Large-Area Slot-Die Coated Organic Photovoltaics with High Efficiencies

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Dedicated to my parents:

Соня Кушарова и Иван Кушаров
Abstract

Commercially available organic photovoltaics (OPV) are commonly fabricated using printing and coating techniques that allow for low-cost, high throughput processing of large-area OPV devices. However, the power conversion efficiency (PCE) of scaled-up OPVs is often lower than that of small-area ones. This is because the deposition techniques typically being used in industry are different to those used in research laboratories (printing/coating vs. spin-coating). Thus, detailed studies of functional materials are required to tailor the characteristics of photoactive D/A blends of OPVs in order to preserve high PCE values for scaled-up device sizes. Therefore, the aims of this thesis were to enhance the PCEs of OPV cells made using a well-known donor material (P3HT), and to develop a structured approach to fabricating large-area OPVs thus easing the transfer of fabrication procedures from laboratory to industry.

To achieve the first goal, indene-C$_{70}$-bis-adduct (IC$_{70}$BA) was chosen as an acceptor material for a photoactive blend with P3HT. A review of P3HT:ICBA-based solar cells indicated a significant variation of reported device PCE values (average of 4.66±1.45%). The majority of reported device efficiencies were measured for OPVs with photoactive areas rarely exceeding 0.1 cm$^2$. Therefore, a detailed study of the intrinsic characteristics of the IC$_{70}$BA molecule and the morphology of the P3HT:IC$_{70}$BA blends was carried out in order to design the optimal fabrication conditions for achieving higher PCEs and up-scaled device areas. Record PCEs approaching 7% were accomplished in this thesis for OPVs with photoactive areas of 0.43 cm$^2$. This was achieved by understanding the correlation between the isomeric properties of the IC$_{70}$BA molecule and the resulting D/A blend morphology depending on the fabrication conditions used.

The second goal of this thesis was accomplished by designing a slot-die coating equipment that allows for the deposition of functional materials over large-areas. Different solubilised materials were deposited in ambient conditions on glass and plastic substrates in order to fabricate OPV devices. Two different photoactive D/A systems were used: P3HT:IC$_{70}$BA and PCDTBT:PC$_{70}$BM. OPV cell and module PCEs approaching 4% were achieved for devices with photoactive areas of about 35 cm$^2$. The quality of the slot-die coated layers was investigated using LBIC, PL, and Raman mapping. This will allow for future improvements in the coating process and, therefore, increased device PCEs and operational lifetimes.

In conclusion, the results obtained in this thesis show a way of fabricating efficient large-area OPVs without the use of the spin-coating deposition technique. The study of materials and the development of deposition procedures allows for an accessible transfer of research outcomes from the laboratory to industry.
Declaration

This thesis and the work to which it refers are the results of my own efforts, other than the areas explicitly noted as being conducted collaboratively. Any ideas, data, images or text resulting from the work of others (whether published or unpublished) are fully identified as such within the work and attributed to their originator in the text, bibliography or in footnotes. Section 2.3.2.1 and Figure 2.10 were prepared with the support of Dr. Maria Lebedeva and Mr. Ilija Rašović. The HPLC, MS, UV-vis, and NMR characterisation discussed in Sections 5.2.1 and 5.2.2 were carried out and analysed by Dr. Maria Lebedeva, Mr. Ilija Rašović, and Prof. Kyriakos Porfyrakis. The TGA and DSC measurements discussed in Sections 5.2.3 and 5.2.4 were conducted by Ms. Violeta Doukova. The analysis is by the author after a discussion with Dr. Ian Hamerton. The CA and SE characterisation in Sections 5.2.5 and 5.3.1 were undertaken by Mr. Alexandros Zachariadis, Dr. Argiris Laskarakis, and Prof. Stergios Logothetidis, while the analysis was carried out by the above mentioned people, and by the author. The LBIC, PL, and Raman characterisation in Sections 6.4.4, 6.4.5, and 6.4.6 were conducted by Dr. Francesco Bausi, Dr. Alina Zoladek-Lemanczyk, and Dr. Fernando A. Castro at the National Physical Laboratory in the UK, while the analysis of the data was undertaken by the above mentioned people, and by the author. This thesis has not been submitted in whole or in part for any other academic degree or professional qualification. I agree that the University has the right to submit my work to the plagiarism detection service TurnitinUK for originality checks. Whether or not drafts have been so-assessed, the University reserves the right to require an electronic version of the final document (as submitted) for assessment as above.

Guildford, 15/05/2017

(Dimitar Ivanov Kutsarov)
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List of publications and awards

Journal papers


• Brett Fisher, Dimitar Kutsarov, Vlad Stolojan, and S. Ravi P. Silva, “Integrated modelling of the optical properties of plasmonic nanoparticles with multiple and graded coatings”, submitted for publication

• Dimitar I. Kutsarov and S. Ravi P. Silva, “P3HT:IC$_{70}$BA-based Organic Photovoltaic devices – A Review”, manuscript in preparation


• Dimitar Kutsarov, Charanadhar Nagavolu, Vadali. V. S. S. Srikanth, and S. Ravi P. Silva, “Solution processed graphene derived electron transport layers for high efficiency, large area polymer solar cells”, manuscript in preparation

• Kiron Prabha Rajeev, Dimitar Kutsarov, Jeremy Allam, and Maxim Shkunov, “Near infrared organic photodiode with nA dark current and high detectivity values at near-zero voltages”, manuscript in preparation

Conference presentations


• Dimitar I. Kutsarov, E. New, M. Shkunov, and S. R. P. Silva, “Large-area hybrid solar cells printed on plastics for integration into buildings”, Poster presentation during the 2016 PGR Conference at the University of Surrey


• Dimitar I. Kutsarov, Keyur Gandhi, Christopher A. Mills, I. Jayawardena, and S. Ravi P. Silva, “A systematic study of P3HT:IC_{70}BA polymer solar cells; towards and beyond the 6% barrier”, Oral presentation during the 8th International Symposium on Flexible Organic Electronics (ISFOE15)

• Dimitar I. Kutsarov, M. Shkunov, and S. R. P. Silva, “Plastic Solar Cells for the bright future of Renewable Energy”, Oral presentation during the 2014 PGR Conference at the University of Surrey

**Conference awards**

• 2016 Poster Presentation Award during the PGR conference at the University of Surrey

• 2015 Best Oral Presentation Award during the 2015 International Nanotechnology conference
Acronyms, materials, and symbols

\( c \)  Concentration
\( d \)  Thickness
\( D \)  Diffusion coefficient
\( k_B \)  Boltzmann constant
\( L \)  Exciton diffusion length
\( n \)  Ideality factor of a diode
\( \text{vol} \)  Volume
\( \text{wt} \)  Weight
\( \tilde{\varepsilon}(\omega) \)  Complex pseudo-dielectric function
\( \varepsilon_r \)  Dielectric constant
\( \mu_h \)  Hole mobility
\( \sigma \)  Conductivity
\( \tau \)  Exciton lifetime
\( \varphi_M \)  Work function of metal contact
\( \varphi_M \)  Metal work function
\( \omega^* \)  Angular velocity
\( \omega \)  Photon energy
\( \Phi_b \)  Injection barrier height
\( A \)  Acceptor
\( \text{ACE} \)  Acetone
\( \text{AFM} \)  Atomic force microscopy
\( \text{Ag} \)  Silver
\( \text{Al} \)  Aluminium
\( \text{AM (G)} \)  Air mass (global)
\( \text{Au} \)  Gold
\( \text{BCP} \)  Bathocuproine
\( \text{BDT} \)  Benzodithiophene
\( \text{BHJ} \)  Bulk heterojunction
\( \text{BPhen} \)  Bathophenanthroline
\( \text{BrAni} \)  4-bromoanisole
\( \text{BT} \)  Benzothiadiazole
\( \text{C}_{60} \) and \( \text{C}_{70} \)  Buckminsterfullerenes
\( \text{Ca} \)  Calcium
\( \text{CA} \)  Contact Angle
\( \text{CB} \)  Chlorobenzene
\( \text{CG} \)  Coating gap
\( \text{CF} \)  Chloroform
\( \text{CN} \)  1-chloronaphthalene
\( \text{CNT} \)  Carbon nanotube
\( \text{CO}_2 \)  Carbon dioxide
\( \text{COSY} \)  Correlation Spectroscopy
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>C-PCBSD</td>
<td>[6,6]-phenyl-C61-butyric styryl dendron ester</td>
</tr>
<tr>
<td>CPDT</td>
<td>Cyclopentadithiophene</td>
</tr>
<tr>
<td>CrOx</td>
<td>Chromium oxide</td>
</tr>
<tr>
<td>Cs</td>
<td>Cesium</td>
</tr>
<tr>
<td>CS</td>
<td>Coating speed</td>
</tr>
<tr>
<td>CT</td>
<td>Charge transfer state</td>
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<tr>
<td>CuOx</td>
<td>Copper oxide</td>
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<tr>
<td>D</td>
<td>Donor</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanolamine</td>
</tr>
<tr>
<td>DI</td>
<td>Deionised water</td>
</tr>
<tr>
<td>DIO</td>
<td>1,8-diiodooctane</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DPP</td>
<td>Diketopyrrolopyrrole</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DTG</td>
<td>Dithienogermole</td>
</tr>
<tr>
<td>DTS</td>
<td>Dithienosilole</td>
</tr>
<tr>
<td>Eg</td>
<td>Exciton binding energy</td>
</tr>
<tr>
<td>Ef,m</td>
<td>Metal Fermi level energy</td>
</tr>
<tr>
<td>Efund</td>
<td>Fundamental energy gap</td>
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<tr>
<td>Eopt</td>
<td>Optical gap</td>
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<tr>
<td>Evac</td>
<td>Vacuum energy</td>
</tr>
<tr>
<td>EA</td>
<td>Electron affinity</td>
</tr>
<tr>
<td>EPBT</td>
<td>Energy payback time</td>
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<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron transporting layer</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FR</td>
<td>Flow rate</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
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<tr>
<td>HMBC</td>
<td>Heteronuclear Multiple-Bond Correlation</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
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<tr>
<td>HSQC</td>
<td>Heteronuclear Single-Quantum Correlation</td>
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<tr>
<td>HTL</td>
<td>Hole transporting layer</td>
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<tr>
<td>IC&lt;sub&gt;60/70&lt;/sub&gt;BA</td>
<td>Indene-C&lt;sub&gt;60/70&lt;/sub&gt; bis-adduct</td>
</tr>
<tr>
<td>ICT</td>
<td>Integer charge transfer</td>
</tr>
<tr>
<td>IEA</td>
<td>International Energy Agency</td>
</tr>
<tr>
<td>IFL</td>
<td>Interfacial layer</td>
</tr>
<tr>
<td>IP</td>
<td>Ionisation potential</td>
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<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>ISOS</td>
<td>International Summit on OPV Stability</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>J&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Current density of minority carriers</td>
</tr>
<tr>
<td>J&lt;sub&gt;dark&lt;/sub&gt;</td>
<td>Dark current density</td>
</tr>
<tr>
<td>J&lt;sub&gt;ph&lt;/sub&gt;</td>
<td>Photogenerated current density</td>
</tr>
<tr>
<td>J&lt;sub&gt;SC&lt;/sub&gt;</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>LBIC</td>
<td>Light Beam Induced Current characterisation</td>
</tr>
<tr>
<td>LCA</td>
<td>Life cycle assessment</td>
</tr>
<tr>
<td>LiF</td>
<td>Lithium fluoride</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass-to-charge</td>
</tr>
<tr>
<td>M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>Molecular weight</td>
</tr>
</tbody>
</table>
MALDI  Matrix-Assisted Laser Desorption Ionization
MEH-PPV  Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
MeO$_x$  Metal oxide
MIM  Metal-insulator-metal
MoO$_x$  Molybdenium oxide
MoO$_3$  Molybdenum (VI) oxide
MS  Mass Spectroscopy
NbO$_x$  Nobium oxide
NEXAFS  Near-edge X-ray absorption fine structure spectroscopy
NiAc  Nickel acetate
NiO$_x$  Nickel oxide
NIR  Near infra-red
NMP  N-methyl pyrrolidone
NMR  Nuclear Magnetic Resonance
NP  Nanoparticle
o-DCB  1, 2 dichlorobenzene
OFET  Organic field effect transistor
OLED  Organic light emitting diode
OPD  Organic photodetector
OPV  Organic PV
OT  1,8-octanedithiol
P$_{\text{light}}$  Power of incident light
P3HT  Poly(3-hexylthiophene)
PAA  Polyallylamine
PBDTP-DTBT  Poly(4,8-bis(4-(2-ethyl-hexyl)-phenyl)-benzo[1,2-b:4,5-b’]dithio-phenylene-vinylene-alt-[4,7-di(4-(2-ethylhexyl)-2-thienyl)-2,1,3-benzothiadiazole]-5,5’-diyl)
PBDTTT  Poly[4,8-bis-substituted-benzo[1,2-b:4,5-b0]dithiophene-2,6-diy1-alt-4-substituted-thieno[3,4-b][thiophene-2,6-diy1]
PC$_{60}$/70BM  [6,6]-phenyl C$_{60}$/70-butyric acid methyl ester
PCDTBT  Poly[9’-hepta-decanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)]
PCE  Power conversion efficiency
PCPDHTBT  Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b2]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]
PD  2,3-pyridinediol
PEDOT:PSS  Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PEI  Polyethyleneimine
PEIE  Polyethyleneimine ethoxylated
PET  Polyethylene terephthalate
PFCa6-K$^+$  Poly[9,9-bis(6’-(18-crown-6)methoxy)hexyl]fluorene]
PffBT4T-2OD  Poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diy1)-alt-(3,3’-di(2-octyldodecyl)-2,2’:5’,2’;5’,2”-quaterthiophen-5,5”-diyl)]
PffBT4T-C$_9$C$_{13}$  Poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diy1)-alt-(3,3’-di(2-nonyltri decyl)-2,2’:5’,2’;5’,2”’quaterthiophen-5,5”’-diyl)]
PFN  Poly[(9,9-bis(3’-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctyfluorene)]
PL  Photoluminescence
POM  Polyoxometalates
PTB7  Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-y1)benzo[1,2-b:4,5-b’]dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate]
<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>PTB7-Th</td>
<td>Poly[4,8-bis(5-(2-ethylhexyl)-thiophen-2-yl)benzo[1,2-b:4,5-b0]-dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]-thiophene-)-2-carboxylate-2,6-diyl]</td>
</tr>
<tr>
<td>PTE</td>
<td>Poly(oxyethylene tridecyl ether)</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
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<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>PVK</td>
<td>Polyvinylcarbazole</td>
</tr>
<tr>
<td>PVP</td>
<td>Poly(vinyl pyrrolidone)</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dots</td>
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<tr>
<td>RS</td>
<td>Series resistance</td>
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<tr>
<td>RSH</td>
<td>Shunt resistance</td>
</tr>
<tr>
<td>R\text{SHEET}</td>
<td>Sheet resistance</td>
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<tr>
<td>Ra</td>
<td>Average roughness</td>
</tr>
<tr>
<td>R\text{MAX}</td>
<td>Maximum height in z-direction</td>
</tr>
<tr>
<td>R\text{RMS}</td>
<td>Root mean squared roughness</td>
</tr>
<tr>
<td>RGO</td>
<td>Reduced graphene oxide</td>
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<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>RI</td>
<td>Regio-isomer</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
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<tr>
<td>RuO\text{2}</td>
<td>Ruthenium oxide</td>
</tr>
<tr>
<td>R2R</td>
<td>Roll-to-roll</td>
</tr>
<tr>
<td>SA</td>
<td>Solvent annealing</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayers</td>
</tr>
<tr>
<td>SE</td>
<td>Spectroscopic Ellipsometry</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SnO\text{x}</td>
<td>Tin oxide</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single walled carbon nanotube</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TA</td>
<td>Thermal annealing</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TiO\text{x}</td>
<td>Titanium oxide</td>
</tr>
<tr>
<td>ToF</td>
<td>Time-of-flight</td>
</tr>
<tr>
<td>TOPD</td>
<td>Titanium(IV) oxide bis(2,4-pentanedionate)</td>
</tr>
<tr>
<td>TPD</td>
<td>Thienopyrroledione</td>
</tr>
<tr>
<td>TS-CuPc</td>
<td>Tetrasulfonate copper phthalocyanine</td>
</tr>
<tr>
<td>TT</td>
<td>Thienothiophene</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra violet-visible</td>
</tr>
<tr>
<td>\Delta V\text{b}</td>
<td>Voltage loss at an ohmic contact</td>
</tr>
<tr>
<td>V\text{2O5}</td>
<td>Vanadium pentoxide</td>
</tr>
<tr>
<td>V\text{bi}</td>
<td>Built-in potential</td>
</tr>
<tr>
<td>VO\text{C}</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>VO\text{x}</td>
<td>Vanadium oxide</td>
</tr>
<tr>
<td>WO\text{x}</td>
<td>Tungsten oxide</td>
</tr>
<tr>
<td>WVTR</td>
<td>Water vapour transmission rate</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Zn(acac)\text{2}</td>
<td>Zinc acetylacetonate</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zink oxide</td>
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1. Introduction

1.1. Energy demand and climate change

The world’s population reached 7.3 billion in 2015, and is expected to continue to grow by approximately 83 million people per year, which means that it will reach 8.5 billion by 2030.[1] This, in addition to improving standards of living in developing countries, means that the world’s energy demand is expected to rise by 30% between now and 2040, which will inevitably result in an increased consumption of energy, still dominated by fossil fuels.[2] However, the conversion of energy from these traditional sources leads to the generation of carbon dioxide (CO\textsubscript{2}), which has a direct impact on climate change given that CO\textsubscript{2} is a greenhouse gas. High CO\textsubscript{2} emissions in the past decades have led to an increase in the global temperature, which is a prime cause for climate change that can be detrimental for life on Earth. Furthermore, it should be noted that hundreds of millions of people will have no access to basic energy services by 2040, which will prevent sustained economic growth, the building of inclusive societies, a reduction of poverty, and access to health and educational services.[2, 3] Thus, there is an emerging need to transform the power sector and focus resources on environmentally friendlier energy conversion technologies, in order to fight climate change and allow for the decentralisation of energy generation so as to assure access to energy for all.

This need for an urgent intervention in the global energy sector led to the “Paris Agreement” which was negotiated at the 21\textsuperscript{st} Conference of the Parties (COP 21) of the United Nations Framework Convention on Climate Change (UNFCCC). This agreement, which officially came into force on the 4\textsuperscript{th} of November 2016, sets out an action plan to limit the global temperature to a maximum of 2 °C above pre-industrial levels.[4] Indeed, according to the International Energy Agency there will be a slow down in the growth of coal and oil use.[2] Simultaneously, an increase of 50% in the use of natural gas is predicted by 2040.[2] Renewable energies such as solar photovoltaics (PV) and wind power are expected to have the fastest growth, and their rapid development will allow for a competitive positioning on the global energy market without the need for subsidies.[2] A reduction of 40%–70% in the average cost of PVs is expected by 2040, especially when considering the rapid expansion of PV technology in China and India.[2]
1.2. Organic photovoltaic technology

The first successful synthesis and controlled doping of conjugated polymers was carried out in the 1970s by Allan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa.[5] This was a milestone in the field of organic electronics as it opened the door to the use of semi-conducting materials made of organic compounds in various opto-electronic devices.[5] The authors were awarded the 2000 Nobel Prize in Chemistry for the discovery and development of conductive polymers.[6] In 1986, interest in organic semiconductors for solar cell applications increased following Ching Tang’s demonstration of an efficient (for the time) solar cell based on a photosensitive layer consisting of two organic semi-conducting materials.[7] Concurrently, the first thin film transistors built with organic polymers and oligomers were fabricated.[8, 9, 10] Another breakthrough was also achieved with the fabrication of electro-luminescent light-emitting diodes made of thermally evaporated molecular films and conjugated polymers.[11, 12] In 1995, a photoactive layer consisting of a Donor/Acceptor (D/A) bulk-heterojunction was reported, which allowed for an unprecedented increase in the efficiency of the carrier collection and in the PCE of polymer PV cells.[13] Since these breakthroughs, the field of organic electronics has been rapidly expanding. Organic light emitting diode (OLED) devices dominate the display market and are expected to start being used for indoors lighting and in the automotive industry. The interest in organic PV (OPV), organic photodetectors (OPD), and organic field effect transistors (OFET) has also been very high.

One of the key advantages of organic-based technology is that products can be fabricated at a low manufacturing cost due to the use of deposition techniques suitable for fast fabrication at temperatures below 140 °C on a continuously moving R2R web. In the particular case of OPVs, this allows for direct competition with traditional inorganic PV technologies such as silicon solar cells. The low price is also determined by the cost of raw materials, which can be as low as €0.83 per m$^2$ when purchased on an industrial scale.[14] An overall fabrication speed of 10 m/min is feasible for OPV cells, and was estimated to allow the production of 1 GW$_{peak}$ every day.[15] Printing, coating, and vacuum deposition techniques can be used for the fabrication of all layers in the solar cell stack, allowing for scalability of the device size. However, when the size of the OPV device is increased, the collection efficiency of charge carriers is reduced.[16] This is usually caused by the limitations of the transparent electrode as well as defects introduced during the coating procedure.[17, 18]

Another challenge associated with OPV technology is improving the operational lifetime of solar cells. Organic materials are prone to chemical reactions with water molecules and oxygen, which alter their characteristics.[19, 20] These reactions are often enhanced when solar irradiance is present, especially UV light, leading to degradation of the OPV devices’ characteristics. This degradation is commonly a consequence of the cut-off wavelength of the barrier foil and delamination due to harsh environmental conditions.[21, 22] Therefore, new encapsulation methods and barrier foils have been developed in order to avoid direct exposure of the OPV device to the environment.[23, 24, 25] In this respect, encapsulation without a UV filter was reported to significantly decrease the operational lifetime of OPV modules, when installed in rural areas in Africa with high temperatures and heavy rainfall.[22] In contrast, tests performed in the milder environmental conditions of Denmark or the Netherlands have shown device T$_{80}$ values (the
1.2. Organic photovoltaic technology

period of time which it takes for the MPP of the solar cell to decrease by 20% after stabilisation) of one to two years.[26, 27, 28] However, a fair comparison between the reported operational lifetimes and stability values of OPVs fabricated in different research laboratories would only be possible when internationally accepted characterisation protocols are used. Therefore, directions for shelf life and outdoor testing, laboratory weathering and thermal cycling characterisation, as well guidelines for reporting the data, were discussed and summarised during the recent International Summit on OPV Stability (ISOS).[29]

Despite the efforts to improve the operational lifetime of OPV systems, and the unquestionable progress in this field, inorganic PV panels have lifetimes that are approximately five times longer.[30] Nevertheless, a major advantage of OPV technology is the ability to reach significantly reduced energy payback times (EPBT; the operational time required to produce the energy that was invested in the fabrication of the solar cell system). Several life cycle assessments (LCA) have already shown that OPV systems can have an EPBT in the order of months or even a day, which is much shorter than that of mature PV technologies such as crystalline silicon (EPBT of 1-2 years).[15, 31] In this respect, the EPBT for OPV technology is dependent on the scale of fabrication, where the EPBT decreases as the production scale increases.

Currently, there are few OPV companies on the market. Some of the most prominent examples are Armor, Eight19, Heliatek, infinityPV, OPVIUS (previously BELECTRIC OPV), and Sunew. However, the first commercially available OPV modules were produced by the US company Konarka, and were designed to be integrated into rooftops of parking lots, hotels, and resorts.[32] Despite the bankruptcy of the company in 2012, Konarka was unarguably a pioneer in the fabrication of large-area OPV modules using printing and coating techniques on a continuously moving R2R web. The modules consisted of multiple OPV stripes that were deposited onto flexible ITO substrates and showed impressive PCEs of above 3%. Moreover, Konarka’s products were the first OPVs in the world to pass the IEC 61646 lifetime tests, required for the qualification and approval of thin film PV modules.[30, 33]

The first grid connected OPV system was installed in 2012 by OPVIUS in Frankfurt, Germany, and delivered a total nominal power of 0.2 kW.[34] The system consists of nine flexible and semi-transparent OPV modules (see Figure 1.1(a)) that are positioned in the form of a sun sail. This was a significant step towards the commercialisation of OPV technology, as it demonstrated the numerous advantages of the technology in terms of static and mechanical integration and short EPBT. The EPBT was reached after only 10 months of operation and, at the time of writing, the system has been running for more than five years. A lot of progress has been made in terms of safety, and OPVIUS recently announced the integration of OPV modules in glass façades, after passing tests to install laminated glass at elevated heights.[34] This allowed the company to cover the lift shaft of a three storey building with OPV panels (see Figure 1.1(b)) which were used to power the ventilation system of the lift shaft.

OPV devices have also been integrated into rigid glass panels, which were surrounded by a metal frame, and mounted on a tracking system.[36] The panels had photoactive areas of up to 9180 cm² and were connected to the grid. More than 3 kWh were generated during the study. However, due to the high cost of the mounting structure and the labour required in addition to the low operational T_80 of 1 month, the system was deemed to fail in terms of
1.2. Organic photovoltaic technology

Figure 1.1: Photographs of (a) the first grid connected OPV system and (b) a stand-alone OPV installation by OPVIUS.\cite{34, 35} (c) first grid connected OPV-based solar park with a total power of more than 1.3 kW. Reprinted with permission from \cite{15}. Copyright ©2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

real world application where it would have to compete against silicon solar technology. Later, Krebs \textit{et al.} significantly improved the fabrication process of OPV modules and reported the first grid connected OPV-based solar park.\cite{15} As shown in Figure 1.1(c), the installation consisted of six lanes of 100 m stretches of solar cell foil in a web width of 305 mm. By solely using printing and coating techniques on ITO-free substrates, 21 000 defect free solar cells were connected in series per lane. All six lanes were then connected in parallel. The complete installation had a photoactive area of 88.2 m$^2$ (126 000 cells) and was able to deliver voltages above 10 kV per lane. The solar park had an operating performance of 1.53% which lead to EPBT of 180 days, when run in a southern European setting with an estimated T$_{80}$ lifetime of at least one year.\cite{15}

Much higher efficiencies are possible when OPVs are fabricated with vacuum deposition techniques, due to the greater control over the material properties and layer thickness that they enable compared to the more common OPV printing and coating deposition techniques. This allows the fabrication of efficient multi-junction OPVs, where an exact control over the thickness of the layers in the solar cell stack is essential. Currently, the world record efficiency of 13.2% for an OPV device is held by the German company Heliatek, who fabricated a triple junction solar cell by using a vacuum deposition process.\cite{37} The cell was able to absorb light in the wavelengths 450 nm – 950 nm. The absorber materials used were developed and patented by the company. On a module scale, efficiency of 9% for a photoactive area of 122 cm$^2$ was reported by the group.\cite{38} The so-called “HeliaFilm®” has been successfully used for various building integrated OPV pilot projects (BIOPV), as shown in Figures 1.2(b) and 1.2(a), where the HeliaFilm® was integrated in metal, concrete, glass, and plastic façades. Despite the numerous colour options available, traditionally only products with a rectangular shape have been demonstrated, which appears to be a limiting factor when aesthetic and architectural freedom is desired. In contrast, other companies have shown solution processed OPVs with a wide range of design and shape options. The real architectural potential of OPV technology was recently demonstrated by the products of OPVIUS, as shown in Figures 1.2(c) and 1.2(d).\cite{39}
Figure 1.2.: Photographs of (a) BIOPV by Heliatek with a peak power of more than 10 kW in Singapore and (b) HeliaFilm® installed on a Biogas Plant in Germany with a total installed power of 5.4 kW.[40, 41] OPV modules by OPVIUS with a (c) leaf shape integrated in glass and (d) hexagon shaped OPV modules in various sizes mounted on a metal construction to generate electricity while serving a purpose of a shading shield against direct sunlight.[42]
1.3. Objectives

The examples given above represent the achievements of some of the leading research groups and companies in the field of OPV technology, but they portray only a fraction of the research and news articles published on the subject. These commercial products are driven by strategic collaborations and substantial financial support, which has allowed for the fabrication of large-area solar cells with sufficient operational stability and acceptable efficiency. The majority of other studies published to date report the fabrication of small area devices, rarely exceeding 0.1 cm$^2$, as shown in Chapter 3. Despite the high PCEs above 10% reported for small device photoactive areas, the preservation of these high efficiencies for large-area OPV modules is questionable. In addition, the majority of research laboratory based high PCE devices are fabricated using the spin-coating technique, which is not a scalable deposition technique and leads to high material waste. Therefore, the challenges associated with the up-scaling of the OPV fabrication process have to be addressed, and a truly scalable deposition process suitable for R2R integration has to be chosen in order to facilitate the commercialisation of the OPV technology.

1.3. Objectives

Traditionally, OPVs consist of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C$_{60}$-butyric acid methyl ester (PC$_{60}$BM) as the fruit fly donor (D) and acceptor (A) materials respectively. OPV devices using this material combination are ubiquitous in the field, and represent a large majority of the D/A bulk-heterojunction (BHJ) systems studied over the last three decades. However, the open circuit voltage ($V_{OC}$) of this D/A system is limited to about 0.6 V, due to a low-lying lowest unoccupied molecular orbital (LUMO) of PCBM, when related to the highest occupied molecular orbital (HOMO) of P3HT. This results in average PCE of 3%.[43]

Therefore, the first objective of this thesis is to carry out a detailed study of the intrinsic characteristics of an alternative to the PCBM acceptor molecule, i.e. indene-C$_{70}$ bis-adduct (IC$_{70}$BA), which has a higher-lying LUMO level than PCBM, which in turn allows for improved device $V_{OC}$ and PCE. Various analytical, thermoanalytical, optical, topographical, and electro-optical characterisation techniques will be used. This will deepen our understanding of the morphological formation of photoactive blends with the well-known donor material P3HT in dependence on the properties of IC$_{70}$BA. The outcomes of these studies will be analysed in order to design optimal fabrication conditions for achieving high PCEs with P3HT-based OPV devices fabricated using the spin-coating technique.

The second objective of this thesis is to demonstrate the fabrication of large-area OPV modules by using the the slot-die coating deposition technique. This technique was chosen because it is a scalable and industrially applicable fabrication technique, in contrast to the spin-coating technique, which is not. To accomplish this objective, a slot-die coating equipment will be designed and tested for the fabrication of large-area OPV modules. Different optical and electro-optical characterisation techniques will be used in order to study the deposition process, and to allow for an improvement of the coating procedure. It is hoped that this will result in the deposition of homogeneous and defect-free functional layers in the OPV stack. Lastly, OPV modules will be fabricated on plastic substrates, as is common in the OPV industry, in order to demonstrate the viability of transferring the coating techniques developed for this thesis to industry.
1.4. Organisation of this thesis

Chapter 2 provides an introduction to the development of organic semiconductors and the theory behind their ability to absorb photons from light and convert them into viable electricity. The photovoltaic conversion process and electrical characteristics of OPV-based devices are also detailed. Moreover, the historical development of materials used in the solar cell stack is described, and ongoing approaches to improve the PCE, stability, and operational time of OPV devices are discussed. The requirements for a successful scale-up of the fabrication procedure of OPV cells are then analysed. Relevant deposition techniques, materials, and a suitable device architecture to accomplish an efficient scale-up process are also set out.

The scientific literature published to date in the field of P3HT:ICBA-based OPVs is reviewed in Chapter 3, in order to benchmark the significance of the experimental results obtained in this thesis. Thereafter, material specific factors that influence the phase separation of photoactive layers and their stability are discussed. Special care is taken to analyse the characteristics of P3HT:ICBA-based devices depending on the structural isomeric characteristics of the ICBA molecule, and the photoactive device area. In conclusion, the relationships between P3HT:ICBA specific properties are detailed, and a comprehensive summary of reported efficiency values in the field to date is provided. Then, the deposition techniques and corresponding fabrication procedures used during this thesis are summarised in Chapter 4. The experimental techniques employed to characterise all samples are also presented.

Chapter 5 summarises the experimental work undertaken in this thesis in order to achieve record PCEs for P3HT:IC$_{70}$BA-based OPV devices. A systematic characterisation of the intrinsic characteristics of the IC$_{70}$BA molecule is first carried out. Two IC$_{70}$BA samples that exhibit different regio-isomeric properties were blended with P3HT to study the effect of the regio-isomer (RI) proportions in the sample on the optical and morphological characteristics of the blend. Analogous studies were conducted for blends of separated RIs and P3HT. The importance of the ratio between the RI on the OPV device characteristics is shown in Section 5.4, where PCEs approaching 7% are achieved for tailored regio-isomeric characteristics of an IC$_{70}$BA sample, whereas rather low PCEs of about 2% are shown for an unfavourable regio-isomeric distribution in a second IC$_{70}$BA sample. In a similar manner, the device PCE was shown to depend on the RI type. Some of these experimental results are published in [44].

The fabrication of large-area OPV modules is demonstrated in Chapter 6. The effect of the deposition technique on the device characteristics is studied by replacing the laboratory-scale spin-coating technique used in Chapter 5 with the slot-die coating technique, which can be used on industrial scale. The latter deposition technique was used to deposit the ETL (ZnO) and D/A system (P3HT:IC$_{70}$BA or PCDTBT:PC$_{70}$BM) of OPV modules with an inverted structure and a photoactive area of about 35 cm$^2$. A customised slot-die coating equipment was designed and build for this purpose. The effect of the coating parameters on the opto-morphological characteristics of the deposited layers was studied and tailored prior to the fabrication of the OPV modules on glass and plastic substrates. The quality of the deposited layers was analysed by LBIC, PL, and Raman current mapping. The stability of the OPV modules was also studied.

Chapter 7 concludes this thesis and gives suggestions for future studies.
2. Organic photovoltaic devices – theory, materials, and characteristics

This chapter starts by stating the theory behind the formation of an energy band structure in organic semiconductors, and continues with an explanation of the operational principles behind photon absorption and charge carrier generation. The chapter then sets out how these processes are applied to the development of photoactive layers in OPV devices. The main characteristics of an OPV device are then discussed together with the different materials used in functional layers of an OPV cell, i.e. the photoactive and interfacial layers. Electrodes are also discussed. OPV device architectures are then introduced, and their respective advantages and limitations addressed. The current status of improvements to the stability and operational lifetime of OPV cells in the field is presented, followed by a discussion of ongoing challenges associated with the accuracy of testing procedures. To conclude, the requirements for a successful scale-up of OPV technology are examined.

2.1. Fundamentals of organic semiconductors

Carbon is the most common chemical element contained in organic materials. It has the atomic number six, thus four of the six electrons of carbon occupy the valence band. According to the Hund’s rule, it therefore has the electronic configuration $1s^22s^22p^2$ (one electron each in $2p_x$ and $2p_y$ orbitals, and no electron in $2p_z$).[45] Generally, organic semiconductors are defined by a sequence of alternating single and double bonds between carbon atoms. This structure, also called conjugation, provides the essential optical and electronic properties required for the material to interact with visible radiation.

To obtain an energetically stable state, the orbitals of carbon atoms tend to hybridise.[46] In an sp$^2$ hybrid, the valence electrons of carbon reside in sp$^2$ hybridised orbitals (3 electrons) both in the plane, and in one p$_z$-orbital (1 electron) perpendicular to the sp$^2$-orbitals. The electrons in the sp$^2$-orbitals form covalent bonds with neighbouring atoms via $\sigma$ molecular orbitals.[47] The remaining electron in the p$_z$-orbital can form a covalent bond with a neighbouring p$_z$ electron and form a $\pi$ molecular orbital as shown in Figure 2.1(a). The carbon atoms in
a sp² hybridised ethylene molecule are depicted by a double bond (σ and π) between the carbon atoms.[47, 48]

An energy diagram of a double bonded carbon molecule is shown in Figure 2.1(b). It shows that two electrons each occupy the σ and π molecular orbitals. The remaining four carbon electrons are non-bonded (“nb” in Figure 2.1(b)), and therefore available for creating bonds.[49] The discrepancy between the energy levels of bonding σ⁻ and antibonding σ⁺ molecular orbitals is very high and beyond the visible light spectra. The electron wave functions in the pₓ-orbitals along the backbone overlap (also known as conjugation), which causes a splitting between the π and π* molecular orbitals.[49] The electrons are delocalised in the conjugated backbone of the molecule and are therefore associated with a molecular orbital. Furthermore, the π-bond strength is significantly weaker in comparison to the σ-bond, which causes an additional splitting between the π and π* molecular orbitals into smaller energy levels depending on the number of conjugated molecules, as shown in Figure 2.2.[47]

A stronger conjugation caused by the increased number of alternating single and double bonds narrows the fundamental energy gap (E_{fund}) and forms a band structure. In this band structure, the electronic levels are defined as the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) as shown in Figure 2.2. The energy of the HOMO level is considered to be the ionisation potential (IP) required to displace an electron from the HOMO level into the vacuum energy (E_{vac}), whereas the energy of the LUMO level is referred to as the electron affinity (EA) of the molecule (the energy needed to inject an electron from E_{vac} into the LUMO). Hence, the E_{fund} is defined as the difference between the IP and the EA of the organic molecule.[50] For organic semiconductors, this energy is typically between 1.5 eV – 3 eV.[45, 47] The absorption of a photon depends on the optical gap (E_{opt}) of the organic material, which is defined as the energy difference between the lowest electronic ground state in the HOMO level of a molecule called singlet (S₀; total spin multiplicity of zero), and the lowest possible singlet excited state (S₁).[51] As illustrated in Figure 2.2, the difference between E_{fund} and E_{opt} is referred to as the exciton binding energy E_B.

![Orbitals of ethylene](image.png)

**Figure 2.1.:** Orbitals of ethylene (a).[52] Energy diagram of the interaction between two carbon atoms (b): sp², and pₓ atomic orbitals combine to form σ, π, and non-bonding (nb) atomic orbitals.[47] Copyright ©2009 Wiley Books.
2.2. Photovoltaic conversion and operations

The absorption of a photon with sufficient energy by an organic semiconductor, leads to the formation of a strongly bound electron-hole pair called an exciton. This strong coulombic attraction between the electron and the hole is due to the low dielectric constant of organic materials (εr ∼ 2–4). The exciton is, therefore, referred to as a Frenkel exciton and has a binding energy of 0.5 eV – 1.2 eV, which is much larger that the binding energy observed for Wannier excitons in inorganic semiconductors (thermal energy of ∼ 26 meV at room temperature is sufficient to create free charge carriers).[53] Due to typically weak intermolecular interactions in organic materials, excitons are localised on molecules and not in energy bands. The generation of excitons in organic materials does not immediately lead to the formation of free charge carriers that contribute to an electrical current. Instead, the binding energy of the exciton first has to be overcome, in order to separate the electron-hole pair. Nevertheless, when sufficient high energy band offset is provided, the exciton binding energy can be overcome, leading to the exciton separation. This is often the case at the interface between p-type donor (D) molecules that exhibit a low IP and therefore high-lying HOMO level, and n-type acceptor (A) molecules with a high EA and thus a low-lying LUMO level.[54]

2.2.1. Donor/Acceptor heterojunctions

A considerable breakthrough in the field of organic-based PVs was made in 1986 when Tang et al. showed a significant enhancement of the dissociation probability of photogenerated excitons by developing the first organic cell with a D/A bi-layer heterojunction.[7] The photoactive layer was deposited by thermal evaporation under high vacuum, and sandwiched between electrodes of ITO and Ag.[7] In this bi-layer structure, as shown in Figure 2.3(a), a photoinduced charge transfer of electrons from a p-type donor (polyethylene diimide derivative) to a n-type
acceptor (copper phthalocyanine) was demonstrated. However, there is a major drawback associated with the bi-layer heterojunction OPVs. To avoid exciton recombination, the thickness of organic layers has to comply with the exciton diffusion length $L$ of $10\text{ nm} - 20\text{ nm}$ ($L = (D\tau)^{1/2}$, where $D$ is the diffusion coefficient and $\tau$ the exciton lifetime).[55, 56] As a result, for bi-layer heterojunctions, an efficient exciton generation and transport can usually be accomplished for photoactive layers with a thickness of approximately $20\text{ nm}$. However, the ability of the D/A system to absorb efficiently light is greatly reduced for such thin layers.[57]

An approach to overcome the limitation of the bi-layer D/A heterojunctions was proposed with the introduction of the bulk-heterojunction (BHJ). The pioneering work in this field was carried out by Yokoyama et al., who showed a twofold increase in photocurrent compared to a double-layered cell, due to an efficient photogeneration in a co-deposited interlayer.[58] Further developments were achieved by Heeger and Sariciftci, who in 1992 patented the “Conjugated polymer–acceptor heterojunctions; diodes, photodiodes, and photovoltaic cells”. [59] The first applications of this invention followed soon after in papers by Heeger et al. and Friend et al., who reported the deposition of BHJ layers from a solution containing a D/A mixture in order to form a layer with an interpenetrating network of both materials. [13, 60] In this respect, if the length scale in the D/A blend is similar to the exciton diffusion length, then the probability of the exciton reaching a D/A interface is significantly increased. By means of this, the recombinaton of excitons is dramatically reduced. Additionally, exciton generation and respectively, dissociation, can occur everywhere in the BHJ due a larger interface area than in the bi-layer heterojunctions. This also allows for the deposition of thicker photoactive layers that absorb a greater photon flux. Since the first reports of BHJ-based photoactive layers, this type of heterojunction has therefore become the standard D/A system for OPV devices.[57]

![Figure 2.3](image)

**Figure 2.3.** Schematic band diagram of (a) bi-layer and (b) BHJ solar cell under illumination and under short-circuit condition. The HOMO and LUMO energy levels of the donor and acceptor materials are shown with continuous blue or long dashed red lines. $E_F$ is the Fermi level of the metal electrode, $E_{\text{vac}}$ the vacuum energy, and CT stays for charge transfer state. The generation of free charge carriers is summarised in five steps.
Schematic band diagrams of OPV cells with a D/A bi-layer and a BHJ system are shown in Figure 2.3. Due to the common use of this system, the fundamental processes that occur in the photoactive blend are described for the BHJ system in Figure 2.3(b). The working principle of the OPV device, however, is identical for both heterojunctions and is described in five fundamental steps: charge carrier generation; diffusion; dissociation; transport; and extraction/collection at the electrodes.

1. Absorption of photons and exciton formation

Organic semiconductors exhibit large absorption coefficients of about $10^5$ cm$^{-1}$, which allows them to efficiently harvest most of the photons within their absorption spectra in thin layers (100 nm – 200 nm).[61] As discussed in Section 2.2, if the energy of a photon is high enough, i.e. superior to the fundamental gap of the organic semiconductor (see Figure 2.2), an electron is promoted from the HOMO to the LUMO level of the material. A neutral entity made of a coulombically bound electron-hole pair called exciton is created. Most of the incident photons lead to the generation of electron-hole pairs in the donor domain, due to the electron-rich nature of the p-type material. Therefore, it is assumed that the photoexcitation of the donor material contributes primarily to exciton generation, although photon absorption in the acceptor phase was shown to play an important role for the generated exciton yield as well.[62]

2. Exciton diffusion

In order to generate free charge carriers, excitons have to diffuse to the D/A interface, where they can relocate from the D to the A domain by a Förster and/or Dexter mechanism of energy transfer.[63, 64] The movement of the exciton is accomplished by hopping along the backbone of adjacent molecules, and is not influenced by an electric field due to the neutral character of the electron-hole pair.[54] Therefore, the conjugation between the $\pi$ molecular orbitals influences the strength of the intermolecular couplings, that together with the presence of traps and impurities in the p-type material, determine the charge carrier mobilities.[51] As a result, rather low mobilities of about $10^{-7}$ cm$^2$ V$^{-1}$s$^{-1}$ to $10^{-3}$ cm$^2$ V$^{-1}$s$^{-1}$ (vs. $10^3$ cm$^2$ V$^{-1}$s$^{-1}$ for crystalline silicon) are observed.[57, 65] Therefore, in order to avoid a decay of the exciton from the excited $S_1$ state to the ground $S_0$ state, a nanoscale phase separation between the D/A components with a length scale within the diffusion length of the exciton is required.

3. Exciton dissociation

Due to the tight bond between the electron-hole pair explained in Section 2.2, a dissociation into free charge carriers at room temperature (as known for inorganic semiconductors) is not possible. In order for an electron to be transferred from the LUMO level of the donor to the LUMO level of the acceptor, the exciton binding energy has to be overcome. This usually occurs due to the induced electric field at the band offset between the donor and acceptor LUMO levels. However, once the electron is transferred to the acceptor, it is still coulombically attracted to the remaining hole in the donor domain. This intermediate state at the D/A interface is called the charge transfer state (CT), as shown in Figure 2.3(b). There is an ongoing controversy about which mechanisms lead to the dissociation of the exciton from the CT state, a balanced review of which is provided elsewhere.[66, 67, 68] As this is beyond the scope of this work, it is assumed here that the energy of the excited $S_1$ state in the donor is energetically higher than the threshold
of the CT state at the D/A interface, and that the energy offset between the D and A LUMO levels is sufficient for an efficient exciton dissociation.

4. Transportation of free charge carriers

After the exciton dissociation, free charge carriers drift and diffuse in their respective domains towards the electrodes (holes in the D and electrons in the A), due to the internal electric field caused by the work function difference of the electrodes.[51, 61] Percolated pathways in both material domains are required for an efficient charge transport. It is important to achieve a balanced transport for holes and electrons in order to avoid the accumulation of free charge carriers at interfaces, which can reduce the characteristics of the OPV device. Additionally, the probability of an electron non-germinately to recombine with a hole are higher in BHJ-based systems than in bi-layer heterojunctions, due to the increased contact area at the D/A interface.[45]

5. Charge carrier collection at the electrodes

Once free charge carriers reach the contacts, they can be collected in order to generate electrical currents. However, there is the likelihood of some charges reaching the “wrong” electrode through reverse diffusion, which can lead to their recombination with charges from the electrode material.[45] In order to avoid this loss mechanism, interfacial layers are used to define the polarity of the electrode and to accomplish a facile and selective charge collection (electrons collected at the cathode and holes at the anode).

2.2.2. Semiconductor contacts

Whenever a metal and a semiconductor are brought in close contact with each other, a junction between both materials is formed. Under the assumption of equilibrium, the Fermi levels of the materials will equalise. The formation and type of the contact can be explained using the classical Metal-Insulator-Metal (MIM) model. As shown in Figure 2.4, if the work function of the metal contact $\varphi_M$ is within the band gap of the semiconductor and higher than its LUMO level, an energy barrier $\Phi_b$ for electrons is formed (Figure 2.4(a)).[69] As a result, a so-called Schottky or a non-ohmic contact at the metal-organic interface is formed, which can impede the extraction of charge carriers and reduce the device characteristics. On the contrary, if the metal work function is lower than the LUMO level of the semiconductor (Figure 2.4(b), $\varphi_{M1}$), a Fermi level pinning of the electrode work function close to the LUMO level of the semiconductor occurs. This effect is ascribed to a charge transfer of electrons from the metal to the semiconductor via surface states. The presence of accumulated charges at the interface leads to band bending as depicted in Figure 2.4(b).[69] As a result, an ohmic contact is formed, which facilitates the charge carrier extraction and increases the OPV device characteristics.

The MIM model provides sufficient information for understanding the basic energy alignment processes that occur within the OPV device stack. However, this model is rather unsuitable for explaining the interfaces between materials with a negligible hybridisation of $\pi$ molecular orbitals such as semiconducting organic/organic interfaces, and interfaces formed with substrates that are passivated by oxides or residual hydrocarbons.[70] The latter is common for OPV devices where the deposition of the functional layers in the stack is carried out on top of a highly
conductive semiconducting metal oxides or polymers that act as an electrode. In these cases, the Integer Charge-Transfer model (ICT) allows for a better explanation of the energy aliment compared to the MIM model. Detailed information about the ICT model can be found in a comprehensive review on the “Energy-level alignment at organic/metal and organic/organic interfaces” provided elsewhere.\[70\]

![Schematic diagram of (a) Schottky (non-ohmic) contact for electrons and holes, and (b) ohmic contact for electrons](image)

**Figure 2.4.** Schematic diagram of (a) Schottky (non-ohmic) contact for electrons and holes, and (b) ohmic contact for electrons. Left images show the energy diagram before the contact between the metal and the n-type semiconductor, whereas the right image shows the energy diagram after the contact and under short-circuit conditions. $E_{\text{vac}}$ is the vacuum level energy, $\Phi_b$ is the injection barrier height for electrons at a non-ohmic contact and $\Delta V_b$ the voltage loss at an ohmic contact. The metal work functions are $\varphi_{M1}$ and $\varphi_{M2}$. Adapted from [69]. Copyright ©2003 AIP Publishing.
2.2.3. Electrical characteristics of photovoltaic devices

Inorganic and organic PV cells can be represented with the circuit diagram shown in Figure 2.5. In the dark, due to the p-n junction of the photoactive layer, a solar cell operates electrically as a diode and can be described with the diode Equation 2.1:

\[
I_d = I_0 \left[ \exp \left( \frac{qV}{n k_B T} \right) - 1 \right] \tag{2.1}
\]

where \( I_d \) is the current flowing through the diode, \( I_0 \) the reverse saturation current of the diode, \( q \) the absolute value of electron charge, \( V \) the applied voltage across the diode, \( n \) the ideality factor of the diode (1 ≤ \( n \) ≤ 2), \( k_B \) the Boltzmann constant, and \( T \) the temperature. Under illumination, however, a photocurrent is generated which is represented by the current source \( I_{ph} \) in the circuit diagram. A solar cell also exhibits an internal series resistance \( R_S \) and shunt resistance \( R_{SH} \), as shown in Figure 2.5. The latter describes the leakage current in the device stack, whereas the former represents the resistance of the device to the current flow. A detailed explanation of the origin of \( R_S \) and \( R_{SH} \) for OPV devices is provided in Section 2.2.4.

Considering Figure 2.5, the current \( I \) on the external load is, therefore, the sum of the current through the diode junction \( I_d \), the photocurrent \( I_{ph} \), and the leakage current \( I_{sh} \) as given in Equation 2.2:

\[
I = I_{ph} - I_d - I_{sh} \\
= I_{ph} - I_0 \left[ \exp \left( \frac{qV}{n k_B T} \right) - 1 \right] - I_{sh} \\
= I_{ph} - I_0 \left[ \exp \left( \frac{q(V + IR_S)}{n k_B T} \right) - 1 \right] - \frac{V + IR_S}{R_{SH}} \tag{2.2}
\]

If the assumption is made that the resistance and recombination processes of the solar cell do not alter with illumination, the current output of the device equals the sum of the diode and photocurrent curvatures. Taking into account Equation 2.2, both current density-voltage (J-V) curves in Figure 2.6 can be divided in three regions depending on the voltage range. Region I

![Figure 2.5: Equivalent circuit diagram of a real PV cell. A diode presents the behaviour of the solar cell in dark; \( I_{ph} \) is the photogenerated current; \( R_{SH} \) and \( R_S \) are the shunt and series resistances of the device.](image-url)
2.2. Photovoltaic conversion and operations

Figure 2.6: Typical J-V curve of an organic PV cell under illumination and in the dark (a) with all characteristic parameters of the OPV device. The slope of the J-V plot in region I is determined by the leakage currents, region II shows recombination currents and region III is related to the $R_S$. A semi-logarithmic plot of the $J_{\text{dark}}$ for better visual interpretation is shown in (b). The data is identical.

represents the J-V curve at negative and low positive voltages, where the slope of the curve is mainly dependent on the $R_{\text{SH}}$. At intermediate positive voltages (Region II) the J-V curve is determined by the diode parameters $I_0$ and $n$. Region III describes the device behaviour at high voltages, where the slope of the curve is governed by the $R_S$.\[73\]

All main parameters of a PV device can be extracted from its J-V curve under illumination and in the dark. As shown in Figure 2.6(a), the short-circuit current density ($J_{\text{SC}}$) of a solar cell is described as the current at zero applied voltage. The open circuit voltage ($V_{\text{OC}}$), on the other hand, is measured where the current is equal to zero. The maximum power point (MPP) is defined as the operation point with the highest electrical power $P$ and is described as a product of the current and voltage at the MPP on the J-V curve:

$$P_{\text{MPP}} = V_{\text{MPP}} \times I_{\text{MPP}}$$  \hfill (2.3)

The fill factor (FF) is a relation between the power of the device at the MPP and the theoretical value, determined by the $V_{\text{OC}}$ and $J_{\text{SC}}$ of the PV cell:

$$FF = \frac{P_{\text{MPP}}}{P_{\text{max}}} = \frac{V_{\text{MPP}} \times I_{\text{MPP}}}{V_{\text{OC}} \times I_{\text{SC}}}$$ \hfill (2.4)

The power conversion efficiency ($\eta$ or PCE) of the PV cell is then calculated as electrical power produced by the device divided by the power of incident light ($P_{\text{light}}$) irradiating the device area, which combines with Equation 2.4 resulting in:

$$\eta = \frac{P_{\text{OUT}}}{P_{\text{IN}}} = \frac{P_{\text{MPP}}}{P_{\text{light}}} = \frac{V_{\text{MPP}} \times I_{\text{MPP}}}{P_{\text{light}}} = \frac{V_{\text{OC}} \times I_{\text{SC}} \times FF}{P_{\text{light}}}$$ \hfill (2.5)
The highest PCE is then achieved for an ideal solar cell with a FF approaching 100%, R_S of zero and R_SH close to infinity. However, in reality, R_S and R_SH never reach their ideal values and recombination processes within the PV device reduce the FF. As a result, low shunt resistance displaces the J-V curve proportionally to higher currents, whereas high series resistance shifts the J-V curve to lower voltages.[65]

2.2.4. Analysis of the characteristics of organic photovoltaic devices

There are fundamental differences between the energetic band properties of organic and inorganic semiconductors, as discussed in Section 2.2.1. Therefore, the photoexcitation in organic semiconductors does not immediately lead to the generation of free charge carriers at room temperature, as is the case for inorganic semiconductors, due to the tight coulombic attraction of the Frenkel exciton. Moreover, the transport properties and loss mechanisms of charge carriers differ for both semiconductor types. The circuit model used for inorganic PVs, shown in Figure 2.5, can nevertheless be used to describe the characteristics of OPV devices and thus, all equations and fundamental figures of merit for traditional inorganic PVs can be used for describing the behavior of OPVs.[74] However, attention is required when analysing the electrical characteristics of OPV-based devices, as factors that affect the V_OC, J_SC, FF, R_S, and R_SH may vary due to the intrinsic properties of organic semiconductors, especially in a D/A BHJ system which is fundamentally different from the typical p-n junction in inorganic semiconductors.

The open circuit voltage V_OC of OPV-based devices is dependent on the type of contact formed between the electrodes and the BHJ layer. For a non-ohmic contact, described in Section 2.2.2, Mihailtechi et al. experimentally proved that the V_OC matches the work function difference between the electrodes, as expected from the MIM model. On the other hand, assuming the presence of an ohmic contact, the maximum theoretical value of the V_OC for BHJ systems, namely the built in potential V_BI, can be obtained (described as the difference between the donor HOMO level and the acceptor LUMO level). For ohmic-contacts at the electrodes, Mihailtechi et al. reported a very low variation of the V_OC of the negative electrode work function. Regardless of the electrode material used (Ca with ϕ_M of 2.9 eV or Au with ϕ_M of 5.1 eV), the V_OC alteration was of only 160 meV. This effect was explained by the pinning of the electrode Fermi level to the redox potential of the fullerene material in the BHJ.[69]

As 1.7 eV – 2.1 eV is the typical optical band gap of light harvesting organic semiconductors, it is reasonable to expect a similar value for the V_OC of an OPV device.[75] In reality, however, the V_OC is often nearly two times lower than the E_opt. This reduction is due to various factors and loss mechanisms: recombination processes, temperature, light intensity, energetic disorder, defect states, CT states, D/A morphology, and interface area, which are reviewed in detail elsewhere.[75, 76, 77] Nevertheless, a good empirical estimation of the V_OC value for OPV-based solar cells was given by Scharber et al. in 2006, which still applies:[78]

\[
V_OC = |E_D(HOMO)| - |E_A(LUMO)| - 0.3 \text{ eV}
\]  

where the 0.3 eV is an empirical factor due to the difference between the V_BI and the actual device V_OC. The origin of the 0.3 eV loss is still a debated topic and no clear explanation for it
has been found yet. Nevertheless, according to Equation 2.6, the device $V_{OC}$ can be increased with the use of a tailored synthesis of novel acceptor materials with a LUMO level closer to the vacuum energy (assuming that the HOMO level of the donor material is constant).[79, 80, 81, 82]

The short circuit current $J_{SC}$ is strongly dependent on the optical and electrical characteristics of the D and A materials used for the BHJ photoactive layer. Some of the factors that need to be considered for achieving high $J_{SC}$ yields and therefore efficient OPV-based devices are: the choice of energetically and optically matching D and A materials; the area of the D/A interfacial contact in the BHJ; and the thickness and morphology of the photoactive layer. In this regard, increasing the BHJ thickness and tailoring the optical band gap to increase the harvest of photons from the solar spectrum, has been shown to successfully improve the $J_{SC}$ of OPV-based devices.[74] Further enhancement can be achieved with an intelligent selection of the BHJ solvent type, the deposition method, and the fabrication conditions.[83, 84] Special attention has to be devoted in order to reduce recombination processes in the BHJ or at interfaces within the device stack due to thick BHJ layers and low charge carrier mobility, which usually reduce the $J_{SC}$.[85]

The series resistance $R_S$ in both inorganic and organic PV cells is attributed to the bulk resistance of the photoactive layer, the resistance of the electrodes and interfacial layers, the contact resistance at any functional interface in the device stack, and the measuring probe resistance. In OPV-based devices, the $R_S$ is additionally dependent on the electric field strength within the stack, whereas in traditional p-n junction solar cell models, the $R_S$ is independent on the applied voltage as previously shown in Equation 2.2.[86, 87] This dependence originates from the fact that organic semiconductors exhibit field dependent mobilities.[73] In other words, in organic semiconductors high mobilities are recorded at high voltages and thus $R_S$ decreases with increasing voltage. As a result, the most accurate measurement of $R_S$ is conducted by evaluating the differential resistance $dV/dJ$ of the J-V slope near the $V_{OC}$ of the device obtained in the dark.[88] Furthermore, the series resistance is dependent on the D and A characteristics (i.e. regio-regularity, molecular packing, and crystallinity) and the phase separation of the BHJ.[89] The length of the photocurrent extraction path towards the electrodes (when bigger than 1 cm$^2$) greatly increases the $R_S$ when TCOs such as ITO are used.[90, 91] This originates from the fact that TCO conductivities are often more than an order of magnitude lower than typical conductivities of metals.[88, 92] Analytical models and guidelines to design large-area OPVs have also been published.[16, 18, 93, 94]

The shunt resistance $R_{SH}$, on the other hand, describes current leakages in the solar cell such as current leakage between the photoactive layer and the electrodes due to presence of pin-holes, or current leakage induced by impurities in the device. Defects on the surface of materials have been reported to serve as recombination centers for free charge carriers.[95] Another study conducted by Kim et al. suggested that there are three reasons for the $R_{SH}$ of P3HT:PCBM-based OPVs: the photoactive layer thickness; the interface between the photoactive film and the electrodes; and the illumination intensity.[89] In this regard, the use of interfacial layers improves $R_{SH}$ by defining the polarity of the device and assuring a selective charge carrier transport towards the electrodes. An increased $R_{SH}$ due to prevention of Al diffusion into the photoactive blend and reducing the surface roughness at the interface has also been observed.[74] Ultimately,
the majority of studies in the literature use a similar method to evaluate the $R_{SH}$: calculating it from the inverse slope of the J-V curve in the dark near the $J_{SC}$.\cite{96}

The fill factor FF appears to be the most sensitive of all the characteristic parameters of OPV devices, due to its complex dependence on various factors such as the fabrication conditions, the device area, the electrode materials, the thickness and morphology of the BHJ, the recombination losses in the BHJ and at interfaces between layers in the device stack, and the type of metal contact.\cite{74, 97} A suitable energetic alignment between the layers in the device structure is also important in order to avoid J-V curves with a characteristic “s-shape”, which drastically reduces the FF.\cite{98, 99, 100, 101} Effectively, the FF is strongly dependent on the $R_S$ and $R_{SH}$ of the device, which furthermore depend on many of the above mentioned factors.\cite{89, 102}

### 2.3. Materials and device characteristics

#### 2.3.1. Electron donors

P-type organic semiconductors such as polymers and small molecules can be efficiently used as electron donating materials. Detailed reviews of the chemistry of conjugated polymers and the synthetic rules for their synthesis, can be found elsewhere.\cite{103, 104, 105} A good summary of current developments on the field of p-type small molecules has been published by Dou et al. and Kang et al.\cite{57, 106} Generally, the structure of a conjugated polymer is determined by three main components: backbone, side chains, and substituents.\cite{107} From these, the conjugated backbone is the most important component as it defines the physical properties of the polymer.\cite{107} For example, homopolymers commonly have optical band gaps above 1.9 eV, due to steric hindrance associated with the repeating single aromatic unit, or fused aromatics of the conjugated backbone.\cite{107} On the other hand, the optical band gap can reduce significantly after an internal charge transfer (see Section 2.2.2) when a repetition of polymers with an electron-rich and electron-deficient moieties are used to construct the backbone.\cite{107} In this respect, depending on the optical band gap of the polymer, p-type donor materials are generally divided into two classes: wide band gap D materials ($E_{opt} > 1.7$ eV) and low band gap D materials ($E_{opt} < 1.7$ eV). The characteristics of some low band gap polymers can be further tailored to absorb the near infrared (NIR) region of the solar spectrum.

#### 2.3.1.1. Materials with a wide band gap

One of the first homopolymers used as a D material for the fabrication of OPV-based solar cells was poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). It was developed and patented by Wudl et al.\cite{108} This polymer is shown in Figure 2.7(a) and was used in 1995 by Yu et al. for the fabrication of the first BHJ-based OPV cell.\cite{13} The development of PVV-based devices has continued since then, and PCEs of about 3.0% have been achieved.\cite{109, 110} However, the combination of the wide band gap of the material (~2.3 eV) that reduces the light absorption and a relatively low hole mobility, limited further developments of this material.\cite{111}
The limitations associated with PVV-based homopolymers such as low light absorption and hole mobility, have been overcome by using poly(3-hexylthiophene) (P3HT), depicted in Figure 2.7(b). This D material is probably the most commonly used and widely investigated organic semiconductor for OPV-based devices to date.\cite{57} Indicative of this is the large number of reviews and book chapters detailing the properties of P3HT-based layers and blends with other materials, depending on the fabrication conditions used.\cite{112,113,114,115} For example, an impressive 1033 articles reporting solely on P3HT:PCBM-based OPVs were published between 2002 and 2010 (PCBM is an n-type acceptor material that will be introduced in the following sections).\cite{43} There are several reasons for this: P3HT is much cheaper than other materials, and a high quantity of the material is easy to source. The synthesis of P3HT is well-controlled and yields high quality output with only a few synthetic steps, due to process improvements made by Rieke and McCullough.\cite{116,117,118} Additionally, due to the efficient charge transport properties of P3HT, the performance of P3HT-based devices is less dependent on the BHJ thickness, than that of low-band gap polymers.\cite{119} Thus, P3HT is a suitable material for large-area R2R processing of OPVs, where large material quantities and thicker photoactive films are required.

P3HT can be produced to a very high quality, and with regio-regular or regio-random arrangement of its molecules, as shown in Figures 2.7(c) and 2.7(d). The regio-regularity of P3HT is crucial for the polymer characteristics. Values of above 95% are required for efficient charge transport and therefore high device $J_{SC}$ and FF values.\cite{120,121} Furthermore, high hole mobility of $\mu_h = 0.1 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1} - 0.3 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$, high crystallinity, and an absorption range of up to 650 nm (corresponding to a band gap of 1.9 eV) can be also accomplished with highly regio-regular P3HT and tailored fabrication conditions.\cite{114,120,122,123} In contrast, devices with low regio-regularity P3HT were reported to exhibit superior thermal stability.\cite{124,125} Using P3HT with high molecular weight $M_w$ can also improve the hole mobility in P3HT films, as reported by several research groups.\cite{126,127} Choosing the right deposition technique is furthermore important for determining the nanostructure of P3HT-based layers.\cite{113} Finally, P3HT can be easily blended with fullerene multi-adducts of C$_{60}$ and C$_{70}$ (see section on electron acceptors below), allowing for device PCEs approaching theoretical values of about 8%.\cite{128}
2.3. Materials and device characteristics

2.3.1.2. Materials with a low band gap

Narrowing the optical band gap of an organic semiconductor allows for greater light absorption, which in turn leads to an increased exciton yield and charge carrier generation. In a D/A BHJ this means that higher \( J_{SC} \) values are achieved for narrower (lower) \( E_{opt} \) of the organic semiconductors, whereas deepening the HOMO level of the D (or increasing the EA of the A) improves the device \( V_{OC} \). This can be accomplished by utilising alternating D/A-type co-polymers to construct the backbone of the donor material. A great deal of work has been done in the last decade, leading to the synthesis of countless novel p-type semiconductors based on donor and acceptor moieties such as cyclopentadithiophene (CPDT), dithienoisole (DTS), benzothiadiazole (BT), benzodithiophene (BDT), diketopyrrolopyrrole (DPP), thienothiophene (TT), dithienogermole (DTG), and thienopyrroledione (TPD).[57, 106]

One of the first successful uses of the BT and carbazole units in a co-polymer was accomplished with the synthesis of poly[9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzo-thiadiazole) (PCDTBT, shown in Figure 2.8(a)) by Leclerc’s group.[129] At the time, PCDTBT-based OPV devices showed a high \( V_{OC} \) of 0.89 V, owing to the low-lying HOMO level of the material (–5.5 eV). Together with a \( J_{SC} \) of 6.92 mA/cm\(^2\) and a FF of 63%, a PCE of 3.6% was measured. It was not long before an internal quantum efficiency of almost 100% was reported for PCDTBT-based BHJs, and a record device PCE of 6.1% (certified by NREL at 5.96%) was measured by Heeger’s group.[130] Nowadays, PCEs above 7% are common for PCDTBT-based systems, and are ascribed to smart device engineering and favourable BHJ nano-morphologies.[131] Moreover, stability tests have been carried out at on PCDTBT-based OPV devices in order to understand various degradation mechanisms.[26, 132] As a result, device lifetimes of over an year under real-world operational conditions have been reported.[133]

However, PCDTBT has an optical band gap of 1.88 eV, which is too large to harvest photons from the NIR part of the solar spectrum. The combination of CPDT and BT units as building blocks for the co-polymer, has shown to reduce the optical band gap due to strong intra-molecular D/A interactions of the co-polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b2]-dithiophene)-alt-4,7-(2,1,3-ben-zothiadiazole)] (PCPDDBT). The development of its derivatives C-PCPDDBT or Si-PCPDDBT depicted in Figure 2.8(b) followed. A detailed review of other conjugated polymers and molecules for use in organic electronics can be found elsewhere.[134] Initially, the PCPDDBT-based donor materials attracted a lot of attention due to their NIR absorption (\( E_{opt} \) of approximately 1.45 eV) and device PCEs approaching 6%.[135, 136, 137, 138] However, despite the high PCE values at the time, a limiting factor for PCPDDBT-based OPV devices is the disadvantageous \( V_{OC} \) of 0.7 V, that hinders any further efficiency improvement. Nevertheless, PCPDDBT has been proven to serve the purpose of an additional NIR sensitisier in ternary BHJs (usually a blend between two D and one A materials). A comprehensive review of the field can be find elsewhere.[139]

Further improvements of the PCE were achieved with the development of the TT and BDT building blocks.[140, 141] A certified PCE of 6.77% was achieved after tailoring the HOMO level of the low band gap polymer poly[4,8-bis-substituted-benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl-alt-4-substituted-thieno[3,4-b]thiophene-2,6-diyl] (PBDDTT).[142] Further improvements were
2.3. Materials and device characteristics

(a) PCDTBT

(b) X–PCPDTBT

(c) PTB7

(d) PTB7-Th

(e) PffBT4T-2OD

(f) PffBT4T-C_{9}C_{13}

Figure 2.8.: Chemical structures of typical donor materials with low band gap: PCDTBT (a); PCPDTBT, C–PCPDTBT, or Si–PCPDTBT (b); PTB7 (c); PTB7-Th (d); PffBT4T-2OD (e); and PffBT4T-C_{9}C_{13} (f).

accomplished following the synthesis of other PBDTTT-based derivatives such as poly[4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7) and poly[4,8-bis(5-(2-ethylhexyl)-thiophen-2-yl)benzo[1,2-b:4,5-b0]-dithiophene -2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]-thiophene-)2-carboxylate-2-6-diyl] (PTB7-Th, also know as PBDTTT-EFT). This has led to a significant enhancement of device PCE for single junction cells, from 7.4% in 2010 to efficiencies approaching or exceeding 10%.[143, 144, 145, 146, 147] Comprehensive reviews of the field of PBDTTT-based polymers can be found elsewhere.[148, 149]

Another promising polymer is poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3’’-di(2-octyldodecyl)-2,2’;5’,2’;5’’-quaterthiophen-5,5’’-diyl)] (PffBT4T-2OD, Figure 2.8(e)) due to the ability of the material to form pure crystalline domains that lead to increased hole mobility. This allows for the fabrication of BHJs with a thickness greater than 300 nm, while maintaining high device PCEs above 10%.[150] An optimisation of this polymer followed, and a
2.3. Materials and device characteristics

certified record PCE for a single junction device of 11.7% was achieved when poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3‴-di(2-nonyltridecyl)-2,2;5′,2″;5″,2‴-quaterthiophen-5,5‴-diyl)] (PffBT4T-C9C13, Figure 2.8(f)) was used.[151]

2.3.2. Electron acceptors

Exciton separation in organic semiconductors takes place at the D/A interface in the photoactive layer, as discussed in Section 2.2.1. Therefore, the role of n-type materials for efficient charge generation in OPV devices, is equally important to the role of the donor material. A distinction can be drawn between fullerene and non-fullerene based n-type organic semiconductors. The latter can be divided into polymers and small molecules, whereas the former is represented by derivatives of the C60 and C70 molecules. In this section, only the properties of fullerene-based acceptors are discussed, due to their relevance to the scope of this work. Information on the development of non-fullerene acceptors can be found elsewhere.[152, 153]

The C60 and C70 fullerenes (buckminsterfullerenes) are considered to be the third allotrope of carbon.[154, 155, 156] These molecules were discovered by Kroto, Smalley, and Curl, who were awarded the 1996 Nobel Prize in Chemistry “for their discovery of fullerenes”. The chemical structures of C60 and C70 consist of a conjugation between 60 or 70 π electrons, that results in a system exhibiting a high electron affinity. This characteristic of the fullerenes was attributed to a low-lying LUMO level (approximately −4.6 eV). C70 showed a better absorption than C60, due to the asymmetric nature of the molecule. As a result, both fullerenes were used as acceptor materials at the early years of OPV-based solar cells. However, C60 and C70 exhibit poor solubility in common solvents, and high crystallisation tendency. Therefore, the fullerenes had to be modified in order to overcome these drawbacks.[113]

The first successful use of a functionalised C60 fullerene was reported in 1995, when the group of Heeger et al. used [6,6]-Phenyl C60 butyric acid methyl ester (PC60BM, synthesised by Wudl et al.) as an acceptor for the first reported BHJ-based OPV device.[13, 157, 158]. PC60BM, depicted in Figure 2.9(a), has a LUMO level of approximately −3.9 eV, good solubility, and relatively high electron mobility of 10−3 cm2 V−1 s−1.[159]. However, a major drawback of PC60BM is poor absorption of light in the visible wavelengths, owed to the high symmetry of the C60 molecule. In order to overcome this limitation, Janssen et al. synthesised the PC70BM molecule, as shown in Figure 2.9(b). The synthesised molecule exhibited higher absorption in the wavelengths 350 nm – 500 nm than PC60BM does.[110] Nowadays, due to its higher absorption PC70BM is prevalently used as acceptor in blends with low band gap donors, which leads to improved device JSC. Despite this obvious advantage, PC70BM is more expensive than PC60BM, because of the long purification process required to yield C70.[158] Nevertheless, PC60BM and PC70BM are still the most commonly used fullerene acceptors for OPV devices.

Finding alternatives to PCBM (hereafter used to represent both PC60BM and PC70BM) appear to be difficult. Ideally, new acceptor materials should exhibit high absorption in the visible region, sufficient electron mobility, and high EA. Additionally, the LUMO level of the acceptor has to be energetically positioned to match the LUMO level of the donor, in order to facilitate efficient exciton separation at the D/A interface, whereas the difference between the LUMO of the acceptor and the HOMO of the donor should be kept as large as possible in order
2.3. Materials and device characteristics

Figure 2.9.: Chemical structures of typical n-type acceptor materials: PC\textsubscript{60}BM (a), PC\textsubscript{70}BM (b), bis-PC\textsubscript{60}BM (c), IC\textsubscript{60}MA (d), IC\textsubscript{60}BA (e), and IC\textsubscript{70}BA (f).

... to yield high device $V_{OC}$ values (see Section 2.2.4). Therefore, acceptors with LUMO levels that are higher than those of PCBM are needed, in order to improve the PCE of P3HT-based OPV systems by increasing the device $V_{OC}$.

The addition of a second side chain to the fullerene cage has proven to lift the LUMO level.\cite{160} An example of this is the bis-adduct analogue of PC\textsubscript{60}BM (bis-PC\textsubscript{60}BM, Figure 2.9(c)). The bis-adduct molecule exhibits a LUMO level of $-3.7$ eV, compared with $-3.8$ eV for the mono-adduct, which leads to an increased $V_{OC}$ of P3HT:bis-PC\textsubscript{60}BM-based OPV cells and a PCE of 4.5\%\cite{81} Much higher device PCEs are possible when P3HT is blended with indene-functionalised C\textsubscript{60} and C\textsubscript{70}, as reported by the group of Yongfang in 2010.\cite{79, 80} In a simple one pot reaction, the group obtained a mixture of non-reacted fullerene, and mono-, bis-, and tris-adducts of indene with the C\textsubscript{60} molecule (hereafter IC\textsubscript{60}MA, IC\textsubscript{60}BA, and IC\textsubscript{60}TA).

As for the number of adducts of PCBM, the IC\textsubscript{60}MA molecule in Figure 2.9(d) showed a LUMO of $-3.86$ eV, whereas the value for IC\textsubscript{60}BA (Figure 2.9(e)) was $-3.74$ eV.\cite{79} Similar trends were reported in the indene-C\textsubscript{70} analogue, which is shown in Figure 2.9(f).\cite{80} In this respect, IC\textsubscript{60}BA and IC\textsubscript{70}BA showed 0.17 eV and 0.19 eV higher-lying LUMO levels than PC\textsubscript{60}BM and PC\textsubscript{70}BM.

As a result, in a D/A blend with P3HT, both ICBA acceptors (hereafter the term ICBA will used to denote both IC\textsubscript{60}BA and IC\textsubscript{70}BA) drastically improved the device $V_{OC}$, and PCEs of about 5.5\% were achieved.\cite{79, 80} Further PCE enhancements were also reported, as a result of smart device engineering and tailored fabrication conditions.\cite{161, 162} In addition, the ICBA molecule has successfully been used as an acceptor material in combination with low band gap donor materials other than P3HT, such as DTBDT or PTB7, and in ternary BHJ systems with PTB7/PCBM or BDT6T/PCBM.\cite{163, 164, 165, 166}

2.3.2.1. Acceptors with isomeric properties

Currently, synthetic routes to obtaining different fullerene derivatives are often carried out in simple one pot reactions. This leads to a simultaneous synthesis of a dissimilar number of
fullerene adducts. However, as was discussed above, the characteristics of the different C\textsubscript{60} and C\textsubscript{70} adducts vary significantly, which alters the OPV device performance. Therefore, fullerene adducts have to be separated to assure high material quality. Nevertheless, even after separation, the properties of isolated molecules can still vary between different samples. This is attributed to the nature of the C\textsubscript{60} and C\textsubscript{70} molecules, that allows for chemical reactions to occur at different locations on the cage, while yielding the formation of fullerene derivatives with isomeric properties.[167]

The geometrical structure of fullerenes can be illustrated with a Schlegel diagram, as shown for C\textsubscript{70} in Figure 2.10(a). The curvature of C–C bonds decreases from the poles to the equator, which causes a higher strain at the polar \( \alpha \) bonds, than at the bonds nearer the equator.[167] The possibilities for a bis-addition of adducts can be explained with a Newman-type projection of the C\textsubscript{70} molecule, as shown in Figure 2.10(b). Taking into consideration the ICBA molecule, there are five possible sites for bis-addition of the indene molecule to a double \( \alpha \) bond, which has the highest reactivity due to the preferential relief of strain energy.[168] The two indene addends,

![Figure 2.10: C\textsubscript{70} Schlegel diagram with reactive \( \alpha \) bonds highlighted in red (a). Simplified Newman-type projection of C\textsubscript{70} with two reactive polar pentagons for an attachment of indene addends (b). Depending on the location of the indene addends on the C\textsubscript{70} cage, three different RIs of IC\textsubscript{70}BA are formed: 5(c), 2 (d), and 12 (e) o’clock.](image)
therefore, predominantly link to the fullerene cage across these bonds at the opposite poles. As a result, the formation of a so-called 5, 2, or 12 o’clock geometric relationship occurs, as shown in Figures 2.10(c), 2.10(d), and 2.10(e) respectively. Thus, a mixture of RIs is inevitable, based on current synthetic routes. There are a handful of reports showing the synthesis of isomerically pure fullerene derivatives.[169, 170, 171, 172] This structural isomerism, owing to the different position of the indene molecules on the fullerene cage, leads to an energetic disorder and affects the molecular packing of the photoactive blend. This furthermore alters the electron mobility and charge carrier transport efficiency of the D/A mixture, and consequently affects the OPV device characteristics.[173, 174, 175]

2.3.3. Interfacial layers

The utilisation of interfacial layers (IFLs) in the OPV stack plays an essential role as it leads to performance and stability improvements. This originates from the various functionalities of the IFLs such as: improving the energy alignment between the photoactive layer and the electrodes; forming a selective contact for free charge carriers; affecting the morphological formation of the photoactive layer; prohibiting a chemical or physical reaction between the D/A materials and the electrode; and acting as an optical spacer for better light distribution within the device.[176, 177, 178] Generally, IFLs can be divided into inorganic and organic-based ones, depending on the materials used. Taking into consideration the electronic properties of the materials, they can be further distinguished between conducting, semi-conducting, and dipole IFLs. A mixture of at least two of the above mentioned IFL types can be defined as a composite IFL. The following sections solely give an overview of IFL which are directly relevant for the fabrication of OPV devices.

2.3.3.1. Inorganic-conducting

Metals are known for their high conductivity. Thin layers (< 30 nm) of thermally evaporated metals appear transparent and can serve as interfacial layers. For instance, the low work function metal calcium (Ca) is commonly used to modify the electrode work function and accomplish an ohmic contact between the BHJ and the electrode. However, low work function materials tend to oxidise easily in ambient conditions, and chemically transfer to insulating metal oxides that cause reduction of the device performance. Besides, they cannot be easily solution processed and are more useful for research purposes than for application in industry.

2.3.3.2. Inorganic-semiconducting

This class of interfacial layers include numerous semiconducting ceramics, most of which are known as transition metal oxide materials (MeO_x). They offer a wide range of advantages over solely metal-based IFLs.[179] Semiconductors can be n-type and p-type, depending on the charge carrier excess in the material (free electrons for n-type or holes for p-type). The presence of a band gap improves the charge selectivity of the contacts, while modifying the electrode work function to allow a facile transfer of free charge carriers. Additionally, MeO_x exhibit high transparency in the visible spectrum due to wide optical band gaps, and can be easily solution processed over large areas.
2.3. Materials and device characteristics

N-type metal oxides

Zinc oxide (ZnO) is a commonly used n-type interfacial material.\cite{180, 181, 182, 183, 184} Due to its high electron mobility, ZnO is ideal as an electron selective contact layer.\cite{185, 186} Moreover, ZnO films exhibit high optical transmittance in the visible range (> 90%) and can be deposited at a low cost by various coating techniques, which makes it ideal as an electron transporting layer (ETL) for OPV cells.\cite{184, 187} There are many different ZnO-based materials available on the market. Depending on the processing temperature required for the deposition of ZnO, the available ZnO samples can be generally divided into R2R compatible and R2R incompatible. In this regard, there are three main solution based deposition methods: an extensively investigated sol-gel process\cite{187, 188, 189}; a nanoparticles approach (NPs)\cite{121, 181, 182, 190, 191}; and approaches that require a ZnO-precursor to be annealed in air in order to convert to ZnO by hydrolysis\cite{192, 193}. Detailed information about the advantages and disadvantages of the different fabrication techniques for ZnO can be found in comprehensive reviews elsewhere.\cite{184, 194}

Titanium oxide (TiO\textsubscript{x}) is another commonly used MeO\textsubscript{x}, which is a good alternative to ZnO.\cite{195, 196, 197, 198} TiO\textsubscript{x} can be efficiently used as an ETL, due to its good electron collecting ability and transparency in the visible range.\cite{199, 200} Commonly reported in the literature is the use of titanium isopropoxide or suboxide.\cite{200, 201, 202} These titania precursors are usually in a liquid phase which allows for an ease application in a sol-gel or dilution process.\cite{199, 203} Detailed information about the different application methods and ETL characteristics can be obtained from reviews prepared by Park et al. and Steim et al.\cite{176, 177}

Tin oxide (SnO\textsubscript{x}) and nombium oxide (NbO\textsubscript{x}) have also been reported to act as ETLs, however their application in OPV devices is limited due to their high processing temperatures and adverse characteristics compared to ZnO and TiO\textsubscript{x}.\cite{204, 205, 206, 207}

P-type metal oxides

Molybdenium oxide (MoO\textsubscript{x}) is probably one of the most used p-type metal oxide for OPV applications. This is due to the high transparency of the material (in the visible spectrum), and deep lying Fermi level, which is close to the conduction band of the material, making MoO\textsubscript{x} a good choice as an efficient hole transport layer (HTL) and electron blocking layer towards the anode. MoO\textsubscript{x} is also processable from solution at low temperatures using various techniques such as sol-gel, spray-pyrolysis deposition, wet-deposition, and NPs approaches.\cite{208, 209, 210, 211, 212, 213, 214} MoO\textsubscript{x} films can also be obtained at room temperatures.\cite{215, 216}

Vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) has similar characteristics to MoO\textsubscript{x}. Therefore, this material is also often used as a HTL in OPVs. There are many published reports of different deposition techniques such as sol-gel processing, NPs approaches, and low temperature wet processing.\cite{217, 218, 219, 220, 221} Nickel oxide (NiO\textsubscript{x}), tungsten oxide (WO\textsubscript{x}), and copper oxide (CuO\textsubscript{x}) have also found use as HTL due to their similar opto-electric characteristics to other p-type semiconductors.\cite{222, 223, 224, 225, 226}
2.3. Materials and device characteristics

2.3.3. Organic

Organic polymers (π-conjugated or not) and small molecules can also be used to improve the charge carrier transport from the BHJ towards a desired electrode, or to modify the work function of an electrode in order to accomplish an ohmic contact between it and the photoactive layer of OPV cells. One main advantage of organic IFLs over their inorganic counterparts is the versatility of possible material combinations, which allows for the fine adjustment of the characteristics of the IFL. This can be used to accomplish a desired orientation of the IFL used, which can induce the formation of permanent interfacial dipoles and alter the work function of the electrode.[106]

N-type semiconducting materials

There are only a few reports detailing n-type doping of polymers for use as IFLs for OPV devices. A good review on the field was conducted by Walzer et al.[227] Fullerene-based n-type small molecules, on the other hand, are widely used as IFLs. A good review of the field can be found elsewhere.[228] Other n-type small molecules such as bathocuproine (BCP) and bathophenanthroline (BPhen), shown in Figures 2.11(a) and 2.11(b), are commonly used as ETLs (and HBLs) in the OPV (and OLED) community.[91, 176, 229]

P-type semiconducting materials

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a widely used and extensively investigated p-type conductive polymer. Due to its low band gap (1.6 eV – 1.7 eV), high optical transparency, and environmental stability, PEDOT is used for diverse applications such as a hole injection layer in OLEDs, and as a flexible electrode in organic electronics. Nevertheless, to improve the solubility characteristics of PEDOT, polystyrenesulfonate (PSS) is commonly used in combination with PEDOT.[230] The resulting organic compound, depicted in Figure 2.12, is furthermore widely used as a hole selective contact and a standard HTL in OPV devices.

However, PEDOT:PSS exhibits low conductivity of typically $10^{-5}$ S cm$^{-1}$ to 10 S cm$^{-1}$. The conductivity can be increased by simple film treatments with methanol (MeOH; $\sigma$ of 1362 S cm$^{-1}$); the addition of high boiling point solvents such as dimethylsulfoxide (DMSO; $\sigma$ of 1418 S cm$^{-1}$), or ionic liquids such as 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM TCB; $\sigma$ of 2084 S cm$^{-1}$).[230, 231, 232] Nevertheless, PEDOT:PSS exhibits an intrinsically acidic and hydroscopic character, which causes the degradation of OPV devices.

![Figure 2.11.](image)

Figure 2.11.: Chemical structures of organic n-type semiconducting materials: BCP (a) and BPhen (b).
2.3. Materials and device characteristics

Figure 2.12.: Chemical structure of the organic p-type semiconducting material PEDOT:PSS.

Conjugated and non-conjugated polymers

There are several comprehensive reviews of water/alcohol soluble conjugated and non-conjugated polymers that can be used as IFLs.[233, 234, 235] Generally, a significant device performance enhancement can be achieved by the use of polyfluorene-based conjugated materials such as poly[9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctyfluorene)] (PFN, Figure 2.13(a)) or poly[9,9-bis(6'-(18-crown-6)methoxy)hexyl]fluorene] chelating to potassium ion (PFCn6:K\(^+\), Figure 2.13(b)).[236, 237, 238, 239]

Some relevant examples of non-conjugated polymers are polyethylenimine ethoxylated (PEIE), polyethyleneimine (PEI), and polyallylamine (PAA).[240, 241] Generally, films formed from non-conjugated polymers are very sensitive to film thickness, due to their large band gap and insulating character, compared to conjugated polymers.

Small molecules

Another approach to efficiently modify the electrode work function is the use of self-assembled monolayers (SAM) of small molecules. In this regard, device performances can be enhanced by modifying the electrode work function with 4-chlorobenzoylchloride (CBC), 4-chlorobenzenesulfonyl chloride (CBS), 4-chlorophenyldichlorophosphate (CBP), chlorobenzoic acid (CBA), or with SAMs containing a –NH\(_2\), –CH\(_3\), or –CF\(_3\) terminal groups.[242, 243]

Figure 2.13.: Chemical structures of conjugated polymers used as interfacial layers: PFN (a) and PFCn6:K\(^+\) (b).
Recently, a novel non-conjugated small-molecule electrolyte named 4,4’-(((methyl(4-sulphonatobutyl)ammonio)bis(propane-3,1-diyl))bis(dimethyl-ammonium-diyl))bis-(butane-1-sulphonate) (MSAPBS) was shown to efficiently serve the purpose of an IFL, and an OPV device PCE above 10% was reported.[246]

2.3.3.4. Composite

The number of publications reporting on IFLs formed from a composite of two compounds (inorganic and/or organic) has increased over the years. Composite IFLs often consist of a mixture between a metal oxide and an inorganic or organic counterpart. In this respect, high device performance characteristics were reported for a ZnO-TiO$_x$ mixture.[247] In another approach, ZnO was doped with cesium (Cs) leading to a smoother IFL surface and reduced bulk resistance.[248] Small et al., on the other hand, reported enhanced device $J_{SC}$ values after adding poly(vinyl pyrrolidone) (PVP) to a sol-gel ZnO, which caused an improved contact between the ZnO nanoclusters and PCBM.[191]

Hybrid composites between metal oxides and reduced graphene oxide (RGO) are also possible, and lead to PCE improvements due to reduced device $R_S$ and improved IFL conductivity as recently shown by Beliatis et al.[249] Similar approaches were also reported by others.[250] Other hybrid composites are metal oxides with incorporated metal NPs.[215, 251]

Organic IFLs such as PEDOT:PSS have also been used in combination with MeO$_x$.[252, 253] The incorporation of Ag and Au NPs, or even a combination of both, in the PEDOT:PSS film is another way to improve device performance and is often credited with improving the electrical properties of the IFL.[254, 255, 256, 257, 258]

2.3.4. Electrodes

The electrodes of any OPV device embody an essential component in its stack, as they collect the free charges that are generated and enable contact with an external circuit. In this regard, electrons are collected at the electron selective contact named cathode, and holes are collected at the hole selective contact named anode. To accomplish an efficient charge transport with few losses, the ideal electrode should show low sheet resistance ($R_{SHEET}<10\ \Omega/\square$) and thus high conductivity.[17] There are many materials exhibiting these characteristics, which can be efficiently utilised as electrodes. However, in OPVs light has to reach the photoactive layer through one, and ideally both electrodes, in order to generate charge carriers. Therefore, it is very important that at least one of the electrodes exhibits high transparency.

The opto-electrical characteristics mentioned above are possible for electrically conducting ceramics (doped metal oxides), also known as transparent conductive oxides (TCOs). A typical example of this type of materials is ITO, which usually has a $R_{SHEET}$ between 15 $\Omega/\square$ and 75 $\Omega/\square$ and a transparency of above 90% in the visible spectrum. The resistivity of the TCO is important and has to be kept low at all times. Otherwise, the device performance decreases for extended conduction paths (above 1 cm), due to reduced $J_{SC}$ and FF values owed to non-geminate recombination processes.[73, 91, 92, 259] Unfortunately, high quality ITO is very expensive and contains indium, which is limited in supply. Additionally, ITO is not solution
2.3. Materials and device characteristics

Figure 2.14.: Top electrode layouts for OPV modules. Source OPVIUS GmbH.[42]

processable and does not have sufficient flexibility for certain fabrication applications on plastic substrates.[260]. Therefore, numerous alternatives to ITO as a bottom electrode have been studied. In this respect, highly conductive polymers alone or in combination with metal grids have also been shown to overcome the conductivity limitations of ITO.[231, 232, 261, 262, 263] Carbon nanotubes (CNTs) and graphene are other promising materials, due to their low-cost and uncomplicated fabrication.[264, 265, 266, 267, 268]

OPVs also have a top electrode. In research laboratories it is usually deposited by vacuum-thermal evaporation of Al or Ag, whereas printing and coating techniques are more common in industry due to the possibility of fast deposition with unlimited design layouts, as shown in Figure 2.14. In this regard, Ag-based inks are exclusively used in industry, despite recent advances that allow for the fabrication of carbon-based electrode systems.[269] Given the possibility to replace ITO as a bottom electrode and/or evaporated metal top electrodes, the fabrication of large area solar cells (aperture of at least 1 cm$^2$) can be easily achieved using R2R fabrication techniques on plastic substrates.
2.4. Device architectures

The ability to modify the electrode work function by means of using different interfacial layers as discussed in Section 2.3.3, has allowed for the development of two type of OPV device architectures, \textit{i.e.} conventional (also known as standard or regular) and inverted device structure. In this respect, the type of architecture is primarily defined by the polarity of the OPV cell, which also determines the transport direction of free charge carriers from the photoactive layer towards the electrodes. Additionally, a division into single-junction and multiple-junction devices can be made, depending on the number of individual D/A layers in the device stack.

2.4.1. Standard stack configuration

A great deal of work has been devoted over the past decades to investigate OPV devices comprising a regular stack geometry as shown in Figure 2.15(a). In this architecture the anode is commonly ITO, functionalised by an organic HTL made of PEDOT:PSS. To enhance the electron extraction towards the cathode, while forming an ohmic contact with the photoactive layer, a low work function metal, \textit{i.e.} Ca, is generally used as an IFL.\cite{61} The outermost or top electrode (the cathode) is commonly formed by Al, as shown in Figure 2.15(a). However, there are a number of issues associated with the use of Ca as the ETL. Due to its low work function of 2.87 eV, Ca is air and water sensitive making it only suitable for processing in an inert atmosphere.\cite{270, 271} Instead of Ca, thin layers of n-type organic materials (\(~5 \text{ nm}\)) such as BCP (see Section 2.3.3) can be used. However, in both cases an expensive and time consuming thermal-vacuum evaporation process is required for the ETL deposition.

Metal oxides such as ZnO and TiO\textsubscript{x} are less reactive with air and humidity than Ca, and therefore they can be used as efficient ETLs. Moreover, most MeO\textsubscript{x} used in OPV devices are solution processable under ambient conditions, due to their improved air stability over Ca.\cite{200, 272, 273} Nevertheless, care must be taken in the selection of deposition solvents so that orthogonality and good wetting on top of the BHJ layer is maintained. Similar considerations apply also for ETLs other than MeO\textsubscript{x}, whenever a deposition from a solution is done.

![Figure 2.15:](image)

**Figure 2.15.** Schematic diagram of a regular/standard device geometry (a), and the corresponding energy diagram for the device stack (b).
As mentioned in Section 2.3.3, a main responsibility of IFLs is to modify the work function of the electrodes, in order to accomplish a suitable energy alignment between layers in the device stack. Thus, Figure 2.15(b) shows the energy band diagram of a typical OPV cell with a standard architecture. It can be seen, that the ITO work function of $-4.7 \text{ eV}$ can be modified by PEDOT:PSS, which effectively changes the contact work function to approximately $-5.1 \text{ eV}$. By doing this, the electrode work function is brought closer to the HOMO level of P3HT, in order to ease hole transport towards the ITO electrode, which becomes the anode. In a similar manner, as can be seen in Figure 2.15(b), the LUMO level of BCP ($-3.5 \text{ eV}$) is positioned above the LUMO of IC$_{70}$BA ($-3.85 \text{ eV}$), allowing for the formation of an ohmic contact with the Al electrode, as discussed in Section 2.2.2. In addition, the deep HOMO level of BCP ($-7.0 \text{ eV}$) blocks holes from the BHJ and defines Al as the cathode of the cell.

### 2.4.2. Inverted stack configuration

In an inverted OPV device architecture as shown in Figure 2.16(a), the flow of charge carriers from the BHJ towards the contacts is the reversal of the regular architecture. This means that electrons are collected at the ITO, while holes at the top metal electrode, which can be formed from Al or other metals with higher ambient stability such as Ag. In order to accomplish a selective contact for electrons, the ITO work function can be modified by various IFLs. N-type metal oxides such as ZnO are commonly used for this purpose, and to improve the energy alignment with the contact, due to their ability to alter the ITO work function by means of Fermi level pinning.[185, 274] As illustrated in Figure 2.16(b), the ITO work function can be effectively changed from $-4.7 \text{ eV}$ to $-4.2 \text{ eV}$, which leads to an efficient transport of electrons from the LUMO of PC$_{70}$BM to the ITO contact. Furthermore, holes are efficiently blocked due to the large band gap of ZnO (valence band at $-7.6 \text{ eV}$). Similarly, as shown in Figure 2.16(b), MoO$_x$ is used for the hole transport from the PCDTBT domains to the metal top contact.

![Figure 2.16](image)
In comparison to conventional OPVs, inverted devices demonstrate better long-term ambient stability. This improvement is mainly ascribed to the replacement of Ca, and to some extent to the utilisation of metal oxides that usually show good resistance against air and humidity. Additionally, the chemical and morphological instabilities of the ITO interface are reduced due to the replacement of PEDOT:PSS, which has acidic nature.[275] This leads to an improved device lifetime and preserved performance.[276, 277, 278] Another approach to improve the device stability is to replace the top Al electrode with metals such as Ag or gold (Au). This is mainly attributed to reducing the diffusion of air and moisture, due to the use of a high work function metals as a top electrode.[121, 183, 199]

2.4.3. Stacks with multiple junctions

Research on improving the PCE of OPVs has led to the development of solar cell concepts such as tandem (double) or triple junction solar cells.[279, 280] These concepts aim to enhance light absorption within the solar cell device with the utilisation of D/A blends that have complementary absorption spectra. In other words, two or three single junction solar cells are fabricated vertically on the same substrate while connected in series with an interconnecting recombination layer. As with single junction solar cells, double or triple junctions also comprise standard or inverted structures, as depicted in Figure 2.17.

PCEs close to 20% are theoretically possible for tandem OPV devices when a front and back cell with approximate bandgaps of 1.6 eV and 1.2 eV are used.[281, 282] However, the maximum PCEs achieved to date are in the range of 11%, despite the tremendous development of novel donor and acceptor materials.[283, 284, 285, 286, 287] Furthermore, joint efforts between research groups has led to important developments in the field of fully solution processed tandem solar cells, allowing for fabrication with R2R compatible printing and coating techniques.[269, 288] However, the fabrication process is challenging and high deposition precision is required in order to ensure a large yield of working devices.[269]

![Figure 2.17.](image.png)

Figure 2.17.: Schematic diagram of tandem (double) (a) and triple (b) junction OPV device architectures. Reproduced from [289] and [283]. Copyright ©2012 Elsevier and 2013 American Chemical Society.
2.5. Device stability

Understanding the degradation processes occurring in OPV cells is vital to preserving high PCEs over a prolonged period of time, and thus improving the operational stability of devices. Increasing the lifetime of OPV cells is also crucial for the successful establishment of this technology in a market that is still dominated by inorganic (Si-based) solar cells. The need to improve the operational lifetime of devices has triggered intense interest in the research community, and numerous studies have been conducted, as summarised in various review articles.[20, 271, 290]

OPV manufacturing companies have also been working on improving device stability. Konarka reported in 2012 $T_{80}$ lifetimes of 4000 h for their modules, which were tested under damp-heat conditions of 65 °C and 85% relative humidity (RH).[291] OPV modules by Heliatek, on the other hand, sustain more than 90% of their initial PCE after 3000 h at 85 °C and 85% RH.[292] In terms of real world operation, OPVIUS has recently reported that “the world’s first grid-connected OPV system has been running reliably” for four years since installation.[35]

Despite these achievements, the stability of OPV-based devices has a complex nature and is dependent on various factors that generally can be divided into degradation due to oxidation, temperature, and interfacial reactions.[106] These three groups are furthermore represented by degradation caused, amongst other factors by: diffusion of oxygen and water; photo-oxidation due to irradiation; heating and mechanical stress; metastable BHJ morphology due to defect states and material migration; and diffusion of electrodes and buffer layers.[290, 293]. Some of these degradation processes can be significantly reduced if encapsulation is used, whereas others require a better understanding of the properties of materials and the development of more stable novel compounds.

Special care must be taken when choosing a testing protocol suitable for characterisation of the operational stability of OPV-based cells. Using already established testing protocols, i.e. IEC 61646, used for analysis of thin film inorganic PV systems might not be the best choice for investigating organic-based PV technologies, due to the fundamental differences between both technologies discussed in Section 2.2.4.[33] Furthermore, stability tests in research laboratories are performed under different conditions, which prohibits a fair comparison of reported results. This has been recognised by the major researcher groups in the field of OPV-based solar cells, and an International Summit of OPV Stability (ISOS) has been initiated in order to set generally agreed directions for testing device stability and operational lifetime.[29] Nevertheless, it is important to note that the ISOS testing standards should be used as guidelines, rather than as rules “written in stone”. In this respect, extrapolated estimations for long term stability might be unreliable (i.e. ISOS-D, ISOS-O, ISOS-L, ISOS-T, or ISOS-LT), as depending on the degradation mode present in a particular device structure, results may vary or be misleading.[294]
2.6. Requirements for a device scale-up

In the last few years, continuous improvements in the fabrication process for large-area OPV modules has lead to an increase in the PCE and operational stability.[295] However, the efficiencies reported for small area devices are extremely hard to match, due to the numerous challenges associated with the scale-up of the fabrication process from a laboratory to an industrial scale. In this regard, special care must be taken to choose the most suitable deposition method depending on the materials used, in order to assure high device performance.

2.6.1. Deposition methods

The choice of a deposition technique for each of the layers in a solar cell stack can have a significant effect on the solidification physics and the ability to precisely control the deposited film’s thickness, which affect the properties of the layers. In particular, remarkably different photoactive layer morphology is observed when a R2R compatible deposition technique is chosen, in comparison to that observed when the spin-coating technique is used.[296] This brings into question how high device PCEs obtained by the spin-coating technique can be transferred to large-area fabrication, where other deposition techniques are used.

The deposition methods used nowadays for the fabrication of large-area OPVs originate from the printing industry. This is due to the fortunate property of organics, and some inorganics semiconductors which allows for their dispersion in the form of liquid inks. Generally, the deposition techniques relevant to OPV technology can be divided into three major groups: coating, printing, and vacuum deposition. There are many exhaustive reviews on this topic, some of which summarise the most recent achievements in the field of printed functional organic materials and electronics.[295, 297, 298] Design rules and guidelines for closing the efficiency gap between small area “hero” devices and R2R printed large-area modules have also been published.[18, 94, 299] Nevertheless, for the sake of completeness, some of the most relevant developments relating to the up-scaling process of deposition techniques, with examples (when appropriate), are listed below.

2.6.1.1. Coating techniques

This category of deposition techniques can be divided into spin, blade or knife, slot-die, and spray. The most employed deposition technique in laboratory environments nowadays is spin-coating. This is due to the affordable cost of the equipment and the possibility of fabricating highly uniform layers with a precisely controlled thickness. Therefore, device PCEs above 10% are achieved in a laboratory environment, when photoactive layers are fabricated with the spin-coating technique.[147, 300, 301, 302] However, this deposition technique has some limitations such as poor material utilisation and not being suitable for fast large-area device fabrication.

Blade and knife coating (see Figure 2.18) allow for the deposition of layers on a large scale. The lateral dimensions of deposited films are determined by the overlap between the blade/knife width and the substrate. These coating techniques can serve as a prototyping tool for the slot-die coating technique (see Figure 2.18) which allows for a continuous deposition of several stripes with different dimensions on a substrate. Compared to spin-coating, the blade/knife and slot-die coating techniques allow much better material utilisation, which lowers fabrication costs.
However, the formation kinetics of the deposited layers differ significantly compared to that in spin-coating, which unavoidably influences the morphology of the deposited layers. This can be critical when a crystallisation in the D/A blend is desired, as is the case for P3HT-based BHJs. In this respect, PCEs for blade/knife coated P3HT:PCBM-based OPV devices rarely exceed 3%, whereas PCEs above 5% have been reported for spin-coated alternatives.[43] The significance of the blend morphology for the device performance is even more pronounced in the case of P3HT:ICBA-based solar cells, where the regio-isomeric content of the IC$_{70}$BA molecule has a dramatic effect on the device PCE, as discussed in Section 2.3.2.1. Nevertheless, development of new materials allows for some D/A blends to have similar device performances for different blend morphologies.[296] As a result, blade coated devices with PCEs up to 9% have been reported, whereas state-of-the-art semi-transparent modules have shown PCEs of 4.5%.[39, 296]

Spray-coating is another scalable deposition technique, which can be used for the deposition of a range of semiconductor materials on a R2R web, as shown Figure 2.18.[303, 304] A major disadvantage of this deposition technique is the low edge resolution.[298] It can be overcome by the use of a shadow mask or with post-patterning treatments of the deposited layers. However, special care must be taken to avoid contamination of the processing equipment, due to the spread of the ink spray through the nozzles. Additionally, spray coated layers tend to de-wet, due to the use of a low material solid content for the ink and the lack of shear motion during deposition which can keep the ink on the substrate surface.[304] Nevertheless, the de-wetting can be overcome by tailoring process parameters such as material concentration, the solvents and additives used, substrate temperature, spray-speed, gas pressure, and head/nozzle height. As a result, on a laboratory scale, OPV device efficiencies above 8% have been realised.[304, 305]
2.6.1.2. Printing techniques

This category of deposition techniques is represented by flexographic, screen and rotary screen, gravure, and ink-jet, as shown in Figure 2.19. During the screen printing method, a desired pattern is created by a mesh. Areas outside the pattern of the mesh are impermeable for the ink that is spread at a particular speed and pressure from a squeegee. The printing result depends on the viscosity of the ink, and on the mesh apertures. Commonly, the screen printing process is carried out on a flat bed surface, which would impede the continuous deposition on a R2R web. Consequently, a rotary screen printing process was developed in which a cylinder with a patterned screen is used. The ink is supplied inside the rotating cylinder, where it is pressed against the wall of the tube by a squeegee.

During the gravure printing process, a cylinder with an engraved pattern is pressed against a substrate in order to transfer ink from the engraved pattern onto the substrate. The gravure cylinder is placed in an ink bath, which allows the pattern cavities to be filled with ink by the continuous rotation of the cylinder. Excessive ink is removed with a doctor blade.

The process of flexographic printing shares many similarities to that of gravure. A fountain roller is partially placed in an ink bath and serves to transport the ink onto an anilox roller (a cylinder with cavities on the surface that can carry only a particular volume of ink). The major advantage of flexographic printing is the ability to control the amount of ink absorbed by the anilox roller, which allows for adjustments of the deposited ink thickness. Optionally, a doctor blade can be used to remove excess ink from the anilox roller. Then, the ink from the anilox cylinder is transferred onto the printing plate roll, which holds the desired pattern (usually made of rubber or photopolymer). An impression cylinder is used to press the substrate against the printing cylinder in order to transfer the ink onto the substrate.

During the ink-jet printing, droplets are ejected from a nozzle in order to form a pattern on the substrate. Compared to spray-coating, the ink-jet printing process allows a precise deposition of single droplets with a resolution of up to 1200 dpi, which can form a pixelated pattern. The most common method of droplet deposition is referred to as drop-on-demand (DOD), where a droplet of the ink is deposited for each pixel where required. Commercial systems nowadays consist of many nozzles, which allow high image resolution on a R2R without having to reduce the web speed. The main advantage of ink-jet printing technology is the use of a digital master, which can be easily changed on a computer. This allows for the deposition of unlimited patterns, without any additional equipment costs.
2.6. Requirements for a device scale-up

2.6.1.3. Vacuum deposition techniques

Deposition of materials such as metals and organic/inorganic semiconductors by means of vacuum based processes has been widely used in the field of organic electronics. For OPVs in particular, this applies to the extensively used transparent electrode ITO and the device’s top metal electrodes (Al, Ag, or Au). The advantage of the vacuum deposition is greater control over the deposited material thickness, which allows the fabrication of highly efficient, multi-junction OPV devices solely by using vacuum deposition, as demonstrated by Heliatek (see Section 1.2). Nevertheless, the complexity of the equipment used and the cost associated are considerably higher than alternative coating and printing techniques. Some groups have adopted a novel approach, in which a combination of printing, coating, and vacuum deposition is used on a R2R scale.[32]

2.6.2. Material considerations for large-area fabrication

The selection of materials used to fabricate an OPV device stack has a direct effect on a solar cell’s characteristics. Special care must be taken to ensure the compatibility of consecutively deposited layers, in order to prevent dissolution effects. A trade off between device PCE and fabrication cost has to be made, especially for materials used in the photoactive layer. In this respect, despite the large number of expensive high efficiency low band gap donor materials available nowadays, only a fraction preserve these high efficiencies in up-scaled device areas.[15] Additionally, air and humidity stable materials are preferable, in order to prolong device operational times and potentially eliminate the need for expensive encapsulation technologies.

Photoactive layer

Enormous progress in developing novel conjugated polymers has allowed for the synthesis of high efficiency low band gap donor materials, resulting in devices PCEs above 10%, as shown in Section 2.3.1.[147, 306, 307] A great deal of work has also been carried out on the field of novel fullerene and non-fullerene based acceptor materials, as discussed in Section 2.3.2.
However, from an industrial point of view, a low cost and simple one or two step material synthesis is desirable, as it will allow high material yields in large quantities.[32] However, the use of many novel low band gap materials for commercial OPV production is impeded by their multi-step material synthesis and consequently high purchase cost. Large material quantities are also difficult to obtain. A good example of these limitations is given by the low band gap polymers PTB7 and PTB7-Th.[140, 144] Additionally, PTB-based co-polymers have been reported to exhibit a reduced photostability in air when compared to carbazole based materials such as PCDTBT.[308] Indeed, the high photochemical stability of PCDTBT suggests indoor and outdoor operational lifetimes of the order of 7–15 years.[26, 133, 309] Moreover, under low light level conditions (300 lux generated by fluorescent laps), PCDTBT has been shown to perform better than PTB7-based devices (13.3 µW/cm² vs. 12.2 µW/cm²).[310]

Polymers such as P3HT, on the other hand, can be easily synthesised in one-pot reactions with reasonable yields, and at a low cost. Furthermore, theoretical PCE of up to 8% have been reported for OPV devices with a photoactive layer consisting of P3HT and a suitable acceptor material.[128] This puts P3HT in direct competition with some low band gap donor materials. An up-scaled synthesis of indene-fullerenes at a significantly lower cost than commercially available alternatives has also been reported, envisioning a promising future for P3HT:ICBA-based OPVs.[32, 311]

Co-polymers based on DTS and TTz units (see Section 2.3) have been reported as an alternative to P3HT, especially when thicker photoactive layers are desired. In this respect, device PCEs of about 3.35% were achieved for fully solution processed OPVs with a PDTSTTz-4:PCBM photoactive layer of 350 – 500 nm thickness.[312] This D/A system was furthermore compared to another three photoactive blends (P3HT:PCBM, PV-D4610:PCBM, and PBDTTTz-4:PCBM) in order to qualify the quality of different encapsulation foils, and showed a T₈₀ value of 135 hours when tested according to the ISOS-L-1 protocol.[21] Nevertheless, all other D/A blends outperformed PDTSTTz-4:PCBM in terms of stability, and a maximum T₈₀ of 195 hours was calculated for PV-D4610, which was developed by the company Merck. In a more recent publication, a PCE of 9.3% on a glass-ITO substrate and 6.5% on a PET-IMI substrate were reported for another material from Merck (PBTZT-stat-BDTT-8).[39]

Interfacial layers

The function and importance of interfacial layers in the OPV device stack has already been extensively discussed in Section 2.3.3. In this section, reports that are particularly useful as interfacial layers in large-area devices are discussed. A comparison of four different inorganic ETLs (CrOₓ, TiOₓ, AZO, and ZnO) was carried out by Andersen et al. for fully R2R fabricated devices with a conventional (standard) architecture.[313] The choice of this architecture, which is rarely used for R2R fabricated OPVs, was justified by the group’s ability to deposit various materials including metal top electrodes by means of sputtering methods. A photoactive layer consisting of P3HT and ICxA (a low cost indene fullerene mixture of 36% ICMA, 53% ICBA, and 11% ICTA) was used. It was shown, that while devices with CrOₓ did not function at all, the highest PCEs were measured for ZnO followed by AZO and TiOₓ (2.2%, 1.23%, and 0.46%). Similarly, the devices with ZnO exhibited the longest operational lifetime, followed by AZO and TiOₓ.
Cha et al., on the other hand, reported improved device characteristics for solar cells with an inverted architecture when AZO is used, compared to ZnO.[314] This was ascribed to a favourable surface morphology of nanoparticles and good charge transport properties. The former also affects the BHJ formation on top and the contact between the ETL and photoactive layer. Further improvements in device characteristics were achieved after slot-die coating PEIE onto the ETL, which passivated the surface traps and voids in the metal oxide layers. PEIE alone has also been reported to act as an efficient ETL in P3HT:PCBM-based OPVs in an inverted architecture.[315] However, photo-oxidative reactions at the surface of the PEIE layer have been observed to alter the work function of the material and hence negatively affect the device characteristics. Therefore, special care must be taken to protect the PEIE layer from oxygen and light.

PEDOT:PSS is a prominent and extensively used material both as a hole transport layer and a transparent conducting layer (TCL), as already mentioned in Section 2.3.3. The purpose of the PEDOT:PSS layer depends mainly on the conductivity characteristics of the material. High conductivity versions of PEDOT:PSS (usually above 500 S cm\(^{-1}\)) are commonly used to facilitate charge carrier transport towards to the metal electrode in semi-transparent OPVs. In this respect, high boiling point solvents such as EG and DMSO are used to tune the characteristics of PEDOT:PSS, especially conductivity, and could potentially have an effect on the long term stability of OPV devices. This was studied by the Krebs’ group while using fully ambient R2R processed ITO free modules under the well-established ISOS testing protocols.[316] It was found that for outdoor applications, EG is the better choice as an PEDOT:PSS additive, rather than DMSO. In contrast, for some indoor tests (ISOS-D-3 and ISOS-L-3), devices with DMSO showed better stability. The discrepancies originate from the position of the PEDOT:PSS layer within the device stack (front or back) and the hydrophilicity difference due to the use of EG and DMSO. Generally, higher hydrophilicity was found to be undesired, as it can cause degradation of the photoactive layer when the PEDOT:PSS is in a direct contact with the BHJ.

**Substrate carrier and electrodes**

A successful transition from laboratory scale OPV to large-area R2R compatible architectures requires the replacement of rigid substrates with flexible alternatives and the substitution of device electrodes.[18] Substitutions of the most commonly used, brittle and expensive, bottom ITO electrode are also required.[14] Similarly, solution processed alternatives to the top thermally evaporated metal electrode are needed, in order to assure fast device fabrication and further reduce the total manufacturing costs, so that economically competitive Watt Peak per production cost values are achieved.

Alternatives to the ITO electrode were discussed by Angmo and Krebs et al. in a recent review, in which highly conductive polymers, metals or metal NWs, a combination of a polymer and a metal, carbon nanotubes, and graphene were suggested.[317] From all of the above the use of a metal (NWs or NPs), in particular Ag, or the combination of a metal with a polymer seemed to match the requirements (sufficient conductivity at a low sintering temperature) for the fabrication of efficient and stable OPV devices. It can also be used both as a bottom or top electrode system, as has been shown by numerous publications.[221, 318, 319, 320] In this
2.6. Requirements for a device scale-up

regard, a great deal of work has been done by the Krebs’s group, who have proven the ability to fabricate 147 000 ITO-free and defect free solar cells over 700 m of foil.[15]

Silver NWs have been used as both front and back electrodes.[321] This makes them an ideal candidate to replace ITO. Due to their semi-transparency and cost efficient processing, they are also a desirable option as a back electrode. Solution processed Ag NWs have also been used in combination with an Ag ink as front and back electrode systems in fully printed organic tandem solar cells with a PCE of 4.85%.[322] In comparison to PEDOT:PSS as a front electrode, Ag NWs have been shown to increase the device operational stability by up to 1000%.[25] Additionally, an almost complete recovery of Ag from OPV devices has been shown to be possible, which fully justifies the use of Ag as an electrode in the scaled production of organic solar cells.[288]

2.6.3. Device geometry requirements

The compatibility of the inverted device geometry with the ability to fabricate all layers in the solar cell’s stack from a solution was realised at an early stage of the scale-up trials, and has therefore become the most common choice. There have also been attempts to sputter Al, in order to allow the fabrication of normal geometry devices. Nevertheless, rather low device PCE and no or limited operational stability data were reported.[313, 323] The main advantage of the inverted device architecture, as discussed in Section 2.4.2, is the ability to use Ag as a back electrode, which leads to improved operational stability. Furthermore, Ag is currently the only material that can be deposited from a solution, and that achieves $R_{\text{SHEET}}$ below 0.1 Ω/□ even for sintering steps at low temperatures. Additionally, the printing of top electrodes normally has to be carried out on top of a thick interfacial layer (several hundred nm), as is the case for inverted devices, in order to prevent direct contact between the electrode and the photoactive layer as they may cause possible dissolution due to the solvents used for the Ag ink.

2.6.4. Encapsulation

The operational lifetime of OPVs can be significantly improved when an encapsulation is used. The encapsulation acts as a barrier against the ingress of oxygen and moisture into the OPV stack, which in turn can lead to undesired chemical reactions in the OPV device. Improved mechanical stability and protection of the OPV device from UV radiation is additionally possible, depending on the properties of the encapsulation foil.[324] Generally, a water vapour transmission rate (WVTR) of $<10^{-3}$ g/m$^2$day is required for OPV lifetimes of several years.[325] Glass, therefore, is an ideal encapsulation material as it has a WVTR of $<10^{-5}$ g/m$^2$day.[326] Nevertheless, glass is brittle and it is not suitable for a R2R fabrication process, where flexible encapsulation materials are required. Good overviews of alternative to glass materials and corresponding fabrication methods for encapsulation of OPV devices can be found in the literature.[327, 328]
2.7. Summary

This chapter introduced the fundamentals of organic semiconductors in order to provide the background required to explain the formation of an energetic band structure. This allowed for the detailed explanation of the photovoltaic effect occurring in organic semiconductors. The challenges associated with the generation, diffusion, dissociation, transport, and collection of electron-hole pairs were addressed. Two models, *i.e.* MIM and ICT, were given to study the type of semiconductor contacts and the charge transfer kinetics at interfaces in the OPV cell stack. This led to a discussion of the importance of the energetic alignment in the device structure. The electrical characteristics of OPV devices were studied after deriving these from the equivalent circuit diagram of a PV cell. The main characteristics of a solar cell such as $J_{SC}$, $V_{OC}$, $FF$, $P_{MPP}$, $PCE$, $R_S$, and $R_{SH}$ were obtained from a typical current-voltage characterisation curve of an OPV device. Special care was taken to analyse the factors that influence these main characteristic parameters.

The chapter summarised the history of organic electron donors and electron acceptor for OPV cells, which together with novel interfacial layers have allowed for the tremendous PCE and stability improvements. Special attention was dedicated to explain the formation of fullerene-based acceptors with structural isomerism, as this characteristic is essential for achieving a favourable BHJ nano-morphology and therefore high device PCEs. Efficiencies above 11% have been reported, while device lifetimes in the order of years are plausible. The challenges associated with the use of TCO-based electrode systems and possible approaches to overcome these were discussed prior to introducing common OPV cell architectures such as regular/standard and inverted device structures. Schematic examples with respective energy band diagrams for each of them were given, in order to furthermore emphasise the importance of interfacial layers for the energy alignment in the device stack and the consequent improvements in PCE and stability, that are possible. OPV devices with multi-junction structures allowed for an increased sun light absorption, and therefore higher PCEs. The degradation mechanisms occurring in the OPV structure were also discussed. Current efforts to improve device stability and operation life time were briefly summarised, where an emphasise on the appropriate testing procedures and protocols was made.

High PCEs are meaningless if the characteristics of the device cannot be preserved after a scale-up. The requirements for fabrication of large-area OPV devices were therefore summarised. It was shown that only deposition techniques suitable for an implementation in a R2R fabrication process are applicable in the industry. Different coating, printing, and vacuum deposition techniques were therefore summarised. Considerations were made for the appropriate choice of materials and architecture of the OPV device stack, that are relevant from an industrial point of view.
3. P3HT:ICBA-based organic photovoltaics

This chapter reviews the scientific literature published to date in the field of P3HT:ICBA-based OPVs in order to benchmark the experimental results obtained in the chapters that follow. After introducing the most well-known and studied material system for OPVs, i.e. P3HT:PCBM, parallels with P3HT:ICBA are drawn, and material specific factors influencing the D/A phase separation and hence device PCE are detailed. The regio-isomerism of the ICBA molecule and the importance of the ICBA source are also studied together with the significance of the device area on the solar cell characteristics. A comparison between the operational stability of devices with P3HT and PCBM or ICBA is also carried out. The relationships between P3HT:ICBA specific properties are detailed and a comprehensive summary of reported efficiency values in the field to date is presented.

3.1. Introduction

The intrinsic properties of pristine materials play a crucial role when high device power conversion efficiencies are targeted. Due to a band gap energy of approximately 1.85 eV, the absorbance of P3HT is limited to about 675 nm, resulting in average J_Sc values of 8 mA/cm^2 to 12 mA/cm^2.[112] The highest recorded V_OC for P3HT:PCBM-based OPVs is approximately 0.66 V.[329] Adding average FF values of 50% to 65% result in moderate device PCEs of about 3.0%.[43] However, interest in P3HT remains due to the various advantages of this donor material such as low cost, wide availability with excellent material quality and high production quantities suitable for a large-area fabrication of OPVs. This has led to the synthesis of novel acceptor materials with advantageous higher lying LUMO energy levels, compared to PCBM. A prominent example is ICBA which, in a blend with P3HT allow for V_OC enhancements of up to 0.2 V and therefore improved device PCEs, as shown in initial reports on the discovery of the acceptor molecule by He et al. in 2010.[79, 80] Since then, a great deal of work has been undertaken to characterise and understand the intrinsic properties of IC_{60}BA and IC_{70}BA.

Similar to the P3HT:PCBM blend, the effect of the fabrication conditions has been shown to affect the P3HT:ICBA device performance.[161, 238, 330, 331] The incorporation of solvent additives into the D/A blend or the usage of co-solvent systems for the dispersion of the D/A
components has also been reported to alter the nano-morphology of the BHJ and influence the device PCE.[332, 333] Lastly, other approaches including patterning of the BHJ, incorporation of NPs or NWs into the BHJ, surface treatments of the BHJ, and utilisation of antireflecting coatings have been shown to positively affect device characteristics.[334, 335, 336, 337]

3.2. P3HT:PCBM – the benchmark system

As with many scientific advances, it took a few years for the community to realise the importance of the D/A BHJ discovery.[112] Since the first report in 1995, the number of publications has been increasing exponentially each year.[13] Therefore, the collection and evaluation of all published reports in the field of OPV-based devices to date is challenging. Thus, the most recent and comprehensive review of the characteristics of P3HT:PCBM-based OPVs was published in 2011 by Dang et al.[43] As shown in Figure 3.1 and Table 3.1, there is a wide spread of reported PCEs over the years that published efficiency values can vary from below 0.5% up to 6.5%. Clearly, there are numerous factors that influence the performance of P3HT:PCBM-based OPVs such as intrinsic donor and acceptor properties (see Section 2.3), D/A dispersion characteristics (i.e. material ratio and concentration; solvent choice), and the fabrication conditions used. Yet, despite the substantial research, the average PCE for P3HT:PCBM devices remains at about 3%.[43]

After nearly 15 years, P3HT:PCBM-based OPVs dominate the D/A BHJ research articles being published. This is not surprising, especially when large-area OPV modules are reported, due to the great deal of work put into understanding factors influencing the characteristics of P3HT:PCBM blends in conjunction with several advantages of P3HT, over alternative novel low band gap donor materials such as low cost, uncomplicated synthesis, controlled intrinsic characteristics, and availability in large quantities. Undoubtedly, the latter material characteristics

![Figure 3.1](image_url)

**Figure 3.1:** PCE review of P3HT:PCBM-based solar cells reported by Dang et al. Reprinted with permission from [43]. Copyright ©2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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**Table 3.1:** Bibliographic data of P3HT:PCBM-based solar cells extracted from the literature by Dang et al. Reprinted with permission from [43]. Copyright ©2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
anticipate that despite relatively low average device PCEs, compared to newer donor materials, P3HT still remains a competitive key player for the fabrication of scaled-up OPVs on a R2R web, where large material quantities at a minimised cost are required.

3.2.1. Donor/Acceptor ratio and concentration

As shown in Figure 3.2, the device performance for P3HT:PCBM blends is strongly dependent on the ratio of P3HT to PCBM and the thickness of the photoactive layer. The presence of the acceptor material in the blend should be high enough to ensure the formation of a percolated network with continuous pathways for efficient charge carrier transport towards the electrodes.[113] Yet, in P3HT:PCBM blends PCBM molecules can disturb the P3HT crystallisation and thus alter the BHJ morphology.[338, 339] This PCBM segregation process is dependent on the material concentration and could be detrimental to the device performance at high annealing temperatures, as observed by Swinnen et al.[340] Hence, as shown in Figure 3.2(a) the majority of fabricated P3HT:PCBM-based solar cells comprise balanced D/A ratios close to 1:1 by wt%, allowing device PCEs to approach 5%.[43, 341, 342] On the other hand, if the ratio of PCBM to P3HT is low, the interfacial area between the donor and acceptor phases will be reduced, leading to decreased exciton dissociation yields and hence inferior device characteristics.

Furthermore, the concentration of the P3HT:PCBM formulation affects the viscosity of the D/A ink which alters the photoactive layer thickness and device performance.[343] Figure 3.2(b) shows a theoretical calculation of the number of photons absorbed in a P3HT:PCBM layer as a function of the thickness of this layer. It can be seen that for a device with a structure of glass (1 mm)/ITO (140 nm)/PEDOT:PSS (50 nm)/P3HT:PCBM (X nm)/Al (100 nm) there are two distinctive light absorption peaks at approximate BHJ thickness of 90 nm and 210 nm.[112]
3.2.2. Solvent choice

The characteristics of the photoactive layer of P3HT and PCBM are also dependent on the intrinsic properties of the materials, and on the device fabrication conditions. The formation kinetics of the nano-morphology of P3HT:PCBM layers is furthermore dependent on the nature of the solvent used for the D/A dispersion. Thus, the boiling point and rate of evaporation of a solvent has strong influence on the distribution and arrangement between the donor and acceptor domains, as Figure 3.3 shows. The UV-vis absorption spectra of PCBM (below 400 nm) is barely influenced by the solvent choice. In contrast, the P3HT absorption is strongly dependent on the solvent used: high boiling point solvents lead to ordering and self-organisation of P3HT molecules, which cause an increased film crystallinity. Nevertheless, the removal of residual high boiling point solvents such as tetralin (THN) or 1,2,4-Trichlorobenzene (TCB) requires high annealing temperatures unsuitable with the fabrication of OPV devices on plastic substrates. Solvents such as CB and o-DCB enable a good compromise between solvent boiling point and resulting BHJ nano-morphology, leading to their wide spread usage for P3HT:PCBM blends.[43]

Solvent mixtures have also been reported to improve the device characteristics, as the use of a solvent mixture is expected to improve the dispersion of blend components, change the drying kinetics of deposited layers, and sequentially alter the D/A nano-morphology, compared to a single solvent. For example, Jin et al. studied the effect of o-DCB used against a mixture of o-DCB with CB and o-DCB with CF in a 1:1 wt% ratio for the P3HT:PCBM blend.[345] As a result, the reference device characteristics (P3HT:PCBM dispersed in o-DCB) were improved when a solvent mixture of o-DCB:CF was used but decreased in the case of o-DCB:CB.

![Normalized Absorption vs Wavelength](a)

![Boiling Points](b)

**Figure 3.3.:** Effect of the solvent choice on the P3HT:PCBM layer absorption. UV-vis spectra of solid P3HT:PCBM layers fabricated from D/A dispersions in toluene (T) and chloroform (CF) before thermal annealing (Tamb), and after thermal annealing at 175 °C for 5 min (T175) (a). Boiling points of different solvents: chloroform (CF), toluene (T), chlorobenzene (CB), ortho-dichlorobenzene (ODCB), tetralydronephthalene (THN), and trichlorobenzene (TCB) are shown in (b). Reprinted with permission from [344]. Copyright ©2011 Elsevier B.V.
Solvent additives can also be used to selectively improve the fullerene solubility and thus alter the phase segregation of the D/A blend. Typical examples of such additives are alkylthiols, oleic acid surfactants, and di-iodoalkanes. Peet et al. reported improved P3HT:PCBM photoconductivity and increased hole mobility with the incorporation of alkyl thiol molecules into the polymer/fullerene solution. In another publication, Wang et al. increased the donor and acceptor interfacial area using oleic acid. This led to improved P3HT:PCBM device PCE from 3.1% to 4.3%. Yao et al., on the other hand, studied the effect of various solvent additives on the BHJ nano-morphology. Using different characterisation techniques the authors found that the D/A phase separation can be optimised if small amounts of 1,8-octanedithiol (OT) are added to the host solvent (o-DCB). Alternatively, poly(oxyethylene tridecyl ether) (PTE) was used by Park et al. as an additive to the P3HT:PCBM blend and resulted to a PCE improvement from 3.89% to 4.41% due to an increased dissociation efficiency of bound electron-hole pairs.

3.2.3. Fabrication conditions

The properties of P3HT:PCBM BHJs can be altered and further tailored with the use of an annealing step as part of the fabrication procedure. The annealing can be differentiated by “pre-” and “post-annealing”, depending on when the annealing step was carried out: after the deposition process of the D/A blend dispersion (pre-annealing), or on the completed device prior to characterisation (post-annealing).

Pre-annealing can be further divided into a slow drying process, also known as solvent annealing (SA), or a thermal annealing step (TA). In the case of SA, the still wet D/A film is covered, usually with a petri dish, in order to increase the solvent evaporation time, which allows for the D/A molecules to rearrange and form a desired morphological network. SA has been reported to improve the hole mobility of the P3HT phase and enhance exciton generation rates. TA, on the other hand, is commonly carried out on a hot plate, where the presence of thermal energy facilitates morphological alterations of the D/A components such as rearrangement, crystallisation, phase transition, and aggregation.

Although SA can promote the formation of self-arranged material phases in the BHJ blend, thermal annealing is often additionally required in order to further improve the characteristics of P3HT-based OPVs. This is related to an improved P3HT crystallinity, enlarged PCBM domain sizes, more efficient charge transport, and enhanced light absorption in the D/A matrix, as reported by Yang et al. and Erb et al. It is worth noting that the sequence of the annealing procedure during the fabrication process is also important and can affect the device characteristics and stability. Furthermore, as shown in Figure 3.4 the temperature and duration of the TA step has to be tailored according to the D/A system used: i.e. annealing temperatures above 150 °C decrease the PCEs of P3HT:PCBM-based devices. This is usually attributed to an excess agglomeration of PCBM molecules that lead to a reduced contact area at the interface between the donor and acceptor domains, and hence, decreased exciton dissociation rates.
### 3.3. Controlling the characteristics of P3HT:ICBA-based OPVs

An examination of the literature suggests that ICBA would be an ideal acceptor material for P3HT-based OPVs, but no comprehensive review of P3HT:ICBA devices has yet been published. Therefore, an analysis of recent (2010 – 02/2017) scientific articles cited in the Thomson Reuters “Web of Science” database was undertaken. In total 191 papers were found for the search keywords “P3HT” and “ICBA” or “Indene-C”. Review papers and publications not related to the OPV field were not considered. Scientific publications were also excluded when the photoactive device area was not stated. Nevertheless, before exclusion an email was sent to the corresponding authors in order to enquire about the size of the device area. Each single paper was thoroughly examined and relevant data was fed in an Excel database. A record included 20 relevant fields such as device architecture, structure, and area, PCE with standard deviation, bibliographic information, facts about the ICBA molecule, solvents and fabrication details used for the D/A blend. Often more than one record was created for a scientific publication. In addition to the records found in the literature, the device characteristics obtained in this work were also added to the database in order to benchmark the experimental results. In total, 217 individual data points were created. Filters were used to sort the data. In addition, the role of various interfacial charge transport layers has also been considered.

#### 3.3.1. The choice of interfacial layers and annealing steps

The choice of interfacial layers for standard (or regular) and inverted device architectures is directly related to the formation kinetics of the above lying D/A layer (see Section 2.3.3). This is related to materials specific characteristics such as work function, surface roughness, surface energy, and wetting properties. In addition to these, and in a similar manner to the

![Figure 3.4:](image)
P3HT:PCBM blend, the properties of the D/A blend between P3HT and ICBA can be altered and further tailored by means of application of a “pre-” or “post-” annealing steps after the photoactive layer deposition.

Pre-annealing was carried out in the pioneering work of He et al., who first reported the fabrication of P3HT:ICBA solar cells with a device architecture of glass-ITO/PEDOT:PSS/BHJ/Ca/Al using the IC\textsubscript{60}BA molecule, which exhibits beneficial characteristics compared to PCBM such as easier synthesis, readily solubility in common organic solvents, and stronger visible absorption.[79] Owing to a 0.17 eV higher LUMO level of IC\textsubscript{60}BA compared to PCBM, a $V_{OC}$ of 0.84 V and PCE of 5.44% (0.58 V and 3.88% for PCBM) were reported. Soon after, the synthesis of IC\textsubscript{70}BA and its application in a blend with P3HT followed, as shown in Figure 3.5.[80]

In comparison to the previously reported P3HT:IC\textsubscript{60}BA fabrication conditions, where only SA of the BHJ was used, now the group carried out TA for 10 min at 150 $^\circ$C after the SA step. As confirmed by AFM studies, the additional TA was reported to induce aggregation of the fullerene molecules and rearrangement within the D/A blend leading to migration of the IC\textsubscript{70}BA molecules to the surface of the BHJ. As a result, a PCE of 5.64% (compared to 3.55% for PCBM) was reported.

After this pivotal moment for the P3HT-based solar cells, a great deal of work has been devoted to understand the formation kinetics of the P3HT:ICBA blend, while tailoring the fabrication conditions to achieve high device PCEs. Zhao et al. was the first to report a PCE of P3HT-based devices above 6%, achieved after tailoring the TA procedure.[161] Starting with a $V_{OC}$ of 0.80 V, $J_{SC}$ of 9.30 mA/cm\textsuperscript{2}, FF of 65.0%, and a PCE of 4.84% for SA only devices the group managed to improve the characteristics after gradually increasing the TA temperature up to 150 $^\circ$C, followed by a decrease in device characteristics for higher temperatures. The best device performance, with a $V_{OC}$ of 0.84 V, $J_{SC}$ of 10.61 mA/cm\textsuperscript{2}, FF of 72.7%, and a PCE of 6.48%, was ascribed to a uniform P3HT:IC\textsubscript{60}BA surface distribution and an improved D/A interpenetrating network, which benefits the exciton charge separation and transport.[161]

![Figure 3.5: J-V curves (a) and EQE (b) of P3HT-based OPVs with different fullerene derivatives as acceptors. Reprinted with permission from [80]. Copyright ©2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.](image-url)
Since then, the number of publications has been constantly increasing, with the majority reporting OPV characteristics for devices comprising standard architectures, where PEDOT:PSS is used as an HTL. Nevertheless, due to the acidic nature of the PSS component resulting in reduced device lifetimes (see Section 2.3.3), alternative anodic interfacial materials have also been explored. P-type metal oxides such as nickel acetate (NiAc), vanadium oxide (VO$_x$), tungsten oxide (WO$_3$), and chromium oxide (CrO$_x$), have been reported to successfully overcome the limitations associated with the acidic PEDOT:PSS and improve device PCEs.[218, 225, 330, 358, 359] Fan et al. used a radio-frequency magnetron sputtered MoO$_3$ and investigated the effect of SA and/or TA on the morphology of the P3HT:IC$_7$BA photoactive layers.[360] The group revealed that the phase separation in the blend is strongly dependent on the formation of IC$_7$BA crystallites, as well as their size, shape, and distribution in relation with the ordered P3HT domains. This favoured exciton separation and charge-carrier transport, and resulted in a high device PCE above 6.7%.

On the cathodic side of standard architecture devices, much has been done to replace the commonly evaporated Ca or BPhen as interfacial layers. Envisaging large-area device fabrication, solution processed alternatives have been considered. Nevertheless, due to the highly hydrophobic nature of the P3HT:ICBA blend only a few reports of successful use of metal oxides, polyethylenimines (PEIE), or conjugated polyfluorene grafted materials (see Section 2.3.3) have been published. Wang et al. reported the use of titanium(IV) oxide bis(2,4-pentanedionate) (TOPD) as an ETL for both P3HT:IC$_6$BA and P3HT:IC$_7$BA devices.[361] The main advantage of the TOPD is its solution processability in protic solvents such as isopropanol, which exhibit good wettability on top of the hydrophobic BHJ. Owing to an increased surface roughness after application of the TOPD on top of the P3HT:IC$_6$BA layer and annealing it for 15 min at 80°C (13.5 nm vs. 18.3 nm measured by AFM), the group reported device PCEs of 5.0% and 5.59% for SA only IC$_6$BA and IC$_7$BA devices, respectively. This PCE improvement, compared to devices without a TOPD ETL (PCE of 3.93%) was ascribed to an increased contact area between the buffer layer and the cathode, which may benefit charge collection at the interface and increase internal reflection and light collection, due to the higher surface roughness.[361]

The deposition of thin layers of amine-containing non-conjugated polymers such as PEIE, between the BHJ and the metal electrode, has also been shown to improve the device characteristics. Khan et al. fabricated P3HT:IC$_6$BA OPVs using a SA step only and showed a significant improvement in electron collection for glass-ITO/PEDOT:PSS/BHJ/PEIE/Al, Ag, or Au devices, compared to reference devices without a PEIE layer.[362] In the case of Al and Ag as electrodes, PCEs of 4.6±0.3% and 4.5±0.2% were measured, which were comparable to the PCEs obtained for a reference device with a Ca/Al electrode (4.6±0.1%). This was assigned to a contact improvement at the interface with the metal, caused by a surface dipole moment originating from a partial electron transfer from the amine-groups in PEIE to the metal.[362]

Liao et al., on the other hand, presented a novel polymers composed of polyfluorene grafted with a K$^+$-intercalated crown ether involving six, five, or four oxygen atoms (PFCn6:K$^+$, PFCn5:K$^+$, PFCn4:K$^+$), which can be used as an ETL.[238] As shown in Figure 3.6, it was reported that the materials provide multiple functionalities such as: (1) an optical spacer for optical interference effects and redistribution of light within the device; (2) ability to reduce
3.3. Controlling the characteristics of P3HT:ICBA-based OPVs

Figure 3.6.: Schematic illustration of the working mechanism of PFCn4-6:K$^+$ as ETL. Reprinted with permission from [238]. Copyright ©2012 American Chemical Society.

the electron-hole recombination at the interface with the cathode; (3) formation of an interfacial dipole that promotes the vacuum level of the cathode metal; and (4) enhancement of the electron conductivity. Indeed, as can be seen in Table 3.2 the PCE of devices without an ETL was increased from 3.87% up to 6.35% and 6.88% by incorporating PFCn6 and PFCn6:K$^+$ between the P3HT:IC$_{60}$BA and Al electrode. More interestingly, using different polyfluorenes as a transition layer between the BHJ and the Ca/Al electrode, the device PCE was significantly enhanced from 5.78% for the reference device up to 7.50% for a device with PFCn6:K$^+$, as shown in Table 3.2. Notably, this value represents one of the highest reported PCEs for P3HT-based OPVs and was measured for devices with a photoactive area of 0.075 cm$^2$, which were subjected to a TA step for 10 min at 150°C.

Table 3.2.: Performance of P3HT:ICBA OPVs with or without PFCn4-6:K$^+$ as an ETL. Reprinted with permission from [238]. Copyright ©2012 American Chemical Society.

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<td>PFCn5:K$^+$</td>
<td>0.88</td>
<td>11.33</td>
<td>71.2</td>
<td>7.10</td>
</tr>
<tr>
<td>ICBA, Ca/Al</td>
<td>PFCn4:K$^+$</td>
<td>0.87</td>
<td>11.12</td>
<td>69.5</td>
<td>6.72</td>
</tr>
</tbody>
</table>
The first inverted architecture P3HT:ICBA OPV with a device structure of glass-ITO/ZnO/C-PCBSD/BHJ/PEDOT:PSS/Ag was reported by Cheng et al. in 2010, who used a cross-linkable fullerene material C-PCBSD ([6,6]-phenyl-C61-butyric styril dendron ester) to induce a spontaneous vertical phase separation to the deposited photoactive layer and enrich the BHJ top surface with P3HT and the bottom contact with ICBA.[363] This advantageous D/A spacial distribution is desired for devices with an inverted architecture and no SA step was required. After carrying out a TA for 10 min at 150 °C, in addition to the use of C-PCBSD, the group reported a modulation of the electronic and orbital interactions at the interface improving the \( J_{SC} \) and resulting in a PCE of 6.22%.

Subsequently, a great deal of work has been done to improve the characteristics of inverted P3HT:ICBA solar cells. The majority of publications however, report on the replacement or tailoring of the properties of the commonly used ZnO and PEDOT:PSS or MoO\(_3\) interfacial layers on the anodic and cathodic side of the device, respectively, rather than on the effect of the SA and TA step on the P3HT:ICBA blend characteristics.

Lee et al. added the organic additives poly(vinylpyrrolidone) or diethanolamine (PVP or DEA) to a ZnO NPs solution and altered the ZnO work function by 0.4 eV through interfacial dipole formation.[364] In the case of DEA a reduced aggregation and spherical NPs formation was observed. This led to PCE improvement of up to 37% for the ZnO:PVP nanocomposite (from 3.75% to 4.11%). In both cases the devices were subjected only to a TA step for 10 min at 170 °C. Much higher PCEs were reported by Braid et al., who modified the ETL of ZnO with two types of phosphonic acids: a conjugated 2,6-difluorophenylvinylphosphonic acid (oF\(_2\)PVPA) and a non-conjugated 2,6-difluorophenylethylphosphonic acid (oF\(_2\)PEPA).[365] Prior to deposition of the BHJ, which was subjected to SA & TA (10 min/155 °C), the effective ZnO work function was modified by spin-coating ethanol solutions of oF\(_2\)PVPA or oF\(_2\)PEPA on top. A work function decrease of 0.78 eV and 0.57 eV for each solution was observed. As a result, a \( V_{OC} \) and PCE increase was noticed, which was correlated with an improvement of the quasi Fermi level alignment between the electrode and the P3HT:ICBA layer. The reported PCEs were 5.24%, 5.64%, and 5.89% for a non-modified ZnO, and modified with oF\(_2\)PVPA, and oF\(_2\)PEPA, respectively.

Other groups have looked at alternatives to ZnO. The use of TiO\(_x\), CsO\(_x\), or a bilayer of both metal oxides was reported by Zhou et al.[366] Compared to an individual TiO\(_x\) or CsO\(_x\) ETL, the combination of both led to an improved surface morphology and enhanced wetting and adhesion properties resulting in a device PCE of 5.65%, compared to 4.91% and 4.95% for a sole TiO\(_x\) or CsO\(_x\) layer. In all cases, the P3HT:IC\(_{60}\)BA layer was subjected to SA & TA (10 min/150 °C). In another approach, tetrasulfonate copper phthalocyanine (TS-CuPc) was used and an ETL resulting to rather moderate device PCE of 4.60%.[367]

The use of PEIE as an ETL has also been reported by several groups. Shim et al. used a P3HT:IC\(_{60}\)BA-based solar cell as a bottom sub cell in a tandem structured OPV. In a glass-ITO/PEIE/BHJ/MoO\(_x\)/Ag configuration, where the BHJ was SA & TA treated (10 min/150 °C), the group reported an average PCE of 4.70%.[368] Again in a tandem configuration, Kim et al. first measured slightly higher PCEs of about 4.93% using a MoO\(_3\) layer.
3.3. Controlling the characteristics of P3HT:ICBA-based OPVs

Instead, while few years later the same group managed to improve the PCE up to 5.11%.\[369, 370]\nIn both publications the P3HT:IC$_{60}$BA layer was subjected to SA & TA for 10 min at 150 °C.

Alternatives to PEDOT:PSS and MoO$_3$ have also been explored. Lee et al. reported the utilisation of either a sole WO$_x$ layer or a modification of PEDOT:PSS with WO$_x$ to serve as the HTL. The group improved the device PCE from 3.93% (PEDOT:PSS as HTL) to 4.77% (WO$_x$ as HTL) and 5.37% when the PEDOT:PSS:WO$_x$ mixture was used.\[371]\ This device PCE increase was mainly attributed to an improved FF, originating from a reduced $R_S$ and increased $R_{SH}$. In another publication, the same group achieved a further PCE increase up to 5.53% by carrying out a post annealing step for 10 min at 150 °C.\[372]\n
Novel solution processed molecular metal oxides or polyoxometalates (POM) have also been reported to act as efficient HTLs. Owing to the unique POM properties such as high degree of crystallinity and extremely low work function of 6.0 eV–6.2 eV, leading to a p-doping of the donor polymer HOMO level, Vasilopoulou et al. reported PCEs of up to 6.70% for the P3HT:IC$_{60}$BA-based devices (see Figure 3.7).\[373]\n
An interesting alternative approach was suggested by Mauger et al., who inserted thin layers of polysulfonic acids between the P3HT:IC$_{60}$BA and the PEDOT:PSS layers to create a higher concentration of acid at the interface.\[374]\ This was reported to mimic the distribution of materials present in a regular device configuration. Furthermore, upon thermal annealing of the acid oxidised P3HT layers, a thin p-type interlayer of P3HT$^+/\text{acid}^-$ was created on top of the BHJ, which acts as a doped interlayer for reducing the dark leakage current and increasing the device $V_{OC}$ and FF.

![Figure 3.7: Device structure (a) and J-V characteristics (b) for P3HT:IC$_{60}$BA-based OPVs with different POMs as the HTL. Reprinted with permission from [373]. Adapted by permission of The Royal Society of Chemistry.](image)
Figures 3.8(a) – 3.8(d) summarise the PCE values of P3HT:ICBA-based solar cells depending on the annealing step which was used for the device fabrication. The data points presented were found in the literature based on the search criteria detailed in Section 3.3. The PCEs of post-annealed devices is also included. However, the PCEs of solar cells where the P3HT:ICBA layer was fabricated with a mixed solvent system, subjected to subsequent structuring/patterning, or used in combination with an antireflective coating, are excluded. They are, however, discussed in the following sections. A star is used in Figure 3.8(d) to show the device PCE obtained in this work.

Figure 3.8.: Effect of the annealing step on the device characteristics for P3HT:ICBA OPVs subjected to: (a) no SA & no TA, (b) SA only, (c) TA only, (d) SA & TA. Square black and circle red symbols are used to distinguish the data for standard and inverted devices, respectively. A star is used in (d) to show the PCE achieved in the experimental section of this work. Device data for post-annealed OPVs is also included.
It can be seen in Figure 3.8(a) that devices not subjected to SA & TA exhibit widely spread PCEs, ranging from 0.1% to 6.43%. The lowest device PCE was reported for a solar cell with a BHJ consisting of a D/A NPs solution, which needed to be thermally annealed to improve the interfacial contact between both phases.[375] The highest efficiency was reported for devices fabricated from a D/A mixture dispersed in CB.[376] It can also be seen that the majority of fabricated OPVs comprised a regular device architecture. The average PCE based on 23 reported values in the case of no SA & no TA P3HT:ICBA devices is 3.8±1.6%.

As shown in Figure 3.8(b), the use of SA significantly improves the device PCE and based on 27 reported efficiency values an average PCE of 4.9±1.2% was calculated. This improvement is commonly ascribed to an increased device J_{SC}, originating from a higher crystallisation of the P3HT domain as described in Section 2.3.1.1. In the case of SA only solar cells, the lowest PCE of 0.95% was reported by Lin et al. for inverted devices, fabricated from a P3HT:ICBA dispersion in CB.[377]. In contrast, the highest PCE was 6.52% and was achieved mainly due to the utilization of a UV-ozone treated NiAc anode buffer layer, contributing to an improved ohmic contact between the BHJ and the anode, reducing the leakage current and improving the device V_{OC}.[330]

Figure 3.8(c) shows the PCE values found for TA only P3HT:ICBA devices. As can be seen, the annealing temperature has a substantial effect on the device characteristics. The lowest annealing temperature of 60 °C was chosen by two different groups.[378, 379] In both cases, solvents with lower boiling points compared to o-DCB such as CF and CB, were used for dispersing the photoactive layer. The highest annealing temperature of 200 °C was used by Gärtner et al., which was required to improve the interfacial contact between P3HT and ICBA NPs.[375] It is also indisputable from Figure 3.8(c), that for the majority of fabricated P3HT:ICBA OPVs a thermal annealing step at 150 °C was chosen. This can be related to the findings reported by various groups, showing that an optimal D/A phase separation is achieved after a TA step at 150 °C, usually for 10 min. Nevertheless, there is a wide spread of PCEs reported for this annealing temperature, ranging between 2.5% and 7.5%. Lastly, based on 82 reported PCE values, an average device efficiency of 4.7±1.4% was calculated.

The highest device characteristics are achieved when SA is carried out in combination with TA. An average efficiency of 5.1±1.2% was calculated based on 51 reported PCE values, as shown in Figure 3.8(d). The highest reported PCE of 7.07% was measured for a device with a photoactive area of 0.04 cm² comprising a standard architecture with a thermal annealing-free ruthenium oxide (RuO₂) anode buffer layer, mainly due to the high light transmittance in the visible range of the layer.[380] The second highest device PCE was obtained in this work for a OPV device with more than ten times larger photoactive area and is shown in Figure 3.8(d) with a star. In comparison, the lowest device PCE was only 0.34% and it was reported by Yeh et al. [337] It has to be noted that this PCE was measured over a photoactive device area of 1.09 cm². After treating the D/A surface with 1-octanol, Yeh et al. improved the PCE greatly up to 4.16%.
Post-annealing is carried out on completed devices. It aims to improve the interfacial contact between the device layers, especially after the evaporation of the top metal electrode, and is also used to regenerate degraded devices. Nevertheless, it has to be noted that in a similar manner to the pre-annealing step, the post-annealing could also introduce further morphological alterations of the device layers.

Kim et al. investigated the effect of post-annealing on glass-ITO/LZO/P3HT:IC_{60}BA/PEDOT:PSS:WO_{x}/Al devices concluding that the device characteristics were improved due to an alteration of the electrical properties of the PEDOT:PSS:WO_{x} layer (change of the surface composition of the HTL as shown with XPS).[372] As a result, the device PCE was increased from 4.47% for non-annealed devices up to 5.54% for devices post-annealed for 10 min at 150 °C. Higher annealing temperatures were also investigated. However, a reduction of the J_{SC} and device PCE was noticed.

Kumar et al. reported the regeneration of glass-ITO/PEDOT:PSS/P3HT:IC_{60}BA/Ca/Ag devices with a 50% performance restoration over several degradation/regeneration cycles of fully degraded OPVs.[381] After investigating the origins of the degradation mechanisms, the group studied the effect of the post-annealing step for subsequent thermal annealing at different time intervals and temperatures. A PCE recovery of up to 50% of the initial value and a V_{OC} increase up to 90% were achieved after the first annealing step. A systematic enhancement of all parameters due to a reversed cathodic oxidation was observed with the temperature increase, where an annealing step for 5 min at 160 °C was chosen as an optimal condition.

### 3.3.2. The solvent choice for the D/A blend

Additionally to the SA and TA steps, the choice of a solubilising agent plays a crucial role for the BHJ formation kinetics and has a direct impact on the D/A phase separation and morphology, as shown in Section 3.2.2. This becomes apparent from Table 3.3 which shows a summary of reported PCEs for different chlorinated solvents used for the P3HT:ICBA blend. Clearly, the majority of reported PCEs were measured for devices fabricated from a D/A dispersion in o-DCB (141 reported PCE values). In comparison, only a tiny fraction of 16, 9, and 6 reported PCE values were found for devices fabricated from CB, a solvent mixture of o-DCB:CB, and CF. Here, Cheng et al. achieved high device PCEs without the use of any SA or TA annealing steps by replacing the commonly used o-DCB with CB as a P3HT:IC_{60}BA blend solvent.[376] This, in combination with tailoring the interfacial layer (MoO_{3}) characteristics such as thickness, surface morphology, transmittance, and film quality, led to PCE of 6.43%. Vasilopoulou at al., on the other hand, also used CB for the D/A blend dispersion, however they utilised solution processed POMs as a HTL and reported PCEs for P3HT:IC_{60}BA devices up to 6.7%.[373] However, despite those high PCEs, the average reported device efficiencies lye at rather moderate values of about 4.2%.[364, 382, 383, 384] A higher average PCE value of 4.6±0.9% was calculated when a mixture of o-DCB:CB was used. Chloroform has also been chosen as a solvent for the P3HT:ICBA blend by a few groups resulting in average PCEs of about 4.3%.[379, 381]

Currently, the focus is shifting away from environmentally unfriendly and toxic chlorinated solvents such as o-DCB, CB, and CF towards the so-called “green solvents” (halogen-free). The
3.3. Controlling the characteristics of P3HT:ICBA-based OPVs

Table 3.3: P3HT:ICBA device PCEs depending on the used chlorinated D/A solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Average PCE (%)</th>
<th>Maximum PCE (%)</th>
<th>Number of publications</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-DCB</td>
<td>4.9±1.3</td>
<td>7.5 [238]</td>
<td>141</td>
</tr>
<tr>
<td>CB</td>
<td>4.2±1.8</td>
<td>6.7±0.2 [373]</td>
<td>16</td>
</tr>
<tr>
<td>o-DCB:CB</td>
<td>4.6±0.9</td>
<td>6.1 [385]</td>
<td>9</td>
</tr>
<tr>
<td>CF</td>
<td>4.3±0.6</td>
<td>5.5±0.1 [386]</td>
<td>6</td>
</tr>
</tbody>
</table>

research has focussed on environmental friendly fabrication of OPVs using halogen-free solvents for the dispersion of the photoactive organic materials. Prominent examples are toluene, isomers of xylene (o, m, or p), anisole, 1,2-dimethylnaphalene, alcohol, or water.[387, 388, 389, 390] Oh et al. reported the fabrication of OPVs with an enhanced air stability due to a reduced P3HT photooxidation behaviour of the BHJ.[391] This was ascribed to the utilization of single P3HT crystalline nanofibris, which were fabricated in a m-xylene solution. Using the same solvent for the P3HT:IC60BA dispersion, the increased air stability was ascribed to a tight π-π staking in the donor phase, which reduces the permeation of oxygen and water into the nanofibris. The PCE of the devices (4.2%) maintained more than 80% of its initial value after 30 days.

Ulum et al., on the other hand, used an aqueous NP dispersion of P3HT and IC60BA to investigate the miscibility properties of polymer:fullerene blends.[392] Upon annealing, a highly intermixed BHJ blend was formed, which was ascribed to an enhanced miscibility of ICBA in crystalline P3HT improving the device PCE from 1.3% up to 2.5%.

A direct comparison of the P3HT:IC60BA device characteristics with respect to the BHJ solvent choice was carried out by Guo et al.[393] As can be seen in Table 3.4, the suggested less-harmful non-halogenated solvents can substitute for the use of o-DCB and comparable PCEs were reported. In the case of toluene, the device performance was even increased, compared to the reference device processed using o-DCB. This was assigned to a high ICBA solubility in toluene (94.5 mg/mL) in conjunction with an optimised BHJ morphology and phase separation, as shown by AFM studies.[393]

Possibly the most environmentally friendly fabrication of P3HT:IC60BA-based solar cells was proposed by Gärtner et al., who synthesised D/A NPs solutions using a surfactant-free precipitation method in methanol.[375] To achieve a more intimate contact between the NPs and hence produce better charge carrier extraction, the group annealed the photoactive layers after deposition at temperatures from 100 °C to 200 °C. As a result, average PCEs of 3.9±0.1% were reported. In another publication, the same group reported the use of ethanol for the organic NP dispersions.[394] Interestingly, for the fabrication of the OPVs, deposition techniques such as doctor-blading and ink-jet printing were employed, emphasising the possibility for large-area device fabrication. Indeed, compared to the majority of device areas reported for P3HT:ICBA-based OPVs (< 0.1 cm²), Sankaran et al. reported device PCEs of 3.4%, measured for active device areas of 1.1 cm².[394]
Table 3.4: P3HT:IC<sub>60</sub>BA device characteristics with respect to the processing solvent. Adapted with permission from [393]. Copyright ©2014 American Chemical Society.

<table>
<thead>
<tr>
<th>Processing solvent</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>PCE average (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-DCB</td>
<td>0.86±0.03</td>
<td>7.0±0.2</td>
<td>66±1</td>
<td>3.8</td>
</tr>
<tr>
<td>toluene</td>
<td>0.84±0.03</td>
<td>7.2±0.2</td>
<td>71±1</td>
<td>4.4</td>
</tr>
<tr>
<td>o-xylene</td>
<td>0.85±0.03</td>
<td>6.3±0.2</td>
<td>72±1</td>
<td>3.8</td>
</tr>
<tr>
<td>m-xylene</td>
<td>0.85±0.03</td>
<td>6.4±0.2</td>
<td>71±1</td>
<td>3.8</td>
</tr>
<tr>
<td>p-xylene</td>
<td>0.83±0.03</td>
<td>7.1±0.2</td>
<td>67±1</td>
<td>3.8</td>
</tr>
</tbody>
</table>

3.3.3. The mixed solvent approach

The device PCE for P3HT:ICBA-based OPVs is strongly dependent on the fabrication conditions and solvent choice for the D/A blend. High device efficiencies are commonly reported for devices subjected to a SA step. However, this annealing step requires a long time to complete and is therefore unsuitable for high throughput fabrication of large-area OPVs. As the SA step is necessary for controlling the D/A morphology and phase separation, alternative approaches to achieve the same goal are required.

A convenient way to form a desired D/A morphology is to use a solvent additive in conjunction with the main solvent for the D/A blend dispersion. In most cases the solvent additive is a material with a higher boiling point, compared to the host solvent, with selective solubility characteristics tailored for one of the D/A materials.

The pioneering work of Guo et al. investigated the effect of various solvent additives on the blend characteristics of P3HT:IC<sub>70</sub>BA.[333] Four solvent additives, i.e. 1,8-diiodooctane (DIO), 1,8-octanedithiol (OT), N-methyl pyrrolidone (NMP), and 1-chloronaphthalene (CN), were used in conjunction with the host solvent o-DCB. It can be seen from the UV-vis absorption spectra in Figure 3.9(a) that layers with additives show stronger absorption in the visible wavelengths. An additional red shift of the absorption spectra was observed for CN. As seen in Figure 3.9(b) and summarised in Table 3.5, the use of additives increases the device J<sub>SC</sub> and FF. More ordered P3HT structure and favourable phase separation, in addition to improved surface roughness, leads to high device PCEs. Indeed, a PCE of 7.4% was reported for TA only devices when CN was used, which represents one of the highest reported efficiencies for P3HT:ICBA-based solar cells to date. Later, the same group reported on the use of the environmentally friendlier solvent toluene for the BHJ dispersion (compared to o-DCB), in combination with NPM as an additive solvent.[393] By using 1% of the additive, Guo et al. achieved an increased P3HT aggregation and crystallinity and a nanoscaled interpenetrating network of P3HT and ICBA resulting in device PCE improvement from 4.4% to 6.4%.

Wu et al. used a different organic additive: 2,3-pyridinediol (PD) which was reported to improve device characteristics without the need of any annealing steps during the fabrication procedure.[395] It was believed that PD acts differently to other additive substances and interacts with both BHJ components, while forming an optimal vertical D/A distribution and facilitating charge transport. This led to PCE improvement from 3.35% up to 5.93%.[395] In
3.3. Controlling the characteristics of P3HT:ICBA-based OPVs

Figure 3.9.: Effect of the solvent additive (DIO: 1,8-diiodooctane; OT: 1,8-octanedithiol; NMP: N-methyl pyrrolidonel; and CN: 1-chloronaphthalene) on (a) the P3HT:IC\textsubscript{70}BA blend absorption spectra and (b) the device characteristics. Reprinted with permission from [333]. Adapted by permission of The Royal Society of Chemistry.

Another publication, the same group reported device PCEs of about 6.4%.[396] However, this time they carried out both SA & TA on the P3HT:ICBA blend. After conducting a detailed characterisation of the BHJ characteristics, Chang \textit{et al.} concluded that the origin of the PCE increase is due to an improved exciton dissociation yields caused by a greater D/A junction interface and a balanced mobility of charge carriers in the blend.[396]

Other groups have also reported the use of CN as an additive solvent. Angmo \textit{et al.} used 0.3 vol\% of CN in addition to the host solvent CB to improve the printability of P3HT:ICBA.[397] Interestingly, despite the rather low reported device PCEs of about 2.26\%, it has to be mentioned that the devices were fully solution processed using a fabrication procedure directly applicable to a R2R fabrication line. Moreover, Angmo \textit{et al.} are one of the few groups reporting device PCEs on areas greater than 1 cm\textsuperscript{2}. Bannok \textit{et al.} also used CN as an additive to CB, but in 1.5 vol\%.[398] Looking at the influence of the polymer purification (P3HT) on the device PCE, they reported much greater PCE of about 6.6\%, however this efficiency was measured over a small device photoactive area of 0.06 cm\textsuperscript{2}. Again, on small areas (0.045 cm\textsuperscript{2}) and using 3 vol\% of CN in addition to o-DCB, Yan \textit{et al.} reported a P3HT:IC\textsubscript{60}BA device PCE of 5.84\%.[399] The use of

Table 3.5.: Performance of P3HT:IC\textsubscript{70}BA OPVs with or without solvent additives. Reprinted with permission from [333]. Adapted by permission of The Royal Society of Chemistry.

<table>
<thead>
<tr>
<th>Solvent additive</th>
<th>V\textsubscript{OC} (V)</th>
<th>J\textsubscript{SC} (mA/cm\textsuperscript{2})</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without</td>
<td>0.87</td>
<td>7.76</td>
<td>61.1</td>
<td>4.12</td>
<td>1.27</td>
</tr>
<tr>
<td>DIO</td>
<td>0.86</td>
<td>10.11</td>
<td>69.0</td>
<td>6.00</td>
<td>0.55</td>
</tr>
<tr>
<td>OT</td>
<td>0.88</td>
<td>10.54</td>
<td>68.4</td>
<td>6.34</td>
<td>0.59</td>
</tr>
<tr>
<td>NMP</td>
<td>0.86</td>
<td>11.53</td>
<td>72.6</td>
<td>7.21</td>
<td>0.47</td>
</tr>
<tr>
<td>CN</td>
<td>0.87</td>
<td>11.35</td>
<td>75.0</td>
<td>7.40</td>
<td>0.43</td>
</tr>
</tbody>
</table>
4-bromoanisole (BrAni) as a solvent additive resulted in reduced J<sub>SC</sub> values (9.82±0.04 mA/cm<sup>2</sup> vs. 11.42±0.06 mA/cm<sup>2</sup> for CN) and hence a device efficiency of 4.83%. In both cases, the PCE was increased compared to a reference device without any additive (PCE of 4.43%). This increase was attributed to an improved J<sub>SC</sub> due to reduced trap-assisted recombination processes and better charge carrier transport, as proven by AFM and transient photocurrent measurements.

Figure 3.10 shows a summary of all reported PCE values found in the literature for P3HT:ICBA-based solar cells, where the mixed solvent approach was used. At a first look it appears that there is a wide discrepancy between the reported PCE values. However, reference 1 and 2 represent the same solar cell, with the only difference being that in reference 2 the device was not subjected to TA.[333] In a similar manner, the PCE for reference pairs 3 and 4, 5 and 6, 12 and 13 varies with respect to the TA step. For the reference pair, 15 and 16, the difference is the weight ratio between the donor and acceptor materials, in addition to the fact that the device area was 1 cm<sup>2</sup>.[397] Subsequently, the figure highlights that some of the highest reported PCEs are accomplished after tailoring the phase separation and morphology of the P3HT:ICBA blend, in particular using CN and NMP as solvent additives. In addition, considering the fact that the slow SA process was not carried out on these devices, it appears that the use of a mixed solvent system can pave a way towards the high throughput fabrication of large-area OPVs on a R2R web. However, it has been reported that additives destabilise the D/A morphology in the long term, leading to a reduced OPVs operational times.[290]
3.3. Controlling the characteristics of P3HT:ICBA-based OPVs

3.3.4. ICBA source

Assuming a straightforward and reproducible synthesis process of high purity (>99%) fullerene derivatives such as ICBA, it is also expected that respective PCEs will not vary significantly, regardless of the ICBA source. This assumption should apply, especially when a well studied polymer such as P3HT is used as the donor material for the photoactive blend. It has already been shown in the previous sections, that P3HT:ICBA device characteristics vary depending on the fabrication conditions. However, even in this case it is expected that regardless of the ICBA origin, similar average device characteristics should be reported.

Figure 3.11 shows a summary of single and average device PCEs reported for ICBA batches obtained from various sources. It is obvious that the largest number of publications, as well some of the highest reported PCEs, were measured for self synthesised ICBA. It is worth noting that the majority of publications come from the group of Yongfang Li, who first synthesised the material and used it as an acceptor in combination with P3HT for fabricating OPV devices. The average PCE achieved with self synthesised ICBA is about 5.4% and is the highest value, compared to any other average PCEs shown in Figure 3.11. There are also numerous publications where the ICBA source has not been detailed and the average PCE is about 4.7%. Nevertheless, it has to be mentioned that for the highest reported PCE to date, the ICBA source is unclear. Looking at commercially available ICBA materials, the majority of groups used ICBA purchased from Lumtec followed by Nano-C, Plextronics Inc, and so on whereas only one group each used ICBA from Frontier Carbon, Rieke Metals, MRT, and UniRegionBio-Tech. The highest PCE for a commercially sourced ICBA was achieved with a material from Lumtec, while the second best device PCE was obtained in this work with a ICBA batch from 1-Material. Although the fabrication of devices and their performance varies from group to group, there is an obvious trend for lower average PCEs when ICBA originates from commercial sources (average PCE of 4.0±1.3%). This puts in question the intrinsic characteristics of the material itself, which arguably could be a determining factor influencing the device PCEs.

3.3.5. Isomers of ICBA

As already inferred in Section 2.3.2, current synthetic routes to fullerene bis-adducts inevitably generate a mixture of RIs, with only a few reports of producing isomerically pure compounds available. This structural isomerism leads to morphological and energetic disorder (different fullerene RIs exhibit dissimilar electronic energy levels and molecular packing), which can alter the D/A nano-morphology and therefore affect the electron mobility in the photoactive region and consequently the OPV device characteristics.[173, 174, 175]

Currently, there is a lack of full understanding how the fabrication conditions affect the formation kinetics of the P3HT:ICBA blend. This is due to the complexity of the ICBA molecule, which has regio-isomeric properties that influence the BHJ formation and therefore the OPV device characteristics. The groundwork in the field was laid by Wong et al., who isolated and characterised a single RI of IC$_{70}$BA and compared its performance to regio-isomeric mixtures of IC$_{70}$BA in P3HT-based OPVs.[400] Using HPLC for the separation process, the group carried out a detailed characterisation of the isolated fractions and managed to assign the regio-isomeric
3.3. Controlling the characteristics of P3HT:ICBA-based OPVs

Figure 3.11: Power conversion efficiency of P3HT:ICBA-based OPVs in respect to the ICBA origin. Square black and circle red symbols are used to distinguish the data for standard and inverted devices, respectively. A star is used to show the PCE achieved in the experimental section of this work. Blue diamonds show the average PCE for each ICBA source with respective standard deviation bars.

2 o’clock geometric structure to one of them. The RI was used to fabricate solar cells in combination with P3HT and displayed a PCE of 5.9±0.25% compared to 4.7±0.35% for the original ICBA mixture. It is interesting to note, that all isolated fractions were tested and the devices fabricated with them exhibited various PCE values, inferring that different regio-isomeric mixtures exhibit dissimilar intrinsic characteristics, which consequently define the BHJ characteristics.

In a similar manner, Hu et al. managed to separate two IC70BA RIs, however the group did not assign them to any particular regio-isomeric geometrical structure. [401] Nevertheless, P3HT:ICBA-based OPVs were fabricated, although showing lower device PCE for both isolated RIs compared to the IC70BA mixture (2.80% and 3.18% vs. 3.23%).

Isomers of IC60BA have also been investigated. The group of Zhao et al. isolated single regio-isomeric crystalline IC60BA molecules and used them to fabricate OPVs in order to compare their performance to that of the pristine IC60BA mixture. [402] Despite elevated LUMO energy levels and higher electron mobility compared with the mixture of RIs, devices with the isolated crystallites exhibited inferior PCEs. This was ascribed to apparent large-scale fullerene aggregation, resulting in excessive phase separation, a reduced exciton dissociation, and charge carrier transportation yields.

Recently, in a follow up publication Wong et al. succeeded in separating and identifying all possible geometrical RIs of IC70BA. [403] Figure 3.12 and Table 3.6 show the experimental results. The highest device PCE of 5.2% was measured after using one of the geometric 2
3.3. Controlling the characteristics of P3HT:ICBA-based OPVs

Figure 3.12: J-V curves of P3HT-based OPVs containing different regio-isomeric fractions of IC\textsubscript{70}BA: 5 o’clock RI–fractions 2 and 3; 2 o’clock RI–fractions 4, 9-1, and 9-2; 12 o’clock RI–fraction 11.[403]

<table>
<thead>
<tr>
<th>IC\textsubscript{70}BA fraction</th>
<th>(V_{OC}) (V)</th>
<th>(J_{SC}) (mA/cm(^2))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix. of RIs</td>
<td>0.82</td>
<td>8.6</td>
<td>64</td>
<td>4.5 ±0.25</td>
</tr>
<tr>
<td>0</td>
<td>0.80</td>
<td>8.1</td>
<td>66</td>
<td>4.4 ±0.20</td>
</tr>
<tr>
<td>3</td>
<td>0.76</td>
<td>8.0</td>
<td>50</td>
<td>3.1 ±0.30</td>
</tr>
<tr>
<td>4</td>
<td>0.74</td>
<td>3.9</td>
<td>34</td>
<td>0.9 ±0.40</td>
</tr>
<tr>
<td>9-1</td>
<td>0.78</td>
<td>8.2</td>
<td>55</td>
<td>3.6 ±0.25</td>
</tr>
<tr>
<td>9-2</td>
<td>0.82</td>
<td>9.3</td>
<td>68</td>
<td>5.2 ±0.15</td>
</tr>
<tr>
<td>11</td>
<td>0.72</td>
<td>5.7</td>
<td>44</td>
<td>1.8 ±0.30</td>
</tr>
</tbody>
</table>

Table 3.6: Performance of P3HT-based OPVs with different regio-isomeric fractions of IC\textsubscript{70}BA used as acceptor materials for the photoactive layer: 5 o’clock RI–fractions 2 and 3; 2 o’clock RI–fractions 4, 9-1, and 9-2; 12 o’clock RI–fraction 11.[403]

o’clock RI of IC\textsubscript{70}BA (fraction 9-2). Interestingly, using a different geometric isomer of the 2 o’clock RI resulted in inferior PCEs of 3.6% and 0.9% (fractions 9-1 and 4). This result suggests, that the device PCE is not solely dependent on the type of RI, but rather on the geometric arrangement of the indene addends for a particular RI. Similar results were observed for fractions 2 and 3, which correspond to the geometric isomer of the 5 o’clock RI. As can be seen in Table 3.6 that despite similar \(J_{SC}\) values of 8.1 mA/cm\(^2\) and 8.0 mA/cm\(^2\) for the latter fractions, a \(V_{OC}\) and FF difference of 40 mV and 16% were reported. Hence, device PCEs of 4.4% and 3.1% were calculated when fraction 2 and 3 were used. In the case of the 12 o’clock RI, the performance of only one geometric isomer is reported, which is much lower compared to the reference device, consisting of a mixture of the RIs (1.8% vs. 4.5% for fraction 11 and the mixture). It becomes clear that material purity and crystallinity affect the BHJ formation and are essential for determining the PCE of P3HT:IC\textsubscript{70}BA-based OPVs. In addition, these results can be directly related to the observations made in Figure 3.11, where a large variation of PCEs with respect to the ICBA source, was reported.

3.3.6. Further P3HT:ICBA device optimisation

It is possible to achieve further tailoring of the P3HT:ICBA blend characteristics by incorporation of a ternary compound (organic/inorganic) or by improving the light distribution within the device structure (i.e. structuring/patterning of the BHJ and/or surrounding media).

Chen et al. used the conjugated polymer polyvinylcarbazole (PVK) to impede the clustering of crystalline ICBA molecules and improve the phase separation in the P3HT:IC\textsubscript{60}BA blend.[404] Using 13 wt% of PVK, complimentary to the D/A blend components, an improved device \(J_{SC}\) and \(V_{OC}\) was reported. This led to a PCE improvement from 2.2% (no PVK) up to 4.5% (with PVK). In a similar approach, but using a DCB/CB co-solvent, Lin et al. managed to improve the device PCE from 2.6% to 3.81%.[405]
Low bandgap IR copolymer sensitisers such as Si-PCPDTBT have also been used for the BHJ blend in order to tackle the narrow absorption window of the P3HT:IC_{60}BA system.\cite{406} Nevertheless, the use of P3HT was crucial, as it serves as an efficient transport matrix which allows one to overcome dominant recombination losses in photoactive blend. In this regard, adding 20 wt\% of Si-PCPDTBT to the P3HT:IC_{60}BA blend, improved the device $J_{SC}$ and FF from 7.9 mA/cm$^2$ and 60.1\% to 10.0 mA/cm$^2$ and 64.9\%, respectively. This increased the PCE from 3.9\% to 5.1\%.

Higher exciton dissociation yields and charge transport properties have also been observed when hybrid nanomaterials such as quantum dots (QD) and n-doped CNT (NCNT) were synthetically incorporated into the P3HT:ICBA BHJ.\cite{385} A substantial device performance improvement from 4.48\% to 6.11\% was reported, owing to an improved exciton dissociation by promoting electron transfer due to the InP QDs, while the NCNTs enhanced the transport of the separated electrons and eventual charge collection.

Zhang et al., on the other hand, incorporated carbon nanoparticles (CNP) in different concentrations into the P3HT:IC_{60}BA blend and observed an improvement of the PCE.\cite{335} The latter was primary ascribed to an initial increase in charge carriers due to a homogeneous interpenetrating D/A network, which benefits charge carrier transport and reduces charge recombination processes. An increased absorption caused by a scattering effect in the photoactive layer was also observed. As a result, the device PCE was increased by 43\% (from 4.12\% to 5.90\%) for a CNP concentration of 3 wt\%.

Alternatively, some groups have worked on tailoring the interfacial layer characteristics in order to increase the interaction between the photoactive layer and the surrounding layers. Yu et al. fabricated one dimensional distributed Bragg reflectors (1D DBR) composed of N pairs of WO$_3$/LiF layers, which reflected the incident light back to the device due to a well matched high reflectance range with the photoactive layer.\cite{407} After using eight 1D DBRs, the group managed to increase the $J_{SC}$ of a semi-transparent device from 6.21 mA/cm$^2$ to 7.59 mA/cm$^2$, which resulted in 24\% PCE enhancement.

Similarly, nanoimprinted PEDOT:PSS gratings have been used to improve the light harvesting and contact area between the HTL and the P3HT:IC_{60}BA layer.\cite{408} In addition, the imprinted PEDOT:PSS gratings were reported to activate hole and electron conducting pathways and induce a favourable ICBA phase separation, improving the characteristics of the device. This resulted in a 38.4\% $J_{SC}$ increase in the case of 600 nm wide gratings and a PCE of 5.5\%, compared to 4.11\% for the reference device without nanoimprinted gratings.

The utilisation of biomimetic nanoarchitectures allows for improving OPV device characteristics, especially the $J_{SC}$, due to an enhanced light harvesting in the solar cell. Using biomimetic moth-eye nanostructures composed of two-dimensional hexagonal periodic grating arrays on the surfaces of both the ETL (ZnO) and the photoactive layer (P3HT:IC_{60}BA), Leem et al. increased the device photocurrent by more than 22\%.\cite{409} The structures were prepared by a simple and cost-effective soft imprint nanopatterning technique, as shown in Figure 3.13(a). The group investigated different periods of gratings for the ZnO and photoactive layer as shown in Figure 3.13(b), concluding that periods of 380 nm for ZnO and 650 nm for the
3.3. Controlling the characteristics of P3HT:ICBA-based OPVs

BHJ contribute to the highest light absorption improvement within the fabricated solar cells. Due to the improved light path length, strong light scattering of reflected light from the metal layer, and surface plasmon resonance (SPR) effects, the $J_{SC}$ of the device was considerably increased from 10.9 mA/cm$^2$ to 13.3 mA/cm$^2$, whilst the PCE was improved from 5.12% to 6.28%.

In a similar approach, Chen et al. improved the P3HT:IC$_{60}$BA photocurrent by more than 24% by using a gradient shaped photoactive layer and an antireflective (AR) coating.[334] An efficient light trapping was reported and attributed to advantages of the photoactive layer such as broad distribution in wavenumber (periodicity) and random directionability (no preferred orientation). The photonic enhancement of light harvesting was experimentally and theoretically supported. It was ascribed to a collective excitation and hybridisation of several factors such as geometric effect on light scattering induced by the biomimetic nanostructured photoactive layer with continuously tapered morphology, SPR caused by the corrugated metallic back electrode, and the AR effect. These factors contributed to a device PCE improvement, as shown in Table 3.7, and the highest PCE reported to date for a P3HT:ICBA-based device of 7.86±0.25%.

![Figure 3.13.](image)

(a)

(b)

Figure 3.13.: Schematic of the fabrication sequence for a full moth-eye configuration (a): (i) Preparation of ITO substrates, (ii) spin coating of sol–gel derived ZnO precursor layers, (iii) nanopatterning process of ZnO layers via PDMS stamps, (iv) moth-eye architecture on ZnO layers, (v) nanopatterning process of photoactive layers via PDMS stamps, (vi) moth-eye architecture of photoactive layers, (vii) thermal evaporation of MoO$_3$ with Ag electrode. (b) 40°-tilted oblique-view SEM images of the OPV device with photoactive gratings for different periods of 380 nm, 500 nm, 650 nm, and 840 nm at the ZnO (P380) gratings. Adapted with permission from [409]. Copyright ©2015 American Chemical Society.

Table 3.7.: Photovoltaic parameters of P3HT:IC$_{60}$BA OPVs with or without biomimetic photoactive layer and antireflective coating. Adapted with permission from [334]. Copyright ©2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat (control)</td>
<td>0.83±0.01</td>
<td>12.20±0.08</td>
<td>64.39±1.03</td>
<td>6.43±0.12</td>
</tr>
<tr>
<td>Flat+AR</td>
<td>0.83±0.01</td>
<td>12.63±0.15</td>
<td>64.07±1.03</td>
<td>6.68±0.12</td>
</tr>
<tr>
<td>Bio-AL</td>
<td>0.83±0.01</td>
<td>14.61±0.25</td>
<td>61.92±1.15</td>
<td>7.55±0.25</td>
</tr>
<tr>
<td>Bio-AL+AR</td>
<td>0.83±0.01</td>
<td>15.16±0.25</td>
<td>62.05±1.18</td>
<td>7.86±0.25</td>
</tr>
</tbody>
</table>
3.4. The significance of the device photoactive area

Device characteristics can be artificially boosted by not using an aperture mask during the J-V characterisation, not considering the dark diode aperture area, or negating the resistance of the ITO, which plays an essential role for scaled-up OPVs.[88, 410] As a result, if the measurement technique is not correctly applied at small areas (<0.1 cm²), the PCE measurement error is considerable, and can lead to overestimation. Therefore, it is arguable whether high PCE values, measured over small device areas, are feasible for up-scaled device areas.[92, 411]

Figure 3.14 shows reported PCE values for P3HT:ICBA-based OPVs depending on the respective photoactive area over which the efficiencies were measured. In addition, the number of reported PCE values is presented with blue bars in a 0.01 cm², 0.02 cm², and 0.1 cm² steps for device photoactive areas between 0.0 cm²–0.2 cm², 0.2 cm²–0.5 cm², and thereafter. From Figure 3.14 it is obvious that the majority of PCEs reported for both standard (black squares) and inverted (red circles) devices were measured over photoactive device areas rarely exceeding 0.1 cm². In fact, the average area for OPVs with a regular architecture is only 0.08 cm², compared to 0.23 cm² for inverted devices, respectively. There are no reports of devices with areas between 0.5 cm²–0.9 cm² followed by handful devices with a photoactive area above 1 cm². It can be seen that only inverted devices have been fabricated on large areas. This is ascribed to better suitability of the inverted device architecture to be fabricated using large-scale coating and printing techniques, compared to the standard architecture.

Figure 3.14: Power conversion efficiency of P3HT:ICBA-based OPVs in respect to the device photoactive area and the number of publications. The device photoactive area is represented with a base-10 log scale. Square black and circle red symbols are used to distinguish the data for standard and inverted devices, respectively. Stars are used to show the PCEs achieved in the experimental section of this work. Blue bars are used to show the number of publications for a particular device photoactive area size.
3.5. Operational stability

The highest reported PCE of 7.86% for P3HT:ICBA-based OPVs with a photoactive area of up to 0.1 cm$^2$ was achieved in an inverted device architecture; after an enhanced light harvesting due to a nanostructuring of the photoactive layer and the utilisation of an antirefective coating.\[390\] In comparison, in a regular device architecture the highest reported PCE value is 7.5%.\[388\] Interestingly, the number of publications on devices with a photoactive area of 0.04 cm$^2$ is surprisingly high. This may be due to the fact that many of the publications in the field of P3HT:ICBA-based solar cells originate from the group who actually synthesised the acceptor material, and hence dominate over any other research group in terms of published papers. The highest PCE for devices with a photoactive area between 0.4 cm$^2$–0.9 cm$^2$ was 6.74% and was achieved in this work after studying the morphological packing of P3HT:IC$_{70}$BA blends consisting of different mixtures of RIs. The highest PCE for a device with a photoactive area above 1 cm$^2$ was 4.71%.\[337\] There is a general trend for reduced device PCEs with the increase in the device area. This is confirmed by the moderate PCE of 0.52% measured for a device with a photoactive area of 5.4 cm$^2$, which was also fabricated in this work. However, compared to the majority of all other OPVs in Figure 3.14, the large-area P3HT:ICBA-based solar cell in this work was processed by using a R2R compatible coating technique for the deposition of the ETL and D/A blend.

3.5. Operational stability

Factors limiting the stability of OPVs such as metastable morphology, diffusion of electrodes and buffer layers, oxygen and water, irradiation, heating, and mechanical stress, as well as strategies to overcome those determinants have been extensively discussed in Section 2.5. However, in the special case of P3HT:ICBA-based OPVs, there seems to be a lack of comprehensive characterisation of all factors reducing stability. The publications found in the literature concentrate mainly on the metastable D/A morphology, diffusion of electrodes, and instability of buffer layers.

3.5.1. Photooxidation of the P3HT:ICBA blend

One of the first studies on the impact of blending P3HT with different electron acceptors including ICBA, was published by Tromhold et al.\[412\] A rigorous analysis presented the influence of the optical density (thickness) of different materials combinations on the photochemical stability (P3HT as a donor material and C$_{60}$, PC$_{60}$BM, PC$_{70}$BM, IC$_{60}$BA, or bis-PC$_{60}$BM as acceptor materials).

As shown in Figure 3.15(a), the degradation rate of single electron acceptors was investigated by comparing their peak absorption in the range of 300 nm–350 nm. A relationship between the oxidation potential of the material, and hence the HOMO level of the acceptor, with the photochemical stability was expected. It was observed that all acceptors exhibited an exponential increase in degradation rates with increasing absorbance. PC$_{60}$BM and PC$_{70}$BM showed higher stability compared to bis-PC$_{60}$BM and IC$_{60}$BA.
Figure 3.15.: Absorbance resolved degradation rates for (a) different acceptors and (b) pure regio-regular P3HT blended with different electron acceptors. Reprinted with permission from [412]. Copyright ©2012 Royal Society of Chemistry.

The stability of the acceptors in a photoactive blend with P3HT is shown in Figure 3.15(b). In a similar manner to the single acceptors, there is an exponential decrease of the degradation rate with the increase in absorbance. However, a variation between the degradation rates was noticed, which in the case of the most stable blend (P3HT:C\textsubscript{60}) vs. the most unstable blend (P3HT:IC\textsubscript{60}BA) was one order of magnitude. The magnitude of stabilisation was in direct correlation with the energy gap between the LUMO levels of the donor and acceptor. Hence, the utilisation of IC\textsubscript{60}BA was reported to destabilise the blend the most. However, it has to be noted that this study did not consider several parameters that influence the photochemical degradation rates such as morphology, phase segregation, and crystallinity of the blend, in addition to the fabrication conditions and solvents used.

In a direct comparison, Endale \textit{et al.} studied the photodegradation of PC\textsubscript{60}BM and IC\textsubscript{60}BA in a BHJ blend with P3HT using spectroscopic and electrical measurements methods[413]. The study revealed that the air stability of the devices with PC\textsubscript{60}BM is much better compared to that of IC\textsubscript{60}BA. This was ascribed to accelerated physical and chemical degradation in the case of IC\textsubscript{60}BA such as reduced light absorption, increased Rs, and decreased hole mobility. A possible explanation was given with regards to the lower electron affinity of IC\textsubscript{60}BA, which was anticipated to boost the photooxidation of the molecule.

Yamane \textit{et al.} compared the photooxidation of IC\textsubscript{60}BA to that of IC\textsubscript{60}MA.[383] Using MALDI-TOF MS and IR spectroscopic analysis, the group revealed that irradiation causes the generation of carbonyl substituents in the fullerene cages. Due to a higher lying HOMO level for ICBA, compared to ICMA, the oxidation rate of the bis-adduct acceptor was also faster than the mono-adduct. P3HT-based OPVs with separately irradiated and hence photooxidised ICBA solution were fabricated showing almost zero PCE when a five hours irradiated ICBA solution was used, compared to 3.7% PCE for non-oxidised ICBA.
3.5. Insufficient photostability and diffusion of buffer layers

The majority of reports on inverted P3HT:ICBA-based solar cells utilize ZnO as an ETL, despite the known photostability issues of this buffer layer, as discussed in Section 2.3.3. Nevertheless, MacLeod et al. recently revealed that the operational stability of two different ZnO precursors can be greatly improved by means of using dipolar phosphonic acid (PA). After modifying the ZnO surface with PA, interstitial Zn\textsubscript{i} defects and their subsequent interactions with the adjacent P3HT:IC\textsubscript{60}BA photoactive layer were passivated, reducing the photooxidation at the interface. As a result, improved and more stable device $V_{OC}$ and FF were observed after 640 h of characterisation leading to a PCE reduction of less than 30% for the PA modified ZnO device, compared to 62% for the reference device.

The interaction between low work function metal electrodes and fullerene derivatives such as PC\textsubscript{60}BM and IC\textsubscript{60}BA was investigated by Huang et al. using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Figure 3.16 shows the NEXAFS spectra of pristine ICBA films and ICBA films coated with 2 nm of Al or Ca. Similar to PCBM, the deposition of the metals leads to the appearance of new resonant peaks together with the loss of the near-edge structure characteristics of the acceptor molecule. It was believed that the deposition of Ca or Al leads to a formation of new chemical bonds at the interface that destroy the extensive electronic delocalisation around the C\textsubscript{60} cage. This effect was further enhanced after TA, implying a modification of the surface chemical structure by a metal-induced degradation and oxidation in the presence of oxygen.

Kumar et al. made similar observations after investigating the possibility for regenerating degraded P3HT:IC\textsubscript{60}BA-based OPVs fabricated with Ca/Al or Ca/Ag electrodes. As shown in a previous study by the authors, reversible and irreversible electrochemical reactions occur at the interface between Ca and Al or Ag. In the case of Ca/Al electrodes, the formation of Al\textsubscript{2}O\textsubscript{3} is an irreversible process. On the contrary, the formation of Ag\textsubscript{2}O in Ca/Ag electrodes can be reversed after a TA in an inert atmosphere.

![Figure 3.16](image-url) 

**Figure 3.16.** Chemical degradation and oxidation observed by NEXAFS spectroscopy of ICBA films coated with (a) 2 nm of Al and (b) 2 nm of Ca. In both cases, spectra for samples as-cast (AC) and thermally annealed (TA) are presented. Reprinted with permission from [415]. Copyright ©2016 American Chemical Society.
### 3.6. Summary

In conclusion, there are numerous factors that play an important role for the fabrication of efficient OPVs with a P3HT:ICBA photoactive layer. Despite the plateau of available interfacial layers, an optimal D/A thickness of about 210 nm is desired for a maximised photon absorption within the photoactive layer. Tailoring the BHJ nano-morphology to achieve advantageous phase separation and material crystallinity is possible when an appropriate device fabrication process including different pre- and post thermal annealing steps is chosen. A SA followed by a TA step for 10 min at 150 °C seem to be the optimal fabrication condition.

Mixed solvent approaches can be used instead or in addition to the annealing step. Small volumes of solvent additives (<3 vol%) complementary to the main D/A solvent, which commonly is o-DCB, have been shown to drastically alter the D/A nano-morphology and solar cell characteristics. However, special care must be taken as residual solvents could adversely affect the operational stability of the OPVs. Unarguably, high device PCEs are meaningless if the fabricated P3HT:ICBA-based devices are prone to destabilisation due to photooxidation of the D/A blend, as discussed in Section 3.5. Smart OPV device engineering incorporating the addition of ternary components into the BHJ or tailoring the light propagation path within the device stack have also been proven to successfully increase the efficiency of the P3HT:ICBA blend.

Figure 3.17(a) summarises the PCE development of P3HT:ICBA-based solar cells over the years since the discovery of ICBA, and Figure 3.17(b) the number of publications for all reported PCEs is presented in 0.2% PCE steps. It took two years for the scientific community to realise the potential of this novel acceptor material. Subsequently however, the number of reported device PCEs has been constantly increasing, reaching more than a sixfold increase in 2014 (58 PCE values vs. 9 in 2010). It can be seen that PCEs close to 7.5% have been reported, although these were single data points with unreported reproducibility. The PCE achieved during this work is shown with a star in Figure 3.17(a) and it represents the second best efficiency reported in 2016 and is in the top five of the highest reported PCEs for standard architecture devices to date. More importantly, the efficiency was obtained for a OPV device with a photoactive area of 0.43 cm$^2$ which is several times larger than the average area of devices with a standard architecture (0.08 cm$^2$).

Only one report of PCE close to 8% can be found in Figure 3.17(b) and PCEs above 7% have been published only a handful of times. The largest number of reported PCEs are widely distributed between 3.5% and 6.5% with an average PCE of 4.7% calculated from 217 reported values. Sadly, the majority of published device efficiencies were measured over small areas, rarely exceeding 0.1 cm$^2$, bringing into question the scalability of the PCE for future large-area fabrication of P3HT:ICBA-based solar cells.

Interestingly in the years after 2014, interest towards P3HT:ICBA-based OPVs seems to decrease. This can be attributed to the intrinsic properties of the ICBA material itself, where batch-to-batch variation results in a diversity of still not completely understood BHJ phase separation properties. Clearly, the mixture of RIs in the ICBA material has a substantial influence on the molecular packing of P3HT and ICBA, which directly impacts the device PCE.
3.6. Summary

Figure 3.17: Power conversion efficiency of P3HT:ICBA-based OPVs with respect to the (a) year of publication and the number of publications per year (shown with blue bars), and (b) number of publications for a reported PCE values in 0.2% steps. Square black and circle red symbols are used to distinguish the data for standard and inverted devices, respectively. A star is used to show the PCEs achieved in the experimental section of this work.

A controlled synthetic synthesis of regio-isomeric compounds has already been accomplished, underlying that the P3HT-ICBA blend characteristics can be tailored by using deliberate mixtures of RIs.\cite{169,172} This can lead to a beneficial D/A molecular packing assuring high exciton generation yields and unimpeded charge carrier transport. Therefore, the effect of single RIs and their mixture on the BHJ formation is crucial knowledge for the fabrication of high efficiency P3HT:ICBA-based solar cells, as will be discussed in Chapter 5.
4. Experimental techniques

This chapter starts by laying out the theory behind the deposition methods used for this thesis. It then sets out how these methods were applied to the fabrication of all functional layers in the device stack of small-area solar cells and large-area modules. Finally, material and device characterisation techniques that are relevant to this thesis are discussed.

4.1. Deposition methods

Fabrication techniques for the deposition of functional materials can be divided depending on their capability to be used on an industrial scale. Thus, the most common and well-known spin-coating technique does not allow for a high throughput fabrication, and it is therefore accepted as a non-scalable, laboratory-scale deposition method. Coating (except for spin-coating), printing, and vacuum-deposition techniques, however, are easily transferable from the laboratory into industry, and they have been successfully implemented for the fabrication of large-area OPV cells, as already discussed in Sections 1.2 and 2.6.1.

4.1.1. Spin-coating technique

Spin-coating is a rotation-based technique for the application of homogeneous and uniform films from an ink (a dispersion of a material) onto a substrate. This technique is widely used for small-area processing of thin films. The working principle can be explained as follows: a sufficient volume of the ink is applied with a pipette onto a substrate so that it covers the complete surface; the ink is then spun off the edges of the substrate, due to a radial flow caused by rotational centrifugal forces. The final thickness of the film is achieved after evaporation of the solvent. The desired film thickness $d$ can be calculated with the empirical relationship:

$$d \propto \frac{c}{\sqrt{\omega^*}}$$  \hspace{1cm} (4.1)

where $c$ is the concentration of the solution, and $\omega^*$ the angular velocity. Further details can be found in the literature.
4.1.2. Slot-die coating technique

The slot-die coating technique was invented by Beguin in 1954.[420] It is a pre-metered coating method, which means that a (pre)defined amount of liquid is fed with a particular flow rate (FR) through a die, which deposits it onto a substrate that moves at a chosen coating speed (CS). The resulting thickness of the deposited wet film is dependent on the parameters above, in addition to the coating width (CW), the concentration of the material in the ink (c), and the density of the material in the deposited film (ρ).[297] It can be calculated with the empirical relationship:

\[ d \propto \frac{FR}{CS \times CW} \times \frac{c}{\rho} \quad (4.2) \]

A schematic diagram of a slot-die head in operation is shown in Figure 4.1. The ink is usually fed using a pump into the die head, where it fills a reservoir. The purpose of the reservoir is to provide uniform ink distribution inside the die.[421] The die head is commonly made of stainless steel, and consists of two main parts: the downstream and upstream lip. As shown in Figure 4.1, a shim can be inserted between both lips, which allows for the deposition of pre-defined stripe patterns with a resolution of approximately 1 mm. When a shim is used, the thickness of the deposited wet film is additionally influenced by the shim length (the part of the shim that reaches out of the slot-die head), and the coating gap (CG; the gap between the outermost point of the die head and the substrate).[422]

The slot-die coating technique is suitable for high precision deposition of wet films, as long the nature of the flow in the coating bead (the droplet formed between the downstream and upstream meniscus of the ink) is kept within the so-called coating/operating window of the technique.[423] Thus, various experimental and theoretical investigations have been conducted in order to study the process parameters that influence the coating window.[423, 424, 425, 426, 427] This, in addition to the closed nature of the deposition equipment allows for the ability to deposit inks with a wide range of viscosities (1 mPa s to several thousand Pa s) at coating speeds ranging from 1 m/min to above 600 m/min.[428]

4.1.3. Vacuum-thermal evaporation technique

Thermal evaporation under high vacuum can be used for the deposition of various materials such as small molecules, metals, and semiconductors. The evaporation process is usually carried out in a vacuum chamber at pressures of less than \(3 \times 10^{-6}\) mbar. This allows for atoms and molecules to travel directly to the surface of a substrate, where they condense to form a film. The material to be vaporised is placed in a crucible or a tungsten filament, which is heated electrically by way of the Joule effect. The evaporation rate and film thickness can be monitored with a quartz oscillator with a resolution limit of about 0.1 Å/s. For this thesis, the vacuum-thermal evaporation of BCP, MoO\(_3\), and Al was undertaken in a Moorfield Nanotechnology Ltd. evaporator.
4.2. Fabrication of small-area OPV devices

4.2.1. Material preparation

The deposition of all functional layers was carried out on glass-ITO substrates (15 Ω/□, Luminescence Technology Corp.) with dimensions (l × w × th) of 15 mm × 15 mm × 0.7 mm. The dimensions of the pre-patterned ITO stripe were 15 mm × 0.9 mm (l × w). The substrates were sonicated for 5 min sequentially in Decon 90 detergent solution with deionised (DI) water, DI, acetone, and methanol. The surface of the substrate was then treated with an oxygen plasma in an Emitech K1050X plasma cleaner for 5 min at an operating power of 100 W and a gas flow of 15 cm³/min.

PEDOT-PSS (Clevios P VP AI 4083, Heraeus Holding GmbH) was used as the HTL. Regioregular P3HT (4002-EE, Rieke Metals Inc) and IC₇₀BA (1-Materials – Organic Nano Electronic) were employed as the D/A components. Two different batches of IC₇₀BA were used: batch# SX6-255 and batch# SZ1009F7-5. Each of the BHJ components was dissolved in anhydrous 1, 2 dichlorobenzene (o-DCB, 99%, Sigma Aldrich) separately for 24 h under vigorous stirring at room temperature (RT). Both materials were then mixed to form the D/A ink. Where it is not stated to the contrary, the D/A material ratio of the dispersion was 1:1 by volume (vol), while the total material concentration was 40 mg/mL by weight (wt). BCP purchased from Luminescence Technology Corp. was used as the ETL and Al (Sigma Aldrich) as the top electrode.

Figure 4.1.: Schematic diagram of a slot-die coating head in operation.
4.2.2. Deposition procedure

PEDOT:PSS was deposited by the spin-coating technique for 60 s at 4000 rpm to form a 40 nm film on the glass-ITO substrate, as shown in Figure 4.2 steps 2-3. The deposition was undertaken in ambient conditions with a PEDOT:PSS solution which was filtered through a 0.45 µm hydrophilic filter (PVDF) directly onto the surface of the substrate until it was completely covered. Subsequently, the samples were transferred into a glove box filled with nitrogen where they were annealed on a hot plate for 30 min at 150 °C. The P3HT:IC70BA dispersion was then spin-coated on top of the PEDOT:PSS layer, as shown in Figure 4.2 steps 4-5. A two step deposition procedure was chosen. During the first step, 80 µL of the dispersion was pipetted onto the surface of the substrate and spin-coated for 80 s at rotation velocities of 500 rpm – 850 rpm. The second step was undertaken for 5 s at 1000 rpm in order to remove residual droplets from the edges of the substrate. Depending on the experimental requirements, the wet film was either allowed to quick dry for approximately 5 s under inert atmospheric conditions at RT, or it was covered with a round petri dish (60 mm diameter, 15 mm height) for 30 min to enable slow drying of the film. Thermal annealing for 10 min at 90 °C – 150 °C on a hot plate was also carried out when required. In order to complete the cell, 2 nm – 3 nm of BCP and a minimum of 75 nm Al were evaporated through a shadow mask at pressures below 3 × 10^{-6} mbar, as shown in Figure 4.2 steps 6-7. The overlap between the Al and ITO electrodes within the devices was 0.9 cm².

Figure 4.2.: Schematic deposition procedure for small-area OPV devices depicted in 7 steps: (1) substrate cleaning; (2-3) PEDOT:PSS deposition; (4-5) BHJ deposition; (6) BCP ETL and Al electrode evaporation; (7) complete device.
4.3. Fabrication of large-area OPV devices

4.3.1. Material preparation

Glass-ITO (15 Ω/□, Luminescence Technology Corp.) or PET-ITO substrates (60 Ω/□, Sigma Aldrich) were used as the bottom electrode. The latter had dimensions (l × w × th) of 110 mm × 78 mm × 0.13 mm, and the former 78 mm × 78 mm × 0.7 mm. The glass-ITO substrates were already pre-patterned with equidistantly distributed ITO stripes (five with l × w dimensions of 78 mm × 10 mm followed by a sixth with dimensions 78 mm × 13 mm), as shown in Appendix Figure E.11, and cleaned according to the procedure in Section 4.2.1. The PET-ITO substrates were pre-patterned with an excimer laser to the layout of the glass-ITO alternative, and cleaned with a clean room wipe soaked in IPA. A ZnO-precursor (Zn(acac)$_2$, Sigma Aldrich) was used as the ETL. The dispersion was prepared in IPA with a concentration of 10 mg/mL and filtered through a 0.45 μm PTFE filter before use. P3HT:IC$_{70}$BA and PCDTBT:PC$_{70}$BM were used as the photoactive layers. The P3HT:IC$_{70}$BA (IC$_{70}$BA batch# SX6-255) dispersions with total material concentrations of 20 mg/mL or 30 mg/mL were prepared according to the procedure set out in Section 4.2.1. PCDTBT (SOL 4280, Solaris Chem Inc.) and PC$_{70}$BM (Solenne BV) were used, and each of the materials was dispersed separately in a 3:1 solvent mixture by vol of anhydrous o-DCB and chlorobenzene (CB) under vigorous stirring at room temperature. After complete dissolution, both materials were mixed in a 1:4 wt ratio to achieve a total material concentration of 35 mg/mL. The D/A mixture was then left to stir further at RT for at least one week before use. The PCDTBT:PC$_{70}$BM dispersion was diluted to a desired concentration depending on the requirements of each experiment. Molybdenum (VI) oxide (MoO$_3$, Sigma Aldrich) and Al were used as the HTL and the top electrode.

4.3.2. Laser patterning

To pattern the PET-ITO substrates, a rapid laser annealing with a Lambda-Physik LPX 210i Excimer KrF laser was carried out. The laser source is a class 4 and it is capable of producing pulses of UV radiation (wavelength of 248 nm) with energies of up to 1 J due to repetition rates of up to 100 Hz. The pulses are produced using a high voltage discharge in the gas mix (maximum 24 kV). The pulse energy was controlled using an attenuator unit, which consists of a series of eight quartz plates. These plates are pneumatically controlled and placed into the beam path in order to alter the energy of the laser pulse by absorption. The sample was placed underneath the laser beam on a x-y moving stage, which was controlled with a program code written in LabVIEW. The stage was moved at a velocity of 20 mm/s.

4.3.3. Deposition procedure

The slot-die coating equipment has a temperature controlled bed, with allows for the tempering of samples. The ETL dispersion was deposited in ambient conditions on top of preheated substrates (65 °C). The coating parameters were studied in a preliminary screening undertaken on glass slides in order to determine a suitable coating window (see Section 4.1.2). Homogeneously deposited ETLs were achieved with a FR of 150 μl/min, a CS of 18 mm/s, and a SG of 200 μm. A shim with a width of 9 mm was used. The coated substrates were then transferred
onto a hot plate and annealed for 1 min at 120 °C in order to convert the ZnO-precursor to an approximately 20 nm thick ZnO film by hydrolysis. The slot-die coating technique was also used to deposit the photoactive layer, which was carried out under ambient conditions on top of the ZnO layers. Various substrate temperatures were screened for the P3HT:IC70BA blend ranging from RT to 90 °C. The substrate temperature in the case of the PCDTBT:PC70BM layers was varied between 50 °C and 90 °C. Preliminary tests were undertaken to study the optimal coating parameters for each of the D/A blends. Where it is not stated to the contrary, FR × CS × SG of 100 µl/min × 18 mm/s × 300 µm were chosen for the coating procedure of the P3HT:IC70BA dispersion, and 100 µl/min × 18 mm/s × 200 µm for the PCDTBT:PC70BM dispersion. The latter had total material concentrations of 10 mg/mL, 12.5 mg/mL, and 15 mg/mL. A 9 mm wide shim was used for the coating procedure of all D/A dispersions. After deposition, the PCDTBT:PC70BM films were annealed for 10 min at 70 °C to ensure the evaporation of any excess solvents. Additional annealing steps were undertaken for the deposited P3HT:IC70BA films (SA/TA), depending on the experimental requirements. The coated substrates were then placed in a shadow mask and transferred to a thermal evaporator, where 7.5 nm of MoO3 as the HTL, followed by an Al top electrode with a minimum thickness of 75 nm were evaporated. The Al electrode additionally served the purpose of a serial interconnection between the cells. Each module consisted of six cells.

4.4. Materials and device characterisation

4.4.1. Analytical characterisation

High performance liquid chromatography

High performance liquid chromatography (HPLC) is a widely used analytical technique for separation and identification of non-volatile organic and inorganic compounds. In a simplified manner, the working procedure of an HPLC system can be described as follows: a small volume of a liquid sample is injected into the HPLC equipment, where the sample is forced through a so-called “column” by a high pressure pump. Then, the column separates the components of the sample by way of various chemical and/or physical interactions. The separated components are detected at the exit of the column by a spectroscopic, a refractive index, or a fluorescence characterisation technique. The concentration of a compound in the sample is determined quantitatively by either evaluating the height or area of a chromatographic peak from the detected liquid chromatogram.

The HPLC spectra in this thesis were obtained with a Japan Analytical Industry (JAI) LC-9103 Recycling Preparative HPLC system, which was equipped with a modular Hitachi L-7150 pump, and a JAI UV Detector 3702. A Cosmosil Buckyprep-M 20.0 mm internal diameter in a 250 mm column was used. All samples were dispersed in toluene and pumped with a flow rate of 16 mL/min. The UV detector was operated at 312 nm.
4.4. Materials and device characterisation

Mass spectroscopy

The underlying principle of Mass Spectroscopy (MS) is based on the ionisation of chemical species followed by a detection of the ions by a mass spectrometer according to their mass-to-charge (m/z) ratio. The ionisation process allows for the fragmentation of a molecule, and the determination of the elementary particles and compounds present in a particular sample. Thus, it is possible to detect the ion abundance (commonly reported as intensity) versus the m/z for a compound. Matrix-Assisted Laser Desorption Ionization (MALDI) is the most common method for producing gas-phase ions.

The MS characterisation undertaken during this thesis was carried out with a Bruker microflex LT using MALDI time-of-flight mass spectrometry (TOF MS) analysis. Negative ionisation was employed, and trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as the matrix material.

Nuclear magnetic resonance

Nuclear Magnetic Resonance (NMR) is a non-destructive technique that requires minimal sample amounts in order to identify, quantify, and characterise the chemical and physical properties of atoms or organic molecules. During the operation of an NMR system, the atomic nuclear spins of a sample are aligned with a strong magnetic field, and an electronic coil is used to generate a radio-frequency pulse that moves the nuclear spins out of their alignment. The differences in response when nuclear spins return to their alignment with the magnetic field are detected with the electronic coil. This data provides detailed information about the molecular composition and structure of a sample. NMR characterisation is applied with respect to the hydrogen isotope $^1$H or the carbon isotope $^{13}$C within the molecules of a substance of interest. Two dimensional NMR methods such as Correlation Spectroscopy (COSY) 2D NMR, Heteronuclear Single-Quantum Correlation (HSQC) 2D NMR, and Heteronuclear Multiple-Bond Correlation (HMBC) 2D NMR can be additionally used to assign all signals in the $^1$H and $^{13}$C spectra to the corresponding protons and carbons of the sample.

The samples used for the NMR spectroscopy in this thesis were dried in vacuo for at least 24 h before being dissolved in deuterated chloroform. All spectra were obtained with a 400 MHz Bruker AVIII400 spectrometer.

4.4.2. Thermoanalytical characterisation

Thermogravimetric analysis

Thermogravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of the temperature or time in a controlled environment (air or a purging gas of interest). This allows the thermal stability of materials to be studied. In this respect, weight loss originates from different mechanisms such as decomposition (breaking apart of chemical bonds), evaporation (loss of volatiles with elevated temperature), reduction (interaction of sample to a reducing atmosphere), and desorption (depending on physical and chemical processes such as decomposition, oxidation, or dehydration). A gain of weight during the characterisation cycle is ascribed to either oxidation (interaction of the sample with an oxidising atmosphere), or absorption.
The TGA characterisation during this thesis was carried out with a TA Q500 analyser. The scans were conducted from RT (\(\sim 27^\circ C\)) to 800 °C or 900 °C with a heating rate of 10 °C/min, and a N\(_2\) sample purge flow of 10 mL/min.

**Differential scanning calorimetry**

A Differential Scanning Calorimeter (DSC) determines the temperature and heat flow associated with physical material transitions as a function of time and temperature.[433] These transitions are attributed to phase changes, melting, oxidation, and other heat-related changes occurring in the material of interest, which allows for studying, quantitatively and qualitatively, the endothermic and exothermic reactions in the sample.[433]

The DSC characterisation conducted as part of this thesis used a TA Q1000 DSC system. The sample of interest was placed and encapsulated in an aluminium weighing pan. This pan and an empty reference pan were placed in the DSC system, which was operated with heating or cooling rates of 10 °C/min, and an N\(_2\) purge flow of 50 mL/min.

**4.4.3. Surface energy characterisation**

The measurements of the surface energy of materials were carried out with a CAM200 Contact Angle (CA) setup (KSV Instruments Ltd). The software controlling the system allowed for the calculation of dynamic contact angles, surface or interfacial tensions of liquids, and surface free energies. The equipment was capable of measuring contact angles between 5° and 180° with an accuracy of 0.1°, and surface tension in the range 0.01 mN m\(^{-1}\) – 999 mN m\(^{-1}\) with an accuracy of 0.01 mN m\(^{-1}\). A static drop technique with a DI water droplet (vol of 5 µl; surface tension of 72.8 mN m\(^{-1}\)) was used for the characterisation. The evaluation of the data was undertaken in accordance with the method set out by Chibowski et al.[434]

**4.4.4. Optical characterisation**

**UV-visible spectroscopy**

A Varian Cary 5000 UV-vis-NIR spectrophotometer was used to record the absorption spectra of solid films as a function of the wavelength. The Cary 5000 is a dual beam spectrometer, able to take transmission or absorbance measurements. The equipment has two light sources: a mercury lamp used to provide UV radiation; and a tungsten lamp used for the visible radiation. Thus a characterisation in the wavelength range 175 nm – 3300 nm can be accomplished. All measurements undertaken during this thesis were conducted relative to a glass reference in the wavelengths 300 nm – 900 nm with a scan rate of 600 nm/min and a sampling interval of 1 nm. The absorption spectra were recorded through a shadow mask with a circular opening (diameter of 5 mm), which was positioned in the center of the deposited layer. The reported spectra represent the average of two spectra.

The UV–vis spectra of the fractions obtained by HPLC were measured with a Jasco V-570 spectrophotometer. The samples were scanned after the HPLC separation, thus the toluene dispersion of the materials was used.
Spectroscopic ellipsometry characterisation

The operation principle of the Spectroscopic Ellipsometry (SE) is based on measuring the polarisation change in a light beam with pre-defined polarisation states. Generally, the optical properties of a material can be described by the complex refractive index $\tilde{n}(\omega) = n(\omega) + ik(\omega)$, and the complex pseudo-dielectric function $\langle \tilde{\varepsilon}(\omega) \rangle = \langle \varepsilon_1(\omega) \rangle + i\langle \varepsilon_2(\omega) \rangle$ where $\omega$ is the photon energy.[435, 436, 437] A theoretical model based on the layer sequence of glass-ITO/PEDOT:PSS/P3HT:IC$_{70}$BA#1/air was used for the analysis of the measured $\langle \tilde{\varepsilon}(\omega) \rangle$. The optical properties of the P3HT:IC$_{70}$BA layer were then modelled by the use of the modified Tauc–Lorentz oscillator model.[435, 436]

In the above described analysis procedure, the blend films were divided into 20 sub-layers (or slices). The volume fractions of the polymer and fullerene were considered to change exponentially from the bottom to the top of the blend layer.[438] The bottom of the layer is located close to the glass-ITO/PEDOT:PSS surface, whereas the top of the layer is located in the opposite direction. The optical response and layer thickness of the intermediate layers (ITO and PEDOT:PSS) and the D/A components (P3HT and IC$_{70}$BA#1, Figure 4.3) were determined prior to characterisation of the P3HT:IC$_{70}$BA#1 blend. The study was undertaken with a phase modulated spectroscopic ellipsometer (Horiba, France) from the NIR to the far UV (0.7 eV – 6.5 eV) in steps of 20 meV with a 70° angle of incidence.

![Figure 4.3: Bulk dielectric functions $\varepsilon_2(\omega)$ of P3HT and IC$_{70}$BA#1 calculated by the analysis of the pseudo-dielectric function $\langle \tilde{\varepsilon}(\omega) \rangle$ of P3HT (a) and IC$_{70}$BA#1 (b) layers.](image)
Photoluminescence and Raman characterisation

The Photoluminescence (PL) and Raman mapping were carried out on a LabRAM 800 spectrometer (Horiba, France) that was operated in an upright configuration. The excitation wavelength used to characterise the PCDTBT:PC$_{70}$BM blend was 532 nm, and a magnification objective (10×) with 0.25 numerical aperture was used for data collection. The spot size of the laser on the sample was $\sim$ 300 nm, and the power of the laser was approximately 22 mW. A combination of two spectra taken with different grating position (150 lines/mm) formed every spectral data point. This was done to achieve full spectral (x-axis) range. A single spectrum was obtained every 0.03 s. A pixel size of 0.2 mm was used for the data collection. A large pixel size was achieved by fast scanning the laser beam with a piezoelectric mirror before the objective aperture. This allowed for faster collection of spectra with higher laser power on the sample without causing any damage to it. Prior to the sample mapping, approximately 20 independent spectra were recorded in order to generate an average reference spectrum of the PL and Raman signals, as shown in Figure 4.4. The Raman peaks were in agreement with those observed for PCDTBT.[439] The obtained spectra were then normalised depending on different signal characteristics, as summarised in Table 4.1.

Figure 4.4.: Typical reference spectrum of PL and Raman signals obtained from PCDTBT:PC$_{70}$BM blends. Red cursors A and B serve for evaluation of the baseline, area, and peak height of the PL signal, whereas red cursors 1 and 2 are used for evaluation of the Raman signal.

Table 4.1.: Normalisation methods used for the evaluation of the PL and Raman signals.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL Baseline</td>
<td>Green line between red cursors A and B</td>
</tr>
<tr>
<td>PL Area</td>
<td>Average area between red cursors A and B</td>
</tr>
<tr>
<td>PL Height</td>
<td>Peak height from baseline</td>
</tr>
<tr>
<td>PL Ratio</td>
<td>Ratio between PL Area and PL Height</td>
</tr>
<tr>
<td>Raman Baseline</td>
<td>Line between red cursors 1 and 2</td>
</tr>
<tr>
<td>Raman</td>
<td>Baselined peak height</td>
</tr>
</tbody>
</table>
4.4.5. Topographical characterisation

Surface profilometry

The surface profile of the samples was characterised with a Dektak 8 profilometer (Veeco Instruments, Inc.). The setup is equipped with a stylus which is moved over the sample surface, where variation in the surface roughness cause a vertical deflection of the stylus. This deflection produces an electrical signal which is in turn converted to a digital signal by an analog-to-digital converter. In order to measure the thickness of a sample, its surface was scratched with a metal tweezers allowing for the depth of the scratch to be measured. Each measurement started/ended at least 200 nm before/after the edge of the scratch. At least two different samples were measured for each variation of the spin-coated layers. The thickness of the slot-die coated films was measured at three equidistant positions along the direction of the coated layer. Two samples of each coating variation were taken. The data from each measurement was evaluated on a computer with the software operating the equipment. An average value with respective standard deviation of each measurement was then generated.

Atomic force microscopy

Atomic Force Microscopy (AFM) is a scanning probe technique which is used to determine the surface texture of a sample with a nanoscale resolution. To accomplish the surface characterisation, a cantilever with a sharp tip is brought into proximity with the sample, where it is deflected by mechanical contact or forces such as van der Waals, magnetic, or electrostatic.[440] This deflection is recorded by a photodiode, which detects the displacement of a laser beam reflected at the cantilever surface.[440]

A Veeco Dimension 3000 AFM system operating in tapping mode was used for the AFM characterisation in Section 5.3.5 of this thesis. In this operational mode all scan parameters such as setpoint, feedback gain, and scan rate have to be manually adjusted. The AFM characterisation in Section 5.3.6 was undertaken with a Solver Next equipment (NT-MDT Spectrum Instruments), which allows for a completely automated characterisation procedure in tapping mode. All AFM measurements were taken at different positions on the sample. Regardless of the AFM equipment used, the collected data was analysed with the free data analysis software Gwyddion, which allowed for the evaluation of surface roughness parameters such as average roughness ($R_a$), root mean squared roughness ($R_{RMS}$), and the maximum height in z-direction ($R_{MAX}$).[440, 441]

4.4.6. Electro-optical measurements

Light beam induced current characterisation

Photocurrent maps were obtained with a Light Beam Induced Current characterisation setup (LBIC) which operates with a 532 nm diode as an excitation source. The laser beam is stabilised by a noise-eater, modulated with a chopper, and focused to a spot with a diameter of approximately 10 $\mu$m. The sample was moved under the laser beam using an x-y stage controlled by stepper motors (Zaber). The laser beam generated a photocurrent signal which
was amplified using a trans-impedance amplifier, and then sent to a lock-in amplifier (Stanford Research System) in order to increase the signal-to-noise ratio. The voltage signal was integrated by the lock-in amplifier every 10 pulses. The mean value over 10 consecutive data points was calculated by a programme, in order to obtain a value proportional to the photocurrent for each point. No bias light was used during the characterisation procedure.

**Current-voltage characterisation**

The current-voltage (I-V) behaviour of all OPV devices was recorded in ambient atmosphere using a four-point probe configuration and a Keithley 2400 source measurement apparatus. The solar cells were not encapsulated. An Abet Technologies 10500 solar simulator (class AAB) was used for the illumination of the spin-coated devices. The slot-die coated cells and modules were illuminated with an ORIEL solar simulator (class ABA). The solar spectrum of both solar simulators was emitted with a xenon lamp through a filter, that matches the requirements of the American Society for Testing and Materials Standards (ASTM) for an Air-Mass Index of 1.5 G.[442] The light intensity of the solar simulator was calibrated with a silicon reference cell (PV Measurements, Inc. 20 mm × 20 mm) to 1 Sun (100 mW/cm²). An aperture of 0.43 cm² was used to define the photoactive area of the spin-coated devices, in order to reduce the measurement error.[410, 443, 444] A characterisation holder with contact pins was used to accomplish an electrical contact with the slot-die coated single cells, arrays of connected single cells, and complete modules. The photoactive area in this case was measured with a ruler, or obtained from the LBIC data where possible. The I-V measurements were controlled with a code written in LabVIEW.

When operational stability studies were undertaken, the module was placed under the illumination source, while the characterisation procedure was started immediately and carried out for 24 h. The I-V characteristics of the module were recorded once every 60 s. An infrared thermometer pointed at the surface of the module was used to measure the temperature of the sample during the study. At the start of the characterisation the temperature of the sample was equal to the ambient temperature, and gradually increased before reaching a steady value of 60.0 ± 3.0 °C after 5 min of characterisation.

**External quantum efficiency**

The External Quantum Efficiency (EQE) of an OPV device gives the ratio of the number of charge carriers generated by a solar cell to the number of incident photons that is absorbed by it.[445, 446, 447] The photogenerated current of a solar cell can then be obtained after integration of the EQE spectrum of the device. Thus, the spectral response of an OPV cell can be studied over a given wavelength range.

A Bentham PV300 solar cell characterisation system was used for the EQE measurements undertaken during this thesis. The system has a Xenon/Quartz halogen light source, which is used to illuminate the sample. The light beam is input into a monochromator, which allows for a coverage over the spectral range 300 nm – 2500 nm. A Si cell was used to calibrate the EQE system in the wavelengths 300 nm – 1100 nm. The actual EQE measurements of the samples were carried out in the wavelength range from 300 nm to 800 nm with a 5 nm step.
4.5. Summary

This chapter started with an introduction of the deposition techniques used for the fabrication of small-area OPV cells and large-area OPV modules during this thesis. The preparation of materials and the parameters of their corresponding deposition procedure were then detailed. All characterisation methods utilised for the analytic thermoanalytic, optic, surface energetic, topographic, and electro-optic studies of materials and/or devices were discussed in conclusion.
5. P3HT:IC$_{70}$BA-based OPVs with 6.7% power conversion efficiency

This chapter begins with an introductory section outlining the state of the art in the field of P3HT:ICBA-based OPVs and continues with a study of the intrinsic properties of two IC$_{70}$BA samples. The dissimilar regio-isomeric proportions believed to affect the vertical distribution and molecular packing of P3HT:IC$_{70}$BA-based blends are analysed. The spectral response and topography properties of P3HT mixed with isolated RIs or mixtures of RIs of IC$_{70}$BA are investigated and the results shown to account for the morphological formation of the P3HT:IC$_{70}$BA blend. The outcomes from the characterisation of the D/A blend are then used to design and tailor the fabrication procedure for OPV devices. PCEs approaching 7% were achieved for a particular regio-isomeric mixture of IC$_{70}$BA. The results are then used for the fabrication of P3HT-based OPVs with another IC$_{70}$BA sample that shows a dissimilar regio-isomeric ratio, or with isolated IC$_{70}$BA RIs. The influence of the IC$_{70}$BA molecule properties on the formation kinetics and molecular packing of the photoactive layer is demonstrated.

5.1. Introduction

The synthesis of novel donor materials has allowed for OPV devices to reach PCEs above 10%.\[146, 147, 286, 306\] However, the majority of novel low band gap polymers require a multi-step chemical synthesis, which leads to a high production cost. Additionally, rather small quantities of material are currently available, due to the challenges associated with the complicated and time-consuming synthesis. This usually means that novel donor materials can primarily be used for the fabrication of small-area devices with a low chance of being scaled-up and used in the commercial sector, where large-area OPVs are typically fabricated on a R2R web.

In contrast, the chemical synthesis of P3HT can be accomplished in a one-pot reaction which leads to low production costs. Additionally, high material yields with a controlled material quality are common. This allows for an unimpeded device scale-up, despite the lower PCEs observed for P3HT:PCBM-based OPVs, as shown in Section 3.1 and demonstrated by some groups.\[299, 448, 449\]. The discovery of the IC$_{60}$BA and IC$_{70}$BA molecules by He et al. has brought new hope for achieving high device PCEs when ICBA is used in a photoactive blend.
5.1. Introduction with P3HT, as extensively studied in Section 3.3. However, reported efficiencies for P3HT:ICBA-based solar cells vary greatly depending on the ICBA sample and the particular fabrication conditions used. A reasonable explanation for this variation is that there are impurities in the ICBA sample such as mono- and/or tris-adducts (ICMA; ICTA) of indene to the fullerene molecule. For example, ICTA molecules have been reported to pack in small fullerene clusters, which impedes the electron transport through the acceptor phase, leading to reduced mobility of electrons.[450] The regio-isomeric characteristics of ICBA are also important for the spatial arrangement and molecular packing density of the fullerene cages, which affect the structural and energetic order of the D/A blend and consecutively govern the mobility of electrons in the ICBA phase and therefore the OPV device characteristics.[174, 175, 403]

Despite a great deal of work carried out in the field of P3HT:ICBA-based OPVs as detailed in Section 3.3, there is currently a lack of understanding of how single RIs of ICBA and/or their mixture affect the D/A nano-morphology depending on the fabrication conditions used. This knowledge is crucial and can provide a greater insight into the vast variation in PCEs reported for P3HT:ICBA-based solar cells, especially when knowing that synthetic conditions used for the synthesis of fullerene bis-adducts lead to a mixture of RIs, which exhibit different ratio and distribution.[451] Chromatographic isolation of single RIs can be used to separate the synthesised materials, however the product yields are low and the procedure is time consuming. Therefore, regio-specific synthesis of bis-adduct molecules has been targeted by some researchers.[171, 172] However, no regio-selective synthesis of ICBA RIs has been demonstrated yet. As discussed in Section 3.3.5, there is only a small quantity of publications that report the effect of the ICBA RI type on D/A molecular packing. Even less attention has been paid to the ratio and distribution between RIs in a mixture, which can furthermore influence the molecular packing of the P3HT:ICBA blend and alter the charge carrier transport properties in the photoactive region. In addition, the device fabrication conditions have to be taken into consideration, as they determine the vertical distribution of the D/A blend components (see Section 3.3.1).

To address the above points, the intrinsic properties of two different commercial IC$_{70}$BA samples obtained from 1-Materials (batch# SX6-255 and SZ1009F7-5, hereafter IC$_{70}$BA#1 and IC$_{70}$BA#2) were studied and explained below. The properties of blends between P3HT and single IC$_{70}$BA RIs or their dissimilar regio-isomeric mixtures were also investigated while taking into consideration the effect of the fabrication conditions on the formation kinetics of the D/A blend. Then, using processing conditions that were tailored according to the D/A blend characterisation, a number of OPVs with a regular architecture as shown in Section 2.4.1 were fabricated. This was in order to detail the effect of the regio-isomeric properties of the IC$_{70}$BA molecule on the characteristics of P3HT-based OPVs.
5.2. Designing the IC$_{70}$BA molecule for efficient OPV devices

The ICBA molecule (both IC$_{60}$BA and IC$_{70}$BA) has proven to be an ideal acceptor material in P3HT-based OPVs, as shown in Section 3.3. However, it was also shown that the PCE for P3HT:ICBA-based solar cells can significantly vary depending on the ICBA precursor source. A reasonable explanation for this was given by the regio-isomeric properties of the ICBA molecule, that influence the molecular packing of the photoactive blend. Therefore, a detailed study of two different IC$_{70}$BA batches is carried out in the following sections, in order to investigate the effect of the IC$_{70}$BA RIs and their mixture on the intrinsic characteristics of the IC$_{70}$BA molecule and the P3HT:IC$_{70}$BA blend.

5.2.1. High performance liquid chromatography

High Performance Liquid Chromatography (HPLC) was used to analyse IC$_{70}$BA#1 and IC$_{70}$BA#2. Both crude materials were dissolved in toluene with a concentration of 4 mg/mL (80 mg of IC$_{70}$BA#1 in 20 mL toluene, and 130 mg of IC$_{70}$BA#2 in 35 mL toluene). The purification was carried out with a Cosmosil Bucyprep-M 20 mm ID × 250 mm column and toluene with a flow rate of 16 mL/min was used as a solvent. Each injection was recycled once prior to the collection of the fractions shown in Figures 5.1(a) and 5.1(b). Six fractions were collected for both IC$_{70}$BA batches with the highest peak area observed for fractions A, B, and C, whereas fractions $\alpha$, $\omega$, and the tail of C were minor. Therefore, the latter were not investigated further. The approximate ratio between the fractions of each batch based on HPLC peak area integration is shown in Figure 5.1. The purity of each of the separated major fractions A, B, and C for IC$_{70}$BA#1 and IC$_{70}$BA#2 was studied by re-injecting each into the HPLC for further recycling as shown in Figures 5.1(c) and 5.1(d). The analysis of fraction A for both IC$_{70}$BA samples at the time of recycling shows a major peak (A2) and two minor shoulders (A1 and A3) with a peak area integration of approximate ratio between A1:A2:A3 of 1:97:2 for IC$_{70}$BA#1 and 2:95:3 for IC$_{70}$BA#2, respectively. These results show that for both IC$_{70}$BA batches, fraction A consists of a pure isolated RI of indene-C$_{70}$ bis-adduct (97% for IC$_{70}$BA#1 and 95% for IC$_{70}$BA#2). This is further evident from the Matrix-Assisted Laser Desorption/Ionisation (MALDI) Mass Spectroscopy (MS) in Appendix A, which displays an isotropic distribution of a peak with a mass-to-charge ratio (m/z) of 1072, which corresponds to the chemical formula of IC$_{70}$BA (C$_{88}$H$_{16}$).

In a similar manner, the main fractions B from Figures 5.1(a) and 5.1(b) were recycled, and both IC$_{70}$BA batches show a minor shoulder B1 followed by a major peak B2. Absorption spectroscopy reveals that both B1 shoulders have identical spectra to those of fractions A, whereas the B2 peaks have an identical absorption spectra to the main B peaks. The absorption spectra of fractions A and B2 are shown in Appendix B and are in agreement with the spectra reported by other researcher.[400] The HPLC peak integration indicates peak area ratios between B1 and B2 of 3.5 and 96.5 for IC$_{70}$BA#1 vs. 3.3 and 96.7 for IC$_{70}$BA#2. As a result, pure regio-isomeric contents above 96.5% are observed in both B fractions. The remaining regio-isomeric impurity of below 3.5% is attributed to remains from fraction A. The main RI was ascribed to the indene-C$_{70}$ bis-adduct molecule, due to an identical MALDI MS spectra that was observed for fraction B (see Appendix A).
5.2. Designing the IC\textsubscript{70}BA molecule for efficient OPV devices

Figure 5.1: HPLC separation of (a) IC\textsubscript{70}BA\#1 and (b) IC\textsubscript{70}BA\#2. Approximate ratio between the fractions in each batch based on HPLC peak area integration is shown in the table. Analysis of the fractions obtained from (c) IC\textsubscript{70}BA\#1 and (d) IC\textsubscript{70}BA\#2.
The main fractions C for IC\textsubscript{70}BA\#1 and IC\textsubscript{70}BA\#2 were also analysed. They reveal four peaks for IC\textsubscript{70}BA\#1 (C1, C2, C3, and C4) and an additional fifth (C0) in the case of IC\textsubscript{70}BA\#2, as given in Figures 5.1(c) and 5.1(d). The approximate peak ratio of IC\textsubscript{70}BA\#1 is 12.6:77:6.3:4.1; and 0.5:12.6:77:1.3:4.1 for IC\textsubscript{70}BA\#2. This implies that for both batches, fraction C consists of approximately 77% pure RI. Absorption spectroscopy revealed that C1 is identical to fraction B and was therefore combined with it. C2, on the other hand, shows a different absorption spectra (see Appendix B) and therefore was recycled again. The recycling process shows 97.5% pure regio-isomeric content in the case of IC\textsubscript{70}BA\#1 and 97.7% for IC\textsubscript{70}BA\#2. Due to an identical MALDI MS spectra for C2, the RI is ascribed to the indene-C\textsubscript{70} bis-adduct (see Appendix A).

In summary, the HPLC analysis shows that both IC\textsubscript{70}BA samples are highly pure (99%). The remaining 1% of the sample is attributed to impurities such as mono-adducts and tris-adducts of indene-C\textsubscript{70} (IC\textsubscript{70}MA and IC\textsubscript{70}TA). However, IC\textsubscript{70}BA\#1 and IC\textsubscript{70}BA\#2 exhibit different regio-isomeric distributions of the fractions A, B, and C (22%/43%/35% vs. 16%/36%/48%). For both IC\textsubscript{70}BA batches, the separated pure RIs were concentrated, suspended in methanol, filtered, washed with methanol, and dried in air in order to be used for further fabrication of P3HT:IC\textsubscript{70}BA-based solar cells and to study the effect of pure RIs on the device characteristics.

5.2.2. Nuclear magnetic resonance characterisation

In order to assign the relative position of the indene addends in each fraction, the IC\textsubscript{70}BA\#1 fractions A, B, and C were analysed by proton and carbon Nuclear Magnetic Resonance (\textsuperscript{1}H NMR and \textsuperscript{13}C NMR) as well Correlation Spectroscopy (COSY) 2D NMR, Heteronuclear Single-Quantum Correlation (HSQC) 2D NMR, and Heteronuclear Multiple-Bond Correlation (HMBC) 2D NMR to assign all signals in the \textsuperscript{1}H and \textsuperscript{13}C spectra to the corresponding protons and carbons. A NMR characterisation of IC\textsubscript{70}BA\#2 was not carried out, due to the similarity of RIs found in the fractions of both IC\textsubscript{70}BA samples during the HPLC analysis in Section 5.2.1.

NMR analysis of IC\textsubscript{70}BA\#1 fraction C

The \textsuperscript{1}H NMR spectrum of fraction C in Appendix Figure C.3 shows a set of two doublets at 2.5 ppm and 2.9 ppm, two singlets at 4.5 ppm–4.7 ppm, and a set of aromatic signals at 7.3 ppm–7.6 ppm. The latter are related to residual solvents in the sample, whereas the former singlets and doublets correspond to the 8 aliphatic protons in the two indene groups and indicate that the two indene groups are identical. This implies a high symmetry of the IC\textsubscript{70}BA molecule (c\textsubscript{2v} point group), which most likely correspond to the highest symmetry “12 o’clock” RI.

The COSY 2D NMR spectrum of IC\textsubscript{70}BA\#1 fraction C is shown in Appendix Figure C.4 and establishes the coupling and connectivity order between the different protons. The sensitivity of the experiment only allows for the detection of coupling between neighbouring protons separated by no more than one C–C bond. The cross-peaks in the aromatic area allows to determine the connectivity order between the aromatic protons as indicated in Appendix Figure C.4. The cross-peaks in the aliphatic area show the strongest coupling between the protons at 2.5 ppm and 2.9 ppm (red cross-peaks), which are linked to the same C-atom and are assigned as the “bridge” protons H\textsubscript{a} and H\textsubscript{b}. The weaker coupling between the 2.5 ppm–2.9 ppm and 4.5 ppm–4.7 ppm protons is also observed (green cross-peaks), and therefore the signals at 4.5 ppm and 4.7 ppm are attributed to H\textsubscript{c} and H\textsubscript{d}. 

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The HSQC spectrum of IC\textsubscript{70}BA\#1 fraction C in Appendix Figure C.5 allows for the establishment heteronuclear H–C coupling through one bond only. The proton NMR is represented on the x axis, and Distortionless Enhancement by Polarisation Transfer edited (DEPT) carbon NMR on the y axis (showing only C atoms linked to protons). The blue of the cross-peaks indicates secondary carbon atoms, and the red corresponds to the CH and CH\textsubscript{3} groups. The HSQC spectrum confirms that the protons at 2.5 ppm and 2.9 ppm correspond to H\textscript{c} and H\textscript{d}, and clearly indicates the “bridge” C\textsubscript{5} atom. It also allows to distinguish aromatic carbons 8, 9 and 10, 11, and establishes the connectivity between H\textscript{a} and C\textsubscript{3}, and H\textscript{b} and C\textsubscript{4}.

The HMBC spectrum of IC\textsubscript{70}BA\#1 fraction C in Appendix Figure C.6 shows heteronuclear H–C coupling through multiple bonds (up to four individual bonds, with the coupling gradually decreasing as the distance increases). The x axis shows the proton spectrum, and the y axis shows a carbon NMR spectrum with only those C atoms which exhibit HMBC coupling with the corresponding protons. The HMBC spectrum allows to clearly distinguish the coupling between the aromatic C and H atoms, identifying C\textsubscript{6} and C\textsubscript{7} atoms as tertiary aromatic carbons in the indene addends, and C\textsubscript{1} and C\textsubscript{2} as the sp\textsuperscript{3} carbons in the fullerene cage, in addition to all of the signals determined by HSQC. It also allows to clearly identify all of the aliphatic protons H\textsubscript{a} – H\textsubscript{d} (see Appendix Figure C.6 bottom). The proton at 2.5 ppm shows strong coupling with the C\textsubscript{1} and C\textsubscript{2} atoms of the fullerene cage (red cross-peak) and weak coupling with the C\textsubscript{6} and C\textsubscript{7} atoms of the indene addend (yellow-green cross-peak), and is therefore attributed to the H\textsubscript{c} atom in the indene bridge pointing towards the fullerene cage. On the contrary, the proton at 2.9 ppm shows strong coupling with the C\textsubscript{6} and C\textsubscript{7} atoms (red cross-peak) and weak coupling with the C\textsubscript{1} and C\textsubscript{2} atoms (yellow-green cross-peak), and therefore is assigned as the H\textsubscript{d} atom in the indene bridge pointing towards the aromatic ring in the indene addend.

Most notably, the coupling between the H\textsubscript{a} and H\textsubscript{b}, and the corresponding sp\textsuperscript{2} atoms in the C\textsubscript{70} fullerene cage can be resolved (red box in Appendix Figure C.6). The proton at 4.5 ppm shows coupling to the C signal at 157 ppm which corresponds to the C atom closest to the pole in the C\textsubscript{70} cage, and therefore is assigned as H\textsubscript{b}. Similarly, the proton at 4.7 ppm shows coupling to the C atom at 148 ppm which corresponds to the more equatorial C atom in the C\textsubscript{70} cage, and therefore is assigned as H\textsubscript{a}.[452]

In addition to the above mentioned and assigned C\textsubscript{1} – C\textsubscript{11} carbon atoms, the \textsuperscript{13}C NMR spectrum of IC\textsubscript{70}BA\#1 fraction C in Appendix Figure C.9 exhibits approximately 32 aromatic sp\textsuperscript{2} carbons corresponding to the C\textsubscript{70} cage and further confirms the c\textsubscript{2v} symmetry of the molecule, and fraction C as being a 12 o’clock RI.

**NMR analysis of IC\textsubscript{70}BA\#1 fractions A and B**

The same set of NMR experiments was carried out for IC\textsubscript{70}BA\#1 fractions A and B. The spectra was analysed in a similar manner and shows more complicated coupling. This indicates that the two indene addends are non-equivalent, and therefore the symmetry of the molecule is lower than in fraction C (either c\textsubscript{1} or c\textsubscript{i}). The signal assignment obtained for fraction C was applied to the spectra of fraction A and B (see Appendix Figures C.3 – C.7, middle and bottom). The \textsuperscript{13}C NMR spectra show 140 sp\textsuperscript{2} C signals that overlay and indicate lower symmetry of the molecules and the presence of at least two notably different diastereomers. The aliphatic
carbon signals for fraction A also show significant splitting, additionally indicating the presence of several notably different diastereomers. The most notable result is obtained in the HMBC experiment (Appendix Figure C.6, middle and bottom red boxes) showing the coupling of the protons a, a’, b and b’ to the four corresponding C atoms in the C\textsubscript{70} cage.

**Comparison of IC\textsubscript{70}BA#1 fractions A, B, and C**

A magnified representation of the couplings for each of the IC\textsubscript{70}BA#1 fractions A, B, and C from Appendix Figure C.6 (\textsuperscript{3}J(H\textsubscript{a}, C\textsubscript{fullerene, eq}) and \textsuperscript{3}J(H\textsubscript{b}, C\textsubscript{fullerene, pole}) in the red boxes) of the HMBC NMR spectra is shown in Figure 5.2. Due to the high symmetry of the 12 o’clock RI molecule in fraction C, the two “pole” and “eq” carbons are identical, as shown in the bottom diagram in Figure 5.2. The latter carbon pair appear at 148 ppm, whereas the former carbon pair at 157 ppm. Compared to the “eq” and “pole” carbons of fraction C, a noticeable downfield shift of the “eq” and “pole” carbons of fraction B can be observed in the middle HBMC NMR spectra in Figure 5.2. The “eq” carbons appear at 148.7 ppm and 149.3 ppm, whereas the “pole” carbons at 157 ppm and 162 ppm. In contrast, for fraction A (top HBMC NMR spectra in Figure 5.2) an upfield shift is observed for the “pole” carbons, which appear at 155 ppm and 156 ppm. The “eq” carbons, on the other hand, appear at 147 ppm and 148 ppm.

A study of the geometrical structure of the IC\textsubscript{70}BA RIs is required to unambiguously define the type of RI for each of the IC\textsubscript{70}BA#1 fractions. As shown in the structural diagrams in Figure 5.2, the shortest distance between the indene addend and the opposite “pole” carbon atom of the C\textsubscript{70} cage is expected for the 2 o’clock RI (distance of 8.36 Å) followed by the 12 o’clock RI (8.42 Å). The longest distance is observed for the 5 o’clock RI (8.48 Å). A downfield shift of the HMBC NMR spectrum is expected for a reduced distance between a “pole” carbon and the opposite indene addend, due to their interaction. On the contrary, an upfield shift corresponds to a longer distance between the indene addend and the “pole” carbon. Hence, the lowest downfield signal of 162 ppm corresponds to the shortest distance of 8.36 Å observed for the 2 o’clock RI in fraction B, followed by 157 ppm corresponding to the distance of 8.42 Å (12 o’clock RI, fraction C). The longest distance of 8.48 Å results in the highest upfield shift (156 ppm), which is attributed to the 5 o’clock RI in fraction A.

**5.2.3. Thermogravimetric analysis**

The thermal stability of IC\textsubscript{70}BA#1 and IC\textsubscript{70}BA#2, as well of P3HT, and the blend between P3HT and IC\textsubscript{70}BA was studied by Thermogravimetric Analysis (TGA) as shown in Figure 5.3. A gradual weight loss of 7% between 87 °C – 230 °C is observed for the pristine (as received) IC\textsubscript{70}BA#1 sample, as given in Figure 5.3(a). A slightly higher weight loss of 8% is detected for the same temperatures in Figure 5.3(b) for IC\textsubscript{70}BA#2. For both IC\textsubscript{70}BA samples, this weight loss was believed to originate from the evolution of solvent residuals due to the material synthesis in addition to the breakage of indene-C\textsubscript{70} C–C bonds and partial structural decomposition or rearrangement within the IC\textsubscript{70}BA phase.[400]. In another study, IC\textsubscript{70}BA samples were subjected to thermal annealing up to 200 °C prior to the TGA analysis. It can be seen in Figure 5.3 that the thermal stability of both IC\textsubscript{70}BA samples improved. No gradual weight loss is observed and the first distinct mass reduction (about 25% for both IC\textsubscript{70}BA samples) initiating approximately above 200 °C and lasting until 320 °C. This is the temperature range where the
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Figure 5.2.: HMBC NMR spectra of IC$_{70}$BA#1 fractions A (top), B (middle), and C (bottom). The spectra show the coupling with the carbon atoms of the C$_{70}$ cage in each fraction (left). The structural diagrams of the three IC$_{70}$BA RIs are also shown (right). Two different projections (right) indicate the sites where the indene addends are attached (red). Red dashed lines in the structural diagrams indicate the shortest through-space distances between the corresponding “pole” carbon atoms and the indene addend at the opposite pole.
decomposition of indene occurs. A final mass loss of approximately 70% is observed at about 600 °C for IC_{70}BA#1 and IC_{70}BA#2, regardless if the samples were thermally annealed or not. This final weight reduction is ascribed to the decomposition of the C_{70} molecule.

The thermal stability of P3HT and the blend between P3HT and IC_{70}BA was also studied. As shown in Figure 5.3(a), P3HT starts to decompose above 400 °C. A total weight loss of 70% is observed at 500 °C, whereas no further mass reduction is seen up to 800 °C. To study the thermal stability of the D/A blend, a P3HT:IC_{70}BA dispersion with a 1:1 D/A ratio by wt in o-DCB was dropcasted on a glass substrate and annealed in a nitrogen atmosphere for 10 min at 150 °C on a hot plate. The dry blend was then removed from the surface of the glass with a spatula and subjected to the TGA analysis. A weight loss of 9% was measured for P3HT:IC_{70}BA#1 between 200 °C – 300 °C. A slightly higher mass reduction of 12% was observed for P3HT:IC_{70}BA#2 for the same temperature range. The fact that the mass reduction observed for both D/A samples is lower than the weight loss of the IC_{70}BA materials only, is attributed to the nature of the TGA measurement, which detects the weight reduction in relation to the total sample mass at the beginning of an analysis. Thus, the total weight of the D/A sample is made up of 50% of the weight of each IC_{70}BA and P3HT. The 12% mass reduction of P3HT:IC_{70}BA#2 is in agreement with the observed weight loss of about 25% for the IC_{70}BA#2 material only. The weight loss of 9% observed for P3HT:IC_{70}BA#1, however, is less than expected and attributed to a denser molecular packing of the P3HT:IC_{70}BA#1 blend (compared to P3HT:IC_{70}BA#2). This is due to the different regio-isomeric ratio of the IC_{70}BA samples (see Section 5.2.1). The molecular packing of the P3HT:IC_{70}BA blend is likely to have an effect on the temperature at which the final material loss occurs - about 550 °C and 650 °C for IC_{70}BA#1 and IC_{70}BA#2 respectively.

Figure 5.3: TGA graphs of (a) IC_{70}BA#1 and of the P3HT:IC_{70}BA#1 blend; (b) IC_{70}BA#2 and of the P3HT:IC_{70}BA#2 blend. Two samples of each IC_{70}BA batch were studied: a pristine sample and a sample subjected to thermal annealing up to 200 °C. The TGA graph of P3HT is shown additionally in (a).
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5.2.4. Differential scanning calorimetry analysis

The behaviour of IC$_{70}$BA#1 and IC$_{70}$BA#2 during the phase transition was studied by Differential Scanning Calorimetry (DSC), as shown in Figure 5.4. An endothermic peak starting at about 90 °C with a center at 101.6 °C and a less pronounced continuing broad tail centred at about 160 °C can be observed for IC$_{70}$BA#1 in Figure 5.4(a). The endothermic reaction is believed to be a consequence of a removal of trapped moisture from the sample followed by a rearrangement and reorganisation of the IC$_{70}$BA#1 molecules in order to accomplish a spatially packed network. This shows that the annealing temperature, and possibly the time used during the fabrication procedure for P3HT:IC$_{70}$BA-based devices, can have a significant influence on the charge carrier transport properties of the blend.[453] There is the likelihood of a subsequent release of solvents from the sample to contribute to the endothermic reaction, as discussed in Section 5.2.3. There are no peaks in the second or third DSC heat-cool cycles, suggesting that the processes occurring in the IC$_{70}$BA#1 lattice are complete after the first heat phase up to 200 °C, and that they are also irreversible. These results are in agreement with the thermal stability behaviour of IC$_{70}$BA#1 in Section 5.2.3, where thermally annealed IC$_{70}$BA#1 samples showed a more stable TGA behaviour.

Figure 5.4(b) shows the DSC behaviour of IC$_{70}$BA#2. There is a broad endothermic peak at the beginning of the scanning cycle, which is believed to be caused by the tempering of the equipment and therefore is not related to the behaviour of the sample studied. In comparison, the broad endothermic tail between 100 °C – 180 °C (centred at about 145 °C) is attributed to a removal of trapped moisture from the sample followed by a rearrangement and reorganisation of the IC$_{70}$BA#2 molecules. This observation is in agreement with the behaviour of the IC$_{70}$BA#1 sample. However, there are no clearly distinguished endothermic peaks for the IC$_{70}$BA#2 sample, which implies that processes occurring in the material are less pronounced. A possible explanation for this reduced reactivity is the different regio-isomeric distribution between both

![Figure 5.4](image-url)

**Figure 5.4:** DSC analysis of (a) IC$_{70}$BA#1 and (b) IC$_{70}$BA#2. Grey arrows show the start/end of the DSC cycles and the direction of the temperature change.
IC\textsubscript{70}BA samples, which can have an effect on the spatial arrangement of the molecules. A short exothermic peak at 183 °C can also be observed in Figure 5.4(b). A possible explanation for this could be a chemical reaction between the impurities in the sample, as shown by the HPLC in Section 5.2.1 (for example, attachment of free indene molecules to ICMA). Similarly to IC\textsubscript{70}BA\#1, the processes in the IC\textsubscript{70}BA\#2 lattice occur only during the first heat cycle of the DSC scan and cannot be observed during any further scanning cycles.

### 5.2.5. Surface energy characterisation

A determination of the surface energy of materials is vital for understanding wetting properties of different surfaces, or intermixing dynamics and adhesion/tension of materials deposited on top of a surface. Therefore, the surface energy of the materials is required in order to study the vertical material distribution and molecule rearrangement dynamics for a bi-material blend such as P3HT:IC\textsubscript{70}BA.

Contact angle (CA) measurements were used for the evaluation of the surface energies of IC\textsubscript{70}BA\#1 and PEDOT:PSS. The latter was calculated from the contact angle between a DI drop and the surface of the material (see Figure 5.5), which in the case of PEDOT:PSS and IC\textsubscript{70}BA is 18.96° and 89.66°, respectively. The corresponding surface energies were calculated at 69 mN m\textsuperscript{-1} and 28.7 mN m\textsuperscript{-1} for PEDOT:PSS and IC\textsubscript{70}BA\#1. A surface energy of 27.2 mN m\textsuperscript{-1} for P3HT is taken from the literature.[438]

In this thesis, OPV cells with a regular architecture were fabricated by the spin-coating technique, where the P3HT:IC\textsubscript{70}BA layers were deposited on PEDOT:PSS coated glass-ITO substrates (see Section 4.2). Thus, in order to reduce the free energy of the D/A system, the lower surface energy material (P3HT) is expected to migrate to the top surface (air). In contrast, the high surface energy material (IC\textsubscript{70}BA\#1) migrates towards the bottom PEDOT:PSS layer which is the highest surface energy interface. Nevertheless, such D/A distribution would be unfavourable for the charge carrier transport and is expected to decrease the characteristics of P3HT:IC\textsubscript{70}BA\#1-based solar cells.

![Figure 5.5](image_url)

**Figure 5.5.** Contact angle measurements for a DI water droplet on the surface of (a) PEDOT:PSS and (b) IC\textsubscript{70}BA\#1 used for calculation of the surface energy of the materials.
5.3. P3HT:IC$_{70}$BA blend characteristics

Prior to the fabrication of complete OPV devices, the characteristics of P3HT-based blends with IC$_{70}$BA\#1, IC$_{70}$BA\#2, and the isolated 5, 2, and 12 o’clock RIs from both IC$_{70}$BA samples were studied with respect to the processing conditions. For this purpose, P3HT:IC$_{70}$BA dispersions with a 1:1 material ratio by weight and a total concentration of 40 mg/mL were used for the deposition of all samples, which was carried out by means of the spin-coating technique. The following sections show studies of the vertical distribution, surface energy, spectral response and layer thickness, and the surface topography of various P3HT:IC$_{70}$BA-based samples.

5.3.1. Vertical distribution of P3HT:IC$_{70}$BA\#1 volume fractions

A study of the vertical distribution of the D/A blend between P3HT and IC$_{70}$BA can provide insights into the formation kinetics depending on the fabrication conditions used for the deposition of the photoactive layer. In addition, the ratio of the RIs in the IC$_{70}$BA mixture has to be considered, as increased presence of particular RIs can influence the molecular packing of the BHJ and alter the charge carrier transport dynamics, as discussed in Section 5.1. Preliminary tests showed significant variation between the characteristics of P3HT:IC$_{70}$BA-based devices depending on the IC$_{70}$BA batch used. Highest device PCEs were measured for the P3HT:IC$_{70}$BA\#1 blend. Therefore, Spectroscopic Ellipsometry (SE) was used to study the effect of the fabrication conditions on the morphological arrangement of the D/A components in the P3HT:IC$_{70}$BA\#1 blend in order to design the optimal processing conditions for the highest possible device efficiencies. Due to much lower PCEs observed for the P3HT:IC$_{70}$BA\#2-based devices compared to P3HT:IC$_{70}$BA\#1, the former system was not characterised in this section as it is believed that the characteristics of the P3HT:IC$_{70}$BA\#2 blend are not prone to significant further improvements due to an excess acceptor segregation.

As discussed in Section 4.4.4, the complex refractive index $\tilde{n}(\omega) = n(\omega) + ik(\omega)$ and the complex pseudo-dielectric function $\langle \tilde{\varepsilon}(\omega) \rangle = \langle \varepsilon_1(\omega) \rangle + i\langle \varepsilon_2(\omega) \rangle$, where $\omega$ is the frequency which correlates to the photon energy, are used to show the optical properties of the D/A layers. The $\langle \tilde{\varepsilon}(\omega) \rangle$ can be further analysed by the Tauc–Lorentz (TL) oscillator model, which is described in detail in Section 4.4.4. In order to analyse the $\tilde{n}(\omega)$ of the P3HT:IC$_{70}$BA\#1 layers, the optical constants of pristine P3HT and IC$_{70}$BA\#1 were first measured (see Section 4.4.4). All P3HT:IC$_{70}$BA\#1 layers were fabricated on top of glass-ITO/PEDOT:PSS coated substrates (GIPP) and are shown in Figure 5.6(a). From this data the volume fractions of P3HT and ICBA in the top regions (located closer to interface with air) or bottom regions (located closer to interface with PEDOT:PSS) of the blend are extracted (%Vol(P3HT)$_{\text{top/bottom}}$ and %Vol(IC$_{70}$BA\#1)$_{\text{top/bottom}}$) as shown in Figure 5.6(b).

An efficient charge carrier transport is expected for a balanced vertical D/A distribution with a trend in increased P3HT content close to the PEDOT:PSS layer and an accumulation of IC$_{70}$BA\#1 molecules towards the top surface of the photoactive layer. This D/A distribution is beneficial, as it will facilitate the charge carrier transport towards the electrodes of the device. In this respect, P3HT:IC$_{70}$BA\#1 layers that were not subjected to any annealing procedure show an unbalanced D/A material distribution (74%Vol P3HT content on the top and 74%Vol IC$_{70}$BA\#1
5.3. P3HT:IC$_{70}$BA blend characteristics

Figure 5.6: Complex refractive indexes of (a) P3HT:IC$_{70}$BA#1 layers deposited at different fabrication conditions. (b) Vertical distribution of P3HT and IC$_{70}$BA#1 in the top and bottom regions of the their blend depending on the fabrication conditions.

content on the bottom of the layer). This unbalanced D/A material distribution indicates a high phase separation and it is furthermore enhanced after a TA step for 10 min/150 °C was carried out resulting in a %Vol(P3HT)$_{\text{top}}$ and %Vol(IC$_{70}$BA#1)$_{\text{bottom}}$ of 91%. The migration of the RI IC$_{70}$BA#1 molecules is attributed to the ability of the IC$_{70}$BA#1 material to remain miscible in the P3HT phase.[454] This effect is enhanced by the different surface energies of P3HT and IC$_{70}$BA#1 (27.2 mN m$^{-1}$ and 28.7 mN m$^{-1}$), as discussed in Section 5.2.5.

A balanced intermixing of the D/A components is achieved if the P3HT:IC$_{70}$BA#1 layers were subjected to an SA step. This can be seen in Figure 5.6(b), where 30 min SA layers show a visible better intermixing between the D and A phase (%Vol(IC$_{70}$BA#1 and P3HT)$_{\text{bottom}}$ of 54% and 46% vs. %Vol(IC$_{70}$BA#1 and P3HT)$_{\text{top}}$ of 36% and 64%), compared to the pristine layers (no SA and no TA). There is no alteration of the vertical D/A distribution after an additional TA step for 10 min at 90 °C. In contrast, TA steps at temperatures of 150 °C and 170 °C seem to provide a further driving force for material migration and rearrangement. The IC$_{70}$BA#1 contents at the bottom is increased to 60%Vol and the P3HT content is reduced to 40%Vol, whereas on the top regions 37%Vol of IC$_{70}$BA#1 molecules and 63%Vol of P3HT are observed for a TA at 150 °C. Further alteration of the vertical distribution is noted for a TA at 170 °C.

The results above suggest that the nano-morphological formation with respective molecular packing between P3HT and IC$_{70}$BA#1 are strictly dependent on the fabrication conditions. The TA step has a low impact on the vertical distribution of the D and A components of SA layers, compared to pristine films which were not subjected to SA. It appears that the SA and TA steps have the opposite effect on the morphological formation and molecular packing of the P3HT:IC$_{70}$BA#1 blend, but a combination of them is required for the formation of a balanced D/A distribution in the layer. Nevertheless, it is arguable that similar results will be obtained for IC$_{70}$BA#2, which exhibits a different regio-isomeric ratio distribution. Therefore, further optical characterisation of single RIs and their mixtures is required, in order to explain the BHJ formation depending on the fabrication conditions.
5.3.2. Thickness study of P3HT blends with regio-isomeric mixtures

The absorption spectra of P3HT:IC\textsubscript{70}BA\#1 layers which were fabricated at different spin-coating speeds from a 40 mg/mL D/A dispersion are presented in Figure 5.7(a). A study of P3HT:IC\textsubscript{70}BA\#2-based layers was not carried out, due to the identical properties of the D/A dispersions (solid material content and ratio) and the fabrication conditions used. It can be seen that highest optical density is achieved for films deposited at the lowest spin-coating velocities (500 rpm – 550 rpm), which result to the thickest layers in Figure 5.7(b). This is attributed to the correlation between the deposition velocity and the layer thickness, as discussed in Section 4.1.1.

The intensity of the absorption profile gradually decreases with the increased rotational velocity until 800 rpm, where an abrupt decrease in absorbance is observed. The UV-vis absorption profiles for layers fabricated at 800 rpm – 850 rpm additionally suggest that semi-dry P3HT:IC\textsubscript{70}BA\#1 layers are produced, which are unresponsive to a subsequent SA step. Despite the higher absorption intensity achieved at low spin-coating velocities, it was already shown in Section 3.2.1 that the optimal layer thickness for P3HT-based OPVs is about 210 nm.\[112\] As given in Figure 5.7(b), this thickness is achieved for a spin-coating velocity of 600 rpm – 650 rpm.

5.3.3. Spectral response of P3HT blends with regio-isomeric mixtures

In this section, the effect of the pre-annealing step (SA and/or TA) on the absorption spectra of P3HT:IC\textsubscript{70}BA layers is studied. The two IC\textsubscript{70}BA batches containing dissimilar mixtures of RIs were used. As shown in Figure 5.8(a), P3HT:IC\textsubscript{70}BA\#1 layers with a 5, 2, and 12 o’clock RI distribution of 22%, 43%, and 35% respectively, exhibit the lowest absorption spectra when they are quickly dried after the deposition procedure (no SA & no TA). In agreement with the observations made in Section 5.3.4, after the SA step the P3HT crystallinity is improved and the spectra is red shifted.\[455\] A maximum absorption peak at 490 nm and two shoulders at approximately 552 nm and 598 nm are observed. Additional broadening of the absorption spectra is seen when a TA step is carried out. A further red shift of the main absorption peak to

**Figure 5.7.** UV-vis absorption spectra of P3HT:IC\textsubscript{70}BA\#1 layers deposited at different spin-coating velocities (a) and the corresponding layer thickness (b).
5.3. P3HT:IC<sub>70</sub>BA blend characteristics

504 nm, is noticeable. The highest crystallinity is achieved for samples subjected to SA & TA, which is shown by the distinct vibronic shoulders of P3HT located at 548 nm and 601 nm, in addition to the shift of the main absorption peak to 510 nm. These vibrational transitions are related to the inter- and intra-chain states of the P3HT film, with a degree of self-organisation and interchain interactions induced by the fabrication conditions. A red shift of the peaks in the absorption spectra is furthermore attributed to stronger delocalisation of the conjugated π electrons and an increased π–π* optical transition within the P3HT blend. This is indicative of a high level of crystallinity within the P3HT phase. [455] Interestingly, there is a continuous increase and broadening of the absorption spectra of the P3HT:IC<sub>70</sub>BA#1 layers with lowest light absorbance observed for no SA & no TA layers, in contrast to the absorption which is achieved after the SA & TA step.

P3HT:IC<sub>70</sub>BA#2 layers have a 5, 2, and 12 o’clock RI distribution of 16%, 36%, and 48%. It is expected that the increased 12 o’clock RI presence will predominantly define the D/A blend formation and characteristics. Indeed, as shown in Figure 5.8(b), all layers exhibit visible lower light absorption profiles, despite that they have been deposited from a D/A dispersion with an identical solid material content, as used for the fabrication of the P3HT:IC<sub>70</sub>BA#1 layers shown in Figure 5.8(a). This general lower absorption, with the exception of TA only layers, is possibly due to the altered distribution of RIs of IC<sub>70</sub>BA. A pronounced P3HT crystallinity, which is less affected by the pre-annealing step is also noticeable in Figure 5.8(b). The main absorption peak of the P3HT:IC<sub>70</sub>BA#2 layers red-shifts depending on the annealing step from 490 nm for no SA & no TA layers over 495 nm for TA only layers, up to 514 nm for SA only and SA & TA. The second and third vibrational transitions of P3HT remain stable at about 548 nm and 600 nm.

The effect of temperature used for the TA step was also investigated, as shown for the P3HT:IC<sub>70</sub>BA#1 and P3HT:IC<sub>70</sub>BA#2 layers in Figures 5.8(c) and 5.8(d). The absorption spectra of P3HT:IC<sub>70</sub>BA#1 layers reveals similar optical characteristics. A slightly lower absorption for all annealing temperatures is observed for the layers thermally annealed at 150 °C and 170 °C. This is attributed to morphological alterations induced by the high thermal energy supplied, as already shown by the TGA and DSC characterisation in previous sections. This leads to segregation of the acceptor phase and disruption of the interplane stacking of P3HT molecules by IC<sub>70</sub>BA#1 clusters. [360]

P3HT:IC<sub>70</sub>BA#2 layers, on the other hand, exhibit much lower absorption profiles and do not show any clear trends in their absorption spectra depending on the annealing temperature used. There is no clear evidence of morphological alteration, occurring at high annealing temperatures. A possible explanation is an already aggregated IC<sub>70</sub>BA#2 phase, as evidenced by the visible layer inhomogeneity on the surface of the layer. This is attributed to the formation of agglomerates caused by the excess presence of the 12 o’clock RI in the IC<sub>70</sub>BA#2 sample.
5.3. P3HT:IC\textsubscript{70}BA blend characteristics

![UV-vis absorption spectra of P3HT:IC\textsubscript{70}BA#1 and P3HT:IC\textsubscript{70}BA#2 layers depending on (a) and (b) the annealing step (SA vs. TA) and (c) and (d) depending on the temperature for the TA step.]

**Figure 5.8.**: UV-vis absorption spectra of P3HT:IC\textsubscript{70}BA#1 and P3HT:IC\textsubscript{70}BA#2 layers depending on (a) and (b) the annealing step (SA vs. TA) and (c) and (d) depending on the temperature for the TA step.

### 5.3.4. Spectral response of P3HT blends with isolated regio-isomers

The spectral response of blends between P3HT and the isolated 5, 2, or 12 o’clock RIs obtained after the HPLC separation of IC\textsubscript{70}BA\#1 and IC\textsubscript{70}BA\#2 was also studied depending on the fabrication conditions. Each RI was mixed in a 1:1 ratio by weight with P3HT to form a 40 mg/mL dispersion. The dispersions were then used for the deposition the corresponding P3HT:IC\textsubscript{70}BA layer, which are given in Figure 5.9. The thickness of the layers deposited for this experimental section was not controlled, which may have caused an alteration of the optical density. Nevertheless, approximate thickness values can be obtained after comparing the optical densities of the absorption spectra in Figure 5.9 to those in Figure 5.7.

Layers deposited from dispersions of P3HT with the 5 o’clock RIs, which were isolated from the two IC\textsubscript{70}BA batches (hereafter IC\textsubscript{70}BA\#1–5 and IC\textsubscript{70}BA\#2–5) show very similar behaviour depending on the fabrication conditions. There is a distinctive red shift in the absorption
Figure 5.9: UV-vis absorption spectra of thin films consisting of P3HT blends with isolated RIs from IC$_{70}$BA#1 (left column) and IC$_{70}$BA#2 (right column): (a) and (b) – 5 o’clock, (c) and (d) – 2 o’clock, (e) and (f) – 12 o’clock RIs.
spectra depending on the annealing step used, as shown in Figures 5.9(a) and 5.9(b). The main absorption peak for no SA & no TA P3HT:IC\textsubscript{70BA} layers is shifted from 470 nm and 489 nm for IC\textsubscript{70BA}#1–5 and IC\textsubscript{70BA}#2–5 to 488 nm and 492 nm after a TA step for 10 min at 150 °C. Further red shift is observed when either SA only, or SA & TA is carried out, as shown in Figures 5.9(a) and 5.9(b). The second and third absorption peaks for the 5 o’clock RI remain nearly constant at 550 nm and 601 nm. There is a weak absorption peak at about 425 nm ascribed to absorption of the 5 o’clock RI, as shown in Appendix Figure B.2. The spectral response for the the 5 o’clock RI in a blend with P3HT exhibits the highest optical response, when the deposited layers are subjected to TA only.

Similar observations are made for blends of P3HT with the isolated 2 o’clock RIs from IC\textsubscript{70BA}#1 and IC\textsubscript{70BA}#2 (hereafter IC\textsubscript{70BA}#1–2 and IC\textsubscript{70BA}#2–2). As shown in Figures 5.9(c) and 5.9(d), there is a clear red shift in the spectral response of the films, in particular for the main absorption peaks located at 477 nm and 475 nm. The lowest P3HT crystallinity is observed for no SA & no TA layers. The main absorption peaks shift towards 488 nm and 486 nm for IC\textsubscript{70BA}#1–2 and IC\textsubscript{70BA}#2–2 when a TA step for 10 min at 150 °C is carried out. The highest P3HT crystallinity is observed for SA only layers and the absorption is red shifted to 515 nm and 514 nm for the IC\textsubscript{70BA}#1–2 and IC\textsubscript{70BA}#2 layers. Interestingly, a slight blue shift is observed when TA is carried out after the SA step and the position of the main absorption peak for both IC\textsubscript{70BA} batches moves to 512 nm. In addition, a relative decrease of the absorption (compared to TA only layers) is noticeable, which is attributed to morphological alterations within the BHJ, originating from a vertical D/A rearrangement (see SE data in Section 5.3.1) and possibly from an altered molecular packing of the blend. Nevertheless, despite an identical material concentration and ratio for all P3HT:IC\textsubscript{70BA} dispersions, the highest absorption profiles are observed for the 2 o’clock RIs. This result correlates with the increased spectral response observed for the P3HT:IC\textsubscript{70BA}#1 layers in Section 5.3.3, which also exhibit the largest presence of the 2 o’clock RI in the IC\textsubscript{70BA}#1 mixture (43%). Nevertheless, in a similar manner to the 5 o’clock RI the absorption profiles in Figures 5.9(c) and 5.9(d) show a nearly constant position of the second and third vibrational transitions of P3HT at 550 nm and 601 nm, regardless of the annealing step. Notably, there is a more pronounced absorption peak at about 425 nm, which can be ascribed to the absorption of the 2 o’clock RI itself, as shown in Appendix Figure B.2.

The absorption spectra of P3HT in a blend with the 12 o’clock RIs differ significantly, compared to these of the 5 and 2 o’clock RIs, as illustrated in Figures 5.9(e) and 5.9(f). For both IC\textsubscript{70BA} batches, the highest absorption profile is observed for layers subjected to TA only, followed by no SA & no TA treated layers. The lowest light absorption is achieved for SA only or SA & TA layers. It has to be emphasised, that compared to the 5 and 2 o’clock RIs, the 12 o’clock RI showed lower solubility. The dispersion with P3HT was less stable and prone to precipitation, as evidenced by the formation of visible agglomerates. Thus, the high level of P3HT crystallinity observed in Figures 5.9(e) and 5.9(f), regardless of the fabrication conditions used, can be attributed to the low solubility characteristics of the 12 o’clock RI, which does not intermix with the P3HT phase. Hence, the self-organisation and arrangement of P3HT is less disturbed by the IC\textsubscript{70BA} molecules and results to a more pronounced crystallisation of the donor phase. The reduced 12 o’clock content in the P3HT:IC\textsubscript{70BA} mixture is furthermore confirmed.
by the lower absorption spectra of the layers, especially in the wavelengths 300 nm – 500 nm where the main absorption peak of the material is (see Figure B.2). These results also explain the lower optical density observed for the blends between P3HT and the regio-isomeric mixture of IC70BA#2 in Section 5.3.3. The main absorption peak for no SA and no TA IC70BA#1–12 and IC70BA#2–12 layers is located at 520 nm and 523 nm, respectively. It is further red-shifted when SA or SA and TA is carried out. In contrast to P3HT blends with the 5 and 2 o’clock RIs, a TA step for the 12 o’clock RI blue-shifts the absorption spectra of the P3HT:IC70BA#1–12 and P3HT:IC70BA#2–12 layers to 507 nm and 514 nm, respectively. This indicates morphological alterations, which reduce the blend crystallinity. Possible reason is segregation of the 12 o’clock IC70BA molecules within the P3HT matrix, impeding the self-organisation and arrangement of P3HT chains. Such excess aggregation could lead to large scale phase separation and have a detrimental effect on charge carrier generation and separation within the BHJ. Furthermore, it is questionable if such a high level of crystallinity, observed for the 12 o’clock RI, is beneficial for the electro-optical properties of the P3HT:IC70BA blend. It is also possible that the defining factor in the alteration of the photoactive layer performance is the proportion of the 12 o’clock RI in the regio-isomeric mixture.

5.3.5. Topography of IC70BA#1 regio-isomeric mixture in a blend with P3HT

Atomic Force Microscopy (AFM) was used to characterise the surface topography of P3HT:IC70BA#1 layers, which were fabricated under various annealing conditions. All samples were deposited from a P3HT:IC70BA#1 dispersion with a 1:1 material ratio by weight and a total concentration of 40 mg/mL, which was spin-coated at velocities below 700 rpm. For this study no optical micrographs of the surface of the samples were taken, due to a visible homogeneity of the layers and the absence of agglomerates on the surface, compared to the samples fabricated from the P3HT:IC70BA#2 dispersion as already discussed in previous sections.

An obvious alteration of the surface topography of P3HT:IC70BA#1 layers subjected to SA is observed in the AFM scans in Figure 5.10. As shown in the 10 × 10 µm height scan in Figure 5.10(a), no formation of a D/A network can be observed on the surface of the no SA & no TA P3HT:IC70BA#1 layers. Clusters with an average size of 304±172 nm can be seen additionally on the surface of the layers. In contrast, different features are observed upon an 30 min SA step, as shown in Figure 5.10(d).

The 1 × 1 µm height scans in Figures 5.10(b) and 5.10(e) show noticeable differences in the topography of the layers. Layers that were not subjected to SA exhibit a root mean squared (R\text{RMS}) and arithmetic average of absolute values (R\text{a}) surface roughness of 1.1 nm and 0.8 nm. In comparison, rougher surfaces are seen for the SA only layers (R\text{RMS} of 2.5 nm and R\text{a} of 2.0 nm). This roughness increase is indicative of the self-organisation of P3HT, and to some extent to agglomeration of the IC70BA#1 molecules, as higher surface roughness is commonly observed for crystalline films.\[352\] The AFM data points to the formation of crystalline phases in the BHJ and confirms the assumptions made, based on the UV-vis spectra of P3HT:IC70BA#1 layers in Section 5.3.3. Nevertheless, the higher surface roughness can lead to an increased interfacial contact resistance which can cause a rise in the R\text{s} of the device and reduce the PCE.\[161\]
5.3. P3HT:IC\textsubscript{70}BA blend characteristics

The morphological alterations of P3HT:IC\textsubscript{70}BA\#1 layers due to the SA step are also visible in the phase images in Figures 5.10(c) and 5.10(f). The surface of no SA & no TA layers is predominantly covered by P3HT nanofibres, whereas the IC\textsubscript{70}BA\#1 molecules appear to have settled at the bottom of the blend. Considering the CA characterisation, carried out in Section 5.2.5, this material distribution can be explained with the different surface energies of P3HT and IC\textsubscript{70}BA.\textsuperscript{[456]} It is judicious to assume, that due to a quick solvent evaporation after the deposition procedure (approximately 5 s) and a following solidification of the D/A layer, there is not sufficient time for the IC\textsubscript{70}BA\#1 molecules to migrate towards the top surface of the layer. This leads to an unfavourable D/A material distribution which is expected to reduce the characteristics of the OPV devices. The introduction of the SA step allows for a reduction of the solvent evaporation rate and therefore there is sufficient time for the formation of a balanced D/A interpenetrating network. This result is in accordance with the SE analysis in Section 5.3.1.

The effect of the TA step on the BHJ nano-morphology was also investigated, as shown in Figure 5.11, where AFM scans of samples annealed for 10 min at four different temperatures ranging from 90 °C to 150 °C are presented. It can be seen from the 5 × 5 \( \mu \)m height scans in Figures 5.11(a), 5.11(d), 5.11(g), and 5.11(j) that all P3HT:IC\textsubscript{70}BA\#1 layers exhibit good interpenetrating D/A networks with similar R\textsubscript{RMS} values (see Table 5.1), independently from the annealing temperature. Layers annealed at 150 °C, exhibit the lowest R\textsubscript{RMS} of 2.6 nm and the maximum height in z-direction R\textsubscript{MAX} of 20.7 nm, compared to all other samples. A closer view of the topography is given in the 1 × 1 \( \mu \)m height scans in Figures 5.11(b), 5.11(e), 5.11(h), and 5.11(k) and the respective phase images in Figures 5.11(c), 5.11(f), 5.11(i), and 5.11(l).
Figure 5.11.: AFM topography scans of P3HT:IC$_{70}$BA#1 layers depending on the temperature used for the TA step. All layers were subjected to a SA step prior to TA for 10 min at (a–c) 90 °C, (d–f) 110 °C, (g–i) 130 °C, and (j–l) 150 °C.
Table 5.1.: Summarised surface roughness values for different annealing temperatures used for the fabrication of the P3HT:IC\textsubscript{70}BA\#1 layers in Figure 5.11. The TA step was carried out after SA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing temp. (°C)</th>
<th>Size (µm)</th>
<th>(R_{\text{RMS}}) (nm)</th>
<th>(R_{a}) (nm)</th>
<th>(R_{\text{MAX}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>90</td>
<td>5 × 5</td>
<td>3.5</td>
<td>2.8</td>
<td>28.8</td>
</tr>
<tr>
<td>(b)</td>
<td>90</td>
<td>1 × 1</td>
<td>2.0</td>
<td>1.6</td>
<td>12.6</td>
</tr>
<tr>
<td>(d)</td>
<td>110</td>
<td>5 × 5</td>
<td>4.6</td>
<td>3.7</td>
<td>30.5</td>
</tr>
<tr>
<td>(e)</td>
<td>110</td>
<td>1 × 1</td>
<td>2.0</td>
<td>1.5</td>
<td>13.2</td>
</tr>
<tr>
<td>(g)</td>
<td>130</td>
<td>5 × 5</td>
<td>3.5</td>
<td>2.7</td>
<td>27.1</td>
</tr>
<tr>
<td>(h)</td>
<td>130</td>
<td>1 × 1</td>
<td>1.7</td>
<td>1.4</td>
<td>10.6</td>
</tr>
<tr>
<td>(j)</td>
<td>150</td>
<td>5 × 5</td>
<td>2.6</td>
<td>2.0</td>
<td>20.7</td>
</tr>
<tr>
<td>(k)</td>
<td>150</td>
<td>1 × 1</td>
<td>2.1</td>
<td>1.7</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Clearly, the surface roughness of all layers is decreased, compared to the non-annealed sample in Figure 5.10(e). In this regard, improved device characteristics are foreseen for P3HT:IC\textsubscript{70}BA\#1 layers subjected to TA after the SA step, due to an expected low contact resistance at the interface between the smooth surface of the BHJ and the layer above.

5.3.6. Topography of IC\textsubscript{70}BA\#2 regio-isomeric mixture in a blend with P3HT

Prior to the AFM characterisation of the P3HT:IC\textsubscript{70}BA\#2 layers fabricated at different annealing conditions, optical micrographs of the surface of the films were obtained. This was needed due to the visible inhomogeneities observed on the surface of the layers, compared to the P3HT:IC\textsubscript{70}BA\#1 layers. Clearly, the layers in Figure 5.12(a), which have not been subjected to SA or TA, exhibit large scale phase separation as evident from the formation of agglomerates with sizes in the µm–range. Similar trends are noted for the layers subjected to SA only in Figure 5.12(c) or SA & TA in Figure 5.12(b). It appears that the SA step induces excess segregation of the D/A blend. Nevertheless, as previously shown by the UV-vis characterisation in Section 5.3.3, the SA step has to be carried out, as it is required for achieving crystallisation of the P3HT phase. Therefore, it is not to be omitted. The highest layer homogeneity is observed in Figure 5.12(d), which shows the optical micrograph of TA only layers. Agglomerate formation is still present, despite being less pronounced, compared to all other samples.

The decreased homogeneity of the layers is attributed to the different mixture of RIs of IC\textsubscript{70}BA\#2, which in comparison to IC\textsubscript{70}BA\#1 contains larger proportion of the 12 o’clock RI (48% vs. 35%). As mentioned in previous sections, a precipitation of the P3HT:IC\textsubscript{70}BA\#1-12 and P3HT:IC\textsubscript{70}BA\#2-12 dispersions has been observed. Hence, the low layer homogeneity for P3HT:IC\textsubscript{70}BA\#2 is attributed to poor D/A intermixing due to the large quantity of the 12 o’clock RI, that forms agglomerates already in the D/A dispersion prior to the deposition process. It appears that P3HT:IC\textsubscript{70}BA blends which contain more 12 o’clock RI are prone to segregation, which is furthermore enhanced when SA is carried out. Nevertheless, the SA step is required for the crystallisation of P3HT. This emphasises, that regardless the tailoring of the device fabrication conditions, the P3HT:IC\textsubscript{70}BA\#2 blend should underperform compared to blends with a lower 12 o’clock content such as P3HT:IC\textsubscript{70}BA\#1.
5.3. P3HT:IC₇₀BA blend characteristics

Figure 5.12.: Optical micrographs of the surface of P3HT:IC₇₀BA#2 layers depending on the annealing step used after the deposition procedure. Layers subjected to (a) no SA & no TA, (b) SA & TA, (c) SA only, and (d) TA only. The TA step was carried out for 10 min at 150 °C. The optical micrographs were captured during the AFM characterisation.

The surface topography of the P3HT:IC₇₀BA#2 layers shown in Figures 5.12(a–d) was also studied by means of using AFM. The scans were carried out at locations on the samples, which were free from agglomerates, in order to gain a better understanding of the topography of the more homogeneous and smoother parts of the P3HT:IC₇₀BA#2 layers. Nevertheless, an expected increased surface roughness, reduced interfacial contact, and altered drying dynamics of the P3HT:IC₇₀BA#2 layers is expected due to the presence of µm–sized agglomerates, as shown in Figure 5.12.

From the 10x10 µm height scans in Figures 5.13(a), 5.13(c), 5.13(e), and 5.13(g) and the summarised surface roughness values in Table 5.2 it can be seen that the highest R₉₅₉ values are measured for P3HT:IC₇₀BA#2 layers that were subjected to SA or SA & TA (17.2 nm and 25.3 nm, respectively). The R₉₅₉ for no SA & no TA layers is decreased to 10.8 nm, which is attributed to a quicker solvent evaporation after the layer deposition process which reduces the time for aggregation of the IC₇₀BA#2 phase. The smoothest layers are observed when TA only was carried out. This result is in a good agreement with the observations made from the optical micrographs in Figures 5.12(a–d) where TA only layers exhibit the highest homogeneity. The low R₉₅₉ value of 1.7 nm is ascribed to the quick drying process of the layer, during which in a similar manner to the no SA & no TA layers, there is not enough time for rearrangement and agglomeration of the IC₇₀BA#2 molecules.

Figures 5.13(b), 5.13(d), 5.13(f), and 5.13(h) show magnified 3x3 µm AFM height scans of the P3HT:IC₇₀BA#2 layers. As shown in Table 5.2, layers subjected to SA or SA & TA exhibit R₉₅₉ surface roughness of 8.1 nm and 6.1 nm. These P3HT:IC₇₀BA#2 layers also show the highest R₉₅₉ (67.6 nm and 39.1 nm). In comparison, lower R₉₅₉ values of 1.8 nm and 1.6 nm were observed for no SA & no TA and TA only layers (R₉₅₉ follows similar trends). Interestingly, for the TA only layers in Figure 5.13(h), features similar to those observed for SA & TA layers of P3HT:IC₇₀BA#1 (see Figure 5.11) are noticeable. It is believed that these features are evident for an already existing IC₇₀BA#2 aggregation within the blend with P3HT, induced possibly due to the larger amount of the 12 o’clock RI. This implies that P3HT:IC₇₀BA#2 layers subjected to TA appear morphologically similar to P3HT:IC₇₀BA#1 layers, subjected to SA & TA. Nevertheless, this assumption is appropriate only for the IC₇₀BA phase. The P3HT phase, in contrast, does not reach a high level of crystallisation, as evident from the UV-vis spectra in Figure 5.8.
5.3. P3HT:IC$_{70}$BA blend characteristics

![AFM topography scans](image)

**Figure 5.13.** AFM topography scans of P3HT:IC$_{70}$BA#2 layers depending on the annealing step. Layers subjected to (a–b) no SA & no TA, (c–d) SA & TA, (e–f) SA only, and (g–h) TA only. The TA step was carried out for 10 min at 150 °C.
Table 5.2.: Summarised surface roughness values for the P3HT:IC$_{70}$BA#2 layers in Figure 5.13 depending on the annealing step.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing step</th>
<th>Size (µm)</th>
<th>( R_{RMS} ) (nm)</th>
<th>( R_a ) (nm)</th>
<th>( R_{MAX} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>no SA &amp; no TA</td>
<td>10 × 10</td>
<td>10.8</td>
<td>6.3</td>
<td>243.9</td>
</tr>
<tr>
<td>(b)</td>
<td>no SA &amp; no TA</td>
<td>3 × 3</td>
<td>1.8</td>
<td>1.4</td>
<td>18.9</td>
</tr>
<tr>
<td>(d)</td>
<td>SA &amp; TA</td>
<td>10 × 10</td>
<td>25.3</td>
<td>18.9</td>
<td>202.7</td>
</tr>
<tr>
<td>(e)</td>
<td>SA &amp; TA</td>
<td>3 × 3</td>
<td>6.1</td>
<td>4.7</td>
<td>39.1</td>
</tr>
<tr>
<td>(g)</td>
<td>SA only</td>
<td>10 × 10</td>
<td>17.2</td>
<td>14.1</td>
<td>135.8</td>
</tr>
<tr>
<td>(h)</td>
<td>SA only</td>
<td>3 × 3</td>
<td>8.1</td>
<td>6.4</td>
<td>67.6</td>
</tr>
<tr>
<td>(j)</td>
<td>TA only</td>
<td>10 × 10</td>
<td>1.7</td>
<td>1.3</td>
<td>38.9</td>
</tr>
<tr>
<td>(k)</td>
<td>TA only</td>
<td>3 × 3</td>
<td>1.6</td>
<td>1.2</td>
<td>17.2</td>
</tr>
</tbody>
</table>

5.3.7. Topography of IC$_{70}$BA regio-isomers in a blend with P3HT

The surface topography of D/A layers fabricated from dispersions of P3HT with the separated 5, 2, or 12 o’clock IC$_{70}$BA RIs was also characterised by AFM. Due to an expected similarity between the RIs for each IC$_{70}$BA batch (i.e. after the HPLC separation IC$_{70}$BA#1-5 should be identical to IC$_{70}$BA#2-5), the topography of P3HT:IC$_{70}$BA#1 layers only was chosen for the study. All layers were deposited at identical conditions (see previous section) and were subjected to SA & TA (10 min/150 °C). Only this annealing step was chosen, based on the experimental results in previous sections.

As shown in Figures 5.14(a–c), optical micrographs of the surface of each P3HT:IC$_{70}$BA#1 layer were obtained prior to conducting the AFM characterisation. Noticeable agglomeration is observed for all samples. The surface of the P3HT:IC$_{70}$BA#1-2 o’clock layer in Figure 5.14(b) visibly exhibits the highest homogeneity and lowest number of agglomerates. Nevertheless, compared to the P3HT:IC$_{70}$BA#1-5 o’clock sample in Figure 5.14(a), the few agglomerates on the surface of the 2 o’clock layer show visibly larger dimensions. The surface of the 5 o’clock sample appears rough, with numerous agglomerates on it. In comparison, the P3HT:IC$_{70}$BA#1-12 layer in Figure 5.14(c) has the lowest homogeneity among all samples. This infers a possible excess 12 o’clock material segregation, as discussed in previous sections.

Figure 5.14.: Optical micrographs of the surface of the (a) 5, (b) 2, and (c) 12 o’clock RI layers deposited from P3HT:IC$_{70}$BA#1 dispersions, which were subjected to SA & TA. The optical micrographs were captured prior to the AFM characterisation.
5.3. P3HT:IC\textsubscript{70}BA blend characteristics

The observations above are strengthened by the AFM characterisation of the layers. A formation of large-sized agglomerates is visible on the surface of the 5 and 12 o’clock layers, as shown in the 10 × 10 \(\mu\)m height scans in Figures 5.15(a) and 5.15(e), respectively. The corresponding \(R_{\text{MAX}}\) for the samples is 498 nm and 900 nm (see Table 5.3). In a good agreement with the observations based on the optical micrographs of the surface, lower \(R_{\text{MAX}}\) of 176 nm is measured for the 2 o’clock sample in Figure 5.15(c).

Further details of the surface of the 5, 2, and 12 o’clock RI layers are visible in the magnified 3 × 3 \(\mu\)m height scans in Figures 5.15(b), 5.15(d), and 5.15(f). Compared to the 2 o’clock layer, the 5 and 12 o’clock layers exhibit lower \(R_{a}\) and \(R_{\text{RMS}}\) values, as summarised in Table 5.3. However, it has to be noted that the AFM scans of the P3HT:IC\textsubscript{70}BA\#1-5 and P3HT:IC\textsubscript{70}BA\#1-12 layers were carried out purposely on agglomerate-free areas of the samples, in order to gain a better understanding of the surface topography of the more homogeneous areas, and to obtain continuous AFM maps. Features similar to fibres, inferring a predominant presence of P3HT on the surface and therefore an unbalanced vertical D/A distribution, can be seen for the P3HT:IC\textsubscript{70}BA\#1-5 sample. The P3HT fibris surround a large-sized agglomerate (approximately 1 \(\mu\)m in diameter), which is attributed to an excess segregation of IC\textsubscript{70}BA. Similar IC\textsubscript{70}BA formations are observed on the surface of the P3HT:IC\textsubscript{70}BA\#1-2 layer. The smoothest layer surface (\(R_{a}\) of 9.1 nm) is observed for the P3HT:IC\textsubscript{70}BA\#1-12 layer in Figure 5.15(f). However, on a larger scale the excess material crystallisation is expected to detrimentally affect the device performance.

**Table 5.3:** Summarised surface roughness values for the P3HT:IC\textsubscript{70}BA\#1 layers in Figure 5.15 depending on the RI type.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>RI Size ((\mu)m)</th>
<th>(R_{\text{RMS}}) (nm)</th>
<th>(R_{a}) (nm)</th>
<th>(R_{\text{MAX}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 5 o’clock</td>
<td>10 × 10</td>
<td>68.6</td>
<td>50.8</td>
<td>498.0</td>
</tr>
<tr>
<td>(b) 5 o’clock</td>
<td>3 × 3</td>
<td>13.1</td>
<td>10.6</td>
<td>77.6</td>
</tr>
<tr>
<td>(d) 2 o’clock</td>
<td>10 × 10</td>
<td>26.0</td>
<td>20.0</td>
<td>175.9</td>
</tr>
<tr>
<td>(e) 2 o’clock</td>
<td>3 × 3</td>
<td>33.2</td>
<td>26.8</td>
<td>181.2</td>
</tr>
<tr>
<td>(g) 12 o’clock</td>
<td>10 × 10</td>
<td>122.0</td>
<td>92.2</td>
<td>900.8</td>
</tr>
<tr>
<td>(h) 12 o’clock</td>
<td>3 × 3</td>
<td>11.6</td>
<td>9.1</td>
<td>73.9</td>
</tr>
</tbody>
</table>
Figure 5.15: AFM topography scans of layers deposited from a dispersion of P3HT with isolated 5 (a–c), 2 (d–f), and 12 (g–i) o’clock RIs of IC\textsubscript{70}BA#1. The layers were subjected to SA and TA for 10 min at 150 °C.
5.4. P3HT:IC\textsubscript{70}BA device characteristics

This section demonstrates the performance of complete P3HT:IC\textsubscript{70}BA-based OPVs which were fabricated from dispersions of P3HT with the regio-isomeric mixtures of IC\textsubscript{70}BA\#1 and IC\textsubscript{70}BA\#2, or the separated 5, 2, and 12 o’clock RIs of the two acceptors. Preliminary results showed significantly higher device PCEs for the regio-isomeric mixture of IC\textsubscript{70}BA\#1, compared to IC\textsubscript{70}BA\#2. Therefore, aiming at achieving high OPV device characteristics an optimisation of the fabrication conditions for the P3HT:IC\textsubscript{70}BA\#1 layer was undertaken at the beginning of the study, followed by a tailoring of the photoactive layer thickness. The knowledge obtained was then transferred onto BHJs between P3HT and the mixture of RIs of IC\textsubscript{70}BA\#2, or the separated RIs of the two IC\textsubscript{70}BA samples, in order to investigate the effect of the regio-isomeric properties of IC\textsubscript{70}BA on the characteristics of the solar cells produced. A device structure of glass (750 \(\mu\)m)/ITO (150 nm)/ PEDOT:PSS (40 nm)/BHJ (X nm)/BCP (3.0 nm)/Al (100 nm) was chosen for all studies in this section.

5.4.1. Tailoring the fabrication conditions for P3HT:IC\textsubscript{70}BA\#1 layers

The spectral response and morphological characteristics of P3HT:IC\textsubscript{70}BA-based layers crucially depend on the annealing step used after the D/A deposition procedure, as shown in previous sections. In this section the effect of the annealing step (no SA & no TA; SA only; TA only; SA & TA) on the P3HT:IC\textsubscript{70}BA\#1-based OPV characteristics is studied in detail. In agreement with the the UV-vis, AFM characterisation data, and device preliminary results, mentioned in previous sections, the study here was carried out on P3HT:IC\textsubscript{70}BA\#1-based devices only, due to their potential for further characteristics improvement.

Figure 5.16(a) and Table 5.4 show the OPV device characteristics with respect to the annealing step used for the fabrication of the photoactive layer. A spin-coating velocity of 600 rpm was chosen for the deposition of the P3HT:IC\textsubscript{70}BA\#1 layer, as discussed in Section 5.3.2. The highest device performance is observed for solar cells subjected to SA & TA (10 min / 150 \(^\circ\)C), which induce high P3HT crystallinity and appropriate molecular packing of the D/A blend. This result is in an excellent agreement with the observations made during the characterisation phase of the P3HT:IC\textsubscript{70}BA\#1 blend in Section 5.3 where according to the SE, UV-vis, and AFM data optimal device characteristics were expected for photoactive layers subjected to SA & TA. Indeed, the combination of these annealing steps induces a balanced vertical distribution between P3HT and IC\textsubscript{70}BA\#1, which facilitates charge carrier transport towards the electrodes of the device. This is evident by the high average FF of 69.7±3.6%. These high FF values are also correlated to a decreased interfacial resistance, due to the smooth P3HT:IC\textsubscript{70}BA\#1 layers, as indicated by the AFM characterisation in Section 5.3.5. As a result PCEs of 5.97±0.40% are measured, as summarised in Table 5.4. These high device characteristics are additionally ascribed to an appropriate dense molecular packing of the P3HT:IC\textsubscript{70}BA\#1 blend, which is accomplished due to the particular regio-isomeric distribution of IC\textsubscript{70}BA\#1 that leads to a beneficial electronic coupling for electron transfer between the acceptor molecules and therefore high charge carrier mobilities.[175, 457]

Slightly lower average FF, J\textsubscript{SC}, and PCE of 65.4±0.6%, 9.93±0.54 mA/cm\textsuperscript{2}, and 5.37±0.76% were measured for P3HT:IC\textsubscript{70}BA\#1 devices subjected to SA only. This is due to comparable
vertical distribution between the D/A materials, as shown in Section 5.3.1. However, the absent TA step reduces the migration and rearrangement of the IC$_{70}$BA#1 molecules in order to form a more closely packed acceptor network, which was shown to start from about 90 °C (see DSC data in Section 5.2.4). As a result, reduced charge carriers mobility within the P3HT:IC$_{70}$BA#1 blend is expected, which can cause increased recombination processes and decreased device FFs.

The importance of a balanced D/A distribution and an appropriate molecular packing of the blend is furthermore evident when the SA step is not carried out. As shown in Figure 5.16, devices with TA only P3HT:IC$_{70}$BA#1 layers exhibit a further decrease in their characteristics. As summarised in Table 5.4, average $J_{SC}$ and FF values of 7.40±0.32 mA/cm$^2$ and 55.7±9.4% were measured, which is due to the P3HT enrichment on top, and IC$_{70}$BA#1 settlement at the bottom of the photoactive layer, as shown by the SE data in Section 5.3.1. It is noteworthy to mention, that according to the SE data the most unfavourable D/A material distribution is achieved for TA only devices. However, the experimental data in this section clearly shows that this in not the case. An explanation is given by the UV-vis absorption spectra in Section 5.3.3, which showed an appropriate crystallisation of the P3HT phase due to the TA step. This controversy shows that there are several factors that influence the characteristics of the P3HT:IC$_{70}$BA#1 blend. The reduced $J_{SC}$ additionally implies insufficient rearrangement and migration of acceptor molecules, due to the absence of the SA step, which results to the unbalanced D/A blend distribution and leads to decreased charge carrier mobilities and device characteristics.[453] Nevertheless, it has to be noted that an excess segregation of the IC$_{70}$BA molecules, which was observed in previous sections for blends of P3HT with the regio-isomeric mixture or some of the isolated RIs of IC$_{70}$BA#2 is unfavourable and can lead to poor device performance.

Figure 5.16.: J-V characteristics of P3HT:IC$_{70}$BA#1-based OPVs with (a) photoactive layers fabricated at different annealing conditions. Corresponding EQE spectra is shown in (b). The J-V data shows the average characteristics over a number of devices (n>5) for each type, while the EQE spectra is representative of the best performing device. The dark current characteristics in (a) are shown with dotted lines.
Table 5.4.: Summarised OPV device characteristics depending on the annealing conditions used for the fabrication of P3HT:IC$_{70}$BA#1 blend of the devices in Figure 5.16.

<table>
<thead>
<tr>
<th>Annealing conditions</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE average (%)</th>
<th>PCE max (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA &amp; TA</td>
<td>0.85±0.01</td>
<td>10.03±0.46</td>
<td>69.7±3.6</td>
<td>5.97±0.40</td>
<td>6.74</td>
</tr>
<tr>
<td>TA only</td>
<td>0.86±0.01</td>
<td>7.40±0.32</td>
<td>55.7±9.4</td>
<td>3.58±0.76</td>
<td>4.34</td>
</tr>
<tr>
<td>SA only</td>
<td>0.83±0.00</td>
<td>9.93±0.54</td>
<td>65.4±0.6</td>
<td>5.37±0.76</td>
<td>5.79</td>
</tr>
<tr>
<td>no SA &amp; no TA</td>
<td>0.87±0.01</td>
<td>4.83±0.18</td>
<td>33.7±1.9</td>
<td>1.42±0.12</td>
<td>1.55</td>
</tr>
</tbody>
</table>

The lowest device characteristics in Figure 5.16(a) are observed when no SA & no TA was carried out after the deposition of the P3HT:IC$_{70}$BA#1 blend. Nearly two times lower average $J_{SC}$ of 4.83±0.18 mA/cm$^2$ is measured, compared to the best performing devices, which were subjected to SA & TA. This is attributed to reduced light absorption within the P3HT:IC$_{70}$BA#1 blend in addition to a lower self-organisation and crystallisation of P3HT as shown by the UV-vis characterisation in Section 5.3.3. It is judicious to believe that these adverse device characteristics are additionally strengthened by a disadvantageous molecular packing between the D and A components in the blend due to incomplete rearrangement and migration of the IC$_{70}$BA#1 molecules closer to the PEDOT:PSS layer. This is supported by the SE and AFM characterisation in Section 5.3 (Figures 5.6(b) and 5.10(c)). These adverse D/A phase separation and distribution are additionally evident from the low device FFs of 33.7±1.9%, which imply an unbalanced charge carrier transport properties and increased recombination yields. As a result, low device PCEs of 1.42±0.12% are achieved with the best performing OPV solar cell exhibiting a PCE of 1.55%.

The EQE spectra of the best performing OPV devices depending on the annealing conditions are shown in Figure 5.16(b). In accordance with the J-V data in Figure 5.16(a), the highest EQE spectra was measured for the device subjected to SA & TA, which is about 60% for the wavelengths $450 \text{ nm} - 630 \text{ nm}$. Slightly lower EQE of 55% is observed when the photoactive layer was subjected to a SA step only. The EQE spectra exhibits further decrease similarly to the reduced $J_{SC}$ values observed for the TA only or the no SA & no TA devices in Table 5.4.

5.4.2. Optimisation of the photoactive layer thickness

An optimisation of the photon flux absorption within the photoactive layer and subsequent resulting exciton generation, separation, and transport processes for the particular device structure mentioned in Section 5.4.1 was carried out in order to achieve optimal OPV characteristics. For the purpose, a step-wise alteration of the P3HT:IC$_{70}$BA#1 thickness was accomplished by varying the rotational velocity of the spin-coating procedure, used for the deposition of the D/A dispersion. The latter was a 40 mg/mL P3HT:IC$_{70}$BA#1 dispersion with a 1:1 material ratio by weight. The optimised fabrication condition for the D/A layer deposition (SA & TA for 10 min at 150 °C) were used for this study, as drawn from the experimental results in Section 5.4.1.

As already stated in the experimental Section 4.2.2, the P3HT:IC$_{70}$BA#1 layer was deposited in a two step spin-coating process: the first step for 80 s with a rotation velocity altered
from 500 rpm to 850 rpm, followed by the second step for 5 s at 1000 rpm. As shown in Figure 5.17 and summarised in Table 5.5, there is a continuous decrease of the devices’ $J_{SC}$, related to the decreased light absorption in the BHJ due to the reduced photoactive layer thickness (see also Figure 5.7(b) in Section 5.3.2). The average $J_{SC}$ is reduced from 10.05 mA/cm$^2$ in Figure 5.17(a) (500 rpm devices, thickness of 238.3±3.86 nm) down to 6.10 mA/cm$^2$ in Figure 5.17(c) (850 rpm devices, thickness of 175.3±4.1 nm). As summarised in Table 5.5, upon increasing the rotation velocity from 800 rpm to 850 rpm, there is an abrupt decrease in $J_{SC}$ from 8.98 mA/cm$^2$ to 6.10 mA/cm$^2$, which cannot be explained solely by a reduction in the BHJ thickness. Based on the UV-vis data in Section 5.3.2, this $J_{SC}$ decrease is dominated by a rapid drying of the P3HT:IC$_{70}$BA#1 layer, leading to reduced P3HT crystallinity and unbalanced vertical D/A material distribution. This is evident from the lower device FFs and consequently PCEs for the 850 rpm solar cells as shown in Table 5.5, when compared to the other OPVs. The highest average $J_{SC}$ values were measured for the solar cells fabricated with a first spin-coating step at 500 rpm – 650 rpm, due to a greater light absorption compared to the other OPVs. The data in Table 5.5 indicates a stable device $V_{OC}$ of approximately 0.86 V. This is correlated to the homogeneity of the P3HT:IC$_{70}$BA#1 layers, which exhibit a nearly defect and agglomerates free surfaces, as evidenced by the AFM characterisation in Section 5.3.5.

The highest PCE values of 5.97±0.40% and 5.95±0.29% are obtained when the photoactive layer was deposited at a velocity of 600 rpm – 650 rpm. This originates from an optimised balance between photon flux absorption and an equalised charge carrier transport, as evidenced by the high average FF values of 69.7±3.6% and 71.3±2.6%, respectively. The best performing P3HT:IC$_{70}$BA#1-based device exhibits $V_{OC}$ of 0.86 V, $J_{SC}$ of 10.91 mA/cm$^2$, and FF of 72%, which result to a peak PCE of 6.74%. It is worth noting that this is a record PCE value that was measured for such a large device active area (0.43 cm$^2$), as shown in Section 3.4.

The highest EQE responses in Figure 5.17(b) are observed for the OPV devices fabricated at 600 and 650 rpm (best performing solar cells with PCEs of 6.74% and 6.45%). These OPVs exhibit EQE spectra above 55% for the wavelengths 400 nm – 500 nm and exceed 60% in the range 500 nm – 630 nm. Lower EQE responses were measured for the devices fabricated at 500 nm and 550 nm. Here, despite comparable $J_{SC}$ values, lower peak PCEs of 5.86% and 5.92% are calculated, mainly due to reduced device FFs, as shown in Table 5.5. This is attributed to the increased BHJ thickness and therefore longer distances which free charge carriers have to overcome in order to reach the electrodes, that lead to higher probability for bi-molecular recombination processes.

The EQE spectra of solar cells fabricated at rotation velocities ranging between 700 rpm – 850 rpm are shown in Figure 5.17(d). It can be seen that highest EQE spectra was measured for the best performing 700 rpm device, that exhibits a peak PCE of 5.73%. A reduction of the EQE spectra is observed for the solar cells fabricated at a higher spin-coating velocity. In accordance with the J-V curves in Figure 5.17(c), the lowest EQE spectra was recorded for the fabrication velocity of 850 rpm, adversely influencing the device output characteristics (best performing solar cell exhibits $V_{OC}$ of 0.87 V, $J_{SC}$ of 6.24 mA/cm$^2$, FF of 56.1%, and PCE of 3.05%).
5.4. P3HT:IC<sub>70</sub>BA device characteristics

Figure 5.17.: J-V characteristics of P3HT:IC<sub>70</sub>BA#1-based OPVs with photoactive layers fabricated at a different spin-coating velocity: (a) 500 rpm – 650 rpm and (c) 700 rpm – 850 rpm. Corresponding EQE spectra are shown in (b) and (d). The J-V data shows the average characteristics over a number of devices for each type, while the EQE spectra is representative of the best performing device. The dark current characteristics in (a) and (c) are shown with dotted lines.

Table 5.5.: Summarised OPV device characteristics depending on the spin-coating velocity used for the deposition of the photoactive P3HT:IC<sub>70</sub>BA#1 layer in Figure 5.17.

<table>
<thead>
<tr>
<th>Spin-coating velocity (rpm)</th>
<th>VOC (V)</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>PCE average (%)</th>
<th>PCE max (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.87±0.01</td>
<td>10.05±0.09</td>
<td>66.6±0.6</td>
<td>5.79±0.07</td>
<td>5.86</td>
</tr>
<tr>
<td>550</td>
<td>0.86±0.01</td>
<td>10.05±0.06</td>
<td>65.9±1.9</td>
<td>5.72±0.19</td>
<td>5.92</td>
</tr>
<tr>
<td>600</td>
<td>0.85±0.01</td>
<td>10.03±0.46</td>
<td>69.7±3.6</td>
<td>5.97±0.40</td>
<td>6.74</td>
</tr>
<tr>
<td>650</td>
<td>0.85±0.01</td>
<td>9.80±0.33</td>
<td>71.3±2.6</td>
<td>5.95±0.29</td>
<td>6.45</td>
</tr>
<tr>
<td>700</td>
<td>0.86±0.01</td>
<td>9.57±0.10</td>
<td>69.4±0.3</td>
<td>5.69±0.03</td>
<td>5.73</td>
</tr>
<tr>
<td>750</td>
<td>0.85±0.01</td>
<td>9.42±0.10</td>
<td>67.7±0.6</td>
<td>5.44±0.10</td>
<td>5.56</td>
</tr>
<tr>
<td>800</td>
<td>0.86±0.01</td>
<td>8.98±0.11</td>
<td>69.7±2.5</td>
<td>5.34±0.24</td>
<td>5.57</td>
</tr>
<tr>
<td>850</td>
<td>0.88±0.01</td>
<td>6.10±0.14</td>
<td>55.8±0.4</td>
<td>2.98±0.07</td>
<td>3.05</td>
</tr>
</tbody>
</table>
5.4.3. Comparison of different regio-isomeric IC$_{70}$BA mixtures

It was extensively discussed in previous sections that dissimilar RI mixtures of IC$_{70}$BA have an effect on the molecular packing of the P3HT:IC$_{70}$BA blend, due to unfavourable material distribution or excess aggregation due to the presence of a particular RI in the IC$_{70}$BA sample. It was experimentally proven in Section 5.2.1 that the IC$_{70}$BA#1 and IC$_{70}$BA#2 samples exhibit dissimilar 5, 2, and 12 o’clock RI distributions (22%, 43%, and 35% vs. 16%, 36%, and 48%). This variation in the regio-isomeric ratio was further shown to influence the absorption and topography characteristics of the P3HT:IC$_{70}$BA layers (see UV-vis data in Section 5.3.3 and AFM characterisation in Sections 5.3.5 and 5.3.6). In this section, the importance of the mixture of RIs of IC$_{70}$BA on the molecular packing and phase separation of the BHJ and hence on the device PCE is studied. To accomplish this, the tailored fabrication conditions found in previous sections for the P3HT:IC$_{70}$BA#1-based devices are used here for the fabrication of P3HT:IC$_{70}$BA#2-based OPVs. Despite the increased agglomeration, observed for the P3HT:IC$_{70}$BA#2 layers subjected to SA, this fabrication step cannot be omitted, as it is essential for the self-organisation and crystallisation of the P3HT phase, which, as discussed in Chapter 3 and experimentally demonstrated in Section 5.4.1, is required for high device PCEs.

It can be seen from the J-V curves of the best performing P3HT:IC$_{70}$BA-based devices for both acceptor batches in Figure 5.18(a) that the distribution of the RIs in their mixture has a direct influence on the device performance. From the HPLC characterisation is known that IC$_{70}$BA#1 contains predominantly the 2 o’clock RI (43%), which has been reported to deliver the highest device PCE for P3HT:IC$_{70}$BA-based OPVs.[400, 403] The ratio of the remaining RIs in the mixture, however, needs to be considered additionally. This is clear from the UV-vis absorption properties and AFM topography scans conducted on separated single RIs (see Sections 5.3.4 and 5.3.7), which showed RI specific P3HT:IC$_{70}$BA blend crystallisation and agglomeration depending on the fabrication conditions used for the D/A layer deposition.

![Figure 5.18](image-url)

\textbf{Figure 5.18.}: J-V characteristics of P3HT:IC$_{70}$BA-based OPVs for (a) IC$_{70}$BA#1 and IC$_{70}$BA#2. Corresponding EQE spectra are shown in (b). The J-V and the EQE data show the characteristics of the best device for each acceptor batch. The dark current characteristics in (a) are shown with dotted lines.
5.4. P3HT:IC$_{70}$BA device characteristics

As evident from Figure 5.18(a), a reduction of the 2 o’clock RI content from 43% to 36% in addition to a variation of the 5 and 12 o’clock RI presence (22% and 35% vs. 16% and 48%) is sufficient to completely alter the device $J_{SC}$, FF, and PCE. These are reduced from 10.91 mA/cm$^2$, 72.0%, and 6.74% for IC$_{70}$BA#1 to 5.42 mA/cm$^2$, 52.0%, and 2.16% for IC$_{70}$BA#2. The alteration of the device characteristics is attributed to the different molecular packing of the P3HT:IC$_{70}$BA blend.[173] After conducting molecular dynamics simulations and examining the material miscibility characteristics of the 2 and 12 o’clock RIs of IC$_{60}$BA, Tummala et al. reported a closer packing density of the fullerene cages and adducts in the case of the 2 o’clock RI compared to the 12 o’clock RI.[175] Thus, the reduced 2 o’clock RI content from 43% in IC$_{70}$BA#1 to 36% in IC$_{70}$BA#2, in addition to the increased 12 o’clock RI content from 35% to 48% alters the molecular packing of the photoactive blend, which in turn affects the charge transport properties. In addition, a $V_{OC}$ of 0.86 V was measured for the P3HT:IC$_{70}$BA#1 device, compared to 0.77 V for the P3HT:IC$_{70}$BA#2 device. This alteration can be correlated to the energetic disorder within the IC$_{70}$BA phase, induced by the dissimilar RI HOMO/LUMO energy levels.[401] Based on the experimental results in Section 5.3.6, however, the primary cause for the reduced $V_{OC}$ of the P3HT:IC$_{70}$BA#2 devices is the significantly larger amount of the 12 o’clock RI in the blend. The predominant 12 o’clock content leads to the formation of agglomerates with sizes in the the µm–range that increases the surface roughness of the P3HT:IC$_{70}$BA#2 layers. Therefore, in agreement with the AFM characterisation in Section 5.3.6, reduced device $R_{SH}$ and increased $R_S$ due to morphological and structural changes are expected to deteriorate the device characteristics, compared to these of the P3HT:IC$_{70}$BA#1 solar cells.

The effect of the ratio of RIs on the D/A blend characteristics, i.e. exciton conversion efficacy, are further confirmed by the reduced EQE spectra for the P3HT:IC$_{70}$BA#2 devices in Figure 5.18(b), compared to the EQE of the device with IC$_{70}$BA#1. This reduction is directly related to a reduced charge carrier mobilities and exciton dissociation yields within the D/A BHJ, lowering the device $J_{SC}$, FF, and PCE.[457, 458]

5.4.4. Regio-isomers of IC$_{70}$BA and their effect on the device characteristics

Reports in the literature suggest that P3HT:IC$_{70}$BA-based OPVs fabricated with isolated RIs of IC$_{70}$BA exhibit higher device PCEs for some of the RIs when compared to the initial RI IC$_{70}$BA mixture.[403] Similar device performance dependence on the regio-isomeric characteristics has been observed for different from ICBA fullerene-based acceptor materials.[173] For example, it is known that P3HT:IC$_{70}$BA blends of the 2 o’clock RI deliver the highest device PCE.[400] An explanation is given by reduced hopping distances and improved electron conduction in the IC$_{70}$BA phase, due to closely packed fullerene-fullerene molecules which improve the electron mobility and carrier transport properties.[457, 458] These results are also supported by the experimental data in Section 5.2.2, which shows that the 2 o’clock RI exhibits the shortest distance between the “pole” carbon atom and the indene addend at the opposite pole (8.36 Å).

Increased aggregation was observed on the surface of the P3HT:IC$_{70}$BA layers in Section 5.3.7 fabricated from the isolated 5, 2, and 12 o’clock RIs, which was attributed to the acceptor phase. Therefore, in this section OPV devices were fabricated in order to study the effect of the spacial arrangement of individual isolated IC$_{70}$BA RIs on their molecular packing.
in a matrix with P3HT. In accordance with the spectral response of the P3HT:IC\textsubscript{70}BA layers is Section 5.3.4, the photoactive blends for the study were subjected to SA & TA (10 min/150 °C). Despite an increased IC\textsubscript{70}BA agglomeration for these fabrication conditions, in particular for the 12 o’clock RI samples, a combination of the SA and TA step was chosen. This is justified by the SA step necessity, which is required for the rearrangement and crystallisation of the P3HT phase that was shown to drastically improve the device PCE (see Section 5.4.1).

The device characteristics for the 5, 2, and 12 o’clock RIs, which were obtained after the HPLC separation of IC\textsubscript{70}BA#1 and IC\textsubscript{70}BA#2 are presented in Figures 5.19(a) and 5.19(c). The detailed device characteristics are summarised in Table 5.6. For comparison, the characteristics of the OPVs, fabricated from the regio-isomeric mixtures for identical conditions from Section 5.4.3 are also included. It is evident from the J-V curves in Figures 5.19(a) and 5.19(c) that the best performing P3HT:IC\textsubscript{70}BA devices for both IC\textsubscript{70}BA batches were fabricated with the 2 o’clock RI. This is in a good agreement with the UV-vis absorption spectra in Section 5.3.4 that showed highest light absorption for the 2 o’clock RI. Consequently, $J_{SC}$ values of 4.45±0.31 mA/cm$^2$ and 6.09±0.58 mA/cm$^2$ were measured for the P3HT:IC\textsubscript{70}BA#1-2 and P3HT:IC\textsubscript{70}BA#2-2 devices. The $J_{SC}$ of the 5 and 12 o’clock OPVs for both IC\textsubscript{70}BA batches are lower, as shown in Table 5.6. This is in agreement with the lower UV-vis absorption spectra seen for the layers. In the case of the 12 o’clock RI, the average $J_{SC}$ is below 0.5 mA/cm$^2$ which is attributed to the low solubility of the RI in addition to the excess acceptor segregation observed in Sections 5.3.4 and 5.3.7. This leads to a reduced acceptor content in the BHJ mixture resulting in an unbalanced D/A distribution. Therefore, the low device $J_{SC}$ is related to a decreased contact area at the interface between the BHJ components and drastically reduced exciton separation yields.

A clear trend in achieving slightly different $V_{OC}$ values depending on the RI or on the mixture of RIs is also noticeable in Table 5.6. This variation is indicative of dissimilar HOMO/LUMO level energies, typical for different RIs.[401, 457] The formation of large scale agglomerates, seen on the surface of the 5, 2, and 12 o’clock layers in Section 5.3.7, corresponds to the standard variation observed for the $V_{OC}$ of all devices in Table 5.6. The 2 o’clock OPVs for P3HT:IC\textsubscript{70}BA#1 and P3HT:IC\textsubscript{70}BA#2 exhibit $V_{OC}$ values of 0.78±0.07 V and 0.82±0.02 V respectively, which can be attributed to pathways generating leakage currents due to the IC\textsubscript{70}BA agglomerates formation. Similar observations apply to the 5 and 12 o’clock devices. However, special attention has to be paid in the case of the 12 o’clock RI, due to the excess agglomerates formation observed. As confirmed by the AFM scan in Figure 5.15(g), these agglomerates exceed sizes of 1 μm in diameter, which leads to electrical shorting and failure of the whole OPV. This is evidenced by the J-V curves and the calculated $V_{OC}$ for the P3HT:IC\textsubscript{70}BA#2-12 devices.

Among all RIs, highest FFs are observed for the OPVs devices fabricated with the 2 o’clock RI (53.2±8.14% and 56.9±4.92% for IC\textsubscript{70}BA#1 and IC\textsubscript{70}BA#2). This is in agreement with the AFM characterisation in Section 5.3.7 that showed high layer homogeneity as well as low $R_{RMS}$ and $R_{MAX}$ values for the P3HT:IC\textsubscript{70}BA#1-2 samples. Therefore, the formation of an appropriate D/A nano-morphology is expected, suitable for an efficient exciton generation, dissociation, and charge carrier transport, that is less prone to recombination processes compared to the D/A blends with the 5 and 12 o’clock RIs (FFs below 50%). This leads to average device PCEs of 1.85±0.36% (2.20% peak) and 2.85±0.22% (3.29% peak), measured for the P3HT:IC\textsubscript{70}BA#1-2
Figure 5.19.: J-V characteristics of P3HT:IC_{70}BA-based OPVs with the 5, 2, and 12 o’clock RIs of (a) IC_{70}BA#1 and (c) IC_{70}BA#2. Corresponding EQE spectra are shown in (b) and (d). The J-V data and EQE spectra are representative of the best performing device for each RI. The dark current characteristics in (a) and (c) are shown with dotted lines.

Table 5.6.: Summarised OPV device characteristics of P3HT blends with different IC_{70}BA RIs of the devices shown in Figure 5.19.

<table>
<thead>
<tr>
<th>Regio-isomeric P3HT:IC_{70}BA</th>
<th>V_{OC} (V)</th>
<th>J_{SC} (mA/cm^{2})</th>
<th>FF (%)</th>
<th>PCE average (%)</th>
<th>PCE max (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1 – mixture</td>
<td>0.85 ± 0.01</td>
<td>10.03 ± 0.46</td>
<td>69.7 ± 3.6</td>
<td>5.97 ± 0.40</td>
<td>6.74</td>
</tr>
<tr>
<td>Batch 1 – 5 o’clock</td>
<td>0.81 ± 0.01</td>
<td>3.18 ± 0.40</td>
<td>47.6 ± 9.9</td>
<td>1.24 ± 0.35</td>
<td>1.52</td>
</tr>
<tr>
<td>Batch 1 – 2 o’clock</td>
<td>0.78 ± 0.07</td>
<td>4.45 ± 0.31</td>
<td>53.2 ± 8.1</td>
<td>1.85 ± 0.36</td>
<td>2.20</td>
</tr>
<tr>
<td>Batch 1 – 12 o’clock</td>
<td>0.15 ± 0.20</td>
<td>0.45 ± 0.22</td>
<td>43.8 ± 28.5</td>
<td>0.04 ± 0.06</td>
<td>0.15</td>
</tr>
<tr>
<td>Batch 2 – mixture</td>
<td>0.80 ± 0.02</td>
<td>4.31 ± 0.95</td>
<td>51.4 ± 5.3</td>
<td>1.76 ± 0.37</td>
<td>2.16</td>
</tr>
<tr>
<td>Batch 2 – 5 o’clock</td>
<td>0.72 ± 0.05</td>
<td>2.07 ± 0.18</td>
<td>45.5 ± 3.1</td>
<td>0.68 ± 0.09</td>
<td>0.78</td>
</tr>
<tr>
<td>Batch 2 – 2 o’clock</td>
<td>0.82 ± 0.02</td>
<td>6.09 ± 0.58</td>
<td>56.9 ± 4.9</td>
<td>2.85 ± 0.44</td>
<td>3.29</td>
</tr>
<tr>
<td>Batch 2 – 12 o’clock</td>
<td>0.03 ± 0.03</td>
<td>0.26 ± 0.18</td>
<td>45.9 ± 31.4</td>
<td>0.00 ± 0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
and P3HT:IC\textsubscript{70}BA\#2-2 solar cells. Lower PCEs were measured for the 5 o’clock devices as shown in Table 5.6. The lowest OPV efficiency is achieved for the P3HT:IC\textsubscript{70}BA\#1-12 devices (0.04±0.06%, peak 0.15%). No device output could be measured for the P3HT:IC\textsubscript{70}BA\#2-12 devices which were electrically shorted due to the excess aggregation of the IC\textsubscript{70}BA\#2 phase.

None of the P3HT blends with the separated IC\textsubscript{70}BA RIs reach the levels of device characteristics observed for the P3HT:IC\textsubscript{70}BA\#1 RI mixture, which shows J\textsubscript{SC} of 10.03±0.46 mA/cm\textsuperscript{2}, FF of 69.7±3.6%, and PCE of 5.97±0.40%. These results are also supported by the device EQE spectra shown in Figures 5.19(b) and 5.19(d). The highest EQE for the RI of the P3HT:IC\textsubscript{70}BA\#1-based OPVs is observed for the 2 o’clock RI, which is in agreement with the higher J\textsubscript{SC} compared to all other RIs. Nevertheless, the peak of the EQE spectra is only about 25% (400 nm – 550 nm) with a slight increase up to 30% for the wavelengths 550 nm – 640 nm. The 5 o’clock device exhibits an average EQE below 15%, and the EQE of the P3HT:IC\textsubscript{70}BA\#1-12 device is 2.5%. Therefore, the importance of the correct balance between the RIs not only for optimal light absorption, but also structural integrity and electrical conductivity is underlined here.

Similar behaviour is noted for the P3HT:IC\textsubscript{70}BA\#2 devices. The P3HT:IC\textsubscript{70}BA\#2-2 device shows the highest EQE response, and therefore the highest PCE when compared to the reference device fabricated with the RI mixture of P3HT:IC\textsubscript{70}BA\#2 (see Figure 5.18). This is not surprising, due to the larger amount of the 12 o’clock RI in the IC\textsubscript{70}BA\#2 sample that was shown to drastically affect the molecular packing of the D/A blend and adversely alter the device performance. Indeed, no EQE was measured for the 12 o’clock OPVs, as shown in Figure 5.19(d), due to the failure of the devices fabricated. These results demonstrate that the highest OPV characteristics are possible for regio-isomeric mixtures with tailored proportions of RIs such as the P3HT:IC\textsubscript{70}BA\#1 mixture.

5.5. Summary

Two commercial samples of IC\textsubscript{70}BA were analysed by HPLC to find the presence of three different RIs of IC\textsubscript{70}BA. For each IC\textsubscript{70}BA batch, the combination of the RIs contributed to 99% of the sample, whereas the remaining 1% was related to impurities due to the synthetic synthesis. An integration of the HPLC peaks obtained during the separation process showed a dissimilar distribution of the three RIs for each of the two IC\textsubscript{70}BA samples. \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and UV-vis absorption spectroscopy were used to unambiguously assign the geometric structure of the 5, 2, and 12 o’clock RIs shown in Section 5.2.2 to the HPLC fractions A, B, and C, respectively. Regio-isomeric distributions of 22%/43%/35% and 16%/36%/48% were calculated for the 5, 2, and 12 o’clock RI of IC\textsubscript{70}BA\#1 and IC\textsubscript{70}BA\#2. A comparison of the fractions A, B, and C was also undertaken. Different distances between the indene addend and the opposite “pole” carbon atom of the C\textsubscript{70} cage were calculated, indicating the formation of dissimilar molecular packing between the RI of IC\textsubscript{70}BA by itself and the RIs of IC\textsubscript{70}BA in a mixture with P3HT.

The thermal stability and phase transition properties of the two IC\textsubscript{70}BA samples were investigated using TGA and DSC analysis techniques. Similar behaviour was observed for both samples during the first and second weight loss that happen between 200 °C and 320 °C and
after 600 °C. The latter was attributed to the fullerene decomposition, whereas the former to the indene molecule. Improved thermal stability was seen when the IC$_{70}$BA samples were mixed in a blend with P3HT. However, different TGA behaviour was observed depending on the IC$_{70}$BA batch used, which was related to a different molecular packing of the D/A system, induced by the dissimilar distribution of RIs for both samples. The variation in the regio-isomeric distribution of IC$_{70}$BA in addition to reactions between impurities in the material are the likely explanation for the different phase transition behaviour of IC$_{70}$BA#1 and IC$_{70}$BA#2.

Differences in the vertical distribution of P3HT and IC$_{70}$BA#1 in their blend, depending on the fabrication conditions used during the deposition of the photoactive layer, was analysed by SE. The results showed that a balanced D/A distribution is only possible after a SA step that allows the migration and rearrangement of molecules in the layer, induced by the different surface energies measured for P3HT and IC$_{70}$BA#1. On the contrary, a TA step of 10 min at 150 °C leads to an unfavourable D/A vertical arrangement. Nevertheless, a combination of both annealing steps (SA followed by TA) was shown to lead to an optimal BHJ formation in the case of the P3HT:IC$_{70}$BA#1 system used in this study.

The spectral response of P3HT:IC$_{70}$BA#1 and P3HT:IC$_{70}$BA#2 layers was characterised using UV-vis spectroscopy and revealed distinctive variations in the absorption spectra depending on the fabrication conditions used. A significant difference in the absorption profiles, depending on the IC$_{70}$BA sample used, was also observed. The highest crystallinity of P3HT when mixed in a blend with IC$_{70}$BA, was generally observed for layers subjected to SA & TA. However, much lower optical density was measured for the P3HT:IC$_{70}$BA#2 samples, despite the identical parameters used for their deposition. The absorption spectra of P3HT in a blend with the separated 5, 2, and 12 o’clock RI of IC$_{70}$BA#1 and IC$_{70}$BA#2 were also analysed. A similar correlation between the fabrication conditions and the absorption profiles of the layers was noted, as well as a significant reduction of the optical density of layers from the 12 o’clock RIs. This was related to the low solubility of the RI and the excess agglomeration, which were shown to reduce the acceptor content in the BHJ and therefore lead to inferior device characteristics compared to all other RIs.

The topography of P3HT:IC$_{70}$BA#1 and P3HT:IC$_{70}$BA#2 layers was characterised by means of an AFM depending on the processing conditions used for the fabrication of the samples. In agreement with the SE data, different surface topography was observed for the samples and the necessity for the SA & TA step was confirmed. Nevertheless, excess agglomeration was observed on the surface of the P3HT:IC$_{70}$BA#2 samples, which was again attributed to the increased content of the 12 o’clock RI, which affects the molecular packing and morphological formation of the D/A BHJ. This was further confirmed by the topography of P3HT:IC$_{70}$BA#1 layers with the separated RIs, which showed the strongest agglomeration for the 12 o’clock RI.

Based on the findings above, optimal fabrication conditions for P3HT:IC$_{70}$BA-based OPV devices were designed and the effect of the annealing step on the solar cell characteristics was investigated. IC$_{70}$BA#1 was chosen for this study, due to the preferential RI distribution known for this acceptor batch (reduced content of the 12 o’clock RI). In excellent agreement with studies of the photoactive layer characteristics, highest device PCEs of above 6.7% were measured for SA & TA P3HT:IC$_{70}$BA#1 layers. Then after a continuous PCE decrease followed for
photoactive layers subjected to SA only, TA only, and no SA & no TA. An optimisation of the P3HT:IC$_{70}$BA#1 layer thickness was also carried out, however no further improvement of the device characteristics was observed. The tailored processing conditions known for the P3HT:IC$_{70}$BA#1-based devices were then utilised for the fabrication of P3HT:IC$_{70}$BA#2-based solar cells. However, much lower device PCEs were measured and the best performing solar cell exhibited a PCE of 2.16%. This low efficiency is due to the different distribution of RIs of IC$_{70}$BA#2, which determines the formation kinetics of the BHJ and leads to an adverse molecular packing and blend morphology.

The device characteristics for BHJ blends consisting of P3HT and the separated RIs of IC$_{70}$BA#1 and IC$_{70}$BA#2 were also studied. No further improvement was observed for any of the separated RI of IC$_{70}$BA#1, compared to their mixture. The highest PCE of 2.2% was measured for the 2 o’clock RI, followed by the 5 o’clock (1.52%), and the 12 o’clock (0.15%). On the contrary, a significant improvement of the device characteristics was observed for IC$_{70}$BA#2. The highest PCE measured for a device with the 2 o’clock RI was 3.29%, which is a significant improvement of the PCE compared to the mixture of RIs (2.16%). The second best performing RI was the 5 o’clock. All devices fabricated with the 12 o’clock RI of IC$_{70}$BA#2 exhibited an electrical shortage, which was related to the excess agglomeration of the acceptor.
6. Fabrication of large-area OPV modules

This chapter shows how the non-scalable spin-coating deposition technique can be substituted by adapting a paint applicator to serve as a fully functional slot-die coater. The custom built slot-die coater was used to fabricate P3HT:IC70BA and PCDTBT:PC70BM-based OPV modules, with photoactive areas of about 35 cm². By tailoring of the deposition process and selecting materials wisely, PCEs approaching 4% were achieved for modules with the PCDTBT:PC70BM blend. LBIC, PL, and Raman mapping were employed to analyse the quality of the deposited layers and identify the nature of defects that occurred during the coating process. This allows for routes in which further improvements may be facilitated to the design of the scaling-up equipment. The operational stability of non-encapsulated modules was also studied for 24 h under constant illumination in ambient conditions.

6.1. Introduction

The formation kinetics of the BHJ depends on the deposition technique used. This is attributed to the dissimilar evolution of solvent evaporation during the fabrication cycle.[459] The formation process of the D/A BHJ is crucial for the phase separation of the photoactive blend and determines the device PCE, as shown in Chapter 5. Special care must be taken when materials with isomeric characteristics are used, as already shown for the IC70BA molecule.

A successful scale-up of OPV technology requires the use of deposition techniques and materials that can be implemented on an industrial scale. In this respect, coating, printing, and vacuum deposition techniques have already proven to be ideal fabrication methods to accomplish the processing of large-area OPV cells, as discussed in Section 2.6.1. In terms of materials for the photoactive layer, low band gap polymers show promising characteristics leading to high device PCEs. However, their cost is high, and purchase quantities above 5 g require waiting times above four weeks (1 g of PCE10 or PCE12 from Ossila costs ~ €2600 in April 2017). The prices of P3HT and PCDTBT are lower (1 g of P3HT or PCDTBT from Ossila costs ~ €380 or €1400 in April 2017). Therefore, P3HT and PCDTBT seem at the time of writing to be a better option for donor materials. PCBM is unarguably the most commonly used acceptor material, and it is a suitable match for most of the donor materials used in OPV-based cells, while ICBA
has shown promising improvements to the device PCE when combined mainly with P3HT. In terms of interfacial layers, MeO$_x$ have been widely employed due to their low material cost and high stability, as discussed in Section 2.3.3.

The choice of device architecture is also an important factor to be considered. Owing to the discussion laid out in Section 2.6.3, the inverted device geometry was chosen for the fabrication of large-area OPV modules in this chapter. The module layout consists of a substrate with six equidistantly distributed 78 mm $\times$ 10 mm ITO stripes (approximately 150 nm thick). A gap of 2 mm was chosen between the stripes, as shown in Appendix E.11. This choice was based on the limitations associated with the ITO conductivity discussed in Section 2.3.4. Initial device processing was performed on pre-patterned glass-ITO substrates, and optimised fabrication procedures were then transferred onto flexible PET-ITO substrates. The latter were patterned with an excimer laser.

Due to the very good processing reproducibility associated with the slot-die coating technique, a custom built slot-die coater was designed and used to deposit the ETL and photoactive layer for the OPV modules fabricated in this chapter.[460] P3HT:IC$_{70}$BA or PCDTBT:PC$_{70}$BM were used as photoactive layers according to the discussion above, while the ETL was deposited from a ZnO precursor dispersion.[192] P3HT:IC$_{70}$BA as a D/A system was also selected in order to compare the characteristics of slot-die coated photoactive layers with those fabricated by means of the spin-coating technique (see Chapter 5). PCDTBT:PC$_{70}$BM, on the other hand, was chosen due to its promising high PCE and operational stability, as discussed in Section 2.6.2. To complete the OPV module, MoO$_3$ and Al were thermally evaporated through a shadow mask, as discussed in Section 4.3.3.

6.2. Design and manufacturing of the coating equipment

A paint applicator from RK PrintCoat Instruments Ltd served as the base unit for the construction of the slot-die coating equipment. The choice was made due to the customisability of the paint applicator. It can be supplied with different types of coating beds (vacuum, magnetic, and heated), with the ability to deposit inks over areas of up to 325 mm $\times$ 250 mm. The speed and pressure applied to the coating applicator are also adjustable. The initial equipment was purchased with a combination of a heated bed and a micrometer adjustable applicator, as shown in Figure 6.1(a). The advantage of this applicator type is that it mimics the doctor-blading coating process, thus allowing an accurate adjustment of the coating gap between the substrate and the blade edge. This allows for a precise control of the thickness of the deposited wet film, commonly required for the fabrication of large scale OPVs.[297] However, during the doctor-blading process, the width of the coated film is defined by the blade width, and no simple patterning and coating of multiple stripes on a single substrate is possible.[298] In addition, there is no continuous ink supply, which limits the length of the deposited film.

6.2.1. Adaptation of existing parts

The design of the micrometer adjustable applicator had to be adapted in order to serve as a holding platform for a slot-die coating head. As shown in Figure 6.1(b), from the original
set-up only the horizontal plate (label 1) was retained. It accommodates two micrometers which are used for adjusting the height between the original blade and the substrate underneath. The horizontal platform was extended at both ends with the metal components #2 in order to increase the range of the coating head carrier’s horizontal movement in Figure 6.1(b)–3. This carrier was attached to a linear guide rail (component #4). However, rotational movement of the head was observed. To overcome this undesired movement, a PTFE cube was added to the coating head (component #5). The original set-up required the utilisation of one spring to hold the metal blade, however due to an increased weight, two additional springs were attached to balance the weight. To accommodate coating heads with different dimensions, the sliding carrier had to be lifted. Therefore, the “push-feet” of the original applicator (Figure 6.1(b)–6) were extended. The design of all components was carried out with a free CAD software called “eMachineshop” and is shown in Appendix D.[461]

![Figure 6.1:](image)

Figure 6.1.: Photographs of the slot-die coater designed for this thesis. (a) original micrometer adjustable applicator. (b) proposed adaptation of the micrometer adjustable applicator consisting of: (1) original horizontal plate; (2) extensions left and right; (3) carrier for the coating head along a (4) linear guide rail; (5) a PTFE cube; (6) extended “push-feet” left and right; (7) a slot-die head. (c) Complete slot-die coating equipment.
6.2.2. Slot-die head design

The limitations associated with the doctor-blading process are overcome in this thesis by means of using a slot-die head (Figure 6.1(b)–7), with an inlet, which allows for a continuous supply of ink. The coating head, designed for this thesis, has a small reservoir and allows the deposition of a single stripe of ink. However, more complex coating heads can be accommodated to allow the deposition of multiple stripes at once.[297] To minimise the amount of ink required during the deposition process, and therefore reduce the fabrication costs, the reservoir of the stainless steel coating head was designed with a very low dead volume of 12 μL. To achieve this, a 50 μm deep milled canal with a width of 12 mm was chosen, as shown in the CAD designs in Appendix D. The access to the reservoir is accomplished through the inlet, which was designed to be used with a fitting and a ferrule suitable for a tubing with an a very low outer/inner diameter of 1/16 in. × 0.031 in. respectively. The tubing is connected to a luer-lock syringe, which is attached to a syringe pump (Aladdin Syringe pump, AL-1000). This allows a precise control over the flow rate of the material ink.

The width of the coated layers was defined with meniscus guides (shims), which were sandwiched between the front and the back part of the slot-die coating head and held by four M3 screws (see Section 4.1.2). The shims were made with different widths and a length of 1 mm from a 0.5 mm thick stainless steel (see Appendix D). Two screws were used to attach the coating head to the carrier component. The complete slot-die coating equipment is shown in Figure 6.1(c).

6.3. P3HT:IC$_{70}$BA-based modules on glass substrates

The effect of the deposition technique on the characteristics of the P3HT:IC$_{70}$BA layers is studied in this section. To accomplish this, modules with an inverted architecture were fabricated, which is in accordance with the discussion in Section 2.6.3. The photoactive layer was deposited by means of the slot-die coating technique from D/A dispersions with a total material concentration of 20 mg/mL or 30 mg/mL and a 1:1 ratio by weight, which were dissolved in o-DCB. Aiming at high device PCEs, the IC$_{70}$BA#1 was used (see Section 5.4.3). The coating window for the photoactive layer ink was determined following preliminary tests, which were carried out on glass substrates under ambient conditions. Homogeneous and reproducible coatings were obtained at a flow/pumping rate (FR) of 100 μL/ min; coating speed (CS) of 18 mm/s; and a coating gap (CG; the gap between the substrate and the top of the exposed coating shim) of 300 μm.

6.3.1. Thickness study of slot-die coated P3HT:IC$_{70}$BA layers

There are several factors that have to be taken into consideration when depositing inks by means of the slot-die coating technique. The film thickness, for instance, is dependent on the shim length, CS, substrate temperature, FR, CG, and ink concentration. In addition, the substrate and/or slot-die head temperature have to be tailored for the particular deposition process, as the viscosity of the ink is reduced for higher coating temperatures, which furthermore alters the
layer thickness.\cite{422} The evaporation process of the solvent or mixture of solvents used for the ink plays an important role in the uniformity of the layer during the drying process, especially when complex D/A material systems are deposited.\cite{462} Therefore, the effect of the substrate temperature on the uniformity of the deposited P3HT:IC\textsubscript{70}BA layers was studied, as depicted in the photographs in Figure 6.2.

As can be seen in Figure 6.2, the homogeneity of the slot-die coated P3HT:IC\textsubscript{70}BA layers is dependant on the substrate temperature that was used during the deposition process. Regardless of the D/A ink concentration (two different material concentrations, 20 mg/mL and 30 mg/mL were used), the uniformity of the layers improves consistently with the increasing substrate temperature. The P3HT:IC\textsubscript{70}BA layers in Figure 6.2(a) that were deposited at room temperature (RT), show visible surface defects and an accumulation of the D/A ink at various points on the sample. This is ascribed to the high boiling point of o-DCB (165 °C), relative to the substrate temperature, which causes a slow solvent evaporation and hence agglomeration of the film.\cite{462} A visible improvement is observed for a substrate temperature of 50 °C. Nevertheless, deposition imperfections are still present. The characteristic pattern along the coating edge is ascribed to a form of capillary flow in which pinning of the contact line of the drying D/A layer ensures that liquid evaporating from the edge is replenished by the liquid from the interior. The resulting outward flow can then carry most of the dispersed material to the edge, which is commonly described as the “coffee stain” effect.\cite{463} A distinguishable increase in the quality of the coated layers is noticeable for the P3HT:IC\textsubscript{70}BA layers coated at 70 °C and 90 °C (the darker area at the bottom corner of the left hand-side layer is a reflection from the surrounding environment). This is due to reduced ink viscosity and quicker solvent evaporation.\cite{422} Similar trends are notable for the layers in Figure 6.2(b).

The accumulation of material at the lateral edges along the coating direction was further analysed with a profilometer. The height profiles of the P3HT:IC\textsubscript{70}BA layers in Figure 6.2(b) are shown in Figures 6.3(a–c). Indeed, it can be seen that the material accumulation at the edges is reduced when higher substrate temperatures are used during the coating process. The highest layer inhomogeneity was observed for samples deposited at a substrate temperature of 50 °C. The profile of these layers appears as a semicircle with two sharp peaks, ascribed to the material

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.2.png}
\caption{Photographs of P3HT:IC\textsubscript{70}BA layers, slot-die coated from a 20 mg/mL (a) and a 30 mg/mL (b) D/A dispersion at different substrate temperatures (RT stands for room temperature).}
\end{figure}
6.3. P3HT:IC\textsubscript{70}BA-based modules on glass substrates

accumulation close to the edges. The height of these peaks is about 500 nm, which is expected to adversely affect the device performance, due to the formation of possible short circuit pathways towards the electrodes. In contrast, P3HT:IC\textsubscript{70}BA layers deposited at substrate temperatures of 70 °C and 90 °C show a rectangular shape with less pronounced edge inhomogeneities (average peak height about 100 nm). A more balanced charge carrier generation is expected due to the improved lateral layer thickness, compared to the layers shown in Figure 6.3(a). The reduced edge effect also implies a better coverage of the upper interfacial layers, which leads to an appropriate separation between the BHJ and the top metal electrode.

The thickness of the photoactive layer was shown to affect the device performance (see Section 5.4.2). For the spin-coated P3HT:IC\textsubscript{70}BA#1-based OPVs an optimal thickness of about 220 nm was found to deliver the highest device photocurrent output. In order to achieve a similar photoactive layer thickness, the relationship between the D/A ink concentration and the

\begin{figure}[h]
\centering
\begin{subfigure}[h]{0.45\textwidth}
\includegraphics[width=\textwidth]{figure6.3a.png}
\caption{(a)}
\end{subfigure}
\begin{subfigure}[h]{0.45\textwidth}
\includegraphics[width=\textwidth]{figure6.3b.png}
\caption{(b)}
\end{subfigure}
\begin{subfigure}[h]{0.45\textwidth}
\includegraphics[width=\textwidth]{figure6.3c.png}
\caption{(c)}
\end{subfigure}
\begin{subfigure}[h]{0.45\textwidth}
\includegraphics[width=\textwidth]{figure6.3d.png}
\caption{(d)}
\end{subfigure}
\caption{Lateral thickness profiles of slot-die coated P3HT:IC\textsubscript{70}BA#1 layers at a substrate temperature of 50 °C (a), 70 °C (b), and 90 °C (c) for a D/A dispersion concentration of 30 mg/mL. The layer thickness with standard deviation bars (six measurements) for different D/A dispersion concentrations and substrate temperatures is shown in (d).}
\end{figure}
substrate temperature during the slot-die coating process was investigated.

It can be seen in Figure 6.3(d), that the substrate temperature has a direct effect on the deposited layer thickness. The thickest layers were measured at a coating temperature of 50 °C. The layer thickness is reduced at higher substrate temperatures and the thinnest P3HT:IC$_{70}$BA layers were measured on samples fabricated at 90 °C. As shown in Figure 6.3(d), a layer thickness close to the optimal value for the P3HT:IC$_{70}$BA-based cells, is achievable at a temperature of 50 °C for the 20 mg/mL D/A dispersion and at 70 °C for the 30 mg/mL dispersion.

6.3.2. Spectral response of thin films

As extensively analysed in Chapter 5, the P3HT:IC$_{70}$BA layers exhibit distinguishable vibrational transitions, which can be revealed by means of studying the UV-vis absorption spectra of the D/A blend. These vibrational transitions change in relation to the fabrication conditions (SA and/or TA) and can be used to determine the presence of self-arrangement and crystallinity of the P3HT, which is essential for achieving high device PCE. Therefore, in Figure 6.2(a) the UV-vis absorption spectra of the P3HT:IC$_{70}$BA layers was studied in relation to the pre-T annealing step that was carried out after the layer deposition. The absorption spectra for each substrate deposition temperature in Figure 6.4 represents the average spectra of two samples.

As can be seen from the UV-vis spectra of the non-annealed samples in Figure 6.4(a), a semi SA step is possible when the P3HT:IC$_{70}$BA#1 layers are deposited at RT. At such temperatures, the solvent in the D/A ink does not dry quickly after the deposition procedure (1 s – 2 s), as observed for layers coated at substrate temperatures above 50 °C. However, the quality of the layers coated at RT is very poor (see Figure 6.2(a)) and a slow SA step would be impractical due to the desired fast R2R fabrication speeds.[15] Indeed, P3HT:IC$_{70}$BA#1 layers slot-die coated at RT required approximately 20 min to visibly dry (without a petri dish coverage). As a comparison, the drying process of spin-coated P3HT:IC$_{70}$BA#1 layers in Chapter 5 occurred within 10 s after the deposition. This discrepancy shows that the solvent evaporation rate depends on the deposition process, which in turn governs the properties of the photoactive layer.[464]

Despite the long drying time observed for the P3HT:IC$_{70}$BA#1 layers deposited at RT, it can be seen from their UV-vis spectra in Figure 6.4(a), that the P3HT phase has not achieved a high degree of self-organisation and crystallisation. This is clear from the less pronounced vibronic shoulders at about 548 nm and 600 nm, compared to the spin-coated and SA samples in Section 5.3.3. The UV-vis spectra of a spin-coated P3HT:IC$_{70}$BA#1 layer that has not been subjected to any pre-T step, is included as a reference in Figure 6.4(a). It can be seen that spin-coated layers exhibit a slight red shift in the absorption spectra, despite the identical annealing conditions. The vibrational transitions of P3HT are also easier to distinguish. Obviously, there is no evidence of a well defined crystallisation in the P3HT phase, despite the long drying time observed for the slot-die coated layers at RT. In addition, a decrease in the absorption profile can be observed after a TA step in Figure 6.4(a). This can be ascribed to the removal of residual solvent from the layer. Clearly, the SA step was not complete, despite the visible vaporisation
of the solvent from the layer surface. This furthermore confirms that a potential SA step is extremely time consuming and not suitable for a high-speed device processing on a R2R web.

The UV-vis spectra of P3HT:IC\textsubscript{70}BA\#1 layers deposited at 50 °C, 70 °C, and 90 °C are shown in Figures 6.4(b), 6.4(c), and 6.4(d), respectively. It can be seen that no SA step can be carried out, due to the quick drying times for substrate temperatures above 50 °C (1 s – 2 s). The lowest light absorption is observed when no pre-T annealing was carried out. A TA step for 10 min at 110 °C broadens the main absorption peak of the P3HT:IC\textsubscript{70}BA\#1 blend and leads to a visible red shift. The vibrational transition at about 600 nm becomes more pronounced, compared to the non-annealed reference sample. Nevertheless, the distinct vibronic shoulder of P3HT, located at about 550 nm, is almost absent. This shows a low degree of self-organisation and interchain interaction within the P3HT phase. Further broadening of the absorption spectra and a better differentiation between the vibrational transitions is noticeable for annealing temperatures of 130 °C and 150 °C for all UV-vis spectra in Figure 6.4. Nevertheless, the absorption profiles do not show any evidence of a high degree of crystallisation within the P3HT:IC\textsubscript{70}BA\#1 blend, when compared to spin coated layers (see Figure 5.3.3). This reduced crystallinity is expected to lead to inferior device PCE compared to the spin-coated devices in Section 5.4.
6.3. P3HT:IC\textsubscript{70}BA-based modules on glass substrates

![Graphs showing UV-vis absorption spectra of P3HT:IC\textsubscript{70}BA#1 layers coated at different temperatures.](image)

**Figure 6.4.** UV-vis absorption spectra of P3HT:IC\textsubscript{70}BA#1 layers coated at room temperature (a), 50 °C (b), 70 °C (c), and 90 °C (d) for a D/A dispersion concentration of 20 mg/mL. The absorption spectra of a spin-coated P3HT:IC\textsubscript{70}BA#1 layer, that has not been subjected to SA or TA is shown as a reference in (a).

### 6.3.3. Opto-electrical characterisation of complete devices

P3HT:IC\textsubscript{70}BA-based modules were fabricated with the slot-die coating technique, in order to study the ease of scale-up from small area solar cells, commonly processed by means of the spin-coating technique, to large-area OPVs. The schematic structure of the modules, used for the study, is shown in Figure 6.5. As illustrated, a glass substrate is used as a carrier media, which is covered with a pre-patterned ITO (see Section 4.3.1), on top of which approximately 20 nm ZnO is slot-die coated. The ZnO deposition was carried out approximately 1 mm away from the ITO edge. The P3HT:IC\textsubscript{70}BA layer (approximately 230 nm thick) is deposited on top of the ZnO. An additional shift of 1 mm from the ZnO edge was used during the deposition, in order to prevent the direct contact between the photoactive layer and the ITO electrode. After the deposition of the photoactive layer, a pre-T annealing step was carried out for 10 min at 130 °C under ambient conditions. This annealing step was chosen based on the UV-vis spectra in Figure 6.4, in order to ensure the evaporation of any excess solvents and to induce morphological
rearrangement and crystallisation within the BHJ. To complete the cells, 7.5 nm MoO₃ and 100 nm Al were evaporated through a shadow mask. The Al top electrode additionally acted as an interconnection between cells, by means of contacting the clean ITO stripe of the adjacent device (on the left of the ZnO layer in Figure 6.5). The photoactive area of each cell was defined by the overlap of the bottom ITO and top Al electrode.

It was shown in previous sections that P3HT:IC₇₀BA layers that were slot-die coated at RT or 50 °C show poor layer homogeneity and exhibit deposition defects that can easily lead to an electrical shortage of the complete cell (Figure 6.3(a)). Additionally, no evident SA step was observed at these temperatures, despite the slow drying of the D/A ink described in Section 6.3.2. For the fabrication of the P3HT:IC₇₀BA-based modules discussed in the following sections, a substrate temperature of 70 °C was therefore chosen, due to the acceptable layer homogeneity of the photoactive layers. A 30 mg/mL D/A dispersion was used, given the suitable film thickness (see Section 6.3.1) that was measured for the layers deposited at substrate temperatures of 70 °C. Based on preliminary tests, the slot-die coating process of the ZnO layer was carried out at a FR of 100 µl/min, CS of 18 mm/s, and a CG of 200 µm. A precursor dispersion with a total material concentration of 10 mg/mL in IPA was used for this purpose. The latter was annealed, immediately after the deposition, for 1 min at 100 °C in air. The P3HT:IC₇₀BA layers were deposited with a FR of 100 µl/min, CS of 18 mm/s, and a CG of 300 µm. The deposition of both layers was accomplished by a shim with a 10 mm width.

Two P3HT:IC₇₀BA#1-based modules were prepared (hereafter M1 and M2). The characteristics of the best cell and the average J-V curve of all working cells on both modules are shown in Figures 6.6(a) and 6.6(b), respectively. The average J-V curve is based on the J-V data of eight working cells (the data of three electrically shorted devices, i.e. M1 cells #3 and #6 and M2 cell #6, is excluded together with the J-V data of M2 cell #4, which could not be measured due to contacting problems).

The best performing cell (M2, cell #2) in Figure 6.6(a) exhibits a V_OC of 0.50 V, a J_SC of 2.33 mA/cm², a FF of 45.5%, and a PCE of 0.52%. Similar results were measured for cells #2 and #4 on M1 (see Table 6.1). It is difficult to compare the characteristics of the large-area cells above with the smaller-area devices fabricated in Chapter 5, which exhibited PCEs above 6.7%. This is due to the different device architectures used (regular for spin-coated and inverted for slot-die

![Figure 6.5: Schematic diagram of an OPV module consisting of three P3HT:IC₇₀BA-based cells which are connected in series.](image-url)
coated cells), which led to the utilisation of dissimilar interfacial layers. Nevertheless, the characteristics of devices with a comparable device stack (glass-ITO/ZnO/P3HT:ICBA/MoO₃/Ag) can be found in the literature, where reported device $V_{OC}$ values rarely exceed 0.8 V.[334, 365, 465]. The highest $V_{OC}$ for the P3HT:IC₇₀BA modules fabricated, however, is approximately 0.3 V lower than values reported in the literature, as shown in Table 6.1. It must be noted, that all comparable devices found in the literature have a photoactive area of about 0.1 cm², while the single cells fabricated in this section are more than 50 times larger (see Table 6.1). The increased device area leads to a higher number of fabrication defects, and therefore reduced device characteristics. Additionally, both the ZnO and P3HT:IC₇₀BA layers were coated under ambient conditions, which can lead to adsorption of contaminants from the atmosphere, and alter the chemical and physical properties of the materials, leading to an overall reduction of the PCE.

The major difference in characteristics of slot-die and spin-coated devices, however, is in the $J_{SC}$. Under optimised fabrication conditions, $J_{SC}$ values of about 10 mA/cm² are mostly reported for spin-coated cells. These are commonly ascribed to an appropriate BHJ nano-morphology. Indeed, under optimised fabrication conditions (SA in combination with TA), average $J_{SC}$ values of 10.03±0.46 mA/cm² were also measured for the regular devices in Chapter 5, which were fabricated by means of the spin-coating technique. However, the slot-die coated P3HT:IC₇₀BA cells in this section show moderate $J_{SC}$ values of 2.33 mA/cm² ($I_{SC}$ of 12.49 mA). This is ascribed to the reduced P3HT self-arrangement and crystallisation (see Section 6.3.2) due to the missing SA step and also consequently an unfavourable D/A morphology.

As can be seen from the slope of the J-V curve in Figure 6.6(a), which represents the average cell characteristics, a large number of the fabricated devices exhibit high leakage currents, due to fabrication defects. These led to a reduction of all device characteristics, as is evident from Table 6.1, where the average $V_{OC}$, $J_{SC}$, FF, and PCE are 0.33±0.14 V, 2.08±0.39 mA/cm²,
Table 6.1: Summarised P3HT:IC\textsubscript{70}BA module characteristics of the devices shown in Figure 6.6, which were fabricated from a 30 mg/mL D/A dispersion on glass substrates.

<table>
<thead>
<tr>
<th>Device description</th>
<th>V\textsubscript{OC} (V)</th>
<th>I\textsubscript{SC} (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Area (cm\textsuperscript{2})</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best single cell</td>
<td>0.50</td>
<td>12.49</td>
<td>45.5</td>
<td>0.52</td>
<td>5.4</td>
<td>7.4</td>
</tr>
<tr>
<td>Average single cell</td>
<td>0.33±0.14</td>
<td>12.47±1.26</td>
<td>33.8±6.6</td>
<td>0.28±0.18</td>
<td>5.56±0.2</td>
<td>4.2±2.1</td>
</tr>
<tr>
<td>M1: cell #1</td>
<td>0.12</td>
<td>13.49</td>
<td>26.1</td>
<td>0.08</td>
<td>5.8</td>
<td>1.7</td>
</tr>
<tr>
<td>M1: cell #2</td>
<td>0.51</td>
<td>14.68</td>
<td>39.7</td>
<td>0.51</td>
<td>5.8</td>
<td>7.4</td>
</tr>
<tr>
<td>M1: cell #3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M1: cell #4</td>
<td>0.51</td>
<td>13.60</td>
<td>39.6</td>
<td>0.47</td>
<td>5.8</td>
<td>6.9</td>
</tr>
<tr>
<td>M1: cell #5</td>
<td>0.24</td>
<td>11.48</td>
<td>25.7</td>
<td>0.12</td>
<td>5.8</td>
<td>2.8</td>
</tr>
<tr>
<td>M1: cell #6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M1: cells #1 to 2</td>
<td>0.66</td>
<td>14.21</td>
<td>38.1</td>
<td>0.31</td>
<td>11.5</td>
<td>9.4</td>
</tr>
<tr>
<td>M1: cells #1 to 3</td>
<td>0.61</td>
<td>13.96</td>
<td>40.3</td>
<td>0.20</td>
<td>17.3</td>
<td>8.5</td>
</tr>
<tr>
<td>M1: cells #1 to 4</td>
<td>1.12</td>
<td>13.68</td>
<td>40.8</td>
<td>0.27</td>
<td>23.0</td>
<td>15.3</td>
</tr>
<tr>
<td>M1: cells #1 to 5</td>
<td>1.37</td>
<td>13.22</td>
<td>36.3</td>
<td>0.23</td>
<td>28.8</td>
<td>18.1</td>
</tr>
<tr>
<td>M1: cells #1 to 6</td>
<td>1.37</td>
<td>13.28</td>
<td>34.2</td>
<td>0.18</td>
<td>34.6</td>
<td>18.2</td>
</tr>
<tr>
<td>M2: cell #1</td>
<td>0.23</td>
<td>11.68</td>
<td>30.5</td>
<td>0.16</td>
<td>5.4</td>
<td>2.7</td>
</tr>
<tr>
<td>M2: cell #2</td>
<td>0.50</td>
<td>12.49</td>
<td>45.5</td>
<td>0.52</td>
<td>5.4</td>
<td>6.2</td>
</tr>
<tr>
<td>M2: cell #3</td>
<td>0.26</td>
<td>11.66</td>
<td>30.3</td>
<td>0.17</td>
<td>5.4</td>
<td>3.1</td>
</tr>
<tr>
<td>M2: cell #4</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>5.4</td>
<td>NA</td>
</tr>
<tr>
<td>M2: cell #5</td>
<td>0.29</td>
<td>10.66</td>
<td>33.1</td>
<td>0.19</td>
<td>5.4</td>
<td>3.1</td>
</tr>
<tr>
<td>M2: cell #6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M2: cells #1 to 6</td>
<td>1.97</td>
<td>11.52</td>
<td>38.2</td>
<td>0.27</td>
<td>32.2</td>
<td>22.7</td>
</tr>
<tr>
<td>M2 (10 min / 120°C)</td>
<td>1.27</td>
<td>11.04</td>
<td>33.1</td>
<td>0.14</td>
<td>32.2</td>
<td>14.0</td>
</tr>
</tbody>
</table>
33.8±6.6%, and 0.28±0.18%, respectively.

Figure 6.6(b) shows the development of the device I-V curve depending on the number of cells on M1 that are connected in series in order to form a complete module. An increase in the module’s \( V_{OC} \) with the addition of each cell is expected, due to the series connection, whereas the \( I_{SC} \) is likely to be limited by the lowest cell’s \( I_{SC} \) and remain constant at this value, regardless of the number of interconnected cells. Indeed, the data in Table 6.1 indicates a voltage increase with respect to the number of connected single cells. Moreover, M1 functions despite the electrically shorted cells #3 and #6. The current output of the module remains relatively constant with the enlarged photoactive area from 5.8 cm\(^2\) to 34.6 cm\(^2\), which implies an efficient series interconnection between the cells on the module.

The I-V curve of M2 is also shown in Figure 6.6(b). The \( V_{OC} \) of the module is larger than the \( V_{OC} \) of the individual cells, as shown in Table 6.1. This is due to the missing characterisation data of cell #4, because of a problem in contacting during the measurement. Compared to M1, a slightly lower \( I_{SC} \) was measured for M2 (13.28 mA vs. 11.52 mA). Nevertheless, due to a better FF, the PCE measured for M2 was higher than for M1 (0.27% vs. 0.18%). The corresponding power outputs for M1 and M2 were 18.2 mW and 22.7 mW, respectively.

The thermal stability of M1 was also studied. As shown in Figure 6.6(b), the I-V curve of M2 is shifted to a lower \( V_{OC} \) after annealing for 10 min at 120 \(^\circ\)C in a nitrogen atmosphere. In addition, the device \( I_{SC} \) and FF are reduced, which consequently reduces the PCE to 0.14%. This could be explained by additional morphological alteration within the functional layers of the device.

6.3.4. Operational stability

The operational stability of M1 was studied, as shown in Figure 6.7. For the study, M1 was placed in a characterisation holder with metal contacting pins. The holder was positioned centred underneath the beam of the illumination source. The intensity of the light was calibrated for operation at 1 Sun. The characterisation procedure was started immediately after placing the module underneath the beam and carried out for 24 h. Records of the module’s I-V data were taken once every 60 s. At the start of the characterisation, the temperature of the module (measured with an infrared thermometer, pointed at the surface of the module) was close to the ambient temperature (28.0 ± 3.0 \(^\circ\)C). During the first 5 min of characterisation, a gradual increase in temperature was observed until a steady value of 60.0 ± 3.0 \(^\circ\)C was reached. The relative air humidity during the characterisation procedure was approximately 35.0±5.0%. These environmental conditions are in a good agreement with the ISOS-L-2 testing protocol.[29]

As can be seen in Figure 6.7 the module’s \( V_{OC} \) shows a slow increase from its initial value, reaching its maximum approximately six hours before the end of the measurement. At this point, the \( V_{OC} \) has improved 10% from its starting value, which corresponds to about 0.2 V higher \( V_{OC} \). A possible explanation for this voltage increase is the filling of oxygen trap states within the ZnO band structure due to the constant illumination, which improves the energetic alignment within the device stack and reduces charge recombination processes.[466] Prior to the measurement end, the increasing \( V_{OC} \) behaviour reverts and a 10% decrease is observed.
6.4. **PCDTBT:PC$_{70}$BM-based modules on glass substrates**

The $I_{SC}$, on the other hand, shows a gradual decrease during the characterisation procedure. At the end of the study, the $I_{SC}$ has decreased 33% from its starting value. This reduction of the module’s photocurrent implies a low photostability of the P3HT:IC$_{70}$BA blend and is attributed to a photochemical bleaching of the BHJ compounds, due to the exposure of the module to air, humidity, and light.$^{[467]}$ These effects lead additionally to the slow reduction of the module’s FF and a decrease of 10% was observed at the end of the stability tests. The PCE of M1 follows the slowly decreasing trend, observed of all other device characteristics, and the $T_{80}$ was reached after approximately 120 min. At the end of the study a total reduction of 37% was measured, which hints at the low operational stability of the P3HT:IC$_{70}$BA-based modules.

**Figure 6.7.:** Time dependent behaviour of P3HT:IC$_{70}$BA M1’s PCE, $I_{SC}$, $V_{OC}$, and FF at a constant AM 1.5G illumination for 24 h. The I-V measurements were carried out in ambient conditions with a device surface temperature of 60.0 ± 3.0 °C and a humidity of 35.0±5.0%. All parameters are normalised to maximum values.

In the experiments reported in this section, all PCDTBT:PC$_{70}$BM layers were deposited using the slot-die coating technique. In order to vary the thickness of the photoactive layer, a pristine 35 mg/mL PCDTBT:PC$_{70}$BM dispersion with a material ratio of 1:4 by weight, was diluted to a desired concentration and then used for the deposition of the photoactive layers. Based on preliminary tests, a FR of 100 µl/min, CS of 18 mm/s, and a CG of 200 µm were chosen in order to achieve a successful and defect-free coating window.
6.4. PCDTBT:PC$_{70}$BM-based modules on glass substrates

Figure 6.8: Photographs of PCDTBT:PC$_{70}$BM layers slot-die coated from 10 mg/mL (a), 12.5 mg/mL (b), and 15 mg/mL (c) D/A dispersions at different coating temperatures.

6.4.1. Spectral response and thickness study of thin films

Figure 6.8 shows photographs of PCDTBT:PC$_{70}$BM layers coated at different substrate temperatures from 10 mg/mL, 12.5 mg/mL, and 15 mg/mL D/A dispersions. There appear to be a trend, whereby layers coated at 50 °C exhibit more distinguishable inhomogeneities than layers coated at higher temperatures. These results are in agreement with the observations made for the P3HT:IC$_{70}$BA layers in Section 6.3.1. The effect is most evident for the visibly thinner layers shown in Figure 6.8(a), which were deposited from the 10 mg/mL dispersion. An increased D/A concentration results in visibly thicker layers with fewer imperfections. One of the PCDTBT:PC$_{70}$BM layers in Figure 6.8(b) that was coated at 70 °C, appears thinner. This is due to the manual handling of the equipment, which can cause minor variation of the CG and result in an altered layer thickness. Noticeable improvement in the homogeneity of the layers is observed when coating was carried out at higher substrate temperatures. An exception is seen in one of the layers in Figure 6.8(c), which was coated at 70 °C. This is ascribed to possible contamination of the glass substrate, resulting in adverse wetting characteristics of the deposited layer.

As has already been set out in Section 6.3.1, the formation kinetic of the D/A blend is dependent on the fabrication technique, which is crucial for the phase separation of the photoactive blend, which in turn determines the device PCE. For this reason, the absorption spectra of slot-die coated PCDTBT:PC$_{70}$BM layers were compared to spin-coated alternatives, using UV-vis spectroscopy. For this purpose, the average of two absorption spectra for each sample variation was used. As shown for the 10 mg/mL PCDTBT:PC$_{70}$BM layers in Figure 6.9(a), regardless of the coating technique used, all layers exhibit similar absorption profiles with an absorption band below 350 nm caused by PC$_{70}$BM. The absorption peak centered at 381 nm and the wide band between 470 nm and 560 nm is assigned to PCDTBT. The dependence of the layer thickness on the substrate temperature during the deposition procedure, seen in Figure 6.8, is additionally confirmed by the UV-vis data in Figure 6.9(a), where lower optical densities of the absorption profiles are observed at higher substrate temperatures.

Higher optical densities are seen in the 12.5 mg/mL and 15 mg/mL PCDTBT:PC$_{70}$BM layers in Figures 6.9(b) and 6.9(c). The dependence of the layer thickness on the coating temperature, however, is less pronounced, and relatively similar spectral responses are observed for all temperatures. Nevertheless, the thinnest PCDTBT:PC$_{70}$BM layers were deposited at the
highest substrate temperatures. This is in agreement with the dependency observed between the substrate temperature and the resulting layer thickness of the P3HT:IC\textsubscript{70}BA-based films in Section 6.3.1.

The thickness of the PCDTBT:PC\textsubscript{70}BM layers, coated from 10 mg/mL, 12.5 mg/mL, and 15 mg/mL dispersions, with respect to the substrate temperature, are shown in Figure 6.9(d). In line with the observations made above, it can be seen that the layer thickness is dependent on both the solid content in the D/A ink, and the substrate temperature both of which affect the ink viscosity. The maximum thickness is measured for layers coated from the 15 mg/mL dispersion, followed by a reduced thickness for dispersions with a lower material concentration. The thinnest layers are coated at 90 °C. It is worth noting the relatively large standard deviation for some of the measured data points, which is due to the short coating distance of 7.62 cm on the glass slides. The latter increases the layer thickness at the start and the end of the coating process due to excess solvent that remains captured between the meniscus guide and the surface of the substrate.
Figure 6.9: UV-vis absorption spectra of PCDTBT:PC<sub>70</sub>BM layers coated at different temperatures for D/A dispersion concentrations of 10 mg/mL (a), 12.5 mg/mL (b), and 15 mg/mL (c). The absorption spectra of a spin-coated PCDTBT:PC<sub>70</sub>BM layer is shown for reference in (a). The corresponding layer thickness with standard deviation bars (six measurements) is shown in (d).
6.4.2. Opto-electrical characterisation of complete devices

To study the effect of the PCDTBT:PC$_{70}$BM layer thickness on the device characteristics, OPV modules with a structure of glass-ITO/ZnO/BHJ/MoO$_3$/Al were fabricated. Figure 6.10 shows a schematic diagram of three cells with the above structure, which are connected in series to form a complete OPV module. The BHJ thickness was altered by using different PCDTBT:PC$_{70}$BM dispersions, with concentrations of 10 mg/mL, 12.5 mg/mL, and 15 mg/mL, which were all deposited at a substrate temperature of 70 °C. This temperature was chosen due to a preferred thickness range and an acceptable layer coating homogeneity. The coating parameters for the PCDTBT:PC$_{70}$BM layer were kept identical to those used in Section 6.4.1. All other layers in the device stack were deposited as described in Section 6.3.3. Two modules of both the 10 mg/mL and 12.5 mg/mL dispersions (hereafter M1 and M2), and one module with the 15 mg/mL dispersion (hereafter M1) were prepared. After depositing all photoactive layers, the samples were annealed for 10 min at 70 °C, to ensure the evaporation of any excess solvents.

To calculate the current density $J$ (mA/cm$^2$) the photoactive area of each cell was defined by the overlap of the bottom ITO and top Al electrode. For the modules fabricated with a 12.5 mg/mL D/A dispersion, the device photoactive area was corrected after evaluating the cell areas mapped with the LBIC characterisation shown in Section 6.4.4. The characteristics of the best cell and the average J-V curve of all cells on the modules fabricated (12 cells for the 10 mg/mL and 12.5 mg/mL and 6 cells for the 15 mg/mL dispersion) are shown in Figures 6.11(a), 6.11(c), and 6.11(e). The device characteristics are summarised in Table 6.2.

The best cells for the 10 mg/mL, 12.5 mg/mL, and 15 mg/mL PCDTBT:PC$_{70}$BM concentrations exhibit very high $V_{OC}$ of 0.90 V, 0.87 V, and 0.89 V, respectively. These $V_{OC}$ values are among the highest reported in the literature for large-area PCDTBT:PC$_{70}$BM devices, implying the effectiveness of the interfacial layers used in the device stack, allowing for an unimpeded charge carrier transport due to an appropriate energy alignment within the device structure.[131, 468] As shown in Figures 6.11(a), 6.11(c), and 6.11(e), the average device $V_{OC}$ is reduced to 0.82 ± 0.09 V, 0.75 ± 0.90 V, and 0.84 ± 0.70 V. A reasonable explanation may be minor inaccuracies in the positioning of the slot-die head shim when coating subsequent layers, leading to reduced diode rectifying characteristics and hence low $R_{SH}$ as seen from the slope of the J-V curves of the cells.

![Figure 6.10.](image-url) Schematic diagram of an OPV module consisting of three PCDTBT:PCBM-based cells which are connected in series.
Figure 6.11.: J-V characteristics of the best performing individual cell and the average J-V curves for devices fabricated from PCDTBT:PC$_{70}$BM dispersions with concentrations of 10 mg/mL (a), 12.5 mg/mL (c), and 15 mg/mL (e). The average J-V curve in (a) and (c) is based on the J-V curves of 12 single cells, while in (e) it is based on 6 single cells. A comparison of the I-V characteristics depending on the number of connected cells in series on a module for the 10 mg/mL, 12.5 mg/mL and 15 mg/mL is shown in (b), (c), and (d), respectively. The I-V curve of a second module is also included in (b) and (d).
The reproducibility of the coated PCDTBT:PC$_{70}$BM layer thickness is confirmed by the small standard deviation of the average $J_{SC}$ values of 9.88 ± 0.24 mA/cm$^2$, 10.41 ± 0.20 mA/cm$^2$, and 9.30 ± 0.37 mA/cm$^2$, measured for the 10 mg/mL, 12.5 mg/mL, and 15 mg/mL dispersions respectively. This demonstrates the quality of the coatings achievable with the custom designed slot-die coater. The exact cell area was measured by way of the LBIC characterisation, which was carried out only on the 12.5 mg/mL modules due to this time consuming characterisation procedure. This allowed for a correction of the calculated device current density $J$. In the case of the 10 mg/mL and 15 mg/mL modules, the area used for the calculation of the $J$ was measured with a ruler, which commonly leads to an overestimation of the photoactive area and an underestimation of the $J$. Interestingly, regardless of the PCDTBT:PC$_{70}$BM layer thickness, which was shown in Figure 6.9(d) to vary significantly with different D/A dispersion concentrations, similar $I_{SC}$ values for all cells were measured here (see Table 6.2). This indicates that the $I_{SC}$ measured for the module is limited by the lowest $I_{SC}$ value of a single cell.

It is known that due to a high $R_{SHEET}$, ITO is not an ideal electrode material for devices with cell widths of more than 1 cm.[92, 411] Indeed, relatively low average FF of 35% – 40% were observed for all single cells fabricated in this section, as evident from the data in Table 6.2. In addition to the resistive nature of the ITO, the low FFs are assigned to the reduced device $R_{SH}$ due to both a misalignment of subsequently coated layers, and a high internal $R_S$ of the cells (device areas of 5.7 cm$^2$ – 6.3 cm$^2$). As a consequence, free charge carriers have to overcome large conduction paths, in order to reach the module electrodes. A maximum FF of 44.4% followed by 42.2% and 39.6% were measured for the best single 15 mg/mL, 10 mg/mL, and 12.5 mg/mL cells. This is in agreement with the reduced $V_{OC}$ for in particular the 10 mg/mL cells.

The highest average PCE of 3.28±0.54% peaking at 3.80% and 3.15±0.57% peaking at 3.86% were measured for the 10 mg/mL and 15 mg/mL cells. A somewhat lower PCE of 2.82±0.55% with the best performing cell of 3.69% was measured for the 12.5 mg/mL D/A dispersion. This reduced average PCE is attributed to inaccuracies during the device fabrication process, in particular for two of the cells of M1 and another one of M2, leading to reduced $V_{OC}$ and hence PCE. Such positioning inaccuracies are easily overcome when alignment cameras are used to assure a precise layer deposition. The respective power output of all cells was in the range 45.0±6.2 to 49.3±5.0 mW.

The development of the I-V characteristics depending on the number of single cells connected in series to form a complete module of six cells for the 10 mg/mL, 12.5 mg/mL, and 15 mg/mL devices are shown in Figures 6.11(b), 6.11(d), 6.11(f), and summarised in Table 6.2. It can be seen that for all modules the $V_{OC}$ increases approximately linearly with the addition of another cell to the module. Maximum values of 5.05 V and 4.65 V are measured for M1 and M2 fabricated with the 10 mg/mL PCDTBT:PC$_{70}$BM dispersion. The slightly higher $V_{OC}$ of M1 indicates a better alignment of the slot-die head shim during the coating procedure. Similar behaviour is noted for all other modules, with the lowest $V_{OC}$ observed for the 12.5 mg/mL modules. The $V_{OC}$ increase in conjunction with the number of connected cells demonstrates a very good interconnection between the cells, where nearly no losses due to leakage current pathways are observed.

The $I_{SC}$ data in Table 6.2 indicates a well balanced photon absorption for all cells and
shows only a minor variation of the $I_{SC}$ depending on the number of single cells connected in series. This points to photoactive areas of similar sizes. The highest $I_{SC}$ values were measured for the 12.5 mg/mL modules (63.35 mA and 61.12 mA). The differential resistance $dV/dI$ of the I-V slope near the $V_{OC}$ increases with the number of monolithically connected devices indicating an increased $R_S$. Nevertheless, FFs of 40.2% and 39.2% were measured for M1 and M2 respectively. This results in PCEs of 3.18% and 3.25% and power outputs of 278.7 mW and 278.1 mW. These values are measured for photoactive areas of 35.2 cm$^2$ and 33.5 cm$^2$ respectively. Similar observations are made for the modules fabricated from 10 mg/mL and 15 mg/mL D/A dispersions, as shown in Table 6.2.

**Table 6.2:** Summarised PCDTBT:PC$_{70}$BM module characteristics of the devices shown in Figure 6.11, which were fabricated from a 10 mg/mL, 12.5 mg/mL, or 15 mg/mL D/A dispersion on glass substrates.

<table>
<thead>
<tr>
<th>Device description</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Area (cm$^2$)</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best single cell</td>
<td>0.90</td>
<td>58.61</td>
<td>42.0</td>
<td>3.80</td>
<td>5.8</td>
<td>52.8</td>
</tr>
<tr>
<td>Average single cell</td>
<td>0.82±0.09</td>
<td>57.71±1.42</td>
<td>40.2±2.4</td>
<td>3.28±0.54</td>
<td>5.84±0.0</td>
<td>47.4±5.6</td>
</tr>
</tbody>
</table>

| M1: cells #1 to 2  | 1.65        | 55.21         | 39.1   | 3.05    | 11.7          | 91.2       |
| M1: cells #1 to 3  | 2.50        | 56.30         | 40.7   | 3.27    | 17.5          | 140.8      |
| M1: cells #1 to 4  | 3.35        | 57.06         | 42.0   | 3.43    | 23.4          | 191.2      |
| M1: cells #1 to 5  | 4.30        | 56.47         | 41.9   | 3.49    | 29.2          | 242.9      |
| M1: cells #1 to 6  | 5.05        | 56.86         | 42.8   | 3.51    | 35.0          | 287.2      |
| M2: cells #1 to 6  | 4.65        | 59.13         | 41.4   | 3.25    | 35.0          | 275.0      |

<table>
<thead>
<tr>
<th>Device description</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Area (cm$^2$)</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best single cell</td>
<td>0.87</td>
<td>59.69</td>
<td>39.6</td>
<td>3.69</td>
<td>5.6</td>
<td>51.9</td>
</tr>
<tr>
<td>Average single cell</td>
<td>0.75±0.09</td>
<td>59.60±1.78</td>
<td>35.5±2.4</td>
<td>2.82±0.55</td>
<td>5.7±0.2</td>
<td>45.0±6.2</td>
</tr>
</tbody>
</table>

| M1: cells #1 to 2  | 1.40        | 59.95         | 34.2   | 2.43    | 11.8          | 80.9       |
| M1: cells #1 to 3  | 2.20        | 61.20         | 35.6   | 2.71    | 17.7          | 134.6      |
| M1: cells #1 to 4  | 2.80        | 62.33         | 37.4   | 2.75    | 23.7          | 174.5      |
| M1: cells #1 to 5  | 3.60        | 62.14         | 38.5   | 2.92    | 29.5          | 223.7      |
| M1: cells #1 to 6  | 4.40        | 63.35         | 40.2   | 3.18    | 35.2          | 278.7      |
| M2: cells #1 to 6  | 4.55        | 61.12         | 39.2   | 3.25    | 33.5          | 278.1      |

<table>
<thead>
<tr>
<th>Device description</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Area (cm$^2$)</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best single cell</td>
<td>0.89</td>
<td>62.05</td>
<td>44.4</td>
<td>3.86</td>
<td>6.3</td>
<td>55.0</td>
</tr>
<tr>
<td>Average single cell</td>
<td>0.84±0.07</td>
<td>58.88±2.36</td>
<td>40.1±3.5</td>
<td>3.15±0.57</td>
<td>6.3±0.0</td>
<td>49.3±5.0</td>
</tr>
</tbody>
</table>

| M1: cells #1 to 2  | 1.52        | 57.83         | 37.5   | 2.59    | 12.7          | 87.6       |
| M1: cells #1 to 3  | 2.42        | 57.44         | 38.5   | 2.82    | 19.0          | 139.2      |
| M1: cells #1 to 4  | 3.28        | 58.49         | 40.4   | 3.06    | 25.3          | 191.8      |
| M1: cells #1 to 5  | 4.14        | 58.15         | 40.8   | 3.10    | 31.7          | 240.5      |
| M1: cells #1 to 6  | 4.94        | 58.70         | 40.7   | 3.10    | 38.0          | 290.1      |
6.4.3. Thermal stability study

The effect of post depositional thermal (post-T) annealing on the module characteristics was also studied. For this purpose, the two PCDTBT:PC$_{70}$BM modules fabricated from the 12.5 mg/mL D/A dispersion were additionally thermally annealed after the initial I-V characterisation. The annealing procedure was carried out under a nitrogen atmosphere. The first annealing step was conducted for 10 min at 120°C, followed by a second annealing step for additional 10 min at 140°C. The corresponding I-V curves of the modules, are shown in Figure 6.12 and the device characteristics are summarised in Table 6.3.

There is no distinguishable degradation of the module characteristics after a post-T annealing step for 10 min at 120°C. In contrast, a slight increase in V$_{OC}$ from 4.40 V to 4.55 V and from 4.55 V to 4.70 V is observed for M1 and M2, respectively. A possible explanation is an improved contact between the electrodes and the interfacial layers of the module. However, an additional 10 min annealing step at 140°C reveals thermally induced alterations of the module characteristics, lowering the V$_{OC}$ of M1 and M2 to 4.30 V and 4.55 V. These alterations are explained by the aggregation of the PC$_{70}$BM molecules, due to the high temperature annealing step and material diffusion within the device.[271] This is confirmed by the gradual I$_{SC}$ reduction of M1, as a consequence of the annealing procedure, from 63.35 mA to 55.24 mA as seen in Figure 6.12(b). In contrast, M2 seems to show a lower variation of the I$_{SC}$.

Despite a very stable FF for both modules, a PCE and consequently power output decrease of the modules was observed due to the annealing step at 140°C, as shown in Table 6.3. Interestingly, a continuous deterioration of the device characteristics was observed for each of the following measurements. Therefore, it is arguable whether the device characteristics were influenced by the ambient atmosphere conditions such as air and humidity. Hence, a further detailed study of the operational stability of preferably encapsulated OPV modules is required.

\[\text{Figure 6.12.: J-V characteristics of PCDTBT:PC$_{70}$BM M1 (a) and M2 (b) depending on the temperature used for the post-T annealing step.}\]
Table 6.3.: PCDTBT:PC$_{70}$BM module characteristics shown in Figure 6.12, which were subject to a first post-T annealing step for 10 min at 120 °C followed by a second one for 10 min at 140 °C.

<table>
<thead>
<tr>
<th>Post-T annealing step</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Area (cm$^2$)</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1: no post-T</td>
<td>4.40</td>
<td>63.35</td>
<td>40.2</td>
<td>3.18</td>
<td>35.2</td>
<td>278.7</td>
</tr>
<tr>
<td>M1: 10 min/120 °C</td>
<td>4.55</td>
<td>59.26</td>
<td>40.7</td>
<td>3.12</td>
<td>35.2</td>
<td>269.8</td>
</tr>
<tr>
<td>M1: + 10 min/140 °C</td>
<td>4.30</td>
<td>55.24</td>
<td>40.6</td>
<td>2.74</td>
<td>35.2</td>
<td>237.6</td>
</tr>
<tr>
<td>M2: no post-T</td>
<td>4.55</td>
<td>61.12</td>
<td>39.2</td>
<td>3.25</td>
<td>33.5</td>
<td>278.1</td>
</tr>
<tr>
<td>M2: 10 min/120 °C</td>
<td>4.70</td>
<td>62.05</td>
<td>40.4</td>
<td>3.51</td>
<td>33.5</td>
<td>291.8</td>
</tr>
<tr>
<td>M2: + 10 min/140 °C</td>
<td>4.55</td>
<td>60.49</td>
<td>39.3</td>
<td>3.22</td>
<td>33.5</td>
<td>275.3</td>
</tr>
</tbody>
</table>

6.4.4. Light beam induced current characterisation

The photocurrent generation of the device is dependent on the uniformity and thickness of the photoactive layer. Fabrication defects such as dust particles, local de-wetting, or non-uniform layer thickness can cause pinholes and malfunctioning of OPV cells, or even the complete electrical shorting of devices.[469, 470] Therefore, mapping and imaging techniques are very useful to investigate the effect of the processing conditions on the uniformity of the photoactive layer and its impact on the final device performance.[471, 472]

In this section, LBIC photocurrent mapping is used to investigate the quality of the layers that were deposited with the custom built slot-die coating equipment. The characterisation and sample preparation was carried out according to Sections 4.2 and 4.4. The normalised photocurrent maps of all single cells on M1 and M2 from Figure 6.11(d) are shown in Figures 6.13(a) and 6.13(c). In both LBIC maps, darker areas correspond to a lower module photocurrent response, and brighter areas correspond to higher photocurrents. According to this colour coding, M1 exhibits higher photocurrent reproducibility along the coated photoactive layers than M2. There are scratches seen in the LBIC maps of both modules, which can be attributed to the manual handling of the substrates during the fabrication procedure and the subsequent transportation of the samples prior to the LBIC characterisation. Such defects deteriorate the device characteristics and can be minimised by atomisation of the fabrication procedure by means of a R2R system with an in-line opto-electrical characterisation unit. Some point defects are also present, which are assigned to dust particles or the agglomeration of the D/A materials. Excess agglomeration of the acceptor domain was already shown to drastically decrease the device performance of the P3HT:IC$_{70}$BA-based OPVs in Chapter 5. Layer non-uniformities are also observed (see the dark lateral lines along the edges of the cells). These are attributed to the “coffee stain” effect discussed in previous sections. Black lines are seen on the LBIC map of M2 (see left hand side), which are likely due to problems in the electrical connection during the long acquisition (three days). Due to the long characterisation period under ambient conditions, an exposure of the non-encapsulated sample to humidity and air is inevitable. This can lead to the formation of areas that do not contribute to the photocurrent generation as seen in cell 1 (45 mm – 70 mm) in Figures 6.13(c) and 6.13(d). Therefore, a reduction of the measurement...
duration is desired in order to prevent the samples from degradation due to their exposure to the ambient atmosphere. This goal is achievable by way of decreasing the scan resolution. However, this will lead to less detailed current maps. In this regard, an in-line compatible contactless LBIC characterisation has already been reported, allowing reduced acquisition times and improved module contacting.\[473\]

The normalised photocurrent profiles of the cells within M1 and M2, which were extracted from the LBIC maps, are presented in Figures 6.13(b) and 6.13(d). The profiles reflect the average of all of the line profiles from the central 70% of the cell width. It can be seen that the cells on M1 show a photocurrent uniformity of approximately 10% – 20% along the deposition direction, except for cell 2. The dark line artefacts along the lateral edges of the cells are not

![Figure 6.13: Normalised LBIC photocurrent map of M1 (a) and M2 (c) from Figure 6.11(d) with a resolution of 0.1 mm. No colour key is reported for the photocurrent map because the amplitude of the different cells is normalised for a better comparison of the defects. Corresponding photocurrent profiles along the direction of deposition of the photoactive layer (b) and (d). The profiles are smoothed to remove the contribution of noise and show the baseline photocurrent profile.](image-url)
taken into account in the photocurrent profiles, as they are due to known imperfections in the coating process. It is assumed that the latter will be improved in order to avoid such defects for fabrication on an industrial scale. More non-uniform photoactive layers can be seen in M2, as shown in the photocurrent profiles in Figure 6.13(d). An abrupt decrease in the photocurrent is observed 7 mm after the coating start, and 10 mm before the coating end. This reduction is due to a temporary loss of signal during the characterisation process, and therefore is not attributed to the quality of the deposited layers.

6.4.5. Photoluminescence and Raman mapping

In addition with the LBIC characterisation carried out in Section 6.4.4, high resolution micro-photoluminescence (PL) and micro-Raman spectroscopy measurements of the whole areas of M1 and M2 from Figure 6.11(d) were also carried out. By using the reference spectrum of the photoactive layer described in Section 4.4.4, the current non-uniformities that occurred on the LBIC maps in Figure 6.13 could be analysed. The nature of the PL characterisation method allowed for excitation at a particular wavelength in order to only study the response of the layer of interest. An excitation wavelength of 532 nm was chosen in agreement with the absorption spectra of the PCDTBT:PC$_{70}$BM layer. Different PL signals can be obtained with regards to the normalisation method used for the evaluation of the spectral data. As shown for M1 in Figures 6.14(a) to 6.14(d), the measurements provide a full PL and Raman spectra per pixel (measurement position), depending on the mapping of the area, the height, the ratio area/height, and the baseline of the PL signal. The measurements for M2 are shown in Appendix G.

As can be seen from the PL profiles in Figure 6.14, the clarity of the photoactive layer defects depends on the normalisation method used. For instance, intensity ripples, perpendicular to the deposition direction of the photoactive layer, are more pronounced in the PL-Area and PL-Height spectra in Figures 6.14(a) and 6.14(b), than in the PL-ratio A/H and PL-baseline spectra in Figures 6.14(c) and 6.14(d). These ripples are due to a spatial modulation of the PCDTBT:PC$_{70}$BM layer thickness, which is generated during the deposition procedure. Possible explanations for this are oscillations associated with the movement of the slot-die head holder, and the non-uniform speed of the slot-die head. The corresponding modulation in the photocurrent is much smaller than the photocurrent amplitude. Photoactive layer non-uniformities with a wave-like appearance are also visible for all cells, and are ascribed to the drying process that happens a few seconds after the deposition of the photoactive layer. Analogous observations were made for the PL profiles of M2, as shown in Appendix G.

The possibility of photoexcitation of only the PCDTBT:PC$_{70}$BM layer allows for a comparison between the LBIC map of the complete module and the PL spectra of the photoactive layer alone. Thus, defects that occur in the PCDTBT:PC$_{70}$BM layer can be differentiated from defects that occur in the surrounding interfacial layers or electrodes. For instance, there is a visible scratch (approximately 3 cm long) across the width of cell 1 on M1 in the LBIC map in Figure 6.13(b). This scratch is not recognisable in the PL spectra in Figure 6.14, which indicates that the defect is not part of the photoactive layer, but rather of the surrounding layers. Similar observations are made for the nearly 1 cm wide and almost 4 cm long scratch across cell 4 and
Figure 6.14: Normalised PL and Raman photocurrent maps of PCDTBT:PC$_{70}$BM M1 from Figure 6.13. The PL spectra were normalised against the signal’s area (a), height (b), ratio A/H (c), baseline (d), and Raman signal (e). Note that every cell in the image for each method was normalised separately for a better comparison of the defects. For this reason no colour key is reported for the maps. The normalised photocurrent, PL, and Raman profiles along the direction of deposition of the photoactive layer of cell 2 on M1 are shown in (f).
6.4. PCDTBT:PC$_{70}$BM-based modules on glass substrates

It is important to note that the intensity of the PL signal reflects the quantity of the polymer in the volume of the photoactive layer. However, the morphology of the D/A blend can significantly affect the exciton quenching and alter the PL signal. For instance, in vertically segregated layers, most of the PL signal is detected from the surface of the layer, therefore a change of the thickness may not affect the PL signal, but it would cause alteration of the Raman signal.

The Raman maps in Figure 6.14(e) show the peak height of the Raman signal normalised by the baseline. The defects observed during the PL mapping are not distinguishable in the Raman maps. This is due to the nature of the Raman measurement, which is characterised by a low signal-to-noise ratio and, therefore, small defects in the photoactive layer cannot be detected easily. Nevertheless, the intensity of the Raman signal is a figure of merit for the amount of the PCDTBT material in the volume of the photoactive layer and can be used to determine alterations in the thickness of the layer.[439] This is due to the proportionality of the Raman signal to the Raman scattering detected from the sampling volume.[474, 475, 476, 477] Thus, regions where no correlation between the LBIC and Raman signals is observed can be used to detect defects in the device stack. For example, the Raman signal intensity and the LBIC photocurrent map of cell 2 on M1 in Figure 6.14(f) are in agreement, which indicates that the photocurrent is proportional to the thickness of the photoactive layer. However, a hypothetical reduction of the LBIC signal could be attributed to losses due to an electrical contact, or to an unfavourable morphology of the PCDTBT:PC$_{70}$BM layer.

6.4.6. Study of deposition defects

Features such as dots, scratches, and film deposition non-uniformities were observed in the LBIC photocurrent and PL maps. Categorisation the defects according to those occurring in the photoactive layer and those occurring in the surrounding layers was also possible by comparing the LBIC and PL maps of the modules. In this section, a study of the defects found in cell 5 of M1 is carried out. For this purpose, eight defects were identified from the LBIC and PL maps in Figure 6.15(a), and their unique PL spectra was measured as shown in Figure 6.15(b). A reference scan of a defect free area in the cell was also obtained for the purposes of comparison.

The spectra of the highlighted defects #1 and #8 observed in Figure 6.15(a), is shown in Figures 6.15(c) and 6.15(j). These defects are attributed to the accidental deposition of dust particles during the device fabrication procedure. The intensity of their corresponding PL spectra varies significantly, which can be explained by different origins of the dust particles. Generally, a reduced PL intensity is related to an efficient exciton quenching which is expected for a well intermixed D/A system such as PCDTBT:PC$_{70}$BM. Defect #5 in Figure 6.15(a) has a visibly similar appearance to the above mentioned other defects, however its PL spectrum in Figure 6.15(g) shows a peak at about 690 nm, which is consistent with PL peaks observed for the PCDTBT polymer.[439, 478] The peak at 580 nm, on the other hand, is attributed to the PC$_{70}$BM emission. The increased PL intensity observed for the spectrum in Figure 6.15(e) compared to the reference PL spectra in Figure 6.15(k), means that that defect #3 may be due to an aggregation of the PCDTBT material.[439] In this respect, a red shift of the PL spectra

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Deposition defects study by means of LBIC and PL mapping of PCDTBT:PC\textsubscript{70}BM modules. Comparison of the LBIC and PL maps of cell 5 of M1 with highlighted defects is shown in (a). The corresponding PL spectra of the defects (b). The PL spectra of each defect (c–j) and the reference scan of a defect free area (k).

Figure 6.15.
of PCDTBT is attributed to an aggregation of the polymer domains, and it is also indicative of altered D/A nano-morphology.\cite{439}

The PL spectra in Figures 6.15(d) and 6.15(i) exhibit comparable signal intensity and spectral response. Therefore, these spectra are indicative of similar type of defects. Based on the appearance of defects #2 and #7 in Figure 6.15(a), they can be generalised as defects caused by coating imperfections. These types of defects are caused either by the deposition of already agglomerated D/A particles, or by the agglomeration of ink of the photoactive layer after coating.

Defect #4 shows another type of feature which looks like halo in the PL map. This can be attributed to adverse phase separation of the D/A blend, or local defects in the photoactive layer. However, a more systematic analysis is needed in order to understand the small spectral changes of defect #4 in Figure 6.15(f) compared to the reference scan. The lowest PL signal intensity is observed for defect #6 in Figure 6.15(h). The origin of this defect is attributed to an agglomeration of the acceptor material. This is due to the lower PL intensity of the spectrum (compared to that of PCDTBT), due to a lower photosensitivity of PC$_{70}$BM at the excitation wavelength of 532 nm.

6.4.7. Operational stability

The operational stability of the non-encapsulated M1 from Figure 6.11(b) was also investigated. The study was conducted in accordance with the characterisation procedure used for the P3HT:IC$_{70}$BA-based modules in Section 6.3.4. As shown in Figure 6.16, the normalised PCE exhibits a slow gradual decrease and a T$_{80}$ value is reached after 24 h of characterisation. This PCE decrease is attributed mainly to a $V_{OC}$ reduction (about 13% at the end of the characterisation phase) in addition to a less pronounced $I_{SC}$ decrease of 8%. The device $V_{OC}$, which was found to initially increase followed by a subsequent gradual reduction in dependance of the post-T annealing step (see Section 6.4.3), was found to gradually decrease during the stability characterisation study. This is primarily a consequence of degradation, due to the lack of encapsulation which can lead to irreversible electrochemical reactions at the electrode interface, or at the interconnection of cells between the Al top and ITO bottom electrodes. For example, the formation of insulating Al$_2$O$_3$ films has been reported to alter the energetic alignment at the electrode interface, reducing $V_{OC}$.\cite{416} Similar to the observations in Sections 6.3.4 and 6.4.3, a gradual $I_{SC}$ decrease due to photochemical bleaching of the BHJ during the characterisation procedure was also noticed.\cite{467} It is worth mentioning that the device FF exhibited very stable behaviour, as shown in Figure 6.16, demonstrating a nearly constant value of 42% – 43% during the complete characterisation cycle. Further improvements in the stability of devices was expected upon encapsulation of the modules.
6.5. PCDTBT:PC$_{70}$BM-based modules on plastic substrates

To study the transfer of PCDTBT:PC$_{70}$BM-based modules from glass to plastic substrates, OPV modules were fabricated on a PET-ITO carrier. In order to accomplish a separation between single cells on the substrate, a structuring of the ITO layer with an excimer laser was carried out. The pre-patterned PET-ITO substrates were then cleaned with a wipe soaked in IPA and placed on the pre-heated slot-die coater bed. The modules were then fabricated with the same coating parameters as for modules on glass substrates (see Section 6.4.2). To prevent any deformation of the PET substrate due to the thermal treatment, the conversion procedure of the ZnO layer was carried out at temperatures below 100°C. The photoactive layer was deposited from a 12.5 mg/mL PCDTBT:PC$_{70}$BM dispersion.

6.5.1. Laser patterning of PET-ITO substrates

The removal of the ITO layer from the PET substrate was studied by varying the laser fluence. A laser operating voltage of 17 kV and a repetition rate of 20 Hz were chosen, while the pulse energy was controlled using the attenuator unit. The effect of the ITO removal upon different laser fluences is shown in Figure 6.17.

There is no visible ablation of the ITO from the PET substrate for a fluence of 2.9 mJ/cm$^2$ (Figure 6.17(a)–1). A notable improvement is seen in Figure 6.17(a)–2 where a fluence of 3.9 mJ/cm$^2$ was used, however a complete removal of the ITO layer was not accomplished.
6.5. PCDTBT:PC$_{70}$BM-based modules on plastic substrates

Figure 6.17: Effect of the laser fluence on the removal of ITO from the surface of a PET substrate at different laser fluences (a). Magnified optical photographs of ablated ITO layers at laser fluences ranging from 2.9 mJ/cm$^2$ (1) to 22.2 mJ/cm$^2$ (6) are shown in (b) to (g). Both optical photographs in (a) depict the same sample, which was placed on a different background.

As shown in Figure 6.17(a), a continuous ablation of the ITO layer along the moving direction of the stage was achieved for laser fluences above 6.3 mJ/cm$^2$ (layer 3). Nevertheless, the desired width of the pattern (2 mm) was possible only when laser fluences above 14.5 mJ/cm$^2$ were used (layers 5 and 6).

A closer look at the ITO removal quality can be obtained from the magnified optical micrographs in Figures 6.17(b)–6.17(g). In agreement with the observations made for Figure 6.17(a), it can be seen that the complete ITO removal is accomplished for laser fluences above 6.3 mJ/cm$^2$ (Figure 6.17(d)). The desired pattern width of 2 mm was possible for laser fluences above 14.5 mJ/cm$^2$ (Figures 6.17(f) and 6.17(g)). An inhomogeneous removal of the ITO layer can be clearly seen in the ablation pattern of layers 3 and 5. This is ascribed to the asymmetric profile of the excimer laser beam used, which causes a sharp increase in the intensity at the maximum peak of the profile of the beam.[479]

6.5.2. Opto-electrical characterisation

Two PCDTBT:PC$_{70}$BM-based modules were fabricated on PET substrates. In order to avoid deformation of the PET substrate, the hydrolysis procedure, used for the conversion of the ZnO precursor to ZnO, was carried out for 5 min at 100 °C for M1 and 5 min at 80 °C for M2. All other fabrication steps were carried out in accordance with the experimental details used in Section 6.4.2. The J-V characteristics of the best single cell and the average cell (calculated for four single cells) of M1 and M2 are shown in Figures 6.18(a) and 6.18(b) and summarised in Table 6.4.
6.5. PCDTBT:PC\textsubscript{70}BM-based modules on plastic substrates

Figure 6.18. J-V characteristics of the best performing single cell and the average J-V curve for M1 (a) and M2 (b), which were fabricated from a PCDTBT:PC\textsubscript{70}BM dispersion with a concentration of 12.5 mg/mL. The average J-V curve in (a) and (b) is based on the J-V curves of 4 single cells in each module.

The best single cell of M1 (cell 2) exhibits a V\textsubscript{OC} of 0.86 V. As shown in Figure 6.18(a), a lower V\textsubscript{OC} of 0.73 ± 0.10 V is observed for the average cell, which primary originates from the lower V\textsubscript{OC} values of the single cells #3 and #4 (see Table 6.4). This lower device V\textsubscript{OC} is due to coating imperfections, as discussed in Sections 6.4.4 and 6.4.5. Similar behaviour was observed for some of the cells of M2 in Figure 6.18(b). The best performing cell has a V\textsubscript{OC} of 0.82 V. The reduced V\textsubscript{OC} is additionally related to the low temperature that was used for the conversion of the ZnO layer (80 °C). It is arguable that the thermal energy is sufficient for the complete conversion of the ZnO precursor, which has to be carried out at 120 °C.[192] Nevertheless, the average device V\textsubscript{OC} shows a slightly higher value of 0.76 ± 0.03 V compared to M1.

Table 6.4 indicates, that the average I\textsubscript{SC} of the single cells of M1 is higher than that of M2 (50.5 ± 2.9 mA/cm\textsuperscript{2} vs. 45.8 ± 2.8 mA/cm\textsuperscript{2}). The I\textsubscript{SC} difference is attributed to the intrinsic characteristics of the ZnO as an ETL (Fermi level position, work function, conductivity) which inevitably depend on the completeness of the ZnO precursor conversion. Nevertheless, the I\textsubscript{SC} observed for the PET cells is generally lower than that of the cells fabricated on glass substrates. This reduction is attributed to the lower transmittance of the PET substrate in the visible wavelengths (approximately 79% at 555 nm) when compared to a glass reference, which leads to a reduced light absorption within the BHJ.

The data in Table 6.4 shows lower FFs for the cells of M1 and M2, compared to identical cells on glass substrates (see Table 6.2). This is due to the R\textsubscript{SHEET} of the ITO on the PET substrate, which is four times higher than the R\textsubscript{SHEET} of the glass reference (60 Ω/□ vs. 15 Ω/□). As a result, average PCEs of 1.93±0.44% and 1.78±0.29% are calculated for the cells on M1 and M2, respectively. The best performing cell of M1 and M2 was cell 2, which exhibited a peak PCE of 2.68% and 2.21%.
**Table 6.4.** Summarised PCDTBT:PC$_{70}$BM module characteristics of the devices shown in Figure 6.18, which were fabricated from a 12.5 mg/mL D/A dispersion on PET substrates.

<table>
<thead>
<tr>
<th>Description</th>
<th>VOC (V)</th>
<th>ISC (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>PCE Area (cm$^2$)</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell #1</strong></td>
<td>0.78</td>
<td>45.80</td>
<td>28.2</td>
<td>1.62</td>
<td>6.2</td>
<td>35.6</td>
</tr>
<tr>
<td><strong>Cell #2</strong></td>
<td>0.86</td>
<td>53.72</td>
<td>36.2</td>
<td>2.68</td>
<td>6.2</td>
<td>46.0</td>
</tr>
<tr>
<td><strong>Cell #3</strong></td>
<td>0.67</td>
<td>51.84</td>
<td>32.6</td>
<td>1.82</td>
<td>6.2</td>
<td>34.5</td>
</tr>
<tr>
<td><strong>Cell #4</strong></td>
<td>0.61</td>
<td>50.64</td>
<td>32.4</td>
<td>1.60</td>
<td>6.2</td>
<td>30.7</td>
</tr>
<tr>
<td><strong>Average single cell</strong></td>
<td>0.73±0.10</td>
<td>50.5±2.9</td>
<td>32.4±2.8</td>
<td>1.93±0.44</td>
<td>6.2±0.0</td>
<td>36.7±5.7</td>
</tr>
<tr>
<td><strong>Connected cells #1 to 2</strong></td>
<td>1.57</td>
<td>51.93</td>
<td>31.5</td>
<td>2.07</td>
<td>12.4</td>
<td>81.3</td>
</tr>
<tr>
<td><strong>Connected cells #1 to 3</strong></td>
<td>2.27</td>
<td>50.77</td>
<td>32.1</td>
<td>1.99</td>
<td>18.6</td>
<td>115.3</td>
</tr>
<tr>
<td><strong>Connected cells #1 to 4 (M1)</strong></td>
<td>2.93</td>
<td>51.58</td>
<td>32.7</td>
<td>1.99</td>
<td>24.8</td>
<td>151.0</td>
</tr>
<tr>
<td><strong>M1 annealed</strong></td>
<td>3.03</td>
<td>53.09</td>
<td>33.6</td>
<td>2.18</td>
<td>24.8</td>
<td>160.7</td>
</tr>
</tbody>
</table>

The properties of M1 and M2 on PET reflect the characteristics of the single cells of each module, as shown in Table 6.4. The VOC of M1 is slightly lower that of M2 (2.93 V vs. 3.08 V). This is in agreement with the behaviour of the average values of the single cells’ VOC. A nearly linear increase in the VOC, depending on the number of interconnected single cells, is observable for both modules in Appendix H. This is due to an efficient series connection between the cells. Additionally, M1 was subjected to a post-T annealing step for 10 min at 120 °C, which resulted in an improvement of the module’s characteristics. This is in agreement with the effect of post-T annealing on modules that were fabricated on glass substrates.

As shown in Table 6.4, the ISC of M1 is slightly higher than that of M2. This difference is possibly due to the properties of the ZnO layers, which were fabricated at different annealing temperatures. Nevertheless, both modules show only a minor variation in the ISC with regard to the number of monolithically connected cells and the increasing photoactive layer area, which shows the quality and reproducibility of the slot-die coated PCDTBT:PC$_{70}$BM layers. This leads to PCE of 1.99% (2.18% after post-T annealing) and 1.83% measured for M1 and M2. The corresponding power output is shown in Table 6.4.
6.5.3. Operational stability

The operational stability of M2 on PET was characterised under conditions and measurement procedure identical to those described in Section 6.3.4. In comparison to the modules fabricated on glass-ITO substrates in Figure 6.16, the modules on PET-ITO exhibit lower PCE at the end of the study. The $T_{80}$ value is reached after approximately 570 min and a 31% lower PCE was observed after 24 h compared to the initial value, as shown in Figure 6.19. Despite the relatively stable behaviour observed for the $V_{OC}$ of the module (6% decrease after 24 h of characterisation), a strongly pronounced $I_{SC}$ and FF decrease is observed, compared to the modules on glass-ITO substrates. In this respect, the $I_{SC}$ in Figure 6.19 shows a reduction of 20% at the end of the characterisation, whereas the FF is decreased by 9%. In addition to the electrochemical reactions and photochemical bleaching of the D/A system, the enhanced device degradation is attributed to the possible non-complete conversion of the ZnO precursor, which was carried out at an annealing temperature of 80 °C instead of 120 °C, as discussed in Section 6.5.2.[192]

![Figure 6.19.](image_url) Ambient stability studies of a PCDTBT:PC_{70}BM module on a PET substrate. Time dependent behaviour of the module’s PCE, $I_{SC}$, $V_{OC}$, and FF at a constant AM 1.5G illumination for 24 h. The I-V measurements were carried out in ambient conditions with a device surface temperature of 60.0 ± 3.0 °C and a humidity of 35.0±5.0%. All parameters are normalised to maximum values.
6.6. Summary

Despite the wide spread consensus that scalable deposition techniques have to be used for OPV device fabrication, the non-scalable spin-coating technique is still currently used in most scientific reports, possibly due to the low cost of the equipment and the good layer deposition reproducibility. In order to overcome the limitations of the spin-coating technique in terms of scale-up, and keep the equipment cost low without scarifying deposition quality, in this chapter the customisation of paint applicator equipment to serve the purpose of a fully functional slot-die coating system was proposed.

A custom built slot-die coater was used for the deposition of the ETL and BHJ of OPV modules. Two different D/A material systems (P3HT:IC$_{70}$BA and PCDTBT:PC$_{70}$BM) were utilised in order to study the effect of the scale-up of the device area and the material selection on the characteristics of the modules. In this respect, due to unfavourable D/A morphology, rather low device PCE were measured for the P3HT:IC$_{70}$BA-based modules, when compared to the spin-coated references from previous chapters. Nevertheless, improvements are expected for a tailored BHJ morphology, for instance when a co-solvent system or an additive is used for the D/A dispersion. In terms of operational stability, a $T_{80}$ value was reached for non-encapsulated P3HT:IC$_{70}$BA modules after approximately 120 min of characterisation under conditions that are comparable to the ISOS-L-2 testing protocol.

The replacement of the P3HT:IC$_{70}$BA material system with the low bandgap-based D/A system PCDTBT:PC$_{70}$BM led to an immediate improvement in the OPV device characteristics. The reproducible coating of homogeneous layers from the photoactive layer ink allowed for an increase in the PCE, when compared to P3HT:IC$_{70}$BA-based modules. This increase was also ascribed to the use of a more stable D/A material system, that allows a facile transfer between different deposition techniques without any major morphological alterations. The use of LBIC in conjunction with PL and Raman mapping facilitated the evaluation of the exact photoactive device area and proved to be a powerful tool for evaluating the layer homogeneity and the quality of the custom built equipment. Defects during the coating process were also analysed. A significantly improved $T_{80}$ value of 24 h, compared to P3HT:IC$_{70}$BA-based modules, was also achieved. The deposition process was then used for the successful fabrication of OPV modules on PET substrates. This way, the ultimate goal of designing a coating equipment and developing a R2R compatible deposition procedure, was achieved.
7. Conclusions

7.1. Summary of achievements

The aims of this thesis were to study and tailor the characteristics of the photoactive blend of P3HT and IC$_{70}$BA in order to achieve record OPV device PCEs, and to develop and test an industrially viable deposition procedure for the fabrication of large-area OPV modules. Both aims were accomplished successfully, as summarised in the sections below, and published in scientific journals (references [44] and [480]).

7.1.1. P3HT:IC$_{70}$BA-based OPVs with record efficiencies

It is shown in Chapter 5 that the morphology of the BHJ formed between the donor and acceptor depends on the isomeric properties of the acceptor material, and that the spatial molecular packing of the D/A blend has an influence on the efficiency of charge carrier generation and overall on the PCE of an OPV device. These findings are crucial for understanding and controlling the formation kinetics of BHJ-based photoactive systems, that use materials with isomeric characteristics, in order to enhance the characteristics of OPV devices.

The inexpensive and off-the-shelf donor material P3HT was used in combination with the acceptor material IC$_{70}$BA for the photoactive layer of OPV devices, which were fabricated using the spin-coating deposition technique. These devices exhibited record PCEs with a maximum value of above 6.7%, which was measured for a device photoactive area of 0.43 cm$^2$. That is several times larger than the average area of similar devices reported in the literature (0.08 cm$^2$), as shown by a review of the literature in Section 3.3.

These record PCEs were achieved after conducting a detailed study of the intrinsic characteristics of the IC$_{70}$BA molecule in Section 5.2, and by investigating the effect of these characteristics on the molecular packing of the BHJ between P3HT and IC$_{70}$BA in Section 5.3. HPLC was used to analyse two commercial samples of IC$_{70}$BA. This showed the presence of three different RIs of IC$_{70}$BA. These RIs also exhibited dissimilar distributions in IC$_{70}$BA#1 and IC$_{70}$BA#2. MS, $^1$H NMR, $^{13}$C NMR, and UV-vis absorption spectroscopy were used to study the RIs, and
7.1. Summary of achievements

to unambiguously assign these to the geometric structures of the 5, 2, and 12 o’clock RIs of IC\textsubscript{70}BA. The spacial molecular packing of these RIs with P3HT was indicated by the different distances between the indene addend and the C\textsubscript{70} cage. Depending on the IC\textsubscript{70}BA batch used, a different D/A nano-morphology was observed, which in turn resulted in the dissimilar thermal stability and phase transition properties of the different P3HT:IC\textsubscript{70}BA blends.

It was shown in Section 5.3.1 that the SE characterisation technique is applicable to studying multi-material blends, and leads to a detailed understanding of the formation kinetics of BHJ systems. Therefore, SE was used to study the influence of the fabrication procedure of the photoactive layer on the vertical distribution of P3HT and IC\textsubscript{70}BA in their blend. A balanced D/A allocation and the formation of domains with an appropriate size was only possible due to the migration, rearrangement, and crystallisation of the photoactive blend caused by the SA and TA step. Morphological variation of the P3HT:IC\textsubscript{70}BA blends depending on the fabrication conditions used, were also revealed and confirmed by the spectral response of the P3HT:IC\textsubscript{70}BA#1 and P3HT:IC\textsubscript{70}BA#2 layers, which were studied by way of UV-vis spectroscopy. Significant differences in the absorption profiles of different IC\textsubscript{70}BA samples were observed depending on the regio-isomeric distribution, despite the identical parameters used for the fabrication of the samples. A similar correlation between the fabrication conditions and the absorption spectra of layers of P3HT with separated 5, 2, and 12 o’clock RIs of IC\textsubscript{70}BA#1 and IC\textsubscript{70}BA#2 was noted. Low solubility of the 12 o’clock RI and excess agglomeration were shown to play an important role for the molecular packing of the D/A blend. Crucially, it was proposed that the content of the 12 o’clock RI impacts negatively on the device characteristics. This was confirmed by the topographical characterisation of P3HT:IC\textsubscript{70}BA layers using AFM, which showed an excess agglomeration for increased content of the 12 o’clock RI in the IC\textsubscript{70}BA sample.

The importance of the RI type and the ratio between the different RIs in their mixture in the IC\textsubscript{70}BA sample was clearly shown in Section 5.4, where complete OPV devices were fabricated. Optimal fabrication conditions for the P3HT:IC\textsubscript{70}BA blend were designed based on the experimental results obtained in previous sections. The highest device PCE of above 6.7% was achieved for the P3HT:IC\textsubscript{70}BA#1 blend, when it was subjected to SA & TA. In contrast, a maximum PCE of 2.2% was measured for P3HT:IC\textsubscript{70}BA#2-based solar cells. This was attributed to the increased content of the 12 o’clock RI, which leads to a disadvantageous molecular packing and morphology of the D/A blend, which drastically impacts the charge carrier generation and transport processes, and reduces the device PCE. This was furthermore confirmed by the subsequent fabrication of OPV devices with photoactive blends of P3HT with the separated RIs of IC\textsubscript{70}BA#1 and IC\textsubscript{70}BA#2. The experimental results clearly showed a dependence of the device’s characteristics on the type of RI, where the lowest PCEs were measured for the 12 o’clock RI.
7.1.2. Fabrication of large-area OPV modules

A scalable deposition technique was developed in Chapter 6 in order to understand the factors that influence the characteristics of large size OPV devices, and to ease the transition from laboratory to industry. A paint applicator equipment was redesigned and engineered to serve as a fully functional slot-die coater, and was then used for the fabrication of large-area OPV solar cells and modules. PCEs approaching 4% were achieved for device photoactive areas of over 35 cm$^2$. LBIC, PL, and Raman mapping were used to study the homogeneity and quality of the slot-die coated layers in order to provide the information needed for further improvements. The experimental results demonstrate a way to potentially replace the non-scalable spin-coating technique, and to bring laboratory scale research closer to industry.

The custom built slot-die coater was deployed for the deposition of the ETL and photoactive layer of the solar cells’ stack. The transition from small- to large-area OPV devices was studied for the P3HT:IC$_{70}$BA and PCDTBT:PC$_{70}$BM material systems. An unfavourable D/A morphology was observed when the slot-die coating technique was used for the deposition of P3HT:IC$_{70}$BA layers, compared to their spin-coated counterparts. This was attributed to the altered drying kinetics and different morphological formation of the blend. Thus, the desired molecular packing of the BHJ was not achieved, and this resulted in rather low device PCEs of the P3HT:IC$_{70}$BA-based modules. The reduced PCEs were also related to imperfections associated with the coating procedure. Nevertheless, suggestions of how to overcome these challenges are given in the following section.

The challenges associated with the unfavourable D/A morphology and the deposition imperfections of slot-die coated P3HT:IC$_{70}$BA layers were overcome by using the photoactive system of PCDTBT:PC$_{70}$BM. This was attributed to the lower sensitivity of the BHJ morphology of the latter material system to the fabrication conditions, which did not entail an SA step. Additionally, the deposition uniformity of the photoactive ink improved due to the use of a mixed solvent system for the dispersion of PCDTBT:PC$_{70}$BM. The substitution of P3HT with the low band gap polymer PCDTBT enhanced the photon yield in the photoactive layer which together with the reproducible coating of homogeneous PCDTBT:PC$_{70}$BM layers allowed for an increase in the device PCE when compared to P3HT:IC$_{70}$BA-based modules.

The quality of the deposited layers was studied using LBIC, PL, and Raman mapping techniques that facilitated the evaluation of the exact photoactive device area and also proved to be a powerful tool for analysing the nature of different coating defects. The use of the PCDTBT:PC$_{70}$BM system instead of P3HT:IC$_{70}$BA additionally led to the significantly improved operational stability of the devices. The ultimate goal to develop a deposition procedure suitable for a R2R implementation was accomplished by fabricating OPV modules on PET substrates.
7.2. Suggestions for future work

The use of solvent additives is a promising approach to controlling the morphology of the P3HT:IC$_{70}$BA system. The beneficial drying properties of the ink after deposition allow for selective material solubility and tailored formation kinetics of the BHJ system. Thus, a suitable D/A molecular packing leading to high device PCEs can be achieved without the need for an SA step. Future work is, therefore, required to study the effect of solvent additives such as DIO, OT, CN, NMP, and others on the morphological formation of the P3HT:IC$_{70}$BA blend. Additionally, it would be of interest to investigate how solvent additives affect the nano-morphology of the photoactive layer depending on their use with either single RIs or a mixture of RIs of IC$_{70}$BA to make blends with P3HT. The UV-vis, AFM, and spectroscopic ellipsometry characterisation techniques are ideal for preliminary testing and facilitate the design of a deposition procedure that allows for the fabrication of P3HT:IC$_{70}$BA films with similar properties to those fabricated using an SA step. Moreover, by avoiding the SA step and tailoring the drying kinetics of deposited layers, the fabrication speed and deposition quality of functional layers in the device stack can be improved. This can address the challenges associated with the homogeneity of P3HT:IC$_{70}$BA layers when the custom built slot-die coater is used, and lead to preserving the high PCEs achieved using the spin-coating deposition technique.

Different interfacial layers can be used in the device stack in order to improve the PCE and operational stability of OPV devices by allowing for better charge carrier extraction properties, enhanced light absorption and distribution in the solar cell stack, and increased resistivity against water vapour and oxygen from the environment. The thermally evaporated MoO$_3$ layer used in this thesis could be replaced by alternative solution processable p-type materials such as MeO$_x$-based precursors, molecular metal oxides, or PEDOT:PSS (see Section 2.3.3). The replacement of the thin MoO$_3$ layer (7.5 nm) used in this work by thicker HTLs such as PEDOT:PSS (i.e. PH1000 with a thickness greater than 300 nm) would allow for the deposition of Ag top electrodes by using printing and coating techniques such as screen, gravure, or flexo-printing (suggestions for possible top electrode layouts are given in Appendix I). This, in turn, would allow for the processability of the complete OPV device by using only R2R compatible deposition techniques.

Although the development and design of the slot-die coating equipment for this thesis demonstrated that uncomplicated fabrication of large-scale OPV modules is possible, optimisations of the custom built equipment can be carried out to improve the coating alignment: an automated and traced-by-a-camera movement of the coating head is desirable in order to allow for more precise positioning and coating accuracy when modules consisting of lanes of cells are fabricated. It is also possible to design a slot-die head which allows for the deposition of several lanes simultaneously, or a wide single lane that can be furthermore precisely structured and divided by a laser into smaller lanes of solar cells. Additionally, the coating head could be redesigned to accommodate a heating element in order to permit better control over the temperature of the ink to be deposited.

The laser patterning procedure could also be tailored to allow for the precise removal of each functional layer in the OPV device stack. The laser source used in this thesis operates at 248 nm. Although it is possible to pattern PET-ITO substrates with this operating wavelength
by ablation of the ITO, it is questionable whether the laser set-up would be suitable for the removal of other layers in the OPV device stack. Therefore, further studies are required to evaluate the compatibility of the laser used for structuring all layers incorporated in the structure of the modules. Nevertheless, by using a suitable laser source, it would be possible to accomplish a more efficient and precise structuring, which can increase the geometrical fill factor of the devices (GFF; the ratio of the photoactive device area to the total area of the module). An improved interconnection between single cells in the module would additionally reduce resistive losses and improve the characteristics of the module. In this respect, it is highly advisable to use a bottom device electrode with $R_{\text{SHEET}}$ below $10 \, \Omega/\square$ in order to allow for an unimpeded charge carrier extraction. This, in turn, would lead to improved device FF and PCE.

Another point of interest would be to improve the operational stability of the modules. Although the PCDTBT:PC$_{70}$BM-based OPVs fabricated in this thesis showed promising operational stability values when characterised unprotected from the environment for 24 h under constant 1 Sun illumination, significant improvements may be expected upon the use of an appropriate encapsulation. Therefore, future work should concentrate on studying different encapsulation foils in order to preserve high device PCEs for a prolonged period of time. Apart from dedicating efforts to identifying suitable encapsulation media with low WVTR (ideally below $10^{-4} \, \text{g/m}^2\text{day}$), it is advisable to look into encapsulation foils that also serve as an UV filter that will protect the organic materials used in the device stack from degradation.
Appendix

A. Mass spectroscopy analysis of IC\textsubscript{70}BA\#1

MALDI MS was carried out on fractions A, B, and C\textsubscript{2} for IC\textsubscript{70}BA\#1 only. The spectrum correspond to indene-C70 bis-adduct with m/z 1072 (C\textsubscript{88}H\textsubscript{16} formula). Figure A.1 shows the MS spectra of IC\textsubscript{70}BA\#1 fraction A only.

![Figure A.1: Mass spectroscopy (MALDI) of IC\textsubscript{70}BA\#1 fraction A (a). Isotopic distribution of the peak of IC\textsubscript{70}BA\#1 fraction A (b) with m/z 1072 which corresponds to the C\textsubscript{88}H\textsubscript{16} formula.](image)

Figure A.1.: Mass spectroscopy (MALDI) of IC\textsubscript{70}BA\#1 fraction A (a). Isotopic distribution of the peak of IC\textsubscript{70}BA\#1 fraction A (b) with m/z 1072 which corresponds to the C\textsubscript{88}H\textsubscript{16} formula.
B. Optical characterisation of IC$_{70}$BA#1

Figure B.2 shows the absorption profiles for the IC$_{70}$BA#1 fractions only. This is due to expected identical UV-Vis absorption profiles for each isomer type, regardless of the IC$_{70}$BA batch. The absorption spectra were recorded in toluene solutions.

![Absorption spectra of the 5, 2, and 12 o’clock RI of IC$_{70}$BA#1 recorded in toluene.](image)

**Figure B.2.** Absorption spectra of the 5, 2, and 12 o’clock RI of IC$_{70}$BA#1 recorded in toluene.
C. Nuclear magnetic resonance characterisation of IC\textsubscript{70} BA\#1

Figure C.3.: \textsuperscript{1}H NMR spectra of IC\textsubscript{70} BA\#1 fractions A (top), B (middle), and C (bottom) with the signals assigned to protons H\textsubscript{a} – H\textsubscript{h}. The peaks at 2.37 ppm, 7.19 ppm, and 7.25 ppm correspond to residual toluene, whereas the peaks at 7.27 ppm and 3.5 ppm to chloroform and methanol.
Figure C.4.: COSY 2D NMR spectra of IC$_{70}$BA#1 fractions A (top), B (middle), and C (bottom). The insets shows enlarged aromatic region with the black lines indicating connectivity order between protons H$_e$ – H$_h$. 
Figure C.5.: HSQC 2D NMR spectra of IC$_{70}$BA#1 fractions A (top), B (middle), and C (bottom). The spectra indicate single-bond correlations between the protons H$_a$ – H$_h$ and the corresponding carbon atoms.
Figure C.6.: HMBC 2D NMR spectra of IC$_{70}$BA#1 fractions A (top), B (middle), and C (bottom). The spectra indicate multiple-bond correlations between the protons H$_a$ – H$_h$ and the corresponding carbon atoms.
Figure C.7.: $^{13}$C NMR spectrum of IC$_{70}$BA#1 fraction A showing the full spectrum (a), an aliphatic (b), and aromatic (c) regions. The spectrum indicates the assigned carbon atoms C$_1$ – C$_{11}$ in each case.
Figure C.8: $^{13}$C NMR spectrum of IC$_{70}$BA#1 fraction B showing the full spectrum (a), an aliphatic (b), and aromatic (c) regions. The spectrum indicates the assigned carbon atoms C$_1$ – C$_{11}$ in each case.
Figure C.9: $^{13}$C NMR spectrum of IC$_{70}$BA#1 fraction C showing the full spectrum (a), an aliphatic (b), and aromatic (c) regions. The spectrum indicates the assigned carbon atoms C$_1$ – C$_{11}$ in each case.
D. Slot-die coater parts – 3D drawings

Figure D.10.: 3D Images of the slot-die coater parts. Horizontal plate extension–left (a), horizontal plate extension–right (b), extended “push-feet”–left (c), extended “push-feet”–right (d), slot-die head–back plate (e), slot-die head–front plate (f), and slot-die head–shim (g).
E. Glass-ITO layout for OPV modules

Figure E.11.: Pre-patterned glass-ITO substrate used for the fabrication of OPV modules.
F. Device characteristics for single PCDTBT-PC$_{70}$BM cells

Table F.1.: Summarised device characteristics for single PCDTBT-PC$_{70}$BM cells, which were fabricated from a 10 mg/mL, 12.5 mg/mL, or 15 mg/mL D/A dispersion on glass substrates.

<table>
<thead>
<tr>
<th>Modules from a 10 mg/mL PCDTBT-PC$_{70}$BM dispersion</th>
<th>V$_{OC}$ (V)</th>
<th>I$_{SC}$ (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Area (cm$^2$)</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1: cell #1</td>
<td>0.77</td>
<td>54.26</td>
<td>39.7</td>
<td>2.84</td>
<td>5.8</td>
<td>41.8</td>
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<tr>
<td>M1: cell #2</td>
<td>0.87</td>
<td>57.13</td>
<td>40.9</td>
<td>3.48</td>
<td>5.8</td>
<td>49.7</td>
</tr>
<tr>
<td>M1: cell #3</td>
<td>0.85</td>
<td>57.98</td>
<td>41.4</td>
<td>3.50</td>
<td>5.8</td>
<td>49.3</td>
</tr>
<tr>
<td>M1: cell #4</td>
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<td>51.1</td>
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<tr>
<td>M1: cell #5</td>
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<td>3.67</td>
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<td>50.2</td>
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<tr>
<td>M1: cell #6</td>
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<td>38.3</td>
<td>2.82</td>
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<td>43.0</td>
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<td>M2: cell #1</td>
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<td>3.42</td>
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<tr>
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<td>M2: cell #5</td>
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<td>42.0</td>
<td>3.80</td>
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</tr>
<tr>
<td>M2: cell #6</td>
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<td>56.58</td>
<td>38.9</td>
<td>1.97</td>
<td>5.8</td>
<td>34.0</td>
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<table>
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<th>Modules from a 12.5 mg/mL PCDTBT-PC$_{70}$BM dispersion</th>
<th>V$_{OC}$ (V)</th>
<th>I$_{SC}$ (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Area (cm$^2$)</th>
<th>Power (mW)</th>
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<tr>
<td>M1: cell #1</td>
<td>0.75</td>
<td>59.50</td>
<td>33.9</td>
<td>2.58</td>
<td>5.9</td>
<td>44.6</td>
</tr>
<tr>
<td>M1: cell #2</td>
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<td>35.7</td>
<td>2.75</td>
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<td>51.0</td>
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<td>33.0</td>
<td>2.27</td>
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<td>30.1</td>
</tr>
<tr>
<td>M2: cell #1</td>
<td>0.80</td>
<td>58.56</td>
<td>35.2</td>
<td>2.97</td>
<td>5.6</td>
<td>46.9</td>
</tr>
<tr>
<td>M2: cell #2</td>
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<td>59.69</td>
<td>39.6</td>
<td>3.69</td>
<td>5.6</td>
<td>51.9</td>
</tr>
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<td>34.8</td>
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<td>1.62</td>
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<table>
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<th>Modules from a 15 mg/mL PCDTBT-PC$_{70}$BM dispersion</th>
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<th>I$_{SC}$ (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Area (cm$^2$)</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>54.38</td>
<td>34.4</td>
<td>2.32</td>
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<td>43.8</td>
</tr>
<tr>
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<td>58.00</td>
<td>41.6</td>
<td>3.38</td>
<td>6.3</td>
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<tr>
<td>M1: cell #3</td>
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<td>58.88</td>
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<td>3.36</td>
<td>6.3</td>
<td>51.6</td>
</tr>
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<td>62.05</td>
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<td>3.86</td>
<td>6.3</td>
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</tr>
<tr>
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<td>M1: cell #6</td>
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<td>36.6</td>
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<td>6.3</td>
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G. PL and Raman photocurrent maps of PCDTBT:PC$_{70}$BM–M2

Figure G.12.: Normalised PL and Raman photocurrent maps of PCDTBT:PC$_{70}$BM–M2 from Figure 6.13. The PL spectra were normalised against the area of the signal (a), height (b), ratio A/H (c), baseline (d), and Raman signal (e). Note that every cell in the image for each method was normalised separately for a better comparison of the defects. For this reason no colour key is reported for the maps.
H. I-V characteristics of PCDTBT:PC$_{70}$BM modules on plastic substrates

Figure H.13.: I-V characteristics of PCDTBT:PC$_{70}$BM modules on plastic substrates with regard to the number of connected cells in series on M1 (a) and M2 (b). The I-V curve of M1, which was subjected to a post-T annealing step for 10 min at 120 °C is included in (a).
I. Top electrode layouts for OPV modules

Figure I.14.: Top electrode layouts for OPV modules with a finger-grid structure (a), and an opaque structure (b). Both layouts are suitable for deposition by the flexographic printing technique.
Bibliography


Bibliography

1995.


Bibliography


Bibliography


