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Studying Morphology Formation and Charge Separation in Organic Solar Cells

Yanfeng Liu

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During the course of research underlying the thesis, Yanfeng Liu was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden.

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Abstract

We are currently living in the era of automation and artificial intelligence, which requires more energy than ever before. Meanwhile, the reduction of carbon footprint is needed for keeping the environment sustainable. Exploring green energy is crucial. Solar power is one of the green energy sources. The apparatus that converts solar energy to electricity is a solar cell. Organic solar cells (OSCs), employing organic materials absorbing solar radiation and converting to electricity have got extensive attention in the last decades due to their unique advantages like lightweight, semi-transparency, and potential industrialization.

In most cases, an OSC composes of two different organic semiconductors as electron donor and acceptor to form a photoactive layer with a bulk heterojunction (BHJ) structure, and sandwiched between the electron and hole transport layers and then two electrodes. The morphology of the BHJ plays a crucial role in the device's performance, and it is a result of a complicated interplay between donor, acceptor, and solvent during the film drying from a solution. Thus, *in-situ* monitoring the film drying during solvent evaporation could deepen understanding of the mechanism of the morphology formation. A versatile multiple spectroscopic setup is assembled for this purpose, which can record laser scattering, steady-state photoluminescence (PL), time-resolved photoluminescence (TRPL), and white-light absorption during film formation.

By comparing the drying dynamics of three different blend systems with their corresponding pristine films, we find that the blend film formation and its final morphology are more dominated by the component with a higher molecular weight. Different PL and TRPL quenching profiles between fullerene- and non-fullerene-based systems provide hints about different donor-acceptor interactions. Moreover, with the help of TRPL, the relative change of quantum yield during film formation can be calculated. Besides, this setup is also proved suitable for studying mechanisms behind device optimization processes, like the usage of solvent additives.

One of the unique features of OSCs based on non-fullerene acceptors is the highly efficient hole transfer from the acceptor to the donor, sometimes even under zero or negative energetic offsets. However, in these cases the mechanism of hole transfer has not been fully understood.

By studying hole transfer at the donor:acceptor interface in different material systems and device configurations, we highlight the role of electric field on the charge separation of OSCs when energetic offsets are not enough.

To achieve better device performance, engineering the photoelectric properties of interfacial layers is equally essential. A good interfacial layer can facilitate carrier extraction and reduce carrier recombination. We demonstrate that adding MXenes into the PEDOT:PSS can increase the conductivity of this composite hole transport layer, without sacrificing its optical transparency and work function.

Populärvetenskaplig sammanfattning

Vi lever för närvarande i en tid av automatisering och artificiell intelligens. Vi vill ha smartphones med lång batteritid och datorer med högre datorkraft. Kort sagt, vi kräver mer energi än någonsin tidigare. Samtidigt kräver vi också att koldioxidavtrycket ska minska. Användningen av grön energi är ett bra sätt att gå tillväga. När det gäller grön energi är solenergi nyckeln till en ren energi framtid.

Lösningen, alltså den anordning som kan omvandla solenergi till elektricitet, kallas solceller. Organiska solceller (OSC), har lovande fördelar som låg vikt, halvtransparent och potential att snabbt produceras industriellt, har fått stor uppmärksamhet den senaste tiden. OSC använder organiska halvledare i form av små molekyler och polymerer som det aktiva skiktet för att omvandla solenergi. Det aktiva skiktet är inklämt mellan ett elektron- och ett håltransportskikt samt två elektroder för att bilda en fungerande OSC.

Det aktiva skiktet av OSC är en blandningsfilm som innehåller två olika organiska halvledare som elektrondonator och acceptor. Morfologin för detta blandningsaktiva lager är avgörande för solcellens prestanda, och den bildas huvudsakligen under lösningsmedelsindunstning vid en lösningsmedelsbaserad process. Under arbetet med den här avhandlingen, har en metod baserad på flera spektroskopier utvecklats för att studera filmbildningsprocessen i realtid. Metoden gör det möjligt att förstå donator-acceptor-interaktioner i olika typer av filmblandningar och att studera mekanismer bakom optimeringsprocesser.

Genom att studera hålöverföringsprocessen vid donator:acceptor-gränsskiktet i olika materialsystem och solcellskonfigurationer, belyser vi rollen som det elektriska fältet har vid laddningsseparering i OSC:er med oegensamma energiska förskjutningar.

För att uppnå bättre enhetsprestanda är optimering av de fotoelektriska egenskaperna lika viktiga för samtliga lager. Det ideala elektron- och håltransportskiktet bör ha en lämpligt utträdesarbete, hög transparens och tillräcklig konduktivitet. Vi har visat att MXener kan adderas till i PEDOT:PSS för att öka konduktiviteten hos detta komposithåltransportlager, utan att kompromissa dess optiska transparens och utträdesarbete.

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Yanfeng Liu
October 2021 at Linköping University

Papers included in this thesis

Paper 1

Mo_{1.33}C MXene-Assisted PEDOT:PSS Hole Transport Layer for High-Performance Bulk-Heterojunction Polymer Solar Cells

Yanfeng Liu, Quanzheng Tao, Yingzhi Jin, Xianjie Liu, Hengda Sun, Ahmed El Ghazaly, Simone Fabiano, Zaifang Li,* Jie Luo, Johanna Rosen,* and Fengling Zhang*

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Paper 2

Revealing Effect of Solvent Additive in All-Polymer Solar Cells with *in-situ* Spectroscopic Characterization

Yanfeng Liu, Qunping Fan, Heng Liu, Yingzhi Jin, Ergang Wang* Xinhui Lu,* Olle Inganäs, and Fengling Zhang*

In Manuscript

Paper 3

In-situ Optical Studies on Morphology Formation in Organic Photovoltaic Blends

Yanfeng Liu, Aymen Yangui, Rui Zhang, Alexander Kiligaridis, Ellen Moons,* Feng Gao, Olle Inganäs,* Ivan G. Scheblykin,* and Fengling Zhang*

Small Methods **2021**, 2100585.

Paper 4

Electric Field Facilitating Hole Transfer in Non-Fullerene Organic Solar Cells with a Negative HOMO Offset

Yanfeng Liu, Jianyun Zhang, Guanqing Zhou, Feng Liu, Xiaozhang Zhu,* and Fengling Zhang*

The Journal of Physical Chemistry C **2020**, 124, 15132-15139.

Contributions to included papers

Paper 1

Conducted all the measurements and data analyses, wrote the manuscript. MXene was synthesized by Quanzheng Tao (Linköping University).

Paper 2

Conducted all the measurements and data analyses, except for the GIXS. Wrote the manuscript. Polymer PF5-Y5 was synthesized by Qunping Fan (Chalmers University).

Paper 3

Conducted all the measurements and data analyses, wrote the manuscript. TRPL measurements were conducted together with Aymen Yanguai (Lund University).

Paper 4

Conducted all the measurements and data analyses, except for the transient absorption. Wrote the manuscript. Materials for active layer were synthesized by Jianyun Zhang (Chinese Academy of Sciences).

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3. Suppressing Co-Crystallization of Halogenated Non-Fullerene Acceptors for Thermally Stable Ternary Solar Cells

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5. Molecular Orientation of Polymer Acceptor Dominates Open-Circuit Voltage Losses in All-Polymer Solar Cells

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10. Laminated Free Standing PEDOT:PSS Electrode for Solution Processed Integrated Photocapacitors via Hydrogen-Bond Interaction

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Table of Contents

Chapter 1 Background	1
1.1 Photovoltaic effect and solar cells	1
1.2 Characteristics of solar cells	1
1.2.1 Current density–voltage characteristics.....	1
1.2.2 External and internal quantum efficiency	4
Chapter 2 Organic solar cells.....	7
2.1 Basics of organic semiconductor	7
2.1.1 Conjugated polymers and molecules.....	7
2.1.2 Energetics of organic semiconductors	9
2.1.3 Optical transitions of organic semiconductors	12
2.1.4 Architecture of organic solar cells.....	14
2.1.5 Interfacial layers.....	14
2.2 Working principle of organic solar cells.....	16
2.2.1 Exciton generation and dissociation.....	16
2.2.2 Charge transport and collection	17
2.2.3 Recombination	19
2.3 Concept of bulk heterojunction.....	19
Chapter 3 Morphology of bulk heterojunction.....	23
3.1 Film formation and phase separation	23
3.2 Coating methods.....	25
3.2.1 Spin coating.....	25
3.2.2 Blade coating	26
3.3 Deposition conditions	29
3.3.1 Solvents	29
3.3.2 Solvent additives.....	30
3.3.4 Solvent vapor and thermal annealing.....	32
3.4 <i>In-situ</i> characterization of solution drying	32
3.4.1 Laser scattering.....	32
3.4.2 Absorption	33
3.4.3 Photoluminescence.....	34
3.4.4 Time-resolved photoluminescence.....	36
3.5 <i>Ex-situ</i> characterization of film morphology	39
3.5.1 Atomic force microscopy.....	39
3.5.2 Grazing-incidence X-ray scattering.....	40
Chapter 4 Charge separation in bulk heterojunction.....	43
4.1 Charge transfer and exciton dissociation	43
4.2 Interfacial dipole at the donor:acceptor interface	43
4.3 Disorder of organic semiconductors	44

4.4 Delocalization of charge carriers	44
4.5 Electric field.....	45
Chapter 5 Voltage losses in organic solar cells	47
5.1 Detailed balance theory.....	47
5.2 Shockley-Queisser limit.....	48
5.3 Quantification of voltage losses	49
Chapter 6 Summary and outlook.....	53
References	55

Chapter 1 Background

1.1 Photovoltaic effect and solar cells

The photovoltaic effect, discovered by French scientist Edmond Becquerel in 1839, refers to the phenomenon that incident light causes a potential difference between different parts of a non-uniform semiconductor.¹ It is a one-step conversion that generates electric potential from light energy. Light can be seen as particles with a certain amount of energy (photons). When light is absorbed by an absorber and the energies of photons are sufficient to overcome the potential barrier for excitation, the excited electron can jump to higher energy states within the materials. If there exists an extra driving force, for example, two electrodes with different electronic properties, the excited electrons could be drifted to one of the electrodes, thus a voltage would be generated between these electrodes, and the resulting device is a solar cell.

In 1945, Daryl Chapin, Calvin Fuller, and Gerald Pearson at Bell Labs in the United States first reported the monocrystalline silicon solar cell.² With the power conversion efficiency (PCE) of 6% under sunlight, this invention opened up the possibilities of utilizing sunlight as a reliable power source in situations when fuel is hard to be delivered, from remote villages to satellites in space.

1.2 Characteristics of solar cells

1.2.1 Current density–voltage characteristics

The current density–voltage (J - V) measurement is one of the most practical techniques to characterize the output power and calculate the maximum PCE of solar cells.³ It is performed by recording the photo-generated current density J with a function of applied voltages V under defined illumination (usually under the AM 1.5G solar spectrum for standard PCE calculation).

Figure 1.1. The J - V characteristics of a solar cell under AM 1.5G illumination (orange) and in the dark (dash grey). The corresponding power-voltage characteristic is plotted as the blue curve.

A typical J - V curve is shown in **Figure 1.1**. Without illumination, a solar cell shows a much higher current under forward bias ($V > 0$) than under reversed bias ($V < 0$), which is also called the rectification effect. As indicated in **Figure 1.1**, under illumination, this characteristic is shifted to the lower quadrants, and the operating window of the solar cell is in the fourth quadrant.⁴ For every operation point in this quadrant, a positive voltage correlates to a current density, thus the output power density P of the solar cell is given by $P = J \times V$. The intersection of the J - V curve with the J axis gives the short-circuit current density J_{SC} whereas the intersection with the V axis specifies the open-circuit voltage V_{OC} . The point at which the product of J and V reaches its maximum (MPP, the maximum power point of a solar cell) can be given as a function of J_{SC} and V_{OC} by defining the fill factor FF :

$$FF = \frac{J_{MPP} V_{MPP}}{J_{SC} V_{OC}} = \frac{P_{MPP}}{J_{SC} V_{OC}}, \quad (1.1)$$

where P_{MPP} is the maximum power density of a solar cell. In **Figure 1.1** the FF can also be graphically understood as the area ratio that the blue rectangle makes up of the orange rectangle. Thus, the PCE can be calculated by

$$\text{PCE} = \frac{P_{\text{MPP}}}{P_{\text{S}}} = \frac{J_{\text{SC}} V_{\text{OC}} FF}{P_{\text{S}}}, \quad (1.2)$$

where P_{S} is the incident light power density. When a solar cell is operated under the standard AM 1.5G illumination, $P_{\text{S}} = 1000 \text{ W m}^{-2}$.

Figure 1.2. Equivalent circuit of an ideal solar cell.

In the ideal case, a solar cell is modeled as a current generator in parallel with a diode, generating two opposing currents under illumination (**Figure 1.2**): J_{SC} delivered by the light, and the dark current density J_{dark} developed by the potential difference between the terminals. For an ideal diode, the J_{dark} is

$$J_{\text{dark}}(V) = J_0 \left(e^{\frac{qV}{kT}} - 1 \right), \quad (1.3)$$

where J_0 is the saturation dark current density of the diode, q is the electronic charge, k is Boltzmann's constant, and T is the temperature in Kelvin.

With both J_{SC} and J_0 , the net current density in the solar cell can be calculated as

$$J(V) = J_{\text{SC}} - J_{\text{dark}}(V) = J_{\text{SC}} - J_0 \left(e^{\frac{qV}{kT}} - 1 \right). \quad (1.4)$$

Based on this equation, the J - V curve of an ideal solar cell under illumination can be constructed. When $J = 0$, the short circuit current and the dark current exactly cancel out, the solar cell reaches its open circuit condition, thus the V_{OC} can be deduced from the following equation:

$$V_{\text{OC}} = \frac{kT}{q} \ln \left(\frac{J_{\text{SC}}}{J_0} + 1 \right). \quad (1.5)$$

1.2.2 External and internal quantum efficiency

The external quantum efficiency (EQE), also known as the incident photon-to-current conversion efficiency (IPCE), is another parameter used to evaluate the performance of solar cells. It indicates the ratio between the number of electrons that reach the external circuit and the number of photons that is incident in the solar cell at a certain wavelength:

$$EQE = \frac{N_e(\lambda)}{N_{ph}(\lambda)}, \quad (1.6)$$

where $N_e(\lambda)$ is the electron flux density in the external circuit, $N_{ph}(\lambda)$ is the incident flux density, λ is the wavelength. As shown in **Figure 1.3**, the J_{SC} is the integration of EQE, as the following equation:

$$J_{SC} = q \int EQE(E) f_s(E) dE, \quad (1.7)$$

where $f_s(E)$ is the spectral photon flux, and the relation between photon energy E and wavelength λ is

$$E = \frac{hc}{\lambda}, \quad (1.8)$$

where h is Planck's constant, c is the speed of light.

Figure 1.3. The EQE curve (orange) and the corresponding integrated J_{SC} (blue) of a solar cell.

While the internal quantum efficiency (IQE), on the other hand, indicates the number of electrons liberated by incident photons that are actually absorbed by the photoactive layer.

$$IQE = \frac{N_e(\lambda)}{N_{ph}^{ab}(\lambda)} , \quad (1.9)$$

where $N_{ph}^{ab}(\lambda)$ is the absorbed photon flux density. The conversion between EQE and IQE is given as $EQE = A \times IQE$, where A is the absorbance of the active layer in the device.

Chapter 2 Organic solar cells

2.1 Basics of organic semiconductor

The term organic solar cell (OSC) implies the materials that construct the photoactive layers are organic semiconductors, which are mainly made up of carbon and hydrogen atoms. Thus, the electric properties of organic semiconductors are significantly different from traditional inorganic semiconductors, such as silicon or gallium arsenide.

2.1.1 Conjugated polymers and molecules

The performance of solar cells highly depends on the choice of light-absorbing materials as the photoactive layers. In OSCs, the photoactive layers are mainly constructed by the conjugated polymers and/or monomers (often referred to as small molecules) as the electron donor and acceptor materials (similar to p-type and n-type inorganic semiconductors). Conjugated materials featuring a backbone of alternating single and double bonds result in π -conjugation by the overlap of the π -orbitals, giving rise to a continuum of energy states called a band structure.

For most of the conjugated materials for OSCs, aromatic rings usually form their conjugated structure, like in the most iconic homopolymer poly(3-hexylthiophene-2,5-diyl) (P3HT) and its derivatives.⁵⁻⁶ With decent thermal stability and hole mobility, P3HT soon became one of the most common electron donors in OSCs and persisted in its prominence for a decade.⁷⁻⁹ In the meantime, researchers also realized that the relatively high bandgap of P3HT and the resulting low absorption range started to hinder the further enhancement of the performance of OSCs.

Alternating electron-donor (D) units and electron-acceptor (A) units within one polymer backbone has been recognized as an effective method in narrowing the bandgap and improving the light-harvesting capability of the polymer by promoting the intramolecular charge transfer (ICT) along the polymer chain.¹⁰⁻¹³ For example, one of the representative D-A copolymer PBDB-T,¹⁴ which is composed of 2-alkylthiophene-substituted benzo [1,2-b:4,5-b'] dithiophene (BDT) as the D unit and 1,3-bis(thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo-[1,2-c:4,5-c']dithiophene-4,8-dione (BDD) as the A unit, exhibits much broader absorption than

P3HT. **Figure 2.1** shows the chemical structures of P3HT and PBDB-T, as well as their absorption spectra.

Figure 2.1 (a) Chemical structures of P3HT and D-A copolymer PBDB-T. (b) Normalized absorption spectra of PBDB-T and P3HT dissolved in chlorobenzene (CB).

Conjugated polymers can be used not only as electron donor materials but also as acceptors in OSCs.¹⁵⁻¹⁶ One of the most widely used polymeric acceptors are polymers based on naphthalenediimide (NDI), like P(NDI2OD-T2), also known as N2200,¹⁷⁻¹⁸ and PNDI-T10.¹⁹ Recently, polymerizing conjugated small molecule acceptors is proven to be an effective strategy to construct polymer acceptors with outstanding performance.²⁰⁻²²

Conjugated small molecules were also used as donor materials,²³⁻²⁶ before the dominance of D-A copolymers. Nowadays, most of the conjugated small molecules are used as acceptors in OSCs. Among them, fullerenes and their functionalized derivatives like PC₆₁BM, ICBA, and PC₇₁BM used to be the most widely used acceptors.²⁷ However, limited tunability of their energy levels, weak absorption in the visible and near-infrared (NIR) regions, and relatively poor thermal and photochemical stabilities restrict the further development of fullerene-based acceptors.

Accompanied with the dominance of D-A copolymers, conjugated small molecules with a similar A-D-A core are also developed for OSCs,²⁸⁻²⁹ mainly to replace fullerene acceptors. Similar to the D-A copolymer, the strong ICT allows extend visible/NIR light absorption.

Their versatilities of chemical structures allow variable energy levels of these molecules. Besides, the close packing of the end units favors electron transport, gifting A-D-A materials high electron mobility. Thus, the A-D-A small molecules are ideal for the acceptor materials in OSCs. Nowadays, OSCs with desirable photovoltaic properties are mostly obtained by using the A-D-A type non-fullerene acceptor (NFA), including ITIC,³⁰ Y6,³¹ and many of their congeners, like IT-M (**Figure 2.2**).³²⁻³⁴

Figure 2.2. Chemical structures of the fullerene acceptor PC₇₁BM, and A-D-A type NFAs including ITIC, IT-M, and Y6.

2.1.2 Energetics of organic semiconductors

Just like we mentioned previously, organic semiconductors are carbon-based materials. Atomic carbon in the ground state has six electrons, two are in a 1s orbital, two in a 2s orbital, and the remaining two in a 2p_x and 2p_y orbital, respectively. If one of the 2s electrons were to move into the empty 2p_z orbital, the carbon atom could make four covalent bonds. Take the ethene molecule as an example (**Figure 2.3 a**), each carbon atom has three 2sp² hybrid orbitals in-plane and one 2p_z orbital out-of-plane. Three 2sp² orbitals give rise to three σ-bonds. The electrons in the 2p_z orbitals of two carbon atoms will be paired, and this shared pair of electrons corresponds to a π-bond (**Figure 2.3 b**). Further antibonding σ*- and π*-orbitals are formed accordingly at higher energy levels. For a more

complex conjugated system, π -orbital is delocalized throughout the full conjugation length.

Figure 2.3. (a) Chemical structure of ethene. (b) A sketch shows the formation of σ - and π -bond from atomic orbitals for ethene, and (c) the corresponding energy level diagram.

Two electrons in each carbon $1s$ orbital are accommodated in both σ - and σ^* - orbitals during the formation of σ -bond. While every $2sp^2$ hybrid orbital on each carbon contains only one electron. When they combine with the electron from the other carbon, the pair will only fill the low-lying bonding σ -orbital yet leave the anti-bonding σ^* -orbital at high energy empty. Similarly, each of two carbon $2p_z$ orbitals contains one electron to be accommodated, they will only fill the π -orbital, leaving the π^* -orbital empty. Thus, as illustrated in **Figure 2.3 c**, the π -orbital here is defined as the highest occupied molecular orbital (HOMO). The next higher orbital, which is the empty π^* -orbital, becomes the lowest unoccupied molecular orbital (LUMO).

Comparing organic semiconductors to the inorganic ones, the LUMO and HOMO are equivalent to the conduction band minimum (CBM) and valence band maximum (VBM), respectively. Thus, the bandgap (electric gap, E_g^{ele}) of an organic semiconductor is defined by the energetic difference between its LUMO and HOMO. As a result, further electronic transitions could happen between its HOMO and LUMO levels.

Inorganic semiconductors usually have small E_g^{ele} , for some materials, the free charges can be created by thermal excitation at room temperature. Furthermore, their relative dielectric constants ϵ_r are large, meaning that

coulomb effects between electrons and holes are weak, thus light absorption can easily create free electrons and holes in the materials.³⁵ In contrast, the E_g^{ele} of organic semiconductors is usually larger than their inorganic counterparts. Besides, their ϵ_r are small, usually around 3.5.³⁶ This indicates that coulomb interactions are significant, thus any electron-hole pair created by light absorption is bound by coulomb energy of about 0.5 – 1.0 eV.³⁶

Figure 2.3 c portrays the orbital diagram of a given molecule, which helps understand the working mechanism of OSCs. However, a lot of photophysical processes of organic semiconductors are discussed in electronic states. **Figure 2.4** presents an orbital diagram and a state diagram. As shown in **Figure 2.4 a**, the different states can be understood as the combinations of different distributions of electrons over the molecular orbitals. When all electrons are paired and sit in the lowest orbitals, the molecule has its ground state (S_0). When one or more electrons sit in the LUMO or the orbital above LUMO, several excited states ($S_1, S_2, \dots$) will be generated. Electrons in orbitals are bound to the nuclei, so all orbital energies are below the vacuum energy at 0 eV. Whereas in the state diagram (**Figure 2.4 b**), the ground state, which is the lowest possible state in a molecule, serves as a reference and is set to be 0. The energy between S_0 and S_1 refers to the optical gap E_g , which can be determined from the intersection of the normalized absorption and emission spectra of the studied molecule (**Figure 2.4 c**).³⁷

Figure 2.4. The ground state and excited states are illustrated in (a) an orbital diagram, note that only the dominating electronic configuration for each excited state is shown. Similar states are also drawn in (b) a state diagram, where the relative energies of every excited state can be defined. Adapted with permission.³⁶ Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Determination of the E_g of IT-M from the crossing point of its normalized absorption and emission spectra.

2.1.3 Optical transitions of organic semiconductors

The absorption and emission properties of conjugated polymers or molecules can be understood by the Franck-Condon principle.³⁶ The Franck-Condon principle is a rule that explains the intensity of vibronic transition. It is based on the approximation that the electronic transition between S_0 and S_1 is most likely to happen without any motion of the corresponding nucleus in its surroundings. Thus, in a Franck-Condon principle energy diagram, as shown in **Figure 2.5**, transitions between S_0 and S_1 are always depicted as vertical arrows, without changes in nuclear coordinates. As the result, the intensity of a vibronic transition is

proportional to the overlap between the vibronic wavefunction of the two involved states.

Figure 2.5. Schematic diagram of the Franck-Condon principle in (a) an absorption, and (b) a fluorescence process. (c) A sketch of the absorption and fluorescence spectrum. Adapted with permission.³⁶ Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In absorption, an electron is excited from the lowest vibration state of S_0 to a vibration state in S_1 . It then goes through a non-radiative relaxation to the lowest vibration state of S_1 , and finally decays to a certain vibration state of S_0 via emitting a photon. This radiative decay is called fluorescence. The Franck-Condon principle is equally applied to both absorption and fluorescence, resulting in an approximate mirror symmetry between absorption and fluorescence spectra (**Figure 2.5**). But for conjugated polymers, the vibronic peaks in their absorption and fluorescence spectrum are not as sharp as they are suggested in **Figure 2.5** but broadened, due to their structural disorder. Nevertheless, both absorption and fluorescence spectrum of a conjugated polymer can be

used for the identification of species as long as the spectrum exhibits vibronic bands.

2.1.4 Architecture of organic solar cells

The configuration of an OSC is a photoactive layer sandwiched between an electron transport layer at the cathode side and a hole transport layer at the anode side. Usually, one of its two electrodes is transparent, the other is preferably to be reflective, so it can reflect the transmitted light back into the photoactive layer again, to increase the overall absorption. The conventional structure of OSCs allows incoming light to reach the photoactive layer from the anode side, while the so-called inverted OSCs generally have a transparent cathode. The photoactive layer is responsible for photoelectric conversion. During the development of OSCs, various types of photoactive layers were introduced into solar cells. Started with the Schottky junction device only contains one photoactive material. Followed by the bilayer heterojunction device, which contains two different photoactive materials (a p-type material as electron donor and an n-type material as acceptor), and the junction between donor and acceptor is planar.³⁸ In a bulk heterojunction device, the donor and acceptor materials are mixed, thus the donor:acceptor junction could distribute in the entire photoactive layer.³⁹⁻⁴⁰ **Figure 2.6** illustrates the typical structure of an OSC with the conventional structure.

Figure 2.6. Schematic diagram of a conventional structure solar cell.

2.1.5 Interfacial layers

The interfacial layers, namely the electron transport layer (ETL) and the hole transport layer (HTL), are significant constituents of OSCs and play

an important role in the device's performance and stability.⁴¹⁻⁴³ These buffer layers can modulate the energy levels of electrodes, thus promoting the formation of ohmic contacts between the active layer and electrodes. Besides, the interfacial layer has selectivity for charge carriers. For example, the HTL should only allow holes to reach the anode and block electrons, which reduces the recombination of interfacial charges. Significant development of various ETLs has been achieved by using polymers, organic small molecules, or inorganic oxides, such as poly(ethylene oxide),⁴⁴ polyethylenimine,⁴⁵ polyfluorene derivatives,⁴⁶⁻⁴⁸ lithium fluoride,⁴⁹⁻⁵⁰ and zinc oxides.⁵¹⁻⁵² However, the studies on efficient HTL are comparatively overlooked.

The conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is the most commonly used solution-processable HTL in OSCs (**Figure 2.7**).⁵³⁻⁵⁴ PEDOT:PSS has advantages such as water-soluble, high transparency in the visible and NIR ranges, and suitable work function. However, as an HTL in OSCs, it also has some drawbacks which need to be improved: a) acidic PEDOT:PSS might corrode the indium tin oxide (ITO) anode, resulting in the diffusion of indium ions into PEDOT:PSS and the active layer, thus compromising the stability of OSCs. b) PEDOT:PSS can absorb moisture and oxygen from the air, which also might accelerate device degradation. c) The conductivity of a thin layer of transparent PEDOT:PSS is relatively low, which impairs the PCE and its compatibility with large-scale printing processes.

Figure 2.7. Chemical structure of PEDOT and PSS.

In **Paper 1** we try to implement highly conductive two-dimensional transition metal carbides, named MXenes, into the PEDOT:PSS layer. Compared to the pristine PEDOT:PSS film, the composite

Mo_{1.33}C:PEDOT:PSS shows increased conductivity, and still maintains a decent optical transparency and work function. As a result, OSCs based on Mo_{1.33}C:PEDOT:PSS exhibited an average PCE of 9.24%, which was ~13% higher than the reference device without Mo_{1.33}C dopant.

2.2 Working principle of organic solar cells

Figure 2.8 demonstrates the working principle of an OSC under illumination. The photon-to-current conversion is completed by the sequential steps as follows:

- Absorption of photons and formation of excitons.
- Excitons diffuse to the donor:acceptor (D:A) interface.
- Formation of charge transfer (CT) exciton at the interface through charge transfer.
- CT exciton dissociation and the formation of free charge carrier.
- Charge carrier transport towards the corresponding electrode.

Figure 2.8. Schematic working principle of an OSC in an orbital diagram.

2.2.1 Exciton generation and dissociation

Upon illumination, light is absorbed by donor and acceptor materials in the active layer, and excitons can be generated in both donor or acceptor phases if the photon energy is larger than the E_g of these materials. To

split the exciton into charge carriers, first, the exciton needs to diffuse to the D:A interface. The diffusion length of the exciton is usually around 10 nm,⁵⁵ thus for efficient exciton dissociation, the donor or acceptor domain size should also be in a range of a few tens of nanometers.

If a photogenerated exciton is generated in the donor phase, once the exciton reaches the D:A interface, the electron can transfer from the donor phase to the acceptor phase. As for the exciton generated in the acceptor phase, a similar hole transfer would happen at the interface as well. These charge transfer processes are usually efficient, within a timescale of femtosecond.⁵⁶

After charge transfer, the distance between the hole and the electron is increased, which decreases the binding energy of the resulting charge transfer exciton (CT exciton). However, at this point the hole and electron are still coulombically bounded, thus the complete dissociation of this electron-hole pair requires extra driving forces. The source of the driving force for CT exciton dissociation is still a debatable topic, and will be discussed in the following chapter. In short, the energetic difference between the HOMO or LUMO levels of donor and acceptor materials (Δ HOMO or Δ LUMO), disorder and charge delocalization on conjugated polymer, thermal energy, and build-in potential are all proposed to contribute to exciton dissociations.

2.2.2 Charge transport and collection

Inorganic semiconductor theories describe charge transport using the band theory, with a continuous conduction and valence band that are separated in energy. Electrons can be effectively conducted through the material in the conduction band, thanks to the high delocalization of charge carriers in inorganic semiconductors.

Comparing to inorganic semiconductors, similar energetic states, as previously described, referring as LUMO to the CBM and HOMO to the VBM, also exist in their organic counterparts. However, the LUMO and HOMO in organic semiconductors are not continuous, since the substantial delocalization of charge carriers only exists in each of the conjugated polymer chains or molecules, rather than the entire donor and acceptor phase. Thus, the LUMO and HOMO in the donor and acceptor phase distribute both in space and energy (**Figure 2.9**), and the charge transport in the photoactive layer is realized by the localized charge hopping between different energetic sites.

Figure 2.9. A sketch that shows the distribution of LUMO and HOMO in energy and space. Transport of electrons and holes is achieved by hopping from one energetic site to another.

The charge transport properties in semiconductors can be evaluated by a parameter called the charge carrier mobility μ . The value of μ can be determined by the space-charge-limited-current method according to the Mott-Gurney law,⁵⁷⁻⁵⁸ by fitting the dark J - V curve of a solar cell with the following equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{(V - V_{bi})^2}{d^3}, \quad (2.1)$$

where the ε_0 is the vacuum permittivity, V_{bi} is the built-in voltage, and d is the thickness of the active layer. In general, high mobility is desirable for organic solar cells, but balanced electron and hole mobilities in the solar cell are also important for achieving high performance.

Photogenerated free charge carriers that do not recombine are finally extracted at the respective electrodes. The potential barrier at the active layer:electrode interface must be reduced to maximize the extraction of charges. Therefore, to achieve an efficient charge collection, the work function of the anode should match with the HOMO of the donor material, accordingly, the work function of the cathode must align with the LUMO of the acceptor material.

2.2.3 Recombination

Recombination occurs upon encounter of opposite charge carriers, and it is the main loss mechanism in OSCs. The rate of recombination R is proportional to the charge carrier density n in the solar cell:

$$R = \beta n^\gamma, \quad (2.2)$$

where β is the recombination coefficient, and γ is the order of recombination.

Charge recombination can be classified as geminate and non-geminate. Geminate recombination, which is a first-order process, occurs when the involved electron and hole originated from the same photon. In OSCs, the recombination from the photon-induced excitons, as well as CT excitons, are geminate recombination.

Whereas the non-geminate recombination occurs when the involved electron and hole come from different photons. There are various mechanisms by which this can occur. The simplest is “band-to-band” recombination, also refers as bimolecular recombination, where two free charge carriers (an electron and a hole) are drawn together at the D:A interface. Thus, bimolecular recombination is a second-order process. Another important non-geminate recombination channel is recombination *via* trap states, it involves two steps where one charge is first captured into a trap and becomes immobilized, and then an oppositely charged carrier may approach and recombine with it. The trap-assisted recombination is still a first-order process, since each step only involves one free charge carrier.

2.3 Concept of bulk heterojunction

The efficiency of charge extraction from an OSC depends on the competition between charge generation, transport, and recombination throughout the device. The efficient charge generation prefers small pure domains and sufficient D:A interfaces, while charge transport requires large domains of pure donor and acceptor. Besides, the excess of D:A interface could also promote bimolecular recombination, which eventually undermines device performances. Thus, the concept of bulk heterojunction (BHJ) solar cells is proposed to balance the aforementioned processes.⁵⁹

As shown in **Figure 2.10 a**, the ideal BHJ is a finely mixed, yet phase-separated network, consisting of a nanoscale blend of donor and acceptor materials. Interfaces throughout the active layer facilitate efficient exciton dissociation, allow thicker devices to be fabricated without substantially increasing losses due to recombination. In order to ensure that the majority of excitons are able to reach an interface prior to relaxation, and facilitate free charge carriers transport to the electrodes, an interpenetrating network of donor and acceptor domains on the length scale of 10 - 20 nm is required. Except for the pure domains, many state-of-the-art BHJ solar cells also contain mixed domains in the active layer, which are in fact advantageous for the charge separation process. Consequently, the introduction of BHJ solar cells once led to drastic improvements in device performance, in comparison to the aforementioned Schottky junction and bilayer heterojunction devices.

Figure 2.10. A sketch of (a) an optimized BHJ, and (b) a dilute BHJ where the donors are well-separated by the excessive acceptors. Adapted with permission.⁶⁰ Copyright 2020. American Chemical Society.

Although the BHJ has been proven as one of the best solutions for constructing OSCs with high performance, it might not be an ideal structure to understand the underlying mechanisms of many fundamentals of photon-to-current conversion, mainly because of the morphological complexity of the BHJ active layers. In this respect, the solar cell comprising mainly acceptor blended with a low amount of donor (around 10% weight ratio), so-called dilute donor BHJ, is an exceptional model system. In the dilute BHJ (**Figure 2.10 b**), the impact of morphology can be decoupled largely from other parameters under

study. In particular, the dilute donor BHJ ensures that each donor molecule is surrounded by acceptors, establishing a well-defined donor:acceptor interface. Recently, such dilute BHJs have been used in lots of studies, including the properties of CT states, impacts of CT states on charge recombination and V_{OC} , and the hole transport mechanism between isolated donor molecules.⁶¹⁻⁶⁷

Chapter 3 Morphology of bulk heterojunction

3.1 Film formation and phase separation

In solution-processed OSCs, the morphology of BHJ develops primarily during solvent evaporation. **Figure 3.1** depicts a possible route of BHJ formation. As the solvent evaporates, donor and acceptor molecules start to rearrange themselves and eventually form a phase-separated blend. The formation of BHJ films during solution processing is complex progress, which usually cannot be interpreted with one simple mechanism. The parameters that can possibly guide BHJ formation include: 1) kinetic parameters, such as the boiling point of the solvent and the viscosity of the ink, and the deposition conditions that influence the drying kinetics of the blend; 2) thermodynamic parameters, such as the self-assembly tendencies of donor and acceptor materials, their solubilities in the main solvent and the possible co-solvent(s), and the solvent-solute and solute-solute interactions.

Figure 3.1. A sketch that shows a possible route of the morphology formation of BHJ during deposition.

The Flory-Huggins theory is particularly useful for predicting the solidification pathway and the final phase separation of the multicomponent blend.⁶⁸⁻⁷⁰ The free energy of mixing for a solvent:donor:acceptor (S:D:A) ternary system can be determined by the following equation:

$$\Delta G_m = k_B T \left(\varphi_S \ln \varphi_S + \frac{\varphi_D}{N_D} \ln \varphi_D + \frac{\varphi_A}{N_A} \ln \varphi_A + \chi_{SD} \varphi_S \varphi_D + \chi_{SA} \varphi_S \varphi_A + \chi_{DA} \varphi_D \varphi_A \right) \quad (3.1)$$

where φ_i is the volume fraction of component i , χ_{ij} is the Flory-Huggins interaction parameter between components i and j , and N_i is related to the degree of polymerization of component i . This equation can be transformed into a phase diagram as shown in **Figure 3.2 a**. Each side of the triangle represents the concentration of one of the components, thus every point inside the triangle represents a specific composition of these three components. The composition space in the diagram is then divided into two parts by the spinodal curve: a stable single-phase region and an unstable two-phase region. The dashed black line represents the changes in composition during solvent evaporation (solvent quench).

Figure 3.2. (a) Schematic phase diagram of a ternary mixture of donor, acceptor, and solvent. (b) A sketch that illustrates possible phase separation processes in a donor-acceptor-solvent system during solvent evaporation.

The possible phase separation processes from an initially homogenous solvent-solute mixture are summarized in **Figure 3.2 b**. Two competing processes, which are liquid-liquid (L-L) or solid-liquid (S-L) phase separation, are driven by solvent evaporation. L-L phase separation begins upon crossing from the single-phase to the two-phase region (spinodal curve in **Figure 3.2 a**), while S-L phase separation occurs when either the donor or acceptor component reaches its solubility limit in the deposition solvent. With different solvent-solute systems, these phase separation processes may occur simultaneously, or one may precede the other. If neither process occurs, the mixture will end up with an intimately mixed morphology, with a minimum level of phase separation.

3.2 Coating methods

3.2.1 Spin coating

On the laboratory scale, BHJ active layers and other solution-processable interfacial layers are conventionally produced by spin coating. As shown in **Figure 3.3**, the substrate is first fixed on a spinner, and the solution is dropped on the substrate which then starts to rotate. With the help of centrifugal force, solutions can be spread on the top surface of substrates, and the substrate rotates continuously with the spinner until the film is dry. Due to its compact size, the spin coater can be easily integrated into a glove box with the desired atmosphere. Besides, for a given material system this method produces highly reproducible coatings. Thus, spin coating becomes the go-to choice for the fabrication of high-performance OSCs on small and rigid substrates in the lab.

Figure 3.3. (a) A sketch of the spin coating process. (b) A half cross-section sketch of a film during spin coating.

Although spin coating has become a well-established coating method in the field of OSCs, it still suffers the following drawbacks: 1) the parameters of spin coating are highly interrelated, which makes it difficult to distinguish the impact of every individual parameter on the quality of the resulting film. For example, changing to a higher spinning speed gives a thinner film, but it increases the speed of airflow above the wet film, which increases solvent evaporation rate as well. 2) The spinning of the substrate generates larger centrifugal flows inside the film, and the centrifugal force is a function of the position on the substrate:

$$f = \rho\Omega^2 R \quad (3.2)$$

where f is the centrifugal force per unit volume, ρ is the density of the fluid, Ω is the spin frequency, and R is the distance from the rotation axis. This might result in an inhomogeneous distribution of donor or acceptor materials along the radius of rotation. 2) The drying kinetics of spin-coated films are different from the films produced by the industrial printing process, meaning a solar cell that is optimized by spin coating in the lab might end up with different performance in large-scale production.

3.2.2 Blade coating

The concerns described for spin coating above can be well addressed by the blade coating technique. The term “blade” refers to the fact that organic films are coated to the substrate with the help of a moving blade.⁷¹

As shown in **Figure 3.4**, due to the intrinsic directionality of the blade coating, this method may favor the formation of aligned molecular packing. The blade coating is suitable for fabricating organic electronic devices on large and flexible substrates, and it is also compatible with continuous printing methods used in the industry, such as roll-to-roll processing. Besides, in spin coating, quite a lot of organic ink is discarded, whereas in blade coating the utilization of inks is much more efficient.

Figure 3.4. A sketch of the blade coating process.

Figure 3.5 summarizes primary deposition regimes in blade coating, defined by the relation between dry film thickness h and coating speed v . A detailed discussion of the relation between h and v can be found in an article published in 2009.⁷² At low coating speeds, the “evaporative regime” features a decreased dry film thickness as a function of an increased coating speed (**Figure 3.5 a**). In this regime the rate of solvent evaporation is comparable with the coating velocity, meaning film coating and drying happen simultaneously. Therefore, the drying process is under the direct influence of fluid flowing under the forward meniscus (**Figure 3.5 b**). Driven by solvent evaporation, a dramatic concentration gradient will be established close to the forward meniscus. As a result, capillary flows toward solid film can be induced. The stick-and-slip behavior, which is assisted by the capillary flow, commonly occurs in the evaporative regime. This cyclic process usually results in unfavorable periodic undulations in dry film thickness.⁷³ Besides, a surface tension gradient may also arise at the forward meniscus, which can induce Marangoni flows in different directions. The combined effect of these flows can dramatically influence the nanostructures of the final films.

At high coating speed, the film thickness starts to increase, and this region is called the Landau-Levich regime. At this regime, viscous effects dominate, the film coating and drying become two separate processes, a thin layer of liquid is first dragged out by viscous force before solvent evaporation. The fluid flow in Landau-Levich deposition is more like

laminar flow, which is parallel with the sample surface. Experimental results showed that the film obtained in the Landau-Levich regime has a sharper distribution of film thickness, with very few pinholes.⁷²⁻⁷³

The position of the transition (mixed regime) between these two regimes are dependent on a number of factors, such as ink concentration, coating temperature, and the boiling point of the solvents.⁷¹

Figure 3.5. (a) Different deposition regimes are characterized by different film thickness versus coating speed relations. Adapted with permission.⁷¹ Copyright 2018. Springer Nature Publishing AG. (b) Schematic illustrations of the evaporative regime and the Landau-Levich regime.

The parameters that determine the film thickness in these two regimes are different as well. In the evaporative regime, the concentration and density of the inks, the distance d between blade and substrate, and the evaporation rate of solvents are all important. In the Landau-Levich regime, the thickness is mainly defined by surface tension and the

viscosity of the inks, the surface energy of the substrates, and the geometry of the blade (mainly the height of the back meniscus *l*).

3.3 Deposition conditions

3.3.1 Solvents

The choice of solvents used for BHJ deposition can significantly influence the morphology of the active layer and the resulting solar cell performance.⁵⁰ Solvents with low boiling points tend to evaporate rapidly, which could “freeze” the molecules into thermal-nonequilibrium conformations in the dry film. Whereas the high boiling point solvents offer plenty of time for the reorganization of molecules, which in some cases lead to donor-acceptor demixing and gives a more phase-separated blend.

Besides the drying kinetics, the quality of solvent regarding the solute (good or bad solvent) plays an equally important role in the final morphology of the blend. The aggregation/conformation of a given polymer can be influenced by its solubility in different solvents, which gives different morphology in its dry film. The absorption or emission spectra are well-established approaches to resolve the level of aggregation or the changes of conformation of polymers. For example, Zhang et al. demonstrated that the absorption spectra of D-A copolymer J51 and N2200 solution exhibited a gradual red-shift as the polymer was dissolved by a good solvent (chloroform, CF) to a bad solvent (cyclopentyl methyl ether, CPME).⁷⁴ The authors suggest that the decreased solubility of polymers in bad solvents leads to increased crystallization driving force, thus, more nuclei are formed, and the resulting polymer films give a more uniform morphology (**Figure 3.6**).

Figure 3.6. (a) Normalized absorption spectra of polymer J51 in different solvents. Atomic force microscopy (AFM) height images of J51 films spin-coated from (b) CF, (c) mesitylene (Mes), and (d) CPME solutions. Reprinted with permission.⁷⁴ Copyright 2019, the Royal Society of Chemistry.

3.3.2 Solvent additives

The blend film casted from a single solvent sometimes results in a non-ideal morphology, which could reduce the device performance. Thus, additional methods to manipulate morphology are usually required. The usage of solvent additives, or in some cases refer to as mixed solvents,⁷⁵ during solar cell fabrication has been proven as a convenient yet efficient strategy to obtain ideal BHJ morphology in OSCs. Solvent additives are used in rather small concentrations, usually less than 3 vol%, but still have tremendous impacts on BHJ morphologies. In general, the purpose of solvent additives is either to tune the extent of phase separation, or enhance the crystallinity of donor or/and acceptor phase.

Solvent additives usually have a higher boiling point than the main solvent, and/or have different solubility for donor and acceptor materials. For a BHJ blend that phase separation mainly follows the L-L demixing process, the role of solvent additive is to either promote or reduce the level of L-L demixing. This can be achieved by promoting earlier aggregation of donor or acceptor in solution to induce more S-L demixing, or by prolonging the overall evaporation time to reduce the solvent quench depth. For a BHJ blend where S-L demixing dominates its phase separation, the role of additives is to help donor or acceptor overcome its crystallization barrier, or prolong its crystallization process.

The first solvent additive for OSCs was reported in 2006, when Peet et al. introduced 1-octanethiol in P3HT:PC₆₀BM blends.⁷⁶ Since then, lots of solvent additives have been demonstrated to effectively enhance the

device performance, such as 1,8-diiodooctane (DIO),⁷⁷⁻⁷⁹ 1-chloronaphthalene (CN),⁸⁰⁻⁸¹ diphenyl ether (DPE),⁸²⁻⁸³ and N-Methyl-2-pyrrolidone (NMP).⁸⁴ Due to the chemical diversity of both additives, main solvents, and material systems, it is challenging to define the function of each additive. For example, CN usually is seen as a compatibilizer that prevents oversized aggregation from a highly crystallized polymer like N2200,⁸⁵⁻⁸⁶ but in **Paper 2** we find that CN can actually promote the aggregation of polymer PBDB-T when it is blended with another polymer PF5-Y5 (**Figure 3.7**). Thus, the additive processing must be tailored to the individual solar cell system.

Figure 3.7. AFM height images of all-polymer blend PBDB-T:PF5-Y5 with different amounts of CN as solvent additive. From left to right, a gradually increased surface roughness was observed as the increase of CN vol%.

3.3.3 Donor:acceptor ratio and deposition temperature

The blend stoichiometry between donor and acceptor greatly influences the performance of BHJ solar cells as it not only affects the overall absorbance of the active layer, but also the crystalline order, phase separation, and phase purity of the resulting films. In order to form a bi-continuous pathway for efficient charge separation and transport, depending on different material systems, the D:A ratio has been reported to vary to a large extent, from 7:3 to 1:4.⁸⁷

Changing deposition temperature is also a method to optimize the BHJ morphology. This method is mostly relevant to polymers that display strong temperature-dependent aggregation behavior, such as PffBT4T and PBDB-T families.^{14, 88-89} By controlling both solution and substrate temperature, polymer aggregation could be fine-tuned to achieve optimal nanostructure in the BHJ. Besides, temperature also influences the viscosity of polymer inks, which in turn determine how mobile polymer chains are in solution, and eventually influence blend morphology.

3.3.4 Solvent vapor and thermal annealing

Besides tuning the composition of organic inks and deposition parameters, sometimes post-deposition treatments are also required for morphological optimization. These include solvent vapor (SVA) and thermal annealing (TA).^{19, 90-92} SVA is conducted by place an as-cast BHJ layer in a partly closed Petri dish with few drops of solvent. This method allows the vapor of the chosen solvent to penetrate the BHJ film and enable the reorganization or diffusion of polymers. While TA is usually done by heating the as-cast blend near the glass transition temperature of one of its components. But in some material systems, TA is only used to ensure complete removal of residual solvent or additive. Overall, the main purpose of these treatments is similar, which is to allow polymers or molecules to rearrange themselves in a more favorable conformation, thus drive the system toward the most thermodynamically stable state.⁹³

3.4 *In-situ* characterization of solution drying

In previous sections, we have discussed the importance of BHJ morphology and its optimization methods. After deposition, the final morphology of the BHJ film can be resolved by a number of *ex-situ* nanostructural analysis methods. However, since the BHJ morphology is mainly developed during solvent evaporation, *in-situ* studies more reliably probe the progress of film formation, allowing the observation of polymer aggregation, crystallization, and phase separation in real-time. In this chapter, we will discuss some *in-situ* characterization methods which are involved in our studies.

3.4.1 Laser scattering

Light scattering is widely used to study the drying process of BHJ layers. The intensity of the scattered light is related to the wavelength of the incident light, size of the particle, scattering angle, and refractive index of the two species. If a contrast in the refractive index exists between the particles and the surroundings, scattering intensity is determined to a great extent by the size of the particles. For the drying of BHJ, during the solvent evaporation, at some point, the donor-acceptor blend will go through the liquid-liquid or solid-liquid phase separation. These phase separations cause a refractive index contrast between two phases, thus the onset of phase separation can be detected by the onset of light scattering.

Besides, the resulting domain size can be correlated to the increase of scattering intensity. This correlation was demonstrated in **Paper 2** and **3**.

3.4.2 Absorption

The UV-vis absorption is extensively used for measuring optical properties, typically the absorbance and vibronic states of organic semiconductors. Conducting the UV-vis absorption *in-situ* offers the possibility to monitor polymeric or molecular aggregation during solution processing. The development of aggregates usually leads to the appearance of new features in absorption spectra, such as new vibronic peaks and band edge shifts. **Figure 3.8 a** shows the evolution of PBDB-T absorption spectra during film formation. From wet film to dry film, an enhanced vibronic peak around 640 nm and the red-shifted absorption edge can be observed. **Figure 3.8 b** gives another example of an *in-situ* absorption study, which shows the differences in drying kinetics of all-polymer blend PBDB-T:PF5-Y5 from CF, CB, and ortho-dichlorobenzene (o-DCB). A longer drying time is observed for o-DCB that has the highest boiling point.

Figure 3.8. (a) Absorption spectra of PBDB-T in CB solution during its solidification. Reprinted with permission.⁹⁴ Copyright 2021, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Normalized absorbance of PBDB-T in PBDB-T:PF5-Y5 blends processed with different solvents, namely CF, CB, and o-DCB, respectively.

The *in-situ* absorption setup is illustrated in **Figure 3.9**. The setup is based on a blade coater. One side of an optical fiber is connected to a white light source, and another side is mounted on top of the blade coater, which illuminates on top of the as-casted wet film. The second optical

fiber is placed underneath the blade coater, to continuously collect transmittance signals, and convert them to absorption spectra through the following equation:

$$A(\lambda) = -\log_{10}T(\lambda) \quad (3.3)$$

where A is the absorbance and T is the transmittance in percentage.

Figure 3.9. Schematic diagram of the *in-situ* absorption setup.

3.4.3 Photoluminescence

Due to the Franck-Condon principle, the fluorescence spectrum also contains information about spectral shifts of vibronic peaks, which can be related to the aggregation of polymers as well. While absorption occurs on a timescale of less than 10^{-15} seconds, the relaxation process from S_1 to S_0 is much slower. Therefore, comparing to the absorption, the corresponding fluorescence can provide more information on the interactions of polymer with surrounding molecules and solvents. This information can be resolved by the changes in fluorescence intensity and its lifetime.

The term photoluminescence (PL) means the fluorescence of a chromophore is induced by photons. In our studies, photons come from a laser beam, and polymers or small molecules in films are chromophores. A schematic diagram of the *in-situ* PL setup is shown in **Figure 3.10**.

Figure 3.10. Schematic diagram of the *in-situ* PL setup. Scattered laser signals from the film are collected simultaneously with the PL spectra.

For a given polymer or small molecule solution, its PL intensity can either increase or decrease (PL quenching) during solvent evaporation. The increase of PL intensity might come from the possibly increased absorbance around excitation wavelength, or the so-called aggregation-induced emission (AIE) enhancement.⁹⁵ AIE stands for the phenomenon that organic molecules show higher PL quantum yield in their aggregated state than in solutions. AIE molecules share a common feature in their structures, that is containing freely rotating groups. When these molecules are excited, energy can be non-radiatively annihilated through these intramolecular rotations. While after aggregation, molecules are closely packed, which restricts those rotations in space, resulting in enhanced fluorescence.

The PL quenching during the film formation from single-component solutions, or binary blends contain donor and acceptor materials, is usually a result of a few mechanisms that occur at the same time. It includes aggregation-caused quenching and concentration-related quenching. The aggregation-caused quenching (ACQ) can be observed for many chromophores that with planar and well-conjugated structures. They exhibit much weaker or quenched luminescence in their aggregated state than in dilute solution. On the other hand, concentration-related quenching can be explained by the Stern-Volmer theory, which classifies quenching into two categories, dynamic quenching and static quenching. As depicted in **Figure 3.11**, dynamic quenching is the result of diffusive encounters between fluorophores and quenchers, while static quenching is due to the formation of the non-radiative complex (blue-black circles in **Figure 3.11 b**).

Figure 3.11. Schematic presentation of (a) dynamic and (b) static quenching mechanisms. [Q] is the quencher concentration. Adapted with permission.⁹⁴ Copyright 2021, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

If the oxidation or laser-induced degradation can be excluded, PL quenching during polymer or BHJ solution drying is dominated by aggregation and concentration quenching. Thus, the recorded PL signal is a direct indication of conformation changes and interactions of donor and acceptor materials.

3.4.4 Time-resolved photoluminescence

Time-resolved photoluminescence (TRPL) spectroscopy is an extension of photoluminescence spectroscopy. In TRPL spectroscopy the fluorescence from the sample is recorded as a function of time right after excitation by a laser pulse, and the duration of the pulse should be as short as possible. In general, the purpose of this technique is to calculate the lifetime τ of fluorescence decay. For a single exponential decay, the lifetime can be determined from the slope of a plot of $\log I(t)$ versus t , as indicated in **Figure 3.12** and the following equation:

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right), \quad (3.4)$$

where $I(t)$ is the time-dependent fluorescence intensity, I_0 is the intensity at time $t = 0$.

Figure 3.12. Schematic of pulse excitation and TRPL lifetime measurement.

In **Figure 3.12** the pulsed excitation has an infinite sharpness, but in reality, the length of the pulse is usually long, thus the overall fluorescence response is the convolution result of the instrument response function and the actual fluorescence response.

From a practical point of view, the measurement of TRPL is the most crucial method to distinguish between dynamic and static quenching. One of the important characteristics of dynamic quenching is the equivalent decrease in PL intensity and lifetime. The decrease in lifetime occurs because dynamic quenching is an additional rate process that reduces the population of the excited state. While static quenching does not decrease the lifetime, because the complexed fluorophores are non-radiative, thus the observed emission only comes from the non-complexed fluorophores, which have an unquenched lifetime. Thus, dynamic and static quenching exhibit different features on TRPL decay kinetics, as illustrated in **Figure 3.13**.

Figure 3.13. Evolution of TRPL decays for the cases of (a) dynamic (b) static quenching and (c) the combination of both mechanisms. Reprinted

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In **Paper 3** TRPL was used to probe the contribution of each mechanism to the total PL quenching during drying of various polymer inks. To the best of our knowledge, this is the first time that TRPL was conducted *in-situ* to monitor the film formation process. A schematic diagram of the *in-situ* TRPL setup is shown in **Figure 3.14**. The recorded PL decay was deconvoluted to get its actual fluorescence decay $I_{PL}(t)$, then a two-exponential function was used to fit this decay:

$$I_{PL}(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right), \quad (3.5)$$

where A_1 and A_2 are the amplitude of each exponential decay, τ_1 and τ_2 are the corresponding decay lifetime. Performing this fitting for every PL decay captured during film formation allows us to study its PL quenching mechanisms by checking two parameters: the amplitude averaged lifetime

$$\langle\tau\rangle = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}, \quad (3.6)$$

which characterizes dynamic quenching, and the initial decay amplitude

$$A = A_1 + A_2 \quad (3.7)$$

which provides information about static quenching (or ultrafast quenching).

Figure 3.14. Schematic diagram of the combined *in-situ* TRPL and PL setup.

3.5 *Ex-situ* characterization of film morphology

3.5.1 Atomic force microscopy

AFM has become a standard technique for imaging the surface topography of BHJ blends. As shown in **Figure 3.15**, a silicon-made cantilever with a sharp tip at the bottom side of the end is used as a scanning probe. During the tip scanning across the surface of a sample, interactions between the tip and the sample may cause extra vibration or torsion of the cantilever. These extra movements are translated into the changes of laser signal that are reflected from the upper surface of the cantilever, and the reflected laser is finally captured by a quadruple photodiode. Thus, the output signal from the photodiode is directly related to the deflection of the cantilever, which in turn represents the topography of the sample.

Figure 3.15. Schematic of a typical AFM setup.

By measuring the surface topography, the resulting AFM height or phase images reveal domain structures in nanoscale, information like surface roughness can also be obtained. Besides, the complementation with other techniques makes AFM even more powerful. For example, conductive atomic force microscopy (C-AFM) allows simultaneous measurement of local conductivity and surface topography; AFM-based infrared spectroscopy (AFM-IR), a hybrid technique that combines the spatial resolution of AFM with chemical analysis capability of IR

spectroscopy, is particularly helpful for mapping the actual donor-acceptor phase separation on BHJ surface.

3.5.2 Grazing-incidence X-ray scattering

Although AFM is helpful to explore surface domain structures with high resolution, it cannot reveal domain structures in the bulk, where most of the charge generation processes take place. Reports also pointed out that for some blend systems, the top-surface morphology is not exactly the same as its inner morphology.⁹⁶⁻⁹⁷

X-ray scattering techniques, on the other hand, are extensively used to study morphology in the bulk. In particular, grazing incidence small- and wide-angle X-ray scattering (GISAXS and GIWAXS) have played a major role in understanding bulk morphology. A sketch of GISAXS and GIWAXS setup is shown in **Figure 3.16**. A monochromatic X-ray impinges onto the surface of the sample in z-plane, with a very small incident angle, usually smaller than 1° . The resulting scattering signal is recorded on a 2D X-ray detector in the x, y-plane, which gives different scattering patterns, like rings, peaks, and diffuse scattering.

Figure 3.16. The geometry of grazing incidence X-ray scattering (GIXS): GISAXS and GIWAXS.

GISAXS can be used to probe length scales relevant to nanoscale separation in BHJ, including the average domain size and domain purity. As indicated in **Figure 3.16**, a GISAXS setup can be converted to a GIWAXS setup by moving the detector towards the sample, thus the

length scale of the nanostructure that can be probed by GIWAXS is down to a few tenths of an Ångström, which is at the molecular level. As the result, GIWAXS is specifically suitable for probing molecular packing direction, crystalline lattice spacing, crystalline correlation length (CCL), and the relative crystallinity of the sample.

Chapter 4 Charge separation in bulk heterojunction

4.1 Charge transfer and exciton dissociation

In Chapter 2.2 we learned that the optical-to-electrical power conversion in an OSC is a sequential process that involves a coulomb-bound electron-hole pair that eventually dissociate into free electron and hole. In order to help the escape of the electron-hole pair from its mutual Coulomb potential, which is usually considered to be around 0.3 eV in typical polymer:fullerene systems, the extra driving force larger than this binding energy is required.

One of the persuasive views regarding the origin of this driving force is the excess energy resulting from charge transfer, namely the electron transfer and the hole transfer at the donor-acceptor interface, which are triggered by the electronegativity differences between donor and acceptor material. This excess energy is related to the energetic difference between the LUMO or HOMO levels of donor and acceptor. As a result, the increased charge transfer and exciton dissociation rate are expected with increased ΔLUMO or ΔHOMO . This idea is indeed supported by lots of experimental results.⁹⁸⁻¹⁰¹ However, weak correlations between energy level differences with solar cell performance are observed in some cases,¹⁰²⁻¹⁰⁴ especially after the booming development of high-efficient non-fullerene acceptor systems. Recent studies show that some NFA solar cells work better under the reduced ΔLUMO or ΔHOMO ,¹⁰⁵⁻¹⁰⁸ and in some cases, a decent hole transfer rate can still be achieved even under a negative ΔHOMO .¹⁰⁹ These observations imply the contribution from other aspects is needed to explain efficient charge transfer and exciton dissociation.

4.2 Interfacial dipole at the donor:acceptor interface

Similar to the interface at the inorganic p-n junction, where a dipolar electric field will be created and shift the vacuum energy level when two semiconductors are brought into contact, the shift of vacuum level is detected at the D:A interface of organic semiconductors.¹¹⁰ The vacuum level shift results in similar interfacial dipoles, thus creating a drop of the

electrostatic potential. Another source of the interfacial dipole is reported to be the partial charge transfer in the dark.¹¹¹ Nevertheless, it has been shown that these dipolar layers at the interface can radically alter the coulomb attraction energy of the electron-hole pair, thus sometimes facilitate the dissociation of CT excitons.^{110, 112-114}

4.3 Disorder of organic semiconductors

Organic semiconductors for OSCs are usually non- or semi-crystalline, meaning they have a higher degree of structural and energetic disorder compared to their inorganic counterparts. The general impression of disorder in polymer and small molecules is negative, because it brings more trap states, decreases the charge carrier mobilities, thus undermines solar cell performances. The LUMOs and HOMOs in organic semiconductors are subject to distributions in state density with a standard deviation around 50-100 meV. Considering the fact that charge hopping usually takes place in the tail states of the distribution, charge carriers might need less thermal energy than estimated to escape from the Coulomb-bounded exciton. The contribution of disorder on exciton dissociation has been demonstrated by both simulations and experimental results.¹¹⁵⁻¹¹⁸

4.4 Delocalization of charge carriers

Another contribution to efficient exciton dissociation is the degree of delocalization of charge carriers in a conjugated system. This contribution was first acknowledged in kinetic Monte Carlo simulations by Deibel et al. in 2009.¹¹⁹ The author found highly efficient exciton dissociation can be explained by delocalized charge carriers within conjugated segments of the polymer chain. The delocalization of holes along the conjugated polymer chains increases its mean distance between the electrons located in fullerenes. This reduces the Coulomb interaction energy within the dissociating electron-hole pairs.

The correlation between CT exciton binding energy and charge delocalization was then proved experimentally by directly comparing the binding energies of a series of donor-acceptor blends.¹¹⁰ Murthy et al. also reported that the binding energy of CT exciton can be reduced down to 7.8 meV by efficient charge delocalization.¹²⁰ Besides the delocalization of holes in polymers, electron delocalization in the

fullerene cluster was also found by Jamieson et al. in 2012.¹²¹ Overall, the importance of electron and hole delocalization after photoinduced charge transfer for efficient free carrier generation has been widely agreed in the field of OSCs.

4.5 Electric field

Electric fields in OSCs can be either generated by interfacial dipoles or polarization effects at the donor:acceptor interface, or by energy level differences between electrodes and external electric fields which exist in the entire active layer. The contribution of the former on exciton dissociation has been discussed in Chapter 4.2, while here we mainly focus on the effect from the latter.

The effect of the electric field on the dissociation of CT excitons can be examined by a lot of techniques, including field-dependent PL quenching, field-dependent transient absorption, time-delayed-collection-field (TDCF) measurement, and field-dependent charge carrier densities and lifetime measurements. Although simulations conclude that stronger electric fields favor efficient exciton dissociations,¹²²⁻¹²⁴ some experimental studies, on the other hand, show different results. In 2014, Vandewal et al. studied the field dependence in different material systems by using the TDCF technique, their results indicate that different material systems have different field dependence of exciton dissociation.¹²⁵

In **Paper 4**, we comparatively studied the hole transfer in two NFA systems with a ΔHOMO of 0.05 and -0.07 eV. The electric field and temperature dependence of the hole transfer process in the dilute donor OSCs indicate these two systems have similar charge generation properties, but the system with the negative ΔHOMO exhibits a stronger bias dependence on the photocurrent. Based on this observation, we proposed the electric field does promote exciton dissociation in the OSCs, but in the scenario that the energetic driving force alone cannot efficiently dissociate excitons.

Chapter 5 Voltage losses in organic solar cells

5.1 Detailed balance theory

The main idea of the detailed balance theory is that a solar cell will exchange thermal radiation with its surroundings *via* the emission of photons during the absorption of solar radiation. The rate of emission from the solar cell must be matched by its rate of photon absorption. This emission is necessary since the concentration of electrons in the active layer needs to remain constant.

For a solar cell in the dark, it will absorb “light” from surroundings, in this case, the dark ambient radiation is like a black body (BB), with the photon flux density normal to the surface of a flat solar cell:

$$\phi_{BB}(E) = \frac{2F_a}{h^3 c^2} \frac{E^2}{\exp\left(\frac{E}{kT}\right) - 1}, \quad (5.1)$$

where F_a is the geometrical factor of the ambient radiation, here $F_a = \pi$; h is the Plank constant; c is the speed of light in the vacuum. Thus, the equivalent dark saturation current density absorbed from BB is

$$J_{abs} = q \int EQE(E) \phi_{BB}(E) dE. \quad (5.2)$$

As the result of detailed balance, J_{abs} is also equal to the equivalent density for photon emission through the surface of the solar cell J_{rad} .

Rau et al. extended the detailed balance relationship from ideal cases to practical solar cells, and showed a reciprocal relationship between the quantum efficiency for current extraction EQE and the quantum efficiency for electroluminescence EQE_{EL}.¹²⁶

$$EQE_{EL}(E) = EQE(E) \phi_{BB}(E) \left(\exp\left(\frac{qV}{kT}\right) - 1 \right). \quad (5.3)$$

The electroluminescence (EL) spectrum is the result of operating a solar cell as a light-emitting diode. Its emission comes from the radiative recombination of charge carriers in the solar cell. Equation 5.3 allows the practical dark saturation current J_0 to be related to the EQE:

$$J_0 = \frac{q}{EQE_{EL}} \int EQE(E) \phi_{BB}(E) dE. \quad (5.4)$$

This reciprocal relationship in Equation 5.3 is important for us to pinpoint charge transfer absorption in high-sensitive EQE spectra, by comparing its absorption features at sub-gap range with the corresponding EL spectra, as illustrated in **Figure 5.1**.

Figure 5.1. EQE, IQE, absorption, and EL spectra of a MEH-PPV:PC₆₁BM device. Adapted with permission.¹²⁵ Copyright 2014. Springer Nature Publishing AG.

5.2 Shockley-Queisser limit

The Shockley-Queisser (S-Q) limit, which was first proposed by Shockley and Queisser in 1961,¹²⁷ is the upper theoretical limit for the efficiency of a single p-n junction solar cell. It was calculated in the ideal case where 1) the only recombination mechanism in the device is radiative recombination, and 2) all incident light with $E > E_g$ is absorbed with 100% quantum efficiency, while no absorption below E_g .

From assumption 1) we know under S-Q condition, the EQE_{EL} of the device is 100%, and from assumption 2) its absorbance and EQE become a step-like function: $EQE = 1$ when $E > E_g$, $EQE = 0$ when $E < E_g$.

Thus, the dark saturation current density under S-Q condition J_0^{SQ} is

$$J_0^{SQ} = q \int_{E_g}^{\infty} \phi_{BB}(E) dE. \quad (5.5)$$

Similarly, under the standard AM 1.5G illumination, the short circuit current density under S-Q condition J_{SC}^{SQ} is

$$J_{SC}^{SQ} = q \int_{E_g}^{\infty} \phi_{AM\ 1.5}(E) dE. \quad (5.6)$$

With the defined J_0^{SQ} and J_{SC}^{SQ} , the J - V relation of the solar cell under S-Q condition is

$$J(V) = J_{SC}^{SQ} - J_0^{SQ} \left(e^{\frac{qV}{kT}} - 1 \right), \quad (5.7)$$

and the maximum open circuit voltage under S-Q condition V_{OC}^{SQ} can be calculated as

$$V_{OC}^{SQ} = \frac{kT}{q} \ln \left(\frac{J_{SC}^{SQ}}{J_0^{SQ}} + 1 \right). \quad (5.8)$$

V_{OC}^{SQ} is an important parameter for the quantification of voltage losses, which will be discussed later. Based on the equations above, one can conclude that when a solar cell is in thermal equilibrium with fixed ambient and solar radiation, the E_g is the only parameter that limits the solar cell's J - V relationship and the resulting PCE.

5.3 Quantification of voltage losses

The voltage loss, or energy loss, in organic solar cells, is mainly due to the recombination of charge carriers. It denotes the energy difference between the optical gap E_g and the measured V_{OC} . By comparing a real solar cell with its ideal counterpart (under S-Q condition), the total voltage loss can be classified into three parts (**Figure 5.2**), denoted as ΔV_1 , ΔV_2 , and ΔV_3 :

$$\begin{aligned} V_{loss} &= \frac{E_g}{q} - V_{OC} = \left(\frac{E_g}{q} - V_{OC}^{SQ} \right) + (V_{OC}^{SQ} - V_{OC}^{rad}) + (V_{OC}^{rad} - V_{OC}) \\ &= \Delta V_1 + \Delta V_2 + \Delta V_3 \end{aligned} \quad (5.9)$$

Figure 5.2. Energy diagram of the voltage loss in different parts, defined by S-Q limit.

ΔV_1 comes from the radiative recombination, which is an unavoidable loss in any solar cells, since according to the detailed balanced theory, a spontaneous emission will always exist as long as solar cells absorb photons. The value of ΔV_1 can be calculated by subtracting $V_{\text{OC}}^{\text{SQ}}$ from E_g .

As we discussed previously, $V_{\text{OC}}^{\text{SQ}}$ is defined based on the assumption that all incident light with $E > E_g$ is absorbed with 100% EQE. by replacing the 100% EQE with the actual EQE(E) which is recorded from the real device, the radiative limit V_{OC} , $V_{\text{OC}}^{\text{rad}}$, can be calculated by

$$V_{\text{OC}}^{\text{rad}} = \frac{kT}{q} \ln \left(\frac{J_{\text{SC}}}{J_0^{\text{rad}}} + 1 \right) = \frac{kT}{q} \ln \left(\frac{\int EQE(E) \phi_{\text{AM}1.5}(E) dE}{\int EQE(E) \phi_{\text{BB}}(E) dE} + 1 \right), \quad (5.10)$$

where J_0^{rad} is the radiative limit dark current density, which equals to J_{abs} in Equation 5.2.

Thus, the origin of ΔV_2 is the mismatch of the EQE in the S-Q condition and the real working device. Research shows that a smaller Urbach energy, which is correlated to the reduced energetic disorder in solar cells, is helpful to reduce ΔV_2 .¹²⁸

Finally, the third part of voltage loss ΔV_3 is mainly due to the non-radiative recombination. The existence of non-radiative recombination in the device will drive its EQE_{EL} from unity to a lower value, therefore ΔV_3 can be calculated by the EQE_{EL} of the real device when the injection current density equals to J_{SC} :

$$\Delta V_3 = -\frac{kT}{q} \ln(EQE_{EL}). \quad (5.11)$$

The voltage loss of a solar cell can also be quantified by the energy of the charge transfer state (E_{CT}). The E_{CT} can be deduced by fitting the sub-gap region of the high-sensitive EQE spectrum, which usually can be assigned to the absorption of CT states. However, in some of the high-efficient NFA systems, the absorption of the CT state is hard to distinguish due to the strong hybridization between the CT state and the locally excited state.¹⁰³ From this point of view, quantifying voltage loss with S-Q limit is more practical for most of the OSC systems.

Chapter 6 Summary and outlook

Due to its importance and complexity, the morphology of the donor:acceptor photoactive layer has become and will continue to be a hot topic in the field of OSCs. *Ex-situ* nanostructure analysis on dry films after deposition can of course reveal the final morphology of the film. However, *in-situ* measurements directly probing the film formation progress, allowing us to “watch” aggregation and phase separation processes in real-time. Driven by the need for deeper insights into nanostructure formation in active layers, we present a versatile *in-situ* detection system that consists of multiple spectroscopic techniques, its capabilities have been demonstrated in our study regarding the film formation processes of three representative material systems in OSCs. Among these techniques, *in-situ* steady-state PL and TRPL show unique advantages since they not only provide real-time information like polymer aggregation, but also resolve interactions between donor and acceptor during film formation. We believe this method can be easily extended to other solution processing techniques for in-depth morphological studies of not only organic, but also perovskite solar cells.

The *in-situ* setup was also utilized to study morphological optimization processes of the all-polymer blend, and reveal the role of solvent additive in all-polymer systems. Other conditions that could potentially influence the final morphology during deposition, like the viscosity of the ink, or the coating atmosphere, are expected to be studied with this method.

The mechanism of efficient exciton dissociation in OSCs with minimum energetic offsets is another debatable topic in the field. Although numerous pieces of literature have aimed to tackle this puzzle, a generalized conclusion is still lacking. Alternative device architectures like bilayer and dilute BHJ could be useful in future studies, since potential impacts from intricate morphologies can be excluded by these structures to some degree.

Modification of interfacial layers in OSCs by introducing a second component can be a practical and effective way to increase the device's overall performance. However, there are also potential limitations of this method. Take MXene as an example, although it has outstanding electronic and optical properties, the instability in aqueous media needs to be addressed before its future application.

We have witnessed a rapid growth of the PCE of OSCs in the last decade, which came from mutual contributions of the rational design of the materials, optimizations of device fabrication, and in-depth understandings of its working mechanisms. The screening of the best material combinations and device fabrication conditions are still trial-and-error processes, which require tedious lab work and massive material consumption. From this point of view, the development of high throughput screening methods based on big data and machine learning could drastically shorten the development cycles for new materials and devices. The mechanisms of morphology formation and exciton separation may be among the most challenging topics in OSCs. I hope the methods and conclusions that we have proposed in this thesis may contribute to future studies related to these topics. The vision of OSCs is the capability to be fabricated by industrial printing on a large scale. The proposed real-time measurements in this thesis could also be converted to a non-destructive imaging method for the in-line quality evaluation of the solar cells during the printing process. The stability of OSCs is another key parameter other than PCE that needs to be optimized before its mass production. Very recently, an article demonstrates the remarkable operation stability of an OSC system,¹²⁹ which further provides great potential for the commercial application of OSCs.

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