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Studies of Morphology and Charge-Transfer in Bulk-Heterojunction Polymer Solar Cells

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To my family

Abstract

The work presented in this thesis focuses on the two critical issues of bulk-heterojunction polymer solar cells: morphology of active layers and energy loss during charge transfer processes at electron donor/acceptor interfaces. Both issues determine the performance of polymer solar cells through governing exciton dissociation, charge carrier recombination and free charge carrier transport.

The morphology of active layers (spatial percolation of the donor and acceptor) is crucial for the performance of polymer solar cells due to the limited diffusion length of excitons in organic semiconductors (5-20 nm). Meanwhile, the trade-off between charge generation and transport also needs to be considered. On the one hand, a finely mixed morphology with a large donor/acceptor interface area is preferred for charge generation because efficient exciton dissociation only occurs at the interface, but on the other hand, proper phase separation is needed to reduce charge carrier recombination and facilitate free charge carrier transport to the electrodes. In this thesis, morphologies of the active layers based on different polymeric donors and fullerene acceptors are correlated to the performance of solar cells with various microscopic and spectroscopic techniques including atomic force microscope, transmission electron microscope, grazing incidence x-ray diffraction, photoluminescence, electroluminescence and Fourier transform photocurrent spectroscopy. Furthermore, methods to manipulate the morphologies of solution processed active layers to achieve high performance solar cells are also presented. Processing solvents, chemical structures of the donor and the acceptor materials, and substrate surface properties are found critically important in determining the nanoscale phase separation and performance of polymer solar cells.

Optimizing morphology of active layers alone does not guarantee high performance devices. In addition to spatial percolation, energy arrangements of donors and acceptors are also essential due to contrary requests of the photocurrent and the photovoltage: Efficient exciton dissociation or charge transfer at donor/acceptor interfaces requires large enough energetic driving force, which is also known as energy loss for charge transfer. However, the energy loss due to charge transfer will unavoidably reduce the photovoltage. In this thesis the balance between the photocurrent and the photovoltage in polymer solar cells due to charge transfer at donor/acceptor interfaces is investigated for different active material systems. The driving force tuned by synthesizing series of polymers is determined by directly measuring the optical band gap via UV-Vis spectroscopy and probing the charge transfer recombination via electroluminescence measurements. Influences of driving force on the photocurrent and the photovoltage are characterized via field dependent photoluminescence and internal quantum efficiency measurements. The results correlated well with the performance of the solar cells.

Populärvetenskaplig Sammanfattning

Denna avhandling behandlar polymera solceller med absorberande lager bestående av en blandning av halvledande polymerer och fullerenderivat och fokuserar på två kritiska frågor för prestandan: blandningens nanostruktur och energiförlusterna vid laddningsöverföringen vid polymer/fulleren gränsytan. Dessa båda är avgörande för prestandan hos solcellen då de bestämmer hur väl excitoner (bundna elektron-hålpar) delas, laddningsbärare rekombinerar och fria laddningar transporteras.

Nanostrukturen hos polymer/fullerenblandningen i det absorberande lagret är kritisk för prestandan hos polymera solceller på grund av den begränsade diffusionslängden i organiska halvledare (5-20 nm). Samtidigt måste hänsyn tas till laddningsgenerering och laddningstransport. Å ena sidan eftersträvas en mycket fin blandning med en stor andel gränssytor mellan polymer och fulleren för att generera laddningar eftersom delningen av excitoner till fria laddningar sker vid dessa gränssytor. Å andra sidan behövs en fassetparation med rena domäner av de båda materialen för att begränsa rekombination och ge fria transportvägar för laddningarna till respektive elektrod. I detta arbete har nanostrukturen hos flera olika typer av polymerer blandade med fullerener studerats och korrelationer mellan nanostruktur och solcellsprestanda har uppvisats med flera olika mikroskopi- och spektrala mättekniker så som atomkraftsmikroskopi, transmissionselektronmikroskopi, röntgendiffraktion, fotoluminescens, elektroluminescens och fourier transform fotoströmsspektroskopi. Vidare presenteras metoder för att kontrollera och styra nanostrukturen för att nå hög prestanda i solceller. Valet av lösningsmedel, kemiska strukturer hos polymerer och fullener och ytegenskaper hos substrat visas kritiskt avgörande för fassetparation och prestanda.

Att enbart optimera nanostrukturen hos det absorberande lagret garanterar inte en högpresterande solcell. Utöver transportvägar till elektroderna krävs att energinivåerna hos polymerer och fullerener optimeras då motsägelsefulla villkor ställs för maximal fotoström och maximal fotospänning. En effektiv delning av excitoner och laddningstransport vid gränssytorna mellan polymer och fulleren kräver en tillräckligt stor drivkraft; den energiförlust som krävs för att överföra en laddning från polymer till fulleren. Tyvärr kommer denna energiförlust oundvikligen att reducera fotospänningen i polymera solceller. I detta arbete studeras den delikata balansen mellan optimerad fotoström och fotospänning för olika materialsystem. Energiförlusten (drivkraften) justeras genom att syntetisera en serie polymerer och kvantifieras via spektroskopimätningar med ultraviolett/synligt ljus samt elektroluminescens där rekombination vid gränssytan studeras. Drivkraftens inverkan på fotoström och fotospänning studeras via fältberoende fotoluminescens och mätningar av den interna kvantverkningsgraden. De uppnådda resultaten korrelerar med uppmätt solcellsprestanda.

Publication List

Papers INCLUDED in this thesis

Paper I

An Isoindigo-based Low Band Gap Polymer for Efficient Polymer Solar Cells with High Photo-voltage

E. G. Wang, Z. F. Ma, Z. Zhang, P. Henriksson, O. Inganäs, F. L. Zhang and M. R. Andersson
Chem. Commun., **2011**, 47, 4908-4910

Paper II

An Easily Accessible Isoindigo-Based Polymer for High-Performance Polymer Solar Cells

E. G. Wang, Z. F. Ma, Z. Zhang, P. Henriksson, O. Inganäs, F. L. Zhang and M. R. Andersson
J. Am. Chem. Soc., **2011**, 133, 14244-14247

Paper III

Enhance Performance of Organic Solar Cells Based on An Isoindigo-based Copolymer by Balancing Absorption and Miscibility of Electron Acceptor

Z. F. Ma, E. G. Wang, K. Vandewal, M. R. Andersson and F. L. Zhang
Appl. Phys. Lett., **2011**, 99, 143302

Paper IV

Synthesis and Characterization of Benzodithiophene–Isoindigo Polymers for Solar Cells

Z. F. Ma, E. G. Wang, M. E. Jarvid, P. Henriksson, O. Inganäs, F. L. Zhang and M. R. Andersson
J. Mater. Chem., **2012**, 22, 2306-2014

Paper V

Influences of Surface Roughness of ZnO Electron Transport Layer on the Photovoltaic Performance of Organic Inverted Solar Cells

Z. F. Ma, Z. Tang, E. G. Wang, M. R. Andersson, O. Inganäs and F. L. Zhang
J. Phys. Chem. C, **2012**, 116, 24462-24468

Paper VI

Quantification of Quantum Efficiency and Energy Losses in Low Bandgap Polymer:Fullerene Solar Cells with High Open-Circuit Voltage

K. Vandewal*, Z. F. Ma*, J. Bergqvist, Z. Tang, E. G. Wang, P. Henriksson, K. Tvingstedt, M. R. Andersson, F. L. Zhang and O. Inganäs
Adv. Funct. Mater., **2012**, 22, 3480-3490

(*Co-first author)

Paper VII

Structure-Property Relationships of Oligothiophene-Isoindigo Polymers for Efficient Bulk-Heterojunction Solar Cells

Z. F. Ma, W. J. Sun, S. Himmelberger, K. Vandewal, Z. Tang, J. Bergqvist, A. Salleo, J. W. Andreasen, O. Inganäs, M. R. Andersson, C. Müller, F. L. Zhang and E. G. Wang
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Author's contributions to the papers Included in this thesis:

- Paper I** All of the experimental work and the writing related to device fabrication and characterization.
- Paper II** All of the experimental work and the writing related to device fabrication and characterization.
- Paper III** All of the experimental work and the first draft of the manuscript.
- Paper IV** All of the experimental work related to device fabrication and characterization and the most part of writing.
- Paper V** All of the experimental work and the writing.
- Paper VI** Most part of the experimental work and part of the writing.
- Paper VII** Most part of the experimental work and the writing.

Papers NOT INCLUDED in this thesis

Paper VIII

A Facile Method to Enhance Photovoltaic Performance of Benzodithiophene-Isoindigo Polymers by Inserting Bithiophene Spacer

Z. F. Ma, D. F. Dang, Z. Tang, D. Gedefaw, J. Bergqvist, W. G. Zhu, W. Mammo, M. R. Andersson, O. Inganäs, F. L. Zhang and E. G. Wang
Submitted, **2013**

Paper IX

An Alternating D-A₁-D-A₂ Copolymer Containing Two Acceptors for Efficient Polymer Solar Cells

W. J. Sun, Z. F. Ma, D. F. Dang, W. G. Zhu, M. R. Andersson, F. L. Zhang and E. G. Wang
J. Mater. Chem. A, **2013**, *1*, 11141-11144

Paper X

Semi-Transparent Tandem Organic Solar Cells with 90% Internal Quantum Efficiency

Z. Tang, Z. George, Z. F. Ma, J. Bergqvist, K. Tvingstedt, K. Vandewal, E. G. Wang, L. M. Andersson, M. R. Andersson, F. L. Zhang and O. Inganäs
Adv. Energy Mater., **2012**, *2*, 1467-1476

Paper XI

Conjugated Polymers with Polar Side Chains in Bulk-heterojunction Solar Cell Devices

D. A. Gedefaw, Y. Zhou, Z. F. Ma, Z. Genene, S. Hellström, F. L. Zhang, W. Mammo, O. Inganäs and M. R. Andersson

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Paper XII

Conformational Disorder Enhances Solubility and Photovoltaic Performance of a Thiophene–Quinoxaline Copolymer

E. G. Wang, J. Bergqvist, K. Vandewal, Z. F. Ma, L. T. Hou, A. Lundin, S. Himmelberger, A. Salleo, C. Müller, O. Inganäs, F. L. Zhang and M. R. Andersson

Adv. Energy Mater., **2013**, *3*, 806-814

Paper XIII

A Triphenylamine-based Four-armed Molecule for Solution-processed Organic Solar Cells with High Photo-voltage

Q. Hou, Y. Q. Chen, H. Y. Zhen, Z. F. Ma, W. B. Hong, G. Shi and F. L. Zhang

J. Mater. Chem. A, **2013**, *1*, 4937-4940

Paper XIV

Side-Chain Architectures of 2,7-Carbazole and Quinoxaline-Based Polymers for Efficient Polymer Solar Cells

E. G. Wang, L. T. Hou, Z. Q. Wang, Z. F. Ma, S. Hellstrom, W. L. Zhuang, F. L. Zhang, O. Inganäs and M. R. Andersson

Macromolecules, **2011**, *44*, 2067-2073

Paper XV

9-Alkylidene-9H-Fluorene-Containing Polymer for High-Efficiency Polymer Solar Cells

C. Du, C. H. Li, W. W. Li, X. Chen, Z. S. Bo, C. Veit, Z. F. Ma, U. Wuerfel, H. F. Zhu, W. P. Hu and F. L. Zhang

Macromolecules, **2011**, *44*, 7617-762

Abbreviations and List of Symbols

PV	Photovoltaic
Si	Silicon
J-V curve	Current density-voltage curve
AM1.5G	Air Mass 1.5 Global
PCE	Power conversion efficiency
J_{sc}	Short-circuit current density
V_{oc}	Open-circuit voltage
FF	Fill factor
EQE	External quantum efficiency
IQE	Internal quantum efficiency
IPCE	Incident photon-to-electron conversion efficiency
TMM	Transfer matrix model
PEDOT:PSS	Poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate)
E_g	Energy bandgap
LUMO	The lowest unoccupied molecular orbital
HOMO	The highest occupied molecular orbital
TQ1	Poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl]
P3HT	Poly(3-hexylthiophene-2,5-diyl)
MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
PTI-1/P1TI	Poly[<i>N,N'</i> -bis(2-hexyldecyl)isoindigo-6,6'-diyl-alt-terthiophene -2,5-diyl]
P3TI	Poly[<i>N,N'</i> -bis(2-hexyldecyl)isoindigo-6,6'-diyl-alt-3,3''-dioctyl-2,2':5',2''-thiophene-5,5''-diyl]
P5TI	Poly[<i>N,N'</i> -bis(2-hexyldecyl)isoindigo-6,6'-diyl-alt-3,3''',3''',4'-tetraoctyl-2,2':5',2''':5'',2''':5''',2''''-quinquethiophene-5,5''''-diyl]
P6TI	Poly[<i>N,N'</i> -bis(2-hexyldecyl)isoindigo-6,6'-diyl-alt-3,3''',3''',4'-tetraoctyl-2,2':5',2''':5'',2''':5''',2''''-sexithiophene-5,5''''-diyl]
PSC	Polymer solar cell
BHJ	Bulk-heterojunction
D/A	Donor/Acceptor
PC₆₁BM	[6,6]-phenyl C ₆₁ butyric acid methyl ester
PC₇₁BM	[6,6]-phenyl C ₇₁ butyric acid methyl ester
ITO	Indium-tin-oxide
LiF	Lithium fluoride
CT	Charge transfer
AFM	Atomic Force Microscopy
TEM	Transmission electron microscopy
GIXRD	Grazing Incidence X-ray Diffraction
PL	Photoluminescence
EL	Electroluminescence
FTPS	Fourier-transform photocurrent spectroscopy

RMS	Root mean square
CF	Chloroform
CB	Chlorobenzene
oDCB	1,2-dichlorobenzene
DIO	1,8-diiodooctane
ZnO	Zinc Oxide
α	Absorption coefficient
q	The elementary charge
ϵ_0	Vacuum dielectric constant
ϵ_r	Relative dielectric constant
T	Absolute temperature
k	Boltzmann constant
φ_p	AM 1.5 solar radiation photon flux
A_{abs}	Absorption of the BHJ active layer in PSCs
R	Reflection of the solar cell
A_{para}	Parasitic electrode absorption of the solar cell
E_{D^*}	Energy of polymer exciton
E_{CT}	Energy of CT states
ϕ_{BB}^T	Black body photon flux
σ	Absorption cross section
d	Thickness of the active layer in PSCs
EQE_{EL}	External quantum efficiency of electroluminescence
J_{inj}	Injected current density
J_0	Dark saturation current density
J_{ph}	Photogenerated current density

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Chapter 1. Introduction

Summary: In this chapter, the history of photovoltaic energy conversion is briefly presented. Definitions of the performance parameters and standard characterization techniques for solar cells are introduced. The bulk-heterojunction concept and the general working principle of polymer solar cells are discussed. The aim and outline of the thesis are also given.

1.1. Solar energy and solar cells

Solar energy is the energy from the sun. The total solar energy reaching the Earth per year is about 3 850 000 exajoules (EJ), which is over 8, 000 times compared with the annual energy consumption of mankind.¹ Solar energy is abundant, green, and sustainable. It is the origin of most of the energy resources that are currently used. Exploring solar energy with photovoltaic (PV) technologies can provide not only a solution to the rapid growing energy needs of mankind, but also a way to alleviate the environmental and climate problems induced by burning fossil fuels.

PV technologies can convert solar energy into electricity by using PV cells (solar cells) constructed with semiconducting materials. The first practical solar cell based on a Si (silicon) p-n junction was fabricated by Daryl Chapin et al. in 1954 at Bell Laboratories. This solar cell exhibited a power conversion efficiency of $\sim 6\%$.² Since then, solar cell technology has been rapidly developing in both academia and industry. Today, the power conversion efficiencies of the best single junction and multi-junction solar cells reach 28.8% and 37.9%, respectively.³ For commercial mono-crystalline inorganic solar cells, the power conversion efficiency is $\sim 22\%$.⁴ From 1995 to 2012, the installed PV capacity has increased from 0.6 Gigawatts (GW) to 100 GW.⁵ (Figure 1-1)

Figure 1-1. The installed PV capacity from 1995 to 2012 in the world. (From Renewables 2013, Global Status Report)

1.2. Characterization of solar cells

The power from a solar cell, dissipating in an external resistive load is a product of current and voltage. Thus the performance of the solar cell depends not only on the illumination

power, but also on the load. A standard method to characterize the performance of a solar cell is to perform current-voltage (I - V) measurement under a standard illumination condition: Air Mass (AM) 1.5G with an intensity of 100 mW/cm^2 . The applied voltage sweep simulates different resistors and the resulting I - V curve is plotted, as in Figure 1-2(b). The power extracted from a solar cell can also be plotted as a function of voltage, as shown in Figure 1-2(a). The maximum power of the solar cell is indicated in the figure. The current and voltage at which the maximum power is obtained are defined as I_{max} and V_{max} . The power conversion efficiency (PCE) of a solar cell is defined as the ratio between the maximum power of the solar cell and the power of the incoming photons. There are three additional parameters that are defined for further analysis of the performance of a solar cell. The first parameter is the open-circuit voltage (V_{oc}), which is the maximum voltage available from a solar cell. It is defined as the generated potential difference between the two electrodes of the solar cell under open-circuit condition. The second parameter is the short-circuit current (I_{sc}), which refers to the flowing current of the solar cell under short-circuit condition. Considering the active area of the solar cell, the short-circuit current density (J_{sc}) is commonly used in academia. Another parameter defined as a kind of quality factor is the fill factor (FF) which is calculated via Equation 1-1:

$$FF = \frac{P_{\text{max}}}{J_{\text{sc}}V_{\text{oc}}} = \frac{I_{\text{max}}V_{\text{max}}}{J_{\text{sc}}V_{\text{oc}}} \quad (1-1)$$

The PCE of a solar cell can thus be expressed as:

$$PCE = \frac{P_{\text{max}}}{P_{\text{in}}} = FF \times \frac{J_{\text{sc}} \times V_{\text{oc}}}{P_{\text{in}}} \quad (1-2)$$

Figure 1-2. (a) P - V and (b) I - V curve of a solar cell. The maximum power point (MPP or P_{max}) generated by the solar cell is indicated. The corresponding V_{max} and I_{max} and also the V_{oc} and the I_{sc} are indicated.

Two other commonly used terms in the field of PV are the external quantum efficiency (EQE) and internal quantum efficiency (IQE). The EQE, also known as the incidence photon-to-electron conversion efficiency (IPCE), is a spectral quantity defined as the ratio between the number of extracted electrons (N_{el}^{out}) and the number of incident photons (N_{ph}^{in}):

$$EQE(E) = \frac{N_{el}^{out}(E)}{N_{ph}^{in}(E)} \quad (1-3)$$

An EQE(E) depends on the photon energy (E) and optical property of absorbing material in a solar cell, and can be related to the J_{sc} of the solar cell under the AM1.5 illumination via Equation 1-4:

$$J_{sc} = \int \varphi_p(E) EQE(E) dE \quad (1-4)$$

where $\varphi_p(E)$ is the photon flux of AM1.5 solar radiation.

IQE is also a spectral quantity and it is defined as the ratio between the number of extracted electrons (N_{el}^{out}) and the number of absorbed photons in the photoactive layer (N_{ph}^{abs}), as shown in Equation 1-5:

$$IQE(E) = \frac{N_{el}^{out}(E)}{N_{ph}^{abs}(E)} \quad (1-5)$$

Because N_{ph}^{abs} can be associated with N_{ph}^{in} through the absorption of the active layer (A), the IQE can be calculated by Equation 1-6:

$$IQE(E) = \frac{EQE(E)}{A(E)} \quad (1-6)$$

where:

$$A(E) = 1 - R(E) - A_{para}(E) \quad (1-7)$$

Here, $R(E)$ is the reflection of the opaque solar cell. $A_{para}(E)$ is the parasitic electrode absorption of the solar cell, which is often calculated using a transfer matrix model (TMM).⁶ The IQE of the solar cell is the product of charge generation efficiency (η_{gene}), free charge carrier transport efficiency (η_{tran}) and charge carrier collection efficiency (η_{col}). It is related to the internal electric losses.

1.3. Polymer solar cells and bulk-heterojunction concept

Today, silicon based inorganic solar cells dominate the PV market. However, due to the high production cost, installation cost and complicated fabrication processes of inorganic solar cells, the market share of solar energy is less than 0.1% of the total energy conversion in the world.⁷ Thus, there is a need for inexpensive solar cells for low cost energy conversion. As a potentially cheap and roll-to-roll printable alternative, organic solar cells based on organic semiconductors are attracting more and more attention. These organic semiconductors can be dye molecules, small molecules or polymers. The main focus of this thesis is on solar cells that use polymers as their active semiconductors and photo-absorbers. This particular topic of research has been under active investigation for the past few decades.

1.3.1. Conjugated polymers

Conjugated polymers are polymers with π -electron-rich systems. They possess appropriate optical and electronic properties for optoelectrics due to their delocalized π -electrons. However, the electrical conductivity of neat conjugated polymers is so low that applications of conjugated polymers in optoelectronic devices are limited. In 1970s, Shirakawa, MacDiarmid and Heeger found that doping improved the conductivity of the conjugated polymer poly(acetylene) (Figure 1-3). This led to a revolution in the field of organic electronics.⁸ PEDOT:PSS (poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate)) (Figure 1-3), is an example of a doped conjugated polymer which is widely used as an electrode in many organic electronic devices.^{9,10}

Figure 1-3. Chemical structures of poly(acetylene) and PEDOT:PSS.

The conjugated polymers used as semiconductors in organic solar cells are undoped. The energy band gap (E_g) for a conjugated polymer is defined as the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular

orbital (LUMO). Conjugated polymers used as photo-absorbers in solar cells, have relatively high absorption coefficients (α) compared with inorganic semiconductors like Si with indirect band gap (Figure 1-4). A thin film ($\sim 1\mu\text{m}$) of a conjugated polymer can absorb most of the photons from the sun with the energy in the absorption band of the polymer. At the beginning, the most studied conjugated polymers in organic solar cells are MEH-PPV (Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]) and P3HT (Poly(3-hexylthiophene)). Their chemical structures are shown in Figure 1-5. However, the large band gaps of these polymers limit the absorption of photons from the sun.^{11,12} In order to broaden the absorption spectrum, conjugated polymers with alternating electron-rich (donor) segments and electron-deficient (acceptor) segments were developed.^{13,14} In the so called D-A-D conjugated polymers, the absorption spectrum can be extended to the near infrared region by the help of intramolecule charge transfer (ICT).¹⁵ Moreover, the D-A-D structure is beneficial for the transport of charge carriers along the conjugated polymer chains.^{16,17} All the polymers used in this thesis have alternating D-A-D structures. Their chemical structures are given in Figure 1-5.

Figure 1-4. The absorption coefficient spectra for Silicon (red) and one of conjugated polymers P3TI (blue) used in this thesis. The AM 1.5 solar radiation spectrum (black) is also given in this figure as a reference.

Figure 1-5. Chemical structures of P3HT, MEH-PPV and other conjugated polymers studied in this thesis.

1.3.2. Polymer solar cells

The first polymer solar cell (PSC), referred to as a single layer solar cell, was presented by Weinberger et al. in 1982, who fabricated it by sandwiching polyacetylene between two metallic conductors (Figure 1-6(a)).¹⁸ After absorbing light, electron-hole pairs or excitons are created in the solar cell. Because of the low dielectric constant of organic materials, the Coulomb interaction between the electron and the hole in the photogenerated exciton is strong, as described in Equation 1-8:

$$F = \frac{q^2}{4\pi\epsilon_0\epsilon_r r^2} \quad (1-8)$$

where, F is the Coulomb force, q is the elementary charge, ϵ_0 is the vacuum dielectric constant, ϵ_r is the relative dielectric constant of the material and r is the distance between the electron and the hole. In the presence of strong Coulomb interactions, the electric field induced in the semiconductor by the different work functions of the two metallic electrodes is not large enough to efficiently separate the photo-generated excitons. That is why the performance of the single layer polymer solar cell was low.¹⁹

Figure 1-6. Polymer solar cells constructed with three different active layer structures: (a) single layer (b) bilayer and (c) bulk-heterojunction.

A real breakthrough came in 1986, when C.W Tang introduced a bilayer heterojunction concept into organic solar cells. In this work, copper phthalocyanine and a perylene tetracarboxylic derivative were used as active materials and $\sim 1\%$ PCE was delivered.²⁰ The first bilayer polymer solar cell fabricated using MEH-PPV and C_{60} was reported by N. S. Sariciftci et al. in 1993.²¹ The bilayer solar cell was fabricated by sandwiching two organic layers (Figure 1-6(b)), one being an electron donor layer and the other being an electron acceptor layer, in between two metallic electrodes. The energy offset between the LUMO levels of the two organic materials facilitated exciton dissociation at the interface between the two organic layers, thus improving the performance of organic solar cells. The energy levels of the donor and the acceptor in the bilayer solar cell need to be well designed for efficient exciton dissociation. The LUMO offset needs to be large enough to provide sufficient energetic driving force for electrons transferring from the donor to the acceptor. However, it cannot be too large as it reduces the chemical potential (related to the photovoltage) inside a bilayer solar cell created by the photo excitation. The voltage of a solar cell is limited by the energy lost during the charge transfer process. The HOMO levels of the donor and the acceptor also need to be well adjusted to prevent energy transfer/exciton transfer to occur at the Donor/Acceptor (D/A) interface. A major problem in bilayer polymer solar cells is the short diffusion length of excitons in organic semiconductors (5-20 nm)²²⁻²⁴. In order to absorb enough light, the polymer donor layer must be sufficiently thick (~ 100 -200 nm). As a result, most generated excitons, which are

located further to D/A interfaces than the exciton diffusion length, would recombine before reaching the interface.

In order to solve the problem of inefficient exciton dissociation due to the short exciton diffusion length in the bilayer PSC, the bulk-heterojunction (BHJ) (Figure 1-6(c)) concept was introduced. Here, the active layer of a BHJ solar cell is a blend of an electron donor (often a polymer) and an electron acceptor (often a fullerene derivative). Ideally, the D/A interface area is maximized in the BHJ active layer. Then all photogenerated excitons can diffuse to a D/A interface within their lifetime. And efficient exciton dissociation can occur when the energy offset between the LUMO levels of the two organic materials is sufficient. Yu et al. reported the first BHJ PSC with a *PCE* of 2.9% under monochromatic light illumination by mixing MEH-PPV with C60 in the active layer in 1995.²⁵ Today, BHJ is the dominant active layer geometry in PSCs. The *PCEs* of the most efficient single and multi-junction PSCs constructed based on BHJ concept are 9.2% and 10.6%, respectively.^{26,27} Solar cells studied in this thesis are also based on the BHJ concept using conjugated polymers as electron donors and fullerene derivatives as electron acceptors.

Depending on the polarity of the bottom electrode, BHJ solar cells can be divided into two different categories: conventional and inverted. As shown in Figure 1-7, solar cells constructed with the bottom electrode as an anode (here ITO) are often referred to as conventional solar cells; and solar cells with a bottom electrode as a cathode (here ZnO modified ITO) are called inverted.²⁸ Both types are investigated in this thesis.

Figure 1-7. The device architecture of the BHJ solar cells used in this thesis: conventional device (top) and inverted device (bottom).

1.3.3. Acceptors for BHJ polymer solar cells

In BHJ PSCs, the electron donors are conjugated semiconducting polymers as previously mentioned. The electron acceptors can be polymers or small molecules with higher electron affinity and large energy offset with the LUMO levels of polymers to provide sufficient driving force for charge transfer. The soluble derivatives of C60: [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) and C70: [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) are the most commonly used acceptors due to their high electron mobilities, good solubilities in most organic solvents and desired energy levels. PC₆₁BM and PC₇₁BM were first synthesized by Hummelen et al. and Wienk et al., respectively.^{29,30} Their chemical structures and absorption spectra are given in Figure 1-8. Compared with PC₆₁BM, PC₇₁BM has a stronger absorption in the visible range, thus could contribute more to the total absorption of the photoactive layer.^{30,31} However, PC₆₁BM has better miscibility with some conjugated polymers than that of PC₇₁BM. Thus active layers based on PC₆₁BM could have better morphology. Sometimes, the trade-off between acceptor absorption and miscibility with conjugated polymers needs to be considered, to optimize the performance of BHJ solar cells.³²

Figure 1-8. Molecular structures and absorption spectra of PC₆₁BM and PC₇₁BM.

1.3.4. Working principle of BHJ polymer solar cells

The basic working principle of a BHJ solar cell is often described in five steps (Figure 1-9):

- Light absorption and exciton generation in the active layer (step 1)
- Diffusion of the photogenerated excitons to the D/A interfaces (step 2)
- Charge transfer to form an excited charge transfer complex at the D/A interfaces (step 3)
- Separation of charge transfer complex, and generation of free charge carriers (step 4)
- Charge carrier transport to electrodes and collection (step 5)

Figure 1-9. The scheme of cross-section of a PSC and working principle for a polymer-fullerene BHJ solar cell.

The maximum number of photons absorbed in the active layer is determined by the absorption band of the active materials. In order to absorb more photons, the absorption spectrum of a polymer needs to be as broad as possible and thus the optical band gap should be as small as possible. However, a smaller band gap leads to lower photovoltage due to thermalization of the excitons excited by high energy photons. This trade-off leads to the optimal band gap of single-junction solar cells to be 1.1~1.3 eV for the theoretical maximum *PCE* of 33%. The limit of *PCE* is known as Shockley-Queisser limit,³³ and can be broken by tandem or multi-junction solar cells. To reach this limit, absorption of the photons with energy larger than the band gap of the active layer needs to be complete.

Thus, the active layer of organic solar cells needs to be thick. However, the low mobility of organic semiconductors causes significant recombination losses in the PSC with a thick active layer (> 100-200 nm). So, efficient light incoupling into a thin active layer is needed for organic solar cells. This is a tricky task. Anti-reflection coating, optical spacer, diffraction gratings etc. are the typical structures employed to improve light harvesting in organic solar cells.

For the BHJ solar cell with conventional architecture, reducing thickness of the active layer for a better constructive interference of light in the active layer may also help. TMM can be used to predict the dissipation of energy in the active layer of organic solar cells. Thus the maximum photocurrent generation can be predicted for solar cells with different active layer thicknesses by assuming a 100% IQE.³⁴

The maximum photocurrent generation predicted with TMM can sometimes be obtained when the internal electric field across the solar cell is sufficiently high, but sometimes can never be obtained due to recombination losses. Recombination of photogenerated excitons found dominantly in single layer and bilayer solar cells also exists in BHJ solar cells. Too large phase separation between the donor and acceptor in the BHJ active layer is most likely the reason for such a loss, due to the fact that excitons can often diffuse only for 5-20 nm.

Even if the excitons can diffuse to a D/A interface, the dissociated electrons and holes are still weakly bound with Coulomb force at the D/A interface. This state is known as the charge-transfer (CT) state and the binding energy for the CT excitons is roughly 0.1-0.4 eV.³⁵⁻³⁸ The geminate CT state recombination has been shown to be the dominant recombination mechanism that limits solar cell performance for different active material systems.³⁹ A commonly used model to describe the CT recombination is the Onsager-Braun-Model, although its validity is still under debate:^{40,41}

$$k_{diss} = \frac{3\beta}{4\pi a^3} \exp\left(\frac{E_B}{kT}\right) \left(1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \dots\right) \quad (1-9)$$

where k_{diss} is the dissociation rate, β is the bimolecular recombination constant, a is the initial distance of the bound electron-hole pair at D/A interface, E_B is the Coulomb binding energy, k is the Boltzmann constant, T is the absolute temperature and b equals:

$$b = e^3 E / 8\pi \epsilon_0 <\epsilon> (k_B T)^2 \quad (1-10)$$

Where, $<\epsilon>$ is the spatially averaged relative dielectric constant. This term describes the relative enhancement of the CT dissociation rate with changing of the electric field E .

From Equation 1-9, one can find that CT recombination is field dependent.

Free charge carriers are generated after the CT exciton separation. They drift towards the electrodes in the presence of an electric field and then contribute to the photocurrent. However, recombination of the free charge carriers can occur during the transport process, which limits the photocurrent. This is called bimolecular recombination. The rate depends on the probability of an electron finding a hole in the active layer. Free charge carrier recombination can also be trap-assisted. The rate then depends on the probability of an electron or a hole to fall to a trap. Surface recombination, which can also limit the photocurrent generation, is due to diffusion of minority carriers towards the wrong electrodes. All recombination losses of the free charge carriers in organic solar cells are field dependent.

1.4. Aim and outline of the thesis

The active layer morphology and the energetic driving force for charge transfer or exciton dissociation are two critical issues for BHJ PSCs. Both of them play crucial roles in determining the performance of the polymer BHJ solar cell. To improve the performance of PSCs, deeply understanding the two issues should be aimed. They are also the focus of the thesis.

In chapter 2, the role of the BHJ active layer morphology in determining the performance of PSCs is presented. Different techniques used to characterize the active layer morphology are introduced. The factors influencing the morphology of BHJ active layers are discussed.

In chapter 3, the energy losses during the charge transfer at the D/A interface in BHJ PSCs are discussed. Energy losses, defined by the energy difference between the energy of CT states and the energy of the polymer exciton, which provide the energetic driving force for exciton dissociation and charge transfer, are introduced. The trade-off between quantum efficiency and the potential loss in BHJ solar cells induced by the energy loss is also discussed.

Chapter 4 summarizes the papers included in this thesis.

An outlook is given in chapter 5.

References and notes are listed in chapter 6.

Chapter 2. Morphology of the Active Layer in BHJ Polymer Solar cells

Summary: In this chapter, the effects of morphology of a BHJ active layer on performance of PSCs are discussed. Methods and tools employed in the characterization of the active layer morphology are introduced. The last section of this chapter deals with the factors that determine the formation of the active layer nanoscale morphology.

2.1. Desired active layer morphology for BHJ polymer solar cells

The nanomorphology of BHJ active layer results from the interaction between the electron donor and electron acceptor. As aforementioned, the bound electron-hole pairs generated in organic BHJ solar cells have high possibility to be split at the D/A interface. Due to the fact that exciton diffusion length in organic semiconductors is short (5-20 nm), active layer morphology is important for optimization of the performance of PSCs. Phase separation between the electron donor and the electron acceptor should not be significantly larger than exciton diffusion length, as the D/A interface area and thus the exciton dissociation efficiency will be severely limited. On the other hand, a too homogenous mixture of donor and acceptor hampers transport of the photogenerated free charge carriers and causes recombination losses.^{42,43} The desired nanomorphology of the active layer for an efficient organic BHJ PSC requires formation of continuous interpenetrating networks and separated donor and acceptor phases with domain sizes comparable with the exciton diffusion length. Thus excitons generated in any spot in the BHJ active layer can always diffuse to a D/A interface to dissociate into free electrons and holes which can be efficiently transported to their respective electrodes before recombining with each other. A schematic representation of an ideal BHJ active layer with a desired nanomorphology is shown in Figure 2-1.

Figure 2-1. The desired nanoscale morphology of the BHJ active layers for efficient PSCs.

2.2. Nanomorphology related losses

As briefly mentioned in the previous section, the nanoscale morphology of the active layer determines both exciton dissociation efficiency and charge carrier transport property of the PSC. In general, IQE of the solar cell is closely related to the nanomorphology of the active

layer. The morphology related losses are often internal electric losses. IQE of the solar cell can be written as a product of the efficiencies of different processes in a working solar cell:⁴⁴

$$IQE = \eta_{gene}\eta_{tran}\eta_{col} \quad (2 - 1)$$

where η_{gene} is the exciton dissociation efficiency, η_{tran} is the efficiency of the free charge transport and η_{col} is the efficiency of the charge carrier collection at electrodes. η_{diss} directly depends on the morphology of the active layer, or the domain size of the donor and acceptor phases in the active layer. Large scale phase separation could induce the exciton to recombine before reaching a D/A interface. Under such conditions, J_{sc} provided by the solar cell would be limited. Free charge carrier transport in PSCs can be limited by recombination losses originated from either the existence of many dead ends in one of the phases or too insufficient vertical transporting pathways that reduce effective charge carrier mobilities. This kind of bimolecular recombination losses could inhibit the J_{sc} , V_{oc} and FF of the solar cell. Accumulation of undesired phases at the active layer/electrode interfaces i.e. donor phases at the cathode, or acceptor phases at the anode, could reduce the efficiency of charge carrier collection due to the induced extraction barriers. The performance of the solar cell thus could be limited.

Therefore, optimizing the nanoscale morphology of the BHJ active layer to reduce recombination losses is essential for efficient PSCs. To optimize nanomorphology, controlling the degree of phase separation of the electron donor and acceptor and formation of percolation pathways during the film formation process should be the goal.

2.3. Characterization of the BHJ active layer morphology

There are many methods and tools used to characterize and investigate the nanoscale morphology of the BHJ active layer. In 1996, Heeger and Yang studied the nanoscale morphology of the BHJ active layer containing a polymer donor and a C60 acceptor using transmission electron microscopy (TEM).⁴⁵ Later on, atomic force microscopy (AFM), X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS), etc. were all reported to be valuable for characterizing morphology of the BHJ active layer.^{46–49} Spectroscopic methods including photoluminescence (PL), electroluminescence (EL) and IQE spectrum are also useful in addressing nanomorphology related studies.^{44,49,50} In this section, we review the commonly used methods for analyzing the morphology of BHJ active layer.

2.3.1. Microscopic Methods

Atomic force microscopy (AFM): AFM is a well-developed imaging tool that can be used to characterize surface topography of specimens.^{51,52} It is extensively employed to characterize the morphology of the BHJ active layer of organic solar cells.^{46,53} A sample for AFM

measurements can be easily prepared and can even be an actual solar cell. Therefore, the results from the AFM accurately reflect the surface property of the active layer of the solar cell.

When AFM is used to study morphology of the soft BHJ active layer of PSCs, a noncontact mode (tapping-mode as shown in Figure 2-2) that prevents damaging the specimen surface should be used. In tapping-mode AFM, a small tip connected to an oscillating cantilever scans about 5-40 nm above the sample surface at a fixed frequency. The change of the topography of the sample leads to a change of the Van der Waals force between tip and the sample surface that disturbs the oscillation frequency of the cantilever and thus the probe scanning process. The cantilever then has to be lifted or lowered to keep the distance between the tip and the sample surface constant and thus the oscillation frequency of the cantilever constant. The movement of the cantilever is recorded to represent the topography of the sample being examined.

Figure 2-2. A scheme of the tip and sample surface interaction in tapping mode (left) and a picture of the AFM instrument used in this thesis (right).

For studying the morphology of the active layer of a solar cell with AFM, the measurements need to be done on either real solar cells or samples prepared following the same procedures as that of the solar cell, but without a top electrode. Usually, a height image and a phase image are simultaneously obtained as output results of the AFM measurement. The height image gives information about the sample surface topography and also the root mean square (RMS) roughness value, which can be related to the nanoscale morphology of the BHJ active layer. AFM images obtained from two active layers of PTI-1:PC₆₁BM are used as examples here (Figure 2-3(a) and (b)). The existence of large domains (~ 200 nm) in the left image indicates the large phase separation between the two components in the BHJ active layer. In the right-hand AFM image, domains were removed after morphology

optimization via introducing a processing additive 1,8-diiodooctane (DIO) into the active system (*cf.* section 2.4.1 below). The phase image arose from the phase difference between the driving signal and the actual oscillation of the cantilever. It can reflect the variations of materials composition, though it cannot provide species identification.

Figure 2-3. The examples of AFM images for active layers of PTI-1:PC₆₁BM (a) without (w/o) DIO and (b) with DIO. (c) and (d) are TEM images corresponding to (a) and (b), respectively.

However, the application of the AFM in morphology investigation is limited because it can only examine surface topography, not bulk property of the sample. Other techniques, such as transmission electron microscopy, are required to study the bulk morphology of the BHJ active layer.

Transmission electron microscopy (TEM): TEM is a microscopic technique that uses electron beams with a short wavelength to detect micro or nanostructures of the specimens. The contrast of TEM images is formed in a transmission mode, thus the samples for TEM need to be thin. A sketch of TEM is shown in Figure 2-4. TEM was used to study the morphology of mixed MEH-PPV with C60 BHJ active layer in 1996 by Yang and Heeger. Phase separation between MEH-PPV and C60 were distinguished after C60 was selectively dissolved using decahydronaphthalene.⁴⁵ Since then, bright-field TEM is commonly used in PSCs to study the active layer morphology with different polymer and fullerene derivatives. The specimen

of the active layer for TEM is prepared on top of PEDOT:PSS film. When the sample is immersed in water, PEDOT:PSS layer will dissolve in water and the active layer will float on the water. Then the floating active layer is easy to move on copper grids. The dark part of the TEM image usually represents the PCBM phase or PCBM-rich phase, since the PCBM has higher proton density. The light part is from polymer phase or polymer-rich phase, due to the smaller proton density. Examples of TEM images obtained from PTI-1:PC₆₁BM active layers with coarse morphology (w/o DIO) and optimized morphology (with DIO) are given in Figure 2-3(c) and (d), respectively.

Figure 2-4. A sketch of the TEM with the electron pathways and important features (left) and a picture of the TEM instrument used in this thesis (right).

Recently, electron tomography (ET) has been developed to study the 3-dimensional (3D) morphology of the active layer.⁵⁴ In this technique, TEM images are collected at various tilt angles and the images thus obtained are reconstructed with the help of software to obtain the final 3D ET image. However, this technique is not used in this thesis. Not all the active layers in PSCs can be studied by TEM or ET due to the limitation of the sample preparation. For example, the active layer of the inverted PSC is spin-coated on top of the buffer layer cannot be selectively dissolved in some solvent. Thus, the application of TEM is limited, and more tools and methods are needed to characterize the nanoscale morphology of the BHJ active layer in PSCs.

2.3.2. Spectroscopic methods

Grazing-Incidence X-ray Diffraction (GIXRD): GIXRD is a powerful tool for studying the nano-crystallites of the thin film samples. In fact, the self-organization of most polymers in the active layers cannot form perfect crystallites as observed in some inorganic materials and only some ordered nano-structures can be detected. This kind of ordered nano-structure can be regarded as crystallites in polymer films and the corresponding crystal parameters are shown in Figure 2-5.^{55,56} Here the semi-crystalline polymer P3HT is used as the example. The (h00) corresponds to the direction of lamella stacking of the polymer, (0k0) is the reflection due to the π - π stacking of the polymer and (00l) corresponds to the direction of polymer backbone chain. While the charge carrier can transport easily along the directions of (0k0)/ π - π stacking and (00l)/polymer backbone chain, it becomes difficult along (h00)/lamellar direction due to the insulating alkyl side chains.

Figure 2-5. (a) Schematic of the ordered nanostructure of conjugated polymers. When XRD is used, the (0k0) reflections are due to π - π stacking, (h00) is the direction of lamellar packing and (00l) reflections are due to polymer main chain. (b) 2D GIXRD patterns obtained from PTI-1:PC₆₁BM blend film.

Charge carriers in the active layer of the PSCs are transported along the out-of-plane direction. Thus the stronger intensities of the signal obtained in (0k0) and (00l) are favorable to the charge carrier transport to the electrodes. Usually, the intensity of the signal obtained from polymer films by GIXRD is much weaker than that of inorganic crystal films. So X-ray

supported by synchrotron radiation is used as the x-ray source. All the GIXRD data in this thesis were collected by our co-workers at the Stanford Synchrotron Radiation Lightsource (SSRL) on the beam line of 11-3. The GIXRD pattern obtained from PTI-1:PC₆₁BM film is given in Figure 2-5(b) as an example.

Photoluminescence (PL) and Photoluminescence quantum efficiency (PLQE): PL detects radiative emission from photo excited state of a sample. When PL is used to investigate the BHJ active layer morphology in PSCs, the quenching of pure polymer emission upon mixing with an electron acceptor is recorded. The PL quenching efficiency (ΔPL) is defined as:

$$1 - \frac{PL_{blend}}{PL_{polymer}} \quad (2 - 2)$$

where PL_{blend} is the recorded PL counts from polymer-fullerene blend film, $PL_{polymer}$ is the PL counts obtained from pure polymer film. ΔPL is proportional to the efficiency of the polymer exciton dissociation in polymer:fullerene BHJ system. If the driving force for charge transfer is sufficient, ΔPL is determined by the nanoscale morphology of the active layer: a fine nanomorphology would induce high ΔPL . The two active layers of PTI-1:PC₆₁BM with coarse morphology and with optimized morphology mentioned in the last section are also used as examples here. PL spectra obtained from the two active layers and together with a film of pure PTI-1 are plotted in Figure 2-6(a). Compared with PL spectrum of pure PTI-1, PTI-1:PC₆₁BM with optimized morphology shows more quenching than that of PTI-1:PC₆₁BM with coarse morphology, thus, more efficient exciton dissociation occurs in the active layer of PTI-1:PC₆₁BM.

Here, ΔPL is qualitatively determined. For quantitative measurements of the PL of samples, the PLQE method was employed.⁵⁷ In this thesis, all the PL spectra are collected with an EMCCD detector and the schematic drawing is given in Figure 2-6(b). A red laser (CW He-Ne 632 nm) is used as the exciting light source. PLQE is collected with the same set up (Figure 2-6(b)), but with one more external integrating sphere.

Figure 2-6. (a) PL spectra for pure PTI-1 film (square), PTI-1:PC₆₁BM film w/o DIO (solid circle) and PTI-1:PC₆₁BM film with DIO (open circle). (b) Schematic drawing of setup for PL emission measurement.

Electroluminescence (EL): The EL measurement can also be employed to study the morphology of the active layer. EL is an optoelectronic phenomenon in which the specimen emits lights through radiative recombination when an electric current or an electric field is applied. When an external voltage is applied to a PV device the injected electrons and holes in the device must recombine. The energy of the emission depends on which states are populated by the charge carriers in the PSC. The most populated states in a BHJ solar cell are the lowest energy states, i.e. charge transfer states.^{50,58} As a result, the injected carriers primarily recombine at the D/A interfaces. EL is thus a useful method to detect the existence and the energy of CT states in PSC.^{50,59} However, if the phase separation between the donor and the acceptor in the PSC is large, recombination can occur in the pure phases. In this case, the ratio between the CT emission and the pure polymer/PCBM emission can be used to analyze the active layer nanomorphology of the PSC. Less CT emission or more polymer/PCBM emission indicates more pure polymer/PCBM matrixes in the PSC or a large phase separation.^{60,61} It should be noted that even when the pure phase EL emission is higher compared with the CT emission, it does not necessarily mean that the recombination is dominantly from the pure phase because the recombination of carriers in pure polymers has a higher probability for radiative recombination than that of CT recombination.^{50,62,63} The EL spectrum was recorded with the same set as used for the PL measurement, but with an external applied voltage on the sample instead of a laser pump.

Internal quantum efficiency (IQE): IQE spectrum can be used to study morphology of the active layer of a solar cell.⁴⁴ Normally, IQE of a solar cell is not expected to be wavelength dependent above the band gap of the active layer. However, for organic BHJ solar cells, excitation can occur either in the polymer phase or in the PCBM phase. When the size of the polymer phase and the size of the PCBM phase are different, incomplete exciton dissociation may exist in one of the phases. In this case, IQE can be expressed as:

$$IQE = \frac{\eta_{col}(\lambda)(\eta_D Abs_D(\lambda) + \eta_A Abs_A(\lambda))}{Abs_D(\lambda) + Abs_A(\lambda)} \quad (2 - 3)$$

Where, Abs_D and Abs_A are the optical contributions of the donor and the acceptor to the active layer absorption spectrum, respectively, and η_D and η_A are the exciton harvesting efficiencies of the donor and the acceptor, respectively. Clearly, due to the fact that absorption in the polymer phase differs from the absorption in PCBM phases, IQE in this case can be wavelength dependent when the exciton dissociation efficiencies in the two phases are different. In general, it has been shown that a larger polymer phase would lead to an inefficient carrier generation in the polymer phase, thus IQE for the photons absorbed in the polymer phase would be limited, while IQE for the photons absorbed in PCBM stays higher when there are no additional losses.

2.4. Determinants for active layer morphology

There are many factors affecting morphology of active layers via controlling the kinetic formation process of films, such as chemical structure of the donor or the acceptor, D/A blending ratio and concentrations of the solution, processing solvents, substrate surface energy, and post-treatment of the active layer film (thermal annealing or solvent annealing).

2.4.1. Processing solvents and mixed solvents

One advantage of PSCs is that they can be fabricated via solution process. The solubilities of polymers vary in different organic solvents. Therefore, the interaction between polymer and PCBM in solution or during the film drying process will be different when different solvents are used which could result in different active layer morphologies.^{49,64–67} Hummelen's group studied the influence of processing solvents on performance of the PSCs and the morphology of the active layer based on MEH-PPV:PCBM (1:4). Three different solvents xylene, chlorobenzene (CB) and *ortho*-dichlorobenzene (oDCB) were used in their experiments. Their experimental results indicated that the solar cell fabricated from CB solution has the best performance due to the optimal active layer morphology with desired phase separation and PCBM crystal packing.⁶⁵ In this thesis, we also observed that the performance of the PTI-1:PC₇₁BM solar cell was enhanced from 0.4% to 1.7% when the

processing solvent chloroform (CF) was replaced with oDCB. Our experimental results also indicated that the enhanced *PCE* was mainly due to the more homogeneous mixture of the donor and the acceptor in the active layer leading to the observed improvement in J_{sc} and *FF* of the solar cells. AFM images of the active layers based on PTI-1:PC₇₁BM spin-coated from CF and oDCB are compared in Figure 2-7. Clearly, the active layer of PTI-1:PC₇₁BM spin-coated from oDCB solution have a smaller nanoscale phase separation. Therefore more D/A interfaces and continuous pathways promote the exciton dissociation.

Morphology of the BHJ active layer in PSCs can be tuned by using mixed solvents with different boiling points.^{68,69} Zhang et al. found that the J_{sc} of the APFO-3:PC₆₁BM solar cell could be significantly improved from 3.2 to 5.2 mA/cm² by adding a small amount of guest solvent CB into a CF solution due to the formation of a more homogeneous nanomorphology.⁶⁸ J. Peet et al. reported that the efficiency of the PCPDTBT:PC₇₁BM solar cell was improved from 2.8% to 5.5% by using alkane dithiols as processing additive solvent.⁷⁰ According to their study, this was also due to the more beneficial active layer morphology. Since then, processing solvent additives are widely used for the nanoscale morphological modification.^{71–73} Lee et al. proposed two criteria for choosing the processing solvent additive to optimize the nanomorphology of the BHJ active layer: one is that the polymer and the fullerene derivative should show selective solubility in the solvent additive; the other is the boiling point of the solvent additive, which should be higher than that of host solvent.⁷⁴ The role of the processing solvent additive 1,8-diiodooctane (DIO) in forming the nanoscale morphology of the active layer was studied by Peet et al..⁷⁵ For the active layer based on P3HT:PC₆₁BM, the processing solvent additive (DIO) extended the drying time of the wet film during spin-coating which gave P3HT more time to crystallize. On the other hand, the processing solvent additive was found to improve the morphology of the active layer based on PCPDTBT:PC₇₁BM via improving the aggregation of the polymer.⁷⁵

In our work, the processing solvent additive DIO was used to improve the nanoscale morphology of the isoindigo-based polymer:PCBM active layers. The *PCE* of the PTI-1:PC₇₁BM solar cell was improved from 1.7% to 3.0% by adding 2.5% DIO (by volume) into the oDCB solution. The improved *PCE* was mainly contributed by the improved J_{sc} of the solar cell induced by more homogeneous phase separation in the active layer as indicated in the AFM images shown in Figure 2-7. *FF* of the solar cell was improved upon using DIO, which should be attributed to the more percolated networks for carrier transport in the active layer. However, the V_{oc} of the solar cell was reduced from 0.92 to 0.89 V after adding DIO into the active solution. This phenomenon was also observed in other studies, and it was ascribed to the fact that there were more ordered polymer domains in the active layers after adding the processing additive.^{70,73,76}

Figure 2-7. AFM images ($5\ \mu\text{m} \times 5\ \mu\text{m}$) for the PTI-1:PC₇₁BM active layers spin-coated from (a) CF, (b) *o*DCB and (c) *o*DCB mixed with DIO (2.5% by Volume) solutions.

2.4.2. The chemical structures of fullerene acceptors or polymer donors

Structural factors can be related to nanomorphology of BHJ active layers in PSCs. Different fullerene acceptors/polymer donors have different solubilities in organic solvents and different miscibilities with polymer donors/fullerene acceptors.

PC₆₁BM and PC₇₁BM are the most commonly used fullerene acceptors in BHJ solar cells. The two fullerene acceptors have more or less the same HOMO and LUMO energy levels. Today, most of the high efficiency BHJ PSCs use PC₇₁BM as the acceptor, mainly due to the higher absorption coefficient of PC₇₁BM in the visible region (Figure 1-8). Absorption in PC₇₁BM can contribute additionally to the generation of the photocurrent in the solar cells.³⁰ However, for some polymers, the better miscibility with PC₆₁BM compared with that of PC₇₁BM allows the formation of better active layer morphology and more efficient exciton dissociation. For these polymers, the trade-off between absorption and exciton dissociation needs to be taken into account when optimizing performance of the solar cell. For instance, the isoindigo-based polymer PTI-1 was found to have better miscibility with PC₆₁BM than PC₇₁BM. Therefore, better mixture of donor and acceptor in the PTI-1:PC₆₁BM active layer was obtained. *PCE* of the PTI-1:PC₆₁BM PSC was higher compared with that of the PTI-1:PC₇₁BM solar cell even though the absorption in the PTI-1:PC₇₁BM solar cell was better.^{30,32}

Compared with fullerene acceptors, the chemical structures of the donors are more varied. They can be changed by varying the building blocks or adjusting the side-chain architectures of the building block. Polymers with different chemical structures could induce different

interaction with acceptors and different polymer packing in the active layer. So, the relationship between polymer and active layer morphologies is complex. In order to simplify investigating the relationship between the chemical structures of polymers and active layer morphology, the chemical structures of polymers were finely adjusted.^{77–79} How the side-chain architecture of the thiophene-quinoxaline (TQ) alternating copolymers affect the active layer morphology was reported by Wang et al.⁸⁰ The influence on the active layer morphology of the spacer group was studied in Ref.73.

2.4.3. Surface properties of the bottom buffer layer

Active layer of a solar cell has to be deposited on top of a bottom electrode, anode or cathode. Thus the surface property of the substrate plays an important role in determining morphology of the active layer.^{81,82} In the PSC with conventional geometry, PEDOT:PSS is used as the bottom anode buffer layer. Peng et al. reported that the performance of the P3HT:PC₆₁BM BHJ solar cell could be improved from 3.4% to 4.7% after the PEDOT:PSS buffer layer was modified with the organic solvent 2-propanol.⁸³ The enhanced *PCE*, according to the authors, was attributed to the more beneficial surface morphology of the PEDOT:PSS buffer layer, which in turn improved the active layer morphology of the solar cell and led to an improved J_{sc} .⁸³ In the inverted PSCs, ZnO is a commonly used bottom cathode buffer layer. Self-assembled monolayer, polymer interlayer, as well as UV-Ozone treatment, plasma treatment of the interfacial layer have been used to modify the surface property of the ZnO layer to improve the performance of the inverted solar cells.^{82,84,85}

In this thesis, the surface roughness of the ZnO layer was tuned to modify surface properties of the interfacial buffer layer, as the surface roughness was correlated to the surface energy of the ZnO layer.⁶¹ In our work, three ZnO films with different surface roughnesses were prepared via chemical method and their AFM images are shown in Figure 2-8. The experimental results indicated that the inverted PSC based on the smoothest ZnO film (RMS=1.9 nm) had the best performance due to the optimized active layer nanomorphology as confirmed by EL measurement(Figure 2-9): smallest ratio between pure polymer emission and CT emission was shown by the EL spectrum of the inverted PSC based on the smoothest ZnO film.

Figure 2-8. The AFM images for the ZnO layers with RMS roughness of (a) 1.9 nm (S-film), (b) 17 nm (M-film) and (c) 48 nm (R-film).

Figure 2-9. Normalized EL spectra for the inverted PSCs based on Smoothest (S) (black line), (b) Moderate (M) (dark-gray line) and (c) Roughest (gray line) ZnO layer, normalized EL spectrum obtained from TQ1 polymer (light-gray line) is also given here as a reference.

Chapter 3. Energy losses in BHJ polymer solar cells

Summary: This chapter introduces the energy losses for charge transfer and recombination in BHJ polymer solar cells. Both energy losses are closely related to charge transfer states, the energy of which is deduced. In addition, the effects of these energy losses on the photovoltage and the photocurrent of BHJ polymer solar cells are also discussed.

3.1. Definition of energy losses in BHJ solar cells

The difference between optical band gap of the photo active layer (E_{opt}) and qV_{oc} (V_{oc} measured under 1 sun conditions) is an energy loss (ΔE) in a solar cell:

$$\Delta E = E_{opt} - qV_{oc} \quad (3-1)$$

In crystalline Si solar cells, ΔE is around 0.4-0.5 eV.⁸⁶ In BHJ organic solar cells with $E_{opt,D} < E_{opt,A}$, E_{opt} equals $E_{opt,D}$,^{87,88} which is also equal to the energy of the polymer excitons (E_{D^*}). ΔE in BHJ polymer solar cells is around 0.8-1.3 eV,⁸⁷ which is much larger than that in inorganic solar cells. ΔE increases in BHJ organic solar cells because additional energy (driving force) is needed to split strongly bound excitons into CT states before the generation of free charge carriers. The introduction of CT states allows us to rewrite Equation as:

$$\Delta E = (E_{D^*} - E_{CT}) + (E_{CT} - qV_{oc}) \quad (3-2)$$

Where, E_{D^*} is the energy of the polymer excitons (in PSCs with $E_{opt,D} < E_{opt,A}$, E_{D^*} equals E_{opt}), E_{CT} is the energy of CT states at the D/A interface. Equation 3-2 enables us to quantify energy losses in BHJ PSCs: the first term on the right-hand side represents the energy loss due to charge transfer, while the second term is the loss due to recombination. The energy losses are schematically depicted in Figure 3-1.

Figure 3-1. The scheme for energy losses in BHJ polymer solar cells with $E_{opt,D} < E_{opt,A}$.

The energy loss during charge transfer, which is also referred to as the driving force, results in the reduction of the V_{oc} of a BHJ solar cell (Figure 3-1). In order to optimize the photovoltage of BHJ PSCs, the driving force for exciton dissociation should be minimized.^{87,89} However, when the driving force is too small, exciton dissociation will be hampered and the

photocurrent generation will be limited.⁸⁹ Therefore, an appropriate driving force is critically important for an efficient PSC with high V_{oc} and high J_{sc} at the same time.^{87,89} The driving force is usually related to the difference between the LUMO energy levels of the donor and the acceptor. Empirically a driving force larger than 0.3 eV is needed for efficient exciton dissociation in organic solar cells.^{90,91} However, the driving force approximated from LUMO energy offset of the donor and the acceptor neglects the influence induced by D/A interfacial interaction.⁷³ Thus, the criterion that driving force should be larger than 0.3 eV for efficient exciton dissociation could be overestimated. For example, in our studies, a driving force as small as ~ 0.1 eV, obtained from $E_{D^*} - E_{CT}$, was found to be large enough for highly efficient exciton dissociation (IQE $\approx 87\%$).⁸⁹

The energy loss due to recombination of charge carriers is more complex and inevitable, which involve both radiative and non-radiative recombination loss.

3.2. Energy of CT states

Both two losses in Equation 3-2 are associated with the energy of the D/A interfacial CT states. Thus, E_{CT} plays a critical role in determining the performance of the BHJ polymer solar cells. The energy of CT states will be deduced in this subsection.

According to Wurfel's generalized Planck law, the two processes of light emission and absorption are reciprocal. This indicates that a light absorbing material will always emit light. The rate of the light emission is proportional to the absorption cross section $\sigma(E)$ of the material. Therefore, the strongly absorbing molecules are always fast emitters. In organic solar cells, the relation between PV and electroluminescent actions was derived by Rau in Ref.92.

Based on the Marcus theory, the absorption cross section of the CT states at photon energy E can be described as:^{93,94}

$$\sigma(E)E = \frac{f_{\sigma}}{\sqrt{4\pi\lambda kT}} \exp\left(\frac{-(E_{CT} + \lambda - E)^2}{4\lambda kT}\right) \quad (3-3)$$

Where, k is Boltzmann constant, T is absolute temperature and f_{σ} represents the strength of the interaction between the donor and the acceptor. f_{σ} is independent of photon energy E but proportional to the square of the electronic coupling matrix element.⁹⁴ λ is a reorganization energy which is related to the CT absorption process (Figure 3-2).⁹⁵

Figure 3-2. Free-energy diagram for the ground state and lowest excited state of the charge transfer complex as a function of a generalized coordinate.

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Since the light absorption and emission are reciprocal, the emission rate I_f at photon energy E can be described as:^{93,94}

$$I_f = \frac{f_{If}}{\sqrt{4\pi\lambda kT}} \exp\left(\frac{-(E_{CT} - \lambda - E)^2}{4\lambda kT}\right) \quad (3-4)$$

where, f_{If} is also proportional to the square of the electronic coupling matrix element. Equation 3-3 and 3-4 give reduced absorption and emission spectra, respectively. The energy of the crossing of the two spectra stands for E_{CT} (Figure 3-3).

The emission spectrum of the CT states can be obtained by measuring the electroluminescent emission.^{50,63} However, the relatively low absorption coefficients (α) of the CT states due to the low oscillator strength of polymer:PCBM BHJ systems, make the CT absorption difficult to detect. Vandewal et al. found that a highly sensitive technique Fourier-transform photocurrent spectrum (FTPS) could be used to measure the PV EQE (EQE_{PV}) spectrum where the low energy CT absorption bands could be resolved.^{63,96} This technique allows for the determination of E_{CT} via EQE_{PV} in the absorption range of the charge transfer state:

$$EQE_{PV}(E) = IQE(E)A_{act} \quad (3-5)$$

Where, A_{act} is the absorption of the active layer in BHJ PSCs. The thickness of the active layer is d , the absorption coefficient of the active layer is α . A_{act} is then approximated to $\alpha 2d$ when a metal back reflector is used. Since the absorption coefficient α in the spectral region

of CT state absorption is the product of absorption cross section σ and the number of CT complexes per unit volume (N_{CTC}). Thus equation 3-5 for CT absorption can be rewritten as:

$$EQE_{PV}(E) = IQE(E)\sigma(E)N_{CTC}2d \quad (3-6)$$

Combining Equation 3-3 and 3-6, we obtain:

$$EQE_{PV} = \frac{f}{E\sqrt{4\pi\lambda kT}} \exp\left(\frac{-(E_{CT} + \lambda - E)^2}{4\lambda kT}\right) \quad (3-7)$$

Where, the prefactor f stands for $IQEN_{CTC}2df_0$. E_{CT} as well as the reorganization energy λ and the prefactor f can thus be determined by fitting the measured EQE_{PV} spectrum using Equation 3-7 (Figure 3-3).

Figure 3-3. Reduced EQE_{PV} and EL spectrum for a MDMO-PPV:PCBM 1:4 PV device. The gray curves are fits of the EQE_{PV} and EL spectra using formulas 1 and 2, using the same E_{CT} and λ values. These parameters, together with the maxima of absorption $E_{abs-max}$ and emission E_{fl-max} are indicated in the figure.

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3.3. Relation between E_{CT} and V_{oc}

To understand the fundamental limit for organic solar cells, we need to find the relation between E_{CT} and V_{oc} of the BHJ solar cell.

We start with the ideal diode equation for a solar cell in dark condition, the injected current ($J_{inj}(V)$) can be described as:

$$J_{inj}(V) = J_0 \left(\exp\left(\frac{qV}{kT}\right) - 1 \right) \quad (3 - 8)$$

In this equation, J_0 is the dark saturation current. As Rau derived in Ref.92, J_0 can be related to the electro-optical properties through the following equation:

$$J_0 = \frac{q}{EQE_{EL}} \int EQE_{PV}(E) \phi_{BB}^T(E) dE \quad (3 - 9)$$

Here, EQE_{EL} is the overall electroluminescence EQE, ϕ_{BB}^T is the black body photon flux at temperature T , and is described by:

$$\phi_{BB}^T(E) dE = \frac{2\pi}{c^3 h^3} \frac{E^2}{\exp\left(\frac{E}{kT}\right) - 1} dE \quad (3 - 10)$$

Since ϕ_{BB}^T strongly decreases with increasing photon energy, only the low energy CT part of the EQE_{PV} spectrum make contribution in Equation 3-9.⁷⁹ Thus, substituting Equation 3-7 and 3-10 into Equation 3-9, we get:

$$J_0 = \frac{q}{EQE_{EL}} f \frac{2\pi}{c^2 h^3} (E_{CT} - \lambda) \exp\left(-\frac{E_{CT}}{kT}\right) \quad (3 - 11)$$

Under illumination, the total current $J(V)$ of the PV device is the sum of photogenerated current (J_{ph}) and the injected current (J_{inj}):

$$J(V) = J_{inj} - J_{ph} = J_0 \left(\exp\left(\frac{qV}{kT}\right) - 1 \right) - J_{ph} \quad (3 - 12)$$

At open-circuit voltage, the total current $J(V)$ in the PV device equals 0 ($J(V=V_{oc})=0$). Therefore,

$$J_{inj}(V = V_{oc}) = J_0 \left(\exp\left(\frac{qV_{oc}}{kT}\right) - 1 \right) = J_{ph}(V = V_{oc}) \quad (3 - 13)$$

Rewriting Equation 3-13, and we can get:

$$V_{oc} = \frac{kT}{q} \ln \left(\frac{J_{ph}(V = V_{oc})}{J_0(V = V_{oc})} + 1 \right) \quad (3 - 14)$$

For an ideal solar cell, $J_{ph}=J_{sc}$. Combine equation 3-11 and 3-14, and we obtain:

$$V_{oc} = \frac{E_{CT}}{q} + \frac{kT}{q} \ln \left(\frac{J_{sc} c^2 h^3}{f q 2 \pi (E_{CT} - \lambda)} \right) + \frac{kT}{q} \ln(EQ E_{EL}) \quad (3-15)$$

Notably, losses due to radiative and non-radiative recombination are separately presented in Equation 3-15. It also becomes clear that V_{oc} of an organic BHJ solar cell, at first approximation, depends linearly on the temperature T and E_{CT} , and logarithmically on the illumination light intensity, which is consistent with previous reports.⁹⁷⁻⁹⁹

Vandewal et al. also studied the relationship between E_{CT} and V_{oc} for several polymer:PCBM systems and summarized their study results in Figure 3-4.^{63,80,100-102} A linear relationship between E_{CT} and V_{oc} is proposed which follows:¹⁰¹

$$V_{oc} = \frac{E_{CT}}{q} - 0.6 \text{ V} \quad (3-16)$$

Figure 3-4. The energy of CT states (E_{CT}) versus V_{oc} of polymer/fullerene solar cells.

3.4. Recombination losses

Equation 3-15 predicts that V_{oc} is determined by both radiative and non-radiative recombination of free charge carriers in the solar cell. The maximum V_{oc} is obtained when

there is no non-radiative recombination path ways. In this case, EQE_{EL} equals unity, and hence the third term on the right-hand side in Equation 3-15 is zero. The expression for V_{oc} is reduced to:

$$V_{oc} = \frac{E_{CT}}{q} + \frac{kT}{q} \ln \left(\frac{J_{sc} c^2 h^3}{f q 2\pi (E_{CT} - \lambda)} \right) \quad (3 - 17)$$

This means that even for an ideal organic solar cell, qV_{oc} is still smaller than E_{CT} due to radiative recombination loss which is represented by the second term on the right-hand side in Equation 3-15. The radiative loss depends on f and λ , which is minimized when the electric coupling between the donor and the acceptor is reduced and the reorganization energy is zero.

For BHJ polymer solar cells, the dominant recombination is, however, non-radiative.⁸⁴ Therefore, the third term in Equation 3-15 contributes more to the overall voltage loss in organic solar cells compared with that of the second term. EQE_{EL} for organic solar cells is typically 10^{-6} to 10^{-9} , which counts for a voltage loss of roughly 0.3-0.5 V.⁶² Minimizing the non-radiative recombination loss can significantly improve the performance of organic solar cells. The recombination of charge carriers at the electrode/active layer interfaces or via trap-states are non-radiative, which limit the V_{oc} . These non-radiative recombination pathways can be eliminated by carefully designing solar cell architecture and choosing proper interface materials. In spite of these advances, the non-radiative bulk recombination that limits V_{oc} of the state-of-the-art organic solar cells is still poorly understood at this stage.

Chapter 4. Summary of Papers

Summary: In this thesis, the active layer nanomorphology of the BHJ polymer-fullerene solar cells and the energy loss during charge transfer in PSCs are studied. Seven publications are included. Their introductions, motivations and mainly experimental results are summarized.

4.1. Paper I and Paper II

An Isoindigo-based Low Band gap Polymer for Efficient Polymer Solar Cells with High Photo-voltage

Ergang Wang, Zaifei Ma, Zhen Zhang, Patrik Henriksson, Olle Inganäs, Fengling Zhang and Mats R. Andersson.

Chem. Commun., **2011**, 47, 4908-4910

An Easily Accessible Isoindigo-Based Polymer for High-Performance Polymer Solar Cells

Ergang Wang, Zaifei Ma, Zhen Zhang, Patrik Henriksson, Olle Inganäs, Fengling Zhang and Mats R. Andersson.

J. Am. Chem. Soc., **2011**, 133, 14244-14247

Nanomorphology of the BHJ active layer plays an important role in determining the performance of a PSC. In these two papers, a processing solvent additive DIO was introduced to improve the performance of PSCs via optimizing the nanomorphology of active layers.

In our experiment, two polymer-fullerene active layer systems were studied. Isoindigo-containing D-A-D copolymers PTI-1 and P3TI were used as electron donor to blend with PC₇₁BM in the two active layers, respectively. After adding DIO (2.5% by volume) into oDCB solutions, the *PCEs* of PTI-1:PC₇₁BM and P3TI:PC₇₁BM solar cells with conventional architecture were respectively improved from 1.7%, 4.8% to 3.0% and 6.3%. These enhancements in *PCE* were mainly contributed by the improved J_{sc} and *FF*. Therefore, more beneficial nanomorphology of the active layer could be expected. This was confirmed by AFM measurements. Large domains existed in the active layers spin-coated from oDCB solutions which were removed after adding DIO. The more homogeneous phase separation and more interpenetration networks in the active layers spin-coated from oDCB:DIO solutions were favorable for the exciton dissociation and free charge transport, thus resulted higher J_{sc} and *FF*.

4.2. Paper III

Enhance Performance of Organic Solar Cells Based on An Isoindigo-based Copolymer by Balancing Absorption and Miscibility of Electron Acceptor

Zaifei Ma, Ergang Wang, Koen Vandewal, Mats R Andersson and Fengling Zhang, *Appl. Phys. Lett.* **2011**, 99, 143302

In the last two papers, the influences of processing solvent additive on the active layer nanomorphology were discussed. Here, the effect of acceptor selectivity on the nanomorphology of the BHJ active layers was investigated.

Two commonly used fullerene derivative acceptors PC₆₁BM and PC₇₁BM were employed to fabricate two active layers via mixing with an isoindigo-containing copolymer PTI-1. Our experimental results indicated that the performance of PTI-1:fullerene solar cell was improved from 3.0% to 4.5% when PC₇₁BM was substituted with PC₆₁BM, even though PC₇₁BM shows higher absorption coefficient in visible region than that of PC₆₁BM. According to our study, this was due to that the better miscibility between PTI-1 and PC₆₁BM resulted in more homogeneous phase separation in the active layer of PTI-1:PC₆₁BM. More efficient exciton dissociation or higher J_{sc} was thus observed in PTI-1:PC₆₁BM solar cell. So, the trade-off between the absorption and compatibility with polymer donor should be considered when selecting electron acceptor for efficient PSCs.

4.3. Paper IV

Synthesis and Characterization of Benzodithiophene–isoindigo Polymers for Solar Cells

Zaifei Ma, Ergang Wang, Markus E. Jarvid, Patrik Henriksson, Olle Inganäs, Fengling Zhang and Mats R. Andersson,

J. Mater. Chem. **2012**, 22, 2306-2014

In this paper, the association between finely adjusted polymer chemical structures and active layer morphology was investigated.

Three isoindigo-containing D-A-D copolymers PBDT-I, PBDT-TIT and PBDT-OIO were used as electron donor to build polymer-fullerene active layer systems. In the three D-A-D alternating copolymers, compared with PBDT-I (only containing alternating isoindigo and benzodithiophene segments), PBDT-TIT and PBDT-OIO respectively took thiophene and octylthiophene as spacer groups in the backbone of copolymers. The experimental results suggested that the thiophene ring made PBDT-TIT exhibit quite planar backbones, which benefited the compatibility with fullerene derivatives. So, the optimal active layer nanomorphology was obtained by PBDT-TIT:PCBM. The PBDT-TIT:PCBM solar cell with conventional architecture presented the best performance with a *PCE* of 4.22%. However, instead of thiophene, when octylthiophene was used as the spacer group, the planarity of the polymer backbones was reduced and an coarse morphology resulted in the PBDT-OIO:PCBM active layer. A low *PCE* of 1.39% was obtained by the solar cell of PBDT-OIO:PCBM.

4.4. Paper V

Influences of Surface Roughness of ZnO Electron Transport Layer on the Photovoltaic Performance of Organic Inverted Solar Cells

Zaifei Ma, Zheng Tang, Ergang Wang, Mats R. Andersson, Olle Inganäs and Fengling Zhang
J. Phys. Chem. C, 2012, 116, 24462-24468

In the last four papers, the influences of processing solvent additive and structural factors on the active layer nanomorphology and the performance of PSCs were investigated. However, all these studies were based on PSCs with conventional architecture (Glass/ITO/PEDOT:PSS /Active layer/LiF/Al), where PEDOT:PSS was used as bottom buffer layer. As the property of the substrate can be strongly associated with the morphology of the active layer on top, tuning the substrate surface property is necessary to be explored to study how the substrate surface property affects performance of the PSC.

In this work, solar cells constructed with inverted architecture (Glass/ITO/ZnO/Active layer/PEDOT:PSS/Ag) were employed. The surface energy of the ZnO layer was tuned by controlling the RMS surface roughness to investigate the influences of the ZnO surface roughness on the performance of the ZnO inverted PSCs. TQ1:PC₇₁BM was used as photo active layer and PEDOT:PSS/Ag was used as top anode. Three ZnO interfacial layers were prepared with RMS decreased from 48 nm, 17 nm to 1.9 nm. The corresponding *PCE* for the ZnO inverted PSCs were increased from 2.7% to 3.9%. According to our experimental results, the surface roughness of the ZnO interfacial layer could determine their surface energy and thus the nanoscale morphology of the active layer on top. The smoother ZnO interfacial layer could induce more beneficial nanoscale active layer morphology which assists exciton dissociation and thus J_{sc} of the inverted PSCs. This was confirmed by EL and FTPS spectra. Moreover, the rougher ZnO interfacial layer had more interfacial area between the ZnO interlayer and the active layer, which could lead to trap-assisted recombination and reduce the *FF* and V_{oc} of the solar cell.

4.5. Paper VI

Quantification of Quantum Efficiency and Energy Losses in Low Bandgap Polymer:Fullerene Solar Cells with High Open-Circuit Voltage

Koen Vandewal, Zaifei Ma, Jonas Bergqvist, Zheng Tang, Ergang Wang, Patrik Henriksson, Kristofer Tvingstedt, Mats R. Andersson, Fengling Zhang, and Olle Inganäs

Adv. Funct. Mater., **2012**, 22, 3480-3490

Energy loss during the charge transfer in BHJ solar cells can also be strongly related to the device performance. Minimizing the driving force of polymer:PCBM system can optimize the V_{oc} of PSCs. But on the other hand, a large enough driving force is needed for efficient exciton dissociation in the PSC.

In this paper, the impact of energy lost due to electron transfer from the polymeric donor to PCBM acceptor on the J_{sc} and V_{oc} is investigated. Two isoindigo-containing copolymers (PTI-1 and P3TI) were employed to construct polymer:PCBM solar cell with conventional device architecture. The experimental results indicated that even though PTI-1 and P3TI have quite similar chemical structures, similar optical and electrochemical properties, solar cells based on these two copolymers are very different in V_{oc} and IQE: PTI-1:PCBM (weight ratio 2:3) solar cell had a higher V_{oc} (0.91 V), but lower IQE ($\sim 45\%$). However, P3TI:PCBM (weight ratio 2:3) based solar cell showed a lower V_{oc} (0.7 V), but higher IQE ($\sim 87\%$). According to our investigation, the underlying reason for these differences in V_{oc} and IQE is that the driving forces ($E_D^* - E_{CT}$) for the two polymer:PCBM systems were different. It was notable that almost no driving force (~ 0.0 eV) could be observed in PTI-1:PCBM system using FTPS and EL. Thus, a higher V_{oc} (0.91 V), but a lower IQE was obtained by PTI-1:PCBM solar cell. Moreover, ~ 0.1 eV driving force made P3TI:PCBM solar cell show a much lower V_{oc} , but a significantly higher IQE ($\sim 87\%$). The active layer morphologies studied by TEM and field dependent PL indicated that the lower IQE of P3TI:PCBM was indeed due to its small driving force, but not the too coarse morphology.

This paper demonstrated a possibility to get high quantum efficiency and a decent V_{oc} at the same time via optimizing the driving force of the BHJ polymer:PCBM system.

4.6. Paper VII

Structure-Property Relationships of Oligothiophene-Isoindigo Polymers for Efficient Bulk-Heterojunction Solar Cells

Zaifei Ma, Wenjun Sun, Scott Himmelberger, Koen Vandewal, Zheng Tang, Jonas Bergqvist, Alberto Salleo, Jens Wenzel Andreasen, Olle Inganäs, Mats R. Andersson, Christian Müller, Fengling Zhang and Ergang Wang

Accepted as publication in *Energy Environ. Sci.*, **2013**

As already discussed, the driving force of the BHJ system is important for PSC via balancing the quantum efficiency and potential loss of the device. Here, the driving force of the polymer-PCBM systems was fine adjusted in a small region (0.0 – 0.15 eV) through tuning the chemical structures of polymers. How the driving force and active layer morphology were related to the performance of the solar cells was also investigated.

In this work, four oligothiophene-isoindigo copolymers ($PnTI$) were used. The number of the thiophene rings in the oligothiophene group increased from 1, 3, 5 to 6, and corresponding four copolymers were named as $P1TI$, $P3TI$, $P5TI$ and $P6TI$. The PV property of all the four copolymers was characterized by polymer-fullerene solar cell with conventional architecture. From the experimental results, it could be found that the V_{oc} of the optimized $PnTI$:PCBM solar cells decreased with increasing number of thiophene rings (n). This was attributed to the increasing driving force during the electron transfer in the solar cells with n increased from 1 to 6. On the other hand, $P1TI$:PCBM solar cell showed the lowest J_{sc} , which was due to small driving force (energy loss) and the exciton recombination at D/A interface. However, J_{sc} of the solar cell containing $PnTI$:PCBM decreased when n was changed from 3 to 6, even the driving force increased. This was ascribed to the large polymer domains excited in the active layers of $P5TI$:PCBM and $P6TI$:PCBM, which made the exciton recombine afore reaching D/A interface and thus limited the J_{sc} of the solar cells. The existence of large polymer domains in $P5TI$:PCBM and $P6TI$:PCBM was confirmed by GIXRD and IQE measurements. All the $PnTI$:PCBM solar cells had quite similar FF as expected from the mobility measurement. In this work, $P3TI$:PCBM contained solar cell showed the highest PCE of 6.9% with the highest J_{sc} and a decent V_{oc} .

Chapter 5. Outlook

The PCE of the PSCs made in lab-scale by spin-coating has been up to 9-10% due to extensive research in the last few decades. The high efficiencies make PSCs commercialization possible. The lab-scale studies not only provide us insight understanding of the operation principle of PSCs, but also helped us identify the important factors, such as active layer morphology, the driving force of a BHJ system etc, to determine the performance of PSCs. However, PSCs commercialized as a low-cost energy conversion should be produced in large-scale using roll-to-roll process instead of spin-coating. Moving from lab-scale to large-scale, the processing conditions of PSCs will be utterly altered. Thus the performance of PSCs will be different.

Roll-to-roll printing is entirely different from spin-coating, and uses non-toxic solvent for the mass production of PSCs at low price are required. When it comes to large-scale manufacturing, the conditions required to achieve the desirable morphology of the active layers will need to be optimized. The methods frequently used to improve the morphology of the active layer of PSCs in labs, such as using processing additives, post-annealing, etc., will not work for the printed PSCs in industrial scale. Alternative approaches will be needed to optimize the performance of large-scale PSCs. The existing methods for detecting morphology of the BHJ active layer in PSCs, such as AFM, TEM, PL, EL etc. will also have to be changed or modified for large-scale production.

The low *PCE* of large-scale PSCs is still the bottleneck for their commercialization. An understanding of the morphology of roll-to-roll printed active layers is critical in improving the performance of the large-scale PSCs. However, studies toward this direction are still limited. Therefore, it will need to be the focus of research in the near future.

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