Loss Mechanisms in Non-Fullerene Organic Solar Cells

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During the course of research underlying this thesis, Huotian Zhang was enrolled in the graduate school Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden.

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Abstract

Photovoltaics are one of the most important sustainable energy sources in the 21st century. Among photovoltaics, organic solar cells (OSCs) offer many advantages such as the ease of processing, light weight, the potential for flexible devices, and tunable properties. Their unique nature and complexity present a fascinating charm, attracting many researchers. Thanks to researchers' efforts, the power conversion efficiency (PCE) of OSCs has been boosted from below 1% to 19% over the last three decades. Despite the exciting PCE, some problems remain unsolved, for example, the large voltage loss and unsatisfying long-term stability. This thesis aims to understand the fundamental physics of the state-of-the-art OSCs, especially the loss mechanisms. Ultimately, properly understanding the mechanisms will serve as the basis of OSC's further improvements and commercialization.

The beginning of this thesis introduces basic concepts about semiconductor physics and donor-acceptor OSCs, explaining the generation of electricity from light and the fundamentals of organic electronics. Subsequently, the detailed balance in a solar cell is reviewed, which is the basis of voltage loss analysis. In this section, we see how the generation, recombination, and output of charges reach a balance. Then, the way to determine the voltage loss is shown, and the most recent understandings in reducing this loss are reviewed. The fill factor, as a measure of the quality of a solar cell, is a complex parameter, especially in OSCs. The latter part of this thesis starts from the photophysical processes in an OSC, and then relates intrinsic parameters to the fill factor. Figure of merits have been employed to express the fill factor analytically. Finally, experimental methods and basic principles for the previous analysis are introduced, including Fourier transform infrared spectroscopy, external quantum efficiency of photovoltaics, spectrograph for electroluminescence or photoluminescence, transient absorption, and time-delayed collection field. Overall, this thesis combines thermal dynamics and charge dynamics to analyse voltage losses and fill factor losses. The author hopes this work can contribute to a better understanding of the loss mechanisms in OSCs.

Keywords: photovoltaics, organic solar cells, non-fullerene, charge recombination, voltage loss, fill factor

POPULÄRVETENSKAPLIG SAMMANFATTNING

Solceller är ett av 2000-talets viktigaste hållbara energikällor. Bland solceller erbjuder organiska solceller (OSC) många fördelar som enkel bearbetning, lättvikt, potential för flexibilitet och avstämbara egenskaper. Dess märkliga natur och komplexitet utgör en fascinerande lockelse som attraherar många forskare. Tack vare forskarnas ansträngningar har OSC:ernas verkningsgrad ökat från 1% till 19% under de senaste tre decennierna. Trots den spännande verkningsgraden återstår vissa problem att lösa, till exempel den stora spänningsförlusten och den långsiktiga stabiliteten. Denna avhandling syftar till att förstå den grundläggande fysiken hos de senaste OSC:erna, särskilt förlustmekanismen. I slutändan kommer en korrekt förståelse av mekanismerna att bli en arbetsgrund för OSC:ers ytterligare förbättring och kommersialisering.

Detta arbete fokuserar på förlustmekanismerna för OSC, särskilt tomgångsspänningen och fyllningsfaktorn. I början av denna avhandling introduceras grundläggande begrepp om halvledarfysik och donator-acceptor-OSC:er. Denna del förklarar elproduktionen från ljus och grunderna i organisk elektronik. Därefter ses den detaljerade balansen i en solcell över, vilket är grunden för spänningsförlustanalysen. I den här delen ser vi hur ingångsparametrar, rekombination och utgångsparametrar hänger samman. Sedan visas sättet att bestämma spänningsförlusten, och de senaste rönen för att minska förlusten ses över.

Fyllningsfaktorn, som ett mått på en solcells kvalitet, är en komplex parameter, särskilt i OSC:er. Den senare delen av denna avhandling utgår från de fotofysiska processerna i en OSC och relaterar sedan inneboende parametrar till fyllningsfaktorn. Godhetstal har använts för att uttrycka fyllningsfaktorn analytiskt. I slutändan introduceras experimentella metoder och grundläggande principer för den tidigare analysen, inklusive Fourier transform infraröd spektroskopi, extern kvanteffektivitet hos solceller, spektrografi för elektroluminescens eller fotoluminescens, övergående-absorption och tidsfördröjd insamlingsfält. Sammantaget kombinerade avhandlingen termisk-dynamik och laddningsdynamik för att analysera spänningsförluster och fyllningsfaktorförluster. Författaren hoppas att detta arbete kan bidra till en bättre förståelse av förlustmekanismerna i OSC.

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CHAPTER 1

Introduction

This chapter presents the background information and motivation for this work. Organic solar cells are widely studied but still rarely used in daily life. There is no doubt that society supports this technology and expects its potential application as renewable energy. However, the role that organic solar cells will play in the future remains unclear. Before answering this question, let us review the history and current state of the field. In the last section of the chapter, the aim and the structure of this thesis will be described.

1.1 Climate change and energy supply

Since the early 2000s, scientists have observed obvious climate changes [2–4]. Global warming, as one of the most significant changes, are most likely driven by human activities [5, 6]. According to the data from NASA [1], global surface average temperature has increased by over 1 degree Celsius since the pre-industry period (**Figure 1.1**). At the same time, extreme weather events are becoming more serious and more frequent. From heatwaves in Sweden[7], droughts in South Africa[8], flooding in Bangladesh[9] to hurricanes in the Caribbean[10] and arctic outbreak in Texas[11], people's daily lives are becoming increasingly disrupted. Mounting evidence is showing the terrible results of global warming, drawing increasing global attention, meanwhile, the warming is accelerating faster than we thought [12].

Global warming is primarily caused by fossil fuel combustion, which increases the level of heat-absorbing greenhouse gases in the earth's atmosphere. The large-scale use of fossil fuels contributed to the Industrial Revolution. Now, fossil fuels have become the cornerstone of modern society due to their importance in transportation, power generation and industrial production. As of 2018, the world's major energy sources include oil (34%), coal (27%), and natural gas (24%), with the share of fossil

Figure 1.1 | Global warming. These graphs illustrate the global surface temperature difference in year (a) 1884, (b) 1943, and (c) 2020. d, The average temperature has increased significantly since 1880. Data source: NASA's Goddard Institute for Space Studies (GISS) and NOAA's National Centers for Environmental Information NCEI[1]. Credit: NASA/GISS, NOAA/NCEI

fuels in the world's primary energy consumption at 85% [13]. Correspondingly, the combustion of fossil fuels produces around 35 billion tons of carbon dioxide (CO₂) per year, far exceeding the amount that can be absorbed by natural processes. As a result, there is a net increase of billion tons of (CO₂) per year [14], which leads to global warming and ocean acidification.

To stop further climate deterioration, the term “Carbon neutrality” is proposed, which refers to achieving net-zero carbon dioxide emissions. One way to implement carbon neutrality is by using renewable energy such as hydro, wind, geothermal, and solar power. According to the electricity generation amount by each energy source from 1990-2018 (Figure 1.2 a), fossil fuels still dominate the power generation despite significant increase of renewable energy sources. Hence, there are still great potentials for renewable energy sources. The solar photovoltaic (PV), as one of the promising methods for clean energy, has surged during last three decades. As shown in Figure 1.2 b, the share of solar PV in both all energy sources and renewable energy sources has increased by over three orders of magnitude from 1990 to 2018, while the total electricity consumption has kept growing. Of course, this initial rapid growth of PV benefits greatly from the support of various countries and regions. Certainly, it is attributed to the distinctive features of PV, for example, no pollution and no emission during operation, no fuel filler required, low safety risk, and great abundance of raw materials.

Figure 1.2 | Energy supply around the world. a, Electricity generation by source, World 1990-2018. **b,** The electricity generation share of solar PV in all sources and renewable sources, World 1990-2018

Data source: International Energy Agency (IEA).

1.2 Organic semiconductors for photovoltaics

The term organic semiconductor implies (1) that the compounds generally contain carbon-hydrogen bonds, possibly with a few heteroatoms such as oxygen, nitrogen and sulfur, and (2) that they exhibit features typically possessed by semiconductor materials [15]. Organic semiconductors are interesting because they have the potential to combine electrical properties of semiconducting materials with chemical and mechanical advantages of organic compounds.

A semiconductor material has an electrical conductivity value falling in between that of a conductor and an insulator. Its conductive properties may be altered by introducing impurities, illumination or by external electric field. Since the middle of 20th century, the information era and the mobile Internet age have arrived one after another with the spread of personal computers and smartphones. At the same time, the semiconductor industry, which is the backbone of electronic products, has experienced booming development. Semiconductor materials have also been widely studied and each of them has its distinctive properties. For example, the high abundance, the good mobilities and the perfect Si-SiO₂ interface make silicon a natural pillar material for general purpose devices. The high charge-carrier mobilities, relatively insensitive to overheating and low noise of gallium arsenide make it perfect for high frequencies application such as radio circuits for 5G. Silicon carbide is widely used as power electronic devices in electric systems and high speed rails due to its high voltage and high temperature resistance.

Daily encountered organics can hardly be related to conductivity or electronics. However, this stereotypical impression has been changed when conjugated polymers with metallic transport came into the scientific spotlight around 1970s [16]. In addition, by manipulating the chemical synthesis, researchers succeeded in making organics work as semiconductors. Based on their semiconducting properties, organic semiconductors have been applied in devices such as photovoltaics (PVs), light-emitting diodes (LEDs), or field-effect transistors (FETs) [17]. However, although the organics show semiconducting properties, they have some intrinsic differences when compared with inorganic semiconductors. Organics typically consist of molecules. The intermolecular forces are widely present in organic matters, giving rise to their characteristics of softness and ease of processing. However, these also bring about localized electronic wave functions and weak dielectric screening. When electrons are excited in semiconductors, they can form a bound state with holes, which is called 'exciton'. According to the degree of charge binding or electric field screening, excitons can be divided into Wannier-Mott excitons or Frenkel excitons, respectively. In typical inorganic semiconductors, excitons are weakly bound Wannier-Mott excitons with large radii and small binding energy, which can directly separate at room temperature. In organic semiconductors, excitons are usually strongly bound Frenkel excitons, which can hardly contribute to the free charge carriers. The mobility of organic semiconductors (including crystalline organic semiconductors) is usually much lower than inorganics, because of their localized charges. Moreover, there are few intrinsic charge carriers in organic semiconductors, which makes them poorly conductive without doping. Despite many drawbacks in electronic qualities and semiconducting properties, organic semiconductor have many distinguished advantages, especially

the good tunability (for example, absorption and emission spectra). Together with their properties of easy process, flexibility and light weight, organic semiconductors are great candidates for special optoelectronic applications.

The photovoltaic effect in organics was observed for the first time by H. Kallmann and M. Pope in 1959[18]. It was not until the 1980s that there was a big breakthrough in organic solar cells, when C.W. Tang reported the first donor-acceptor organic solar cell with a bilayer structure. At that time the power conversion efficiency (PCE) was about 1%. Now, the best organic solar cell has achieved more than 18% PCE [19, 20], which is approaching silicon or perovskite solar cells. Encouraging initial lifetime (>8,000 h unencapsulated) has been achieved in commercialized products [21]. However, silicon solar cells have achieved more than 26% PCE [22, 23], and the performance of commercial modules can keep 95% after 20-years outdoor usage [24]. Considering the efficiency, cost and stability issues, the status of silicon in the power grid is unshakable. However, just like the application of particular inorganic semiconductor in special fields as mentioned above, organic photovoltaics may also occupy a place in the subdivision of photovoltaics, for example, semi-transparent PV for greenhouse, PV for indoor applications, and PV for mobile devices.

Currently, the commercialization of organic solar cells is already underway. However, there are still many scientific issues that plague academia. For example, controversial studies and debates on the mechanism of charge separation are going on. Moreover, new problems continue to arise with the emergence of new materials, while old problems may fade with the retirement of old materials. For example, the development of non-fullerene acceptors has brought opportunities to reduce the voltage loss and additional requirements for understanding charge separation and recombination, meanwhile, researchers may care less about the tunability of fullerene.

1.3 Aims and structure of this thesis

The aim of this thesis is to understand the loss mechanisms in organic solar cells, especially those based on non-fullerene acceptors. The mind map to achieve this goal is exhibited in (**Figure 1.3**). The thesis focuses on two main fundamental questions on the topic “loss mechanisms of organic solar cells”: what is affecting the open-circuit voltage and what is affecting the fill factor.

To answer these questions, we have to be equipped with basic knowledge of semiconductor physics and donor-acceptor organic solar cells (chapter 2), including the origin and the characteristics of the photovoltaic effect, and the special features of organic photovoltaics. After the basic concepts and theory, the loss analysis can be overall analysis of a system based on thermal dynamics, or individual analysis of electronic states. On the one hand, recombination at the open-circuit condition dominates the open-circuit voltage (chapter 3). On the other hand, the charge separation and recombination process as a function of bias influences the current generation and the maximum power point, which is the physical origin of FF (chapter 4). To study those processes in organic solar cells, steady-state and transient techniques are required (chapter 6). The last part of the thesis (chapter 7) summarizes the results of the appended papers.

Figure 1.3 | Factors determining the performance of a typical organic solar cell. The terms in green squares are phenomenon or matters, which are mainly dealt with in material synthesis, film formation and device fabrication. The terms in purple squares are physical parameters, which rely on the matters as indicated by the slim green arrows. FF and V_{oc} in the dashed red frame are main investigation objects of this thesis. (This mind map is inspired by [25])

CHAPTER 2

Basic concepts

In this chapter, some basic concepts and theories of semiconductors physics and organic semiconductors for photovoltaics are introduced.

2.1 The photovoltaic effect

The word "photovoltaic" consists of "photo" and "voltaic", indicating the straightforward working principle, photons in and voltage out. The realistic working process in a solar cell is more than pure voltage output. From the perspective of energy, it is the conversion of photo energy into electric potential. Here comes the question, what drives the conversion?

2.1.1 From photonic energy to chemical potential

The absorption of photons occurs through the excitation of electrons into states of higher energy. As with other optical and electrical properties, the absorption of metals, semiconductors, and insulators can be completely different. The fundamental reason is their difference in electronic structures. With calculation of the wave function in a semiconductor, it is found that the allowed electron energy is not continuous. The ranges of energy levels that electrons may have are called bands and the ranges that they may not have are called band gaps or forbidden bands [26]. In equilibrium conditions, Fermi-Dirac statistics can describe the distribution of electrons over energy states,

$$f(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1} \quad (2.1)$$

where $f(E)$ is the occupation possibility of a state with energy E , k_B is Boltzmann constant, T is the temperature, and E_F is the Fermi level which is also the chemical

potential of electrons.

Figure 2.1 | Fermi-Dirac distribution and density of states. **a**, Fermi-Dirac (FD) statistics at 0, 150, 300 and 600 K. The abscissa is energy, and the ordinate is occupation probability. **b**, Demonstration of electron and hole densities under the FD distribution at 300 K, in conduction and valence bands with the parabolic density of states (DOS). (Credit: Wolfgang Tress.)

As for a semiconductor, the Fermi level lies within the band gap, and the gap is small enough for electrons to be "thermally populated". The bands closest to the Fermi level are called the conduction band and the valence band, both of which have decisive impacts on the conductivity of the semiconductor. At absolute zero, the conduction band is located at the lowest range of empty electronic states, while the valence band is the highest range of occupied electronic states. A solid conducts only if the valence band is not fully occupied or the conduction band is not entirely empty, because the total momentum of electrons may be changed in an electric field, and there would be a net current. The occupation of the density of states can be described in **Figure 2.1**. The empty states can be treated as quasi-particles, which are called holes. The Fermi level and electron occupation can be changed by doping electron donors or acceptors, which changes the conductivity and chemical potential in equilibrium conditions. Any deviation from the thermal equilibrium changes the level of occupation of the electronic states, hence altering the concentrations of electrons and holes. Light-induced excitation, electrical injection or a sudden increase in temperature can produce fresh charge carriers, creating a non-equilibrium condition.

When semiconductors are illuminated by photons with energy higher than the gap, electrons at the valence band can be excited by absorbing photons. The photo-excited electrons initially reside at an energy higher than the conduction band edge. Since there are many density of states at a lower energy, the hot carriers may thermalize

within femtoseconds to the band edge by absorbing and releasing phonons. Before they recombine and eventually reach thermal equilibrium, the charge carriers exist in their bands for their “lifetime”, which is much longer than their thermalization time [27].

Under continuous illumination, the generation and recombination reach thermal and chemical equilibrium, and a certain amount of charges always remain in the bands. The distribution can still be described by Fermi-Dirac distribution because the thermalization process is short, which originates from the collision between electrons and phonons, while the recombination process is much longer, which originates from the collision between electrons and holes. To describe the occupation of the states in the conduction band and the valence band separately, two quasi-Fermi levels ($E_{f,n}$, $E_{f,p}$) can be used, as shown in **Figure 2.2**. The splitting of quasi-Fermi levels denotes the increase of chemical potential in the semiconductor.

Figure 2.2 | Quasi-Fermi level splitting. **a**, The distribution of electrons and holes in the DOS in the equilibrium condition. **b**, Electrons and holes under continuous light illumination, where the density of electrons and holes need to be described by two quasi-Fermi levels, individually.

The equilibrium point may move due to the change of the recombination rate or extraction of the charges. Accordingly, faster recombination or extraction will lead to a lower chemical potential. The detailed process will be discussed in chapter 3.

2.1.2 From chemical potential to electrical energy

In the previous subsection, we have introduced the photo-induced chemical potential change in semiconductors. However, a homogeneous semiconductor cannot produce a voltage output, because voltage requires spatial variations in electric poten-

tial, for example, a spatial gradient of charges or electrochemical potentials. To create voltage via semiconductors, one of the simplest ways is to make electrical junctions [28].

An electrical junction is a point or area where multiple conductors or semiconductors make physical contact. For example, the homojunction, the heterojunction, and the metal-semiconductor junction. A spatial difference in Fermi level indicates the difference in charge carrier density, which leads to the diffusion of charge carriers from high intensity to low intensity. The diffusion breaks electrical neutrality, creating the space charge region and the electric field. The electric field drives charge carriers to drift back. Only when the electric field is large enough, and the drift current cancels out the diffusion current, the system can reach an equilibrium. The most commonly known solar cell is configured as a p-n junction (for example, p-type silicon and n-type silicon). Another commonly used configuration for solution-processed solar cells is p-i-n (or n-i-p) structure, which consists of p-type hole transport layers, n-type electron transport layers, and an intrinsic semiconductor layer as the light absorber.

To describe the diffusion and drift process in a semiconductor junction, one can use the following equations,

$$\mathbf{J}_{\text{diffusion}} = eD_n \nabla n - eD_p \nabla p \quad (2.2)$$

$$\mathbf{J}_{\text{drift}} = en\mu_n \mathbf{F} + ep\mu_p \mathbf{F} \quad (2.3)$$

where $\mathbf{J}_{\text{diffusion}}$ is the diffusion current, e is the elementary charge, D_n or D_p is the diffusion constant for electrons or holes, ∇ is the vector differential operator, n or p is the density of electrons or holes, $\mathbf{J}_{\text{drift}}$ is the drift current, μ_n or μ_p is the electron or hole mobility, and $\mathbf{F}$ is the internal electric field.

Using Einstein relation, the diffusion constant can be transformed and expressed by the mobility of carriers. Using Boltzmann approximation, carrier densities can be expressed as a function of fermi levels [26]. Hence, the total current can be expressed in the following form,

$$\mathbf{J} = \mathbf{J}_n + \mathbf{J}_p = n\mu_n \nabla E_{F,n} + p\mu_p \nabla E_{F,p} \quad (2.4)$$

where $\mathbf{J}$ is the total current, $\mathbf{J}_n$ is the electron current, and $\mathbf{J}_p$ is the hole current. There would be a net electron (or hole) current if there is a quasi-Fermi-level gradient of electrons (or holes). As shown in a simulation result via SCAPS (**Figure 2.3 a and d**), there is no Fermi-level splitting for a zero-bias p-n junction in the dark. The conduction band and valence band are bent near the boundary between the p-type semiconductor and the n-type semiconductor because of the built-in field and the vacuum level shift. Here, the contacts at both ends are preset to have the same Fermi level (or work function) as that of the semiconductor, which is for flat bands at both ends. When there is continuous light illumination from the left side, quasi-Fermi levels split and reach quasi-equilibrium. In **Figure 2.3 b**, where the p-n junction is at the open-circuit condition, there is a significant difference between $E_{F,p}$ at the left end and $E_{F,n}$ at the right end. The quasi-Fermi levels have slight bending, but the electron and hole currents cancel each other out. The difference between them equals eV_{OC} . In **Figure 2.3 e**, the overall charge density is increased but the change

in minority carriers is more pronounced (note that the asymmetry is caused by the one-side illumination and hence the generation difference between two sides). In **Figure 2.3 c**, where the p-n junction is at the short-circuit condition, the conduction and valence band bending is similar to that at the dark condition, while the quasi-Fermi level splitting is significant and the bending around space charge region (the junction) is notable.

Figure 2.3 | Energy levels and charge densities in a p-n junction. **a-c**, Energy levels at dark and zero bias condition, light and open-circuit condition, and light and short-circuit condition respectively **d-f**, Electrons and holes density at dark and zero bias condition, light and open-circuit condition, and light and short-circuit condition respectively. The One-dimensional results are simulated through SCAPS, with contacting, with or without illumination from the left side.

A balance of diffusion and drift current is achieved within the junction in the dark state, and the built-in field cancels out the chemical potential difference between the two sides of the junction. Upon light shining, the drift current is enhanced and the equilibrium starts to move. In this case, either the drift current is extracted out of the junction or the charge is accumulated to form a voltage until a new equilibrium. To summarize, the force converting the chemical potential within a semiconductor into electrical potential is the built-in electric field, and the built-in electric field comes from the joint of two sites with different fermi levels, which is a semiconductor junction. No matter it is a p-n junction or a p-i-n junction, the internal field, charge diffusion/drift ability, charge density, and recombination processes have significant impacts on the performance of a solar cell.

2.1.3 Characteristics of solar cells

The performance of a solar cell is commonly characterized by scanning the voltage and measuring the current under illumination. Although solar cells in real-world applications may work in an ever-changing natural environment, academia and industry need a standard to measure their performance. The typical standard test conditions for power output are radiation of Air Mass 1.5 Global (AM1.5G) and a cell temperature of 25°C. "Air Mass 1.5" means 1.5 atmosphere thickness, corresponding to a solar zenith angle of 48.2° [29]. "Global" implies the inclusion of both direct and diffuse radiation. The AM1.5G spectrum standard can be found in ASTM G-173, and the spectrum has an integrated power of 1000 W/m² (100 mW/cm²) [30]. During indoor laboratory testing, solar simulators are usually used to provide controllable illumination approximating standard AM1.5G. Several types of lamps have been used as the light source within solar simulators, including Xenon arc lamps, light-emitting diodes (LED), and metal halide arc lamps. As shown in **Figure 2.4 a, b**, the spectra of Xenon lamp-based and LED-based simulators are compared with AM1.5G. Here, both simulators meet the class A specification in the spectral match, despite obvious spectral differences between the simulators and AM1.5G [31].

Figure 2.4 | Basic characteristics of a solar cell. Spectral match of (a) the LED (VeraSol) and (b) Xenon (Sol3A) solar simulator to the AM1.5G spectrum. (Reproduced with permission.[31] Copyright 2016, IEEE.) c, The typical current density versus voltage characteristic curve of a solar cell under a solar simulator

Using a sourcemeter (for example, Keithley 2400) to sweep applied voltage and to

measure current, one can get a current density versus voltage (JV) characteristic curve of a solar cell (**Figure 2.4 c**). In a short-circuit condition, where the output voltage bias is zero, the external load has zero or negligible resistance. The current density recorded at the short-circuit condition is called short-circuit current density (J_{SC}). In an open-circuit condition, where no net current flows out of the device, the external load has infinitely or extremely large resistance. The voltage recorded at the open-circuit condition is called open-circuit voltage (V_{OC}). There is no output power at both short-circuit and open-circuit conditions. The output power reaches a maximum power (P_{max}) when the load is optimized, and the maximum power point (MPP) can be extracted from the JV curve when voltage sweep effectively simulates the presence of different loads. The power conversion efficiency (PCE) of a solar cell is defined as the ratio between P_{max} and the power of the incident light (P_{in}),

$$PCE = \frac{P_{max}}{P_{in}} = \frac{J_{MPP} V_{MPP}}{P_{in}} \quad (2.5)$$

where J_{MPP} and V_{MPP} refer to the current density and the voltage at the MPP, respectively.

Another term to describe the overall performance of a solar cell is the fill factor (FF). The fill factor is defined as

$$FF = \frac{J_{MPP} V_{MPP}}{J_{SC} V_{OC}} \quad (2.6)$$

Using FF, PCE is then presented as

$$PCE = \frac{FF J_{SC} V_{OC}}{P_{in}} \quad (2.7)$$

The benefit of using this expression is that FF, J_{SC} and V_{OC} can be related to the physical properties in a solar cell. For example, J_{SC} depends on how many photo-generated charges can be extracted from the device, and it can be related to the external quantum efficiency of the solar cell. V_{OC} depends on the fermi level splitting and the charge amount staying in the device. FF depends on the competition between charge recombination and extraction. The details regarding V_{OC} and FF is discussed in **chapter 3** and **chapter 4**.

Besides PCE which is a measure of the overall conversion efficiency, quantum efficiency is a spectrally resolved measure of a solar cell's efficiency. The external quantum efficiency (EQE) is the ratio of the amount of charge carriers yielded by a solar cell to the amount of incident photons,

$$EQE(\lambda) = \frac{n_{\text{carrier, out}}(\lambda)}{n_{\text{photon, in}}(\lambda)} \quad (2.8)$$

where λ is the wavelength, $n_{\text{carrier, out}}$ is the number of collected charge carriers per unit time, and $n_{\text{photon, in}}$ is the number of incident photons during the same period. To be distinguished from the EQE of LEDs, the EQE of photocurrent conversion is expressed as EQE_{PV} in the following text.

In addition to the characterization performed under illumination, the JV in the dark condition is also an important part of the characteristics of a solar cell. The barrier

Figure 2.5 | Jablonski scheme with light excitation and decay process. S₀ is the ground state. S₁ and S₂ are the first and the second excited state of singlet. T₁ and T₂ are the first and the second excited state of triplet.

and built-in electric field of a junction give a solar cell rectifying characteristics, which means it passes current in one preferred direction. Moreover, the reverse current contains the information about the parallel resistance, the forward current contains the information about diode features and the series resistance.

2.2 Donor-acceptor organic solar cells

As mentioned in section 1.2, organic semiconductors are very different from inorganic semiconductors. In organic solar cells, the most interesting phenomenon is that tightly bound charges in single components are hard to be extracted, while specific organic blends generate long-lived free charge carriers which can be collected by electrodes easily. The former occurs due to the energetic features of organic semiconductors, and the latter involves a kind of interfacial state. The details are introduced in the following subsections.

2.2.1 Energetics of organic semiconductors

From atoms to molecules, orbitals of atoms hybrid and form new orbitals. This is the same for both organic and inorganic semiconductors. In conventional inorganic

semiconductors, covalent or ionic bonds are everywhere within a crystal and the electron cloud can extend three-dimensionally. In organics, however, the same interaction may end within a much shorter length than inorganics, and the overlap of orbitals may be limited in certain dimensions. Essentially, without the widespread intermolecular interactions, organics may lose those soft and lightweight properties as well.

Typical organic semiconductors are conjugated molecules. Due to the discontinuous energy and localized wave function, the terms “conduction band” and “valence band” are not suitable for describing energy levels of organic semiconductors [15, 32]. Instead, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are used to analyze and interpret the optical and electrical properties of organic semiconductors. By changing molecular structure, for example, the length of conjugation, the electron withdrawing or donating ability of functional groups, the HOMO and the LUMO can be easily tuned. From benzene (1 ring) to pentacene (5 rings), the gap between HOMO and LUMO is decreased by about 3.8 eV, which corresponds to their absorption change [33]. HOMO and LUMO are very important. However, they are not sufficient to describe the entire optical transitions in organics.

To illustrate the electronic states of a molecule and the transition between them, a Jablonski diagram can be used. As shown in **Figure 2.5**, the states represented by horizontal lines are arranged vertically by energy and grouped horizontally by spin multiplicity [15]. A radiative transition from an energy level to a higher level is mediated by the absorption of a photon, while a transition to a lower level involves the emission of a photon. Non-radiative transitions can occur through vibrational relaxation of the excited state to its lowest vibrational state. This transition process cannot occur for isolated molecules because it involves the dissipation of energy from the molecule to its surroundings. Another kind of radiationless transition is internal conversion (IC), which occurs through the coupling between vibrational states of two electronic states. A third kind of non-radiative transition is intersystem crossing (ISC), which involves two electronic states with different state spin multiplicity and is highly related to the spin-orbit coupling of the molecule. ISC can be followed by phosphorescence.

Molecular bonds are always vibrating and the motion of nuclei causes vibrational energy levels. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to absorption or emission of a photon [36]. To explain the intensity of vibronic transition within molecules, one can refer to the Franck-Condon principle. This principle states that an optical transition is most probable for a vertical transition when the nuclear coordinates keep the same position, while two vibrationally relaxed states have a small transition probability due to their different nuclei positions. This is the origin of Stokes shift. From the perspective of quantum mechanics, the probability of radiative transition depends on the wavefunction overlap. **Figure 2.6 b** is the Schematic diagram of the absorption and emission spectra corresponding to the energy diagram in **Figure 2.6 a**. An identical shape of the ground and excited-state potential wells lead to the symmetry of absorption and emission spectra.

Organic semiconductors naturally tend to be disordered. Organic polymers have in-

Figure 2.6 | Franck–Condon principle energy diagram. **a**, The overlap of vibrational wave functions determines the transition propability. Here, the most favored transitions are between $v'' = 0$ and $v' = 2$ for the absorption (blue line), and between $v' = 0$ and $v'' = 2$ for the emission (green line). **b**, The absorption and fluorescense spectra corresponds to the energy diagram. Isolated narrow peaks usually only appear for dispersed gas molecules, while liquids and solids show inhomogeneous broadening of the same transitions as indicated by the black curves. Transitions between the lowest vibrational levels of the electronic states (the zeroth to zeroth transition) have the same energy in both absorption and emission. Figures by Mark Somoza under CC-BY-SA 4.0 and GFDL license.[34, 35]

homogeneous chain lengths and conformational defects (twists and kinks), resulting in divers site energies (disorder) [37]. Further disorder can be introduced by the morphology of the whole condensed phase. Crystallinity, aggregation, molecular orientation, and any charged species may affect the energetic landscape of a material. The energetic disorder is thus a collective property of both morphology and chemical structures. A widely assumed distribution of the density of states (DOS) in organic semiconductors is a Gaussian distribution,

$$g(E) = \frac{N_0}{\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right) \quad (2.9)$$

where N_0 is the concentration of sites, σ is the standard deviation of the distribution, E is the energy of sites, and E_0 is the average energy. A schematic of energy sites along with the space is shown in **Figure 2.7**, which is randomly generated based on Gaussian distribution. Here, the σ is the commonly referred energetic disorder in charge transport simulations. The charge transport between energetic sites will be discussed in chapter 4.

Figure 2.7 | Schematic illustration of energy sites with a Gaussian distribution. The energy of 100 sites along the space are generated randomly following a Gaussian distribution with mean energy E_0 and standard distribution σ .

2.2.2 Interfacial charge-transfer states

Generally, charge transfer (CT) can happen from electron-donating sites (donor, D) to electron-accepting sites (acceptor, A), within a molecule or between molecules [38, 39], in the ground state, or in the excited state [40–43]. This subsection focuses, however, on the CT in organic solar cells happening in the excited state at D-A interfaces. A state related to the ground state by a CT transition is called the CT state [44]. Such CT states are intermediates in essential electrical processes, for example, charge separation and recombination [45, 46].

Due to the weak oscillator strength between the CT state and the ground state, the absorption of the CT state is usually very weak. A CT absorption, 100-1000 times weaker than the pristine material, was detected by the high-sensitive photothermal deflection spectroscopy [47]. The existence of CT was also proved in the spectral-resolved-photocurrent spectroscopy, by observing additional free-charge-carrier generation at long wavelengths, which is attributed to direct excitation of CT states [47, 48]. Typically, a clear difference between the blend and the pristine material appears at the small energy part of the log-scale sensitive absorption spectra [49]. In addition, radiative transitions from CT states to the ground state have been observed in blends at energies below both the donor and the acceptor emission in photoluminescence

(PL) [50] and electroluminescence (EL) [51] spectra.

As shown in **Figure 2.8**, when the donor is excited by photons, the electron can transfer from the LUMO of the donor molecule to the low-lying LUMO of the adjacent acceptor molecule. The remaining hole at the HOMO of the donor and the transferred electron at the acceptor form a CT exciton due to the Coulomb interaction. A similar hole transfer process can happen when the acceptor is excited. Several studies reported that the electron transfer process from donor polymers to acceptor molecules occurs on a timescale of 10 to 100 fs, using ultrafast pump-probe spectroscopy [52–54]. Moreover, the charge transfer rate was found to be correlated to the frontier energy level difference [40, 54–57].

The energy of the CT state (E_{CT}) is determined by the frontier orbital energy levels of D and A, and some other material parameters. Despite a formula expression for E_{CT} has been derived for complexes of D-A molecules in solutions using a solvent-continuum model [58], an quantitative description of E_{CT} in a solid state is very hard. Multiple factors, including Coulomb binding energy, polarization, and aggregation-caused delocalization, are expected to influence E_{CT} . The energy difference between the lowest-energy excited singlet state, or called local excited (LE) state, and E_{CT} is usually considered as the driving force of the charge transfer. Empirically, a lower limit, around 0.3 eV, of energy difference between the LE state and the CT state (ΔE_{LE-CT}) is required for the efficient CT in typical polymer:fullerene blends [40]. However, there have been arguments whether a similar driving force is needed in some non-fullerene blends, to accomplish efficient CT and charge dissociation [49, 59–62].

Figure 2.8 | Charge transfer. Schematic illustration of an electron transfer process from the LUMO of the donor (D) to the LUMO of the acceptor (A).

Thermal dynamics and the voltage loss

From the perspective of energy conversion, as shown in **chapter 2**, the operation of a solar cell is the process of converting photonic energy into chemical energy and subsequently into electrical energy. During the processes, the solar cell and its surrounding environment obey the conversion of energy and thermal dynamic principles. This allows us to theoretically calculate the upper limit, as well as the losses of a solar cell's performance. This chapter introduces the detailed balance in solar cells. Later, the voltage loss in solar cells is discussed. Finally, the latest studies on reducing the voltage loss in organic solar cells are reviewed.

3.1 Detailed balance

The operation of a solar cell involves the sun, the cell, the environment and the output load. Energy and matter cannot be created or destroyed. They conserve and form a balance within the system.

3.1.1 Solar spectrum and the black-body radiation

Any object above absolute zero emits electromagnetic radiation, which is called thermal radiation, or the black-body radiation for an idealized opaque, non-reflective black body. It has a specific shape of spectrum depending only on the temperature of the object. The spectrum can be described by Planck's law due to the quantized nature of light. Planck's law states that

$$I(E, T) = \frac{2E^3}{h^3 c^2} \frac{1}{\exp(\frac{E}{k_B T}) - 1} \quad (3.1)$$

Figure 3.1 | The solar and the blackbody radiation. The standard AM1.5G solar spectrum as well as the 300 K blackbody radiation expressed in photon flux as a function of energy. The dark blue curve is the EQE of PM6:Y6 with an optical gap around 1.40 eV.

where $I(E, T)$ is the equilibrium spectral radiance (the power per unit solid angle and per unit of area normal to the propagation) density of energy E per unit energy at temperature T , h is the Planck constant, c is the speed of light in vacuum, k_B is the Boltzmann constant, and T is the absolute temperature of the body. Our surrounding environment emits thermal radiation due to the background temperature. Matters within the environment emit and absorb electromagnetic radiation, and may eventually reach an equilibrium.

The energy potentially harvested by a solar cell comes from the thermal radiation of the sun, which is to very similar to the radiation of a black body radiator at about 5 780 K [63]. As it passes through the atmosphere, solar radiation is attenuated by scattering and absorption. As mentioned in the previous chapter, the standard solar spectrum for solar cell characterization is AM1.5G. As shown in **Figure 3.1**, the solar spectrum is expressed by the photon flux as a function of the energy. Many gaps in the spectrum are caused by specific gases, such as water vapor and oxygen. Note that the solar spectrum has a considerable density of photons in the near-infrared (NIR) region, which might be counterintuitive because the solar irradiance as a function of the wavelength has the maximum power density at around 500 nm (**Figure 2.4**). This is because, firstly the wavelength interval does not correspond to a constant energy interval, and secondly the energy of photons varies at wavelengths. As a result, the EQE_{PV} at the infrared region can affect the short-circuit current of a solar cell greatly.

Figure 3.2 | The analogy for charge generation, recombination and output.

a, In the dark condition, radiative recombination equals radiative generation. A similar equilibrium occurs for non-radiative processes. There is no current nor voltage output. **b**, In the short-circuit condition under illumination, all the photogenerated charges are extracted. **c**, With light illumination, when a voltage bias is maintained in the working condition, a part of the photogenerated charges are output and the other part becomes additional recombination. **d**, All the charges recombine in the open-circuit condition.

3.1.2 Shockley-Queisser limit

In 1961, Shockley and Queisser initially proposed a theory to derive a thermodynamic limit for solar energy conversion efficiency of photovoltaic cells based on the detailed balance principle. The theory is valid for both inorganic and organic single-junction solar cells. Several fundamental assumptions were proposed for an ideal solar cell: (1) Semiconductor absorbs all photons above the optical gap (Note that it is “band gap” in the original paper. Here, it is adapted to “optical gap” for a unified description of organic and inorganic semiconductors.), and no absorption below the optical gap, which is also called a step function like absorption; (2) Each absorbed photon can only generate one electron-hole pair; (3) Perfect charge transport and collection.

As shown in **Figure 3.2**, a complete process starts from radiative or non-radiative generation and ends in radiative or non-radiative recombination (note that the output is recombination outside the solar cell). Thus, an equation is built,

$$F_S + R(0) = I/q + F_C(V) + R(V) \quad (3.2)$$

where F_S is the photon flux of solar radiation, $R(V)$ is the non-radiative recombination current of voltage V , $R(0)$ is the non-radiative recombination current at zero voltage, I is the output current, q is the elementary charge, $F_C(V)$ is the radiative recombination current of voltage V . The left side of the equation is the generation and the right side is the recombination. Here, some transformation has been made. For example, the non-radiative generation has been replaced by $R(0)$ because they cancel out each other at zero bias. For an ideal diode, the equation becomes

$$I = q(F_S - F_C(0)) - q(F_C(0) + R(0))(1 - \exp(qV/kT)) \quad (3.3)$$

where an ideal factor of 1 has been assumed. This equation describes the output current as a function of the applied voltage bias. Given a specific optical gap and the environment temperature, the only uncertain parameter $R(0)$ can be deduced from the luminescence efficiency. If the EQE_{EL} is 100%, there is no non-radiative recombination nor $R(0)$, enabling a quantitative relation between I and V for the theoretical

limit conversion. A series of limits can be obtained when the energy of the optical gap changes. The limits are usually referred to as the Shockley-Queisser (SQ) limit, often expressed in terms of several parameters, including the V_{OC} , the J_{SC} , the FF and the PCE , as a function of the energy (Figure 3.3).

Figure 3.3 | Schematic illustration of the Shockley-Queisser limit. The theoretical limits of any type of single junction solar cells as a function of gap energy are shown in (a) the short-circuit current, (b) the open-circuit voltage, (c) the fill factor, and (d) the power conversion efficiency

3.1.3 Reciprocity between absorption and emission

We have shown the equilibrium of charge generation and recombination. Below, we discuss the equilibrium between light absorption and emission.

Kirchhoff's law states that: For a body of any arbitrary material emitting and absorbing thermal electromagnetic radiation at every wavelength in thermodynamic equilibrium, the ratio of its emissive power to its dimensionless coefficient of absorption is equal to a universal function only of radiative wavelength and temperature [64]. In simpler language: For an arbitrary body emitting and absorbing thermal radiation in thermodynamic equilibrium, the emissivity is equal to the absorptivity[64].

A solar cell also absorbs and emits radiation all the time. An analogous reciprocity relation between the photovoltaic and the electroluminescence properties of solar

cells have been proposed and verified [65–68].

$$\begin{aligned}
 EQE_{EL}(E) &= \frac{\phi_{emission}(E, V)}{J(V)} \\
 &= \frac{\phi_{emission}(E, 0)(\exp(\frac{eV}{k_B T}) - 1)}{J_0(\exp(\frac{eV}{k_B T}) - 1)} \\
 &= \frac{eEQE_{PV}(E)\phi_{BB}(E)}{J_0} \tag{3.4}
 \end{aligned}$$

where $EQE_{EL}(E)$ is the electroluminescence quantum efficiency of energy E per unit energy, $\phi_{emission}(E, V)$ is the solar cell emission photon flux of energy E at bias V per unit energy, $J(V)$ is the current flow at bias V , J_0 is the total recombination current in the dark equilibrium condition, e is the elementary charge, k_B is the Boltzmann constant, $EQE_{PV}(E)$ photocurrent quantum efficiency of energy E , and $\phi_{BB}(E)$ is the thermal radiation of the solar cell of energy E .

The significance of this reciprocity includes, that 1) electroluminescence emission and photovoltaic quantum efficiency are quantitatively linked following the detailed balance (**Equation 3.4**); 2) light-emitting diode quantum efficiency can be used for V_{OC} analysis (**Equation 3.5**); 3) the emission and the absorption spectra can validate the overlapped range and complement the missing parts of each other (**Figure 3.4**); and 4) it emphasizes that a good solar cell is also a good light-emitting diode.

Equation 3.4 provides a relationship between J_0 and the quantum efficiency. Thus, the V_{OC} can be expressed as

$$\begin{aligned}
 V_{OC} &= \frac{K_B T}{e} \ln\left(\frac{J(V_{OC})}{J_0} + 1\right) \\
 &= \frac{K_B T}{e} \ln\left(\frac{J(V_{OC})}{\frac{\int EQE_{PV}(E)\phi_{BB}(E)dE}{\int EQE_{EL}(E)dE}} + 1\right) \\
 &= \frac{K_B T}{e} \ln\left(\frac{\int EQE_{PV}(E)\phi_{sun}(E)dE}{\frac{1}{EQE_{EL}} \int EQE_{PV}(E)\phi_{BB}(E)dE} + 1\right) \\
 &\approx \frac{K_B T}{e} \ln(EQE_{EL} \frac{\int EQE_{PV}(E)\phi_{sun}(E)dE}{\int EQE_{PV}(E)\phi_{BB}(E)dE}) \\
 &= \frac{K_B T}{e} \ln\left(\frac{\int EQE_{PV}(E)\phi_{sun}(E)dE}{\int EQE_{PV}(E)\phi_{BB}(E)dE}\right) + \frac{K_B T}{e} \ln(EQE_{EL}) \\
 &= V_{OC,rad} + \frac{K_B T}{e} \ln(EQE_{EL}) \tag{3.5}
 \end{aligned}$$

where $\phi_{sun}(E)$ is the solar emission photon flux of energy E , EQE_{EL} is the overall electroluminescence quantum efficiency of all wavelength. $V_{OC} = V_{OC,rad}$ when there is only radiative recombination and $EQE_{EL} = 1$. This equation helps with the analysis of voltage losses, especially non-radiative loss, which will be discussed in the following section.

Figure 3.4 | Spectral reciprocity. Normalized EQE_{PV} and EL spectra of the device based on PM6:Y6 are plotted in black. The dashed curves in grey are calculated according to the reciprocity principle, which overlap the measured ones. The ratio of ϕ_{EL} and ϕ_{BB} was used to calculate the EQE while the product of FTPS-EQE and ϕ_{BB} was used to calculate the EL, where ϕ_{EL} and ϕ_{BB} represent the EL photon flux and the black-body-radiation photon flux at room temperature, respectively.

3.2 Voltage losses in single-junction solar cells

Voltage loss is the loss that occurs when a solar cell maintains electrons in high energy states (or charge carrier density) at the open-circuit condition. To better understand this, one can refer to the description in **subsection 2.1.2**, which indicates the nature of voltage in a solar cell is the difference of the quasi-fermi level at two ends.

In a narrow sense, “voltage loss” refers to the voltage difference between the optical gap over elementary charge (E_g/e) of a solar cell and its open-circuit voltage (V_{OC}). Broadly speaking, it can be the difference of an ideal V_{OC} and a more realistic V_{OC} (for example, non-radiative voltage loss). The most ideal V_{OC} is determined by the intrinsic gap of a material and the unavoidable thermal dynamic processes, which is well described in the previous chapter. Once the optical gap is determined, the upper limit of V_{OC} is also determined with idealized assumptions. Moreover, imperfect features of realistic devices cause additional losses and lower V_{OC} . In general, this section describes the analysis of voltage losses in any type of single-junction solar cells.

3.2.1 Defining an optical gap

The optical gap is the threshold for photons to be absorbed. In the SQ limit, the optical gap is described as the turning point where EQE changes from 1 to 0. However, “turning point” is “turning points” in reality. There are multiple interpretations and analysis methods of this vague “threshold” point. Some may be the point where absorption just begins, while some others may be the point with significant photocurrent remaining, which makes it difficult to compare the voltage losses of solar cells. There-

fore, to better understand the physical meaning of the optical gap, and to choose an appropriate method for voltage loss analysis, several commonly used methods and their characteristics are discussed below.

One of the most widely used “optical gap” for semiconductors comes from the intersection of the extrapolation of the absorbance edge and the horizontal axis or the extrapolation of the absorbance tail (**Figure 3.5 a**) [69–71]. This method is easy to use because it only requires an absorbance measurement and the analysis is straightforward. However, a manual extrapolation is arbitrary and may introduce some errors. In addition, the absorbance edge can significantly change once made into a device. On the one hand, conditions (e.g. additional components or annealing) during processing can change the condensed state of the film [69, 72], and on the other hand, the structure (e.g. optical cavity) of the device also changes its light absorption [73, 74]. Moreover, determining the optical gap this way lacks physical meaning and overlooks the steepness of the absorption edge when calculating voltage losses, especially not fair for devices that exhibit a sharp edge. Therefore, this method is well suited as a preliminary comparison method, for example, during the synthesis stage of materials, but not appropriate for voltage loss analysis.

An alternative method with more definitive estimation of the optical gap adopts the intersection of the normalized absorption and emission spectra (**Figure 3.5 b**) [49, 75]. The feasibility of this method is based on that the zero to zero transitions have the same energy in both absorption and fluorescence, as shown in **Figure 2.6**. However, despite its straightforwardness, there might be a few difficulties. For example, it might be tricky to normalize a spectrum with multiple peaks when the absorption and emission spectra are asymmetrical (In **Figure 3.5 b**, imagine that the absorption peak at 1.7 eV becomes much higher, almost containing the peak at 1.55 eV, and the emission remains the same.). Moreover, if the absorption and emission spectra are not obtained from the device but a film, the same problems mentioned in the previous method occur. Nevertheless, determining the optical gap at the intersection of absorption and emission is physically motivated and usually well reproducible [76]. A similar method is used to define the CT state energy by the absorption and emission spectrum of CT states in organic solar cells.

Recent reports also proposed to determine the optical gap from the EQE spectrum. One method is to use the crossing point of the extrapolated line of the EQE edge and the horizontal tangent of the EQE peak (**Figure 3.5 c**) [77, 78]. In sharp contrast to the first, this method takes a point with a significant photocurrent remaining as the optical gap, maximizing the assessment of the steepness of the absorption edge during the voltage loss calculation. The other method treats a solar cell as a superposition of multiple ideal solar cells, by dividing the actual EQE into an infinite number of step-function-like EQE of various optical gaps [25, 76, 79]. The gaps form a distribution $P(E)$ along energy which can be obtained by taking the derivative of the EQE with respect to energy (**Figure 3.5 d**). A widely used way to assign an optical-gap value is

$$E_g = \frac{\int_a^b P(E)E dE}{\int_a^b P(E) dE} \quad (3.6)$$

Here, the boundary a and b are selected where $P(a) = P(b) = 0.5 \max[P(E)]$, aiming to exclude the influence of noisy data and negative value of $P(E)$. Overall, determin-

Figure 3.5 | Methods for determining the optical gap. The optical gap can be extracted from (a) the onset of the absorption spectrum, (b) the intersection between the normalized absorption and emission spectra, (c) the intersection of the extrapolated EQE edge and the EQE isoline which passes through the local EQE peak at the edge of the EQE spectrum, and (d) the distribution of optical gaps

ing an optical gap from the EQE spectrum is a quantitative and reproducible method, with physical meaning. It is not only related to the internal characteristics of the absorbing material but also depends on the device structure (the thickness of the active layer, the optical characteristics of the interlayers, and the electrodes). This method requires device fabrication, EQE measurement and calculation, which seems a large workload. However, considering that many reports on organic solar cells have provided the EQE data, this is a very good method for summarization and comparison. Depending on the characteristics of these methods, researchers can choose the one that is suitable for a particular occasion. However, it is essential to use a consistent method to obtain the optical gap values during a comparison. Additional attention to the physical meaning of the optical gap is also necessary when calculating the voltage loss.

3.2.2 Quantifying voltage losses

Given the optical gap value E_g , the total voltage loss can be obtained by subtracting the V_{OC} from the E_g/e . But why do we compare the V_{OC} with the gap? That is because optical gaps have fundamental but homogeneous influences on V_{OC} . After excluding the homogeneous influences, we can analyze the different physical processes remaining and attribute the loss channels to the undesirable properties of materials or

devices. As shown in **Figure 3.6**, the total loss can be divided into three parts,

$$\begin{aligned}
 \Delta V_{loss} &= E_g/e - V_{OC} \\
 &= (E_g/e - V_{OC}^{SQ}) + (V_{OC}^{SQ} - V_{OC}^{rad}) + (V_{OC}^{rad} - V_{OC}) \\
 &= (E_g/e - V_{OC}^{SQ}) + \Delta V_{OC}^{rad, below\ gap} + \Delta V_{OC}^{non-rad} \\
 &= \Delta V_1 + \Delta V_2 + \Delta V_3
 \end{aligned} \tag{3.7}$$

where e is the elementary charge, ΔV_{loss} is the total voltage loss, E_g is the optical gap, V_{OC}^{SQ} is the maximum voltage according to the Shockley-Queisser limit, V_{OC}^{rad} is the open-circuit voltage where only radiative recombination occurs, $\Delta V_{OC}^{rad, below\ gap}$ is the voltage loss due to the sub-gap absorption induced radiative recombination, and $\Delta V_{OC}^{non-rad}$ is the voltage loss of the non-radiative recombination.

$\Delta V_1 (E_g/e - V_{OC}^{SQ})$ is due to radiative recombination originating from the absorption above the gap, which is unavoidable for any single-junction solar cell. As shown in **Figure 3.3**, ΔV_1 is a function of E_g . When the E_g changes from 1 eV to 2 eV, the ΔV_1 changes from 0.24 V to 0.30 V.

$\Delta V_2 (\Delta V_{OC}^{rad, below\ gap} = V_{OC}^{SQ} - V_{OC}^{rad})$ is due to the additional radiative recombination from the absorption below the optical gap. According to the reciprocity relation, the radiative recombination is directly proportional to the photon absorption of the room-temperature blackbody radiation. As shown in **Figure 3.1**, the room-temperature blackbody radiation at the low-energy region is much stronger than that in the high-energy region. The analytical expression for V_{OC}^{rad} is shown in Equation 3.5. As a result, any sub-gap absorption can cause a large radiative loss even though it may hardly contribute to the photocurrent. For inorganic or perovskite solar cells with steep absorption edges, $\Delta V_{OC}^{rad, below\ gap}$ is negligible. Therefore, a steep absorption edge is preferred to avoid this part of loss.

$\Delta V_3 (\Delta V_{OC}^{non-rad} = -\frac{kT}{e}(EQE_{EL}))$ arises from the non-radiative recombination. As also shown in Equation 3.5, EQE_{EL} is the electroluminescence quantum efficiency of the solar cell when charge carriers are injected into the device in the dark. The enhanced EQE_{EL} makes it possible to achieve low non-radiative energy losses. In other words, a good solar cell with low non-radiative recombination loss should also be a good light-emitting diode.

3.3 Reducing voltage losses in organics solar cells

Despite the increase in PCE, the V_{OC} loss, especially the non-radiative loss, is still a substantial challenge for organic solar cells when compared to inorganic or hybrid solar cells. Recently, researchers devoted many efforts to understanding and decreasing the V_{OC} loss of organic solar cells, and achieved remarkable results. Some of the understandings are presented in the following subsections.

Figure 3.6 | Schematic illustration of voltage losses. An ideal solar cell has step-function-like EQE_{PV} and EQE_{EL} of 100%. A realistic solar cell has EQE_{PV} with absorbing features extending to below the gap, which is attributed to the distribution of DOS or specific sub-gap states. These weakly absorbing features lead to additional radiative recombination and voltage losses. A realistic solar cell also has EQE_{EL} below 100%, which results in non-radiative voltage losses.

3.3.1 Energy gap law

In the condensed phase, polyatomic molecules with narrow gaps tend to exhibit low emission efficiency. This quenching phenomenon and its non-radiative deactivation pathway have been recognized as the ‘energy gap law’ [80–82]. This law indicates that the relaxation of an excited state to a ground state can be promoted by the wave-function overlap between the zero vibration level of the excited state and the higher iso-energetic vibration levels of the ground state, subsequently rapid thermalization to the zeroth vibration level of the ground state. This vibrational relaxation accelerates if the emissive states possess low energy and hence large wave-function overlap, drastically reducing the emission intensity, as evidenced by the lack of organic light-emitting diodes in the deep red and NIR region [82, 83].

A recent study shows that the ‘energy-gap law’ also works for organic solar cells with a trend that the non-radiative voltage loss increased with decreasing CT energy of fullerene-based solar cells (Figure 3.7) [84]. In the study, non-radiative recombination was attributed to intramolecular vibrations of the organic molecules. This model implied that high vibrational carbon-carbon frequency modes have a significant impact on non-radiative recombination. Based on the model, a visible-light-emitting D-A system with simultaneous occurrence of a high photovoltaic and emission quantum yield was reported [85]. The strongly enhanced emission indicates an effective way to reduce ΔV_3 by increasing E_{CT} and reducing electron-phonon coupling. However, this model cannot explain the performance of some non-fullerene solar cells

Figure 3.7 | Schematic illustration of the energy gap law. Non-radiative (k_{nr}) and radiative (k_r) transitions from the CT state to the ground state are demonstrated for (a) a large E_{CT} and for (b) a small E_{CT} . The non-radiative transition is facilitated by the wave-function overlap between the relaxed CT state ($i = 0$) and the vibrationally excited ground state ($j = n$), followed by vibrational relaxation to the zeroth level ($j = 0$). The wave-function overlap of the states is indicated by the green area. Radiative transitions from the CT state to lower vibrational modes of the ground state are denoted by red arrows. c, ΔV_{nr} as a function of the E_{CT} presents an empirical trend that a small E_{CT} tends to yield a large non-radiative loss. (Reproduced with permission.[84] Copyright 2017, Springer Nature.)

with both narrow gaps and decent emissive efficiency, which indicates that the non-radiative loss is more complicated than what the energy-gap law can predict.

3.3.2 Energetic offsets

Early studies widely observed a correlation between V_{OC} and the energetic difference between the HOMO of the donor and the LUMO of the acceptor [86, 87]. Later investigations on fullerene-based solar cells revealed the CT state as the origin of V_{OC} [46]. The reason for a good correlation between the V_{OC} and the E_{CT} , as discussed in the previous section, is that sub-gap absorption features dominate the radiative recombination (ΔV_2). As a result, increasing the LUMO of acceptor or decreasing the HOMO of donors have been the most followed pathways to increase the V_{OC} [88–90]. But it is not until recently, when non-fullerene solar cells with small driving energies emerged, that the importance of the relationship between non-radiative loss and the energetic offsets was revealed.

Recent studies show that the energetic offsets between the CT states (E_{CT}) and the local excited states (E_{LE}) of narrow gap materials have evident impacts on non-radiative voltage losses of organic solar cells (Figure 3.8) [49, 61, 91, 92]. D-A systems with small offsets tend to give strong emission and small voltage losses [69, 75, 93, 94]. For those D-A blends with small offsets, a distinct phenomenon is that the high-sensitive EQE and EL spectrum almost overlap between the blend and the narrow-gap pristine-material devices. The absence of red-shifted CT absorption and emission bands are attributed to the strong interplayed LE-CT state [49, 92]. These interplayed LE-CT states, in form of thermal population and hybridization, are capable to significantly

Figure 3.8 | Non-radiative voltage losses as a function of ΔE_{LE-CT} . **a**, Radiative recombination rate (k_r) and non-radiative recombination rate (k_{nr}) at various electronic coupling between LE and CT states (t_{LE-CT}). **b**, Calculated non-radiative loss as a function of energetic offsets and electronic coupling. **c**, Measured non-radiative loss as a function of energetic offsets. (Reproduced with permission.[91] Copyright 2021, Springer Nature.)

enhance the emission efficiency through the way of oscillator strength borrowing from LE to CT states [91]. In addition, a few state-of-the-art organic solar cells with NIR absorption edge but without distinct CT optical transition have achieved reduced non-radiative losses and record efficiency, which marks the practical feasibility of this method [20, 95]. However, the energetic offsets cannot be reduced indefinitely. On the one hand, small energetic offsets hinder the charge separation and cause a low photo current [61]. On the other hand, the suppression of non-radiative loss seems to slow down with the proceeding of reducing energetic offsets [91].

3.3.3 Other methods to reduce non-radiative losses

A typical electroluminescence quantum efficiency can be expressed as

$$EQE_{EL} = f_{e-h} \beta \eta f_{outcoupling} \quad (3.8)$$

where f_{e-h} is the probability of balanced charge injection (when the numbers of electrons and holes injected are equal), β is the probability of forming a correlated electron-hole pair or exciton from each pair of injected carriers, η is the emission quantum yield of the correlated electron-hole pair or exciton, and $f_{outcoupling}$ is the optical outcoupling coefficient. From this equation, some pathways for reducing non-radiative losses become apparent. Optimizing the injection barriers at both sides and the mobility balance, will ensure the recombination center within the active layer, make f_{e-h} approach 1, and thus increase EQE_{EL} . A device with good light outcoupling can also increase the emission efficiency. For a light-emitting diode with only one emissive species, β usually denotes the ratio of singlets (typically 1/4), and η implies the photoluminescence quantum yield. Both β and η are expected to be increase for a high EQE_{EL} . However, for blends where multiple kinds of excitons with different η may compete with each other, Equation 3.8 shall be transformed to

$$EQE_{EL} = f_{e-h} f_{outcoupling} \sum \beta_i \eta_i \quad (3.9)$$

where β_i and η_i correspond to the same type of exciton i . In a certain case, when η_i and $\sum \beta_i$ are constant, increasing the portion of β with higher η can also increase the final EQE_{EL} . In a blend film with negligible driving energy, the overlap of EL spectra between the blend and the pristine material implies that the radiative recombination in the blend is possibly determined by the emission properties of the pristine material with the lowest bandgap [49, 96]. As also discussed in the previous subsection, the thermal population and electronic coupling have been reported as pathways to this phenomenon [91]. In other words, it also indicates the importance of enhancing the emission efficiency of the narrow-bandgap material to decrease the non-radiative recombination loss of the blend film. In a very popular system, PM6:Y6, it is also reported that the radiative recombination of free charges is almost entirely due to the re-occupation and decay of Y6 singlet excitons, but this pathway contributes less than 1% to the total recombination [97]. The paper claims that the properties of the Y6 singlet excitons are almost irrelevant for the V_{OC} of the PM6:Y6 devices. Indeed, the total recombination is almost irrelevant with singlet excitons but is instead dominated by the CT state decay properties, which may give the impression that the decay rate change of singlets does not affect the total rate. However, if the singlet emission efficiency increases in EL, the total recombination rate including both radiative and non-radiative processes has to be reduced to ensure that the radiative recombination rate is constant according to the reciprocity principle, which leads to the a reduce V_{OC} loss. Nevertheless, it is difficult to draw general conclusions, especially considering lacking adequate device examples.

Charge dynamics and the fill factor

This chapter reviews the basic processes of charge carrier generation in bulk heterojunction organic solar cells and discusses the loss channels behind the equilibrium. Parameters have been extracted from photophysical processes to describe the inherent properties of materials or devices. Finally, the fill factor in organic solar cells are discussed and linked to those parameters.

Figure 4.1 | Photons in and charges out. Schematic illustration of the photophysical processes in a bulk-heterojunction organic solar cell.

Generating photocurrent in a bulk-heterojunction organic solar cell requires several steps. Initially, photons are absorbed by the donor or the acceptor molecule, followed by exciton generation. The excitons undergo random walking, and they may diffuse toward the D-A interface, where a type of interfacial excited state is formed through ultrafast charge transfer. The interfacial state, which is called the CT state, is typically regarded as the precursor to free electrons and holes. The free charge carriers can drift and diffuse in the bulk materials, finally extracted at the electrodes. Excitons may recombine directly before they diffuse to the D-A interface, and CT states may also relax

before forming charge-separated states. These steps are summarized in **Figure 4.1**. Note that, some photophysical processes in bulk-heterojunction organic solar cells are still controversial and need further understanding. The reason might be complex and diverse experimental phenomenon depending on the detailed material system and its specific micro-structures, while direct and effective observation is limited by disordered or unstable properties of organics.

4.1 Charge-carrier photogeneration

4.1.1 Photon absorption and exciton generation

In a D-A bulk heterojunction layer, both photoactive constituents can contribute to light absorption. However, despite tunable gaps, organic semiconductors tend to have a narrow absorption range compared to inorganic semiconductors. Fortunately, state-of-the-art organic photovoltaic materials with intramolecular electron push-pulling effects alleviate the problem by broadening the absorption range (over 300 nm) yet maintaining strong extinction coefficients (over $10^5 \text{ M}^{-1} \text{ cm}^{-1}$) [96, 98]. A D-A blend with complementary absorption can absorb most (over 80%) of the light above the gap with only 130 nm-thick film [20, 95].

Frenkel excitons form in the donor and acceptor molecules after light absorption. The excitons of organic material can relax to the ground state within hundreds of picoseconds without external influences [15, 61].

4.1.2 Exciton diffusion

Excitons diffuse within the condensed phase from one site to another via energy transfer before they decay to the ground state. The energy transfer can occur through Föster (through-space) or Dexter (through-bond). The exciton diffusion length in amorphous π -conjugated polymers covers a range of 5-15 nm [99–103]. while the latest study shows long exciton diffusion lengths in the range of 20 to 47 nm within non-fullerene acceptor films [71].

At D-A interfaces, the exciton from a donor unit dissociate via electron transfer from the donor to an acceptor unit and subsequently form CT excitons. A similar process can happen for an acceptor exciton via hole transfer. To ensure efficient charge transfer in a D-A blend, the donor or acceptor phase has to be small enough for excitons to reach the D-A interfaces before they decay, that is why the phase separation is so important for high device performance.

4.1.3 Charge transfer

In a molecular orbital picture, the driving force for charge transfer comes from the energy difference, also referred to as the energy offset, of either the LUMO of D and A in the case of electron transfer, and the HOMO in the case of the hole transfer. In condensed phases, the same must be true for the difference in electron affinity (EA) for electron transfer, and for the difference in ionization potential (IP) for hole transfer.

Note that the EA and IP are often approximated by the LUMO and HOMO in molecular solids, ignoring the effects of intermolecular interactions. In an energy level picture, the driving force is the energy offset between the LE and the CT state. The driving force determines the favourable charge transfer direction from high energy to low energy, and also affects the transfer rate. Classical Marcus theory describe the electron transfer rate between individual molecules in solution as [104]

$$W = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda kT}} \exp \left[-\frac{(\lambda + \Delta G_0)^2}{4\lambda kT} \right] \quad (4.1)$$

where J is the electronic coupling, λ is the reorganization energy, ΔG_0 denotes the difference in Gibbs free energy of two states, $\hbar$ is the reduced Planck constant, k is the Boltzmann constant, and T is the temperature. If the tunneling between the initial and the final state needs to be taken into account, a more complete quantum mechanical treatment is required that incorporates both the effect of high and low-frequency molecular modes, which is Marcus-Levich-Jortner expression [105].

$$W = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda_0 kT}} \sum_{n=0}^{\infty} e^{-S} \frac{S^n}{n!} \exp \left[-\frac{(\lambda_0 + \Delta G_0 + n\hbar\omega)^2}{4\lambda_0 kT} \right] \quad (4.2)$$

where n is the quantum number of final vibrational state, S is the Huang-Rhys factor, $\hbar\omega$ is the average vibrational energy spacing.

In fullerene solar cells, a number of studies using ultrafast pump-probe spectroscopy state that electron transfer occurs on a timescale of 10-100 fs, much faster than other photophysical processes, including singlet relaxation to the ground state (100 ps - 1 ns) [52, 53, 106, 107]. These studies denote a CT yield near 100% independent of the energy difference between E_{LE} and E_{CT} . Some contradictory results are shown in time-resolved microwave conductivity and photoluminescence lifetime investigations on polymer-fullerene blends, where high CT rates only occur for an energetic offset of around 0.4 eV [40, 56].

Several reports on polymer:non-fullerene systems report a reduced CT rate on the picosecond time scale, attributed to the low driving force [108, 109]. A recent study demonstrates that hole transfer remains at hundreds femtoseconds with a negligible driving force [54]. The transfer rates are shown to be consistent with the prediction of Marcus theory. In addition, the study shows the electron transfer is generally faster (<0.1 ps) which cannot be described within the non-adiabatic Marcus limit. Another study challenges previous understandings, showing that the ultrafast donor-to-acceptor energy transfer precedes hole transfer from the acceptor to the donor and thus renders the EA offset virtually unimportant [62]. It also indicates the energy-level bending at the D-A interface is caused by the acceptors' quadrupole moments. This energy-level bending prevents efficient transfer from excitons to CT states at low IE offsets, while the same bending can facilitate the dissociation of CT excitons.

4.1.4 Charge-pair dissociation

After charge transfer, two scenarios are possible: either the electron and the hole are still weakly bound due to Coulombic interaction - or they are not and thus are free

Figure 4.2 | Illustration of the Marcus theory for electron transfer. The potential diagram of a transition is shown from an initial state to a final state, mediated by a surrounding solvent. The donor molecule, the acceptor molecule, and the solvent are regarded as a system. The system is described by a generalized configuration coordinate Q and the related potential energy curve that is approximately a parabola. ΔG_0 is the Gibbs free energy difference between the initial and final states, and λ is the reorganization energy describing the energy required to match the geometries of the final and initial states. Credit: Dr. Jiangbin Zhang.

carriers. If CT excitons are generated upon singlet exciton dissociation, an additional driving force is needed to overcome the Coulomb binding energy.

The Braun-Onsager model is widely used to describe the field-dependent dissociation of charge pairs,

$$P(F) = \frac{k_{diss}(F)}{k_{diss}(F) + k_f} \quad (4.3)$$

where $P(F)$ is the dissociation yield of electrical field F , $k_{diss}(F)$ is the rate of dissociation with F , and k_f is the recombination rate to the ground state. The field-dependent dissociation rate k_{diss} is expressed as

$$k_{diss}(F) = \frac{e\mu}{\epsilon_r \epsilon_0} \frac{3}{4\pi a^3} \exp\left(-\frac{E_b}{k_B T}\right) \left(1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \dots\right) \quad (4.4)$$

where μ is the sum of electron and hole mobility, a is the initial distance of its constituents, $E_b = e^2/4\pi\epsilon_r\epsilon_0 a$ is the binding energy, k_B is the Boltzmann constant, T is the temperature, and $\epsilon_r\epsilon_0$ is the dielectric constant. The last factor in brackets is the Taylor expansion of a first-order Bessel function, with the reduced electric field $b = e^3 F/8\pi\epsilon_r\epsilon_0 (k_B T)^2$.

Despite the binding energy of tens to hundreds of meV [43, 110–112], the CT state dissociation yield has been shown to approach 100% even when directly exciting the

vibrationally relaxed CT state [113]. There have been many explanations for efficient charge generation. High local mobility in crystalline PCBM clusters was proposed to facilitate dissociation by performing a Braun-Onsager fit in polymer fullerene films [114]. Another study indicates that the Coulomb binding energy of the CT can be reduced by electrostatic screening and delocalization of charges, enabling separation from thermally relaxed CT states [115]. Moreover, the importance of delocalization and the crystallinity of the acceptor phase for efficient separation has been suggested by others as well [116–119]. It has also been suggested that CT separation is entropy-driven [120, 121]. The density of states is drastically increased for free charges as compared to bound charges at the interface, leading to an increase in entropy and making charge separation energetically favourable. Recent studies show barrierless CT state to free charge conversion in high-performance non-fullerene acceptor solar cells, and the origin has been revealed to be the energy level bending at D-A interface caused by quadrupole moments of the acceptors [62, 72].

4.1.5 Charge-carrier transport

To be collected by electrodes, free electrons and holes have to transport within condensed phases. As mentioned in subsection 2.1.2, charge motion can be driven by an electric field (drift) or a charge-concentration gradient (diffusion). A key parameter that describes the motion ability is mobility μ , which is defined as the drift velocity v per unit electric field F

$$\mu = \frac{v}{F} \quad (4.5)$$

Note that, μ is not necessarily a constant and it may change along with the electric field. [122–124].

In an organic semiconductor, charge transport is accomplished by the transfer of an electron from the LUMO of a site to the empty LUMO of another site. Equivalently, a hole can be transferred between HOMO levels of sites. Here, the site may be a molecule or a conjugated segment of a polymer. In an ordered crystal, carriers can move within a band of states formed by the frontier orbitals. The acceleration under an electric field ends at a finite velocity due to the increasing scattering along with the increasing velocity. This is the reason for a finite mobility. As long as this scattering process is only a weak perturbation of the overall electronic coupling between the neighboring molecules, charge transport can be described by the band-transport model [125]. In this model, a mobility decreases with increasing temperature due to increasing scattering. At higher temperatures, intra-molecular vibrations also become important. This can be described by the local phonon coupling, where the “phonon” is molecular vibrations and the “coupling” is of the vibronic type [126]. If the strength of vibronic coupling is at the same level as that of electronic coupling between sites, a band-transport model is no longer suitable for describing the charge transport process. In the extreme case, the transport becomes a hopping-like motion when the charge motion comes across scattering at every site [127, 128]. Furthermore, when the material is microscopically disordered, transport is controlled by (i) the electronic coupling among the constituent molecular units, (ii) the coupling to intra-molecular as well as inter-molecular vibrations, and (iii) the static intra- and

inter-molecular disorder [15].

Figure 4.3 | The band-like transport and the hopping charge transport. For the band-like transport, electronic coupling between molecules is dominating, and the mobility decreases with increasing temperature. For the hopping transport, thermally-assisted tunneling is dominating, and the mobility increases with increasing temperature. Credit: Dr. Nakul Jain.

The charge transport mode in organic solar cells is disorder controlled due to the amorphous nature of the organic blend films, despite some crystalline or semi-crystalline domains. A commonly used model to explain charge carrier transport in disordered organic solids on a microscopic level is the Bässler model, also called the Gaussian disorder model (GDM) [129]. In this model, the DOS can be described by a Gaussian distribution as discussed in Equation 2.9. This approach assumes that the energies of adjacent sites are uncorrelated, which is not necessarily true. The jump rate ν from site i with energy E_i to j with E_j is assumed to be of Miller-Abrahams type [130],

$$\nu_{ij} = \nu_0 \exp(-2\gamma r_{ij}) \begin{cases} \exp\left(-\frac{E_j - E_i}{k_B T}\right), & E_j > E_i \\ 1, & E_j \leq E_i \end{cases} \quad (4.6)$$

where the first exponential term of this equation describes the wave-function overlap and a tunneling probability, r_{ij} is the jump distance between site i and site j , γ is the inverse localization radius which is a wave-function decay parameter, ν_0 is the attempt-to-hop frequency.

The Miller-Abrahams equation neglects the polaronic effect as described by Marcus theory, such as changes in molecular conformation upon charge transfer. The hopping rates given by both theories are typically applied in Monte Carlo simulations [129, 131, 132] or hopping master equations [133, 134] to study the macroscopic charge carrier transport properties in organic disordered semiconductors.

4.2 Geminate and non-geminate recombination

4.2.1 Recombination of geminate pairs

The recombination of a positive charge and a negative charge may occur geminately or non-geminately. In organic solar cells, geminate recombination (GR) is closely related to the free charge generation, while non-geminate recombination (NGR) mainly competes with charge extraction.

Figure 4.4 | Geminate and non-geminate recombination in an energy diagram. Singlets and CT excitons recombine geminately by relaxation directly to the ground state. Free charge (FC) carriers recombine non-geminately through back-transfer, bimolecular and trap-assisted processes. Credit: Dr. Nakul Jain.

Originally, the term “geminate recombination” refers to the reaction of two transient species produced from a common precursor in solution [135]. The pair of species from a common precursor is called a geminate pair. If a recombination reaction occurs before any separation of the geminate pair due to diffusion, this reaction is termed primary GR. If the interacting particles have been separated and come together through diffusion, this reaction is termed secondary GR. In organic heterojunctions, electron-hole pairs which are still correlated due to their mutual Coulomb attraction, are also called geminate pairs. The recombination of such an electron-hole pair is called GR as well. Therefore, a geminate pair in organic solar cells comes from the same parent exciton. If positive and negative charges are injected at the anode and the cathode, subsequently move through the organic semiconductor film, encounter each other, and finally relax to the ground state or form a geminate pair, then this is a NGR process. Similarly, photogenerated free charge carriers undergo NGR as well.

GR and NGR are not two competing processes. Instead, they are describing the spontaneous recombination processes of geminate pairs and free charge carriers, respectively. A geminate pair undergoes GR spontaneously, or dissociates via a driving force. A charge carrier undergoes NGR spontaneously, or gets extracted (recombining elsewhere). Moreover, geminate pairs can also come from NGR in addition to the same

excitation. This is because GR includes secondary GR in its definition. In addition, there is no proof that a geminate pair can discriminate its origin and recombine differently. Accordingly, NGR should not be considered as complete recombination process, to avoid the description of the later process and the argument whether it is a relaxation to the ground state or the source of geminate pairs.

4.2.2 Recombination of free carriers

Photogenerated or injected free charge carriers can meet each other and recombine non-geminately during the charge transport. Langevin theory is often used to describe the charge recombination in materials with low charge mobility ($\mu < 1 \text{ cm}^2/(\text{V} \cdot \text{s})$) [136]. This theory was developed by Langevin in 1903 to describe recombination of ions in gases [15, 137].

$$R = -\frac{dn}{dt} = -\frac{dp}{dt} = -\gamma np \quad (4.7)$$

where R is the recombination rate per unit volume, n and p are the concentration of electrons and holes, and t is time. The recombination coefficient, γ , is the product of the charge-moving velocity and reaction cross-section. If $n = p$, $R \propto n^2$. Since this recombination involves two molecules and the recombination order is two, the recombination process is called bimolecular recombination (BMR). This model assumes a recombination critical point where the Coulomb potential equals the thermal energy $k_B T$, which can be expressed as

$$r_c = \frac{e^2}{4\pi\epsilon_r\epsilon_0 k_B T} \quad (4.8)$$

where r_c is known as the Coulomb capture radius, as the Langevin capture radius or as the Onsager radius. With a collision sphere of this radius, the recombination coefficient can be described by

$$\gamma = 4\pi r_c (D_n + D_p) \quad (4.9)$$

where diffusion coefficients of positive and negative charges are expressed as D_n and D_p , respectively. Using Einstein relation $D = \mu k_B T / e$ and Equation 4.8, Equation 4.9 becomes

$$\gamma = \frac{e}{\epsilon_r \epsilon_0} (\mu_n + \mu_p) \quad (4.10)$$

where e is the elementary charge, ϵ_r is the relative permittivity, ϵ_r is the vacuum permittivity, and μ_n and μ_p are mobilities of negative and positive charges, respectively. However, Langevin recombination theory is often found to deviate from experimental results, especially for the recombination coefficients of efficient organic solar cells [138–141]. Recombination coefficients, that are one to three orders of magnitude lower than the prediction of Langevin theory, have been reported for both fullerene and non-fullerene organic solar cells [111, 142–145]. Therefore, a reduced Langevin recombination coefficient is introduced. One possible reason for reduced recombination probability is that electrons and holes stay at donors and acceptors respectively, and the recombination can take place only at the D-A interfaces [138]. Interestingly,

the reduction factor has not been explained comprehensively due to a strong dependence on the material system and its processing condition [146].

For several material systems, a recombination order above two has been observed [147, 148]. Although recombination of order 3 is often considered as Auger recombination, it is less possible in organic solar cells. Because AM 1.5G illumination is commonly not enough to provide the high charge carrier densities for Auger recombination. The high recombination order is usually explained by effects depending on the charge-carrier density, for example, density-dependent mobilities or recombination coefficients

4.3 The fill factor

The definition of a fill factor is shown in **Equation 2.6**. A fill factor (FF) measures whether a solar cell can output a current and a voltage approximating its conversion limit simultaneously. Note that, for a large-scale solar cell, the series resistance significantly limits the FF, which is not discussed in this work. Physically, the FF is resulting from the competition between charge recombination and charge extraction as a function of the voltage bias. The following subsections introduces how these processes are affecting the FF of solar cells, especially organic solar cells.

4.3.1 Analytical expressions

In **Figure 3.3**, we show the numerical expression of maximum FFs. In this subsection, we discuss the analytical expressions for FFs, as well as impacts from recombination coefficient, mobilities, and thickness.

Independent of the relationship between an current output J and a voltage output V , the condition for maximum power yields

$$d(JV) = JdV + VdJ = 0 \quad (4.11)$$

and thus

$$\left(\frac{dJ}{dV} \right)_{MPP} = - \left(\frac{J}{V} \right)_{MPP} \quad (4.12)$$

where MPP represents the maximum power point. An ideal exponential J-V characteristic is expressed as

$$J = J_0 \left(\exp \left(\frac{eV}{n_{id} k_B T} \right) - 1 \right) + J_{SC} \quad (4.13)$$

where n_{id} represents the ideal factor, J_0 the reverse saturation current, e the elementary charge, k_B the Boltzmann constant, T the temperature, and J_{SC} the short-circuit current. With Equation 4.13, Equation 4.12 becomes

$$J_0 \frac{e}{n_{id} k_B T} \exp \left(\frac{eV_{MPP}}{k_B T} \right) = - \frac{J_{MPP}}{V_{MPP}} \quad (4.14)$$

With

$$J_{MPP} = J_0 \left(\exp \left(\frac{eV_{MPP}}{n_{id}k_B T} \right) - 1 \right) + J_{SC} \quad (4.15)$$

and

$$\frac{J_{SC}}{J_0} = 1 - \exp \left(\frac{eV_{OC}}{k_B T} \right) \quad (4.16)$$

Equation 4.14 becomes

$$V_{MPP} = \frac{n_{id}k_B T}{e} \left[\exp \left(\frac{e(V_{OC} - V_{MPP})}{n_{id}k_B T} \right) - 1 \right] \quad (4.17)$$

If we divide the voltage by $n_{id}k_B T/e$ and use the symbol v for this normalized voltage, we get

$$v_{MPP} = v_{OC} - \ln(v_{MPP} + 1) \quad (4.18)$$

which leads to a precise implicit relationship for FF

$$FF = \frac{v_{MPP}}{v_{MPP} + 1} \frac{v_{OC} - \ln(v_{MPP} + 1)}{v_{OC}(1 - \exp(-v_{OC}))} \quad (4.19)$$

If we do a first approximation, replacing v_{MPP} with v_{OC} and neglecting $\exp(-v_{OC})$

$$FF = \frac{v_{OC} - \ln(v_{OC} + a)}{v_{OC} + 1} \quad (4.20)$$

where $a = 1$. Emperially, setting $a = 0.72$ greatly increases the accuracy of the expression, as proposed by Green [149]. This equation is derived from the Shockley equation and only valid if the V_{MPP} is close to the V_{OC} .

4.3.2 Figure of merits for organic solar cells

A figure of merit is a single quality parameter extracted from a multifactorial system or a device to describe its performance. A FF itself is a figure of merit of a solar cell. However, it is difficult to analytically relate the fill factor to the mobility, the film thickness, and the recombination coefficient. From the perspective of those parameters, new figure of merits (FOMs) have been proposed to describe the device performance, as well as the FF of organic solar cells.

In organic solar cells, a low mobility (typically below $10^{-2} \text{ cm}^2/\text{Vs}$) severely limits charge extraction and causes considerable pile-up of photogenerated charges in the active layer [150]. The pile-up results in significant NGR and screens the electric field from the externally applied bias, which leads to non-ideal JV characteristics. A dimensionless parameter θ has been proposed under consideration of both recombination and extraction [151]

$$\theta = \frac{k_2 G d^4}{\mu_n \mu_p (V_i)^2} \propto \frac{J_{rec}}{J_{extr}} \quad (4.21)$$

where k_2 is the second order NGR coefficient, G is the generation rate, d is the active layer thickness, μ_n and μ_p are the electron and hole mobilities, V_i is the internal bias

(here taking the electrode work function difference minus 0.4 V), and J_{rec} and J_{extr} . A clear dependence of fill factors on θ is shown in **Figure 4.5** with little scatter, by varying θ -related parameters to simulate the JV characteristics.

Figure 4.5 | Simulated FF- θ . Scattered points show a clear “S” shape, which indicates the correlation between two parameters. Reproduced under a Creative Commons Attribution 4.0 International License.[152]

Another dimensionless parameter α [150] is defined as

$$\alpha^2 = \frac{e^2 k_2 J_G d^4}{4 \mu_n \mu_p (k_B T)^2} \quad (4.22)$$

where e is the elementary charge, and $k_B T$ is the thermal energy. An approximate value for V_{int} is obtained by assuming constant gradients of the quasi Fermi levels across the device. This parameter omits the impacts from the electrodes and transport layers, but focuses on the bulk recombination within the active layer, which describes the electronic quality of a photovoltaic layer. To get an analytical expression, which relates a FF to the parameter α , an equation similar to **Equation 4.20** is needed. Considering that the Shockley equation is incomplete to describe an organic solar cell, the following empirical expression is used to describe the FF

$$FF = \frac{v_{OC} - \ln(0.79 + 0.66 v_{OC}^{1.2})}{v_{OC} + 1} \quad (4.23)$$

with v_{OC} written as

$$v_{OC} = \frac{e V_{OC}}{(1 + \alpha) k_B T} \quad (4.24)$$

to provide a viable analytical description of the FF of solar cells with transport-limited photocurrents [150].

As shown in **Figure 4.6**, the simulation results in the FF versus α plots, which include a wide range of mobilities, recombination coefficients, and thicknesses, have small

Figure 4.6 | Illustration of the new figure of merits. Open circles are simulated FF- α points. Dashed and solid lines show analytical FF- α dependencies according to Equation 4.20 and Equation 4.23. Reproduced under a Creative Commons Attribution 4.0 International License.[150]

scatter with the analytical expression curve. Note that the simple expression **Equation 4.20** only works well for the ideal behavior ($\alpha < 1$), while **Equation 4.23** provides a much better description of the full data, especially the transport-limited region ($\alpha > 1$).

Another study presents a facile method to extract the photoactive layer's electronic quality by using only common device parameters [153]. The FF is normalized to reduce the scatter shown in the previous method and the simulation results, by mapping the FF onto the range (-1, 1)

$$FF_n = 2 \frac{FF - FF_{min}}{FF_{max} - FF_{min}} - 1 \quad (4.25)$$

where FF_{min} is set 0.25, corresponding to non-rectifying device with a linear JV curve, and FF_{max} a simple relation proposed in an early work

$$FF_{max} = \frac{aV_{OC}}{V_{OC} + b} \quad (4.26)$$

where a and b are constant parameters, 0.92 and 0.09, respectively, to be found by fitting. By assuming that FF_n follows hyperbolic tangent function due to the S shape of scattered data points, authors did fitting with this equation

$$FF_{n,fit}(\gamma) = \tanh [\alpha \ln(\gamma/\gamma_0)] \quad (4.27)$$

where α and γ_0 are fit parameters as well. γ is the collection coefficient

$$\gamma = \frac{V_{OC}^2}{d^{3.5} J_{SC}^{0.5}} \frac{\mu^2}{k^{0.8}} \quad (4.28)$$

where μ is the mobility when balanced mobilities are assumed, and k is the recombination coefficient. After fitting, they obtained γ , equivalently the electronic quality $\mu^2/k^{0.8}$ for a direct recombination (to be distinguished with Shockley-Read-Hall recombination)

$$Q_{fit} = \gamma_0 \frac{d_{3.5} J_{SC}^{0.5}}{V_{OC}^2} \exp\left(\frac{\text{arctanh } FF_n}{\alpha}\right) \quad (4.29)$$

where γ_0 is $2 \times 10^{17} \text{ mA}^{-0.5} \text{ s}^{-1.2} \text{ cm}^{-0.9}$, and α is 0.29. This method is facile because it can get the competition between extraction and recombination by measuring only the device thickness and the JV curve. But the mathematical processing, including the normalization of FFs and the selection of hyperbolic tangent function for fitting, lacks physical meaning, which is also reflected in the irregular dimension of Q .

Figure 4.7 | Mobility imbalance and contact barriers. Simulated FFs shown in terms of the Figure-of-merit α to illustrate (a) the influence of a mobility imbalance and (b) the effect of increasing electrode work function mismatch at the contacts (decreasing built-in voltage). The FF expected based on the model of Neher et al.[150], is indicated by the grey line. (Reproduced with permission.[154] Copyright 2021, Wiley-VCH GmbH.

All the analytical analysis above assumes that i) space charge effects are insignificant, and ii) the bimolecular process dominates the recombination, while surface recombination and trap-assisted recombination are negligible. However, when mobilities of electron and hole are not balanced, the accumulation of slow charge results in space charge effects, causing additional NGR. This mobility mismatch has been widely blamed for non-optimal FFs [155–158]. As shown in **Figure 4.7 a**, a simulation result of several mobility ratios is compared with the model (Figure 4.6) in a recent review paper [154]. Another recombination pathway, considerable in organic solar cells, is surface recombination. The origin can be the reduction of the built-in field caused by inappropriate contact workfunction, surface pinning effects, and surface traps. The effect of built-in voltage on the FF is demonstrated in **Figure 4.7 b**.

In general, the models above can predict the impacts from mobility, recombination rate, and thickness on the fill factor well. However, major deviation occurs when the

charge generation is dominated by the external voltage bias, which might be a problem in organic solar cells with a negligible driving force.

4.3.3 Development of the fill factor in organic solar cells

Looking back at organic solar cells, the FF did not rise steadily with the record efficiency. In 2013, the device based on PTPD3T:PC₇₁BM achieved a 79.6% FF with EQE close to 80% and PCE near 8% [159]. This is very impressive compared to MDMO-PPV:PC₆₁BM (61% for FF and 2.5% for PCE) and P3HT:PC₆₁BM (67.4% for FF and 4.4% for PCE) [160, 161]. Fullerene solar cells reported with PCEs around 10% did not show improvements in the FF values [162–164]. Later, the record efficiency gradually moved to non-fullerene. In 2016, the benchmark non-fullerene device based on PBDB-T:ITIC obtained FF 71%–74%, PCE close to 11% and EQE around 75% [165]. The device based on PM6:Y6 has FF around 75%, PCE above 15% and EQE above 80% [166]. For the state-of-the-art non-fullerene solar cell with efficiency approaching 20%, most of them have a FF around 80% [19, 20, 167]. Two decades ago, the low FF was due to limited material choices, insufficient understanding of mechanisms, or lacking device fabrication experience. During the age of fullerene, when great progress has been made in all aspects of organic solar cells, high FF and high EQE have already been achieved simultaneously. These achievements are attributed to the high electronic qualities of the active layer and the prolonged device optimization. However, the organic solar cell has a feature that significantly distinguishes it from silicon solar cells and perovskite solar cells, that its development relies heavily on the renewal of the main constituent materials. As a result, although the device physics and fabrication experience can be sustained and developed steadily, material and devices properties may show fluctuations. These fluctuations create difficulties for phenomenon understanding, but they also bring the ground for discovering general mechanisms and deep science.

Recently, it is reported the FF of organic solar cells decreases when the energetic offset goes down [168]. This raises the question that is there a relation between the FF and the driving energy. If there is, how are they related? Furthermore, this phenomenon is often related to a voltage-loss change, posting another question whether there is a relation between the FF and the voltage loss. These questions remain to be answered.

Figure 4.8 | Schematic for decreasing fill factors and decreasing voltage losses with decreasing energetic offsets.

CHAPTER 5

Summary and Outlook

The core of this thesis is to understand the loss mechanisms of organic solar cells. To cope with this challenge, the thesis understands an organic solar cell from the perspective of thermal dynamics and equilibrium states, and the perspective of charge dynamics and intermedium states. Based on these two aspects, the open-circuit voltage and the fill factor in organic solar cells are analyzed.

The detailed balance in a solar cell works perfectly for the voltage loss analysis. To further relate the voltage loss to material properties, however, more internal and microscopic parameters of molecules and condensed phases should be taken into consideration. Currently, the voltage loss of the best organic solar cell is still greater than that of the best perovskite solar cell. To continue to improve the power conversion efficiency of organic solar cells, more efforts are needed to reduce the voltage loss, especially the non-radiative voltage loss. Compared with the open-circuit voltage, the fill factor lacks physical meaning and is more complicated. The process of charge generation, recombination, and transport, as well as their field dependence, have an impact on the fill factor. Thanks to previous studies on analytical expressions and new figure of merits, the fill factor in organic solar cells has been well described with assumptions. However, the assumptions limit their usage, and there are exceptional cases and trends that require additional investigation. Besides the voltage and the fill factor, the photocurrent, precisely the charge separation process, in organic solar cells is not entirely clear. Particularly, there are still debates on the energetic offsets, interfacial dipoles, interfacial electrostatic potentials, and the charge-transfer excitons.

Organic solar cells have been developing for over three decades. Achievements are in various fields, including material synthesis, mechanism understanding, characterization techniques, and device fabrication. With the efficiency approaching 20%, the commercialization of organic solar cells is on the way. Therefore, several points should be considered in moving towards commercialization. Firstly, long-term sta-

bility, especially stability under light, is essential for organic solar cells. There is a need for in-depth understandings of degradation and stability in high-performing non-fullerene acceptors for future commercialization. Considering the unstable nature of organics under sunlight, we may use organic solar cells in weak light situations (for example, indoor) or for short-term use. Secondly, the use of green solvents is necessary for the large-scale commercialization of organic solar cells. Although unprecedented efficiency of over 16% in green-solvent processed non-fullerene organic solar cells has been achieved [169], there is a dearth of studies aimed at understanding the detailed morphology and device physics in these systems. Thirdly, some powerful tools such as the high-output automatic screening and machine learning in molecule design may accelerate the development. Although current reports are still rare, with the rapid development of artificial intelligence, the two fields are likely to collide and generate new sparks.

This chapter introduces the major experimental methods and equipments in this work.

6.1 Sensitive-external-quantum-efficiency characterisation

6.1.1 Monochromatic technique

Figure 6.1 | Schematic illustration of the EQE_{PV} measurement through the monochromatic and the lock-in technique.

The definition of EQE is described in Equation 2.8. To experimentally measure the photocurrent at each wavelength, particularly the weak response of the absorption tail, researchers often use the lock-in technique to increase the signal-to-noise ratio. As shown in **Figure 6.1**, the light from a quartz tungsten halogen (QTH) lamp is focused into a monochromator (Bentham TMC300). A monochromator is an optical device that selects a specific narrow band of wavelengths of light from the input light. The output monochromatic light is modulated with an optical chopper (Thorlabs MC2000B) with frequency ω (165 Hz in my experiments). The frequency should avoid common AC signals and their integer multiples. Then the light passes through

a long-pass filter (LPF), subsequently a beamsplitter. A part of light shines upon the device to generate photocurrents as the sample signal, while the other part of light goes to a silicon detector for calibration. The electrical signals from both the sample and the detector are received by a preamplifier (SR570) and subsequently a lock-in amplifier (SR830). The lock-in amplifier multiplies the sample signal by the reference signal ω , integrates it over a specified time, and outputs a DC signal which is proportional to the amplitude of only ω in the sample signal, excluding noises of other frequencies. In our EQE measurements, the DC signals which are proportional to the photocurrent amplitudes are transferred to a homemade LABVIEW program. Using the EQE of the silicon detector and the light intensity ratio between the detector and the sample, the EQE of the sample can be calculated.

The working mechanism of a monochromator with the common Czerny–Turner design is shown in **Figure 6.2**. The incident light (A) is aimed at an entrance slit (B). The slit is placed at the effective focus of a concave cylindrical mirror (C) to collimate the reflection light. The collimated light is diffracted by a grating (D) and dispersed according to the color. The diffraction light is collected by another concave cylindrical mirror (E), which focuses the dispersed light on the plane of an exit slit (F). The exit slit with a finite width outputs the dispersed light selectively. A rotation of the grating changes the incident and diffraction angle, to project the desired wavelength onto the center of the exit slit.

Figure 6.2 | Schematic illustration of a Czerny-Turner monochromator. The wide-range light (A) is focused at an entrance slit (B), and subsequently collimated by a cylindrical mirror (C). The collimated beam is diffracted from a grating (D). The dispersed light is focused by another cylindrical mirror (E) onto the plane of the exit slit (F). Each wavelength of light is focused at a different position, and only the desirable range (G) can pass through the exit slit by rotating the grating and adjusting the slit. Figures by FeuRenard under CC-BY-SA 4.0 license [170]

The basic grating equation determines the discrete directions into which monochromatic light of wavelength λ is diffracted, which is expressed as

$$m\lambda = d_G(\sin\alpha + \sin\beta_m) \quad (6.1)$$

where α is incident angle, d_G is the groove spacing of the grating, and β_m is the set of

angles the light diffracted along. For every beam of monochromatic light incident on a grating, the light is diffracted in directions corresponding to $m = 0, \pm 1, \pm 2, \pm 3, \dots$. Typically only the first order, positive or negative, is desired. However, the first-order diffraction of a specified frequency is in the same direction as the higher-order diffraction of its multiple frequencies. As a result, higher order diffraction peaks may need to be blocked. It is especially important to block high-order radiation when measuring the tail-state absorption. For example, if a solar cell has EQE of 1 at 500 nm and EQE of 10^{-5} at 1000 nm, the second-order diffraction of 500 nm needs to be 6 orders of magnitude weaker than the first-order diffraction of 1000 nm, to ensure the system error less than 10%. This is why an additional LPF is often needed for the measurement of sub-gap features.

6.1.2 Fourier-transform technique

Figure 6.3 | Schematic illustration of a Fourier transform spectrometer, which is essentially a Michelson interferometer with one mirror movable.

Another technique often used to get a sensitive EQE is the Fourier-transform Photocurrent Spectroscopy (FTPS). Instead of using a monochromatic light, this technique uses a dispersive white light to illuminate the sample. The white light is time-modulated at each wavelength via a Fourier-transform spectrometer (see **Figure 6.3**). In the interferometer, the incident light is split into two by a beamsplitter, and subsequently reflected by two mirrors. Depending on the distance of two mirror, a path length difference $\delta=2d$ is created between the two reflection beams. Accordingly, constructive or destructive interference occurs when they come together. The analytical expression for the intensity of the output light at a specified wavenumber σ is

$$s(\sigma)(1 + \cos(2\pi\sigma\delta)) \quad (6.2)$$

where $s(\sigma)$ is the incident light irradiance of wavenumber σ . If this output beam in

incident on a detector with a response $R(\sigma)$, the detector produces a photocurrent $I(\delta)$ as

$$I(\delta) = \int_0^{\infty} s(\sigma)(1 + \cos(2\pi\sigma\delta))d\sigma \quad (6.3)$$

The response at each wavelength $R(\sigma)s(\sigma)$ can be obtained by convolving the output signal.

$$R(\sigma)s(\sigma) = 4 \int_0^{\infty} \left(I(\delta) - \frac{1}{2}I(0) \right) \cos(2\pi\sigma\delta)d\delta \quad (6.4)$$

The actual operation is to input the photocurrent to the Fourier-transform instrument after passing through the preamplifier. And the instrument can do the inverse Fourier transform easily.

For a monochromator, the light output is positively correlated to the slit width, resulting in a trade-off between the spectral resolution and the signal-to-noise ratio. In contrast, FTFS allows very fine spectral resolution while maintaining a high signal-to-noise ratio. However, since the finite mirror distance and the finite scanning time, the spectral bandwidth of FTFS may be limited. Moreover, if a sample has uneven photocurrent responses over frequencies, the photocurrent spectrum would exhibit deformation, because every σ is correlated to a different f while f is typically around 5 kHz or higher. A correction procedure is usually performed at several mirror scanning speeds $V_1, V_2, \dots, V_n$. For each wavenumber, this introduces frequencies $f_1 = 2\sigma V_1$, $f_2 = 2\sigma V_2, \dots, f_n = 2\sigma V_n$, which is a part of the relative frequency response. Here, 'relative' means no absolute value but ratios between each frequencies. By changing the wavenumber, we can get a continuous response by matching the frequency response curves in their overlapping frequency region.

6.2 Steady-state spectrum

6.2.1 Spectrograph

A spectrograph (spectrometer) is an instrument used to measure the light intensity over a specific wavelength. As mentioned in the last section, the method to measure a wavelength-dependent parameter can be either monochromatic or Fourier-transform. In this section, we focus on only the spectrograph using a monochromatic technique. As shown in **Figure 6.2**, a diffraction grating or a prism is used to disperse the light according to the wavelength. The dispersive light with different colors is focused into a detector, which is usually a CCD array. The response of the detector at each wavelength can be recorded and shown in a computer as a spectrum. The spectrograph (Shamrock 303i) in our lab is equipped with a silicon array detector (Andor Newton EM-CCD) and an InGaAs detector (Andor). The silicon detector works in the wavelength range of 300 nm - 1100 nm and is cooled to -45°C during the measurement. the InGaAs detector works in 800 nm - 1700 nm and is cooled to -80°C during the measurement. A Mercury lamp is used for wavelength position calibration and a standard halogen lamp (AvaLight-HAL-S-Mini) is used for wavelength intensity calibration.

6.2.2 UV-VIS-NIR absorption

Measuring the material absorption is a standard technique that allows easy yet effective characterisation of material features. In our lab, we used a commercial setup (Perkin Elmer Lambda 950 UV/VIS/NIR). In this setup, the light of a Tungsten lamp or a Deuterium lamp passes a monochromator and comes out as monochromatic light. The monochromatic light is collimated and directed onto the sample. For transmission measurement, the sample is put before an integrating sphere and the transmitted light enters the integrating sphere. For reflection measurement, the sample is put after the integrating sphere and the reflected light enters the integrating sphere. There are two detectors under the integrating sphere. A photomultiplier tube (PMT) is used in the UV/VIS range while a lead sulfide (PbS) detector is used in the NIR range.

6.2.3 Photoluminescence and quantum yield measurement

Figure 6.4 | A schematic for a PL measurement.

The PL is excited by a collimated laser-diode-pumped laser module. A short-pass filter is used after the laser to reduce the tail light. A long-pass filter is used before the spectrograph to protect the detector. The PL excitation and detection were performed via an objective, a 45° placed long-pass dichroism glass and optical fibers. For bias-dependent PL measurement, a source meter Keithley 2400 was connected to the photovoltaic devices to sweep the voltage bias and to record the current.

When measuring the PLQY of solids, a “Direct & Indirect Excitation” method is used to reduce the scattering impact. The measured spectrum is composed of that from the un-absorbed pump laser and that from the sample emission. We refer to the amount of un-absorbed pump laser as L , and that of the emitted light as P . In the “off” experiment, we assume that a fraction μ of the scattered light is absorbed by the sample. In the “on” experiment, we assume that a fraction A of the incident light is absorbed by

Figure 6.5 | Schematic for a PLQY measurement of film samples. **(a) Blank:** reference samples in both sample position 1 and 2; **(b) On:** the test sample in position 2 and the reference sample in position 1; **(c) Off:** the reference sample in position 2 and the test sample in position 1

the sample. We have

$$L_{off} = L_{Blank} (1 - \mu) \quad (6.5)$$

$$L_{on} = L_{Blank} (1 - A)(1 - \mu) \quad (6.6)$$

From these two equations, we have

$$A = 1 - \frac{L_{on}}{L_{off}} \quad (6.7)$$

In the “off” experiment, the number of photons striking the detector is $L_{off} + P_{off}$. In the “on” experiment, this part of light will be decreased to $(1 - A) \times (L_{off} + P_{off})$. However, in the “on” experiment, we also have light emitted directly due to the absorption of collimated laser light, which is $PLQY \times L_{Blank} \times A$. Hence

$$L_{on} + P_{on} = (1 - A) \times (L_{off} + P_{off}) + PLQY \times L_{Blank} \times A \quad (6.8)$$

From this equation, the PLQY can be calculated as

$$PLQY = \frac{P_{on} - (1 - A)P_{off}}{L_{Blank}A} = \frac{P_{on} - P_{off} \frac{L_{on}}{L_{off}}}{L_{Blank}(1 - \frac{L_{on}}{L_{off}})} \quad (6.9)$$

6.2.4 External quantum efficiency for electroluminescence

As shown in **Figure 6.6**, the electroluminescence (EL) of a sample is focused into a spectrograph for EL spectra. The setup is the same as bias-dependent PL measurement, as shown in the last subsection. A large area silicon photodiode (Hamamatsu 1010B) is used for the measurement of EQE_{EL} (**Figure 6.6**). A Keithley 2400 SourceMeter is used to apply voltage and record the injected current. A Keithley 485 Picoammeter is used to measure the signal of the silicon photodiode for the emitted light intensity. The EQE_{EL} is calculated according to a wavelength response which depends on both the EQE_{PV} of the silicon photodiode and the instrument loss. The response is calibrated with a standard LED.

Figure 6.6 | Schematic for the EQE_{EL} measurement.

6.3 Time-resolved measurements

6.3.1 Transient absorption spectroscopy

Figure 6.7 | Schematic illustration of the transient absorption measurement.

Each excited state has its distinct absorption and emission. However, some excited states have very short lifetime and constitute very little proportion in the steady state. To map the evolution of those states over time, an excited-state absorption measurement called transient absorption spectroscopy (TAS) is often used by researchers. In TAS, the absorbance over a specific wavelength range of a sample is measured as a function of time after excitation by a flash of light. A typical technique for measurement is called pump-probe spectroscopy (PP), in which both the light for excitation ('pump') and the light for measuring the absorbance ('probe') are generated by a pulsed laser. The 'pump' is typically a broad-band pulse generated by a non-collinear optical parametric amplifier (NOPA) and a fundamental laser. If no short pulse duration is needed, an optical parametric amplifier (OPA) can be used to gen-

erate narrowband pump pulses. The ‘probe’ is typically a supercontinuum (white-light pulse) generated by tightly focusing intense ultrashort pulses in crystals such as yttrium aluminum garnet (YAG), lithium fluoride (LiF), or sapphire. The time delay between the pump and probe light can be mechanical (typically between ps and ns) or electronic (typically between ns and ms). PP spectra are obtained by comparing the transmission of the probe light (white light supercontinuum) when the sample is excited, $T_{pump\ on}$, with the transmission when the pump is blocked by the chopper, $T_{pump\ off}$

$$\frac{\Delta T}{T} = \frac{T_{pump\ on} - T_{pump\ off}}{T_{pump\ off}} \tag{6.10}$$

As illustrated in **Figure 6.8**, the main features in typical PP spectra include the ground-state bleaching (GSB), the stimulated emission (SE), and the photo-induced absorption (PIA). These features come from the disappearance or the appearance of electronics states. By decomposing the raw signal into these individual components, we can observe the evolution of the corresponding states. A typical analysis may involve mathematical models of physical processes with the help of other steady or time-resolved spectroscopy.

Figure 6.8 | Schematic illustration of features contributing to a transient absorption spectrum. The ground state bleaching (blue) comes from $S_0 \rightarrow S_n$ transition. The stimulated emission (green) originates from the inverse process $S_0 \leftarrow S_1$. The photo-induced absorption (red) is from $S_1 \rightarrow S_n$ transitions. Credit: Dr. Andreas Jakowetz.

The GSB signal is the result of reduced absorption when the sample is excited. The ab-

sorption of molecules in the ground state can be measured by steady-state absorption spectroscopy, as described in subsection 6.2.2. After excitation, the depopulation of the ground state causes the transmitted probe light less absorbed at the energies that correspond to the ground state absorption hence a GSB. ΔT gives a positive signal with a shape similar to the steady-state absorption spectrum. GSB cannot differentiate the type of excited states. Its intensity is proportional to the density of total excited states.

The SE signal is the result of stimulated emission from molecules in an excited state. The excited state can randomly decay to the ground state by emitting a photon, which is usually measured in the steady-state PL or the time-correlated single-photon counting (TCSPC). However, the radiative decay can be stimulated by a photon of energy corresponding to the transition to a lower energy state and emits a second photon of the same energy. This process is called stimulated emission. The SE caused by the probe light is detected as increased transmission, thus producing a positive ΔT . Its shape roughly matches the PL spectrum and its intensity represents the population of excited states that can undergo radiative transitions.

The PIA signal is the result of absorption by excited states that transition to higher excited states. The excited states provide new transitions and absorb additional probe light, which results in a negative ΔT . In contrast to the SE signal, PIA also comes from states that can not undergo radiative transitions to the ground state, such as triplet excitons and charges.

6.3.2 Time-delayed collection field

Time-delayed collection field (TDCF) is a transient technique to monitor the evolution of charge carriers in a device after excitation by a flash of light. The TDCF measurement has similarities to the transient photocurrent (TPC) and the transient photovoltage (TPV) measurements, but is more powerful in investigating the charge generation and recombination process. Compared with TAS, TDCF typically provides a longer observation time scale for the long-lived charge carriers in ready-made devices.

In TDCF, the sample device is excited by a pulsed laser. Before the excitation, a pre-bias is applied and maintained on the device. The charge generation process accomplishes during the pre-bias. After a specified time delay, a large reverse collection field is applied on the device to extract all remaining charges before significant recombination. Monitoring the extraction current can provide information about charge density in the device. By varying the pre-bias and making the time delay short, we can investigate the field dependence of charge generation. By varying the time delay and keeping the pre-bias, we can study the recombination process of free charge carriers. As indicated in **Figure 6.9**, the pre-bias and collection field are applied by a low-jitter function generator. A synchronization and delay generator (SDG) is used to trigger both the laser pulse and the function generator. Fast charge extraction requires a small measurement resistor (10 Ohms) and a small capacitance (100 pF) which results in a short and large recharging current of ca. 1 A within 2.7 ns [146]. A high-definition oscilloscope with very low noise input amplifiers is needed to reach an overall high sensitivity for monitoring the extraction current.

Figure 6.9 | Schematic illustration of the TDCF measurement. The synchronization and delay generator (SDG) controls the laser and delivers a trigger to the function generator and the oscilloscope. The filter wheel (FW) controls the excitation intensity. Credit: Dr. Jona Kurpiers.

CHAPTER 7

Results and included pappers

The results obtained from my research leading up to this thesis are presented in the form of three scientific papers published in peer-reviewed journals and a manuscript.

7.1 List of publications

Papers appended in the thesis:

[I] **Barrierless Free Charge Generation in the High-Performance PM6:Y6 Bulk Heterojunction Non-Fullerene Solar Cell**

Lorena Perdigón-Toro, Huotian Zhang, Anastasia Markina, Jun Yuan, Seyed Mehrdad Hosseini, Christian M Wolff, Guangzheng Zuo, Martin Stolterfoht, Yingping Zou, Feng Gao, Denis Andrienko, Safa Shoaee, Dieter Neher
Advanced Materials, 32, 1906763 (2020).

Contribution: I fabricated the devices, did the initial characterization, and performed the temperature-dependent measurements. I did the TDCF measurements and analyzed the data with L.P.-T. I contributed to the revision of the manuscript.

[II] **From Generation to Extraction: A Time-Resolved Investigation of Photo-physical Processes in Non-fullerene Organic Solar Cells**

Rokas Jasiūnas, Huotian Zhang, Jun Yuan, Xuehong Zhou, Deping Qian, Yingping Zou, Andrius Devizis, Juozas Sulskus, Feng Gao, Vidmantas Gulbinas
The Journal of Physical Chemistry C, 124, 21283-21292 (2020).

Contribution: I participated in conceiving the idea. I fabricated the devices. I contributed to the revision of the manuscript.

[III] **Effect of the Energy Offset on the Charge Dynamics in Non-fullerene Organic Solar Cells**

Yunhao Cai, Huotian Zhang, Linglong Ye, Rui Zhang, Jinqiu Xu, Kangning Zhang, Pengqing Bi, Tengfei Li, Kangkang Weng, Ke Xu, Jianlong Xia, Qinye Bao, Feng Liu, Xiaotao Hao, Songting Tan, Feng Gao, Xiaowei Zhan, Yanming Sun
ACS Applied Materials & Interfaces, 12, 43984-43991 (2020).

Contribution: I did the EL, PL and FTPS-EQE measurements, and analyzed the voltage loss data. I contributed to the first draft and the revision of the manuscript.

[IV] **The relation between Fill Factor and Open-circuit Voltage Loss in Non-fullerene Organic solar cells**

Huotian Zhang, Rui Zhang, Xuehong Zhou, Jun Yuan, Rokas Jasiūnas, Wenchao Huang, Vidmantas Gulbinas, Arkady Yartsev, Feng Gao
Manuscript

Contribution: I initiated and coordinate the project. I collected and analyzed the data. I wrote the first draft of the manuscript.

Additional publications not included in the thesis:

- **Optical gaps of organic solar cells as a reference for comparing voltage losses**
Yuming Wang, Deping Qian, Yong Cui, [Huotian Zhang](#), Jianhui Hou, Koen Vandewal, Thomas Kirchartz, Feng Gao
Advanced Energy Materials, 8, 1801352 (2018).

Contribution: I contributed to the discussion and the revision of the manuscript.

- **A near-infrared photoactive morphology modifier leads to significant current improvement and energy loss mitigation for ternary organic solar cells**
Lingling Zhan, Shuixing Li, [Huotian Zhang](#), Feng Gao, Tsz-Ki Lau, Xinhui Lu, Danyang Sun, Peng Wang, Minmin Shi, Chang-Zhi Li, Hongzheng Chen
Advanced Science, 5, 1800755 (2018)

Contribution: I measured the FTPS-EQE and the EQE of EL. I did the voltage loss calculation.

- **Oriented quasi-2D perovskites for high performance optoelectronic devices**
Rong Yang, Renzhi Li, Yu Cao, Yingqiang Wei, Yanfeng Miao, Wen Liang Tan, Xuechen Jiao, Hong Chen, Liangdong Zhang, Qing Chen, [Huotian Zhang](#), Wei Zou, Yuming Wang, Ming Yang, Chang Yi, Nana Wang, Feng Gao, Christopher R McNeill, Tianshi Qin, Jianpu Wang, Wei Huang
Advanced Materials, 30, 1804771 (2018)

Contribution: I measured the EQE of EL.

- **Enabling low voltage losses and high photocurrent in fullerene-free organic photovoltaics**
Jun Yuan, Tianyi Huang, Pei Cheng, Yingping Zou, [Huotian Zhang](#), Jonathan Lee Yang, Sheng-Yung Chang, Zhenzhen Zhang, Wenchao Huang, Rui Wang, Dong Meng, Feng Gao, Yang Yang
Nature Communications, 10, 44204 (2019)

Contribution: I did the FTPS-EQE, EL, EQE_{EL} , PL and PLQY measurements. I did the voltage loss calculation and the time-resolved PL analysis. I wrote a part of the first draft and contributed to the revision of the final manuscript.

- **The crucial role of end group planarity for fused-ring electron acceptors in organic solar cells**
Jeromy J Rech, Nicole Bauer, David Dirkes, Joseph Kaplan, Zhengxing Peng, [Huotian Zhang](#), Long Ye, Shubin Liu, Feng Gao, Harald Ade, Wei You
Materials Chemistry Frontiers, 3, 1642-1652 (2019)

Contribution: I did the PLQY measurement.

- **Sulfur vs. tellurium: the heteroatom effects on the nonfullerene acceptors**
Lei Yang, Linqing Qin, Yunxiao Xu, [Huotian Zhang](#), Lei Lv, Kepeng Chen, Xinyu Sui, Yangguang Zhong, Yuan Guo, Feng Gao, Jianzhang Zhao, Yuhao Li, Xinfeng Liu, Yuanping Yi, Xinhui Lu, Aidong Peng, Hui Huang
Science China Chemistry, 62, 897-903 (2019)

Contribution: I measured the FTPS-EQE and the EQE of EL. I did the voltage loss calculation and the reciprocity fitting.

- **Realizing Efficient Charge/Energy Transfer and Charge Extraction in Fullerene-Free Organic Photovoltaics via a Versatile Third Component**

Hao-Wen Cheng, Huotian Zhang, Yu-Che Lin, Nian-Zu She, Rui Wang, Chung-Hao Chen, Jun Yuan, Cheng-Si Tsao, Atsushi Yabushita, Yingping Zou, Feng Gao, Pei Cheng, Kung-Hwa Wei, Yang Yang
Nano Letters, 19, 5053-5061 (2019)

Contribution: I did the FTPS-EQE, EL, EQE_{EL}, PL and PLQY measurements. I did the voltage loss calculation.

- **Experimentally Validated Hopping-Transport Model for Energetically Disordered Organic Semiconductors**

Tanvi Upreti, Yuming Wang, Huotian Zhang, Dorothea Scheunemann, Feng Gao, Martijn Kemerink
Physical Review Applied, 12, 64039 (2019)

Contribution: I fabricated the devices. I did the temperature-dependent JV measurement.

- **Bright free exciton electroluminescence from Mn-doped two-dimensional layered perovskites**

Liangdong Zhang, Tao Jiang, Chang Yi, Jiquan Wu, Xiao-Ke Liu, Yarong He, Yanfeng Miao, Ya Zhang, Huotian Zhang, Xinrui Xie, Peng Wang, Renzhi Li, Feng Gao, Wei Huang, Jianpu Wang
The Journal of Physical Chemistry Letters, 10, 3171-3175 (2019)

Contribution: I did the PLQY measurement.

- **Tuning the electron-deficient core of a non-fullerene acceptor to achieve over 17% efficiency in a single-junction organic solar cell**

Can Zhu, Jun Yuan, Fangfang Cai, Lei Meng, Huotian Zhang, Honggang Chen, Jing Li, Beibei Qiu, Hongjian Peng, Shanshan Chen, Yunbin Hu, Changduk Yang, Feng Gao, Yingping Zou, Yongfang Li
Energy & Environmental Science, 13, 2459-2466 (2020)

Contribution: I measured the FTPS-EQE and the EQE of EL. I did the voltage loss calculation and the reciprocity fitting.

- **Promoting charge separation resulting in ternary organic solar cells efficiency over 17.5%**

Qing Ma, Zhenrong Jia, Lei Meng, Jinyuan Zhang, Huotian Zhang, Wenchao Huang, Jun Yuan, Feng Gao, Yan Wan, Zhanjun Zhang, Yongfang Li
Nano Energy, 78, 105272 (2020)

Contribution: I measured the FTPS-EQE and the EQE of EL. I did the voltage loss calculation and the reciprocity fitting.

- **Reliability of charge carrier recombination data determined with charge extraction methods**

Juliane Kniepert, Andreas Paulke, Lorena Perdigón-Toro, Jona Kurpiers, Huotian Zhang, Feng Gao, Jun Yuan, Yingping Zou, Vincent M Le Corre, L Jan Anton Koster, Dieter Neher

Journal of Applied Physics, 126, 205501 (2019)

Contribution: I fabricated and characterized the devices.

- **Reducing voltage losses in the A-DA' DA acceptor-based organic solar cells**

Jun Yuan, Huotian Zhang, Rui Zhang, Yuming Wang, Jianhui Hou, Mario Leclerc, Xiaowei Zhan, Fei Huang, Feng Gao, Yingping Zou, Yongfang Li
Chem, , (2020)

Contribution: I contributed to the discussion, draft and revision of the manuscript.

- **Understanding energetic disorder in electron-deficient-core-based non-fullerene solar cells**

Jun Yuan, Chujun Zhang, Honggang Chen, Can Zhu, Sin Hang Cheung, Beibei Qiu, Fangfang Cai, Qingya Wei, Wei Liu, Hang Yin, Rui Zhang, Jidong Zhang, Ye Liu, Huotian Zhang, Weifang Liu, Hongjian Peng, Junliang Yang, Lei Meng, Feng Gao, Shukong So, Yongfang Li, Yingping Zou
Science China Chemistry, 63, 1159-1168 (2020)

Contribution: I contributed to the discussion and revision of the manuscript.

- **Emerging approaches in enhancing the efficiency and stability in non-fullerene organic solar cells**

Fuwen Zhao, Huotian Zhang, Rui Zhang, Jun Yuan, Dan He, Yingping Zou, Feng Gao
Advanced Energy Materials, 10, 2002746 (2020)

Contribution: I contributed to the discussion, draft and revision of the manuscript.

- **Highly efficient fused ring electron acceptors based on a new undecacyclic core**

Fuwen Zhao, Dan He, Jingming Xin, Huotian Zhang, Jixiang Zhou, Baojun Lin, Yongju He, Jiang Li, Wei Ma, Bao Li, Feng Gao, Yongfang Li, Chunru Wang
Materials Chemistry Frontiers, 5, 2001-2006 (2021)

Contribution: I measured the FTPS-EQE and the EQE of EL. I did the voltage loss calculation.

- **Revealing Morphology Evolution in Highly Efficient Bulk Heterojunction and Pseudo-Planar Heterojunction Solar Cells by Additives Treatment**

Qiannan He, Wangping Sheng, Ming Zhang, Guodong Xu, Peipei Zhu, Huotian Zhang, Zhaoyang Yao, Feng Gao, Feng Liu, Xunfan Liao, Yiwang Chen
Advanced Energy Materials, 11, 2003390 (2021)

Contribution: I did the voltage loss calculation and analysis.

- **Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells**

Chao Li, Jiadong Zhou, Jiali Song, Jinqiu Xu, Huotian Zhang, Xuning Zhang, Jing Guo, Lei Zhu, Donghui Wei, Guangchao Han, Jie Min, Yuan Zhang, Zengqi Xie,

Yuanping Yi, He Yan, Feng Gao, Feng Liu, Yanming Sun
Nature Energy, 6, 605-613 (2021)

Contribution: I did the FTPS-EQE, EL and EQE_{EL} measurements. I did the voltage loss calculation. I contributed to the discussion and revision of the manuscript.

- **Carrier Mobility Dynamics under Actual Working Conditions of Organic Solar Cells**

Rokas Jasiūnas, Vidmantas Jasinskas, Huotian Zhang, Tanvi Upreti, Feng Gao, Martijn Kemerink, Vidmantas Gulbinas

The Journal of Physical Chemistry C, 125, 14567-14575 (2021)

Contribution: I fabricated the devices.

7.2 Summary of included papers

Paper I

Barrierless Free Charge Generation in the High-Performance PM6:Y6 Bulk Heterojunction Non-Fullerene Solar Cell

Summary

The efficiency of photocurrent generation is studied in the high-efficiency non-fullerene PM6:Y6 blend, using a combination of field- and temperature-dependent optoelectronic measurements. These experiments reveal barrierless free charge generation, despite a small driving force. Theoretical modeling suggests the existence of a large electrostatic interfacial field, which repels charges from the donor–acceptor interface.

Author's contribution

I fabricated the devices, did the initial characterization, and performed the temperature-dependent measurements. I did the TDCF measurements and analyzed the data with L.P.-T. I contributed to the revision of the manuscript.

Paper II

From Generation to Extraction: A Time-Resolved Investigation of Photophysical Processes in Non-fullerene Organic Solar Cells

Summary

The photophysical process from sub-ps to μ s is studied in organic solar cells based on three non-fullerene combinations with negligible HOMO offsets, using several transient investigation techniques. The experiments show inefficient hole transfer and enhanced geminate recombination for the low offset system.

Author’s contribution

I participated in conceiving the idea. I fabricated the devices. I contributed to the revision of the manuscript.

Paper III

Effect of the Energy Offset on the Charge Dynamics in Non-fullerene Organic Solar Cells

Summary

Three devices are presented with the HOMO offset changed from 0.15 eV to -0.1 eV by polymer chlorination, which is cross verified by CV and UPS. This work indicates the feasibility of the free carrier generation and the following charge separation under the condition of a negative offset.

Author's contribution

I did the EL, PL and FTPS-EQE measurements, and analyzed the voltage loss data. I contributed to the first draft and the revision of the manuscript.

Paper IV

The relation between Fill Factor and Open-circuit Voltage Loss in Non-fullerene Organic solar cells

Summary

A large number of data about the FF and the V_{OC} are summarized. The data together with theoritical simulations show no competition between FF and V_{OC} in a non-geminate recombination dominated condition. However, field-dependent charge dissociation may harm FF when geminate recombination is dominating.

Author's contribution

I initiated and coordinate the project. I collected and analyzed the data. I wrote the first draft of the manuscript.

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Papers

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