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**NANYANG
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**PLASMON-POLARON COUPLING IN
CONJUGATED POLYMERS ON
INFRARED METAMATERIALS**

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**SCHOOL OF PHYSICAL & MATHEMATICAL
SCIENCES**

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Plasmon-Polaron Coupling in Conjugated Polymers on Infrared Metamaterials

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Abstract

Plasmonic nanostructures that strongly enhance local electric fields are widely considered to improve the efficiency of thin film polymer photodetectors and photovoltaics, where absorption and charge photogeneration are limited by the active layer thickness (~100-200 nm).

Compared to conventional inorganic semiconductors, conjugated polymer photophysics is further complicated by strong electron-electron interactions, which often results in the photogeneration of strongly bound electron-hole pair (excitons) and the formation of charge carriers coupled to the lattice (polarons). Since excitons are neutral species, the density of mobile charged polarons generated either directly or indirectly (e.g. by dissociation of excitons) upon photoexcitation is overall responsible for device photocurrent. While common approaches for plasmonic enhancement of polymer photocurrent rely on absorption enhancement by nanostructures resonant with excitonic interband transitions, *in this thesis work we propose and demonstrate a completely different approach based on the resonant coupling of the polymer photoinduced polaron states to properly designed infrared (IR) metamaterials.*

IR photoinduced absorption (PIA) measurements were used to directly gauge the density of photogenerated charge carriers, probing the polaronic transitions and the infrared-active-vibrational modes (IRAV) of the polymer induced by photodoping. We first considered bare P3HT, a well-known photoconductive polymer, and fully characterized its polaron and vibrational response by PIA measurements and *ab initio* modeling. We then studied conventional plasmonic enhancement

of P3HT absorption by coupling the polymer to surface plasmons of metal nanoparticles with resonance at visible frequencies and various degrees of overlap with the excitonic transitions of P3HT. We find that IR-PIA reflects well the enhancement of charge carrier photogeneration induced by the metal nanoparticles.

To verify the concept of plasmon-polaron coupling, we then fabricated large area IR-nanoantenna arrays with resonances matching the P3HT polaron relaxation energy. Even in this case, PIA measurements clearly indicate enhancement of both polaronic transitions and IRAV modes due to near-field interaction between charged polarons in the polymer and localized surface plasmons in the IR-nanoantennas. This idea was further extended to the case of P3HT:PCBM “bulk heterojunctions”, showing that the concept of charge generation enhancement by plasmon-polaron coupling is also applicable to donor-acceptor systems with greater relevance to light detection and photovoltaic applications.

In our conclusions, we argue that these new plasmon-polaron hybrid quasi-particles could also be exploited in functional materials other than conjugated polymers, like tuning the photogenerated polaron or bipolaron density in superconducting cuprates, discovering strong coupling between polaron and plasmons, or designing dispersion relation of propagating hybrid surface-polaron-plasmon polaritons.

Introduction

At present, electronic devices fabricated from organic semiconductors are no more pure topics for academic studies. For instance, displays using organic light emitting diodes (OLED) are already mass produced for mobile phone screens and television sets with OLED start competing with LCD TVs.

The study of optoelectrical properties of organic semiconductors may date back to the early 20 Century, when Pochettino¹ in the year of 1906 discovered the photoconductive properties of solid anthracene.^{2,3} Ever since, substantial research was carried out on the photoexcitation and charge carrier properties of organic molecular crystals. In early days, studies were mostly focused on the fundamental understanding of organic electronics. Electroluminescence (EL) devices were later fabricated starting from the year of 1962⁴ though with rather poor performances; the breakthrough of OLED devices occurred much later, in 1987.⁵

Since 1970s the discovery of doping mechanism that make insulating conjugated polymer conducting and, as later realized, semiconducting, has opened up another field of study in the realm of organic electronics.^{6,7} Thanks to the large freedom in the synthesis of materials and their tunable electronic properties, π -conjugated polymers have become one of the major fields of study in both chemistry and physics academics. Figure I1 shows different electrical conductivity of different conjugated polymer compared to their inorganic counterparts.⁸

Figure 11. Electrical conductivity range of conjugated polymers and typical numbers of inorganic materials.

Practically, the low cost and ease of processing even on flexible substrates of conjugated polymers make them more than promising for device applications, such as the organic thin film (photo-) transistors (OFETs) for logic circuits or RFID,⁹ OLEDs or polymeric light emitting diodes (PLEDs) for displays,¹⁰ organic photo detectors (OPD) for sensing¹¹ and organic photovoltaics (OPVs) for light harvesting and electric conversion.^{12,13} Particularly, the OPV devices are widely considered as possible green energy technology for new generation solar cell devices after silicon. Thanks to the efforts of both academic and industrial research, the highest single junction power conversion efficiency (PCE) of conjugated polymer solar cells is now over ~12%.^{14,15} The trends of OPV efficiency (in black curve) achievements against time can be found in figure I2, compared with cells fabricated from other materials.

Figure I2. The trend of development for solar cell efficiency. Black circle indicates the achievement of organic solar cells efficiency since 2001. (Adopted from National Renewable Energy Laboratory (NREL), USA)

To improve the OPV device performance, different methods are applied, such as synthesizing new polymer materials, adopting new device structures, or using new light trapping techniques. Hybrid plasmonic organic solar cells that utilize plasmonic effects of metal nanostructures to enhance charge carrier generation are one of the most studied methods, not only because of the strong light concentration abilities of plasmonic nanoparticles but also due to their tunable optical properties by structural design. Beyond the simple concept of light concentration, the presence of plasmonic metallic materials, nanoparticles or nanoantennas, in semiconducting polymers films will inevitably alter the physical properties of the polymers, not only the morphology but more importantly the photophysics dynamics. Therefore, the aim of my thesis is to study the interaction between plasmons and different species of photoexcitations in conjugated polymers using spectroscopic techniques.

More specifically, based on the concept of plasmon coupling to different degrees of freedom, for

example, plasmon-exciton coupling, plasmon-phonon coupling, we have discovered a new coupling mechanism, which is the plasmon-polaron coupling using infrared, not visible, metamaterials. We argue that this mechanism can be used to enhance polaron (charge carriers) photogeneration in conjugated polymers and further applied for improving organic bulk heterojunction solar cell performance. In addition, plasmon-coupling may also be found in other material systems with strong electron-phonon interactions.

To describe all the steps performed to achieve our goal of realizing plasmon-polaron coupling, the thesis is organized in the following structure. First of all I will introduce the basics of photoexcitations in conjugated polymer, especially the existence of polarons, as well as other neutral species. Characterization of the polymers' optical properties and their application in organic solar cells (*Chapter 1*). This will be followed by spectroscopic studies of a prototypical π -conjugated polymer, P3HT, in *Chapter 2*, to provide detailed background on the morphologies, electronic & optical properties. As a comparison for our new concept, I will start from the investigation of conventional methods of plasmon enhanced excitonic transition (absorption) in gold nanoparticle/P3HT system with IR-PIA spectroscopy (*Chapter 3*).

The discovery of plasmon-polaron coupling in IR metamaterial/P3HT hybrid system (*Chapter 4*) will be introduced in following the general concept of plasmon-polaron coupling, the design strategies and metamaterial fabrication process, and the experimental results showing plasmon-polaron coupling and polaron photogeneration enhancement by IR-PIA spectroscopy. Possible applications of plasmon-polaron coupling in organic bulk heterojunction solar cell will be finally discussed in *Chapter 5* with preliminary IR-PIA results of IR metamaterials/P3HT:PCBM system

showing enhanced photoinduced polaronic transitions. In conclusion, I will also discuss some other material systems that also contain polarons as charged species, where plasmon-polaron coupling could potentially be observed.

Chapter 1. Polarons in π -conjugated polymers

1.1 Primary photoexcitations in π -conjugated polymers

Above bandgap photoexcitation of semiconductors generates electron-hole pairs. Depending on their binding energy, these can be directly formed as free electrons in conduction band and holes in valence band (the case of most bulk inorganic semiconductors); or remain bound to form neutral quasi particles, excitons (the case of most organic materials). Excitons in conjugated polymers are neutral quasi particles of Coulombically bound electron-hole pairs with the electron localized on LUMO orbital and the hole on HOMO orbital.² To generate free polarons in conjugated polymers, the excitons need to undergo a secondary step of dissociation separating these bound pairs. An efficient organic photovoltaic device requires efficient exciton dissociation and subsequently reduced recombination during the charge transport process, as well as efficient charge collection at the electrodes.¹⁶⁻¹⁸

A general photophysical picture of transitions in π -conjugated polymers upon photoexcitation can be seen from the Jablonski diagram of a single molecule shown below (figure 1.1):²

(i) Light absorption (A): Light absorption is a typical inter-band transitions by which photons with energy above the (optical) bandgap are absorbed by the polymer and excite electrons from lower to higher energy levels. Excitation from neutral singlet ground state to neutral excited state forms electron-hole pairs (excitons). The transitions labeled as 0-0, 0-1, 0-2, and 0-3 stem from the Franck-Condon principle by which transitions occur between the lowest level (0) in the ground state and

different (0, 1, 2, 3) vibrational levels in the excited state, which are determined by the degree of electron wavefunction overlap. Subjected to optical excitation, electrons can either be promoted to the first excited state (S_1 state) or to higher states (S_n states). Only transitions between singlet states are allowed due to the conservation of total spin number ($\Delta S=0$).

(ii) Relaxation: fluorescence is a radiative relaxation process arising from exciton relaxation from excited to ground state, also known as exciton radiative recombination or radiative quenching of excitons. According to Kasha's rule,¹⁹ once excited the electron energetically relax to the bottom of the excited state (mostly S_1 state) within several femtoseconds (fs) or picoseconds (ps), and emission occurs from the bottom of the S_1 state to different vibrational levels in the ground state. Note that the non-radiative relaxation from S_1 to S_0 and internal conversion from S_n to S_1 via vibrational levels (in the form of heat) is not shown in figure 1.1.

(iii) Photoinduced absorption (PIA) of charged states: The grey dotted arrows in figure 1.1 indicates the dissociation process of (singlet) excitons into different excited states; excitons in higher excited states are referred as "hot" excitons, which possess excess energy due to the high excitation photon energy. Dissociation of excitons generates charges and charge states. Photoinduced absorption can then occur between charged states.²⁰ Polarons in polymers can be either delocalized over several units of one or two polymer chains, or localized onto a single site, both of which reorganize the polymer energy levels with new levels appearing within the bandgap and resulting in characteristic PIA spectral signatures.²¹⁻²³

(iv) Photoinduced absorption of excitons: once excited, electrons in the excited state can be further

promoted to higher excited states before relaxation; or they can undergo a non-radiative intersystem crossing process from S_1 state to triplet state (T_1) by flipping their spin, resulting in PIA from T_1 state to higher triplet states. The relaxation from T_1 state to ground state (S_0) (phosphorescence) is manifested at much longer lifetimes as compared to fluorescence, a process which is favorable for OLED applications.¹⁰ Despite of the large binding energy, it is still possible for triplet excitons to dissociate into free charges (process is not shown in figure 1.1). For instance, they can dissociate through either energy or charge transfer processes.²⁴⁻²⁶

Figure 1.1 Jablonski diagram of singlet, triplet exciton states and charged (polaron) states with a few vibrational side bands. Other processes such as non-radiative decay ($S_1 \rightarrow S_0$) or ($S_n \rightarrow S_1$), geminate and non-geminate recombination of excitons and polarons, and others, are not shown here.

1.2 Excitons in conjugated polymers

Excitons are one of the primary photogenerated species not only in organic materials but also in inorganic low dimensional systems such as quantum wells, quantum dots, two dimensional materials, etc. Their properties are widely exploited in optoelectronic applications, such as photovoltaics or light emitting diodes. Meanwhile, coupling of plasmons to excitons, especially in the strong coupling regime in which plasmon-exciton complexes or polaritons are formed, are also

important in the field of plasmonics (see *introductions in Chapter 4*). Here I will mainly introduce the exciton species in organic materials, especially conjugated polymers.

1.2.1 Excitons in organic molecules or crystals

Excitons in crystals are usually categorized into three types according to their radius and binding energy:²

Figure 1.2 Exciton types in crystals (a) Frenkel exciton with radius smaller than the lattice constant a_L ; (b) Wannier-Mott exciton with radius larger in comparison with the lattice constant; (c) charge-transfer exciton is an intermediate type of exciton.²

Frenkel type excitons are strongly bound and have small radius, thus reside on a single molecular site or monomer. They can usually be found in molecular, noble gas and ionic crystals, which have weak interaction between units. Moreover, the coupling between molecules in aggregates (e.g. J- and H-aggregates) results in the splitting of degenerated exciton level as in single molecules and subsequently forms non-degenerate exciton bands (with exciton bandwidth, W) in the excited state. The coupling between excitons and intramolecular vibrational modes (or intermolecular vibrations) leads to a distortion of single molecule vibronic progressions. Both absorption and fluorescence spectra contain information about the excitons and the optical properties of the aggregates (figure 1.3).

Figure 1.3 Frenkel exciton energy level splitting in dimer and N-aggregates for two types of aggregates: J-aggregates (Left) and H-aggregates (Right).

Wannier-Mott excitons have large radius and hence low binding energies; their energy spectrum resembles the one of hydrogen atoms, with a series of modified Rydberg transitions below the conduction band. From the classical solid state theory,²⁷ the exciton energy levels E_n^K are expressed as, $E_n^K = E_g - \frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 \epsilon^2 n^2} + \frac{\hbar^2 K^2}{2(m_e^* + m_h^*)}$, where E_g is the band gap of the solid (the zero of energy is at the top of the valence band), μ is the reduced effective mass derived from the effective mass of electrons (m_e^*) and holes (m_h^*), and ϵ is the dielectric constant of the surrounding material.

Figure 1.4 The Wannier-Mott exciton levels below the conduction bands at the vicinity of $K=0$.

Charge-transfer (CT) excitons are an intermediate type of excitons, for which electron and hole

reside in neighboring sites or molecules; these type of excitons are mostly observed in donor and acceptor molecules.

1.2.2 Excitons in conjugated polymers

In the context of conjugated polymers, both of Frenkel excitons and Wannier-Mott excitons exist in the quasi-one dimensional intra-molecular chains. Inter-chain excitons, however, are given different names based on their separation distance, for example “charge transfer excitons” or “polaron pairs”.²⁸ Frank Spano *et al.*, adopted the ideas developed by Kasha and coworkers for small molecular chromophore aggregation effects (J- and H-aggregates) to study the packing behavior, exciton bandwidth, and the exciton coherence length of conjugated polymers from their absorption and fluorescence spectra.^{29,30}

The binding energy magnitude of excitons in polymers can be estimated from Coulomb interaction,

$$V = \frac{e^2}{4\pi\epsilon_r\epsilon_0 r},$$

where ϵ_r is the dielectric constant of the surrounding medium, ϵ_0 is the vacuum

permittivity, r is the electron-hole separation distance. The low dielectric constant (~ 3) in conjugated polymers leads to weak charge screening and results in a strong Coulomb interaction with an exciton binding energy of 0.2-0.5 eV, that is larger than the thermal energy $k_B T$ (~ 25 meV).³¹

To develop efficient organic photovoltaics or photodetectors, such large exciton binding energy must be overcome to facilitate exciton dissociation. Apart from applying additional electric fields, the charge transfer process between two different donor (D) and acceptor (A) materials is widely used to achieve efficient charge separation.¹⁸ Interfacial charge transfer (CT) states/exciton reside between D-A interfaces with holes remaining in donor and electron being transferred to acceptors,

but remaining bound by Coulombic attraction. The electronic processes occurring at D-A interfaces and the role of CT states for charge separation have been under intensive investigations.³²⁻³⁴

1.3 Polarons in conjugated polymers

Polarons are quasi particles formed by strong coupling of charge carriers and phonons (also referred as localized lattice distortion), which can be described as charge carriers self-trapped within potential wells of the lattice (note that weak-coupling polarons, on the other hand, are not self-trapped species, and they are not considered here).^{35,36} They are usually found in polar and ionic solids, molecular crystals, and polymers thanks to the strong electron-phonon interaction.

The formation of polarons or self-trapping, according to solid state theory, requires that the final states of the system (polarons or coupled charge and phonon) should have reduced energies as compared to those of delocalized charge carriers and distorted lattices, which can be expressed as: $\delta E_1 + (\delta E_2 + \delta E_3) < 0$, where $\delta E_1 > 0$ is the localization energy of the final stabilized system, $\delta E_2 < 0$ is the lattice distortion energy, and $\delta E_3 < 0$ is the charge delocalization energy or, in other words, the binding energy.² This can also be described in terms of the self-trapped polaron formation requiring its electronic frequency $E_{binding}/h$ to exceed the atoms' characteristic vibrational frequency ν .³⁶ Polarons have large effective mass and low mobilities since charge carriers need to move in association with atom or molecular distortion, and they display characteristic phonon-broaden absorption band corresponding to the photoexcitation of self-trapped carrier, similar to immobile carriers captured by traps.

In the following we introduce polaron properties in more detail, such as their formation, their formal

description, transport behavior and optical properties, first in inorganic materials and molecular crystals and then in conjugated polymers.

1.3.1 Polarons in inorganic solids

Landau in 1933 first introduced the general concept of polaron, in a short paper describing the self-trapping properties of electronic carriers traveling through ideal ionic crystals.³⁷ Theories and experiments concerning the physical properties of effective mass, binding energies, transport behavior, etc. of polarons, were subsequently brought out by scientists.^{36,38,39} Depending on the electron-phonon interaction range and size, polarons in solids are mainly categorized into two species: **large polaron** and **small polaron** (bipolaron and other species with extended polaron concepts, such as magnetic polarons, piezopolarons, polaron-excitons, etc. will not be considered here).

The classification of these two species mainly depends on their size; **large polarons** have a large size with radius larger than the lattice constant, and are subjected to long-range electron-phonon interactions. Large polarons are often referred as *Fröhlich polarons* and modeled by the *Fröhlich Hamiltonian*, which describes the electron-phonon coupling by electrons and constant longitudinal-optical (LO) phonons and take the continuum approximation assuming the spatial extension of the polaron is large enough compared to the lattice parameters (this is quite true for large polaron).³⁹⁻⁴¹

The *Fröhlich Hamiltonian* can be expressed as

$$H = H_e + H_{e-ph} + H_{ph} = \frac{p^2}{2m_b} + \sum_k (V_k a_k e^{i\mathbf{k}\cdot\mathbf{r}} + V_k^\dagger a_k^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}}) + \sum_k \hbar\omega_k a_k^\dagger a_k ,$$

where the first term is the kinetic energy of electron in the band with effective mass m_b , the second

is interaction of electron with LO phonon with a constant angular frequency ω_{LO} , and V_k are the Fourier components of the electron-phonon interaction, $V_k = -i \frac{\hbar \omega_{LO}}{k} \left(\frac{4\pi\alpha}{V} \right)^{1/2} \left(\frac{\hbar}{2m_b \omega_{LO}} \right)^{1/4}$ with dimensionless *Fröhlich coupling constant* α , $\alpha = \frac{e^2}{\hbar} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \sqrt{\frac{m_b}{2\hbar \omega_{LO}}}$, ϵ_∞ and ϵ_0 are electronic and static dielectric constant of the solid, respectively. The *Fröhlich coupling constant* characterizes the electron-phonon coupling strength with $\alpha > 1$ for strong coupling, while $\alpha < 1$ for weak coupling. The large polaron has a large mobility ($\mu > 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) and its transport is dominated by phonon scattering. The optical absorption of large polaron resides in infrared to THz region, where light can excite the self-trapped polaron in “donor” levels below the unbound delocalized state up to several excited bound states, or directly into delocalized states. The threshold for photoexcitation, or in other words the ground state of large polarons in the potential well, is $3E_p$ where E_p is its net polaron binding energy.³⁶

Figure 1.5 (Left) The electronic levels of large-polaron type of self-trapped carriers below the unbound continuum states. (Right) The large polaron absorption coefficient plotted against the excitation photon energy in units of polaron binding energy.³⁶

Small polarons are small in size with radius comparable to the lattice constant, therefore small polarons are more or less localized in the unit cell of the solid. Different from large polarons, the formation of small polarons is mainly due to short-range forces, which make the *Fröhlich continuum approximation* no longer adequate. A complete analysis of small polaron requires *ab*

initio calculations, while the relatively simpler **Holstein model** originally based on ideal molecular crystal⁴²⁻⁴⁴ is widely considered as a generic model for studying small polarons. Unlike the large polaron, the transport of small polaron is a phonon assisted hopping process, therefore its mobility is thermally activated, $\mu \sim e^{-\frac{E_a}{k_B T}}$ and it can be distinguished from the appearance of two different temperature dependent hopping components: adiabatic hopping, $\mu \sim \frac{1}{T} e^{-\frac{E_a}{k_B T}}$ and nonadiabatic hopping, $\mu \sim \frac{1}{T^{3/2}} e^{-\frac{E_a}{k_B T}}$. Since a small polaron is in most cases confined on a single site, the absorption of photon excites the small polaron in low-lying state of one site to higher energy state of an adjacent site. Therefore its absorption spectrum peaks at $2E_p$, correspond to the transition from ground state on one site to an adjacent site without atomic displacement (in accordance to the Franck-Condon principle). And its absorption coefficient can be written as,

$$\alpha \propto \frac{1}{\hbar\Omega} \exp\left(-\frac{(2E_p - \hbar\Omega)^2}{4E_p \hbar\omega_0}\right);$$

$\hbar\Omega$ is the photon energy, and ω_0 is the average phonon frequency.^{36,45} Meanwhile, an elevated temperature leads to a broader absorption band, as its width results from the atoms of both states vibrating around their equilibrium positions.

Figure 1.6 (Left) Photoexcited transition for a small-polaron. (Right) The small polaron absorption efficient plotted against the excitation photon energy with elevated temperature (a $\rightarrow$ c).³⁶

In addition to conventional polar, ionic materials and molecular crystals, the concept of polaron and its theoretical description has also been extended to other emerging materials, such as colossal

magnetoresistance perovskites, high- T_c superconductors (bipolaron in this case),⁴⁶⁻⁴⁸ fullerenes and carbon nanotubes,⁴⁹ semiconductor nanostructures⁵⁰ and, as will be discussed below to conjugated polymers.

1.3.2 Polarons in conjugated polymers

To introduce polarons in conjugated polymers, their formation, energy states, and transport, we shall start describing their electronic structure, namely electronic properties due to π -electrons.

Electronic structure of conjugated polymers

π -conjugated polymers are carbon-based molecules consisting of π -electrons as a result of sp^2 hybridization. The ground state of the carbon atom is $1s^2 2s^2 2p^2$, with two paired s electron and two unpaired p electron. To form C-C bonds, one of the $2s$ electron is excited to $2p$ orbital resulting in four outer valence orbitals, $2s$, $2p_x$, $2p_y$, $2p_z$, and these excited electron undergo a hybridization process with new hybrid electron states (orbitals). In the sp^2 hybridization, $2s$ electron mix with p_x , p_y orbitals to form three hybrid sp^2 orbitals that are coplanar and oriented 120 apart from each other, while the remaining $2p_z$ orbital lies perpendicular to the plane.

Figure 1.7 sp^2 hybridization and formed bonds in ethylene, C_2H_4 .

Two σ bonds from sp^2 orbitals connect two carbons to form the backbone of the polymer with highly localized electrons, while the overlapping of two neighboring $2p_z$ orbitals creates a π -bond that establishes delocalized electron density above and below the plane. In the case of sp^2 hybridization polymers, there is one π -electron per carbon atom corresponding to a half-filled π -electron band.^{2,51}

Take the simplest conjugated polymer polyacetylene (PA) as an example, instead of showing metallic behavior due to the half-filled π -electron band, the one-dimensional structural instability leads to a structural distortion (referred as Peierls distortion⁵²) which opens up a bandgap in the band structure with filled valence band (HOMO, bonding states, π) and empty conduction band (LUMO, antibonding states, π^*), in figure 1.8 (b) to (c). Specifically, the Peierls distortion results in the dimerization of the equal length σ bonds transforming them into alternating “single” and “double” σ -bonds states with two different bond lengths.⁵³ As a result, the PA preserve twofold *degenerated ground states* of two phases, shown in figure 1.8(a).

Figure 1.8 (a) The degenerate ground state of polyacetylene structure with two phases having the same energy, and the undimerized structure that forms an unstable state (the potential curve is plotted against the dimerization coordinate). (b) Band structure of undimerized structure of $E_k = 2t_0 \cos ka$ in the reduced zone, where a is lattice constant. (c) Band structure of dimerized structure in the reduced zone with an optical bandgap of $E_g = 2\Delta_0$. The Fermi level is at the wave vector of $k_F = \pi/2a$.⁵³

Nondegenerate ground state polymers are another class of widely studied conjugated polymers.

They have two structures with different free energy, so that the aromatic structure is stable structure in the neutral state, while the quinoid structure has a lower ionization potential and larger electron affinity, as shown in figure 1.9. Upon doping, a local structural deformation around the charges shifts the deformation coordinate by Δr causing a lattice distortion, and hence the molecule relaxes to the quinoid structure (see more detailed in next section **polaron states in bandgap**).^{54,55}

Figure 1.9 Schematic potential curve of nondegenerate ground state poly (p-phenylene) (PPP), where the aromatic and quinoid structures have two different energies (the potential curve is plotted against the deformation coordinate).

According to the molecular orbital (MO) theory, the bonding π -bands (π) are highest occupied molecular orbitals (HOMO) lying above the σ bands, and the antibonding π -bands (π^*) are lowest unoccupied molecular orbitals (LUMO). The relatively low band gap of π - π^* transitions and delocalization of π -electrons are responsible for the semiconducting properties of π -conjugated polymers.⁵⁶

Polaron states in bandgap

Polarons in conjugated polymers are radical cation and radical anion carrying charge 1 and spin 1/2, and they can be either positive or negative, respectively. Conversely *bipolarons* have charges 2 and spin 0, and can be either positive (dication) or negative (dianion).

Figure 1.10 Polaron and bipolaron species formed via chemical doping that is oxidation and reduction processes.

To explain the formation of polarons and their intra-bandgap states, we shall start considering the picture of polaron formation in molecular monomer and extend it to molecules with repeating monomer units in the frame work of molecular orbital theory; meanwhile the prediction of polaron levels from SSH model will also be explained.

For molecular monomer with non-degenerated ground state, the ionization process can follow two different pathways.^{54,55,57,58} Path (a) follows the Franck-Condon principle by which electrons in the ground state (A) are ionized by direct vertical transitions, and ionized states then relax to stable ionized ground states having different lattice coordinates. The relaxation energy gained in this process is represented by E_{relax} . From the structural point of view, the molecule possesses equilibrium benzenoid-like geometry at neutral ground state (A), while quinoid-like geometry with radical cation (or anion) at ionized ground state with a shift of conformational coordinate (D) (see previous section); therefore, it can be understood as a vertical ionization transition exciting the molecule to an unstable benzenoid-like structure with charges (red dash curve, B, in figure 1.11), which then relaxes to quinoid-like equilibrium geometry accompanied by lattice distortion, Δr . On

the other hand, path (b) sees the molecule with stable molecular structure to be initially distorted to the excited state with quinoid-like geometry at the expense of elevated energy, E_{dis} . Electrons in this state can be subsequently ionized to stable charged states. It is easy to deduce that E_{dis} is also the relaxation energy of the molecule, E_{relax} , when molecules in unstable ionized state relax back to the equilibrium state. Combining path (a) and (b), the polaron formation condition hence requires

$$E_{relax} = E_{ipv} - (E_{ipd} + E_{dis}) = \Delta E - E_{dis} > 0.$$

Figure 1.11 (Left figure) Electron ionization process in single molecule following Franck-Condon principle, path (b) represents the formation of polarons. (Right) The HOMO and LUMO shift upon lattice distortion, the two ionization energies are shown in respect to the Fermi level.

In the MO picture considering one-electron levels, the ionization process accompanied by the lattice distortion corresponds to an up shift of the HOMO level to (HOMO+1) level, and a down shift of the LUMO level to (LUMO-1) level, forming two new localized electronic levels. The energy is elevated by ΔE respect to the HOMO level of neutral states. In the molecular picture considering the intra-molecular contribution only, the polaron binding energy E_{pol} is equal to the geometry relaxation energy, and since the charged state relaxation energy E_{relax} and the neutral state distortion energy E_{dis} are equal, $E_{pol} = E_{relax} = E_{dis}$. The reorganization energy (λ_{reorg}) is one of the key factors in Marcus theory^{59,60} in describing the charge transfer process, and the intra-molecular

reorganization energy associates with the monomer geometry changes upon charge transfer taking place; since the inter-molecular is not considered here, the reorganization energy is given by

$\lambda_{reorg} = \Delta E = E_{relax} + E_{dis}$. Therefore, the polaron binding energy is half of the reorganization energy,

$$E_{pol} = \lambda_{reorg} / 2.^{58}$$

In the molecular picture, coupling between the repeating units results in the formation of π and π^* bands via the splitting from the monomer degenerate HOMO and LUMO levels. Considering the conjugated polymers' semiconducting features, π and π^* bands can be viewed as valence bands and conduction band, respectively. Similar to the single molecule description, the ionization process and formation of localized polaron can be conceptually divided into: first the local lattice distortion of the polymer shifts the HOMO and LUMO of the polymer leading to the appearance of two new intra-bandgap states, one filled and the other empty; further removal of electron (in the case of positive polaron) leaves one of the intra-bandgap states half filled, while the other remains empty.⁵⁷

Figure 1.12 Conceptual illustration of polaron formation in polymers. (Left) Electron excitation from valence band. (Middle) the local lattice distortion shifts the HOMO and LUMO states of the polymer leading to the appearance of two new intra-bandgap states, one fully filled and the other empty. (Right) the formation of positive polaron states, one half filled, and the other one empty.

SSH and other models⁵³

The *Su-Schrieffer-Heeger (SSH) model* was first used to describe the excitations of polyacetylene

(PA), and was widely studied and developed by researchers. The SSH model is essentially a “single-electron” model on one dimensional polymer chain, where the interactions between the σ -electrons and π -electrons are neglected and only π -electrons from each carbon atom site are considered mobile. While the many body electron-electron interactions are also neglected, the electron-phonon coupling is emphasized and takes a dominant role. Under the tight-binding scheme (with assumption of nearest-neighbor interactions), the quasi-1D model where dimerization coordinates “ u ” are used to characterize nuclei or lattice displacement, leads to the SSH Hamiltonian:

$$H_{SSH} = H_{\pi} + H_{\pi-ph} + H_{ph}$$

where

$$H_{\pi} = -t_0 \sum_{n,s} (c_{n+1,s}^{\dagger} c_{n,s} + c_{n,s}^{\dagger} c_{n+1,s})$$

is the electron-transfer Hamiltonian describing the hopping of single π -electron between nearest-neighbor sites, and t_0 is the electron transfer energy. The second term:

$$H_{\pi-ph} = \alpha \sum_{n,s} (u_{n+1} - u_n) (c_{n+1,s}^{\dagger} c_{n,s} + c_{n,s}^{\dagger} c_{n+1,s})$$

describes electron-phonon coupling, where only linear lattice displacements u_n are considered, and α is the coupling constant. The phonon term is given by the conventional phonon model:

$$H_{ph} = \sum \frac{p_n^2}{2M} + \frac{K}{2} \sum (u_{n+1} - u_n)^2,$$

where p_n is the momentum conjugated to u_n , M is the mass of (CH) group, and K is the spring constant.

The SSH model is essentially based on the **Hückel model** with more refined approximation, which includes the electron-phonon interaction term in the Hamiltonian. However, by neglecting the many body electron-electron interaction, the existence of excitons and their properties are not accounted by this model. To solve this problem, several other models have been developed with inclusion of

more interactions terms, for example the *Pariser-Parr-Pople (P-P-P) model* that also takes into account long-range electron-electron interactions.^{56,61}

Though it is a rough approximation, the SSH model has successfully predicted the properties of characteristic charged species in polymers formed upon doping, and resulting modifications of electronic structure. Specifically, the charge conjugation symmetry or electron-hole symmetry feature of the continuum model SSH Hamiltonian naturally predicts the appearance of two polaron states with an equal separation away from valence and conduction band; moreover in this tight-binding model, the polaron level above the valence band is associated with the polaron binding energy, E_{pol} .

Meanwhile, several works have attempted to model polarons in polymers starting from the *Holstein* molecular crystal model, which yielded similar results of the SSH model.^{62,63} The Holstein model has been further applied to describe polymer π -stacking aggregates, and to predict the resulting spectroscopic signatures of delocalized polarons.⁶⁴

Doping of polarons and polaron generation enhancement

Similar to inorganic semiconductor counterparts, the semiconducting polymers can be doped by introducing extra charges onto the polymer chains to alter their electrical properties. Doping can be achieved by chemical and electrochemical doping, photo-doping and charge injection.^{7,55,65}

In **chemical and electrochemical doping**, the polymer undergoes a charge transfer process through the mechanism of oxidation or reduction by electron donors or acceptors for p-type or n-type doping,

respectively (refer to figure 1.10). Taking the polaron generation for example, by removing one electron from the non-degenerate ground state type polymer results in the formation of a radical cation, meanwhile the localized structure relaxes to quinoid-like charged ground state; the further removal of one electron leads to the formation of another polaron or bipolaron with a total charge 2 and spin 0.

Charge injection doping consists of injecting the charge directly from a metal surface via a charge-transfer process. Charge injection doping can be used for fabricating light emitting diode (OLED) and field effect transistor (OFET) devices with conjugated polymers as active materials.

In the case of **photo-doping** by photoexcitation, photogenerated excitons (electron-hole pairs) undergo a series of processes to dissociate into free charge carriers (as described in *Section 1.1*). The mechanism of photo doping plays an important role in photovoltaics applications (OPV). In studies of polymer photoexcitation mechanisms, the debates of whether the polarons can be directly generated last for decades.⁶⁶⁻⁷⁷ According to the SSH tight-binding model, the exciton binding energy is so small that polarons can be directly generated; whereas in the molecular picture, the generation of polarons has to be a secondary process after the tightly bound exciton dissociation. Various ultrafast experiments on different material systems have been carried out and results interpreted in either of these two ways; although a definitive conclusion is still lacking, it somehow acceptable that polaron photogeneration is an ultrafast process occurring at a time scale smaller than 200 fs, regardless whether it is a direct or an indirect process. The branching ratio of polaron and exciton direct photogeneration at ultrafast time scale can be as high as 30%.⁷³

1.4 Donor-acceptor systems for polymer solar cells

To enhance charge photogeneration in conjugated polymers, donor-acceptor systems are widely studied in solar cells applications. Electron acceptor materials (n-type) are blended with the polymers (usually p-type); the built-in field created by the HOMO and LUMO levels offset of the two materials interface provides additional energy to overcome the exciton binding energy, and hence enhance exciton dissociation.^{16,18} In the general picture of charge photogeneration in solar cells, excitons have to migrate to the donor-acceptor interface to be separated; in order to compensate the short exciton diffusion length, so called “bulk heterojunctions” that blend polymer with electron acceptors, typically fullerene and its derivatives, have become the classical structure for polymer solar cells.⁷⁸⁻⁸⁰ Ultrafast charge transfer processes complete at the polymer-fullerene interface within the first 100 fs upon photoexcitation.^{81,82} Separated charges can then be transported via the polymers and fullerene network and be collected at the electrodes. While the bulk heterojunction contains a large number of internal junctions, the discontinuous blend structure is not favorable for charge transport. Additional treatments are required to induce the phase separation between polymer chains and the fullerenes. Optimal power conversion efficiency of OPV devices results from the trade-off between large interfacial area and improved phase separation, thus the morphology of the blend film is one of the key parameters for thin film processing.^{83,84}

The most accepted charge generation scheme in bulk heterojunction consists of^{17,85} (a) light absorption in the polymer generates spatially localized excitons; (b) excitons diffuse to donor-acceptor interfaces; (c) exciton dissociate directly to free charges nearby the interfaces, or fall into the manifold of charge transfer (CT) states in the form of charge transfer excitons or polaron pairs, with hole in polymer and electron in fullerene; (d) the charge transfer excitons can further dissociate

into free charge carriers forming hole polarons in the polymer and electron polarons in the fullerenes;

(e) charge carriers move under the influence of the internal electric field and are eventually collected at the electrodes. This process is schematically shown in figure 1.13 with single-particle representation.

Figure 1.13 Schematic representations of the charge generation processes in a donor acceptor system.

As will be discussed in the next chapter, P3HT:PCBM bulk heterojunctions can yield higher photocurrent as well as characteristic spectroscopic signatures of polarons, all of which indicate an enhancement of charge carrier photogeneration due to the increased probability of exciton dissociation.

1.5 Spectroscopic characterization of conjugated polymer photoexcitations

1.5.1 Linear absorption spectroscopy

Inter-band transitions

In the molecular picture where the dominant photoexcitations are excitons, photons absorbed by polymer molecules promote electrons from the neutral ground states S_0 to neutral excited states S_1 to S_n , according to the Franck-Condon principle.

Light absorption due to inter-band transitions follows the Lambert-Beer's law $I = I_0 10^{-A}$, where I_0 and I are the incident light intensities before and after the sample and A is the absorbance (or optical density, OD) given by $A = -\lg(\frac{I}{I_0}) = -\lg(T) = \varepsilon \cdot C \cdot l$; where T is the transmittance, ε is the molar extinction coefficient, C is the concentration of absorbing species, l is the path length. This formula is mostly used by chemists in characterizing the absorption of molecules in solution.

Another form of expression mostly used by physicists to characterize bulk samples is $I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)d}$, where α is the linear absorption coefficient and d is the sample thickness. This can be derived from $dI(\lambda) = -\alpha(\lambda) \cdot I(\lambda) \cdot dx = -\sigma_{abs}(\lambda) \cdot N \cdot I(\lambda) \cdot dx$, where $\alpha(\lambda) = \sigma_{abs}(\lambda)N$, $\sigma_{abs}(\lambda)$ is the absorption cross-section, N is the density of absorbing centers with a unit of cm^{-3} . Considering also the Fresnel type losses through surface reflection R , the formula becomes $I(\lambda) = (1 - R(\lambda))^2 I_0(\lambda)e^{-\alpha(\lambda)d}$. This is because the light intensity used in the equation of $I_{in} = I_{in,0}e^{-\alpha d}$ is that at the inner surface of the solid material.⁸⁶ Hence the absorption coefficient can be measured and calculated by $\alpha(\lambda) \cong \frac{1}{d} \{-\ln T(\lambda) + 2\ln[1 - R(\lambda)]\}$. From electrodynamics

theory, one can easily correlate the absorption coefficient with the imaginary part of the complex refractive index ($\hat{n} = \sqrt{\hat{\epsilon}} = \sqrt{\epsilon' + i\epsilon''} = n + i\kappa$) through $\alpha = 4\pi \frac{\kappa}{\lambda}$, where λ is the light wavelength and κ is the extinction coefficient.

Intra-band transitions and Raman scattering: vibrational absorption

Thermally excited molecular vibrations (and rotations for small molecules) can be probed by the absorption of radiation energy in the mid- and far- infrared spectral region. These vibrational modes can be represented as sub-levels within each electronic state potential surface as shown in figure 1.14; transitions between these levels are referred to intra-band transitions.⁵¹ Practically, the frequencies of different vibrational modes are *fingerprints* for specific functional groups and particular chemical structure motions.⁸⁷

Figure 1.14 Vibrational transitions within the potential well of one electronic state.

Raman scattering provides another way of detecting vibrational modes of the molecules based on the photon scattering.⁸⁸⁻⁹¹ The scattering of an incident photon can be either elastic, corresponding to the Rayleigh scattering, or inelastic, accompanying with the emission or absorption of (optical) phonons. The frequency shift due to inelastic light scattering corresponds to the Raman scattering

of Stokes or anti-Stokes processes, respectively (in figure 1.15). Spontaneous Raman scattering doesn't require the existence of higher excited states, instead molecules can be excited to intermediate "virtual" states and relax back to different vibrational levels of the ground state. If the "virtual" state coincides with one of the real excited states of the molecules, the process is referred to resonance Raman scattering. The resonant coupling of incident light to the molecules' excited states can enhance the scattering intensity by several orders of magnitude compared to spontaneous Raman scattering. Resonance Raman scattering lifetime is much shorter than that of fluorescence process. As a result, fluorescence is independent to the excitation light wavelength according to the Kasha's rule, while resonance Raman scattering is incident light wavelength dependent as shown schematically in figure 1.15.

Figure 1.15 (Left) Rayleigh scattering and spontaneous Raman scattering with Stokes and anti-Stokes shift shown. (Right) Resonance Raman scattering and fluorescence following Kasha's rules.

Selection rules

Both inter- and intra-band transitions between different states or levels are subjected to certain dipolar transition selection rules. The absorption cross section can be expressed as

$\sigma \sim |\mu|^2 = |\mu_{ij}(Q_0)|^2 \left| \langle \chi_{iv} | \chi_{ju} \rangle \right|^2 = |\mu_{ij}(Q_0)|^2 F_{vu}$; the selection rule of electronic transitions is set by

the electronic dipole moment, $\mu_{ij} = \langle \psi_i | \hat{\mu} | \psi_j \rangle \cong \mu_{ij}(Q_0)$, where j and i are initial and final states, respectively, and $\hat{\mu}_e$ is the electronic dipole operator. A dipole allowed inter-band transition requires μ_{ij} being nonzero, which requires the j to i transition preserving inversion symmetry inversion (initial and final states must have different parity). From *Section 1.1*, the conservation of electron spins from the electronic transitions is also required.

For intra-band transition, one expand the dipole operator as a function of the normal mode coordinates, similar to the derivation of the Franck-Condon principle, we get

$$\hat{\mu} \cong \mu(Q_0) + \sum_{k=1}^{3N-6} \left(\frac{\partial \hat{\mu}}{\partial Q_k} \right)_0 (Q - Q_0) + \dots$$

For the electron within one potential well, its vibrational dipole transition moment becomes

$$\mu_{ij} = \langle \psi_i | \hat{\mu} | \psi_j \rangle \cong \mu(Q_0) \langle \psi_i | \psi_j \rangle + \sum_{k=1}^{3N-6} \left(\frac{\partial \hat{\mu}}{\partial Q_k} \right)_0 \langle \psi_i | (Q - Q_0) | \psi_j \rangle,$$

where $\langle \psi_i | \psi_j \rangle = 0$ due to the orthogonal property of the two wavefunction. Therefore, molecules

are vibrational “infrared active” when $\frac{\partial \hat{\mu}}{\partial Q_k} \neq 0$, which means molecules should possess a dipole

change respect to one of its normal mode coordinate when vibrating.

As for in Raman scattering, the light scattering process is determined by the electric field induced dipole with moment $P = \alpha E$, where α is the polarizability. The polarizability can be expanded respect to the normal mode coordinate in a similar way, thus Raman modes are active only when the term

$$\frac{\partial \alpha}{\partial Q_i} \text{ is nonzero.}$$

Symmetry and group theory

The symmetry requirement in selection rules can be clearly illustrated using the irreducible representation of the molecule point group. Most π -conjugated polymers with quasi-one-dimensional chain-like structure have C_{2h} point group and its irreducible representation is shown in the table 1.^{53,92} The interband photoexcitation process in single molecule in the formalism of Jablonski diagram can be further depicted in terms of the irreducible representations, A_g and B_u , where g stands for gerade (even) and u stands for ungerade (odd) parity, as shown in figure 1.16. From the selection rules of dipolar transitions, only transitions between u and g states are allowed, while u to u and g to g transitions are forbidden.

Table 1. (Right) Irreducible representation of C_{2h} group. (Figure on the left) The polyacetylene molecule belong to C_{2h} group.

C_{2h}	E	C_2	i	σ_h	$h=4$	
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y

Figure 1.16 Electronic transitions together with molecular symmetry. Arrows indicate allowed (dipolar) transitions, which are typically $g \rightarrow u$ or $u \rightarrow g$.

The vibrational infrared absorption corresponds to the dipole operator, x, y, z , in Table 1; while the

Raman scattering corresponds to the second order terms. Specifically for polymers with C_{2h} point group (P3HT is one of them), the infrared active modes correlate to B_u symmetry, and the Raman active modes correlate to A_g symmetry.⁹³ In this case the infrared vibrational spectroscopy and Raman scattering are complementary to each other.

1.5.2 Photoinduced absorption spectroscopy

Polaron states and photoinduced absorption (PIA)

Polaron absorption in semiconducting conjugate polymers is a nonlinear response to light: photogeneration of polarons modifies the energy bands of the polymer with inducing two new intra-bandgap energy levels, the P_1 and P_2 states. Photoinduced absorption (PIA) spectroscopy requires two beams to detect the polaron states: one beam is used for light excitation, while the second broadband light is used to probe the transitions between polaron states, HOMO and LUMO.

For positive polarons (radical cations), the P_1 state is singly occupied and the P_2 state is empty with total spin 1/2, while for negative polarons (radical anions), the P_1 state is doubly occupied and the P_2 state singly occupied with total spin 1/2.^{53,55,94} Figure 1.17 labels the allowed infrared polaron transitions. With the same transition energies between HOMO to P_1 state in positive polaron and P_2 state to LUMO in negative polaron, one cannot distinguish the positive and negative polarons simply by photoinduced absorption spectra. Since the new transitions that appear upon photoexcitation are also subjected to dipole transition and selection rules, the transitions of HOMO to P_2 and P_1 to LUMO are symmetrically forbidden (see *Section 1.5.1*).

Figure 1.17 Schematic representations of electronic states of positive and negative polarons. Black arrows indicate the electron spins, red thick arrows indicate allowed electronic transitions.

In the case of doubly charged conjugated polymers, two new bipolaron (dication or dianion) states appear within the bandgap. For positive bipolarons both of the two new states are empty, while, for negative bipolarons, they are both doubly occupied. Since the structural distortions for bipolarons are larger than those for polarons, the bipolaron states are further separated from the HOMO and LUMO level of the polymer.

Figure 1.18 Schematic representations of electronic states of positive and negative bipolarons. Black arrows indicate the electron spins, red thick arrows indicate allowed electronic transitions.

Infrared-active vibrational (IRAV) modes

With charge carriers, generated either by photo or by chemical doping, present on the in polymer

chains, polaron transitions accompanied by *infrared active vibrational (IRAV) modes* manifest as sub bandgap absorption spectra.⁵³ The IRAV modes are symmetric even parity Raman-active vibrational modes (A_g) which become visible in IR spectroscopy (infrared active, odd parity) because of the local translational symmetry breaking of polymer chains due to the charge. IRAV modes have one-to-one correspondence to the strongest polymer Raman-active modes that can be observed in resonance Raman scattering spectroscopy. Their intensity is proportional to the charge carrier concentration, which makes them unique signatures for charge carriers.⁹⁵

Specifically, as a result of the distortion around the charge carriers, one (or more) for each of the localized optical-phonon modes (with enhanced infrared oscillator strength) are split off. IRAV modes frequencies are determined by the restoring force that resists the translation of charges, characterized by a “pinning” potential; the lowest frequency mode correlates directly to the strength of the pinning potential. In 1982, Horovitz first described these IRAV modes in *trans*-(CH)_x (PA)⁹⁶ analytically using amplitude mode formalism (AM), which was successfully applied for the description of resonance Raman-active A_g modes. The theory was originally derived with adiabatic approximations, and the renormalized “bare” phonon frequencies (IR frequencies) were given by the equation,

$$D_0(\omega) = \sum_n \left(\frac{\lambda_n}{\lambda} \right) \frac{(\omega_n^0)^2}{\omega^2 - (\omega_n^0)^2} = -\frac{1}{1-\alpha} \quad (1.1)$$

where $D_0(\omega)$ is the phonon response function, ω_n^0 are the “bare” phonon frequencies, λ_n are the electron-phonon coupling constant for the n th mode with $\lambda = \sum_n \lambda_n$, and α is the pinning parameter related to the pinning potential. The number of IRAV modes equals that of bare phonon modes. The frequencies of IRAV modes are given by the equation above, which are intersections between $D_0(\omega)$ and $-1/(1-\alpha)$ (line a) (in figure 1.19). Their conductivity $\sigma(\omega)$, and hence strength of IRAV

absorption ($\text{Re}[\sigma(\omega)] \approx \alpha_{abs}(\omega)$), are given by,

$$\sigma(\omega) = -i\omega \left(\frac{e^2 \rho_c}{M_d \Omega_0^2} \right) \frac{D_0(\omega)}{1 + (1 - \alpha) D_0(\omega)} \quad (1.2)$$

where ρ_c is the average charge density, M_d is the kinetic charge mass and $\Omega_0^{-2} = \sum_n \left(\frac{\lambda_n}{\lambda} \right) (\omega_n^0)^{-2}$.

Figure 1.19 Phonon response $D_0(\omega)$ intersected with the $-1/(1-\alpha)$ to give the IR frequencies (intersection of line a, $-1/(1-\alpha) = -1.26$), which shifts respect to bare phonon and Raman frequencies (intersection of line b).⁹⁶

The experimental features of IRAV modes can be predicted from the formula (1.1) & (1.2):⁹⁷ (1)

The lower shift of their frequencies respect to resonance Raman frequencies are due to the pinning potential from the electron-phonon interaction; (2) The relatively strong absorption of IRAV modes is due to the large charge oscillation strength due to the small kinetic mass of charged excitations.

Several theories were later developed with better refinements, for example Zerbi, et al. used the effective conjugation coordinate (ECC) to describe the correlation of the IRAV modes with infrared activation of totally symmetric modes.⁹⁸⁻¹⁰⁰ ECC describes the molecule geometry changes along the so-called 6-coordinate due to the transitions from ground state to the excited electronic state, and the bare phonon frequencies are calculated from first principles, adjusted by experimental results; Ehrenfreud and Vardeny found a link between the doping induced sub-bandgap electronic states and the doping induced IRAV modes based on the linear response theory proposed by Soos et al.¹⁰¹ Horovitz et al. later extended the amplitude mode (AM) model to a nonadiabatic situation

to explain the anti-resonance and quantum interference features found in RR-P3HT photoinduced absorption spectroscopy, where the IRAV modes overlap with the polaronic transitions in the spectra.¹⁰²

Chapter 2. P3HT: A prototype polymer for charge photogeneration and transport

2.1 Introduction to P3HT and its applications

Poly(thiophene) (PT) is a typical nondegenerate ground state polymer exhibiting unique properties of high environmental and thermal stability, electrical conductivity and synthetic versatility.¹⁰³⁻¹⁰⁵, A group of polymers, the *poly*(3-alkylthiophenes) (P3ATs), with improved solubility and fusibility is obtained by attaching different length of the alkyl side-chain on the conjugated PT backbones. Among the family of P3AT, the *poly*(3-hexylthiophene) (P3HT), which was firstly synthesized in the early 1990s, has been widely studied during the past decades as a model polymer for both device performance optimization and fundamentals studies of charge photogeneration, charge transport, and morphology-function relationships owing to its ease of synthesis, high purity, and good optoelectronic properties.^{106,107}

Figure 2.1 Molecular structure of regioregular P3AT, where R represents the alkyl side chain; In the case of regioregular P3HT, and R is the hexyl group.

The first reported P3HT:PCBM photovoltaic device had a power conversion efficiency of 0.2% in year 2003,¹⁰⁸ and was soon increased to 3.5% during the same year by tuning the weight ratio of P3HT:PCBM and introducing thermal annealing treatment of the active layer at 75 °C.¹⁰⁹ The

current highest power conversion efficiency is of P3HT photovoltaic devices is well over 5%.¹¹⁰ As introduced in *Chapter 1*, studies on the photophysical properties of blend films and device physics focus mainly on the polaron dynamics under light illumination; for example the ultrafast charge photogeneration,^{84,111} the role of charge transfer states (CT) during exciton dissociation and geminate recombination process at the interfaces^{33,34,112,113}, or the non-geminate recombination during the charge transport and charge extraction.¹¹⁴⁻¹¹⁶ Moreover, the field effect hole mobility of P3HT can be higher than $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (up to $3.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) in high carrier concentration conduction channel induced by doping from electrolyte gate dielectric,^{117,118} while field effect transistors (FETs) with normal dielectric materials show mobility in the range of $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ depending on the crystallization and molecular packing of P3HT chains within the conduction channel.¹⁰⁷

2.2 Structure, morphology, and electronic properties

2.2.1 Molecular packing and morphology of P3HT films

It is well studied up to now that the conformation and aggregation of the polymer play key roles in charge transports as well as the optical properties of the film.^{83,107,119-121} Various methods and strategies have been used to control the crystallization and morphology of polymers, such as the choice of solvents, the use of different substrates, their functionalization thermal treatments, solvent additives, changing molecular weight, and regioregularity of polymers.

The regioregularity denotes the percentage of the monomers adopting head-to-tail configuration; specifically in P3AT, the alkyl side chain attaches to the 3rd position of the thiophene rings to form a stereoregular order.^{105,122} In regioregular polymer aggregates, the alkyl side-chains are

interdigitated with each other, as shown in figure 2.2, bringing the thiophene rings closer together and forming interchain π -stacking. Hence domains with crystalline structure can be found in regioregular polymer films; whereas in regiorandom polymer films the side chains twist the polymer backbone leading to amorphous microstructures. Within the microcrystalline domain, the polymer has a *lamellar structure* that is a two-dimensional conjugated planar structure with interchain π -stacking shown, as in figure 2.2.^{119,120,123}

Figure 2.2 (Left) Lamellar structure in microcrystalline domain of RR-P3HT with typical length scale and orientations. (Right) Schematic diagrams for edge-on and face-up orientation of lamellar structures assembled on the substrates.

Films of self-assembled regioregular polymer have different morphology because of different conjugation length of the polymer depending on its molecular weight: for low molecular weight polymer, films show only one-phase, non-entangled, polycrystalline (of *paraffinic-like* structure); while for molecular weight larger than the onset of chain folding and entanglement, the film contains a mixed structure of crystalline domain embedded in an amorphous matrix, whereby individual macromolecules interconnect multiple ordered domains.¹²⁴ The morphology of polymers with high regioregularity and high molecular weight is crucial for efficient charge carrier generation and transport.¹²⁵⁻¹²⁸

The typical regioregular-P3HT (RR-P3HT) lamellar structure has inter plane distance around 0.38 nm and interchain distance in plane around 1.6 nm.¹²³ The packing geometry affects the transport properties of polymer in the way that charge transport is favorable along the backbone of the single polymer (intrachain transport), lower in mobility between the π - π stacking of two adjacent polymer chain (interchain transport), and lowest in mobility along the hexyl side groups between two backbone chains in plane. Two orientations of lamellar structures have been identified: one is the plane and oriented perpendicular to the substrate, referred to as “edge-on” structure, the other one is a “face-on” structure with preferential (010) orientation normal to the substrate (figure 2.2).^{119,120}

2.2.2 Influence of molecular packing on the electronic properties of P3HT

Linear optical spectra & excitons

As introduced in *Chapter 1*, absorption and fluorescence spectra contain both the exciton-intramolecular vibration coupling with and the intermolecular coupling (J) of polymer chains in aggregated films. Both experimental and theoretical studies have been carried out treating the lamellar packing of RR-P3HT as H-type aggregate; experimentally it has been shown that the 0-0 peak in the RR-P3HT absorption spectrum is mainly due to interchain interactions.¹²⁹ Theoretically, Spano, et al.^{29,30,130} treated the RR-P3HT as a two-dimensional excitonic system considering both intramolecular and intermolecular interactions. Results show that the vibronic replica in the absorption spectrum can be fitted with inhomogeneous broaden Gaussian curves, and that the intensities of the first (0-0) and the next vibronic peak (0-1) relate to the free exciton bandwidth

($W=4J$) by the equation, $\frac{A_{0-0}}{A_{0-1}} \approx \left(\frac{1 - 0.24W / E_p}{1 + 0.073W / E_p} \right)^2$, where E_p denotes the intrachain phonon energy

coupled to the electronic transition (it is assumed that the Huang-Rhys factor is $S=1$). Specifically,

E_p is the energy of ring symmetric stretching mode in RR-P3HT with the magnitude of 0.18 eV.

The amplitude of W (or J) is linked to the microstructure and the average molecular conformation in RR-P3HT film prepared by different methods, which can be used to characterize the degree of crystallinity of P3HT films.

Figure 2.3 Typical absorption and photoluminescence spectra of RR-P3HT films.

Delocalized polaron states and IRAV modes

Interchain interactions in RR-P3HT strongly modify the electronic properties polarons. Polarons are no longer localized inside the polymer chain; but rather they become delocalized over the neighboring polymer chains. Both experimentally and theoretically^{21,23,64,131} it has been shown that the increase of interchain coupling leads to a splitting of energy levels from that of one dimensional localized polaron; as a result new photoinduced polaronic transitions appear with red shifted polaron absorption peak in the low energy region (mid-IR) and blue shifted in the near infrared (NIR)

spectral region.

Figure 2.4 Schematic representations of localized and delocalized polaron (hole) states with P_1 , P_2 , DP_1 , DP_2 , denoting the dipole allowed polaronic transitions.

The spectral overlap of broadband DP_1 transition with sharp IRAV modes results in Fano-type anti-resonances and quantum interference, which manifest as spectral dips rather than peaks. Theoretically, Horovitz et al.^{102,132} explained the appearance of IRAV modes as Fano-resonances by extending the amplitude mode (AM) model to the nonadiabatic case.

2.3 Optoelectronic properties of RR-P3HT

2.3.1 Photocurrent of RR-P3HT

Photocurrent of organic semiconductors

Photoconductivity or photocurrent measurements probe the nature of the charged photoexcitations of a system yielding information about the exciton-charge conversion, charge mobility and charge carrier lifetime. In steady-state photoconductivity experiments, a photoconductor (conjugated polymers in our cases) is excited by a continuous stream of photons, generating charge carriers that move and are collected at the electrodes under an externally applied electric field F .

According to Ohm's Law, the current density depends on the electric field according to the equation $J_{ph} = \sigma F = qnv = qn\mu F$, which holds under the assumption that the drift current is dominant and ignoring diffusion current; here σ is the electrical conductivity, n is the charge carrier density, and the drift velocity is $v = \mu F$, where μ is charge carrier mobility. The intensity of transmitted light upon absorption of incident photons throughout a bulk material is described by the Lambert-Beer's Law, $I = I_0(1-R)e^{-\alpha z}$, where z is the light penetration depth in the material, and R is the reflectance of the material. Consider the rate equation $\frac{dn}{dt} = G - R = -\eta \frac{dI}{dz} - \frac{n}{\tau}$, where $G = -\eta \frac{dI}{dz}$ is the charge photogeneration rate and $R = \frac{n}{\tau}$ is the charge monomolecular recombination rate under low light intensity condition; at steady-state ($\frac{dn}{dt} = 0$) the photogenerated charge carrier density is given by $n = -\hbar \frac{dI}{dz} \tau = \hbar \alpha \tau I_0 (1-R)e^{-\alpha z}$, where η is the quantum efficiency describing the amount of charge carriers generated per absorbed photon; and τ is the charge carrier lifetime. Finally the current density can be expressed as $J_{ph} = q\eta\mu\tau\alpha I_0(1-R)e^{-\alpha z} F$. In our photocurrent measurement with coplanar stripline contact geometry (figure 2.5), the total current I_{ph} collected by the electrodes can be calculated as

$$I_{ph} = \int_0^d J_{ph} w dz = q\eta\mu\tau\alpha I_0(1-R)(1-e^{-\alpha d}) \frac{V}{l} \quad (2.1)$$

where d is film thickness. From this equation (2.1), it is easy to conclude that the steady-state photocurrent is combined results of (i) light absorption as determined by the term $I_0(1-R)(1-e^{-\alpha d})$, which depends linear on the incident light intensity; (ii) the multiplicity of quantum efficiency η , drift mobility μ , and charge carrier lifetime τ ; (iii) the electric field or the applied bias, on which it depends linearly for first order approximation. This type of charge carriers predominant in the material determine the mobility μ ; meanwhile the quantum efficiency η and the carrier lifetime τ are mainly determined by the charge photogeneration and recombination mechanisms. All of these

factors, namely absorption coefficient α , reflectance R , charge carrier mobility μ and lifetime τ can be determined by independent experiments such as absorption and reflection measurements (for R and α), time of flight photocurrent¹³³ or fitting of field effect transistors curves (for μ),^{134,135} and transient absorption and transient photocurrent (for η and τ).¹³⁶

The photocurrent action spectrum can be obtained by measuring the photocurrent with respect to the wavelength of incident light. One of the figures of merit for photocurrent measurements is the

responsivity (R) to a certain light wavelength: $R[\text{A/W}](\lambda) = \frac{J_{ph}[\text{A/cm}^2]}{I_0[\text{W/cm}^2](\lambda)}$, which can also be

understood as normalized photocurrent per incident light intensity.

Figure 2.5 Device geometry for photocurrent measurement: coplanar stripline with typical dimensions labeled.

In more complicated scenarios, the photocurrent can have different behaviors. First of all, an additional diffusion current term, $qD\nabla n$ needs to be considered in the current density equation.

Instead of monomolecular recombination, bimolecular recombination processes are dominant in materials with a recombination rate of $R=\gamma n^2$ under high incident light intensity; thus the photocurrent light intensity dependence becomes $J_{ph} \propto I^{0.5}$. The charge carrier mobility can also depend on electric field dependence, for example due to the Poole-Frenkel effect in disordered material system,²⁰ making the photocurrent nonlinear with respect to the electric field. Moreover, the photocurrent is also affected by the electrodes geometry and charge injection conditions in a

way that current-voltage characteristics are modified even in dark condition, for example the superlinear current-voltage dependence in the space charge limited (SCL) region yields space charge limited dark and photo currents (SCLCs) in materials, $J_{dark} = \frac{9}{8} \mu \epsilon \epsilon_0 \frac{V^2}{L^3}$.^{2,137,138}

Photocurrent measurements of RR-P3HT film

The photocurrent measurements of spin cast RR-P3HT film were conducted by fabricating devices with coplanar stripline contacts, which is a symmetric contact structure at two sides (insert of figure 2.6(a)). 200 nm Au was thermally evaporated onto the film a through shadow mask, forming the electrodes. The Au work function is around 5.1 eV, close to the HOMO level of P3HT, ~5 eV; therefore, the devices are expected to have barrierless Ohmic contacts, as confirmed by the I-V curve measured in dark condition (figure 2.6(a)). This also shows that space charge limited effects do not affect in our photocurrent measurements.

Figure 2.6 (a) I-V curve of P3HT device under dark condition. (b) Photo response spectrum (red solid curve) of the device at room temperature, with the applied electric field of 7 kV/cm. The absorption spectrum of P3HT film is also shown

(black dashed curve).

The photoresponse spectrum of pristine P3HT (photocurrent action spectrum with normalized incident light intensity), shows good correspondence with its linear absorption spectrum, with comparable onset. This symbiotic behavior suggests that the absorption of P3HT is the primary step for generating photocurrent, while photocurrent spectrum of some other organic materials may show antibatic behavior respect to the absorption.¹³⁹ Note that to obtain photocurrent from this devices fabricated from pristine P3HT film require large electric field, comparing to the devices fabricated from P3HT:PCBM film as will be shown later.

The temperature dependence of the photocurrent was measured with monochromatic incident light ($\lambda=532$ nm) at two different electric fields, 7 kV/cm and 20 kV/cm. Both fields show thermally activated behavior at relatively high temperature ($T>100$ K), with an obvious deviation at the lowest temperature investigated. The thermal activation energy can be obtain by fitting the Arrhenius plot, which leads to $E_a \sim 0.3$ eV. The temperature independent behavior of low temperature, as suggested by Heeger and Mose, et al.,¹⁴⁰ can be attributed to of a fast sweep-out of charge carriers prior to being trapped.

Figure 2.7 Temperature dependent photocurrent of P3HT film with monochromatic incident light at two different applied

electric fields.

The light intensity dependence of the photocurrent measured was done at both room temperature and low temperature (78 K), with applied electric field of 7 kV/cm and 20 kV/cm, respectively. Single wavelength incident light ($\lambda=532$ nm) was used for photoexcitation. Though with much lower photocurrent amplitude at low temperature compared to that room temperature, photocurrent shows that almost identical intensity dependence with $\alpha=0.68$ at room temperature and $\alpha=0.63$ at low temperature (figure 2.8). The exponent power (α) falls into the range of $0.5 < \alpha < 1$, suggesting an bimolecular recombination process due to the energy distribution of traps.^{141,142}

Figure 2.8 Light intensity dependent photocurrent of P3HT under monochromatic light illumination measured at (a) room temperature, 7 kV/cm applied electric field and (b) 78 K, 20 kV/cm.

2.3.2 Photoinduced absorption of RR-P3HT

Photoinduced absorption spectroscopy and polaron states

Photoinduced absorption spectroscopy relies on a two-beam experiment with one beam of light photoexciting electrons to different electronic states and the other broadband beam probing these electronic states. The transmission spectra of samples measured from the probe light both with and without the pump beam are recorded and calculated as normalized transmittance difference,

$$-\frac{\Delta T}{T} = -\frac{I_{on} - I_{off}}{I_{off}} = 1 - \frac{T_{on}}{T_{off}}, \text{ where } I_{on} \text{ and } I_{off} \text{ denote the transmitted probe light intensity with}$$

excitation light on (T_{on}) and off (T_{off}), respectively. Considering the Lambert Beer's law,

$$T = (1 - R)^2 e^{-A}, \text{ the differential transmittance can be expressed as, } -\frac{\Delta T}{T} \cong \Delta A + \frac{2}{1 - R} \Delta R. \text{ If the}$$

sample has negligible reflectance (R) or reflection change (ΔR), the equation explicitly expresses

the correlation of $-\frac{\Delta T}{T}$ and the change of absorption upon excitation, $-\frac{\Delta T}{T} \cong \Delta A = \Delta \alpha d$ (or

$$\Delta A \cong -\frac{\Delta T}{T} \cdot \frac{1}{2.3}). \text{ Specifically, in polymer } -\frac{\Delta T}{T} > 0 \text{ (or } \Delta \alpha > 0) \text{ corresponds to photoinduced}$$

absorption (PIA) due to the emergence of new states for instance photoinduced polaron absorption;

conversely photo bleaching (PB) signal ($-\frac{\Delta T}{T} < 0$, or $\Delta \alpha < 0$) is associated to the depletion of

ground state population due to photoinduced inter-band transitions.

Our steady-state photoinduced absorption spectroscopy setup operates under quasi-steady-state excitation that a continuous wave laser is used as a pump and a broadband light source from a commercial FT-IR is used as a probe beam; the pump light is kept on and off while the T_{on} and T_{off} spectra are recorded alternatively. Both spectra are averaged over more 5000 times in order to ensure high signal to noise ratio. Unlike transient absorption spectroscopy that probes the excited states at the time scale of hundreds of femtosecond to picoseconds, the steady-state photoinduced absorption

experiment measures the long-lived states/species with lifetimes up to several micro- to milliseconds, such as long-lived polarons or triplet excitons. Long-lived polarons and their photoinduced sub band-gap transitions are particularly of our interest.

Infrared polaronic transitions of RR-P3HT film

Figure 2.9 shows the photoinduced absorption (PIA) spectra measured in the same conditions with a thick RR-P3HT film drop-cast from chloroform solution (top panel) and with a thin P3HT film spin-cast from 1,2-dichlorobenzene solution (bottom panel). Both spectra have transitions at around 0.35 eV (P_1) and 1.24 eV (P_2) which are attributed to localized polarons residing in amorphous region of the polymer film, while the transitions around 0.08 eV (DP_1) and 1.85 eV (DP_2) are attributed to delocalized polarons due to the well-ordered lamellar packing and interchain interaction.

The PIA spectrum of spun-cast film (on the bottom) shows lower delocalized polaron peaks especially for DP_1 transitions at 0.08 eV due to the smaller film thickness, and new transitions appear at 1.05 eV and around 1.66 eV. The first photo-bleaching peak at 1.94 eV also becomes visible. The transition at 1.05 eV (labeled as EX in bottom figure of 2.9(b)) is attributed to the absorption of remaining/trapped singlet exciton that has been assigned by detected magnetic resonance (DMR),²¹ whereas the 1.66 eV peak most likely originates from triplet excitons with a different symmetry.¹⁴³

Figure 2.9 Photoinduced absorption spectra of (top) drop-cast RR-P3HT film and (bottom) spin-cast RR-P3HT film, with DP_1 , DP_2 denoting two delocalized polaron transitions, P_1 , P_2 for localized polaron transitions and PB representing photo bleaching signal. Grey arrows indicate corresponding transitions.

The differences of PIA spectra of drop-cast and spin-cast films arise not only from the different film thickness but also from the different morphology of the polymer films: the more intense delocalized polaron transitions (such as DP_2) as compared to localized polaron transitions (P_2), together with the absence of singlet exciton absorption in spectrum of drop-cast film, are clear indications of the presence of microcrystalline domains can be found in drop-cast film. Indeed, the formation of well-ordered microcrystalline domains in drop-cast films is known in the field of OFET devices.¹⁴⁴ Moreover, the vanishing of singlet exciton absorption peak at 1.05 eV (EX) in PIA spectrum of drop-cast films indicates that the well-ordered structure facilitates exciton dissociation compared to spun-cast films.

Raman and IRAV modes

The IRAV modes of RR-P3HT reside in far side of the PIA spectrum below 0.2 eV. As a result of symmetry breaking by the presence of charges, IRAV modes appearing in spectra may serve as a

unique gauge of charge density in polymers (refer to *Chapter 1*). Instead of showing positive peaks, the IRAV modes in RR-P3HT manifest anti-resonances. This Fano-type interferences originate from the spectral overlap of delocalized polaron band (DP_I) and spectrally narrow IRAV modes. Experimentally these IRAV modes can be assigned either to IR vibrational modes or to Raman modes. The enhanced DP_I and IRAV mode signal (black curve compare to red) in figure 2.10(b) is partly due to the larger film thickness of the drop cast sample.

Figure 2.10 (a) Infrared absorption peaks of drop-cast RR-P3HT film. (b) Photoinduced IRAV modes of drop-cast (black curve) and spin-cast RR-P3HT film (red curve). (c) Resonance Raman modes of RR-P3HT.

The assignments of IR active modes, Raman modes as well as IRAV modes are summarized in table 1. Their origin can be theoretically explained with the help of amplitude mode model under nonadiabatic limits.¹³² Meanwhile, these modes can also be calculated by quantum chemical simulations using density function theory, DFT.^{23,145} The frequencies in bracket in the table below are simulated results from DFT theory and figure 2.11 shows the calculated IR and Raman spectra

with the polymer in neutral ground states (e and f), neutral excited states (c and d), and charged ground states (b and c). These results show that the characteristic IRAV modes of P3HT (figure 2. 11(a)) are actually a combination of both IR and Raman modes of these three states.

Table 1 Experimental IR, PIA-IRAV, Raman vibrational modes and assignments to calculated frequencies (in bracket)

Modes No	IR (cm ⁻¹)	Assignments	PIA-IRAV (cm ⁻¹)	Raman modes (cm ⁻¹)	Assignments
1				599 (595)	C _α -S-C _α ring deformation
2			678	678 (661)	C _α -S-C _α symmetric deformation
3	726 (720)	Hexyl rocking vibration	725	727	C _α -S-C _α asymmetric deformation
4	817 (815)	C _β -H out-of plane vibration	817		
5				837	C _β -H out-of plane vibration
6			872		
7			888		
8			978		
9			1002		
10				1005	C _β -C _{alkyl} stretching
11			1084		
12				1090	C _α -H and C _β -H bending
13			1156		
14				1170,1183	
15			1205		
16	1378 (1386)	Terminal CH ₃	1375	1383 (1358)	C _β -C _β symmetric stretching
17	1456 (1451)	C _α =C _β Symmetric stretching	1450	1450 (1430)	C _α =C _β symmetric stretching
18	1512 (1500)	C _α =C _β asymmetric stretching	1512	1512 (1512)	C _α =C _β asymmetric stretching

Figure 2.11 (Left) DFT calculated IR and Raman spectra of P3HT. (a) Experimental PIA results of drop-cast RR-P3HT film. (b)-(f) Calculated IR and Raman peaks of P3HT in different states. (Right) Molecular structure of P3HT in different states (ground state, first excited state, polaron and bipolaron states).

2.4 Optoelectronic properties of P3HT:PCBM bulk heterojunctions

2.4.1 Absorption and photocurrent of P3HT:PCBM

Absorption and PL of P3HT:PCBM

The absorption spectrum of P3HT:PCBM spun-cast film is shown in figure 2.12 (red solid curve) together with the absorption of pristine P3HT thin film (black solid curve). The vibronic replica (0-0, 0-1, and 0-2) from the exciton absorption of P3HT can also be seen in P3HT:PCBM absorption spectrum between 400 and 700 nm. On the other hand, the increase of the absorption below 400 nm and the peak at around 335 nm can be attributed to the absorption of PCBM.¹⁴⁶⁻¹⁴⁸ The quenching of PL signal for P3HT:PCBM film (red dash curve) as compared to that of pristine P3HT film (black dash curve) reveals the fact that the charge transfer processes occur at the P3HT and PCBM

interfaces and effectively dissociate excitons, thus greatly in reduce the exciton radiative recombination rate.

Figure 2.12 Absorption spectra of pristine P3HT (black solid curve) and P3HT:PCBM (red solid curve), as well as photoluminescence spectra of P3HT (black dash curve) and P3HT:PCBM (red dash curve) film.

Photocurrent of P3HT:PCBM

The linear dependence of the dark current to the applied voltage indicates to the Ohmic behavior of the device. The photo response spectrum measured at room temperature with applied electric field of 0.7 kV/cm (red solid curve) is shown in figure 2.13(b). Comparing to the previously shown photocurrent spectrum of pristine P3HT, the P3HT:PCBM film yields a factor of 10 higher responsivity or photocurrent, even with 10 times lower electric field applied. Thanks to the efficient charge transfer process at the donor-acceptor interfaces, excitons dissociate much more efficiently in P3HT:PCBM films. Meanwhile, the photocurrent spectrum of P3HT:PCBM thin film (black dash curve) has similar shape as its absorption spectrum. The peaks at around 700 nm as well as 340 nm in the photocurrent spectrum can be assigned to the absorption of PCBM, meaning that charge generation occurs not only in P3HT but also in PCBM domains, suggesting that hole transfer

process can also happen at the P3HT-PCBM interfaces.

Figure 2.13 (a) I-V curve of P3HT:PCBM device in dark condition. (b) Photoresponse spectrum (red solid curve) of the device at room temperature, with the applied electric field of 0.7 kV/cm. The absorption spectrum of P3HT:PCBM film is also shown (black dashed curve).

Figure 2.14 shows the temperature dependent photocurrent under green laser light illumination ($\lambda=532$ nm, $I_0=21$ mW/cm²), with applied electric field of $F=0.7$ kV/cm. In this case the thermal activation energy extracted from the Arrhenius plot in the figure 2.14 is $E_a=0.268$ eV, indicating thermally activated behavior of the blend film. This is mainly attributed to the polaron hopping transport processes, while the relatively low thermal activation energy as compared to pristine P3HT may be due to the lowering of the barrier for hopping transport by the applied electric field on the film.^{20,58}

Figure 2.14 Temperature dependent photocurrent of P3HT:PCBM film with monochromatic incident light, the activation energy is around 0.268 eV.

2.4.2 Photoinduced absorption of P3HT:PCBM

Comparing the spin-cast P3HT:PCBM blend film to the pristine RR-P3HT film, its PIA spectra in figure 1.15 also shows the localized and delocalized polaron transitions in both mid-IR and NIR regions, as well as photo bleaching peaks below 1.9 eV, which confirms the efficient formation of polarons. The factor of 2 enhancement of PIA intensity confirms the increased exciton dissociation efficiency due to the donor-acceptor blend. In addition, the quenching of exciton peaks at 1.05 eV and 1.66 eV indicates an efficient charge transfer between donor and acceptor in the blend film leaving no interchain excitons in the blend film.

Figure 2.15 (Top) Photoinduced absorption spectra of as-cast RR-P3HT/PCBM film (red curve, labeled as NA) and thermally annealed RR-P3HT/PCBM film (black curve, labeled as TA). (Bottom) Photoinduced absorption spectra of the two films in the mid-IR region.

As introduced in *Chapter 1*, the morphology of blend films obtained from solution plays an important role in optimizing the performance of solar cell devices. Specifically, one should find a trade-off between the degree of mixing between donors and acceptors which favors efficient charge generation and phase separation at the nanoscale, which favors charge transport by reducing non-geminate charge recombination. Several methods have been used to this aim, such as thermal annealing treatments, solvent annealing, solvent additives, etc. Here we compare the photoinduced absorption spectra of as-cast RR-P3HT:PCBM film and that after thermal annealing treatment (figure 2.16). Both two samples are prepared and measured under the same conditions. The intensity of polaron signals in PIA spectra of the as-cast film, except for the P_2 peak, are significantly larger than those of thermally annealed film, and both DP_1 and photobleaching peaks are spectrally shifted. The enhanced polaronic transitions and IRAV modes in the as-cast film indicate more efficient

charge photogeneration in well-mixed donor-acceptor film with interpenetrating structures, while the phase separation induced by thermal annealing reduces the amount of photo generated charges. Indeed, this can also be confirmed by ultrafast transient absorption spectroscopy, which shows delayed charge carrier generation in thermally annealed P3HT:PCBM film, attributed to exciton diffusion from the interior of P3HT domains to the interfaces can be found;^{111,149} on the other hand, the as-cast P3HT:PCBM film mainly suffers from inefficient charge collection efficiency. Meanwhile, it has been shown that the peak of DP_1 (E_{max}) is a sensitive indicator for the polaron relaxation energy and the shift of E_{max} reflects the change of film morphology: the more ordered the film, the smaller the polaron relaxation energy.²² The red shift of E_{max} in the thermally annealed sample indicates improvement of the morphology, likely, due to the formation of more ordered lamellar structure. The morphology difference between the as-cast P3HT:PCBM film and the thermally annealed film can be directly seen from the topography AFM images (figure 2.17).

Figure 2.16 AFM topography height images of P3HT:PCBM spin-cast film. The brightest yellow color corresponds to a maximum height of 10 nm. (Left) As-cast P3HT:PCBM film shows uniform distribution of P3HT in the film. (Right) P3HT:PCBM film after 120 °C thermal annealing shows aggregation of P3HT (bright yellow color).

2.5 Solvent additive effects in P3HT:PCBM

As discussed above, the morphology of the bulk heterojunction film plays a critical role in achieving highly efficient organic solar cells; film morphology affects both charge photogeneration (by modifying the light absorption spectrum and the donor-acceptor interfacial area) and charge

transport and extraction processes (by determining the degree of phase separation and crystallinity of P3HT aggregates). However, optimum morphology can hardly be achieved immediately after film deposition from solution; the formation of as-cast film morphology depends strongly on the materials' solubility and miscibility as well as their molecular dynamics during the processing from solution.¹⁵⁰

Several methods have been brought out and studied extensively in order to tune the nano- or micro-morphology of spin-cast blend film; such as the post processing thermal annealing, solvent slow drying, and the use of processing solvent additives.^{121,150,151} The processing solvent additive technique is widely considered as a promising method because it is a simple one-step procedure, and it is especially useful when thermal annealing is not applicable to some materials. The additive processing technique consists of adding a small amount of volatile solvent into the host solvent of the two materials, with the additives having different, usually higher, boiling temperature and different solubility.¹⁵² Different boiling temperature and solubility of the additives in solution can alter greatly the molecular dynamics during the spin casting process, therefore the degree of phase separation can be easily controlled by carefully selecting different types of additives.

In addition to photovoltaic device characterization, we used steady-state optical spectroscopy techniques (linear UV-vis absorption and mid-IR photoinduced spectroscopy) to study the influence of additives on the crystalline order and charge photogeneration in RR-P3HT:PCBM films. The RR-P3HT:PCBM films were prepared by adding 1%, 2% and 5% 1,8-Octanedithiol (ODT) additives, and results are compared with films prepared by thermal annealing (TA) treatment and as-cast films (NA) without any treatment.

Steady state absorption shows enhancement of absorbance of P3HT:PCBM accompanying with clear 0-0 and 0-1 vibronic features due to better crystallinity of P3HT after process treatments, both for thermally annealed and with solvent additive samples. The absorption spectra of treated P3HT:PCBM film were normalized to the 0-1 vibronic peak in order to compare the relative intensity between 0-0 and 0-1 vibronic peaks of different samples. Free exciton bandwidth (W) can be calculated similar to that of pristine P3HT films using the equation $\frac{A_{0-0}}{A_{0-1}} \approx \left(\frac{1 - 0.24W / E_p}{1 + 0.073W / E_p} \right)^2$ introduced in *Section 2.2.2*. Calculated W of different samples assuming $E_p=0.18$ eV are shown in figure 2.17(b); the decrease of W implies better crystallinity of the blend film with increasing additive concentration, so that thermal treatment has equivalent effect as the film with additive concentration between 2-5%.

Figure 2.17 (Top) Normalized absorption spectra of P3HT:PCBM films. (Bottom) Free exciton bandwidth calculated from the 0-0 and 0-1 vibronic peak.

The additives and thermal treatment effects on the blend films can better be seen from the topography images of AFM measured in tapping mode. Figure 2.18(a) to (e) clearly demonstrate

the trend of P3HT crystallinity with different treatments: the image of the as-cast sample shows uniformly distributed P3HT, while the sample prepared with 5% additive shows highly aggregated P3HT forming different domains. The thermally annealed sample shows larger P3HT crystalline domain than the sample prepared with 2% additive however less aggregated and less rough than the one prepared with 5% additive, which is consistent with the trend shown by the free exciton bandwidth calculation.

Figure 2.18 Topography images of AFM measurements of P3HT:PCBM film (a) as-cast; (b) with 1% additive; (c) thermally annealed; (d) with 2% additive; (e) with 5% additive.

Steady-state photoinduced absorption spectroscopy was carried out on different samples at 78 K, with results shown in figure 2.19(a). To better illustrate the effects of additives on the photogenerated charge carriers, the PIA spectra were normalized by the absorbance of each sample at the light excitation wavelength ($\lambda=532$ nm). The normalized PIA spectra are shown in figure 2.19(b); the as-cast P3HT:PCBM film shows highest the localized (P_I) and delocalized (DP_I)

polaron signal as well as the IRAV modes below 0.2 eV, while the thermally annealed film has the lowest polaron signals and IRAV modes; the polaron peaks intensity of the sample prepared by 1% additive is between the ones prepared by 2% and 5% additive. I-V curves of fabricated solar cell devices under AM 1.5 white light illumination are shown in figure 2.20(c). The short circuit currents are enhanced by the treatments, while the open circuit voltage remains almost the same for all five samples. The additive and thermal annealing treatments influence the power conversion efficiency through increasing photocurrent and thus filling factors of the photovoltaic devices. The best performance device is the one with 2% additive, having power conversion efficiency (*PCE*) up to 2.86%, while only 1.89% *PCE* for devices fabricated from as-cast film; the 5% additive sample has the lowest device performance among the samples with additive treatments.

Figure 2.19 (a) PIA spectra in MIR region of P3HT:PCBM films. (b) PIA spectra in MIR region of P3HT:PCBM films normalized over absorption spectra of each film. (c) I-V curve of solar cell devices fabricated from P3HT:PCBM with different treatments.

To better correlate the measured PIA spectra with devices performance, the polaron signal from figure 2.19(a) was integrated over the mid-IR spectral region ($N \sim \int_{\omega_1}^{\omega_2} I(\omega) d\omega$) and plotted against

the additive concentration. Note that in this way the overall light absorption enhancements due to the additive or thermal annealing are also included. The devices performances were also summarized by plotting the short circuit photocurrent against different additive concentrations in figure 2.19(c). Figure 2.20(a) and (b) reflect the phenomenon observed in figure 2.19, however in a clearer way, showing that (i) with the additive increase from 1% to 2%, the improvement of morphology leads to polaron signal intensity decrease but the device performance increases with the best performance among the samples tested; (ii) though the sample with thermal annealing has lowest polaron intensity, still it yields the second best device performance; (iii) the 5% additive samples have the best crystallinity of P3HT and polaron intensity, but the lowest device performance. The observed phenomena can be explained as: (i) from as-cast sample to 1% sample, the increase of polaron intensity is due to the improved absorption; while the increased *PCE* is also due to the phase separated P3HT providing transport networks for charges; (ii) in the region between 1% and TA, the trend of photovoltaic performance is a trade-off between reduced charge intensity and improved morphology for charge transport; (iii) the deleterious effect of 5% additive on the device performance (*PCE*) is because of the excessive film surface roughness, as seen from AFM measurement in Figure 2.18(e).

Figure 2.20 (a) Polaron signals integrated over the MIR region from PIA spectra. (b) Short circuit current extracted solar cell devices I-V curve.

To conclude, I have demonstrated that steady-state PIA in mid-IR spectral region is a sensitive technique to study the additive effects on photovoltaic device performance. Results show that the morphology of the P3HT:PCBM film is crucial in both aspects of charge photogeneration and charge transport for optimizing devices performance.

2.6 Conclusions

In this chapter, I gave a broad review of the optical and optoelectronic properties of P3HT, one of the most studied photovoltaic conjugated polymers; I introduced the polymers structures, aggregated morphologies, polaron states and their photoinduced spectra in steady-state, as well as its photocurrent properties of both pristine films and P3HT:PCBM “bulk heterojunctions”. With

this in mind, we are to further discuss plasmonics effects on charge carrier photogeneration processes in both metal particles blends (*Chapter 3*) and P3HT/IR-nanoantenna hybrid structures (*Chapter 4*).

Chapter 3. Plasmonic enhancement of charge photogeneration in conjugated polymers

3.1 Introduction to particle plasmons

3.1.1 Drude model and bulk plasmons

Plasmons are collective electron oscillations in metals induced by external electromagnetic (light) fields.

Treating electrons in metals as a free electron gas, their optical and electrical properties can be modeled as a classical conductivity model, the Drude model.^{27,153} In this model, electrons drift freely and are scattered by nuclei, as described by a typical damping parameter γ or relaxation time $\tau=1/\gamma$; their motion can be modeled by the damped oscillation function, $m\ddot{\mathbf{x}} + m\gamma\dot{\mathbf{x}} = -e\mathbf{E}(t)$, where $E(t)$ is the time varying oscillating electric field $E(t) \sim \cos(\omega t)$ with frequency ω . From the macroscopic polarization, one can obtain the dielectric function in terms of the plasma frequency,

$$\hat{\varepsilon}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}.$$

The **plasma frequency** ω_p is defined as $\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m}$, where N is the electron density, and m is electron

mass. The real and imaginary parts of the dielectric function are $\varepsilon' = \text{Re}(\hat{\varepsilon}) = 1 - \frac{\omega_p^2 \tau}{\omega^2 \tau^2 + 1}$ and

$\varepsilon'' = \text{Im}(\hat{\varepsilon}) = \frac{\omega_p^2 \tau}{(\omega^2 \tau^2 + 1)\omega}$. Assuming relative permittivity $\mu=1$ in Maxwell's equations, the relation

of complex refractive index and dielectric function is $\hat{n} = \sqrt{\hat{\varepsilon}} = \sqrt{\varepsilon' + i\varepsilon''} = n + i\kappa$, hence $\varepsilon' = n^2 - \kappa^2$,

and $\varepsilon'' = 2n\kappa$.

In large frequency regime ($\omega\tau \gg 1$), the dielectric function becomes $\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$. If $\omega < \omega_p$, where the (real) dielectric function is negative ($\varepsilon(\omega) < 0$), metals still preserve their metallic characteristics with free electron plasma. If $\omega > \omega_p$, where the dielectric function becomes positive ($\varepsilon(\omega) > 0$), the Drude contribution in metals becomes unimportant and they act like nonabsorbing dielectric media.

In the very low frequency regime ($\omega\tau \ll 1$) on the other hand, the real (n) and imaginary part (κ) of the refractive index are both large and comparable, making $n \approx \kappa = \sqrt{\frac{\varepsilon''}{2}} \approx \sqrt{\frac{\omega_p^2 \tau}{2\omega}}$ and $\alpha = \sqrt{\frac{2\omega_p^2 \tau \omega}{c^2}}$, which describes the absorbing properties of metals within the skin depth $\delta = \frac{2}{\alpha}$. In

a relatively high frequency regime ($1 \leq \omega\tau \leq \omega_p\tau$), metals have the reflectivity close to unity.¹⁵⁴

Figure 3.1 (Left) Real and imaginary parts of the dielectric function of aluminum calculated from the Drude model. The parameters used are $\omega_p = 15.3$ eV and $\gamma = 0.5984$ eV. (Right) Reflection spectrum of aluminum (black dash line) and Drude model (black solid line), with the red dash line indicating a sudden drop at the plasma frequency. The left and right arrows indicate the metallic and dielectric regions respectively, the dip at 1.5 eV is from electron inter-band transitions of Al.²⁷

In the spectral regime $\omega \sim \omega_p$, both of n and κ are small, the reflection spectrum shows a sudden drop at ω_p . The dispersion relation of propagating transverse electromagnetic waves becomes

$$\omega(k) = \sqrt{\omega_p^2 + k^2 c^2}, \text{ so that below the plasma frequency propagating wave solutions are forbidden,}$$

while above the plasma frequency the metal plasma supports propagating waves with group velocity smaller than the speed of light ($v_g = d\omega / dk < c$).

At plasma frequency ($k=0$) and in the low dielectric limit $\varepsilon(\omega_p)=0$, collective longitudinal oscillation of electrons occurs at the plasma frequency. The quanta of these charge oscillations are called plasmons (or bulk plasmons); the longitudinal bulk plasmons cannot be excited by the transverse external field ($\mathbf{k} \cdot \mathbf{E} = 0$).^{153,155}

Since the Drude model treats the metal as a free electron gas, it can only describe its optical properties at frequencies below ω_p . A more general model for dielectrics materials including metals is the Drude-Lorentz model, which is valid for broadband exciting frequency:

$$\hat{\varepsilon}_r(\omega) = \hat{\varepsilon}_r(\infty) + \omega_p^2 \sum_{m=0}^M \frac{f_m}{(\omega_m^2 - \omega^2) - i\omega\gamma_m},$$

where $\hat{\varepsilon}_r(\infty)$ is the dielectric function of higher frequencies, and f_m , ω_m and γ_m are the oscillator strength, oscillation frequency and damping parameter for the m th oscillator, respectively.

3.1.2 Surface plasmon polaritons

Surface plasmon polaritons (SPP) are coupled electromagnetic waves and collective electron oscillations that can propagate along dielectric-metal interfaces.^{153,155}

Figure 3.2 Schematic of for SPP propagation at single interface between a metal and a dielectric material.

The propagation and dispersion relations can be derived directly from the classical Maxwell's equations modeled by two media imposing continuity of the normal and transverse fields at interface as boundary conditions.¹⁵⁴ It can be shown that surface modes cannot be excited by transverse electric (*TE*) mode fields; the exciting transverse magnetic (*TM*) mode field can be written as $\mathbf{E}_i = (E_{i,x}, 0, E_{i,z})e^{i\omega t - i\mathbf{k}_i \cdot \mathbf{r}}$ and $\mathbf{H}_i = (0, H_{i,y}, 0)e^{i\omega t - i\mathbf{k}_i \cdot \mathbf{r}}$, where, $\mathbf{k}_i$ are wave vectors explicitly expressed as $\mathbf{k}_i = (\beta, 0, k_{i,z})$, and $i=1, 2$ denoting the two different media (1 for dielectric, 2 for metal). By applying the boundary conditions, one can obtain the relation of following ($k_i = k_{i,z}$)

$$\frac{\varepsilon_1}{k_1} + \frac{\varepsilon_2}{k_2} = 0.$$

Given that k_1 and k_2 are always positive, surface waves exist only when ε_1 and ε_2 have opposite signs, condition of which can be satisfied between an insulator and a metal at the frequency below the plasma frequency ω_p . The longitudinal and transverse components of wave vectors (β and k_i) represent the two propagation modes of electromagnetic waves in both media; which one exponentially decays into the bulk described by k_i , and the other propagates along the interface as described by β .

Figure 3.3 Schematic representation of SPP propagating at a metal-dielectric interface.

The dispersion relation of surface waves with negligible losses of the electrons oscillations

($Im(\epsilon_1)=0$) can be further derived to be $\beta = \frac{\omega}{c} \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}}$. In the limit of large wave vectors ($\beta \rightarrow \infty$),

the oscillation frequency approaches to that of the surface plasmon frequency, $\omega_{SPP} = \frac{\omega_p}{\sqrt{1 + \epsilon_2}}$,

when $\epsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$. Figure 3.4 shows the dispersion relation of plasmons; the surface plasmon

mode has electrostatic character with frequency ω_{SPP} when β goes to infinity, and its group velocity

goes to zero.

Figure 3.4 Dispersion relations of both SPP (red solid line) and bulk plasmons (blue solid line). The light cones in air (black solid line) and in dielectrics (black solid line) are shown.

Excitation of surface plasmon polaritons

As shown in figure 3.4, the entire dispersion of electron oscillations in metals resides below the light cones, therefore free space light illumination cannot directly excite surface plasmon modes. Thus, different coupling techniques are required to fulfill the momentum conservation requirement (phase matching). Several coupling strategies have been brought out for SPP excitation (figure 3.5);¹⁵⁶ for example, the Kretschmann method of coupling prism onto a metal film (A in the figure), grating coupling (B), highly focused optical beams (C), near field coupling (D), end-fire coupling (E), and step-gap leakage coupling (F), where method E relies on spatial mode matching coupling rather than phase matching.

Figure 3.5 Excitation methods for SPP: A, prism coupling; B, grating coupling; C, highly focused optical beam; D, near field coupling; E, end-fire coupling and F, step-gap leakage coupling.¹⁵⁶

3.1.3 Localized surface plasmons

Scattering in nanostructures/nanoparticles

While the coupling of electromagnetic waves to electron plasma of metals results in propagating surface plasmon polaritons (SPP) at dielectric-metal interfaces, localized surface plasmon resonances (LSPR) are non-propagating excitations with electrons in metallic nanostructures coupled directly to external oscillating electromagnetic fields.^{155,157} The LSPR in nanoparticles can be analytically obtained by solving Maxwell's equations for the scattering of electromagnetic waves by sub-wavelength sizes conductive particles, which was first carried out by Mie.¹⁵⁸ Upon plane-wave excitation, for example, the conduction electrons inside nanoparticles move in phase with exciting light field, leaving the polarization charges on the opposite side of the metal surface. As a result, the displaced electrons are driven by the restoring forces from polarization charges and oscillate at a certain frequency (figure3.6). Therefore, the electric field is amplified both inside the particle and within the near field zone, due to the excited electron oscillations.

Figure 3.6 (Left) Metal sphere excited by an electromagnetic field. (Right) Localized dipole-type electric field formed in the metal sphere upon plane-wave excitation.

Near field enhancement and resonance condition

For small spherical nanoparticles with typical diameter of $a \ll \lambda$ in isotropic and non-absorbing surrounding medium, the electrostatic approximation is valid, hence only the dipolar term needs to be considered. By solving the Laplace equation, $\nabla^2 \Phi = 0$, in spherical coordinates, the electric field distribution inside and outside the metal nanosphere can be derived as,

$$\mathbf{E}_{in} = \frac{3\epsilon_2}{\epsilon_1 + 2\epsilon_2} \mathbf{E}_0 \quad \text{and} \quad \mathbf{E}_{out} = \mathbf{E}_0 + \frac{1}{4\pi\epsilon_0\epsilon_2} \frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}}{r^3},$$

where ϵ_1 and ϵ_2 are the dielectric functions of the metal and the surrounding medium.¹⁵⁴ The polarizability α , defined by $\mathbf{p} = \epsilon_0\epsilon_2\alpha\mathbf{E}_0$, is

$$\alpha = 4\pi a^3 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2}.$$

Therefore, resonant enhancement occurs at the *Fröhlich frequency* when $\text{Re}[\epsilon_1(\omega)] = -2\epsilon_2$ and the denominator of the polarizability becomes minimum, equaling the imaginary part of ϵ_1 . The resonant frequency ω_{LSPR} can be linked to the plasma frequency of metals through the metal dielectric function using the Drude model ($\omega_{LSPR} = \omega_p / \sqrt{3}$ for spherical particles). Generally, the plasmon resonance frequency also depends on the particle shape, the type of metal, and the dielectric constant of the surrounding medium.

Near field enhancement effects can be directly seen from the electric field distribution outside the nanosphere (E_{out}), where the second term is the expression of typical electric dipole radiation in the near field zone. E_{out} has maximum intensity when $\mathbf{n} \cdot \mathbf{p} = 1$, which means the dipole moment has the same direction of the external electric field; the field enhancement factor η can be written as

$$\eta = \frac{|E_{out}|^2}{|E_0|^2} = \left| 1 + \frac{\alpha}{2\pi r^3} \right|^2 = \left| 1 + \frac{2a^3}{r^3} \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \right) \right|^2.$$

Therefore the field enhancement factor is strongly dependent on the distance from the metal nanoparticles and the size of nanoparticles roughly scaling as $(\frac{a}{r})^6$. The largest field enhancement factor is obtained at the position $r=a$,¹⁵⁹ in addition, the resonant near field enhancement occurs at the *Fröhlich frequency*.

Far-field spectra and particle size dependence

The LSPR of nanostructures are usually characterized optically by their far-field extinction spectrum, which is defined as the sum of absorption and scattering (or $I-R-T$). For small particles satisfying the Rayleigh approximation ($\lambda \gg 2\pi a$), the extinction cross-section calculated using the Poynting's theorem is given by $\sigma_E = \sigma_{abs} + \sigma_s$, where $\sigma_{abs} = k \text{Im}[\alpha] = 4\pi k a^3 \text{Im}[\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2}]$, and

$$\sigma_s = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8\pi k^4 a^6}{3} \left| \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \right|^2.$$

The particle size a affects the extinction spectra and hence the color of the particles: for small sizes, the absorption is dominant, then the particles' color is complimentary to those that are absorbed; for relative large sizes, scattering effects become dominant, then the particles show the colors that are scattered. The particle total extinction can be expressed as^{158,160}

$$E(\lambda) = \frac{(1 + \chi)^2 24\pi^2 N a^3 \varepsilon_2^{3/2}}{\lambda \ln(10)} \left[\frac{\varepsilon_i(\lambda)}{(\varepsilon_r(\lambda) + \chi \varepsilon_2)^2 + \varepsilon_i(\lambda)^2} \right], \text{ where } \varepsilon_r = \text{Re}(\varepsilon_I) \text{ and } \varepsilon_i = \text{Im}(\varepsilon_I) \text{ are the}$$

real and imaginary parts of the metal dielectric function, respectively and χ is the shape factor: $\chi=2$ for sphere, and $\chi>2$ for other spheroidal shapes^{161,162} with higher aspect ratio. Only spherical and spheroidal structures have analytical solution for the extinction, while for other shapes one needs to rely on numerical simulations.¹⁶³⁻¹⁶⁵

For nanoparticles with sizes beyond the Rayleigh approximation ($\lambda \ll 2\pi a$), Mie theory considering higher order modes has to be applied, and higher order resonances begin to appear in the spectra. Meanwhile, the dipolar resonances are red shifted due to the overall effect of retardation of exciting field, reduction of depolarization field inside the particles, and broadening due to the radiative damping process with a characteristic dephasing time T_2 .^{155,157,163,166}

3.2 Plasmon enhancement of excitonic absorption in organic photovoltaics

In organic photovoltaics, the organic active film thickness is limited to be around 100- 200 nm by the trade-off between light absorption for charge photogeneration and the charge carrier mobility for transport; therefore, light trapping and field-enhancement techniques are highly beneficial. To enhance the power conversion efficiency of thin film photovoltaics, various light trapping techniques have been considered, for example the use of antireflective coatings, surface texturing,¹⁶⁷ optical spacers,^{168,169} and plasmonic metallic nanostructures.¹⁷⁰⁻¹⁷⁶

Plasmons in metallic nanostructures can largely increase light absorption of solar cells. Generally

three enhancement mechanisms are considered,¹⁷² which are: (i) the light scattering from the particle plasmons (figure 3.7(a)); (ii) the near field enhancement induced by the surface plasmon resonances (LSPR) (figure 3.7(b)); and (iii) traveling electromagnetic fields supported by surface plasmon polaritons (SPP) at the metallic nanostructure-dielectric interfaces (figure 3.7(c)). Additionally, other mechanisms to plasmonically enhance light absorption have been developed, for example magnetic mirrors supported by metasurfaces¹⁷⁷ can be designed to tune the phase of reflected electromagnetic waves: as a result the amplitude of light waves can be engineered to peak inside a specific active layer as shown in figure 3.7(d).

Figure 3.7 Three mechanisms of plasmonic enhancement solar cell efficiency based on different nanostructures. (a) Metal or dielectric particles on top of the solar cell scatter light into the active layer. (b) Localized surface plasmons excited by incident light concentrate the electric field in the near-field zone. (c) Surface plasmon polaritons excited between the nanostructures and the active materials propagate along their interface. (d) Magnetic mirrors fabricated from metasurfaces can control the phase of reflected light, hence enhance light interaction with the active layer.

The light trapping mechanisms of metallic nanoparticles, absorption or scattering, rely on their different sizes. Specifically, large size nanoparticles trap light by far-field scattering. For example, 100 nm diameter Ag particle in air has an albedo (light scattering efficiency defined as

$Q = \frac{\sigma_s}{\sigma_s + \sigma_{abs}}$) of over 0.9, as calculated by Mie theory. A good selection of light scattering particles should aim at achieving highest albedo or, in other words, at reducing absorption (Ohmic losses) of metal nanoparticles as much as possible. On the other hand, smaller size nanoparticles are preferred for near-field enhancement due to their high absorption. In this case, nanoparticles serves as optical nanoantennas that store and radiate energy in the near field region. Typically, 5-20 nm nanoparticles are used, in which their absorption dominates the extinction with very low albedos (below 7×10^{-3} for 12 nm diameter Ag nanoparticles in air).^{160,171,178} To take full advantage of the near field enhancement, the absorption rate of the active material in the vicinity of metal nanoparticles should be high enough to avoid energy dissipation (Ohmic losses) in the nanoparticles.¹⁷²

In addition to particle size, other factors need to be considered for optimizing plasmonically enhanced organic solar cells such as shape, concentration and distribution position of metallic nanoparticles within the different layers and interfaces of the device.^{170,175} The presence of metallic nanoparticles may affect the solar cell performance through LSPR enhanced light absorption,¹⁷⁹⁻¹⁸¹ modification of active film morphology,¹⁷⁵ change of charge transport mobility or charge collection efficiency,¹⁸² and other subtle effects. In addition, the plasmons-exciton interaction also alter the photoexcitation dynamics in the way that it either enhance the exciton dissociation¹⁸³⁻¹⁸⁵ or it leads to exciton quenching on the metal surface or on the metal particle capped ligands¹⁸⁶⁻¹⁸⁸. To achieve the best enhancement, all those factors must be systematically considered simultaneously.

3.3 Plasmonically enhanced charge generation in P3HT on Au nanoparticles

To determine the charge generation enhancement in plasmonics solar cells, methods like steady state photocurrent (or EQE) and current-voltage (I-V) measurements are often used. However, these methods characterize the overall plasmonic enhancement on charge photogeneration, transport and collection properties of solar cells. Photoinduced absorption spectroscopy, on the other hand, can provide direct and unique evidence of charge photogeneration enhancement without the need to fabricate solar cell devices. Despite its importance, only few works have utilized this technique either in the steady-state or in the time domain.¹⁸⁴ Steady-state PIA studies conducted so far focused mostly on the visible-NIR spectral region and were not conclusive in showing enhancement of carrier photogeneration in metal nanoparticle/P3HT composite films.^{186,189}

Figure 3.8 Schematics of (a) Au NPs on substrate and (b) Au NPs/P3HT composite samples.

Here we used steady-state mid-IR photoinduced absorption spectroscopy, a technique which is very sensitive to photogenerated polarons in polymer film (see *Chapter 2*), to tackle this problem. The system we studied consists of Au nanoparticles (Au NPs)/P3HT composite films. Two different sizes of colloidal gold nanoparticles, 5 nm and 10 nm, exhibiting different resonance frequencies were used in our experiments. The samples were prepared by drop casting the Au NPs solution onto CaF₂ substrates (figure 3.8(a)) and subsequently spin casting the P3HT films on top of the particles (figure 3.8(b)). To obtain samples with higher Au NPs density, the drop cast procedure was repeated multiple times. In the following experiments, samples are labeled based on particles size and their

density, for instance 5NM_2 represents the sample with 5 nm Au NPs and drop cast deposition of particles was repeated twice. AFM images, both topography and phase images in figure 3.9 show the distribution of different amounts of Au NPs (5 nm) on substrates. 5NM_1 sample with lowest density shows well dispersed Au NPs on the substrates, while increasing particles density (5NM_2 and 5NM_3 samples) leads to particle aggregation on the substrates.

Figure 3.9 (a-c) AFM Topography images of different amounts of Au NPs (5NM_1, 5NM_2, 5NM_3) deposited on CaF₂ substrates. (d-f) Corresponding AFM phase images of the samples.

Figure 3.10(a) & (c) show the extinction spectra of 5 nm and 10 nm Au NPs film deposited on CaF₂ substrates. All three 5 nm Au NPs samples have the same resonance frequency at 566 nm which is close to the photoexcitation frequency (green laser, $\lambda=532$ nm, grey dash lines in figure 3.10) of our PIA experiment and extinction intensity increases proportionally to the particle density as shown in figure 3.10(a). This confirms that, although particles with higher density aggregate on substrates (figure 3.9), the plasmonic resonance peaks remain unaltered. Figure 3.10(c) shows the 10 nm Au NPs having plasmon resonance frequency away from the light excitation frequency with broad resonant structure centered at 660 nm, i.e. below the P3HT optical bandgap (figure 3.10(d)). The 10 nm Au NPs samples can be used as “off-resonance” control samples and compared with 5 nm

Au NPs to further understand the importance of spectral overlap between the resonant frequency of Au NPs and light absorption of the polymer films.

Figure 3.10 (a) Extinction spectra of 5 nm Au NPs with different density (5NM_1 red curve, 5NM_2 blue curve, 5NM_3 green curve) deposited on CaF₂ substrate. The inset shows the picture of an actual Au NPs film. (b) Optical density spectra of pristine P3HT (black), 5NM_1/P3HT (red), 5NM_2/P3HT (blue) and 5NM_3/P3HT (green) film. Au NPs extinction spectra (dash curve) obtained by subtracting pristine P3HT spectrum from Au NPs/P3HT OD spectra. (c) Extinction spectra of 10 nm Au NPs with different density (10NM_1 pink curve, 10NM_2 yellow curve) deposited on CaF₂ substrate. The inset shows the picture of an actual Au NPs film. (d) Optical density spectra of 10 nm Au NPs/P3HT composite films (solid curve) and Au NPs extinction spectra (dash curve) obtained by subtracting pristine P3HT spectrum from Au NPs/P3HT OD spectra. The dash line in (a)-(d) indicate the photoexcitation wavelength ($\lambda=532$ nm).

Optical density (OD) spectra of all five Au NPs/P3HT composite samples (5NM_1/P3HT, 5NM_2/P3HT, 5NM_3/P3HT, 10NM_1/P3HT and 10NM_2/P3HT) were measured as shown in figure 3.10(b) & (d). Both 5 nm and 10 nm Au NPs/P3HT composite samples exhibit enhanced OD. The Au NPs effects in composite samples can be represented as “subtracted extinction” spectra, in figure 3.10(b) & (d) dash lines, by first subtracting the OD spectra of composite samples by that of pristine P3HT spectrum and then converting the subtracted spectra into extinctions spectra following the equation, $E=1-T=1-10^{-Abs}$. Subtracted extinction spectra reproduce the shape of bare Au NPs (5 nm and 10 nm) shown in figure 3.10(a) & (c), with comparable intensity.

Figure 3.11 Infrared transmission spectra of 5 nm Au NPs/P3HT (a) and 10 nm Au NPs/P3HT (b) composite films; red area indicates the IR absorption of P3HT C-H stretching modes.

To exclude the possibility that the enhanced optical density may be due to the larger polymer film thickness, infrared transmission spectra of the composite films were measured and shown in figure 3.11. We chose the intensity of three vibrational peaks between 2800 and 3000 cm^{-1} (indicated in the red area) as characteristic parameters for evaluating the film thickness. All of these three vibrational peaks originate from C-H stretching modes of P3HT: 2857 cm^{-1} for CH_2 symmetric stretching mode, 2871 cm^{-1} for CH_3 symmetric stretching mode and 2928 cm^{-1} for CH_2 asymmetric stretching mode. The equal intensity of these three vibrational peaks in all six samples further confirm that all P3HT films have the same thickness. The appearance of vibrational peaks around 1583 cm^{-1} in Au NPs/P3HT composite samples (indicated by grey dash line in figure 3.11) is due to the ligands of Au NPs. Therefore, the enhanced OD of samples shown in figure 3.10(b) & (d) must result from the incorporation of Au NPs and their plasmonic effects.

To study the effects of Au NPs on polymer charge photogeneration, steady-state mid-IR photoinduced absorption measurements were subsequently carried out with results shown in figure 3.12(a) & (b). The mid-IR PIA spectra consist of broadband long lived localized (~ 0.35 eV) and delocalized (below 0.2 eV) polarons absorption in the polymer, thus the higher PIA signal as well as enhanced IRAV modes (below 0.2 eV) intensity suggest that more charges are photogenerated in Au NPs/P3HT composite film. The 5nm Au NPs/P3HT samples show similar PIA spectra to the pristine P3HT film with increased intensities. The PIA signal of the composite sample with highest Au NPs density, 5NM_3/P3HT, shows an enhancement factor of 1.8 compared to pristine P3HT (figure 3.12(a)). On the other hand, though enhanced in optical density, the PIA signal and the IRAV modes of 10nm Au NPs/P3HT composite samples increase very little (pink and yellow solid curves in figure 3.12(b)). The PIA spectra of both 10NM_1/P3HT and 10NM_2/P3HT samples (figure 3.12(b)) reveal that the enhanced OD with 10 nm Au NPs could not effectively improve the final charge density in P3HT polymer films as compared to the on-resonance samples, for instance, the PIA of 5NM_3/P3HT (green curve in figure 3.12(a)). The fact that no enhanced polarons are photogenerated is consistent with the observation that the plasmons in 10 nm Au NPs are not resonantly excited (both the 10 nm Au NPs extinctions and the subtracted Au NPs extinctions in figure 3.10 have the lowest intensity at the pump wavelength). Therefore, we confirmed that the resonant excitation of plasmons in Au NPs is the key for enhancing polymer excitonic absorption, regardless of the enhancement of OD observed in the 10 nm Au NPs/P3HT samples. As already discussed in *Section 3.2*, the enhanced OD of the composite samples can either result from the actual improved absorption of the polymer, as in the 5 nm Au NPs/P3HT samples, or from losses in the Au NPs, as in the 10 nm Au NPs/P3HT samples.

Figure 3.12 (a) IR-PIA spectra of pristine P3HT (black), 5NM_1/P3HT (red), 5NM_2/P3HT (blue) and 5NM_3/P3HT (green) film. The inset shows the schematic of IR-PIA setup. (b) IR-PIA spectra of pristine P3HT (black), 10NM_1/P3HT (yellow), 10NM_2/P3HT (pink) and 5NM_3/P3HT (green) film.

To confirm that increased polaron signals in 5 nm Au NPs/P3HT composite samples are actually due to enhanced polymer absorption, we estimated the total number of charges generated in the polymer film (N) by integrating the polaron signal in the PIA spectra from 0.1 to 0.6 eV, $N \sim \int_{\omega_1}^{\omega_2} I(\omega) d\omega$. Results are plotted against the total OD of each sample at the excitation wavelength ($\lambda=532$ nm). The linear dependence shown in figure 3.13(a) clearly indicates that the increase in number of charges with different density of Au NPs is caused by the plasmonic enhancement of the excitonic absorption of P3HT.

Figure 3.13 (a) The polaron yield plotted against the total OD of different 5 nm Au NPs/P3HT composite film. (b) Photoluminescence spectra of pristine P3HT (black), 10NM_1/P3HT (pink), 10NM_2/P3HT (yellow) and 5NM_3/P3HT (green) film.

We then measured the steady state photoluminescence of 10NM_1/P3HT, 10NM_2/P3HT and pristine P3HT samples. Results show that the sample with lower Au NPs density (10NM_1/P3HT sample) exhibited the highest photoluminescence intensity compared to pristine P3HT films, while both of the two off-resonance samples (10NM_1/P3HT and 10NM_2/P3HT) have higher PL intensity than those on-resonance and pristine samples (i.e. 5NM_3/P3HT in figure 3.13(b)). Measured photoluminescence can be characterized microscopically by the molecular detection efficiency (MDE),¹⁹⁰ $MDE(r_0) = \Gamma_{exc}(r_0) \times Q \times MCE(r_0)$ where $\Gamma_{exc}(r_0)$ is the excitation rate, Q is emission quantum yield and MCE is the molecular collection efficiency. The excitation rate, below saturation, is $\Gamma_{exc}(r_0) \propto |\mathbf{p} \cdot \mathbf{E}|^2$, where $\mathbf{p}$ is the transition dipole moment and $\mathbf{E}$ is the electric field. And the emission quantum yield is defined as $Q = \frac{\Gamma_{rad}}{\Gamma_{rad} + \Gamma_{nonrad}}$, where Γ_{rad} is the exciton radiative recombination rates and Γ_{nonrad} corresponds to the nonradiative process. Therefore, the enhanced

PL found in figure 3.13(b) can arise from the increased excitation rate due to electric field enhancement (i.e. enhanced absorption of the polymer, for example in 5NM_3/P3HT), from modified emission quantum yield or from improved light collection efficiency. Our results are consistent with previous work on Ag NPs/Si solar cell system.¹⁹¹

3.4 Conclusions

In conclusion, we have studied plasmonic effects of Au NPs on enhancing the above bandgap excitonic absorption in conjugated polymer P3HT using a combination of absorption, PL, and mid-IR PIA spectroscopy. With Au NPs having resonant frequency close to that of the excitation light (5 nm Au NPs), the plasmonic near field effects enhance effectively the excitonic absorption of P3HT, resulting in increased charge photogeneration. With Au NPs having resonant frequency away from the excitation light wavelength (10 nm Au NPs), though enhanced optical density is also observed in composite films, no enhanced polaron signal is found in PIA spectra. Instead, Au NPs enhance the exciton radiative recombination process while the charge photogeneration yield is unaltered.

Overall, mid-IR PIA spectroscopy has proven to be a reliable method to provide direct information about charge photogeneration in the polymer. However, we should emphasize that this conclusion is only suitable for Au NPs/polymer two component systems; with the presence of PCBM in bulk heterojunctions, exciton dissociation is greatly enhanced by charge transfer at donor-acceptor interfaces, as seen from the complete PL quenching (refer to figure 2.12 in *Chapter 2*). Therefore, a different approach should be used to determine the effects of plasmonic enhancement of Au NPs on bulk heterojunctions, as will be discussed later in *Chapter 5*.

Chapter 4. Plasmon polaron coupling in P3HT

4.1 Plasmon coupling to various degrees of freedom

Plasmonics are collective electron oscillations of free electrons induced by an electromagnetic field (*Chapter 4*). The interaction of the plasmonic modes with surrounding materials may occur in two ways: (i) the plasmonic resonance is affected by the dielectric function of the surrounding, thus different materials cause different shifts of the plasmonic resonance frequency for plasmonic modes; and (ii) the strong electric field in the vicinity of plasmonic nanostructures can modify the inherent optical properties of the surrounding material through either weak or strong coupling; for example the weak coupling of plasmonically enhanced fluorescence (SEF)¹⁹⁰ or Raman scattering (SERS).¹⁹² In the case of strong interaction, the coupling of plasmons and material excitations forms complexes or polaritons with mixed physical properties, such as altered dynamics and/or dispersion relations.¹⁹³ From a slightly different point of view, the formation of complexes due to strong coupling can be considered as the interactions of two species with similar discrete field energies, similar to state coupling in molecules.¹⁹⁴

Both of weak and strong couplings of plasmons with various degrees of freedom have been widely studied for their fundamental interest and intriguing applications. Plasmons can couple with excitons to form plasmon-exciton polaritons,¹⁹⁵⁻¹⁹⁹ with phonons in to form strongly coupled plasmon-phonon polaritons,^{200,201} and with IR molecular vibrations in the case of plasmonically enhanced IR absorption (SEIRA).²⁰²⁻²⁰⁴ Polaron species found in many organic and inorganic material systems, especially in conjugated polymers, are interesting excitations to study their

interactions with plasmons, the plasmon-polaron coupling.

In plasmonic organic solar cells, most of plasmonic enhancement methods were developed to enhance excitonic transitions at energies above the HOMO and LUMO gap, as discussed in *Chapter 3*. In these methods, light trapping or absorption enhancement is the dominant mechanism; meanwhile reports also show that of exciton dynamics in plasmonic organic solar cells may be altered by plasmon-exciton coupling.^{184,185,205}

Here we study the coupling between the surface plasmons in properly designed IR-nanoantennas and polarons in P3HT and show, for the first time, that plasmon-polaron coupling can be used as a means to modify the photophysical properties of conjugated polymers.

Figure 4.1 Conceptual representation of plasmon-polaron coupling presented in this chapter.

The proposed concept is shown in figure 4.1. The photogenerated polaron delocalized within the polymer interacts with surface plasmons in the adjacent plasmonic metamaterial. Since the relaxation energy of polarons in polymers is in the mid-IR, in order to achieve plasmon-polaron coupling our plasmonic metamaterial (IR-nanoantennas) is designed to resonate around this energy, far from the visible excitonic absorption. Plasmon-polaron coupling is expected to increase the probability of reaching final polaron states, through either direct or indirect pathways, by resonant

enhancement of polaron relaxation and exciton dissociation processes.^{206,207}

4.2 Design and fabrication of IR-nanoantennas

To test the concept of plasmon-polaron coupling, we chose the well-characterized organic photovoltaic material RR-P3HT to provide the photogenerated polarons. The design of the IR-nanoantennas had to satisfy the following requirements: (1) IR-nanoantennas have plasmonic resonances in mid-IR region overlapping with the P_I polaron band of the polymer. We avoid coupling with other polaron bands, DP_2 , P_2 , because the overlap of these bands with the broadband exciton (EX) absorption (interchain singlet exciton at 1.05 eV and triplet exciton absorption at 1.66 eV), may further complicate interpretation of the results;²¹ (2) IR-nanoantennas should have no resonance in the visible region, so that the spectral changes could be directly correlated to the plasmons-polaron coupling without having to consider effects on polaron photogeneration due to plasmonically enhanced light absorption; (3) large area samples are required for our steady-state PIA measurements, meanwhile such samples will prove feasibility for future device applications on large scale.

IR-nanoantennas were fabricated using the hole-mask colloidal nanolithography with tilted-angle-rotation evaporation technique. This technique was previously proven to be suitable for low-cost and large-area fabrication of complex plasmonic nanostructures and metamaterials.²⁰⁸⁻²¹¹

4.2.1 Structure design and simulation results

Design of IR-nanoantennas is based on the commonly used split-ring-resonator (SRR) structure,

which can be easily fabricated by our technique. 3D full-wave simulation software *COMSOL Multiphysics* was used to simulate the far-field transmission curves and field maps of the SRR with periodic boundary conditions (See *Appendix C* for detail). By carefully tuning the geometrical parameters of the SRR, we obtained nanoantenna structures with desired IR resonant positions.

SRR was modeled as a periodical lattice above the substrate, with period of 900 nm and gaps oriented horizontally. Optimized dimensions of the rings consist of inner radius of 214 nm, outer radius of 397 nm and gap subtending an angle of 33 degrees from the center, as shown in figure 4.2.

Refractive indexes for all the materials were retrieved from the literature.

Figure 4.2 (Left) The unit cell model of split-ring-resonator with geometrical parameters labeled. (Right) List of optimized parameters deduced from the simulations.

Simulated transmission curves of the SRR are shown in figure 4.3(a) together with the typical RR-P3HT PIA spectrum (figure 4.3(b)). As can be seen from figure 4.3(a), the simulated transmission curves of SRR have a single resonance around 0.37 eV (A in figure 4.3(a)) that is excited by mid-IR light with 90° polarization, while two resonances appear in the same spectral region, at 0.19 eV (B) and 0.53 eV (C) for 0° polarization of the incident light. These polarization dependent resonances have similar energies as the polaronic transitions of RR-P3HT (figure 4.3(b)). For clarity the spectral position of these resonances are shown in an energy diagram together with RR-P3HT

polaronic transitions (figure 4.3(c)). The extracted plasmonic resonance frequencies are further red-shifted when taking into account the high-index polymer film, and resulting energy alignment are shown in figure 4.3(d); note that A and B plasmonic resonances are optimally aligned with the P_I transition and the IRAV modes of P3HT. The normalized field distribution of the electric field component perpendicular to the plane of the structure (E_z) 20 nm above the substrate plane for each SRR resonance is plotted in figure 4.3(d), showing near field confinement of the field due to surface plasmon resonant modes in the SRR. Clear dipolar modes can be identified for A and B, while a quadrupolar mode is excited at higher frequency (C).

Figure 4.3 (a) Simulated transmission spectra of bare IR-nanoantennas for 0° (light pink curve) and 90° (blue curve) polarized light; A, B, and C correspond to resonant modes in panel (d). (b) PIA spectrum of RR-P3HT thin film spun-cast on CaF2 substrate. (c) Energy level of localized polaron transitions and resonance transitions extracted from (a). (d) Simulated near field maps of E_z above the split ring resonator. To better represent the figure, the zero electric field outside the perimeter of rings was set as white color rather than the green in color scale bar.

4.2.2 Fabrication of IR-nanoantennas

From the design and optimized parameters, large-area SRR were fabricated using the hole-mask colloidal nanolithography with tilted-angle-rotation evaporation technique. The description of such technique and the fabrication details of IR-nanoantennas can be found in *Appendix B*.

SEM image of resulting IR-nanoantennas samples shown in figure 4.4(a) reveal that single SRR structure can be experimentally produced according to the simulation design. Instead of orderly arranged array, such nanoantennas assemble into a dense array with random spatial distribution. However, all SRRs share a common rotational orientation throughout the entire substrate. Consequently, large-area IR transmission spectra of fabricated samples exhibit light polarization dependence (figure 4.4(c)), in good agreement with simulation results (figure 4.4(d)). Following the design requirements, the fabricated IR-nanoantennas have very low absorbance ($OD < 0.1$) in the visible part of the spectrum overlapped with absorption of P3HT (yellow dashed curve in figure 4.4(b)). Absence of plasmonic enhancement of polymer absorption is confirmed by the slight quenching of a ~ 70 nm-thin P3HT film absorption (black solid curve in figure 4.4(b)) on the metamaterial (yellow solid curve in figure 4.4(b)). This ensures that visible excitation (e.g., at 532 nm, green arrow in figure 4.4(b)) of the hybrid sample photo excites the polymer, but not the IR-nanoantennas.

Figure 4.4 (a) SEM image of fabricated large area IR-nanoantennas with split-ring-resonator (SRR) structures. (Inset) Enlarged scale of SEM image. (b) Absorption spectra of pristine RR-P3HT thin film on CaF₂ substrate (black solid curve), P3HT/IR-nanoantennas hybrid sample (yellow solid curve) and bare IR-nanoantennas (yellow dash curve). (c) Measured IR transmission spectra of bare IR-nanoantennas for orthogonal polarizations (0°, dark pink and 90°, dark blue curve). (d) Simulated IR transmission spectra of bare IR-nanoantennas (0°, light pink and 90°, blue curve).

Meanwhile off-resonance-antenna samples were also fabricated as a control in order to rule out any other factor that may affect the overall polaron photogenerations, e.g. charge or energy transfer between the polymer and the metamaterial,²¹² or improved morphology of polymer films spun-cast on metals.²¹³ By shortening the length of the rings, i.e. increasing the gap angle of the SRR (see SEM image in figure 4.5(a)), we were able to blue shift the SRRs resonances outside the P_I polaron absorption band. This blue shift of resonances can be confirmed by the IR transmission spectra of bare off-resonance-antenna (figure 4.5(c)), showing little spectral overlap with the pristine P3HT PIA spectrum in mid-IR region (figure 4.5(d)). Similar to IR-nanoantenna samples, the control sample exhibits negligible absorption in the visible (yellow dash curve in figure 4.5(b)), with no plasmonic enhancement of polymer absorption observed in the off-resonance-antenna/P3HT hybrid sample (blue and black solid curve in figure 4.5(b)).

Figure 4.5 (a) SEM image of fabricated large area, off-resonance antenna sample. (Inset) Enlarged SEM image. (b) Absorption spectra of pristine RR-P3HT thin film on CaF₂ substrate (black solid curve), P3HT/off-resonance antenna hybrid sample (yellow solid curve) and bare off-resonance antenna (yellow dash curve). (c) Measured IR transmission spectra of bare off-resonance antenna for orthogonal polarizations (0°, dark pink curve and 90°, dark blue curve). (d) PIA spectrum of pristine P3HT thin film on CaF₂ substrate.

4.3 Plasmon-polaron coupling in IR-nanoantennas/P3HT hybrid systems

4.3.1 P3HT on IR-nanoantennas

To ensure the homogeneity and thickness identity of polymer films on different sample substrates, we measured samples with Atomic Force Microscopy (AFM) and characterized both the samples' surface topography and polymer films thickness.

Figure 4.6 shows the surface topography images (10 $\mu\text{m} \times 10 \mu\text{m}$) of the IR-nanoantenna, IR-nanoantennas/P3HT, and pristine P3HT samples on CaF₂ substrates, respectively, measured by AFM. Single split ring resonator IR-nanoantennas can be resolved clearly in the uncoated samples

on both height and phase images, while the phase image of IR-nanoantennas/P3HT sample (figure 4.6(e)) confirms a well coated P3HT film on top of the IR-nanoantennas. The pristine P3HT film topography images are shown in figures 4.6(c) & (f) for comparison. The root mean square (rms) roughness of IR-nanoantenna/P3HT is around 8 nm, which, compared to the 4 nm value obtained for the pristine P3HT sample, indicates that the presence of nanoantennas does not alter the polymer film's homogeneity, even if still affecting the surface's roughness.

Figure 4.6. Topography of samples with both height (a-c) and phase images. IR-nanoantenna (a, d), IR-nanoantenna/P3HT (b, e), and pristine P3HT (c, f).

The thicknesses of P3HT in both IR-nanoantenna/P3HT and pristine P3HT samples are determined by AFM measurements of a scratch in each polymer film which reaches the substrate surface (figure 4.7). The cross-section profile in figure 4.7(b) and (d) show that the pristine P3HT and IR-nanoantenna/P3HT have almost identical thickness of, namely $h = 68.8$ nm and $h = 64.9$ nm. These identical values are also consistent with the visible absorption of pristine P3HT and IR-nanoantenna/P3HT shown in figure 4.4(b).

Figure 4.7 (a) Topography images of pristine P3HT with a ditch. Light yellow, the polymer film. Brown, the substrate. (b) Surface profile of IR-nanoantennas/P3HT. Light yellow, the polymer film. Brown, the substrate. (c) Topography images of IR-nanoantennas/P3HT with a ditch. (d) Surface profile of IR-nanoantennas/P3HT.

To confirm repeatability of sample preparation and reliability of thickness from one realization to another, we prepared 5 P3HT thin films under the same conditions and measured their thickness. Results show good repeatability of thickness as shown in figure 4.8.

Figure 4.8. Film thickness statistics of 5 spun cast P3HT films.

4.3.2 Polarized photoinduced absorption spectra of IR-nanoantennas/P3HT

To probe the interaction between resonant surface plasmons and polarons in the hybrid IR-nanoantennas/P3HT system we conducted broadband probe-polarized steady-state PIA experiment, as introduced in *Chapter 2*. Corresponding differential transmittance spectra are reported in figure 4.9. The PIA of the hybrid IR-nanoantennas/P3HT sample is found to be independent of pump beam polarization but strongly dependent on the polarization of the probe. For both 0° and 90° polarizations, the amplitude of PIA resonances is enhanced by a factor of 2 (in figure 4.9(b) & (c)) compared with the reference pristine P3HT film (figure 4.9(a)). Such enhancement of polaron signal is an indication of plasmon-induced increase of polaron generation in the polymer film. Strong modulation features appear at 0.14 eV and 0.41 eV for the 0° polarization, and at 0.29 eV for the 90° polarization (figure 4.9(b) & (c)). This polarization dependence clearly demonstrate the modulations originates from the SRR resonance. To further understand this phenomenon, we compare it with its IR transmission spectra.

Figure 4.9 PIA spectra of (a) pristine P3HT (black curve) (b) P3HT/IR-nanoantennas hybrid sample for 0° (dark pink curve) and (c) 90° polarized probe light (dark blue curve).

4.3.3 IR transmission and near field modeling

IR transmission spectra of IR-nanoantennas/P3HT hybrid sample

The IR transmission spectra of IR-nanoantennas/P3HT hybrid sample with polarized incident light are shown in figure 4.10(a). Spectra of both 0° and 90° polarizations (dark pink and dark blue curves) present characteristics of P3HT (e.g., the hexyl C-H stretching vibrational modes at ~0.36 eV) as well as of the nanoantennas (e.g., polarized resonances A, B and C). The high refractive index ($n \sim 1.85$) of the polymer film induces a small red shift (0.06 eV) of the nanoantenna resonance with respect to the bare antenna (figure 4.4(c)). More importantly, the modulations found in PIA are red shifted compared to the IR-nanoantennas resonant frequencies (figure 4.10(a)).

Figure 4.10 (a) Measured IR transmission spectra of IR-nanoantennas/P3HT hybrid sample for 0° (dark pink curve) and 90° (dark blue curve) light polarization. A, B, C label the resonant modes corresponding to the bare IR-nanoantennas, red and blue arrows indicate the incident IR light polarization. (b) Calculated near field resonances of the SRRs using a damped harmonic oscillator model (light pink curve for 0° and light blue curve for 90° polarized light). (c) Subtracted PIA spectra of P3HT/IR-nanoantennas hybrid sample from pristine P3HT spectrum. Dark pink curve: 0° polarized probe light; Dark blue curve: 90° polarized probe light. Vertical dashed lines are guidelines to highlight the resonance shift from the far- to the near-field of the SRRs. (d) Schematics of plasmon-polaron coupling. (Table) Fitting parameters used for calculating near field resonances with the damped, driven harmonic oscillator model.

Near-field modeling and plasmon-polaron coupling

As introduced in *Chapter 3*, the field distribution of LSPR in the vicinity of metallic nanostructure is significantly different from what can be measured in the far-field; nevertheless, plasmonic coupling only occurs in the near field region. The red shift observed in figure 4.10(c) (or figure 4.9) can be explained by the near field interactions, or else found in other systems.

The red shift of resonances is well described by the simple damped driven harmonic oscillator model, where external IR light electric field provides the driving force (figure 4.10(b)).²¹⁴⁻²¹⁶ The primary equation that describes the motion of the oscillator is $m\ddot{x} + m\gamma\dot{x} + kx = F_0 \cos(\omega t)$, where

the time varying driving term $F_0 \cos(\omega t)$ is from the external electric field, γ is the intrinsic damping parameter and k is the spring constant that characterizes the restoring force due to the displacement of conduction electrons. The steady-state solution of the above equation has the form of $x(t) = A(\omega) \cos(\omega t - \delta)$, where A is the frequency dependent oscillation amplitude, ω is the oscillation frequency and δ the phase. The amplitude of the oscillation, A , relates to the line-shape of near field plasmon resonance expressed as $A(\omega) = \frac{F_0}{m} \frac{1}{\sqrt{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}}$, where $\omega_0 = (k/m)^{1/2}$ is the plasmon resonance frequency, and the amplitude maxima reside at frequency $\omega_{NF} = \sqrt{\omega_0^2 - \gamma^2/2}$, which is red-shifted respect to the plasmon resonance frequency. On the other hand, the average power absorbed per oscillation period correlates to the far field absorption (extinction) spectrum of the nanoantennas, which can be calculated as $\langle P(t) \rangle = \frac{F_0^2 \gamma}{2m} \frac{\omega^2}{[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]}$, where the maximum absorption occurs at the plasmon frequency, ω_0 .

In practice, the values of the parameters in the equations above are determined by fitting the extinction spectra of the nanoantennas. This was done by subtracting the P3HT absorption from the measured IR transmission spectra shown in figure 4.10(a), and the extinction spectra were calculated by $E = 1 - T - A$, where E represents the extinction of the nanoantennas, T is the overall transmittance of the hybrid sample, and A is the absorbance of the P3HT thin film, which is obtained by measuring the pristine film IR transmission spectrum spun-cast on CaF_2 substrate. A Lorentz function was then used to fit the resonance peaks for both polarizations with $y = y_0 + A\gamma\omega^2 / [(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]$, where γ is the damping parameter and ω_0 is the plasmon resonance frequency. The fitted parameters are tabled in figure 4.10 according to different plasmon

resonances (resonance A, B, C) found in figure 4.10(a). Simulated near-field spectra are finally calculated as $y = B / \sqrt{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$ for both two polarizations. The spectrum of 0° polarization was obtained by combining the two fitting results for resonances B and C, with necessary adjustment of their amplitudes. The near-field resonances have a typical ~0.03 eV energy difference respect to the far-field ones, as can be seen in figure 4.10(b).

To better understand the coupling mechanism, the IR-nanoantennas/P3HT PIA spectra of two polarizations are subtracted by the spectrum of pristine P3HT. The subtraction is done according to

$$\text{Subtracted}(-\Delta T / T) = (-\Delta T / T)_{\text{IR-nanoantennas/P3HT}} - 2.3 \times (-\Delta T / T)_{\text{P3HT}},$$

where $(-\Delta T / T)_{\text{IR-nanoantennas/P3HT}}$ are the IR-nanoantennas/P3HT PIA spectra and $(-\Delta T / T)_{\text{P3HT}}$ is the pristine P3HT PIA spectrum shown in figure 4.9, and 2.3 is enhancement factor due to the plasmon-polaron coupling. In addition to the enhancement, the modulation features (0.14 eV and 0.41 eV for the 0° polarization and at 0.29 eV for the 90° polarization) are more clearly represented as photo-bleaching of polaron absorption of P3HT ($\text{Subtracted}(-\Delta T / T) < 0$) induced by IR-nanoantennas. As anticipated, the photo-bleaching signal in IR-nanoantennas/P3HT PIA spectra (figure 4.10(c)) matches well with the near-field resonances calculated in figure 4.10(b), indicating the near-field interaction occurring in the vicinity of IR-nanoantennas. The near-field interaction is a strong evidence for plasmon-polaron coupling. Moreover, the photo-bleaching by plasmon-polaron coupling can be clearly seen from figure 4.10(d), where the excitation of IR-nanoantennas induces resonant transfer of charges into corresponding polaron states, and thus bleaching corresponding transitions. To further confirm this hypothesis, ultrafast time-correlated measurements will be needed.

4.3.4 IRAV modes

To clarify the effect of plasmon-polaron coupling and correlate the enhancement of polaron signal to the actual charge carrier photogeneration, we further analyzed the changes of IRAV modes in the PIA spectra of IR-nanoantennas/P3HT hybrid sample.

As described in *Chapter 2*, the appearance of strong IRAV modes results from the conversion of even parity symmetric Raman-active vibrational modes (A_g modes) into IR-active modes by the local symmetry breaking of polymer chains produced by charge localization. Experimental infrared absorption spectra induced by photo- or chemical-doping show peaks with one-to-one correspondence to the strongest Raman-active modes of the polymer observed in resonance Raman scattering. The intensity of these IRAV modes is directly proportional to charge carrier concentration, making them a unique optical probe for charge carrier density and dynamics in conjugated polymers. Instead of manifesting as PIA peaks, IRAV modes of P3HT films possess a Fano-type anti-resonance line shape (figure 4.11(b)), created by the superposition of the narrow IRAV modes with the broadband delocalized polaron absorption.²¹ In figure 4.11(b) we compare the IRAV modes of the pristine polymer film (black curve) with those obtained from the hybrid IR-nanoantennas/P3HT sample with orthogonal probe polarizations. For 90 ° polarization (dark blue square curve), the IRAV modes appear in a spectral region not strongly modulated by the plasmon-polaron coupling resonance at ~0.3 eV; nevertheless, their intensity is enhanced by more than a factor of 2 and all modes are preserved without spectral shift with respect to the pristine film. In both pristine and hybrid samples at 90 ° probe polarization (black and dark blue square curves in figure 4.11(b)), the assignment of IRAV modes to P3HT IR-absorption (figure 4.11(a)) and resonance Raman (figure 4.11(c)) modes is hindered by the presence of anti-resonances (indicated

by grey arrows). In contrast, at 0° probe polarization the IRAV modes overlap with the plasmon-polaron coupling resonance at ~0.15 eV, and their peaks are easily resolved (dark pink curve in figure 4.11(b)): from 900 to 1300 cm⁻¹, the anti-resonances become positive IRAV peaks perfectly matching the Raman active modes, whereas in the tail of the modulation, from 1300 to 1700 cm⁻¹, the IRAV peaks become anti-resonances, also in correspondence with Raman active modes. We therefore speculate that the near-field coupling of plasmons and polarons offsets the effect of broadband delocalized polaron absorption in the spectra, thus making IRAV modes of P3HT clearly distinguishable. These experimental results are consistent with the description from nonadiabatic amplitude mode theory developed by Horovitz and colleagues.^{102,132} The enhancement of IRAV modes in both 0° and 90° polarized PIA spectra provides strong evidence of the fact that more charges are generated in the presence of resonant IR-nanoantennas.

Figure 4.11 (a) IR absorption spectrum of P3HT thick film. (b) IRAV modes below 1700 cm⁻¹ in PIA spectra for pristine P3HT film (black solid curve) and IR-nanoantennas/P3HT hybrid film at 0° (dark pink solid curve) and 90° (dark blue square solid curve). Dashed grey line arrows indicate IR and Raman active modes; solid grey arrow indicate typical IRAV anti-resonances in 90° polarized PIA spectra which become clear peaks for 0° polarization. Pink area indicates the typical IRAV modes area in spectrum. (c) Resonance Raman scattering spectrum of P3HT thin film.

4.3.5 Control experiments

PIA spectra of off-resonance-antennas/P3HT

With control samples, the IR transmission spectra (figure 4.12(a)) confirm that the plasmon resonances are still red-shifted by the presence of P3HT, despite being well separated from the P3HT polaronic transition in mid-IR region. Specifically, the resonance at ~ 0.8 eV (0° polarization) is at the energy gap of polaronic transition (P_1) and singlet exciton absorption (EX), while the resonance at ~ 1.0 eV (90° polarization) and at ~ 1.25 eV (0° polarization) overlap with exciton absorption and P_2 polaron transition, respectively (figure 4.12(b)).

The probe-polarized PIA spectra in mid- to near-Infrared (NIR) spectral response are shown in figure 4.12(c) & (d). Resonances in NIR induce modulations in PIA spectra, and the P_2 band is slightly enhanced with both polarizations. However, interpretation of this phenomenon becomes difficult because overall three different species (plasmons, excitons, and polarons) may be involved in the interaction. On the other hand, the PIA spectra of the off-resonance-antennas/P3HT hybrid sample in MIR spectral region, as shown in figure 4.12(e) on an enlarge scale, exhibit similar behavior to the pristine P3HT films, with no significant enhancement of polaron signal and IRAV modes.

Figure 4.12 (a) Measured IR transmission spectra of off-resonance-antennas/P3HT hybrid sample for 0 °(dark pink curve) and 90 °(dark blue curve) light polarization. (b) PIA spectrum of pristine P3HT thin film sample. (c) PIA spectrum of off-resonance-antennas/P3HT hybrid sample for 0 ° probe light polarization. (d) PIA spectrum of off-resonance-antennas/P3HT hybrid sample for 90 °probe light polarization. (e) PIA spectra of off-resonance sample for 0 °(dark pink curve) and 90 °(dark blue curve) light polarization and pristine P3HT thin film in MIR spectral region on an enlarge scale.

The presence of mid-IR light plays a rather important role in the PIA measurements, since it not only probes the charge species in the polymer but also excites the plasmonic resonances of the nanoantennas, while charges are photogenerated by the visible light. Our mid-IR PIA setup satisfies the conditions stated above (see *Appendix A* for more details). Therefore, the absence of enhancement with resonances excited in off-resonance antenna/P3HT sample (figure 4.12(e))

further proves the existence of plasmon-polaron coupling in IR-nanoantennas/P3HT. More importantly, it emphasizes the necessity of having nanoantennas resonant at the polaron relaxation energy in order to achieve coupling and polaron photogeneration enhancement.

Chemical doping on IR-nanoantennas/P3HT hybrid sample

To further confirm that plasmon-polaron coupling modifies the inherent photophysical properties of the polymer particularly enhancing the polaron photogeneration process, we compared the mid-IR PIA spectra with the differential transmittance spectra obtained by chemical (redox) doping (figure 4.13). By chemically introducing charge carriers in polymer, we could rule out the possibility that the enhancement observed in PIA spectra may arise from the spectroscopic summation of plasmonic resonances and polaronic absorption, and conclude instead that the near-field resonant coupling actually induces a change of the polymer excited state.

Chemically induced absorption spectra were calculated similarly to PIA, using transmission spectra of the same undoped films as a reference (figure 4.13(a)). Both plasmonic resonances and polymer vibrational features are clearly visible in far-field IR transmission spectra of the hybrid IR-nanoantennas/P3HT film (figure 4.13(a)). Doping-induced absorption spectra of the two samples shown in figure 4.13(b)(c) exhibit the following features: (i) broad polaron absorption, centered around 0.4 eV, similar to PIA spectra of pristine P3HT, and polarized modulations induced by resonant plasmon coupling in the hybrid sample; (ii) no significant enhancement or spectral shift of the resonances induced by near-field coupling, for either of the polarizations; (iii) no enhancement of IRAV mode intensity (below 0.18 eV) in the hybrid film compared to the pristine P3HT film, with either probe polarization. Both (ii) and (iii) indicate that polarons cannot be generated due to

the coupling to surface plasmons in addition to those that have already been (chemically) induced. Therefore we conclude that the mechanism leading to enhanced polaron photogeneration in the presence of resonant IR-nanoantennas must be dynamic, and based on the thermal activation of either direct polaron excitation or exciton dissociation which do not occur in the case of static, chemical doping. Here we emphasize again that the PIA experiments involve a three-level system comprising of the main excitonic transition of the polymer in resonance with the pump, as well as photoinduced polaronic transitions and IR-nanoantenna plasmonic modes in resonance with the infrared probe. It appears that both infrared resonances must be excited simultaneously to lead to cooperative enhancement of polaronic transitions during the photoexcitation process.

Figure 4.13 (a) IR absorption spectrum of undoped IR-nanoantennas/P3HT sample with 0° (dark pink curve) and 90° (dark blue square curve) light polarizations. (b) Chemical doping induced absorption spectra for pristine P3HT film (black curve) and hybrid sample at 0° (dark pink curve) and 90° (dark blue square curve) polarizations. Dashed lines indicate the spectral position of far-field transmission resonances. (c) Doping induced absorption spectra in the region of IRAV modes on an enlarge scale.

4.4 Discussion and conclusions

The generally accepted scheme for polaron photogeneration in conjugated polymers sees a competing pathway between direct photoexcitation and exciton dissociation. While the first process does not require any excess energy, the second requires thermal, photon energy, or electric field activation.^{70,217} Experiments clearly demonstrate that both exciton and polaron photogeneration are ultrafast ($t < 100$ fs) events.^{67,75,136} Polaron/exciton branching ratios are varying from 10 to 30% in pristine polymer films.^{71,72} There are three possible mechanisms by which plasmon-polaron

coupling with IR-nanoantennas could lead to enhanced polaron photogeneration yield: (i) formation of plasmon-polaron complexes may favor direct polaron relaxation through resonant energy transfer; (ii) the effect of the resonance on the dissipation path of a coherent state made by the superposition of the singlet state (“exciton”) and the charge separated state. The decay of such coherent superposition might be affected by the resonance with the IR-nanoantennas, enhancing the yield of the charge separation channel; (iii) absorption of IR light by the coupled resonant nanoantennas may provide excess thermal energy needed for exciton dissociation. These arguments, especially (i), can be understood considering the polaron formation mechanism introduced in *Chapter 1*. The polarons formation energy: $E_{relax} = E_{ipv} - (E_{ipd} + E_{dis}) = \Delta E - E_{dis} > 0$ and the plasmon-polaron coupling mechanism could enhance either of the formation pathways (a) and (b) shown in figure 4.11. Taking the polaron formation pathway (b) for example, the presence of IR plasmonic nanoantennas could enhance the (A)→(C) process by providing additional thermal energy to the system, or the molecule potential surface could be altered due to the formation of plasmon-polaron complexes.

Figure 4.14 Electron ionization process in single molecule according to the Franck-Condon principle.

Additional studies will be required to elucidate these arguments as well as the charge-transfer mechanism discussed before. For instance, “Pump-Push-Probe” experiments^{68,218} or measurements

of photocurrent generation in working device structures are two possible options to be pursued in future research.

In conclusion, with photoinduced absorption spectroscopy we have observed both plasmon-polaron coupling and enhanced polaron photogeneration in pristine semiconducting polymer P3HT films by engineering the plasmonic nanoantennas resonance to overlap in energy with the P3HT polaron absorption. Applying this concept to donor-acceptor bulk heterojunction solar cell devices may open up a new route for improving the performance of organic solar cells, either through plasmon-polaron coupling or by recycling the thermal solar radiation otherwise wasted. It may also be possible to engineer plasmonic nanostructures with resonances in the Vis-NIR spectral region to enhance photon absorption and in the mid-IR to enhance polaron photogeneration simultaneously.

Chapter 5. Perspectives and future work

5.1 Towards photovoltaic device implementation

5.1.1 Plasmon-polaron enhancement of bulk heterojunction solar cells

The schematic of a typical organic bulk heterojunction solar cell is shown in figure 5.1, together with the chemical structure of a number of donor (D) and acceptor (A) molecules. The large variety of active materials, especially polymer electron donors, show the vast potential for improving organic solar cells performance by developing compounds with tailored optical and electrical properties. For example, low optical bandgap matches better the solar spectrum, or the relative LUMO-HOMO alignment with acceptor materials leads to better charge separation. However, the excitonic behavior of organic solar cells upon photoexcitation poses inherent limits for device structure optimization, and it is mainly constrained by the film thickness. To solve this problem, light trapping techniques are developed to enhance above bandgap absorption. Meanwhile, even with low bandgap materials and light trapping techniques, certain amount of solar light with energy below bandgap will always be wasted, in addition to the energy lost in the thermalization during the charge separation process.^{12,219} In the following, we outline some opportunities that will be investigated in the future to use the new concept of plasmon-polaron coupling I demonstrated in this thesis to enhance power conversion efficiency of actual bulk heterojunction solar cells. We propose that plasmon-polaron coupling could be used to facilitate thermally activated process and to resonantly enhance polaron relaxation.

Figure 5.1 Chemical structures of representative donor and acceptor materials, and typical structure of a bulk heterojunction solar cell. HTL stands for holes transporting layer, the substrate is usually glass, and the cathode is usually aluminum, depending on the energy alignment with the active materials. Additional layers can be inserted in between the cathode and active layer, such as electron transporting layer (ETL) or layers to modify the interface between the active layer and the cathode.

Continuing the discussion started in *Chapter 4*, we hereby emphasize that the mechanism of enhancing organic solar cells performance by IR-nanoantennas plasmonics may act in two ways: it may change the photoexcitation dynamics upon formation of plasmon-polaron coupled complexes, and it may enhance thermal solar light concentration by IR plasmonics induced field enhancement.

5.1.2 Plasmon-polaron enhanced polaron photogeneration in bulk heterojunctions

While it has been shown in *Chapter 4* that the plasmon-polaron coupling can inherently change the photophysical properties of the polymer, we expect it to function similarly in donor-acceptor systems. On the other hand, the photophysical picture of donor-acceptor systems is profoundly

different from that of polymer/IR-nanoantennas system; here the efficient charge transfer process which occurs at the donor-acceptor interfaces becomes the major charge generation source, and the effect of plasmon-polaron coupling mechanism in this process should be discussed.

We have gathered preliminary results performing polarized PIA measurements of IR-nanoantennas/P3HT:PCBM hybrid systems. Figure 5.2 shows similar spectral modulation as the case of IR-nanoantennas/P3HT (presented in *Chapter 4*), indicating near-field interaction of the plasmons in IR-nanoantennas and the polarons in conjugated polymer, P3HT. Similar to IR-nanoantennas/P3HT, the PIA spectra exhibit approximately a factor of two polaron signal enhancement in IR-nanoantennas/P3HT:PCBM compared to P3HT:PCBM. PIA results clearly reveal the effects of plasmon-polaron coupling do also apply to bulk heterojunctions; however, additional transient spectroscopy experiments are still needed to understand the details of charge photogeneration in this more coupled 4-level system.

Figure 5.2 (a-c) Photoinduced absorption on P3HT:PCBM sample (black curve) and IR-nanoantennas/P3HT:PCBM hybrid sample for 0° (dark pink curve) and 90° (dark blue curve) polarizations. (d-f) Photoinduced absorption on P3HT sample (black curve) and IR-nanoantennas/P3HT hybrid sample for 0° (dark pink curve) and 90° (dark blue curve) polarizations.

5.1.3 Thermally assisted charge photogeneration in organic solar cells

The enhanced thermal absorption due to the IR-nanoantennas can also be helpful for solar cell performance improvement by facilitating the thermally active processes in organic active films. In the following, we review a few thermally activated processes as discussed in the literature of organic solar cells.

Onsager theory

Some researchers suggest that the charge separation process can be modeled by the Onsager/Onsager-Braun theory. The Onsager theory²²⁰ is widely used model for dissociation and recombination of photogenerated geminate electron-hole pair in both organic molecular crystals and polymers.^{31,34,221} More specifically the model is based on the picture shown in figure 5.3, where (1) the absorption of photon excites the molecule to S_n state, after which the photoexcited molecule can either undergo a rapid phonon assisted relaxation to S_I state in process (2) forming “cold” exciton, or generate free charges directly from “hot” exciton state in process (3) (a process referred as autoionization), or thermalize to become charge transfer (CT) exciton; CT excitons are bound by Coulomb force, have separation a (the thermalization distance), and reside in the Coulombic potential well. This geminate pair, CT exciton, can either dissociate into a free charge pair or recombine depending on the magnitude of Coulombic interaction in the potential well. A characteristic parameter defined by Onsager is the Coulomb capture radius $r_c = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$, i.e. the distance for which the Coulomb potential energy equals the thermal energy ($k_B T$). A geminate pair with radius a will dissociate into free charge carriers if $a > r_c$, while it will have certain probability to recombine or dissociate if $a < r_c$. In his original formulation, Onsager assumed unitary

recombination probability when the electron gets in contact again with the hole, while Braun later modified the theory by considering the CT exciton with a certain lifetime $\tau(E)$, which could also be regenerated from free charge carriers within the lifetime (bimolecular process).²²² Therefore in the

Onsager-Braun model, the dissociation probability $f(E)$ can be expressed as

$$f(E) = \frac{k_{diss}(E)}{k_{diss} + k_{recom}} = k_{diss}(E)\tau(E), \text{ where } k_{diss}(E) \text{ is the field-dependent dissociation rate, and}$$

$k_{recom}(E)$ is the geminate recombination rate constant including both radiative and nonradiative relaxation processes. The dissociation rate in the low electric field limit is defined as

$$k_{diss}(E) = \frac{\langle \mu \rangle}{\langle \epsilon_r \rangle \epsilon_0} \cdot \frac{3}{4\pi a^3} \cdot e^{-\frac{\Delta E}{k_B T}} \left[1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \dots \right], \text{ where } \langle \mu \rangle \text{ is the charge carriers' average}$$

mobility, $\langle \epsilon_r \rangle$ is the average dielectric constant of the surrounding medium, ΔE is the Coulomb

binding energy of the thermalized exciton $\Delta E = \frac{e^2}{4\pi\epsilon_0 \langle \epsilon_r \rangle a}$, and $b = \frac{e^2}{8\pi\epsilon_0 \langle \epsilon_r \rangle (k_B T)^2} E$. In zero

external field, the dissociation rate becomes $k_{diss}(0) = \frac{\langle \mu \rangle}{\langle \epsilon_r \rangle \epsilon_0} \cdot \frac{3}{4\pi a^3} \cdot e^{-\frac{\Delta E}{k_B T}}$. The Coulomb potential

can be lowered in high electric field as described by the Frenkel-Poole effect. Thus the dissociation

of geminate excitons or CT excitons may depend both on temperature and external electric field.

Figure 5.3 Photoexcitation and relaxation of an organic material represented by its potential energy diagram. The curve shows the potential well of Coulomb attraction as a function of exciton separation distance. The labeled processes are (1) photoexcitation and exciton generation. (2) Thermalization of electron to a position with geminate pair separation a . (3) Autoionization process that directly separates the charges. (4) Infrared excitation to promote electrons to higher states prior to their recombination, thus enhancing the charge separation yield.

Meanwhile, it is also likely that excitation of the geminate excitons with additional thermal energy before they recombine may enhance charge separation probability and overall amount of charge collected in a device (see figure 5.3 (4)+(2) process). Indeed, thermally assisted dissociation of geminate pair has been observed experimentally by “pump-push” transient measurements.^{223,224} Therefore, with the help of simultaneously absorbed thermal energy, our IR plasmonic nanoantennas can act similarly, by either maintaining the exciton “hot” in higher electronic states, or by elevating it from the Coulomb potential well after thermalization; both mechanism could enhance geminate pair dissociation.

Thermal excess energy for charge transfer states in bulk heterojunctions

The study of charge transfer exciton or charge transfer states started from the organic molecular crystals in the framework of Onsager-Braun theory for geminate pair dissociation and recombination.² It was later proposed that intermediate states may be formed during the charge

transfer process at donor-acceptor interfaces in bulk heterojunctions.^{31,34,218,221,225-229} Some macroscopic factors of organic solar cells are found to be closely related to the CT states, such as the open circuit voltage (as discussed in *Chapter 2*). However, more questions are waiting for answers on CT states in bulk heterojunctions, for example the achievement of 100% internal quantum efficiency organic solar cells^{169,230} may require either an extremely efficient dissociation of CT excitons, or the direct charge transfer of electrons from the donor to the acceptor.

Current understanding of charge photogeneration processes involved in CT states are shown in figure 5.4(a), which include: (1) above bandgap photoexcitation generating “hot” excitons in the polymer; (2) direct generation of interface CT excitons by sub bandgap photoexcitation; (3) charge transfer forming CT excitons with the hole in the polymer and electron in the acceptor or direct charge transfer inducing free electrons in the acceptor; (4) thermalization of CT excitons from “hot” states to the bottom of the state (CT_0); (5) possible thermally assisted excitation route promoting excitons from the CT_0 state back to the CT_n states; (6) dissociation of CT excitons found both from CT_0 and CT_n states. After several years of debates on the necessity of excess thermal energy for CT exciton dissociation (“hot” CT exciton dissociation vs. dissociation from CT_0 state), the community seem to have accepted that the degree of delocalization of the CT exciton rather than the excess thermal energy plays a key role.^{107,221,231} Recent results show that delocalized electron-hole pairs at interfaces, even in CT_0 states can have lower binding energy than the room temperature thermal energy, thus leading to spontaneous exciton dissociation.^{227,229,232} Whether the geminate pair in “cold” CT_0 states is delocalized or localized seems to depend on the materials and their morphology quality between interfaces.^{221,231} What is important for us is that it has been experimentally shown that by pushing the electron in single occupied CT_0 state to more delocalized doublet CT_n states

with additional thermal energy of ~ 0.3 eV enhance the measured photocurrent at ultrafast time scale (see figure 5.4(b), corresponding to the process (5) in figure 5.3(a)).²¹⁸

Figure 5.4 (a) Energy diagram of exciton dissociation into free charges via the formation of CT excitons. (1) Above gap photoexcitation and exciton generation process. (2) Sub-gap photoexcitation directly generate charge transfer excitons. (3) Charge transfer process or internal conversion of exciton in both “hot” and “cold” states to CT states. (4) Thermalization of exciton in manifold of CT states to CT_0 state. (5) Additional push pulse for promoting the exciton from CT_0 to “hot” CT_n state. (6) Charge separation into free charges (b) Band diagram for the splitting of charge transfer exciton with the help of infrared push energy.

Similar to the argument in the previous discussion, the IR-nanoantennas could help the exciton stay in more delocalized “hot” CT states by pushing it with addition thermal energy, as shown in figure 5.4(a), process (5); or more directly alter the exciton status, for example making it more delocalized, even before it reaches to the donor-acceptor interfaces through the plasmon-polaron coupling mechanism. The polaron photogeneration enhancement in IR nanoantenna/P3HT:PCBM deduced from PIA results may be due to both mechanisms described above.

5.1.4 Device implementation

Based on the experimental results and discussion above, we propose that the concept of plasmon-

polaron be applied for the design of more efficiency devices with carefully engineered metamaterials that can recycle the infrared solar radiation to promote carrier photogeneration and exciton dissociation in polymers and bulk heterojunctions. In addition, one could design plasmonics nanostructures with resonances both in visible, above polymers' optical bandgap, and in mid-IR, coupled to polaron relaxation energy, to further enhance the organic solar cell efficiency. One way is to drop cast Au NPs (as discussed in *Chapter 3*) onto the IR-nanoantennas, and study the overall effects of both excitonic and polaronic generation enhancement. Two possible device structures are shown in figure 5.5, with Au NPs and IR-nanoantennas employed simultaneously for plasmonic enhancement. To fully utilize the IR radiation, infrared transmitting substrates should be used in normal solar cell structure (figure 5.5(a)), as solar light must pass through the substrate. Since most of the cheap glass substrates are not transparent in the IR, plastic substrates may be a good option. On the other hand, an inverted solar cell architecture (figure 5.5(b)) could avoid such problem, since TiO₂ layers have relatively good IR transparency, and ITO, carbon nanotubes (CNTs) or graphene could be used as IR transparent cathodes.

Figure 5.5 Proposed organic solar cell structures combining Au NPs and IR-nanoantenna enhancement. (a) Normal and (b) inverted solar cell architectures.

5.2 Effect of plasmon-polaron coupling on polaron transport

In addition to charge photogeneration processes coupling of polaron resonances with IR-nanoantennas, could also affect directly charge transport processes in conjugated polymers.

Under IR illumination, the nanoantennas could enhance thermally assisted polaron transport processes by local concentration of thermal energy in the polymer. Indeed, both experimental and theoretical works have shown that the mobility of organic polymers is thermally activated,^{58,233,234} which means that delocalization of polarons can be energetically enhanced providing thermal energy. This enhancement mechanism would be especially relevant in disordered systems, i.e. polymer films with low mobility and disordered morphology, where polarons migrate via hopping transport. Conversely, concentrating thermal energies by IR-nanoantennas in highly ordered materials like organic crystals, in which polaron transport occurs via delocalized bands, may even reduce charge carrier mobility.² To observe similar effects in experiments, an additional beam of IR light would be required.

Another interesting opportunity is to improve the electric properties of polymers via formation of plasmon-polaron coupling complexes, even in dark. E. Orgiu, T. W. Ebbesen et al. have recently demonstrated that by designing an exciton-plasmon strongly coupled system using organic small molecules, dark carrier mobility increased by one order of magnitude; this was attributed to coherent traveling of polariton in metal nanostructures.^{235,236} By directly coupling to charged polarons, our IR nanoantenna system could provide a more straightforward way to enhance charge carrier mobility than neutral exciton-plasmon polaritons. To achieve this experimentally, randomly distributed IR-nanoantennas as shown in *Chapter 4* are not suitable: one should design ordered IR-

nanoantenna arrays (as depicted in figure 5.6) in which the collective plasmon oscillations could carry polarons as a means of transport in polymer films (strong coupling is required in this case) without the need for additional IR light excitation of the nanoantennas. Such study would not only elucidate some fundamental issues raised by Ebbesen and coworkers, but also provide a pathway for implementing plasmon-polaron coupling to improve the performance of organic electronic devices such as solar cells or transistors (figure 5.6(b)).

Figure 5.6 (a) Possible design of IR-nanoantenna array and electrical measurement scheme. (b) Transistor structure for charge carrier mobilities measurement.

5.3 Extending the concept to other material systems

The existence of polarons in different conjugated polymers and small molecules besides P3HT provide a well-understood platform to further study and exploit the plasmon-polaron coupling mechanism. Table 1 summarize three typical low bandgap polymers (PCDTBT, PCPDTBT and PTB7) as well as two types of small molecule of their bandgap and polaron peak positions.

Table 1. Polaron peaks of three typical low bandgap polymers.

Polymer	Bandgap E_g (eV)	Polaron peak position (eV)	Polaron peak position (μm)	assignment
PCDTBT ²³⁷	1.85	0.35	3.54	P_1
		1.24	1	P_2
		1.8	0.69	DP_2
PCPDTBT ^{74,145,238}	1.7	0.35	3.54	P_1
		1	1.24	P_2
PTB7 ²³⁹	1.8	0.5	2.48	P_1
		1	1.24	P_2
Thiophene oligomers (nT) (α -6T)	2.1 (α -6T)	0.8 (α -6T)	1.55 (α -6T)	P_1 (α -6T)
		1.54 (α -6T)	0.81 (α -6T)	P_2 (α -6T)
		1.1 (α -6T)	1.12 (α -6T)	BP (α -6T)
Star-shaped small molecules (nT) (1T)	2.0 (1T)	1.03 (1T)	1.2 (1T)	P_1 (1T)

However, the mid-IR polaron transitions (P_1) of these polymers make it difficult for both plasmonic nanostructure fabrication and spectroscopic characterization, especially if one would like to implement the pump-push-probe ultrafast measurements. Therefore, materials with distinguishable near infrared polaron bands are desirable for the next stage of experiments. The well-characterized

series of thiophene oligomers (nT , $n=3, 4, 5, 6$)²⁴⁰⁻²⁴³ fulfill this requirement, especially the sexithiophene (6T) oligomer and its solution process derivatives. Similar to the thiophene oligomer series, the star-shaped small molecules (SSMs) with generic structure of N(phenylene- n thiophene-dicyanovinyl-alkyl)₃ ($n=1-3$) could be another option. By changing the number thiophene rings in SSM from 3 to 1, their P₁ polaron absorption peak can be tuned from ~0.6 eV to ~1 eV.²⁴⁴

Finally, as introduced in *Chapter 1*, polarons are not unique photoexcitations of conjugated polymer. Therefore, the plasmon-polaron coupling mechanism demonstrated here may have further implications in other functional material systems, like high- T_c superconducting cuprates, carbon nanotubes, semiconductor nanostructures, etc., for the purpose of tuning their photo response properties or charge transport properties.

More fundamentally, exploiting strong coupling of plasmon and polarons could be another direction of work; specifically, this could be used to design dispersion relation of propagating hybrid surface-polaron-plasmon polaritons or to study high- Q factor coupled plasmon modes with Fano resonances²⁴⁵ and exploit their possible applications.

Conclusions

In this thesis, I have proposed and shown a completely new photoexcitation mechanism based on the resonant coupling between plasmons in IR-nanoantennas and photoinduced polarons in conjugated polymers.

This subject was developed step by step, starting from the complete characterization of optoelectronic and spectroscopic properties of on one of the classical conjugated polymers, P3HT and the typical bulk heterojunction system, P3HT:PCBM. Infrared photoinduced absorption spectroscopy was first used to study the effects of volatile additive effects on the P3HT:PCBM organic solar cells performance. Conventional plasmonic photogeneration enhancement achieved by blending Au nanoparticles with P3HT was also tested by infrared PIA spectroscopy; demonstrating how the plasmonic enhancement of charge photogeneration by Au nanoparticles is mainly induced by the enhancement of excitonic absorption.

Plasmon-polaron coupling was then demonstrated by PIA spectroscopy in mid-IR region by defining designing and fabricating IR nanoantenna/P3HT hybrid samples. Prior to the measurements, the IR nanoantenna structure were fully modeled and characterized. Experiment and modeling have confirmed the plasmon-polaron coupling due to near-field interactions; meanwhile, enhanced polaron photogeneration has also been shown from the PIA spectra, even without additional excitonic absorption in the conjugated polymer. We have extensively discussed how this plasmon-polaron coupling mechanism can further be extended to the case of P3HT:PCBM bulk

heterojunctions system, where it could be effective for enhancing the power conversion efficiency of actual bulk heterojunction solar cells. Finally we have emphasized that since polarons are not unique species of conjugated polymers, more applications of this concept could be found in other material systems: by the method we proposed, polaronic properties could be tuned by IR plasmonics either exploiting the concentration of electric field/thermal effects, or the near-field coupling of polarons to selected plasmonic resonances.

Since this is a new and exciting field, much work waits to be done. My future studies may still root on the conjugated polymer/small organic molecules and IR plasmonics system, for example to design and implement actual devices utilizing the plasmon-polaron coupling or to study it from a more fundamental point of view with ultrafast spectroscopy by the use of multiple laser beams, i.e. the “pump-push-probe” technique.

Appendix A. Experimental methods

A.1 Fourier transform infrared (FT-IR) spectroscopy

A Fourier transform infrared spectrometer (FT-IR) is a classical apparatus used for infrared transmission and reflection measurements. Different from UV-visible spectrophotometer consisting of diffraction grating, the FT-IR is based on the two beam interferometers that was originally designed by Michelson in 1891.²⁴⁶ The Michelson interferometer generates an interference pattern, i.e. an interferogram, by recombining two light beams divided from the same original source after traveling different lengths of path (figure A.1). One beam is divided into two (50:50) after passing through a beam splitter (50:50), and recombine again at the beam splitter after being reflected by fixed mirror or movable mirror. The optical path difference (OPD, δ) (or retardation) is the path difference of the two beams traveled, $\delta=2(OM-OF)$. Different intensity as a function δ probed by the photodetectors result in the interferogram. A subsequent Fourier transform process converts the interferogram in δ domain (in essence time domain) into spectra in wavenumber (frequency)

domain; the wavenumber is defined as $\tilde{\nu}[\text{cm}^{-1}] = \frac{1}{\lambda[\text{cm}]}$.

Figure A.1 Michelson interferometer. Back solid line indicate the light ray, black dash line indicate the extremes of collimated beam. The movable mirror traveling direction is also indicated.

In conventional FT-IR, scanning modes are used: one is the rapid-scan mode that the movable mirror travels at a constant velocity for each scan (usually larger than 0.1 mm/s) and data are sampled at a regular interval. The signal to noise ratio (SNR) can be increased by a factor of $\sqrt{N}$ by averaging N times of repeating scans; the other is step-scan mode that the movable mirror move in discrete steps and halt at each retardation position until data acquisition is finished. The step scan mode allows a time resolved measurement acquiring time dependent signal on each step with the time resolution limited by the frequency bandwidth of the acquisition electronics. Resulting time resolved interferograms are reconstructed as a function of retardation and time, and then converted into temporal spectrum for each wavenumber by Fourier transform.

A.2 Steady-state photoinduced absorption spectroscopy

Steady state photoinduced absorption measures the transmittance (and then absorption) difference of samples between two equilibrium states: one is under pump light illumination, the other is in

dark state. Different from time resolved measurements, the steady state photoinduced absorption focuses on the long-lived charges, which has strong correlation to device applications such as photovoltaics and photodetectors.

A.2.1 Photoinduced absorption spectroscopy

To take steady state photoinduced absorption spectra, usually a continuous wave laser is used as a pump to populate the excited states of material with charge excitations (polarons in P3HT), and a broadband light source, usually incoherent lamps, as probe beam. After collecting the transmitted probe light with either pump on or off, the normalized transmittance difference is calculated as,

$$-\frac{\Delta T}{T} = -\frac{I_{on} - I_{off}}{I_{off}} = 1 - \frac{T_{on}}{T_{off}}$$

Where I_{on} and I_{off} are the intensity of transmitted probe light after sample with laser excitation on and off, respectively, T_{on} and T_{off} denote the transmittance of the sample with light on and off, respectively. The signal is referred to photoinduced absorption (PIA) when $-\frac{\Delta T}{T} > 0$ ($\Delta\alpha > 0$) that is new states with additional absorption appear upon excitation; signal referred to photo bleaching (PB) ($-\frac{\Delta T}{T} < 0$, or $\Delta\alpha < 0$) signal when ground state population is reduced or even depleted due to the inter-band transitions.

A.2.2 Experimental setup for steady-state photoinduced absorption spectroscopy

Figure 4.2 shows the experimental setup for steady-state photoinduced absorption spectroscopy. A Nd-YAG continuous wave laser (green, $\lambda=532$ nm) was used as pump, and a vacuum FT-IR spectrometer (Bruker Vertex 80v) as probe for the steady-state photoinduced absorption

spectroscopy. The laser beam that is deflected by an acousto-optic modulator (ME-402) that is triggered by the FT-IR for each states of scans (“on” and “off”). The laser beam is expanded by a beam expander in order to ensure the pump beam spot size is larger than the IR probe beam spot. To obtain a higher signal intensity as well as signal to noise ratio, polymer samples are usually measured under low temperature condition (78 K) in a liquid nitrogen cooled cryostat kept in vacuum below 5×10^{-5} mbar.

Figure A.2 Experiment setup: low temperature photoinduced absorption measurement with FT-IR. The light grey area indicate the position of reflection/transmission accessory in FT-IR whose optics alignment is shown as inset.

Depending on the desired spectral region, different detectors and beam splitters in FT-IR are used for measurements to have spectra from visible to mid-IR. Table A.1 summarizes the measurement configuration for different spectral regions, which can be categorized as “Vis-NIR configuration”, “NIR configuration”, and “MIR configuration”. Measurements are done with Bruker reflection/transmission accessory (A510/Q-T), where probe beam has an 11 °incidence angle with respect to the normal direction of the sample and external pump beam is normal incident to the sample.

Table A.1 Key parameters of FT-IR setting for steady-state photoinduced absorption (PIA) measurements.

	Light source	Beam splitter	Detector	Sensitive spectral region (cm ⁻¹)	Laser filters $\lambda=532$ (CW)	Accessory	Cryostat window materials
Vis-NIR configuration	Tungsten	CaF ₂ -UV enhanced	RT-Si	8000-24000	long pass filter >550nm	Reflectance accessory	CaF ₂
NIR configuration	Tungsten	CaF ₂	RT-InGaAs	5700- 12000	long pass filter >550nm	Reflectance accessory	CaF ₂
MIR configuration	Globar (thermal radiation)	KBr	MCT LT-Photovoltaic	680-7500	Si wafer (double polished)	Reflectance accessory	KBr
			RT-DTGS	400-7500	Si wafer (double polished)		

The transmitted light intensities are recorded with and without photoexcitation (I_{on} and I_{off}) in turns by FT-IR under rapid scan mode. In order to reduce the heating effects induced by the laser, each cycle of measurement contains 5 to 10 scans for each “on” and “off” states and are repeated for 800-1000 cycles. Therefore a total 8000-10000 scans for each “on” and “off” states are taken and averaged in order to achieve desired signal to noise ratio.

Other experiments that have been set up with FT-IR

Charge modulation spectroscopy (CMS) in conducted on transistors have been done as well with the FT-IR microscope. Similar to PIA, FT-IR microscope measures the transmitted or reflected probe light intensity for each gate bias “on” and “of” states with the drain-source voltage remaining constant. Polaron signals due to the charge injections from transistor electrodes and the IRAV modes can be observed from the normalized difference spectra. With the help of computer controlled sample stage of the FT-IR microscope and customized Macro coding, mapping of charge distribution along the transistor conduction channel was done with the highest spatial resolution of 15 μm .

The time resolved photoinduced absorption spectroscopy can also be done in our lab with FT-IR operating in step scan mode. A nanosecond laser, $\lambda=532$ nm generated from the second harmonic generation (SHG) of Nd: YAG 5 ns pulse laser $\lambda=1064$ nm, is used as pump. The FT-IR is installed with a transient DAQ card with maximum time resolution of 2.5 ns. Time resolved photoinduced absorption measurements can be done with time resolution up to 5 ns, and the polaron dynamic in nanosecond to millisecond time scale can be measured.

A.3 Steady-state photocurrent spectroscopy

Steady-state photocurrent spectroscopy was done with the conventional light modulation technique that light modulated by a mechanical chopper is focused onto the sample generating AC photocurrent signal. This photocurrent signal is filtered and detected by a lock-in amplifier.

The steady state photocurrent setup is shown below in figure A.3, which consists of two light sources (tungsten and Xenon lamps), one monochromator (Horiba iHR550), one voltages source (Keithley 6487), one mechanical chopper (Stanford SR540), one optional current preamplifier (Stanford SR570), and one lock-in amplifier (Stanford SR830). White light from the light source is dispersed by the grating of the monochromator, and the output single-wavelength light beam is collimated and then focused at sample surface by a pair of aluminum parabolic mirrors. A voltage source (Keithley 6487) is used to electrically bias the sample. In general, resulting currents from the sample consist of both photocurrent (AC) and dark current (DC). Only the AC photocurrent with the same frequency as referencing mechanical chopper frequency is selected and amplified by the lock-in amplifier and it generates two channels output DC signals that are finally collected by a digital-analog acquisition (DAQ) card and recorded by the computer.

Figure A.3 Steady-state photocurrent measurement setup. The optical elements and light beams are represented by thick solid lines, while electrical connections are represented by thin solid lines.

The two channel output signals from the lock-in amplifier can be either in the form of R and θ or in the form of X and Y . And they are linked by $R = \sqrt{X^2 + Y^2}$ and $\theta = \arctan(\frac{Y}{X})$, where R is photocurrent amplitude, θ is photocurrent phase shift angle respecting to the referencing signal and X, Y are referred as *in-phase* and *out-of-phase* signals.

Samples can be measured either on a home-built probe station equipped with four probes or in a home-built high vacuum chamber (up to 10^{-5} mbar). The high vacuum chamber with two electrical feedthroughs are used for either low temperature measurements or for preventing samples from degrading as in ambient air. The P3HT and P3HT:PCBM photocurrent measurements, both room temperature and low temperature, were done with samples mounted in vacuum chamber.

In addition, CW lasers of different wavelengths ($\lambda=532$ nm Nd: YAG laser, $\lambda=633$ nm He-Ne laser) provide higher light intensity than white light source for steady-state photocurrent spectroscopy measurement, which is useful for light intensity dependent photocurrent measurement. With other

optic components installed, frequency dependent, light polarization dependent photocurrent measurement can also be done with this setup.

The responsivity (R) of a sample is its photocurrent amplitude normalized with the incident light intensity (I_0). Therefore, incident light intensity need to be calibrated for each time of photocurrent measurement. This can be done by first measure the photocurrent of calibrated photodiodes, Si diodes for the spectral region of 240 nm to 1100 nm and Ge diodes for the region of 800 nm to 1500 nm. The incident light intensity (I_0) is then calculated using the calibrated responsivity (R_d)

datasheet of photodiodes, $I_0[W/cm^2] = \frac{i_d[A]}{R_d[A/W] \cdot S_d[cm^2]}$, where i_d is the photocurrent of

photodiodes, S_d is the active area of the photodiodes when light beam is larger than the active area of photodiodes, or it should be the area of the beam spot. Then the actual responsivity of samples

is calculated following $R[A/W] = \frac{i_s[A]}{I_0[W/cm^2] \cdot S_s[cm^2]}$, where i_s is the photocurrent of samples, S_s

is the active area of samples when the light beam is larger than the active area of the sample, or it should be the area of the beam spot.

Other experiments that can be done with this system

Since this is a home-built experiment setup, it can be reconfigured for many other electrical and optoelectronic measurements, such as the I-V curve measurement with and without light illumination, the characterization of transistors (output and transfer curves) and photo-transistor measurements. Photoinduced absorption measurements in the visible and near infrared can also be done with light modulation and phase-sensitive detection (Lock-in amplifier) technique. All the measurements are computer controlled with different customized LabView programs.

A.4 Characterization of solar cell devices

Solar cell devices usually have diode like I-V characteristics in dark and ideal conditions,

$J = J_0 (e^{\frac{qV}{k_B T}} - 1)$ (Shockley equation). With light incident on the devices, the I-V curve is shifted downwards and an additional **short circuit photocurrent** term must be added to the equation at zero bias,

$$J = J_0 (e^{\frac{qV}{k_B T}} - 1) - J_{SC}. \quad (\text{A.1})$$

In short circuit conditions, charges drift towards the electrodes due to the internal electric field. The open circuit voltage is defined as the voltage at which the total current $J=0$, therefore

$$V_{OC} = \frac{k_B T}{q} \ln\left(\frac{J_{SC}}{J_0} + 1\right). \quad (\text{A.2})$$

In polymer solar cells, the open circuit voltage can expressed as

$$V_{OC} = \frac{1}{e} (|E_{LUMO}^{fullerene}| - |E_{HOMO}^{Donor}|) - \frac{k_B T}{e} \ln\left(\frac{n_e n_h}{N_C^2}\right), \quad (\text{A.3})$$

where n_e and n_h are electron and hole densities, N_C is the corresponding conduction density of states near the fullerene LUMO ($N_C=N_A$) and the polymer HOMO level ($N_C=N_D$), which are assumed to be equal.^{247,18,121} The empirical number for the offset of 0.3 V to the fullerene LUMO and polymer

donor HOMO energy level difference $\frac{1}{e} (|E_{LUMO}^{fullerene}| - |E_{HOMO}^{Donor}|)$, derived from the second term of the equation (2.4). The V_{OC} is found experimentally²⁴⁸ to have direct correlation to the charge transfer

(CT) states, as expressed by $V_{OC} = \frac{k_B T}{q} \ln\left(\frac{J_{SC}}{J_0} + 1\right)$, similar to that of inorganic solar cells shown

above. However, the original short circuit current is replaced by the injection current (J_{SC}) that induces the measured charge transfer state electroluminescence (EL). The dark saturation current

J_0 can be calculated from the equation $J_0 EQE_{EL}(E) = q EQE_{PV}(E) \phi_{BB}(E)$ by integrating J_0 over the

desired spectrum, where EQE_{EL} is the electroluminescence quantum yield, EQE_{PV} is the solar cell external quantum efficiency and ϕ_{BB} is the black body spectrum at a given temperature, 300 K for example.^{34,248} Finally the derivation above it shows that the energy level difference, $|E_{LUMO}^{fullerene}| - |E_{HOMO}^{Donor}|$, can be used to coarsely estimate the energy level of CT states.

The **external quantum efficiency (EQE)**, also known as incident photon-to-current efficiency (IPCE) is defined as the ratio of number of charge carriers collected in the solar cell to the number

of absorbed photons, $\eta_{EQE}(\lambda) = \frac{N_{electron/sec}}{N_{photon/sec}} = \frac{J_{sc}}{I_0} \cdot \frac{hc}{\lambda e}$, where J_{sc} is the short circuit photocurrent and

I_0 the incident light intensity. By integrating the product of EQE and incident light irradiance (AM 1.5) over the spectrum, one can obtain another expression of the short circuit current density (J_{sc}).

It is therefore clear that the EQE is correlated to the responsivity by $\eta_{EQE}(\lambda) = R([A/W], \lambda) \cdot \frac{hc}{\lambda e}$.

Figure A.4 Typical J-V curve of an organic solar cell fabricated from P3HT:PCBM thin film. The pink area indicates the maximum output power of the solar cell, which can be used to calculate the power conversion efficiency (PCE) dividing it by the solar radiation power. The ratio of pink and grey area is the filling factor (FF).

Appendix B: Sample preparation

B.1 P3HT and P3HT:PCBM film preparation

B.1.1 Samples for Chapter 2

Regioregular-P3HT (RR-P3HT) polymer was purchased from Rieke Metals, Inc. with regioregularity larger than 90% and averaged molecular weight 50-70 kDa. It was dissolved in 1, 2-dichlorobenzene (2 wt%, 20 mg/mL). A ratio of 1:1 (2 wt%, 20 mg/mL: 20 mg/mL) was used for P3HT:PCBM solution, where PCBM was purchased from Nano-C.

For PIA measurements, P3HT and P3HT:PCBM were spun-cast onto blank KBr substrates at the speed of 800 rpm for 120 s, and a subsequent 2000 rpm spin process for 60 s in order to dry the film. Samples were thermally annealed at 120 °C for 10 min. All samples were prepared in N₂ atmosphere. Resulting film thickness is ~70 nm as determined by AFM. Thicker samples were prepared by drop-casting RR-P3HT from chloroform solution with 3 wt% (30 mg/mL) onto KBr substrate.

For steady-state photocurrent measurement, samples were spun-cast on glass substrate with the same procedure. The coplanar stripline contacts were prepared by thermally evaporating gold (100 nm) under high vacuum (10^{-6} mbar) through shadow masks. The gap of between electrodes is 100 μ m.

P3HT:PCBM films for additive experiments were prepared by first dissolving P3HT and PCBM

into 1,2-dichlorobenzene with 1:1 ratio (20 mg/mL: 20 mg/mL); different volume of 1,8-octanethiol as additive (1%, 2%, and 5%) were then added to the solutions. The solutions were spun-cast onto CaF₂ substrates at the speed of 800 rpm for 120 s and then at higher speed of 2000 rpm for 60 s. The samples were then kept in ultra-high vacuum overnight in order to make sure all solvent and additives are evaporated. Solar cell devices were fabricated by cleaning the patterned ITO substrate (ultrasonic cleaning in acetone, IPA, and water for 10 min in sequence, and then O₂ plasma cleaning for 15 min); then the PEDOT: PSS solution was spun-cast onto ITO substrate at the speed of 5000 rpm for 30 s, and thermally annealed at the temperature of 150 °C for 5 min. P3HT:PCBM films were deposited from solutions with different percentage of additive by spin-cast, Al contacts as cathodes were thermally evaporated for 100 nm through shadow masks. The entire devices were then thermally annealed for another 20 min in order to improve the metal-semiconductor contact.

B.1.2 Samples for Chapter 3, 4

Two sizes of (5 nm and 10 nm) colloidal gold nanoparticles were purchased from Ted Pella, Inc., Ligand exchange of Au NPs with Polyvinyl acetate (PVA) was done in solutions prior further step. Au NPs films were prepared by drop casting from their solutions onto CaF₂ substrate. To obtain Au NPs on substrates with different density, the drop-cast procedure were repeated multiple times. P3HT films were spun-cast from 1,2-dichlorobenzene solution (20 mg/mL) onto the prepared Au NPs films.

The IR-nanoantenna and off-resonance antenna samples were prepared by the hole-mask colloidal nanolithography with tilted-angle-rotation evaporation as will be shown in *Section B.2*. P3HT

solution (1 wt%, 10 mg/mL) was spun-cast onto nanoantenna samples as well as blank CaF_2 substrates at the speed of 800 rpm for 120 s. All the samples were thermally annealed at 120 °C for 10 min. The chemically doping samples were prepared by dipping the IR-nanoantennas/P3HT and samples into solution of FeCl_3 (0.001 M) in nitromethane for 7 h, then repeatedly washed with methanol, and dried in nitrogen gas atmosphere.

B.2 Fabrication of plasmonic IR-nanoantennas on large scale

The hole-mask colloidal nanolithography with tilted-angle-rotation evaporation technique was initially developed by Harald Giessen group in University of Stuttgart; with their help we were able to fabricate the plasmonic IR-nanoantenna samples for experiments.

The samples were fabricated as follows:

(a) PMMA film coating. A 480 nm thick PMMA layer was first spun-cast and baked under 165 °C for 120 s to form a flat and uniform mask layer on CaF_2 substrate.

(b) Polystyrene (PS) sphere immobilization. The resulting PMMA film then undergo a series of surface treatments, (1) oxygen plasma cleaning for 18 s to improve the surface wettability, (2) 0.2% of poly(diallyldimethylammonium chloride) (PDDA) drop cast on the surface and then rinsed away and blew to dry in order to charge the surface for the next step PS sphere self-assembly. The substrate is then covered with a layer of well separated PS sphere with a diameter of 220 nm by first drop-casting the PS sphere from solution and rinsed with water; the wetted substrate undergoes a 3 min hot water bath to ensure the PS sphere has immobilized onto it.

(c) Au evaporation. A 20 nm thick Au layer was deposited on the sample by thermal evaporation.

(d) O₂ plasma etching. Removal of the PS spheres in an ultrasonic bath yielded a perforated gold layer on top of the PMMA. Isotropic oxygen plasma etching for 11 min was then used to extend hole cavities in PMMA underneath the gold mask layer.

(e) Tilted-angle-rotation evaporation. To “write” the structure, the sample was loaded into a thermal evaporator with motorized sample stage, with azimuthal angle of 31 ° respected to the source-sample line; the sample stage was rotated with a polar angle of 340 ° while evaporating Au.

(f) Lift-off. The sacrificial PMMA layer was finally peeled off the substrate and organic residues removed by rinsing and ultrasonic in acetone. A subsequent plasma cleaning can further remove the residual PMMA around the structure.

Figure B.1 (Left) The fabrication process of hole-mask colloidal nanolithography with tilted-angle-rotation evaporation. (Middle) The layout of tilted-angle-rotation evaporation in thermal evaporator. (Right) Dimensional parameters of the split-ring-resonator structure.²⁰⁸

The thickness of PMMA layer (h_0), the size of PS sphere, in other words, the size of the hole mask (w), the setting of the azimuthal angle (θ) and polar rotation angle (ϕ) and the thickness of Au deposited after tilted-angle-rotation evaporation (h_1) are key parameters in determining the dimension and shape of the final fabricated structures. From figure B.1, a typical split-ring-

resonator dimension, central diameter (r) and thickness (h) can be set following the equation,

$$r = h_0 \tan \theta \quad \text{and} \quad h = h_1 \frac{45^\circ \cdot w}{\varphi \cdot h_0 \cdot \tan \theta}.$$

Practically, the azimuthal angle has a limitation of smaller than

31 °. The plasma etching intensity and time during the process **(d) O₂ plasma etching** also affect the resulting structure quality, which too much etching of PMMA will result in the a merge of isolated structures, destroying the structure plasmon features, insufficient etching creates smaller cavities and hence limit the final structure size deviating from the original design.

Appendix C: Numerical simulations of IR-nanoantenna electromagnetic response

The plasmonic modes of IR-nanoantennas responding to different incident light polarization are numerically simulated. The software used was the *COMSOL Multiphysics*, a commercial program that is capable of numerically solving the Maxwell's equations in three dimensions.

C.1 Finite element method (FEM) and multiphysics simulations

The finite element method (FEM) is a numerical technique for solving complex system problems that generally require the solutions of ordinary or partial differential equations.^{249,250} Originally developed for solving solid mechanics problems, FEM is now widely used for multiphysics problems. The principal idea of FEM is first to discretize a body into several smaller units (finite elements) that are interconnected by nodes and/or boundary lines and/or surfaces. Instead of solving the equations for the whole body, the equations for each finite element are formulated with certain approximation methods. Finally, the solutions from that the finite elements are reconstructed to obtain the solution of the entire body. To make the calculation results close to actual physical behavior, care must be taken for each step stated above, for example, the use of discretization methods, the mesh density, the choice of element for analysis, the boundary conditions, the solution parameters, the assemble of element solutions, etc.

COMSOL Multiphysics uses the finite element method for modeling and simulating various

physics-based problems, especially for the coupled or multiphysics phenomena.²⁵¹ It takes 3D full-wave simulation for solving electromagnetic problems, which means the Maxwell's equations are solved on each desired wavelength under the condition of steady state for each elements. Therefore, simulated results contain all the physical parameters in terms of electromagnetics, such as the amplitude and direction of electromagnetic fields at each point, the energy and the currents flows in space.

C.2 FEM simulations of IR-nanoantennas

The far field transmission and near field maps of the split-ring resonators are calculated using COMSOL. The optimized geometry for unit cell, shown in figure C.1, consisting of: the inner and outer radius of 0.214 μm and 0.397 μm , respectively; gap subtending an angle of 33 $^\circ$ from the center. The structure thickness is 8 nm. In addition, in order to reproduce the real structures fabricated in experiments, two ends of the ring at the gap was further cut into round shape. The rings were modeled as periodically arranged above the substrate with the lattice constant of 0.9 μm with gaps oriented horizontally as per experiment. Refractive indexes for all the materials, gold for SRR and CaF_2 for substrate, have been retrieved from literature.

Figure C.1 The unit cell model of split-ring-resonator with geometrical parameters labeled. (Right) List of optimized parameter for IR-nanoantennas.

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List of publications

Manuscripts in preparation

1. Multipoles of n-fold rotational symmetry planar metamolecules, H. Liu, **Z. Wang**, H.J. Fan, C. Soci, N. Zheludev, to be submitted.
2. A study of IR/V modes in conjugated polymers by density functional theory, J. Yin, D. Fazzi, **Z. Wang**, C. Soci, to be submitted to J. Phy. Chem. C.
3. Enhanced carrier mobility in n-type OFETs by semiconductor-dielectric interface treatment, X.Y. Chin, A. Luzio, **Z. Wang**, J. Yin, D. Fazzi, M. Caironi, C. Soci, to be submitted.
4. Polarization dependence of photocurrent in bilayer graphene, M. Eginligil, F. Hipřito, B. Cao, **Z. Wang**, X. Shen, V. M. Pereira, C. Soci, T. Yu, to be submitted to Light Sci. Appl.
5. Photoinduced polaron formation in Rubrene single crystal: steady-state photocurrent and ultrafast spectroscopy. Z. Wang, L. Ma, K. K. Zhang, C. Soci, G. G. Gurzadyan, C. Kloc, in preparation.

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1. Plasmon-polaron coupling in conjugated polymer on Infrared nanoantennas, **Z. Wang**, J. Zhao, B. Frank, Q. Ran, G. Adamo, H. Giessen, C. Soci, Nano Lett. 15, 5382 (2015).
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Patents and technology disclosures

Mid-IR plasmonic antenna to polaron coupling for organic solar cells, organic photodetectors, and other organic electronic applications, C. Soci, **Z. Wang**, H. Giessen, disclosed to NTU, ETPL ref: TD/261/14 (2014), provisional patent to be filed.