Evaporation induced self-assembly and characterization of nanoparticulate films: a new route to bulk heterojunctions

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EVAPORATION INDUCED SELF-ASSEMBLY AND CHARACTERIZATION OF NANOPARTICULATE FILMS:
A NEW ROUTE TO BULK HETEROJUNCTIONS

A Dissertation Presented

by

YIPENG YANG

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

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EVAPORATION INDUCED SELF-ASSEMBLY AND CHARACTERIZATION OF NANOPARTICULATE FILMS: A NEW ROUTE TO BULK HETEROJUNCTIONS

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ACKNOWLEDGEMENTS

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Polymer-based semiconducting materials are promising candidates for large-scale, low-cost photovoltaic devices. To date, the efficiency of these devices has been low in part because of the challenge of optimizing molecular packing while also obtaining a bicontinuous structure with a characteristic length comparable to the exciton diffusion length of 10 to 20 nm. In this dissertation we developed an innovative evaporation-induced nanoparticle self-assembly technique, which could be an effective approach to fabricate uniform, densely packed, smooth thin films with cm-scale area from home-made P3HT nanoparticles. Unlike the previous reports of nanoparticle-based film formation, we use a mixture of two solvents so that the solvent quality slowly decreases over time and particles aggregate at the air-liquid interface. The charge mobility of P3HT nanoparticle film fabricated using this technique is very similar to that
of drop-cast P3HT films. Sintering (i.e. formation of contact discs between particles) and the effect of different size distribution of nanoparticle dispersion on film charge mobility were also studied.

Binary films composed of P3HT and PCBM can be obtained using the same method from a suspension containing both P3HT and PCBM nanoparticles. The existence of PCBM in binary films was confirmed, and the relative composition of the two types of particles as a function of film-formation time was measured.

Moreover, we show how to control the internal, molecular-scale structure within the P3HT nanoparticles and the absorption spectra by slowing the process of particle formation. These results provide an example of manipulating one phase of the active layer of OPV devices independently of the other phase.
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CHAPTER 1

INTRODUCTION

1.1 Organic photovoltaic devices

1.1.1 Prologue

The increasing energy consumption and limited fossil fuel resources have led to an intense search for alternative, renewable energy sources in the past 40 years. Among recent studies, there has been a rapidly growing attention on polymer-based organic photovoltaic materials, which are considered promising for solar energy conversion because of these advantages:

(a) They rely on inexpensive, commercially available materials.

(b) They are light in weight compared to inorganic counterparts.

(c) They are simple and fast to manufacture into thin film devices [1].

(d) They exhibit high absorption coefficients over $10^5$ cm$^{-1}$ [2], leading to the possibility of ultra-thin device with good efficiency.

(e) Their band gap energy can be synthetically engineered [3].

(f) The charge carrier mobility can be as high as $10$ cm$^2$/V$\cdot$s [4], comparable with amorphous silicon [5, 6].

Despite the intense research and substantial progress in OPV science and device fabrication, there remain significant challenges. A primary challenge is to first design and then manufacture the optimal spatial arrangement of the semiconducting materials in the active layer. As will be
described later in this introduction, the ideal structure is thought to consist of a bicontinuous structure, in which the electron-donating and electron-accepting phases have large area of contact with one another, and at the same time each forms a continuous pathway to the electrodes. That is, each point in the active layer must be close to (perhaps within 20 nm or so) of both phases, and must then find a short pathway to either electrode. In this thesis, Part 1.1 will introduce the structure and mechanism of a characteristic organic solar cell, the optimization of its performance, and the choice of materials.

Part 1.2 will give an overview of this thesis: an approach to fabricating high efficiency bulk heterojunctions by self-assembly of organic semiconductor nanoparticles. In Section 1.3 the methods of making well-controlled, large-area thin films from nanoparticles will be reviewed and discussed.

### 1.1.2 Structure of polymer/fullerene solar cells

A characteristic structure of polymer-based organic solar cell is shown in Figure 1.1 [7], where the active layer is sandwiched between electrodes.

![Figure 1.1 Schematic illustration of the device structure of polymer-based organic solar cell (Figure copied from Gunes, S., et al. [7])](image)
The anode is commonly made of ITO (indium tin oxide) due to its high transparency and conductivity, while the cathode is made of a lower work-function metal such as aluminum.

The PEDOT:PSS (i.e., poly(ethylene-dioxythiophene) doped with polystyrenesulfonic acid, chemical structure shown in Figure 1.2) layer is coated (usually from aqueous solution) on ITO-coated glass electrode in order to eliminate the shorts and improve surface quality. Moreover, the work function of the PEDOT layer can also be tuned chemically or electrochemically [8], and in turn influence the efficiency [9].

Most importantly, the active layer should be a composite of electron donors (p-type semiconductor) and electron acceptors (n-type semiconductor), i.e. heterojunctions.

1.1.3 Materials and morphology in heterojunctions of active layers

Fullerenes are an excellent electron acceptor due to their high electron affinity [10] and electron mobility (up to 1cm²V⁻¹s⁻¹) [11]. Because of the limited solubility of C₆₀, Wudl et al. synthesized a soluble derivative of C₆₀, PCBM (1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C₆₀) [12], which has been widely used as the electron acceptor in organic solar cells.

On the other hand, two most commonly used electron donor materials are MDMO-PPV (poly[2-methoxy-5-(3,7-dimethloctyloxy)-1,4-phenylen] -alt-(vinylene)) and P3HT(poly(3-hexyl...
(thiophene). Figure 1.3 shows the chemical structures and band structures of P3HT, MDMO-PPV and PCBM [13].

**Figure 1.3** Band structure diagram illustrating the HOMO and LUMO energies of MDMO-PPV, P3HT, and an “ideal” donor relative to the band structure of PCBM. (Figure copied from Thompson, B., et al. [13])

**Figure 1.4** Band gap illustration of the operating principle of polymer/fullerene solar cells

The band gap illustration of the operating principle for a polymer/fullerene (p3HT/PCBM) heterojunctions is shown in Figure 1.4. The polymer (electron donor) should be able to transfer the generated charge to fullerene. In order to dissociate and transfer the charge, a driving
potential drop of at least 0.3 eV [14, 15] is required to overcome the exciton binding energy. This energetic drive can be empirically provided by the energy difference between the LUMOs of the donor and acceptor. But an energy difference bigger than 0.3 eV only turns into energy loss and thus not favorable. Furthermore, it has been claimed that the optimal band gap value for a polymer absorber is 1.5 eV [16, 17]. This is how the authors were able to structure an “ideal” donor polymer conjugated with PCBM in Figure 1.3.

A good similarity to the ideal conjugated band structure, as well as ultrafast photo-induced charge transfer (ca. 45 fs) [18, 19] and good solubility, has made P3HT/PCBM system a “best seller” [20] for polymer-based organic solar cell.

Despite all these advantages, polymer-based organic photovoltaic materials (e.g. P3HT/PCBM heterojunctions) do have some drawbacks: (a) most semiconducting polymers have a band gap of 2 eV or higher, which can only possibly harvest solar photons with a wavelength of 620 nm or less. This is only about 30% of all the solar energy; (b) unlike inorganic semiconductors (e.g. silicon), exciton diffusion lengths in polymers and organic semiconductors are usually around 10-20nm. Thus, the choice of material in the heterojunctions of active layer and its morphology are both dominant factors determining the efficiency of the device.

In terms of their morphology, heterojunctions can be classified into two types (Figure 1.5) [7]:
Commonly fabricated by vacuum deposition, a bilayer heterojunction (left in Figure 1.5) is structured by simply stacking p-type donor and n-type acceptor semiconductors on top of each other, then the device can work as a classical p-n junction [21, 22]. Given the generally accepted 10-20 nm exciton diffusion length, the effective thickness of the bilayer heterojunction is limited.

A bulk heterojunction (right in Figure 1.5) is ideally a bicontinuous blend of electron donor and acceptor phases with maximized interfacial area between them. “Bicontinuous” refers to the requirement that a charge be able to flow across the sample in either the p- or n-type material. Figure 1.6 [7] shows an ideal (but not necessary) structure of a bulk heterojunction in a polymer/fullerene solar cell, where the domain length scale is 10-20 nm, matching the exciton diffusion length.
However, in reality the ideal structure is difficult to construct. Instead, the current technique of fabricating bulk heterojunction is casting or spin-coating the active layer solution followed by post-treatment such as annealing [23-25]. The morphology has been controlled by the choice of solvent, the compound ratio, the solution concentration, annealing temperature, etc. As of 2009, the best device efficiency is a relatively low 6.5% [26, 27] because it is hard to avoid phase segregation and in such blended layers. PCBM clusters with a domain size around 100 nm or bigger was observed, which is much larger than the exciton diffusion length. Figure 1.7 [23] shows the typical morphology of a bulk heterojunction made in this way.

![Diagrams](image)
Therefore, it is still a big question to build bulk heterojunctions with controlled morphology at the scale of 10 nm, which is exactly the advantage of using nanoparticles. A new route of fabricating bulk heterojunctions based on organic semiconductor nanoparticles will be discussed in 1.2.

**1.1.4 Mechanistic principles of energy conversion in bulk heterojunctions**

It is widely believed that in a bulk heterojunction, the mechanism of solar energy conversion of light into electricity has four steps [13]: (1) Light is absorbed by the electron donor phase and excitons are generated, (2) excitons diffuse in donor phase until associating with the acceptor at the interface, (3) excitons dissociate and an electrons are transferred to the accepter phase (a process known as charge transfer), (4) generated charges are transported to electrodes and collected.

Figure 1.8 [13] is a schematic illustration of photoenergy conversion in a typical bulk heterojunction solar cell.

In order to increase the efficiency of organic photovoltaic devices, tremendous efforts have been made recently to synthesize low band gap photovoltaic materials absorbing larger portion of the solar spectrum, and to tune the parameters influencing the morphology of the active layers.

The approach presented in this prospectus focuses on self-assembly of nanoparticles made of photovoltaic materials in order to control the molecular packing in bulk heterojunctions and improve the efficiency of polymer/fullerene photovoltaic devices. The principle and methods will be thoroughly discussed.
Figure 1.8 Mechanism for photoenergy conversion in bulk heterojunction solar cell
(Figure copied from Thompson, B., et al [13])
1.2 Disordered packing of nanoparticles with continuous pathways for efficient charge transport

As shown in previous parts, fabricating heterojunctions with characteristic length comparable to the exciton diffusion length is one of the biggest bottlenecks in developing high-efficiency organic photovoltaic systems. A recent perspective (Labastide et al., by researchers in the Venkataraman, Barnes, and Dinsmore groups at UMass [28]) has brought up a new approach of constructing binary nanoparticle superlattices for organic photovoltaic applications.

Figure 1.9 (Top) Superlattice crystal structures obtained by the assembly of nanoparticles with specific radius ratios. (Bottom) Expanded view of the AlB₂ structure showing continuous pathways for electron/hole transport to the anode/cathode, respectively. (Figure copied from Labastide, J. A. et al. [28])

Figure 1.9 [28] shows the structures of nanoparticle superlattices under different radius ratios. Therefore, if we can turn p-type (e.g., P3HT) and n-type (e.g., PCBM) organic semiconductor materials into spherical nanoparticles of 10-20 nm (preparation methods will be introduced in
detail in chapter 2), it is possible to assemble them into various stable superlattices [29-32] providing continuous but separate paths for the transport of excitons in both donor and acceptor phases, and heterojunction characteristic structural length comparable to the exciton diffusion length.

It is, however, difficult and unnecessary to build crystalline structures as shown in Figure 1.9 because: (a) it requires highly monodisperse nanoparticles, which is hard to obtain by our current miniemulsion technique, (b) superlattices is ideally formed under equilibrium conditions, which may also be difficult to achieve, (c) some superlattices are anisotropic, which may cause some orientation problem in bulk heterojunctions.

On the other hand, the amorphous composite based on nanoparticles of donor and acceptor materials is much more realistic to fabricate. Figure 1.10 gives a comparison of a typical bicontinuous bulk heterojunction and an amorphous heterojunction made of nanoparticles. One can conclude that the latter one can also be an efficient bicontinuous system providing pathways for both photogenerated electrons and holes with optimal molecular packing.

![Figure 1.10](image-url) A comparison of a general bicontinuous bulk heterojunction (left) and an amorphous heterojunction made of nanoparticles (right) (Left figure copied from Thompson, B., et al [13], right figure copied from Labastide, J. A. et al. [28])
1.3 Making well-controlled and large-area thin films

In 1.2 we have introduced the route of fabricating high efficiency bulk heterojunctions by nanoparticles of organic donor and acceptor materials. Realizing these goals, however, requires further exploration of methods to make nanoparticle-based films that are densely packed, and consisting of two or more different kinds of particles that are well mixed. Moreover, the film surface should be smooth and the thickness should be uniform across cm scales and adjustable in the range of 10-100 particle diameters. These goals must be met without addition of wetting agents or other materials that may become trapped within the device and hinder performance.

It is not a trivial task to use P3HT nanoparticles for the construction of an optimal thin film structure that would be ideal for the fabrication of organic photovoltaic devices. Three different approaches that have been reported extensively in the literature: drop-casting, spin-coating, and spray-coating. We focus here on methods of making films composed of particles from suspensions, rather than of polymers from solution. Drop casting is perhaps the simplest method: a droplet of particle suspension is placed on the substrate and allowed to dry. Eventually a thin film of solvent remains and the meniscus formed around each particle leads to capillary forces that pull the particles together into close-packed arrays. Variations on this technique, sometimes referred to as convective assembly or the doctor blade method [33] have been used to make ordered arrays of particles for photonic applications [33-37]. Two potential drawbacks of this method are the requirement of high concentration of particles in suspension, and the observed heterogeneity in film thickness or particle packing at length scales of 0.1-1 mm (typically). Heterogeneity arises from either pinning of the 3-phase contact line (causing the coffee-ring stain [38]) or stick-slip motion of the interface across the substrate. Larger-area (cm²-size) films up to a
few particles in thickness can be made with care by moving the drying front across the substrate at a controlled speed [33, 39, 40]; thicker films by careful drying of alcohol suspensions have also been made [41]. These films might have uniform thickness over large areas but this has not been demonstrated. Spin-coating of particle suspensions can be used to make cm-sized films of particles in solvents that are either polymerized afterward [42, 43] or evaporate during the spinning [44-46]. This technique is rapid but has a limited maximum area, radially varying thickness [45], and wastes much of the sample [1], which is impractical for some applications. Finally, spray-coating yields rapid, large-area coating of particulate films over cm² surfaces [43, 47, 48]. All of the above approaches require control of substrate wettability and/or sample viscosity, which is not always practical, especially for deposition on a hydrophobic substrate. We also note that although the above approaches can yield large-area coverage, it is not clear how uniform the thickness is across the full area because thickness is rarely sampled over a large region. A disadvantage of spray coating and convective assembly methods is that the solution is deposited along with the suspended particles. Therefore, solutes including surfactants remain dried onto the film at the end of the process. In applications such as OPVs, where the residual solutes may hinder transport, this can be a disadvantage.

Another approach to particle-based-film formation uses a fluid interface, such as an oil-air interface, as a ‘substrate.’ There are three advantages to forming films at a fluid interface: (i) the evaporation rate and hence the particle deposition flux are uniform across a large area, leading to large-area films, and (ii) the fluid interface is not rigid, so the contact line is not pinned and, moreover, as the film ages and contracts, internal stresses and cracking [49, 50] are minimized, and (iii) the film can be transferred to any solid substrate without drying the solvent down and
retaining solute. Dong, et al. [51] demonstrated this technique by floating a layer of nanoparticles in a volatile solvent (hexane) atop a non-volatile subphase (diethylene oxide); after the hexane evaporated, the authors found beautifully ordered particle superlattices with one, two, or three types of particles [51]. We followed this technique and the results were briefly shown in section 2.5. However, because the water-air interfacial tension is very large, water does not spread over other liquids, but instead forms oddly shaped droplets that yield films of irregular thickness. Therefore, the films that were made by this method do not have an ideal thin-film shape for OPV devices.

The remaining chapters of this thesis describe the experiments and results. In Chapter 2, we introduce an evaporation-induced nanoparticle self-assembly technique of fabricating uniform, densely packed, cm-scale thin films. In chapter 3, binary films composed of P3HT and PCBM will be studied, and the relative composition of the two types of particles will be calculated. In chapter 4, the internal, molecular-scale structure within the P3HT nanoparticles and its absorption spectra will be explored.
CHAPTER 2
EVAPORATION INDUCED SELF-ASSEMBLY OF P3HT NANOPARTICLES

As was discussed in section 1.3, it is not a trivial task to use aqueous-based nanoparticles for the construction of an optimal thin film structure that would be ideal for the fabrication of organic photovoltaic devices. Here we report on a straightforward evaporation-induced self-assembly method and use it to fabricate uniform films of nanoparticles composed of an organic electron-donating material, as well as binary mixtures of nanoparticles of organic electron-donating and –accepting materials. As a model, we chose poly(3-hexylthiophene) (P3HT) and phenyl-C61 butyric acid methyl ester (PCBM), which are efficient and widely used in OPV studies[13]. The assembly technique works by suspending the particles in a mixture of a volatile good solvent (water) and a less volatile, unfavorable solvent (dimethylsulfoxide). As the water evaporated under heat, a film formed at the air-liquid interface and grew in thickness over time (as illustrated in Figure 2.3). Subsequently, the liquid was drained from the vessel to lower the film onto a pre-mounted substrate, which was then left to dry. The experimental details of this technique will be shown in 2.2.1.

The P3HT nanoparticle films that we made with this technique were as large as 5×5 cm² and thickness was varied between approximately 0.5 µm and 2 µm, which corresponds to approximately 4-15 particle diameters. As will be shown in detail later in this section, the films were remarkably smooth and uniform over large distances, which is an important point because measurements of film thickness over large areas have seldom been reported previously. We
measured a volume fraction (filling fraction) of 0.56 ± 0.07, which is consistent with random close packing. We measured the charge (hole) mobility in P3HT-nanoparticle films and found mobility values \( \sim 8 \times 10^{-4} \text{ cm}^2/(\text{V} \cdot \text{s}) \), which is comparable to cast polymer films made from the same polymer. These results indicate that the nanoparticle films have high filling fraction and intimate particle-to-particle contact without intervening surfactant layers.
2.1 Formation of P3HT and PCBM nanoparticles

Nanoparticles composed of either P3HT or PCBM were prepared using the miniemulsion technique developed by Venkataraman group and refined in collaboration of the Venkataraman, Barnes, and Dinsmore groups [28, 52-54]. In brief, the method consists of dissolving the polymer in a solvent (chloroform), then emulsifying this solution in a water-surfactant mixture to obtain stable droplets. These droplets are then heated so that the solvent evaporates and the polymer particles form by precipitation. The particles remain in suspension, stabilized by the adsorbed surfactant. The structures of P3HT and PCBM nanoparticles as well as the chemical structures of P3HT, PCBM and SDS are shown in Figure 2.1

Poly(3-hexylthiophene) (P3HT) of molecular weight 79 kDa and 92% regioregularity was purchased from Rieke Metals (Lincoln, NE) and used as received. In order to make nanoparticles of average diameter 120 nm, the P3HT was dissolved in chloroform at 5mg/mL concentration. Anionic surfactant, sodium dodecyl sulfate (SDS) (Sigma Aldrich, cat#: L4509-100G), was dissolved in Millipore-filtered water at 1 mM concentration. A 0.3-mL aliquot of the P3HT solution was injected into 2.5 mL of SDS solution in a glass vial, resulting in a large droplet of P3HT solution at

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**Figure 2.1.** Schematic illustration of the structure of P3HT and PCBM nanoparticles

Poly(3-hexylthiophene) (P3HT) of molecular weight 79 kDa and 92% regioregularity was purchased from Rieke Metals (Lincoln, NE) and used as received. In order to make nanoparticles of average diameter 120 nm, the P3HT was dissolved in chloroform at 5mg/mL concentration. Anionic surfactant, sodium dodecyl sulfate (SDS) (Sigma Aldrich, cat#: L4509-100G), was dissolved in Millipore-filtered water at 1 mM concentration. A 0.3-mL aliquot of the P3HT solution was injected into 2.5 mL of SDS solution in a glass vial, resulting in a large droplet of P3HT solution at
the bottom of the vial. The vial was ultrasonicated for 2 min using a probe sonicator (Ace Glass, model GEX750-5B, 39% power, 6.4 mm micro tip, pulsed 0.1 s on/0.1 s off). The vial was then immediately immersed into a preheated oil bath at 120 °C for approximately 5 min, during which time the chloroform evaporated. The average diameter of P3HT nanoparticles made by this method can be adjusted in the range of 15 nm to 160 nm by modifying the following five conditions: the concentration of P3HT chloroform solution, the concentration of SDS aqueous solution, the duration of sonication, the heating temperature of the oil bath, and the shape of the vial used. For example, nanoparticles with average diameter of 80 nm were obtained by using P3HT chloroform solution of 1.5mg/mL and everything else the same as above. Figure 2.2 shows a typical TEM (Transmission electron microscopy) image of P3HT nanoparticles around 150 nm. This TEM image was taken by JEOL 100CX with a CCD camera.

![Figure 2.2. A TEM image of P3HT nanoparticles around 150 nm in diameter.](image)

Phenyl-C61 butyric acid methyl ester (PCBM) was obtained from Nano-C (Westwood, MA) and dissolved in chloroform at 5.5mg/mL concentration, and then PCBM nanoparticles were made following the same procedure.

The original solvent for P3HT can also be toluene or a mixture of chloroform and toluene [52]. The surfactant used for these nanoparticles can be changed too. For example, if CTAB (cetyltrimethylammonium bromide) is used as the surfactant, the nanoparticles will be positively
charged. The absorption and photoluminescence spectra of these nanoparticles was carefully analyzed [52, 53], but it is beyond the scope of this thesis.

In chapter 4 a slightly different method of synthesizing P3HT nanoparticles will be discussed, where the evaporation of chloroform was significantly slower, and the internal structure and absorption spectra of nanoparticles are distinguishable.
2.2 Film formation, collection and initial characterization

2.2.1 Experimental details of evaporation-induced self-assembly technique

A P3HT nanoparticle aqueous suspension was centrifuged and the supernatant discarded to achieve a desired concentration. In some cases, excess SDS was rinsed out by diluting the sample in water by a factor of 2000, then removing the excess aqueous solution to retain the particles.

While a glass vial with a mixture of dimethyl sulfoxide (DMSO) and water was being sonicated, the concentrated suspension was injected into the glass vial, and at that point, the resulting mixture was sonicated for another 2 min to ensure a uniform consistency. Then the mixture was transferred to a shallow dish containing a preset substrate, and the dish was placed under a heat lamp (Eagle electronic, Cat #: 415-A, 660W) to induce water evaporation and film formation. The temperature of the suspension was controlled by varying the distance to the heat lamp; separate experiments with the same lamp distance and solvent ratios but without nanoparticles were conducted to measure the solution temperature. After a film formed on top of the mixture,
(typically 1-1.5 h), the residual DMSO was drained with a preset syringe so that the film settled on the substrate. Finally the collected film was placed into a covered dish for a slow air-dry over two days. (Drying much faster than this resulted in more cracks.) Figure 2.3 shows a schematic illustration of the film formation and collection. Note that the water evaporation here can instead be induced by placing the dish on a hot plate around 55 °C or inside a vacuum chamber heated to around 55 °C. However, it has not been the best practice, since it is preferable to heat the solution from above to minimize thermal convection, and since it was difficult to observe the film formation inside the vacuum chamber.

There are two advantages in using the fluid interface for assembly: first, heating leads to evaporation at an approximately uniform rate across the surface, which in turn leads to an approximately uniform flux of liquid to the surface, and a uniform growth rate across the film, which can be controlled by the heating temperature. By contrast, in the drop-casting technique the evaporation rate is higher near the sample perimeter, leading to a thick rim of material and a very sparse interior coating unless excess surfactant is used (which is undesirable in our case). Second, the air/water interface is a compliant surface, so that as the film grows and dries and the particles aggregate, there is no build-up of stress at the surface. By contrast, when films are cast at a solid surface, solvent evaporation causes shrinkage of the film; once the film becomes solid, then further contraction leads to stress and cracking [55, 56].

The same technique was applied to latex particles (SPHERO Streptavidin Polystyrene, 2.1 µm diameter) and silica particles (AS-40 Ludox, 30 nm diameter). Latex particles form a film at the interface, but the film was no more than two particles in thickness and was fragile. Thicker and more robust films may be possible using a different starting concentration of particles or a
different water-DMSO composition. AS-40 ludox silica particles, however, aggregated in the bulk suspension and did not form a film at the interface. We attribute it to different surface chemistry and density of silica particles, which are much denser than P3HT and therefore do not move freely in the suspension after they aggregate.

2.2.2 Structure and morphology at the macroscopic and microscopic scales

Evaporation-induced self-assembly provided a fast solution-processed method of fabricating nanoparticle-based organic thin films with cm-scale extent and good uniformity. Figure 2.4 shows images of two typical cm-scale nanoparticle films before they were collected on substrate. These films were fabricated by suspending P3HT nanoparticles in a mixture of water and DMSO (typically 60 vol% and 40 vol%, respectively) and then allowing the water to evaporate. Figure 2.4(a) shows a film that formed at and covered the top of a dish completely. To make the region of the film more visible, we show in Figure 2.4(b) a film that grew on the surface of an isolated droplet, approx. 6 cm across, placed in a large dish. After the film formed, water was added to float the film. The area and shape of the film is clearly visible in the image and correspond to the size and shape of the starting droplet. This process is repeatable. The limiting step is draining the liquid and lowering the film on the substrate, which may cause cracks in the film. For instance, we were able to make a 1.5 cm × 1.5 cm films without cracks approximately a third of the time. (In the other cases, we obtained films but cracks were visible.) These cracks form because the suspension is pinned at the wall of the dish, which leads to a curved meniscus that applies stress on the film. We expect that straightforward measures such as moving the substrate up through the surface rather than lowering the liquid level will enhance the rate of crack-free films and the
The thickness profile of a typical P3HT nanoparticle film, measured using a surface profiler, is shown in Figure 2.5. The average film thickness was 1.683 \( \mu \text{m} \). The roughness at scales up to
several hundreds or thousands of µm was approximately 100 nm, which is similar to the diameter of P3HT nanoparticles. This is approximately as smooth as could be expected for particle-based film. We show below that the average thickness can be varied from 0.5 to 5 µm by controlling the growth time and temperature.

Scanning electron microscopy (SEM) images reveal the surface and internal structure of these films (Figure 2.6). The nanoparticle morphology is preserved in the film, and the nanoporous

Figure 2.6 Scanning electron microscope (SEM) images of two P3HT-nanoparticle films. In (a), we focus on the edge of the film and in (b) we focus on a macroscopic crack in the film to reveal the interior structure.
structure provides tremendous surface area. The smooth surface confirms the result of the profile measurements of Figure 2.5.

The volume fraction $\phi$ of P3HT particles within a typical nanoparticle film, defined as the volume of spheres divided by the volume of the film, was also measured. Once the film was air-dried, the thickness $h$ and the roughness were measured using an Alpha-Step IQ Surface Profiler. The volume fraction of particles within the films was measured based on the thickness $h$ and area $A$ of the film, the mass density of P3HT ($\rho$) and the mass of the substrate with the film $m_{\text{before}}$ and without the film $m_{\text{after}}$, as follows:

$$ f = \frac{V_{\text{film}}}{V_{\text{film}}} = \frac{\Delta m}{h \cdot A \cdot \rho} = \frac{m_{\text{after}} - m_{\text{before}}}{h \cdot A \cdot \rho} $$

The masses, $m_{\text{after}}$ and $m_{\text{before}}$, were measured by analytical balance (Sartorius 4504). The area $A$ of the film was measured from a top-view image of the substrate, and $\rho$ is approximately 1.1 g/L for the high molecular weight batch that we used.

We measured $\phi = 0.56 \pm 0.07$ in a 2-µm-thick film composed of approx. 100-nm particles. This fraction is similar to random close packing of hard spheres (0.637 [57]), which is the maximum value obtainable by packing spheres randomly. This value of filling fraction implies efficient packing with few internal voids.

It should be noted that to obtain the smooth and densely packed films, it is important that water and DMSO have the right ratio in the initial mixture. When the DMSO content was greater than approx. 50 vol%, P3HT nanoparticles immediately aggregated in the bulk. An in-depth exploration to optimize the film quality will be presented in 2.2.3.
2.2.3 Growth rates and film formation mechanism

In order to understand the dynamics of this film-formation technique, the thicknesses of the films were measured using a profilometer at multiple spots after different growth times and under various temperatures. Figure 2.7 shows the time evolution of the film formation at solution temperatures $T = 40, 45$ and $55 \, ^{\circ}\text{C}$ for up to 90 min. The starting composition of the liquids were 40 vol% DMSO. The error bars of each point represent the local roughness of the measured spots. Different symbols at a given $T$ and time represent thickness measured at well-separated regions on the same film and account for the long-range roughness across the film. When $T = 35 \, ^{\circ}\text{C}$, the film grew linearly and showed small local roughness (~0.1 µm), and the thickness was consistent in separate regions of the film. When the temperature was higher, the film grew more rapidly and both local and long-range roughness increased substantially. We propose that the evaporation-induced self-assembly is based on different volatility of water and DMSO (boiling temp. = 189 °C). When the suspension of nanoparticles in water and DMSO is heated, water evaporates from the liquid-air interface at a much faster rate than does DMSO, creating a vertical concentration profile with low water content near the air interface. Separate control experiments showed that these SDS-stabilized P3HT particles aggregated when the DMSO composition exceeded a typical value of 50%. Thus the nanoparticles aggregate at the DMSO-enriched interface and form a film there. Simultaneously, the bulk concentration of DMSO rises, leading to nanoparticle aggregation in the bulk. This process leads to aggregates that are visible in suspension.
Forming a smooth film requires a balance of aggregation of particles at the air interface (which yield a good film) vs. aggregation of particles in the bulk. The latter process leads to random clusters, some of which are carried to the film surface by thermally-driven convection, where they pack inefficiently and cause roughness. The results of Figure 2.7 show that at the elevated T (45, 55 °C), the films were rough, which we attribute to bulk aggregates being convected to the surface.

For more insight into the film-formation mechanism, we compare the growth-rate data to a simple model. We assume, as a start, that if a volume $\Delta V$ is lost to evaporation, then all of the particles within that volume accumulate in the film. This is equivalent to assuming that the motion of particles from convection and diffusion are negligible over the timescale of film formation; that is, as the interface moves downward it accumulates all the particles in the lost volume. The volume of particles that join the film during a given time interval is therefore $(\Delta m_w / \rho_w) \phi_s$, where $\Delta m_w$ is the mass of solvent (mostly water) lost to evaporation, $\rho_w$ is the mass
density of water, and $\phi_s$ is the volume fraction of particles in the starting suspension. If all of these particles join a film of area $A$ and interior volume fraction $\phi$, then the film thickness grows by $\frac{(\Delta m_w \phi_s)}{(\rho_w \phi A)}$. We therefore find that the change of film thickness ($h$) per unit of mass lost to evaporation is $h/\Delta m_w = \phi_s/(\rho_w \phi A)$. In our experiments, $A = 3.8$ cm$^2$ and $\phi_s = 1.4 \times 10^{-4}$, so we predict $h/\Delta m_w = 0.7$ µm/g as the film growth efficiency in the absence of strong convection of particles to the film. Sources of convection such as connective rolls could carry bulk aggregates to the surface, and are not included in this model.

For comparison to our model, we measured the mass-loss, $\Delta m_w$, for water-DMSO mixtures under the same conditions as in Figure 2.7 but without particles. Combining this result with the film-growth data, we measured $h/\Delta m_w = 4.6$ µm/g for $T = 40 ^\circ C$ after 60 min. This value is approximately 6× greater than predicted by our model, which implies that convection currents from the temperature gradient are an important source of the flux of particles onto the film. Furthermore, at the higher temperature, $T = 45 ^\circ C$, we measured $h/\Delta m_w = 8.0$ µm/g after 60 min. This is nearly a 2× enhancement in the convection-driven flux of particle and aggregates from the bulk; we propose that this is the reason for the much greater roughness at 45 °C. This analysis indicates that reducing the temperature should lower the ratio of $h/\Delta m_w$ toward the theoretical limit, where the convection of bulk aggregates is negligible; this should be the regime of the smoothest and most densely packed films. This result is consistent with the film-growth data of Figure 2.7.

Although the largest films we made were approximately 5 cm across, we anticipate that the same method should allow formation of arbitrarily large films, with the size limited by the container size. Similarly, a wider range thickness should be readily obtained by changing particle size or
concentration, or by changing the film-formation temperature or duration of film-formation process. No additives are needed to promote wetting of the substrate, which is important for photovoltaic and other applications that rely on transfer of charge or energy across particle interfaces.

However, these structural characterizations cannot guarantee change transport performance. One might wonder whether the surfactant that was used to stabilize nanoparticles could potentially hinder change transport in an OPV device. Therefore, more characterization of the electric properties of these self-assembled films is needed, which is going to be discussed in detail in Part 2.3.
2.3 Charge Mobility measurement

2.3.1 Mobility

Charge carrier mobility is one of the most important properties of semiconductors that are used in photovoltaic devices. It is defined as average drift velocity of a carrier for unit electric field ($\mu = v/E$) with a unit of m$^2$/(V*s) or cm$^2$/(V*s). In the four-step energy conversion mechanism introduced in 1.1.4 [13], step (4) “generated charges transported to electrodes and collected” mainly relies on mobility. In order to have high energy conversion efficiency, the charges need to be transported to electrodes prior to carrier recombination. In other words, we want the transit time to be smaller than the lifetime of excitons [58].

P3HT is a p-type semiconductor, i.e. the main charge carriers are holes, while the main charge carriers in PCBM (n-type) are electrons. Hole mobility is a very important property to measure especially for P3HT nanoparticle films shown in Part 2.2 because the contact between nanoparticles could be an issue. Since in suspension, all the nanoparticles are covered by electrically insulating surfactant, it was not clear whether the nanoparticles were separated by surfactant (figure 2.8 left) or they are actually touching (figure 2.8 right) in the film.

![Figure 2.8 Loose packing (left) and compact packing (right) of nanoparticles](image-url)
2.3.2 Time-of-flight technique

The question raised in 2.3.1 can be answered by measuring the hole mobility of P3HT nanoparticle film using time-of-flight (ToF) technique, a conventional method for measurement of charge carrier mobility of organic semiconductor materials. The set up of a classical ToF device is shown in figure 2.9 schematically [59].

![Figure 2.9 Scheme of the ToF apparatus (Figure copied from Sworakowski, J. et al. [59])](image)

A laser pulse is applied on one side of a film sample sandwiched by two electrodes, and charge carriers are generated and propagated toward the other side under applied bias. The measurement then consists of determining the time necessary for the carriers to reach the counter electrode (transit time, $t_{tr}$) under a given biasing voltage $V$. The drift mobility $\mu$ can be calculated from the equation:

$$\mu = \frac{V}{E} = \frac{L}{t_{tr}} \frac{1}{V/L}$$

$$\mu = \frac{L^2}{t_{tr} V}$$

where $L$ is the thickness of the sample. For a sample film with known thickness $L$ and biasing voltage $V$, the mobility will be determined by the transit time $t_{tr}$. 
The output data from a ToF experiment is a photocurrent transient collected by an oscilloscope at the counter electrode, which is used to determine the transit time \( t_{tr} \). The charge carriers generated by the laser pulse can be considered as a series of propagating packets [60]. As a packet moves towards the opposite electrode, the diffusion of charges is in effect as well. Figure 2.10 [61] shows a typical current transient collected by the oscilloscope, which is a result of both charge propagation and diffusion. The log-log scale was usually used to make the transient more obvious.

![Figure 2.10. A typical transient current in log-log scale collected by oscilloscope in Figure 2.9 (F is the electric field here, F=V/L, the inset shows the same data in linear scale, figure copied from Lebedev, E. et al. [61])](image)

The following model is often used to describe the detected photocurrent variation before and after the transit time:

\[
I(t) \propto \begin{cases} 
  t^{-(1-\alpha_i)}, & t < t_{tr} \\
  t^{-(1+\alpha_f)}, & t > t_{tr}
\end{cases}
\]

where \( \alpha_i \) and \( \alpha_f \) are dispersion parameters before and after the transit time.
Therefore, the photocurrent transient before and after the transit time can be fitted into two straight lines in log-log scale, and the transit time can be determined by the crossover point of the fitted lines, as shown in Figure 2.10. Then charge carrier mobility can be calculated by: \( \mu = \frac{L^2}{(V \cdot t_{tr})} \). Classically, this process was done by manually placing two straight lines along the photocurrent transient in Origin and recording the horizontal ordinate of the crossover point. No advanced analysis technique has been reported so far in literature. In this thesis a simple script was written to determine the transit time and calculate the mobility by a least-square fitting. A typical output of this program is shown in Figure 2.11. This program was written in a Python script (Enthought EPD Free 2.7.2). The algorithm of this script is explained in Appendix A and the source code can be found in Appendix B.

\[ \mu = \frac{L^2}{t_{tr} V} \]

Figure 2.11 A typical output of the program determining the transit time and mobility
The error bars were always missing in mobility measurement in literatures because of the manual fit, but it is provided by this program. The analysis of the measurement error propagation is shown in Appendix A.6. It turns out that most of the error of the mobility measurement comes from the measurement error of film thickness, while the error of estimation on transit time has been significantly reduced by the least-square fit and a scan of possible straight-line-fit range.


2.3.3 Hole mobility measurement of self-assembled P3HT nanoparticle film

Although we observe fairly dense packing in the film from the SEM images and filling fraction measurement, the charge-transport properties of these nanoparticulate films cannot be predicted with confidence because there may still be nm-scale gaps between particles or surfactant remaining on the particle surfaces. These would not be visible in structure characterizations but could significantly slow charge transport. Moreover, if there were too few effective contacts between nanoparticles, transport paths may be too tortuous for efficient transfer. To test transport properties, therefore, we measured the charge carrier mobility of films using a time-of-flight (ToF) technique [58].

Figure 2.12 shows the hole mobility in our self-assembled nanoparticulate films composed of P3HT. In order to make the measurement, a nanoparticulate film with \( h = 2 \cdot 3 \) µm was collected and dried on a substrate, half of which was coated with indium tin oxide (ITO). Then a 100...
nm aluminum layer was deposited on top of the film in a vacuum thermal evaporator (MBraun) and a sandwich structure with two electrodes was obtained. Two silver wires were attached to the ITO layer and Al layer using conductive epoxy adhesive to ensure good conductivity (Figure 2.12, inset). A pulsed laser with wavelength of 355 nm, 10 Hz repetition rate and pulse duration of 4-6 ns was directed through the ITO electrode to generate charge carriers within the film. Then, under a given biasing voltage $V$, the average time necessary for the carriers to reach the counter electrode (the transit time $t_{tr}$) was determined and the hole mobility $\mu$ was calculated using the method shown in 2.3.2. Uncertainty in this measurement mainly comes from the uncertainty of the transit time and the measurement of film thickness.

Using the as-made P3HT particles, we obtain mobility approximately $2 \times 10^{-4}$ cm$^2$/(V·s). However, when we first rinsed the particles to remove excess SDS surfactant (maintaining the same particle concentration), we found that the mobility more than doubled to $4-8 \times 10^{-4}$ cm$^2$/(V·s). We repeated this measurement over 5 times and found the results to be consistent within the range of $4-8 \times 10^{-4}$ cm$^2$/(V·s), which is a 2-4 fold enhancement.

It should be noted that ToF measurement requires continuous films, because the existence of pin holes would allow the deposited Al to short the sandwich structure in the films and disable the whole measurement. Therefore, the fact that ToF measurement can be properly conducted is a demonstration that these large-area films are pin-hole free.

For comparison, we measured the ToF mobility of drop-cast films made using the same batch of P3HT. The mobility was approximately $1 \times 10^{-3}$ cm$^2$/(V·s) when the applied electric field was
(150)^2 \text{ V/m}, and decreases when the electric is larger. This mobility of drop-cast P3HT film agrees with the figures of P3HT with similar molecular weight in literature [62-64]. Hence the mobility of our nanoparticle films is very similar in magnitude to that of the drop-cast film.

### 2.3.4 Hole mobility vs. nanoparticle size distribution

It was shown in 2.3.3 that the hole mobility of self-assembled P3HT nanoparticle film has hole mobility that is very similar to drop-cast P3HT films, which is an important electric property of active layers of OPV devices. In this section an exploration of optimizing the hole mobility of P3HT nanoparticle film by manipulating the nanoparticle size distribution will be demonstrated.

**Figure 2.13** Size distribution of P3HT nanoparticles from different batches, measured by DLS. Z-average diameter: (a) 134 nm, (b) 110 nm, (c) 59 nm. The schematic plots of particle spheres on the right were drawn in size.
As was stated in 2.1, we have very good control of the average size of P3HT nanoparticles, which can be adjusted in the range of 15 nm to 160 nm by modifying the concentration of P3HT chloroform solution, the concentration of SDS aqueous solution, etc. However, comparing to commercially-available particles such as silica particles and latex particles that we have worked on, these home-made nanoparticles have a much wider size distribution. Figure 2.13 shows a set of size distribution measurement with dynamic light scattering (DLS) on the 3 different batches of P3HT nanoparticles that were used in this experiment. The average particle sizes were measured as 134 nm, 110 nm and 59 nm, and a schematic plot of average particle size on the right of each distribution plot in Figure 2.13.

![Figure 2.14](image)

**Figure 2.14** Charge mobility (holes) of the poly-dispersed P3HT nanoparticle film measured by time-of-flight (ToF). The horizontal axis is the square root of the electric field, $E$, applied to the film. 1+1+1 means the nanoparticle dispersion that was used for self-assembly was a mixture of 3 different batches of P3HT nanoparticles shown in Figure 2.13 with a volume ratio of 1:1:1.
The 3 batches of P3HT nanoparticle dispersions were then mixed at a volume ratio of 1:1:1 and 1:2:2 (134 nm : 110 nm : 59 nm), and the resultant dispersions were expected to have much wider size distributions. After the mixing, these dispersions were washed, self-assembled, collected and dried using our innovative technique introduced in 2.2.1, and the same process of electrode deposition, time-of-flight measurement and programming-based analysis as 2.3.3 were followed. Figure 2.14 showed the summarized hole mobility measurements on the self-assembled P3HT nanoparticle films from the mixed dispersions, where 1+1+1 means that the volume ratio of 134 nm, 110 nm and 59 nm nanoparticles is 1:1:1, and 1+2+2 means that this ratio is 1:2:2.

These mobility measurements as well as the error bars suggest that the polydispersed nanoparticle dispersion (i.e. the standard deviation of nanoparticle sizes in the dispersion is large) may lead to denser packing and higher hole mobility than mono-dispersed nanoparticle dispersion. However, there has been some inconsistency in ToF mobility measurement. For

![Figure 2.15 Second charge mobility (holes) of the poly-dispersed P3HT nanoparticle film measured by time-of-flight (ToF) done in May 2013. Repeated measurement of Figure 2.14](image-url)
example, the pink points in Figure 2.14 show charge mobility that is similar to the red points, which are the mobility measured on films made from mono-dispersed nanoparticle dispersion.

Therefore, repeated experiments have been done to confirm the above conclusion, as shown in Figure 2.15 and Figure 2.16. In each set of experiment, the ToF mobility of nanoparticulate film made from poly-dispersed nanoparticle dispersion is consistently higher than that from mono-dispersed nanoparticle dispersion.

This result may be the opposite of people’s intuition that single-sized particles and ordered structure, such as crystals, usually yield better performance. However, it should be noted that the packing structure in our P3HT nanoparticle films is always random packing. An analogy of the poly-dispersed nanoparticle dispersion is a mixture of basketballs, tennis balls and ping-pong balls. The gaps between basketballs can be filled with smaller balls and the packing structure is denser and more defect-free than a structure that is solely made of basket balls.
Therefore, this experiment has shown an advantage of the particle-packing approach: not only can we make better films, we may be able to rationally control the geometry and topology by tuning particle size distribution, etc.

However, it should also be noted that there is a huge variation in ToF mobility measurement if we compare from day to day. For example, 150 nm washed/diluted 20,000x: obtained 4E-4 on one day, and 18E-4 on another day. This could be due to different batch of P3HT samples, the set-up of ToF devices, depreciation of coupling resistance, electrode coating and other treatment, etc.
2.4 Sintering in P3HT nanoparticle films

We have shown in Section 2.3 that the self-assembled P3HT nanoparticle films have decent charge mobility, which means that these large-area films are pin-hole free, and the surfactant on the surface of P3HT nanoparticles do not hinder charge transport. Yet the contacts between nanoparticles in these films have not been fully studied and understood, e.g. how many neighbors do particles have on average, how big the contact areas are, etc. In this section, we will look into the contacts between nanoparticles in these films.

Figure 2.17 is a scanning electron microscope (SEM) image of a P3HT nanoparticle film, top surface.

Figure 2.17 is a scanning electron microscope (SEM) image of a P3HT nanoparticle film at the top surface. According to this image, the film seems to be sintered and many nanoparticles clearly
have very good contact with each other, which is expected given the good charge mobility of the whole film. It should also be noted that many nanoparticles have significant elastic deformation, possibly due to van der Waals attraction between particles or to capillary pressure when DMSO evaporates in the air-drying process. Therefore, these nanoparticles cannot be treated as hard spheres, which is why we adopted JKR theory [65, 66] to understand the contacts between them.

Figure 2.18 Illustration of interactions in a JKR mode.
(Figure copied from Johnson, K. L, et al. [65])

The force diagram of JKR (Johnson, Kendall, Roberts) Theory is shown in Figure 2.18, which is a fully elastic model considering adhesion in the contact zone. JKR theory predicts contact area of adhesive elastic contacts between two spheres to be:

\[
R_c = \left( \frac{\pi \omega R_1 R_2}{E^*} \right)^{1/3}
\]

where \( R_c \) is the contact radius, \( R_1 \) and \( R_2 \) are the particle radii, \( \omega \) is the adhesion energy per unit area of contacting surfaces, and \( E^* \) is the reduced Young's modulus \( E^* = E / (1-v^2) \) where \( E \) is the Young's modulus and \( v \) is the Poisson ratio. Therefore, we have the following relationship:

\[
R_c^3 \propto R_1 R_2, \quad D_c^3 \propto D_1 D_2
\]

Since \( R_c, \ R_1, \ R_2, \ D_c, \ D_1 \) and \( D_2 \) can all be measured from the SEM image, we can check if the contacts between nanoparticles in the self-assembled film agrees with the prediction from JKR theory.
Figure 2.19 A SEM image of a P3HT nanoparticle film showing how the diameter of particles and contacts were measured.

Figure 2.20 A SEM image of a P3HT nanoparticle film showing all 30 selected contacts.
We chose 30 contacts from an SEM image of P3HT nanoparticle film, according to the requirement that the contact area is only between 2 nanoparticles and mostly perpendicular to the image plane. Figure 2.19 shows how the diameter of both particles and the diameter of contact area were measured, and figure 2.20 shows all the 30 selected contact areas. All these measurements are plotted in Figure 2.21, which shows a systematic increase of $D_c$ with $D_1D_2$. Although there is significant scatter in the plot, the results are consistent with a linear relationship between $D_c^3$ and $D_1D_2$ as predicted by the JKR theory of elastic adhesive contact area between two spheres.

![Figure 2.21 The contact diameter $D_c^3$ vs. particle diameter $D_1D_2$](image)

It should be noted, however, the measured $D_c^3$ and $D_1D_2$ are not perfectly proportional in the above plot, which could be due to the following reasons:

(a) Particles are not perfectly spherical

(b) Contact surfaces may not be normal to surface

(c) There may be a third (or more) particle touching the dimer near the contact,
underneath the visible particles.

(d) The number of measurements is low so that a fit to the overall trend is not reliable.

The above analysis provides a quantitative evaluation of the sintering effect on the nanoparticle film. We are unable to provide a quantitative link between the extent of sintering and the high measured charge mobility. However, at a qualitative level, it may be that the finite-sized contact discs make it possible for these particle films to achieve ToF mobility close to that of the cast polymer films. If the particles had very large modulus or low adhesion so that they remain undeformed, then the effective contact area for charge transport would be smaller and the mobility might be greatly reduced. On the other hand, using particles with low modulus or softening them with vapor may lead to larger contact areas and larger charge mobility.

Future experiments to understand the sintering phenomena would be very useful and may enhance charge separation and transport. For instance, different temperatures in the film-formation process may lead to different levels of sintering. Different solvents in the drying process may also affect sintering. One might also try annealing the film and see the effect of annealing on sintering and the effect of sintering on mobility measurement.
2.5 Brief summary of the method of drying droplet on a liquid substrate

In this part we are going to introduce a different film-formation technique, which was developed prior to the evaporation-induced self-assembly technique in 2.2.1. This method is listed here mainly for reference, as a later section 3.3 is based on this method. This method led to a very striking in-plane segregation of particles into micron-scale domains. However, the overall film morphology was not well suited to further study or to devices, so that this line of research was stopped.

This method is developed following the paper from Dong, A. G. et al. [51]. An aqueous suspension of P3HT nanoparticles (or a mixture of P3HT and PCBM nanoparticles) was dropped in a glass vial on top of OFPA (2, 2, 3, 3, 4, 4, 5-octafluoropentyl acrylate, purchased from Sigma-Aldrich, catalog#: 474401-25ML), which was chosen as a liquid substrate because of its high boiling point, high mass density and immiscibility with water. Then the container can be closed (or partial closed) in order to control the evaporation rate. A film of the nanoparticles formed at OFPA-air interface after about 24 hours. Figure 2.22 shows this film formation method.

![Figure 2.22](image-url) Images of a typical drop-drying process on a liquid substrate (The scale bar in the right image is 100 μm)

However, due to the relatively large surface tension between water and air, the shape of the aqueous droplet on OFPA was almost spherical, far away from an ideal thin layer. And the film
obtained with this method was too thick (100 μm) for the active layer of organic photovoltaic devices.

Moreover, in a binary film of P3HT and PCBM nanoparticles formed with this method, the morphologies on the two sides were different (figure 2.23). A mesoscopic structure was observed on the side facing air, while the side facing OFPA showed a better mix of the two species, and quenching effect was observed. The quenching experiment will be discussed in 3.3.

In a similar experiment mainly conducted by Ryan Horton from the same research group, a hexane suspension of PMMA (Poly(methyl methacrylate)) nanoparticles stabilized by ligands PHSA (Poly(hydroxystearic acid)) was placed on top of water substrate, and uniform film with large area was obtained (figure 2.24).
This experiment indicates if P3HT and PCBM nanoparticles could be suspended in hexane or some other low-density solvent that is immiscible with water, this method of drying droplet on a liquid substrate may potentially produce uniform large-area films of P3HT or binary films of P3HT and PCBM. Efforts have been made to disperse P3HT nanoparticles in hexane, but no good particles were obtained due to highly limited choice of solvents and surfactants.
CHAPTER 3

P3HT/PCBM BINARY FILM

3.1 Formation of P3HT/PCBM binary film

In chapter 2 the self-assembly fabrication and characterization of packing structure and electric property of P3HT single component films have been thoroughly presented. A natural next step in this dissertation is to fabricate P3HT/PCBM binary films that can be used as the active layer in OPV devices.

In fact, binary films composed of P3HT and PCBM could be obtained by the same self-assembly technique as introduced in 2.2.1, using a suspension containing both P3HT nanoparticles and PCBM nanoparticles. A binary film made from P3HT/PCBM mixed dispersion with a 1.82:1 mass ratio (P3HT dispersion of 0.75mg/mL and PCBM dispersion of 0.825mg/mL mixed with a volume ratio of 2:1) is shown in Figure 3.1. Fluorescent images have shown good mixing and no segregation of P3HT from PCBM at scales larger than 1 µm was observed.
The appearance of the above binary film is, however, almost the same as P3HT single-component films. Therefore, additional validation is needed to prove that the PCBM nanoparticles have become part of the film. An easy way of checking the existence of PCBM would be dissolving the film and comparing its UV-Vis absorption spectra with the absorption spectra of pristine P3HT and PCBM, which will be shown in 3.2.
3.2 Absorption spectra of binary film

In this part, we will prove the existence of PCBM in binary films, and we will also calculate the relative composition of the two types of particles as a function of film-formation time, by measuring the absorption spectra of chloroform solutions made from dissolved binary films.

To be specific, the P3HT/PCBM binary films were dissolved in chloroform, and the absorption spectra of the solution were measured using a SHIMADZU 3600 UV-vis-NIR Spectrometer. Meanwhile, absorption spectra of solutions of pristine P3HT (peak $\lambda = 450$ nm) and PCBM (peak $\lambda = 327.5$ nm) with known concentration were also measured for calibration. The concentration of the binary film solution is unknown, but if we assume that the absorption of the mixture solution is just the sum of the absorption from its P3HT component and its PCBM component, we have the following relationship between the sample spectra and calibration spectra:

$$\text{Abs}_{\text{mix}} = \text{Abs}_{\text{P3HT}*} \frac{C_s,\text{P3HT}}{C_o,\text{P3HT}} + \text{Abs}_{\text{PCBM}*} \frac{C_s,\text{PCBM}}{C_o,\text{PCBM}}$$

where $\text{Abs}_{\text{mix}}$ is the measured absorption of chloroform solution made from dissolved binary films, $\text{Abs}_{\text{P3HT}*}$ is the measured absorption of the reference pristine P3HT solution, $\text{Abs}_{\text{PCBM}*}$ is the measured absorption of the reference pristine PCBM solution, $C_s,\text{P3HT}$ is the unknown concentration of P3HT in binary film solution, $C_o,\text{P3HT}$ is the known concentration of the reference pristine P3HT solution, $C_s,\text{PCBM}$ is the unknown concentration of PCBM in binary film solution, $C_o,\text{PCBM}$ is the known concentration of the reference pristine PCBM solution.

Note that the above relationship exists for the whole spectra. Since there are only 2 unknown variables $C_s,\text{P3HT}$ and $C_s,\text{PCBM}$, we can pick 2 wavelengths 327.5 nm and 450 nm and solve the following equations:
Abs_{mix, 327.5nm} = Abs_{P3HT, 327.5nm} * C_s,P3HT / C_o,P3HT + Abs_{PCBM, 327.5nm} * C_s,PCBM / C_o,PCBM

Abs_{mix, 450nm} = Abs_{P3HT, 450nm} * C_s,P3HT / C_o,P3HT + Abs_{PCBM, 450nm} * C_s,PCBM / C_o,PCBM

Solving the top equations, we have:

\[
\frac{C_s,P3HT}{C_s,PCBM} = \frac{C_o,P3HT}{C_o,PCBM} \times \frac{Abs_{PCBM,327.5nm} \times Abs_{mix,450nm} - Abs_{P3HT,450nm} \times Abs_{mix,327.5nm}}{Abs_{P3HT,450nm} \times Abs_{mix,327.5nm} - Abs_{P3HT,327.5nm} \times Abs_{mix,450nm}}
\]

The relative composition of P3HT/PCBM within the binary film was then determined following the above equation, given the known mass concentration of the reference pristine P3HT and PCBM solution, and the measured spectra of dissolved binary films and reference pristine P3HT and PCBM solutions. The mass concentration of the reference pristine P3HT and PCBM solution were kept the same, and all the measured spectra intensity used in the calculation is listed below in table 3.1:

<table>
<thead>
<tr>
<th></th>
<th>55/45 vol%</th>
<th>60/40 vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 min</td>
<td>40 min</td>
</tr>
<tr>
<td>C_{o,P3HT} / C_{o,PCBM}</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Abs_{PCBM,450nm}</td>
<td>0.02774545</td>
<td>0.02774545</td>
</tr>
<tr>
<td>Abs_{mix,327.5nm}</td>
<td>0.26405</td>
<td>0.151338</td>
</tr>
<tr>
<td>Abs_{PCBM,327.5nm}</td>
<td>0.6126545</td>
<td>0.6126545</td>
</tr>
<tr>
<td>Abs_{mix,450nm}</td>
<td>0.57045</td>
<td>0.24173</td>
</tr>
<tr>
<td>Abs_{P3HT,327.5nm}</td>
<td>0.15399</td>
<td>0.15399</td>
</tr>
<tr>
<td>Abs_{P3HT,450nm}</td>
<td>0.73159</td>
<td>0.73159</td>
</tr>
<tr>
<td>C_s,P3HT / C_s,PCBM</td>
<td>3.25</td>
<td>1.96</td>
</tr>
<tr>
<td>wt% P3HT</td>
<td>76%</td>
<td>66%</td>
</tr>
</tbody>
</table>

Table 3.1 Spectra intensity measurements in calculation of mass concentration ratio

The resulting fits agree well with the experiment across the absorption spectra (Figure 3.2). The
absorption spectra of a synthetic mixture of P3HT and PCBM solution with a mass ratio of 3.25:1 almost perfectly overlaps with the absorption spectra of the dissolved binary film, which not only confirmed the existence of PCBM, but also provided a good estimate of the relative mass composition of the two types of particles in the binary film.

The above measurements and calculation of relative composition were done on multiple samples. We begin with a nanoparticle suspension containing 67 wt% P3HT and 33 wt% PCBM in a 55/45 vol% water/DMSO mixture. In a film formed after 20 min, we found a composition of 76 wt% P3HT. In a film formed after 40 min, the composition changed to 66 wt% P3HT, indistinguishable from the suspension composition (Figure 3.2). Starting from a nanoparticle suspension with the same 67/33 wt% of P3HT/PCBM but with 60/40% water/DMSO, we found a slightly lower incorporation of PCBM: a 20-min film had 76 wt% P3HT and a 40-min film had 72% P3HT. In all

![Absorption spectrum of a dissolved two-component film containing nanoparticles of P3HT and PCBM. Also shown are the control measurements of pure solutions of P3HT and of PCBM, and a 3.25:1 combination of these controls, which approximate matches the film data.](image)
cases, the composition in the film was close to the initial concentration, but at early times there was a slight enhancement of P3HT. This selective partitioning of P3HT into the film may be a result of PCBM particles being more stable in the presence of DMSO. It is likely that there is a modest gradient in composition, where the air side of the film being slightly enriched in P3HT. For OPV devices, this indicates the potential, by separately tuning the surface chemistry of the two finds of particles, to build in a gradient to enhance separation of electrons and holes.
3.3 Fluorescence quenching experiment on binary film

3.3.1 Fluorescence quenching and charge transfer

In 3.1 and 3.2, the charge transport characteristic (i.e., mobility) was measured, which is associated with step 4 in the four-step energy conversion mechanism introduced in 1.1.4 [13]. Here the transfer of charge associated with step 3 will be checked by a fluorescence quenching experiment.

Fluorescence is a result of radiative recombination [67], which is a process competing with charge transfer [58, 68]. Therefore, fluorescence quenching, which usually refers to a decrease in fluorescence intensity, can be monitored as an evidence of charge transfer. In a P3HT/PCBM binary composite, the better they mix, the more likely charge transfer happens and hence the lower the fluorescence intensity should be [69].

3.3.2 Method of quenching experiment

Classically, quenching experiment consists of a series of photoluminescence measurements with intrinsic fluorescent spectrum and quenched ones. Attempts have been made on a photoluminescence spectrometer to check the quenching effect on binary films made by the drop-drying way with different stoichiometries (compound ratio), but the result was limited by the sensitivity of the photoluminescence spectrometer on solid films given the small area of films made with that method.

Therefore, an alternative method using optical microscope was designed as follows: (a) binary films with different stoichiometries (volume ratio of PCBM: P3HT=0:2, 1:2, 2:2, 3:2, 4:2, 8:2) were
formed with the drop-drying method introduced in 2.2, (b) when excited by arc lamp, fluorescence images of each film were taken on a optical microscope by a digital camera, (c) fluorescent intensity was obtained by Image J in multiple positions of each image, (d) the values of intensity were normalized by the density of P3HT in each film. In order to keep consistent, all the images were taken on the same day using the same objective with the same exposure time and the same arc lamp turned on for over half an hour.

However, although it was done carefully, the reliability of this experiment is still based on the following assumptions:

(a) The intensity that measured by the digital camera is a quantitative and repeatable measure of real photon intensity, which is the promise of the manufacturer.

(b) The arc lamp is steady during the whole experiment, which is probably not true.

(c) All films are uniform, which is not true given the different structures on two sides of the films

(d) The absorption is mainly by P3HT

(e) Reflection is not significant or light source (green field) = transmitted + absorption, which is not true when the film is thick.

Therefore, if possible, the measurement still needs to be done on a photoluminescence spectrometer, since large-area thin film is available now.

3.3.3 Data analysis and discussion

Although the experiment designed in 3.3.2 has its drawbacks, the result is demonstrated in figure
3.3 since the data would be analyzed in the same way no matter how the fluorescence intensity was measured.

It should be noted that the films studied by this method are the ones from section 2.5, not the large-area ones that was introduced in 2.2. However, even though the films are different, the same P3HT and PCBM nanoparticles were used. Therefore, if we demonstrate effective charge transfer in these films (when there is no mesoscale segregation), we assume that the other films will also have effective charge transfer.

Figure 3.3. Quantitative fluorescence measurement vs. stoichiometry

As was shown in figure 3.3, when the volume ratio was PCBM:P3HT=1:2, significant quenching in the binary film was observed, indicating a great mix at particle level. However, when the volume fraction of PCBM nanoparticles increased more, the intensity of fluorescence increases and quenching was not that significant, which is probably because of a worse mixing in the binary film owing to the mesoscale particle segregation, and a smaller chance of charge transfer.

It should be noted that having a structure with characteristic length comparable to the exciton diffusion length and a great chance of charge transfer is one of the biggest advantage of using
nanoparticle structures. One could expect a more significant quenching effect on a binary film when smaller nanoparticles were used.

The fluorescent images were taken by CoolSNAP HQ² CCD camera (Phohometrics Inc., Tucson, AZ).

The P3HT film were excited by green light, and the fluorescent images were taken after a red filter.

The arc lamp used here is HBO 100.
CHAPTER 4

EXPLORATION OF CONTROLLING INTERNAL STRUCTURE
OF P3HT NANOPARTICLES

4.1 Synthesis of fast- and slow-processed P3HT nanoparticles

Besides what have been shown in chapter 2 and 3, one of the advantages of our approach of fabricating bulk heterojunctions from nanoparticles is that it allows the manipulation on one phase of the bulk heterojunction without changing the other one. An example of this phase-specific manipulation will be discussed in this chapter.

In 2.1 we described the synthesis of P3HT nanoparticles using the miniemulsion technique, which we call “fast-processed” P3HT nanoparticles in this chapter. In brief, P3HT chloroform solution was emulsified in a water-SDS mixture to obtain stable droplets, and then the emulsion was heated so that chloroform would evaporate and P3HT particles formed by precipitation and were stabilized by the absorbed surfactant in 5 to 10 minutes. In this chapter we modified the technique by slowing down the evaporation of chloroform. Figure 4.1 shows a schematic of the synthesis of slow-processed P3HT nanoparticles. After sonication, instead of being heated in an oil bath, the emulsion was stirred in a loosely capped container for approximately 24 hours to allow chloroform to evaporate slowly. Figure 4.2 shows the TEM images of slow- and fast-processed P3HT nanoparticles synthesized using the technique described above. It appears that the slow-processed P3HT nanoparticles are also fairly spherical, but they may have a wider distribution in size than the fast-processed ones.
In section 4.2 and 4.3, the internal molecular-scale structure of both fast- and slow-processed P3HT nanoparticles and their absorption spectra will be studied. Given the extended duration of
solvent evaporation and particle formation, it would be interesting to see if there is any difference between the internal structure of the slow-processed P3HT nanoparticles and the fast-processed ones, *e.g.* denser molecular packing, different alignment between polymer chains, etc.. This would be an interesting and useful example of manipulating the P3HT phase of the self-assembled bulk heterojunction without changing the PCBM phase.

It should be noted that there is no quantitative control on levels of isolation, *i.e.* the evaporation rate of chloroform in different slow-processed samples here. Therefore, the internal molecular packing within slow-processed P3HT nanoparticles might vary from sample to sample.
4.2 GIWAXS of fast- and slow-processed P3HT nanoparticles

To characterize the internal, molecular-scale structure of fast- and slow-processed P3HT nanoparticles, 5 samples, labeled as sample 1-5 or YY1-5, were made on the same day from the same chloroform solution, and cast on silicon wafers. Sample 1 and 2 are fast-processed P3HT nanoparticle samples made at the same time following exactly the same procedure. Sample 3 and 4 are slow-processed P3HT nanoparticle samples made at the same time following the same

![GIWAXS pattern of 5 samples](image)

**Figure 4.3** GIWAXS pattern of 5 samples. Sample 1 (YY1: Fast-processed-1s), sample 2 (YY2: Fast-processed-5s), sample 3 (YY3: Slow-processed-1s), sample 4 (YY4: Slow-processed-5s), sample 5 (YY5: drop-cast P3HT polymer film-5s)
procedure, except that the evaporation rate may differ because of small differences in the sealing layer on the vials. Sample 5 is drop-cast P3HT polymer film.

Figure 4.3 shows the Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) measurements of these 5 samples performed at the Lawrence Berkeley National Laboratory (LBNL) by Feng Liu in April 2015 (X-ray Energy=10 keV). There is a significant difference in orientation between nanoparticle films and drop-cast polymer films. Only the drop-cast film has an anisotropic

![Figure 4.3 GIWAXS Measurements](image1)

**Figure 4.4** (Top, bottom left) GIWAXS of fast- and slow-processed P3HT nanoparticle and drop-cast P3HT polymer film. (bottom right) Example of fitting Lorentz function to (100) and (200) peak.

GIWAXS pattern, while all the first 4 films are isotropic, which is expected since the nanoparticles
were randomly packed in these film.

The angular averages of GIWAXS intensity of the 5 samples were plotted in Figure 4.4. There is a noticeable shift at (100) and (200) peaks between fast- and slow-processed P3HT nanoparticles (Figure 4.3(bottom left)). In order to analyze the data at a finer granularity, the (100) and (200) peaks were fitted to Lorentz function (Figure 4.3(bottom right) shows fairly good fit quality) after the baselines were cut. Then the peak position, area under the peak and FWHM were measured for each peak and the d-spacing and domain size were calculated for all the 5 samples. The results were summarized in table 4.1, and the implied D-spacing of fast-processed nanoparticles agree with the previously reported range of 1.66nm to 1.68 nm in literature [62, 70-72], while slow-processed nanoparticles and drop-cast samples suggest a smaller D-spacing.

<table>
<thead>
<tr>
<th>Sample-exposure time</th>
<th>100 peak</th>
<th>200 peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position</td>
<td>Area</td>
</tr>
<tr>
<td>YY1. Fast-processed-1s</td>
<td>0.37669</td>
<td>131.94</td>
</tr>
<tr>
<td>YY2. Fast-processed-5s</td>
<td>0.37669</td>
<td>804.28</td>
</tr>
<tr>
<td>YY3. Slow-processed-1s</td>
<td>0.38909</td>
<td>104.46</td>
</tr>
<tr>
<td>YY4. Slow-processed-5s</td>
<td>0.38289</td>
<td>690.89</td>
</tr>
<tr>
<td>YY5. Drop-cast-5s</td>
<td>0.38909</td>
<td>831.49</td>
</tr>
</tbody>
</table>

Table 4.1 GIWAXS measurements summary of fast- and slow-processed P3HT nanoparticles and drop-cast P3HT polymer film
The results in table 4.1 shows that the d-spacing in (100) direction in fast-processed nanoparticles is much larger (by as much as 3%) than that in the drop-cast P3HT, and one of the slow-processed nanoparticle film is very similar to the drop-cast film, while the other one is between fast-processed nanoparticle films and the other slow-processed nanoparticle film. As was discussed at the end of 4.1, this inconsistency in slow-processed nanoparticles may be due to different evaporation rate of chloroform. The d-spacing in (020) direction is relatively stable across the 5 samples, and there is also no systematic difference in domain size between the 3 types of samples. It should also be noted that the thickness of the cast films was not controlled, so the area below peaks (without normalization) cannot be compared across samples.

**Figure 4.5** Schematic of molecular packing in P3HT
Figure 4.5 is a schematic of the packing structure of P3HT polymer chains. A decrease in d-spacing in (100) direction in slow-processed nanoparticles represents a denser packing, which could be a result of the slow evaporation of chloroform.
4.3 Absorption spectra

4.3.1 Absorption spectra of fast- and slow-processed P3HT nanoparticles

After exploring the internal structure of fast- and slow-processed P3HT nanoparticles, we discuss the measurements of their absorption spectra with the UV-vis-NIR Spectrometer SHIMADZU 3600 in this section.

Firstly, we demonstrate that the difference in absorption spectra is not just an effect of nanoparticle size. Figure 4.6 shows the absorption spectra of two fast- and slow-processed P3HT nanoparticle suspension samples (another set of samples, different from the 5 samples that are extensively discussed in this section). Their size distributions measured by Nanosight are almost the same, but their absorption spectra are distinguishable. Therefore, this difference is likely to be due to different treatment in the synthesis process.

![Absorption spectra of fast- and slow-processed P3HT nanoparticles](image)

**Figure 4.6** Absorption spectra of fast- and slow-processed P3HT nanoparticle (inset shows the size distribution of both samples)
To further understand the connection between the internal structure and absorption spectra in P3HT nanoparticles, we measured the UV absorption spectra of the samples 1-4, i.e. fast- and slow-processed P3HT nanoparticles that we discussed in section 4.2 (Sample 5 is a drop-cast polymer film and therefore not quantifiable by this solution-based method). Figure 4.7 shows the 4 sets of absorption spectra, in which we can see that the two fast-processed samples (1 and 2) have very similar spectra, but sample 3 is very different from them. Sample 4 is somewhere between sample 3 and sample 1, 2.

In order to further understand the physical meaning of this difference, we turn to studies that correlate the relative intensities of vibronic features in the absorption spectra of P3HT with the P3HT aggregate structure, specifically the H/J aggregate model developed by Spano [52, 73, 74]. According to this theory, the dominant coupling types, H-type (face-to-face) or J-type (end-to-end), are related to the intensity ratio of the transition from the energy origin to the first vibronic satellite, called $A_{0,0}/A_{0,1}$. To find the intensity of these specific peaks, we decompose of the spectra.

**Figure 4.7** Absorption spectra of sample 1-4, i.e. fast- and slow-processed P3HT nanoparticle suspension samples discussed in section 4.2
Following Spano’s theory, we decomposed the absorption spectra of both fast- and slow-processed P3HT nanoparticles into 5 Gaussian peaks (Figure 4.8, Figure 4.9), based on the following rules:

1. The distance (energy difference) between adjacent peaks should be approximately the same;

2. The above distance should be close to 170 meV;

3. From lower energy state to higher energy state, the distance between adjacent peaks may only increase or remain the same, not decrease;

4. From lower energy state to higher energy state, the variance of peaks may only increase, if not the same, and this increase should be within 30%.

**Figure 4.8** Decomposed absorption spectra of Sample YY1 (fast-processed P3HT nanoparticles)
The fit parameters extracted from the samples YY1-YY4 (the same as were used for x-ray diffraction) were summarized in table 4.2, where “Amorphous” is the coefficient associated with P3HT chloroform solution that was used to subtract from the whole spectra, \( A_{0-0} \) to \( A_{0-4} \) are the intensity of the 5 decomposed Gaussian peaks, \( e_{00} \) is the position of the first peak (0-0) center, \( w_1 \) is the distance between the 0-0 peak and 0-1 peak, \( w_2 \) is the difference in energy between the 0-1 peak and 0-2 peak, the 0-2 peak and 0-3 peak, and the 0-3 peak and 0-4 peak (these three energy shifts are forced to be the same), \( \sigma_1 \) is the standard deviation of the first Gaussian peak, \( \sigma_2 \) is the standard deviation of the second peak, and \( \sigma_3 \) is the standard deviation of the last 3 peaks.

Figure 4.9 Decomposed absorption spectra of Sample YY3 (slow-processed P3HT nanoparticles)
<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>0.52</td>
<td>0.52</td>
<td>0.5</td>
<td>0.52</td>
</tr>
<tr>
<td>A$_{0-0}$</td>
<td>0.44</td>
<td>0.45</td>
<td>0.60</td>
<td>0.48</td>
</tr>
<tr>
<td>A$_{0-1}$</td>
<td>0.73</td>
<td>0.73</td>
<td>0.81</td>
<td>0.74</td>
</tr>
<tr>
<td>A$_{0-2}$</td>
<td>0.7</td>
<td>0.7</td>
<td>0.75</td>
<td>0.73</td>
</tr>
<tr>
<td>A$_{0-3}$</td>
<td>0.36</td>
<td>0.36</td>
<td>0.38</td>
<td>0.37</td>
</tr>
<tr>
<td>A$_{0-4}$</td>
<td>0.07</td>
<td>0.07</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>e$_{00}$</td>
<td>2.055</td>
<td>2.051</td>
<td>2.305</td>
<td>2.046</td>
</tr>
<tr>
<td>w$_{1}$</td>
<td>0.175</td>
<td>0.175</td>
<td>0.172</td>
<td>0.173</td>
</tr>
<tr>
<td>w$_{2}$</td>
<td>0.176</td>
<td>0.176</td>
<td>0.174</td>
<td>0.174</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>0.103</td>
<td>0.102</td>
<td>0.092</td>
<td>0.092</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>0.122</td>
<td>0.124</td>
<td>0.116</td>
<td>0.117</td>
</tr>
<tr>
<td>$\sigma_3$</td>
<td>0.134</td>
<td>0.134</td>
<td>0.130</td>
<td>0.130</td>
</tr>
<tr>
<td>A$<em>{0-0}$/A$</em>{0-1}$</td>
<td>0.60</td>
<td>0.62</td>
<td>0.74</td>
<td>0.65</td>
</tr>
<tr>
<td>A$_{0-0}$/Amorphous</td>
<td>0.85</td>
<td>0.87</td>
<td>1.2</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Table 4.2 Fit parameters of the Gaussian components assigned to the different vibronic components of fast- and slow-processed P3HT NP absorption spectra

This decomposition analysis of P3HT absorption spectra is introduced in detail in Appendix C. The analysis was written in R code, and the source code can be found in Appendix D.

We see from table 4.2 that the A$_{0-0}$/Amorphous ratio in slow-processed P3HT nanoparticles is much higher than that in fast ones, which indicated a larger portion of aggregates in slow-processed P3HT nanoparticles.

Moreover, both fast- and slow-processed P3HT nanoparticles show an A$_{0-0}$/A$_{0-1}$ ratio of less than 1, which suggests a weak presence of H-type aggregate. But a higher A$_{0-0}$/A$_{0-1}$ ratio from the
slow-processed P3HT nanoparticles implied more J-type aggregate component.

Furthermore, taking our finding about the internal structure within P3HT nanoparticles in section 4.2 into consideration, the data shows a trend, in which the d-spacing is smaller for the two slow-grown samples relative to the fast-grown samples, and the $A_{0,0}/A_{0,1}$ ratio is larger for these samples. Fig 4.10 shows these results in a plot. We propose that there may be a connection between d-spacing and the extent of J-aggregate behavior. The data are consistent with this but do not prove it, since it may be that both parameters are set by another property in an unknown way. The smaller d-spacing and denser packing in the more slowly formed particles might be a result of a higher degree of planarity of thiophene rings in a structure with more J-type aggregates. The drop-cast P3HT film made from chloroform solution takes approximately 10-15 minutes to dry, which is closer to the 5 minutes processing time of fast-grown samples, but GIWAXS data shows that they actually represent more slow-processed nanoparticles instead of fast ones.

![Figure 4.10](image.png)

**Figure 4.10** Plot of $A_{0,0}/A_{0,1}$ vs D-spacing for samples YY1-YY4. The rectangle represents the range of $A_{0,0}/A_{0,1}$ values in section 4.3.2
4.3.2 In-situ experiment of slow-processed P3HT nanoparticles

We showed in 4.2 and 4.3.1 that the internal molecular-scale structure (d-spacing, H/J aggregate components, etc.) of the slow-processed P3HT nanoparticles is slightly different from fast-processed ones. However, little has been known so far about the 24-hour formation process of slow processed P3HT nanoparticles.

We know that when chloroform evaporates, the droplets of P3HT solution gradually become nanoparticles by precipitation. But there are 2 possible routes: (1) fast-processed nanoparticles formed in the suspension first, and then they annealed and became slow-processed nanoparticles; (2) the slow-type aggregates formed in P3HT nanoparticles from the very beginning, and then they just grew over time. The two possible routes should have different absorption spectra during the nanoparticle-formation process. Figure 4.11 shows the hypothetical ratios of \( A_{0-0}/A_{0-1} \) and \( A_{0-0}/\text{Amorphous} \) of the two routes qualitatively.

![Figure 4.11 Hypothetical ratios of \( A_{0-0}/A_{0-1} \) and \( A_{0-0}/\text{Amorphous} \) of the two possible formation routes of slow-processed P3HT nanoparticles](image-url)
Therefore, an in-situ experiment was conducted to measure the absorption spectra of the emulsion/suspension during the 24-hour formation of slow-processed P3HT nanoparticles. The measured spectra were shown in Figure 4.12.

![Absorption spectra of P3HT droplet/nanoparticle suspension during the formation of slow-processed P3HT nanoparticles.](image)

**Figure 4.12** Absorption spectra of P3HT droplet/nanoparticle suspension during the formation of slow-processed P3HT nanoparticles.

We see from Figure 4.12 that the signal was very poor in the first 2 hours when scattering dominated. As time goes by, more and more chloroform evaporated, and the absorption from the aggregated phase gradually surpassed the absorption from the amorphous phase. After 10 hours, there is very minimal change in the spectra. The decomposition analysis introduced in 4.3.1 was done on all the spectra above, and the results were summarized in Table 4.3. Although the results in the first 3 hours may not be as precise as later ones due to the poor signal, the “shoulder” is quite visible even in the 2h spectrum, and the trend implies that ratio $A_{0.0}/A_{0.1}$ was never less
than the 24-hour value in the whole process.

<table>
<thead>
<tr>
<th>Time(hr)</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>0.9</td>
<td>0.98</td>
<td>0.76</td>
<td>0.59</td>
<td>0.57</td>
<td>0.56</td>
<td>0.54</td>
</tr>
<tr>
<td>A_0-0</td>
<td>0.32</td>
<td>0.41</td>
<td>0.5</td>
<td>0.51</td>
<td>0.51</td>
<td>0.51</td>
<td>0.52</td>
</tr>
<tr>
<td>A_0-1</td>
<td>0.44</td>
<td>0.54</td>
<td>0.73</td>
<td>0.77</td>
<td>0.77</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>A_0-2</td>
<td>0.42</td>
<td>0.55</td>
<td>0.69</td>
<td>0.72</td>
<td>0.71</td>
<td>0.72</td>
<td>0.73</td>
</tr>
<tr>
<td>A_0-3</td>
<td>0.22</td>
<td>0.24</td>
<td>0.32</td>
<td>0.37</td>
<td>0.39</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
<td>A_0-4</td>
<td>0.03</td>
<td>0.03</td>
<td>0.05</td>
<td>0.07</td>
<td>0.08</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>e_00</td>
<td>2.042</td>
<td>2.036</td>
<td>2.036</td>
<td>2.036</td>
<td>2.038</td>
<td>2.038</td>
<td>2.038</td>
</tr>
<tr>
<td>w_1</td>
<td>0.167</td>
<td>0.17</td>
<td>0.173</td>
<td>0.173</td>
<td>0.17</td>
<td>0.17</td>
<td>0.172</td>
</tr>
<tr>
<td>w_2</td>
<td>0.169</td>
<td>0.17</td>
<td>0.173</td>
<td>0.173</td>
<td>0.172</td>
<td>0.173</td>
<td>0.173</td>
</tr>
<tr>
<td>σ_1</td>
<td>0.074</td>
<td>0.091</td>
<td>0.092</td>
<td>0.095</td>
<td>0.092</td>
<td>0.092</td>
<td>0.092</td>
</tr>
<tr>
<td>σ_2</td>
<td>0.103</td>
<td>0.11</td>
<td>0.117</td>
<td>0.119</td>
<td>0.121</td>
<td>0.12</td>
<td>0.118</td>
</tr>
<tr>
<td>σ_3</td>
<td>0.129</td>
<td>0.129</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>A_0-0/A_0-1</td>
<td>0.73</td>
<td>0.76</td>
<td>0.68</td>
<td>0.66</td>
<td>0.66</td>
<td>0.66</td>
<td>0.68</td>
</tr>
<tr>
<td>A_0-0/Amorphous</td>
<td>0.36</td>
<td>0.42</td>
<td>0.66</td>
<td>0.86</td>
<td>0.89</td>
<td>0.91</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Table 4.3 Fit parameters of the Gaussian components assigned to the different vibronic components of the absorption spectra during the formation of slow-processed P3HT nanoparticles.

![Figure 4.13](image_url)

Figure 4.13 Fitted intensity ratio vs. time during the formation of slow-processed P3HT nanoparticles, comparing to those of fast-processed P3HT nanoparticles
The evolutions of decomposed intensity of peak A$_{0-0}$, A$_{0-1}$, A$_{0-2}$ and Amorphous part normalized by their final states were plotted in Figure 4.13. Focusing on time between 5h and 15h, when there were good signals and an obvious evolution, we see that there is a significant increase in A$_{0-0}$, A$_{0-1}$ and A$_{0-2}$, and a huge decrease in amorphous part over a period of approx. 5 h, while the ratio of A$_{0-0}$/A$_{0-1}$ stays almost unchanged. Taking the following facts into account: (1) the growth of A$_{0-0}$, A$_{0-1}$ and A$_{0-2}$ were at similar pace; (2) the ratio of A$_{0-0}$/A$_{0-1}$ in the spectra of slow-processed P3HT nanoparticles was never as low as that of fast-processed P3HT nanoparticles in the whole formation process, we conclude that the second formation route of slow-processed P3HT nanoparticles is correct. The slow-type aggregates formed in P3HT nanoparticles from the very beginning, and then they just grew over time and took the space of the amorphous part. Recalling that the GIWAXS showed a larger D-spacing for the slow particles, we would also hypothesize that these crystallites nucleated with larger D-spacing and grew with that same spacing. By contrast, it appears that the fast-processed crystallites nucleated with smaller d-spacing and the spacing might not have evolved over time.

These results show that in order to form the same crystalline structures as in drop-casting, it appears that slowing the rate of precipitation in the miniemulsion method is critical. In particles, based on the rates seen in Fig 4.13, the chloroform evaporation process should be drawn out for at least five hours. It might be that further reducing the rate of chloroform evaporation could lead to great J-type behavior and less amorphous material.
APPENDIX A

FITTING ALGORITHM AND ERROR ANALYSIS OF
TIME-OF-FLIGHT TECHNIQUE

1. Determine the fitting range

The goal of this step is to create an algorithm to find proper fit range automatically from the data, since not the whole current transient is used to do the least-square fit. My algorithm is:

a. Choose a proper starting point before the transit time, which should be in the range that you want to use to fit the straight line

b. Choose a proper window size and do a trial straight-line fit of log-log data within the window (Figure A.1)

c. Define a confidence interval of the fitted slope by allowing one, two or more standard deviation from the fitted slope

d. Choose a proper block size, then move the window to the right by one block

e. Do another straight-line fit in the new window. If the new slope is within the confidence interval of the previous slope, move the window further to the right; if not, stop.

f. Back to the starting point, do the same thing as (d)-(e), but this time move the window to the left

g. The window + the distance it moves in both directions is going to be the range we really want to fit to find $\alpha_i$ and $\alpha_f$.

h. Choose a proper starting point after the transit time, do the same thing as (a)-(g)
2. Real fit

After the fitting range is determined, two least-square fits of log(I) ~ log(t) are done (before and after the transit time). The region used in the real fit is shown in the plot.
3. Adjusting parameters

In addition to the 2 starting points, there are some parameters that can be tuned from sample to sample. One of them is the tolerance, the number of standard deviations from the fitted slope that are used to construct the confidence interval.

From Figure A.3 and Table A.1, it is obvious that as the tolerance increases, the allowed range for the fit expands, and chi-square gets bigger, while the processing time increases a bit and calculated transit time changes a little.

Figure A.3 Tuning the tolerance (the number of standard deviations from the fitted slope that are used to construct the confidence interval)
Other parameters (window size, block size, etc) can be tuned similarly.

4. Calculate transit time and mobility

The transit time $t_r$ is determined as the crossover point of the two fitted lines $y=m_1x+b_1$ and $y=m_2x+b_2$, where $x=\log(t)$, $y=\log(I)$, thus:

$$t_r = \frac{b_2 - b_1}{m_1 - m_2}$$

the mobility is calculated using Equation: $\mu=\frac{L^2}{(t_rV)}$

5. Error of transit time

Since $b_1$ and $m_1$, $b_2$ and $m_2$ are correlated, we need to use the error matrix to calculate the error of transit time $\sigma_{t_r}$:

$$D = \begin{pmatrix} \frac{\partial T_r}{\partial b_1} & \frac{\partial T_r}{\partial b_2} & \frac{\partial T_r}{\partial m_1} & \frac{\partial T_r}{\partial m_2} \\ \frac{\partial^2 T_r}{\partial b_1^2} & \frac{\partial^2 T_r}{\partial b_1 \partial b_2} & \frac{\partial^2 T_r}{\partial b_1 \partial m_1} & \frac{\partial^2 T_r}{\partial b_1 \partial m_2} \\ \frac{\partial^2 T_r}{\partial b_2 \partial m_1} & \frac{\partial^2 T_r}{\partial b_2 \partial m_2} & \frac{\partial^2 T_r}{\partial m_1^2} & \frac{\partial^2 T_r}{\partial m_1 \partial m_2} \\ \frac{\partial^2 T_r}{\partial m_2^2} & \frac{\partial^2 T_r}{\partial m_2^2} & \frac{\partial^2 T_r}{\partial m_2^2} & \frac{\partial^2 T_r}{\partial m_2^2} \end{pmatrix} = \begin{pmatrix} \frac{1}{m_1 - m_2} & -\frac{b_2 - b_1}{(m_1 - m_2)^2} & \frac{1}{(m_1 - m_2)^2} \\ -\frac{b_2 - b_1}{(m_1 - m_2)^2} & \frac{1}{(m_1 - m_2)^2} \\ \frac{b_2 - b_1}{(m_1 - m_2)^2} & \frac{b_2 - b_1}{(m_1 - m_2)^2} & \frac{1}{(m_1 - m_2)^2} \end{pmatrix} = \begin{pmatrix} \frac{m_2 - m_1}{(m_1 - m_2)^2} & \frac{h_1 - h_2}{(m_1 - m_2)^2} \\ \frac{h_1 - h_2}{(m_1 - m_2)^2} & \frac{m_1 - m_2}{(m_1 - m_2)^2} \end{pmatrix}$

\[ \sigma_{t_r} = \sqrt{|D|} \]
\[
\sigma^2_{\mu} = D'ED = \frac{1}{(m_1 - m_2)^2} (m_2 - m_1 \ b_1 - b_2 \ m_1 - m_2 \ b_2 - b_1)
\]

\[
\begin{pmatrix}
\text{cov} \_ p1[0][0] & \text{cov} \_ p1[0][1] & 0 & 0 \\
\text{cov} \_ p1[1][0] & \text{cov} \_ p1[1][1] & 0 & 0 \\
0 & 0 & \text{cov} \_ p2[0][0] & \text{cov} \_ p2[0][1] \\
0 & 0 & \text{cov} \_ p2[1][0] & \text{cov} \_ p2[1][1]
\end{pmatrix}
\begin{pmatrix}
m_2 - m_1 \\
b_1 - b_2 \\
m_1 - m_2 \\
b_2 - b_1
\end{pmatrix}
\]

6. Error of mobility

The film thickness, transit time and applied voltage have no correlation with each other. According to the equation: \( \mu = \frac{L^2}{(t_rV)} \), we have:

\[
\sigma^2_{\mu} = \left( \frac{\partial \mu}{\partial L} \right)^2 \sigma^2_L + \left( \frac{\partial \mu}{\partial t_r} \right)^2 \sigma^2_{t_r} + \left( \frac{\partial \mu}{\partial V} \right)^2 \sigma^2_V
\]

\[
\sigma_{\mu} = \frac{\mu}{L} \sqrt{4 \left( \frac{\sigma_L}{L} \right)^2 + \left( \frac{\sigma_{t_r}}{t_r} \right)^2 + \left( \frac{\sigma_V}{V} \right)^2}
\]

If \( L = 1.8 \mu m, \ \sigma_L = 0.1 \mu m, V = 10V, 30V, 50V, 70V, 90V \) respectively, and \( \sigma_r = 0.1V \), the error of the mobility measurement can be calculated accordingly. It turns out that most of the error typically comes from the estimation of film thickness, and the error of transit time has been significantly reduced by the least-square fit and a careful choice of fitting area.
APPENDIX B

SOURCE CODE OF CALCULATING TRANSIT TIME AND MOBILITY IN TIME-OF-FLIGHT DATA ANALYSIS

(The parameters that can be adjusted are in red)

```
from scipy import *
from pylab import *
from scipy.optimize import leastsq
from time import clock

starttime = clock()

a = loadtxt('90Vd1.txt')
a = a - array([0,0.0008])

id = np.where((a[:,1]>0) & (a[:,0]>0))
time, current = a[id].T

start1=100
start2=3800
window=200
block=50
tolerance=2
thickness=1.8
thickness_err=0.1
voltage=90
voltage_err=0.1

x=zeros(window)
y=zeros(window)
b=zeros(len(time)/block)
m=zeros(len(time)/block)
b_err=ones(len(time)/block)
m_err=ones(len(time)/block)
c=zeros(len(time)/block)
c[0]=-1

c[1]=-1
i1=1

while (c[i1-1]<0):
    for j in range(window):
        x[j]=log10(time[start1+block*(i1-1)+j])
y[j]=log10(current[start1+block*(i1-1)+j])

    model_func=lambda p,x : p[0]+p[1]*x
    error_func=lambda p,x,y : y-model_func(p,x)
    gradient=(y[window-1]-y[0])/(x[window-1]-x[0])
```
intercept=mean(x)-gradient*mean(x)
p0=array([intercept,gradient])
pfit,cov_p,infodict,mesg,ier=leastsq(error_func,p0,args=(x,y),full_output=True)
b[i1]=pfit[0]
m[i1]=pfit[1]
chisq=sum(infodict['fvec']**2)
npars=len(pfit)
dof=window-npars
cov_p=cov_p*chisq/dof
b_err[i1]=sqrt(cov_p[0][0])
m_err[i1]=sqrt(cov_p[1][1])
if i1>1: c[i1]=(m[i1]-m[i1-1]-tolerance*m_err[i1-1])*(m[i1]-m[i1-1]+tolerance*m_err[i1-1])
i1=i1+1
i2=1
while (c[i2-1]<0):
    for j in range(window):
        x[j]=log10(time[start1-block*(i2-1)+j])
y[j]=log10(current[start1-block*(i2-1)+j])
model_func=lambda p,x : p[0]+p[1]*x
error_func=lambda p,x,y : y-model_func(p,x)
gradient=(y[window-1]-y[0])/(x[window-1]-x[0])
intercept=mean(x)-gradient*mean(x)
p0=array([intercept,gradient])
pfit,cov_p,infodict,mesg,ier=leastsq(error_func,p0,args=(x,y),full_output=True)
b[i2]=pfit[0]
m[i2]=pfit[1]
chisq=sum(infodict['fvec']**2)
npars=len(pfit)
dof=window-npars
cov_p=cov_p*chisq/dof
b_err[i2]=sqrt(cov_p[0][0])
m_err[i2]=sqrt(cov_p[1][1])
if i2>1: c[i2]=(m[i2]-m[i2-1]-tolerance*m_err[i2-1])*(m[i2]-m[i2-1]+tolerance*m_err[i2-1])
i2=i2+1
x1=zeros(window+block*(i1+i2-6))
y1=zeros(window+block*(i1+i2-6))
for j in range(window+block*(i1+i2-6)):
    x1[j]=log10(time[start1-(i2-3)*block+j])
y1[j]=log10(current[start1-(i2-3)*block+j])
model_func1=lambda p,x1 : p[0]+p[1]*x1
error_func1=lambda p,x1,y1 : y1-model_func1(p,x1)
gradient=(y1[window+block*(i1+i2-6)-1]-y1[0])/(x1[window+block*(i1+i2-6)-1]-x1[0])
intercept=mean(x1)-gradient*mean(x1)
p0=array([intercept,gradient])
pfit1, cov_p, infodict, msg, ier = leastsq(error_func1, p0, args=(x1, y1), full_output=True)
b1 = pfit1[0]
m1 = pfit1[1]
chisq1 = sum(infodict['fvec']**2)
npar = len(pfit1)
dof = window - npar
cov_p1 = cov_p * chisq1 / dof
b_err1 = sqrt(cov_p1[0][0])
m_err1 = sqrt(cov_p1[1][1])

i3 = 1
while (c[i3-1] < 0):
    for j in range(window):
        x[j] = log10(time[start2 + block*(i3-1)+j])
y[j] = log10(current[start2 + block*(i3-1)+j])

model_func = lambda p, x : p[0] + p[1]*x
error_func = lambda p, x, y : y-model_func(p, x)

gradient = (y[window-1] - y[0])/(x[window-1] - x[0])
intercept = mean(x) - gradient*mean(x)
p0 = array([intercept, gradient])
pfit, cov_p, infodict, msg, ier = leastsq(error_func, p0, args=(x, y), full_output=True)
b[i3] = pfit[0]
m[i3] = pfit[1]
chisq = sum(infodict['fvec']**2)
npar = len(pfit)
dof = window - npar
cov_p = cov_p * chisq / dof
b_err[i3] = sqrt(cov_p[0][0])
m_err[i3] = sqrt(cov_p[1][1])
if i3 > 1:
    c[i3] = (m[i3] - m[i3-1] - tolerance * m_err[i3-1]) * (m[i3] - m[i3-1] + tolerance * m_err[i3-1])
i3 = i3 + 1

i4 = 1
while (c[i4-1] < 0):
    for j in range(window):
        x[j] = log10(time[start2 - block*(i4-1)+j])
y[j] = log10(current[start2 - block*(i4-1)+j])

model_func = lambda p, x : p[0] + p[1]*x
error_func = lambda p, x, y : y-model_func(p, x)

gradient = (y[window-1] - y[0])/(x[window-1] - x[0])
intercept = mean(x) - gradient*mean(x)
p0 = array([intercept, gradient])
pfit, cov_p, infodict, msg, ier = leastsq(error_func, p0, args=(x, y), full_output=True)
b[i4] = pfit[0]
m[i4] = pfit[1]
chisq = sum(infodict['fvec']**2)
npar = len(pfit)
dof = window-npar
cov_p = cov_p*chisq/dof
b_err[i4] = sqrt(cov_p[0][0])
m_err[i4] = sqrt(cov_p[1][1])
if i4 > 1:
c[i4] = (m[i4]-m[i4-1]-tolerance*m_err[i4-1])*exp((m[i4]-m[i4-1]+tolerance*m_err[i4-1]))
i4 = i4+1
x2 = zeros(window+block*(i3+i4-6))
y2 = zeros(window+block*(i3+i4-6))
for j in range(window+block*(i3+i4-6)):
    x2[j] = log10(time[start2-(i4-3)*block+j])
y2[j] = log10(current[start2-(i4-3)*block+j])
model_func2 = lambda p, x2: p[0]+p[1]*x2
error_func2 = lambda p, x2, y2: y2-model_func2(p, x2)
gradient = (y2[window+block*(i3+i4-6)-1]-y2[0])/(x2[window+block*(i3+i4-6)-1]-x2[0])
intercept = mean(x2)-gradient*mean(x2)
p0 = array([intercept, gradient])
pfit2, cov_p2, infodict, mesg, ier = leastsq(error_func2, p0, args=(x2, y2), full_output=True)
b2 = pfit2[0]
m2 = pfit2[1]
chisq2 = sum(infodict['fvec']**2)
npar = len(pfit2)
dof = window-npar
cov_p2 = cov_p2*chisq2/dof
b_err2 = sqrt(cov_p2[0][0])
m_err2 = sqrt(cov_p2[1][1])
figure()
plot(log10(time), log10(current), label='Photocurrent transient')
plot(log10(time), model_func1(pfit1, log10(time)), '--', color='r', linewidth=1.5, label='Fitted lines')
plot(log10(time), model_func2(pfit2, log10(time)), '--', color='r', linewidth=1.5)
bar(log10(time[start1-(i2-3)*block]), 0.4, width=0.005, bottom=log10(current[start1-(i2-3)*block])-0.2)
bar(log10(time[start1+window+(i1-3)*block]), 0.4, width=0.005, bottom=log10(current[start1+window+(i1-3)*block])-0.2)
bar(log10(time[start2-(i4-3)*block]), 0.4, width=0.005, bottom=log10(current[start2-(i4-3)*block])-0.2)
bar(log10(time[start2+window+(i3-3)*block]), 0.4, width=0.005, bottom=log10(current[start2+window+(i3-3)*block])-0.2)
xlim(log10(time[0]), log10(time[len(time)-1]))
ylim(log10(current[len(time)-1]), log10(max(current))+1)
legend(loc='lower left')
xlabel('log(time(s))')
ylabel('log(current(A))')
grid(linestyle='--')
ttr=(b2-b1)/(m1-m2)
D=matrix([[m2-m1,b1-b2,m1-m2,b2-b1]]/(m1-m2)**2)
E=matrix([[cov_p1[0][0],cov_p1[0][1],0,0],[cov_p1[1][0],cov_p1[1][1],0,0],[0,0,cov_p2[0][0],cov_p2[0][1]],[0,0,cov_p2[1][0],cov_p2[1][1]]])
ttr_err=array(sqrt(D*E*D.T))
mu=thickness**2/((10**ttr)*voltage)
mu_err=mu*sqrt(4*((thickness_err/thickness)**2)+((10**ttr_err-1)**2)+((voltage_err/voltage)**2))
print"The transit time Ttr= %.6f+/-%.6f us" %((10**ttr)*1000000,(10**ttr_err-1)*(10**ttr)*1000000)
print"The charge carrier mobility= %.3f+/-%.3f*E-3 cm2/Vs" %(mu/100000,mu_err/100000)
print"The Chi square for the two fitting = %.4f, %.4f" %(chisq1, chisq2)
elapsed = (clock() - starttime)
print"The processing time for the program = %.3f s" %elapsed
show()
APPENDIX C

DECOMPOSITION AND ANALYSIS OF UV-VIS ABSORPTION SPECTRA

1. Subtract baseline

The baseline was determined by the tail of the spectra, i.e. the last 10 points of the spectra intensity, as shown in Figure C.1.

![Figure C.1 Absorption spectra baseline subtraction](image)

2. Subtract amorphous part

![Figure C.2 Subtraction of amorphous part](image)
Figure C.2 shows the subtraction of amorphous part in the P3HT nanoparticle absorption spectra. The absorption spectra of the amorphous portion was estimated by measuring the absorption spectra of P3HT chloroform solution, and the magnitude of this part was manipulated so that the left shoulder (~ 420 nm) matches. The result of the subtraction was considered as the absorption at the aggregated part in P3HT nanoparticles, which we are going to decompose in the following part.

3. Transform into energy space

The result of step 2 was then transformed into the energy space following the equation: $E=1240\text{nm}\times\text{eV}/\lambda$. The motivation of this step is that the decomposed peaks in energy space should be approximately evenly spaced, which will make the fitting easier by applying some constrain. The transformed data is shown in Figure C.3, in which we can see that the shoulder flips from the right to the left.
4. Decompose into 5 peaks

![Figure C.4 Decomposition into 5 peaks](image)

Figure C.4 Decomposition into 5 peaks
(black solid line: spectra to be decomposed; black dash lines: decomposed 5 Gaussian peaks; red line: sum of the decompositions (5 black dash lines))

Following the method introduced in literatures [52, 75, 76], the spectra were then decomposed into 5 Gaussian peaks with similar width and were approximately evenly spaced. The amplitudes of the 5 peaks were manipulated so that the sum of the 5 peaks almost overlapped with the spectra obtained in step 3.

5. Transform back to wavelength space

![Figure C.5 Transformation back to wavelength space](image)

Figure C.5 Transformation back to wavelength space

This is the opposite of step 3. All the lines in Figure C.4 were transformed into Figure C.5. This is an optional step, mainly for reporting purpose.
6. Summary

![P3HT NPs UV absorption spectra decomposition](image)

**Figure C.6 Summary of UV absorption spectra decomposition**

The 5-step decomposition analysis was shown in Figure C.6. As a result of this analysis, the fit parameters of the 5 decomposed Gaussian components were recorded, and the relative intensity of some of these vibronic features were calculated (Table C.1), which may infer the P3HT aggregate structure within nanoparticles.

<table>
<thead>
<tr>
<th>Amorphous</th>
<th>A₀⁻₀</th>
<th>A₀⁻₁</th>
<th>A₀⁻₂</th>
<th>A₀⁻₀/A₀⁻₁</th>
<th>A₀⁻₀/Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>0.44</td>
<td>0.73</td>
<td>0.63</td>
<td>0.60</td>
<td>0.85</td>
</tr>
</tbody>
</table>

**Table C.1 Fit parameters of the Gaussian components assigned to the different vibronic components of the P3HT nanoparticle absorption spectra**
APPENDIX D

SOURCE CODE OF UV-VIS ABSORPTION SPECTRA DECOMPOSITION AND ANALYSIS

(The parameters that can be adjusted are in red)

```r
# loading P3HT CHCl3 solution data --------------------------------------------
setwd("D:/Lab/Data/UV/Absorption/140716 P3HT slow NPs in-situ")
amorphous <- read.table('P3HT dilute x30.txt', skip=322)[1:441 * 2 -1, ]

# define utility functions --------------------------------------------------------
load_data <- function(name) {
  data <- read.table(name, skip=2)
  names(data) <- c('wavelength', 'intensity')
  data$baseline <- mean(tail(data$intensity, 10))
  plot(data$wavelength, data$intensity)
  data
}

cut_amorphous <- function(data, c1) {
  data$intensity <- data$intensity - data$baseline
  data$intensity <- data$intensity / max(data$intensity)
  data$amorphous <- c1 amorphous$V2
  data$subtract <- data$intensity - data$amorphous
  plot(data$wavelength, data$intensity, type='l', col='brown', lwd=2, lty=2,
       main='P3HT NPs UV absorption spectra decomposition',
       xlab='Wavelength(nm)', ylab='Intensity(a.u.)')
  lines(data$wavelength, data$amorphous, type='l', col='darkorange', lwd=2, lty=3)
  lines(data$wavelength, data$subtract, type='l', col='black', lwd=3)
  data
}

plote <- function(data) {
  data$fit <- data$peak1 + data$peak2 + data$peak3 + data$peak4 + data$peak5
  plot(data$ev, data$subtract, type='l', col='black', lwd=2, xlim=c(1.5, 3.0),
       main='P3HT NPs UV absorption spectra decomposition',
       xlab='Wavelength(nm)', ylab='Intensity(a.u.)')
  lines(data$ev, data$fit, type='l', col='red', lwd=2.5)
  lines(data$ev, data$peak1, type='l', lty=2, lwd=2)
  lines(data$ev, data$peak2, type='l', lty=2, lwd=2)
  lines(data$ev, data$peak3, type='l', lty=2, lwd=2)
  lines(data$ev, data$peak4, type='l', lty=2, lwd=2)
  lines(data$ev, data$peak5, type='l', lty=2, lwd=2)
}
```

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```r
lines(data$ev, data$subtract - data$fit, type = 'l', col='blue')
}

plotw <- function(data) {
  data$fit=data$peak1+data$peak2+data$peak3+data$peak4+data$peak5
  plot(data$wavelength, data$intensity, type='l', col='brown', lwd=2, lty=2,
       xlim=c(370,825), main='P3HT NPs UV absorption spectra decomposition',
       xlab='Wavelength(nm)', ylab='Intensity(a.u.)')
  lines(data$wavelength, data$amorphous, type='l', col='darkorange', lwd=2, lty=3)
  lines(data$wavelength, data$subtract, type='l', col='black', lwd=3)
  lines(data$wavelength, data$fit, type='l', col='red', lwd=2.5)
  lines(data$wavelength, data$peak1, type='l', lty=2, lwd=1.5)
  lines(data$wavelength, data$peak2, type='l', lty=2, lwd=1.5)
  lines(data$wavelength, data$peak3, type='l', lty=2, lwd=1.5)
  lines(data$wavelength, data$peak4, type='l', lty=2, lwd=1.5)
  lines(data$wavelength, data$peak5, type='l', lty=2, lwd=1.5)
  legend(630,1, legend=c("Original spectra w/o baseline","Amorphous component","Aggregate component","Fitted aggregate component","Decomposed peaks"),
         lty=c(2,3,1,1,2), col=c("brown","darkorange","black","red","black"), lwd=c(2,2,3,2.5,1.5))
}
## 1
# load data to be analyzed ---------------------------------------------
data <- load_data('150222-1 FF P3HT-1.txt')

# cut amorphous part ------------------------------------------------------
data <- cut_amorphous(data, 0.52)

# setting decomposition parameters --------------------------------------
e00=2.055
w1=0.175
w2 <- 0.176
s1 <- 0.0106
s2 <- 0.015
s3 <- 0.018

data$ev=1239.842/data$wavelength
data$peak1=0.44*exp(-(data$ev-e00)^2/s1)
data$peak2=0.73*exp(-(data$ev-e00-w1)^2/s2)
data$peak3=0.7*exp(-(data$ev-e00-w1-w2)^2/s3)
data$peak4=0.36*exp(-(data$ev-e00-w1-2*w2)^2/s3)
data$peak5=0.07*exp(-(data$ev-e00-w1-3*w2)^2/s3)

# plot results ----------------------------------------------------------
```

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plote(data)
plotw(data)
REFERENCES


62. Shen, X. B. et al., *A Study on the Correlation Between Structure and Hole Transport in*


