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Organic Electronic Devices for Solar Energy Conversion and Storage

Yingzhi Jin

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

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Abstract

This thesis focuses on two types of organic electronic devices: organic photovoltaic (OPV) devices for solar energy conversion, and photo-capacitors for energy storage.

OPVs have been under the focus of research for decades as an effective technique to convert solar energy to electricity. So far, the efficiency of bulk heterojunction OPV consisting donor and acceptor materials is approaching to 18% with non-fullerene acceptor (NFA), which make it close to commercialization. The process of charge generation and recombination are two competing processes in OPVs, since their requirements for the active layer morphology are contradictory. Large donor/acceptor interfaces facilitate charge generation but hinder the transporting pathways for charge transportation. The simultaneously enhanced charge generation and transportation are achieved by using the ternary strategy in my first paper. The fully mixed donors and NFAs are beneficial for the charge generation and fullerene is introduced as an extra electron transport channel. The hierarchical morphology of the blend film is confirmed by the TEM results. The voltage loss analyses indicate that the hierarchical morphology could suppress unfavorable charge transfer state and non-radiative recombination loss. In my second paper, efficient charge generation with low voltage loss are achieved in the solar cells by rational designing a series of NFAs. The detailed voltage losses are discussed in these binary systems, revealing the critical relationship between radiative efficiency and device performance.

To harvest photocurrent in OPVs, long lifetime triplet excitons are highly expected to be good candidates. The potential of triplet materials in OPVs has been explored since 1970s. However, the performance of the triplet materials-based OPVs is far behind. The voltage loss in triplet OPVs is intensively studied in my third work. A higher open circuit voltage (0.88 V) is observed for Ir(FOtbpa)₃-based devices than those of Ir(Ftbpa)₃ (0.80 V) despite a lower charge transfer state energy. To understand above result, the voltage losses through radiative and non-radiative recombination pathways in two devices are quantitatively investigated, which indicate a reduced non-radiative recombination loss in the Ir(FOtbpa)₃-based devices.

The fluctuation of sun irradiation resulting the unstable output power of solar cells. Therefore, it is important to store electricity of solar cells for later use. Integrated photo-capacitor (IPC), combining a solar cell and a super-capacitor by sharing one common electrode, is able to simultaneously realize the energy harvesting and storage. Building upon this advantage, IPC devices received tremendous research attention. In my fourth and last papers, we introduced super-capacitors to construct IPC devices with OPV device or modules. A free standing thick-PEDOT:PSS film is successfully integrated into an all solution-processed IPC device as the common electrode. Resulting devices demonstrate good performance and outstanding stability. With solar PV modules, a higher voltage can be generated and stored by asymmetric super-capacitors, which could be used as a portable power unit.

Populärvetenskaplig Sammanfattning

Efterfrågan på el ökar dramatiskt och det finns därmed ett starkt behov av utveckling av förnyelsebara energikällor. Solenergi är en ideal energikälla på grund av dess låga miljöpåverkan. Organiska solceller (härefter benämnda solceller) använder konjugerade organiska molekyler eller polymerer som ljusfångande aktivt material för att absorbera solljusets energi och omvandla denna till elektricitet. För att effektivt kunna fånga upp solljusets energi behöver man i det aktiva lagret ha en blandning av minst två typer av molekyler, där den ena typen (kallad en donor) har förmåga att ge bort en elektron när den interagerar med ljus, och den andra typen (kallad en acceptor) har förmågan att ta emot en elektron. Fram till nyligen användes nästan uteslutande kolbollar (olika fullerener) som acceptorer. Men under senare tid har nya typer av acceptor-molekyler utvecklats vilket lett till snabba förbättringar i prestanda. Solcellers prestanda kan utvärderas kvantitativt i procent med hjälp av begreppet effektomvandlingseffektivitet (Där förkortningen PCE, från engelskans Power Conversion Efficiency, brukar användas). Det tog mycket lång tid att utveckla solceller med PCE på 10%, men efter att nya typer av acceptorer introducerades har PCE ökat snabbt. I labbskala har man lyckats uppnå PCE på 18% och processtekniken bör inom snar framtid kunna skalas upp för industriell tillverkning. En inneboende begränsning med solceller är att solljuset inte är konstant, utan varierar till exempel med dygnet samt molnighet. Därför behövs energilagringseinheter, såsom batterier och superkondensatorer, kopplas samman med solceller. Dessa hybrider kallas fotokondensatorer, vilka både kan omvandla solljus till elektricitet och lagra denna elektricitet. Fotokondensatorer kan därför användas som självdrivna enheter oberoende av anslutning till elnätet. Denna avhandling fokuserar på 1) utveckling av organiska solceller för att kunna fånga upp solljuset energi och omvandla denna till elektricitet, och 2) utveckling av fotokondensatorer för att både kunna generera och lagra elektricitet.

List of Publications

Papers **included** in this thesis

Review paper:

Limitations and Perspectives on Triplet-Material-Based Organic Photovoltaic Devices.

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Yingzhi Jin, Yanxin Zhang, Yanfeng Liu, Jie Xue, Weiwei Li, Juan Qiao, Fengling Zhang

Research papers:

1. High-efficiency small-molecule ternary solar cells with a hierarchical morphology enabled by synergizing fullerene and non-fullerene acceptors.

Nature energy, 2018, 3, 952–959.

Zichun Zhou, Shengjie Xu, Jingnan Song, **Yingzhi Jin**, Qihui Yue, Yuhao Qian, Feng Liu, Fengling Zhang and Xiaozhang Zhu

2. Asymmetric Electron Acceptors for High-Efficiency and Low-Energy-Loss Organic Photovoltaics

Advanced Materials, 2020, 32, 2001160.

Shuixing Li, Lingling Zhan, **Yingzhi Jin**, Guanqing Zhou, Tsz-Ki Lau, Ran Qin, Minmin Shi, Changzhi Li, Haiming Zhu, Xinhui Lu, Fengling Zhang, Hongzheng Chen

3. Investigation on voltage loss in organic triplet photovoltaic devices based on Ir complexes.

Journal of Materials Chemistry C, 2019, 7 (47), 15049-15056

Yingzhi Jin, Jie Xue, Juan Qiao, Fengling Zhang

4. Laminated free standing PEDOT:PSS electrode for solution processed integrated photo-capacitors via hydrogen-bond interaction.

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Yingzhi Jin, Zaifang Li, Lei qiang Qin, Xianjie Liu, Lin Mao, Yazhong Wang, Fei Qin, Yanfeng Liu, Yinhua Zhou, Fengling Zhang

5. All solution processed organic photovoltaic module integrated with asymmetric super-capacitors as a self-powered unit

Manuscript

Yingzhi Jin, Lulu Sun, Lei qiang Qin, Zaifang Li, Yinhua Zhou, Fengling Zhang

My contributions to the papers

Review paper:

Wrote the main part of the manuscript, except for the part relevant to material design. Revised the manuscript together with co-authors.

Research papers:

1. Did the energy loss part experiments and analyzed the data, wrote the manuscript relevant to energy loss and revised with co-authors.
2. Did the energy loss part experiments and analyzed the data, revised the manuscript with co-authors.
3. Performed most of the experiments and data analyses, except for the material synthesis and characterization, wrote the manuscript and revised it together with co-authors.
4. Performed most of the experiments and data analyses. Wrote the manuscript and revised it together with co-authors.
5. Designed and performed most of the experiments. Wrote the manuscript.

Papers **not included** in this thesis

1. “Double-cable” conjugated polymers with linear backbone toward high quantum efficiencies in single-component polymer solar cells.

Journal of the American Chemical Society, 2017, 139 (51), 18647-18656.

Guitao Feng, Junyu Li, Fallon JM Colberts, Mengmeng Li, Jianqi Zhang, Fan Yang, **Yingzhi Jin**, Fengling Zhang, Rene AJ Janssen, Cheng Li, Weiwei Li

2. Design rules for minimizing voltage losses in high-efficiency organic solar cells.

Nature materials, 2018, 17 (8), 703-709.

Deping Qian, Zilong Zheng, Huifeng Yao, Wolfgang Tress, Thomas R Hopper, Shula Chen, Sunsun Li, Jing Liu, Shangshang Chen, Jiangbin Zhang, Xiao-Ke Liu, Bowei Gao, Liangqi Ouyang, **Yingzhi Jin**, Galia Pozina, Irina A Buyanova, Weimin M Chen, Olle Inganäs, Veaceslav Coropceanu, Jean-Luc Bredas, He Yan, Jianhui Hou, Fengling Zhang, Artem A Bakulin, Feng Gao

3. Printed nonfullerene organic solar cells with the highest efficiency of 9.5%.

Advanced Energy Materials, 2018, 8 (13), 1701942.

Yuanbao Lin, **Yingzhi Jin**, Sheng Dong, Wenhao Zheng, Junyu Yang, Alei Liu, Feng Liu, Yufeng Jiang, Thomas P Russell, Fengling Zhang, Fei Huang, Lintao Hou

4. A Free-Standing High-Output Power Density Thermoelectric Device Based on Structure-Ordered PEDOT: PSS.

Advanced Electronic Materials, 2018, 4 (2), 1700496.

Zaifang Li, Hengda Sun, Ching-Lien Hsiao, Yulong Yao, Yiqun Xiao, Maryam Shahi, **Yingzhi Jin**, Alex Cruce, Xianjie Liu, Youyu Jiang, Wei Meng, Fei Qin, Thomas Ederth, Simone Fabiano, Weimin M Chen, Xinhui Lu, Jens Birch, Joseph W Brill, Yinhua Zhou, Xavier Crispin, Fengling Zhang

5. Charge transfer dynamics and device performance of environmentally friendly processed nonfullerene organic solar cells.

ACS Applied Energy Materials, 2018, 1 (9), 4776-4785.

Luana Cristina Wouk de Menezes, **Yingzhi Jin**, Leandro Benatto, Chuanfei Wang, Marlus Koehler, Fengling Zhang, Lucimara Stolz Roman

6. Effect of Side Groups on the Photovoltaic Performance Based on Porphyrin–Perylene Bisimide Electron Acceptors.

ACS applied materials & interfaces, 2018, 10 (38), 32454-32461.

Yiting Guo, Yanfeng Liu, Qinglian Zhu, Cheng Li, **Yingzhi Jin**, Yuttapoom Puttisong, Weimin Chen, Feng Liu, Fengling Zhang, Wei Ma, Weiwei Li

7. A diketopyrrolopyrrole-based macrocyclic conjugated molecule for organic electronics.

Journal of Materials Chemistry C, 2019, 7 (13), 3802-3810.

Cheng Li, Chao Wang, Yiting Guo, **Yingzhi Jin**, Nannan Yao, Yonggang Wu, Fengling Zhang, Weiwei Li

8. Mo_{1.33}C MXene-assisted PEDOT:PSS hole transport layer for high performance bulk-heterojunction polymer solar cells.

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

List of Abbreviations and Symbols

terawatts	TW
organic photovoltaic device	OPV
light emitting diode	LED
molecular orbital	MO
highest occupied molecular orbital	HOMO
lowest unoccupied molecular orbitals	LUMO
power conversion efficiency	PCE
bulk heterojunction	BHJ
poly(phenylene vinylenes)	PPV
polythiophenes	PT
[6,6]-phenyl-C61-butyric acid methyl ester	PC ₆₁ BM
[6,6]-Phenyl-C71-butyric acid methyl ester	PC ₇₁ BM
open circuit voltage	V_{oc}
short circuit current density	J_{sc}
current density	J
air mass	AM
current density-voltage curves	J - V curves
fill factor	FF
incident light power	P_{in}
external quantum efficiency	EQE
internal quantum efficiency	IQE
number of collected charge carriers	N_e^{out}
number of incident photons	N_{ph}^{in}
number of absorbed photons	N_{ph}^{ab}
exciton binding energy	E_B^{exc}
exciton diffusion length	L_D
Charge transfer	CT
Förster resonance energy transfer	FRET
bonding energy of CT excitons	E_B^{CT}
ground state	GS
charge-separated state	CS
non-fullerene acceptor	NFA
density of states	DOS

space-charge-limited-current	SCLC
poly(3-hexylthiophene)	P3HT
indene-C60bis-adduct	ICBA
Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)	PEDOT:PSS
Polyethylenimine	PEI
optical bandgap	E_g
Shockley–Queisser	SQ
electroluminescent	EL
external quantum efficiency of EL	EQE_{EL}
Photothermal deflection spectroscopy	PDS
Fourier-transform photocurrent spectroscopy	FTPS
energy of CT state	E_{CT}
photoluminescence	PL
triplet material based OPVs	T-OPVs
intersystem crossing	ISC
spin-orbit coupling	SOC
internal conversion	IC
electrical double layer capacitor	EDLC
cyclic voltammetry	CV
galvanostatic charge discharge	GCD
two-dimensional	2D
integrated photo-capacitor	IPC
dye-sensitized solar cell	DSSC
perovskite solar cells	PVSC

Chemical structures of materials involved in this thesis

Donor materials involved in this thesis

Acceptor materials involved in this thesis

Interface or electrode materials involved in this thesis

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Chapter 1 Introduction

1.1 Solar Energy Conversion

The enormous energy delivered by the sun to the earth is 1.2×10^5 terawatts (TW), which surpasses any other energy resource. However, the usage of solar energy is less than 1.8% among the total energy consumption in 2017.¹ Solar energy is usually converted into three types of energy: electricity, fuel, and heat. Solar photons can be converted into electricity by photovoltaic devices. Solar fuel is a synthetic chemical fuel that produced by natural and artificial photosynthesis, electrolysis, and photocatalysis.² Heat can be directly captured by an absorbing medium. In my thesis, we focus on the electricity conversion because of the dramatically increasing of electricity demand in our daily life. The sources of electricity generation have changed a lot from 1973 to 2017 (**Figure 1.1**), it is exciting to see the remarkable increase in the share of electricity generated from Non-hydro renewable energy.

Figure 1.1 Electricity generation sources in 1973 and 2017.¹

To date, silicon solar cells, due to their high power conversion efficiencies (PCEs) and excellent stability, are the most successful commercial photovoltaic (PV) devices, which dominate more than 90% of the PV market. However, the complicated fabrication process and the rigid device structure hinder their applications in the field of flexible and portable electronics. In contrast, organic

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PV (OPV) devices with the advantages of easy fabrication, low cost, lightweight and flexibility, have more potential applications than silicon solar cells.

1.2 Solar Energy Storage

Solar cells have been investigated as an effective technique to convert solar energy to electricity. However, this process can only work when the sun is shining. Moreover, the fluctuation of sun irradiation causes an unstable output power of solar cells. Therefore, it is important to be able to store solar energy for later use. Batteries, fuel cell and super-capacitors are widely used as energy storage devices. All these devices are consisting of two electrodes in contact with an electrolyte, but the operating mechanisms are different. Batteries are closed systems that convert chemical energy to electrical energy *via* oxidation-reduction (redox) reactions at the anode and cathode. Fuel cells are open systems, which need fuels (hydrogen, hydrocarbons) and oxygen to run the chemical reaction. In super-capacitors, charges are stored by fast and reversible redox reactions at the interface of the electrode/electrolyte. The performance evaluation of the different energy storage devices is shown in a Ragone plot (**Figure 1.2**) by comparing the energy density and the power density. Fuel cells can generate high energy with low power, whereas super-capacitors deliver high power with low energy. Batteries have intermediate power and energy density.

Figure 1.2 Ragone plot of batteries, fuel cells and super-capacitors. The figure is adapted with permission.³ Copyright 2004, American Chemical Society.

When the energy storage devices are installed as a part of PV modules, the excess solar electricity can be stored for later use without sunlight. Demands for solar energy storage are different for different applications. The solar electricity installation can be classified into two types: utility-scale solar power facility and distributed solar power facility. A utility-scale solar power facility can generate large amounts of electricity. As a result, 1-20 MW maximum power of the energy storage systems is expected, and 2-6 h storage lifetime is required for delivery to the electric grid. The storage system with such capacity can provide huge advantages for the efficiency and production of solar power.⁴ On the other hand, a distributed solar power facility is able to produce moderate amounts of electricity compared to the utility-scale solar power facility. Therefore, robust energy storage systems with repeating charge/discharge are required to provide inherent high service reliability to local electrical systems.

1.3 Organic Semiconductors

Organic semiconductors have been widely used in electronic devices including light emitting diodes (LEDs), OPVs, field effect transistors, photodetectors and memories.⁵⁻⁷ The semiconducting property of organic materials is derived from the π -conjugated structure consisting of alternating single and double bonds between carbon atoms. A conjugated structure can occur in both polymers and small molecules. Although the carrier mobility and stability are lower than those of inorganic materials, organic semiconductors have their other advantages, such as easy fabrication, mechanical flexibility, and low cost.

Figure 1.3 σ - and π -bond are formed by the orbital overlap.

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The molecular structure of organic semiconductors can be described by valence bond theory or molecular orbital (MO) theory. Valence bond theory explains the formation of a chemical bond by the overlapping atomic orbitals (hybridization) between two atoms. As shown in **Figure 1.3**, σ - and π -bond are formed by different types of orbital overlap. σ -bonds are formed by s-s overlap, head-to-head p-p overlap, and s-p overlap. π -bonds are formed by the parallel overlap of two p orbitals. The single bond only has one σ -bond, while the double bond has one σ - and one π -bond. In contrast with the valence bond theory, MO theory describes the distribution of electrons delocalized over the entire molecule rather than being localized on atoms. MO theory is more helpful to understand the properties of organic semiconductors.

The concept of bonding and antibonding molecular orbitals, such as σ/σ^* and π/π^* (**Figure 1.4 a**), which is proposed in MO theory, well predicts the process of electron transition between different energy levels. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbitals (LUMO) are very important for organic semiconductors. In solid films, the π - π stacking of polymers or small molecules broadens the distribution of the bonding and antibonding molecular orbitals (**Figure 1.4 b**), which result in the energetic landscape of HOMO and LUMO bands.

Figure 1.4 (a) σ/σ^* and π/π^* molecular orbitals are formed by the combination of two s orbitals and two p orbitals, respectively. (b) LUMO and HOMO energy distribution due to inter molecular or inter-chain π - π stacking.

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2.1 The Development of OPVs

In the early stage of OPVs (1970s), Schottky barrier cells were utilized to investigate the photovoltaic effects of organic materials.⁸⁻¹⁰ The common structure of the Schottky cell is metal/organic materials/metal ($M_1/P/M_2$) (**Figure 2.1a**), where one metal electrode should be semi-transparent. However, this type of device show poor performance due to the high exciton binding energy of organic materials, leading to inefficient exciton dissociation.

Figure 2.1 The architecture of OPVs: (a) Schottky junction (b) Bilayer-heterojunction (c) BHJ. (d) Ternary. The figure is adapted with permission.¹¹ Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

After about one decade, A bilayer-heterojunction device containing a donor (electron donating material) layer and an acceptor (electron accepting material) layer (**Figure 2.1b**) with an impressive PCE about 1% was fabricated *via* vacuum deposition in 1986.¹² In bilayer devices, the interface between donor and acceptor facilitate exciton dissociation into free charges. In addition, the donor and acceptor layers provide continuous pathways for the transport of charge carriers to the corresponding electrodes. However, the performance of bilayer solar cells

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is still limited by the short exciton diffusion length (~ 10 nm),¹³ which limits the thickness of active layers and results in inefficient absorption.

The development of the bulk heterojunction (BHJ) structure (**Figure 2.1c**) with interpenetrating donor/acceptor domains in one film has become the standard geometry of OPVs nowadays. The idea of mixing donor and acceptor materials was first reported by Yokoyama et al. using a co-deposition method in 1991,¹⁴ after that, the BHJ concept was realized in solution processed organic films by A. J. Heeger et al.¹⁵⁻¹⁹ The ideal BHJ geometry has a much larger interfacial area comparing to that in the bilayer-heterojunction. To achieve efficient exciton dissociation, a large interfacial area is required, while continuous donor and acceptor phases are needed for charge transportation. Therefore, the morphologies of the BHJ layer have strong influence on the device performance.

The ternary concept (**Figure 2.1d**) is a facile and effective way to further improve the performance of binary OPV devices. Not only can the third component (either as donor or acceptor) provide a broadened band of light absorption, but also has other important roles, such as facilitating exciton dissociation and charge transport, as well as the possibility of influencing the film morphology.

Figure 2.2 The trend of PCE development of BHJ OPVs since 2001. The data are from reference.²⁰⁻³²

The trend of PCE development of BHJ OPVs since 2000 is shown in **Figure 2.2**, which is divided into three stages. Before 2000, the PCE is less than 1% and the illumination light is not the standard air mass (AM) 1.5G, thus the

development is not included in Figure 2.2. At that time, poly(phenylene vinylenes)(PPV) or polythiophenes (PT) based polymers were used as donors and C₆₀ was used as acceptor.³³ To increase the solubility of C₆₀ in organic solvents, [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) was developed.³⁴ The devices with configuration of Ca/MEH-PPV:PC₆₁BM/ITO were investigated in 1995.¹⁹ At stage I (2001~2007), the development of fullerene acceptors from C₆₀ to PC₆₁BM to [6,6]-Phenyl-C71-butyric acid methyl ester (PC₇₁BM)³⁵, accompanied by device engineering (interface engineering^{36, 37}, thermal annealing²¹, solvent annealing²²), contributed to the improvement in photocurrent and PCEs. In 2001, the breakthrough in this field was achieved by Shaheen et al. in Linz. The device structure was ITO/PEDOT/MDMO-PPV:PC₆₁BM/LiF/Al. By changing solvent from toluene to chlorobenzene, an improved PCE from 0.9% to 2.5% was achieved.²⁰ The use of alternating copolymers with small band gaps consisting of electron rich and electron deficient units in the conjugated main chains were reported by Havinga et al. in 1992.³⁸ Copolymers based on fluorine-thiophene-A-thiophene units (APFOs) and phenylene-thiophene-A-thiophene units (LBPPs) were synthesized and applied as donors in OPVs by Andersson/Inganäs et al. in 2003.³⁹⁻⁴⁵ OPVs based on these donor materials with extended absorptions showed only slight improvement in PCEs compared to PT based donor materials. However, it still indicated the direction for the design of new copolymers materials. From 2007 to 2015 (stage II), more efforts were made in designing and synthesizing new alternating copolymers with low band gaps. Leclerc and co-workers introduced the carbazole with thiophene-benzothiazole-thiophene (TBT) units as the main chain to obtain copolymer PCDTBT.⁴⁶ A high PCE of 6.1% was achieved by device engineering with a device configuration of ITO/PEDOT:PSS/PCDTBT:PC₇₁BM/TiO_x/Al.⁴⁷ The alternating copolymers based on benzo[1,2-b:4,5-b']dithiophene (BDT) and different conjugated units further improved the performance of OPVs from 7% to 10%.^{24, 25, 48} From 2015, the development of non-fullerene acceptors (NFAs) has further boosted the efficiency of OPVs up to 18% for single junction devices.³²

2.2 Performance Characterization of OPVs

2.2.1 J-V Curves

In dark condition, a diode behavior (rectifying feature) with a much higher current at forward bias than that at reverse bias is characteristic of a OPV device. (**Figure 2.3a** red dash curve). Therefore, the dark current density of an OPV device can be expressed by the Equation for an ideal diode:

$$J_{dark} = J_0 \left(e^{\frac{qV}{k_B T}} - 1 \right) \quad (2.1)$$

where J_0 is the reverse saturation current density, q is charge in one electron, V is the applied voltage, k_B is Boltzmann constant, and T is absolute temperature.

Figure 2.3 (a) Typical J - V curves under light and dark for an OPV device, as well as the calculate P - V curve. (b) Equivalent circuit for an ideal OPV device.

Under light illumination, OPVs will generate power when a load is connected into the circuit. With infinite load resistance (the circuit is open), the voltage developed is called the open circuit voltage (V_{oc}). While negligible load resistance leads to the short circuit condition, giving the short circuit current density (J_{sc}).

The equivalent circuit of an ideal OPV is shown in **Figure 2.3b**. The net current density (J) that flows in the circuit is the sum of the short circuit current density J_{sc} and dark current density J_{dark} .

$$J = J_{sc} - J_{dark} \quad (2.2)$$

$$J = J_{sc} - J_0 \left(e^{\frac{qV}{k_B T}} - 1 \right) \quad (2.3)$$

For the ideal diode, at open circuit condition, no current is flowing in the circuit, which indicates that all the photo-generated charge carriers are recombined. With $J = 0$ in Equation 2.3, we obtain,

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{J_{sc}}{J_0} + 1 \right) \quad (2.4)$$

The efficiencies of OPVs are measured under illumination of a simulated AM 1.5G solar irradiation with intensity of 100 mW cm^{-2} . Typical current density-voltage (J - V) curve (Figure 2.3a, black curve) for an OPV device under light can be recorded by applying sweep voltage on the device. The J - V curve pass through

three quadrants, which indicate three different applications. When $V < 0$, the device acts as a photodetector. At $V > V_{oc}$, the device work as an LED. OPVs operate at bias from 0 to V_{oc} , in which the device generates power. The device output power density (P) is given by

$$P = J \times V \quad (2.5)$$

From the P - V curve shown in **Figure 2.3a** (blue), the maximum output power (P_{max}) occurs at a particular point with the current density J_{mp} and voltage V_{mp} . For an ideal solar device, the value of J_{mp} is close to J_{sc} and V_{mp} is close to V_{oc} , which means the J - V curve would follow the blue rectangle as shown in **Figure 2.3a**. The fill factor (FF) is an important parameter defined as

$$FF = \frac{J_{mp} \times V_{mp}}{J_{sc} \times V_{oc}} \quad (2.6)$$

FF characterizes squareness of the J - V curve and represents the extraction property of the OPV device. Then the PCE of a device is defined as the ratio between the maximum output power and the incident light power (P_{in}).

$$PCE = \frac{P_{max}}{P_{in}} = \frac{J_{mp} \times V_{mp}}{P_{in}} = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}} \quad (2.7)$$

The equivalent circuit with series and shunt resistances for a real device is shown in **Figure 2.4**. Series resistance includes the bulk resistance and contact resistance. The shunt resistance arises from the leakage current in the device. Taking both types of resistance into consideration, the J - V curve can be expressed by Equation 2.5,

$$J = J_{sc} - J_0 \left[\exp \left(\frac{q(V + JR_S)}{nk_B T} \right) - 1 \right] - \frac{V + JR_S}{R_{Sh}} \quad (2.8)$$

where n is ideality factor of the diode, R_S is series resistance and R_{Sh} is shunt resistance.

Figure 2.4 Equivalent circuit of a real OPV device.

2.2.2 External and Internal Quantum Efficiency

Quantum efficiency describes the photon to electron conversion efficiency of a solar cell. There are two types of quantum efficiencies in OPVs: the external quantum efficiency (EQE) and internal quantum efficiency (IQE). EQE is calculated by the ratio of the number of collected charge carriers (N_e^{out}) to the number of incident photons (N_{ph}^{in}) at a specific wavelength, see Equation 2.9; IQE is the ratio of the number of collected charge carriers to the number of absorbed photons (N_{ph}^{ab}), Equation 2.10.

$$EQE(\lambda) = \frac{N_e^{out}(\lambda)}{N_{ph}^{in}(\lambda)} \quad (2.9)$$

$$IQE(\lambda) = \frac{N_e^{out}(\lambda)}{N_{ph}^{ab}(\lambda)} \quad (2.10)$$

As the number of absorbed photons is always smaller than that of incident photons, the IQE is always larger than EQE. The J_{sc} of an OPV device can be calculated by integrating over the product of the EQE and the photon flux of the AM1.5G solar spectrum (**Figure 2.5a**).

$$J_{sc} = q \int EQE(E) \phi_{AM1.5}(E) dE \quad (2.11)$$

The relationship between photon energy and wavelength is defined by

$$E = \frac{hc}{\lambda} = \frac{1240}{\lambda} \quad (2.12)$$

where E in eV and λ in nm.

As a concrete example, the EQE spectrum and corresponding integrated current based on the high efficiency blend PM6:Y6 are shown in **Figure 2.5b**. EQEs of around 80% are achieved over wide range from 500 to 800 nm. Both donor and acceptor are contributing to the photo-generation. The calculated J_{sc} obtained by integrating the EQE spectrum using Equation 2.11 is quite close to the measured J_{sc} from the J - V curve.

Figure 2.5 (a) AM 1.5G solar spectra irradiance and photon flux. (b) EQE spectrum and corresponding current density of OPV device based on PM6:Y6.

2.3 Working Principle of BHJ OPVs

The working mechanism of BHJ OPVs is converting photons into free charges, which can be achieved by five steps (**Figure 2.6**).

1. Donor and acceptor absorb light to form excitons (bound electron-hole pairs). This process is determined by the bandgap, absorption coefficient and thickness of active materials as well as the device geometry. The photo-generated excitons (Frenkel excitons) are strongly bound due to a strong Coulomb interaction, generally present in organic materials, with a binding energy (E_B^{exc}) typically 0.2-0.5 eV.⁴⁹⁻⁵¹
2. Excitons diffuse to the donor and acceptor interface. The exciton diffusion length (L_D) is defined by the Equation $L_D = \sqrt{D \times \tau}$. Here, D is the exciton diffusion coefficient or diffusivity and τ is the exciton lifetime. The short exciton diffusion length (~10 nm) restrict the domain size of pure phase in active layers.
3. Charge transfer (CT) excitons are formed at the interfaces. The Frenkel excitons need to be dissociated by electron or hole transfer at the donor/acceptor interfaces. The E_B^{exc} is overcome by the charge transfer from Frenkel excitons to CT excitons, which is an ultrafast process in femtoseconds (fs) timescale.⁵²⁻⁵⁴
4. CT excitons dissociate into free charge carriers (holes/electrons). This process is influenced by the binding energy, electric field, electrostatic landscape at interface, entropy, disorder and delocalization. More discussion will be given on the CT exciton dissociation in **2.3.2**.

5. Free charge carriers diffuse or are driven by the built-in potential in the active layer and collected at corresponding electrodes. This process is dominated by the carrier mobility, property of interfacial layers and the work functions of electrodes.

Figure 2.6 Schematic working principle of BHJ OPVs. The bounded Frenkel excitons are represented by electron (red) and hole (blue) within a dash circle. CT exciton is represented by electron and hole within yellow circle. The figure is adapted with permission.¹¹ Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.3.1 Exciton Diffusion

Excitons generated by the photon absorption in organic semiconductors are electrically neutral. Thus, the transportation of excitons in organic materials is electrical field independent, meaning that an exciton moves by random diffusion. Exciton diffusion is facilitated by either Förster or Dexter transfer. The Förster resonance energy transfer (FRET) process is based on a dipole–dipole coupling and requires overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor. The FRET process occurs in a range of 1–10 nm. Dexter energy transfer refers to the actual exchange of electrons between the donor and the acceptor when they have an overlapping wave function. The overlap requirement means that it's a short range process only occurring when the donor and the acceptor are within 1 nm.

Figure 2.7 Exciton diffusion process with downhill and thermally activated hopping at different temperatures. The Gaussian density of states are represented by the distribution of the excitonic energy states. (a) At low temperature, the downhill migration dominates. (b) At room temperatures, both downhill migration and thermally activated hopping contribute to the excitons diffusion process. Reproduced with permission.⁵⁵ Copyright 2008, American Chemical Society.

The dynamics of exciton diffusion is complex. Both coherent and incoherent transport are used to characterize the process of exciton diffusion. In the well-ordered crystalline region, the delocalized excitons migrate in a coherent way. However, most organic films have amorphous feature, the localized excitons migrate by incoherent hopping. The disorder in solid state organic semiconductor materials, due to co-existence of both ordered and amorphous phases, leads to a Gaussian distribution of energy states. One way to try to quantify the energy disorder in the material is given by the half-width σ of the Gaussian peak. The processes of exciton diffusion in a disordered system at different temperatures are shown in **Figure 2.7**.⁵⁵ At low temperature (Figure 2.7a, 4K), the created excitons of high energy go through downhill migration toward lower energy sites. Excitons are trapped in the low energy sites due to the lack of thermal energy and insufficient density of states (DOS) for hopping. Thus, downhill migration process limits the excitons diffusion at low temperature. Whereas at room temperature (Figure 2.7b, 300K), the high energy excitons first go through downhill migration to lower energy sites then thermally activated hopping to the neighbour sites ended closer to the middle of the Gaussian states. Therefore, the exciton diffusion process is temperature dependent.

2.3.2 CT Exciton Formation and Dissociation

CT excitons are formed by ultrafast electron or hole transfer between donors and acceptors (Figure 2.5). The bonding energy of a CT exciton (E_B^{CT}) is smaller than that of the Frenkel excitons (due to the increased electron-hole distance), but still higher than the thermal energy at room temperature (0.025 eV).⁵⁶ Thus, further dissociation of CT excitons is essential for the charge generation in OPVs. So far, there is no consensus of the specific mechanism of the dissociation process of the CT states into free charge carriers. The energy diagram of charge generation and recombination in OPVs is shown in **Figure 2.8**. Under illumination, photons are absorbed by donors and acceptors and Frenkel excitons with large binding energy are generated. At the donor/acceptor interface, CT excitons are formed by electron or hole transfer between donors and acceptors. Then CT excitons can either decay to the ground state (GS) (process 7) or dissociate to the charge-separated (CS) state (process 3 and 4). The recombination of free charge carriers can form both singlet CT state (1CT_1) and triplet CT state (3CT_1), with a 1:3 ratio due to spin statistics (process 5). The back transfer from 3CT_1 to lower triplet state (T_1) may occur as a loss pathway (process 6).

Figure 2.8 A schematic Jablonski diagram for the working process in OPVs. 1. Singlet excitons formed by photon absorption; 2. Radiative decay of singlet excitons; 3. The hot CT excitons can directly dissociate into CS state; 4a. The relaxed CT state is formed by thermal relaxation from hot CT to the lowest CT state (1CT_1); 4b. Dissociation from 1CT_1 into the CS state; 5. The separated electrons and holes recombine to form CT excitons (both singlet and triplet); 6. The triplet CT excitons relax to the triplet state (T_1); 7. The singlet CT excitons recombine to the ground state. The figure is adapted with permission.^{57, 58} Copyright 2013, Springer Nature Publishing AG. Copyright 2014, the Royal Society of Chemistry.

As illustrated in Figure 2.8, there are two proposed processes for CT exciton dissociation.^{58, 59} One is that free charge carriers are generated through the dissociation from the hot CT state (CT_n) (process 3). Hot CT state means CT state with excess thermal energy due to the energy difference between singlet and CT states. Another is that the hot CT state first relax to the lowest CT state (1CT_1) and then dissociate into free charge carriers (process 4a and 4b). The hot CT state theory suggests that the excess thermal energy facilitates the dissociation. This has been supported by the ultrafast pump-probe spectroscopy measurements and simulations.⁶⁰⁻⁷¹ However, charge generation that is independent of excess excitation energy has also been reported.⁷²⁻⁷⁴ In addition, the development of the NFAs shows weak dependence between the dissociation efficiency and the energy offset ($LUMO_{donor}-LUMO_{acceptor}$ or $HOMO_{donor}-HOMO_{acceptor}$).⁷⁵⁻⁷⁸ Besides, the strong evidence of the relaxed CT state dissociation has also been reported.⁷⁹⁻⁸³ The relaxed CT dissociation indicates that the IQE of the system should not depend on the photon energy, even in the CT state region. This phenomenon was confirmed by Vandewal et al. as shown in **Figure 2.9**. The IQE for two material systems were independent with the excitation energy, which proves the relaxed CT dissociation.

Figure 2.9 The IQE of MEH-PPV:PC₆₁BM blend (a) and PBDTTPD:PC₆₁BM blend (b). Reproduced with permission.⁸¹ Copyright 2013, Springer Nature Publishing AG.

The hot CT theory is supported by the ultrafast pump-probe spectroscopy measurements, however, opposite results can also be found in some publications.^{84, 85} For the relaxed CT state dissociation, the driving force to split CT excitons need to be considered. Intensive research has been conducted to correlate the dissociation process with multiple factors, such as electric field, electrostatic landscape at the interface, entropy, disorder and delocalization. The

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electric field dependent or independent charge generation is more related to the material systems. Nowadays, the material systems with high efficiencies show almost independent charge generation on the electric field.⁸⁶ Due to the dipole formed at the interface by the ground state energy transfer, the electrostatic landscape at the donor/acceptor interface has been studied and is believed to contribute to the dissociation process.^{87, 88} The exciton dissociation is determined by the free energy which include the effect of entropy. The electronic degeneracy increases with CT exciton dissociation, which will lead to an increase in entropy and decrease in free energy. This effect has been proved by both experimental and simulation results.⁸⁹⁻⁹² Due to the amorphous nature of organic materials, the energetic disorder will always exist. In general, disorder has negative effect on the charge transport process and increases the recombination loss. However, it has shown positive effect on CT exciton dissociation, indicated by both theoretical simulations and experimental results.⁹³⁻⁹⁸ A larger disorder gives a broader DOS distribution, in which excitons can further relaxed to overcome the remaining binding energy. This should be the reason why disorder facilitate charge generation. Among the above factors, the charge delocalization is considered to play a critical role in free charge carrier generation. The importance of hole or electron delocalization in exciton dissociation has been emphasized and reported.⁹⁹⁻¹⁰² Actually, the above factors do not affect the dissociation of excitons alone, but usually work together to influence the dissociation process.¹⁰³⁻¹⁰⁷ There is at present no consensus for the dissociation process. It is assumed that above factors do have relations and more studies have to be done. In fact, the above factors do not affect the dissociation of excitons alone, but usually work together to influence the dissociation of excitons.

2.3.3 Charge Transport and Collection

After CT excitons have dissociated into free charge carriers, electrons and holes need to be transported in the acceptor and donor phases and then be collected at corresponding electrodes. Therefore, bi-continuous pathways are necessary for efficient charge transport: Note that this requirement stands in opposition to the requirement of charge generation (a large donor/acceptor interface). Thus, the morphology of the blend films has a huge effect on the performance of OPVs.¹⁰⁸ Unlike the electrically neutral excitons, the transportation of free charge carriers depend on the electric field. Thus, both field and concentration affect the transport process. The intrinsic disorder in organic semiconductors results in a different charge transport mechanism compared to that in inorganic materials. The band transport with high mobility is fast in inorganic materials with high delocalization. While in organic materials, localized charges transport occur through hopping

between different energy sites in the DOS. Photo-generated carriers undergo fast diffusive motion, and then drift to the electrode. The combination of diffusion and drift motion for charge carrier transport is shown in **Figure 2.10**.¹⁰⁹

Figure 2.10 Charge carriers transport undergo diffusion and drift motion. Reproduced with permission.¹⁰⁹ Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Mobility is a common characteristic that describe the charge carrier transportation property. In OPVs, the steady state mobility of electrons or holes is usually determined by the space-charge-limited-current (SCLC) method according to the Mott-Gurney law.¹¹⁰ By fitting the dark J - V curves according to the Equation (2.13).

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{(V - V_{bi})^2}{d^3} \quad (2.13)$$

where ϵ_0 is the vacuum permittivity, ϵ_r is the relative dielectric constant of the blend, μ is the zero-field mobility, V_{bi} is the built-in voltage, and d is the thickness of the active layer.

As mentioned before, charge transport is field dependent, Murgatroyd and Gill¹¹¹ considered the electric field effect on the mobility and extended the Equation (2.13) with a field enhancement factor gamma (γ), giving

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{(V-V_{bi})^2}{d^3} \exp\left(0.891\gamma \sqrt{\frac{V-V_{bi}}{d}}\right) \quad (2.14)$$

2.4 Recombination

The extracted charges at steady state are equal to the generated charges minus the recombined charges.

$$J = q \times (G - R) \quad (2.15)$$

where G is the generation rate and R is the recombination rate.

R is proportional to the charge carrier density n in the device.

$$R = \beta n^\gamma \quad (2.16)$$

where β is the recombination constant and γ is the order of recombination.

Figure 2.11 Illustration of geminate and non-geminate recombination process.

Recombination in OPVs can be divided into two main types, geminate and non-geminate recombination (**Figure 2.11**).¹¹² Geminate recombination is the recombination of an electron-hole pair originating from a single photon. The recombination of excitons that relax to the ground state before dissociating to CT excitons, and CT exciton relaxation before separating into free charge carriers are geminate, which are also considered as monomolecular recombination. Geminate recombination is a first order process, $\gamma = 1$, as R is proportional to the number of excitons in the device and thus is proportional to the illumination intensity and

the dissociation rate of excitons. Accordingly, recombination between an electron and a hole created by different photons are non-geminate, which include bimolecular, trap-assistant, surface and auger recombination.

Bimolecular recombination, also called Langevin recombination, is a second order process ($\gamma = 2$), which mainly occurs at the donor/acceptor interfaces *via* CT. Therefore, reducing the donor/acceptor interfaces would reduce the likelihood that opposite charge carriers will meet each other thereby suppressing the bimolecular recombination.

Trap-assistant recombination, also named as Shockley-Read-Hall recombination, is a first order process where free charges recombine with the trapped opposite charges resident in trap states. Trap-assistant recombination usually originates from impurities present in organic semiconductors, creating energy levels inside the forbidden band gaps. Energy states at the tail of DOS could also act as traps in organic materials.

Surface recombination, or rather diffusion driven charges being collected at the opposite electrode due to a non-selective contact, generates a current opposite to the drift photocurrent, and is thus not really a recombination. However, it results in a reduced collected photocurrent just as does recombination.

All non-geminate recombination depend on the densities of free charge carriers and the charge carrier generation rate. The carrier density upper limit is determined by light intensity. Therefore, the light intensity and temperature dependent current-voltage measurements will provide information to differentiate between geminate and non-geminate recombination.

Under short circuit conditions, most generated charge carriers can be extracted from the bulk under a high enough built-in field. The relationship between J_{sc} and light intensity I can be found as $J_{sc} \propto I^\alpha$, where α ranges typically from 0.85 to 1. Thus, the deviation from $\alpha = 1$ has been conjectured to arise from a small loss of carriers *via* bimolecular recombination. It is found that a large difference in electron and hole mobility leads to space-charge limited photocurrents at high intensity due to the unbalanced transport of electrons and holes. Thus, space-charge effects will reduce α value. As shown in **Figure 2.12 a**, two different systems with α values of 0.93 and 0.92, which indicate comparable bimolecular recombination occurs at short circuit conditions. (Paper 3)

Figure 2.12 Light intensity dependence of J_{sc} (a) and V_{oc} (b) for two blend systems. Reproduced with permission.¹¹³ Copyright 2020, the Royal Society of Chemistry.

Under open circuit conditions, all photo-generated charges will be recombined. The dominating type of recombination can be distinguished by the dependence of V_{oc} on the natural logarithm of the light intensity. Bimolecular recombination has a slope of $1\text{ }k_B T/q$, while trap-assisted recombination has a slope of $2\text{ }k_B T/q$. A slope less than $1\text{ }k_B T/q$ may be due to surface recombination. As shown in **Figure 2.12b**, two different blends give different slopes, $1.03\text{ }k_B T/q$ for $\text{Ir}(\text{FOtbpa})_3$ -based devices and $0.95\text{ }k_B T/q$ for $\text{Ir}(\text{Ftbpa})_3$ -based devices. This result suggests that bimolecular recombination dominates in $\text{Ir}(\text{FOtbpa})_3$ -based devices and surface recombination may occur in the $\text{Ir}(\text{Ftbpa})_3$ -based devices.

2.5 Tandem Cells and OPV Modules

The configuration of tandem solar cells with two junctions is illustrated in **Figure 2.13a**. The tandem devices (series connected in the vertical direction) typically consist of a front cell, intermediate layers (consisting of one electron transport layer and one hole transport layer for charge recombination), and a rear cell. The materials used in the front cell usually have high band gap, and for the rear cell low band gap materials are usually used. Compared with the single-junction cells, the tandem strategy is an effective way to overcome the thickness limitation. With the complementary absorption of the two sub cells, a reduced optical loss can be achieved with a high V_{oc} , which leads to high PCE. In tandem cells, the voltage is the sum of two sub cells and the generated current is limited by the low current sub cell.

Figure 2.13 Schematic diagram of the device structure of a tandem solar cell with two junctions (a) and a sample solar module with three sub cells (b).

There are two main issues that need to be considered to improve the performance of tandem devices: 1) active layer materials with suitable energy band gaps; and, 2) efficient charge recombination in the intermediate layers. The previous issue can be easily addressed thanks to the rapid development of novel organic semiconductors with various band gaps. Thus, the key challenge for the fabrication of tandem cells is the solution processing step involving the intermediate layers.¹¹⁴ There are several requirements for the intermediate layers: 1) Ohmic contacts with two sub cells; 2) transparency; 3) no harmful effect on the rear cell when sequentially casting the solutions of the intermediate layers; 4) preventing solvent penetration when depositing the rear cell; 5) resistance for further treatments, such as thermal annealing.

We have tried to fabricate all-solution-processed (including the top electrode) tandem solar cells with poly(3-hexylthiophene):indene-C60bis-adduct (P3HT:ICBA) as the active layer materials in order to obtain a higher V_{oc} . The intermediate layers here consist of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) with different conductivities (the hole transport layer) and polyethylenimine (PEI) (the electron transport layer). The tandem solar cell with the device configuration of ITO/PEI/P3HT:ICBA/PH1000:4083(1:3)/PEI/P3HT:ICBA/PH1000 and an active area of 1 cm^2 was fabricated. The device performance was recorded by illuminating it from both sides due to the semi-transparency of the device. From the J - V curves shown in **Figure 2.14**, similar results were obtained with the illumination either from the PH1000 side or the ITO side and the corresponding parameters are summarized in **Table 2.1**.

Figure 2.14 J - V curves of a tandem solar cell illuminated either from the anode (PH1000) or the cathode (ITO) side.

Table 2.1 Summary of photovoltaic parameters for the tandem solar cell illuminated either from the anode (PH1000) or the cathode (ITO) side.

illumination	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
PH1000	1.59	2.30	0.57	2.09
ITO	1.59	2.20	0.58	2.02

The upscaling OPVs from small area to modules (**Figure 2.13b**) could deliver appreciable electrical power. The design and fabrication methods change drastically when moving from small-area to large-area modules. The performance reduction during the upscaling fabrication process can be attribute to electrical and geometric losses. Electrical losses are mainly caused by an increase in the resistance from the bottom and top electrodes, as well as the introduced interconnect resistance derived from the modules. In large-area OPV modules, the dimensions of the electrodes are of outmost importance to avoid unnecessary losses. To keep the resistive losses in the electrode as small as possible, the width has to be narrowed with the contacts taken on the long sides. This minimizes the distance that the charge carriers extracted from the active layer have to travel in the resistive ITO electrode.¹¹⁵ Similarly, geometric losses are caused by the “dead area” in the modulation of OPVs, where the patterning part between single cells is incapable to generate photocurrent. The ratio of active area to the total area of the module is defined as the geometric fill factor. Therefore, the patterning length is the decisive parameter, which can be optimized to give a geometric fill factor value of 98.5% by a pattern-assisting technique, laser patterning.

Chapter 3 Voltage losses in OPVs

The voltage loss in OPV is defined as the energy difference between the optical bandgap (E_g) and qV_{oc} . To comparing the voltage losses in OPVs, the first thing needs to do is unifying the definition and determination of E_g . The larger voltage losses are found in OPVs than those in inorganic or perovskite solar cells. Therefore, minimizing voltage losses in OPVs has been extensively pursued. There are two ways to quantify the voltage losses in OPVs, which are based on detailed balance and thermal equilibrium conditions. On the one hand, voltage losses could be relating to the CT states. On the other hand, voltage losses could also be calculated based on Shockley-Queisser (SQ) theory.

3.1 E_g of Organic Semiconductors

Different methods have been utilized to determine E_g of organic semiconductors. More discussion about the different definition methods or how to determine E_g can be found in the literature.¹¹⁶ The most commonly way is just taking the absorption onset of pristine or blend films as E_g .¹¹⁷⁻¹²⁰ However, it is inaccurate when relate to voltage loss in OPVs due to the broaden absorption spectra with shallow tails. The broaden peaks in absorption and emission spectra of organic thin films are mainly attribute to the low frequency vibrations as illustrated in **Figure 3.1**.¹²¹ Therefore, E_g can be appropriately obtained by the cross point of normalized absorption and emission spectra of pristine or blend films.

Figure 3.1 Low frequency vibrations in organic thin films is illustrated in the energy diagram with reorganization energy λ_L (left). The broaden absorption and emission peaks (right). E_{0-0} refers to E_g . Reproduced with permission.¹²¹ Copyright 2018, the Royal Society of Chemistry.

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The determination of E_g from EQE spectra is another way. In paper 2 we have calculated E_g of three blend systems by using this method as shown in **Figure 3.2**. E_g is determined from the derivatives of the EQE curve, and a mean peak energy is calculated by the Equation 3.1.

$$E_g = \frac{\int_a^b E_g P(E_g) dE_g}{\int_a^b P(E_g) dE_g} \quad (3.1)$$

where the integration limits a and b are chosen as the $P(a)=P(b)=0.5\text{Max}P(E_g)$.

Figure 3.2 E_g from the derivatives of the EQE curves for PM6:Y6, PM6:BTP-S1, and PM6:BTP-S2 blends.

3.2 The Principle of Detailed Balance

To quantify the voltage losses, the detail balance theory should be considered. By decomposing dynamic systems into elementary processes, the principle of detailed balance has been introduced to study kinetic systems such as collisions, chemical reactions, and absorption and emission process. At equilibrium, each elementary process is in equilibrium with its reverse process. In the field of OPVs, the rate of photon absorption must be counterbalanced by the rate of emission in thermal equilibrium condition based on the principle of detailed balance.

When the devices are in the dark condition, which indicates that the system is in thermal equilibrium with ambient. The ambient radiation is assumed like a black body radiation and into a hemisphere. Then the absorbed thermal photon flux is equal to the black body photon flux,

$$\phi_a(E) = \phi_{BB}(E) = \frac{2\pi}{h^3 c^2} \left(\frac{E^2}{\exp\left(\frac{E}{k_B T}\right) - 1} \right) \quad (3.2)$$

where h is Plank constant, c is vacuum speed of light. The current density absorbed from the ambient is

$$J_{abs} = q \int EQE(E) \phi_a(E) dE \quad (3.3)$$

According to the principle of detailed balance, in equilibrium, there must have the inverse process (photon emission) to balance J_{abs} . Therefore, the current density for photon emission (J_{rad}) should be equal to J_{abs} . When the device is under a forward bias voltage, the injected current leads to the radiative emission of photons, which follows an exponential law. The excess emission photon flux (ϕ_{EL}) is giving below,

$$\begin{aligned} \phi_{EL}(E, V) &= \frac{J_{rad}}{q} \exp\left(\frac{qV}{k_B T}\right) - \frac{J_{abs}}{q} \\ &= \int EQE(E) \phi_{BB}(E) dE \left(\exp\left(\frac{qV}{k_B T}\right) - 1 \right) \end{aligned} \quad (3.4)$$

This Equation reveals the reciprocity relation between EQE and electroluminescent (EL) emission in OPVs. The EL is from the radiative recombination of free charge carriers. The existence of non-radiative recombination in OPVs resulting the EQE of EL (EQE_{EL}) is smaller than unity. EQE_{EL} is defined as the ratio between the radiative recombination current density and the injected current density.

$$EQE_{EL} = \frac{J_{rad}(V)}{J_{inj}(V)} \quad (3.5)$$

$$J_{inj}(V) = \frac{q\phi_{EL}(E, V)}{EQE_{EL}} = \frac{q}{EQE_{EL}} \int EQE(E) \phi_{BB}(E) dE \left(\exp\left(\frac{qV}{k_B T}\right) - 1 \right) \quad (3.6)$$

Equation 3.6 can also be written as

$$J_{inj}(V) = J_0 \left(\exp\left(\frac{qV}{k_B T}\right) - 1 \right) \quad (3.7)$$

With J_0

$$J_0 = \frac{q}{EQE_{EL}} \int EQE(E) \phi_{BB}(E) dE \quad (3.8)$$

Equation 3.7 resembles the ideal diode Equation 2.1.

While under light illumination, both solar photon and thermal photon will contribute to the absorbed current density.

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$$J_{abs}^L = q \int EQE(E) (\phi_{AM\ 1.5}(E) + \phi_{BB}(E)) dE \quad (3.9)$$

With illumination, a chemical potential (μ) will be developed and result in an increased emission. Then the emitted photon flux is given by

$$\phi_e(E, \Delta\mu) = \frac{2\pi}{h^3 c^2} \left(\frac{E^2}{\exp\left(\frac{E-\Delta\mu}{k_B T}\right) - 1} \right) \quad (3.10)$$

This is also called the generalized Plank law.

3.3 CT States Characterization

The dissociation of CT excitons is discussed before, which indicates the significance of CT states in operation of OPVs. In this section, we focus on the characterization of CT states. Highly sensitive techniques are required to detection CT states due to the low electronic coupling between CT states and ground states. The CT state at donor/acceptor interface is a lower energy state compared to the singlet state of the low bandgap material in the blend, which resulting in a sub-gap absorption and a red shift emission.

3.3.1 Absorption of CT States

It is usually difficult to conducting the CT absorption measurement due to the low electronic coupling, which results low absorption coefficient of the CT state in organic films. Photothermal deflection spectroscopy (PDS) with high sensitivity has been developed to characterize the CT states absorption of polymer fullerene systems.^{122, 123} Besides PDS, Fourier-transform photocurrent spectroscopy (FTPS) has been widely employed to measure the EQE of OPVs in the sub-gap absorption regime.^{124, 125} The measurement is conducted by holding devices under light illumination from a Fourier transform infrared spectrometer, and collecting the generated photocurrent with a preamplifier. The light beam irradiation needs to be calibrated by measuring a standard Si photodetector. The spectra resolution is much higher than the monochromatic EQE.

According to Marcus theory,¹²⁶ the EQE for the CT absorption regime is expressed by Equation 3.11. The energy of CT state (E_{CT}) could be obtained by fitting the sub-gap regime of EQE spectrum using Equation 3.2. An example of FTPS-EQE spectrum for BTR:PC₇₁BM blend is shown in **Figure 3.3** (Paper 1).

$$EQE(E) = \frac{f}{E \sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(E_{CT} + \lambda - E)^2}{4\lambda k_B T}\right) \quad (3.11)$$

Where f is proportional to the electronic coupling strength of CT states and the density of the donor/acceptor interfaces, λ is the reorganization energy of CT states.

Figure 3.3 FTPS-EQE spectrum with fitted curve for OPVs based on BTR:PC₇₁BM. The sub-gap tail in low energy is attributed to the CT state. Reproduced with permission.¹²⁷ Copyright 2018, Springer Nature Publishing AG.

3.3.2 Emission of CT States

Radiative decay of CT excitons giving a red shift emission in photoluminescence (PL) spectrum compared to that from the individual components. The PL signals of the CT states have been detected in several materials systems.¹²⁸⁻¹³² However, in the systems with high PL intensities from donor or acceptor, the weak CT PL emission is still hard to detect. Therefore, in many OPVs systems, no CT emission was observed. In contrast, EL from the CT state is easier to capture by applying a forward voltage on the devices.¹³³ When charge carriers are injected from the electrode into the devices, they will recombine in non-radiative or radiative ways. By increasing injection current or applied voltage, electrons and holes will first occupy the lowest energetic state, which is the CT state, and then go to the higher energetic state. Thus, the radiative recombination at the lowest energetic state (CT state) will generate the CT EL emission. The spectra change under different injection current is an excellent way to distinguish the original emission states.

Figure 3.4 (a) PL spectra for the pristine donor BTR, acceptor PCBM and BTR:PC₇₁BM blend films. (b) Normalized PL spectra. (c) EL spectra of devices based on pristine donor BTR and BTR:PC₇₁BM blend. (d) EL spectra of device based on BTR:PC₇₁BM blend with different injection current. Reproduced with permission.¹²⁷ Copyright 2018, Springer Nature Publishing AG.

The PL spectra for the pristine donor BTR, acceptor PC₇₁BM, and BTR:PC₇₁BM blend films are shown in **Figure 3.4 a**. There are no additional peaks or even shoulders could be found in the blend PL spectrum. The PL signal for the blend film is quenched comparing to the pristine donor emission, which indicates efficient charge transfer between donor and acceptor. The PL peak of the blend films is blue shift comparing to the BTR emission shown in the normalized PL spectra (**Figure 3.4 b**), which indicates that the introducing PC₇₁BM in the blend films might affect the π - π stacking of BTR donors. The EL spectra for the pristine donor and BTR:PC₇₁BM blend are shown in **Figure 3.4 c**. The blend shows a new peak located at round 1.25 eV, far away from the donor emission at around 1.71 eV, which is attribute to CT emission. When increasing the injection current, pristine donor emission is occurred in blend system (**Figure 3.4 d**). This might due to the existence of the pure donor domain in the blend films. The EL spectra of CT state could also be fitted by Equation 3.12,

$$\frac{I_f}{E} = \frac{f_{If}}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(E_{CT}-\lambda-E)^2}{4\lambda k_B T}\right) \quad (3.12)$$

where I_f is the emission rate at photon energy E , f_{If} is relate to the electronic coupling. This is called the reduced EL spectra. It should be noticed that if the emission was measured as photon per unit time per unit wavelength, it needs to be divided by E^3 . The reduced EQE spectra can be obtained by multiplying E on equation 3.2. The cross point of the reduced emission and EQE spectra is E_{CT} . The normalized reduced FTPS-EQE and EL spectra for BTR:PC₇₁BM are shown in **Figure 3.5**. The E_{CT} value from the cross point is consistent with that obtained in **Figure 3.3**.

Figure 3.5 Reduced FTPS-EQE and EL spectra for the device based on BTR:PC₇₁BM blend.

3.4 Relate V_{oc} with CT States

As discussed before the E_{CT} could be obtained by fitting the low energy regime of PFTS-EQE spectrum with Equation 3.11. In chapter 2, V_{oc} for an ideal diode has been derived by Equation 2.4, in which J_0 is defined as Equation 3.8. By substituting Equation 3.2 and 3.11 in Equation 3.8, J_0 is given by

$$J_0 = \frac{q}{E_{QE_{EL}}} \frac{f 2\pi}{h^3 c^2} (E_{CT} - \lambda) \exp\left(\frac{-E_{CT}}{k_B T}\right) \quad (3.13)$$

An approximation for Equation 3.2 is used during the substitution. The relationship between V_{oc} and E_{CT} could be achieved by combining Equation 2.4 and 3.13, giving

$$V_{oc} = \frac{E_{CT}}{q} + \frac{k_B T}{q} \ln\left(\frac{J_{sc} c^2 h^3}{f 2 \pi q (E_{CT} - \lambda)}\right) + \frac{k_B T}{q} \ln(E Q E_{EL}) \quad (3.14)$$

Figure 3.6 Energy diagram demonstrates the voltage losses relate with CT state.

As shown in **Figure 3.6**, the voltage losses consist of two part: one loss is between E_g and E_{CT} due to radiative recombination during charge transfer process. Another loss is between E_{CT} and qV_{oc} . According to Equation 3.14, the loss between E_{CT} and qV_{oc} composed two terms: radiative recombination loss ($q\Delta V_{rad}$) via the CT state and non-radiative recombination loss ($q\Delta V_{non-rad}$), which are

$$q\Delta V_{rad} = -\frac{k_B T}{q} \ln\left(\frac{J_{sc} c^2 h^3}{f 2 \pi q (E_{CT} - \lambda)}\right) \quad (3.15)$$

$$q\Delta V_{non-rad} = -\frac{k_B T}{q} \ln(E Q E_{EL}) \quad (3.16)$$

It has been found that the loss between E_{CT} and qV_{oc} is around 0.6 eV for fullerene based OPVs.¹³⁴ Reducing voltage losses is an important topic in OPVs. One effective way to reduce voltage losses is decreasing the donor/acceptor interfacial area, while that may also result in a low charge carrier generation. In addition, recent research found a more efficient way to minimise voltage losses by reducing $q\Delta V_{non-rad}$ with high PL yields materials.⁷⁶ In Paper 1, we investigate the voltage losses related with CT state in ternary system and compared with that in binary systems. FTPS-EQE spectra and EQE_{EL} were shown in **Figure 3.7**. E_{CT} can be deduced by fitting the low energy region of the FTPS-EQE spectrum according to Equation 3.11, and the corresponding parameters are summarized in

Table 3.1. When we take a look on the two binary systems, we could find that a larger E_{CT} for fullerene-based devices compared to the NF based devices. However, a larger V_{oc} was obtained for the NF based devices, which is contradict with common sense that a larger E_{CT} will result a larger V_{oc} . A more detailed analyse on the radiative and non-radiative loss indicates that a reduced non-radiative loss with much higher EQE_{EL} in the NF based devices. The loss between E_{CT} and qV_{oc} in NF devices is reduced to 0.48 eV. Moreover, in ternary system with small amount of NF, the non-radiative loss is reduced compared to that in the BTR:PC₇₁BM devices. Therefore, it is believed that NITI could block the non-radiative decay channels in BTR:PC₇₁BM. The results from voltage losses also support the morphological study in ternary blends.

Figure 3.7 (a) Normalized FTPS-EQE spectra for the binary and ternary devices. (b) EQE_{EL} of the binary and ternary devices. Reproduced with permission.¹²⁷ Copyright 2018, Springer Nature Publishing AG.

Table 3.1 Voltage losses relate with CT states in binary and ternary systems. Summary of the parameters. Reproduced with permission.¹²⁷ Copyright 2018, Springer Nature Publishing AG.

BTR: NITI:PC ₇₁ BM	qV_{oc} [eV]	f [eV ²]	λ [eV]	E_{CT} [eV]	$q\Delta V_{rad}$ [eV]	EQE_{EL} [%]	$q\Delta V_{non-rad}$ [eV]
1:0:1	0.90	1.0×10^{-3}	0.24	1.49	0.19	1.8×10^{-5}	0.40
1:1:0	0.95	3.0×10^{-3}	0.1	1.43	0.22	4.0×10^{-3}	0.26
1:0.4:1	0.94	7.0×10^{-4}	0.08	1.42	0.18	8.2×10^{-4}	0.30

3.5 Shockley-Queisser (S-Q) Limit

Shockley and Queisser initially proposed an upper theoretical limit for the efficiency of solar cell in 1961, called the detailed balance limit of efficiency.¹³⁵ The theory is based on several assumptions. (1) A step-function-like absorption, which means absorb all photons above E_g and no absorption below E_g . (2) One photon could only generate one electron-hole pair, which indicates no multiple carrier generation. (3) No potential loss in the circuit during charge transport and collection. (4) Only radiative recombination loss in devices. With all the assumptions, the PCE of an ideal cell is only affected by E_g and incident light. Then we have,

$$EQE(E) = \begin{cases} 1 & E \geq E_g \\ 0 & E < E_g \end{cases} \quad (3.17)$$

and EQE_{EL} is equals to 1. Thus, we could rewrite Equation 3.8 and 2.11 under the S-Q limit condition.

$$J_0^{SQ} = q \int_{E_g}^{\infty} \phi_{BB}(E) dE \quad (3.18)$$

$$J_{sc}^{SQ} = q \int_{E_g}^{\infty} \phi_{AM1.5}(E) dE \quad (3.19)$$

The V_{oc} also can be rewrite as

$$V_{oc}^{SQ} = \frac{k_B T}{q} \ln \left(\frac{J_{sc}^{SQ}}{J_0^{SQ}} + 1 \right) = \frac{k_B T}{q} \ln \left(\frac{q \int_{E_g}^{\infty} \phi_{AM1.5}(E) dE}{q \int_{E_g}^{\infty} \phi_{BB}(E) dE} + 1 \right) \quad (3.20)$$

The ultimate efficiency of the solar cell for a 6000 K black body sun is given by

$$\eta = \frac{E_g \int_{E_g}^{\infty} \phi_{BB}(E) dE}{\int_0^{\infty} E \phi_{BB}(E) dE} \quad (3.21)$$

As shown in **Figure 3.8a**, the maximum efficiency is around 44% at a bandgap of 1.10 eV, which is calculate by Equation 3.21.

Figure 3.8 (a) The theoretical efficiency limit of solar cells under 6000 K black body sun based on the S-Q limit. (b) Energy diagram demonstrates the voltage losses relate with S-Q limit.

The voltage loss in OPVs is due to charge carrier recombination. According to the principle of detailed balance, the process of photon emission is always accompanying with photon absorption, resulting the unavoidable radiative recombination in all type of solar cells. As shown in **Figure 3.8b**, based on S-Q limit, the voltage losses can be divided into three parts.

$$E_{loss} = E_g - qV_{oc} = \Delta E_1 + \Delta E_2 + \Delta E_3 \quad (3.22)$$

ΔE_1 is the energy difference between E_g and qV_{oc}^{SQ} , whereas V_{oc}^{SQ} is the maximum V_{oc} for materials with a certain E_g . Thus, this radiative loss above bandgap exist in all type of solar cells and only dependent on E_g if the light source and temperature is fixed.

ΔE_2 is the energy difference between E_g and qV_{oc}^{rad} , whereas V_{oc}^{rad} is the radiative limit V_{oc} , which indicate only radiative recombination occurs in devices ($EQE_{EL}=1$). In real cells, especially in OPVs, the bandgap is not like step function. The sub-gap absorption has a large influence on the reverse saturation current density J_0 , thus increase the losses. By replacing the step function like EQE with real measured EQE in Equation 3.20, V_{oc}^{rad} can be calculate by

$$V_{oc}^{rad} = \frac{k_B T}{q} \ln \left(\frac{J_{sc}^{rad}}{J_0^{rad}} + 1 \right) = \frac{k_B T}{q} \ln \left(\frac{q \int_{E_g}^{\infty} EQE(E) \phi_{AM1.5}(E) dE}{q \int_{E_g}^{\infty} EQE(E) \phi_{BB}(E) dE} + 1 \right) \quad (3.23)$$

It should be noticed that the black body photon flux has an exponential effect at low energy regime. Highly sensitive technology should be used to measure EQE.

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ΔE_3 is the energy difference between qV_{oc}^{rad} and qV_{oc} , which is assigned to the non-radiative loss. In real cells, the non-radiative recombination result in a low EQE_{EL} . Then the V_{oc} and ΔE_3 can be calculate by

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{J_{sc}}{J_0} + 1 \right) = \frac{k_B T}{q} \ln \left(\frac{q \int_{E_g}^{\infty} EQE(E) \phi_{AM1.5}(E) dE}{q EQE_{EL}^{-1} \int_{E_g}^{\infty} EQE(E) \phi_{BB}(E) dE} + 1 \right) \quad (3.24)$$

$$\Delta E_3 = qV_{oc}^{rad} - qV_{oc} = -k_B T \ln(EQE_{EL}) \quad (3.25)$$

Therefore, the voltage losses can be clearly quantified by this method with different recombination losses. It was found that no obvious CT state emission was detected in some NFA based OPVs. Thus, the voltage loss could not always relate with CT states. Quantifying voltage losses based on S-Q limit is more universal method compared to that of the CT states. In paper 2, we applied this method to analyse the voltage loss in asymmetric NFA based devices with high efficiency.

Figure 3.9 Normalized EL spectra for devices based on pristine acceptor and blend films (a) Y6 and PM6:Y6; (b) BTP-S2 and PM6:BTP-S2. Normalized FTPS-EQE spectra for devices based on pristine acceptor and blends (c) Y6 and PM6:Y6; (d) BTP-S2 and PM6:BTP-S2.

As shown in **Figure 3.9 a and b**, comparing to the EL from the pure acceptor devices, there is no new peak or even red shift shoulder can be seen in both PM6:Y6 and PM6:BTP-S2 blend systems. On the contrary, slightly blue shift EL emissions for both blend systems were observed compared to pure acceptor EL emissions. This could be explained by slightly different packing behavior of the acceptor molecules. In the pristine acceptor films, molecules should be well ordered. While in the blend films, the donor polymer may affect the packing of acceptor molecules, which may result in a slightly blue shift emission. Similar phenomenon was revealed in the FTPS-EQE spectra shown in **Figure 3.9 c and d**, which confirms that CT state transition in these two blend systems is unobservable.

Figure 3.10 (a) FTPS-EQE spectra for devices based on PM6:Y6, PM6:BTP-S1 and PM6:BTP-S2 blends. (b) EQE_{EL} of the devices based on PM6:Y6, PM6:BTP-S1 and PM6:BTP-S2 blends. Reproduced with permission.¹³⁶ Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

As a result, the voltage losses in these blend devices was investigate based on the S-Q limit method. To calculate detailed voltage losses, E_g was firstly determined and discussed in pervious section. FTPS-EQE spectra and EQE_{EL} of the three devices are shown in **Figure 3.10**. The calculated losses are summarized in **Table 3.2**. PM6:BTP-S2-based device shows the lowest losses (0.53) in all the three blend systems. The main differences in voltage losses are originated from ΔE_3 , non-radiative losses. As shown in **Figure 3.10b**, PM6:BTP-S2-based device shows the highest EQE_{EL} of $2.3 \times 10^{-2}\%$, thus, the non-radiative loss is the lowest (0.22 eV). The results indicate that EQE_{EL} can realize one order of magnitude of improvement by introducing more halogen atoms, and chlorine atom is better than fluorine atom.

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Table 3.2 Summary of detailed voltage losses parameters for OPVs based on PM6:Y6, PM6:BTP-S1 and PM6:BTP-S2 blends. Reproduced with permission.¹³⁶ Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Active layers	E_g (eV)	qV_{oc} (eV)	E_{loss} (eV)	qV_{oc}^{SQ} (eV)	ΔE_1 (eV)	qV_{oc}^{rad} (eV)	ΔE_2 (eV)	EQE_{EL} (%)	ΔE_3 (eV)
PM6:Y6	1.42	0.84	0.58	1.16	0.26	1.09	0.07	4.4×10^{-3}	0.26
PM6:BTP-S1	1.49	0.93	0.56	1.22	0.27	1.15	0.07	1.1×10^{-2}	0.24
PM6:BTP-S2	1.48	0.95	0.53	1.21	0.27	1.15	0.06	2.3×10^{-2}	0.22

Chapter 4 Triplet materials based OPVs

4.1 Singlet and Triplet States

The excited states are created by promoting one electron from the HOMO to the LUMO. There are two types of excited states, the singlet state ($S_1 \dots S_n$) and the triplet state ($T_1 \dots T_n$) which is defined by the total spin quantum number. **Figure 4.1a** illustrates the orbital configuration for the ground state (S_0), S_1 and T_1 state. In the ground state the electrons are paired, which indicate antiparallel spin of the two electrons. When light or a magnetic field with excitation energy is applied, one electron can be excited. If the spin of the excited electron remains the same, it is the excited singlet state. If the spin of the excited electron changed, the result is the excited triplet state.

Figure 4.1 (a) S_0 , S_1 and T_1 in an orbital configuration scheme. The blue arrows represent the electron spin. Only one spin configuration is shown for the triplet state. (b) Vector diagram for singlet and triplet states with the relative orientations of two electron spins around a local magnetic field in z-direction. Adapted with permission.¹³⁷ Copyright 2009, Elsevier.

According to quantum mechanics, the excited states consisting of unpaired electrons in π^* and π orbitals can be regarded as a two particle system with spin angular momentum. Thus, it has simultaneous eigenvectors of $\mathbf{S}^2$ and S_z with eigenvalues S and M_s . $\mathbf{S}$ is the spin angular momentum operator and S_z denotes its z-component. For one particle with spin $s = 1/2$, the values of quantum number m_s are $\pm 1/2$. The two basic spin wave functions α and β are denoted as spin-up and spin-down states with eigenvalues $s = 1/2, m_s = 1/2$ and $s = 1/2, m_s = -1/2$.

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Therefore, the two particles system have four eigenstates with spin wave functions as below

$$\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \quad S = 0 \text{ and } M_s = 0$$

$$\alpha_1\alpha_2 \quad S = 1 \text{ and } M_s = 1$$

$$\frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \quad S = 1 \text{ and } M_s = 0$$

$$\beta_1\beta_2 \quad S = 1 \text{ and } M_s = -1$$

As shown in **Figure 4.1b**, the left part represents the first spin wave function with $S = 0$ and $M_s = 0$ indicating only one single possible value of the z-component, and is therefore referred to as singlet. While the right part of the three spin wave functions have $S = 1$, and only the z-component of the spin is different with eigenvalues $M_s = 1, 0, -1$. Therefore, this arrangement is called a triplet. The phase change should be noted for the singlet (180° out of phase) and triplet states (in phase).

4.2 The Generation of Triplet Excitons

Excitons can be created by light absorption of organic semiconductor or electrical injection into the electronic devices. Generally, only singlet excitons can be directly generated by absorbing photons due to the selection rule in the electronic dipole transition processes. On the other hand, electrical injection leads to the formation of both singlet and triplet excitons. In triplet material based OPVs (T-OPVs), we are more interested in the optical generation of triplet excitons. The triplet excitons can be obtained by flipping the spin orientation of singlet excitons through the effective intersystem crossing (ISC), triplet sensitizers and singlet fission.^{138, 139}

4.2.1 Intersystem Crossing

The ISC rate depends on two factors, the strength of the spin-orbit coupling (SOC) and the vibrational overlap between the wave functions of the S_1 and triplet state involved. As show in **Figure 4.2**, there are two ISC processes. One process involves a transition from S_1 into a nearby high-energy triplet state followed by internal conversion (IC) to T_1 . The other process is a direct transition from S_1 to T_1 . Effective ISC can be realized by either enhancing ISC or/ and suppressing the radiative and non-radiative decay transition of S_1 state. In order to enhance ISC, several strategies have been proposed including generating a strong SOC and

minimization of the energy gap between the singlet and triplet states.¹⁴⁰ Generally, the SOC is weak in organic materials (consisting mainly of carbon and hydrogen) because the SOC is proportional to the atomic number.¹⁴¹ Consequently, introducing heavy atoms, especially heavy metals, into organic molecules and polymers is a promising approach to enlarge SOC and enable formation of triplet excitons. As for minimization of the energy gap between the singlet and triplet states, using twisted strong D-A molecular structures have been proved to be an effective way.¹⁴² On the other hand, effective triplet excitons generation can also be realized by largely suppressing the radiative and non-radiative decay transition of S_1 even with small ISC rate, which could be achieved by specific molecular packing motifs such as H-aggregates or crystal engineering, host-guest doping method and so on.¹⁴³⁻¹⁴⁶

Figure 4.2 A schematic Jablonski diagram for the photophysical process of organic materials under photoexcitation. A: absorption, R: radiative decay transition, NR: non-radiative decay transition, IC: internal conversion, ISC: intersystem crossing, VR: vibrational relaxation; $n \geq 2$. Reproduced with permission.¹¹ Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.2.2 Triplet Sensitizers

It has been reported that phosphorescence signal could be observed in organic materials (host) with the help of triplet sensitizers.^{147, 148} In order to have successful sensitization, the system should meet the following requirements: 1) the triplet state of the host is below that of sensitizer, and, 2) the sensitizer has a high ISC yield. There are two ways to generate triplet excitons by triplet sensitizers. As shown in **Figure 4.3**, one way is to first generate the triplet excitons

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on the sensitizers *via* ISC, the triplet exciton is then transferred to the lower lying triplet state of the host. Another way is photoexcitation of the host which generates singlet excitons that then transfer to the singlet state of the sensitizer, followed by ISC and transfer from triplet state of the sensitizer to the triplet state of the host.

Figure 4.3 A schematic Jablonski diagram for the triplet excitons generation through triplet sensitizers. (a) Photoexcitation on triplet sensitizers to generate triplet excitons *via* ISC, then transfer to the lower lying triplet state of the host material. (b) Photoexcitation on the host material with generated singlet excitons, then transfer to the singlet state of the sensitizer, following by the ISC and energy transfer from triplet state of the sensitizer to the triplet state of the host.

4.2.3 Singlet Fission

Singlet fission is a process where an organic molecule in an excited singlet state, shares its excitation energy with a neighbouring ground-state molecule, and finally, both are converted into triplet excited states (**Figure 4.4**).¹³⁸ The bimolecular singlet fission is an alternative but rare way to generate triplet excitons. The two molecules can be the same (“homofission”) or different (“heterofission”). The critical condition for singlet fission is that the energy of S₁ state is close to the sum of the energy of the two T₁ states.

Figure 4.4 Singlet fission: 1 the molecule A was excited to S_1 , 2 the excited singlet exciton shares energy with the neighbouring molecule A or B, creating two triplet excitons. Adapted with permission.¹³⁸ Copyright 2010, American Chemical Society.

4.3 Charge Generation in T-OPVs

The mechanism of converting photons into charges in OPVs has been intensively investigated in last decade, while few studies have concerned the corresponding mechanism in T-OPVs. It should be noticed that the binding energy of the triplet excitons is higher than those of singlet excitons due to the attractive exchange interaction of the same spin orientation. Thus, the higher binding energies of triplet excitons may affect the exciton dissociation process.

4.3.1 Exciton Diffusion Length

As we discussed in Chapter 2.3, exciton diffusion is an important step in the working process of OPVs. The possible long exciton diffusion length is considered as one of the motivations and possible advantage of utilizing triplet excitons in T-OPVs, which may break the trade-off on charge generation and recombination with large domain size. However, it is debatable on whether triplet excitons will diffuse longer distances than singlet excitons. It has been reported that exciton diffusion length of triplets is in the range of 10-140 nm which is indeed longer than the values of the singlet materials (3-10 nm).¹⁴⁹ In some materials comparable diffusion lengths of triplet and singlet excitons have been demonstrated.^{150, 151} The exciton diffusion length is proportional to the diffusivity-lifetime product as shown in the previous chapter, where the diffusivity describes the mobility of excitons inside the material. Therefore, a long exciton lifetime does not guarantee a long diffusion length, as the diffusion length is also influenced by the diffusivity and crystallinity of materials.¹⁵²

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Exciton diffusion is facilitated through either Förster or Dexter energy transfer as discussed before. In general, only singlet excitons can be transported *via* the Förster mechanism. The efficiency of FRET usually outperforms that of Dexter energy transfer for singlet excitons as the dipole-dipole coupling is more efficient than exchange interaction. Triplet excitons may be transferred between non-phosphorescent molecules only by the Dexter mechanism due to the forbidden transition. Thus, the diffusivity of triplet excitons can be several orders of magnitude smaller than those of singlet excitons due to the different (Förster or Dexter) energy transfer mechanisms. Therefore, exciton diffusion length is comparable for triplet and singlet excitons when triplet excitons undergo Dexter energy transfer. However, it has been reported that triplet excitons generated from a phosphorescent molecule can also undergo FRET process,¹⁵³⁻¹⁵⁵ which may increase the diffusivity for triplet excitons. As a consequent, the excitons diffusion length of triplet excitons may be longer than that of singlet excitons.

4.3.2 Do the Charges Generated *via* Triplets?

There are many reports about the use of triplet materials in OPVs, but these rarely concern the mechanistic aspects. As electron transfer and ISC process have a similar timescale (fs) in T-OPVs, it is hard to distinguish if the electron transfer occurs from the singlet state or the triplet state. There are some studies by Schanze's group^{156, 157} on the dynamics of singlet and triplet excited states in T-OPVs based on several Pt-based polymers. They found that the energy levels of the singlet and triplet state play a crucial role in T-OPVs. Two possible energy level diagrams are shown in **Figure 4.5**. When the energy of T_1 is lower than the CT shown in **Figure 4.5a**, then electron transfer will occur from the S_1 state to the CT. In this case, the longer lifetime triplet state will not facilitate the charge generation process. Furthermore, the competition between ISC from S_1 state to T_1 and electron transfer process, as well as the back transfer from the 3CT to the T_1 will increase the recombination loss. When the energy of T_1 is higher than the CT state shown in **Figure 4.5b**, then the electron transfer will occur from the T_1 to the 3CT . As a result, the long-lifetime triplet state will participate in the charge generation process and the recombination loss from the 3CT to the T_1 will be reduced.

Figure 4.5 Two possible energy level diagrams for T-OPVs. (a) Charge generation from singlet state and (b) charge generation from triplet state.

4.4 Voltage Losses in T-OPVs

In general, the energy level of T_1 is lower than S_1 , and the energy difference between these two states is called the exchange energy. The exchange energy is depending on the interaction of the electron in the HOMO with that in the LUMO. A significant wave functions overlap between the electron in the HOMO and that in the LUMO leads to a large exchange energy about 0.7-1.0 eV.¹⁵⁸⁻¹⁶⁰ On the other hand, in metal complexes, the metal-to-ligand CT transition (MLCT) produces localizations of holes and electrons at different parts of the molecule, with a small exchange energy about 0.2-0.3 eV.^{161, 162} As a result, the utilization of triplet excitons will lead to a decreased V_{oc} because the S_1 -to- T_1 conversion will lower the energy level of excited states.

The voltage losses in T-OPVs based on iridium (Ir) complexes as sole donors and PC₇₁BM as acceptor were investigated in Paper 3. Two homoleptic Ir complexes based on extended π -conjugated benzo[g]phthalazine ligands, Ir(Ftbpa)₃ and Ir(FOtbp_a)₃, were synthesized as triplet electron donors. As shown in **Figure 4.6**, CT state emission was observed by both PL and EL measurement. Obvious red shift CT PL emission peaks were observed for both the two systems compared to their corresponding pristine donor emissions. Furthermore, it shows a clear trend of CT PL from the films with a higher donor content in both the two systems. The EL emissions from devices based on pristine Ir complexes and their blends are shown in Figure 4.6c and d. The CT state EL emissions are consistent with the CT state PL emissions. Therefore, the voltage losses in these systems were relate to the CT state.

Figure 4.6 (a) PL spectra of pristine Ir(Ftbpa)₃ and Ir(Ftbpa)₃:PC₇₁BM blends with different weight ratios; (b) PL spectra of pristine Ir(FOTbpa)₃ and Ir(FOTbpa)₃:PC₇₁BM blends with different weight ratios. The films are excited by a 532 nm laser; (c) EL spectra for devices based on pristine Ir(Ftbpa)₃ and Ir(Ftbpa)₃:PC₇₁BM blends with different weight ratios; (d) EL spectra for devices based on pristine Ir(FOTbpa)₃ and Ir(FOTbpa)₃:PC₇₁BM blends with different weight ratios. Reproduced with permission.¹¹³ Copyright 2020, the Royal Society of Chemistry.

FTPS-EQE spectra of these two Ir complexes blends were shown in **Figure 4.7a** and **b**, respectively. The fitting parameters were summarized in **Table 4.1**. For the optimized devices with 1:1.5 weight ratio, E_{CT} is 1.47 eV and 1.38 eV for Ir(Ftbpa)₃-based and Ir(FOTbpa)₃-based devices, respectively. However, a higher V_{oc} was obtained in Ir(FOTbpa)₃-based devices than Ir(Ftbpa)₃-based devices. The contradiction between E_{CT} and V_{oc} for two systems motivated us to further investigate the voltage losses here. The radiative and non-radiative losses were calculated and are listed in Table 4.1. The $q\Delta V_{rad}$ s for both Ir(Ftbpa)₃ and Ir(FOTbpa)₃-based devices are independent of blend ratios. From the EQE_{EL} measurements (Figure 4.7c and d), the EQE_{EL} s of the Ir(Ftbpa)₃ and Ir(FOTbpa)₃-based devices increased with increasing donor content, which lead to low $q\Delta V_{non-rad}$ for both Ir(Ftbpa)₃ and Ir(FOTbpa)₃-based devices. The EQE_{EL} of the device based on Ir(FOTbpa)₃ is more than one order of magnitude higher than that of the Ir(Ftbpa)₃. This leads to calculated $q\Delta V_{non-rad}$ of 0.31 eV for the Ir(FOTbpa)₃-based

devices, about 0.11 eV lower than that of the Ir(Ftbpa)₃-based devices. Both radiative and non-radiative recombination for the Ir(FOTbpa)₃-based devices are lower than that of the Ir(Ftbpa)₃-based devices, which result in a higher V_{oc} for the Ir(FOTbpa)₃-based devices.

Figure 4.7 FTPS-EQE spectra for Ir(Ftbpa)₃:PC₇₁BM (a) and Ir(FOTbpa)₃:PC₇₁BM (b); EQE_{EL} of the Ir(Ftbpa)₃:PC₇₁BM (c) and Ir(FOTbpa)₃:PC₇₁BM (d). Reproduced with permission.¹¹³ Copyright 2020, the Royal Society of Chemistry.

Table 4.1 Summary of fitting parameters and calculated $q\Delta V_{rad}$ and $q\Delta V_{non-rad}$ values for T-OPVs. Reproduced with permission from reference.¹¹³

Donor	Ratio	qV_{oc} (eV)	f_1 (eV ²)	E_{CT} (eV)	λ (eV)	$q\Delta V_{rad}$ (eV)	EQE _{EL} (%)	$q\Delta V_{non-rad}$ (eV)
Ir(Ftbpa) ₃	2:1	0.85	6×10^{-3}	1.46	0.27	0.25	1×10^{-4}	0.36
	1:1.5	0.80	6×10^{-3}	1.47	0.25	0.25	1×10^{-5}	0.42
	1:3	0.78	9×10^{-3}	1.48	0.27	0.26	5×10^{-6}	0.44
Ir(FOTbpa) ₃	2:1	0.93	9×10^{-4}	1.41	0.19	0.21	2×10^{-3}	0.27
	1:1.5	0.88	6×10^{-4}	1.38	0.12	0.19	7×10^{-4}	0.31
	1:3	0.85	1×10^{-3}	1.38	0.18	0.20	3×10^{-4}	0.33

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Capacitors are classified into two types: electrical double layer capacitors (EDLCs) and pseudo-capacitors or super-capacitors.¹⁶³ The energy storage mechanism is different for these two capacitors. In EDLCs the charge is stored in a non-faradaic way by electrostatic attraction (adsorption) at the electrode surface. Thus, the surface area and conductivity are important parameters determining the capacitance. Carbon nanomaterials are commonly used as electrodes in EDLCs. On the other hand, in the case of pseudo-capacitors, charges are stored through redox (Faradaic) reactions with charge transfer processes occurring at the electrode/electrolyte interfaces. Super-capacitors have higher specific capacitance than EDLCs due to the additional redox reactions, which leads to a lower cycle stability. Transition metal oxides and conductive polymers are widely employed as electrodes for pseudo-capacitors. The performance of the electrode materials or energy storage devices are evaluated by electrochemical measurements like cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and self-discharge.

5.1 Electrochemistry Technology

Electrochemistry is a branch of physical chemistry that studies the chemical reactions involving electrons or ions moving between electrodes and electrolyte. The movement of electrons or ions generate electricity and the chemical reaction is known as a redox reaction. Energy storage devices such as batteries, fuel cells and super-capacitors can convert chemical energy to electrical energy *via* redox reactions. Thus, electrochemistry is an essential way to investigate energy storage devices. Energy storage devices can be viewed as two electrode systems, consisting of a working electrode, a counter electrode and electrolyte. The three-electrode system (**Figure 5.1**), with an additional reference electrode, is important in voltammetry, which can determine potentials within the cells. In an electrochemical cell, the chemical reaction takes place at the working electrode, the potential is measured against that of the reference electrode, and the current is passing through the counter electrode.

Figure 5.1 Schematic illustration of three electrode cell system.

5.1.1 Cyclic Voltammetry

CV is a powerful and standard electrochemical method to investigate the redox reaction accompany with electron transfer and ion moving in electrode materials. In the CV measurement, the scan potential range and scan rate need to be set first. The current will be recorded as a function of the applied potential with cycles of ramps. The cyclic voltammogram trace unfortunately have two conventions, US and IUPAC (IUPAC convention is used in my thesis). The scan from high potential to low potential (cathodic trace) is a reduction process with a reduction peak. In contrast, the scan from low potential to high potential (anodic trace) is an oxidation process with an oxidation peak. The peak width and height are strongly dependent on the electrode material, scan rate and electrolyte.

For example, the reversible redox of ferrocene (Fc) and ferrocenium (Fc^+), at a scan rate (s) of 100 mV s^{-1} is shown in **Figure 5.2**. During the initial forward scan with an applied positive potential ramp, an oxidation peak at potential E_{pa} with an anodic peak current i_{pa} is observed. The anodic current initially increases over this period when Fc located near the electrode is steadily oxidized to Fc^+ . The peak current depends on the diffusion of additional Fc from the bulk solution to the electrode area at certain concentration. At the same time the oxidized Fc^+ at the surface of the electrode forms a diffusion layer, which hampers the diffusion of Fc to the working electrode. Consequently, upon scanning to more positive potentials, a decrease of anodic current (after E_{pa}) is displayed. During the reversed scan with a negative potential ramp, a reduction peak at potential E_{pc} with a cathodic peak current i_{pc} is observed. Meanwhile, the concentration of Fc^+ at the electrode is decreased as it is reduced back to Fc with the decreasing

potential. The equilibrium between Fc and Fc⁺ can be described by the Nernst Equation 5.1.

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{O_x}{Red} \right) = E^{0'} + \frac{RT}{F} \ln \frac{[Fc^+]}{[Fc]} \quad (5.1)$$

where E is the potential of an electrochemical cell, E^0 is the standard potential of a species, $E^{0'}$ is the formal potential, R is the universal gas constant, T is the temperature, F is Faraday's constant, n is the number of electrons, O_x and Red are the concentrations of the oxidized and reduced analytes, respectively. The potential difference between E_{pa} and E_{pc} mainly results from the effects of Fc and Fc⁺ diffusion rates. The halfway potential ($E_{1/2}$) between E_{pc} and E_{pa} indicates the equal concentration of Fc⁺ and Fc at the electrode surface, which provides a straightforward way to estimate the formal potential $E^{0'}$.

Figure 5.2 CV curve of the reversible redox of Fc/Fc⁺, at a scan rate of 100 mV s⁻¹.

The electrochemical reversibility of electrode materials can be easily observed by the CV redox peaks or alternatively be evaluated by the difference between E_{pa} and E_{pc} , called peak-to-peak separation (ΔE_p). ΔE_p in a one electron reversible reduction process is 57 mV at 25 °C and the full-width half max on the forward scan peak is 59 mV.¹⁶⁴ A larger ΔE_p will be observed if the electrochemical reaction is non-reversible.

The CV curves are also representing the energy storage capability. The enclosed area of a CV curve is proportional to the capacitance of the material or

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device. The specific capacitance from the CV data is determined by the following Equation 5.2.

$$C = \frac{1}{s\Delta V} \int_{V_0}^{V_0+\Delta V} j dV \quad (5.2)$$

C is specific capacitance (F g^{-1} , F cm^{-2} , F cm^{-3}), j is the current density (A g^{-1} , A cm^{-2} , A cm^{-3}), s is the scan rate (V s^{-1}), ΔV is the voltage window (V). It should be noted that the integral part in Equation 5.1 should be either area A1 or A2 in **Figure 5.3**. If the enclosed area of the CV curve ($A1 + A2$) was used, then the voltage window should be $2\Delta V$.

Figure 5.3 A typical CV curve for free standing PEDOT films. At a scan rate of 50 mV s^{-1} .

5.1.2 Galvanostatic Charge Discharge

The galvanostatic charge discharge (GCD) is also called chronopotentiometry, which is different from the CV method. The constant current is applied on a cell and the potential changes are recorded as a function of time. The GCD technique is widely used in the field of super-capacitors to evaluate the capacitance and stability of materials or devices. As shown in **Figure 5.4a**, the GCD profile of a super-capacitor based on free standing PEDOT electrodes showed similar charging curves to discharging curves. A voltage drop may occur when current is inversed due to the intrinsic resistance or at high charge-discharge current density (**Figure 5.4b**). The specific capacitance of electrode materials or devices could be calculated by Equation 5.3.

$$C = \frac{I\Delta t}{\Delta V} \quad (5.3)$$

where I is the applied current density (A g^{-1} , A cm^{-2} , A cm^{-3}), Δt is the discharge time, and ΔV is the operating voltage obtained from the discharge profile excluding the voltage drop.

Figure 5.4 (a) GCD profiles of a super-capacitor based on free standing PEDOT electrodes at different current density. Reproduced with permission.¹⁶⁵ Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) A voltage drop can be observed at high charge-discharge current density.

The energy density (E_{ca}) and power density (P_{ca}) of electrode materials or super-capacitors are given by the following Equations.

$$E_{ca} = \frac{1}{2} C (\Delta V)^2 \quad (5.4)$$

$$P_{ca} = \frac{E_{ca}}{\Delta t} \quad (5.5)$$

5.2 Electrode Materials and Devices

Numerous materials such as active carbon, carbon nanotubes, graphene, metal nitride, metal oxides, polymers, and MXenes have been developed as electrode materials for super-capacitors. In my study, polymers and MXenes were utilized as electrode materials to fabricate the super-capacitors.

5.2.1 PEDOT Electrode

PEDOT:PSS with tuneable conductivity is widely utilized in organic electronic devices. The commercially available PH1000 suspension is one of the commercial PEDOT:PSS products with high conductivity. Super-capacitors based on PEDOT electrodes have also been reported.^{166, 167} PEDOT films prepared by vapor-phase

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and electrochemical polymerizations are utilized as the electrode for super-capacitors with specific capacitance around 175 F g^{-1} and 130 F g^{-1} .^{168, 169} Super-capacitor based on PEDOT hydrogel fibre has also been investigated, which has a specific capacitance of 203 F cm^{-3} at discharge current 0.54 A cm^{-3} .¹⁷⁰ In paper 4, a free standing PEDOT film was obtained and used as electrode for super-capacitors. The fabrication method of free standing PEDOT film is shown in **Figure 5.5**.

Figure 5.5 Preparation of the free standing PEDOT film.

The electrochemical properties of the free standing PEDOT films were investigated in three electrode setups with $1 \text{ M H}_2\text{SO}_4$ as electrolyte. The CV curves of a PEDOT electrode is shown in **Figure 5.6**, which kept nearly a rectangular shape as the scan rate increased from 25 to 100 mV s^{-1} . No obvious redox peaks could be detected, which is similar with other reported studies.^{166, 167} The rectangular shape of the CV curves indicate that the free standing PEDOT:PSS electrodes possess a low resistance and high reversibility.

Figure 5.6 The CV curves of a free standing PEDOT electrode at scan rates of 25, 50, and 100 mV s^{-1} .

5.2.2 MXene Electrode

MXenes are a family of two-dimensional (2D) inorganic materials consisting of transition metal carbides, nitrides, which is first made in 2011.¹⁷¹ MXenes are synthesized by etching away the A layer from the $M_{n+1}AX_n$ phases, where M is a transition metal, A is an IIIA-group element (Al, Si), and X is carbon or nitrogen. MXenes with metallic conductivity and hydrophilic surfaces are widely investigated in energy storage devices. $Ti_3C_2T_x$ is the first developed MXene material and has been widely studied as an electrode material for electronic devices due to its high conductivity, easy solution processability, and good flexibility.¹⁷²⁻¹⁷⁴ The fabrication process of $Ti_3C_2T_x$ MXene solution is shown in **Figure 5.7**. Solid state super-capacitors based on $Mo_{1.33}C$ MXene hybrid with PEDOT:PSS electrode exhibited high performance with a specific capacitance of 568 F cm^{-3} .¹⁷⁵

Figure 5.7 Schematic of the fabrication process of $Ti_3C_2T_x$ MXene solution. Reproduced with permission.¹⁷¹ Copyright 2011, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In my fifth study, $Ti_3C_2T_x$ MXene solution is fabricated according to the literature.¹⁷⁴ Free standing $Ti_3C_2T_x$ MXene films are fabricated through filtration from the water suspension. The CV curves of the $Ti_3C_2T_x$ MXene electrode are shown in **Figure 5.8**. The oxidation peak is more pronounced than the reduction peak in CV curves, which might be due to the low reduction speed.

Figure 5.8 The CV curves of a $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrode at scan rates of 25, 50, and 100 mV s^{-1} .

5.2.3 Device Configuration

As described above (5.1), super-capacitors are two electrode systems. Super-capacitors can be divided into two types: symmetric and asymmetric devices (**Figure 5.9**), depending on the electrode materials. In symmetric super-capacitors, the same material is used as both the anode and cathode electrodes. In contrast, the asymmetric super-capacitor consists of different electrode materials, which could extend the potential window by using suitable anode and cathode combinations. Therefore, higher energy density can be achieved in asymmetric devices than that in symmetric ones.

Figure 5.9 Schematic illustration of symmetric (a) and asymmetric (b) super-capacitors in sandwich type.

Super-capacitors have various configurations. The most typical configuration is the sandwich type, which is fabricated by sandwiching electrolyte between two flat electrodes. The advantages of this configuration include easy processing and that it is suitable for many different types of materials. The super-capacitors in this thesis are of the sandwich type. The symmetric device with two free standing PEDOT films as electrodes shows a potential window of 0.8 V (**Figure 5.10a**).

An asymmetric device with a free standing PEDOT film as an anode and a $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film as a cathode displays a larger potential window of 1.5 V (**Figure 5.10b**), which results in a higher energy density than that of the symmetric one.

Figure 5.10 (a) CV curves of a symmetric super-capacitor based on free standing PEDOT electrodes. Reproduced with permission.¹⁶⁵ Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) CV curves of an asymmetric super-capacitor based on free standing PEDOT anode and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene cathode.

Chapter 6 Photo-capacitors

6.1 The Development of Photo-capacitors

The combination of energy conversion and storage systems, for example silicon solar panels and batteries, have been commercialized.¹⁷⁶ Physical integration with wires was adopted in these kind of devices and the large internal resistance limit the possible applications. In addition, the large, bulky, and heavy devices limit their applications in portable and wearable electronics. Combining solar cells and super-capacitors by a common electrode, which simultaneously realize energy harvesting and storage, resulting in self-powered autonomous systems named as integrated photo-capacitors (IPCs). Different types of solar cells such as dye-sensitized solar cell (DSSC), OPVs and perovskite solar cells (PVSC) have been successfully integrated with super-capacitors for self-powering systems.

The first planar IPC was reported by Murakami et al. in 2004.¹⁷⁷ They achieved the *in situ* energy harvesting and storage by integrating a DSSC and capacitor with two electrode configuration, which caused high internal resistance. Later, a common electrode was introduced between the photo-electrode and counter electrode, which currently constitute the main configuration of IPC.¹⁷⁸ A number of studies have been reported based on DSSCs.¹⁷⁹⁻¹⁸¹ However, the usage of liquid electrolytes in most DSSCs have the risk of leakage. Thus, IPCs based on OPVs emerged because OPVs possess the advantage over DSSCs of being all-solid state. Furthermore, OPVs have additional advantages such as low cost, lightness, mechanical flexibility, and for the possibility of large area manufacture. Srinivasan et al. demonstrated an IPC utilizing a single-walled carbon nanotube network as a common interface between an OPV and a capacitor, which reduced the internal resistance up to 43% compared to devices where external wires connect the OPVs and super-capacitors.¹⁸² A high overall efficiency of 10% was also achieved by laterally integrating a PVSC and a super-capacitor with external copper tape in 2015.¹⁸³ They found that a high V_{oc} and PCE was obtained for the PVSC when the super-capacitor was discharged at some potentials. In addition to the planar type IPC discussed above, fibre type IPCs were developed with the unique advantages of weaving compatibility, flexibility, and independence of incident light angle. The fibre type IPC consisting of a DSSC and a super-capacitor was first reported by Wang et al.¹⁸⁴ Later, fibre type IPC combined with OPV and super-capacitor was achieved.¹⁸⁵ However, the poor performance and complicated fabrication process hindered the application.

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The common electrode plays an important role in the IPC. The requirements for the common electrode are high conductivity and high capacitance. Currently, metal materials are the most commonly used type of electrodes; however, metal electrodes are not favorable for low-cost and large area industrial manufacture. Other materials like TiO₂, Graphene, carbon and silicon were reported to replace the metal electrodes. However, high temperature treatment was needed. Therefore, it is important to find a suitable common electrode for all solution processed large area production. In paper 4, the conducting polymer PEDOT:PSS was used as a common electrode due to its high conductivity and capacitance, which make it possible for developing all solution processed IPCs.

6.2 Performance Evaluation

The overall efficiency (η_{overall}) of a photo-capacitor is determined by the PCE of solar cell and the energy storage efficiency (η_{storage}) of the super-capacitor. The PCE of OPV has been discussed in Chapter 2. The energy density of the light (E_{light}) illuminating the solar cell during the photocharging time (t , s) is calculated by the Equation 6.1.

$$E_{\text{light}} = P_{\text{in}} \times t \quad (6.1)$$

The energy density of a super-capacitor is calculated through Equation 5.3. Thus, the η_{overall} is determined by the Equation 6.2.¹⁸⁶

$$\eta_{\text{overall}} = PCE \times \eta_{\text{storage}} = \frac{E_{\text{ca}} \times A_{\text{ca}}}{E_{\text{light}} \times A_{\text{OPV}}} = \frac{\frac{1}{2}C(\Delta V)^2 \times A_{\text{ca}}}{P_{\text{in}} \times t \times A_{\text{OPV}}} \quad (6.2)$$

where A_{ca} and A_{OPV} are the active area of the super-capacitor and OPV, respectively. Therefore the η_{storage} of the super-capacitor can be calculated by Equation 6.3.

$$\eta_{\text{storage}} = \eta_{\text{overall}} / PCE \quad (6.3)$$

In the ideal case, the charge voltage of the super-capacitor should be close to the V_{oc} of the OPVs. However, a decrease in voltage always exist, that maybe attribute to the resistance between these two parts. As the charging process of super-capacitors is time dependent, thus the performance of the photo-capacitor is also related to the charging time.

In paper 4, a new lamination method was developed to fabricate the all solution processed photo-capacitors, which consist of an OPV based on P3HT:ICBA as active layer and a capacitor based on free standing PEDOT:PSS as electrodes. The device structure and performance of the photo-capacitor are shown in **Figure 6.1**.

The reason to choose parallel configuration is to avoid the penetration of the electrolyte in super-capacitor to the active layer of the OPV. The η_{overall} increased with the photo-charge time, then it reached a maximum and finally showed a downward trend slightly. The photo-charge time is very fast, which within 5 s, and the energy storage capability for the capacitor is very low. The maximum η_{overall} is about 2% for the IPC, which is main limited by the PCE of the OPV according to the calculation Equation 6.2.

Figure 6.1 (a) Device structure of a photo-capacitor consist of an OPV and capacitor with PEDOT:PSS as the common electrode. (b) The η_{overall} of the photo-capacitor versus the photo-charge time. Reproduced with permission.¹⁶⁵ Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The self-discharge or leakage current of super-capacitors limits the low current density charge process, which indicates the inefficient photo-charging under low incident light. When the current generated by OPV is large enough and the resistance between OPV and super-capacitor is small, the photo-charge and discharge profile will be similar to the auto-lab charge discharge profile, as shown in **Figure 6.2**. The discharge time for the IPC after photo-charge is a little longer than that after auto-lab charge, which could attribute to the increased ion mobility, due to the enhanced temperature by light illuminate. When an OPV is under low light illumination (1000 flux), the photo-charge process takes 1230 s with a charging potential of 1.5 V (**Figure 6.3a**). When the light illumination increases to 150000 flux, the photo-charge time is shorted to 50s and a high charging potential of 3 V is achieved (**Figure 6.3b**). Therefore, the incident light intensity has a huge influence on the performance of the IPCs.

Figure 6.2 (a) The photo-charge under AM 1.5 simulated sunlight (100 mW cm⁻²) illumination and galvanostatic discharge at different discharge current densities in dark. (b) Auto-lab charge at the same charging current density as the photo-charge (7 mA cm⁻²) and galvanostatic discharge at different discharge current densities. Reproduced with permission.¹⁶⁵ Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 6.3 (a) The photo-charge under LED with intensity 1000 flux illumination and galvanostatic discharge at 0.5 mA cm⁻² in dark. (b) The photo-charge under LED with intensity 150000 flux illumination and galvanostatic discharge at 0.5 mA cm⁻² in dark.

6.3 Applications

The distinguished features of super-capacitors are the fast charge/discharge rates, high power density, and long cycle lifetime. However, the energy density of super-capacitor is lower than that of battery. Therefore, the applications of such photo-capacitors are more suitable for suppressing fluctuations of the incident light, mini-power portable and wearable electronics. In paper 5, we demonstrated a self-powered unit consisting of an organic solar module and an asymmetric

super-capacitor. The super-capacitor could light on a blue LED for tens of seconds, which indicates the relatively low energy density when used for such application. However, under a LED illumination with light intensity about 500 flux (the intensity is comparable to those in a library or shopping malls), the IPC could power a digital thermometer (**Figure 6.4**). During about 5 h testing, there is no obvious drop in the display contrast of the digital thermometer, which indicates the high stability of the IPC under such light illumination. Therefore, the IPC may be used to power the digital price display in supermarket as a self-powered unit.

Figure 6.4 A digital thermometer is powered by the IPC under a LED light illumination with intensity about 500 flux.

Chapter 7 Summary and Outlook

In this thesis, we focused on two kinds of organic electronic devices. For the OPVs, we mainly investigated the voltage losses with both singlet and triplet materials. Low voltage loss has been achieved with novel NFA, which is attributed to the reduced non-radiative recombination. However, for the triplet materials, the combination with NFAs need to be explored, and more importantly, the deeper understanding on charge generation and transport in T-OPVs is needed in the future. Besides, the role of triplet materials in the field of OPVs need to be carefully considered.

For the IPCs, the performance evaluation is based on the total photo-electric conversion efficiency. The energy storage power should match with the generated power by the OPVs. The self-discharge and low energy density are the main shortcomings for the super-capacitors. Although the asymmetric super-capacitors show larger energy density with a much wider operation window, it is still far behind the Li-ion batteries. Therefore, it is necessary to develop novel electrode materials with reasonable architecture to achieve higher surface areas, excellent electronic conductivity, and better ion transmission paths, thus further improve the energy density. In addition, the connection between two devices or the circuits need to be well designed to reduce the resistance losses.

The technology of all solution processed (vacuum free) OPVs or solar modules for large scale production are urgently needed. Conducting polymer PEDOT:PSS is considered as promising electrode materials for OPVs. However, when it is used as the top electrode, the interaction with active layers needs to be studied. In addition, preliminary study on the PEDOT-based solar cells found that the stability of the devices is not ideal under 1 sun illumination. Therefore, how to overcome the light stability problem is critical for its commercial applications. Room light application of OPVs may be a good choice to avoid the light stability problem.

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