Tailoring device-scale properties in organic electronics: morphological, optical and electrode-interface related approaches

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Tailoring device-scale properties in organic electronics: Morphological, optical and electrode-interface related approaches

by

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A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

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Iowa State University
Ames, Iowa
2015

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DEDICATION

I dedicate this dissertation to my country Egypt, my wife Wafaa and daughters: Menaallah, Kenazy, and Retal. Also, I would like to dedicate this work to my parents and my family; without their support I would not have been able to complete it.

Last but not least, I would like to dedicate this dissertation to the people who supported me to join the graduate college, namely Prof. Nabil Kinawy, Prof. Maher El-Tonsy, Prof. Hassan Elhadidey, Prof. AbdelRahamn Lashin as well as my friends Dr. Hytham Alatfey and Dr. Ihor Hlova.
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ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious and the Most Merciful Alhamdulillah, all praises to Allah for the strengths and his blessing in completing this work.

First and foremost, I offer my sincerest gratitude to my country Egypt for their funding and continuous support. I would like to express my deepest gratitude to my supervisor, Prof. Sumit Chaudhary, for his respectful guidance, precious discussions and perspective views throughout my doctoral studies. Mostly important, I also appreciate all the committee members, Prof. Vikram Dalal, Prof. Rana Biswas, Prof. Kristen Constant and Prof. Scott Beckman, for their continued guidance.

I wish to express my warm and sincere thanks to my colleagues in the Nanolab research group and all MRC students for their valuable advice and help. Special thanks go out to Max Noack for his technical assistance and fruitful discussions.

During this work, I have closely collaborated with many colleagues at Argonne National Lab (ANL) and South Dakota State University. I would like to thank all of them for sharing their research equipments and being always kind.

Last but not least, no words are enough to thank my wife Wafaa and my daughters Menaallah, Kenzy, and Retal for their unwavering support throughout my PhD studies. Finally, the love and mental support of my parents and family made my accomplishments possible.

Moneim Elshobaki
FUNDING

This work is supported and funded by the Ministry of Higher Education of the Arab Republic of Egypt and National Science Foundation (NSF).
In era of dwindling fossil fuel supplies, increasing energy demand and high rates of carbon emission, investment in the clean and renewable-energy market is now the goal of many governments. This global prospect pushes the countries to consolidate new policies and rules to increase the production of cost-effective resources and grow the deployment in renewable energy. Sunlight, wind, waves and geothermal heat are the natural energy resources that strongly contribute to our global energy consumption. Organic materials - restricted to those that have conjugated structure and exhibit semiconducting properties - have gained intense interest in research and academia, leading to efficient and commercially applicable devices. Organic photovoltaic (OPV), organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs) are the most prominent devices in the field of organic electronics. These devices are promising due to potentially low cost, mechanical flexibility, lightweight as well as high and ease of processability from solution (such as, spin-coating, drop casting, roll painting, and ink jet printing). Significant improvements have been achieved - especially for OLEDs, which have now been commercialized for cellular telephone applications as well as high-definition television screens. For OPVs, however, inferior performance and short lifetimes hinder their successful commercialization. The work presented in this dissertation focuses on three different performance-related issues and strategies for OPVs; electrode-interface engineering, morphology tuning, and optical absorption enhancement. The work on morphology tuning is also extended and applied to OLEDs and OFETs.

In chapter one, a schematic showing the organization of this dissertation is presented. In the same chapter, a general introduction on organic materials and thin-films is also discussed. Furthermore, the architecture and basic operation of OPV, OFET and OLED devices are considered.
Chapter two discusses the possibility of fabricating new OPV devices on previously used Indium-Tin-Oxide (ITO) substrates, which went through prior device processing with popular acidic interfacial layer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). We show that, contrary to the concerns in the literature, only the top few nanometers of ITO are etched by PEDOT:PSS in typical device processing and storage thereafter. Conductivity losses are offset by transmission gains leading to an increased power conversion efficiencies (PCE) for PTB7-based (PTB7: poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]) OPVs on used ITO substrates compared to devices on fresh ITO.

In chapter three, we introduce a generic morphology tuning technique with anisotropic applicability -exposure to static electric-field (E-field) gradient during the solidification of solution-processed polymeric thin-films. This technique improves the connectivity between polymer chains; by changing the E-field direction, radiative pathways in polymeric thin-films can be altered, charge transport in- and out-of-plane can be improved, and phase-separation in polymer-fullerene blends can be coarsened in the bulk and perpendicular to the substrate. In exemplary cases, we improved the hole mobility in OFETs, power conversion efficiency in OPVs, and electroluminescence efficiency in OLEDs.

In the last part of this dissertation, we studied the effect of using microlens array (MLA) to increase the light absorption inside the active-layer of OPVs. Our MLA approach does not hinder the fabrication of the OPV because MLA lies on the non-conductive side of the ITO glass. In chapter four, we initially investigated the effect of using MLA with 2000 nm feature size. We found that thick (P3HT:PCBM) and thin (PCDTBT:PCBM) OPVs exhibit an improved short-circuit current. This enhancement stems from the increased light path coupled with the constructive interference patterns inside the OPV photoactive layer. In chapter five, we used MLAs with smaller feature sizes. In addition to feature size of 2 micrometer, 1.5 micrometer, 1 micrometer and 0.6 micrometer MLAs were also investigated. The experimental and simulations results show agreement on an increased light absorption inside the photoactive layer; improved current-density and PCE were realized for PTB7:PCBM and PCDTBT:PCBM OPVs (w.r.t. control) using 1 micrometer and 1.5 micrometer feature size MLAs, respectively.
NOMENCLATURE

P3HT: Poly(3-hexylthiophene-2,5-diyl)
PCBM: Phenyl-C61-butyric acid methyl ester
E-field: Electric field
VDG: Van de Graaff
OPVs: Organic solar cells
OFETs: Organic field effect transistor
OLEDs: Organic light-emitting diode
ITO: Indium-tin oxide
PEDOT:PSS: Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PVP: poly(4-vinylphenol)
PMF: poly(melamine-co-formaldehyde)
SS-PL: Steady-state photoluminescence
AFM: Atomic force microscopy
c-AFM: Conductive atomic force microscopy
KPFM: Kelvin probe force microscopy
HOMO: Highest occupied molecular orbital
LUMO: Lowest unoccupied molecular orbital
MoOx: Molybdenum Oxide
CS2CO3: Cesium Carbonate
Ca: Calcium
IDrain: Source/drain Current of OFET
VDrain: Source/drain voltage of OFET
VGate: Gate voltage of OFET
n: Diode ideality factor
V: Voltage
I: Current
J: Current density
PCE: Power conversion efficiency
MLA: Microlens array
Al: Aluminum
Ag: Silver
LiF: Lithium fluoride
EQE: External quantum efficiency
GIWAXS: Grazing Incidence wide angle X-ray scattering
CELIV: Charge extraction by linearly increasing voltage
XPS: X-ray Photo electron Spectroscopy
MEH-PPV: Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
BPhen: Bathophenanthroline
CHAPTER 1. General Introduction

1.1 Introduction

In era of dwindling fossil fuel supplies, increasing energy demand and high rates of carbon emission, investment in the clean and renewable-energy market is now the goal of many governments. This global prospect pushes the countries to consolidate new policies and rules to increase the production of cost-effective resources and grow the deployment in renewable energy. Sunlight, wind, waves and geothermal heat are the natural energy resources that strongly contribute to our global energy consumption. Organic materials - restricted to those that have conjugated structure and exhibit semiconducting properties - have gained intense interest in research and academia, leading to efficient and commercially applicable devices. Using the organic devices, including organic photovoltaics (OPVs), organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs), chemical sensors as well as photodetectors and memory cells has a great demand in the last few years. These devices are promising due to potentially low cost, mechanical flexibility, lightweight as well as ease of processability from solution (such as, spin-coating, drop casting, roll painting, and ink jet printing). Significant improvements have been achieved - especially for OLEDs, which are now commercialized in cellular telephone applications, chemical and biological sensors as well as high-definition television screens. For OPVs, however, inferior performance and short lifetimes hinder their successful commercialization. More efforts are still needed to overcome the low performance and short-lifetime of these technologies.
1.2 Dissertation Organization

This dissertation is composed of a number of journal articles published or submitted for publication and organized as shown in Figure 1.1 and as follows:

- Chapter one covers the history and recent progress of organic electronic materials and devices, and introduces the basic device structure and operation of OPVs, OFETs, and OLEDs.

- Chapter two discusses the possibility of making new solar cells on previously used Indium-Tin-Oxide (ITO) substrates, which were subjected to an acidic interfacial layer such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). The structural, compositional, optical and electrical properties of both fresh and previously used ITO substrates were investigated. This work was published in the journal *ACS Applied Materials & Interfaces*.

- Chapter three presents a new method to control the stacking and phase distribution of organic semiconductors blends via the exposure to a static electric-field (E-field) gradient during their solidification from wet state. The active-layer of OPVs, OFETs, and OLEDs were fabricated under the influence of electric field in different directions. Several structural and optoelectronic properties were characterized.

- Chapter four presents the effect of using microlens array (MLA) on the non-conductive side of the ITO substrate to increase light absorption inside the active layer of OPVs. Optical and electrical properties of OPVs fabricated with and without 2µm feature size-MLA were investigated for thick (P3HT:PC$_{60}$BM) and thin (PCDTBT:PC$_{70}$BM) OPVs. This work was published in the journal *Physical Chemistry Chemical Physics*.

- In chapter five, which is an extension of the work presented in chapter four, we studied the effect of using MLAs with smaller feature sizes on the properties and performance of PTB7:PC$_{70}$BM and PCDTBT:PC$_{70}$BM polymer systems. Experimental work was tightly coupled with simulation. This work was also published the the journal *Physical Chemistry Chemical Physics*. 
Figure 1.1  Schematic shows the organization of this dissertation.
1.3 Organic Electronic Materials

In general, conjugated organic materials are subdivided into two groups: small-molecules and polymers. Figure 1.2 shows typical examples of common small molecules and polymers. Polymers - such as polythiophenes - consist of many identical repeating units bonded together in a long chain, whereas small-molecules consist of few units. The semiconducting property of these polymeric materials stems from the alternating single and double bonds configuration that leads to an overlapping between the carbon $p_z$ orbitals, creating a delocalized $\pi$-electron cloud.

Figure 1.2 Chemical structures of common small molecules (PC$_{60}$BM, SMPV1 and p-DTS(FBTTh$_2$)$_2$) and polymers (P3HT, MEH-PPV and PCDTBT) used as p-type or n-type semiconductors in organic electronic devices, respectively.
Organic photovoltaics (OPVs), organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs) are the most extensively studied devices in academia. Their low cost of fabrication, mechanical flexibility, light-weight and ease of processing from solution gave these applications superiority over their inorganic counterparts. As Figure 1.3 shows, the aforementioned devices are fabricated by different methods, including drop-casting, spin-coating, printing (brush, inkjet, stamp and spray coating) and meniscus-guided coating (drop-coating, zone casting, hollow pen writing, blade coating, slot die coating and solution shearing). Currently, OLEDs are now implemented in smartphones and high-definition television screens, showing strong development in the field of organic electronics. Unfortunately, the low performance and short-lifetime of organic electronics are the main drawbacks of organic electronics. Therefore, scientist in academia and industry are paying more attention to understand the physics and chemistry of organic materials and to present new materials to overcome the aforementioned problems.

In 1996, Harold W. Kroto, Robert F. Curl, and Richard E. Smalley were awarded the Nobel prize in chemistry for their discovery of soccer-ball-shaped cages, known as fullerences. A few years later, the same award was given to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa for the discovery and development of electrically conductive polymers. Either one
Figure 1.4 Chemical structures of common fullerene-derivatives\textsuperscript{21}.

or two materials are implemented in the active layer of different organic electronic devices\textsuperscript{1-3}. In the next few paragraphs will shed the light on the properties of (n-type) small molecule-materials such as phenyl-C61-butyric acid methyl ester (PC\textsubscript{60}BM) and (p-type) $\pi$-conjugated polymers such as poly (3-hexylthiophene-2,5-diyl) (P3HT)\textsuperscript{20}.

Fullerene derivatives have been adopted widely as n-type semiconductors since their discovery. They remain the most commonly used material in solution processed OPVs\textsuperscript{10}. PC\textsubscript{60}BM (Figure 1.4) molecule is a single isomer, which is synthesized by the addition of the diazoalkane\textsuperscript{11}. Incorporating fullerene derivatives into the active layer of OPVs as an acceptor is associated with the highly efficient architectures\textsuperscript{1, 12-15}. Upon intimate blending with P3HT, the hole mobility of the donor is balanced by the electron mobility of PCBM, which is typically in the order of $10^{-4} \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}\textsuperscript{16, 17}$. Furthermore, it beneficially absorbs in the UV and slightly in infrared\textsuperscript{18} and increases the trapped light inside photoactive layer of the solar cell. Recently, tuning the PCBM energy level has yielded several fullerene derivatives – such as PC\textsubscript{70}BM\textsuperscript{19}, ICBA and Bis-PCBM - that achieve high power conversion efficiency solar cells\textsuperscript{20}.

Among the semiconducting polymers that have been commonly studied in the last two decades, the thiophene-based materials remain among the most interesting candidates. Two reasons account for this conclusion: (1) the chemistry of thiophene is well established, in which modifying and tuning the electronic properties of conducting polymer is possible\textsuperscript{22}; (2) the existence of sulfur atom in the thiophene ring leads to the stabilization of the conjugation chains and excellent charge transport\textsuperscript{23}. Furthermore, the small size of the thiophene building block
facilitates the polymer aggregation, higher mobilities, and; thus, better device performance. P3HT - a well-known organic semiconductor- is one of the \( \pi \)-conjugated polymers that belongs to the polythiophene family. The semiconducting property of P3HT originates from the alternating single and double bonds\(^\text{24}\). In addition to OPVs, P3HT was originally studied in the field of OFETs\(^\text{25}\). Figure 1.5a shows the structure of P3HT chain. Starting with its building unit, monomer, P3HT polymer is polymerized forming long chains with length depending on the polymer molecular weight.

Figure 1.5  a) Chemical structure of a region-regular P3HT chain and, b) Isomer conformation of the thiophene rings, and possible regioisomeric combinations [image taken from reference\(^\text{26}\)].
Because of having an asymmetric monomer, the P3HT polymer is cast in two conformations: regioregular (RR) and regiorandom (RRa). The degree of regioregularity, which measures the extent of a perfect alternation of head-to-tail (HT) arrangement, determines whether the polymer is regioregular or regiorandom. Basically, the uncontrolled coupling of 3-substituted thiophenes at the 2- and 5-positions yield polymers with different degrees of regioregularity because of the formation of head-to-tail (HT), head-to-head (HH), and tail-to-tail (TT) isomers (see Figure 1.5b). As a result, combinations of these isomeric configurations lead to four regioisomeric triads in the polymer chain: (1) HT–HT, (2) TT–HT, (3) HT–HH and (4) TT–HH. The degree of HT regioregularity is defined as the percentage of thiophene rings that adopts a HT orientation. The regioregular HT polymer has a nearly planar configuration, displaying efficient packing and better intra- and interchain stacking. Conversely, the regiorandom polymer has a twisted configuration, exhibiting a limited conjugation, poor packing, and moderate carrier mobilities.

In contrast to inorganic semiconductors, \( \pi \)-conjugated polymers are designated with their semi-crystalline or amorphous nature. The disordered species found in the polymer matrix coupled with the insulating alkyl chains, which are responsible for dissolving the polymer in organic solvents, severely hindering the carrier mobility. It is worth mentioning that the charge transport is fastest in the direction of conjugation. When chains pack, a partial overlap between \( \pi \)-orbitals assists charge transfer between chains, enhancing the mobility in two orthogonal di-
Figure 1.7  The grazing incidence-wide angle x-ray diffraction of P3HT-based thin-films in OFET. The cartoon shown on each GIWAXS image displays the (a) edge on, and (b) plane on orientation [image taken from reference 32].

rections. In the third direction, however, the insulating alkyl chains impede charge transport, making mobility in this direction inherently low. The schematic diagram, shown in Figure 1.6, displays the chain stacking of P3HT. P3HT exhibit well-ordered lamellar stacks in the direction normal to the substrate, which is called “edge-on” orientation. The directions of π-π stacking and backbone are the most relevant to charge transport, with the π-stacks being the most important for intermolecular charge transfer. In contrast, the charge transport along the alkyl stacking direction is the slowest, suppressing the hole mobility. In OFET devices, the orientation of P3HT thin-films was previously identified by grazing-incidence X-ray diffraction (see Figure 1.7). In this work, Sirringhaus et al. showed that polymers with high HT regioregularity adopt an “edge-on” arrangement in which the side chains are normal to the substrate, whereas polymers with low regioregularity favor a “plane-on” orientation in which the side chains are parallel to the substrate. Achieving one of the aforementioned orientations relies strongly on the polymer regioregularity, surface properties of the substrate as well as deposition method.
1.4 Organic Electronic Devices

1.4.1 Organic solar cells: Architecture and operation

Over the last decade, OPVs have made rapid progress by achieving a power conversion efficiency (PCE) increase from 2% to 12%\textsuperscript{13, 15, 33-39}. This rapid improvement of PCE has primarily been due to the following aspects: (1) new materials, especially small band-gap donor polymers with appropriate energy level offsets to the fullerene acceptors\textsuperscript{40-42} (2) improved anodic and cathodic buffer layers\textsuperscript{43-45} and (3) the optimization of the bulk-heterojunction morphology using approaches such as annealing and additives\textsuperscript{46-50}. In addition to tailoring the band-gap of materials to absorb more solar spectrum, several device architectural approaches have been explored to improve light absorption in OPVs. These include utilizing textured substrates\textsuperscript{51-53}, substrates with wrinkles and deep folds\textsuperscript{54}, metal nanoparticles in or adjacent to the active-layers\textsuperscript{55, 56} and patterning the active-layers\textsuperscript{57}. The best research-cell efficiencies that have been verified by the National Renewable Energy Research Laboratory (NREL) are shown in Figure 1.8\textsuperscript{58}. Currently, organometal halide perovskites solar cells, which are an emerging class of semiconductors, records efficiencies higher than 20%\textsuperscript{60-61}. Although, the perovskite thin-films have charge diffusion length (mobility and lifetime product) in the range of 1 micron\textsuperscript{62}, this new technology faces a big challenges related to short-term and long-term stability due to high water-solubility of the perovskites materials.

As Figure 1.9a shows that typical OPVs have a layered structure with active layers that can be realized in three different ways: (1) a single layer of organic material sandwiched between two electrodes, (2) double-layer junction between donor and acceptor materials and (3) an intimate blend of donor and acceptor (bulk heterojunction)\textsuperscript{59}. The OPV device generally consists of on a transparent electrode [typically indium-tin oxide (ITO) or fluoride-doped tin oxide(FTO)], an active layer and a top metal electrode (typically aluminum). The basic operation of OPV device is shown in the schematic of Figure 1.9c, which depicts the different steps after which a photocurrent is generated from the solar cell. These steps are (1) absorption of an incident photon to create an exciton, (2) diffusion of an exciton toward the donor-acceptor interface, (3) dissociation of the exciton at the interface by charge transfer of an electron in the acceptor and
Figure 1.8 The most recent “best research-cell efficiencies” that have been verified by the National Renewable Energy Research Laboratory (NREL), June 201538.
Figure 1.9  a) The basic device architecture of organic solar cells, b) typical lab-scale solar cell device and c) a schematic view of energy diagram of organic solar cell, which describes the different processes leading to the generation of photocurrent.

hole in the donor, and (4) transport of charges to and collection at the contacts.

The equivalent circuit of solar cells is shown in Figure 1.10a. Under illumination, the solar cell current versus voltage (IV) relationship is expressed in terms of the photocurrent $I_L$ and dark current $I_D$ with the non-ideality factor taken into account through the shunt resistance $R_{\text{shunt}}$ and the series resistance $R_{\text{series}}$. The IV characteristic is then described by equation [1.4.1]^{63}:

$$I = I_L - I_o\left(e^{\frac{q(V-I \times R_{\text{series}})}{nkT}} - \frac{V + IR_{\text{series}}}{R_{\text{shunt}}}\right)$$ (1.4.1)

where, $I$ and $V$ are the current and voltage over the external load, $q$ is the charge of electron, $k$ is the Boltzmann constant, $T$ is the temperature, and $n$ is the diode ideality factor. It is worth mentioning that the series and shunt resistance are extracted from the slopes of the I-V curves near the open circuit voltage ($V_{\text{OC}}$) and short circuit-current ($I_{\text{SC}}$) points (Figure 1.10b), respectively.
Figure 1.10  (a) The equivalent circuit of the solar cells; $I_D$ and $I_L$ represent the currents in dark and under illumination, and $R_{shunt}$ and $R_{series}$ are the shunt and series resistances, respectively. (b) A typical current-voltage (I-V) curve that shows the diode parameters: short-circuit current ($I_{SC}$), open-circuit voltage ($V_{OC}$), maximum current ($I_{max}$), maximum voltage ($V_{max}$) and maximum power point ($P_{max}$).

The power conversion efficiency (PCE or $\eta$), which is defined as the percent ratio of the output electric power ($P_{out}$) and the input light power ($P_{in}$), is represented by equation [1.4.2]:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{V_{OC} \times I_{SC} \times FF}{P_{in}}$$  \hspace{1cm} (1.4.2)

where FF is the fill factor, which is defined as the ratio between the maximum power ($P_{max}$) and the product of the open-circuit voltage and short-circuit current as expressed by equation [1.4.3]:

$$FF = \frac{P_{max}}{V_{OC} \times I_{SC}} = \frac{V_{max} \times I_{max}}{V_{OC} \times I_{SC}}$$  \hspace{1cm} (1.4.3)

where $V_{max}$, $I_{max}$ and $P_{max}$ represent the maximum voltage, current and power (see Figure 1.10b), respectively.
1.4.2 Organic field-effect transistors: Architecture and operation

Organic field-effect transistors (OFETs) act as electronic switches in the integrated circuits for memories and sensors as well as for controlling individual pixels in active matrix displays. As Figure 1.11 shows, OFETs can be fabricated in four different configurations: (1) bottom-gate top-contact, (2) bottom-gate bottom contact, (3) top-gate top-contact and (4) top-gate bottom-contact. This OFET consists of a bottom gate electrode, a dielectric layer, organic semiconducting material, and source/drain electrode. Because of their ease deposition, thermal stability, and high transparency, organic dielectrics are promising candidate that can replace the extensively used SiO$_2$ or Al$_2$O$_3$ counterparts. The field-effect mobility is largely sensitive to the morphology of the semiconductor/gate interface. The smoother the dielectric, the higher mobility is.

![Schematic diagram of the four types of OFET configurations](image)

Figure 1.11 Schematic diagram of the four types of OFET configurations: (a) top-gate bottom-contact, (b) top-gate top-contact, (c) bottom-gate bottom-contact, and (d) bottom-gate top-contact.

To further differentiate between the n- and p-channel OFETs, energy level diagram of the HOMO-LUMO levels and the source/drain metal electrodes is shown in Figure 1.12. At zero
gate voltage \( (V_{\text{Gate}} = 0) \), the undoped organic semiconducting layer does not show any carrier transport (see Figures 1.12e and f). The only way to get a flowing current is the injection from the source/drain electrodes. Therefore, when a positive bias is applied to the gate \( (V_{\text{Gate}} > 0) \), negative charges are induced at the semiconductor/dielectric interface (n-channel) as shown in Figure 1.12g. If the Fermi level of source/drain is far from the LUMO level of the organic semiconductor so that electron injection/extraction is very unlikely, then a low Drain/source current \( (I_{\text{Drain-source}}) \) is expected due to high contact barrier. Conversely, selecting a source/drain metal with work function close to the LUMO level of the polymer facilitates the charge extraction and OFET conducts. In contrast, when a negative voltage is applied \( (V_{\text{Gate}} < 0) \), positive charge are drifted to the organic semiconductor/dielectric close to gate dielectric (p-channel) as shown in Figure 1.12h. If the Fermi level of source/drain metal is close to the HOMO level of the organic semiconductor, then positive charges can be extracted by applying a voltage \( V_{\text{Drain}} \) between drain and source.

The carrier mobility \( (\mu) \) is calculated from the linear and saturation regions of the \( I_{\text{Drain}}-V_{\text{Gate}} \) curve. For p-type OFET devices, at low source-drain voltage \( (V_{\text{Drain}}) \), source/drain current \( (I_{\text{Drain}}) \) increases linearly with the \( V_{\text{Drain}} \), and is determined from equation [1.4.4]:

\[
I_D = \frac{WC_i}{L} \mu (V_{\text{Gate}} - V_T) V_D
\]

where, \( L \) is the channel length, \( W \) is the channel width, \( C_i \) is the capacitance per unit area, and \( V_T \) is the threshold voltage. For \( V_{\text{Drain}} \) more negative than \( V_{\text{Gate}} \), \( I_{\text{Drain}} \) tends to saturate. In the saturation region, the relation between \( I_{\text{Drain}} \) and \( V_{\text{Drain}} \) is governed by the following equation [1.4.5]:

\[
I_D = \frac{WC_i}{2L} \mu (V_{\text{Gate}} - V_T)^2
\]
Figure 1.12 Schematic shows the structure of a) OFET with highlighted accumulation of b) electrons (n-type OFET), and c) holes (p-type OFET), respectively. d) Schematic shows the energy level diagram of n- and p-type OFETs at $V_{\text{Drain}} = V_{\text{Gate}} = 0$ V. (e-g) and (f-h) are the energy level diagrams of n- and p-channel OFETs at zero and non-zero drain voltage, respectively.
1.4.3 Organic light-emitting diodes: Architecture and operation

Organic light emitting diodes (OLEDs) are fabricated based on small molecules, dendrimers and polymers. Recently, OLEDs have been implemented in different applications - including high-definition television screens, computer monitors, mobile smartphones, sensors as well as digital cameras and car lighting. 1.13 shows typical industrial OLEDs applications. OLED devices possess several advantages over the conventional display devices, such as high luminous efficiency, wide viewing angle, high resolution, light weight, low power consumption and their low power drain. In addition, the R&D of OLEDs yielded unlimited choices of colored devices with high stability and good potential of low manufacturing cost. Based on the type of manufacturing and their use, OLEDs are classified into several types; passive-matrix OLEDs, active-matrix OLEDs, transparent OLEDs, foldable OLEDs, and white OLEDs.

![Figure 1.13 Photograph of a) white OLED flat Lamps, b) foldable blue OLED lamp; c) curved OLED TV, and d) the Samsung Galaxy edge smartphone with an OLED display.](image)

In general, most state-of-the-art OLEDs consist of multiple organic devices in which the light-emitting layers are sandwiched between two electrodes, a cathode and anode (1.14a). At least one of two electrodes is (semi)transparent, such as Indium tin oxide (ITO). Tuning the device thickness and the work function of the interfacial layers surrounding the OLED emissive
Figure 1.14  Schematic shows a) double heterostructure OLED device and b) its corresponding energy level diagram.

layer(s) are crucial to optimize the injection of charges, and also to improve the device stability. 1.14b shows the energy level diagram an OLED device. When a forward bias is applied, injected electrons and holes recombine in the organic emissive layer to generate light.
1.4.4 References


CHAPTER 2. EFFICIENT POLYMER SOLAR CELLS FABRICATED ON POLY(3,4-ETHYLENEDIOXYTHIOPHENE): POLY(STYRENESULFONATE)-ETCHED OLD INDIUM TIN OXIDE SUBSTRATES


Moneim Elshobaki, James Anderegg and Sumit Chaudhary

2.1 Abstract

In organic electronic devices, indium tin oxide (ITO) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) are the most common transparent electrode and anodic buffer layer materials, respectively. A widespread concern is that PEDOT:PSS is acidic and etches ITO. We show that this issue is not serious: only a few nanometers of ITO are etched in typical device processing conditions and storage thereafter; conductivity losses are affordable; and optical transmission gains further offset these losses. Organic photovoltaic (OPV) devices fabricated on old ITO (with PEDOT:PSS history) were similar or higher in efficiency than devices on fresh ITO. Poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) devices on old ITO showed efficiencies up to 9.24%, compared to 8.72% efficient devices on fresh ITO. This reusability of ITO is potentially impactful for economics of organic electronics because ITO accounts for almost 90% of energy embedded in organic devices such as OPVs.
2.2 Introduction

Owing to its high optical transmission and electrical conductivity, indium tin oxide (ITO) is the most popular transparent electrode in liquid crystal displays and optoelectronic devices. In organic electronic devices, such as organic photovoltaics (OPVs), ITO is widely used also because its work function is easily tuned by cleaning processes, surface treatments, and buffer layers. Because indium is rare and demand for ITO is high, primarily in liquid crystal displays, prices of indium have been fluctuating. This has led to efforts toward replacing ITO with new materials, such as metal nanowires, carbon nanotubes, graphene, and conductive polymers. However, most alternatives are still inferior to ITO in overall performance. Replacements are also being sought for poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which is the most common anodic buffer layer in organic devices. PEDOT:PSS smoothen the surface, increases the work function of ITO for efficient collection (or injection) of holes, and protects the overlying active layer from oxidative effect of ITO. However, PEDOT:PSS is acidic and known to etch ITO, thus, spurring research in alternatives, such as MoO$_3$, NiO$_x$, graphene oxide, and V$_2$O$_5$. Still, PEDOT:PSS remains the most popular anodic buffer layer and is a rather mature material; formulations of different conductivities are available for different applications. Motivated by our observation that an unencapsulated, ambient-stored, old ITO substrate-coated with PEDOT:PSS and other OPV layers can be cleaned and reused to fabricate efficient OPV devices, we investigated the impact of etching of ITO by PEDOT:PSS in detail. This paper discusses our several characterizations on this issue. Our key findings are that (1) PEDOT:PSS etches only a few nanometers of ITO, which does not seriously affect the charge collection and transport in OPV devices, and (2) affordable conductivity losses are further offset by the gain in optical transmission of ITO, making PEDOT:PSS-etched ITO effective in increasing optical absorption in OPVs of promising contemporary materials such as Poly[4,8-bis(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyll][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyll]] (PTB7). Cleaning and reusing 2.5-year-old (PEDOT:PSS-coated) ITO, we fabricated 9.24% efficient OPV devices based on the PTB7 polymer compared to 8.72% efficient devices on fresh (new) ITO substrates. Considering that...
most OPVs currently have a lifetime of around 3–4 years,\textsuperscript{14} suitable only for consumer electronic applications, it thus becomes unproblematic and even advantageous to continue using ITO and PEDOT:PSS and then reuse ITO from degraded or discarded OPVs to fabricate new batches. This can significantly impact the cost structure of OPVs; life cycle assessment has shown that ITO accounts for \(~90\%\) of energy embedded in an OPV module.\textsuperscript{15} Although light has not been shed on the seriousness of etching, prima facie, there is no doubt that PEDOT:PSS etches ITO. It was shown using Rutherford backscattering technique that this etching initiates In diffusion in PEDOT:PSS, and diffusion saturates after a few days.\textsuperscript{16} We probed the impacts of etching using several structural, electrical, and optical characterizations. OPV cells were also fabricated on old and fresh ITO substrates. Throughout this paper, old ITOs refer to ITO substrates that were coated with PEDOT:PSS/active layer/cathode and stored in ambient for the indicated amount of time or age, and fresh ITOs refer to recently purchased ITOs with no PEDOT:PSS or device processing history. For all of the characterizations and re-fabrication on old ITOs, previously coated device layers were removed by typical ITO cleaning processes.

2.3 Experimental Procedure

2.3.1 Materials

P3HT, PTB7, PC\textsubscript{60}BM, and PC\textsubscript{70}BM were purchased from 1-Material; ITO on glass (5–15 ohms/square) was purchased from Delta Technologies; and PEDOT:PSS (VP 4083) was purchased from HC Stark.

2.3.2 Solar cell fabrication

Device layers from old ITOs were removed by the sonication in chloroform. Both the fresh and old ITOs were further cleaned in detergent, deionized water, methanol, ethanol, and 2-propanol. After drying the ITO slides with N\textsubscript{2} on a hot plate at 150 °C for 15 min, they were exposed to high-dose air plasma for 5 min before depositing PEDOT:PSS (spin coating of 4000 rpm/ 60 s) and annealing at 150 °C for 30 min. Then, the substrates were transferred into a N\textsubscript{2}- filled glovebox with oxygen and water levels less than 10 and 0.1 ppm, respectively.
The P3HT:PC$_{60}$BM blend (1:1, w/w; 10 mg/mL) was dissolved in ortho-dichlorobenzene by stirring overnight. The blend solution was filtered using plastic syringes and 0.2 μm filters, before spincoating the active layer at 500 rpm/40 s. P3HT:PC$_{60}$BM cells had a structure of ITO/PEDOT:PSS (40 nm)/active layer/Ca (20 nm)/Al (100 nm) (see Figure A.1 in Appendix B). Calcium and aluminum were thermally evaporated in a 10-6 mbar vacuum at rates less than 1 and 4 Å/s, respectively. For PTB7:PC$_{70}$BM devices, the blend (1:1.5; 10 mg/mL) was dissolved by stirring overnight in mixed solvents (97% 1,2-dichlorobenzene and 3% 1,8-diiodooctane) and the active layer was spin-coated at 1000 rpm/60 s. The device structure was the same as P3HT:PC$_{60}$BM cells. A total 96 devices, each with an effective area of 0.1256 cm$^2$, were fabricated on fresh and used ITO substrates. Cells within a comparison set were fabricated on the same day using the same active layer solution.

2.3.3 Characterization of ITO substrates and solar cells

The crystal structure and the elemental composition of ITO were investigated using Siemens D500 x-ray diffractometer and X-ray photoelectron spectroscopy, respectively. The current-voltage characteristics (1 sun) were obtained by using ELH Quartzline halogen lamp. External quantum efficiency was measured using a custom setup built from a single grating monochromator (Horiba Jobin Yvon), 100 W halogen-bulb (OSRAM Bellaphot), and a current pre-amplifier (Ithaco, Inc.). An optical chopper (Thor Labs) coupled with a lock-in amplifier (Stanford Research Systems) were used to reduce noise in the system. Optical absorption/transmission was measured in Varian Cary 5000 UV-Vis-NIR Spectrophotometer. C-AFM measurements were done using Veeco Multimode Nanoscale III, and images were analyzed using Nanotec Electronica WSxM software.\textsuperscript{17}

2.4 Results and Discussions

ITO consists of a matrix of In$_2$O$_3$ and SnO$_2$. As the atomic radii of Sn and In are comparable (0.71 and 0.81 Å, respectively), Sn substitutes In in the ITO matrix.\textsuperscript{18} Thus, by increasing the Sn concentration, ITO lattice constant decreases and its conductivity increases until a point, after which the dopants arrange interstitially and conductivity deteriorates.\textsuperscript{19} Figure 2.1a shows the x-
Figure 2.1 (a) X-ray diffraction spectra showing the position shift of the (222) peak as a function of the age of ITO. (b) XPS binding energy spectra of fresh and used ITOs. And, c) conductivity box plots of more than 30 old ITO substrates of different ages.

Ray diffraction spectra of the fresh, and some old ITO substrates. It is known that PEDOT:PSS etches In$_2$O$_3$ more than SnO$_2$; this increases the relative Sn content on the ITO surface, and reduces the lattice constant of the (222) peak from 10.26 Å in fresh ITO to 10.21 Å, 10.23 Å and 10.19 Å in the one month, six months and one year old ITO (see Figure A.2a in Appendix B), respectively. At 2θ of 35.3° and 37.5°, the In$_2$O$_3$ (400) and (411) peaks seem to increase in old ITO. However, these peaks strongly overlap with the SnO$_2$ (021) and (012) peaks because of the comparable atomic radii of Sn and In, and thus are also indicative of increased Sn content on the surface of old ITOs.

X-ray photoelectron spectroscopy showed that etching by PEDOT:PSS only changes the elemental composition of the top few nm (~ 5 nm) of ITO film. As shown in Table 2.1 and Figure A.2b-d, fresh ITO had higher In content or lower Sn/In ratio at the surface, than one month, six months and one year old ITOs, in agreement with the x-ray diffraction results. However, after 5 min. of Ar ion etching, which etches nearly 5 nm of ITO, elemental composition of fresh ITO was found to be similar to old ITOs (see values in parenthesis in Table 2.1).
Table 2.1  Elemental Composition of the Fresh and Old ITOs before and after Ar Ion Etching, as Measured by XPS.

<table>
<thead>
<tr>
<th></th>
<th>O 1s</th>
<th>In 3d</th>
<th>Sn 3d</th>
<th>Sn/In ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh ITO</td>
<td>64.3</td>
<td>32.3</td>
<td>3.4</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>(53.9)</td>
<td>(43.2)</td>
<td>(2.9)</td>
<td>(0.07)</td>
</tr>
<tr>
<td>One-month ITO</td>
<td>65.4</td>
<td>31.2</td>
<td>3.4</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>(53.5)</td>
<td>(43.8)</td>
<td>(2.7)</td>
<td>(0.06)</td>
</tr>
<tr>
<td>Six-months ITO</td>
<td>69.5</td>
<td>27.0</td>
<td>3.5</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>(53.7)</td>
<td>(43.3)</td>
<td>(3.0)</td>
<td>(0.07)</td>
</tr>
<tr>
<td>One-year ITO</td>
<td>66.1</td>
<td>29.6</td>
<td>4.3</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>(53.9)</td>
<td>(43.1)</td>
<td>(3.0)</td>
<td>(0.07)</td>
</tr>
</tbody>
</table>

The values in ( ) are the atomic concentration of ITO constituents after surface etching.

Figure 2.1b shows the electrical conductivity box plots of fresh and several old ITOs, as measured by the four-point probe method. Overall, old ITOs exhibited lower conductivity, variations being between -10% to +5% with respect to average conductivity of fresh ITO. To investigate morphology and conductivity at nanoscale, we employed conductive atomic force microscopy (c-AFM). Morphology and current maps for fresh and old ITOs of three different ages are shown in Figure 2.2a-h. Root-mean-square surface roughness decreased from 2.20 nm for the new ITO to 1.72, 1.48 and 1.69 nm for the six months, one year and two years old ITOs, respectively. This slight roughness decrease in old ITOs can be due to preferential etching of certain sharp features by PEDOT:PSS. Evidence of etching also appears in grain sizes, which are overall smaller in old ITOs. The c-AFM current maps were measured at an applied bias of +0.5V. Root-mean-square current values of the fresh, six months, one year and two years old ITOs were 846 pA, 227 pA, 359 pA and 77 pA, respectively. It can be noted that among the old ITOs, four-point probe and c-AFM measurements do not show a clear trend with the age of ITO. This can be due to different histories or manufacturing variabilities; manufacturer itself specifies the sheet resistance of these ITOs to be not a precise number, but in a range of 5-15
Figure 2.2 The (a-d) C-AFM height and the (e-h) current map images of the fresh and old ITO substrates. The current distribution images were captured at +0.5 V using a Pt–Ir-coated tip.

Omega/□. Fresh ITO, however, was notably different and more conductive than the old ones. This raises the question: if old ITOs are reused for OPV device fabrication, how do conductivity losses impact device performance?

To investigate this, we first fabricated and characterized poly(3-hexylthiophene-2,5-diyl): [6,6]-phenyl C61 butyric acid methyl ester (P3HT:PC\textsubscript{60}BM) based OPVs on fresh and some old ITO substrates. Figure 2.3a shows representative current-voltage characteristics and Table 2.2 summarizes the performance parameters of these devices under 1 sun illumination. Owing to better fill-factors, P3HT:PC\textsubscript{60}BM OPVs on fresh ITO were slightly more efficient than the ones on old ITOs. Better fill-factors in fresh ITO based devices are ascribed to slightly lower series resistance and higher shunt resistance; the latter also results in a decreased dark current in the reverse bias (J\textsubscript{o}) as shown by dark current-voltage characteristics (Figure 2.3b). Two surprising observations were: (1) Of the three old ITOs used, devices fabricated on the two oldest ones showed higher short-circuit-current (J\textsubscript{SC}) than the fresh ITO based devices; (2) external and normalized quantum efficiency curves for all the old ITO based devices were blue
shifted compared with the fresh ITO based devices (Figure 2.3c and Figure A.3). To understand the reason behind this blue-shift, we measured the transmission of our ITO substrates. Figure 2.3d shows that the old ITOs transmitted more light than fresh ITO in the 350 - 450 nm wavelength range, and transmission peak intensified with the increasing age of ITOs. This explains the quantum efficiency blue-shift and $J_{SC}$ enhancement in the case of old ITO based devices, and demonstrates that the conductivity loss in old ITOs is to some extent offset by the gain in visible-light transmission.

Figure 2.3 Current–voltage characteristics of P3HT:PC$_{60}$BM OPVs (a) under illumination and (b) in the dark. (c) External quantum efficiency of P3HT:PC$_{60}$BM OPVs. Shown current–voltage and quantum efficiency curves were from a single cell on a substrate containing six cells in total. Averages of all cells are presented in Table 2.2. (d) Optical transmission of fresh and old ITO substrates without any device layer.
Table 2.2 Photovoltaic Parameters of P3HT:PC$_{60}$BM and PTB7:PC$_{70}$BM Polymer Solar Cells.

<table>
<thead>
<tr>
<th></th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta_{average}$ ($\eta_{best}$) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PC$_{60}$BM</td>
<td>Fresh ITO</td>
<td>0.59</td>
<td>7.62 ± 0.28</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>1-months-old ITO</td>
<td>0.61</td>
<td>6.98 ± 0.23</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>6-months-old ITO</td>
<td>0.61</td>
<td>7.79 ± 0.14</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>1-year-old ITO</td>
<td>0.60</td>
<td>7.93 ± 0.34</td>
<td>50</td>
</tr>
<tr>
<td>PTB7:PC$_{70}$BM</td>
<td>Fresh ITO</td>
<td>0.70</td>
<td>16.74 ± 0.37</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>1-months-old ITO</td>
<td>0.75</td>
<td>17.16 ± 0.52</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>6-months-old ITO</td>
<td>0.75</td>
<td>17.37 ± 0.37</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>1-year-old ITO</td>
<td>0.75</td>
<td>16.36 ± 0.66</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Fresh ITO</td>
<td>0.73</td>
<td>16.26 ± 0.62</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>30-months-old ITO</td>
<td>0.73</td>
<td>16.61 ± 0.56</td>
<td>64</td>
</tr>
</tbody>
</table>

The transmission spectra of ITOs showed that, in addition to the 350–450 nm wavelength range, old ITOs also transmit more light in wavelengths around 600 nm and above. Old ITO-based P3HT:PC$_{60}$BM devices did not benefit from this higher wavelength transmission enhancement because of low overlap with the P3HT absorption spectrum. However, emerging OPV materials, such as PTB7, do absorb these wavelengths in the red/NIR region; it is an important region where a significant amount of solar flux lies. Therefore, owing to its wide absorption range (400–750 nm), we chose and characterized the PTB7:PC$_{70}$BM system on our fresh and old ITOs. Figure 2.4a shows representative current–voltage characteristics, and Table 2.2 summarizes the performance parameters of PTB7:PC$_{70}$BM devices under 1 sun illumination. The fill factor of old ITO-based devices was similar to that of fresh ITO-based devices, showing that conductivity loss in the top few nanometers of ITO does not affect charge transfer.
Figure 2.4 (a) Current−voltage characteristics of PTB7:PC$_{70}$BM OPV devices under illumination, (b) absorbance of ITO/PEDOT:PSS/PTB7:PC$_{70}$BM structures, and (c) external quantum efficiency of PTB7:PC$_{70}$BM devices. Shown current−voltage and quantum efficiency curves were from a single cell on a substrate containing six cells in total. Averages of all cells are presented in Table 2.2. (d) Current−voltage characteristics of PTB7:PC$_{70}$BM devices on the fresh and oldest ITO tested in this study.

However, results from PTB7:PC$_{70}$BM clearly indicate that the near broadband transmission gain in old ITOs is notably beneficial. Devices based on 1-month-old and 6-month-old ITOs show on average 2.5 and 3.8% higher Jsc, respectively, than fresh ITO-based devices. The absorption spectra (Figure 2.4b) of PTB7:PC$_{70}$BM films showed that, while absorption of
fresh and 1-month-old ITO-based films are similar, films on older ITOs have higher absorption at lower and higher wavelengths, the same regions in which old ITOs transmit more than the fresh ITOs. External and normalized quantum efficiency curves (Figure 2.4c and Figure A.4) of PTB7:PC70BM devices show that the improved transmission of old ITOs notably contributes to photocurrent in these devices. The devices on 6-month-old ITO showed power conversion efficiency as high as 9.24%, which rivals the highest efficiencies in the PTB7:PC70BM system. In another experiment, we also tested an even older ITO, 30-month-old ITO. PTB7:PC70BM devices fabricated on this 30-month-old ITO showed a 2% enhancement in JSC over the fresh ITO-based devices; open-circuit voltage and fill factors were nearly the same (Figure 2.4d and Table 2.2). Considering that 30 months is approaching the current lifetime (3–4 years) of OPVs and that our old ITOs were ambient-stored rather than encapsulated, the prospect of reusing ITO from discarded OPV cells in consumer electronics clearly appears promising.

Lastly, we investigated whether buffer layers other than PEDOT:PSS can have a similar effect on ITO or not. We fabricated and characterized P3HT:PC60BM devices on old ITOs that were previously coated with different buffer layers, such as poly(9,9-bis(6′-(N,N,N-trimethyl)ammonium)hexyl)-2,7-fluorene) (PFN), molybdenum oxide (MoOx), and cesium carbonate (Cs2CO3). PFN and Cs2CO3 are coated on ITO for inverted OPV cells in which ITO acts as a cathode, whereas MoOx is a common anodic buffer layer like PEDOT:PSS. We found that old ITOs with MoOx or PFN history were similar to fresh ITOs in terms of device performance and optical transmission (see panels a and b of Figure A.5). However, Cs2CO3 seems to also etch ITO like PEDOT:PSS, as we noted that devices fabricated on old ITOs with Cs2CO3 history showed (1) slightly higher short-circuit current than the fresh ITO-based devices and (2) slightly higher transmission in blue and associated blue shift in quantum efficiency of the device. In content on the surface was also the least for ITO with Cs2CO3 history (see Table A.1). This apparent etching of ITO must be due to the basic nature of Cs2CO3. Surprisingly, the devices based on old ITOs with PFN history showed a quantum efficiency curve that was red-shifted in comparison to the fresh ITO-based devices (see Figure A.5c); the reason for this is unclear, and further investigation is required.
2.5 Conclusion

In conclusion, we showed that the issue of ITO being etched by PEDOT:PSS is not a serious issue; only a few nanometers of ITO is etched, which does not hinder the charge collection, akin to the charge being easily able to tunnel through very thin insulating cathodic buffer layers, such as alkaline halides. These few nanometers of ITO etching in fact seem advantageous because it increases the ITO optical transmission by $\sim$10\% in the blue/green region and 3\% in the red/NIR region, which, in turn, leads to enhancement in the photocurrent of OPVs (that absorb these wavelengths) fabricated on the reused ITO substrates. Thus, reusing ITO from degraded and discarded OPV cells that include PEDOT:PSS is feasible and potentially impactful for the dollars/watt figure of merit.

2.6 Acknowledgement

This work was supported by the U.S. National Science Foundation (Award CBET 1236839). Moneim Elshobaki thanks the fellowship support from the Egyptian government under Contract GM915. The authors gratefully acknowledge John Carr, Max Noack, and Joydeep Bhattacharya for the fruitful discussions and help with providing old ITO substrates.
2.7 References


CHAPTER 3. SOLIDIFYING SOLUTION-PROCESSED ORGANIC-ELECTRONIC THIN-FILMS IN ELECTRIC-FIELD FOR ANISOTROPIC MORPHOLOGY CONTROL


3.1 Abstract

Tuning morphology in conjugated-polymer based optoelectronic devices has relied on material-specific approaches like annealing and solvent-selection. Here, we introduce a generic technique with anisotropic applicability – exposure to a static electric-field (E-field) gradient during solidification of solution-processed thin-films. This technique improves the connectivity between polymer chains; by changing the E-field direction, radiative pathways in polymeric thin-films can be altered, charge transport in- or out-of-plane can be improved, and phase-separation in polymer-fullerene blends can be coarsened in the bulk and perpendicular to the substrate. In exemplary cases, we improved hole-mobility in organic thin-film-transistors from $7.13 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ for the control to $12.1 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ by applying E-field parallel to the substrate, power conversion efficiency in organic photovoltaics from 3.5% to 4.1% by applying E-field perpendicular to the substrate, and electroluminescence efficiency in organic light-emitting-diodes from $\sim 70$ Cd/m$^2$ to $\sim 178$ Cd/m$^2$ by applying E-field at an angle. Properties were correlated with morphological changes using several characterizations. Simplicity of our technique opens
avenues for tailoring structure and properties across multiple organic-electronic materials and devices.

3.2 Introduction

Photovoltaic, transistor, and light-emitting devices of conjugated-polymers have attracted tremendous interest owing to promises such as light-weight, mechanical flexibility, and scalable fabrication. However, their electrical properties remain inferior to inorganics due to disordered internal nanomorphology, which is intricately linked to chemical structure, molecular weight, and processing conditions. Several morphology-tuning techniques have been reported, mostly from the perspective of photovoltaic device application. These include thermal annealing, solvent annealing, slow growth, and using low-vapor-pressure solvents and solvent mixtures. Typically, these techniques improve polymeric crystallinity, or affect phase separation in donor-acceptor blends, or both. However, these effects are largely isotropic, and their applicability and optimization are material specific; for example, thermal annealing improves structural order in classic polythiophenes, but worsens it in a recent high efficiency polymer system. In this article, we introduce a multifaceted and anisotropic morphology tuning technique for polymer and polymer:fullerene thin-films – exposure to a static electric-field (E-field) gradient as the films solidify from wet state. We show that morphological effects of E-field exposure are different from contemporary techniques, anisotropically dependent on the direction of E-field, and generally applicable across multiple organic materials. E-field, as in electrophoresis, is commonly used for assembling one-dimensional nanostructures and biomolecules. In the organic semiconductor community, E-field has been used to position and orient pentacene single crystals, and align liquid crystals in ternary photovoltaic blends. However, the effects of E-field on the properties of polymer and polymer:fullerene thin-films and devices are not well understood. Thus far, there are only two conflicting reports; one shows that E-field parallel to the substrate improves photovoltaic device performance and perpendicular field has no effect, whereas the second shows that perpendicular field improves the device performance. In this study, we report the effects of static E-field – in horizontal, tilted and vertical directions with respect to the substrate – on several structural, optical, and optoelectronic properties of thin-
films of neat-polymer and polymer:fullerene blends. Photovoltaic, light-emitting and transistor devices with better performance were also realized and characterized in different E-field configurations. Initially, we speculated that the E-field may align polymer chains, similar though not identical to the effect on inorganic nanowires, as morphology in these paracrystalline films is more complex. Using several characterizations, we show that E-field does affect chain orientation, aggregation and connectivity in these thin-films, and notably improves charge transport anisotropically dependent on the direction of E-field. Phase separation is also coarsened in polymer:fullerene blend films due to differential electric forces on polymer and fullerenes. In this study, immediately after spin-coating, while the films were still wet, we exposed them to three exemplary directions (horizontal, tilted and vertical) of E-field around a Van de Graaff generator (Fig. 3.1a). Several characterizations and resultant understanding leads to guiding principles on utilizing E-field to fabricate more efficient photovoltaic cells (OPVs), light-emitting-diodes (OLEDs), and field-effect-transistors (OFETs). The material system investigated was primarily poly(3-hexylthiophene-2, 5-diyl) (P3HT) and blends of P3HT and [6,6]-phenyl-C61-butyric acid methyl ester (PC<sub>60</sub>BM). To probe generality, OPVs of PTB7 and OLEDs of MEH-PPV were also investigated [PTB7: poly(4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl){3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno[3,4-b]thiophenediyl})] [MEH-PPV: poly(2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene)].
Figure 3.1  Photograph of the Van de Graaff generator showing the directions of E-field applied to our films. The effect of E-field on (b-d) P3HT (concentration: 10mg/ml in oDCB) and pure oDCB drops, and (e-g) PC$_{60}$BM drop (concentration: 10mg/ml in oDCB). The normalized steady-state photoluminescence spectra of P3HT thin-films following excitation at 500 nm wavelength for (h) parallel, and (i) perpendicular polarization (insets shows the measurement sample structure and $S_r$ vales). The standard deviations of the Sr values were statistically insignificant. (j) Raman spectra of an exemplary set of P3HT:PC$_{60}$BM films deposited on PEDOT:PSS-coated ITO substrate following laser excitation at 532 nm wavelength (inset shows device structure and the average FWHM values of the C=C peak). (K) UV-Vis absorption of P3HT:PC$_{60}$BM thin-film.
3.3 Results and Discussions

Effect of E-field on photophysical and morphological properties First, to inspect attraction of conjugated polymers and fullerenes to E-field, three droplets were placed near a Van de Graaff generator dome (Fig. 3.1b-g). The control droplet of solvent ortho-dichlorobenzene showed no response. In contrast, P3HT and PC$_{60}$BM dissolved in ortho-dichlorobenzene were pulled towards the dome in $\sim$50 seconds and $\sim$3 seconds, respectively. Quicker response of PC$_{60}$BM can be imputed to its smaller size. To probe the effect of E-field on the photophysics of P3HT thin-films, steady-state photoluminescence (PL) was measured. The PL spectra of P3HT is discerned by 0-0 (wavelength $\sim$620 nm) and 0-1 (wavelength $\sim$720 nm) emission peaks. The ratio between the intensities of these peaks ($S_r = I_{0,0} / I_{0,1}$) designates H- or J-aggregate polymer chain conformation. In H-aggregates, interchain interactions stem from side-by-side stacking of chromophores, suppressing 0-0 transition and $S_r<1$. In J-aggregates, head-to-tail conformation of chromophores promotes a one-dimensional interchain interaction, suppressing 0-1 transition and $S_r>1$. Furthermore, the PL spectra exhibit red (blue) shift in H- (J-) aggregation. We measured the PL of P3HT films in parallel (||) and perpendicular (⊥) polarizations with respect to the incident polarized excitation (Fig. 3.1h and i). In || polarization, relative contribution of the 0-0 peak is lower and PL curves are slightly red-shifted in E-field samples (Fig. 3.1h), revealing $S_r$ ratios of 0.89, 0.81, 0.77, and 0.76 for the control, horizontal, tilted and vertical E-field films, respectively. This shows that E-field increases H-aggregation behavior. In contrast, in ⊥ polarization, the control, horizontal, tilted, and vertical E-field films recorded $S_r$ ratios of 0.71, 0.98, 0.88, and 0.85, respectively (Fig. 3.1i). These ratios for E-field films are even higher than in || polarization, demonstrating less H-aggregation, with horizontal film nearly approaching J-aggregation behavior. Higher ratios are also accompanied by slight blue-shifts. The ⊥ polarization PL results show that in E-field films, the minority J-aggregate chromophores tend to self-assemble orthogonally to H-aggregates, and channeling of photogenerated dipoles to these emissive J-aggregates is strengthened. Regardless of polarization and E-field direction, photogenerated excitons in E-field films decay more radiatively than the control, as evident from higher PL intensities in all E-field films (Fig. B.1a-b). Within
E-field films, consistent anisotropy is revealed in both polarizations with horizontal E-field films showing the least H-aggregate nature, vertical E-field films showing the most, and tilted E-field films being intermediate. To probe molecular order, P3HT:PC_{60}BM thin-films (structure: ITO/ PEDOT:PSS/ P3HT:PC_{60}BM) were examined by Raman spectroscopy. It is known that in Raman spectra, structural ordering narrows the full-width half maximum (FWHM) of the C=C symmetric stretch (peak at $\sim 1450$ cm$^{-1}$). In one of our measurements, FWHM of C=C peak of the horizontal (33.8 cm$^{-1} \pm 0.15$), tilted (32.6 cm$^{-1} \pm 0.08$) and vertical (32.3 cm$^{-1} \pm 0.09$) E-field films were slightly higher than the control (32.1 cm$^{-1} \pm 0.07$) (Fig. 3.1). These differences are insignificant to conclude any difference in molecular order. Repeated measurements also showed fluctuations in trends (Fig. B.2a and b), indicating similar molecular order in all films. This may be expected as all films were dried under petri-dishes and underwent slow self-organization. Equally pronounced peak and vibronic shoulders in the optical absorption curves (Fig. 3.1k) also indicate similar molecular packing. For an unclear reason, the E-field films exhibit slightly reduced optical absorbance compared to the control, in spite of which they show larger background luminescence in the Raman spectra, consistent with the PL measurements (inset of Fig. 3.1k and B.1a-b). Thus, we concluded that E-field does not improve or hamper molecular packing as reflected in Raman and optical absorption spectra. However, PL results show that polymer aggregations and orientations are certainly impacted.

To probe the internal morphology, grazing incidence wide-angle x-ray scattering (GIWAXS) measurements were performed on P3HT and P3HT:PC_{60}BM thin-films. In thin-films, P3HT is known to have edge-on, face-on or mixed conformations depending on processing conditions. In our measurements, film surface was selectively probed using 0.15° incident angle (below the polymer critical angle), and the bulk was probed using 0.2° angle. All P3HT:PC_{60}BM films display out-of-plane (100), (200), and (300) lamellar stacking peaks along $q_y = 0$ Å$^{-1}$ and an in-plane (010) $\pi-\pi$ stacking peak ($q = 1.65$ Å$^{-1}$), indicating edge-on conformation of P3HT (Fig. 3.2a-h). Line-cuts of the (100) peak (0.35 < $q$ < 0.45) showing the intensity versus polar angle in the detector plane, $\chi$, for the 0.15° incident angle case display FWHM of 17.8°, 18.4°, 17.6° and 12° for the control, horizontal, tilted and vertical E-field thin-films, respectively (black bars in Fig. 3.3). Lower FWHM in E-field films indicates increased edge-on conformation and
decreased mosaicity. Vertical E-field films showed most significant reduction in FWHM, together with diminished PC_{60}BM ring for incident angle of 0.15° (red arrow in Fig. 3.2d), implying that vertical E-field depletes PC_{60}BM from the film surface. Higher concentration of PC_{60}BM away from the surface is further corroborated by probing the bulk of the film at the grazing incident angle of 0.2°, at which the vertical E-field film displays the most intense fullerene ring (red arrow in Fig. 3.2h). Given the smaller size, higher mobility and shorter response time of PC_{60}BM in the droplet experiment (Fig. 3.1b-g), it is not surprising that vertical E-field pulls PC_{60}BM down towards the film-substrate interface. In the bulk spectra (Figs. 3.2e-h), At the grazing incident angle of 0.2°, the vertical E-field thin-film exhibits FWHM of 20.1° for the (100) peak, which is significantly lower than the control (25.8°), horizontal (26°) and tilted (25.7°) E-field thin-films (red bars of Fig. 3.3), respectively. GIWAXS data on neat-P3HT films also show that FWHM for (100) peak in E-field films is slightly lower than the control, for both surface and bulk patterns (see Fig. B.3a-h and Fig. 3.3).

Figure 3.2 2D-GIWAXS images of P3HT:PC_{60}BM thin-films at grazing incidence angles of (a-d) 0.15° and (e-h) 0.2°.
Figure 3.3 The FWHM of the line cuts of the (100) peak obtained from the 2D-GIWAXS images of P3HT:PC₆₀BM thin-films at the aforementioned grazing incidence angles.

Kelvin probe force microscopy (KPFM) was employed to image the surface phase distribution in P3HT:PC₆₀BM films. Fig. 3.4a-d show the surface-potential maps, quantitatively depicted by histograms in Fig. B.4. The surface-potential map of the control displays both fine and coarse P3HT and PC₆₀BM domains, in good agreement with the previous work. Horizontal E-field film shows more refined P3HT and PC₆₀BM domains and more relative PC₆₀BM contribution than the control. PC₆₀BM contribution increases further in tilted E-field films showing that PC₆₀BM is partially pulled to the surface. The vertical E-field film is strikingly different from others with negligible PC₆₀BM on the surface, in agreement with the GIWAXS measurements showing diminished PC₆₀BM ring on the surface. It can be speculated from the KPFM images that in conventional OPVs – devices in which cathode is deposited on the top of active-layer – vertical E-field and tilted E-field morphologies lead to the worst and best performances, respectively. That was indeed the case, as discussed shortly.
Figure 3.4 Surface-potential KPFM images (1.5 μm x 1.5 μm) of P3HT:PC_60BM thin-films captured at bias of -0.5 volts in dark. The P3HT-rich and PCBM-rich agglomerations are represented in red and blue colors, respectively.

Effect of E-field on charge transport and device (OFET, OLED, and OPV) characteristics

For nanoscale imaging of charge transport in P3HT thin-films, we performed conductive-atomic force microscopy (c-AFM). The c-AFM roughness maps (Fig. 3.5a-d) of P3HT-only thin-films (structure: ITO/ PEDOT:PSS/ P3HT) reveal RMS roughness of 6.5 nm for the control, which slightly reduces for the horizontal (3.9 nm), tilted (5.7 nm) and vertical (5.1 nm) E-field films. Though the differences are slight, minimum RMS roughness for the horizontal case is also shown by P3HT:PC_{60}BM films (Fig. B.5a-h). The c-AFM current maps (Fig. 3.5e-h) show that the tilted and vertical E-field films exhibited peak currents of 31.9 pA (RMS = 6.39 pA) and 20.1 pA (RMS = 3.61 pA) compared to 13.2 pA (RMS = 1.91 pA) for the control. The horizontal E-field film exhibited minimum peak current of 9.9 pA (RMS = 1.99 pA). Thus, the tilted E-field films show the best charge injection/transport, whereas the horizontal E-field film shows the worst. The worst current-map of the horizontal case correlates with its highest degree of edge-on orientation at the surface (see Fig. 3.3); in this orientation, mediation of alkyl side-chains is expected to prohibit charge injection from the c-AFM tip.

To probe the anisotropic effect of E-field exposure on hole mobility, P3HT-only OFETs (charge transport parallel to substrate) and OPV-type sandwich devices (charge transport perpendicular to substrate) were investigated. Bottom-gate top-electrode P3HT OFETs were fabricated (structure: Fig. 3.6a inset). Horizontal E-field OFETs exhibit highest drain current (I_D) at a given drain voltage (V_D) and gate voltage (V_G) (Fig. B.6b-e). Hole mobility and
threshold voltage ($V_{th}$) were extracted from the transfer characteristics ($I_{DS}$ versus $V_{GS}$) at $V_{DS} = -100$ V (see Fig. B.7). As Fig. 3.6 shows, the control and vertical E-field OFETs have comparable hole-mobilities. Hole mobilities of the horizontal and tilted E-field OFETs are higher. Horizontal E-field devices exhibit the highest mobility, 70% higher than the control. Interestingly, tilted E-field devices showed the lowest $V_{th}$ (Fig. 3.6a inset). This is not surprising since OFETs turn on when holes accumulate at the P3HT-dielectric interface, and this accumulation happens via injection from the top electrode and vertical transport through the film. In this regard, tilted E-field films are the most effective as shown by c-AFM maps. Hole mobility was also probed in P3HT hole-only devices using the space-charge-limited-current (SCLC) model; hole mobility was extracted from the SCLC region\textsuperscript{34} of the dark-current versus voltage curves (Figs. 3.6b and B.8a). Affirming the c-AFM current maps and $V_{th}$ in OFETs, tilted E-field devices show the highest hole mobility, 144% higher than the control. Hole mobilities of horizontal and vertical E-field devices are also higher than the control by 98% and 36%, respectively.
Figure 3.6  (a) Hole-mobility of P3HT OFETs as calculated from the straight-line fitting of $I_{DS}$-$V_{GS}$ transfer characteristics at $V_{DS} = -100$ volts (see supplementary information Fig. B.6b-e, Fig. B.7 and Table B.1). The inset shows the threshold voltages and device structure of OFETs. (b) Hole-mobility obtained from straight-line fitting of SCLC regime of the dark current-voltage curves of P3HT hole-only diodes. Inset shows the device structure.
Although P3HT is not a promising material for OLEDs, we also investigated its electroluminescence properties to see if enhanced charge transport in select E-field films translates to more efficient OLEDs. We observed that all E-field films show higher current-density, higher electroluminescence intensity, and lower turn-on voltage than the control (Fig. B.9a and 3.7a).
We also fabricated OLEDs from a popular OLED material MEH-PPV; all E-field devices show higher electroluminescence efficiency than the control (Figs. 3.7b and B.9b-c). Tilted E-field are the most efficient showing electroluminescence efficiency of ≈ 420 Cd/A, which is 460% higher than the control (≈70 Cd/A) (see Fig. B.9c). It can be noted that there are some differences in trends between P3HT and MEH-PPV OLEDs, and between the OLED and charge-transport characteristics. These differences are not fully understood, though not surprising because OLED functionality not only depends on carrier transport, but also factors such as carrier recombination. A noteworthy similarity across the two materials is that the trend of SCLC hole mobilities in P3HT (Fig. 3.6b) is same as the trend of electroluminescence efficiencies in MEH-PPV (Fig. B.9c).

We also measured hole mobilities in P3HT:PC$_{60}$BM devices using two methods: SCLC, and photo-CELIV (CELIV: photogeneration and charge extraction with linearly increasing voltage ramp). SCLC hole mobility was $8.93 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ in the control hole-only diode (Fig. 3.8a and Fig. B.8b); it increases by 117%, 106% and 76% for the horizontal, tilted and vertical E-field devices, respectively. Consistency between P3HT and P3HT:PC$_{60}$BM SCLC hole mobility results is that the control shows the least mobility, and among E-field devices, horizontal and tilted E-field devices exhibit higher mobility than the vertical. However, whereas tilted E-field device records the highest mobility in the P3HT-only devices, horizontal E-field device is marginally higher than the tilted in P3HT:PC$_{60}$BM. We expected this deviation could be due to differences in phase separation in P3HT:PC$_{60}$BM films. To probe the phase separation in the bulk of the films, PL lifetimes were measured using time-correlated single-photon counting technique.$^{35}$ All films exhibit a bi-exponential decay with two time-constants, in agreement with previous work (Fig. 3.8b).$^{36}$ Higher time-constants imply more polymer-fullerene demixing. All E-field films show slight (tilted E-field film) to large (vertical E-field film) increase in polymer-fullerene demixing. Vertical E-field films display maximum demixing as also evident from GIWAXS and KPFM data. Demixing in the horizontal E-field film is higher than the tilted case, implying larger P3HT domains. This can explain higher hole-mobility in the horizontal E-field P3HT:PC$_{60}$BM films, contrary to the tilted case being better for P3HT-only films.
Figure 3.8  (a) Hole-mobility of P3HT:PC$_{60}$BM thin-films obtained from straight-line fitting of SCLC regime of the dark current-voltage P3HT:PC$_{60}$BM hole-only diodes. Inset shows the device structure. (b) PL lifetime plots of P3HT:PC$_{60}$BM thin-films. Inset displays the bi-exponential decay lifetimes and device structure. (c) Photo-CELIV hole-mobility data of P3HT:PC$_{60}$BM devices as a function of the delay time.
Using Photo-CELIV method, hole-mobility in P3HT:PC_{60}BM devices was measured for delay times (t_{delay}) of 0.25 µs – 500 µs (Fig. 3.8c). Increase in hole-mobilities at higher t_{delay} is attributed to decreased maximum time (t_{max}) and current change (ΔJ).\(^{37}\) Photo-CELIV measurements agreed with the SCLC measurements to the extent that at least one of the E-field devices always exhibits a higher mobility compared with the control. Up to t_{delay} of 10.3 µs, the horizontal E-field device displays the highest mobility as in the case of SCLC method. At t_{delay} > 10.3 µs, either the tilted or the vertical E-field devices show similar or better carrier mobility than the horizontal case and all are still better than the control. Hole-mobility values for all structures studied are also statistically tabulated in table B.1. On the mechanism behind improvements in charge-transport, we claim that since crystallinity of control and E-field films is nearly similar as shown by UV-Vis absorption and Raman spectra, improved charge transport in E-field films must be due to change in orientation of and connectivity between aggregates and individual chains in these paracrystalline films. Our results offer strong indirect evidence of this; direct visual evidence of partial orientation of chains in these films is beyond the resolution of even the most sophisticated imaging techniques employed in the organics community.\(^{38}\)

The photovoltaic characteristics of P3HT:PC_{60}BM OPVs were examined (Fig. 3.9a). Over eight batches, devices were highly reproducible and tilted OPVs exhibit PCE comparable or higher than the control (Table 3.1). The horizontal E-field devices exhibit short-circuit current density (J_{SC}) ~13% lower than the control, which can be ascribed to larger polymer aggregates as indicated by PL lifetimes (Fig. 3.8b). Vertical E-field OPVs have poorest performance, which strongly correlates to highest P3HT:PC_{60}BM de-mixing and migration of the PCBM toward ITO, as shown by GIWAXS, KPFM, and PL lifetimes results. Other electrical signatures of demixing and poor vertical phase separation in the vertical E-field OPVs are increased series resistance (~3 kΩ), slope (~2) of the open-circuit-voltage versus light intensity curve, poor (~2) diode ideality factor, and increased saturation current in reverse bias (Table 3.1 and Fig. B.10a and b). Inverted P3HT:PC_{60}BM OPVs show the same general trend. Tilted E-field OPVs record an average PCE of 2.79%, which is 5% better than the control (Fig. 3.9b and Table 3.1). Similar to conventional OPVs, horizontal E-field devices are worse than the control. Vertical E-field device, though poorest, are not as poor as in the case of conventional devices because
PCBM segregation in inverted OPVs is towards the desirable electrode (cathode). Based on these results, we hypothesized that if polymer-fullerene demixing can be limited, vertical E-field can be utilized to achieve desirable vertical phase separation, that is, more fullerenes near the cathode, and more polymer near the anode. In an attempt to do so, we fabricated inverted devices in which the active-layer was exposed to vertical E-field for a short time (90 seconds was chosen as an exemplary short time). The series resistance decreases in this vertical E-field device from 161 $\Omega$ (control) to 59 $\Omega$, enhancing $J_{SC}$ and fill factor by $\sim$9% and $\sim$5%, respectively. This indeed results in 4.1% efficient OPVs, which are 17% better than the control (Fig. 3.9c and Table 3.1). 4.1% efficiency is impressive considering that these inverted OPVs were fabricated in air. Finally, we explored the generality of the effects of E-field exposure by fabricating PTB7:PC$_{70}$BM OPVs. These devices also show the same trend as P3HT-based devices (Fig. B.10c); this demonstrates that the effects of different directions of E-field translate across different material systems.
Figure 3.9  Effect of E-field on the photovoltaic characteristics of P3HT:PC_{60}BM OPVs. Current-density versus voltage curves under AM 1.5 G illumination at 100 mW cm\(^{-2}\) of (a) conventional, (b) inverted, and (c) inverted vertical E-field (E-field applied for duration of 90 s) P3HT:PC_{60}BM OPVs.
Table 3.1  Effect of E-field on the open-circuit-voltage ($V_{OC}$), current-density ($J_{SC}$), fill factor (FF), power conversion efficiency (PCE) and series resistance ($R_S$) of air-processed conventional and inverted P3HT:PC$_{60}$BM OPVs under AM 1.5 G illumination.

<table>
<thead>
<tr>
<th></th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE(%)</th>
<th>$R_S$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conventional</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>0.59</td>
<td>8.46 ± 0.2</td>
<td>59</td>
<td>2.91 ± 0.1</td>
<td>87</td>
</tr>
<tr>
<td>Horizontal</td>
<td>0.59</td>
<td>7.32 ± 0.3</td>
<td>58</td>
<td>2.91 ± 0.1</td>
<td>93</td>
</tr>
<tr>
<td>Tilted</td>
<td>0.59</td>
<td>8.40 ± 0.4</td>
<td>60</td>
<td>2.95 ± 0.2</td>
<td>89</td>
</tr>
<tr>
<td>Vertical</td>
<td>0.18</td>
<td>0.14 ± 0.0</td>
<td>32</td>
<td>0.01 ± 0.0</td>
<td>3828</td>
</tr>
<tr>
<td><strong>Inverted</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>0.55</td>
<td>9.94 ± 0.4</td>
<td>50</td>
<td>2.73 ± 0.2</td>
<td>121</td>
</tr>
<tr>
<td>Horizontal</td>
<td>0.53</td>
<td>8.25 ± 0.8</td>
<td>54</td>
<td>2.35 ± 0.3</td>
<td>98</td>
</tr>
<tr>
<td>Tilted</td>
<td>0.56</td>
<td>9.75 ± 0.2</td>
<td>51</td>
<td>2.79 ± 0.2</td>
<td>127</td>
</tr>
<tr>
<td>Vertical</td>
<td>0.41</td>
<td>4.51 ± 0.3</td>
<td>50</td>
<td>0.93 ± 0.1</td>
<td>130</td>
</tr>
<tr>
<td>Control</td>
<td>0.60</td>
<td>10.48 ± 0.0</td>
<td>56</td>
<td>3.5 ± 0.0</td>
<td>161</td>
</tr>
<tr>
<td>Vertical*</td>
<td>0.60</td>
<td>11.51 ± 0.4</td>
<td>59</td>
<td>4.1 ± 0.4</td>
<td>59</td>
</tr>
</tbody>
</table>

* This inverted device was exposed to E-field for 90 s.
3.4 Conclusion

In summary, we applied static E-field on solution-processed conjugated-polymer based thin-films and devices. We initially observed that pure solvent drop shows no response to E-field, whereas P3HT and PC$_{60}$BM solutions move in response to it. Though molecular packing in P3HT is not affected by E-field as shown by Raman and UV-Vis absorption spectra, E-field films show reduced mosaicity and increased edge-on orientation as shown by GIWAXS, and more aggregations, chain-connectivity and radiative-pathways as shown by steady-state PL results. In polymer-fullerene blend films, fullerenes can be pulled through the polymer phase to the surface or the substrate depending on the direction of E-field, which can be used to fabricate efficient conventional or inverted OPVs. Hole transport is also significantly enhanced by E-field exposure, with anisotropic dependence on E-field direction; this translates to applicability in more efficient OLEDs and OFETs.

3.5 Acknowledgement

Moneim Elshobaki thanks the fellowship support from the Egyptian government, under the contract No. GM915. This work was supported by National Science Foundation (Award # CBET – 1236839). The work at the Ames Laboratory was supported by the Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-07CH11358. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357.
3.6 References


CHAPTER 4. MICROLENS ARRAY INDUCED LIGHT ABSORPTION ENHANCEMENT IN POLYMER SOLAR CELLS


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4.1 Abstract

Over the last decade, polymer solar cells (PSCs) have attracted a lot of attention and highest power conversion efficiencies (PCE) are now close to 10%. Here we employ an optical structure – the microlens array (MLA) – to increase light absorption inside the active layer, and PCE of PSCs increased even for optimized devices. Normal incident light rays are refracted at the MLA and travel longer optical paths inside the active layers. Two PSC systems – poly(3-hexylthiophene-2,5-diyl):(6,6)-phenyl C61 butyric acid methyl ester (P3HT:PC\textsubscript{60}BM) and poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]:(6,6)-phenyl C71 butyric acid methyl ester (PCDTBT:PC\textsubscript{70}BM) – were investigated. In the P3HT:PCBM system, MLA increased the absorption, absolute external quantum efficiency, and the PCE of an optimized device by \(\sim 4.3\%\). In the PCDTBT:PC\textsubscript{70}BM system, MLA increased the absorption, absolute external quantum efficiency, and PCE by more than 10\%. In addition, simulations incorporating optical parameters of all structural layers were performed and they support the enhancement of absorption in the active layer with the assistance of MLA. Our results show that utilizing MLA is an effective strategy to further increase light absorption in PSCs, in which optical losses account for \(\sim 40\%\) of total losses.

\(^1\)Moneim Elshobaki equally contributed to this work.
MLA also does not pose materials processing challenges to the active layers since it is on the other side of the transparent substrate.

4.2 Introduction

In this era of depleting fossil-fuel based energy sources, and their environmental impact, focus on renewable energy sources is becoming increasingly important. Direct conversion of solar energy to electricity is very attractive due to the abundance of solar energy resource, which dwarfs all other energy resources combined. Within the solar cell community, polymer-based solar cells (PSCs) have received heightened attention due to advantages such as flexibility, potentially low cost production, light weight and easy integrability into building products, clothes and fabrics. PSCs have been making rapid progress in research and development in academia and industry; maximum power conversion efficiencies (PCE) have increased from around 2% to 10% in the last decade.\(^1\),\(^2\) This progress is owing to the development of new materials, and novel device structures and processing conditions. So far, the majority of studies on PSCs have focused on the development of new materials,\(^3\)–\(^5\) interlayers,\(^6\)–\(^8\) and morphology optimization.\(^9\)–\(^13\)

Another important way to enhance the PCE of PSCs is by increasing light absorption inside the active layers using various optical approaches. Enhancing light absorption is important because active layers in PSCs are quite thin, which leads to optical losses accounting for ~40% of total losses.\(^14\) In true bilayer donor–acceptor heterostructures, active layers can only be ~10 nm thick due to short exciton diffusion lengths (around 5–10 nm\(^15\)). On the other hand, in bulk-heterojunction structures, in which the donors and acceptors are intimately mixed together in a single layer, higher thickness can be afforded. However, such thicknesses (~100–200 nm, at times less) are still not enough to efficiently absorb light, and thicknesses cannot be indiscriminately increased further because of low charge carrier mobilities in most organic materials. Hence, to boost efficiencies further, it is imperative to improve light absorption within existing PSC architectures.

Some optical approaches enabling light trapping in PSCs have been proposed and implemented. These include approaches like textured substrates,\(^16\) wrinkles and deep folds,\(^17\) metal nanospheres,\(^18\)–\(^19\) and microlens arrays.\(^20\) However, these methods suffer from one or more weak-
nesses. In the case of textured substrates, topographical dimensions of textures (gratings) need to be designed optimally to enable a conformal coating of active layers. High aspect-ratio gratings can result in shunts between top and bottom electrodes, underfilling, and air gaps inside active layer film.\textsuperscript{16} Whereas, narrow pitch gratings lead to overfilling of trenches and increased losses from carrier recombination.\textsuperscript{16} Another challenge is that for different polymer systems with different optimum active-layer thicknesses, grating dimensions need to be redesigned and retested for conformal polymer coating. The approach of utilizing substrates with wrinkles and deep fold features suffers from similar issues. Besides, it is challenging to have a quantitative and precise control on the dimensions of self-assembled wrinkles and folds. Utilizing metal nanospheres inside active layers employs plasmonic near-field enhancement effects to trap more light. However, this approach also has drawbacks such as inclusion of metallic and surface group impurities, which could act as recombination centers and degrade charge transport.

Utilizing a microlens array (MLA), as an additional structure on the side of the transparent substrate opposite to the active-layer, is another approach to increase light absorption inside the active layer of PSCs. Since MLA is located on the other side of the substrate, this approach is non-intrusive in nature, and has no effect on the device fabrication processing or internal morphology of the active-layer. It has also been demonstrated as a universal method of light absorption enhancement in different organic photovoltaic systems.\textsuperscript{20} In this previous demonstration, MLA consisted of hemispherical microlenses with a diameter of 100 $\mu$m. These 100 $\mu$m microlenses reduce surface-reflection, and refract the incoming light towards the active layer, thus increasing the optical path. In this study, we utilized the near-hemispherical microlenses of 2 $\mu$m diameter. With a sharper peak, the near hemispherical shape is better than a pure-hemispherical shape towards refracting incoming light. These microlenses, with diameter close to visible light wavelength, not only reduce surface reflection and refract incoming light like 100 $\mu$m microlenses, but also utilize optical interference to enhance light intensity inside the active layer. Even though 100 $\mu$m MLAs act as gratings, the diffraction angles are small, which makes the diffraction small and hard to observe. However 2 $\mu$m MLAs have a period closer to visible light wavelength, which makes the diffractive angles larger than that of 100 nm MLAs. Thus we expected that the more diffractive nature of the 2 $\mu$m period compared to the 100 $\mu$m period
will make the light enhancement in 2 μm MLAs higher. This is indicated by simulations on MLAs with diameters of 2 μm and 6 μm. Since 6 μm is much larger than visible light wavelength (short wavelength limit), light absorption in the PSCs can be studied with geometrical optics, or ray optics, where optical effects such as diffraction and interference are not accounted for (the diffraction effect is very small as discussed above). In this short wavelength limit, the 6 μm and 100 μm MLAs yield the same light absorption enhancement. We show these simulation results in the simulation section of this paper. We fabricated two types of PSCs on our MLA substrates and compared their performance with devices without MLA. Performance enhancement in MLA devices is demonstrated in the following sections through different characterizations and discussion.

4.3 Methods and Experimental Details

4.3.1 Microlens array

The MLA is composed of arrays of microlenses as shown in Fig. 4.1 and see Fig. in appendix C. Microlenses were near-hemispherical with a diameter of 2 μm, and they sit on the side of a glass substrate facing the incident light. The array is fabricated by imprinting a polydimethylsiloxane (PDMS) mold on a UV curable polyurethane (PU) drop placed on the glass. More details about fabrication of MLA on glass are described elsewhere.  

![Figure 4.1 SEM image of the PU layer with the MLA pattern.](image)
4.3.2 P3HT:PCBM PSC and PCDTBT:PBM PSC systems

P3HT (Solarmer Inc.) and PCBM (Nano-C Inc.) were dissolved in 1,2-dichlorobenzene (o-DCB) with 20 mg ml\(^{-1}\) concentration for each and stirred at 800 rpm on a hot plate at a temperature of 45 °C for around 20 hours to make active layer solution. Indium Tin Oxide (ITO) coated glass (Delta Technologies) and ITO coated glass with the MLA pattern were ultrasonicated in 2-propanol/acetone, and de-ionized water, respectively, for 2 minutes. Then both substrates were dried with nitrogen and exposed to air plasma for 1 minute. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin-coated on the ITO side of the glasses at 3000 rpm for 60 s. Spin-coated devices were annealed on a hot plate at 100 °C for 10 minutes. Both substrates were then transferred inside a glovebox filled with nitrogen. The previously prepared active layer solution was filtered through a 0.2 \(\mu\)m filter. Filtered solution was dropped on the PEDOT:PSS film devices and spun at the speed of 500 rpm for 45 seconds, to yield an active layer thickness of around 200 nm. After spin-coating, devices were covered under separate petri dishes for 1 hour. This amount of time is long enough to dry the active layer and its color changes from orange to dark purple. Devices were then taken out from petri dishes and annealed on a hot plate at 110 °C for 10 minutes. After annealing, devices were transferred to a thermal evaporator with loaded calcium (Ca) and aluminum (Al) sources. Under a vacuum level of around 10\(^{-6}\) mbar, 25 nm of Ca was evaporated on the active layer, followed by 100 nm of Al layer. Following the same fabrication process, six cells were fabricated in one batch. In total, two batches were fabricated.

PCDTBT of molecular weight 50 kDa was purchased from 1-material. MoO\(_X\) (99.99%), LiF (99.98%) and PC\(_{70}\)BM were purchased from Sigma Aldrich. For the PCDTBT:PC\(_{70}\)BM system, 10 nm of MoO\(_X\) anode buffer layer was thermally evaporated on ITO under a vacuum of about 10\(^{-6}\) mbar at a rate 0.5 Å s\(^{-1}\). A solution of PCDTBT and PC\(_{70}\)BM (weight ratio 1:3.5), with a concentration of 7 mg mL\(^{-1}\) in o-DCB was kept stirring on a hot plate at 90 °C and 650 rpm for eight hours. After that, the temperature of the solution was reduced to 60 °C at the same stirring speed. After several days, the active layer was spin coated on the top of the MoO\(_X\) layer at 2000 rpm for 45 seconds. The devices were dried under petri dish for 20 min,
and then annealed for 15 min on a hot plate at 70 °C. Finally, LiF (2 nm) and Al (130 nm) were thermally evaporated over the active layer with a shadow mask of area 0.1256 cm² with an evaporation rate of less than 0.5 and 8 Å s⁻¹, respectively. Following the same fabrication process, six cells were fabricated in one batch, and a total of three batches were fabricated.

4.3.3 Characterization

Several characterizations were carried out as described below. Current–voltage characterization was done using the ELH Quartzline halogen lamp at 1 sun intensity, which was calibrated using a reference crystalline Si solar cell coupled with a KG-5 filter. Absolute external quantum efficiency (EQE) was determined using a custom setup built from a single grating monochromator (Horiba Jobin Yvon Srl), 100 W halogen bulb (OSRAM Bellaphot), and a current preamplifier (Ithaco, Inc.). An optical chopper (Thor Labs) coupled with a lock-in amplifier (Stanford Research Systems) were also used to reduce noise in the system. EQE was carried out at room temperature in the presence of ambient light. For absorption characterization, ITO coated glasses were deposited with PEDOT:PSS (for the P3HT system) or MoOₓ (for the PCDTBT system) and an active layer following the fabrication process in the previous sections. Then these active-layer coated substrates were optically characterized using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Global reflection and global transmission were obtained from the spectrophotometer. Then absorption was calculated using 100% subtracting global reflection and global transmission.

4.4 Results and Discussion

We chose to investigate the P3HT:PCBM system because it is the most widely investigated system in the field of PSCs. Even though new promising materials have emerged recently, P3HT:PCBM systems remain relevant for one of the sub-cells in tandem structures. Illustrated in Fig. 4.2(a) is a conventional P3HT:PCBM device, which is our control device in this study. The corresponding P3HT:PCBM device with an additional layer of MLA on one side of glass (called the MLA device) is schematically shown in Fig. 4.2(b). The performance parameters of current–voltage characterization of the two devices are listed in Table 4.1. The performance
Figure 4.2  Schematic structures of different PSC systems: P3HT:PCBM system (a) without MLA and (b) with MLA; PCDTBT:PC_{70}BM system (c) without MLA and (d) with MLA.

Parameters of each device in the table are averaged from six cells in one batch. Since the devices were fabricated under optimized conditions from our experience and through the literature, it can be observed that even the control device has a quite high PCE of around 4.69%, one of the highest among P3HT:PCBM devices in the literature. The performance of the MLA device increases by 4.3% to 4.89%. This improvement is due to enhancement of current density ($J_{SC}$), which increases from 11.78 mA cm$^{-2}$ in the control device to 12.19 mA cm$^{-2}$ in the MLA device. The performance enhancement in percentage is not as high in our case as in the previous P3HT:PCBM study with 100 μm microlenses. However, it should be noted that our fabrication conditions are more optimized, and even our control P3HT:PCBM device performs better than the MLA P3HT:PCBM device in that study.

In Fig. 4.3(a), the MLA device shows higher absolute EQE than the control device in the wavelength between 400 nm to 800 nm. From a quantitative view of this enhancement as in Fig. 4.3(c), the enhancement from the MLA reaches up to 5% in the shorter wavelength range below 600 nm, while in the wavelength range above 600 nm the enhancement can be as
high as 20%. Since the MLA layer is on the separate side of the glass substrate from device structure, the microlenses do not affect the process of exciton diffusion/dissociation, charge transport and collection. However, the MLA layer can change the direction and distribution of incoming light in the active layer. Incoming light beams get refracted through MLA and have longer optical paths compared to those without MLA. Longer paths give light more chance to be absorbed inside the active layer. Besides, light beams, which get reflected on one microlens would encounter another neighboring microlens and get refracted into the active layer, thus reducing surface reflection. At the same time, a close-packed MLA with diameter 2 μm close to visible light wavelength acts as a structured grating to produce a diffraction pattern inside the active layer. This diffraction would enhance light intensity inside the active layer, contributing to more exciton creation and hence charge carriers. The light absorption spectra inside the active layer of P3HT:PCBM devices are measured and depicted in Fig. 4.3(b). As shown in Fig. 4.3(c), between wavelengths 400 nm and 650 nm, MLA leads to broadband enhancement of light absorption inside the active layer, with the highest enhancement up to 10%. In the wavelength range between 650 nm and 780 nm, there is reduction in light absorption in the MLA device compared to the control device. It may be caused by light interference in this wavelength region, which reduces light intensity inside the active layer. However the light absorption in this range is far smaller than that below 650 nm. This little reduction of light absorption does not significantly change the total light absorption enhancement. Thus, it can be seen that by simply adding a MLA layer on the glass substrate, the P3HT:PCBM device gets more light absorption in the active layer, leading to higher current density and PCE.

Table 4.1 Parameters of current–voltage characterization of two PSC systems with and without 2 μm MLA

<table>
<thead>
<tr>
<th></th>
<th>P3HT:PCBM</th>
<th></th>
<th>PCDTBT: PC70BM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J&lt;sub&gt;SC&lt;/sub&gt;</td>
<td>PCE</td>
<td>V&lt;sub&gt;OC&lt;/sub&gt;</td>
</tr>
<tr>
<td>Control</td>
<td>mA cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>%</td>
<td>V</td>
</tr>
<tr>
<td>MLA</td>
<td>12.29</td>
<td>4.89</td>
<td>0.60</td>
</tr>
<tr>
<td>Enhancement %</td>
<td>4.3</td>
<td>4.3</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 4.3  (a) Absolute EQE of P3HT:PCBM and PCDTBT:PC$_{70}$BM devices without (control) and with (MLA) MLA. (b) Absorption of P3HT:PCBM and PCDTBT:PC$_{70}$BM devices without (control) and with (MLA) MLA. (c) Absolute EQE ratio of MLA device to control device (black color); absorption ratio of MLA device to control device (red color).

In PCDTBT:PC$_{70}$BM devices, with similar structure and same function of MLA in PSC devices, we expected that the light absorption, absolute EQE and the current density will also increase. In fact, we expected higher enhancement because PCDTBT:PC$_{70}$BM active layers are only 70 nm thick in optimized devices.\textsuperscript{22} In order to verify our hypothesis, the similar characterization of the PCDTBT:PC$_{70}$BM system as the P3HT:PCBM system was carried out. From Table 4.1 it is clear that the short circuit current density is enhanced by 10.7\%, and PCE is increased from 5.6\% to 6.4\%. The spectra of the absolute EQE in Fig. 4.3(a) also clearly show an enhancement in the case of the MLA device, supporting the current density enhancement. In the wavelength region between 450 nm to 800 nm, the enhancement of EQE is slightly larger than 10\% as seen in Fig. 4.3(c). The light absorption spectra, shown in Fig.
4.3(b) also support our expectation about the effect of the MLA. The light absorption inside the active layer is enhanced from MLA in the entire region between 400 nm and 700 nm, except for a little reduction between 700 nm and 800 nm. As seen in Fig. 4.3(c), between 400 nm and 550 nm, the enhancement falls below 10%. The enhancement between 550 nm and 650 nm becomes higher than 10% and reaches a maximum of 26% at 625 nm.

The existence of the diffraction effect from MLA is demonstrated in Fig. 4.4. The measurement was carried out on a surface. On the surface there was a hole, which was larger than PSC devices. One halogen lamp was put just under the hole at some distance so that light can shine through the hole. Three devices with a P3HT:PCBM active layer: control device, MLA device, and ITO coated glass with MLA were put above the hole in turn experiencing the same light conditions. Then optical photos were taken from above the devices using a digital camera with the same setup. The control device, which has no MLA layer, shows conformal light mapping as seen in Fig. 4.4(a). However, Fig. 4.4(b) and (c) show diffraction patterns in a device with MLA and glass with MLA, respectively. Microlenses behave like small diffraction gratings on the micrometer scale, which generate colourful mapping from the visible light. Thus the combination of hundreds of small diffraction gratings obviously forms diffraction and interference patterns inside the active layer as well, thus further increasing the effective optical path. The enhanced light intensity contributes to more exciton creation and charge carriers inside the active layer. The above colourful mappings on the surface are for substrates with 2 μm MLA, obviously showing the diffraction effect. However the substrate with 100 μm MLA did not show the colourful mapping on the device surface (not shown here in this paper). Even though 100 μm MLA is a periodical grating structure, the diffractive angle is very small since the period is far larger than visible wavelength. So there is barely any diffraction effect observed in 100 μm MLA devices. With the MLA grating period reduced to 2 μm, the diffractive angle increases and shows a diffraction effect as seen in the colourful mapping. Thus, the 2 μm MLA enhances more light absorption than the 100 μm MLA.

In summary, MLA brings enhancement in these two PSC systems. Because the thickness of the active layer in P3HT:PCBM (around 200 nm) is far larger than that in PCDTBT:PC70BM (around 70 nm), the light absorption in the first system is already high enough while the light
Figure 4.4 Optical photos taken above devices with light of halogen lamp shining through devices from the bottom. (a) Control device without MLA, (b) MLA device with MLA, and (c) ITO coated glass with MLA.

Absorption in the second system is lower. So the light absorption enhancement effect of the MLA in the second system is more prominent than that in the first system. This indicates that MLA is an effective way to enhance light absorption in PSC systems, especially when light absorption in the original device is not very high.

Simulation

Light absorption simulation is done for both PSC systems with both control and MLA devices as shown in Fig. 4.5(a). The simulation of these devices is based on the structures in Fig. 4.2. The planewave-based transfer matrix method is applied as a full-field electromagnetic approach to obtain the absorption spectrum. In the simulation, the wavelength range is restricted to 400 nm to 800 nm to match the solar spectrum and the two PSC systems' absorption. Optical parameters such as refractive indices n and the extinction coefficients k are obtained from the literature. Fig. 4.5(a) shows the simulated absorption for both PSC systems with control and MLA devices, revealing the higher absorption in MLA devices than that in control devices. In the wavelength range between 400 nm and 650 nm, where most of the light was absorbed for P3HT devices, the light absorption in the MLA device shows enhancement as large as 10% around 400 nm and 570 nm, with an average improvement of around 4% compared to the control device. The simulated light absorption of PCDTBT devices experiences average of 9% enhancement in the MLA device than the control device between light wavelength of 400 nm and 650 nm. In order to confirm our expectation of higher light absorption with 2 μm MLA than that with 100 μm MLA, simulation with both 2 μm MLA and 6 μm MLA is employed and shown in Fig. 4.5(b). MLA with diameter 6 μm is far larger than visible light wavelength,
Figure 4.5 (a) Simulation of light absorption inside active layers of P3HT:PCBM and PCDTBT:PC$_{70}$BM devices without (control) and with (MLA) MLA. (b) Absorption simulation spectra of PCDTBT:PC$_{70}$BM devices with MLA of diameters 2 μm and 6 μm.

which only plays a ray optic effect to increase the light optical path inside the active layer, similar to MLA with diameter 100 μm. Below 600 nm, the absorption spectra show an average of 4% higher absorption in 2 μm MLA than in the case of 6 μm MLA, where most of light absorption happens. From these simulations, we can more confidently say that employing 2 μm microlens arrays is a more effective way to enhance the performance of PSCs, than MLAs with much greater dimensions. Of course, 2 μm might not be the most optimal dimension and in the vicinity of these dimensions, there might be one that can perform better. That exploration is a part of our current and future studies.

4.5 Conclusion

In this work, two types of PSC systems: P3HT:PCBM and PCDTBT:PC$_{70}$BM are investigated with a 2 μm microlens array on one side of the glass substrate. Devices with MLA have a better performance than that without MLA. In the P3HT:PCBM system, MLA increases the absorption, absolute external quantum efficiency, and PCE by 4.3%, even for a conventional device with fabrication conditions optimized for high efficiency. In the PCDTBT:PC$_{70}$BM system, MLA increases the absorption, EQE and PCE by more than 10%. All of these enhancements are due to the increased light path and absorption inside the active layer from refracted light
through the microlens as well as diffraction induced light intensity enhancement. This improvement of light absorption is further supported by simulations in the two PSC systems. Our MLA approach is more effective in devices with a thinner active layer than that with a thicker active layer. MLAs also do not pose materials processing challenges to the active-layers since they are on the other side of the transparent substrate.

4.6 Acknowledgements

SC acknowledges National Science Foundation for financial support (Award # CBET – 1236839). Y. Chen thanks financial assistance from Chinese Scholarship Council (CSC). M. Elshobaki thanks financial support from the Egyptian Government.
4.7 References


CHAPTER 5. REDUCING OPTICAL LOSSES IN ORGANIC SOLAR
CELLS USING MICROLENS ARRAYS: THEORETICAL AND
EXPERIMENTAL INVESTIGATION OF MICROLENS DIMENSIONS


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5.1 Abstract

The performance of organic photovoltaic devices is improving steadily and efficiencies have now exceeded 10%. However, the incident solar spectrum still largely remains poorly absorbed. To reduce optical losses, we employed a microlens array (MLA) layer on the side of the glass substrate facing the incident light; this approach does not interfere with the processing of the active-layer. We observed up to 10% enhancement in the short circuit current of poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b0]-dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}):(6,6)-phenyl C71- butyric acid methyl ester (PTB7:PC71BM) OPV cells. Theoretically and experimentally investigating several MLA dimensions, we found that photocurrent increases with the ratio of the height to the pitch size of MLA. Simulations reveal the enhancement mechanisms: MLA focuses light, and also increases the light path within the active-layer by diffraction. Photocurrent enhancements increase for a polymer system with thinner active-layers, as demonstrated in PCDTBT:PC71BM OPVs with 17% improvement in short circuit current.

1Moneim Elshobaki equally contributed to this work.
5.2 Introduction

Solar-electric conversion using organic semiconductors has been a very active research area within the photovoltaic community. Organic photovoltaics (OPVs) have the advantages of flexibility, light weight, and potentially low cost roll-to-roll production. In the last decade, the power conversion efficiency (PCE) of OPVs has increased from 2% to 11%. The rapid improvement of PCE has primarily been due to the following aspects: (1) new materials, especially small band-gap donor polymers with appropriate energy level offsets to the fullerene acceptors, (2) improved anodic and cathodic buffer layers, and (3) the optimization of the bulk-heterojunction morphology using approaches such as annealing and additives. Although the OPV efficiencies have improved steadily, they are still lower than those of contemporary thin-film inorganic solar cells. The efficiency losses in OPV cells include thermalization, exciton recombination, energy losses required for exciton dissociation, charge-carrier recombination, and optical losses. Among them, optical losses have been estimated to be nearly 40% of total losses. This is primarily because the thicknesses of OPV active-layers, as optimized for efficient charge transport, are only 100–200 nm or less. Therefore, methodologies to improve light absorption are necessary for further advancement of OPV technology.

In addition to tailoring the band-gap of materials to absorb more solar spectra, several device architectural approaches have been explored to improve light absorption in OPVs. These include utilizing textured substrates, substrates with wrinkles and deep folds, metal nanoparticles in or adjacent to the active-layers and patterning the active-layers. However, these approaches bring along several challenges and bottlenecks. In the textured substrate approach of Nalwa et al., texture dimensions need to be tailored, or rather discovered by trial-and-error for conformal coating of active-layers. Low-aspect ratio structures lead to over-filling of trenches and increased charge-carrier recombination, and high-aspect ratio structures lead to catastrophic shunts between the electrodes. Additionally, for contemporary polymer systems, which typically have thinner active-layers, achieving conformal coatings will be more challenging. Overall, conformally patterned cells may have good theoretical performance for optimum optical designs, but realizing conformal coatings by solution-processing is non-trivial and an
open problem. The microprism approach,\textsuperscript{17} and the one of utilizing substrates with wrinkles and deep folds\textsuperscript{19} suffer from similar issues. In the latter, it is also challenging to have a quantitative and precise control on the dimensions of self-assembled wrinkles and folds. Incorporating metal nanoparticles in or adjacent to the active-layer can also improve light absorption by surface plasmon polarization assisted field enhancement, and lateral propagation of light in the plasmonic mode.\textsuperscript{20, 21, 23–25} However, metal nanoparticles are centers for exciton quenching and charge-carrier recombination. In summary, all of the above approaches are intrusive to the active-layer, and optical enhancement often comes at a cost of disrupting the charge dynamics.

An alternative non-intrusive approach involves employing the microlens array (MLA) on the side of the transparent substrate opposite to the active-layer, such that light traverses the MLA and transparent substrate before entering the active-layer. Being on the other side, MLAs do not affect the fabrication or morphology of the active-layer. The MLA approach has been successfully used in organic light-emitting diodes to enhance light extraction.\textsuperscript{26–29} More recently, the MLA approach was also demonstrated to be useful for OPVs. Myers et al. utilized hemispherical microlenses with a 100 μm diameter;\textsuperscript{30} this led to refraction of light towards the active-layer and reduced surface reflection. Since the light was no longer traveling perpendicular to the substrate, the overall path length inside the active layer was increased and thus the absorption increased. In our previous publication,\textsuperscript{31} we showed that MLA with smaller feature sizes can be more promising because besides reduced surface reflection and refraction, they can also benefit from diffraction. In that report, we only investigated 2 μm diameter microlenses, but by smaller feature sizes we more generally mean feature sizes in or near the regime of optical wavelengths. Feature sizes (diameters) smaller than 2 μm have not been explored; neither has been the effect of changing the height of microlenses. That is the focus of this report, in which we show that both the pitch and height of microlens structures critically affect the device performance. We couple experimental investigations with theoretical predictions for two contemporary polymer systems (PTB7 and PCDTBT). Simulations also elucidate the mechanisms behind enhancement in light-absorption.
5.3 Methods

5.3.1 Microlens array fabrication

Periodic MLA with square lattice symmetry, having a structure similar to a closely packed egg tray (see Fig. D.1 in appendix E), was fabricated by soft lithography imprinting on polyurethane (Summer Optical Lens Bond Type J-91) from a polydimethylsiloxane (PDMS) mold (appendix C: Fig. C.1). Polyurethane was then cured under UV light for 3 hours, forming a solid MLA pattern after peeling off the PDMS mold. The polyurethane has negligible absorption for wavelength greater than 300 nm. In addition, the operating temperature range of ~50 to 110 °C is suitable for photovoltaic applications. MLAs with different pitches were fabricated from PDMS molds of different pitches. The PDMS molds with varying pitches and the desired inverse relief patterns were obtained from holographic interference lithography of photoresist. Further details about fabrication of the MLA pattern and PDMS molds are described elsewhere.32, 33 The fabricated MLA with different pitch sizes can be seen in Fig. 5.1.

![SEM images of MLAs with pitch sizes](image)

Figure 5.1 SEM images of MLAs with pitch sizes (a) 0.6 μm, (b) 1 μm, (c) 1.5 μm, and (d) 2 μm.
5.3.2 Device fabrication

PTB7 (1-Material) and PC$_{71}$BM (1-Material) with a weight ratio of 1 : 1.5 were dissolved in 1,2-dichlorobenzene : 1,8-diiodoctane (97%: 3% by volume) with 25 mg ml$^{-1}$ total concentration, and stirred at 800 rpm on a hot plate at a temperature of 60 °C for around 20 hours. Indium tin oxide (ITO) coated glasses (Delta Technologies) with and without an MLA pattern were pre-cleaned by sonicating in 2-propanol–acetone and then de-ionized water for 10 min each. The substrates were then dried with nitrogen and exposed to air plasma for 1 minute. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was spin-coated on ITO substrates at 4000 rpm for 60 s, followed by annealing on a hot plate at 120 °C for 10 min. The substrates were then transferred inside a nitrogen-filled glovebox. The previously prepared active-layer solution was filtered through a 0.2 μm filter, dropped on the PEDOT:PSS coated ITO, and spin-coated at 1000 rpm for 60 s. After spin-coating, the devices were covered with separate petri dishes for two hours. This length of time was long enough to dry the active-layers. To finish the device fabrication, 20 nm calcium and 100 nm aluminum were thermally evaporated on the active-layer at a pressure of around 10$^{-6}$ mbar. The preparation of substrates for PCDTBT based devices was done similar to that of PTB7. PCDTBT of molecular weight 50 kDa was purchased from 1-Material. MoO$_X$ (99.99%) and LiF (99.98%) were purchased from Sigma Aldrich. For the PCDTBT:PC$_{71}$BM system, 10 nm of a MoO$_X$ anodic buffer layer was thermally evaporated on ITO under a vacuum of about 10$^{-6}$ mbar at the rate of 0.5 Å s$^{-1}$. Solution of PCDTBT and PC$_{71}$BM (1 : 3.5, w/w), with a concentration of 7 mg mL$^{-1}$ in 1,2-dichlorobenzene, was continuously stirred on a hot plate at 90 °C and 650 rpm for 8 hours. The temperature of the solution was then reduced to 60 °C at the same stirring speed. After that, the active-layer was deposited on the top of the MoO$_X$ anodic layer at 2000 rpm for 45 seconds. The films were then dried under petri dishes for 20 min, and then annealed for 15 min on a hot plate at 70 °C. Finally, LiF (2 nm) and Al (100 nm) were thermally evaporated on the active-layer at the rates of 0.5 and 8 Å s$^{-1}$, respectively. PTB7 and PCDTBT based device architectures without and with MLA are depicted in Fig. 5.2.
5.3.3 Experimental characterization

For global transmission measurements, 0% and 100% were first calibrated for the integrating sphere. ITO coated glass substrates with and without MLA were placed in front of the opening of the integrated sphere with the ITO layer facing the opening. Then global transmission spectra were recorded on an optical fiber coupled spectrometer (Ocean Optics). For current density–voltage characterization, an ELH Quartzline halogen lamp provided 1 sun illumination after being calibrated with a reference crystalline Si solar cell coupled with a KG-5 filter. All the samples were measured under the same light intensity. In order to measure external quantum efficiency (EQE), a 100 W halogen bulb (OSRAM Bellaphot) was used as a light source with a single grating monochromator (Horiba Jobin Yvon Srl). An optical chopper (Thor Labs)
coupled with a lock-in amplifier (Standford Research Systems) was employed to reduce system noise. The EQE spectra were calculated after comparing the sample signal to the crystalline Si reference signal. Light angle dependent current density was measured using a customized setup in the lab. One sun illumination was obtained using a light source (LS150 Abet Technologies) and calibrated with a reference crystalline Si solar cell. A rotating sample stage was used to change the incident angles from 0 to 80 degrees (appendix D: Fig. D.2), and short-circuit current was measured using a Keithley 2400 sourcemeter.

5.3.4 Simulations

We used the rigorous scattering matrix (SM) method\textsuperscript{34,35} where Maxwell’s equations are solved in Fourier space, i.e. on the basis of plane waves for both polarizations. We divided the OPV devices into slices in the z-direction, wherein the dielectric function depends periodically on x and y in each slice i.e. the in-plane coordinates $r = (x,y)$. The dielectric function $\varepsilon$ has Fourier components $\varepsilon(G)$ given by

$$\varepsilon(r) = \sum \varepsilon(G) \exp(iG \cdot r)$$  \hspace{0.5cm} (5.3.1)

where $G$ are reciprocal lattice vectors. The electric E and magnetic H fields are also expanded in Fourier components of strength $e$ and $h$, which are functions of $G$ and $z$.

$$E(r) = \sum e(G, z) \exp(-i(k + G) \cdot r)$$  \hspace{0.5cm} (5.3.2)

$$H(r) = \sum h(G, z) \exp(-i(k + G) \cdot r)$$  \hspace{0.5cm} (5.3.3)

where $k$ is a Bloch vector. We solve an eigenvalue equation for the transverse x and y components of the fields $e$, $h$ in each layer.\textsuperscript{34} We obtain the SM for each layer by solving the Maxwell’s equations with the boundary conditions, that the parallel components of the fields $e$ and $h$ are continuous at each interface. The SM of each layer was combined by a standard convolution procedure\textsuperscript{34} to obtain the SM of the entire structure, which relates the incoming (incident) fields to the outgoing (reflected and transmitted) fields. The SM yields the total
reflectance $R$ (including diffraction), transmittance $T$ ($\sim 0$) and absorbance $A$ (=$1-R-T$) at each wavelength. This SM technique has advantages over real-space methods in being able to simulate fully 3-dimensional geometries, without added memory requirements, since a real space grid is unnecessary. The SM method is fully parallelized with each frequency being sent to a different processor, and we have efficiently simulated complex textured organic solar cells with this method. The results are well converged for $N_G = 270–300$ plane waves ($G$ vectors) for each polarization of the field, leading to a scattering matrix size of order $540–600$ ($2N_G$). Our simulations utilize experimental values for the wavelength dependent dielectric functions for the materials including measurements for PCDTBT and PTB7, and standard tabulated values for other materials.

5.4 Results and Discussion

MLAs with four pitch sizes (0.6 $\mu$m, 1 $\mu$m, 1.5 $\mu$m, and 2 $\mu$m) were fabricated and evaluated. In order to compare the optical properties of the substrates with and without MLA, the global transmission spectra of these substrates (structure: MLA/glass/ ITO) were measured as well as simulated; they are plotted in Fig. 5.3(a). As the experimental plots in Fig. 5.3(a) show, all substrates have similar spectra; only the 0.6 $\mu$m MLA substrate showed slightly lower transmission between 400 nm and 550 nm wavelengths. This lower transmission is due to stronger scattering of light passing through the 0.6 $\mu$m pitch microlenses. We visually observed that part of the scattered light escaped out through the side of the substrates before entering the integrating sphere. The 1 micron case also differs from simulation, showing a decrease at longer wavelengths. This could be due to a similar issue of light scattering at high angles and escaping the integrating sphere aperture. The global transmissions of all of the MLAs were comparable. The calculated spectra from simulation support this conclusion. The calculated spectra in Fig. 5.3(b) are very similar to the experimental data. All substrates have similar global transmission spectra including the 0.6 $\mu$m MLA substrate, since calculations include the scattered light that escaped in the experiment. The positions of maxima are near 530 nm from multiple interference effects, depending on ITO thickness (appendix D: Fig. D.3). Even though all these substrates had similar global transmission spectra, they exhibited very different diffraction patterns. These
Figure 5.3  (a) Experimental and (b) simulated global transmission spectra of substrates without MLA (reference) and with MLA (0.6 μm, 1 μm, 1.5 μm and 2 μm pitches).

Figure 5.4  Photographs of light diffraction patterns through reference and MLA devices.

patterns are shown in the photographs of Fig. 5.4. To obtain these images, devices were illuminated with a white light beam normal to the substrates, through a hole at the bottom. A sheet of white paper was placed next to the devices to project the diffraction patterns. No diffraction pattern was observed for the reference device. The MLA substrates, however, being two-dimensional diffraction gratings, showed rainbow like diffraction patterns. According to the grating equation \( d \sin \theta_m = m\lambda \), diffraction order \( m \) is directly proportional to grating period \( d \). Thus, a larger period (pitch) leads to additional diffraction modes. On the other hand, diffraction angle \( \theta_m \) is inversely proportional to the pitch. Thus, larger pitch leads to decreased spacing between different diffraction orders. Both additional modes and decreased angles for larger pitches are evident in the photographs of Fig. 5.4.
Figure 5.5 (a) JV curves, and (b) EQE spectra of PTB7 reference and MLA devices (p = 0.6 μm, h = 250 nm; p = 1 μm, h = 350 nm; p = 1.5 μm, h = 900 nm; p = 2 μm, h = 1000 nm).

Table 5.1 $J_{SC}$ and PCE of PTB7:PC$_{71}$BM OPV devices for MLAs of different pitch sizes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$J_{SC}$ enhancement (%)</th>
<th>PCE (%)</th>
<th>PCE enhancement (%)</th>
</tr>
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<tbody>
<tr>
<td>Reference</td>
<td>16.10</td>
<td>-</td>
<td>7.73</td>
<td>-</td>
</tr>
<tr>
<td>0.6 μm (h=250 nm)</td>
<td>17.39</td>
<td>8.01</td>
<td>8.14</td>
<td>5.3</td>
</tr>
<tr>
<td>1 μm (h=350 nm)</td>
<td>18.00</td>
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<tr>
<td>1.5 μm (h=900 nm)</td>
<td>17.70</td>
<td>9.94</td>
<td>8.25</td>
<td>6.73</td>
</tr>
<tr>
<td>2 μm (h=1000 nm)</td>
<td>17.50</td>
<td>8.7</td>
<td>8.25</td>
<td>6.73</td>
</tr>
</tbody>
</table>

To characterize the effect of MLAs on the performance of OPVs, PTB7:PC$_{71}$BM devices were fabricated on the reference substrate (no MLA) and substrates with MLA of different pitch sizes. Current versus voltage measurements were performed under illumination; the results are plotted in Fig. 5.5(a). Open circuit voltages of MLA devices were similar to the reference. However, short circuit current densities ($J_{SC}$) of all MLA devices were notably higher than the reference. As tabulated in Table 5.1, $J_{SC}$ and PCE of the reference were 16.1 mA cm$^{-2}$ and 7.73%, respectively, among the highest in the literature for PTB7 based devices. Variation of the enhancement is shown in boxplots in Fig. D.4. Among the MLA devices, devices with 1 μm pitch MLA showed the highest $J_{SC}$ and PCE, 18 mA cm$^{-2}$ and 8.55%, respectively. $J_{SC}$ and PCE increased going from 0.6 μm pitch MLA to 1 mm pitch MLA, and then slightly decreased for 1.5 μm and 2 μm pitch MLA. The values of heights of all MLAs are also listed in Table 5.1. EQE spectra of the reference and MLA devices are plotted in Fig. 5.5(b). As can be seen,
MLA devices exhibit broadband enhancement across the range of wavelengths absorbed by the PTB7:PC_{71}BM system, especially in the 400–500 nm and 600–800 nm wavelength regions.

In addition to the pitch sizes, heights of microlenses also affected the OPV device performance (Fig. 5.6). To investigate the effect of heights, two to four height values were evaluated experimentally for each pitch. Optical simulations for these dimensions were also performed on corresponding device structures. Different heights for each pitch were realized by intuitive variation of photoresist spin-coating parameters during MLA fabrication; all the heights for a given pitch were such that the height/pitch ratio (h/p ratio) was \( \leq 1 \). Fig. 5.6 shows the combined (experimental and simulated) \( J_{SC} \) enhancement data for different pitches and heights; enhancement versus the height to pitch ratio (h/p ratio) is also plotted. As can be seen, for a given pitch, mostly enhancement increased as the height of MLAs increased.
First, we discuss the experimental results of height variations (Fig. 5.6(a) and (b)). For the 0.6 μm pitch MLA device, $J_{SC}$ enhancement was 6–8% at around a h/p ratio of 0.4. For the 1 μm pitch MLA device, there was a significant jump in enhancement from 6% to 12% when the h/p ratio increased from 0.2 to 0.4, following which the enhancement began to saturate. The enhancement values increased less sharply with height in the 1.5 μm pitch MLA device; enhancement was ~7% for smaller h/p ratios (0.2–0.4), and ~10% for higher h/p ratios (0.6–1). In the devices with the largest MLA pitch of 2 μm, the enhancement increased rapidly with increasing h/p ratio, similar to the 1 μm pitch MLA devices. Around the h/p ratio of 0.3, the enhancement was 2.5%, while it increased to 9% at the ratio of 0.5, and to the highest value of 11% at the ratio of 0.7.

Simulations agree with the experiments on a general trend that for a given MLA pitch, enhancement increases as height increases (Fig. 5.6(c) and (d)). Regarding the absolute enhancement values, there are some differences between experiments and simulations, which can be due to differences in the MLA structure employed in simulations and the one actually realized by fabrication. Fabricated structures have some unintentional imperfections and local irregularities, examples of which are some depressions in the valleys, as can be seen in SEM images (Fig. 5.1 and Fig. D.5). Nevertheless, simulations agree with measurements on the central trend that enhancement increases with an increasing h/p ratio. Simulations also reveal an interesting feature relevant for MLA architecture design: that across different MLA pitches, enhancement values are similar or close for a given h/p ratio. The h/p ratio of around 0.4 is a pronounced example of this.

The current–voltage measurements under illumination are typically done with incident light normal to the substrates. However, for non-tracking PV systems, the incident angle of sunlight changes throughout the day. In order to probe the angle dependence, we carried out current–voltage measurements with different incident light angles. Devices were rotated from the normal angle (0°) to almost parallel to the light source beam (80°), and $J_{SC}$ was measured at 10° intervals. Angle dependent enhancement ratios were obtained by dividing $J_{SC}$ of MLA devices by that of the reference device (Fig. 5.7). For the MLA devices with 1 μm, 1.5 μm and 2 μm pitch, enhancement slightly decreases with an increasing angle up to 50°. This is be-
cause with increasing angle, light path in the reference device increases as the reflectance (R_p) of p-polarized light decreases, vanishing at the well-known Brewster angle of 50° for glass. At higher angles above the Brewster angle the reflectance (R_p) increases again for the reference and increasingly less light is absorbed in the active-layer. In contrast, MLA reduces the reflection and enhancement ratios in MLA devices rapidly rise to 1.4–1.5 at 80°. The enhancement ratio for 0.6 µm pitch MLA device showed a consistently increasing trend as the incident light angle increased, different from devices of other pitch sizes. This might be due to diffraction effects being strongest in the 0.6 µm device. The angle dependence trends had no evident correlation with heights as the h/p ratios of MLA devices were 0.4, 0.5, 1 and 0.7 (for 0.6, 1, 1.5 and 2 µm pitch MLAs, respectively).
Figure 5.8  Simulated electrical field distribution (for wavelength 610 nm) inside the MLA devices with (a) $p = 0.6 \, \mu m$, $h = 600 \, nm$, (b) $p = 0.6 \, \mu m$, $h = 1000 \, nm$, (c) $p = 1 \, \mu m$, $h = 1000 \, nm$.

To better understand the enhancement mechanisms in MLA devices, electrical field distributions in MLA devices were simulated for different MLA dimensions. Fig. 5.8 shows the electrical field distribution for 610 nm wavelength in the 0.6 $\mu m$ and 1 $\mu m$ pitch MLA devices. To probe into the height dependence, two heights were simulated for the 0.6 $\mu m$ pitch MLA device. One can see that field intensities in the PTB7:PC$_{71}$BM active layers exhibit a periodic distribution
of high intensity focused regions. The incident electrical field intensity was 1. In the 0.6 μm pitch MLA devices (Fig. 5.8(a) and (b)), as the MLA height increases from 600 nm to 1000 nm, the light focusing increases, which contributes to higher electrical field intensity in the higher height device. However, as the field intensities at the periodic focused spots get higher, the field intensities in the intermediate regions decrease, even below 1 in some regions. However, overall there is a gain. Comparing Fig. 8(b) and (c), the MLA height in these two devices is the same at 1000 nm, but (b) has a smaller pitch of 0.6 μm than (c) of 1 μm. The maximum field intensity of (b) is slightly larger than that of (c), which agrees with the observed phenomena. Although the focusing regions are closer for the 0.6 μm pitch, portions of the enhanced |E|^2 lie in the PEDOT:PSS layer. Thus, there is a trade-off between the spatial separation of the focusing spots dictated by the pitch and the location of the focus spots within the active layer. The balance of this trade-off determines the optimal MLA configuration.

In OPVs based on several contemporary polymers, optimal thicknesses of the active-layer are smaller as optimized for charge transport; for example, 60–70 nm thickness in devices based on PCDTBT. We also fabricated MLA and reference devices with the PCDTBT polymer. Current–voltage and EQE curves of these devices are plotted in Fig. 5.9 and performance parameters are listed in Table 5.2. MLA devices showed very similar open circuit voltage to the reference. However, the J_{SC} of all MLA devices was higher than the reference. As shown in Table 5.2, the reference has a J_{SC} of 10.03 mA cm^{-2}, and a PCE of 5.19%. MLA devices showed improvement in J_{SC} by between 10.47% for 0.6 μm MLA to 10.67% for 1 μm pitch MLA. As MLA pitch increased to 1.5 μm, the enhancement increased to 16.95% and then dropped to 13.86% for 2 μm pitch MLA. The enhancement of PCE in MLA devices also increased from 5.59% for 0.6 μm pitch to 7.71% for 1 μm pitch, and then peaks to 13.10% for 1.5 μm and drops to 11.56% for 2 μm MLA. EQE data shows that the MLAs (1 mm, 1.5 μm and 2 μm) mainly have enhancement in the wavelength region of 480–800 nm. However, there is a drop for wavelengths between 400 nm and 460 nm. The enhancement from the 0.6 μm MLA is higher in the longer wavelength region of 600–800 nm than the other MLAs. These results, together with the PTB7 results discussed previously, show that OPV systems with very thin active layers suffer from poor absorption efficiency and can greatly benefit from optical enhancement schemes.
Figure 5.9  (a) JV curves and (b) EQE spectra of PCDTBT based reference and MLA devices.

Table 5.2  $J_{SC}$ and PCE of PCDTBT:PC$_{71}$BM OPV devices for MLAs of different pitch sizes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$J_{SC}$ enhancement (%)</th>
<th>PCE (%)</th>
<th>PCE enhancement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>10.03</td>
<td>-</td>
<td>5.19</td>
<td>-</td>
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<td>0.6 μm (h=250 nm)</td>
<td>11.08</td>
<td>10.47</td>
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<td>5.59</td>
</tr>
<tr>
<td>1 μm (h=350 nm)</td>
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<tr>
<td>1.5 μm (h=900 nm)</td>
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<td>5.87</td>
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<td>2 μm (h=1000 nm)</td>
<td>11.42</td>
<td>13.86</td>
<td>5.79</td>
<td>11.56</td>
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</table>

5.5 Conclusion

We demonstrate that by adding a MLA layer on the light-facing side of the transparent substrate in OPV devices, optical absorption in the active-layers improve due to reduced reflection, and increased light path achieved by light focusing and diffraction. Optical field intensity increases at periodical spots inside the active layer. All of these effects combine to enhance short-circuit currents and power conversion efficiencies. We get around 10% enhancements in PTB7:PC$_{71}$BM devices with a MLA pitch size of 0.6 μm, 1 μm, 1.5 μm and 2 μm, even when the reference devices were high efficiency devices with optimized processing conditions. The enhancement generally increases with increasing height of microlenses. When the angle of light incidence changes away from the normal, the enhancements for 1 μm, 1.5 μm or 2 μm pitch MLAs drop slightly, and then increase significantly at large angles. For 0.6 μm pitch MLA, enhancement increases at all non-normal angles. Simulations using the scattering matrix approach support the central experimental observations and provide insights into the enhancement mecha-
nisms. The enhancement was as high as 17\% in PCDTBT based MLA devices. The simple stamping technique to fabricate the MLAs can be scaled readily to larger areas. Moreover, the MLA is on the substrate side opposite to the active layer and does not hinder the cell fabrication or electrical characteristics. It is also generally applicable to all types of solar cells due to its non-intrusive and external nature.

5.6 Acknowledgement

YC thanks Chinese Scholar Council, and ME thanks Egyptian government for financial support. We acknowledge funding from National Science Foundation (CBET-1236839; ECCS-1232067; CBET-1336134; CHE-1213582). We acknowledge partial support from the Ames Laboratory, operated for the Department of Energy by Iowa State University under contract No. DE-AC0207CH11385. We also acknowledge use of computational resources at the National Energy Research Scientific Computing Center (NERSC). Thanks Geyuan Liu for the help and discussions.
5.7 References


APPENDIX A. SUPPLEMENTARY RESULTS OF CHAPTER TWO

Figure A.1 Schematic describes the different stages of cleaning old ITOs, fabrication of new OPVs and characterization of fresh and old substrates and solar cells.
Figure A.2  X-ray diffraction spectra showing the position shift of the (222) peak as a function of the age of ITO. b) XPS binding energy spectra, c) Atomic composition of new fresh ITO substrates, and d) the Sn/In ratio of the investigated ITO substrates.
Figure A.3  Normalized quantum efficiency (QE) of P3HT:PC$_{60}$BM solar cells.

Figure A.4  Normalized quantum efficiency (QE) of PTB7:PCBM solar cells.
Figure A.5  Investigation of old ITO substrates previously coated with some selected buffer layers other than PEDOT:PSS: ITO previously coated with Cs$_2$CO$_3$ yielded an OPV of 2.23% power conversion efficiency compared with 2.14% for the fresh ITO based devices. ITO slides previously coated with MoOx and PFN had slightly a lowered PCE of 2.07% and 2.03%, respectively. a) Current-voltage characteristics under illumination, and c) normalized QE of P3HT:PC$_{60}$BM OPVs. (b) Transmission of ITO substrates with buffer layers and P3HT:PCBM layers present on the substrates.
Table A.1  Elemental composition of the new, and old ITO substrates previously coated with different buffer layers.

<table>
<thead>
<tr>
<th>Atomic concentration (%)</th>
<th>O 1s</th>
<th>In 3d</th>
<th>Sn 3d</th>
<th>C 1s</th>
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<tr>
<td>Fresh ITO</td>
<td>53.37</td>
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<td>16.97</td>
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<td>MoOx-cleaned ITO</td>
<td>52.29</td>
<td>25.26</td>
<td>3.18</td>
<td>19.27</td>
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<tr>
<td>Cs$_2$CO$_3$-cleaned ITO</td>
<td>47.98</td>
<td>23.30</td>
<td>3.59</td>
<td>25.13</td>
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<td>PFN-cleaned ITO</td>
<td>56.40</td>
<td>27.17</td>
<td>3.04</td>
<td>13.39</td>
</tr>
</tbody>
</table>
APPENDIX B. SUPPLEMENTARY RESULTS OF CHAPTER THREE

Experimental Section

Substrate preparation. ITO coated glass slides (5-15 Ω/□) from Delta Technologies were sonicated in detergent, de-ionized water, methanol/ethanol and 2-propanol. The substrates were dried with nitrogen and on a hot plate at 150 °C for 5 minutes before receiving a medium dose of air plasma treatment for 5 minutes. The ITO slides were blown again with N₂ gas before any depositions.

Solution preparation. Neat P3HT (1-materials Inc.) and a 1:1 P3HT:PC₆₀BM (1-materials Inc.) were dissolved in 1, 2-dichlorobenzene (o-DCB) with dilution of 20 mg/ml. The solutions were stirred at 850 rpm on a hot plate at a temperature of 50°C, then, filtered through a 0.2 μm filter before use.

OFETs fabrication. The gate dielectric consisted of ploy (4-vinylphenol) (PVP) and poly (melamine-co-formaldehyde) (PMF) (Sigma Aldrich), which were mixed together in propylene glycol methyl ether acetate. The dielectric solution was spin-coated at 1000 rpm 60 s⁻¹ on cleaned ITO. Then, it was baked at 200 °C for 20 minutes. The dielectric thickness and capacitance per unit area were 600 nm and 8 nF cm⁻². P3HT (20 mg/ml) solution was spin-coated on top of the thermally treated dielectric, and then subjected to the E-field at the aforementioned directions. 150 nm of silver was thermally evaporated at pressure of a 4 × 10⁻⁷ torr with a shadow mask. The source and drain electrodes had a channel width and length of ~ 2000 and 50-60 micron.

OPVs fabrication. 40 nm of PEDOT:PSS (VP 4083 from HC Stark) was spin coated at 4000 rpm for 60 seconds on cleaned ITO, and then annealed at 150 °C for 30 minutes. P3HT:PC₆₀BM blend (1: 1 by weight; 20 mg/ml) was spin-coated at 500 rpm/ 40s. The P3HT:PC₆₀BM devices had a structure of ITO/ PEDOT:PSS (40 nm)/ active-layer (260 ± 20
nm)/ Ca (20 nm)/ Al (100 nm). Ca and Al were thermally evaporated in 10^-6 mbar vacuum at rates less than 1 and 4 Å/s, respectively. On the other hand, replacing PEDOT:PSS by Cs₂CO₃ and Ca with MoOₓ yield inverted solar cells with structure of ITO/ Cs₂CO₃/ P3HT:PC₆₀BM/ MoOₓ/ Al. The concentration and the spin speed conditions were kept the same in both conventional and inverted OPVs.

**OLEDs fabrication.** OLEDs were fabricated on 140 nm thick ITO-coated glass substrates. After cleaning the ITO substrates, PEDOT:PSS was spin-coated at a speed of 1000 rpm for 60 s, followed by baking at 150 °C for 50 min. In P3HT-based OLEDs, P3HT (15 mg/ mL o-DCB) was deposited at speed of 1500 rpm 10 s⁻¹, whereas, in MEH-PPV-based OLEDs, MEH-PPV (10 mg/ mL o-DCB) was deposited at 1000 rpm 10 s⁻¹. After that, BPhen (an electron transport/ hole blocking layer), LiF cathode buffer layer and Al were thermally evaporated through a mask (1.5 mm diameter) at pressure of 10^-6 mbar. The structure was: ITO/ PEDOT:PSS (60 nm)/ (P3HT or MEH-PPV)/ BPhen (50 nm for P3HT - 30 nm for MEH-PPV)/ LiF (1 nm)/ Al (100 nm).

**GIWAXS.** Samples for Grazing-Incidence Wide Angle X-ray Scattering (GIWAXS) were spin-coated at 500 rpm/ 40 seconds on 1 inch × 1 inch bare silicon wafers. GIWAXS measurements were carried out at the Beamline 8-ID-E of the Advanced Photon Source, Argonne National Lab.1 X-rays with photon energy of 7.35 keV were incident upon the sample at angles \( \alpha_i \) of 0.15°, below the critical angle for the organic thin film, or 0.2°, above the critical angle of the thin film but below the critical angle of the Si substrate, in order to probe the region near the top surface of the film, or to probe the entire thickness of the thin film, respectively. For P3HT, chemical formula \((C_{10}H_{14}S)n\), mass density 1.1 g/cm³, corresponds to an electron density 0.359 e/A³. At E=7.35 keV, the critical angle is \( \alpha_c = 0.1735 \) deg. The beam size was defined by slits 200 μm horizontally and 20 μm vertically, so the x-ray footprint along the beam extended to about 7.6 mm for the smaller incident angle. Samples were enclosed in a chamber purged with helium gas to minimize concerns about radiation damage. A mica entrance window and an internal beamstop before the kapton exit window of the chamber minimized parasitic scattering from the chamber. Two-dimensional data were obtained with a Pilatus 1M detector (Dectris) at two different vertical positions, and the images were combined to eliminate rows.
of inactive pixels using the software package GIXSGUI for Matlab (Mathworks). This also applied corrections for detector non-uniformity, pixel sensitivity, geometry and polarization, and mapped the data from pixel-space to the photon wave-vector transfer vector, \( \mathbf{q} \). All the 2-D data shown were collected for the same exposure time and are displayed on the same pseudo color intensity scale.

**Conductive and Kelvin probe force microscopy imaging.** C-AFM measurements were done using Veeco Multimode Nanoscope III. Kelvin probe force microscopy was performed using Agilent 5500 SPM in single pass and frequency modulation mode. NANOSENSORS PtSi-NCH probe was used for all samples. Two lock-in amplifiers were utilized where the first lock-in amplifier was used to track the topography. The AFM tip was vibrated close to its first mechanical resonance using lock-in amplifier 1 (LIA1) which was used to track the topography and phase. Lock-in amplifier 2 (LIA2) was used to apply AC excitation to the conductive tip at 4kHz frequency and dc bias of -0.5V. The Y component of LIA 1 was fed as input for LIA2. The phase shift of both LIA1 and LIA2 were adjusted to maximize the X component and minimize the Y component of each lock in amplifier to obtain an optimum signal to noise ratio. Both topography and surface potential were tracked simultaneously. All the images were analyzed using Nanotec Electronica WSxM software.²

**Van de Graaff generator (VDG) description.** A Van de Graaff generator, which can produce an electric potential of 325,000 volts or more, was utilized to produce an E-field of 5.8 kV/ m at its surface. The wet active layers were aligned 1 cm from the dome surface, where the E-field strength was calculated to be 5 kV/ m.

**Thin-film characterization.** The current-voltage characteristics (1 sun illumination) were obtained by using an ELH Quartzline halogen lamp. UV-Vis absorption was measured using a Varian Cary 5000 UV-Vis-NIR Spectrophotometer. C-AFM measurements were done using Veeco Multimode Nanoscope III, and images were analyzed using Nanotec Electronica WSxM software.³ PL lifetime measurement was investigated by the time-correlated single-photon counting setup at a probing fluorescence wavelength of 400 nm.⁴ PARSTAT 2273 was utilized with a solar simulator in order to measure \( V_{OC} \) versus light intensity dependence. A Keithley 2400 source meter was used to measure mobility of P3HT and P3HT:PC\(_{60}\)BM devices. The same
instrument was utilized with Keithley 617 source meter to examine the OFETs at room temperature under ambient conditions. For OLEDs, devices were characterized by current – voltage – luminescence measurements, using a Kepco DPS 40-2M programmable power supply, a Keithley 2000 multimeter, and a Minolta luminance meter LS-110.
Figure B.1 The raw data of steady-state photoluminescence spectra of P3HT-only thin-films following 500 nm light excitation for the (a) parallel and (b) perpendicular polarization.
Figure B.2  The FWHM of the C=C peak (located at 1450 cm\(^{-1}\)) of (a) all the different sets of P3HT: PC\(_{60}\)BM thin-films, and (b) their average with the standard deviation depicted on each bar.
Figure B.3 (a-h) Effect of E-field on the crystal structure of P3HT-only thin-films. 2D- GI-WAXS images of neat P3HT thin-films, which were spin-coated at 500 rpm/40 seconds on 1 inch × 1 inch silicon wafer, at grazing incidence angles of (a-d) 0.15° and (e-h) 0.2°. (i) The FWHM of the line cuts of the (100) peak obtained from the 2D-GIWAXS images of P3HT-only thin-films at the aforementioned grazing incidence angles.
Figure B.4 Histograms of surface potential values as extracted from the KPFM images (Fig. 2k-n) for the control, horizontal, tilted and vertical P3HT:PC$_{60}$BM thin-films. The red (black) arrow depicts the direction of increased P3HT (PCBM) aggregates on the surface. Compared to the control (in green), it is clear that the histogram of surface potential values of the horizontal film (in red) shows narrow distribution as well as decreased peak position, implying increased PCBM on the surface. Similarly, the histogram of surface potential values of the tilted KPFM image (in blue) also exhibit more PCBM compared to the control and tilted films. The histogram of the vertical E-field film (in orange) displays an opposite trend, with a wider distribution and increased peak position (~380 mV).
Figure B.5 The tapping mode AFM surface roughness (top) and phase (bottom) maps of the control, and the E-field P3HT:PC_{60}BM thin-films. These films were prepared by spin-coating the active layer at 500 rpm/40sec on PEDOT:PSS-coated ITO substrate. These images were captured simultaneously with the Kelvin probe force microscopy.
Figure B.6  a, Typical schematic of P3HT OFETs with a PVP dielectric, which has thickness and capacitance per unit area of 600 nm and 8 nF cm$^{-2}$, respectively. (b-e) The effect of the E-field on the ($I_{DS}$-$V_{GS}$) characteristics of the P3HT-OFETs (structure: ITO/PVP: PMF (600 nm)/ P3HT (500 rpm/40 sec)/ Ag) at different gate voltages ($V_{GS}$) voltages.
Figure B.7  Transfer characteristic (I_{DS}-V_{GS}) of the control, horizontal, tilted and vertical E-field P3HT-OFETs at V_{DS} = -100 volts. The hole-mobility of the P3HT OFETs is calculated from the straight-line fitting of the linear region of the I_{DS}-V_{GS} curve.
Table B.1  The average, standard-deviation and the number of samples tested for hole-mobility measurements of P3HT-based devices. High values of the standard deviations is because data is from different sets fabricated and characterized in ambient at different times during the last two years. Regardless, the relative trends of mobility enhancement were consistent across different sets.

Average Mobility ± standard deviation (cm$^2$V$^{-1}$s$^{-1}$)

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<th>Device type*</th>
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<td>Control</td>
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<td>Horizontal</td>
<td>$12.1 \times 10^{-3} \pm 3.05 \times 10^{-3}$</td>
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<td>Tilted</td>
<td>$8.28 \times 10^{-3} \pm 1.78 \times 10^{-3}$</td>
</tr>
<tr>
<td>Vertical</td>
<td>$6.97 \times 10^{-3} \pm 2.35 \times 10^{-3}$</td>
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<td>Horizontal</td>
<td>$10.7 \times 10^{-4} \pm 7.77 \times 10^{-4}$</td>
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<td>Tilted</td>
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<td>Vertical</td>
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<td>Vertical</td>
<td>$15.7 \times 10^{-4} \pm 5.84 \times 10^{-4}$</td>
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</table>

* The values in parenthesis represent the number of measured devices.
The space charge limited current (SCLC) regime of the dark current density-voltage (J-V) curve was investigated for hole-only devices (Fig. B.8). From the SCLC fitting, $\mu_h$ was calculated from the Mott-Gurney equation, $J = \frac{9\varepsilon_0\varepsilon_r \mu V^2}{8L^3}$ ($L$, $\varepsilon_0$ and $\varepsilon_r$ are the devices thickness, dielectric constants of free space or vacuum and polymer, respectively).\(^4\)

Figure B.8 Dark current versus voltage characteristics of control and E-field air-processed (a) P3HT and (b) P3HT:PC\textsubscript{60}BM hole-only devices. The thickness of P3HT and the P3HT:PC\textsubscript{60}BM active layer were 200 nm ± 20 nm and 260 nm ± 20 nm, respectively. AFM was used to determine the thicknesses of the examined films by imaging the surface profile of needle-scratched active layer.\(^6\)
Figure B.9 The current density-voltage of (a) P3HT and (b) MEH-PPV OLEDs. (c) The electroluminescence efficiency ($\text{EL}_\text{eff}$) verses current density curves of MEH-PPV-based OLEDs.
Figure B.10  a, Open-circuit-voltage ($V_{OC}$) versus light intensity characteristics for P3HT:PC$_{60}$BM OPVs (inset shows the diode ideality factor).\textsuperscript{7}  b, Dark I-V characteristics of P3HT:PC$_{60}$BM OPVs (inset shows the diode ideality factor calculated from the ideal diode regime of the dark I-V curve).  c, Current-density versus voltage under illumination of conventional PTB7:PC$_{70}$BM OPVs (structure: ITO/ PEDOT:PSS (40 nm) / active layer (100 nm)/ Ca (20 nm)/ Al (100 nm)).

2. Z. Jiang.


APPENDIX C. SUPPLEMENTARY RESULTS OF CHAPTER FOUR

Figure C.1  Schematic describes the fabrication steps of MLA. (a) PFMS stamp has the MLA structure is (b) placed atop of polyurethane (PU) drop. (c) The PU is cured under UV light. Then, (d) the PDMS stamp is removed yielding the MLA on the non-conductive side of the ITO glass substrate. As Fig C.2 and C.3 show, SEM and AFM images confirms the successful fabrication of the 2 m MLA.
Figure C.2  Top and angle views of AFM images of the 2 µm MLA.

Figure C.3  SEM image shows the exact dimensions of the 2 µm MLA.
Figure D.1 Schematic represents an egg tray-like structure that mimics the fabricated MLA.
Figure D.2  Rotating stage on which the photovoltaic characteristics were measured as a function of the angle of light incidence.
Figure D.3  (a) Global transmission spectra of 1μm pitch MLA substrates with different ITO thickness.  (b) Spectra of spectral and global transmission in 1 μm pitch MLA substrate.
Figure D.4 Box plots showing the variation in enhancement of short circuit current and power conversion efficiency for PTB7 (a, b) and PCDTBT (c, d) devices. 18 cells were tested for each condition.
Figure D.5  Side view of AFM image of the 600 nm MLA.
APPENDIX E. LabVIEW CODES

Figure E.1 LabVIEW VI for photovoltaic solar cell characterization.
Figure E.2  LabVIEW VI for $V_{OC}$-light intensity measurement of organic solar cell.
Figure E.3  LabVIEWVI for the characterization of OFETs.
APPENDIX F. LIST OF PUBLICATIONS

Journal publications:


**Manuscripts in preparation:**

1. M. Elshobaki and S. Chaudhary, “Tuning the degree of donor/acceptor intermixing towards efficient inverted solar cells processed under a static electric field”.
2. M. Elshobaki and S. Chaudhary, “Universality of electric-field toward reducing structural disorder of organic thin films and devices”

3. M. Elshobaki and S. Chaudhary, “Effect of electrostatic field on the carrier transport in solution processed polymer/small molecule-based OFETs”.


Conference presentations:


