanced carrier mobility had also previously been observed

by the same research group to be a favourable product of the inverted stack [68]. When using identical ETL and HTL of ZnO and MoO₃ respectively for both stack architectures they found that the inverted stack was “serendipitously optimized”, proving this naturally dependent on material choice and optimisation of the stack, with a particular importance tied to the choice of donor and acceptor molecules with balanced carrier mobilities. The concepts of work function, open-circuit voltages and short-circuit current are explored further on in this Chapter. Inverted stack devices can also allow for increased photon absorption when implementing higher transparency layers before the PAL, as well as good stability in air, thanks to the ability to evaporate high work function metals as the top electrode, and avoid the use of hygroscopic and sometimes corrosive PEDOT:PSS [75]. However, the metal oxide ETLs that are currently commonly used in inverted stacks do result in device stability problems under the irradiation of UV light. It is for these reasons that this thesis heavily focuses on the ETL particularly within OPV in the inverted device architecture, with the aim of exploring an alternative to metal oxides.

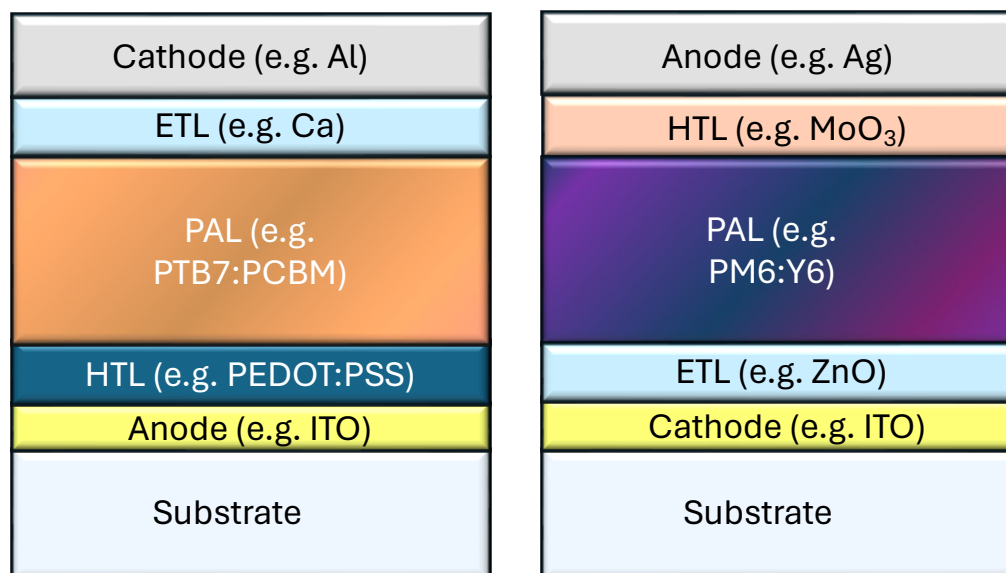


Figure 2.2 - Diagram of the two different organic photovoltaic device architectures. These are known as the ‘conventional’ (left) and ‘inverted’ (right) architectures, respectively.

In this stack configuration considered, it is important that the bottom electrode is transparent to allow photons a path to the photoactive layer. The photoactive layer is responsible for charge carrier generation. It is comprised of organic semiconductor materials that respectively act as donor and acceptor molecules for photo-excited charge carriers. Carbon based conjugated polymers or small molecular materials typically form the donor molecules and small molecules, both fullerene and non-fullerene, have been used as the acceptor [76]. These donor and acceptor materials can be layered to form what is called a bilayer or blended together to form a bulk heterojunction [77]. The latter is preferred for organic solar cell devices, due to the resulting increase in interfacial area between the donor and acceptor molecules. This leads to shorter diffusion distances for bound electron-hole (exciton) pairs produced in the donor materials upon absorption of a photon, to reach the donor/acceptor interface where they are separated. This allows for film thicknesses larger than the exciton diffusion length to be fabricated, thus improving the light absorption and consequently the quantum efficiency (the incident photon to free electron ratio) by several orders of magnitude [78].

2.1.2 Energy levels, charge generation and transport

The organic semiconductor materials used in OPV form a conjugated bonding structure along the carbon backbone. What this means is the carbon molecules in the carbon chain are alternating between being single and double bonded to one another, i.e. $C - C = C - C = C$. This formation is a result of carbon’s electronic structure. Carbon has an

electronic configuration of $(1s^2 2s^2 2p^2)$, meaning it has four valence electrons that have filled the respective s - and p -orbitals according to the Aufbau principle, Hund's rule (although it should be noted that this is not strictly always the case [79]) and Pauli's exclusion principle [80-82], two in the outer s -orbitals and two in the outer p -orbitals. The p -orbitals consists of three degenerate molecular orbitals, namely p_x , p_y and p_z , each of which can hold two electrons with opposing spin. Elements form bonds by sharing their valence electrons with one another to fill these outer orbitals and achieve full occupation of the electron shells surrounding their atomic core. This is known as covalent bonding. In the case of carbon, in perhaps the simplest case it may share its four valence electrons with hydrogen atoms to form the molecule methane (CH_4). Here, the $2s$ and $2p$ orbitals of carbon atoms respectively overlap with the $1s$ orbitals of each hydrogen atom, allowing the four valence electrons of carbon to be shared between four hydrogen atoms, filling the outer $1s$ orbital of the hydrogen atoms, and each hydrogen can share one electron to fill the outer $2p$ orbital of the carbon atom. Now both have a complete outer shell and are more energetically stable. Specifically for the case of methane, one electron from the $2s$ orbital is promoted to the $2p_z$ orbital, resulting in the overlapping of these orbitals, to allow for the hydrogen atoms to attach efficiently, making up for the energy required to rearrange the electron distribution. This overlapping of different orbitals is known as hybridisation, and in methane, this is known as sp -hybridisation due to the overlapping of s - and p - orbitals specifically. With three $2p$ - and one $2s$ - orbitals overlapping each other, this is classified as sp^3 hybridisation. As the orbitals in methane overlap in-plane, linearly or end-to-end, depending on the nomenclature followed, the covalent bonds formed are sigma (σ) bonds. Here the electrons distribution is concentrated between the nuclei of the bonding atoms. The molecular orbital electron distribution is depicted in Figure 2.3.

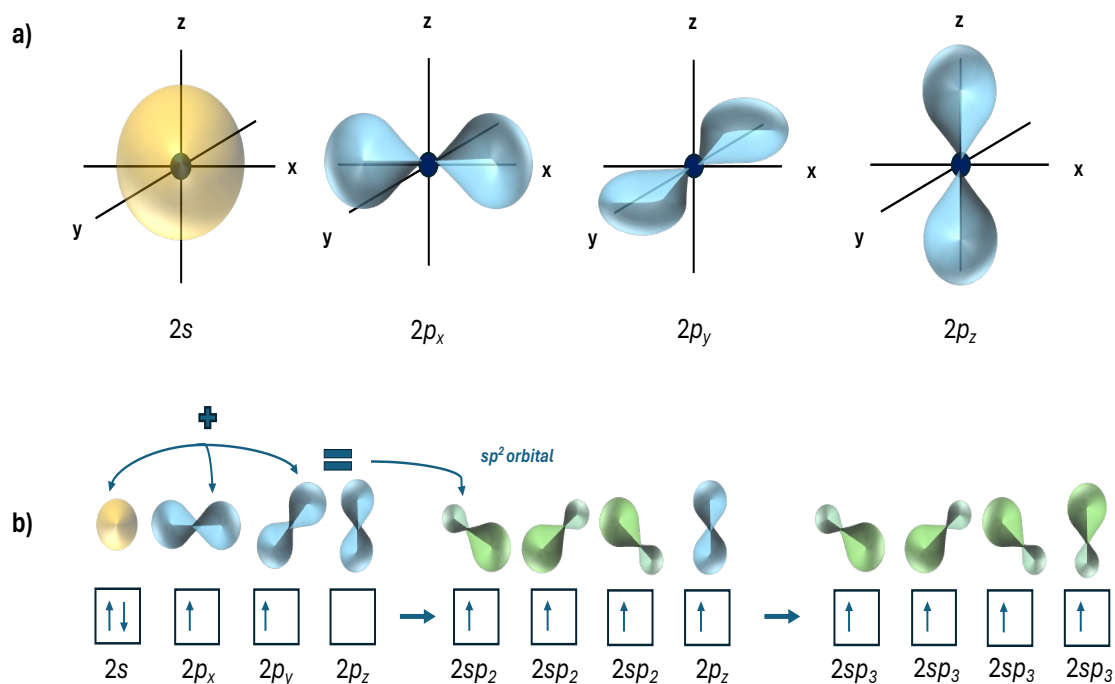


Figure 2.3 – Molecular orbital configurations a) s and p orbitals. b) Orbitals of a carbon atom in the ground, sp^2 and sp^3 hybridised states, exemplifying the redistribution of electrons across the orbitals that occurs in molecules such as methane.

This of course is just one example of orbital hybridization and covalent bonding. Take benzene (C_6H_6), comprised of six sp^2 -hybridised carbon atoms, conjugately bonded to each other and each bonded to a further hydrogen atom. In this molecule, every other pair of carbons are double bonded, between which both a σ -bond and a pi (π) bond form, a bond between molecules formed out-of-plane, non-linearly or side-by-side. This results in a total of 12 σ -bonds and 3 π -bonds for the molecules. According to molecular orbital theory however, the six carbon atoms overlap to then form one continuous π -bond. Here, in contrast to a sigma bond, the electron distribution concentrated above and below the plane of the nuclei of the bonding atoms, which in benzene presents itself as a torus shaped cloud, occupying the plane above and below

that of the carbon atoms [65,80], resulting in delocalisation of electrons across the whole molecular system. The orbital arrangement for methane and benzene are shown in Figure 2.4. In the case of both sigma and pi bonds, depending on the spin configuration of the electrons in each of the orbitals, they are termed bonding (σ or π) or antibonding (σ^* or π^*). Bonding orbitals are the produce of constructive interference between electrons when considering their wave behaviour, and such these orbitals attractively interact more strongly and the electron density between the atoms is increased. Opposingly, antibonding orbitals or states are destructively interfering and have a region of zero electron density between the nuclei. As a result, bonding orbitals are lower in energy. This fundamental bonding chemistry is the basis to forming these organic molecules and plays a critical role in determining their optoelectronic properties.

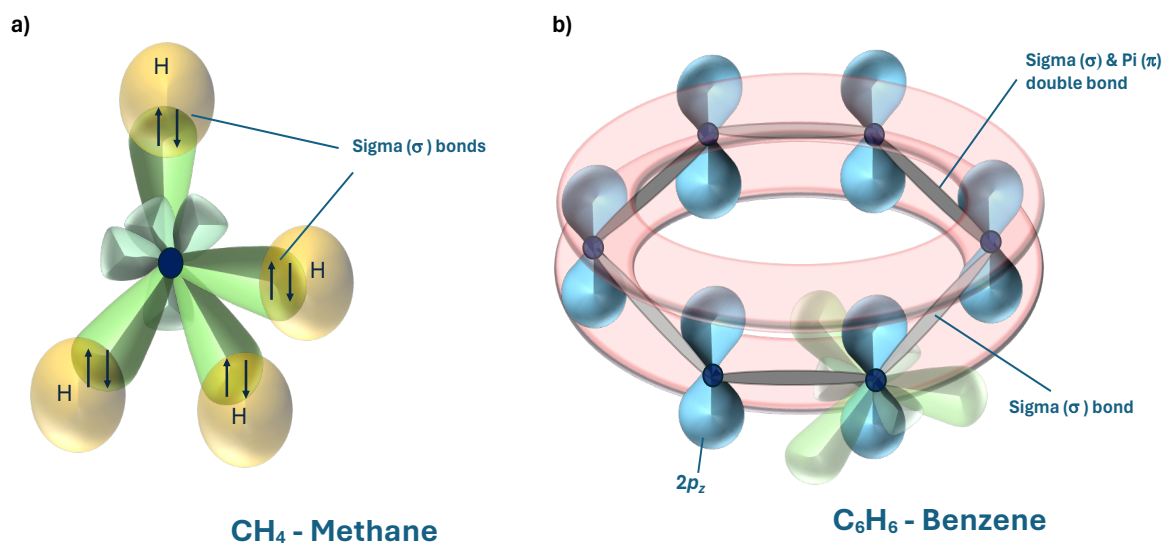


Figure 2.4 – The orbital arrangement for methane (a) and benzene (b), displaying the sp^2 -hybridisation of orbitals in methane and the six conjugately bonded sp^2 -hybridised carbon atoms in benzene. The sigma (σ) and pi (π) bonding exhibited in these systems is highlighted.

As previously mentioned, the HOMO and LUMO orbitals are separated by an energy gap, defines the energy that is required to excite electrons from the HOMO into the LUMO, consequently leaving behind a hole. This term ‘energy gap’ is accurate for finite systems, while in extended infinite systems such as periodic crystals, the orbital energy levels overlap to form degenerate energy bands and thus in these cases it is called a ‘bandgap’. To more thoroughly understand charge generation and separation inside the active layer, we must explain this energetic structure in more detail, to make more sense of the transitions taking place upon photoexcitation, discussing the key difference between the optical gap and fundamental gap of an organic thin film. Additionally, changes in energetic structure of the thin film with illumination and the principles of excitonic generation and dissociation are discussed, considering excitonic binding energies and charge transfer states.

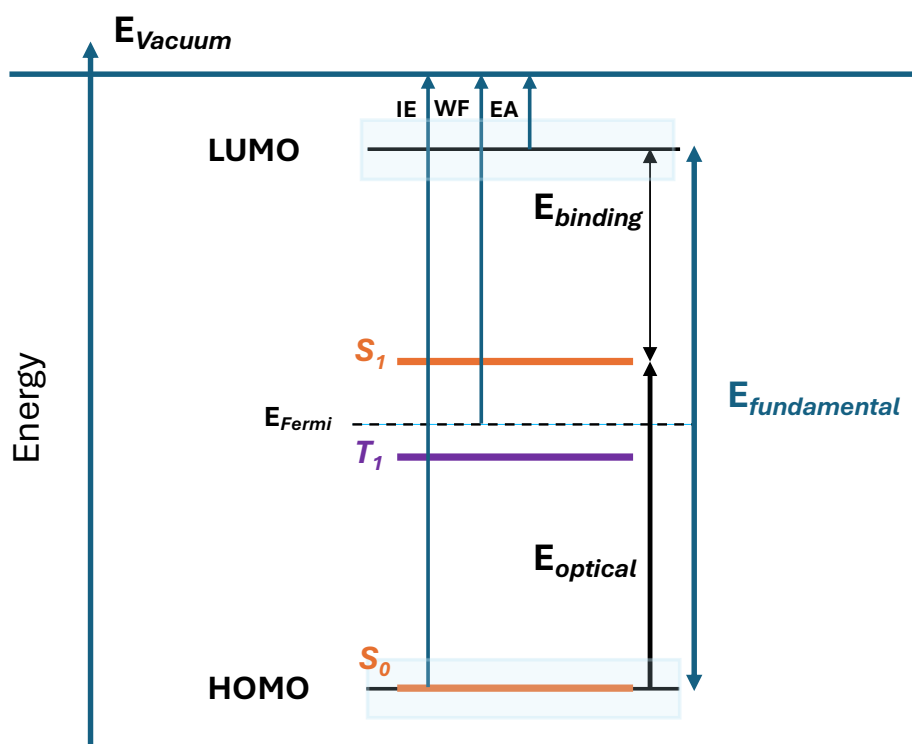


Figure 2.5 – Energy level schematic of an organic semiconductor thin film, detailing the optical gap (E_{optical}), and the exciton binding energy (E_{binding}), that together

describe the fundamental gap ($E_{\text{fundamental}}$). Singlet electronic ground state (S_0) and excited state (S_1) are also highlighted, along with triplet state (T_1). The ionisation energy (IE), work function (WF) and electron affinity (EA) of the film are shown. In this example the zero-energy point is dependent on the frame of reference, i.e. the $E = 0$ can be given as the Fermi, or as the vacuum, provided all other energetic values are then given with respect to that reference.

Figure 2.5 is an energy level schematic for a thin film organic semiconductor. Notable transitions are the ionisation energy (IE), work function (WF) and electron affinity (EA). The work function is the energy required to ionise an electron from the Fermi level. The Fermi level denotes the energetic position of the maximum energy state that electrons can occupy at absolute zero (0K) temperature.

According to semiconductor theory, the number of free charge carriers in a semiconductor, along with energies of the conduction band (E_{CB}) and the valence band (E_{VB}), can be related to the Fermi energy (E_F) from the Fermi-Dirac distribution, provided the effective density of states of the CB (N_{CB}) and valence band (N_{VB}) energy levels are known or can be determined. The position of the Fermi level with relation to the HOMO and LUMO is crucial in determining the electrical properties of semiconductors. At low temperatures in intrinsic organic semiconductors, including room temperature, the Fermi level lies somewhere mid-gap between the HOMO and the LUMO, as described by equation 2.1, as the majority of electrons are in the lower energy HOMO states at these conditions and require more energy to be promoted to the LUMO. If free charge carriers are added for example via doping, the position of the Fermi level in the semiconductor host will shift. For example, with n-doping the Fermi level will shift towards to LUMO due to the introduction of free electrons.

$$E_F = \frac{E_{CB} + E_{VB}}{2} + \frac{k_B T}{2} \ln \frac{N_{VB}}{N_{CB}} \quad (2.1)$$

It should again be noted that there are physical differences between organic and inorganic semiconductors that come in to play here, potentially affecting these relations. Most important are the high exciton binding energies (0.5-1 eV) [64,65] and the low dielectric function ($\epsilon \approx 3-4$) in organic semiconductors, which makes it challenging for the doping-created charge carriers to move away from the ionised dopant molecule. As a result, the doping efficiency in organic semiconductors is rather low [83]. This should be kept in mind when investigating the doping effects on Fermi level position and charge carrier transport in organic semiconductors. Notably, while in Si typical doping concentrations are in the range of 10^{-5} dopants/matrix atom, the ratio is rather in the order of 10^{-1} for organic semiconductor systems [83,84].

According to Koopmans' theorem [85], the ionisation energy is the energy required to excite an electron from the HOMO level to vacuum, i.e. to free or ionise an electron from the HOMO. The electron affinity is the energy difference between the LUMO and the vacuum level. The difference in energy between the ionisation energy and the electron affinity is therefore equivalent to the energy difference between the HOMO and the LUMO, and this is equal to the fundamental gap, $E_{\text{fundamental}}$. The fundamental gap is comprised of an optical gap, E_{optical} and an exciton binding energy, E_{binding} . Typically, the first allowed optical transition for electrons is the transition from singlet state S_0 , an energetic state with spin-paired electrons existing within the HOMO, to singlet state S_1 , conserving electron spin and promoting it into a state within the fundamental gap. This transition is equal to E_{optical} . The difference between the

$E_{\text{fundamental}}$ and E_{optical} is E_{binding} , which needs to be overcome to free the charge carrier. We will discuss these singlet states, expected transitions and triplet states, T_n , when considering inter-system crossing and charge transfer states, a little later in this section.

When a device is illuminated, the energy levels exhibit quasi-Fermi level splitting [80]. In an ideal device stack, the active layer quasi-Fermi levels (E_{Fe} & E_{Fh}) should respectively align with the Fermi levels of the charge transport layers, as shown in Figure 2.6. This allows for the largest open-circuit voltage to be achieved (see 2.1.5), with minimal losses. Misalignment here can cause losses in V_{OC} across the interface [86,87].

The quasi-Fermi levels describe the population of charge carriers within the LUMO and HOMO of organic materials separately, when their distributions are displaced from equilibrium. These represent the energy states from which charge transfer between successive materials takes place and hence with good alignment, minimal voltage losses at the interfaces between each material can be achieved. Focusing on the ETL, if we consider the E_{Fe} to be higher than that of the photoactive layer, then this provides a barrier for electron transport and thus electrons would require more energy for transport to the cathode. Conversely, if we shifted the E_{Fe} of the ETL to be lower in energy, then energy would be lost in the form of thermal emissions as the electrons transfer to lower energy states at the interface. Thus, interfacial transport layers can be used to aid in the energetic alignment between the photoactive layer materials and the electrodes for improved charge carrier extraction [88,89].

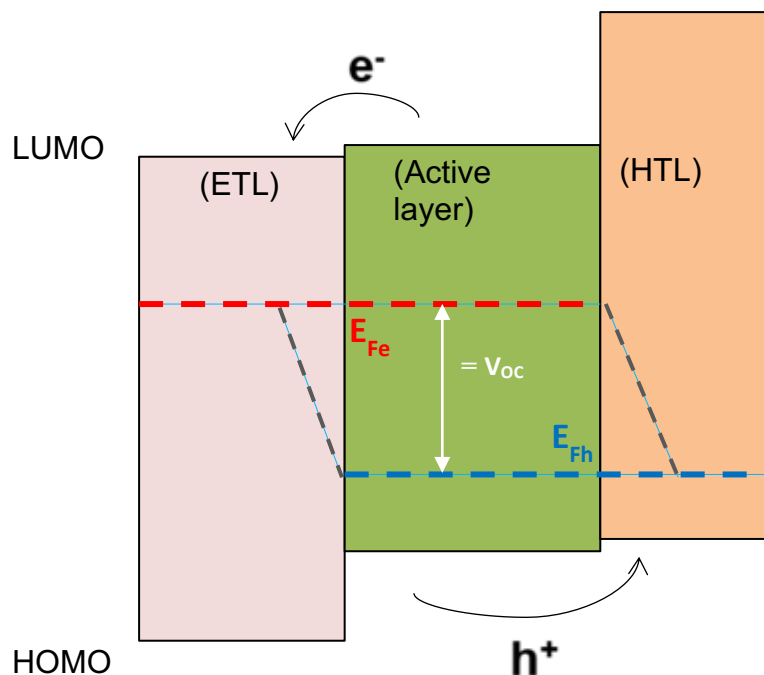


Figure 2.6 – Example of quasi-Fermi level band alignment between active layer and charge transport layers, showing how this relates to open-circuit voltage (V_{oc}). The direction of charge carrier flow is shown.

Upon photoexcitation of electrons in the active layer, the charge carriers are still bound by Coulomb forces in an excitonic state, with the electron excited from a ground (S_0) singlet state, to an excited (S_1) singlet state, leaving behind a hole in the S_0 state, as shown in Figure 2.5 and in the Jablonski diagram in Figure 2.9. These electron-hole pairs that are produced via photoexcitation are known as excitons. The excitons typically formed in organic materials are known as Frenkel excitons, in contrast to Wannier-Mott excitons that are typically formed in inorganics [90,91]. Frenkel excitons describe those local to the same molecule after photon absorption. These are more tightly bound with a much smaller radius, comparable to the interatomic distance, resulting in higher binding energies typically larger than 0.5 eV [92]. Contrastingly, Wannier-Mott

excitons are highly delocalised, often across many molecules in a molecular solid. These excitons have a much lower binding energy, sometimes lower than the thermal energy ($k_B T$) at room temperature, and as such they readily dissociate at room temperature. It is also important to note that excitons can be generated between two adjacent molecules, where the hole and electron each occupy molecules across the donor/acceptor interface. This is different to a Wannier-Mott exciton and in this case is known as a charge-transfer (CT) exciton.

In this work we will now exclusively consider generation of Frenkel and CT excitons. After forming a Frenkel exciton, the exciton will diffuse to the donor/acceptor (D/A) interface due to an electron concentration gradient [80, 93-95]. The charge carriers seek to reach a state where their potential energy difference is minimised and hence when the D/A interface is reached, the bound excitonic electron can lower its potential energy by transitioning into the LUMO of the acceptor material. This step can occur provided the LUMO of the acceptor material is deeper in energy than the donor S_1 state that is occupied by the excitonic electron, and that the LUMO offset, and such the electron affinity offset between the two materials is larger than the exciton binding energy, then electrons can transfer into the acceptor material LUMO. Likewise, the bound hole will transition into the donor HOMO provided this is shallower (closer to vacuum level), and that the HOMO offset and in turn ionisation energy offset is larger than the exciton binding energy.

Making this transition of the electron to the lower energy LUMO states of the acceptor material results in the delocalisation of the Frenkel exciton across the interface between the two molecules and forms a CT exciton. This CT exciton has a lower binding energy than the localised Frenkel exciton, and as a result, the bound charges can now more easily separate [80,93,95]. The complete dissociation of charge carriers bound

within the CT excitonic states into charge separated (CS) states is then thought to be thermally activated and built-in field dependent, i.e. helped by the electric field produced by the asymmetrical work functions of the electrodes in the OPV stack [48]. The exact mechanisms of this complete dissociation from CT to CS states is still a matter of controversial discussion, and for a more detailed exploration of CT state physics, please see the thesis of Anna Jungbluth [93]. This complete dissociation competes with the relaxation of the CT state and recombination of the charge carriers, as discussed further around the topic of the Jablonski diagram (Figure 2.9). This process of exciton generation and diffusion is depicted in Figure 2.7, displaying the heterojunction energy levels, the diffusion of the electron-hole pair to the D/A interface, and the dissociation steps as just described.

Following complete dissociation, free charge carriers are able to travel to the active layer/charge transport layer interface provided the gradient of the quasi-Fermi levels is such that they can follow the direction of the built-in potential. This propels the charge carriers to their respective electrodes which occurs via an energy level cascade, as shown simply in Figure 2.8 [96]. Here we see that the free holes correspondingly move from the donor HOMO states directly into the HOMO states in the HTL. At the electrodes, the potential energy difference between the two charge carriers is at its lowest in the circuit. This figure also exemplifies the diode behaviour of an OPV device, as charge carriers readily flow in one direction with no reverse current exhibited.

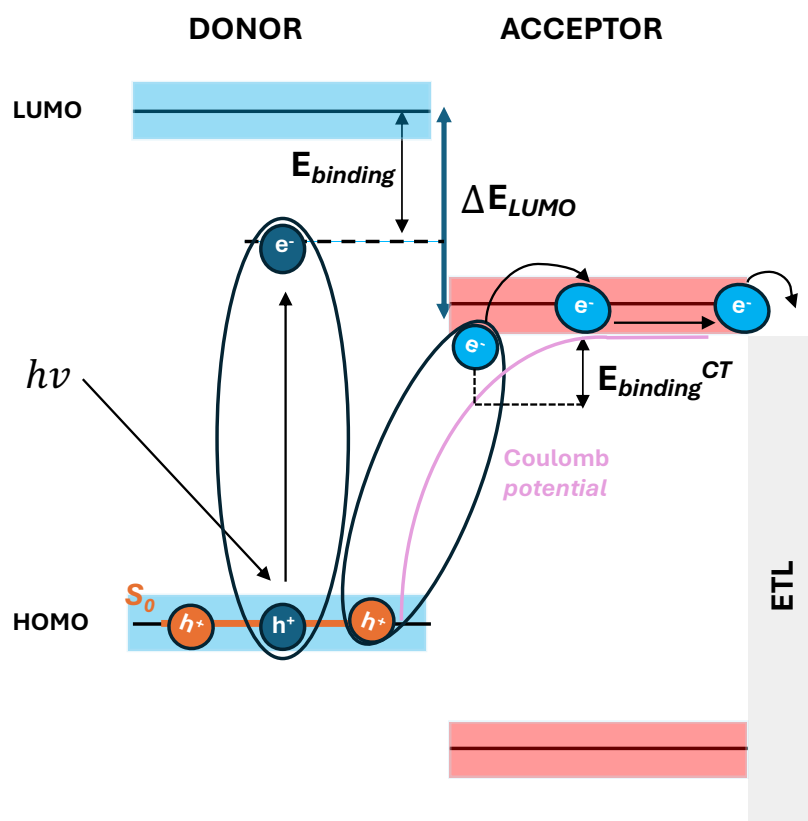


Figure 2.7 – Depicts the formation of a Frenkel exciton with photoexcitation and the necessary lowest occupied molecular orbital (LUMO) offset between the donor and acceptor molecule for the Frenkel exciton to move into the acceptor and dissociate into free charge carriers. Inspired by and adapted from Figure 3.11 in Wolfgang Tress’ thesis and book [80,95].

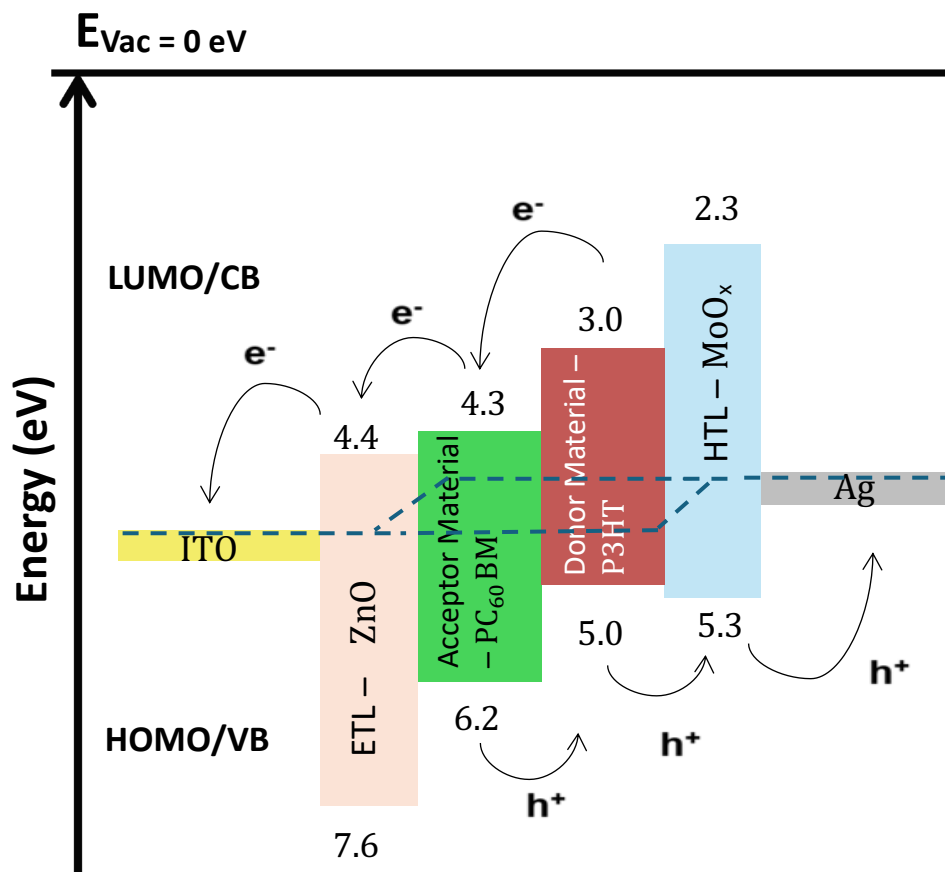


Figure 2.8 - Energy level diagram of a typical OPV device stack, with an inverted architecture and a type-II heterojunction [97,98]. The gradients of the quasi-Fermi levels are shown by the dotted lines. The charge carrier transport from layer to layer in the direction of the built-in potential created by use of electrodes with asymmetric work functions. HOMO and LUMO energy values for separately measured films of ITO, ZnO, PCBM, P3HT and Ag have been extracted from [97], while the values MoO_x have been taken from [98]. In this case, a zero-energy reference of the vacuum energy level is used. Figure adapted from my Master's thesis (2020) [96]. Length scales are estimated but not accurate.

The Jablonski diagram, see Figure 2.9, is named after the Polish physicist Aleksander Jabłoński from his work in 1933 and 1935 [99-101]. It is a prominent and excellent depiction of the possible transitions between energy states in semiconductor

materials, with solid horizontal lines representing transitions between ground and excited states and dashed horizontal lines representing vibrational manifolds, i.e. states in which the electron can drop too via emission of a phonon. The diagram outlines radiative (solid arrows) and non-radiative (dotted arrows) transitions, highlighting where either a photon will be emitted, or vibrational losses occur via phonons or heat transfer respectively. The spin-forbidden transitions are also highlighted (dashed arrows). Singlet states are labelled S_0 , S_1 , up to S_n , and the triple states shown are labelled as T_1 . Once electrons have been excited from ground state (S_0) to an excited singlet state, they will land in one of the vibrational manifold states, or they can be directly excited into a CT state. The rate of excitation of charge carriers into these states is G_S and G_{CT} respectively. Exciton transfer from an excited singlet state to a charge transfer state occurs via a hole or electron transfer at a rate of κ_{CT} . Thermal relaxations of excitonic states, also known as internal conversion, happen at rate κ_{IC} . The rate of radiative decay of singlet states is labelled as $\kappa_{S,rad}$ while the rate of triplet state decay, which is a non-radiative process, is $\kappa_{T,nr}$. The spin-forbidden singlet-triplet transitions are only possible due to spin-orbit coupling and occur via a process called inter-system crossing (ISC) [93,95], at rate κ_{ISC} . This is a non-radiative transition, along with back charge transfer, where CT state will transfer back to a triplet state at a rate κ_{BCT} . The CT state can also radiatively decay at rate $\kappa_{CT,rad}$ or non-radiatively at rate $\kappa_{CT,nr}$. Charge carriers in CT states can dissociate into the CS state at a rate of κ_{diss} , but this process competes with the decay processes. When charge carriers decay, they can recombine. This recombination can be either geminate, describing recombination processes involving an electron-hole pair produced from a single photon event, or non-geminate, involving electrons or holes from differing excitonic pairs. Once in the CS state, charge carriers can also reform CT complexes non-geminately.

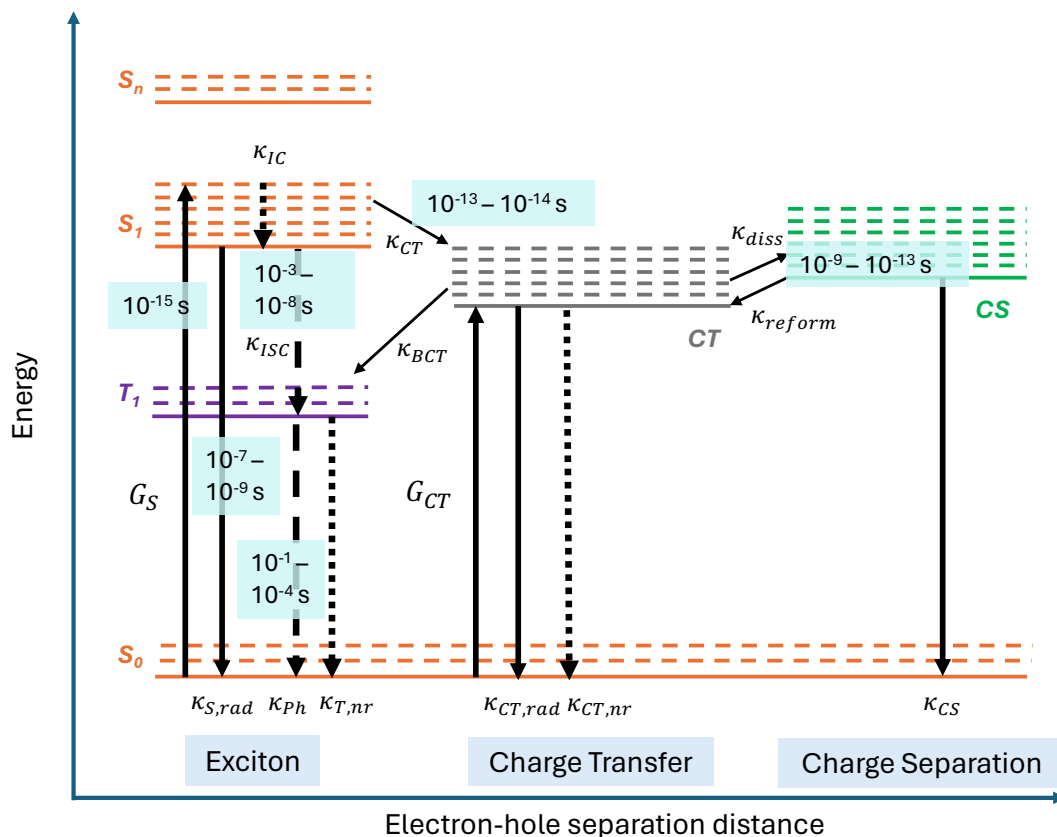


Figure 2.9 – Jablonski diagram. Depicts singlet (S_n) and triplet (T_n) states. Solid horizontal lines represent transitions between ground and excited states and dashed horizontal lines represent vibrational manifolds. Radiative transitions (solid horizontal lines), non-radiative (dotted arrows) transitions, non-possible, spin-forbidden transitions are also highlighted (dashed arrows) are also depicted. CT and CS represent charge transfer and charge separated states respectively. Charge carrier excitation rates are described by G_S and G_{CT} respectively, while the rates of other charge transfer and decay processes are described by κ_x , where x is the respective process taking place. The blue boxes contain values for the typical lifetimes of each process detailed. Timescales for the rates are taken from [80,93,102,103]. An adaption on Figure by Vandewal, 2014 [104], with inspiration from Figure 2.10 by Anna Jungbluth, 2022 [93].

This diagram can be referred to as a comprehensive picture of the mechanisms of photoexcited charge carriers within a semiconductor and a complete photoactive layer.

2.1.3 Intrinsic and doped interfaces

Here we can begin to consider interface interactions between layers, and to keep specific to the work in this thesis, we will focus on interface interactions at the electron transport layer interfaces and the use of n-type dopants. In this work, organic thin film ETLs are predominantly deposited onto ITO substrates. For this reason, it is important to understand the interactions at the interface between organic molecules and metals or highly conductive metal oxide layers. Furthermore, once an ETL is established and is to be used within a device stack, the active layer will then be processed atop it, therefore an understanding of organic/organic interfacial mechanisms is also highly useful. In intrinsic organic semiconductors the concentration of free charge carriers is very low, for example in intrinsic Buckminsterfullerene (C60) is $4.2 \times 10^{14} \text{ cm}^{-3}$, and upon doping this can typically rise to values in the range of around 10^{18} cm^{-3} to 10^{20} cm^{-3} , for weakly and strongly doped samples respectively [84]. The first part of this section will focus on the interface energetics and interactions for intrinsic organic thin ETLs, while the interactions at the interfaces involving doped organic ETLs, with higher charge carrier concentrations, will be discussed successively to this.

We will start this section with an explanation of p-n junctions in classical semiconductors, as this is a great reference point from which the theory on organic semiconductor interfaces can be explained.

p-n and p-i-n junctions

In a typical p-n junction we observe the coming together of a p-type semiconductor and an n-type semiconductor. Before bringing these two components together, we see a step function across the energy levels and upon combining these two materials, due to a

gradient in the electron concentration and a potential energy difference across the material interface, electrons diffuse from the n-type material into the p-type material, leaving positively charged ions in the n-type region. The flowing of charge carriers between the two materials results in Fermi level alignment, as shown in Figure 2.10. Similarly, holes at the interface diffuse from the p-type material into the n-type material, leaving behind negatively charged ions. The accumulation of these ions creates charged regions in which charge carriers are depleted. This region is aptly named the depletion region, and has a width, ω . The build-up of ionised species on either side of the junction generates an electric field, from which a built-in potential voltage (V_{bi}) is generated, that opposes the diffusion of both holes and electrons, acting as an opposing electrical force to the flow of charge carriers. The built-in voltage can be described as the difference in work functions between the two materials (equation 2.2). We also exhibit bending of the energy levels across this depletion region, a product of the electric field produced from the build-up of ionised species. The width of the depletion region (ω) is related to the built-in voltage, the dielectric constant of the material (ϵ), the number of ionised acceptors (N_{A-}) and donors (N_{D+}) in each of the materials and the charge of the electron (q), by equation 2.3.

$$V_{bi} = W_{F_{p+}} - W_{F_{n-}} \quad (2.2)$$

$$\omega = \sqrt{V_{bi} \left(\frac{N_{A-} + N_{D+}}{N_{A-} N_{D+}} \right) \frac{2\epsilon}{q}} \quad (2.3)$$

Therefore, depending on the doping concentration of the semiconductor, the width of the depletion region can be modified. With a large built-in potential, charge carriers

will not be able to flow in the forward direction, but with application of a forward bias voltage, the built-in potential can be reduced. With very high doping concentrations the depletion width becomes very narrow, the electrons can tunnel from the n-type layer, into the more p-type layer. This means the diode is no longer blocking charge flow in the reverse direction. It is because of this that in some semiconductor devices, an intrinsic layer is introduced between the two doped layers, across which the built-in voltage drops, resulting in a wider depletion width, reducing potential charge carrier recombination at the interface. In this case, this is known as a p-i-n junction.

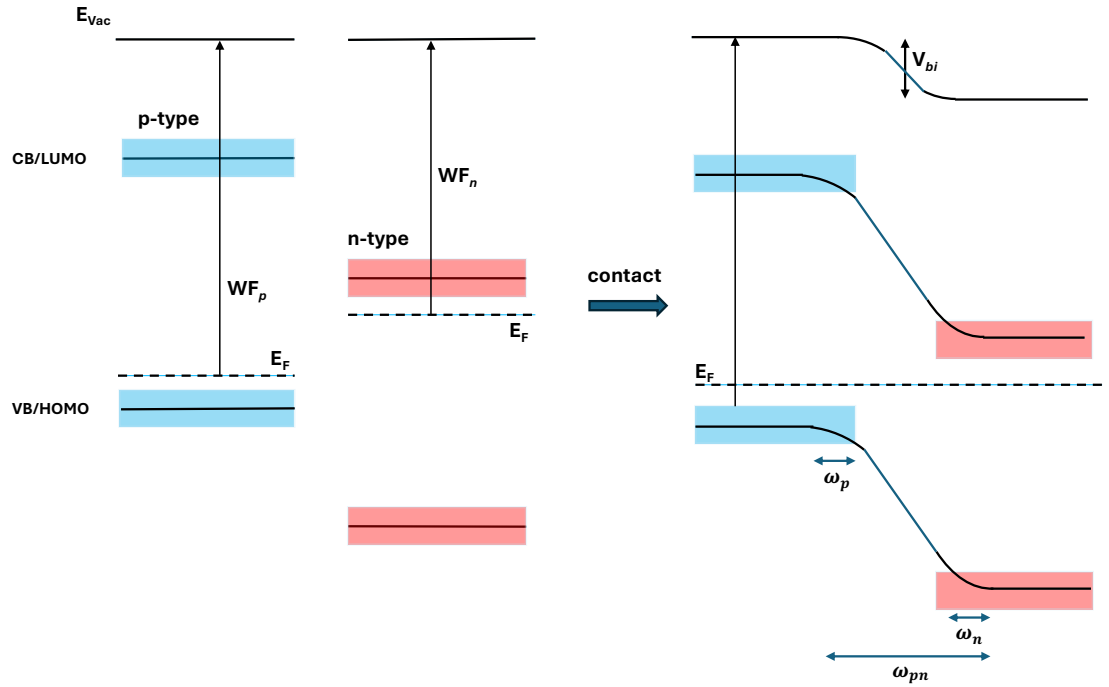


Figure 2.10 – p-n junction with and without contact, showing Fermi level alignment in two different semiconductor materials. The depletion width contributions from the p- and n- type materials are described by ω_p and ω_n respectively and the combined depletion width is ω_{pn} . A general example of the work functions of the materials (WF_n or p) are highlighted, as are the approximated Fermi levels. V_{bi} is the built-in potential across the junction. E_{vac} is the vacuum energy.

In the case of intrinsic materials such as our organic semiconductors that have a much lower concentration of free charge carriers, we typically do not observe the formation of a depletion region as charge carriers cannot flow between the two materials due to the greater energy needed at operating temperatures, to free them from their bound ground states. This means that for typical layer thicknesses the Fermi level is not aligned. With that in mind, we turn our attention to interfaces involving intrinsic organic materials, as an example of where this alternative behaviour exists.

Metal (or highly conductive metal oxide) / intrinsic organic interfaces

At the interface between a metal (or highly conductive metal oxide, e.g. ITO with $10\sim 15\ \Omega/sq$ sheet resistance [105], $\sigma = \sim 10^3 - 10^4\ \text{S/m}$ [106]) substrate and a thin film (order of 10-100 nms) of intrinsic organic semiconductor, we typically do not expect a significant exchange of charge carriers between the semiconductor and the metal, due to the lack of free electrons available in the organic (intrinsic charge carrier concentration of $\sim 10^{15}\ \text{cm}^{-3}$), and the misaligned Fermi levels. In this case, the depletion region is extremely wide and well beyond the layer thickness in organic solar cell devices ($< 200\text{nm}$), for example in intrinsic C60 on a clean metal substrate (Cu, Ag or Au), the depletion region is in the region of $\sim 400\text{-}500\ \text{nm}$ [107].

Now considering the configuration of energy levels at a metal and intrinsic organic film interface; we do not expect vacuum level alignment due to the formation of interface dipoles that occur in the first few nm between the materials. This is particularly prevalent in the case of evaporated organic monolayers on high work function metals and metal oxides, such as gold (5.1 eV), silver (4.26 eV) [107,108] or ITO (typically reported to be between 4.4 - 4.8 eV) [109]. There are a variety of possible origins of such interface dipoles; ion formation at the interface as a product of electron transfer, a

chemical reaction between the organic molecule and the metal is also possible, which can result in electronic distribution rearrangement. Similarly, if interface states are already present on the metal these can act as a buffer to charge carriers at the interface between the two materials. Furthermore, charge carriers at the interface can also rearrange and be pushed back into the metal surface more deeply in what is known as a ‘pillow’ or ‘push-back’ effect, a consequence of organic molecules reducing the electronic tailing of the metal into the vacuum [84].

If the substrate does not have to have a high work function, this effect can be negated by passivating the surface of the metal. In some cases, this is as simple as exposing the surface to air. More recently, passivating agents such as self-assembled monolayers (SAMs) have been used to alter the work function of ITO substrates for more compatible substrate surface energies for subsequent layer deposition and improved energetic alignment throughout the device stack [110-115]. Another example of passivation, again commonly used to alter the surface energy of ITO substrates is a cleaning procedure involving the use of 2-propanol (IPA) or ethanol, covering the sample with hydrocarbons, & UV-Ozone, oxidising the surface of the ITO and changing its work function [116,117]. This reduces the ionisation energy of a clean metal or metal oxide surface, reducing the pushback effect.

This section focuses purely on organic materials deposited onto metals, while the interface interactions that occur when metals are thermally deposited onto organic layers, as is often the case in solar cell applications, are more complicated, due to the thermal energy the metals carry leading to a mixing of the metal and organic materials at the interface. This goes beyond the scope of this thesis as we are concerned with the physics involved in the ETL and those sandwiching it within an inverted stack. For more on this, see for example Chapter 2.3.4 from the PhD thesis of Dr. Selina Olthof [84].

Intrinsic organic / organic interfaces

The intermolecular forces that exist between the organic molecules are weak Van-der-Waals forces, and at undoped organic/organic interfaces, these intermolecular forces are not strong enough to result in any significant interactions or charge transfer between molecules at the interface. Therefore, between two organic layers we typically expect vacuum level alignment [84,118], and in these cases, differences in the IE and EA of the two materials can provide us with estimations for their HOMO and LUMO offsets. Only in the case of organic/organic interfaces with extreme HOMO and LUMO offsets a partial charge transfer can take place, in particular if the EA of one material is larger than the ionisation energy of the other component, which is the case for some molecular dopants, or more generally if two materials with non-overlapping fundamental gaps are in contact [84,119-121]. In this case a charge transfer is necessary, leading to an interface dipole, in order for the Fermi level to be positioned within the two material's fundamental gaps. In these cases, we would also exhibit energy level bending of the HOMO and LUMO states at the interface between the two materials.

Doped organic interfaces with metals and organics

Upon doping, organic and inorganic semiconductors behave similarly. By doping the organic material, higher densities of free charge carriers ($\geq 10^{18} \text{ cm}^{-3}$ can be achieved) are reached and conductivity increases considerably (see chapter 3.2 for an example with PCBM), resulting in a significantly reduced depletion width that can now be on the order of a few nanometres. In the case of most doped organic / doped organic interfaces, the materials will behave as a p-n junction as described above, and in the case of doped organic / intrinsic organic, this will follow the example of the p-i or i-n interfaces from the p-i-n junction, depending on the respective type of doping of the organic.

In the case of a metal / doped organic interface, taking the example of an n-doped organic semiconductor, the mobile electrons flow from the organic into the metal, provided the electron affinity of the organic is lower than that of the metal. The p-side is in this case the metal, which has an infinitesimal depletion region due to the vast number of free charge carriers therefore no potential drops on the metal side. This type of contact is known as a ‘Schottky contact’ (see Figure 2.11)., in which current preferably flows in one direction, following the direction of the built-in potential, and the current will be asymmetrical if the polarity of an applied bias voltage is changed, i.e. exhibits diode behaviour. The built-in voltage can now be described as in equation 2.4, taking account of an additional interface dipole (Δ) that may be present and result in a small charge carrier injection barrier (Φ). Furthermore, the depletion width can be calculated from equation 2.5. Doping the organic semiconductor further will decrease the width of the depletion region and induce a more ohmic style contact.

$$V_{bi} = WF_{organic} - WF_{metal} \quad (2.4)$$

$$\omega = \sqrt{\frac{2\epsilon\epsilon_0 V_{bi}}{q^2 N_{D+}}} \quad (2.5)$$

We will discuss chemical doping of organic semiconductors and how it works to increase the number of free charge carriers in organic semiconductor thin films, in chapter 3.2.

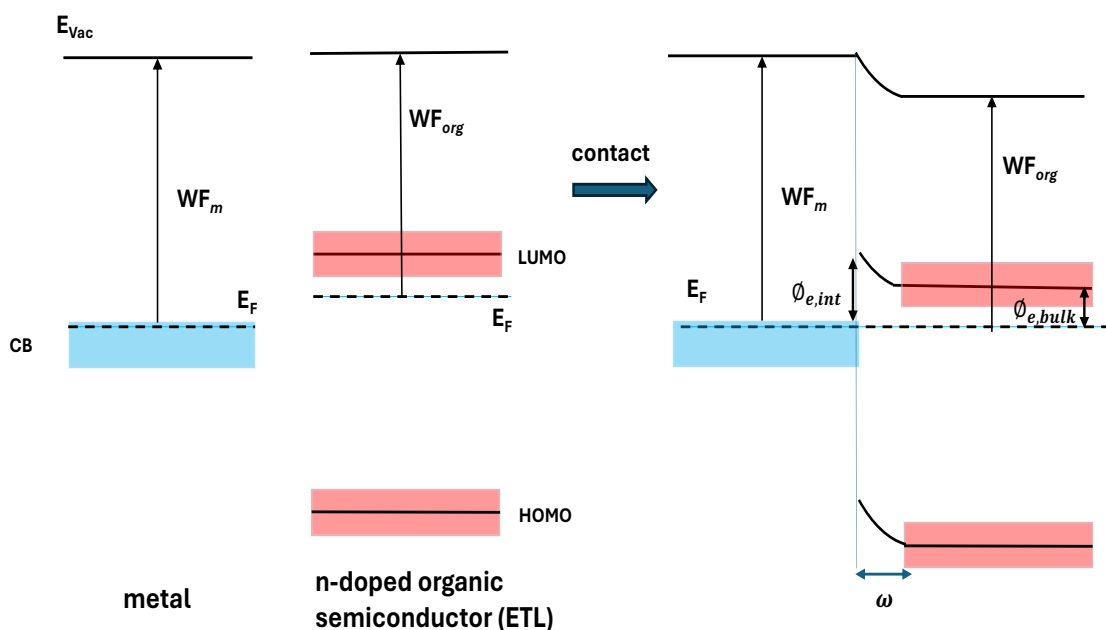


Figure 2.11 – General schematic depicting the formation of a Schottky contact at the interface between a metal and n-doped organic semiconductor film upon contact. ϕ represents an electron injection barrier.

2.1.4 Morphology

The morphology of each layer within the device stack should be considered, as morphological features can have a key role in determining device performance. Structural variations, i.e. crystallinity and orientation of molecules in each layer of the device stack, can influence the optoelectronic properties and processes occurring in a thin film. Additionally, the microstructural variations will have an influence on final film formation and large-scale morphology, including surface properties at the interface, which not only affects electrical properties but can affect how subsequent layers deposit and grow, leading to effects on charge transport through the stack, which we will now explore.

When thinking about morphology and microstructure in organic solar cells we must consider a broad range of length scales, with local molecular interactions and packing taking place on the order of angstroms and even a sub-angstrom scale, and large-scale order extending across centimetres. The optoelectronic properties of organic semiconductors arise from the conjugated bonding structure of the molecules, taking place on a which is particularly present in fused ring small molecules such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and other fullerene derivatives [122]. The small molecules close together interact with one another via weak intermolecular Van-der-Waals forces, holding the material together. In order to tune the films optoelectronic properties, such as local charge transport within the film and absorption, the molecular packing through the film (all on a small scale of up to a few nanometres) can be controlled to some degree by selection and tuning of molecules and their structure within the thin film. However, changes on this small-scale often extend across the film, influencing the crystalline order of the film and the roughness of the film surfaces, and ultimately affecting the size of crystalline grains throughout the film up to entire crystalline domain sizes, and even phase segregation that can take place on the order of micrometres [122].

On the order of angstroms to around ten nanometres, we can consider the molecular chemistry, local molecular packing and defects within a thin film. The chemistry and ordering of molecules, as previously discussed in some detail in 2.1.2., influences the energetics of the system and the potential for the material to generate free charge carriers through orbital hybridisation and electron delocalization. The positioning of energy levels of a thin film determines properties such as its absorption spectrum, while the respective alignment of these levels as part of the complete device stack determine the potential for charge carrier extraction. These properties root from

the molecular scale and the structure of the molecules that make up these thin films, such as size, rigidity, side group solubility and interactions, governing the local packing of the molecules throughout the film. Some local scale molecular ordering is necessary for high charge carrier mobilities, to allow for adequate transport of carriers. Organic materials are often less ordered than inorganic semiconductors, and even poly- or semicrystalline organic materials include amorphous or poorly ordered regions. It is common for clusters of small molecules or polymers to organise into more highly ordered segments via intermolecular interaction, while other areas of a thin film exist in more disorder. Repeating units of a polymer than align in the planes of their conjugated backbones are a good example of this segmented order, which results in efficient pi-orbital overlap [122]. This is also an example of what might be considered aggregation but not quite crystallite formation. Throughout these ordered regions, defects such as impurities—degraded or byproduct molecules, or faults in the molecular stacking, can occur and alter the properties of the material, often introducing trap states into the optical gap or providing a scattering site for charge carriers. Where defect density is high, changes in the spacing and tilt of neighbouring molecules might disrupt the alignment and interaction between molecular side groups and consequently disorder can arise. This is known as static disorder as it remains fixed and independent of ambient conditions.

The size and structure of crystalline regions and their interfacial surface areas contribute to the ability for charge transport to readily occur across thin films, necessary for solar devices to function efficiently. Charge carriers transport is more efficient across pathways through more highly ordered crystalline regions than through disordered regions, and such ordering can be beneficial to charge carrier mobility, particularly important when significant distances (tens to hundreds of nanometres) must be travelled such as in the active layer, where Frenkel excitons must diffuse across molecules to first

reach the D/A interface, and then dissociated free charge carriers must travel further to their respective transport layer interfaces. The molecular ordering making up the transport layers is somewhat less important than in the active layer, as these films are typically very thin, on the order of a few to a few tens of nanometres, and such charge carriers have much less trouble traversing these layers provided crystalline ordering does not entirely inhibit vertical travel, which is highly unlikely.

The crystalline ordering is not only affected by the molecular interactions but is also a product of the processing steps taken to fabricate the thin film. For example, when solution processing, the solvent used and its rate of evaporation has some influence over the speed at which crystallites form [123]; the dispersion of the molecules across the substrate is influenced by the speed at which the film is deposited, i.e. the spin-speed in the case of spin-coating [122,124]. Using additives can too affect the size of crystalline grains and film crystallinity [122], and of course, annealing the films and the conditions used to do so will have a huge influence on packing, orientation and density of crystalline grains or regions formed, as this can increase the rate of solvent evaporation and crystallite formation.

Across larger scales up to 100s of nanometres, we must consider effects such as phase segregation throughout the stack, this is particularly important in the active layer. In order for efficient exciton dissociation, exciton diffusion lengths should be on the scale of around 10 nm, meaning donor and acceptor domains of 10-20 nm [122,125]. Phases can also separate vertically due to interface energetics [126,127], which can of course affect charge transport pathways and thus charge mobility, either negatively by for example disrupting exciton dissociation due to reduced surface area between the donor and acceptor domains in the active layer, or via introduction of vertical interfaces for charge carriers, that can behave as a greater energetic barrier than if the active layer

is well mixed. Or this could have a positive effect, if not too significant a segregation, charge carriers could be produced closer to their respective electrodes and can be more readily transported in the correct direction, increasing mobility.

Finally, when considering the complete film, morphological features such as surface roughness and physical defects come into play. The roughness of a surface can affect its surface energy and wettability. A rough surface may often bind better to a solution than a smooth one, as this provides a grip for the solution to hold to and form a film [128-132]. Defects that come into play are pinholes or debris on the surface, that could lead to shunting of a device and should therefore be minimised.

The two types of stacking we are concerned with here are pi (or π - π) and lamellar stacking, as shown in Figure 2.12. Pi stacking occurs between conjugated groups on the organic molecules, while lamellar stacking typically refers to the separation of the conjugated and aliphatic moieties [133]. In the context of this thesis, it is important to consider the stacking modes available in order to understand how for different molecules this could lead to different growth modes. If molecules have a preference to stack in a certain direction, then we might see areas of a thin film that is highly oriented. This preferential ordering could also change with layer thickness, and the crystalline orientation of the domains in the films may shift with film growth, known as different growth modes. Alternatively, we may see no preference in stacking throughout the film and observe isotropic disorder of molecules.

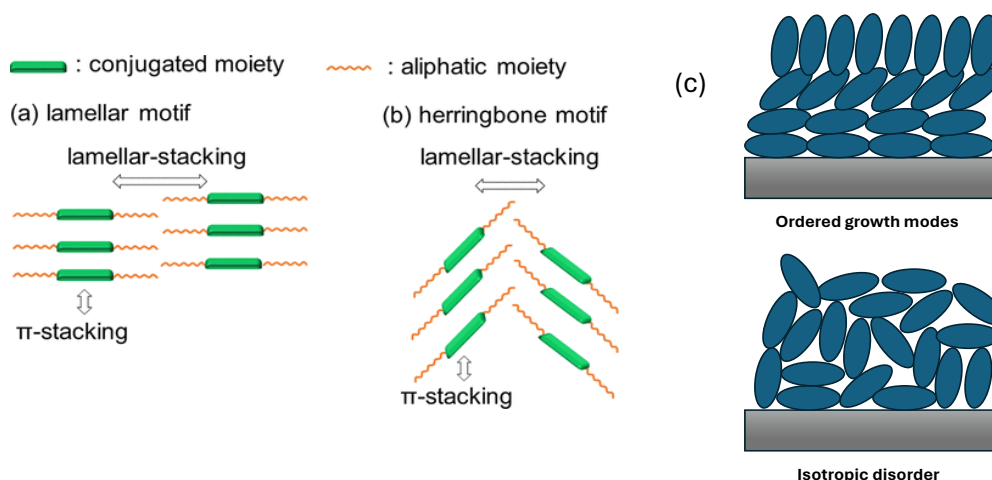


Figure 2.12 – (a) and (b) display examples of both lamellar- and π - stacking in different orientations. These parts were taken directly from Lai et. al, 2018 [133], and amended by addition of (c), following the copyright licensing usage agreement from the American Chemical Society. (c) is an example of order and orientation throughout a film and how this could change at different depths from the substrate it is deposited on, compared to isotropic disorder.

The orientation of a thin film at its interface can have an impact on how the next layer will grow onto it, which in turn can affect optoelectronic properties at the interface. As the different types of stacking, which can be probed by scattering techniques (see chapter 3.4), tell us about the orientation of our molecules throughout a film, if we observe such morphological changes, we can infer from this charge transport and energetics might vary across the film, particularly between the bulk and at the interface. To probe this, we can use other techniques such as photoelectron spectroscopy (PES) to study these optoelectronic properties.

2.1.5 Solar cell performance metrics; V_{OC} , J_{SC} , Fill Factor & PCE

When measuring the current output of solar cell device, a linearly increasing voltage can be applied and the current that is generated over the solar cell area can be measured. In the dark, a negligible current will be measured in the reverse bias direction, however if a forward bias is applied, current increases exponentially. Dark measurements are essential in understanding how the device works without the impacts of the extra photocurrents, while illuminated measurements are necessary to obtain values for the open-circuit voltage - the maximum voltage when the current flow is zero - and short-circuit current (I_{SC}) - the maximum current when applied voltage is zero, can be found. Similarly, the short-circuit current density is the current per area of the device.

In the dark, an ideal photovoltaic device follows the Shockley-diode equation (2.6);

$$J = J_{dark} \left(e^{\frac{qV}{k_B T}} - 1 \right) \quad (2.6)$$

For a device under illumination, this equation contains an extra term;

$$J = J_{dark} \left(e^{\frac{qV}{k_B T}} - 1 \right) - J_L \quad (2.7)$$

Here J is the total current density or current per area. The term J_{dark} is the current per area across the device in the dark, that can be extrapolated from a current density-voltage (JV) curve when the net value of the two opposing current components, drift and diffusion, is equal to zero. The load current J_L is the current per area or generated photocurrent measured under illumination, in the direction opposite that of the conventional

current. The term q refers to the intrinsic charge of the electron, V is the applied voltage, T the absolute temperature (Kelvin) and k_B , Boltzmann's constant.

Due to the generation of charge carriers under illumination, the current is increased which also increases the power available. An example of a JV curve produced from measuring the cell performance can be seen in Figure 2.13. This Figure will be revisited in chapter 7 when discussing device performance results. In order to take measurements under illumination, a light set to simulate the spectrum (AM1.5) and intensity of the sun (1 sun) is used.

The fill factor (FF) and power conversion efficiency, $\eta_{Efficiency}$, of the solar cell are also calculated from these two values and are defined by equations 2.8 and 2.9 respectively [60,77]. The fill factor is the ratio of the maximum electrical power generated to the product of the V_{OC} and J_{SC} , where V_{MaxP} is the voltage at the maximum power point (MPP) in a JV curve, and likewise J_{MaxP} is the current at MPP. This is a characteristic that can be described by the 'squareness' of the JV curve, as shown in Figure 2.13.

$$FF = \frac{V_{MaxP} \times J_{MaxP}}{V_{OC} \times J_{SC}} \quad (2.8)$$

The power conversion efficiency, with respect to the light source used, is ratio of the maximum electrical power generated by the device to the total incident power. Here P_{Max} is the maximum power, the point of which (MPP) can be determined from the turning point on the JV curve, and $P_{Incident}$ is the total incident power on the device.

$$\eta_{Efficiency} = \frac{P_{Max}}{P_{Incident}} \times 100\% = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}} \times 100\% \quad (2.9)$$

Correspondingly, dark measurements are recorded to obtain the injection and leakage currents. The injection current represents the amount of current injected into the device per area under forward bias at a given voltage. This is used as a measure for the serial resistance. The leakage current is the current loss escaping through any unwanted conduction paths under reverse bias at a given voltage.

Once a module has been characterised, high series resistance can be determined from low injection and J_{SC} values, meaning the current flowing through the solar cells is lower than expected, while a low shunt resistance can be deduced from high leakage currents, or reduced V_{OC} due to non-functioning parts of the module [134-136]. The series and shunt resistance of the devices can be estimated from the gradients along different regions of the graph, as shown by the lines drawn on the JV curve in Figure 2.13.

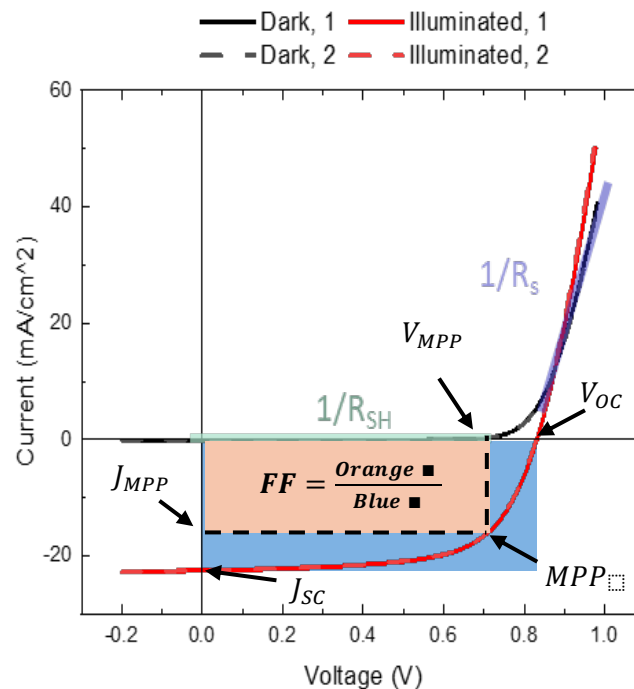


Figure 2.13 – Example current density v voltage curve for an OPV device, with lines highlighting approximations for the shunt (R_{SH}) and series (R_s) resistances. J_{SC} is the short circuit current density and V_{OC} the open-circuit voltage. The maximum

power point (MPP) is highlighted, with JMPP the current at this point and VMPP the voltage at this point. The fill factor can be calculated as the ratio between the area of the orange rectangle and the large blue rectangle.

Chapter 3

Transport layer materials, their functional characteristics, chemical doping & experimental setups

Chapter 3 discusses transport layers and the characteristics necessary for a transport layer for well-performing, device. Conventional materials, both inorganic and organic, are presented and those currently used in more state-of-the-art OPV devices and for scale-up applications. Use of fullerene-derivative materials as a transport layer with the potential to improve device stability as compared to devices using conventional metal oxides is explored. The chapter also highlights 'PCBCB' as a molecule of interest as a potentially stable ETL that has been explored in perovskite applications, with the potential to improve OPV stability when energetically and electrically tuned via the addition of n-type dopant molecules.

3.1. Transport layer materials

In order for a material to be a successful electron transport layer, it should be an n-type material, that should have high electron conductivity and be of low work function to match with the LUMO level of the photoactive layer acceptor material, with a slight offset such that its LUMO is deeper, to achieve successful electron extraction with minimal energy losses [137,138]. In addition, these materials should have good alignment with the cathode and a deeper HOMO than that of the acceptor material, to effectively suppress hole and exciton transport across the interface. In contrast, an effective HTL should be a p-type material, with high work functions to match HOMO level of the donor material in the photoactive layer, again with a slight offset such that it has a shallower HOMO, and good alignment with the anode. This should have a high hole conductivity to minimise series resistance [137] and a shallower LUMO than the donor material, to block electrons and excitons from travelling across this interface. These layers and their energy offsets also minimise charge carrier recombination at the interfaces [139]. For a visual representation of this, refer to Figures 2.6 & 2.8, in chapter 2. Furthermore, we should ensure that the transport layer material adjacent to the ITO electrode does not have an absorption range similar to that of the active layer donor material, and ideally has a wide optical gap to maximise transparency, in turn maximising absorption in the active layer and the potential for free charge carrier generation.

Both Yin, Wei & Zheng [137], and Dahiya et. al [140] provide comprehensive tables, detailing a range of electron and hole transport layers from a large variety of referenced work, in conjunction with the active layers used as part of full device stacks,

with the review from Yin, Wei & Zheng also provided the electrodes used.

3.1.1 Inorganic and metal oxide transport layers and the relationship with UV-irradiation

Typically, inorganic hole transport materials exist in the form of metal oxides. A notable inorganic hole transport material is MoO_3 , due to good optical and electronic properties [141,142], as well as stability [143]. Another commonly used hole transport material is PEDOT:PSS, which is organic and is used due to its comparable ionisation energy to ITO and clean gold [84]. However, this material has a low free charge carrier concentration and weak conductivity compared to inorganic materials, and unless a pH neutral version is used, can cause accelerated degradation due to its acidity [144]. Not only this but dependent on the formulation of PEDOT (solvent) used and the substrate to be deposited on, it often does not typically spin-coat to form uniform layers easily.

Similarly for electron transport materials, inorganic Ca and ZnO are commonly used as the ETL, thanks to their optoelectronic properties, though Ca is very readily oxidised to form CaO [145], and while ZnO has a direct optical bandgap of 3.3 eV meaning it allows around 80% of visible light to pass through into the solar cell active layer, it absorbs in the UV region [67,146-148]. The absorption of UV-light by ZnO has shown to contribute to the instability of organic materials, typically active layer materials that are processed atop the ETL. Ultraviolet light is one of the key contributors to degradation in solar cell devices with its high energy of $\sim 3\text{-}12$ eV, able to break down the carbon-carbon and carbon-hydrogen bonds in organic material. Its ability to cause photocatalysis at material interfaces by forming free radicals that can propagate through the organic thin films and breakdown polymers via scission of conjugated bonds can

lead to absorption and consequently voltage losses [149-157]. These effects are accelerated in the presence of oxygen and are particularly prevalent at the interface between active layer materials and metal oxide transport layers due to the need for UV “light-soaking” to significantly increase the conductivity of these films [158,159]. The outcome of this can be the formation of interface dipoles and unfavourable photocatalytic doping [160] of the active layer material, resulting in voltage losses [161].

Zinc oxide works as an effective transport layer due to its intrinsic n-type nature, the root of which has been a subject of debate and research. In recent studies, it appears that the unintentional incorporation of impurities such as hydrogen during growth or annealing are the cause of the n-type conductivity of ZnO, and that these impurities act as shallow donors [162]. It has been shown by means of density-functional calculations that interstitial hydrogen forms a strong bond with the oxygen in the ZnO to act as a shallow donor. As these interstitials are highly mobile and can diffuse out of ZnO samples, the stability of n-type conductivity at high temperatures has been attributed to hydrogen also acting as a substitute for oxygen in ZnO. Irradiation of ZnO films with UV-light marginally blue-shifts the bandgap of the films and increases conductivity further, with the UV-induced photocatalysis reaction decomposing carbon-based impurities present in the film [163,164]. This results in further hydrogen and carbon atoms becoming doped into the ZnO films, with the hydrogen providing further free charge carriers to the films. This increase in conductivity has also been attributed in part due to the neutralisation of acceptor states present in surface oxygen-based moieties at the grain boundaries in ZnO with holes generated when ZnO is exposed to UV-light, in turn reducing the potential barrier at the grain boundaries, allowing for improved transport of electrons and increased population of conduction band electrons [165].

These effects of UV-irradiation are only temporary, with the pre-irradiation state returning over the course of hours or days without UV-exposure [166]. The effects of UV-irradiation of the conductivity values of ZnO films have been studied further in this thesis, see Chapter 6.2.

Due to this requirement of UV light exposure, the use of materials that allow for limited UV transmission, or the use of UV filters that block that range of radiation are not feasible within this device stack as this can cause performance issues. So, with the use of metal oxide ETLs in devices, we have a situation where UV light is necessary for them to perform well, but photocatalytic activity under UV light leads to the fast decomposition of high-performance active layer materials, such as non-fullerene acceptors. In addition to this, the absorbed UV light induces oxygen desorption, that has been reported to result in shunting and increased charge carrier recombination [158,167,168]. TiO_x is another common ETL that exhibits reduced performance characteristics over time under UV-irradiation, but due to formation of an interface dipole between the ETL and the active layer, with the same effective consequence as increasing the work of the ITO substrate, reducing V_{OC} . In devices fabricated using P3HT:PC₆₀BM active layers with both these metal oxides respectively as the ETL, rapid loss of performance along with a linear loss over a longer duration and a rapid failure have been exhibited, due to photoinduced degradation. The effect causing this is known as photoinduced burn-in and results in a loss of J_{SC} , that has been attributed to increased dimerisation of PC₆₀BM in the active layer, and a loss in V_{OC} , induced by UV exposure and accelerated by the degradation mechanism taking place with the use of a ZnO ETL and the interface dipoles formed when using a TiO_x [161]. In addition, reported cross-linking of polymer chains such as PCDTBT [157], and even co-polymerisation between polymer chains and fullerenes [169], has been observed as a product of UV-irradiation

and also resulted in reduced device performance. We will discuss cross-linked and polymerised organic semiconductor materials further in 3.1.2.

Some ZnO-based (ETL), solution processed OPV, with initial PCEs of 9-12% have shown the potential for increased stabilities, maintaining 80% of their initial PCE (T_{80}) for an extrapolated lifetime of 30 years of outdoor operation, with aid from the incorporation of a SAMs layer between the ZnO and active layer [170]. While these devices and other solution processed OPV devices incorporating ZnO, with initial PCEs of ~ 8 -10%, have also shown the potential for $T_{80} > 10$ years operational lifetime [171], these lifetimes are often extrapolated through ageing tests in which ultraviolet (UV) light from the solar spectrum that is radiated onto the samples is filtered out due to its ability to cause photocatalysis at material interfaces. This filtering is done either via implementation of a blocking layer in the stack [170] and/or removal of the UV from the lamp via a filter, and sometimes through carefully controlled oxygen exposure levels [171]. From these pitfalls it is clear why alternatives are imperative to improved stable efficient solution processed solar cell devices, particularly if the best efficiencies possible are to be achieved. This is why use of materials that are less prone to interactions under UV light, or to some degree block UV light from reaching sensitive layers, are of interest and essential to improving the stability of such devices.

Solutions to the photocatalysis problems with both ZnO and TiO_x based transport layers have been trialled, such as with the application of an aluminium doped ZnO electron transport layer [159]. The doping of the ZnO layer appears to eliminate the need for the UV spectral components of the AM1.5 solar spectrum and in doing so the degradation mechanisms are greatly reduced. Another alternative is to use a SnO_2 ETL, while still a metal oxide material, it is less sensitive to UV irradiation due to its wide bandgap and has proven to be very stable as an ETL in OPV [172]. Definitely one viable

solution if utilized correctly, though it should be noted SnO_2 can be difficult to process consistently and has shown to have drastic layer to layer variation, leading to changes in the quantity of defects and with film morphology [173]. Various surface passivation of ZnO layers have also proven effective to remove surface defects at transport / active layer interface [174]. Moreover, devices above 15% PCE have exhibited 72% of their initial performance after 10,000+ hours of ageing under specific conditions (i.e. nitrogen atmosphere), through careful selection of the electron transport layer (Ir/IrO_x) that results in an absence of photocatalysis [175]. This is an ETL of nanoparticles that can be deposited via spin-coating and proves to work well, resulting in highly stable organic solar cells with regards to resistance to temperature and solar spectrum irradiation at 1 sun intensity. However, as is the case with most of these alternatives, the methods required to obtain these metals and synthesise the material compositions required to make the alternative ETL layers comes at a cost and could prove quite expensive for large scale production of OPV. For this reason, we would like to investigate organic materials as an alternative to metal oxide ETLs, with the aim of producing devices that can compete with those comprising metal oxides, without the negative consequences of UV-radiation exposure. In addition, it is hoped that synthesis of these organic materials on a larger scale could prove to be less costly than sourcing the metals required for metal oxide transport layers and have a reduced carbon footprint as compared to that from metal extraction.

3.1.2. Organic ETL materials (polymerisable fullerene-derivatives)

Many organic materials are richly abundant on Earth and readily synthesisable thanks to their predominantly hydrocarbon composition. As such, some organic semiconductors can offer as a cheaper alternative ETL material to metal oxides, that

rely heavily on less abundant and more costly materials such as zinc, titanium or iridium. Fullerene-derivative semiconductors are chemically stable due to their maximum entropy geometry [176] and quite unreactive with strong covalent bonds existing between the carbon atoms [177], allowing for their longevity, particularly if protected from the atmosphere and elements via encapsulation methods, as are commonly used for solar cell devices [178-181]. In addition, thin films of organic material can be deposited that are semi-transparent. While many metal oxides are fully transparent with regards to interactions with light from the visible spectrum, organic materials may absorb a fraction of the light in this range. Nevertheless, provided that the transparency is high enough, in addition to using an active layer that does not significantly overlap with the absorption of the transport layer, organic semiconductors can still prove to be a robust and cost-effective option. Even with these beneficial factors in mind, organic materials still come under question when considering their conductivity, however, using an effective dopant to increase the conductivity of the films tune the energetics of the material allows it to reach the conductivities needed to be used as a transport layer in photovoltaic devices. The minimum theoretical conductivity required for an ETL of known thickness, for a solar cell to produce a current of 20 mA/cm², with an ~1% voltage drop of 10 mV across the device (presuming a V_{oc} of $\sim 0.8V$), can be calculated according to Kirchoff's circuit laws [182]. This considers the contributing series resistance (R) of the layer, which can be calculated and converted into a conductivity using the following equations (3.1 - 3.4), where l is the thickness of the film (we will use 25 nm based on what we expect for the film thickness of PCBCB films and an upper limit of the ETL to be), A is the vertical cross-sectional area of the film (1 cm²), and ρ is the resistivity of the film.

Using the above parameters, the necessary conductivity of the ETL to achieve these device performance characteristics is calculated to be $\sim 1 \times 10^{-4}$ S/m. All transport layer materials used must therefore achieve conductivities greater than or equal to this value to achieve typical device performance characteristics.

$$\frac{V}{I} = R \quad (3.1)$$

$$R = \frac{l}{A} \rho \quad (3.2)$$

$$\frac{1}{\rho} = \sigma \quad (3.3)$$

$$\therefore \sigma = \frac{\left(\frac{l}{A}\right)}{R} \quad (3.4)$$

Organic polymerisable fullerene-derivatives, such as PCBM, have proven effective solution processible ETLs or ETL-interlayer components within both organic [88,183-189] and perovskite solar cell device stacks [190-205], in which many have exhibited improved device stabilities with use of cross-linked and polymerised materials. The thesis of Ivan Ramirez [206] is a good summary of their use in both technologies. To keep within the scope of this thesis, we will now focus on those used within OPV devices. The polymerisation and/or cross-linking of these materials in thin films improves the insolubility of the films, allowing for solution-processing atop them. This work by Ma et al. [207] gives an extensive review of examples of cross-linkable organic semiconductors that have been used as electron transport layers, including those outside the category of fullerene-derivative materials, e.g. polymers. Interestingly, these

cross-linkable materials have been rarely employed in organic systems with an NFA-based active layer [208], opening an avenue for novel research in this area which this thesis begins to explore (see chapters 6 & 7).

3.1.3 Phenyl-C61-butyric acid benzocyclobutene ester (PCBCB)

Let us now focus on the specific fullerene-derivative molecule, phenyl-C61-butyric acid benzocyclobutene ester (PCBCB), as this is the material that is investigated throughout the primary work in this thesis. This molecule resembles quite closely that of the more commonly known fullerene derivative PCBM, simply differing by a single benzocyclobutene group in place of the pre-existing the methyl group. This molecule was synthesised by the Marder group when at Georgia Tech (now based at CU Boulder) [209] and has been shown to be soluble in chlorine-based solvents, such as 1,2-dichlorobenzene.

While this material has been studied in previous literature, it has so far only been used as an acceptor component in OPV and as an ETL in perovskite solar cells. This material was studied in more detail, again in perovskite devices, in the thesis of Ivan Ramirez [206], in which it was concluded that it could compete and outperform C60 as an ETL. Its use has resulted in improved power output and V_{oc} , both maximum and stabilised, along with reduced surface recombination and increased stability, when compared to C60 [192]. Devices created from this material have also resulted in good stability [190]. From these perovskite results and considering the material's ability to oligomerise and remain robust and intact when processed upon, we understand that PCBCB can be realised as an ETL particularly in an inverted OPV configuration, resulting in greater stability than the conventionally used zinc oxide transport layer, provided its conductivity and energetics are tuned with doping. This work aims to

explore this hypothesis, to determine the optimal processing conditions for a PCBCB ETL via solution processing, and to confirm and adapt accordingly the annealing conditions necessary for a complete and insoluble film with good morphology and surface properties for further solution processing of the active layer.

PCBCB proves to be particularly interesting thanks to its ability to oligomerise under the right conditions—enabling fabrication of a fully insoluble film upon which one can continue with solution processing without solvent mixing and removal of the now robust layer. Through the process of thermal annealing, $PCBCB \rightarrow (PCBCB)_n$, where $n = 2$ dimers are the major product, and this process has been shown to occur after annealing for 10 minutes at around 190 - 200°C [206,210]. It is proposed that this process happens via two possible pathways, as shown in Figure 3.1 [211], and has been reported to lead to cross-linking across the films [210].

As discussed in 3.1.1 when considering UV-irradiation, polymerisation or cross-linking can result in reduced device performances [157,169], due to effects like photoinduced burn-in when used as active layer components [161]. However, it should be noted that in some examples cross-linking can also result in reduced phase segregation of organic molecules within the thin films and increased device stability [212,213]. The stability of these materials could be exploited by implementation as a transport layer to further improve overall device stability.

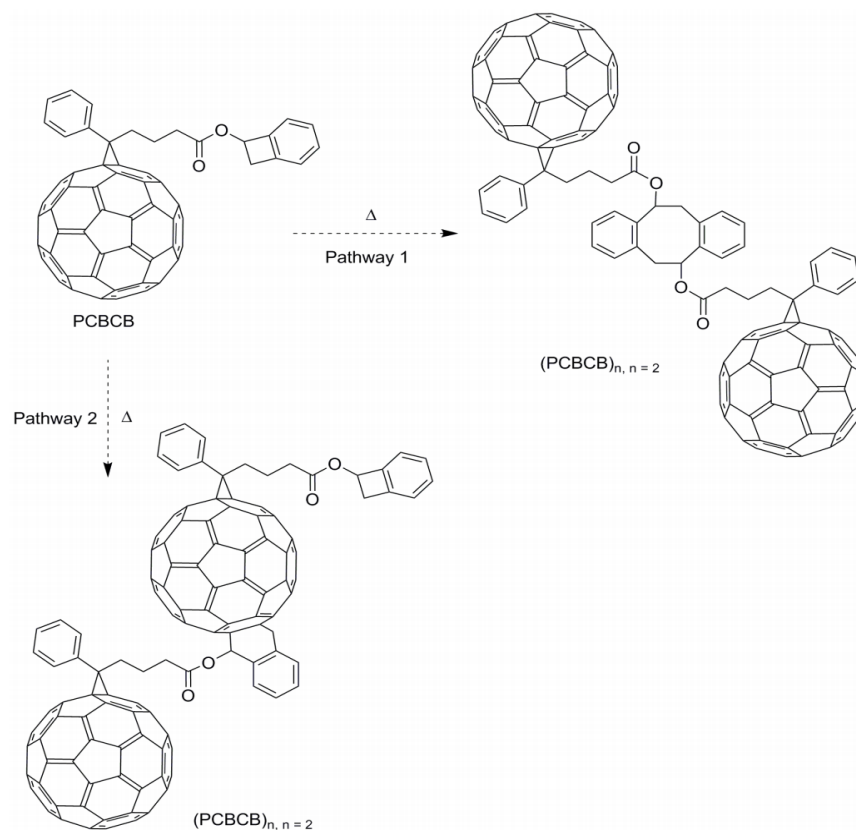


Figure 3.1 – Dimerisation pathways of phenyl-C₆₁-butyric acid benzocyclobutene ester (PCBCB) monomers into $(PCBCB)_{n=2}$ dimer molecules, a process that takes place with thermal annealing at 200°C, rendering thin films insoluble. Reprinted with permission from Deb, N. et al. [211], copyright (2015), Royal Society of Chemistry.

Focusing on a PCBCB ETL in OPV aims to motivate and advocate for more attention to be spent on discovering and investigating new transport layer materials, particularly those that appear to exhibit good stability under solar irradiation. This is an aspect of the OPV device stack that receives a lot less attention than the active layer materials. This work also allows us to dive deeper into the effects of processing on thin film formation and in turn on device performance. While we currently focus on spin-coating methods to fabricate the thin films studied in this work, a good understanding

of the processing conditions can help provide a route to scale-up of these and similar materials. Furthermore, the effects of processing and doping of PCBCB thin film energetics is explored in detail via characterisation techniques such as photoelectron spectroscopy (chapters 5 & 6). Sticking with an ETL material that is expected to be stable and rather inert also provides a good platform on which to investigate the efficacy of different dopant molecules on a single system.

3.2. Chemical doping of organic semiconductors

Let us first consider extrinsic doping of a conventional single crystalline inorganic material, such as silicon. Introduction of impurities within the lattice structure can create defect states close to the band edges, shifting the Fermi level [214,215], and in some systems can change the material's bandgap and optoelectronic properties to some degree [216]. In the case of n-doping of an inorganic semiconductor, the introduction of these gap states, or otherwise known as donor energy level, close to the conduction band of the material, means that with reduced activation energy, charge carriers can be excited into the empty conduction band, in which they are delocalised and can move freely through the material.

Intrinsic organic semiconductor materials have lower free charge carrier concentrations and therefore lower conductivities than in inorganic semiconductors. Chemical doping can be used to increase the number of free charge carriers within an organic thin film, for example by transferring electrons from dopant molecules to the organic host molecule, in turn increasing the conductivity of the layer. Doping will also shift the Fermi level of the organic layer accordingly [217-220]. If the number of free electrons in the organic layer is increased by increased n-doping density,

this affects the charge distribution in the organic semiconductor layer and shifts the Fermi level towards the LUMO (and likewise towards the HOMO if the number of free holes was to be increased by p-doping). This process can allow for ohmic contact with the metal electrodes, which can be beneficial for transport layers as it can result in less voltage loss during the charge carrier transition from active layer to transport layer. There is extensive literature on the general principles of doping in organic semiconductors [217-220], with examples of both p- [221] and n- doping [222], and our focus will now turn to the specific case of n-doping of an organic semiconductor ETL.

In the case of doping an organic semiconductor in order to improve its functionality as an ETL within a solar cell device, n-type dopant molecules are added to an organic host to form a mixed matrix of host and dopant molecules across the thin film. Electrons from the dopant molecules are shared with the host material, increasing the total free electron concentration and consequently conductivity of the thin film, and shifting the Fermi energy of the ETL material to become closer to the LUMO—a desirable characteristic for improved electron transport. For this to happen, we can expect that firstly the free charge carriers must be created, which involved the formation of a charge transfer complex, a Coulomb bound state in which the donor interacts with the host, $[H^+D^-]$. This state must dissociate so that the electron can be completely free from the Coulomb force of the ionised donor molecule. Once dissociated, the electron can then hop across the matrix of molecules that makeup the organic thin film, moving through the layer as a free charge carrier.

Dissociation of the $[H^+D^-]$ complex into a free electron and an ionised donor involves appropriate energetic alignment between dopant and host, such that charge carriers can flow into the host material. In the case of an n-type dopant, for this species to interact with the intrinsic semiconductor material, the EA of the dopant must be

smaller than the host material in order for the electrons to easily ionise, and the HOMO, or in some cases singly occupied molecular orbital (SOMO), as in the case of n-type dopant N-DMBI [223], should be shallower than the LUMO of the semiconductor host, so that electrons can move readily into the host with little activation energy required, see Figure 3.2.

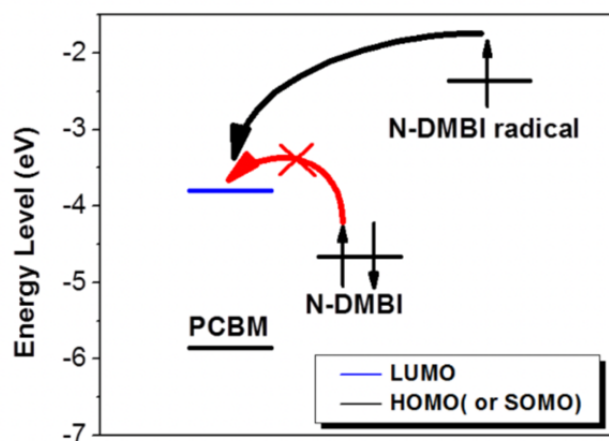


Figure 3.2 – Energy diagram of PCBM, N-DMBI and N-DMBI neutral radical, highlighting the energetic offset between the singularly occupied molecular orbital (SOMO) of the N-DMBI radical and the lowest occupied molecular orbital (LUMO) of PCBM, allowing electron transfer to PCBM. Reprinted with permission from [224], copyright (2010), American Chemical Society. Explain N-DMBI function.

In this thesis we are concerned with the doping of an organic fullerene-derivative semiconductor ETL with n-type dopants, primarily using N-DMBI and derivatives of this dopant molecule. The doping mechanisms by which this molecule works has been studied by Naab et. Al [225] and Bardagot et. Al [226], and it has been shown that this material works by forming a radical that has a singularly occupied molecular orbital (SOMO) at an energy level, in this case, above the LUMO of PCBCB. It has been shown

that by heating N-DMBI to 80°C (or via UV-irradiation), the N-DMBI undergoes thermal activation. This activation means the radical forms a cation which exhibits improved air stability [226]. This dopant can significantly increase the conductivity of organic semiconductor films, and has demonstrated its effectiveness in PCBM films, increasing conductivities by greater than four orders of magnitude [223], from 8.1×10^{-6} S/m to , 1.9×10^{-1} S/m.

Increasing the electron density via n-doping serves to increase the electronic conductivity of the material, in accordance with equation 3.5, where q is the charge of the electron, n_e is the electron carrier density in the material, and μ_e is the electron mobility in the material.

$$\sigma = q \cdot n_e \cdot \mu_e \quad (3.5)$$

Typical doping concentrations in organic semiconductor layers are in the range of 1 to 10 dopant molecules per 100 matrix molecules, a number that is dependent on the doping efficiency (change in the number of free charge carriers per dopant atom added) of the system [84]. The amount of doping of a system can be quantified by mole percent (mol%), as is the case with all doped systems within this thesis. This is the relative number of dopant molecules, n_D , to the total number of molecules, where n_H is the number of host molecules (equation 3.6). The effects of doping the organic ETL material were primarily investigated using conductivity measurements, as explained in chapter 3.4, and photoelectron spectroscopy techniques (UPS & XPS) as described in chapter 4.

$$mol\% = \frac{n_D}{n_D + n_H} \times 10 \quad (3.6)$$

3.3. Sample preparation

In this section we will describe the fabrication methods involved for preparation of any samples to be referred to throughout this thesis. This will be broken down into small subsections as to be easier to follow or refer to.

3.3.1. Materials

**All the materials used within these studies and referred to in this thesis are outlined here, separated by their function within this work and presented in the tables below accordingly. Molecular structure schematics have been provided for PCBCB and the dopant materials.*

Electron and hole transport solute materials:

ETL/HTL & Acronym	Chemical Name and formula	Purity and molecular weight	Supplier and CAS No.
ETL – PCBCB	Phenyl-C61-butyric acid benzocyclobutene ester Formula: C ₇₉ H ₁₈ O ₂ *Primary material investigated in this work.	Grade: 99% purity Molecular weight: 998.93 g/mol	Not commercially available but synthesised by the Seth Marder group, specifically by Raghunath R. Dasari. Also named ‘ <i>DRR-XII-4</i> ’. CAS no.: None

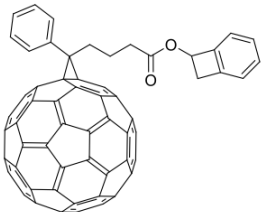
			
ETL –	Zinc acetate dihydrate Formula (Zinc acetate dihydrate): $C_4H_6O_4Zn \cdot 2H_2O$	Grade: 99.999% trace metals basis Molecular weight: 219.51 g/mol	<i>Sigma-Aldrich</i> CAS No.: 5970-45-6
HTL –	Molybdenum(VI) oxide pieces (sintered), 3-6mm length Formula = MoO_3	Grade: 99.95% pure Molecular weight: 143.94 g/mol	<i>Testbourne</i> Product No.: M4-5011-M

Table 3.1 – Electron and hole transport layer materials used within this thesis, their chemical names, formulas, purities, molecular weights, supplier and product/CAS numbers.

Photoactive layer solute materials:

A bulk heterojunction of the polymer-NFA system, PM6:Y6, is used as the active layer material for all devices considered in this thesis, as it is a well-studied system that can produce some of the highest efficiency organic solar cell devices currently possible, with a breadth of research behind its optimisation [227-232].

Acronym	Chemical Name and formula	Purity and molecular weight	Supplier and CAS No.
PM6	PBDB-T-2F Formula: $(C_{68}H_{76}F_2O_2S_8)_n$ *Donor material	Grade: > 40000 (GPC) Molecular weight: 10000 - 100000 g/mol (GPC)	<i>Luminescence Technology Corporation. (LumTec)</i> CAS No.: 1802013-83-7
Y6	BTPTT-4F Formula: $(C_{82}H_{86}F_4N_8O_2S_5)$ *Acceptor material	Grade: 99% (NMR) Molecular weight: 1451.93 g/mol	<i>LumTec</i> CAS No.: 2304444-49-1

Table 3.2 – Active layer materials used within this thesis, their chemical names, formulas, purities, molecular weights, supplier and product/CAS numbers.

Contact (electrode) materials:

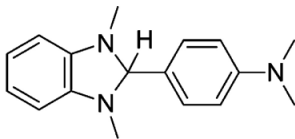
**Alumina nanoparticles are included here as we consider them to be a surface treatment to ITO (cathode).*

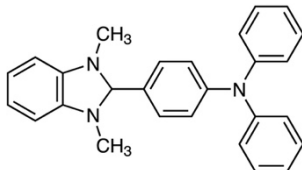
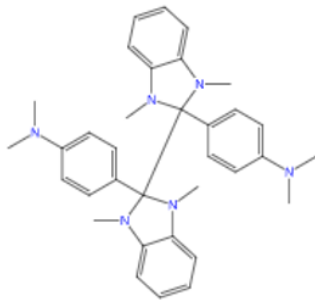
Acronym / symbol	Chemical Name and formula	Purity and molecular weight	Supplier and CAS No.
Ag	Silver pellets, 1-3mm length Formula: Ag *Anode	Grade: 99.99% pure silver Molecular weight: 107.87 g/mol	<i>Testbourne</i> Product No.: S5-5005-M

Au	Gold pellets, 1-3mm length Formula: Au *Anode	Grade: 99.99% pure gold Molecular weight: 196.97 g/mol	<i>Testbourne</i> Product No.: G4-5005-M
Alumina nanoparticles	Alumina nanoparticle suspension Formula: Al ₂ O ₃ *Cathode	<50 nm particle size (DLS), 20 wt.% suspended in isopropanol	<i>Sigma-Aldrich</i>

Table 3.3 – Contact (electrode) materials used within this thesis, their chemical names, formulas, purities, molecular weights, supplier and product/CAS numbers.

Dopant materials:

Acronym / symbol	Chemical Name and formula	Purity and molecular weight	Supplier and CAS No.
N-DMBI	(4-(2,3-Dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzenamine) Formula: C ₁₇ H ₂₁ N ₃ 	Grade: 98% (HPLC) Molecular weight: 267.37 g/mol Pellet length: 1-3 mm	<i>Sigma-Aldrich</i> CAS No.: 302818-73-1

N-DPBI	(4-(1,3-Dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)-N,N-diphenylaniline Formula: $C_{27}H_{25}N_3$ 	Grade: 98% Molecular weight: 391.51 g/mol	<i>Sigma-Aldrich</i> CAS No.: 1400191-57-2
(N-DMBI)2	(2,2'-Di(4-dimethylaminophenyl)-2,2',3,3'-tetrahydro-1,1',3,3'-tetramethyl-2,2'-bi-1H-benzimidazole) Formula: $C_{34}H_{40}N_6$ 	Grade: 99% Molecular weight: 532.72 g/mol	Dopant supplied by the University of Boulder, Colorado, Stephen Barlow and Junxiang Zhang. CAS No.: 2599852-02-3

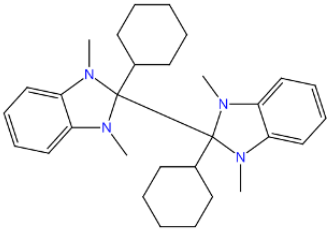
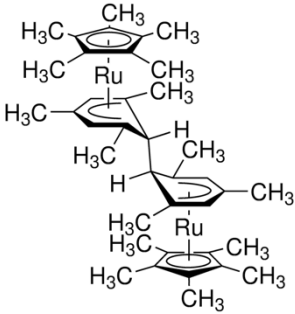
(Cyc-DMBI)2	(2,2'-Dicyclohexyl-2,2',3,3'-tetrahydro-1,1',3,3'-tetramethyl-2,2'-bi-1H-benzimidazole) Formula: $C_{30}H_{42}N_4$ 	Grade: 99% Molecular weight: 458.68 g/mol	Dopant supplied by the University of Boulder, Colorado, Stephen Barlow and Junxiang Zhang. CAS No.: 1620569-09-6
(RuCp*Mes)2	[μ-[(2,3,4,5,6-η:2',3',4',5',6'-η)-2,2',4,4',6,6'-hexamethyl[bi-2,4-cyclohexadien-1-yl]-6,6'-diyl]]bis[(1,2,3,4,5-η)-1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl]diruthenium Formula: $C_{38}H_{54}Ru_2$ 	Grade: 99% Molecular weight: 712.97 g/mol	Dopant supplied by the University of Boulder, Colorado, Stephen Barlow and Junxiang Zhang. CAS No.: 184587-91-5 (a.k.a. Mesitylene pentamethylcyclopentadienyl ruthenium dimer)

Table 3.4 – Dopant materials used within this thesis, their chemical names, formulas, purities, molecular weights, supplier and product/CAS numbers.

Solvents for material dissolution:

Acronym / symbol	Chemical Name and formula	Purity and molecular weight	Supplier and CAS No.
	1,2-dichlorobenzene / ortho-dichlorobenzene Formula: C ₆ H ₄ Cl ₂	Grade: anhydrous, 99% Molecular weight: 147.00 g/mol	<i>Sigma-Aldrich</i> CAS No.: 95-50-1
	Chloroform Formula: CHCl ₃	Grade: > 99.8%, contains 0.5-1.0% ethanol as stabiliser. Molecular weight: 119.38 g/mol	<i>Sigma-Aldrich</i> CAS No.: 67-66-3
	2-methoxyethanol Formula: C ₃ H ₈ O ₂	Grade: anhydrous, 99.8% Molecular weight: 76.09 g/mol	<i>Honeywell</i> CAS No.: 109-86-4
	Ethanolamine Formula: C ₂ H ₇ NO	Grade: puriss. p.a. ACS reagent, ≥ 99.0% (GC/NT). Molecular weight: 61.08 g/mol	<i>Sigma-Aldrich</i> CAS No.: 141-43-5
	2-propanol (Isopropanol) Formula: C ₃ H ₈ O	Grade: puriss., meets analytical specification of Ph.	<i>Sigma-Aldrich</i> CAS No.: 67-63-0

		Eur., BP, USP, $\geq$ 99.5% (GC). Molecular weight: 60.10 g/mol	
	Acetone Formula: C ₃ H ₆ O	Grade: puriss., meets analytical specification of Ph. Eur., BP, NF, $\geq$ 99% (GC). Molecular weight: 58.08 g/mol	<i>Sigma-Aldrich</i> CAS No.: 67- 64-1
	Hellmanex® III cleaning concentrate.	1L bottle.	<i>Hellma®</i>
	decon 90	5L bottle.	decon®

Table 3.5 – Solvents (and cleaning solutions) used within this thesis, their chemical names, formulas, purities, molecular weights, supplier and product/CAS numbers.

Miscellaneous materials studied (chapter 9):

- Materials studied for the intention of use as active layer components in OPV; **DCV3T**, **SubNC** and **HB194**. The thin film samples were fabricated in Oxford by Ming Zhu via vacuum thermal deposition (see chapter 9.1). All materials are used as received, whose information can be found in Table 3.6 below.

These materials have been tabulated below:

Acronym	Chemical Name and formula	Purity and molecular weight	Supplier and CAS No.	Density (gcm ⁻³)
HB194 <i>*(used here as acceptor in PAL)</i>	2-((Z)-2-((E)-2-(1,1-Dimethyl-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-ylidene)ethylidene)-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile Formula: C ₂₇ H ₂₁ N ₃ O	Grade: Sublimed >99% Molecular weight: 403.48 g/mol	Lumtec (LT-S9047) CAS No.: 1207961-82-7	1.4
SubNc <i>*(donor or acceptor in PAL)</i>	Boron sub-2,3-naphthalocyanine chloride Formula: C ₃₆ H ₁₈ BClN ₆	Grade: Sublimed >99% Molecular weight: 580.83 g/mol	Lumtec (LT-S947) CAS No.: 142710-56-3	1.6
DCV3T <i>*(acceptor in PAL)</i>	3',4'-Dibutyl-5,5"-bis(dicyanovinyl)-2,2':5',2"-terthiophene Formula: C ₂₈ H ₂₄ N ₄ S ₃	Grade: >99% Molecular weight: 512.71 g/mol	Lumtec (LT-S9125) CAS No.: 908588-68-1	1.45

Table 3.6 – Materials used within chapter 9 of this thesis, their chemical names, formulas, purities, molecular weights, supplier and product/CAS numbers.

3.3.2. Solution preparation; weighing, stirring, doping

**All organic materials are stored under nitrogen atmosphere in a dry (no solvents) glovebox. After weighing into vials in conditions specified below, these organic materials are then transferred to a wet (solvent/processing) glovebox for the addition of solvents, which are stored here.*

PCBCB – This material was weighed out inside a nitrogen filled glovebox, to eliminate air exposure. 1,2-dichlorobenzene was added as the solvent under nitrogen atmosphere also. The solution was stirred overnight in the glovebox. All solutions were used within

2-3 weeks as it was found that leaving them for durations longer than this could result in reduced performance in desired film properties, likely due to degradation in the electronic properties of the material. Doping of the PCBCB stock solutions was performed in the same glovebox, directly before spin-coating, via addition of the dopant and any excess solvent to produce solution of the required concentration and molar dopant percentage.

ZnO – This recipe produces a zinc oxide sol-gel solution. 100 mg of zinc acetate dihydrate (solute) was used for every 1 ml of 2-methoxyethanol (solvent). Ethanolamine was added as a stabilizer to the solution at 28 μL for every mL of solvent. The solution was then stirred at 60°C for 3 hours, followed by a room temperature stir for ≥ 12 hours. Prior to first use, solutions were sonicated for 15 minutes. All solutions were refrigerated and used within 3 months, re-sonicating before use if precipitation formed. All materials were weighed and stirred in air and solution was deposited in a fume hood in air, for production of ZnO. The processing of ZnO films has been informed by the following sources [233-235].

PM6:Y6 – A ratio of 1:1.2, PM6 to Y6 was used for all samples in this thesis. The materials were weighed in air and a total of 17 mg of solute materials per mL of solution was used (except when thinner films were prepared as again specified in chapter 6.3.1). Chloroform (solvent) was added to the solution in the N_2 -filled glovebox. The solution was stirred in the glovebox for ≥ 5 hours, typically overnight to allow for full dissolution. Best device performance results were exhibited when the solution was used within 48 hours of adding the solvent. Use of the solution after this resulted in drops in device performance if. The processing of PM6:Y6 was primarily informed by [232].

N-DMBI & all other dopants studied – Dopants were weighed in N₂-filled glovebox and same solvent as used for PCBCB (1,2-dichlorobenzene) was added under nitrogen atmosphere also. Stock solution was made and added to the host organic semiconductor solution in N₂-filled glovebox, directly before deposition. No stirring needed, just shake solution upon initial mixing and before use. N-DMBI solution can be stored for several months—(uncertain on storage time of other dopant solutions, as has not been tested).

Alumina (Al₂O₃) nanoparticle suspension – Alumina nanoparticles suspended in IPA (<50 nm particle size (DLS), 20 wt.% suspended in isopropanol), were added to IPA (>99% purity) with a specified dilution ratio. Dilution ratios of 1:x alumina nanoparticle suspension to IPA have been used based on work by Jin et. al [236,237]. The dilution concentration was tuned sample specifically, with 1:150 and 1:300 dilution ratios predominantly used in this work. Vortex mixer was used before spin-coating. Deposited under the fume hood, in air. Can be stored for several months.

3.3.3. Substrate preparation; cleaning, UV-Ozone, alumina nanoparticles

**Substrates include glass substrates (Soda lime glass; 30 × 30 × 1.1 mm, Biotain Crystal Co., Ltd) and pre-patterned ITO coated substrates (ITO coated glass(Etched); 30 × 30 × 1.1 mm, 135 nm ITO layer with > 86% transmittance and 10~15 ohm/sq sheet resistance, Biotain Crystal Co., Ltd) [105]; multiple suppliers have been used for ITO substrates, the supplier that was most heavily used has been listed here.*

Glass and ITO substrates – The cleaning procedure involves first manually scrubbing the surface of each substrate individually with Decon™ decon 90 or Hellmanex® solution, at a concentration of 1-2 % in de-ionised water, using a manual

toothbrush. Substrates are then placed in soap solution of the same concentration and placed into ultrasonic bath for 10-12 minutes. Following this, substrates are rinsed with deionised water thoroughly, before being placed in de-ionised water and back in the ultrasonic bath for a further 10-12 minutes. Substrates are then rinsed thoroughly with acetone to remove any remaining soap, before being placed in acetone for a further 10-12 minutes in the ultrasonic bath. Lastly, substrates are rinsed in 2-propanol (*Sigma-Aldrich*, > 99.5 % purity) and placed in 2-propanol for a final 10-12 minutes in the ultrasonic bath. The substrates are then dried using an N₂-gun.

In preparation for spin-coating, substrates are then placed into the UV-Ozone cleaner for 10 minutes, directly before spin-coating the first material layer onto the substrate. The time between UV-Ozone cleaning and placing into the N₂-filled glovebox is estimated to be 1-2 minutes, while the time between UV-Ozone cleaning and spin-coating of the final substrate was kept to a minimum and estimated to be less than 30 minutes. UV-Ozone can act to improve the wettability of films to the substrate, as is the case with PCBCB [238].

For glass substrates to be coated in PCBCB, alumina nanoparticles (concentration variable and discussed in chapter 6) are used to improve the wettability of the solution to the substrate. The nanoparticles are deposited following UV-Ozone cleaning, in the fume hood (in air), using the spin-coating recipe as described in 3.3.4.

3.3.4. Spin-coating; alumina nanoparticles, ETL & PAL

**Spin-coating parameters will be presented in the following format: Spin speed (rpm), acceleration (rpm/s), duration (s). Location/environment.*

Spin-coating involves casting a material solution onto a substrate through the process of spinning the substrate at high speeds on a rotating chuck. This allows for a somewhat even distribution of the solution to be deposited onto the substrate, forming a thin film. It is the centrifugal motion that spreads the solution across the substrate. Once the rotation reaches the desired speed, most of the applied solution is expelled from the substrate and the remaining solution's rotational speed matches up with the substrate's, allowing for the fluid-film to become level. The film becomes thinner as more fluid is expelled and as the solvent evaporates. The thickness of a thin film produced via spin-coating is generally proportional to the inverse of the spin speed squared [124]. The exact thickness of a film will depend upon the concentration of the solution to be spun, in addition to the solvent evaporation rate (which in turn depends upon factors such as the solvent viscosity, ambient pressure, temperature and local humidity, as well as the solvent atmosphere in which it is being deposited). Furthermore, the degree of film thickness inhomogeneity that can exist also depend on factors including the substrate shape, roughness, how clean it is, its and the solvents polarity and hydrophobicity solvent. For this reason, spin thickness curves for new material solutions are usually determined empirically. Typically, thin film will be deposited, and the thickness measured either by XRR, surface ellipsometry or surface profilometry (Dektak). The spin speed and the concentration of the solution can then be adjusted respectively, to give the desired film thickness.

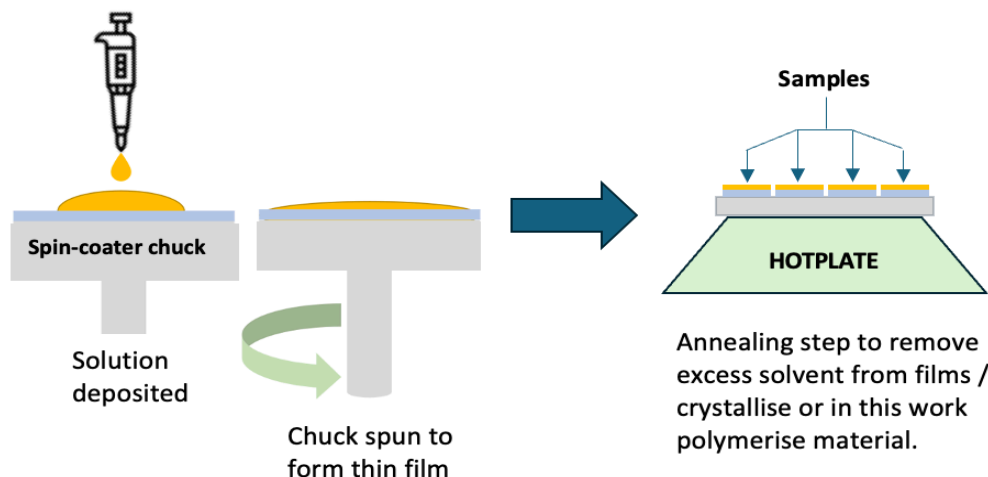


Figure 3.3 – Schematic of spin-coating process for fabrication of thin films. Adapted from the thesis of Michael Farrar [239].

All the spin-coating for the films detailed in this thesis was done dynamically. The recipes used for each material are listed below:

Alumina nanoparticles – 2000 (rpm), 2000 (rpm/s), 20 (s). Fume hood / In air.

PCBCB – 2000 (rpm), 2000 (rpm/s), 45 (s). Glovebox / N₂.

PM6:Y6 – 2000 (rpm), 2000 (rpm/s), 20 (s). Glovebox / N₂.

ZnO – 4000 (rpm), 2000 (rpm/s), 45 (s). Fume hood / In air.

3.3.5. Annealing procedures

The annealing processes involved in the oligomerisation of PCBCB is a key investigation as part of this thesis, playing a key contribution into improving the quality of thin films and reducing shunting in devices. The full details of how the annealing process evolves is described in chapter 5, however the general annealing process is described here, along with the final, optimal condition, used for device and film

preparation.

Annealing of PCBCB thin films – In N₂-filled glovebox. Final anneal conditions are as follows; the hotplate (*Stuart CD162*) is first set to 60°C and samples are set on an aluminium block and placed onto the hotplate for a 10-minute ramping period, in order to drive solvent out of the films. The hotplate is then dialed up 200°C with a 7-minute ramp period to allow for the aluminium block to homogenously reach the correct temperature. Finally, a cap is then placed over the samples while they anneal for the next 15 minutes, to remove light exposure and allow for a partial solvent atmosphere. Remove and leave to cool.

Annealing of PM6:Y6 thin films – In N₂-filled glovebox. Set hotplate (*Stuart CD162*) to 110°C and place samples directly onto hotplate. Anneal for 10-minutes. Remove and leave to cool.

Annealing of ZnO thin films – In fume hood/air. Set hotplate (*Stuart SD160*) to 200°C and place samples directly onto the hotplate. Anneal for 45 minutes. Remove and leave to cool.

The actual temperature of substrates placed onto the hotplates were tested using a thermocouple attached to a glass substrates (30 mm²) that was placed centrally onto the SD160 hotplate. For a more precise measurement of actual substrate temperature for the CD162 (glovebox), a carbon black sample (60 mm²) was placed centrally, and its temperature was measured in different position with an infra-red detector. From these substrate temperature measurements, calibration curves have been plotted such that the

actual temperature of the substrates can be extrapolated from the set temperatures, see appendix A. The offset of the SD160 is slightly larger than the almost zero offset of the CD162. A heatmap of both the SD160 hotplate and of the CD162 with the aluminium block on top, each set to 200°C, have been provided in appendix A also. The CD162 appeared to result in the most homogenous temperature transfer across the aluminium block upon testing.

3.3.6. Thermal evaporation; HTL & top contacts

The HTL and top contact components of the device stacks studied have been fabricated via thermal deposition under vacuum. Thermal evaporation of materials was conducted inside a N₂-filled dry glovebox, using an LC-Technology inc. designed evaporation chamber. The pressure of the chamber before beginning any evaporation was always on the order of 10⁻⁹ mbar according to an internal sensor. An image of the inside of the evaporation chamber can be seen in Figure 3.4.

Shadow masks were used for device fabrication following a design as shown in Figure 3.5, to separate each sample into individual solar cell pixels. Material beneath the evaporated layers was scratched away prior to evaporation of top layers in order to ensure cell separation. Recipes for evaporations are detailed below:

Thermal evaporation of MoO₃ – Molybdenum boat (*Testbourne*); 4" length x $\frac{1}{2}$ " width, dimple dimensions are $\frac{1}{8}$ " depth, $\frac{7}{16}$ " inch diameter. Source 4, rate = 0.2 Å/s.

Thermal evaporation of Au – Tungsten boat (*Testbourne*); 4" length x $\frac{1}{2}$ " width, dimple dimensions are $\frac{1}{8}$ " depth, $\frac{7}{16}$ " inch diameter. Source 2, rate = 0.2 A/s $\rightarrow$ 0.8 A/s at 20 nm thickness $\rightarrow$ 1.5 A/s at 30 nm thickness.



Figure 3.4 – Inside of vacuum chamber used for thermal evaporation of hole transport layer (MoO_3) and cathode (Ag) as the top electrode in the studied device stack. The QCMs used for film thickness calibrations, along with the sources used for heating of the materials are highlighted.

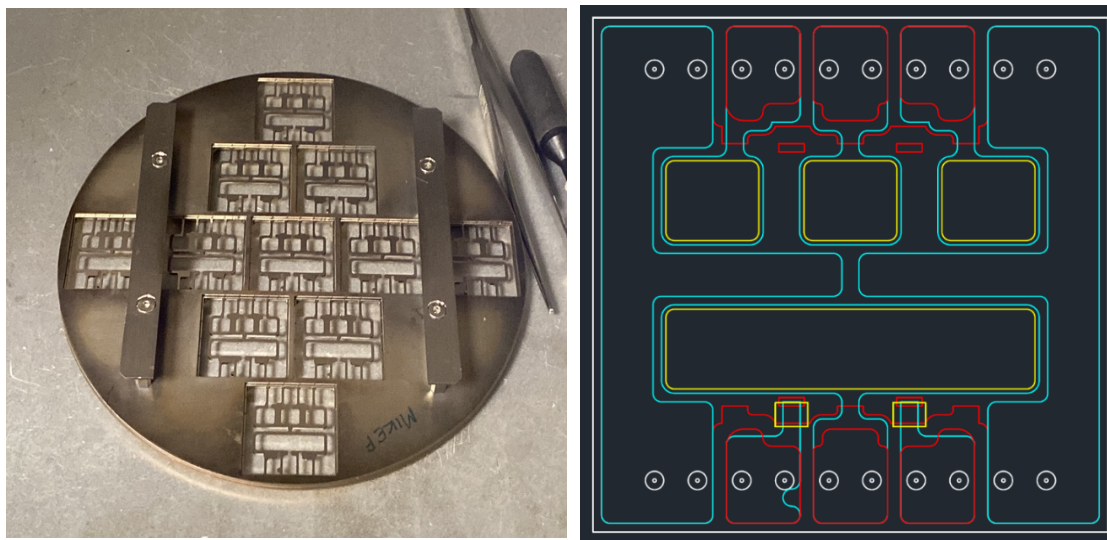


Figure 3.5 – (Left) Shadow masks for the evaporation of the HTL and top electrode, inside the sample plate holder that slots into position in the thermal evaporation chamber. (Right) design schematic for shadow masks. The design allows for each sample to be separated into individual solar cell pixels.

3.3.7. Encapsulation

Encapsulation of samples was done using glass cavity slides and was carried out by first removing all material outside the perimeter of the glass cover slips, to ensure that the glue was in contact with the substrate and the glass cover slip for improved adhesion. A UV curable epoxy (*Everlight 341*) was used and a glass coverslip (*AMG, Korea*). Curing time was approximately 3 minutes per sample.

3.4. Characterisation techniques for determining physical and optical properties of thin films

There are many properties we must consider and characterise when optimising thin film charge transport layers, namely the thickness and morphology of the layer, layer energetics, conductivity and the absorption spectrum of the film, in order to determine the suitability of the material. The thickness of the transport layer impacts how effective the layer is. An electron transport layer that is too thick will provide a high series resistance to the device unless it has particularly high conductivity, as charge carriers must travel further to reach the cathode. A thick ETL may also absorb too much incoming light, reducing that which can be absorbed by the active layer. An ultra-thin layer can allow charge carriers of the opposite charge to tunnel through. This could also result in a higher density of pinholes throughout the film, meaning areas of non-conformality in the film that can expose material underneath and lead to a higher frequency of shunts in a device. To avoid these problems, we should consider materials that do not have an absorption spectrum significantly overlapping with the active layer material. A thickness range should be used that allows for enough transparency for light to reach the active layer, and for the quasi-Fermi level within the charge transport layer to collapse to a single Fermi level (see Chapter 2.1.2, Figure 2.6), such that only electrons travel through the ETL and holes through the HTL, while also producing good film coverage and conformality. Other physical properties such as a particularly high or low surface roughness, can be detrimental to the active layer formation, and thus not all materials are suitable.

X-ray reflectivity

Techniques such as X-ray reflectivity (XRR) can analyse film thickness, density and roughness by producing reflectivity spectra from the surface of the layer [240]. This technique uses total external reflection of X-rays to determine these properties accurately for samples with layer thicknesses between 0.5-35nm [240]. The positions of the fringes are related to the film thickness by the modified Bragg equation, relating the thickness of the layer, the critical angle and the observed angle of fringes in the spectra to the integer number of fringes and the wavelength of the incident X-ray [240].

The equipment used for XRR measurements in this thesis was a Rigaku SmartLab [241]. Analysis of data was done using the software '*GenX 3*'.

Profilometry

Surface profilometry can be used on thicker films deposited directly onto a hard substrate (i.e. glass or ITO) to determine film thickness, provided the material is not too soft such that it coats the profilometer tip when measuring. A groove can be made in the film using a razor blade, and the depth of the groove can be measured by dragging the probe across the groove. The depth between the edge of the groove (film surface) and down to the substrate is determined and this gives an estimation for the film thickness. The equipment used for this measurement is a Dektak profilometer.

Scanning electron microscopy

Scanning electron microscopy (SEM) can be used to assess the quality of a film surface by assessing the topology of a thin film surface [242]. This is useful in determining film roughness and defects on the surface. This technique works by scanning a focused beam of electrons across the surface of the sample and detecting the secondary electron

radiation that is emitted from the sample. An accelerating voltage is applied to the electron beam to control the penetration depth of the electron beam and in turn the resolution of certain features. The SEM equipment used for these studies was a Hitachi S-4300 SEM at an accelerating voltage of 5.0 kV. Samples were prepared on conductive ITO substrate and held in place with conductive carbon tape. All SEM images were taken from top-view by Dr. Alexandra Ramadan, while at the University of Oxford (now University of Sheffield) [243].

Atomic force microscopy

Atomic force microscopy (AFM) involves the use of a physical probe; a sharp tip attached to a cantilever that has three possible modes, non-contact, tapping or contact [244]. In this work we have used tapping mode, as this reduces direct contact with the sample and the damaging lateral forces that are applied in contact mode. In this mode the cantilever is vibrated close to its resonant frequency and brought very close to the sample surface, such that the probe comes into contact with the sample surface intermittently, oscillating between experiencing the electrostatic repulsion of the surface and the attractive Van-der-Waals forces when in close contact. The tip-sample interaction is measured as changes in the amplitude of the cantilever oscillation. Three different pieces of AFM equipment were used for these studies:

- Oxford, Begbroke: AFM was performed using an Agilent 5400 AFM. These measurements were performed in tapping mode using HQNSC35/ALBS tips (manufacturer's suggested resonance frequency of ~ 198 kHz). Images from this setup were processed using *ImageJ* by applying a noise reduction by despeckling. Images were sharpened and passed through a fast fourier transform bandpass filter

to further reduce noise, smears and shadows on the sample surface – this filtered large structures down to 10 pixels and small up to 1 pixel.

- Oxford, Beercroft: AFM was performed in tapping mode using an Asylum Research MFP-3D AFM (Oxford Instruments) with HQ-150-Au model cantilever tips.
- In Cologne, AFM was performed using an MFP-3D Infinity by *Oxford Instruments Asylum Research*. The measurements were performed in tapping mode, using an AC 200 TS cantilevers by *Olympus*.

All raw datasets were analysed using the imaging softwares *ImageJ* and *Gwyddion*. The root mean square (RMS) parameter was determined using the statistical analysis tool provided by *Gwyddion*. The specific setup used for each measurement will be specified alongside the dataset.

Contact angle

Contact angle measurements were conducted by Philipp Weitkamp (University of Cologne), by dropping solvent or solution onto the sample surface and measuring the angle between the flat surface and the slope of the droplet that forms on the surface.

These measurements were performed using an OCA 200 instrument provided by *Data physics instruments*. For all measurements a drop volume of 2 μL was used. As liquids de-ionised water (*rotipure*®), ethylenglycole (*Sigma Aldrich*) and glycerol (*Sigma Aldrich*) were used. The surface tension was calculated according to the Owens, Wendt, Rabel and Kaelble (OWRK) method [245], [246].

2D GIWAXS

Crystal structure of thin films was also considered, as changes in the crystalline ordering of the molecules can affect charge transport throughout the layer. This can be achieved using diffractometry techniques, such as grazing-incidence wide-angle X-ray scattering (GIWAXS) [247].

For 2D GIWAXS measurements, two setups were used, and the exact setup used will be specified with each data set as either the internal or external setup. The first, an internal setup at the University of Oxford is a Rigaku SmartLab [248]. In this setup, parallel beam micro-focusing optics were used, together with a 2D-XRD attachment head which includes a knife edge to prevent background scatter. X-rays were collected with the 2D detector with the sample-to-detector distance set to 65 mm. Data was collected at an incidence angle of 1° and with a detector 2θ angle of 16.5° . The acquired data was then resampled into Q-space with the assistance of Dr. Joel Smith (accounting for the ‘missing wedge’ introduced by the GI geometry), using scripts based on the PyFAI and pygix libraries [249,250]. Sector profiles were generated by azimuthally integrating over a 30° range of χ angles (where 0° is the Q_z direction) for the in-plane (60° to 90°) and out-of-plane (-15° to 15°) 1D Q vs. intensity profiles, exemplified in Figure 3.6.

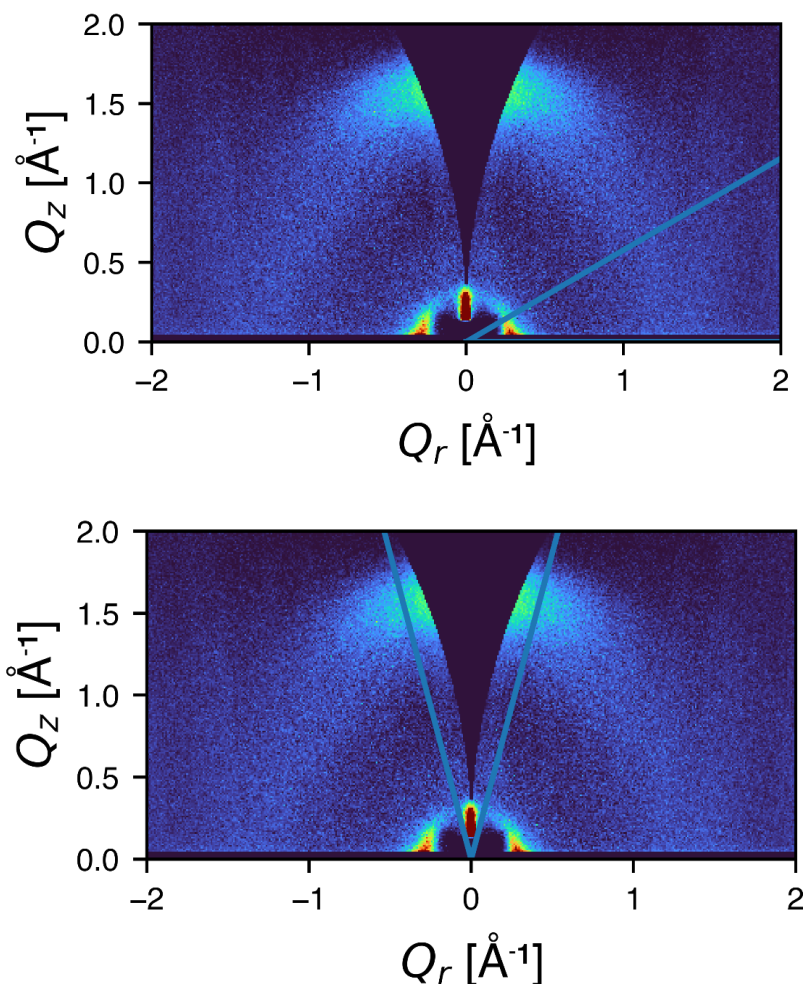


Figure 3.6 – Acquired X-ray data converted into Q space for the PM6:Y6 layer deposited on a PCBCB film. Blue lines mark the boundary of the sector over which data was azimuthally integrated, to produce an in-plane (top) 1D Q_r (or Q_{xy}) vs intensity profile, and an out-of-plane (bottom) 1D Q_r vs intensity profile.

The external setup was at the A28-1-1380 XMaS, ESRF beamtime. I would like to acknowledge the beamline scientist, Oier Bikondoa. The dataset can be found at [251], although is currently under embargo. Samples were measured here by Rachel Kilbride and Pascal Kaienburg and analysed by Olivia Gough. All samples were measured at an angle of 0.075° and with 100s of beam exposure. The detector was a Pilatus M1. Beam energy was 12.4 keV. “The calibration was done using the LaB6

which has well-defined crystalline peaks, meaning we can define the experimental geometry via generating a 'PONI' (point of normal incidence) using pyFAI-calib2.” – Olivia Gough. The code used for analysis was the same as used for the internal setup.

Sector profiles were generated by azimuthally integrating over a 30° range of χ angles (where 0° is the Q_z direction) for the in-plane (50° to 80°) and out-of-plane (0° to 30°) 1D Q vs. intensity profiles.

Two-point probe – lateral conductivity

Conductivity or sample resistance measurements using a four-point or two-point probe, are necessary for determining the conductivity of a thin film and allow for the effect of doping on conductivity to be investigated. Two-point probe measurements will be discussed here as this is within the scope of this thesis. This measurement uses two gold probes to measure the lateral conductivity across a sample. Thin films are deposited onto glass and contacts are deposited onto the samples using thermal evaporation of gold, and shadow masks as shown in Figure 3.7 are used. These masks allow gold to be deposited in thin channels across the thin films, across which the sample resistance can be determined using a Keithley 2636, by measuring the current across the channel (I) with applied voltage (V). This setup has a picoamp and nanovolt resolution. The measurements from each channel were averaged to produce an average conductivity for each sample.

Lateral films resistances (R) were then determined from the gradient of the plotted current against voltage graphs. Conductivities (σ) were then be calculated using the same equations as described in 3.1.2, when calculating the minimum theoretical conductivity necessary for an ETL in a typical OPV device stack. In this case, l is the length of the channel and A is the horizontal cross-sectional area across the channel.

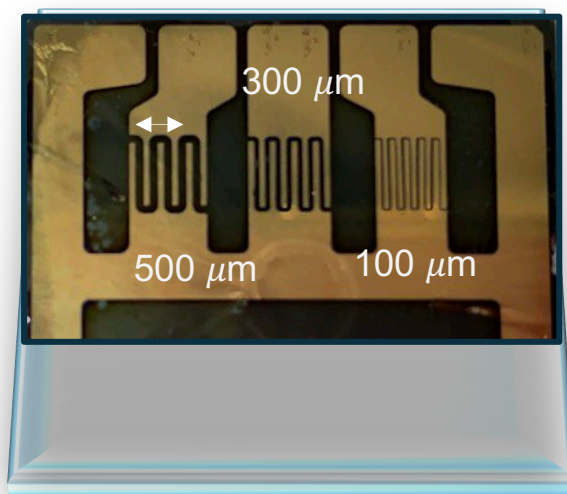


Figure 3.7 – Layout of shadow masks for top contact deposition for use in two-point probe measurements. This design allows for resistivity to be measured across the three channels of specified width, to in turn be able to calculate the conductivity of thin films.

The total dimensions of each channel are as follows:

500 μm : spacing = 500 μm , length = 23.23 mm

300 μm : spacing = 300 μm , length = 31.60 mm

100 μm : spacing = 100 μm , length = 39.51 mm

Ultraviolet-visible spectroscopy

Electronic absorption or ultraviolet-visible (UV) spectroscopy is a technique that can measure the transmission and reflectance spectra of a material layer over a range of wavelengths [252]. This is useful for determining absorptive properties of the layer and helps to determine if a thin film ETL is transparent enough and has a complimentary absorption spectrum to the active layer, to reduce parasitic absorption. This technique can also check the effects of processing on the absorption spectra, a particularly useful

tool to check the effects of doping the material on optical gap, by assessing for any changes in the spectra.

UV-Visible spectroscopy works by measuring the amount of light that either passes through or reflects from a sample placed in front (transmission) or behind (reflectance) a detector. In a typical setup, a panchromatic light source introduces light in through a cavity and is collimated onto a grating, to disperse the light. A monochromator is then used to ensure approximately monochromatic light (depending on the spectral resolution) is incident on the sample. The diffraction grating is rotated to select the specific wavelength to be incident on the sample. An integrating sphere can be used to obtain diffuse transmission and diffuse reflection measurements, by collecting light that has a change in optical path upon passing through the sample. The light undergoes multiple reflections, and this results in a uniform intensity. This avoids significant portions of the spectra becoming lost, by allowing the light to be collected over all angles, which is not the case for a specular reflectance/transmission measurement. The UV-Vis spectrophotometer determines the amount of light that is transmitted or reflected through a sample by ratioing the intensity of the incident light with that of the transmitted [reflected] light. In this work we are interested in the relative absorptance between spectra, and the absorptance (A) can be calculated simply from the transmittance (T) and the reflectance (R) as in equation 3.7.

$$A = 1 - T - R \quad (3.7)$$

Two UV-Vis setups were used for these studies, and the one used will be specified alongside each dataset:

-
- Early UV-Vis measurements were performed with a Lambda 1050 spectrophotometer from *Perkin Elmer*. An integrating sphere was used.
 - Later UV-Vis measurements were conducted using a UV-Vis-NIR Cary 5000 spectrophotometer from *Agilent*. An integrating sphere was used.

Raman spectroscopy

This form of spectroscopy uses high intensity monochromatic laser light at controlled frequencies to probe the chemical bonds in a sample, producing a unique “fingerprint spectrum” that can be used to identify the material [253,254]. The technique relies on Raman scattering from the sample, a phenomenon that has a low occurrence rate of one in one million excitation photons producing a single Raman photon [255]. The scattered photons are filtered and detected. These have a different frequency from the incident photons and this difference in frequency is known as a Raman shift. When the energy associated with the scattered photons is less than the energy of the incident photons, this scattering is known as Stokes scattering. Conversely, when the energy of the scattered photons is more than that of the incident photons, the scattering is known as anti-Stokes scattering.

Upon detection of the scattered light, the wavelengths of the scattered photons are converted to wavenumbers, and these are plotted against the photon intensity. The Raman shifts can be used to identify bonds within molecules, to which incident photons have lost energy in the form of photons, producing a unique Raman spectrum.

This measurement was performed using an *inVia* Raman microscope from *Renishaw*, at the University of Cologne. The samples were excited with a 500 mW laser at a wavelength of 532 nm, with a laser intensity set to 10% of the maximum power.

The Raman shift was recorded with a single acquisition in the range of 100 cm^{-1} - 3000 cm^{-1} selected by a syncroscan 2400 lmm^{-1} grid.

Solar simulator (Wavelabs)

Devices were tested under simulated AM1.5 solar radiation at 100 mW/cm^2 irradiance, with a Wavelabs Sinus-220 (light-emitting diode array) solar simulator. This setup was calibrated with an Si reference cell (Fraunhofer ISE). Current-Voltage characterisation is performed in air using Keithley 2400 series source meters, with a scan rate of 0.3 V/s . This setup has a picoamp and nanovolt resolution. Characterisation measurements are conducted done in the following order: V_{OC} , dark JV, light JV, J_{SC} .

Due to the nature of the light sources used in research and testing to approximate the Sun's spectrum (AM1.5), spikes and dips in the spectrum can arise which cause the spectrum of the simulator to deviate from AM1.5. The spectral mismatch is also dependant on the optical gap of the material within the device being tested. The spectral mismatch between the Wavelabs Sinus-220 light source at 1 sun intensity and the optical gap for the material in this study was calculated [256] and found to be negligible, meaning the testing setup extremely accurate.

Stability testing

Films and devices for stability testing were encapsulated as described in 3.3.7, before being placed under light-soaking conditions in an ageing box (kept in air, standard room pressure), set to emit the same as AM1.5 solar radiation at 1 sun intensity, with a pulsed light source at 20Hz frequency. The ambient temperature was set to either 65° or 85°C (specified with dataset), as calibrated using a reference cell consisting of a PT1000 temperature sensor, embedded in plastic encapsulant with a black matte surface, placed

centrally inside the box. The relative humidity was calculated to be 0.8% (based on a 45% humidity outside of the ageing box).

The photoelectron spectroscopy techniques used to investigate the energetics of thin films are described in detail in chapter 4.

Chapter 4

Characterisation of thin films using photoelectron spectroscopy

In this chapter, we explore the photoelectron spectroscopy techniques that can be utilised to investigate the energetics of molecules and thin films, as well as their composition. These techniques are extremely surface sensitive and give us great insight into the energetics at interfaces, allowing us to explore energetic changes with material growth or increasing film thicknesses. Furthermore, the effects of doping a material can be investigated and the efficacy of different dopants can be compared by implementing these into thin films and probing them respectively.

4.1. Ultraviolet Photoelectron Spectroscopy

4.1.1. UPS measurement setup

Ultraviolet photoelectron spectroscopy (UPS) involves directing a beam of UV-light onto a sample to photoexcite surface electrons, leading to their emission. The freed electrons are then guided towards an electron detector using field voltages, to then have their kinetic energy measured by an electrostatic analyser. This kinetic energy ($E_{kinetic}$) depends on the excitation energy provided by the UV light ($E_{photon} = h\nu$) as well as the binding energy ($E_{binding}$) of the electron in the sample. The general relation between the binding energy and the kinetic energy is given in equation 4.1.

$$E_{binding} = h\nu - E_{kinetic} \quad (4.1)$$

From this technique, the density of state of the delocalized valence band of inorganic materials and the HOMO states of organic materials can be studied. Photon energies of less than 50 eV are typically used for this technique, and a helium gas-discharge lamp is the most common UV-emission source, from which predominately photons with 21.22 eV energy are produced. While these photons penetrate on the order of micrometres into the sample, only electrons from the very surface of the sample will be collected. This is because the mean free path of the electrons relates to its kinetic energy, and as shown in Figure 4.1, electrons with a kinetic energy of 10-20 eV will have a mean free path of a few monolayers, which is on the order of around 10 angstroms, as each monolayer is less than 1 nm thick [257]. The resulting surface sensitivity of this technique allows for the analysis of the energetic alignment at the interface of two materials. By growing (sub-) monolayer at a time, this can be studied

over a series of thickness gradients to understand how the energetics of a material are affected at the interface compared to the bulk, investigating its depletion width and if gap states are formed at the interface due to potential chemical interaction. This change in energetics over the first few monolayers often referred to as level bending [84]. These investigations on a monolayer scale are much more difficult with solution processed films than with films fabricated via vacuum deposition, as the exact thicknesses of thin films deposited from solution processing are much harder to control. However, this can be achieved to some degree by altering the concentration of the solution used, or the speed at which the solution is deposited across the substrate, allowing for thickness adjustments—albeit this level of control is much less precise.

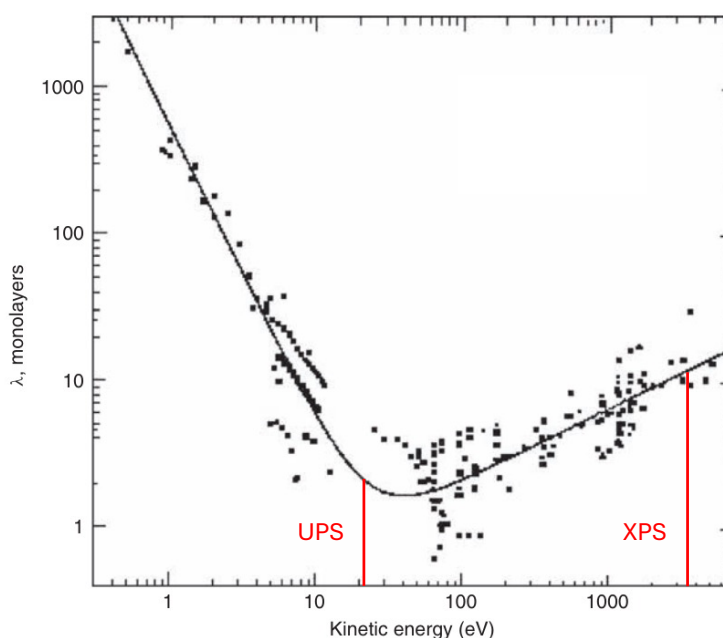


Figure 4.1 – Mean free paths of an electron in a solid, λ (given in monolayers, each equal to < 1 nm) as a function of its kinetic energy. Energies used for ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) are labelled. Inspired by adaption from Olthof (2010) [84] of a figure in Briggs & Seah (1983) [258], which is a reprint from [259].

The general setup for photoelectron spectroscopy measurements is depicted in Figure 4.2, and is based on the setup belonging to Dr. Selina Olthof, based in the group of Klaus Meerholz, at the University of Cologne; Department of Chemistry. This equipment was used for the majority of PES measurements in this thesis. The UV-emission source used here is a helium discharge lamp (VUV5000) from *Scienta Omicron*, from which a helium plasma, contained at a pressure on the order of 10^{-1} mBar, is ignited to produce helium radiation, predominately an energy of $h\nu = 21.22$ eV, referred to as He I α . In addition, a monochromator is used in this setup to filter out additional unwanted excitations. The photoelectrons, which are excited when this UV light is illuminating a sample, therefore have kinetic energies < 20 eV which results in mean free paths of around 1-3 nm (see red line in Figure 4.1). These escaping electrons are focused into by a set of lenses and directed towards a slit, S1. The lens mode can be selected to determine the area of the sample from which electrons can be collected as well as the angle under which the electrons are collected. Both, the size of S1 and an additional iris in the path of the electrons can control the number of electrons entering into the analyser and therefore eventually the signal at the detector.

In the conventional measurement mode, the *Fixed Analyzer Transmission Mode*, a retardation voltage (V_0) is applied between the sample and S1 in order to control the kinetic energy of the electrons entering into the detector to a specific value called the ‘pass energy’ E_{pass} . In order for a range of kinetic energies to be analyzed during a measurement of the density of states (DOS), this retardation voltage is swept. Once electrons have passed through the first slit, they have then entered the analyser. Analysers usually have a hemispherical configuration, comprising two half spheres, and in this case the setup contains a ‘*PHOIBOS 100*’ hemispherical analyser from *SPECS*.

In here, the electron path is controlled by application of radial electric fields between the two half-spheres, deflecting the electrons with the desired E_{pass} onto a trajectory towards the second slit, S2. Importantly, this pass energy is related to the energy resolution of the detector ($\Delta E_{detector}$) and has therefore to be set as low as possible but can be increased to improve the count rate if necessary. The energy resolution follows equation 4.2, where s_1 and s_2 are widths of slits 1 and 2 respectively, α is the electron angle of entry into the detector, and R_0 is the equal to half of the summation of the radii of the inner and outer hemispherical half spheres. Additional contributions to the measured linewidth come from the width of the excitation energy $\Delta E_{excitation}$ and that of the intrinsic width of the atomic energy levels themselves ΔE_w , resulting in a thus the full width half maximum as stated in equation 4.3. At the pass energies used ($E_{pass} < 10$ eV), the largest effect contributing to ΔE_w is thermal broadening from heating of the sample during the measurement.

$$E_{pass} = \Delta E_{detector} \cdot \frac{1}{\left(\frac{s_1 + s_2}{4R_0} - \frac{\alpha^2}{4}\right)} \quad (4.2)$$

$$FWHM = \sqrt{(\Delta E_{detector})^2 + (\Delta E_w)^2 + (\Delta E_{excitation})^2} \quad (4.3)$$

Upon passing through the second slit, the electrons are detected by a phosphor screen which lights up when hit by electrons. A charge-coupled device (CCD) camera aimed towards the phosphor screen detects the light that is emitted, and the amount of light measured results in the count intensity. The CCD camera and the analyser are controlled using a high voltage *HSA3500* power supply, and the detector and the power

supply are connected to a PC via an ethernet cable that then processes the data. The spectroscopy setup and the sample are both grounded to the chamber, to ensure that the Fermi levels align, and their Fermi energies are at the same reference level. The measurement software for UPS is provided by the company *SPECS*. The initial software provide was '*SPECS-Lab*' (version 2.79), this was then later updated to a new software called '*Prodigy*' (version 4.102.2).

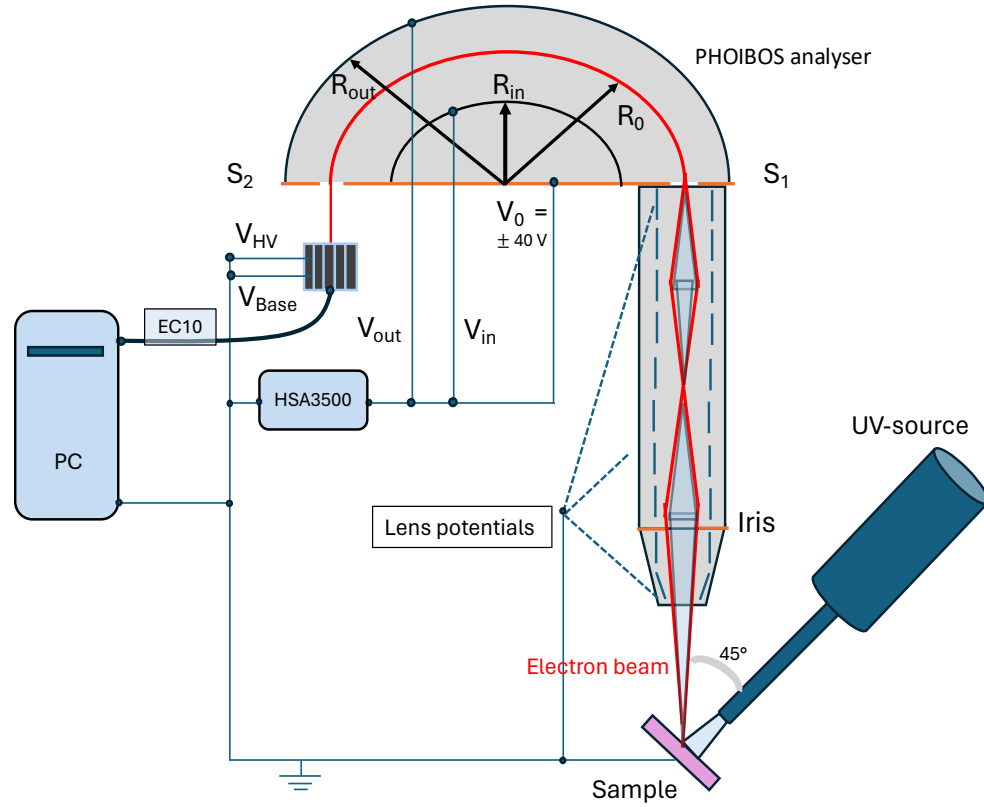


Figure 4.2 – Schematic view of typical UPS setup (based on University of Cologne setup). The photoionisation process is shown, highlighting the direction of the electron beam into the analyser and detector, its path channelled via the use of lenses and applied potentials ($V_{in}-V_{out}$) between across the hemispheres of radius R_{out} and R_{in} respectively. The radius from the centre of the analyser to the electron beam is R_0 . Photons from a UV source free electrons (red lines) from a sample positioned in 40 mm from the detector. A retardation voltage (V_0) is used to slow the electrons and control the kinetic energy of the electrons entering the analyser. the detector to a

specific value called the ‘pass energy’. The analyser entrance and exit slits (S_1 and S_2) are labelled, along with the iris, which is situated at the entrance to the lens system and can be adjusted to control the number of electrons that can enter the analyser. The HSA3500 power source, EC10 ethernet cable, and PC are also highlighted. Adapted and redrawn based on figure from Olthof (2010) [84].

The counts are plotted against either the binding energy or the kinetic energy of the electrons. The system is calibrated such that on the binding energy scale, the Fermi energy of the material is always set to 0 eV. This is achieved by aligning the Fermi level to the equivalent measured kinetic energy during calibration of the detector work function. This is done using a material with a known Fermi edge, in this case a silver calibration foil, and the spectrum of its detected Fermi edge is shown in Figure 4.3. As the Fermi energy of the UPS analyser and the sample are always aligned, this proves a suitable reference point as opposed to the vacuum level of the material, which can differ in position between samples. Furthermore, the width of this Fermi edge gives the uncertainty or energy resolution of the detector. For the experimental setup in Cologne, this linewidth measures as 110 meV and is quoted as the uncertainty in the detector, while uncertainties that arise between samples, highlighting potential issues with reproducibility and comparability, are considered separately per sample set.

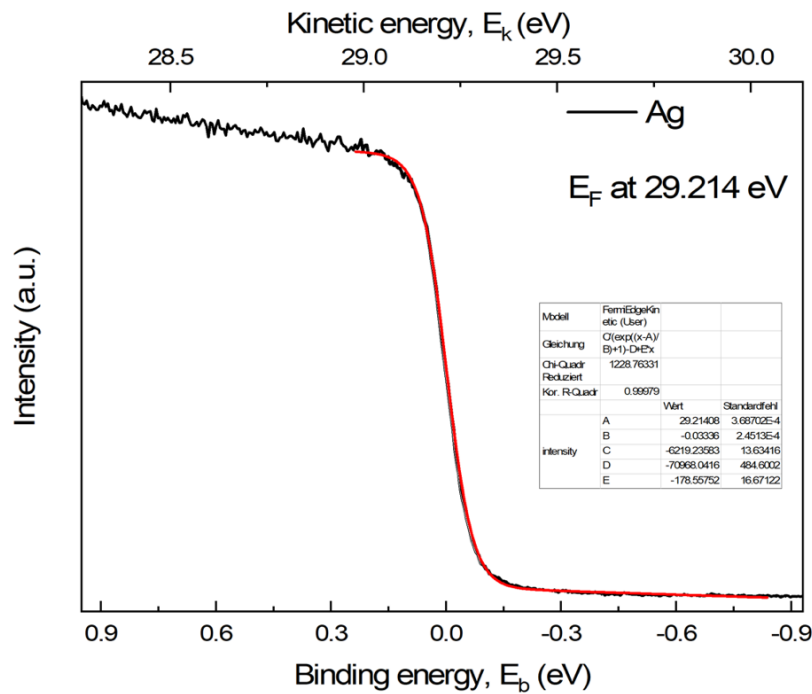


Figure 4.3 – Fermi edge of silver foil, plotted on both a binding energy and kinetic energy scale, used to calibrate the energy scale of the electron detector. The width of this feature gives us our detector resolution.

The system is held under ultra-high vacuum (UHV) and is integrated into a chamber in which the sample is placed to be measured. The sample must be deposited onto a conductive substrate to eliminate charging effects taking place, otherwise shifting of the spectrum will be observed over time. An ideal system base pressure of at least 5×10^{-9} millibar (as was used for this system) or lower should be used, to avoid contamination of the sample surface with traces of oxygen and moisture and potential contaminants that could stick to the surface of the sample and affect the measurement. Depending on the sticking coefficient of residual gases, monolayers of these gases can form very quickly under pressures higher than that quoted above (this can be on the order of minutes to less than a second with a sticking coefficient of unity), so the lower the pressure the better for these measurements. The samples in this work were also

prepared as close as possible to the time at which they entered the chamber, and the time over which these samples were stored in the chamber for measurements was likewise reduced whenever possible.

It is also important to highlight that UPS is measuring energies at the surface of a sample, while in solar cell devices most charge transport takes place in the bulk of the materials, and there will be small differences in the energetics between these two regions. This is an essential distinction to keep in mind when interpreting and analysing UPS data.

4.1.2. UPS data interpretation

Revisiting equation 4.1, the general expression for the binding energy of the electron, in this equation we related the binding energy of an electron to the Fermi level of the semiconductor material or thin film. Typically, when taking UPS measurements, this equation will be amended to include the work function of the detector itself, as well as a bias voltage that is applied to the sample. This bias allows slow electrons (low energy) to avoid stray fields, both electric and magnetic, that may change the path of the electron and result in loss of counts, improving the photoelectron yield. In the case of the setup used at the University of Cologne, described in section 4.1.1., the applied voltage, V_{bias} is $-8V$, which must be subtracted as in equation 4.4, where q is the charge of the electron.

$$E_{binding} = h\nu - E_{kinetic} - WF_{detector} - qV_{bias} \quad (4.4)$$

Figure 4.4 depicts data that has been acquired from a UPS experiment, both from an organic thin film of neat PCBM, as well as a silver foil, to show how the spectra of

the two materials differ, particularly in the position of the onset of the spectra and the features across the spectra, which relate to electronic states. The upper x-axis shows the kinetic energy of the detected electrons, while the lower x-axis displays the binding energy of those same electrons. The y-axis displays the normalized intensity or counts. Towards lower kinetic energies, the spectrum shows a polynomial background of secondary electrons that have been inelastically scattered prior to leaving the sample surface and thereby lost energy as well as any information about the DOS [84]. This background ends abruptly from which we can determine the ‘high binding energy cutoff’ (HBEC). The electrons here are provided with just enough energy to be excited above the vacuum level and we therefore use this HBEC energy to calculate the work function of the material (equation 4.5).

$$WF_{sample} = h\nu - E_{HBEC} \quad (4.5)$$

$$IE = h\nu - (E_{HBEC} - E_{HOMO}) \quad (4.6)$$

On the other end of the spectrum, we can find the Fermi energy, E_F , which is equal to a binding energy of zero electron-volts, $E_{binding} = 0$ eV. In the case of metals, the density of states is occupied up to the Fermi energy, therefore the high kinetic energy electrons will be freed from this Fermi edge, as seen in Figure 4.4. In the case of semiconductors, there are no states around E_F due to the presence of the bandgap, and the first states visible will be a slightly higher binding energy $E_{binding} > 0$ eV and correspond to the onset of the valence band for inorganic material or synonymously in the case of an organic semiconductor, they originate from the HOMO DOS. The rest of the spectrum indicates the energies of other electronic states deeper within the occupied

DOS. The ionisation energy is calculated as the energy required to release an electron from the HOMO to vacuum and can be calculated by obtaining a value for E_{HOMO} and a value for the work function, see equation 4.6.

Figure 4.5 exemplifies how the UPS data is analysed, using data from a thin film of PCBM. This shows how values for the HBEC and the HOMO level onset are extracted by a linear extrapolation. To determine values for the HBEC and HOMO, we are interested in the regions of the spectrum at both high energies (for HBEC) and low energies (for HOMO), and so only these two relevant regions are shown here, instead of the complete UPS spectrum. In both cases, the leading edge of the data is determined by drawing a line to the leading edge of the DOS and reading out the intersection with the background intensity.

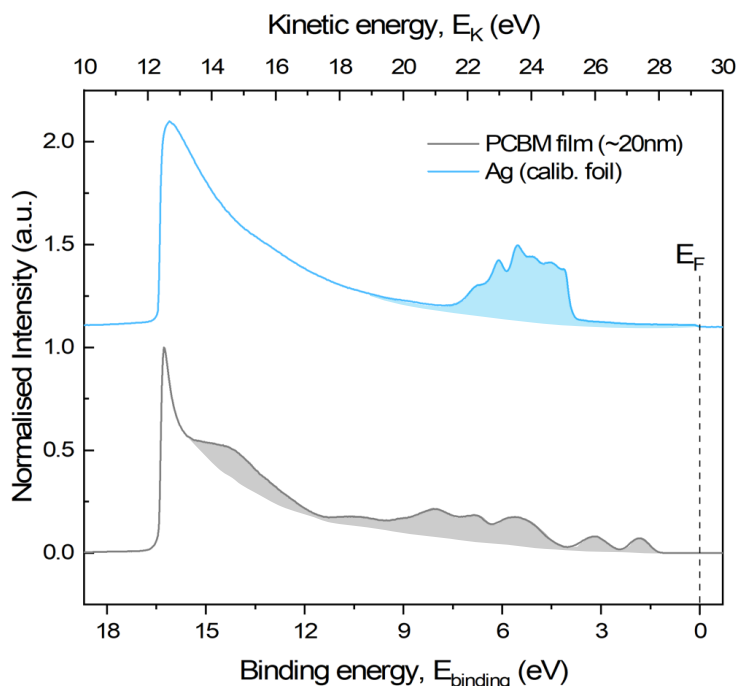


Figure 4.4 – Typical UPS measurements of a thin film of PCBM and a silver calibration foil as a function of binding energy and kinetic energy, highlighting the difference in the onset of occupied states between the two materials, with the valence band onset of the silver foil sitting at the Fermi energy.

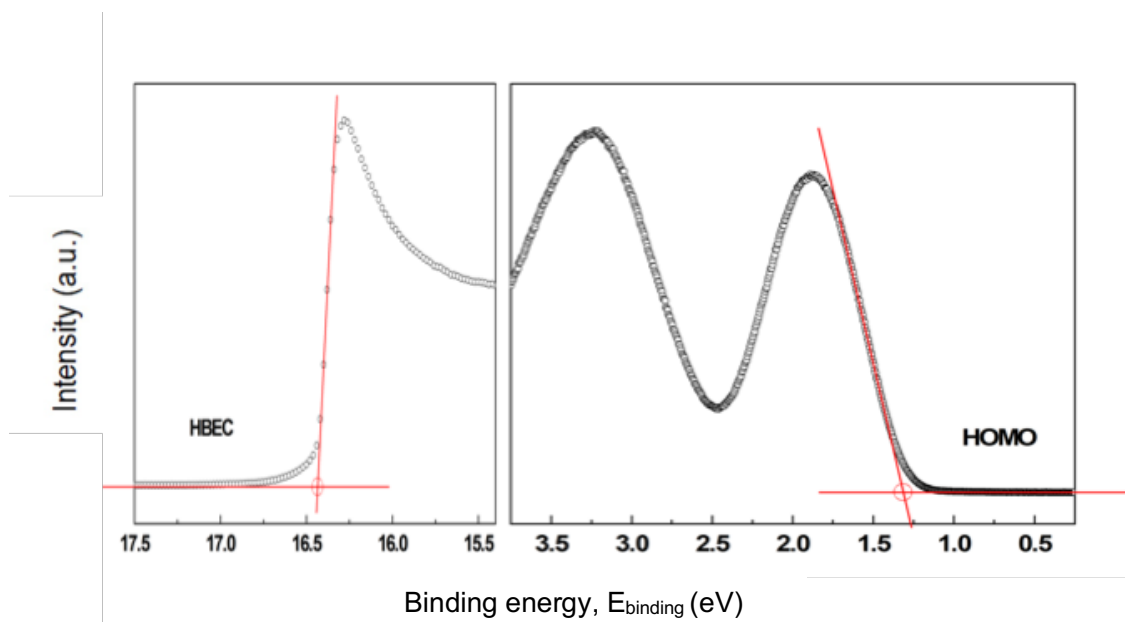


Figure 4.5 – Typical diagram of the UPS measurement, taken from UPS spectrum of PCBM thin film (full spectrum presented in Fig. 4.4), displaying how the high binding energy cutoff (HBEC) and highest occupied molecular orbital (HOMO) onset position are determined.

If we deposit a material onto another material, such that there is contact between them, it is possible using this technique to examine how their energy levels align at the interface. It is commonly observed that the vacuum level (E_{vac}) at an interface is not consistent across the two materials, but rather interface dipoles can occur (see chapter 2.1.3.), resulting in a difference in HBEC energies for the two materials and thus a different work function for the two materials (see Figure 5.21, chapter 5).

For all measurements taken using the UPS setup described in this chapter, a pass energy of 2 eV was used, with energy step widths between 0.01 eV and 0.03 eV, depending on the scan taking place, at an integration time of 0.1s. The spectra are collected by measuring over an area of approximately 3 mm². When necessary, especially when measuring the HBEC, the entrance slit of both the iris and lens are

reduced to ensure that the count rates of the detector do not exceed the acceptable limit of one million count/s. Typical exposure times are less than 5 minutes for any scan.

Additional information can be gained with complimentary spectroscopy such as UV-Vis to determine the optical gap, and with IPES to build up a more detailed idea of the density of states at the LUMO or conduction band. The elemental composition, or chemical changes taking place in the sample can also be investigated with techniques such as XPS. Both IPES and XPS data can be acquired using the same UHV system, as will now be detailed in chapter 4.2.

4.2. Complimentary spectroscopy techniques; IPES, XPS

The two complimentary spectroscopy techniques this thesis will focus on are inverse photoelectron spectroscopy (IPES) and X-ray photoelectron spectroscopy (XPS) [260,261]. Both techniques are conducted in the same UHV chamber as UPS, at the University of Cologne. Starting with IPES, this technique is the inverse of UPS, allowing us to study the unoccupied conduction band or LUMO states of a material or thin film deposited onto a conductive substrate (as with UPS). IPES uses a Kimball ELG-2 electron source to emit electrons at an emission current of 2 μ A. The electrons have a set kinetic energy, such that they interact with these unoccupied electronic states within the first few monolayers or nanometres of the sample. Upon relaxation into these states UV-light is emitted, corresponding to the energy difference. A UV bandpass photon detector comprising a SrF₂ window and a NaCl solid state detector (IPES 2000), supplied from *Omnivac*, is used to collect counts. From this technique, the position of the LUMO energy onset can be determined with respect to the Fermi level. If the work function of the sample is known, e.g. from a prior from UPS measurement, the electron

affinity of the sample can be calculated using equation 4.7. Combining spectra from this measurement with spectra from UPS, allows for a more complete mapping of the electronic density of states of a material.

$$EA = h\nu - (E_{HBEC} + E_{LUMO}) \quad (4.7)$$

This technique however has its limitations. The signal is typically very low, leading to a high noise level in the data. Furthermore, the energy resolution is limited by the rather broad transmission of the bandpass detector to $\sim 450\text{-}600\text{meV}$ and finally the technique can be rather destructive, with high energy electrons hitting the molecules, they can often degrade, making it difficult to interpret the data correctly, or even making the data invalid if too much degradation takes place. The value of the LUMO onset is determined from the IPES spectra in the same way as with UPS, by drawing a line to the leading edge of the DOS and reading out the intersection with the background intensity.

X-ray photoelectron spectroscopy is slightly different from the other two techniques in its purpose, in that it involves the use of a soft X-ray source to probe the chemical composition of a sample. The technique is also known as electron spectroscopy for chemical analysis, *ESCA*. The X-ray source is equipped with a twin anode, one made from aluminium and the other magnesium, that can be excited independently to choose the desired energy of the X-ray emissions. The corresponding energies are $\text{Al K}\alpha_{1/2} = 1486.61$ and $\text{Mg K}\alpha_{1/2} = 1253.64$ eV [84,262]. In this thesis we have used the Mg anode as the X-ray source. In XPS, the X-rays are penetrating further into the bulk of a material or thin film, and the electrons are provided with enough energy such that they have an ~ 10 nm mean free path (see Figure 4.1), hence

only electrons released from the first 10 nm of a sample are measured. Due to this greater probing depth, in addition to allowing for chemical composition analysis, this technique can also reveal any changes in energetic positions of a thin film with deposition of another thin layer of different material on top, highlighting interactions between the two materials, by looking for shifts in the energetic position of chemical bonds.

The technique works by releasing core level electrons from the individual atoms making up the molecules of the sample. These core level electrons have characteristic energies that are measured and correspond to the element from which they were released. Depending on the number of electrons from each element, a characteristic peak will be built-up on the spectrum. The shape of such a peak is determined by several factors, including the number of electronic states available from which electrons can be released, and splitting in the peak may represent electrons from differing orbitals or from spin-orbit splitting within an orbital [84,260,261]. Importantly, the exact binding energy of a core electron is also affected by bonds created by outer electrons in an atom, due to the reorganization of the electron density distribution within the atom when that atom binds to another. This can lead to a ‘chemical shift’, or in other words a shift in the binding energy of that core electron. There are of course examples where two bonds cannot be clearly distinguished from one another due to two atoms with similar electronegativities bonding. Identification of these characteristic signatures within XPS spectra is a key aspect to its analysis and understanding the make-up of a material or thin film.

In order to determine if any compositional changes happen within a given sample, XPS can be used to measure the samples before and after the changes are expected. However, if the exact elemental composition of a sample is to be analysed quantitatively, then the relative heights of each peak can be compared, with many factors coming into

play here, most notably the concentration of each element in the sample, in addition to the cross-section of interaction between the photon and the observed transition. The influence of the cross-section is considered by dividing the measured intensities by a relative sensitivity factor, which need to be calibrated for a given system.

In this work we are not concerned with identifying the exact elemental composition but rather using XPS to detect any changes in spectra with variations in sample processing or doping of thin films. To analyse these differences, changes in intensity of peaks corresponding to the characteristic binding energies of electrons in a given element are analysed. An example spectrum from an XPS measurement of ITO is given in Figure 4.6. This figure highlights some of characteristic peaks of interest.

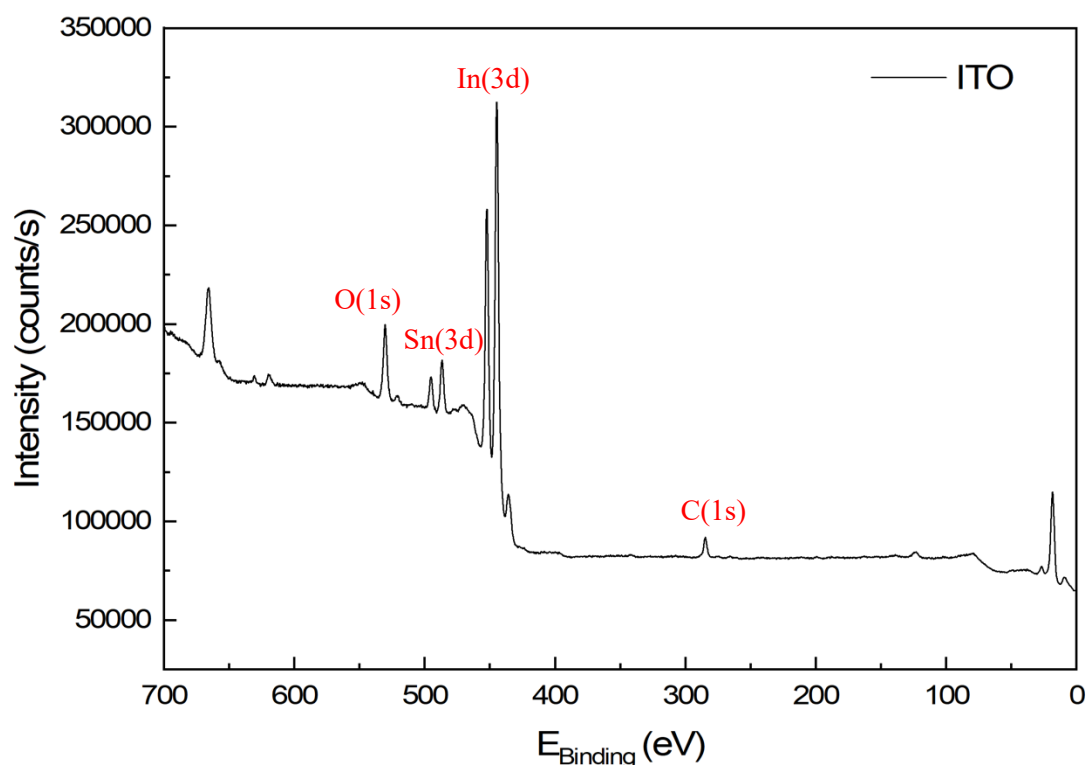


Figure 4.6 – Spectrum from the X-ray photoelectron spectroscopy (XPS) measurement of an ITO substrate, highlighting the peaks correlating to the release of core electrons from elemental carbon, indium, tin and oxygen, and the orbitals from which they originated.

Each spectrum will have a background that corresponds to the signal that arises from scattered electrons. When analysing and fitting a core level signal, appropriate backgrounds must be considered. In the software package used in this thesis (XPSPeak4.1), either a Shirley (e.g. for Oxygen) or Linear (e.g. for Indium) background was used depending on the element being analysed. For quantitative analysis, the characteristic peaks are fit with either a single peak fit or multiple peak fits if there are multiple energetic contributions to the data peak. The line shape of the fits is produced with a combination from both Lorentzian and Gaussian fits. Further fit parameters involve the position of the peak relative to binding energy, the area under the curve and the full-width half-maximum (FWHM). When multiple peaks are involved in a fit, identical Lorentzian-Gaussian ratios and FWHM values are assumed for each contribution to the signal originating from the same element. For spin-orbit split peaks, the relative peak intensities are also fixed, and these intensities are known from the degeneracy. Typical values for the FWHM at the used pass energy of $E_{\text{pass}} = 20$ eV are 1.2-1.4 eV and generally fit contributions are typically 20-40% Lorentzian with the rest a Gaussian contribution. In this setup, it is common for the parameters for different elements to be comparable as they mainly depend on the analyser transmission function and pass energy [84].

XPS measurements must also be done on samples deposited onto conductive substrates to eliminate charging effects taking place and potential shifting of the spectra. After an XPS measurement, a UPS scan should be conducted once more, to investigate for any energetic change, for example through degradation, during the XPS.

In this thesis, XPS has been conducted using the system of Dr. Selina Olthof, at the University of Cologne. A magnesium $K\alpha$ source was used, operated at a power of 240 W. The X-ray source is a dual anode x-ray gun from VG, and the angle between the

sample surface and the detector is 90° . A pass energy of $E_{\text{pass}} = 70 \text{ eV}$ is used for detection, in order to achieve a good resolution with higher count rates than at lower energies. An energetic step width of 0.03 eV is used and an integration time of 0.1 s . For XPS measurements, the *HSA3500* power supply is also used, and the same measurement software is used as with UPS.

For further details on the general principles of any of these techniques, please see [84,260,261,263].

Chapter 5

Investigating the relationship between the fabrication steps of PCBCB thin films and film properties

In this chapter we are investigating the solution processing parameters for organic semiconductor thin films, namely PCBCB as an electron transport layer. When preparing devices, it is crucial the thin films within the stack have optimised properties, both physical and optoelectronic. Here we assess how the parameters used during fabrication can be tuned and adapted in order to attain films with appropriate thickness, complete substrate coverage and a defect-less surface. Furthermore, these physical properties coincide with the optoelectronic properties of the films, determining the absorptance spectrum of a material, how crystalline and ordered its molecular packing may be and how conductive a material it is, along with effects of its energetics. All of these properties are explored and optimised for use in a device stack.

**Within this chapter, all UPS, XPS and IPES measurements were conducted at the University of Cologne, using the setup of Selina Olthof and Klaus Meerholz, as described in chapter 4.*

*** The work in chapter 5, 6 & 7 is yet to be published but will likely be used (with adapted text and figures) within a paper publication/s. Potential name of primary publication: ‘An investigation into energetically tuneable ‘PCBCB’ as robust electron transport layer in OPV applications’.*

5.1. Understanding the effects of fabrication steps on the physical and optoelectronic properties of PCBCB thin films

The initial fabrication parameters adopted for PCBCB thin films have been taken from a combination of the literature as described in chapter 3.1.3 and optimised further to understand better the relationship between the quality of film formation and the concentration of PCBCB solution. It was important to ensure the formation of complete thin film across the substrate with minimal surface defects, whilst ensuring film thickness was not too great ($> \sim 30\text{nm}$), as to reduce both excess light absorption in the ETL and the series resistance contribution from the layer. In the case of spin-coating it is of course important that the processing parameters should when possible be optimised for each individual spin-coater, with differences in conditions—including pressure, solvent and oxygen atmosphere, humidity and temperature to name the key contributors—all playing a key role in the final properties of a thin film.

Thin films of PCBCB were first processed via spin-coating onto a series of ITO substrates using a solution concentration of 15mg/ml of PCBCB monomer powder in 1,2-dichlorobenzene. The exact processing conditions follow that as described in chapter 3.3.

The oligomerisation process of PCBCB is a crucial step in forming an insoluble film, to allow for solution processing atop of it. While the annealing conditions required for this process have been studied by Deb et. al [210], and it was determined an annealing time of at least 10 minutes at 190-200°C is optimal, confirmation of the timing and temperature required for complete oligomerisation in a different lab setup is essential. A series of PCBCB samples were prepared as above, in the same conditions and annealed for differing durations at 200°C. Following the annealing step, the absorbance spectrum for each sample was studied, focusing on the absorbing regions of $\lambda = 310 - 590$ nm. The thin film samples were then rinsed in 1,2-dichlorobenzene (o-DCB) and the absorbance was remeasured. A photograph taken of the samples post-rinse vs an unrinsed sample as a reference is depicted in Figure 5.1.

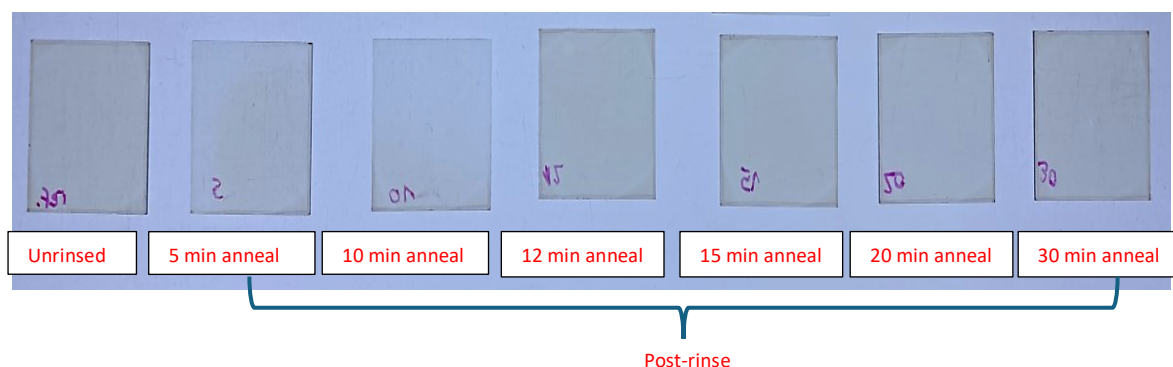


Figure 5.1 – Photograph of PCBCB films pre- and post- rinsing with o-DCB. From left to right, the samples have been annealed over increasing time periods and then subsequently rinsed with dichlorobenzene, indicating the necessary time for full oligomerisation to be at least 12 minutes. The first sample of the left is an unrinsed reference sample for comparison.

From the photograph, it appears that a 10 minute anneal is insufficient, which transparent patches of exposed substrate present across the sample after rinsing with o-DCB, confirming it has partially rinsed away the film. After 12 minutes, the

oligomerisation process appears complete as the film remains complete after rinsing. As there may be some uncertainty in the exact time necessary, a 15 minute anneal was chosen as the one to move forward with, to provide some extra certainty that the oligomers would form, rendering the films insoluble to the chlorinated solvents used. Although this is a nice qualitative determination of at which duration oligomerisation occurs, the UV-Vis absorbance data over the region that can confirm the presence of PCBCB can be seen in Figure 5.2 for a more qualitative confirmation of this result, with a reduction in the peak intensity around 340 nm indicating the removal of the material. Additionally, XRR was used once again to determine that the thicknesses of the films and confirm that the film was still present, and the amount rinsed away post-rinse. A sample fit for PCBCB is shown in Figure 5.3. A total film thickness of ~ 27 nm was confirmed and compared to that of ZnO, also measured with XRR (Table 5.1). This concentration was chosen as the initial thickness for the films, as it matched nicely with the thickness of the chosen control ETL layer, zinc oxide, which was also measured using XRR to have a thickness of ~ 27 nm. Uncertainties are provided based on differences in thickness along the measured samples, with slight variations in thickness and roughness exhibited. It should be kept in mind that sample to sample variation can also occur as with different processing atmospheres (solvent content % for example) and substrate variations etc. Further, a larger uncertainty has been given for ZnO films, as a small differences between the measured data and the fit for these films was observed and understood to be a result of the ranging size of crystallites formed during the fabrication of the sol-gel film, meaning these measurements can only provide an average across the film.

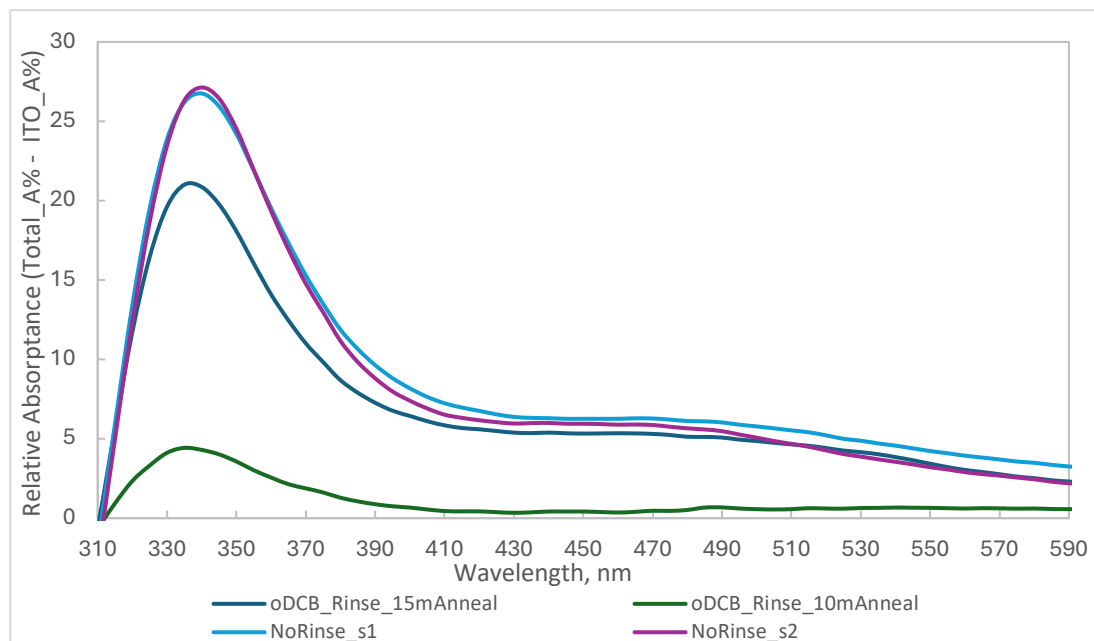


Figure 5.2 – UV-Vis absorbance spectra (Lambda 1050) for samples of PCBCB with and without an o-DCB rinse, showing how a 15 minute anneal is necessary for the oligomerisation, rendering the films insoluble in the solvent. This can be confirmed by no shifting of the spectra post-rinsing. The signal from the ITO background has been subtracted, hence the drop at lower wavelength. Notation s1 and s2 refer to samples 1 and 2 respectively.

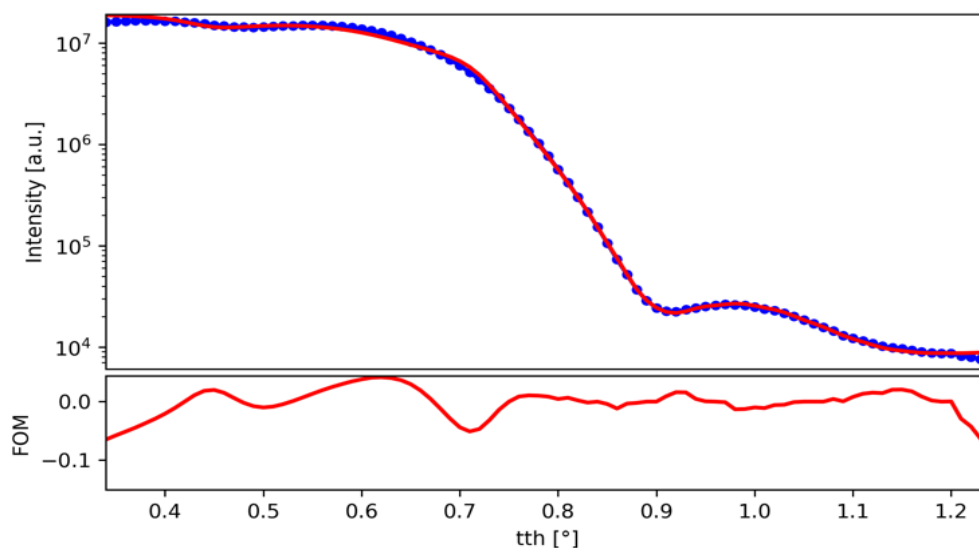


Figure 5.3 – Example XRR fit for PCBCB (15 mg/ml) thin film. The blue dotted line represents the data measured and the red line represents the fit to the data, from which surface roughness and film thickness can be extrapolated.

Film parameter	PCBCB (15 mg/ml) pre-rinse:	PCBCB (15 mg/ml) post-rinse:	ZnO
Thickness (Å)	276.6 ± 20	272.8 ± 21	265 ± 14
Roughness (Å)	16.2 ± 4	17.6 ± 6	16 ± 5

Table 5.1 – Thickness and roughness of ZnO film and PCBCB films pre- and post-rinse, determined via XRR.

With the optimal annealing temperature and duration for oligomerisation confirmed, it was important to assess the quality of the films, to ensure they were complete across the substrate with minimal defects, for use in a device stack. SEM and AFM were two techniques used to assess the film surface quality. Firstly, SEM was used to take a larger scan of the sample surface (Figure 5.4), from which bumps across the surface could be identified. AFM was then used to zoom into the surface and look at a smaller area in finer detail, and with this measurement pinholes up to 2 µm in diameter and up to 20 nm in depth were defined across the surface (Figure 5.5), which would coincide with increased shunting in devices. The harsh annealing temperature of 200°C was determined to have affected the degree of pinholes within the film. We suggest the sudden increase in temperature leads to an explosive phenomenon within the films, resulting in rapid expansion of the solvent trapped within the films and the formation of solvent bubbles that explode and leave behind craters (pinholes) within the films. From the contrast on the AFM image, it appears that debris build up surrounds each of the craters also. Decreasing the number of pinholes throughout the film is essential in decreasing the likelihood of short-circuiting of a device and will result in much more reproducible and consistently performing devices. Therefore, to test this further, a series

of further optimised and less ‘aggressive’ annealing conditions were tested, by implementing a more gradual temperature increase to assess the effect on degree of pinholes before re-assessing the film quality.

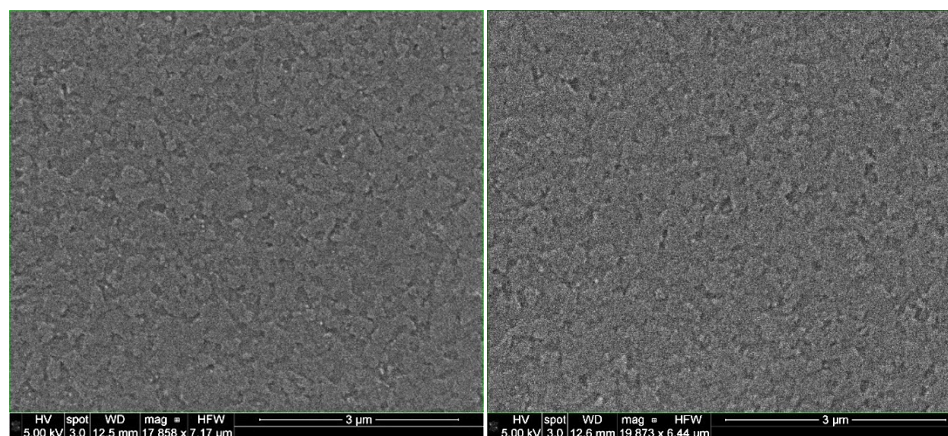


Fig 5.4 – Top-down SEM images of PCBCB thin film surface from a 10 mg/ml solution (left) and (right) and a 15 mg/ml solution (right). The films are determined to have some surface roughness from the contrasting colours across the sample surface. Dark regions indicate deep defects across the sample surface. Images taken by Dr. Alexandra Ramadan.

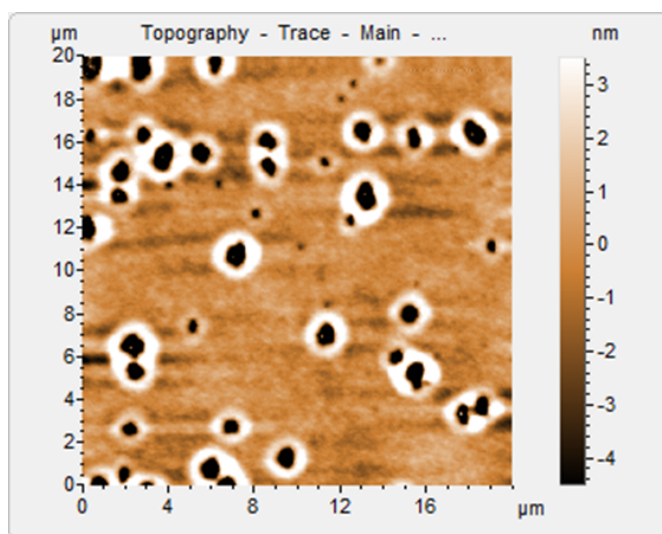


Figure 5.5 – AFM image of PCBCB film annealed directly on hotplate at 200°C following spin coating. Pinholes up to a diameter of $2\mu\text{m}$ and a depth of up to 20 nm were detected (dark features). Measured with Begbroke setup (chapter 3.3), by Nicola Mason.

A set of fresh samples were annealed on top of an aluminium block to homogeneously distribute the temperature across the films and introduce a gradual temperature increase while the block reached 200°C. A further set were prepared with a primary 10-minute, 60°C gentle annealing step, in order to drive solvent out of the films, before ramping up to 200°C on the block. A ramp time of 7-minutes was determined necessary for the samples to reach 200°C on the block (as tested using a thermocouple). The films were then annealed for a further 15 minutes after the ramping period. The solubility of these films in o-DCB had to be tested once more to ensure these new conditions still resulted in oligomerisation as expected, by checking the absorbance spectra of the films with a solvent rinse after annealing (Figure 5.6). The figure compares the previous anneal ('No Block'), to the use of a block ('15m 200C Block') and then with the further 7-minute ramp time included to heat up the block to temperature ('22m 200C Block'), proving the ramp time crucial to the oligomerisation process, with a loss of film material indicated by a change in spectrum between ~ 300-400 nm. A reduction in the peak intensity around 360 nm is indicative of a change in the packing of the film and thus the successfulness of the oligomerisation process [210]. Figure 5.7 is a photograph of the samples tested with (right) and without (left) a rinse, in the same order as presented on the absorption spectrum.

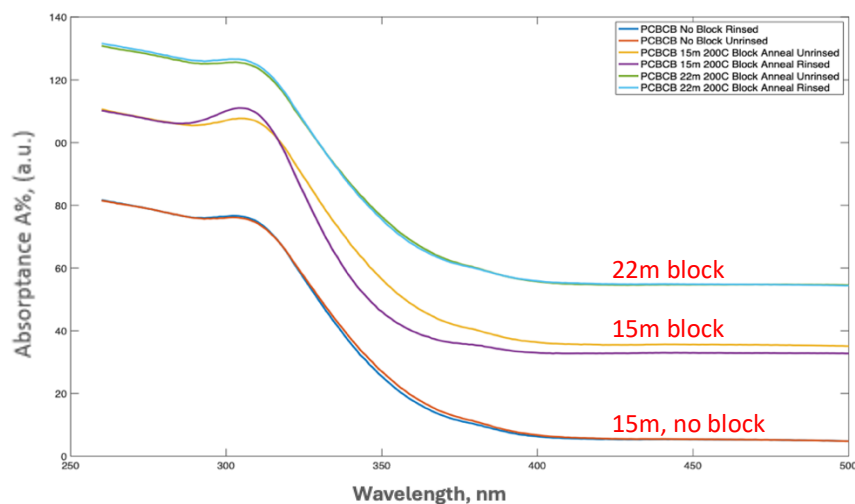


Figure 5.6 – UV-Visible absorption spectra (Cary 5000) from three sample sets with differing anneal conditions. The spectra compared consist of that from samples prepared using the original anneal condition of 200°C for 15 minutes with no block for homogenous thermal distribution or gradual temperature increase (‘No Block’), to the use of a block for 15 minutes also (‘15m 200C Block’) and then with a further 7-minute ramp time included (‘22m 200C Block’). The spectra comparing rinsed and unrinsed samples post-anneal details the loss of material upon rinsing of PCBCB films with o-DCB, without the use of a full 22-minute annealing period when incorporating a block into the annealing step. Changes in the spectra around 300-400 nm indicate this loss of material when rinsed.

These films were then compared with AFM once again, which highlighted the improvements in surface defects with improved annealing conditions (Figure 5.8). The data here was greyscaled to better show the contrast in surface features. Introducing a ramping period to gradually increase the temperature proved to significantly reduce the degree of pinholes in the film, however pinholes were not completely eliminated. The top left of the figure shows the original annealing condition, while the top right is with the introduction of the new improved annealing parameters. The bottom right shows this same result, but with AFM taken on fresh samples with upgraded equipment to enhance the resolution of the film. The bottom left shows a film with an additional rinsing step post-anneal, resulting in removal of the debris.

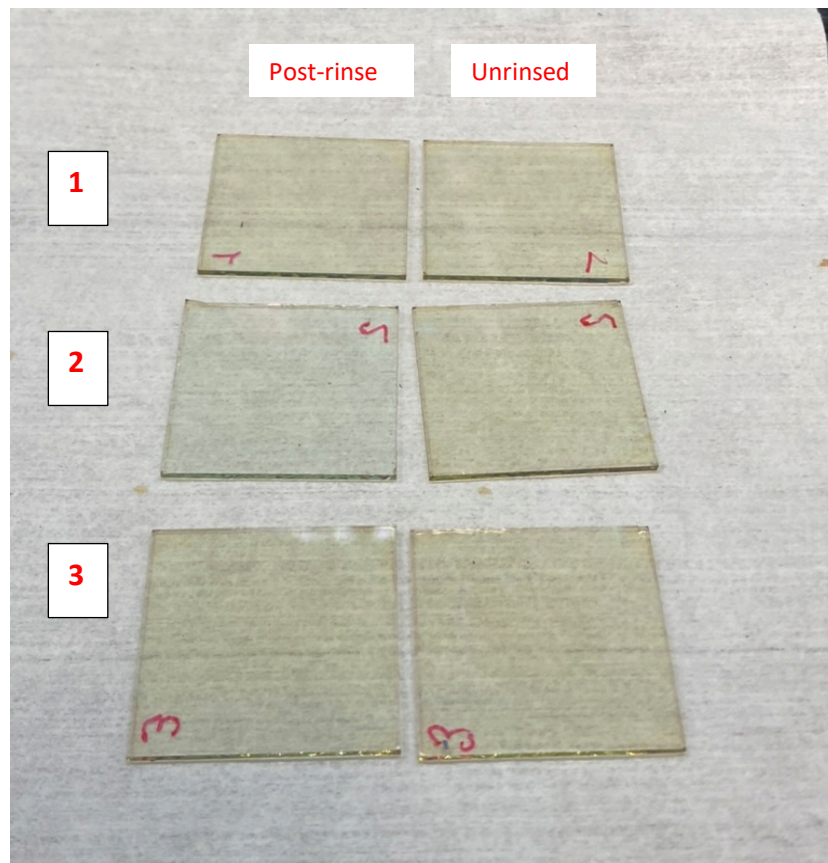


Figure 5.7 - Photograph of samples that have been prepared with three different annealing conditions, with the final optimal condition being condition 3. Condition 1 involves placing samples directly onto a hot plate at 200°C after spin-coating for 15 minutes. Condition 2 involves placing samples onto an aluminium block before placing the block on to the hotplate at 200°C for a 15-minute time period. Condition 3 involves using the same block anneal for 15 minutes but first allowing for a 7-minute ramping period for the block to reach the correct temperature, resulting in a total annealing time of 22 minutes.

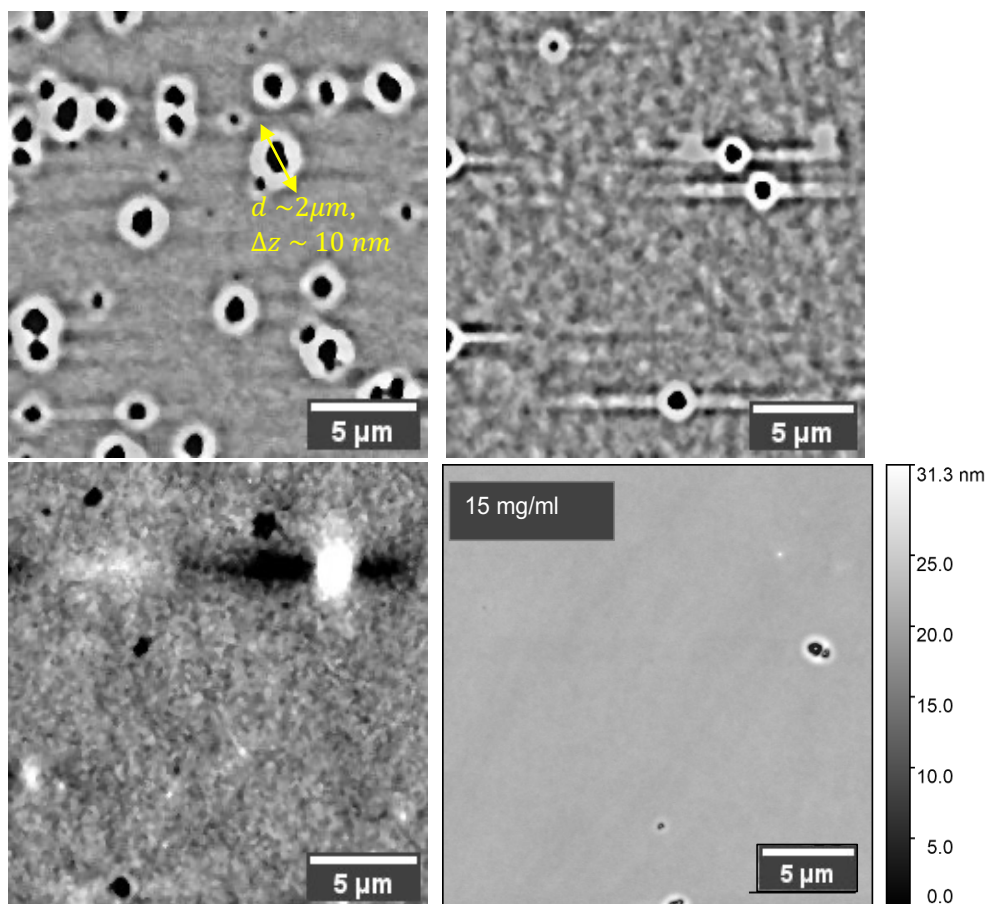


Figure 5.8 – AFM images of different annealing conditions applied to PCBCB films. Top left is a anneal for 15 minutes directly after spin coating on a 200°C hotplate, top right is with application of a 60°C primary anneal for 10 minutes on an aluminium block, followed by an increase in temperature to 200°C, over a ramping period of 7 minutes, followed by a further 15 minutes anneal. Bottom left is the same as top right but with an added rinsing step (bright feature is dust). These three were taken with the Begbroke AFM (chapter 3.3). Bottom right is the same as top right but taken with better equipment (Beercroft setup, ch. 3.3) and shows sample to sample variation. Images taken by Nicola Mason (left, top & bottom and right, top) and Olivia Gough (right, bottom).

From this AFM data, the percentage of the sample covered with pinholes and debris was extrapolated by analysing segmented areas of the film using the software ‘*ImageJ*’. In addition, the correlation between pinholes, debris, the root mean square roughness and the annealing process used, has been plotted in Figure 5.9, showing a clear reduction in pinhole and debris coverage with improved anneal conditions. Interestingly an increase in the overall root mean square surface roughness (RMS) was observed. Giving samples a 10-minute rest period between the spin-coating and annealing step and then placing them directly onto the hotplate at 200°C for 15 minutes was also tested. Increasing the rest period pre-anneal allows time for the solvent trapped within the films to evaporate out before being subjected to higher temperatures. This too resulted in reduced pinholes but was less effective than the introduction of the metal block, and the combination of the 60°C primary anneal and ramped block anneal (denoted as ‘best anneal’ in the figure).

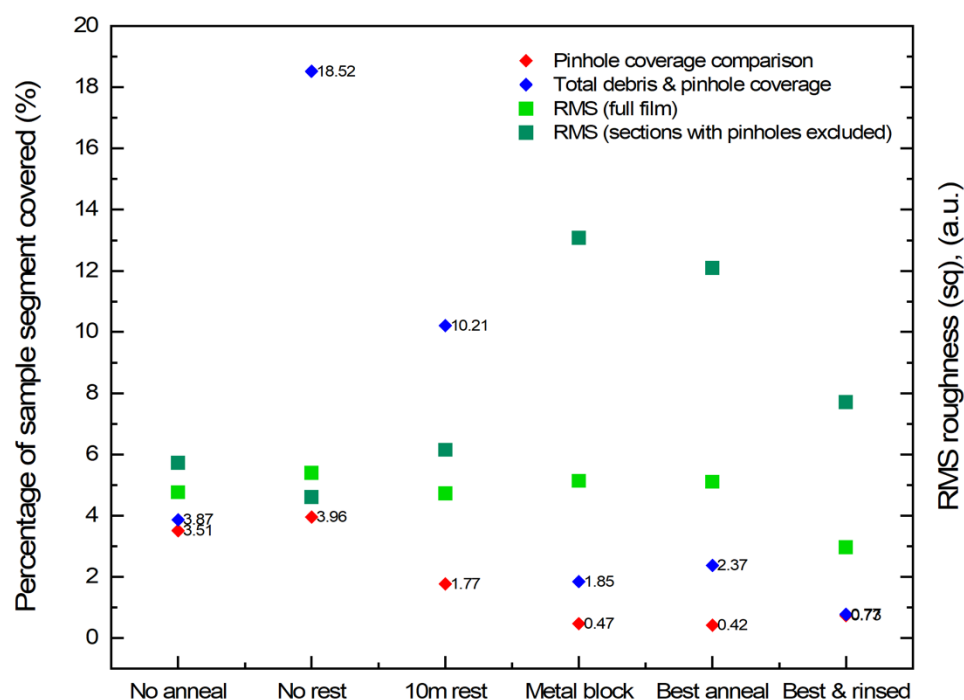


Figure 5.9 – Plot depicting debris and pinhole coverage across PCBCB films with varied annealing conditions, along with the root mean square roughness, scaled to fit (on the order of nanometres). Improving the anneal proves to significantly reduce the percentage of sample segment covered in both pinholes and pinholes and debris surrounding the pinholes. The full film roughness remains mostly consistent throughout, but when excluding pinholes, the use of a metal block appears to increase the roughness of the films as compared to those annealed directly on the hotplate.

Understanding this pinhole problem would also prove to be constructive on a wider scale, helping to understand and solve a problem encountered across the research group when using PCBM layers in particular. This layer had been resulting in inconsistencies in the performance of devices, which has now been proven to also be, at least in part, due to these pinhole formations in such fullerene-derivative materials during fabrication.

These improvements were also observed in the analysis of XPS data from scans of PCBCB films (Figure 5.10), in which the degree of indium signal that appears was a signifier of the degree of pinholes. The indium signal comes from the indium tin oxide substrates upon which the substrates are fabricated. Improving the annealing conditions leads to a reduced indium signal. The X-rays emit electrons from the first ~ 10 nm of the sample they are penetrating, thus when more pinholes are present, we see more indium signal due to the reduced thickness of the PCBCB in these regions. All indium peaks across the XPS data have been fitted using a linear background, a spin-orbital splitting of 7.62 was set, and an asymmetry parameter in the d-orbital was introduced, to account for a plasmon loss tail.

Following these experiments with the annealing parameters, it was decided that this new annealing condition using an initial anneal, which to summarise consisted of: An initial 10-minute, 60°C gentle annealing step, followed with ramping up to 200°C on the aluminium block over a ramp time of 7-minutes to achieve temperature, with a further 15 minutes at this temperature after the ramping period. This anneal procedure resulted in the least number of pinholes, as well as the best energetic compatibility (as will be discussed in 5.2), would be selected to move forward with for device studies. This optimal condition is also described fully in chapter 3.3.

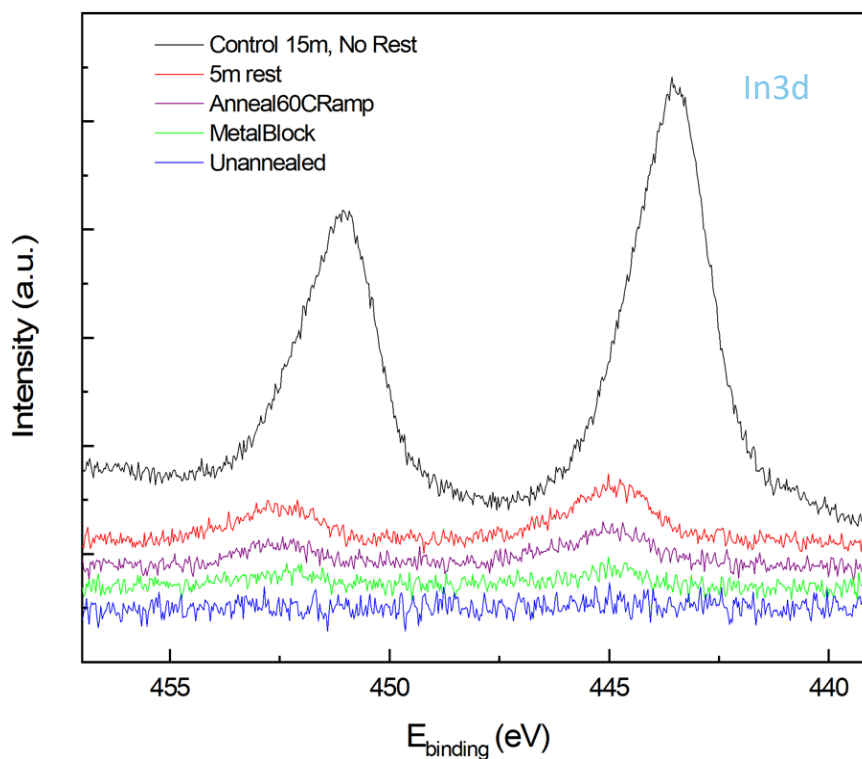


Figure 5.10 – XPS data of characteristic indium 3d peaks indicative of ITO presence in PCBCB films, changing in intensity with annealing conditions.

A series of PCBCB films of varying concentrations were prepared using the optimal annealing conditions, in order to determine the limit at which a thin film with full substrate coverage can be formed and assess the film quality. Raman spectroscopy was first used to detect characteristic carbon bond with wavenumber $1440\text{-}1480\text{ cm}^{-1}$, present in PCBCB but not in the ITO substrates. These measurements were conducted over a $7\times 7\text{ }\mu\text{m}$ area on each sample, see Figure 5.11. From this it could be determined that even at low concentrations of 1 mg/ml had some coverage from PCBCB solution, with some counts appearing in the characteristic region as compared to the data from ITO, albeit low counts. Heat maps were plotted to map the homogeneity of the coverage across the sample, suggesting presence of the material across every $1\times 1\text{ }\mu\text{m}$ square measured (size of the beam spot). This of course does not mean that there is complete coverage across these squares but could also indicate spotted or ‘island’ coverage across these areas, rather than a complete film formation. To investigate this, AFM and contact angle analysis measurements were conducted to determine the concentration at which a complete film forms (Figure 5.12).

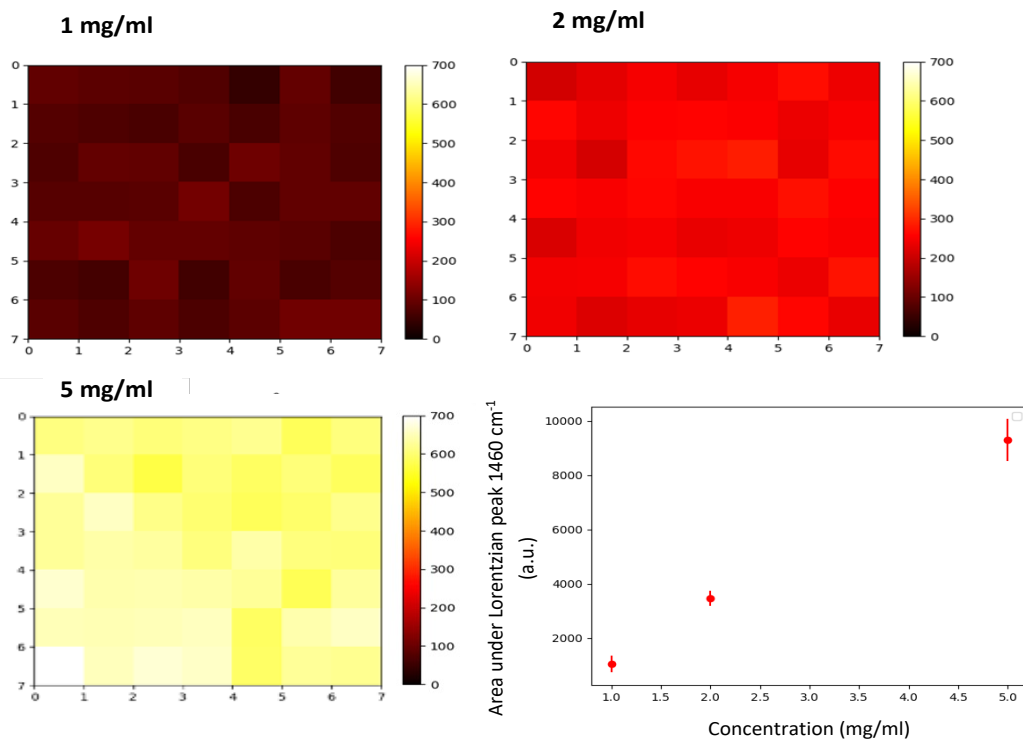
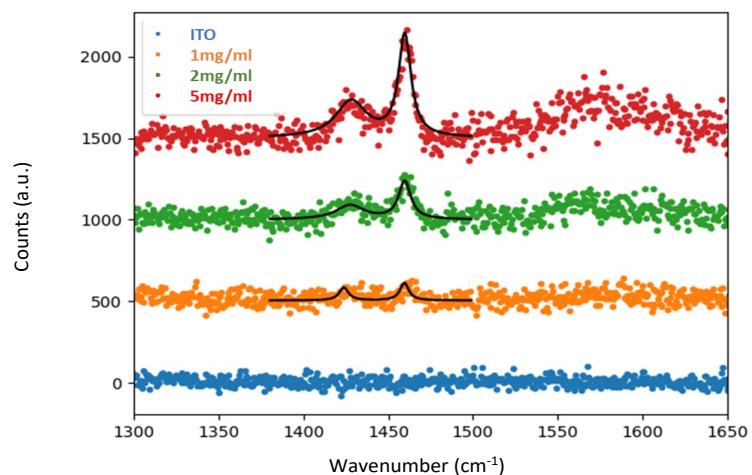


Figure 5.11 – Raman spectroscopy to detect signature carbon bond with wavenumber $1440\text{-}1480\text{ cm}^{-1}$, present in PCBCB films but not in ITO. Heat-maps detail presence of PCBCB across the substrates at different solution concentrations.

From AFM (Cologne setup) and contact angle analysis, it could be shown that at a concentration of around $1\text{-}2\text{ mg/ml}$ in order is needed to see some wetting of the material to ITO substrates, as can be seen by the yellow islands of material on the darker

substrate background. For a complete film to form, a concentration of around 8 mg/ml was required. This is also highlighted by the two linear regimes in the surface tension and contact angle when plotted as functions of PCBCB solution concentration. The concentration at which a complete film forms is somewhere between 5-10 mg/ml, with a turning point in the plot at around 8 mg/ml.

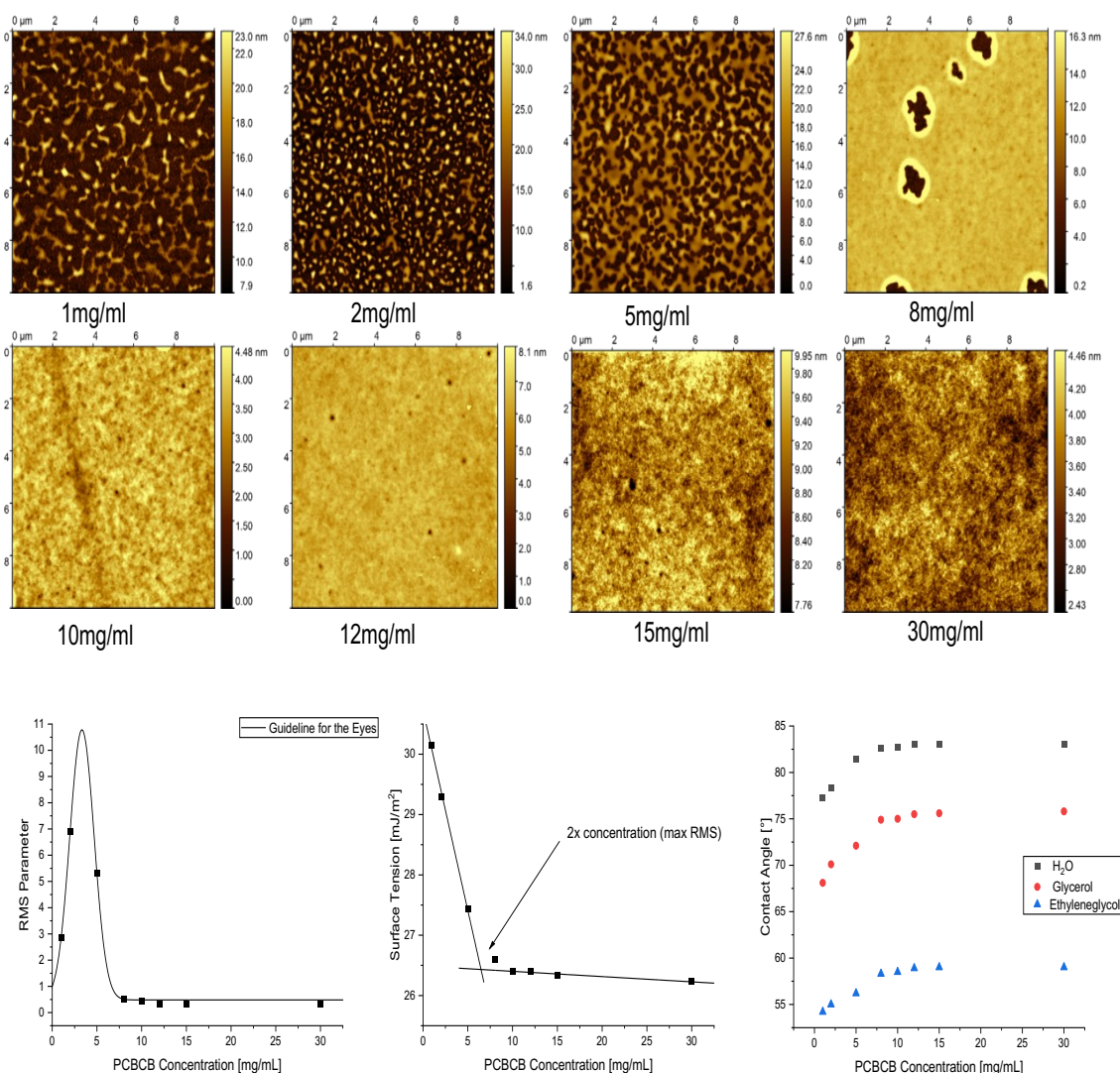


Figure 5.12 – AFM and contact angle measurements for thin films comprised of different concentrations of PCBCB solution. RMS, surface tension and contact angle are plotted as a function of concentration. Complete films are formed at around a concentration of 8 mg/ml. AFM images taken and analysed by Philipp Weitkamp.

XPS analysis highlights the changing indium signal in the thin films (Figure 5.13), with increased suppression of this signal as the film concentration and thus thickness increases, as expected. It can be seen that the indium peak fit does slightly change with increasing thickness, likely due to the depth at which the indium substrate itself is probed. This means that in thinner films, electrons are emitted from slightly deeper into the ITO, while in thicker films, a greater proportion of the indium signal is from surface ITO, and these likely have slightly different chemical composition.

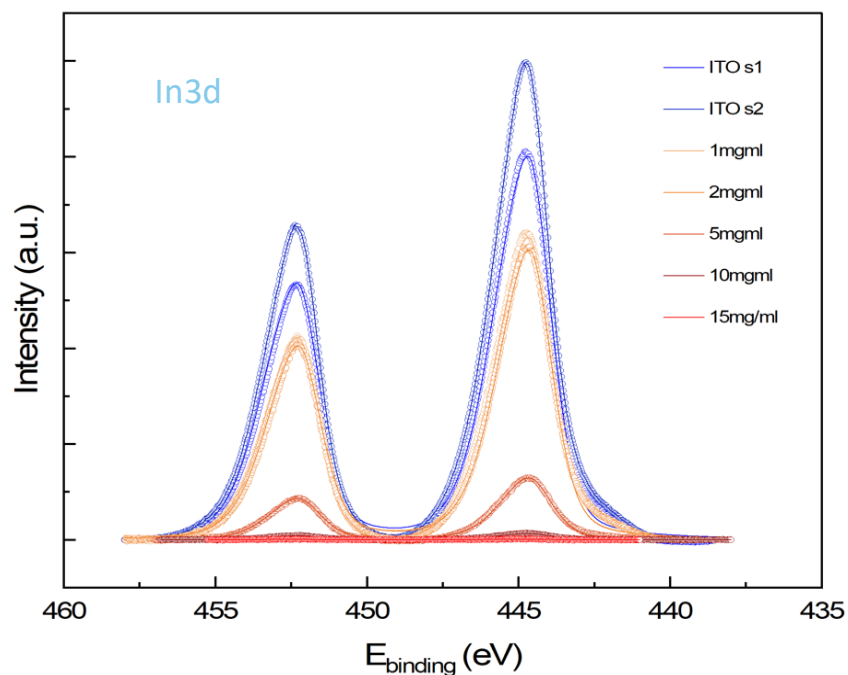


Figure 5.13 – XPS spectra of characteristic indium 3d peaks indicative of ITO presence in PCBCB films of varying concentration, indicative of thickness changes. The notation s1 and s2 refer to two separate samples, labelled 1 and 2 respectively.

5.2. Understanding the effects of fabrication steps on the energetic properties of ITO glass and intrinsic PCBCB thin films

Having understood better the relationship between our variable thin film processing parameters during sample fabrication, it was important to understand how these affect the energetics of the layer and the effects this may have on the system. We first consider the example of nominally intrinsic PCBCB thin films. UPS data has been collected to examine energetic shifts in the position of the HOMO level and the work function of PCBCB thin films with changes in the fabrication steps. We will then consider a thin film of PCBCB prepared using optimised processing conditions against that of other notable semiconductor thin films, namely C60, PCBM and the control, ZnO.

5.2.1. Spectroscopic study on the effects of thin film processing parameters

In order to get a clear understanding of the PCBCB layer, it is useful to first study the substrate upon which it is processed to be able to discern the background substrate signal features. A study of ITO substrates reaffirms that ITO can have some variation in surface energetics from substrate to substrate, and over time on a single substrate, due to many factors including varying surface composition and quantity of surface impurities, time between UV-Ozone cleaning and deposition of the film matter, in addition to slight differences in the cleaning process before use of the substrates themselves. Having a good average for our substrate energetics and trying to be consistent in all cleaning and fabrication processes that can induce changes in the substrate energetics allows us to

have more confidence in our subsequent ETL layer. The variation in ITO work function from sample to sample, as exemplified in literature [84,109,119-121], could occur due to variations in the surface composition of the ITO, as well as differences in substrate preparation such as with cleaning methods, and could also be due to an induced reduction from the UV-light during UPS [121]. These can be seen from the shifts in the HBEC cutoff energies, displayed in Figure 5.14. These substrate dependent shifts in work function, in addition to the possible energetic shifts with small variations in processing conditions, must be kept in mind when analysing thin film energetic deposited onto these substrates, as this can also lead to small shifts in their energetic properties. Films of intrinsic PCBCB shows a range of possible values for the work function and HOMO with respect to Fermi level dependent on the preparation of the substrate. For this reason, a fresh control PCBCB thin film sample was always prepared with every data set, so energetic shifts between samples can be compared fairly with respect to the control from the same data set.

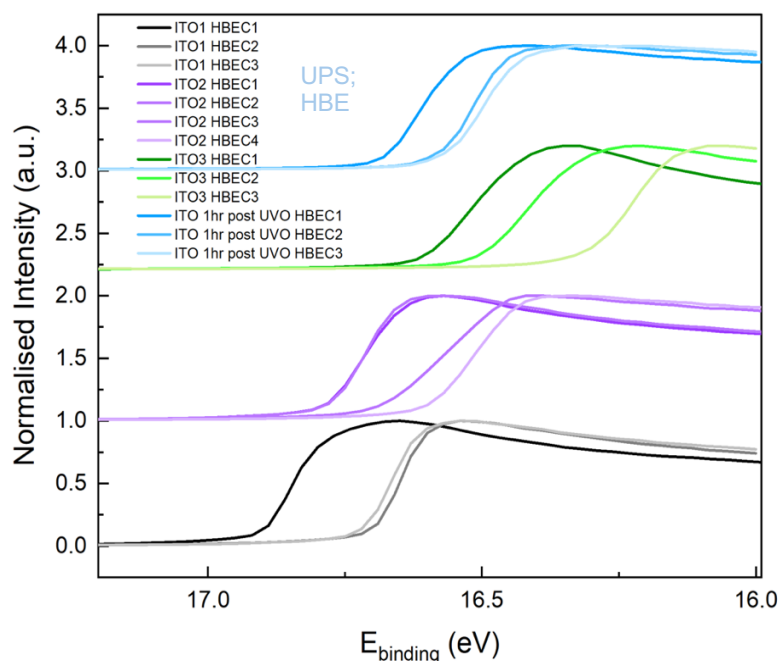


Figure 5.14 – UPS data exemplifying sample to sample variation in ITO work function, as shown by shifting HBEC onsets. *UVO refers to UV-Ozone cleaning.

The energetic shifts in PCBCB films (15 mg/ml) with different annealing temperatures and time were first studied using UPS, as shown in Figure 5.15. A HOMO scan was not taken for the 30m, 190°C, 1-hour post-UV-Ozone sample, hence its omission from the second half of the figure. A longer annealing time may have resulted in more crystallisation and potentially increased oligomerisation throughout the film, which could have resulted in this energetic shift. This could also be a result of substrate variation again influencing the PCBCB work function.

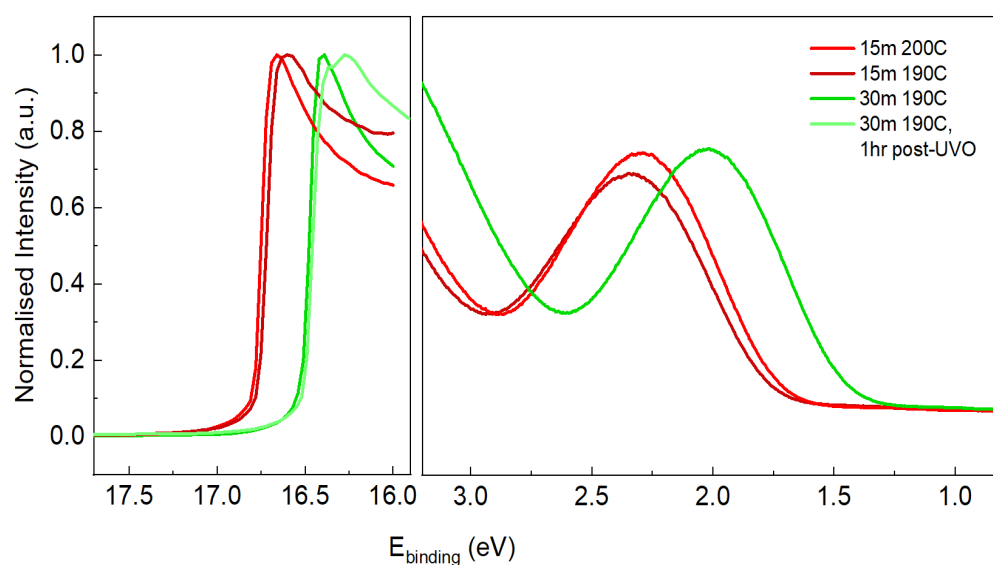


Figure 5.15 – UPS data of PCBCB films with varying annealing steps, showing a shift in energetics with a 30 minute anneal step vs a 15 minute anneal.

Following on from this, the improved annealing conditions, as described in 5.1, were tested to determine first if rest time before annealing had any effect on the film energetics. Interestingly, a shift in the energetics of the films was observed with increased rest time when films are exposed to air after annealing, but negligible changes with no air exposure (Figure 5.16).

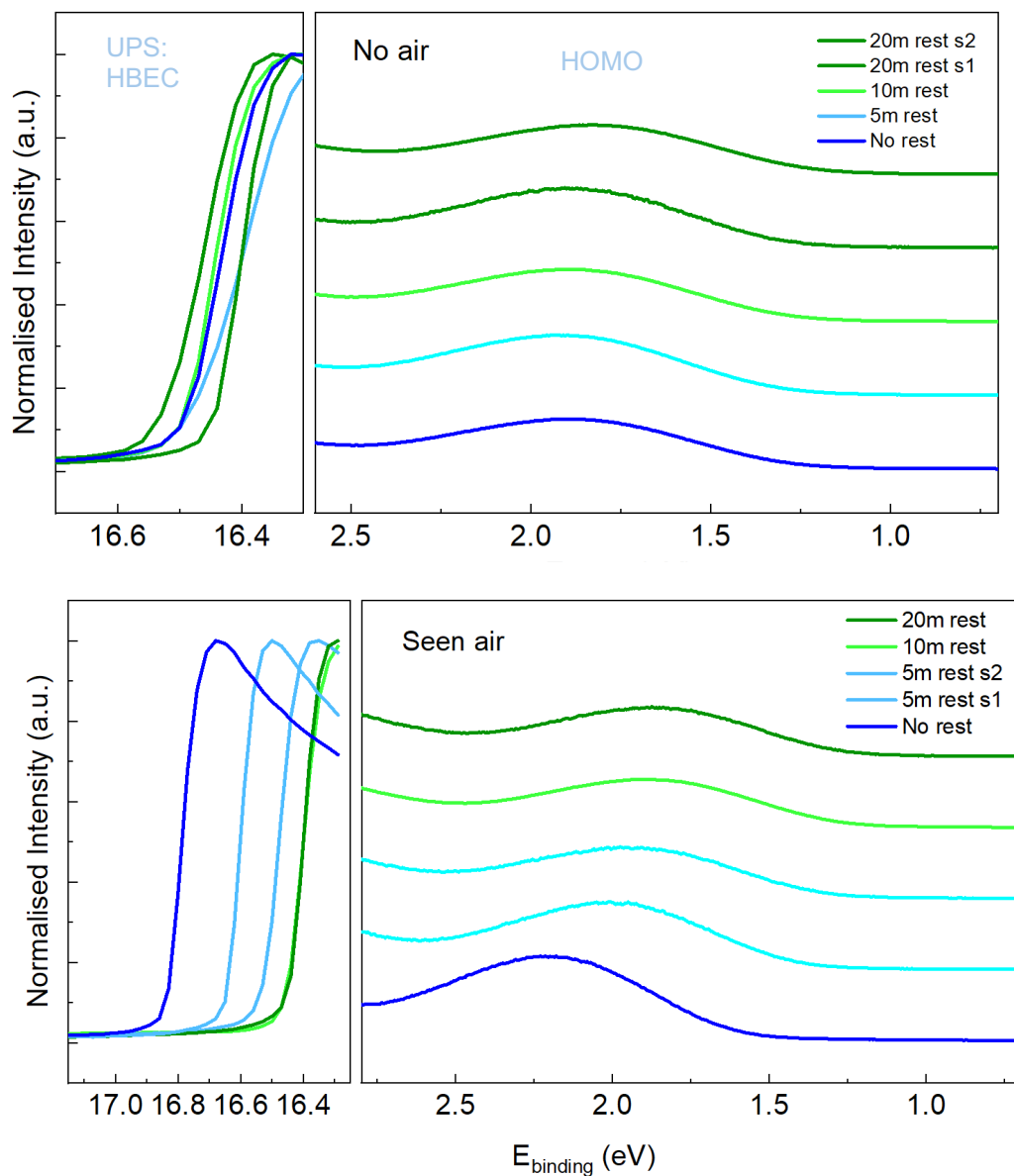


Figure 5.16 – Showing the effects of air exposure post-anneal in samples with varying rest time between spin-coating and annealing. The notation s1 and s2 refer to two separate samples, labelled 1 and 2 respectively, showing some sample-to-sample variation.

We interpret this a difference in the density of the films post-annealing depending on the amount of rest time they were given before annealing, changing the porosity of the films. With reduced rest time we see more craters and thus a film with more pores

(pinholes). We expect air to be adsorbing to the film and increasingly so throughout the film when more pinholes are present, accounting for the even further reduced work function with air exposure as shown. Oxygen is known to have exhibited p-doping effects in organic materials by generating deep trap states which would shift the Fermi level of the organic towards its HOMO [264,265], and to also oxidise electrodes, which can change the work function of the material as already seen with ITO. However, curiously in this case an n-doping effect is exhibited. The exact causes of this doping effect have yet to be confirmed.

In order to test this effect of air further, data from unannealed films was also compared to the data collected from annealed films, investigating further the effect of air on annealing. Here we see that the oligomerisation process has an effect on the positioning of the Fermi level within the material, with oligomerisation leading to a more n-type material, as shown by a shift in the Fermi level away from the HOMO of ~ 300 meV and a significant shift in the work function of ~ 500 - 800 meV between annealed and unannealed samples that have had no air exposure. We again observe air exposure reducing the work function in unannealed samples as in the annealed samples, as shown by the Figure 5.17, with less considerable shifts in energy but still in the region of ~ 150 - 250 meV. This figure takes several samples processed using the compared conditions to exhibit the reproducibility of these results. From this point onwards, samples were not exposed to air in order to replicate device stack conditions, i.e. no air exposure, as to improve stability by reducing potential interfacial trap formation in the stack.

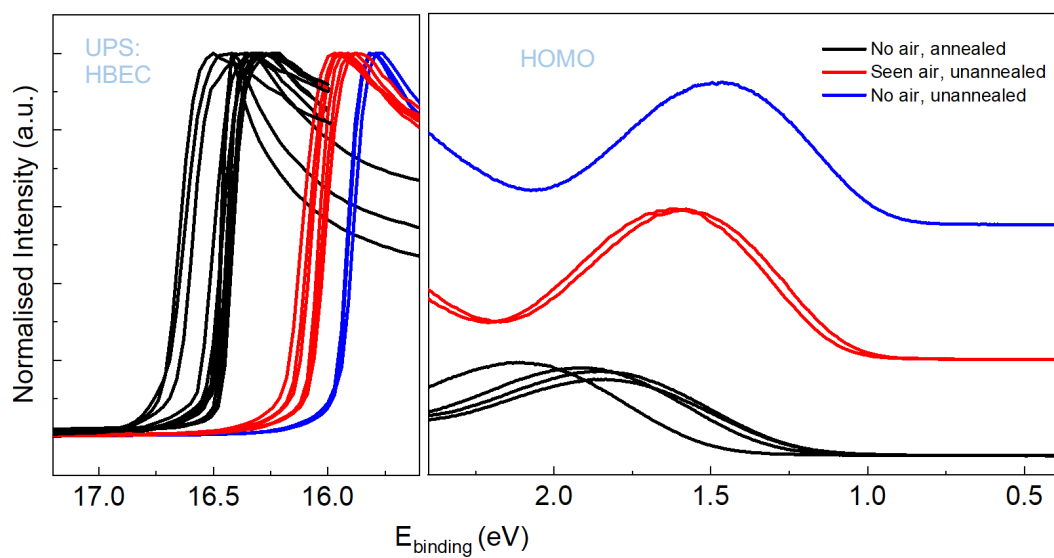


Figure 5.17 – UPS spectra for annealed vs unannealed PCBCB films, with and without air exposure. A significant shift in energetics is observed with annealing and a smaller shift with air exposure.

The effects of the further optimised annealing conditions were investigated for their effects on the work function and HOMO of the thin films, i.e. the use of a metal block for ramped and homogenous heating of samples, and the additional incorporation of a 60°C ramping period in conjunction with the metal block (Figure 5.18).

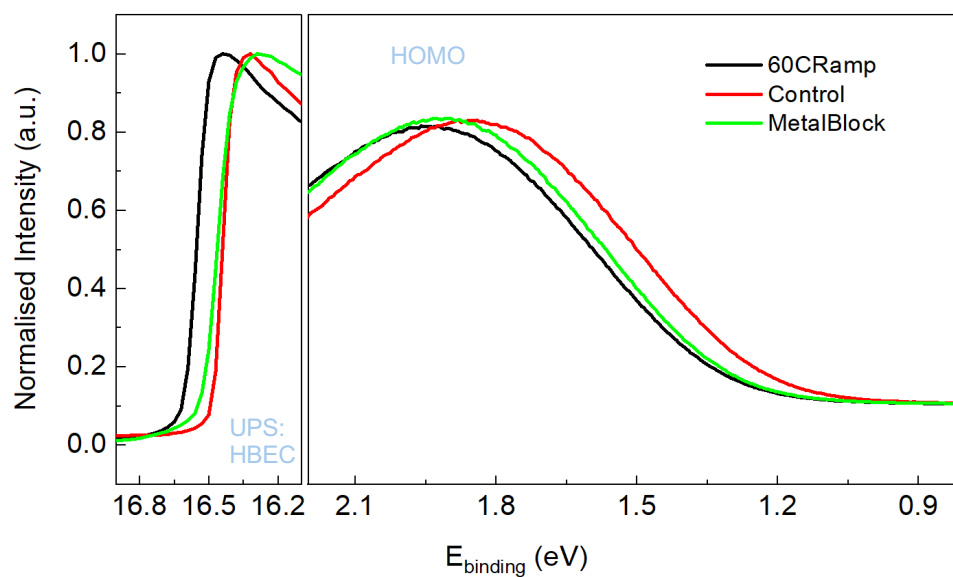


Figure 5.18 – UPS spectra for PCBCB films with varying annealing processes. A small reduction in work function is observed for the best annealing parameter (60Cramp), as described earlier in the chapter and chapter 3.3.

With the incorporation of a ramp period and use of the metal block resulting in a film that exhibited a marginally lower work function than without, a PCBCB (15 mg/ml) sample was prepared using these optimised annealing conditions and measured with both UPS and IPES in order to map out the density of states of the film and determine the LUMO onset (Figure 5.19). From this data, the onset of the HOMO with respect to the Fermi level was determined to be 1.28 ± 0.11 eV, and the onset of the LUMO with respect to the Fermi level was determined as -0.54 ± 0.7 eV. This results in a fundamental gap of PCBCB equal to ~ 1.82 eV ± 0.81 . This means we would expect an optical transition at this energy, however, electronic transitions of lower energies such as this one between the HOMO and LUMO and the $S_1 \rightarrow S_0$ transition are symmetry forbidden in C60 [266,267], and so is also the case in PCBCB as it is a C60 fullerene derivative. Thus, from UV-Visible spectroscopy measurements, no distinct features were present at the equivalent wavelength region covering 650-730 nm. It should be noted that the LUMO onset has a large uncertainty associated, due to the fact that the resolution of the detector is ~ 500 meV. In addition, while measuring these organic samples there is minor degradation that occurs to the films, which can be detected by measuring the HOMO onset before and after the IPES scan and looking for peak shifts or changes. We note here that minor degradation may have taken place with a small distortion of the HOMO onset peak, so a large uncertainty of ± 0.7 eV is estimated for the LUMO position.

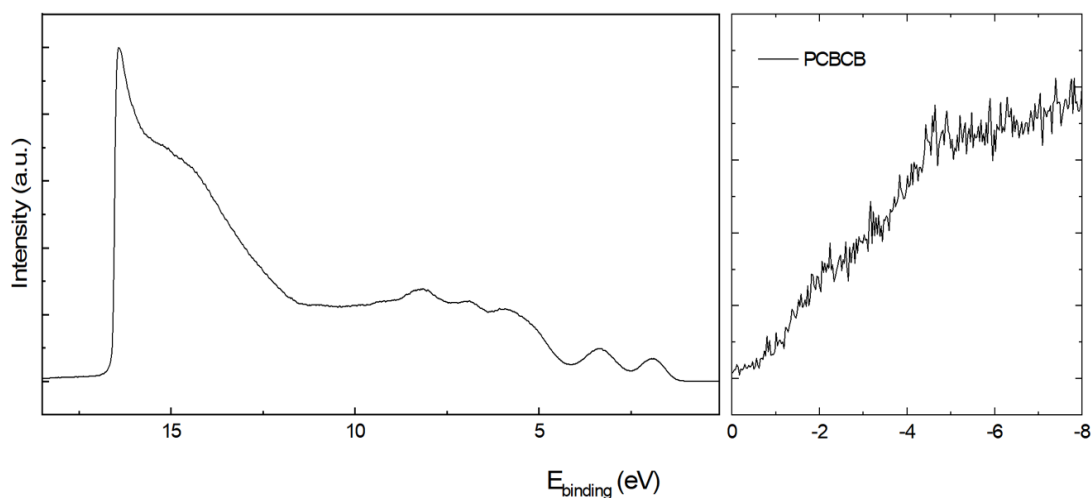


Figure 5.19 – Full density of states (DOS) spectrum from PCBCB (15 mg/ml) film, annealed with optimal annealing condition. Obtained via UPS and IPES measurements.

Samples of C60, PCBM and ZnO on ITO were also prepared via spin-coating and measured with UPS (Figure 5.20), in order to plot their relative work functions and HOMO positions against PCBCB, to highlight its relative intrinsic energetic configuration (Figure 5.21).

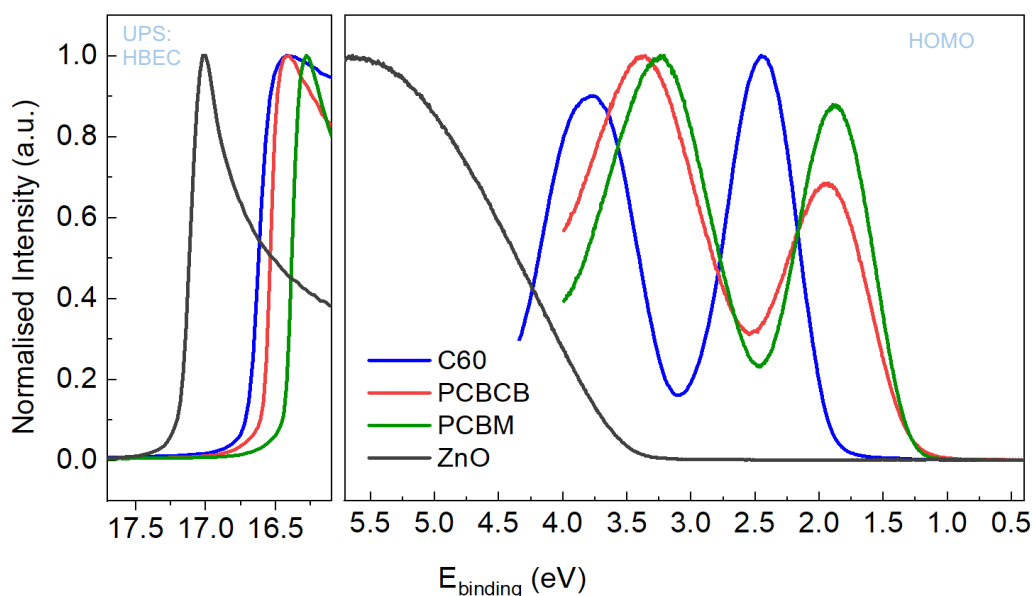


Figure 5.20 – UPS spectra for C60, PCBCB, PCBM and ZnO films deposited on ITO, showing relative positions of the HOMO band onset and HBEC onset.

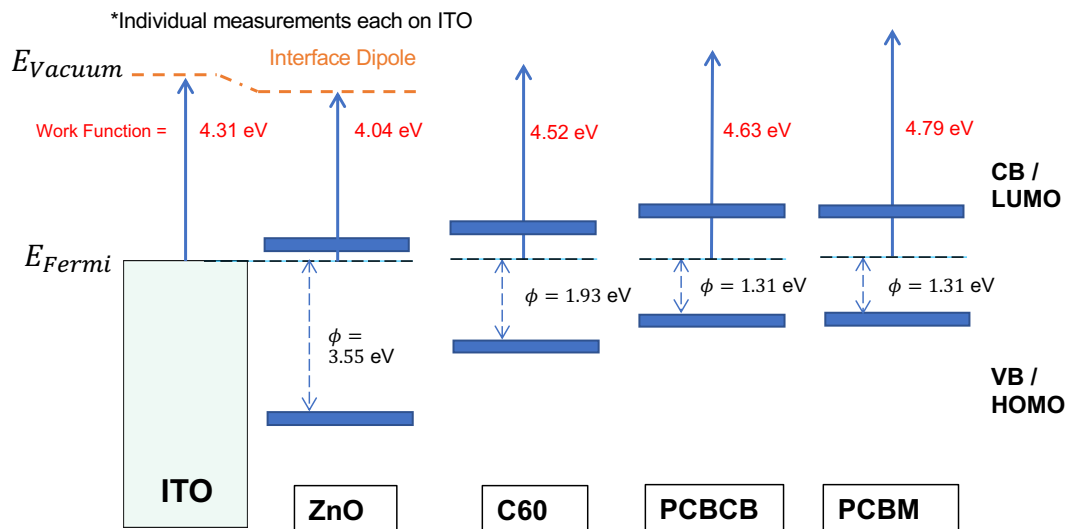


Figure 5.21 – Schematic of energetic configuration of the ETL films, each deposited separately on ITO substrates. Energy gaps are estimated from IPES measurements of the LUMO of each material. The work functions and HOMO to Fermi level gaps (ϕ) are shown. The zero of the energy scale refers to the common, aligned Fermi-level with that of the UPS analyser.

5.2.2. Spectroscopic study on the growth of PCBCB films

As UPS has a penetration depth of 1-2 nm, in order to study the interface energetics between two thin films we should have a good control over thickness of the film being deposited so we can examine and map energetic shifts in work function and HOMO level with changes in thickness. This makes mapping the energetics of PCBCB with layer growth difficult, as it is solution processed and not evaporated, a technique with less precision when it comes to film growth. However, by using a series of concentrations as was done in 5.1, we can begin to build an impression of how the cathode (ITO) interacts with the ETL (PCBCB). It was observed that reducing the concentration of the PCBCB solution below 5 mg/ml, and thus deposition of a thinner film resulted in a shift in the position of the HOMO with respect to the Fermi level such

that it is deeper (further from the Fermi level). The work function of PCBCB was also decreased by an equal amount of ~ 0.1 eV. As we reach particularly low concentrations, we begin to see the peaks associated with the HOMO states dampen in intensity, see Figure 5.22. It is only at concentrations of 2mg/ml and greater that we can consistently observe clear PCBCB signal.

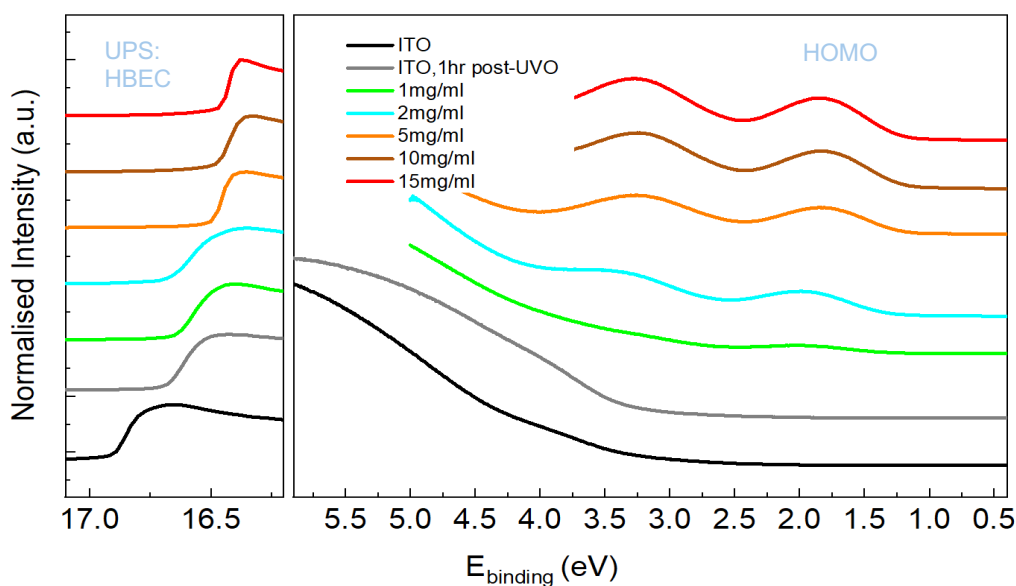


Figure 5.22 – UPS spectra for PCBCB films of different concentrations (thicknesses). Reduced concentrations result in a reduction in work function and a shallower HOMO onset position with respect to the fermi level.

The work function, HOMO with respect to Fermi level and ionisation energy of PCBCB vs concentration of the films have all been plotted below to show the trend in how these develop (Figure 5.23). With this understanding of the nominally intrinsic PCBCB thin films, the effects of doping the PCBCB films can now be explored with the aim of increasing the conductivity of the films and tuning the energetics to result in low work function and a Fermi level closer to the LUMO of the material.

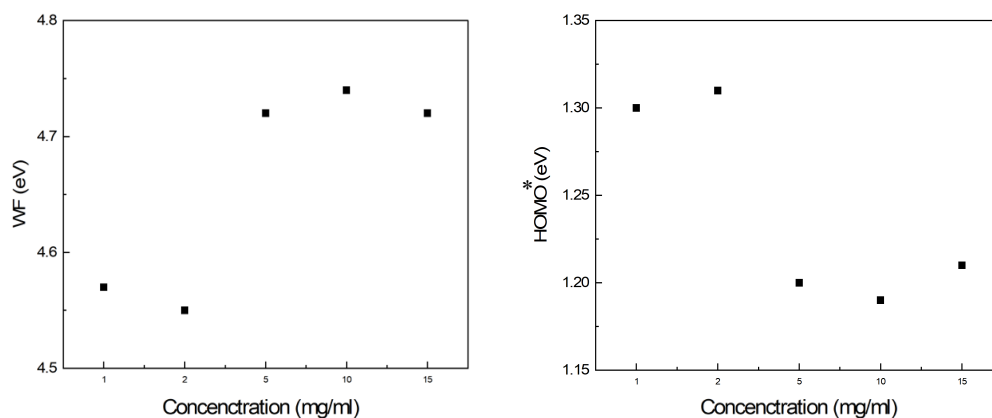


Figure 5.23 – Work function and HOMO onset (*with respect to Fermi level) as a function of PCBCB sample concentration, as measured by UPS.

In this chapter we showed how the processing conditions used to fabricate thin films of PCBCB have a role in the quality of the film produced, as well as on the energetics of the film. It has been shown how subtle changes can greatly influence the film properties, both physical and energetic, and how great care must be taken when processing the films. The effects of annealing on film quality, with regards to pinhole formation and surface roughness have been discussed. The optimal processing conditions for producing the ETL layer have been highlighted.

The concentration of PCBCB solution necessary to form a complete film was determined to be around 8 mg/ml. The effects of the annealing on energetics, as well as the effects of air exposure have been explored and determination of the complete density of states of an optimal PCBCB film was acquired with UPS and IPES measurements. This was compared to the energetics of other organic materials on ITO, namely C60, PCBM and inorganic ETL material ZnO. Finally, the changes in energetics with film concentration and therefore thickness of the PCBCB film were determined, in order to understand changes that might take place at the interface between the ETL and ITO, as opposed to the bulk of the film.

Chapter 6

Investigating the effect and efficacy of different dopants on PCBCB thin film properties and energetics

One disadvantage of organic semiconductors compared to those comprised of a metal oxide is the reduced conductivity in intrinsic organic materials. Conductivity is a crucial property for efficient charge extraction into and transport throughout the layer, so this drawback should be tackled, and can effectively be done so through the technique of doping. The addition of an electron-donating additive into the thin-films can tune the electronic properties of the film, increasing conductivity and reducing work function when n-doped. In this chapter, we explore the effects of n-type doping on PCBCB by considering changes in thin film surface properties, morphology, conductivity and layer energetics, in addition to the consequential effects these have on the active layer (PM6:Y6) energetics and morphology.

6.1. Properties of PCBCB – Intrinsic vs Doped

Doped PCBCB films (15 mg/ml) were prepared as described in chapter 3.3. The primary dopant used throughout this study was the n-type dopant, N-DMBI (4-(2,3-Dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzenamine), due to its proven use as an effective dopant in PCBM [223]. Films were doped by molar percentage, and firstly a series of films from 0 mol% to 50 mol% dopant were prepared on ITO substrates to mimic device structure, and the morphology of these films were studied using 2D GIWAXS. Figure 6.1 depicts the 2D-GIWAXS images produced using the internal Rigaku setup, from an undoped sample (a) vs 20 mol% doped (b) vs 50 mol% doped (c) and of plain ITO substrate (d). Figure 6.2 provides the normalised in-plane line-cut from each sample in this dataset. Each sample received 1800s of beam exposure, with exception to the plain ITO which received 600s.

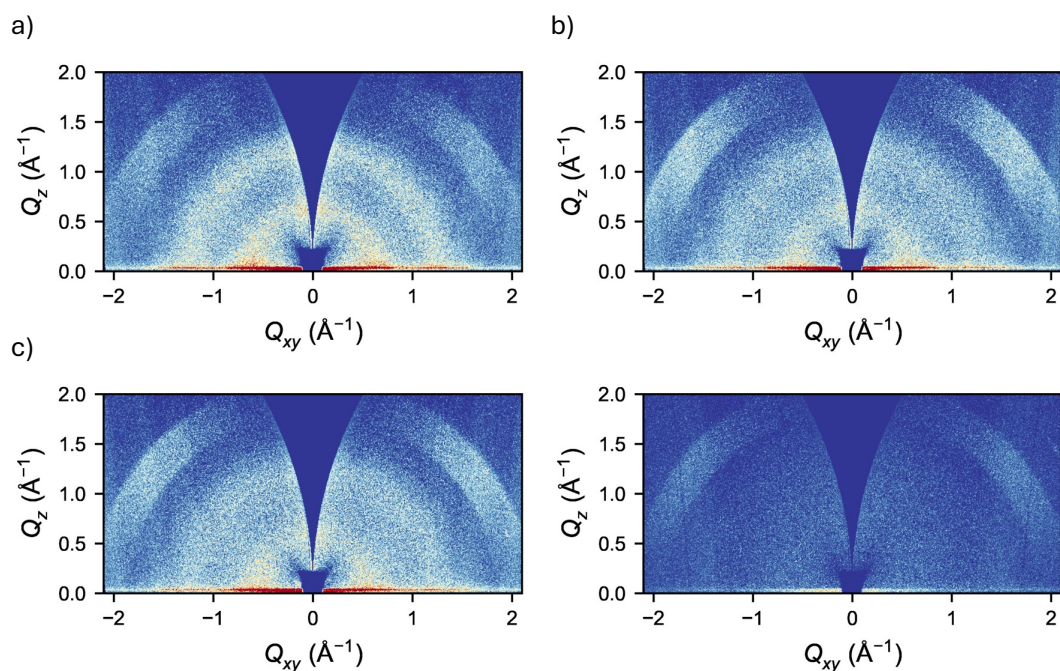


Figure 6.1 – GIWAXS from an undoped PCBCB sample on ITO (a) vs 20 mol% doped (b) vs 50 mol% doped (c) and of plain ITO substrate (d).

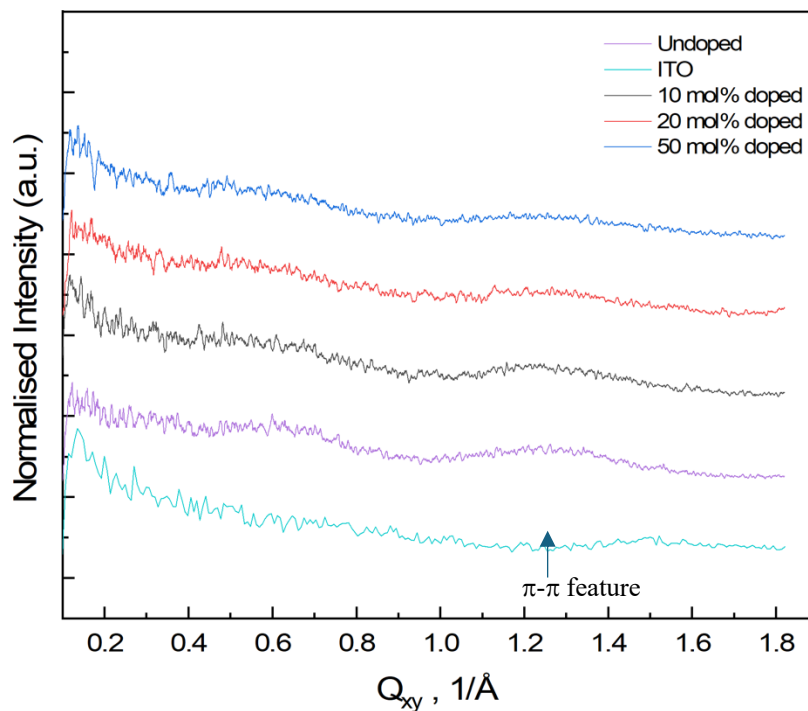


Figure 6.2 – Normalised in-plane 1D line-cut from an undoped PCBCB sample on ITO vs 10 mol% doped, 20 mol% doped and 50 mol% doped films and a plain ITO substrate. The spectra have no sharp features, appear to show mostly isotropically amorphous features with a wide peak feature in the higher-Q region of $Q = 1\text{-}1.5 \text{ Å}^{-1}$, indicative of pi stacking, that seemingly reduced with increased doping.

All films show predominantly isotropically amorphous features, with little variation coming as a product of increased doping. The high-Q features associated with pi stacking, as shown by the arrow in Figure 6.2, may slightly decrease in intensity with increased doping. Further, the ITO substrate appears to be particularly amorphous, with no crystalline features appearing.

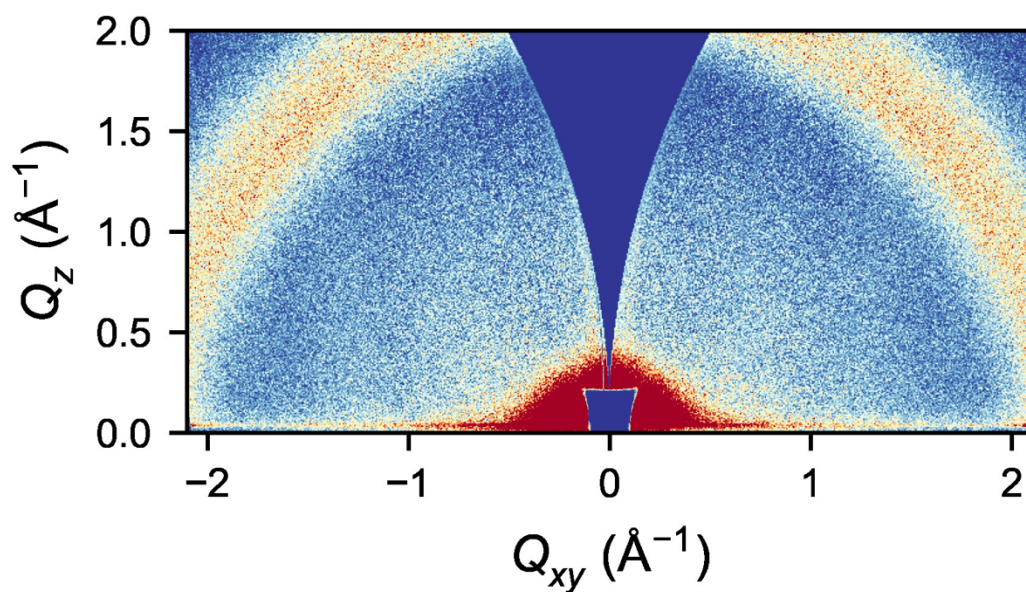


Figure 6.3 – 2D-GIWAXS image of a ZnO film on ITO, exhibiting crystalline features as shown by the yellow and red features.

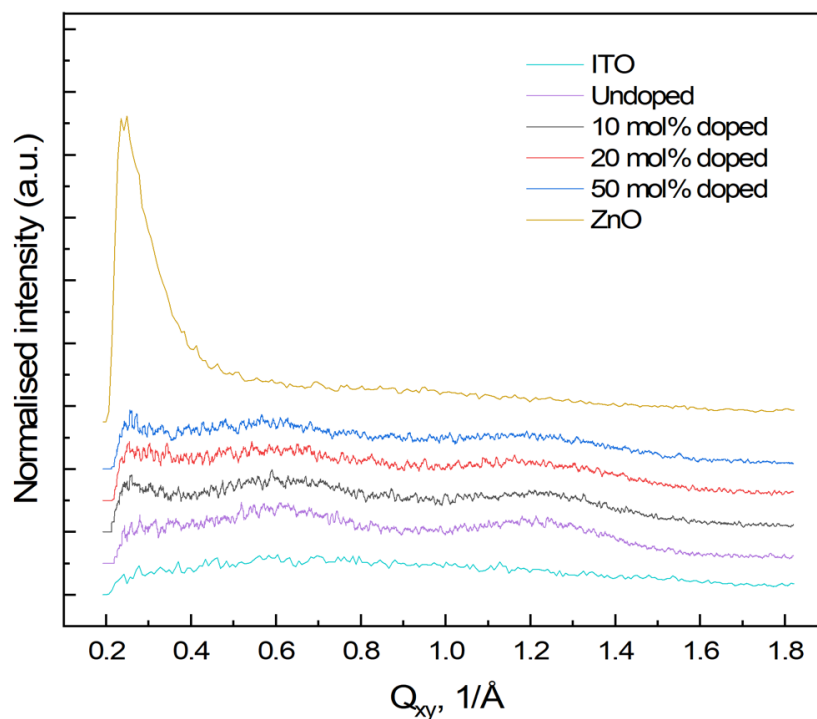


Figure 6.4 – Shows the same spectra as in Figure 6.2, but with the added addition of ZnO, to highlight the difference in ordered features in small- Q , indicative of lamellar stacking.

Comparing these with a 2D-image from a ZnO film (same measurement conditions), as in Figure 6.3, we can see that the low-Q features are much more prominent. Figure 6.4 shows the out-of-plane line-cut from all the samples, with the addition of ZnO, and it is clear to see how much more prominent the small-Q features, relating to lamellar stacking, are in ZnO. This contrast is even larger in-plane. However, interestingly, the larger-Q features correlating pi stacking, are seemingly more prominent in PCBCB films. It is difficult to confidently say whether increased pi stacking, or lamellar stacking are indicative of improved charge transport throughout the layers but are particularly informative with regards to the effect of doping on the ETL morphology, which appears to be minimal with potentially a slight decrease with doping, that could possibly suggest some minor aggregation of dopants in areas of the film disrupting the stacking.

Having confirmed very little change in the crystallinity of the films with doping, we proceed to examine the films with UPS and XPS (Figure 6.5), in order to establish how the doping affected the energetics of the films. It was clear that doping, as expected, shifted the HBEC onset and HOMO onset of the doped films compared to the intrinsic values. Increased doping resulted in a lower work function, a desirable feature of an ETL, and shifted the Fermi level closer to the LUMO due to the increase in charge carrier density, improving energetic alignment at the interface between the ETL and ITO (Figure 6.6), reducing voltage losses across the device. The XPS data again shows indium 3d peaks and how an increase in doping further suppresses the indium signal from ITO, suggesting doping helps with film formation and reducing the number of pinholes throughout the film. Following this, the same sample series was fabricated but with a thin film that can tell us more about the interactions at the interface between ITO and PCBCB, rather than just the bulk of the PCBCB (as penetration depth of UPS is $\sim 2\text{nm}$).

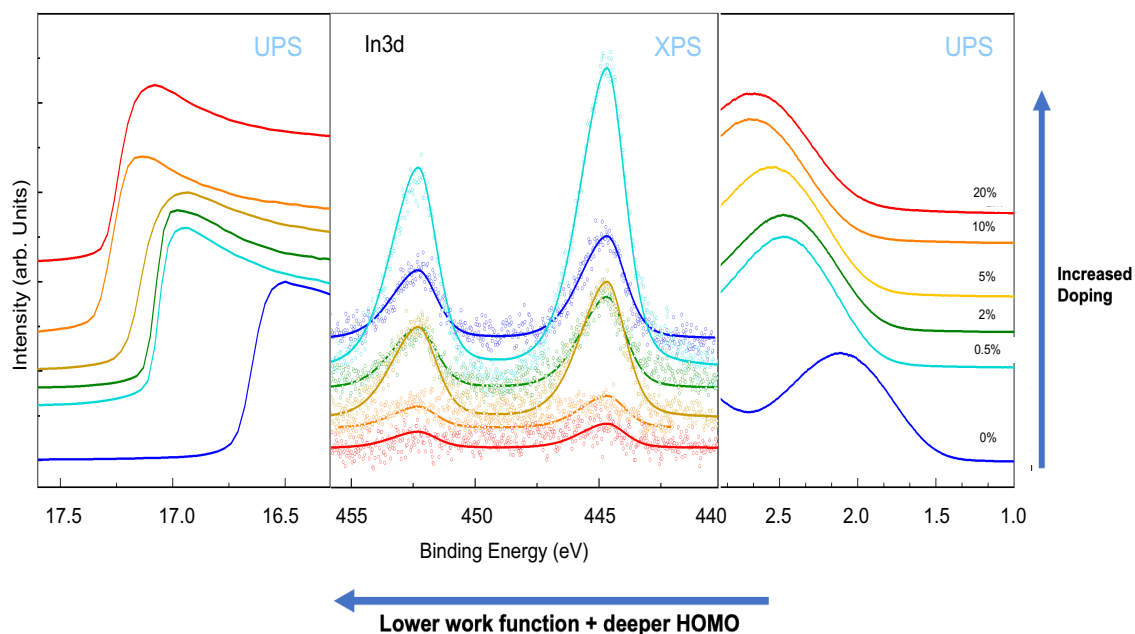


Figure 6.5 – UPS and XPS spectra detailing the shift in work function and HOMO onset of doped PCBCB (15 mg/ml) films, dependent on their doping concentration. The decrease in pinholes in the films is exhibited with a reduction in indium signal with increased doping.

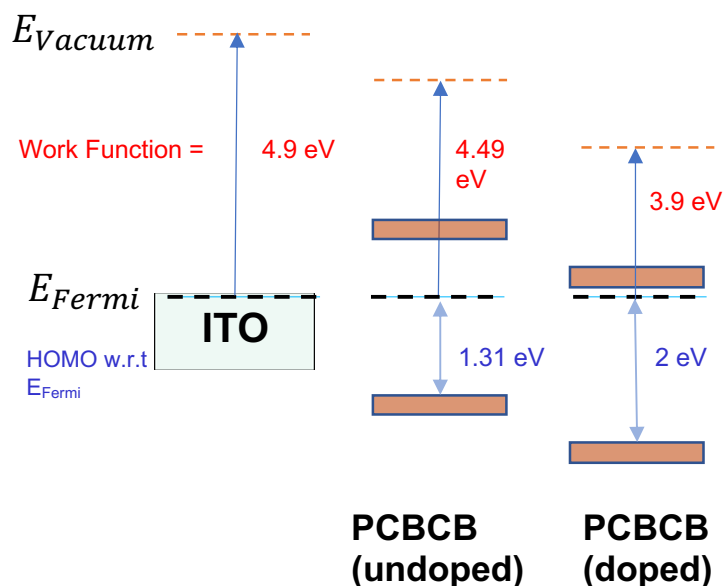


Figure 6.6 – Diagram of energetic configuration at the PCBCB/ITO interface between undoped and doped films, showing alignment of the Fermi levels with doping. The

zero of the energy scale refers to the common, aligned Fermi-level with that of the UPS analyser.

The HOMO position with respect to the Fermi level has been plotted as a function of doping concentration for ‘bulk’ films of 15 mg/ml PCBCB and ‘interface’ films of 2 mg/ml PCBCB (Figure 6.7). The work function of the films follows the same trend. Although a complete film isn’t formed at 2 mg/ml, we still have island formation, that leads to a dominant signal from the PCBCB and can still inform us about how this material interacts at the interface.

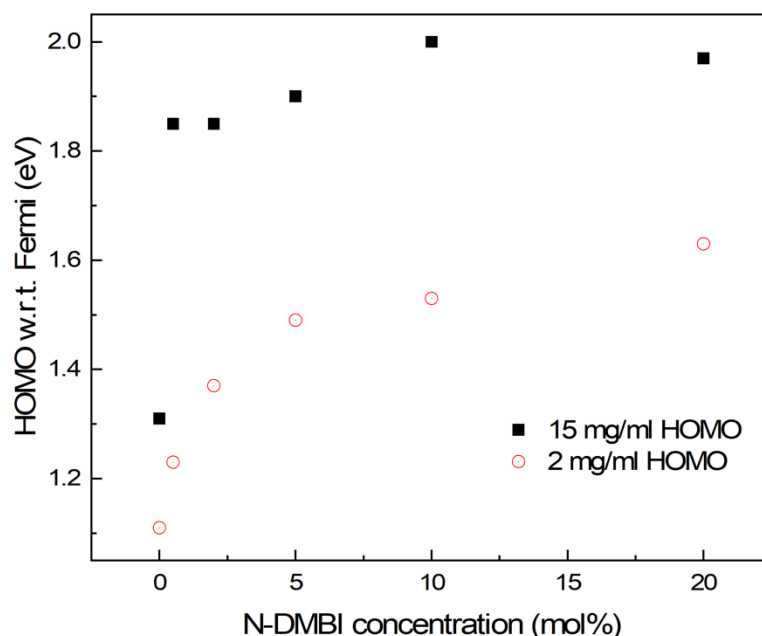


Figure 6.7 – HOMO level onset vs doping concentration in PCBCB films of both 15 mg/ml and 2 mg/ml.

By considering previous literature studies on doping of organic semiconductors [217,221], we understand that as the doping concentration increases, the energy levels change until a doping saturation point is reached, at which point the Fermi level is positioned close to the LUMO (in the case of n-doping) and there can be no more shifts.

Here we exhibit this at doping concentrations of around 10 mol%. From an understanding of the literature and the fact that an interface dipole forms (Figure 6.6), we can expect that as we get closer to the interface, we exhibit some energy level bending away from the flat energy levels picture. When considering the fact that the depletion width decreases with increased doping, and the fact that at 2 mg/ml we don't see this bending take place with high doping as we do with low doping, we can expect our energy level diagram to exhibit a more extreme level bending with increased doping, as shown in Figure 6.8. The stars represent measured values from our system.

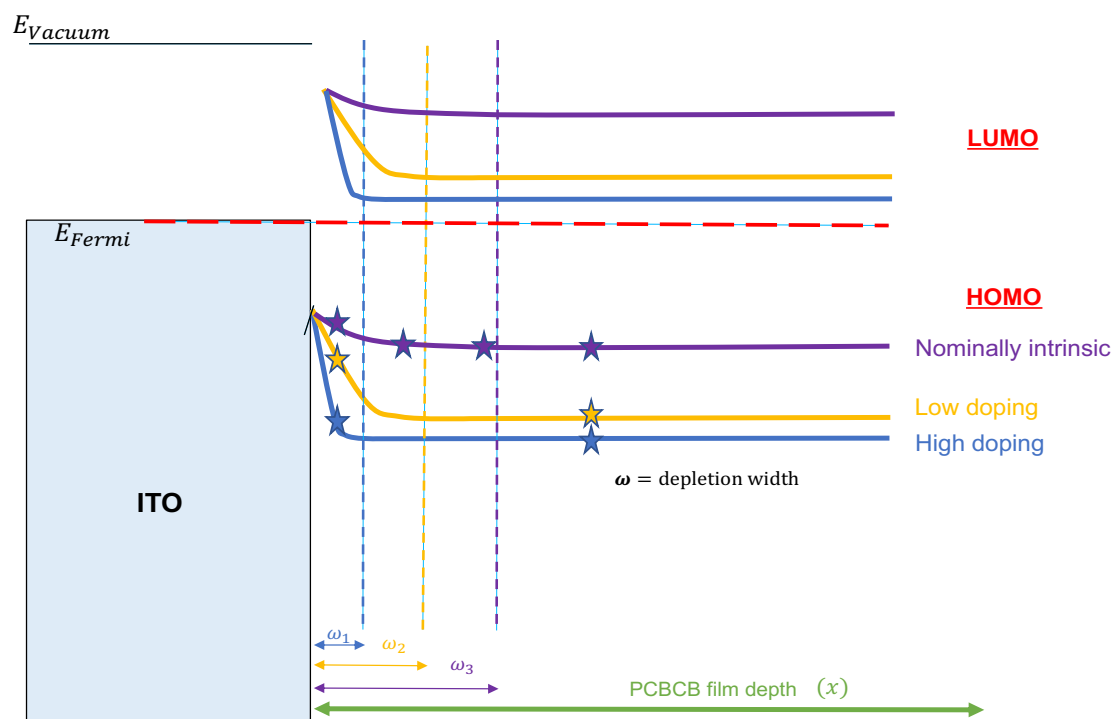


Figure 6.8 – Schematic to depict the energetic alignment of the ITO and PCBCB layer, showing the effects of band bending at the interface with increased doping. The doped PCBCB films align at the Fermi level, and the depletion width decreases with increased doping, leading to a more extreme band bending in doped films. The stars in the schematic here represent data points taken and shown in Figures 5.23, for the nominally intrinsic sample, and 6.7, for both the low and high doping samples, where low doping refers to 1-2 mol% N-DMBI, and high doping refers to > 10 mol% N-DMBI. The dotted lines represent the onset of the depletion region.

Alongside UPS, UV-Vis was conducted to compare the absorptance of a 20 mol% film and an undoped film, to assess the effects of the dopant on the optical properties of the film (see Figure 6.9). The spectra overlap, showing no significant shift in transparency of the film, with the negligible difference between 340-400 nm typical of sample-to-sample variation and some inhomogeneity across the films.

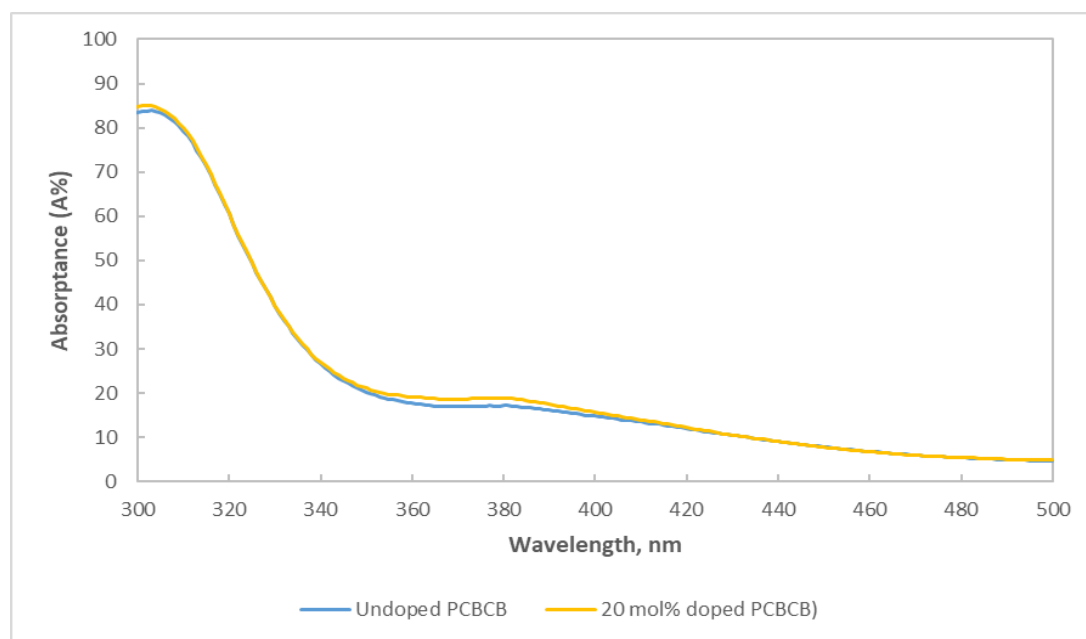


Figure 6.9 – UV-Vis absorbance data (Cary 5000) as a function of wavelength for an undoped PCBCB film compared to a 20 mol% doped PCBCB film. The spectra show no significant differences, meaning no significant changes in the optical properties with doping.

To examine the effects of N-DMBI on conductivity of PCBCB, thin films were prepared on glass substrates, this avoids charge carriers simply travelling through the ITO as the conductivity of ITO is much higher than that of PCBCB. Deposition of PCBCB on glass proves difficult as it has a poor wettability due to the smoother surface of glass substrates as compared to ITO substrates and the resultant reduced surface

tension. This results in a non-continuous film and rather patches of material dispersed unevenly across the substrate, see Figure 6.10.

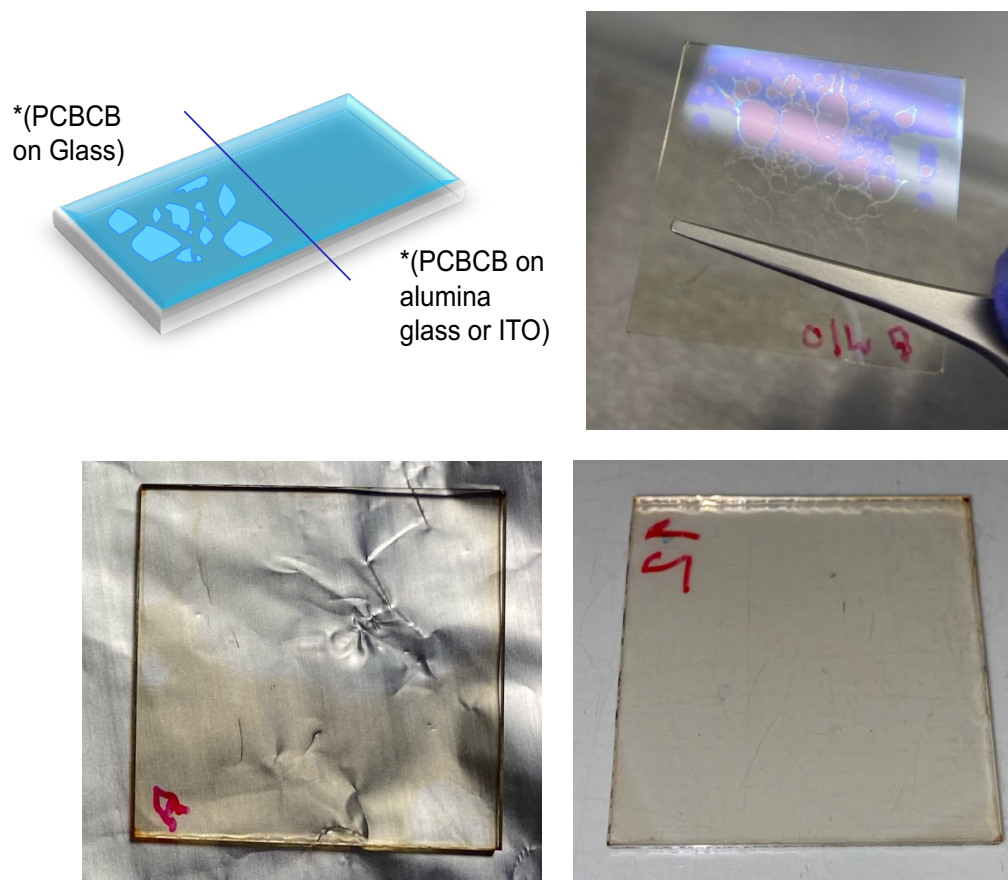


Figure 6.10 – Top left is a schematic of PCBCB wetting on glass vs on alumina coated glass or ITO. Top right is a photo of poor coverage of PCBCB on a glass substrate due to bad wettability. Bottom left shows okay coverage on glass with extra cleaning and UV-Ozone treatment. This is an inconsistent and unpredictable occurrence that still doesn't result in complete substrate coverage. Bottom right shows a complete film of PCBCB deposited onto alumina on glass.

Due to this wetting issue on glass, most films had to be prepared on glass coated in non-conductive alumina nanoparticles, resulting in much improved wettability (Figure 6.10), with few partial films on bare glass achieved. These few were used to assess the effect of the alumina on the conductivity. It was determined that alumina at a

1:150 dilution in IPA reduced the conductivity of the films by approximately an order of magnitude compared to those on bare glass. The alumina nanoparticles are on the order of 10s of nanometres in diameter and so may however have more of a negative impact on lateral conductivity than on vertical conductivity, as charge carriers must travel further around these particles. Using alumina at a 1:300 ratio still produced the desired wettability, with slight improvements in conductivity, but 1:500 reduced wettability. All other conductivity measurements discussed have been conducted using alumina on 1:300 alumina in IPA. The effect of the alumina nanoparticles on the absorbance of the films was also assessed using UV-Vis and determined to be negligible.

Shadow masks (image in chapter 3.3) were used to deposit gold top electrodes onto the films, so that lateral conductivity measurements could be conducted. The lateral electrical conductivities of doped PCBCB (15 mg/ml) films were determined using two-point probe measurements as discussed in chapter 3.4. Two-point probe was chosen as the resistivity in the wires should be negligible compared to that of the PCBCB, in addition to the shadow masks available for the two-point probe allowing for much shorter channel widths, resulting in greater precision in the measurement than the larger channel width of the four-point probe setup. While the path of charge transport that we are concerned with in devices is predominantly vertical, this proves a more difficult measurement, as electrodes must be placed beneath and atop the layer of interest, and direct contact to these electrodes must be ensured. Further, this is likely to change the wettability of the PCBCB layer if it was to be deposited onto a gold contact and consequently change its properties, from morphology to energetics. Lateral conductivity measurements avoid the uncertainty of electrode contact and issues with wettability on top of gold. By depositing the PCBCB onto alumina coated glass, this results in a similar

wettability as with ITO substrates and thus maintaining device relevancy. Measuring the conductivity laterally provides us a lower estimate for the conductivity through the sample in any direction, as the molecular domains within the thin films are isotropically oriented, as shown in the GIWAXS data. The distance over which charge carriers travel in the vertical direction would also be an order of magnitude lower than the channel width they travel for these measurements. A minimum theoretical conductivity required across the ETL to achieve a current of 20 mA/cm², and a minimal voltage drop across the device of 10 mV, was previously determined (chapter 3.1.2) to be equal to 1×10^{-4} S/m. This will be the lower bound we require from our layer conductivity, and if the lateral conductivity is above this, we can expect the vertical conductivity to be so also.

The prepared PCBCB thin film samples were annealed overnight at 80°C, to ensure ‘activation’ of the dopant to improve its stability [226], before completing the annealing procedure for oligomerisation the following day. Upon attempting two-point probe conductivity measurements, it was soon realised that only those samples with a 10 mol% doping concentration or higher would be conductive enough for a conductivity output using our equipment, as any lower than this and the conductivity was too low to be detected. This doping concentration coincides with the maximum shift in Fermi level in PCBCB thin films as was shown in the UPS data. From previous work on PCBM [223], we would expect PCBCB to have an intrinsic conductivity on the order of 10⁻⁶ S/m. Using the equations detailed in chapter 3.4, an average conductivity of a 10 mol% doped PCBCB thin film was determined to be 1.71×10^{-2} S/m, as determined from three samples, averaging the measurements across all channels (see mask design, Figure 3.7). This average conductivity of PCBCB films doped with N-DMBI will now be compared to that of films comprising alternative dopants, in chapter 6.2. It should be noted, the effect of the 80°C overnight anneal was tested and small improvements in

conductivity of half to an order of magnitude were exhibited when comparing to samples only annealed for the process of oligomerisation. Non-annealed films also exhibited increased conductivity of up to an order of magnitude, suggesting oligomerisation must either reduce the electron mobility, according to equation 3.5 (chapter 3.2), which we speculate could arise from more frequent scattering as a product of an increase in defects and disorder. This is a different result to that of Ramirez [206], when measuring the change in mobility with annealing, however it is one that they also expected to observe, due to the pathways involved in the oligomerisation and potentially cross-linking reaction increasing disorder [210].

6.2. Efficacy of alternative n-type dopants

A series of different dopants, detailed in 3.3, were used as alternatives to N-DMBI, in order to test if another dopant could be more effective in increasing the conductivity of PCBCB and tuning its energetics. To determine this, the conductivities of neat, doped PCBCB thin films were studied using the different dopants at 10 mol% each. Each film was encapsulated as described in chapter 3.3.7. Average conductivities for each film were determined from at least 2 films, measured across each channel, using the two-point probe setup. The best of each variation of thin film was then taken and subjected to accelerated ageing at 85°C, light-soaking (described in 3.4), and measuring 48 hours later, to test their short-term stability and investigate the effects of solar irradiation on their conductivities. Conductivity values from the day of fabrication (day 0) and the following day (day 2) are provided in Tables 6.1 And 6.2.

Molecule	Avg. conductivity (S/m), day 0
N-DMBI	1.71×10^{-2}
N-DPBI	6.97×10^{-3}
(N-DMBI) ₂	3.02×10^{-2}
(Cyc-DMBI) ₂	8.44×10^{-3}
(RuCp*Mes) ₂	5.64×10^{-3}
ZnO	1.96×10^{-1}

Table 6.1 – Day 0. Conductivity measurements for PCBCB films incorporating different dopants. *Values given to 3 significant figures (sig. fig.).

Molecule	Conductivity (S/m), day 2
N-DMBI	2.10×10^{-3}
N-DPBI	9.75×10^{-4}
(N-DMBI) ₂	1.82×10^{-3}
(Cyc-DMBI) ₂	4.88×10^{-4}
(RuCp*Mes) ₂	3.60×10^{-3}
ZnO	5.91×10^2

Table 6.2 – Day 2. Conductivity measurements for PCBCB films incorporating different dopants. *Values given to 3 sig. fig.

From these results it could be seen that all dopants successfully worked in enhancing the conductivity of the PCBCB thin films. All doped films have exhibited conductivities greater than the minimum theoretical conductivity limit of $\sim 1 \times 10^{-4}$ S/m (calculated chapter 3.1.2). ZnO clearly has the initial highest conductivity by

an order of magnitude, improving significantly with UV-irradiation by 3 orders of magnitude. Of the other dopants, the N-DMBI dimer appears to produce the highest conductivity films on day 0, however all organic films appear to drop in conductivity by approximately an order of magnitude over the 48 hours, except for those comprised with the organic/inorganic hybrid dopant, (RuCp**Mes*)₂. This material may therefore be the most effective of these options for use in future doping work.

6.3. PM6:Y6 energetics and physical effects of differing PCBCB thin film transport layers on active layer properties

In order to determine whether PCBCB as the ETL is compatible in a device stack, it is also useful to examine its effects on the subsequent active layer, both energetically and physically in terms of film formation.

Let us first consider PM6:Y6 and its energetics when deposited on PCBCB. PM6:Y6 is a thicker layer, determined by profilometry to be 115-140 nm when deposited as the active layer within the device stack. Considering it is solution processed with highly volatile solvents, it is quite difficult to bring its thickness down to the range of a couple of nanometres to measure interface interactions, so instead we just consider effects on the bulk film. However, to ensure films were conductive enough, thinner films of 30-40 nm, measured by profilometry, were fabricated from 5.5 mg/ml PM6:Y6 solution.

6.3.1 Evaluating the energetics of PM6 to Y6 on ETL

It is known that PM6:Y6 as a bulk heterojunction undergoes some phase segregation [268], with one component expected to dominate the surface of the film. With the use of UPS, we wanted to confirm if this was the case, as phase segregation would result in a dominating energy spectrum from one component, rather than equal features of the two components. Neat films of PM6 and Y6 were prepared following the same recipe outlined in chapter 3.3. UPS data displaying the energetics of the neat films is shown in Figure 6.11.

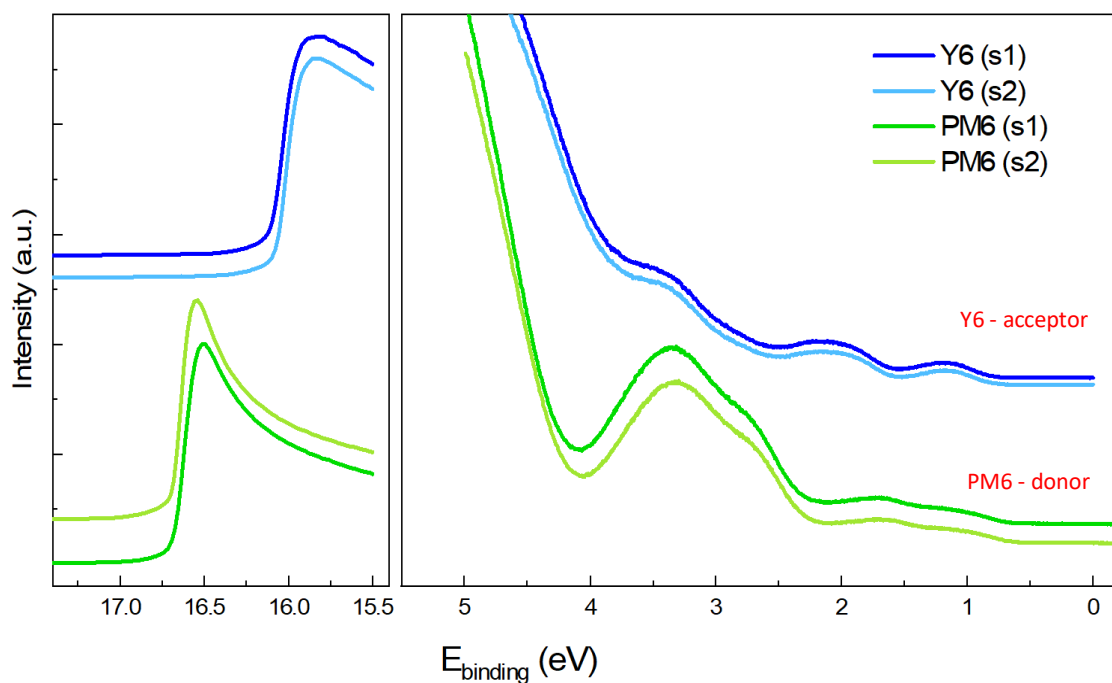


Figure 6.11 – UPS spectra of neat films of Y6 and PM6. The notation s1 and s2 refer to two separate samples, labelled 1 and 2 respectively, showing slight sample to sample variation.

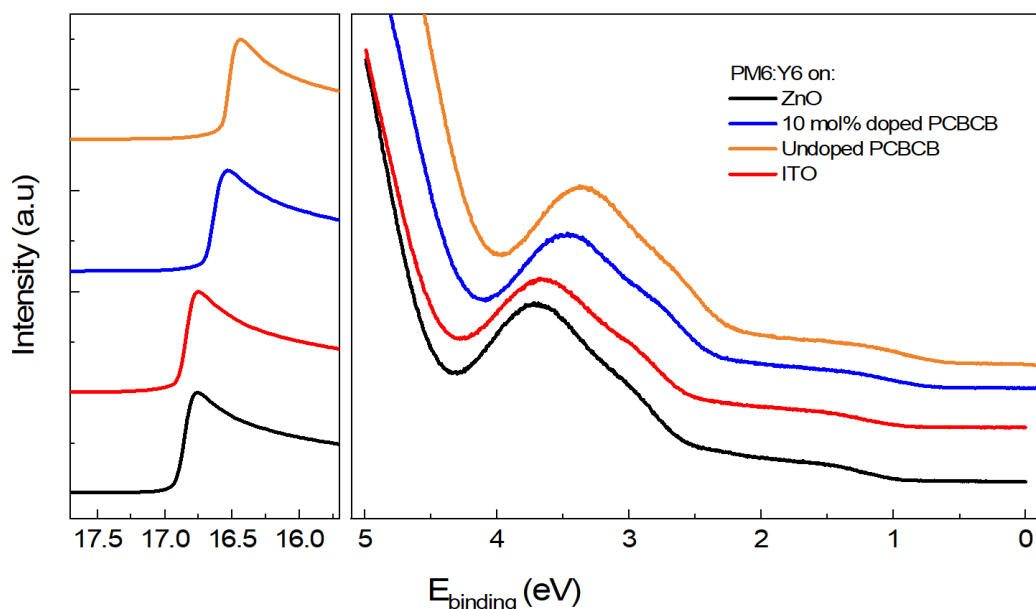


Figure 6.12 – UPS spectra of PM6:Y6 films on varying ETLs, showing the difference work functions of the active layer in addition to shifts in the HOMO onset with respect to the Fermi level. The PM6 component of the film is found to have dominated the sample surface, which can be seen by comparing features with Figure 6.11 and seeing stronger presence of PM6 features, likely a result of phase segregation.

Measuring PM6:Y6 films on different ETL (Figure 6.12), we see a shift in the work function and the HOMO onset position depending on the layer it is on. This could be a function of changing growth modes or improved stack alignment; however, we suggest the primary reason is due to subtle changes in segregation within the film. This can be seen by comparing features with Figure 6.11 and seeing stronger presence of PM6 features and a suppression of features arising from Y6. For example, in undoped PCBCB, the position of the HOMO onset is closer to that of neat PM6, while the work function is larger as in Y6. On the other hand, ZnO has a HOMO onset position closer to that of neat PM6 and a smaller work function, suggesting PM6 dominance in the first

few nanometres as a result of reduced mixing of the film, in other words, greater phase segregation of the two components. Thick 17 mg/ml films (115-120 nm) were also prepared, to ensure phase segregation effect wasn't affected considerably with thickness.

6.3.2 Changes in morphological properties

The growth of PM6:Y6 films and its morphology is very much dependent on the surface it is grown upon. We know this to be true from works such as that by Jiang et. al, whom investigated PM6:Y6 on different 'buffer' layers also [268]. The substrate or surface upon which a thin film is grown or deposited can have variable surface energy and roughness, two properties which have a strong influence on the wetting and morphological features of the subsequent layer. However, we wished to explore whether the changes in dopant concentration throughout the PCBCB layer would have any effect on PM6:Y6 morphology. Lamellar and pi stacking within the bulk of the PM6:Y6 layer when deposited on intrinsic and doped PCBCB thin films were studied using 2D GIWAXS. Most significant features were visible out-of-plane, particularly in larger-Q = 1.4–1.9 Å⁻¹, with in-plane cuts showing less crystalline features, so out-of-plane line-cuts have been shown in Figure 6.13. In this figure we can compare features that are present in neat films of PM6 and Y6, found in [268], to those when deposited on the different underlayers.

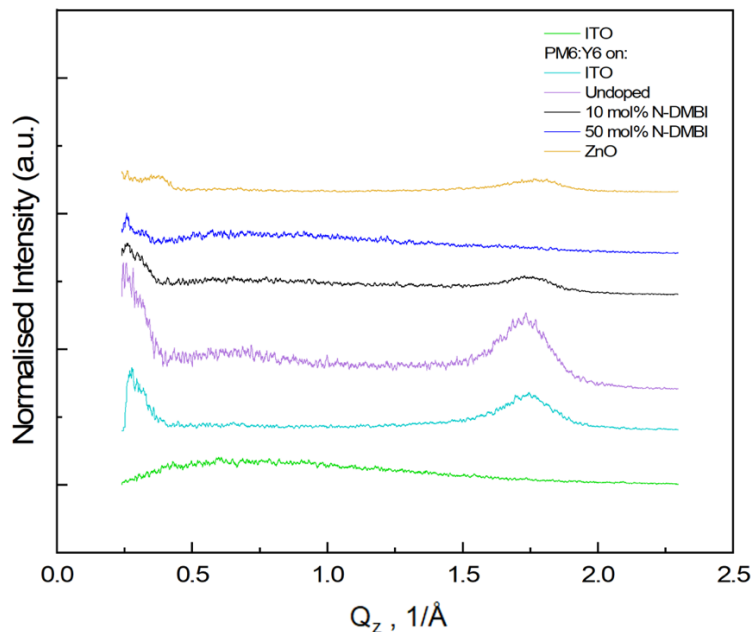


Figure 6.13 – Normalised out-of-plane 1D line-cuts of PM6:Y6 on different ETLs. The effect of doping appears to be significant, suppressing the large- $Q = 1.4\text{--}1.9 \text{ \AA}^{-1}$ feature considerably.

Interestingly, it appears that π stacking in PM6:Y6 films is encouraged on a PCBCB ETL as compared to ZnO, but dependant on the doping of the films. With increased doping we see a reduction in this stacking. We also see that the π stacking is more present in PM6:Y6 on plain ITO. Features in small- Q appear to be more prevalent in PM6:Y6 films deposited on PCBCB as compared to ZnO. This is thought to relate to changes in the surface of the ETL, affecting the surface tension and subsequently the contact angle between the ETL and active layer upon spin-coating, leading to changes in stacking of the active layers. This could then relate to the phase segregation throughout the film and at the interface as stated by Bing-Huang Jiang et al., linking a greater π - π stacking to a greater phase segregation of the active layer, thus reducing the degree of non-geminate recombination and increasing geminate recombination [269]. If

this is the case, we can expect a greater phase segregation of the PM6:Y6 components, increased geminate recombination and decreased non-geminate recombination with less doping.

PM6:Y6 was then deposited on bilayer films of ZnO followed by PCBCB, in order to experiment with the effects of a bilayer ETL on active layer morphology. The out-of-plane linecut again exhibits more significant large-Q features, as displayed in Figure 6.14. These samples once more show increased peak intensities in the regions representing both pi and lamellar stacking for the PM6:Y6 film on PCBCB, with the bilayers showing decreased intensity in the larger-Q peak.

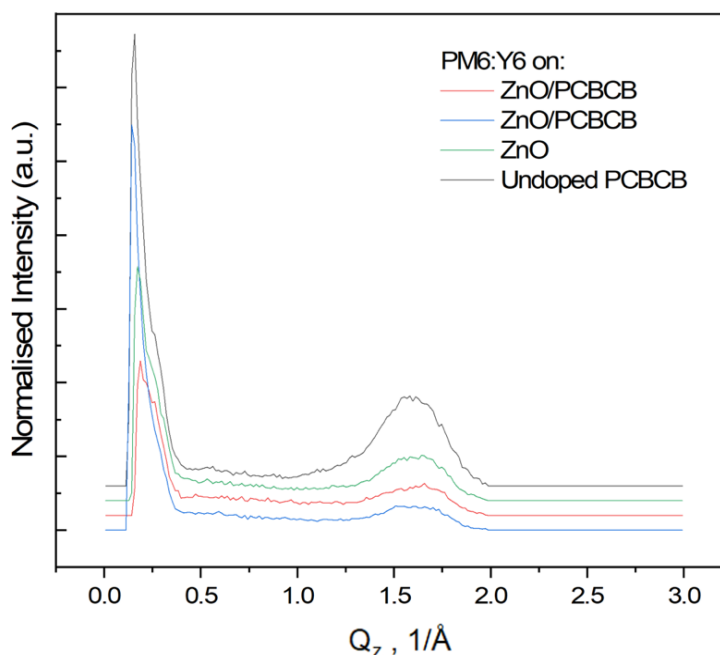


Figure 6.14 – Normalised out-of-plane 1D line-cuts of PM6:Y6 on different ETLs. The effect of a bilayer ETL appears to suppress the large- $Q = 1.4\text{-}1.9 \text{ \AA}^{-1}$ feature considerably, while it appears to be most prominent on undoped PCBCB.

To investigate this a bit further and consider the effect of a second layer on the active layer morphology, samples of PM6:Y6 deposited on different ETL either on ITO

or alumina nanoparticle coated ITO, were taken at a beamtime (detailed in chapter 3.4), and the 2D-GIWAXS images from these measurements are shown below (Figure 6.15).

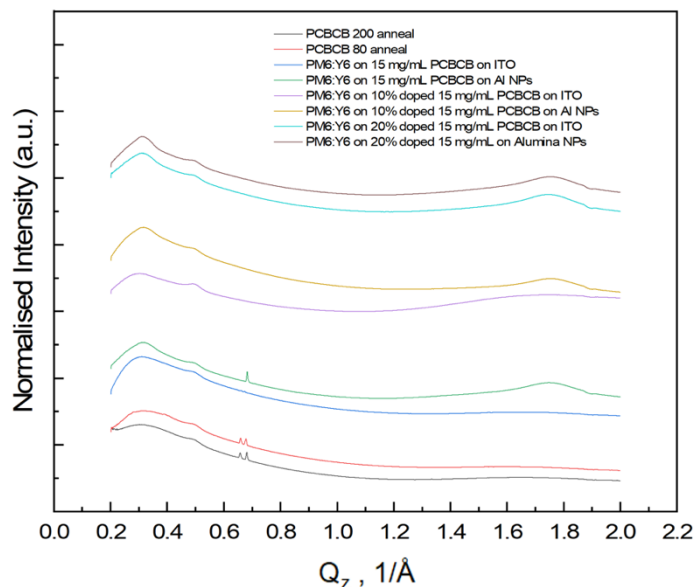


Figure 6.15 – Normalised out-of-plane 1D line-cuts of PM6:Y6 on different ETLs. The effect of a doping is less clear than before, but the effect of alumina nanoparticles on the $Q = 1.4\text{--}1.9 \text{ \AA}^{-1}$ feature is clear, with alumina seeming to increase pi stacking as compared to PM6:Y6 on an ETL on just ITO. Data collected at the A28-1-1380 XMaS, ESRF beamtime by Rachel Kilbride and Pascal Kaienburg and analysed by Olivia Gough.

Contrastingly, the data here showed a stronger peak at $Q = 1.4\text{--}1.9 \text{ \AA}^{-1}$ for the 20 mol% doped PCBCB sample, suggesting more stacking in the large- Q region than those with undoped PCBCB, although this is less clear. This could be a consequence of using a much shorter detector time of 100 seconds compared to a 30-minute exposure time as with the Rigaku, although it would be expected with the increased beam energy that this is not an issue. However, the reduced detector angle here may make a difference to the received spectrum, with the angle changing the probing depth [269]. Further, PM6:Y6 deposited on ETLs that were themselves deposited on alumina appears to clearly exhibit more stacking.

As the effects of stacking with doping were clearer from the previous data, it was concluded that doping appears to reduce the degree of phase segregation which should help improve the device performance.

It would be interesting to research the effects of ETLs on morphology further, perhaps utilising XPS as a tool to look for changes within the active layer films dependent on the ETL layer underneath. This could unveil differences in degrees of phase segregation dependent on the characteristic peaks detected from the first 10 nm of the active layer film. Cross-sectional microscopy imaging could also be an interesting technique to exploit here.

In this chapter we have exemplified how doping can be used to tune the energetics of an organic oligomerisable fullerene-derivative, PCBCB, into a suitable n-type material to be used as an ETL in an OPV device stack. The shift in Fermi energy towards the LUMO has been exhibited, with a doping saturation being reached at around 10 mol% of N-DMBI in PCBCB. The effects of band bending, and depletion width have been discussed. Any effect on optical properties from the dopant was ruled out with UV-Vis absorbance measurements. The conductivity of doped PCBCB was checked to ensure an adequate value is reached for the purpose of an ETL, which appears to be the case, with a conductivity of 1.71×10^{-2} S/m achieved, again with a 10 mol% N-DMBI concentration. The efficacies of other dopants were studied, with both (RuCp**Mes*)₂ and the dimer of N-DMBI, (N-DMBI)₂, proving promising for a potential upgrade in terms of their efficiency and stability.

Finally, the effects of different ETL on the energetics of the active layer were considered, in addition to the effects on morphology, linking this to surface properties, phase segregation and potential changes in the prevalence of certain recombination mechanics.

Chapter 7

Characterisation of devices; PCBCB ETL, Intrinsic vs doped

In this chapter we discuss the fabrication and characterisation of devices comprising a PCBCB electron transport layer and PM6:Y6 active layer. The device performance is determined through the use of JV characterisation. The influence of doping the PCBCB layer in terms of current output, open-circuit voltage capabilities, fill factor and power conversion efficiencies is discussed and compared to the device performance of control zinc oxide OPV devices.

7.1. PCBCB ETL in OPV devices

Control devices were fabricated by me in Oxford, with an active layer of PM6:Y6 and an ETL comprising ZnO, using the recipe as described in chapter 3.3. The highest PCE that was obtained was 12.0 %, this was then determined to be our benchmark for the PCE of

our OPV devices, fabricated using this equipment setup and the specified stack materials, when using a control of ZnO as the ETL. Importantly, it must be acknowledged that when fabricating devices, while higher PCEs are possible and have been achieved, this is variable and subject typically to the atmosphere of the gloveboxes being used to fabricate each layer, the humidity and temperature of the device and their surroundings during fabrication, the quality of the materials being used to fabricate the devices and the quality of encapsulation of the devices, as to reduce their exposure to air and moisture.

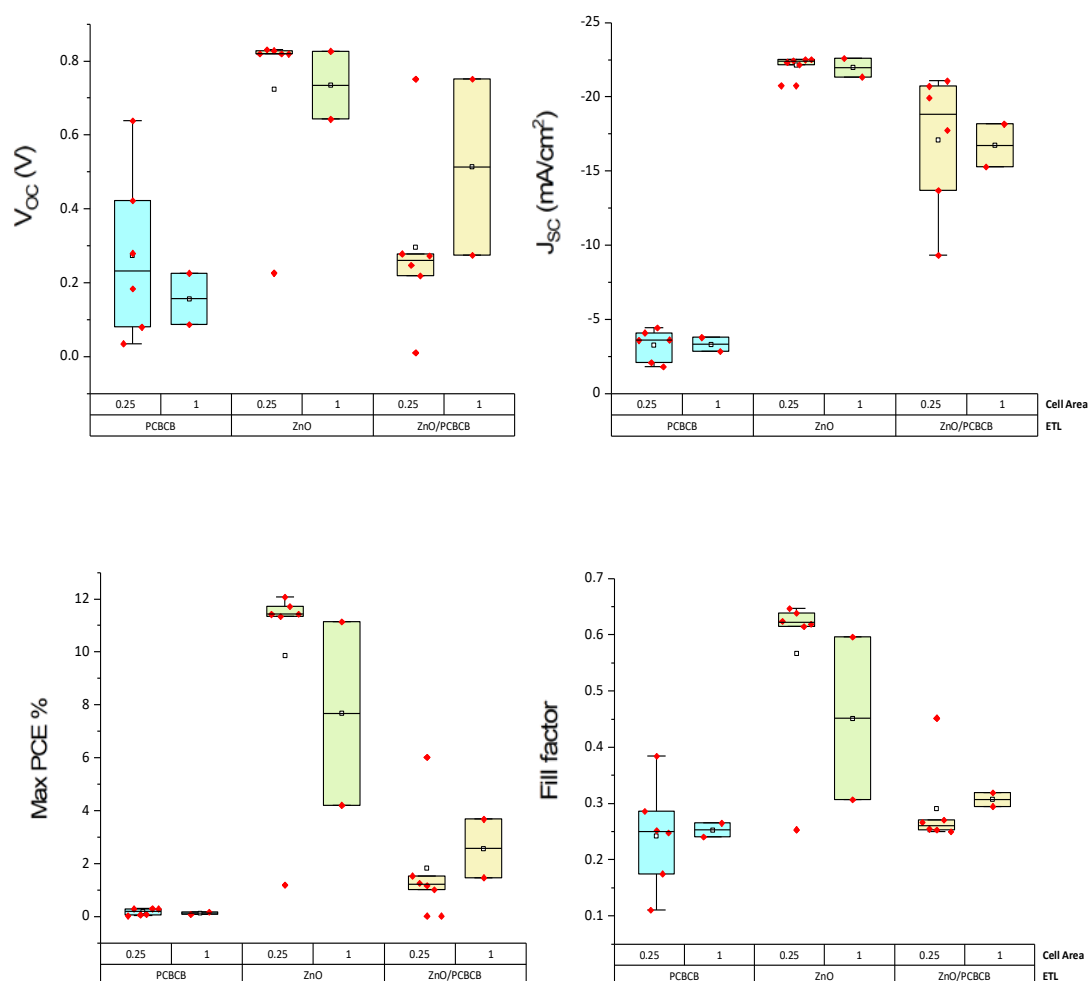


Figure 7.1 – Box plots depicting the open circuit voltage (V_{oc}), short circuit current density (J_{sc}), maximum power conversion efficiency (PCE %) and fill factor FF, for

device stacks comprising a PCBCB ETL, a ZnO ETL and a ZnO/PCBCB bilayer ETL respectively. Cell area (cm^2) is denoted.

Figure 7.1 displays a first set of devices, comparing intrinsic PCBCB (15 mg/ml), ZnO and a ZnO/PCBCB bilayer as the ETLs in the device stack. JV curves for the champion devices are shown in Figure 7.2. The contrast in the device performance metrics shows that in this case ZnO was clearly far more effective as a transport layer. These devices were made as a preliminary test, before optimising the anneal steps involved in oligomerisation of the PCBCB layer. For that reason, we observe shunting of most of the PCBCB devices, with improvements when ZnO is placed underneath as it partially blocks contact between the active layer upwards and the ITO through the PCBCB pinholes. Better energetic alignment throughout the stack is also achieved with ZnO, as we see improved V_{OC} . We expect this as an intrinsic PCBCB layer will not have energetic alignment with the ITO, due to the lack of free charge carriers, resulting in reduced current flow, also a product of its low conductivity. This can also be seen from the dark JV curves by estimating the series and shunt resistances from their slopes, where a pure PCBCB layer shows a very poor series resistance even in the champion device.

A following set of devices containing undoped and doped PCBCB (15 mg/ml) ETLs were fabricated to show how doping works to improve the current in the device and decrease the series resistance due to improved energetic alignment throughout the device stack (Figure 7.3) in comparison to a ZnO ETL. Devices comprising of bilayer ETLs of intrinsic PCBCB atop doped PCBCB and a layer of doped PCBCB atop ZnO respectively, using the same concentrations of material for each layer as used in the monolayer devices, were fabricated to see if this happened to enhance device properties across any metric.

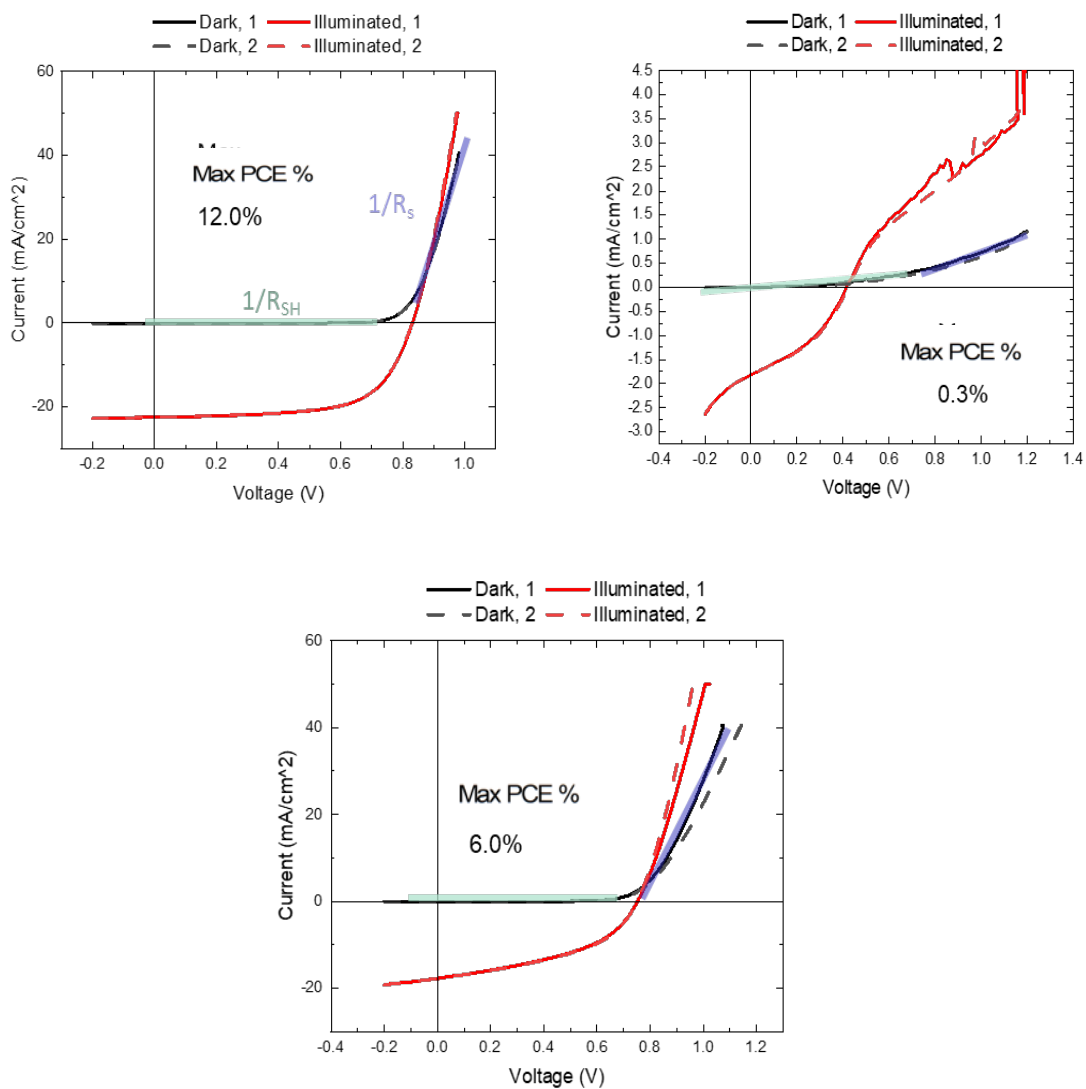


Figure 7.2 – JV curves for devices comprising an ETL of zinc oxide (a), PCBCB (b) and a ZnO/PCBCB bilayer (c). Slopes to estimate the shunt and series resistances are shown, along with max PCE (%) values.

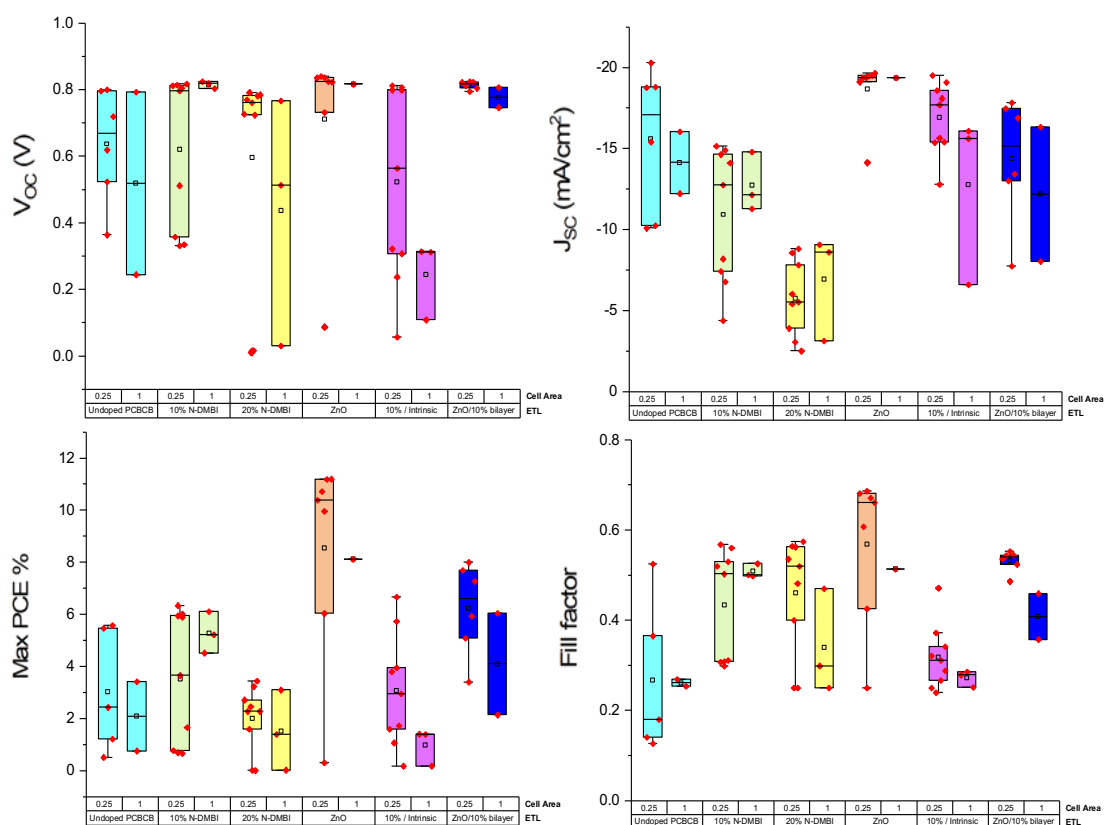


Figure 7.3 – Box plots depicting the open circuit voltage (V_{oc}), short circuit current density (J_{sc}), maximum power conversion efficiency (PCE %) and fill factor FF for device stack containing undoped and doped PCBCB ETLs, a ZnO ETL and bilayer ETL combinations. The bilayers are comprised of a layer of intrinsic PCBCB atop doped PCBCB and a layer of doped PCBCB atop ZnO, respectively. Cell areas are denoted (cm^2).

The improvement in current generated and decrease in series resistance are shown by elimination of s-shaped kinks in the JV-curve [270] and the improved current densities. Too much doping can result in current drops, not likely due to significant dopant aggregation as shown with GIWAXS, but more likely due to charge carrier quenching at the active layer interface. Use of an intrinsic PCBCB layer atop the doped layer appeared to improve this, however the series resistance was increased due to the increased ETL layer thickness. Implementation of a very thin layer of intrinsic PCBCB

should be explored next, as this could retain a good series resistance and reduce charge carrier quenching at the interface. Promising early results from 10 mol% doped PCBCB devices and even higher, up to $\sim 8\%$ in devices comprising a ZnO/doped PCBCB bilayer. The devices were also made before fully optimising the annealing conditions. We suggest that the increase in device metrics for intrinsic PCBCB based devices compared to the last batch maybe due to small amounts of dopant in the atmosphere of the glovebox increased the current of the PCBCB and its energetic alignment, however this is not certain, and could be a product of improved film quality and reduced pinholes and perhaps a slightly thinner layer deposited in this device set.

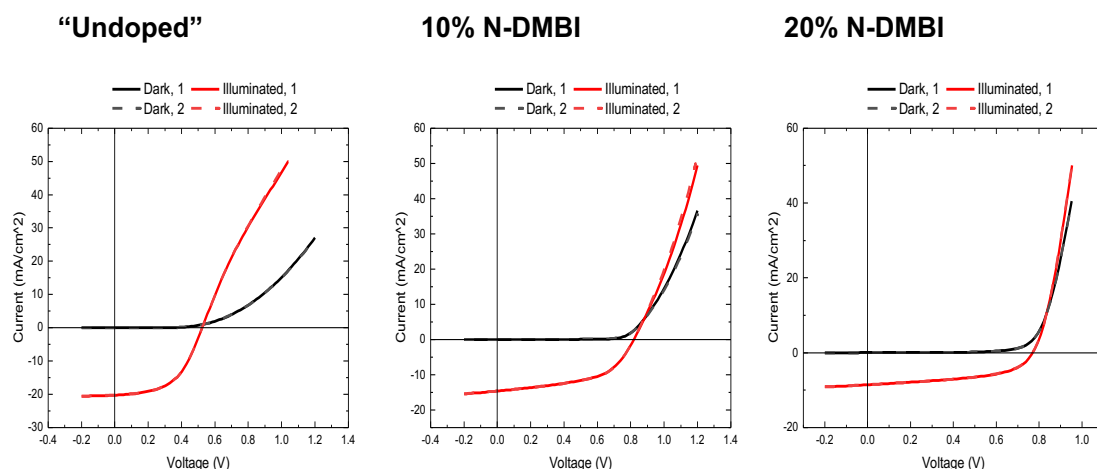


Figure 7.4 – JV curve examples from devices as shown in Figure 7.3. Series resistance improvements can be seen with doping, but increased doping also results in reduced current. Increased doping does improve energetic alignment and remove the s-shaped kink.

Following this, the introduction of both improved annealing and alumina beneath doped PCBCB ETLs was tested, with the aim of further improve the quality of the films with improved wettability as exhibited when depositing on glass. This did appear to

result in improved film quality, with consistently well-performing devices achieving V_{OC} s of around 0.8 eV (Figure 7.5), suggesting less shunting so less pinholes. Alumina appeared to marginally improve the current also, suggesting it does not have a negative influence on conductivity in the vertical direction.

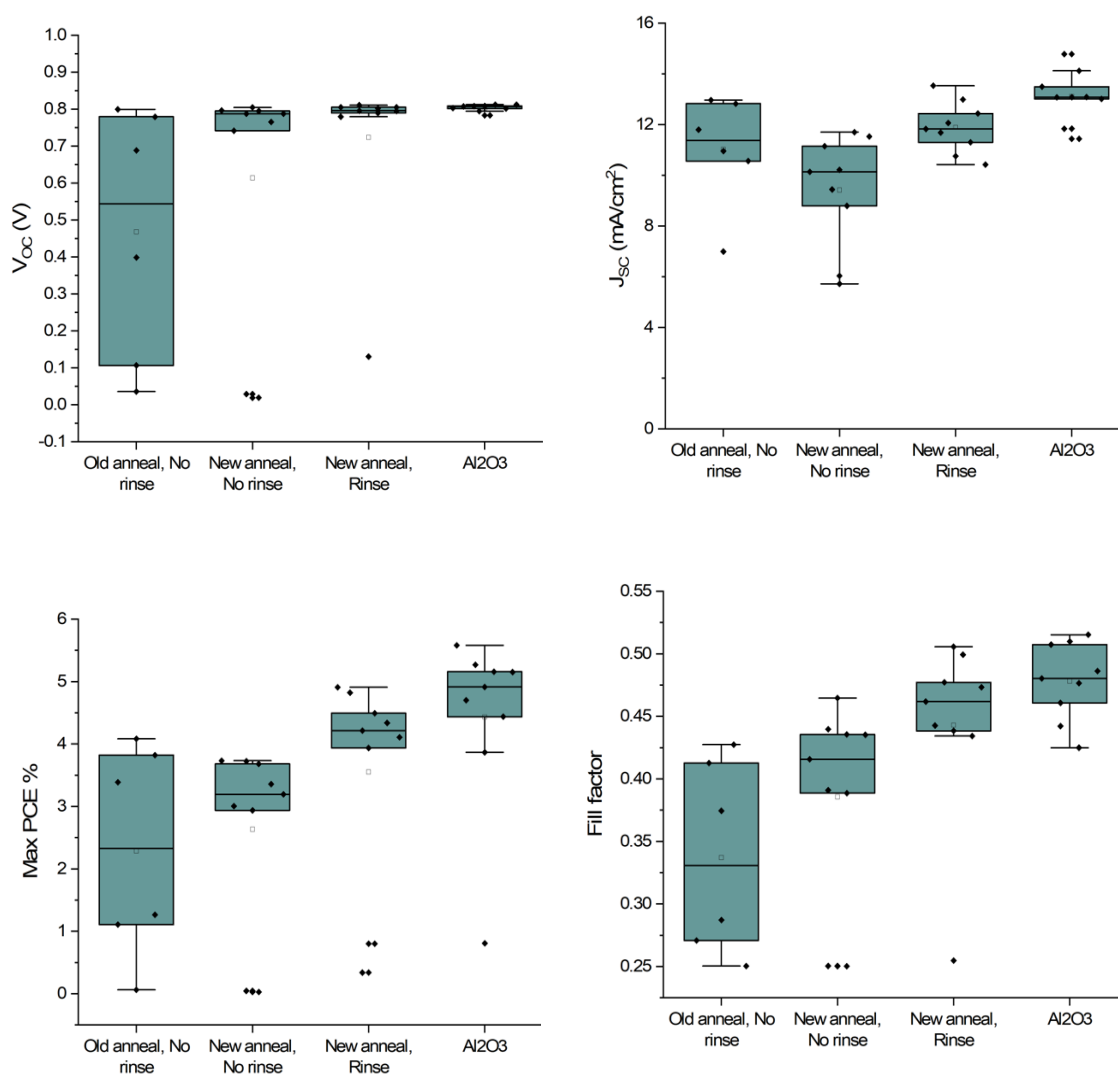


Figure 7.5 – Box plots depicting the open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF) and maximum power conversion efficiency (PCE) for devices comprising 10 mol% doped PCBCB, with different anneal conditions for the PCBCB film, and a set on alumina nanoparticle coated ITO. All devices here have a cell area of 0.25 cm².

7.2 Preliminary stability studies of PCBCB-based devices

The choice of PM6:Y6 active layer was decided early on in this project and was to be kept consistent as its deposition has been studied and used to optimise the ETL layer for a full device. Due to this, we expect to see a reduced stability due to degradation of the active layer with ZnO due to the photocatalysis effect at the interface. Differences in stability we attribute to the ETL as it is the only change during device fabrication. In this study, devices were encapsulated following the method described in chapter 3.3.7, using glass cavity slides and UV-curable epoxy glue, and stability was tested under light-soaking conditions in an ageing box (kept in air, standard room pressure), set to emit the same as AM1.5 solar radiation at 1 sun intensity at 65°C, using the setup as described in Ch 3.4. Figure 7.6 shows the normalised average PCE over a period of 35 days, for devices containing ETLs comprising ZnO, 20 mol% N-DMBI doped PCBCB (15 mg/ml) and a bilayer of 10 mol% N-DMBI doped PCBCB (15 mg/ml) atop intrinsic PCBCB (15 mg/ml), respectively.

If we take a closer look at the first four days, as in Figure 7.7, we can see that the PCBCB monolayer and bilayer devices both retain above 50% efficiency for 4 days (T50), whereas ZnO loses this in 24 hours. The first 24-48 hours shows this drop off in ZnO devices, then the same degradation trend across all samples which we attribute to degradation of the active layer material. However, these first 24 hours in particular exhibit how quickly degradation takes place in this environment with a ZnO transport layer. This is a preliminary study however and is still being investigated with the hope to improve on this result with more conclusive data. It should also be noted that all devices considered are 0.25 cm² cells. They were all aged under direct illumination,

with the top electrode side the exposed side facing the light until day 4, at which point devices were flipped so glass side was exposed to light, represented by highlighted region in the figures. This could have affected the degradation pattern to some degree between days 4 and onwards, due to the light travelling through the cover slip and reflection at the top electrode, rather than directly through the ITO glass up until this point. Figure 7.8 also depicts the champion devices and their respective degradation trends.

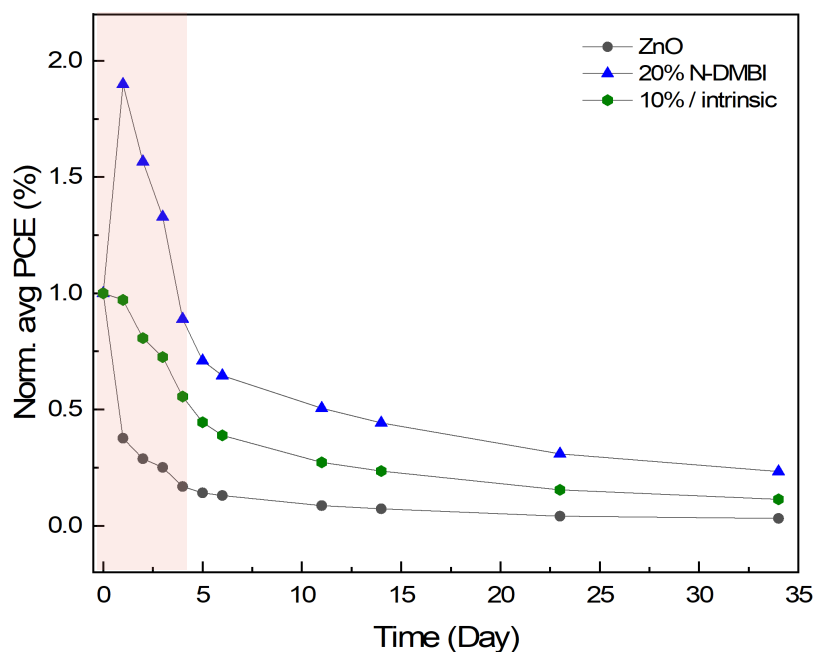


Figure 7.6 – Normalised average PCE of devices from this dataset over a period of 35 days. Comparing ETLs of ZnO to a 20 mol% PCBCB (15 mg/ml) ETL and a bilayer of 10 mol% PCBCB (15 mg/ml) and an intrinsic layer of PCBCB (15 mg/ml). The devices were all aged under direct illumination, with the top electrode side exposed to the light until day 4, at which point devices were flipped so glass side was exposed to light, represented by highlighted region in the figure.

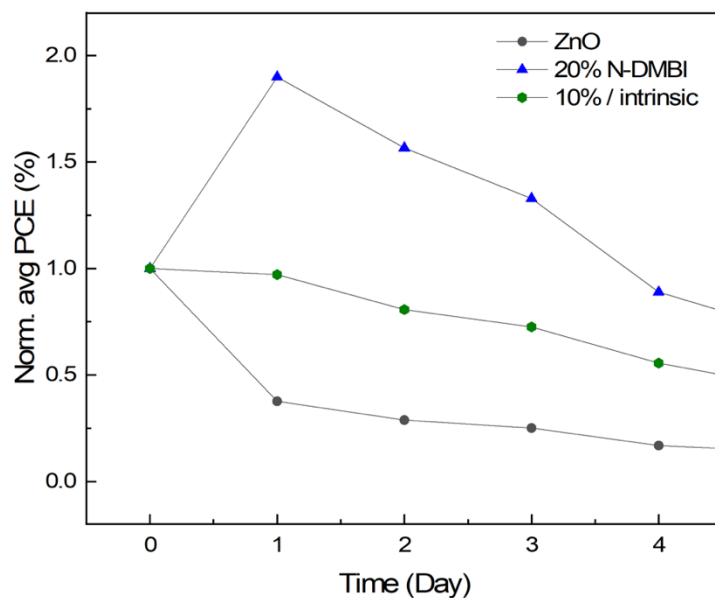


Figure 7.7 – Zoom of Figure 7.6, to show the lifetime of the devices from days 0-4 more clearly.

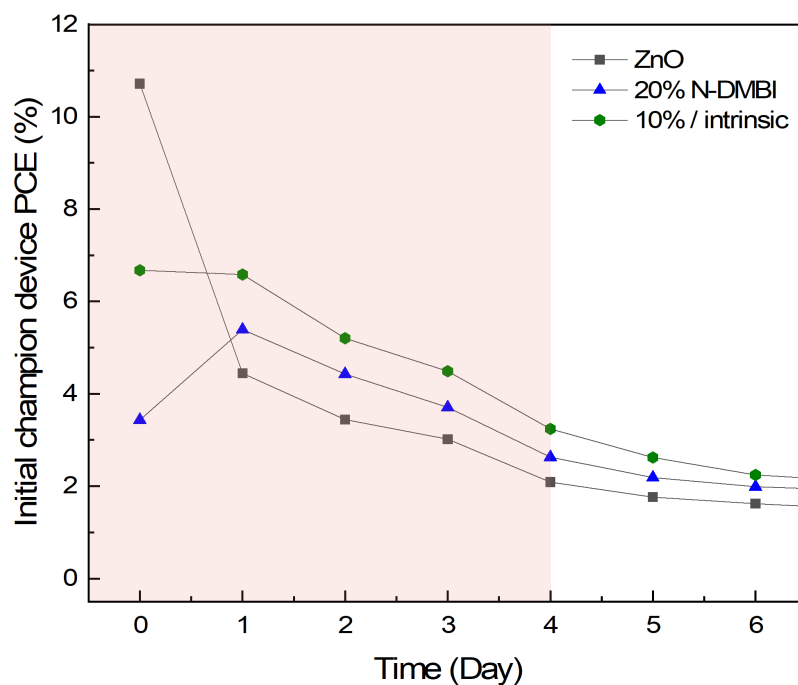


Figure 7.8 - Champion cell PCE degradation over first week. Comparing ETLs of ZnO to a 20 mol% PCBCB (15 mg/ml) ETL and a bilayer of 10 mol% PCBCB (15 mg/ml) and an intrinsic layer of PCBCB (15 mg/ml).

Chapter 8

Design, integration and setup of Ultraviolet Photoelectron Spectroscopy tool, as part of the EPSRC National Thin-Film Cluster Facility (NTCF) for Advanced Functional Materials

This chapter outlines the design of the Ultraviolet Photoelectron Spectroscopy tool and its integration into the Engineering & Physical Sciences Research Council (EPSRC) National Thin-Film Cluster Facility (NTCF). I was allocated lead user for this equipment, having spent a period of nearly 7 months at the University of Cologne in the sub-group of Selina Olthof, as part of the wider group supervised by Klaus Meerholz. This time allowed me to have hands on experience using another UPS setup to collect and analyse data exploring the energetics of PCBCB as an ETL, as exhibited in Chapter 5 & 6, with the aim of honing my expertise towards UPS. This was a major part of my DPhil and I have been heavily involved in all stages, from purchase and design of the equipment—to first stage integration and setup, testing, primary data collection and training other users.

The steps along the way to the finished and fully integrated system are covered, including necessary upgrades and amendments made to the setup since initial installation, and setup of the tool in preparation for first measurements.

8.1. Design, integration and setup

The UPS system that has been setup here in the Department of Physics at the University of Oxford is part of the Engineering and Physical Sciences Research Council (EPSRC) National Thin-Film Cluster Facility (NTCF) for Advanced Functional Materials; a multi-user shared research facility, supporting researchers from other universities and industrial partners across the UK. The purpose of this tool is to enable characterisation of the energetic band structure of thin films and material interfaces, for their use in optoelectronic and semiconductor devices. The NTCF is made up of a series of connected gloveboxes containing fabrication equipment including a thermal vacuum deposition chamber and atomic layer deposition system, alongside tools for device characterisation, meaning films can be developed and characterised without any exposure to air. The addition of the UPS tool to this system means that films can be processed using the thin film vacuum deposition tool that is housed within the system (or through spin-coating), and directly transferred to the UPS under vacuum between deposition chambers. As a result, samples remain in the conditions as similar as possible to those as when fabricated, eliminating the risk of contamination by air or particulates that can occur when transferring out of and between chambers, also reducing risk of degradation from air or changes in moisture. Combining these two tools also allows for the energetic properties of the thin-films or multi-layer stacks to be determined at different stages of growth, either by sequential layer deposition and measurement, or

using a wedge tool installed as part of the vacuum deposition tool, allowing for a gradient in thickness of the material deposited across a substrate. The sample can then be measured using UPS in different locations across the substrate to build up a picture of energetic changes with layer thickness, resulting in a system that is currently unparalleled in terms of the possibilities on offer for thin film deposition and direct characterisation. This system fills a previous critical gap in Oxford's materials and device characterisation capabilities, with researchers previously having to send samples to commercial UPS service providers such as *Kratos Analytical Ltd.* or having to travel to other higher education institutions such as University of Cambridge, UCL, HU Berlin or University of Cologne for access to a UPS tool; now this can be done in-house. This not only allows for improved sample quality in terms of reducing time between fabrication and measurement and risk of contamination, but also allows for productivity to increase by mitigating the time required for samples to be shipped or for travelling.

As part of my DPhil, I was offered the role of lead user of this UPS system, which involved taking on a lot of responsibilities with regards to the designing of the tool, ensuring a tool that has everything necessary to reach the correct vacuum pressure of $< 5 \times 10^{-9}$ mbar, and incorporates all of the correct instrumentation for UPS measurements to take place. The system was designed by me, Professor Moritz Riede, Professor Henry Snaith and Dr. Jin Yao, together with engineers from both *Angstrom engineering* and *SPECS Group*, in order to put together a tool that could be integrated directly as part of the cluster facility system. A 3D model of the system is displayed in Figure 8.1. As the vacuum deposition tool was designed by *Angstrom.*, the main chamber for the UPS tool, along with the sample transfer apparatus including the bellows and the x-y stage (see Figure 8.2) and its accompanying software, were supplied by them also. This allowed for seamless integration of the sample handling processes required for bringing samples

to and from the UPS tool into the already existing cluster facility hardware and software. The x-y stage is made from components comprising both stainless steel and aluminium 6061-T6; all the chamber material that interacts with the sample is required to be conductive and non-magnetic. It was decided that with a magnetic permeability (μ) of 1.02, a stainless-steel holder should have a low enough residual magnetic field to not affect electron path travel. This will be tested further, and a molybdenum holder, with a comparative magnetic permeability of 1.00012, is currently being developed. Stainless steel (304) was also used as the holder material with the UPS setup in Cologne. The magnetic permeabilities were calculated using equation 8.1, where χ_m is the magnetic susceptibility of the material, as found at [271], and μ_0 is the magnetic permeability of a vacuum.

$$\mu = \mu_0 (1 + \chi_m) \quad (8.1)$$

The chamber was designed with several ports, in order to allow for connection of a UVS 10/35 UV-source (*SPECS*) as in Figure 8.3 (a), a PHOIBOS 100 electron analyser (*SPECS*) and 1D-delayline detector (1D-DLD) (Figure 8.3 (b)) and two vacuum pumps, one Pfeiffer Vac Hi Pace 700 turbo pump for achieving ultra-high vacuum pressures, and a backing pump (Figure 8.4) to further improve the pull from the chamber. In addition, some currently unused ports were included to accommodate the future addition of an X-ray source as part of an XPS setup. The chamber was lined with Mu-metal liners (*Argon services*), to shield the sample electrons against external electromagnetic fields that can disrupt the path of the flight, which would ultimately change the UPS measurements.

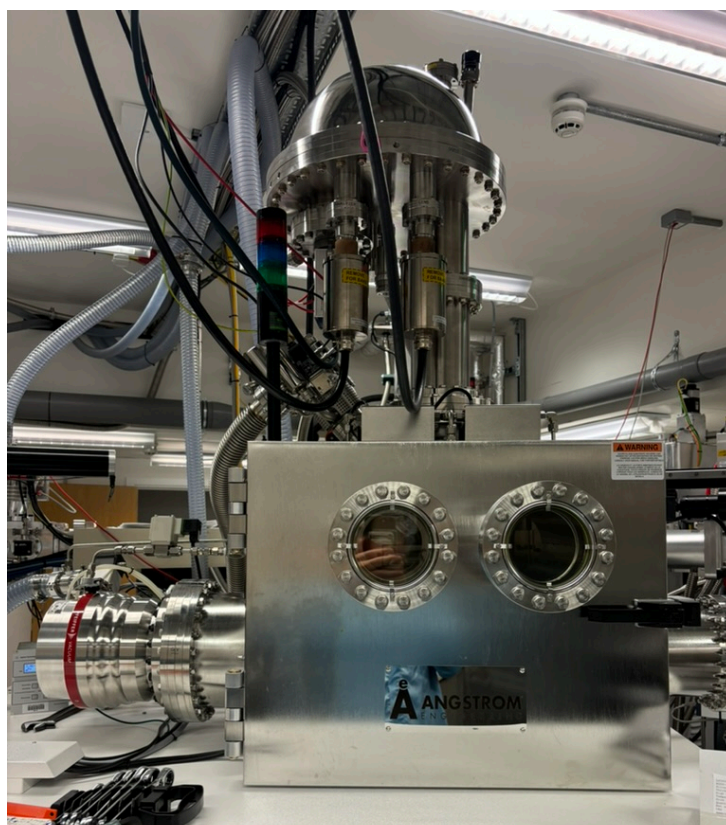
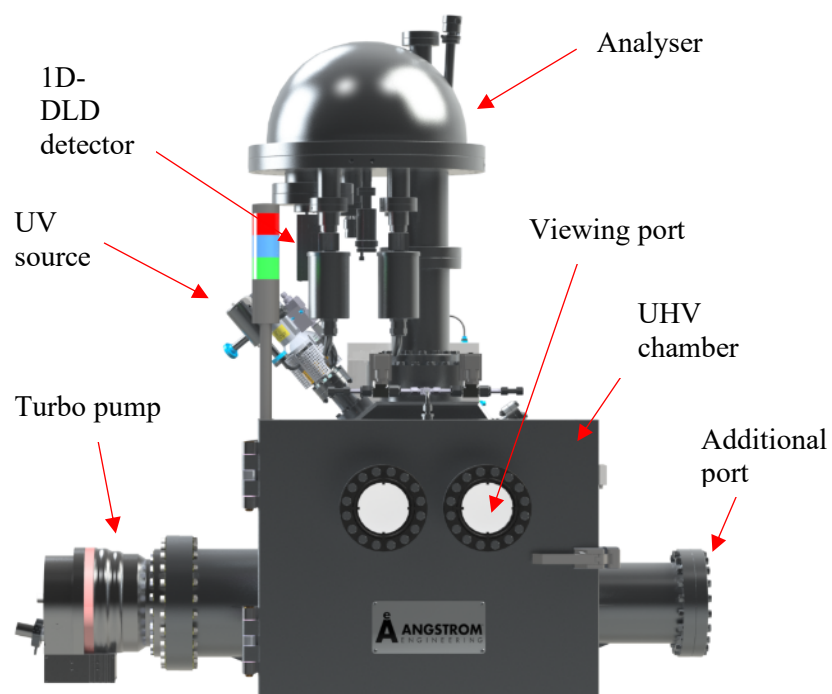


Figure 8.1 – 3D schematic of UPS chamber and components (top) and photo of UPS chamber (bottom).



Figure 8.2 – Bellows controlling x-y stage inside the UPS chamber, used for transfer of samples and aligning sample with UV-source for UPS measurements.



Figure 8.3 – UV-source (left) and PHOIBOS 100 analyser (right).

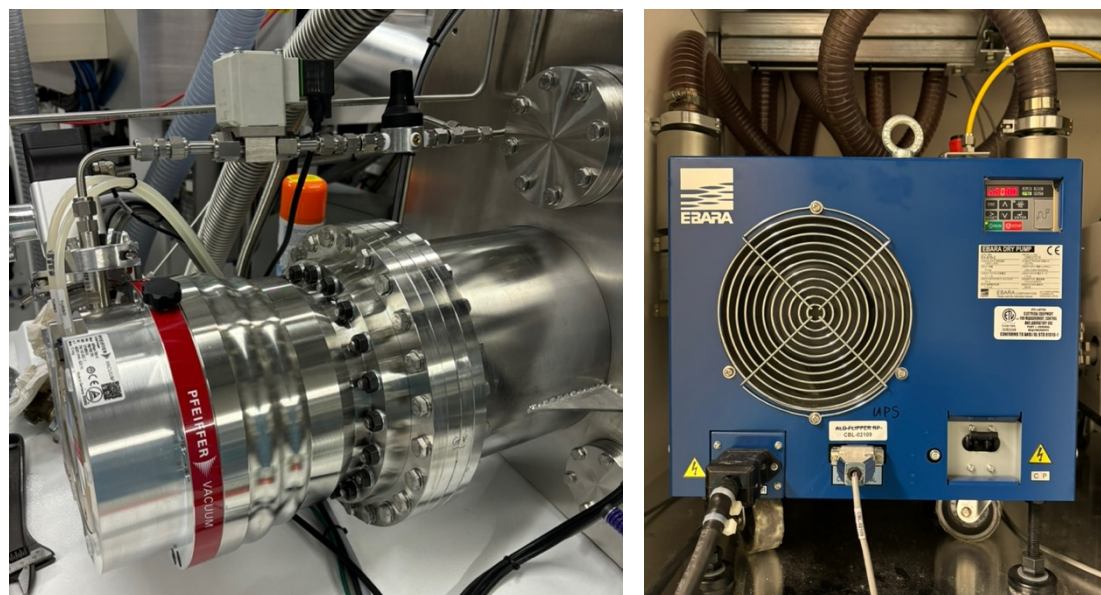


Figure 8.4 – Turbo pump (left) and backing pump (right) attached to UPS chamber.

The actual integration of the tool into the cluster facility was managed with oversight from *Angstrom* and *SPECS* themselves. It was integral to be understand how each part of the UPS works and is connected, in order to ensure its smooth running and to be able to pass on the knowledge to properly operate and maintain the system to future users and to mitigate any problems. With all parts installed, it was also my job to first review whether any additional amendments to the system were required before ensuring the UPS system was at ready to use status. Firstly, the sample stage had to be isolated from the rest of the chamber by adding a layer of insulating tape between the sample plate holder and the x-y stage upon which it sits, as depicted by the schematic in Figure 8.5. This allows for complete isolation of the samples to the rest of the chamber, so that the bias can be directly applied to the samples without passing through the rest of the chamber, ensuring safe application of a voltage when in use. The next step before closing the chamber was to install a connection to the voltage source to allow for this biasing of the samples, for improved detection of slow electrons (as described in chapter 4.1). To do this, Jin Yao and I both worked to guide silver plated copper wires through the hollow pillar central to the x-y stage and coated this in ceramic beads to insulate them. We then installed a feedthrough into the base of the x-y stage pillar through which the external wires from the voltage source and the installed biasing wires could be connected (Figure 8.5 also). The correct installation of the wires was tested by checking the resistance between the plate and wire was indeed 0Ω , and the isolation from the rest of the chamber was ensured by measuring the resistance between the wire and the chamber wall, which was on the order of $M\Omega$. Following this, the chamber was sealed and pumped down and the analyser and other metal components were heated to between 100 – 150 C (component dependent) using heating cables, for a period of 72 hours, to

eliminate moisture that was stuck to the metal insides of the chamber and analyser and reduce the vacuum pressure further, in a process known as bake-out of the chamber.

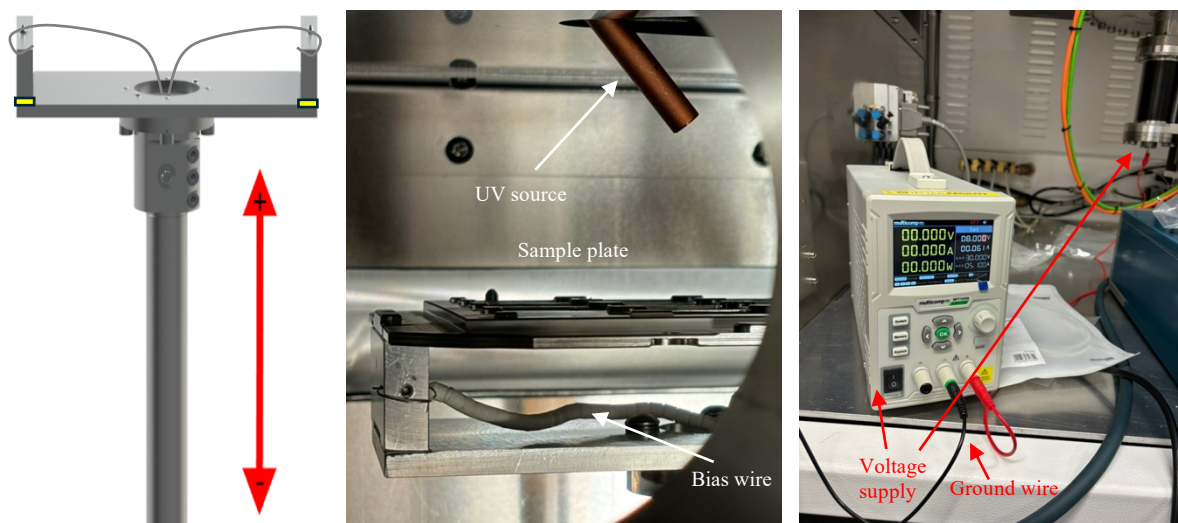


Figure 8.5 – Schematic of UPS stage and sample plate holder (left), with insulating tape to isolate sample plate from the rest of the chamber highlighted in yellow. Arrow to indicate the direction in which the stage moves along the z-axis. Biasing wires are also shown in schematic. UPS sample plate with respect to the UV-source exit and bias wire (middle). Bias setup (right).

During bake-out the chamber pressure was recorded to monitor its reduction and to ensure pressures of $< 5 \times 10^{-9}$ mbar could be reached. The lowest pressure obtained with the current pumping setup post bake-out 4×10^{-9} mbar. The setup was then turned on and the detector voltages were ramped using the prodigy software to 1770V (the recommended optimal voltage for detecting an electron signal with high enough intensity) over a period of 1.5 hours to degas the detector. Following this, the analyser was degassed also by running a scan from $E_{\text{kin}} = 0$ to $E_{\text{kin}} = 1499$, at a pass energy $E_{\text{pass}} = 10$ eV. The helium line attached to the UV-Source and chamber was then flushed with

helium to avoid introduction of oxygen to the system, before introducing helium in the lamp cavity where it is to be ignited. This is controlled by a leak valve on the UV-source (see Figure 8.6). Upon ignition of the helium, the correct pressure within the lamp cavity for production of He I α ($h\nu = 21.22\text{ eV}$) was determined. This system does not have a monochromator so the He II is also present in the UV-beam that reaches the sample, however the pressure can be tuned to improve the intensity of He I, by adjusting the leak valve and monitoring the colour of the ignited flame. He I produces an identifiable orange-pink flame, while He II produces a whiter flame. The pressure determined for igniting the lamp was around 5×10^{-1} mbar. Pressures lower than this will result in a higher intensity of He II and the lamp may not ignite, pressures higher than this result in a greater intensity of He I but the pressure should not be too high as this will result in an overall higher UPS chamber pressure; this needs to be monitored accordingly and one should always aim to keep this in the order of 10^{-9} mbar or lower if possible.

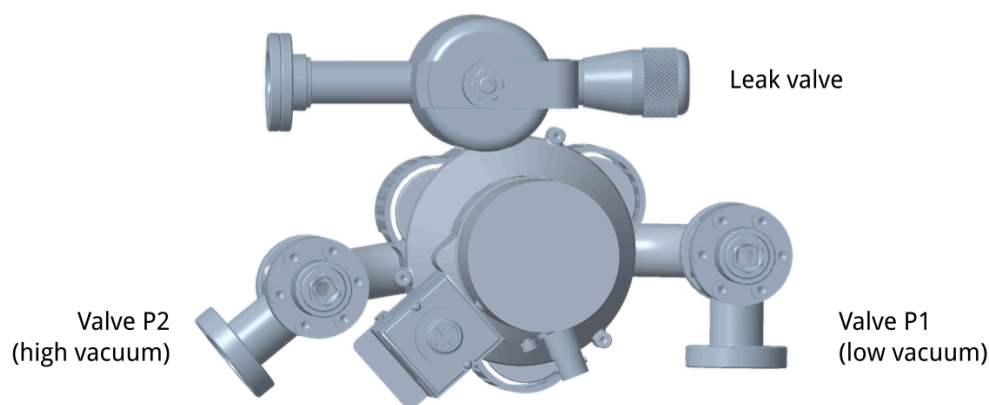


Figure 8.6 – Location of valves on the UVS 10/35, highlighting the leak valve used to control the injection of helium and pressure in the helium lamp.

Having completed these steps, the UPS system is now ready for preliminary testing and calibration. This is the next step in setting up this system, before beginning regular use for collecting data as part of material and sample studies.

Chapter 9

Spectroscopic characterisation investigations into other materials

The work in this chapter highlights the spectroscopic characterisation that I, alongside collaborators at the University of Cologne (Dilara Öz & Selina Olthof), have conducted as part of a collaborative projects headed by a colleague at the University of Oxford, Ming Zhu. This chapter will focus on the energetic characterisation of donor and acceptor components for use in a bilayer planar heterojunction in OPV devices, in order to better establish the energetic alignment of these material as compared to literature measurements from techniques such as cyclic voltammetry.

9.1. Investigating the energetics of a SubNc and NFAs for bilayer planar heterojunction in OPV devices

** This work is yet to be published but will be used (with adapted text and figures) within a paper publication. Potential publication name:*

‘Exploiting Förster Resonance Energy Transfer in Evaporated Organic Solar Cells’ [272]

In this section we investigate the energetics of SubNc and NFA materials, namely HB194 and DCV3T (please see table 3.6, chapter 3 for full names), to be used as components in bilayer planar heterojunctions. This project is part of a collaboration with Ming Zhu who is leading the project on studying vacuum thermally deposited organic systems comprising SubNc|NFA heterojunctions, that mimic solution processed ones and investigating the exploitation of Förster Resonance Energy Transfer (FRET) [273] in OPV devices. As the detailed physics involved in FRET goes beyond the scope of this thesis, we just refer to this specific portion of the study and its contributions.

Recent studies have demonstrated the importance of determining accurate values for the HOMO and LUMO levels of organic components comprising solution processed non-fullerene acceptor based organic solar cells with low offset in their ionisation energies [274,275]. In some cases, the more accessible technique of cyclic voltammetry can be used to determine these energy levels but often yields very different HOMO[LUMO] values from UPS[IPES], causing some well-performing donor/acceptor (D/A) material systems to appear to have ‘no energetic offset’ [275]. These ‘zero-offset’ systems have led to questions regarding the minimum energetic

offset that is necessary for efficient charge separation at the D/A interface, previously concluded from fullerene systems [1]. Furthermore, reported values have often been obtained using different measurement techniques or analysed differently, leading to inconsistencies in the literature. For some materials, HOMO and LUMO values are not reported at all. Reliable HOMO and LUMO values of these NFA systems are crucial for identifying possible energy barriers at the donor/acceptor interface and for understanding the Voc, Jsc and charge separation in devices.

Using UPS (University of Cologne), the energetics of each material (thin film) were studied respectively, by preparing neat film samples deposited on silicon wafers (Inseto Ltd, W-Si Wafer 04/005). All substrates are cleaned in a Hellmanex solution, de-ionized water, acetone and isopropanol in ultrasonic bath before the deposition. Each sonication lasts for 10 mins at a bath temperature of 55°C and 37kHz. Then 10 mins of O₃ plasma treatment is done before the substrates being loaded into the vacuum deposition chamber. The thin films were fabricated via vacuum thermal deposition in the Evaporation CHamber Oxford (ECHO, CreaPhys GmbH, EVAP300). The chamber pressure is brought down to 10⁻⁶ -10⁻⁷ mbar during evaporation using roughing (Pfeiffer GmbH, Adixen ACP15) and turbomolecular (Pfeiffer GmbH, HiPace 700) pumps. The materials to be evaporated are loaded in ceramic crucibles, which are located around 50cm below the substrates in the chamber. During evaporation, crucibles enclosed in water cooled copper shields, are gradually heated to target temperatures by tungsten coils. A substrate shutter is installed to prevent premature deposition of the molecules onto the substrate. These samples are 30nm thin films deposited at the rate of 0.3 Å/s, which are measured via quartz crystal microbalances (QCMs). The substrate shutter is opened when the target deposition rate is reached and closed after reaching the target thickness. The substrate was held at room temperature for these samples. The

evaporation rates and thicknesses are displayed on the deposition controller (Inficon, SQC-310) and carry an error of 5% based on the manufacturer specifications. After the deposition, the substrates are transferred into a N₂-filled glovebox directly, packed and sealed (without any air exposure) to be transported to UPS/IPES chamber.

The exact energetics of the neat films were measured using UPS and IPES (University of Cologne) and analysed to determine accurate HOMO and LUMO values and build a picture of the potential energy offsets at the interface between the donor and acceptor components. From this, the work functions, ionisation energies and electron affinities of the thin films could be determined. The optical gaps were determined by Ming Zhu from surface ellipsometry data, and with these, the expected fundamental gaps were first calculated using equations from [276] and compared to those found using UPS and IPES. The UPS and IPES spectra are shown together in Figure 9.1, while the values extracted from these spectra are displayed in Table 9.1. Literature values for the HOMO and LUMO values and IE and EA values found for SubNc, their sources [277, 280] and the measurement techniques used to obtain these have also been provided here. The respective positions of the HBEC, HOMO and LUMO onsets were determined via a linear fit to the onset regions, taking the first leading edge for each. We account for an additional uncertainty of ± 40 meV to fit of the first leading edge for the HBEC of HB194, in addition to the ± 110 meV energy resolution of the analyser (as determined by the width of the Fermi edge). Due to the poor energy resolution of the detector and difficulty in precise determination of the exact onset of the leading edge, the uncertainty in the IPES values has been stated as ± 550 meV.

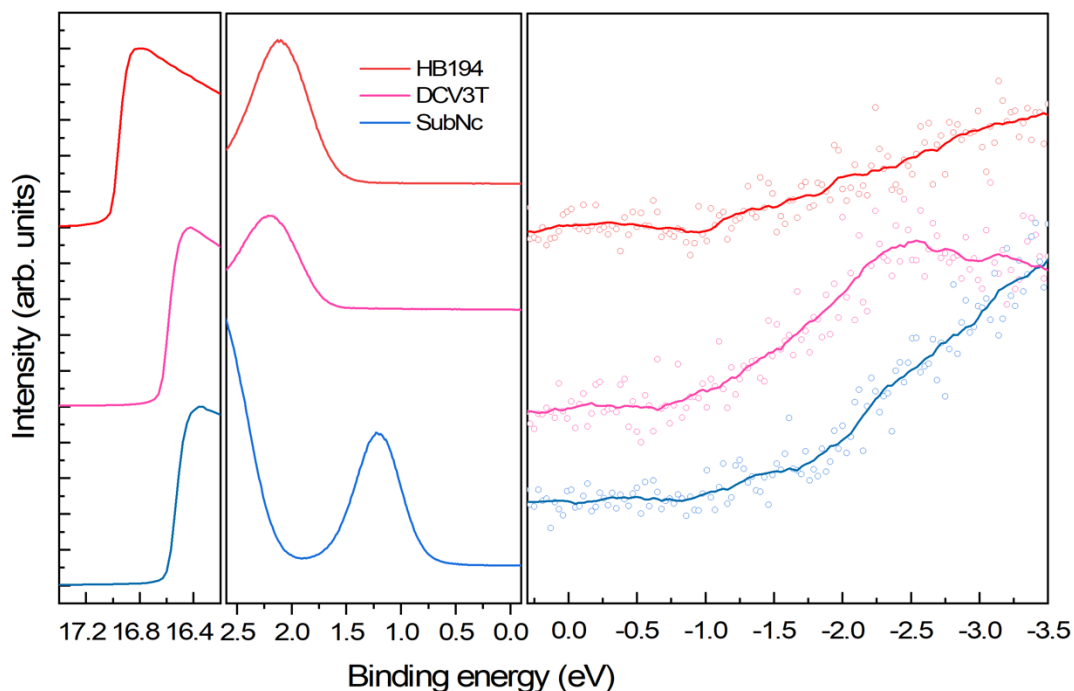


Figure 9.1 – UPS and IPES spectra of respective active layer components, SubNc, HB194 and DCV3T. The left-hand panel shows the UPS data for the position of the HBEC, while the other two panels show the HOMO onset region (from UPS) and the LUMO onset region respectively (from IPES). The grey dashed lines indicate the HBEC onset position used to calculate the WF, while the black dashed line represents the first leading edge used to determine the HOMO onset position. The respective HOMO and LUMO onset energies are marked by black vertical lines.

Molecule Name	Work Function	HOMO w.r.t Fermi	Ionisation energy	LUMO w.r.t Fermi	Fundamental bandgap	Electron affinity
DCV3T	4.57 ± 0.11 eV	1.70 ± 0.11 eV Comparison from literature [277]: - 6.09 eV, measured with cyclic voltammetry with reference to vacuum.	6.27 ± 0.22 eV	-1.03 ± 0.55 eV Comparison from literature [277]: - 3.9 eV, measured with cyclic voltammetry with reference to vacuum.	2.73 ± 0.66 eV $E_{\text{optical}} = 1.99$ eV Expected $E_{\text{fund}} = 2.73$ eV	3.54 ± 0.66 eV
HB194	4.21 ± 0.15 eV	1.60 ± 0.11 eV Comparison from literature [278]: - 5.75 eV, measured with cyclic voltammetry with reference to vacuum.	5.81 ± 0.26 eV	-1.02 ± 0.55 eV Comparison from literature [278]: - 3.6 eV, measured with cyclic voltammetry with reference to vacuum.	2.62 ± 0.66 eV $E_{\text{optical}} = 1.86$ eV Expected $E_{\text{fund}} = 2.55$ eV	$3.19 \text{ eV} \pm 0.70 \text{ eV}$
SubNc	4.62 ± 0.11 eV	0.8 ± 0.11 eV Comparison from literature [279]: - 5.37 eV, measured with cyclic voltammetry with reference to vacuum.	5.42 ± 0.22 eV Comparison from literature [280]: 5.35 eV, measured with UPS.	-1.48 ± 0.55 eV Comparison from literature [279]: - 3.6 eV, measured with cyclic voltammetry with reference to vacuum.	2.28 ± 0.66 eV $E_{\text{optical}} = 1.70$ eV Expected $E_{\text{fund}} = 2.33$ eV	3.14 ± 0.66 eV Comparison from literature [280]: 3.47 eV, measured with UPS.

Table 9.1 – Table of energetic values for respective active layer components, determined via UPS and IPES. Expected fundamental gap determined from equation in [276]. Comparative literature values are also provided, along with the source reference.

From IPES data, we identify there is negligible LUMO offset between thin films of SubNc and HB194 and a sizable offset of 0.4 eV between SubNc and DCV3T. With UPS results, a HOMO offset around 0.39 eV is found for SubNc and HB194, 0.85 eV for SubNc and DCV3T. These results suggest efficient hole transfer at SubNc|HB194 interface and electron (hole) transfer at SubNc|DCV3T interface. Along with other device and thin film characterizations, these results enhance our understanding of how their device performance relates to the intrinsic properties of the molecules.

Chapter 10

Conclusions and outlook

This work investigates the use of electron transport layers in organic solar cells and the effects of doping on organic semiconductor ETLs, through electronic and spectroscopic characterisation techniques. Films of organic semiconductor PCBCB were fabricated, to show its effectiveness as an ETL in an inverted device stack due to its ability to oligomerise and form insoluble films upon thermal annealing. However, this alone does not allow the material to be a functional ETL, because of its lack of free charge carrier resulting in poor energetic alignment with the ITO substrate, and low conductivity. Therefore, doping the ETL allows for improvements in these areas, rendering a useable ETL that has exhibited favourable characteristics in terms of high conductivity, a Fermi level close to the LUMO and improved energetic alignment with ITO. There is still work to be done in terms of device optimisation, but this thesis hopes to shine light on the potential for materials like this to be used for improved device stability by eliminating the photocatalytic effects of metal oxides at the ETL/active layer interface.

The main conclusions to be drawn from this thesis, in addition to a summary of how it expands the current understanding of the field of, can be summarised as follows: There is much interesting research that can be done in the field of electron transport layers to enhance the device performance and stability of organic photovoltaic devices, with polymerisable and cross-linkable fullerenes proving promising in this area. The effects of processing on organic semiconductor thin film properties, in this case electron transport layers, is often undervalued and we have demonstrated that these effects can have a considerable contribution to the physical, optoelectronic and energetic characteristics of an organic ETL.

Furthermore, PCBCB as an electron transport layer is possible, with doping acting as a key component in improving device performance due to its conductivity enhancing properties and its ability to tune the work function and Fermi level of the PCBCB, producing a more favourable, n-type film for charge carrier extraction and transport to the anode.

Through this work we have highlighted the effectiveness of photoelectron spectroscopy as a technique to firstly understand the aforementioned energetic characteristics of a thin film, but also to develop fabrication processes that can be used to tune the properties of not only thin films but consequentially the whole device stack in which they are a component. This was demonstrated when evaluating the morphology and energetics of the active layer atop different ETLs and confirming changes in these properties that can be traced back to how the ETL was fabricated and its doping concentration.

It has been shown that the first steps have been taken towards implementing PCBCB into a device stack, with the necessary conditions for improved performance highlighted. Furthermore, in preliminary tests, it was exhibited that over a 24–48-hour

period, devices comprising PCBCB maintained 50% of their PCE, while ZnO devices dropped considerably below this. Whether this material can compete with metal oxides in terms of device performance is still to be explored further, in order to further improve OPV device efficiencies with the use of a doped PCBCB ETL, and to monitor stabilities over a longer time period. It would also be of interest to take this device work further and study the effects of a thin intrinsic layer of PCBCB atop the doped ETL, to limit the effects of charge carrier quenching at the interface.

The importance of PES techniques has again been highlighted in chapter 9, exhibiting its use in characterising the energetics of known systems in solution-processed OPV for future use in vacuum thermally deposited organic systems. The characterisation of donor and acceptor materials for use in bilayer planar heterojunction allows for improved tailoring of device stacks and ultimately enhanced device performances through better energetic alignment at the donor/acceptor interface. Building on this, the development and setup of a UPS tool into the cluster lab is an excellent step to allow for characterisation of the energetics of materials here in the physics department of Oxford, something previously not possible.

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Appendix A –

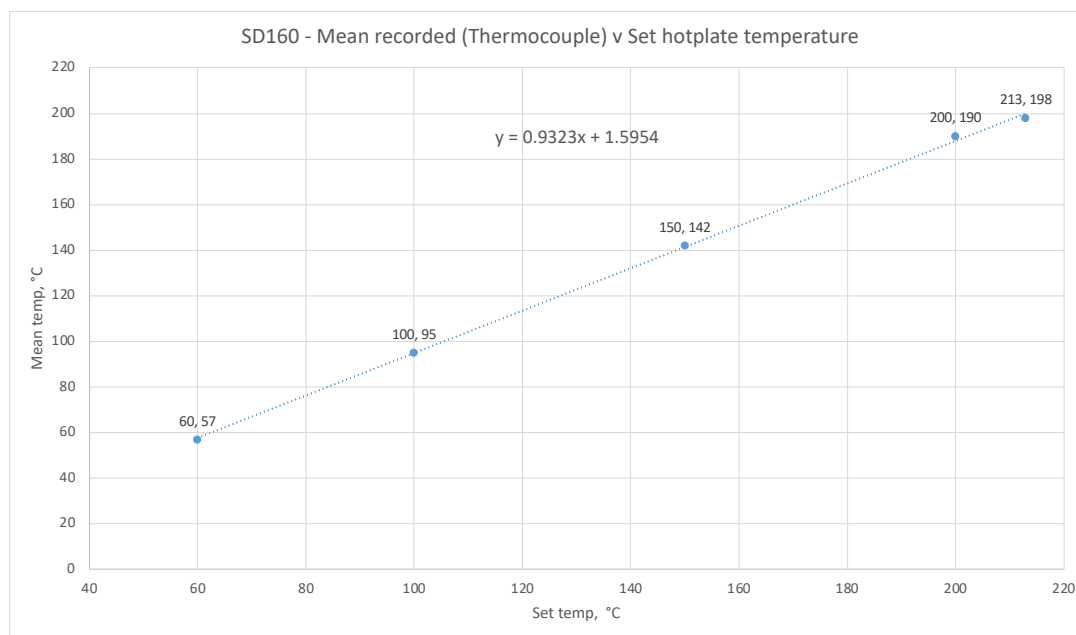


Figure A1 – Hotplate calibration curve (SD160). Based on thermocouple readout, placed central on glass 30 mm x 30 mm glass substrate, outside glovebox

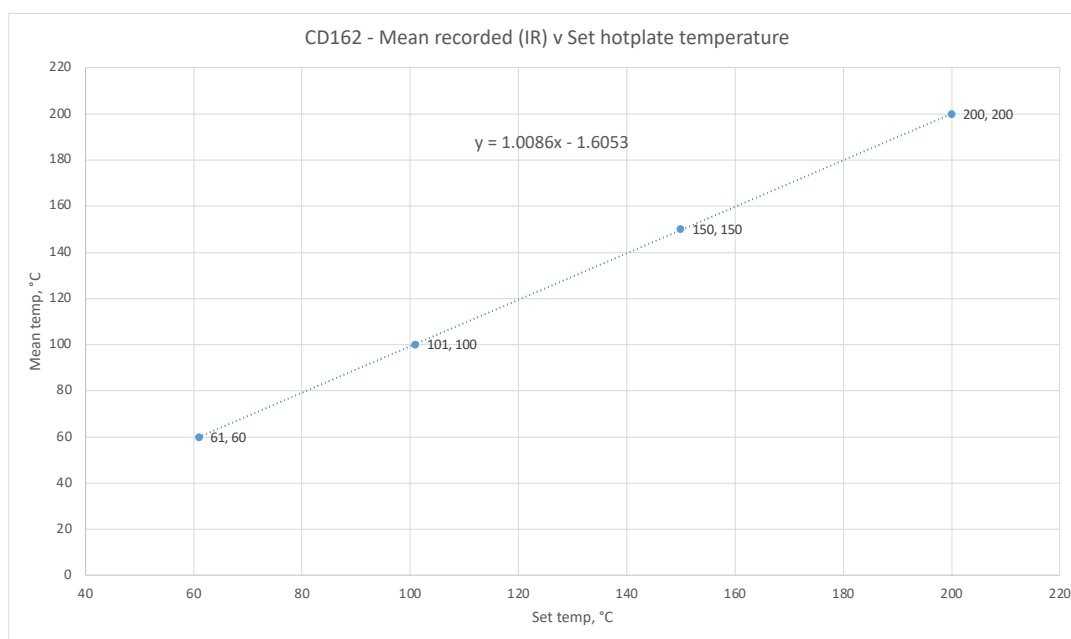


Figure A2 – Hotplate calibration curve (CD162). Based on 60mm x 60mm, Carbon black sample, central on plate, inside glovebox.

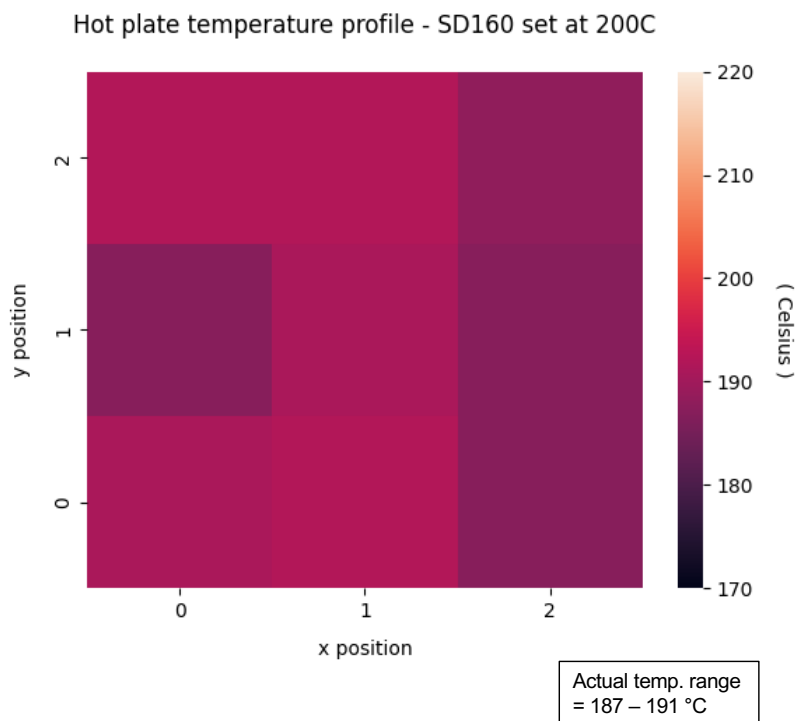


Figure A3 – Heatmap of SD160 hotplate, used to calibrate the set temperature to the actual temperature, as discussed in chapter 3.3.

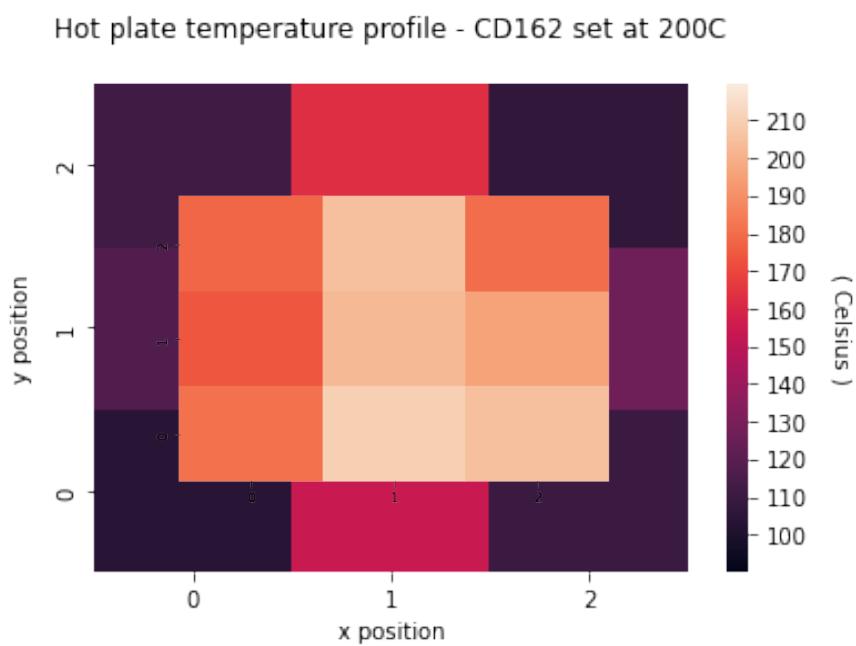


Figure A4 – Heatmap of CD162 hotplate, with the heatmap of the metal block used for annealing samples in this work. Data used to plot this was also used to calibrate the set temperature to the actual temperature, as discussed in chapter 3.3.

Appendix B –

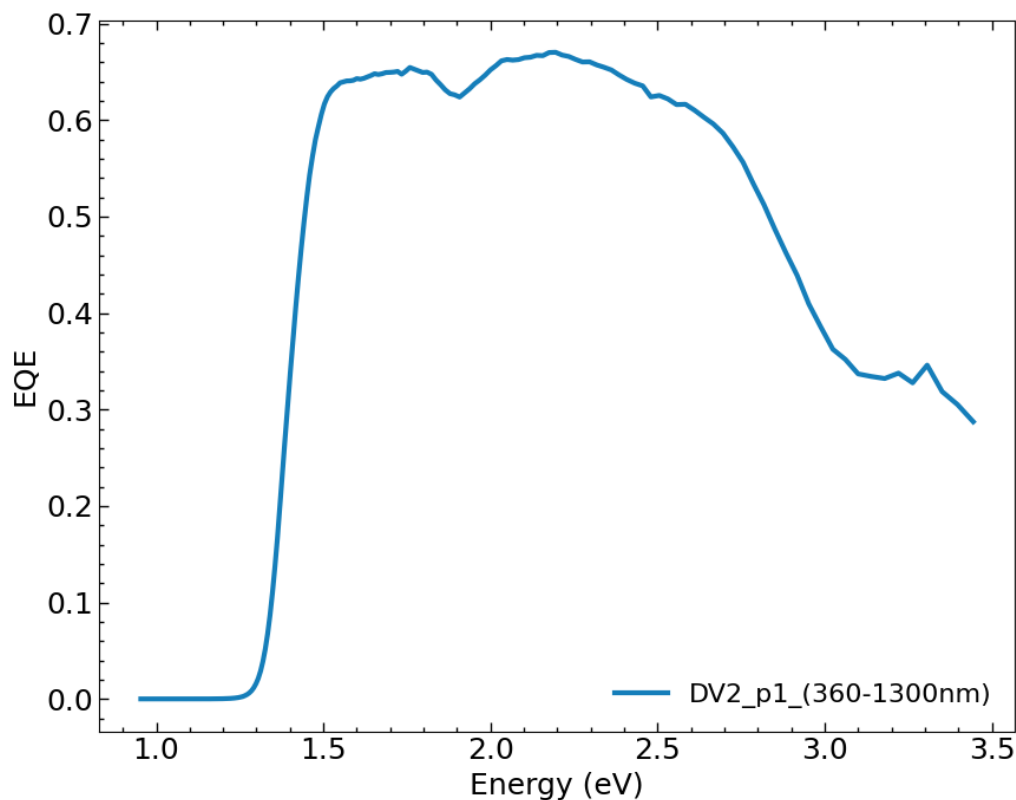


Figure B1 – EQE spectrum for control device stack of ITO/ZnO /PM6:Y6/MoO₃/Ag, to compare to literature spectra. Measured from 0.01cm² pixel, with beam spot... The EQE was calibrated to a Thorlabs FDS100 (Si diode, covers 360-1100nm) and FGA21 (InGaAs diode, covers 800-1500nm). The calculated J_{sc} from this EQE is around 20.05 mA/cm². Measured with Ming Zhu.