

Alcohol Dispersible Semiconducting Polymer Nanoparticle for Application in Organic Solar Cells

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Abstract

A potential route to achieve eco-friendly fabrication of organic solar cells (OSCs) is to prepare nanoparticle (NP) dispersions of the semiconducting materials in environmentally friendly solvents such as water or alcohol. The literature discusses two approaches of forming NP dispersions- a) using commercial surfactants such as sodium dodecyl sulfate (SDS), and b) surfactant-free approach. The former approach resulted in devices with low performance due to presence of residual surfactant in the photoactive layer. Devices with an improved performance could be fabricated using the latter approach, but it provides less control on NP formation. This PhD was directed to study the limitations associated with surfactant-free approach and address them by synthesizing active surfactants which could provide control on NP formation without hampering device efficiencies.

The effect of molecular weight of poly(3-hexylthiophene) (P3HT) polymer on P3HT: indene- C_{60} bis-adduct (ICBA) dispersions prepared from dispersion method was investigated by synthesizing defined molecular weights (5,000 g/mol to 40,000 g/mol) P3HT with high regioregularity and low dispersity (D). The results indicated that the size of NPs increases with the increase in molecular weight of the polymer. Further, the properties of these dispersions were compared with dispersions prepared from commercially available Rieke P3HT (22,000 g/mol) indicating that the size of NPs in the latter was considerably lower than the former. These results, taken together, demonstrated that the properties of NP dispersions prepared using dispersion method are dependent on the batch of the polymer used. For the dispersions prepared

from the same batch of the polymer, the size of NPs is affected by molecular weight of the polymer.

In order to achieve better control on NP formation, three end-capped P3HT polymers- pyridine end-capped P3HT (P3HT-Py), benzoic acid end-capped P3HT (P3HT-COOH) and tri-ethylene glycol monomethyl ether end-capped P3HT (P3HT-TEG) were synthesized to be used as active surfactants (AS). It was hypothesized that P3HT-Py could be converted into $\text{P3HT-PyH}^+\text{AcO}^-$ upon addition of acetic acid while P3HT-COOH could be converted into $\text{P3HT-COO}^-\text{PyH}^+$ upon addition of pyridine base. The presence of these ionic forms in the NP dispersion could improve NP stability of P3HT:ICBA dispersion via an electric double layer (EDL) formation on NP surface as with conventional ionic surfactants. The remarkable property of these surfactants is reversibility of ionic pair (deactivation of active surfactant) i.e., the ionic forms could dissociate to regenerate P3HT-Py and P3HT-COOH with the removal of acid/base on thermal treatment of the NP films. The P3HT-TEG was synthesized to act as a neutral or non-ionic active surfactant to stabilize dispersions via steric repulsion.

The synthesized end-capped polymers were used to obtain reproducible, stable, and concentrated NP dispersions of Rieke P3HT and ICBA. Amongst the three end-capped polymers, only P3HT-Py resulted in controlled synthesis of NPs. The results indicated that using small amount of P3HT-Py and AcOH (together referred as AS-1), NP dispersions of concentration as high as 30 mg/mL in MeOH were obtained and dispersions showed stability for up to 2 months. The AS-1 was also used to achieve controlled NP formation with the synthesized P3HT polymer of well-defined molecular weights. These results evidenced that AS-1 could be successfully used to overcome the batch-to-batch variation associated with different P3HT polymers.

Finally, the effect of using P3HT-Py as active surfactant on device performance was investigated. The NP dispersions of P3HT:ICBA of different concentrations were formed in

methanol (MeOH) and ethanol (EtOH), both with and without using AS-1. OSCs with an inverted architecture were fabricated using these dispersions. The efficiencies of annealed devices fabricated from NP dispersions with and without AS-1 were similar indicating no significant effect of P3HT-Py on electronic properties of BHJ. Further, devices fabricated with concentrated NP dispersions in MeOH stabilized with AS-1 exhibited efficiency similar to devices fabricated from chlorinated solution of P3HT:ICBA.

Declaration

This is to certify that:

1. The thesis comprises only my original work towards the PhD
2. Due acknowledgement has been made in the text to all other material used
3. The thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices

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Publications and Conferences

Publications:

The candidate's contribution to the publications listed below is less than 50% unless stated otherwise:

1) In preparation: **Conjugated Polymer Based Active Surfactant to Stabilize Nanoparticle Dispersions for Application in Organic Photovoltaics** (60 % contribution)

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4) Material Research Society Spring Meeting, 2019, Phoenix, Arizona, USA.

Title: Enhancing Nanoparticle Stability and Reproducibility for Surfactant Free Dispersions with Maintained Efficiencies of Organic Solar Cells.

Dedication

This thesis is dedicated to my late grandfather Sh.

Suresh Chand Saxena.

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Abbreviations

^1H NMR	Proton nuclear magnetic resonance spectroscopy
AcOH	Acetic acid
AFM	Atomic force microscopy
AS	Active surfactant
AS-1	Combination of P3HT-Py and AcOH
AS-1'	Combination of P3HT-Py and TFA
AS-2	Combination of P3HT-COOH and pyridine
AS-3	P3HT-TEG
BHJ	Bulk heterojunction
CHCl_3	Chloroform
CV	Cyclic voltammetry
$\bar{D}$	Dispersity of polymers
$\bar{D}_{\text{np}}$	Dispersity of nanoparticles
DCM	Dichloromethane

DLS	Dynamic light scattering
DLVO	Derjaguin-Landau-Verwey-Overbeek
DSC	Differential scanning calorimeter
EDL	Electric double layer
E _g	Band gap
EtOH	Ethanol
FF	Fill factor
FSO-100	Fluoro surfactant
GIWAX	Grazing incident wide angle X-ray
GPC	Gel permeation chromatography
GRIM	Grignard metathesis
HTL	Hole transport layer
<i>i</i> -PrMgCl	<i>Is</i> o-propyl magnesium chloride
ICBA	Indene-C ₆₀ bisadduct
IPA	Isopropanol
IR	Infra-red
ITO	Indium tin oxide
J _{sc}	Short current density
MALDI-TOF MS	Matrix-assisted laser desorption/ionisation time-of- flight mass spectrometry

MeOH	Methanol
M_n	Number average molecular weight
M_w	Weight average molecular weight
NP	Nanoparticle
<i>o</i> -DCB	<i>Ortho</i> dichlorobenzene
OSC	Organic solar cell
P3CPenT	Poly[3-(5-carboxypentyl)thiophene-2,5-diyl]
P3HT	Poly(3-hexylthiophene)
P3HT-COOH	Benzoic acid end capped poly(3-hexylthiophene)
P3HT-Py	Pyridine end capped poly(3-hexylthiophene)
P3HT-TEG	Tri-ethylene glycol monomethyl ether end capped poly(3-hexylthiophene)
PBDTTPD	Poly[(5,6- dihydro-5-octyl-4,6-dioxo-4H-thieno[3,4-c]pyrrole-1,3-diyl)- [4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6- diyl]]
PBDTTT	Poly(benzodithiophene-co-thienothiophene)
PC ₇₁ BM	Phenyl-C ₇₁ -butyric acid methyl ester
PCBM	Phenyl-C ₆₁ -butyric acid methyl ester
PCDTBT	Poly([9-(1'-octylnonyl)-9Hcarbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3- benzothiadiazole4,7-diyl-2,5-thiophene-diyl)
PCE	Power conversion efficiency
PDPP5T	Diketepyrrolopyrrole–quinquethiophene alternating copolymer

PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)
PET	Petroleum spirit, Petroleum ether
P_{in}	Incident power or incident light intensity
PL	Photoluminescence
PSBTBT	Poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl]
PTEBS-Na	Poly(2-(3-thienyl)-ethoxy-butylsulfonate sodium salt)
PV	Photovoltaic
RBF	Round bottom flask
RR	Regioregularity
RT	Room temperature
SDS	Sodium dodecyl sulphate
SVA	Solvent vapour annealing
TA	Thermal annealing
TEM	Transmission electron microscopy
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TQ1	Poly[2,3-bis-(3-octyloxyphenyl)-quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl]
UV-Vis	Ultraviolet-visible spectroscopy

V_{oc} Open circuit voltage

ZnO Zinc oxide

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Chapter 1 Introduction

1.1 World energy demand and potential of solar energy

Today in the 21st century, energy has become one of the lifelines for human civilization. The availability of energy resources is central to foster economic growth and technological advancements in a society.¹ With an ever-growing world population and anticipated future infrastructural and industrial development, energy demand is expected to rise rapidly. In the current scenario, more than 80% of world's energy requirement is met by non-renewable fossil fuels such as coal, oil and natural gas.^{2,3} The above-mentioned resources have limited reserves and are also associated with environmental pollution. For instance, burning of fossil fuels solely contributes to over 50% of global greenhouse gas emissions⁴ (e.g. CO₂, N₂O), which in turn are related with global climate change, global warming, acid rain and air pollution.⁵ Unequivocally, a sustainable way forward to satisfy increasing energy demand is to harvest energy from renewable resources such as the sun, wind, water or biomass.

Amongst the available renewable energy resources, solar energy has the highest potential to cater for future energy demands due to its safe, clean and inexhaustible nature.⁶ Studies have claimed that sunlight received by the earth surface in an hour is sufficient to meet whole year's energy demand of the world.⁷ Solar radiation can be converted into electricity or thermal energy for both small- and large-scale applications using photovoltaic (PV), concentrated solar thermal and concentrated solar power technologies.⁸⁻¹¹

The direct conversion of sunlight into electricity, known as photovoltaic effect, has received a lot of attention since middle of the 20th century. Although this effect was first observed in 1839,¹² the first conversion of solar energy into electricity via silicon p-n junction cell was demonstrated in 1940.¹³ The photovoltaic process can be fundamentally understood as release of free charge carriers (electrons and holes) within the semiconducting material upon absorption of light (photons) with higher energies than its band gap.¹⁴ The separation of electron and hole pair occurs at the junction (p-n junction) from where the charges get transported to respective electrodes. Later in 1954, Chapin *et al.*¹⁵ reported 6% efficient modern silicon solar cell at Bell laboratories and in late 1950s the first commercial use of silicon based solar cells occurred for US space satellites.¹⁶

The oil embargo in 1970 provided a significant boost to PV technology¹⁷ and the years followed saw evolution of this technology across three generations.¹⁸ The first-generation solar cells were based on wafers of mono-crystalline and/or polycrystalline silicon semiconductors and showed high efficiency of up to ~26%.¹⁹ The second-generation evolved to reduce the production cost of previous generation and composed of thin films of inorganic semiconducting materials such as amorphous silicon, cadmium-telluride and copper indium gallium sulfide/selenide.²⁰ The environmental hazards related to use of toxic and heavy metals such as cadmium and tellurium are one of the major drawbacks of this generation solar cells. The third generation in PV technology is motivated to achieve higher power conversion efficiencies, 2-3 times more than the limit of single junction solar cells (31%), by modifying the fundamental designs on which solar cells are based.²¹ Further, the new concepts need to be incorporated into thin film technology which could promise use of low-cost and environmental friendly materials.

1.2 Organic solar cells

The characteristic of photoconductivity in an organic material was observed in anthracene by Pochettino in 1906.²² Later, several dyes such as methylene blue were among the early materials to exhibit photovoltaic effect. OSCs employ thin layer of organic materials, such as small molecules or polymers, to convert solar radiation into electricity. Unlike the generation of direct charge carriers in inorganic materials, organic semiconductors generate excitons (coulombically bound electron-hole pair) upon absorption of photons. The dissociation of excitons into free charges should occur in order to generate current. Organic materials have high absorption coefficient compared to silicon which enables efficient photon absorption with a much thinner application of organic semiconducting layer. This makes the process both cost and material effective. Another primary motivation behind using organic materials is that they could be coated or printed from a solution on a flexible substrate in a continuous process. Consequently, high-speed roll-to-roll fabrication of solar cells is achievable without any processing at higher temperatures as opposed to conventional solar cells based on inorganic materials. The basics of OSCs including their structure, components and detailed working principle are discussed in subsequent sections.

1.2.1 Architecture and basic principle of organic solar cells

A typical OSC is a multi-layered device as shown in Figure 1.1. The most important layer is the photoactive layer which is responsible for charge generation and it comprises of an electron donor and an acceptor material. This active layer is sandwiched between two electrodes which extract the charges and deliver the generated current to an external circuit. Interlayers (electron/hole transport layers) are also incorporated into the device architecture to improve the flow of charges.

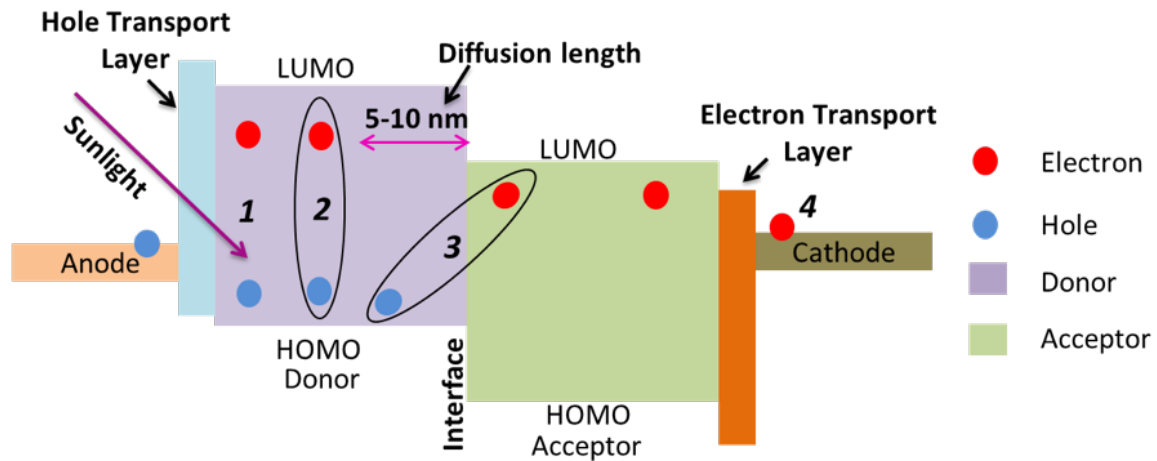


Figure 1.1: Schematic representation of working principle of a bulk heterojunction OSC device.

1) photon absorption generates an exciton, 2) diffusion of the exciton to an interface of the donor and acceptor material, 3) dissociation of the exciton into free charges, (4) transportation of free carrier charge to respective electrodes where charge collection occurs.

There are four steps involved in the functioning of an OSC²³ (Figure 1.1):

- 1) Absorption of photon and generation of an exciton.
- 2) Diffusion of excitons towards the interface of donor/acceptor materials
- 3) Dissociation of excitons into separate charges
- 4) Charge transport towards the electrodes and charge collection.

When light falls on the active layer, the photons are absorbed, and excitons are generated. These excitons are coulombically bound positive and negative charges. For a solar cell to generate electricity, these excitons need to be separated into free charges. Since the excitons have a short lifetime before the electrons recombine with the holes, the characteristic distance between an excitons' generation site and a donor/acceptor interface must be on order of 5-10 nm. Dissociation of excitons into free charges occurs at the interface of donor and acceptor material. It is energetically favored step because energy loss associated with donor/acceptor band offset drives the dissociation of exciton.²⁴ The transportation of free charges towards electrodes can

occur either by diffusion alone or sometimes it can be assisted by a built-in electric field generated through difference in work function of electrode materials.²⁵

1.2.2 Evolution of device structures of organic solar cell

The evolution of the structural configuration of organic solar cells can be represented in three stages. The first ever cells were built by simply replacing the inorganic semiconducting material sandwiched between two electrodes with a single layer of organic semiconducting material.²⁶ Due to low dielectric constant of organic materials, photo-absorption resulted in generation of tightly bound excitons instead of free charge carriers. The field generated in the cell due to difference between work functions of the two electrodes was not strong enough to dissociate the excitons and thus, these devices yielded very low power conversion efficiencies. Later in 1986, Tang²⁷ fabricated a bilayer OSC with photoactive layer consisting of a bi-layer (Figure 1.2A) of a p- and an n-type organic semiconductor and yielding an efficiency ~1%. These bi-layer devices are also known as a planar donor-acceptor heterojunction. For these cells to work efficiently, the excitons generated upon photon absorption must reach the interface between the donor and acceptor materials and then undergo charge separation. It can be recalled that a typical exciton diffusion length should be ~10 nm due to short lifetime of excitons. In bi-layer devices, the excitons generated from only a small area close to interface of the two photo-conducting materials potentially contributes in generation of free charges.²⁸ Therefore, a simple bi-layer structure is not an optimal device layout. Ideally, a 3D nanoscale phase separation in the active layer (Figure 1.2B) is required to sufficiently increase the junction areas. However, such nanoscale structuring of soft material is complicated to achieve.²⁹ Thus, to overcome the limitation of not all excitons reaching the interface, a bulk heterojunction (BHJ) cell was proposed in 1995.³⁰ The donor and acceptor materials are thoroughly mixed so that the interfacial area between the two is spread all through the bulk as oppose to a bi-layer cell. Upon drying, the materials separate into distinct phases, which

effectively distribute the heterojunction throughout the bulk of the active layer, and thereby regarded as bulk heterojunction. Consequently, the distance travelled by excitons to reach the interface is reduced and more excitons contribute in generation of free-charges. However, the challenge is the efficient migration of photogenerated charges through the composite material to the respective electrodes. This preferably requires mixing of donor/acceptor materials into a bicontinuous interpenetrating network within the blend films.³¹ Although subject to intensive research in recent years, there is yet an incomplete understanding on how the ideal nano-morphology of a bulk-heterojunction should look like.

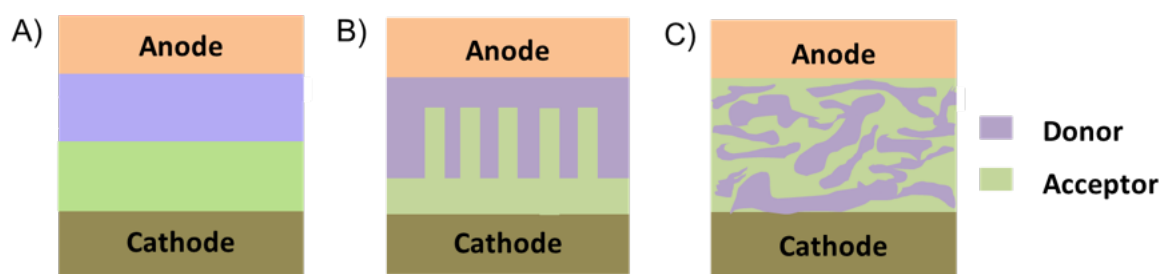


Figure 1.2: Active layer architectures. A) a bi-layer structure, the disadvantage of this architecture is that the excitons within the range of 5 to 10 nm diffusion lengths are utilized whereas, others most of the excitons undergo recombination, B) an ordered 3 D nano-structure, where the heterojunction aligns perfectly with in the exciton diffusion length and C) The bulk heterojunction architecture, enabling a thick enough with the possibility of the heterojunction existing within an exciton diffusion length.

1.2.3 Organic semiconductors

Traditionally, organic polymers are electrical insulators due to restricted mobility of valence electrons that are present in sp^3 hybridized orbitals of carbon atoms. In 1977, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa discovered a new class of conjugated polymers, which were doped with electron attracting species such as chlorine, bromine and iodine to conduct electricity.³² In year 2000, they were awarded with the Noble prize in chemistry for this discovery. The backbone of conducting polymers consists of sp^2 hybridized carbons with a single valence electron lying in p_z orbital. The overlapping of p_z orbitals between carbon

atoms results in formation of π bonds which contain electrons that are less localized compared to σ bond electrons. The property of delocalization of π electrons enables them to move freely along the polymer backbone which contributes to the semiconducting nature of a conjugated polymer.

To qualify to be used in solar cell technology, a material should hold two inevitable properties- a) generation of exciton after photon absorption and b) subsequent transport of the free charges. The materials that have an extended delocalized π -electron system generally exhibit both the properties. Both polymer and small molecules have been utilized as donor materials while small molecules are largely applied as acceptors.

1.2.3.1 Organic donor material

Currently, a number of semiconducting materials have been synthesized to optimize their suitability for OSCs. Semiconducting donor polymers comprises of conjugated backbone and solubilizing side chains. Poly(3-hexylthiophene) (P3HT) has been the commonly used electron donor material with a band gap of ~ 1.9 eV. It is easy to synthesize and also holds high charge carrier mobility with reasonable photo-stability.³³ It has been observed that the material properties of polymers such as molecular weight, dispersity (D) and regioregularity significantly affect the device performance as they vary between different batches of same polymer material.³⁴ These properties will be discussed in detail in the following paragraphs.

Molecular weight

Molecular weight is a physical property of a polymer.³⁵ It is the sum of the atomic weights of each atom that constitute a molecule. Polymer is composed of repeating monomer units (3-hexylthiophene in this case) due to which its molecular weight varies and can be determined by degree of polymerization (DP). All polymer molecules of a particular grade or batch have

different molecular weight therefore, there is a range or distribution of molecular weights in polymers. The two most common ways of expressing molecular weight of polymers are; a) number average of the size distribution (M_n), and b) weight average of the size distribution (M_w).

Dispersity

As mentioned above that polymers are a mixture of molecular weight distributions due to the complicated nature of polymerizations. Generally, the distribution of monomer and initiator molecules occurs in solution to form polymer chains in case of chain growth polymerization. If active polymer chain ends carry more than one access sites for unreacted monomer then each chain can grow to a different extent. The dispersity of a polymer, also recognized as distribution of molecular weight, is important to determining its properties. Although the average molecular weight for two polymer samples could be similar, but their bulk properties could differ significantly if they exhibit different range (wide or narrow) of molecular weight.³⁵ Dispersity index ($\mathcal{D}$) is used as a measure of molecular weight distribution of a sample and is given by the equation: $\mathcal{D} = M_w/M_n$.

Regioregularity

Regioregularity is an essential property of polymers especially when working with an asymmetrical monomer structure. For instance, the P3HT is synthesized by polymerizing asymmetric 3-hexylthiophene resulting in three regioisomers that is, head-to-tail (HT), head-to-head (HH) and tail-to-tail (TT) (Figure 1.3) during dimer formation. These three regioisomers can give rise to four different regioisomeric triads during coupling; HT-HT, HH-TH, HH-TT and TT-HT in which HT-HT isomer is a regioregular isomer whereas, the other three are regio-random or regio-irregular. The property of regioregularity of a polymer can significantly affect its structural, electronic, and optical properties.³⁶ In case of regio-irregular

polymer, the molecule contains torsion between the side groups causing a twist in the backbone which effectively reduce the conjugation length.³⁷ In a regioregular polymer chain, the backbone remains planar enabling efficient π -stacking between neighboring polymer chains. Polymer with high regioregularity shows better crystallinity along with improved charge carrier mobility.³⁸

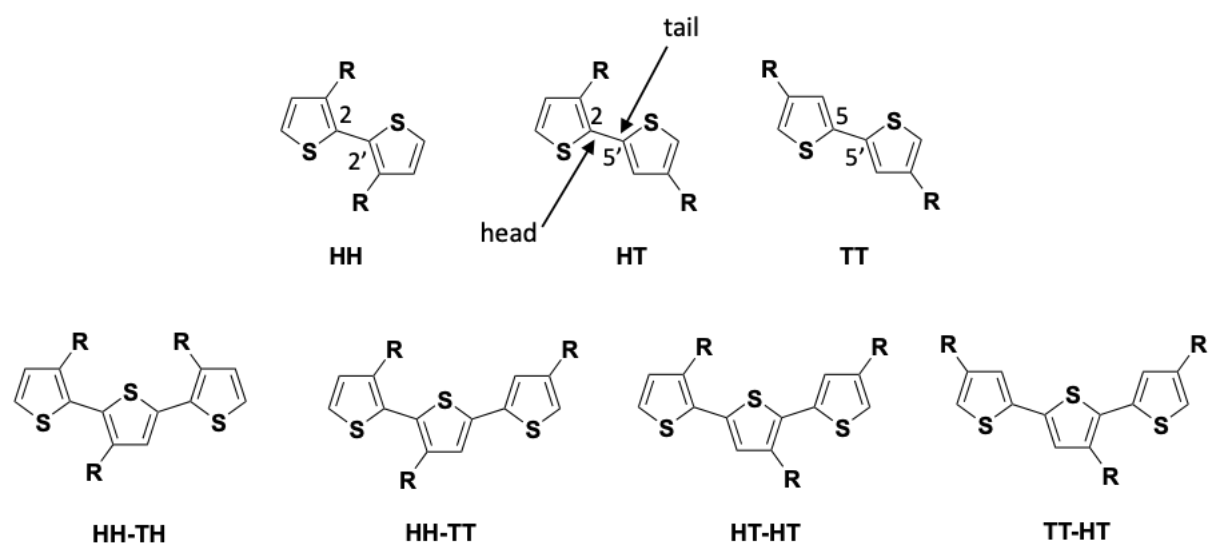


Figure 1.3: Carbon atoms on the thiophene ring are numbered to indicate the head and tail positions of the ring. Possible regiochemistry of P3HT isomers obtained after polymerization.

Literature discusses many synthetic routes to synthesize P3HT polymers and out of all Grignard Metathesis (GRIM) is the most promising approach to synthesize well defined and highly regioregular P3HT with low D .^{39, 40} Small molecules have also been explored as donor materials in heterojunction solar cells. The discrete structure of small molecules facilitates their reproducible and controlled laboratory synthesis whereas, synthesis of polymer can suffer from batch-to-batch variations.

1.2.3.2 Organic acceptor material

Fullerenes and their derivatives were among the first materials to be employed as acceptors due to their symmetrical structure and high electron mobility.³⁰ Phenyl- C_{61} -butyric acid methyl

ester (PC₆₁BM) and its corresponding C₇₀ derivative phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) have been extensively used in last few decades. Compared to PC₆₁BM, PC₇₁BM has a stronger absorption in the visible region which makes it more suitable for OSC devices. Indene-fullerene adducts such as indene-fullerene monoadduct (ICMA), indene-fullerene bis-adduct (ICBA) and indene-fullerene multi-adduct are also used as acceptor materials. ICBA has exhibited higher absorption in spectral range of 300-500 nm and higher LUMO level than PCBM. Consequently, higher power conversion efficiencies have been reported for devices based on P3HT in combination with ICBA (6.5%)⁴¹ than with PCBM of (5%).³⁸ The chemical structures of P3HT and fullerene-based acceptors are given in Figure 1.4. Non-fullerene based acceptors have been also used in conjunction with small molecule and polymer-based donors.⁴² However, detailing of non-fullerene-based acceptors is out of scope of this research work.

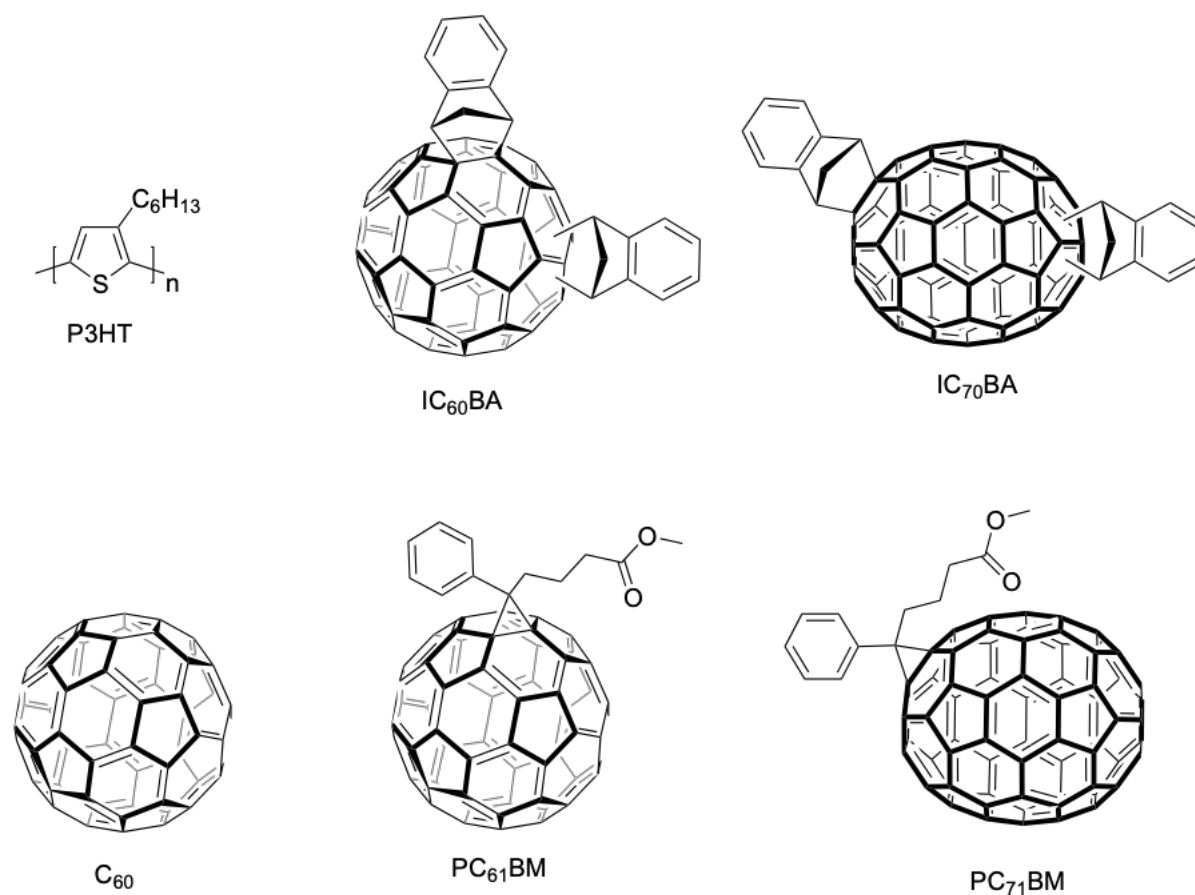


Figure 1.4: Most common semiconducting materials used for application in organic solar cells

1.2.4 Device fabrication and characterization

As discussed above typical OSC consist of several layers, and it can be classified into two architectures – conventional and inverted⁴³ (Figure 1.5). In a conventional OSC, a glass substrate is coated with indium tin oxide (ITO) or fluorine doped tin oxide (FTO) to form a transparent and high work function electrode (anode). A layer of poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), used as a hole transport layer, is spin cast on ITO which also smoothens its surface.⁴⁴ Next comes the BHJ active layer (mixture of donor/acceptor materials) which is responsible for exciton generation, followed by electron transport layer such as ZnO. On top of ZnO, a low work function metal such as aluminium (Al) or barium (Ba) is deposited to act as a cathode. The drawbacks such as etching of the ITO electrode due to persistent contact with acidic PEDOT:PSS layer and high fabrication costs associated with metal deposition have encouraged development of an inverted device architecture for OSCs.⁴⁵ ⁴⁶ For an inverted device, a high work function metal such as Gold (Au) or Silver (Ag) acts as an anode and the ITO or FTO as cathode. Due to reversing of nature of charge collection, the PEDOT:PSS layer no longer comes in contact with ITO.

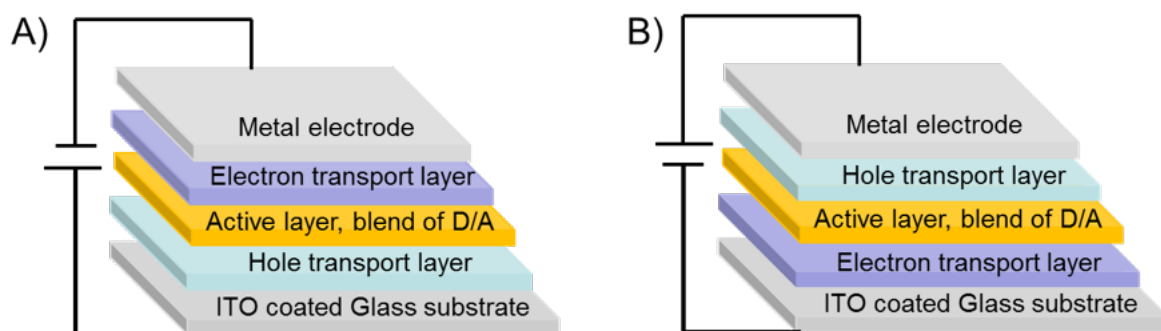


Figure 1.5: Schematic representation of OSC device structure A) conventional geometry of OSC devices where hole transport layer is deposited on ITO which is a high work function electrode B) an inverted geometry of OSC devices where high work function electrode is fabricated on top of hole transport layer.

The device performance and its characteristics are determined from the measurements of current density (J) and voltage (V).^{23, 28} Three important parameters derived from J-V curves (Figure 1.6) are open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF).⁴⁷

V_{oc} is defined as the maximum voltage across the cell under illumination condition when $J=0$,

J_{sc} is defined as the current density at zero applied voltage under illumination, and

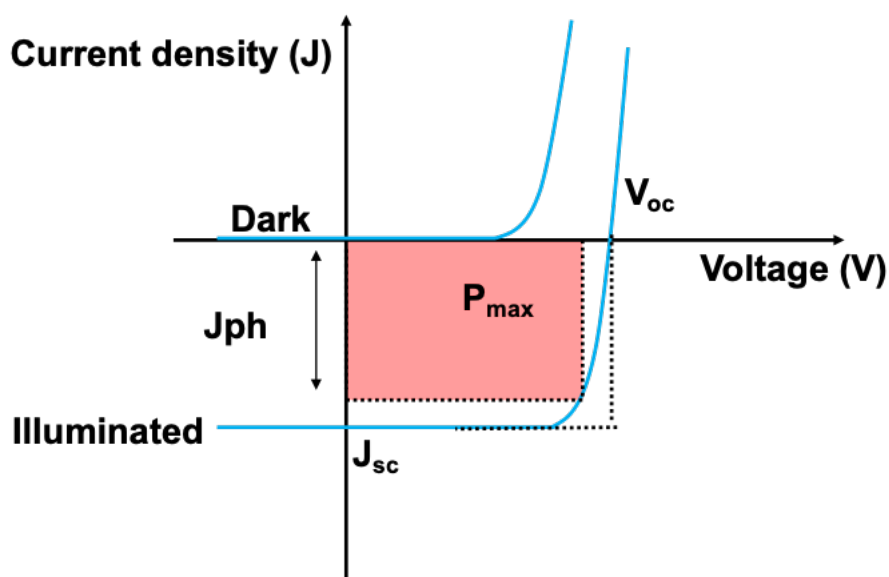
FF is defined as the ratio of maximum power that can be delivered by the cell under illumination and maximum theoretical power that can be obtained (Equation 1.1). Practically, FF gives an idea about how far the formulated device is from an ideal photovoltaic solar cell.

$$FF = \frac{P_{max}}{V_{oc} * J_{sc}} \quad (Eq. 1.1)$$

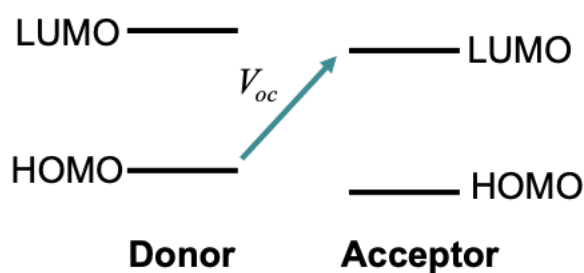
An approximate value for V_{oc} can be theoretically determined from the difference between HOMO of the donor and LUMO of the acceptor materials as illustrated in Figure 1.6.^{48, 49}

And finally, the most important parameter, the power conversion efficiency (PCE) is defined as ratio of maximum output power and incident power (P_{in}) on the cell (Equation 1.2). According to air mass 1.5 (AM 1.5) standard, the P_{in} of solar simulators is typically considered as 1000 W/m².

$$PCE = \frac{V_{oc} * J_{sc} * FF}{P_{in}} \quad (Eq. 1.2)$$



A)



B)

Figure 1.6: Schematic presentation of current density vs. voltage (J-V) curve to obtain short current density, J_{sc} , open circuit voltage V_{oc} and maximum power that can be drawn from device P_{max} B) conceptual diagram of determining V_{oc} by the difference between HOMO of donor and LUMO of acceptor material

1.2.5 Processing techniques

It can be recalled that the primary merit of OSC technology is both material and cost-effectiveness. It is achieved by deposition of thin film of organic semiconducting materials from a solution on a substrate. The categorization of deposition techniques is done based on their scale of application.⁵⁰ Some of the common coating and printing techniques are briefly discussed below.

Spin coating:^{51, 52} It is the most widely used technique for forming thin homogenous films in laboratories owing to its reliability and high reproducibility. The underlying mechanism lies in the name itself i.e., the substrate spins upon application of the solution. Only a part of solution stays on the substrate to form a thin film while most of it falls off the surface of rotating substrate. However, high throughput production is not achievable due to discrete handling of substrates and thus, this technique fails to qualify for large area roll-to-roll processing of OSCs.

Doctor blading:⁵³ This technique utilizes a sharp blade that is kept at a known height above the substrate as it moves after the coating solution is placed in front of the blade. The thickness of the obtained wet film is affected by several factors such as surface tension and viscosity of coating liquid, and meniscus formed at the point of contact between the blade and liquid. Roll-to-roll processing is enabled using the same principle but with a slight modified technique, known as knife coating, which uses a knife instead of a blade.

Wire-bar coating:⁵⁴ This deposition technique requires a metal bar wound with a wire which moves over the substrate to spread the solution through the gaps between the wire. The film thickness in this case depends on many parameters such as bar height and pressure, deposition speed, and concentration and viscosity of the solvents.

Inkjet printing:⁵⁵ This technique was considered suitable for small area application in the beginning. Roll-to-roll processing of OSCs have been demonstrated in recent research works using inkjet printing technique. It involves ejection of a fixed amount of ink from the nozzle to the surface of a substrate. It is a drop-on-demand technique that provides control on the amount of ink being used in deposition process and therefore is material conservative. It also allows for imprinting different patterns on different cells and modules during fabrication.

Slot die coating⁵⁶: It is one of the most actively used printing techniques for fabricating OSCs as it enables the deposition of homogenous and defect-free thin films on a large scale in a roll-

to-roll fashion. It is a pre-metered coating method in which the ink is delivered to the moving substrate through a fixed slot gap. The major advantage of this method is that the thickness of the wet coating could be easily estimated from the flow rate of the ink and speed of the substrate. Further, this technology reduces the dissipation of the material due to the pre-metered volume flow and could be used for coating solvents with a wide range of viscosity.

In addition to above-discussed techniques, several other coating and printing techniques have been explored. Techniques such as spray coating⁵⁷ and gravure coating⁵⁸ techniques have been used in roll-to-roll production of layers in OSCs. Some of the other printing techniques include screen printing⁵⁹ and flexographic printing.⁵⁵

1.3 Industrial scale processability of OSCs

Traditionally, organic semiconducting materials require toxic chlorinated and/or aromatic solvents such as chloroform, chlorobenzene and 1,2-dichlorobenzene (DCB) for their dissolution, and therefore, large scale production of OSCs can be harmful to human health and environment.⁶⁰ The early approaches to achieve safer processability of OSCs involved the use of non-halogenated and aromatic solvent for dissolving semiconducting materials.⁶¹ Researchers have also taken steps towards using alcohol and water to completely omit the use of aromatic solvents.⁶² The order of decreasing toxicity of the solvents used in fabrication of OSCs is presented in Figure 1.7.

1.3.1 Chemical modification of semiconducting materials to make them aqueous processable

Chemically modified polythiophene based materials have been extensively used in fabricating OSCs with non-toxic solvents. There are a number of reports on the synthesis of water soluble conjugated polymers for application in organic solar cells.⁶² A widely used approach to increase the solubility of conjugated polymers is by attaching ionic groups like carboxylic acids,

sulfonic acids, pyridiniums or ammonium salts to the alkyl chain of polymers. Various aqueous soluble conjugated polymers have been prepared and a few of them are commercially available

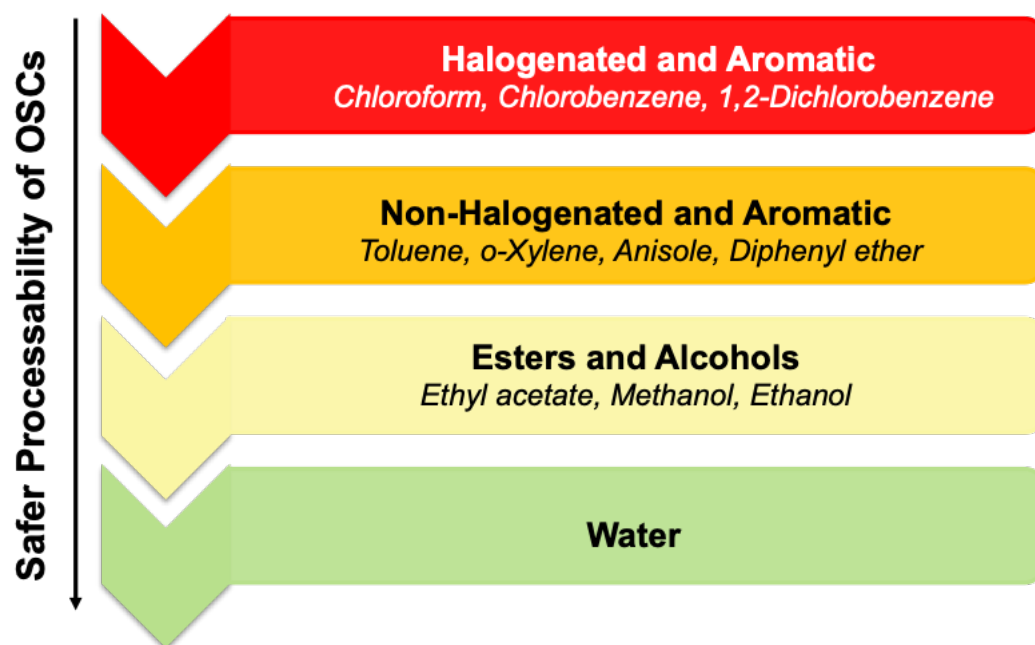


Figure 1.7: Different solvents arrange in order of high to low toxicity from top to bottom

Broadly, the non-toxic fabrication of active layer can be achieved in two ways.⁶³ First, by chemical modification of the semiconducting materials with the addition of polar group to make them water or alcohol soluble. Second, by producing emulsions or dispersions of semiconducting materials in water/alcohol to fabricate OSCs. In this process, hydrophobic polymers are dissolved in small amount of organic solvents and then dispersed in water to produce emulsions or solid nanoparticles.

like poly[3-(5-carboxypentyl)thiophene-2,5-diyl] (P3CPenT) and poly(2-(3-thienyl)-ethoxy-butylsulfonate sodium salt) (PTEBS-Na).⁶³ In earlier studies using these water-soluble semiconducting materials, devices exhibited poor efficiencies, which were attributed to lower charge mobility of the ionic material compared to their non-ionic forms. For example; for devices made with P3CPT and fullerene, the active layer has a charge mobility of $10^{-7} \text{ cm}^2/\text{Vs}$,

which is 100 times lower than the charge mobilities ($10^{-5}\text{cm}^2/\text{Vs}$) observed in regioregular P3HT and fullerene devices.⁶³

One of the major concerns with aqueous soluble conjugated polymers is their incompatibility with generally used hydrophobic acceptor materials. Initial studies with materials such as poly(2-(3-thienyl)-ethyloxy-butylsulfonate sodium salt) (PTEBS-Na) (cast with water as solvent) and C_{60} exhibited a low efficiency of 0.43%.⁶⁴ The PTEBS-Na: C_{60} system showed large phase segregation upon casting. This can be clearly attributed to difference in hydrophilic and hydrophobic nature of PTEBS-Na and C_{60} respectively. To overcome the problem of miscibility, another study utilized poly{*N*-7'-[(1',13'-bis(*N*',*N*'-diethylamino)tridecanyl)]-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)} (PCDTBT-N) and *N,N*-diethyl-5-phenyl-5-[(6',6')- C_{71} -pentyl]-1-amine (PCBM-N) as donor and acceptor materials respectively, and casted the active layer from n-butanol:acetic acid mixed solvent.⁶⁵ These materials revealed good miscibility, but possessed poor photovoltaic properties because in this case the amino groups acted as hole traps which disabled efficient hole transportation.

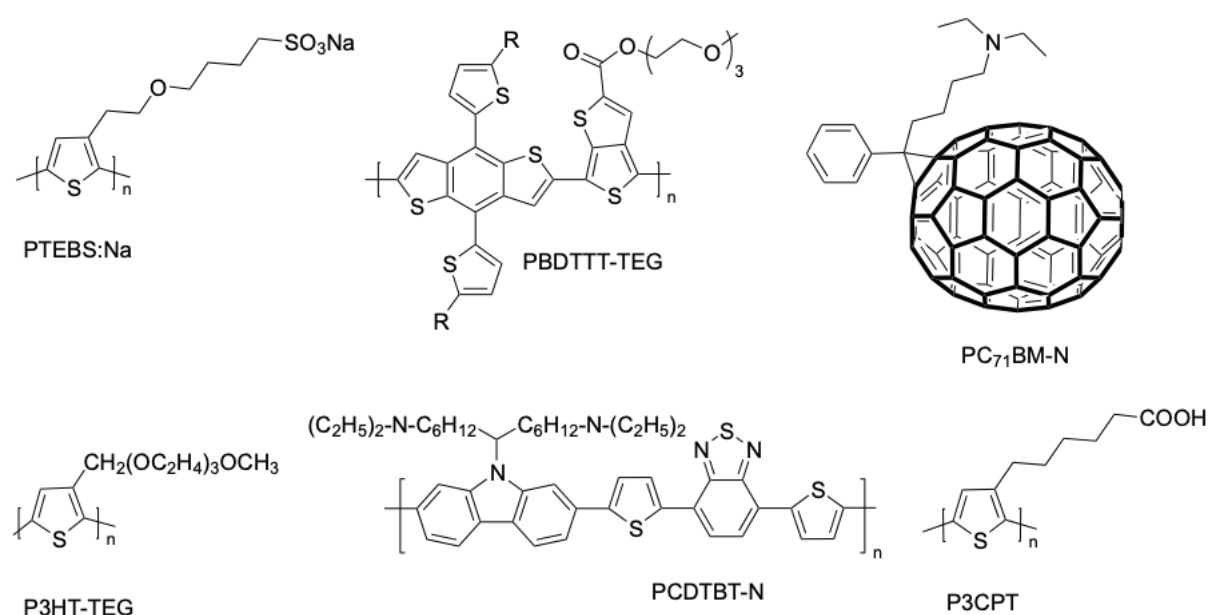


Figure 1.8: Examples of side chain modified conjugated polymers

Another approach of making a water-soluble material is to attach neutral polar substituent on a polymer side chain rather than an ionic group. Xiao *et al.*⁶⁶ synthesized a water soluble polythiophene derivative by introducing triethylene glycol mono-methyl ether (TEG) chain which resulted in charge mobility comparable to P3HT. In another study, a TEG chain was introduced as the side chain to the low band gap polymer poly(benzodithiophene-co-thienothiophene) (PBDTTT).⁶⁷ The device efficiency of PBDTTT-TEG/PC₇₀BM processed with non-halogenated and non-aromatic “N-methyl-2-pyrrolidone” solvent was 5.23%. The chemical structures of some of the side chain modified semiconducting materials are presented in Figure 1.8.

1.3.2 Nanoparticulate OSCs

Nanotechnology offers a path to achieve safer processability of OSCs, a big step towards their industrialization. Using the concept of colloidal chemistry, particles of semiconducting material can be dispersed in either water or alcohol. These water/alcohol-based dispersions can further be used as an ink for roll-to-roll processing of OSCs.

1.3.2.1 Methods of preparing nanoparticle inks

Polymer-based nanoparticles can be prepared by post-polymerization dispersion method which involves dispersion of pre-synthesized polymers. These dispersions can be formulated by two approaches a) miniemulsification⁶⁸ via ultrasonication and b) the dispersion method.⁶⁹

1.3.2.2 Miniemulsion technique

Miniemulsion are those systems in which stable emulsions consisting of small droplets with a size 50-500 nm are created in the continuous phase. These small droplets are generated by applying shearing force using an ultrasonicator on a system containing, water, oil, surfactant and most importantly a hydrophobe (water insoluble compound). Nanoparticles of

semiconducting polymer in aqueous phase using miniemulsion technique was reported by Landfester *et al.*⁷⁰ and Kietzke *et al.*⁷¹ In their studies, a pre-synthesized polymer was dissolved in solvent which constitutes the non-polar phase (dispersed phase). The polymer solution is then mixed with an aqueous solvent containing surfactant to create macroemulsion which is sonicated with ultrasound to achieve miniemulsion. The non-polar phase/ organic solvent captured inside droplets can then be removed by heating, resulting in stable polymer dispersion in water (Figure 1.9). An excess of surfactant can be removed through dialysis process.

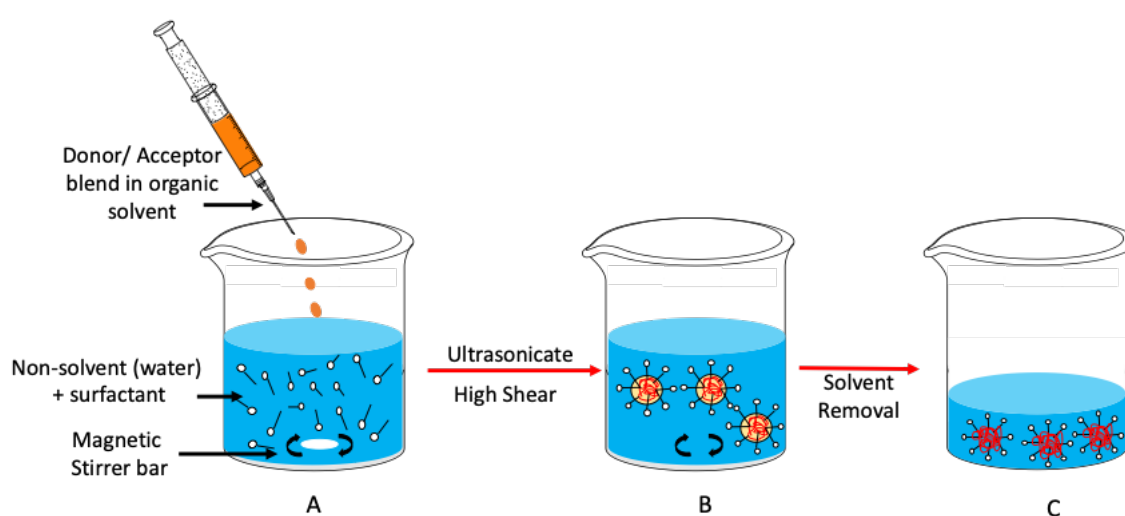


Figure 1.9: A schematic presentation of miniemulsion technique to prepare stable nanoparticles of semiconducting materials with the help of surfactant A) blend of donor/ acceptor material in organic solvent added dropwise into non-solvent (water) containing surfactant, B) high shear using ultra-sonicator results in formation of miniemulsion of semiconducting materials and C) heating is applied to evaporate organic solvent and also for concentrating dispersion by removing some non-solvent

1.3.2.3. Background on surfactants and their self-assemblies

Surfactants are surface acting agents. They are amphiphilic in nature consisting of polar hydrophilic group usually named as the *head* which is joined to non-polar hydrophobic long chain called as the *tail*.^{72, 73} Surfactants have the ability of reducing interfacial tension in a homogenous liquid or the interfacial tension between the two liquids of different polarity. They

are classified into four categories depending on the charge of the head group after dissociation in water⁷⁴- a) ionic (cationic/ anionic), b) non-ionic, c) zwitterionic and d) amphoteric (whose charge changes depending on the pH of the solvent). Surfactant molecules have a tendency to self-aggregate, yielding a variety of assemblies depending upon the nature of amphiphile and experimental conditions such as temperature, pH concentration and ionic strength.⁷⁵ The most common and widely discussed self-assembly of amphiphilic molecules in water is the micelle, which is discussed below in brief.

Micelles

Micelle formation is a spontaneous and reversible process in solution, which occurs by the self-association of amphiphilic molecules, above critical micelle concentration (CMC; minimum concentration to form micelle) and above the Kraft temperature (temperature at which aggregation occurs).⁷⁴ Micelle formation can be imagined as a sheet folded back onto itself. The direction of folding depends on the surrounding medium. A common characteristic of a micelle in an aqueous medium is that the hydrophobic chains point inward while the polar heads point outward. However, in case of organic solvents, these directions are often reversed; polar heads pointing inward with the hydrophobic chains pointing outward therefore, this type of self-assembly is known as reverse micelle (Figure 1.10).⁷⁶

1.3.2.4 Mechanisms of nanoparticle stabilization

A nanoparticle solution is an example of a colloidal system constituting of nanoparticles (dispersed phase) and a solvent (continuous phase). Nanoparticles in a dispersion medium exhibit Brownian motion and thus tend to collide with each other and the container walls. The interaction between two particles is based on the attractive and repulsive forces between them.⁷⁷ Van der Waals forces (attractive force) originate from permanent dipole-permanent dipole (Keesom), the permanent dipole-induced dipole (Debye) and transitory dipole-transitory

dipole (London) forces. Amongst the 3 forces, only London forces are responsible for long range attractive interactions between the particles and are predominantly considered in developing stabilizing strategies for colloids. For colloids to be stable, this long-range force must be outweighed by the repulsive forces. Traditionally, there are two mechanism of colloidal stability^{78, 79}- electrostatic and steric stabilization (Figure 1.11).

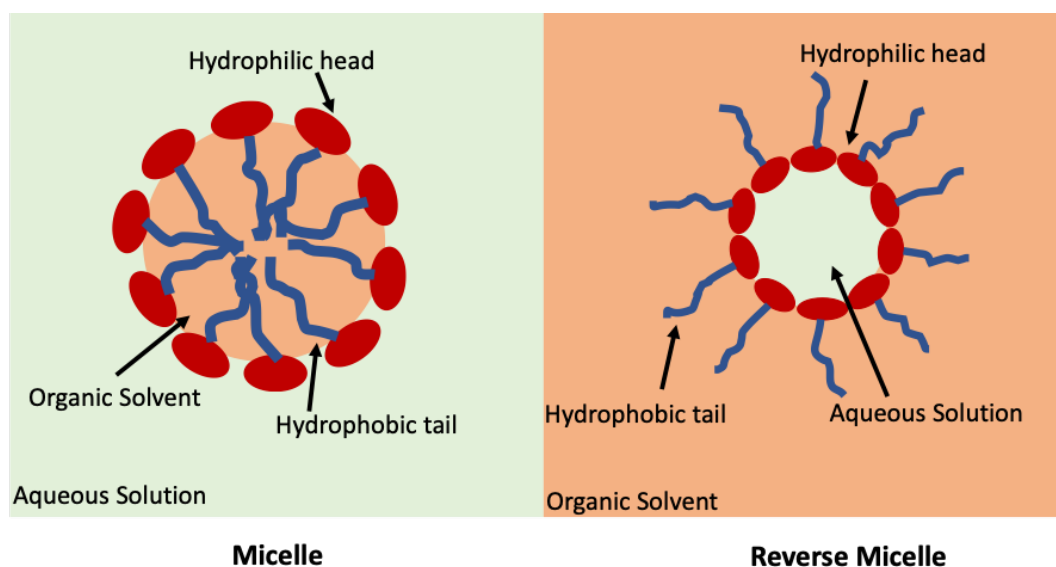
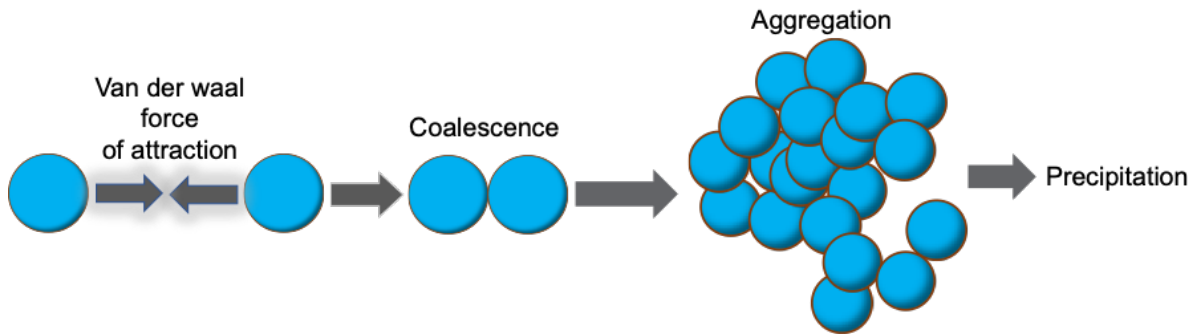


Figure 1.10: Schematic presentation of micelle formation on addition of surfactant. Considering that surfactant is added in aqueous solution then their hydrophilic head groups (red) align themselves in outward direction (towards water side) whereas, hydrophobic group pointing inward leading to the formation of A) micelle. If the surfactant is added into organic solvent (orange) then their hydrophilic part points outward whereas, hydrophobic points inward resulting in formation of B) reverse micelle.

Electrostatic stabilization of colloidal particles is fundamentally based on the presence of an electric double layer (EDL).⁸⁰ Nanoparticles dispersed in a polar solvent such as water acquire a surface charge as ionic groups of surfactant assemble on their surface to form a charged surface layer. It causes build-up of another layer of opposite charge to maintain charge neutrality. This electrically-neutral double layer is referred as EDL. The EDLs of two nanoparticles repel each other and provide stability to the dispersions. This phenomenon of EDL stabilization of nanoparticles can occur if ionic surfactants are used.

Interaction between particles

A) Attractive Force



B) Repulsive Force

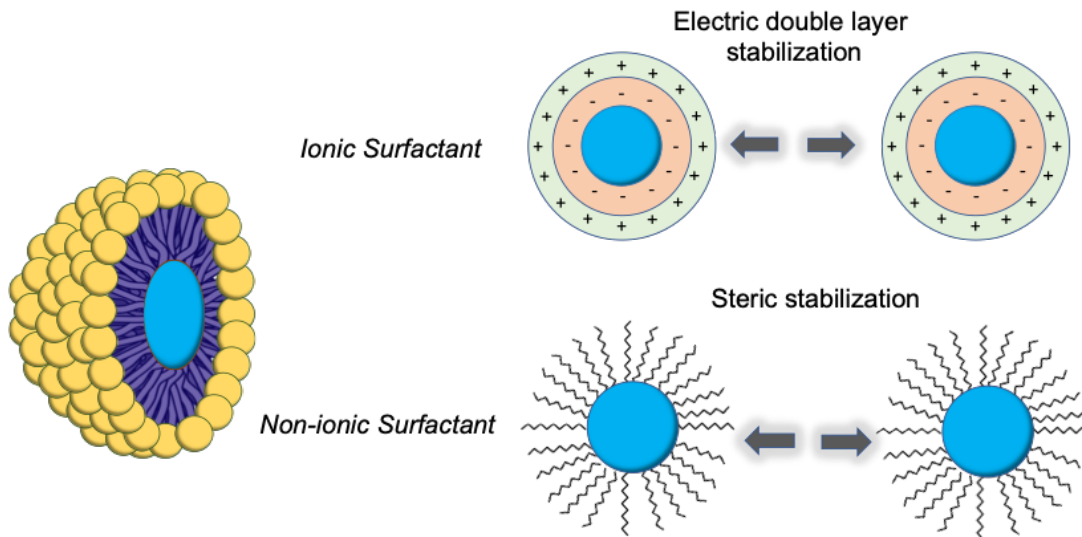


Figure 1.11: A schematic presentation of interaction between two nanoparticles A) in absence of surfactant, the Van der waal force of attraction dominates between two particles bringing them closer and eventually leading to aggregation B) mechanism of surfactant to stabilize nanoparticle. Ionic surfactant develops two layers of opposite charges (electric double layer) on nanoparticle surface and stabilize them through electrostatic repulsion as each nanoparticle contains similar charges in the outer layer. Ionic surfactant also stabilizes nanoparticle through steric repulsion between their long hydrophobic chains and non-ionic surfactant also works on same principle

The colloidal stability via electrostatic interactions between two particles is classically explained via Derjaguin-Landau-Verwey-Overbeek (DLVO) theory developed in 1940s.^{77, 81} It considers the potential energies of Van der Waal attraction and double layer repulsion and

describes the net potential energy as a function of distance from the surface of a spherical particle. For instance, when distance between two particles is large, there is no attractive or repulsive force acting on the particles. A repulsive force is generated due to interaction of two EDLs as particles move close to each other. Aggregation of particles occur when they are very close to one another and Van der Waal attraction dominates over the electrostatic repulsion.

Steric stabilization in a dispersion medium can be achieved by adding surfactant having a long hydrophobic chain.⁸² The assembly of surfactant molecules onto the surface of nanoparticles prevent their aggregation through steric repulsion acting between long hydrophobic chain of surfactant. This repulsion between two particles is not a long-range interaction which is the case for electrostatic repulsive forces. Thus, particles are constantly attracted towards each other under the action of Van der Waal force until the hydrophobic tails of surfactant begin to interfere. This phenomenon of steric stabilization can be seen in both ionic and non-ionic surfactants but more often it occurs in non-ionic surfactants.

It has been observed in the past that the presence of surfactant (an electrically inert species) in a bulk heterojunction reduces device efficiency by creating improper distribution of donor/acceptor domains.⁸³⁻⁸⁵ Therefore, surfactant-free dispersions have been prepared using precipitation/re-precipitation method as discussed below. Hereafter, these methods will be referred as dispersion method in this work.

1.3.2.5 Nanoparticle formation - Dispersion method

Using the dispersion method to form nanoparticles requires a combination of two miscible solvents; one is good for dissolving semiconducting material like chloroform (solvent phase), and another is good for material precipitation like methanol or ethanol (non-solvent phase).⁶⁹ In the dispersion method, the blend of the donor and acceptor materials in an organic solvent is added in one lot or dropwise to the stirred non solvent phase (Figure 1.12). The stirring of

both the phases at high rate result in interdiffusion of the solvent and non-solvent leading to NP formation in continuous phase via nucleation. The dispersions can be heated to remove the organic solvent and also to adjust the concentration of dispersion by evaporating some amount of the non-solvent.

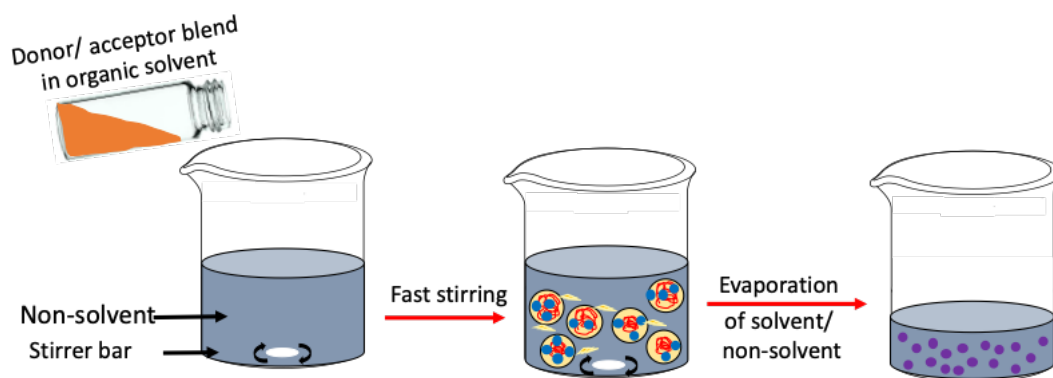


Figure 1.12: A schematic presentation of dispersion technique to prepare stable nanoparticles of semiconducting materials without surfactant A) blend of donor/ acceptor material in organic solvent added instantly/ dropwise into non-solvent, B) fast stirring results in formation of nanoparticles in continuous phase and C) heating is applied to evaporate organic solvent and also for concentrating dispersion by removing some non-solvent

Many researchers have applied dispersion method to formulate nanoparticles of semiconducting material as it enables the formation of dispersion in less toxic solvents without the need of a surfactant.^{86, 87} In this PhD project, the dispersion method has been used for preparing nanoparticle of semiconducting materials.

1.3.2.6 Literature review of nanoparticulate OSCs

The aim of this literature review is to give an insight of the recent published work (in the last 10 years) regarding nanoparticulate OSCs (NP OSCs). These NP OSCs were fabricated using dispersions prepared from surfactant-based miniemulsion method and surfactant-free dispersion method. The chemical structures of different donor and acceptor materials used for NP formation (discussed in this literature review) are presented in Figure 1.13.

Surfactant based nanoparticulate OSCs

In 2011, Andersen *et al.*⁸³ fabricated nanoparticle inks via miniemulsion method and demonstrated that NP OSC devices can be printed via roll-to-roll methods. A series of low band gap polymers poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT), poly[2,3-bis-(3-octyloxyphenyl)-quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1) in conjunction with PCBM were dissolved in chloroform to form nanoparticles with water as the non-solvent and PCEs of 0.55% and 0.15% respectively were obtained. They used the non-ionic fluoro surfactant (FSO-100) as a wetting agent and a large area (4 cm²) inverted OSC cells were prepared by printing via roll-to-roll slot-die coating methods on flexible substrates.

D'Olieslaeger *et al.*⁸⁸ formulated a NP dispersion of the low bandgap polymer poly[(5,6-dihydro-5-octyl-4,6-dioxo-4H-thieno[3,4-c]pyrrole-1,3-diyl)-[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]] (PBDTTPD) in combination with PC₇₀BM with the help of surfactant (SDS). Chlorobenzene was used to dissolve PBDTTPD polymer due to its poor solubility in low boiling point solvents. NP films were annealed at different temperatures, varying from 150 °C to 200 °C for 4 min. The devices annealed at 180 °C resulted in highest PCE of 2%. This efficiency was further improved to 3.8% by annealing the NP film at same temperature (180 °C) for 20 min.

Ullum *et al.*⁸⁹ fabricated NP OSCs using NP dispersions of P3HT:PCBM. These dispersions were made using miniemulsion technique in which P3HT and PCBM were dissolved in chloroform to form nanoparticles in water with the help of surfactant (SDS). The reported device efficiency of NP OSC was 1.3%. After this, they also reported a NP OSC replacing PCBM with ICBA which showed a higher device efficiency of 2.5% due to increased miscibility of P3HT:ICBA domains than P3HT:PCBM domains.⁹⁰ The morphology of

nanoparticles was studied through scanning transmission X-ray microscopy (STXM). Nanoparticles exhibited a core-shell morphology; with a PCBM/ ICBA rich core and P3HT rich shell depending on their relative surface energies. For instance, P3HT has a lower surface energy than PCBM/ ICBA which is why it moves to the outermost surface of the nanoparticle forming a shell during nanoparticle synthesis.⁹⁰ It was found that there was some degree of blending in core and shell domains that enabled the charge transport which was further improved after thermal treatment of NP films.

PDPP5T and PCBM aqueous nanoparticle dispersions from chloroform solution were formed using miniemulsion method.⁹¹ They controlled the size of PDPP5T:PCBM nanoparticles by varying the surfactant (SDS) concentration. Using too much SDS resulted in dewetting of the substrate, while a low concentration of SDS resulted in aggregated nanoparticles. Controlled addition of surfactant resulted in reproducible solar cell formation. They reported power conversion efficiencies of 2.0 and 2.4% for optimized nanoparticulate OSC based on PDPP5T with PC₆₀BM and PC₇₀BM respectively.

A recent study has also demonstrated the stabilization of NP dispersions of different donor and non-fullerene acceptor systems (P3HT: o-IDTBR, PCE10: o-IDTBR, PBQ-QF: o-IDTBR and PBQ-QF: ITIC) using a micelle forming poloxamer, Pluronic F127.⁹² The advantage of using Pluronic F127 as a surfactant is that the excess surfactant could be eliminated by modulating the temperature. Lowering the temperature of dispersions to 0 °C resulted in an increase in critical micelle concentration (CMC). This stimulated the conversion of micelles back to linear poloxamers which could be subsequently removed by centrifugal filtration. Efficiencies reported for water processable devices of P3HT: o-IDTBR, PCE10: o-IDTBR, PBQ-QF: o-IDTBR and PBQ-QF: ITIC were 5.2%, 5.2%, 6.5% and 7.5% respectively.

Non-surfactant based NP OSCs using dispersion method

Darwis *et al.*⁶⁹ reported device efficiency of P3HT:PCBM (1:1) NP OSC of 1.09%. The nanoparticles were made using dispersion method in which chloroform was used as the solvent to dissolve P3HT: PCBM and ethanol as the non-solvent for precipitation. The NP film showed blended morphology and annealing helped in reducing the voids between nanoparticles resulting in more homogenous film.

Gärtner *et al.*⁹³ also formulated a P3HT: IC₆₀BA (1:0.8) NP ink in both methanol and ethanol using dispersion method with a concentration of 10 mg/mL and 2.5 mg/mL respectively. The prepared nanoparticles had a diameter of 125 – 160 nm, with a dispersion stability of a couple of days. To fabricate the active layer, 8 to 25 spin coating steps were required, followed by annealing treatments at 100 – 200 °C for 10 min. The reported PCEs were 4.1% and 3.5% for inverted devices made from methanol- and ethanol- based P3HT:ICBA NP inks respectively.

In 2018, Geoffrey *et al.*⁸⁷ fabricated organic solar cell from aqueous dispersion of poly([9-(1'-octylnonyl)-9Hcarbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole4,7-diyl-2,5-thiophene-diyl) (PCDTBT) and PC₇₀BM. THF was used as solvent to dissolve PCDTBT and PC₇₀BM and a nanoparticle ink was prepared by precipitating this solution into water. They could achieve a maximum concentration of NP ink of 0.3 mg/mL, with average NP diameter of 133 ± 20 nm. In their study, the effect of different composition of PCDTBT: PC₇₀BM and along with the effect of annealing on NP OSC was observed. They reported an optimum composition of 30:70 wt.% for composite nanoparticles of PCDTBT: PC₇₀BM, with a device efficiency of 0.33% on annealing at 160 °C. The maximum concentration of NP dispersions achieved in their study was 10 mg/mL and about 6-8 coating steps were required to attain optimum active layer thickness.

The overall summary of results obtained by the studies discussed in this literature review are presented in Table 1.1.

Table 1.1: Summary of literatures based on NP OSCs

Donor	Acceptor	BHJ % PCE	Surfactant	NP dispersion conc. (mg/mL)	Solvent/ Non- solvent	Z.avg. (nm)	NP OSC % PCE
PSBTBT	PCBM	5.6 ⁹⁴	FSO-100	40	CHCl ₃ /	32	0.55 ⁸³
TQ1		5 ⁹⁵			H ₂ O	87	0.15 ⁸³
PBDTTPD	PC ₇₀ BM	8.1 ⁹⁶	SDS	35	CB/ H ₂ O	32 ± 3	3.8 ⁸⁸
P3HT	IC ₆₀ BA	6.5 ⁴¹	SDS	30	CHCl ₃ / H ₂ O	35 ± 2	2.5 ⁹⁰
P3HT	PCBM	5 ³⁸	SDS	30	CHCl ₃ / H ₂ O	32 ± 3	2.15 ⁸⁹
PDPP5T	PCBM	5.8 ⁹¹	SDS	37	CHCl ₃ / H ₂ O	50 ± 2	2.0 ⁹¹
P3HT	PCBM	5 ³⁸	-	10	CHCl ₃ / EtOH	130 ± 13	1.09 ⁶⁹
P3HT	IC ₆₀ BA	6.5 ⁴¹	-	10	CHCl ₃ / EtOH	135 ± 13	4.1 ⁹³
PCDTBT	PC ₇₀ BM	3.6 ⁹⁷	-	0.3	THF/ H ₂ O	133 ± 20	0.3 ⁸⁷

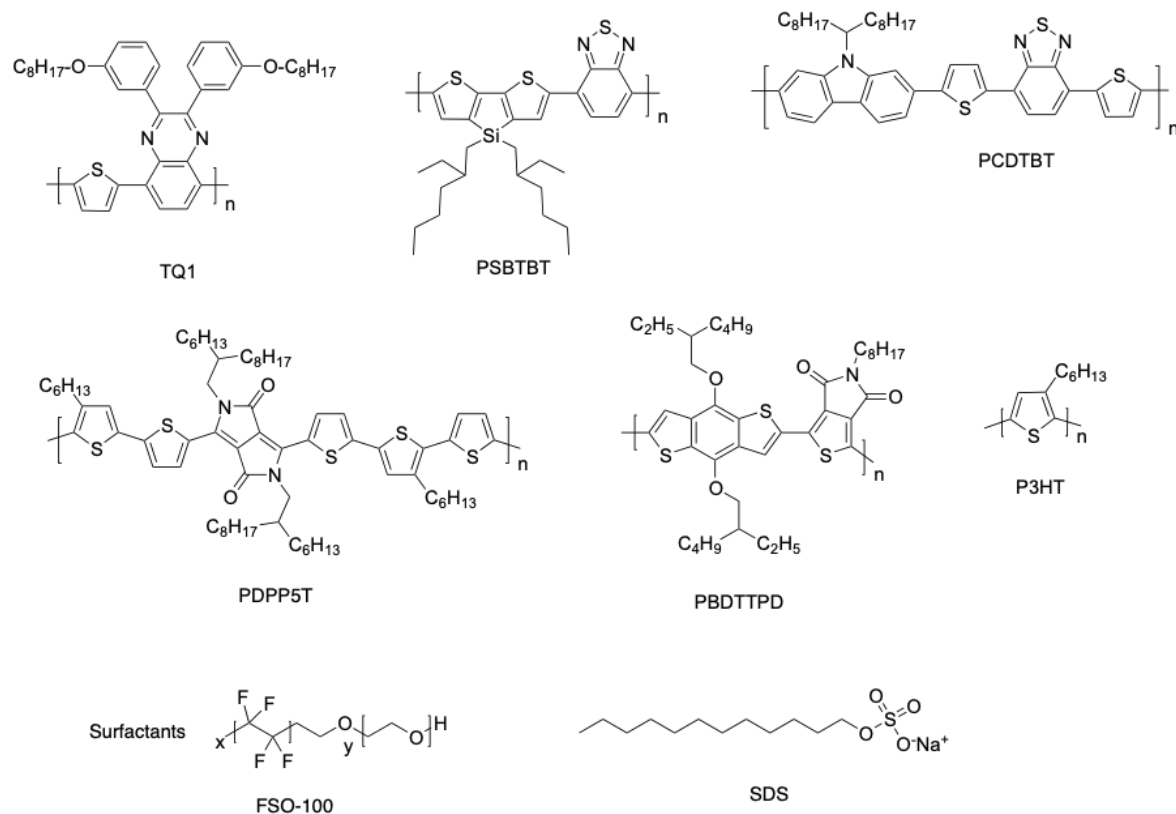


Figure 1.13: Different donor and acceptor materials used for nanoparticle formation with and without the help of surfactant.

Higher concentration of dispersions will reduce the number of coating steps leading to more facile device production and potentially increasing device reproducibility. However, reproducible synthesis of highly concentrated NP dispersions, with controlled size distribution and without surfactant has not been demonstrated thus far.

1.4 Research gaps

Literature survey reveals that devices fabricated using surfactant stabilized dispersions generally exhibit lower power conversion efficiency compared to the devices processed from chlorinated solvents.^{83, 88-90} The lower device efficiencies were attributed to persistence of the surfactant in the active layer, as residual surfactant is electrically inert and potentially inhibits charge transport in the active layer. For instance, the reported device efficiency for devices

fabricated from surfactant stabilized P3HT:ICBA dispersions was 2.5%.⁹⁰ To overcome the limitations with surfactant stabilized dispersions, an alternate approach of preparing surfactant-free NP dispersion via dispersion method was demonstrated. The NP dispersions of P3HT:ICBA were prepared without using surfactant and the reported device efficiency was improved to 4%.⁹³ Despite achieving improved device efficiency, the surfactant-free approach involves lesser control on NP formation and the properties of NPs such as NP size vary with the batch of P3HT polymer used. This variability could be attributed to difference in material properties such as molecular weight, dispersity (D) and regioregularity among different batches of the same polymer. The influence of batch-to-batch variation of P3HT polymer on NP formation has not been investigated in detail.

Other issues related with surfactant-free dispersion method include- a) non-reproducible NP formation, b) poor NP stability, and c) low concentration of dispersions. These factors inhibit application of this approach in industrial settings. The maximum concentration of P3HT:ICBA NP dispersions achieved so far is 10 mg/mL in MeOH and EtOH. At this concentration, 6-8 coating steps were required to attain optimum active layer thickness.⁹³ Such high number of coating steps reduces the efficiency and applicability of this approach and could result in lower device reproducibility. Although roll-to-roll processes such as inkjet printing or spray coating can compensate low concentration of dispersions,⁹⁸ but reducing the number of coating steps at lab-scale using spin coater can be overcome only by forming concentrated NP dispersions.

1.5 Thesis objectives

Based on the research gaps, specific aims of this project are described below:

- 1) What will be the effect of molecular weight and batch-to-batch variation of P3HT on P3HT:ICBA NP dispersions formulated using dispersion method?

- 2) Can a surfactant assist in producing reproducible, stable and concentrated NP dispersions without affecting device performance?
- 3) Is it possible to overcome material dependency of dispersion method?

1.6 Thesis structure

Chapter 2: Synthesis and characterization of defined molecular weight P3HTs and end-capped P3HTs

This chapter focuses on synthesis of P3HT polymers with defined molecular weights and three end-capped P3HT polymers, P3HT-COOH, P3HT-Py and P3HT-TEG which will be used to accomplish first and second research objectives. The defined molecular weights of P3HT were synthesized using McCullough's approach of Grignard metathesis.^{39, 40} The two end-capped polymers (P3HT-COOH and P3HT-Py) were synthesized by end-capping P3HT using Suzuki coupling condition⁹⁹ whereas, the third end-capped polymer, P3HT-TEG was synthesized by initiating P3HT polymerization via Grignard metathesis.¹⁰⁰⁻¹⁰² These end-capped polymers will be used as additives to stabilize P3HT:ICBA dispersions in chapter 3. The prime advantage of synthesizing these end-capped polymers is that unlike conventional surfactants, they carry semiconducting properties as they are based on P3HT unit. All the polymers were purified, particularly the end-capped polymers, to acquire high end-group fidelity as they were to be used as additives for NP formation. The structural characterization of polymers was done using GPC, ¹H NMR spectroscopy, MALDI-TOF and DSC whereas, their photophysical and electrochemical properties were studied using UV-Vis spectrophotometer and cyclic voltammetry.

Chapter 3: Preparation of P3HT: ICBA NP dispersions using dispersion method

Chapter 3 presents the physical parameters affecting NP formation in dispersion method such as temperature and choice of solvent and non-solvent while NP formation, the stirring rate of

dispersion and temperature required for evaporating solvent and non-solvent. NP dispersions of defined molecular weight P3HTs and ICBA were prepared to study the impact of polymer length on NP formation. The properties of these NP dispersions were compared with dispersions prepared from commercial P3HT to understand the impact of batch-to-batch variation of polymers. In this chapter, the idea of using end-capped polymers for producing stable, reproducible and concentrated dispersions has also been discussed in detail. The P3HT-Py and P3HT-COOH can be converted into ionic forms on treatment with acid and base respectively, to behave as ionic surfactants while forming NP dispersions. It can be anticipated that the activated ionic forms of P3HT-Py and P3HT-COOH would improve NP stability of P3HT:ICBA dispersion via EDL formation. Although EDL stabilization of NPs can be expected from any other conventional ionic surfactant, but the advantage of using P3HT-Py and P3HT-COOH is their property of reversibility of ionic pair (deactivation of ionic forms). After NP film deposition, the thermal treatment of these would dissociate ionic pair to regenerate P3HT-Py and P3HT-COOH with the removal of respective acid and base. The P3HT-TEG can be expected to behave neutral or non-ionic active surfactant to stabilize dispersions via steric repulsion. NPs were characterized using DLS and TEM. The idea of reversibility of ionic pair has also been proven in this chapter.

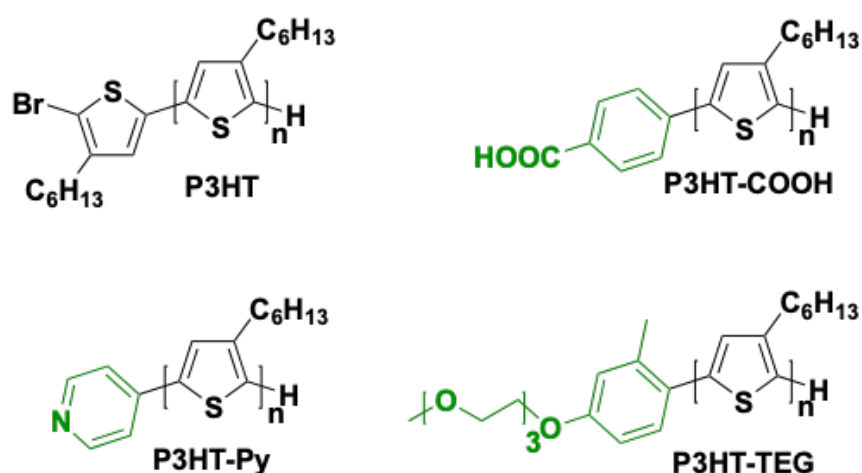
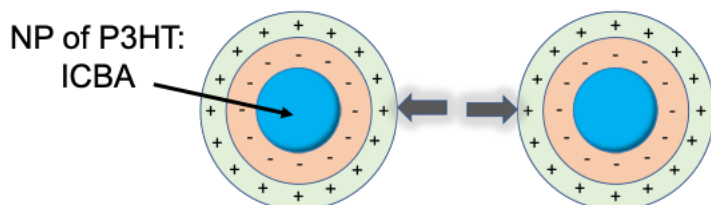


Figure 1.14: Polymers to be investigated in this work

During NP formation

Ionic forms of P3HT-Py and P3HT-COOH stabilizing P3HT:ICBA NPs via Electric double layer in dispersion



During thermal treatment of NP film

Reversibility of ionic pair on thermal treatment resulting in nanoparticle with no charge

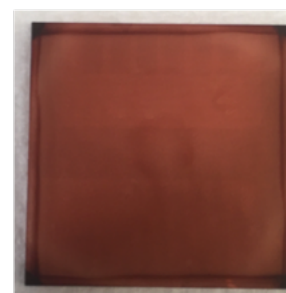
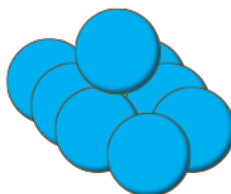


Figure 1.15: The idea of designing P3HT-Py and P3HT-COOH end-capped polymers for nanoparticle stabilization.

Chapter 4: To study the impact of end-capped P3HT on NP film and device formation

The effect of end-capped polymer on devices has been investigated in this chapter. Devices were fabricated using DCB solution and NP dispersions of P3HT:ICBA in MeOH and EtOH. The optimization of active layer thickness for these devices was performed using Dektak profilometer. The performances of as-cast and annealed devices were correlated with the spectroscopic analysis (UV-Vis and photoluminescence quenching measurements). Surface morphology of the films processed from DCB solution and NP dispersions of P3HT:ICBA were studied using atomic force microscopy (AFM). The crystalline nature of these films was examined by conducting grazing incident wide angle X-ray scattering (GIWAXS) analysis.

Chapter 5: Summary and conclusions

This chapter gives an overall summary of the PhD work and also discusses the future aspect related to this work.

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Chapter 2 Synthesis of P3HT and End-Capped P3HT

2.1 Introduction

The groundbreaking work in the direction of synthesizing highly regioregular P3HT was conducted by McCullough¹ and Rieke² independently. The synthesis and characterization of two sets of P3HT-based materials are discussed in this chapter. First, a series of P3HT with molecular weight variation from 5000 to 40000 g/mol was synthesized to highlight the dependence of NP formation on the polymer batch-to-batch variations and polymer length as discussed in Section 1.4. Second, end-capped P3HTs: P3HT with benzoic acid (P3HT-COOH), pyridine (P3HT-Py) and triethylene glycol monomethyl ether (P3HT-TEG) end-caps were synthesized with the goal of using these materials as active surfactants for NP stabilization. Two different synthetic strategies were used to synthesize end-capped P3HTs (a) post-polymerization modification of P3HT, and (b) using functional Ni-based initiators to initiate the polymerization.

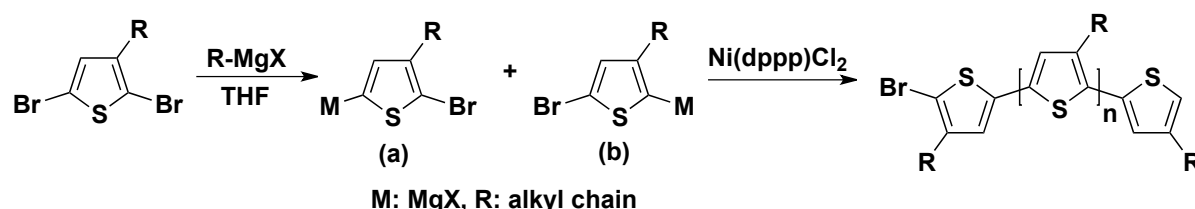
It should be noted that NP dispersions stabilized with end-capped polymers will be utilized to formulate devices to study the impact of these polymers on device performance. Therefore, it is important to synthesize end-capped polymers with controlled molecular weight and low regio-defects. Also, the molecular weight of P3HT ranging from 5,000 to 40,000 g/mol must

be well-defined as it would assist in providing effective understanding of dependence of NP formation on molecular weight of polymer. In order to fulfill these requirements, the polymerization in this work was performed using Grignard metathesis (GRIM).

The characteristics of the GRIM method makes it one of the most popular approach to synthesize well defined and highly regioregular P3HT with low dispersity (D)^{3, 4} as described in the next section.

2.1.1 Overview of Grignard metathesis (GRIM)

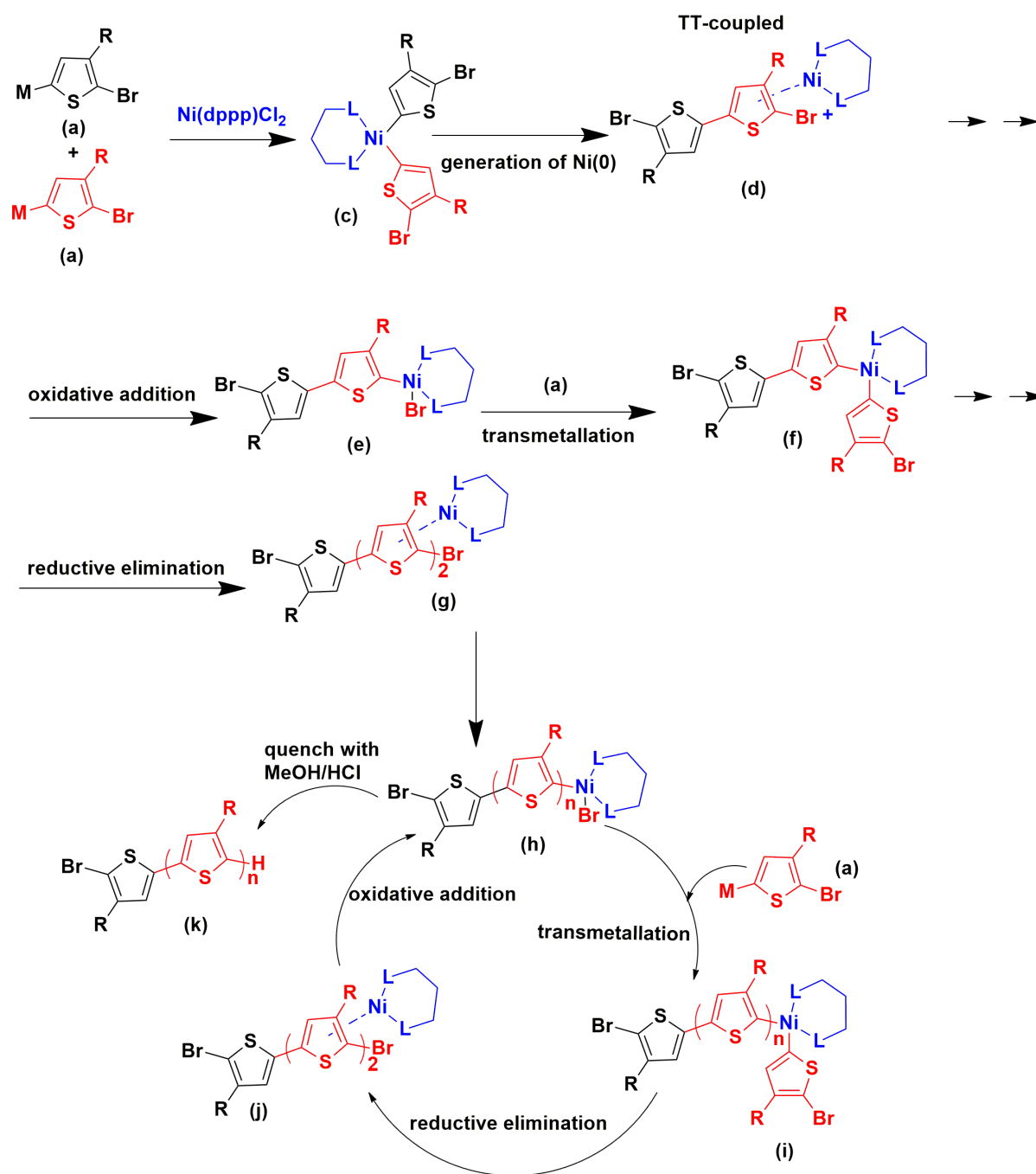
McCullough's group in 1999 discovered a convenient route to synthesize highly regioregular P3HT by Grignard metathesis (Scheme 1). It is a type of poly condensation reaction using Ni (II) as a catalyst and is also known as Kumada Catalyst Transfer Polycondensation reaction (KCTP). Addition of Grignard reagent to the dibromo alkyl thiophene monomer results in formation two regioisomers **(a)** and **(b)**, out of which only one regioisomer **(a)** takes part in polymerization and other one **(b)** remains unreacted in solution due to steric hinderance.



Scheme 1: General route to synthesize P3HT from GRIM polymerization

The mechanism of GRIM polymerization involves three steps: 1) oxidative addition, 2) transmetalation, and 3) reductive elimination. The monomeric unit keeps adding on to the active chain end using these three steps to form a polymeric chain (Scheme 2). The first step involves the reaction of 2 equivalents (eq.) of regioisomer **(a)** with 1,3-bis(diphenylphosphino)propane nickel(II) chloride (Ni(dppp)Cl₂) giving rise to organonickel compound **(c)**, and reductive elimination immediately occurs to form an associated pair of 2,2'-

dibromo-3,3'-dialkyl-5,5'-bithiophene (tail-tail (TT) - coupling) and Ni(0) dimer **(d)**. Compound **(d)** undergoes fast oxidative addition to the nickel center affording a new organonickel compound **(e)**.



Scheme 2: Mechanism of GRIM polymerization; where R, M and L denote to C_6H_{13} , MgBr and PPh_2 respectively.

Transmetalation with another **(a)** give rise to compound **(f)** which undergoes reductive elimination resulting in an associated pair of the terthiophene and Ni(0) **(g)**. Yokozawa's and McCullough's group demonstrated that synthesis of P3HT follows chain growth mechanism.⁵

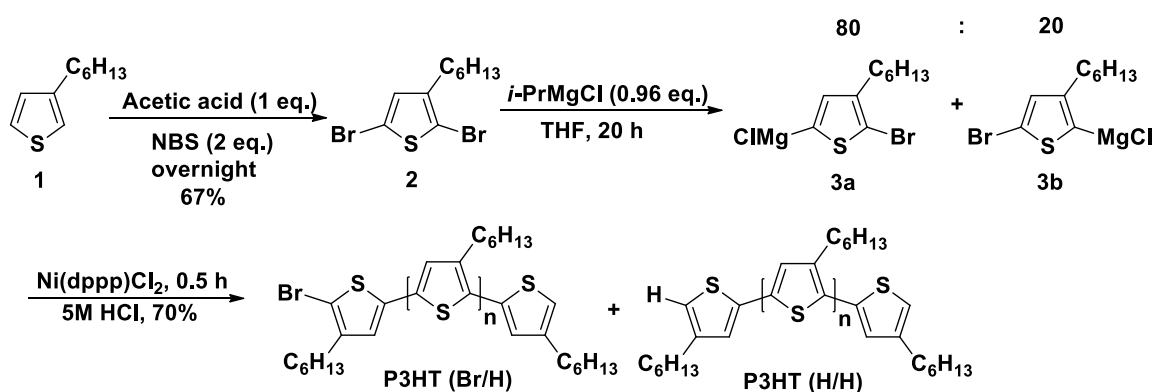
⁶ The association of nickel catalyst with thiophene monomer via π -complex allows the catalyst to remain intact with the growing chain leading to an intramolecular oxidative addition, facilitating a chain-growth mechanism. Therefore, the number average molecular weight of polymer (M_n) should be directly proportional to the feed ratio of monomer to catalyst, and during the reaction, the increase in molecular weight of the polymer is directly proportional to the consumption of monomer. Further investigations by McCullough's group suggested that polymerization via GRIM is a quasi-living reaction.⁶ The quasi-living nature enables the controlled synthesis of polymers with different end functionalities or block copolymers as the polymer chains are active even when the reaction approaches to completion.

The reaction mechanism of GRIM polymerization involves an initial tail-tail (TT) coupling reaction (Scheme 2, compound **(c)**) causing at least one regiodeflect in the polymer chain. This regiodeflect can be eliminated through initiation of polymerization from an external moiety which would also prevent the formation of Br-terminal groups originated from the initial TT coupling reaction.⁷⁻¹¹ It is expected that this initiation should retain the quasi-living nature of GRIM. Moreover, the initiation with aromatic group can also help in preserving the aromaticity of the polymer backbone. Small molecules or polymeric based initiators can be used for external initiation of the polymerization to synthesize end-functionalized P3HT.

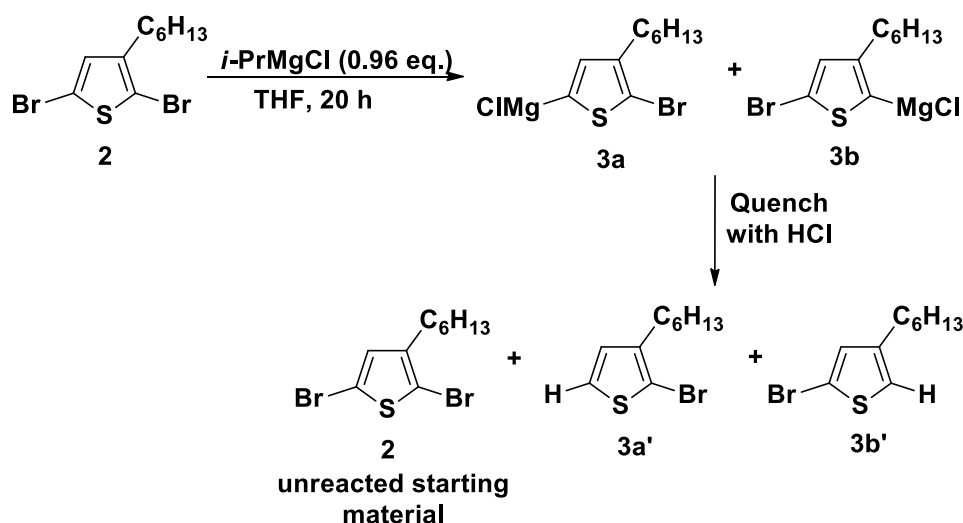
2.2 Synthesis of P3HT polymers of defined molecular weight using GRIM polymerization

Efforts were made to synthesize defined molecular weights of P3HT varying from 5,000 to 40,000 g/mol using GRIM polymerization as published in literature (Scheme 3).¹² The

monomer 2,5-dibromo-3-hexyl thiophene **2** was prepared by bromination of 3-hexylthiophene **1** using acetic acid and N-bromosuccinimide. Conversion of monomer **2** into active Grignard regioisomers was done by using 0.96 eq. of *iso*-propyl magnesium chloride (*i*-PrMgCl). According to literature, the regioisomers **3a** and **3b** shown to be approximately in ratio 80:20.¹² In this work, the ratio of these regioisomers was confirmed by quenching a small aliquot of the sample with one drop of hydrochloric acid (HCl).



Scheme 3: Synthesis of P3HT using GRIM polymerization

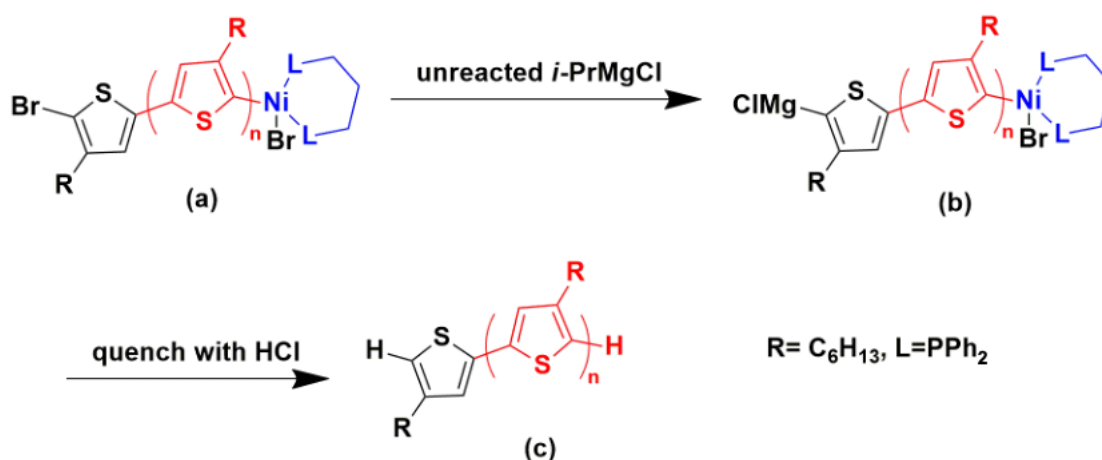


Scheme 4: Possible quenching products of regioisomers **3a** and **3b**.

The possible products (**2**, **3a'** and **3b'**) after quenching are shown in Scheme 4. The relative integration of protons at the respective position of MgCl group after quenching was used to calculate the ratio of regioisomers via ^1H NMR spectroscopy. Upon confirmation of the ratio

of regioisomers **3a** and **3b** to be approximately 80:20, the Ni catalyst was added to initiate polymerization. Addition of Ni catalyst allowed regioisomer **3a** to undergo catalytic cycle, while sterically hindered regioisomer **3b** remained unreacted in solution. The molar ratio between catalyst and regioisomer **3a** was varied according to the required molecular weight of P3HT (Table 2.1). Quenching with 5M HCl terminated the reaction resulting in the synthesis of P3HT with Br/H and H/H ends.

If the polymerization results in 100% Br/H end P3HT then it is considered as a perfect end-group controlled polymerization. The Br end of P3HT originates from initial TT-coupling between regioisomer **3a** whereas, the H end comes from quenching the polymer chain end with HCl. The presence of P3HT with H/H ends is mainly due to incomplete formation of active Grignard monomer resulting in unreacted *i*-PrMgCl in solution. In previous work, the effect excess Grignard reagent on P3HT end groups has been studied.¹³ There are three possible end groups of P3HT that can be obtained from unreacted *i*-PrMgCl; Br/*i*-Pr, H/*i*-Pr and H/H. The Br/*i*-Pr and H/*i*-Pr end groups are expected when *i*-PrMgCl reacts with the active chain end. One of the possibilities of obtaining H/H end groups of P3HTs are when unreacted *i*-PrMgCl generate another active Grignard species by reacting with Br-end of polymer chain (Scheme 5).



Scheme 5: Unreacted *i*-PrMgCl in solution give rise to P3HT with H/H end.

Subsequently, the quenching of polymer chain with HCl results in P3HT with H/H ends. The amount of Br/H in such cases can only be increased by decreasing the polymerization time because the formation of H/H is comparatively slower than formation of Br/H.¹³ Synthesized P3HT polymers of defined molecular weights were purified through Soxhlet extraction which is a common route to separate mixed chemical species based on their solubility differences in various solvents. For example, methanol was used to remove metal salts and unreacted monomer, acetone and petroleum ether removed low molecular weight chains. In the end, the purified polymer was collected using chloroform.

2.2.1 Structural characterization of defined molecular weight P3HT

2.2.1.1 Gel permeation chromatography of P3HT polymers

The polymers were characterized using gel permeation chromatography (GPC) and ¹H NMR spectroscopy (see experimental section for detail). GPC is a type of size exclusion chromatography which is calibrated against polystyrene standards. It separates the polymer based on their molecular weight. GPC plot of retention volume vs. normalized refractive index for defined molecular weight P3HT polymers shows that high molecular weight polymer elutes faster than low molecular weight polymer (Figure 2.1). A long tail observed in high molecular weight polymer is attributed to presence of small oligomers. The *M_n* of synthesized polymers obtained from GPC (Table 2.1) shows that polymer molecular weight increases by reducing the ratio of catalyst to regioisomer 3a. The observed molecular weights were in good agreement with targeted molecular weight up to 30,000 g/mol. However, the synthesis becomes less controlled for higher molecular weight polymers which may be attributed to minimum loading of catalyst leading to incomplete consumption of monomer at a given reaction time. The dispersity for all synthesized polymers up to 25,000 g/mol varied between 1.01 < *D* < 1.2. An increase in *D* value up to 1.6 was observed for higher molecular weight polymers (28,000

g/mol). It could be because the associated complex of Ni (0) with thiophene did not always remain associated with the growing chain resulting in some termination or chain-transfer reactions, causing an increase in $\bar{D}$ value. Due to this unavoidable termination, the synthesis of high molecular weight conjugated polymers via controlled chain growth mechanism is challenging. The molecular weight of synthesized polymers was also determined using ^1H NMR spectroscopy (see section below for details) which followed the same trend of M_n values as obtained from GPC (Table 2.1). There is a slight difference in M_n values obtained from GPC and ^1H NMR experiments. In general, GPC instrument is calibrated using polystyrene standards. The molecular weight of conjugated polymers is estimated assuming that hydrodynamic radii of conjugated polymer and polystyrene standard are same at equivalent chain length. However, polystyrene standards are coil-like and conjugated polymers are mostly rigid and rod-like, which is why an assumption of their same hydrodynamic radii at equivalent chain length leads GPC to overestimation of molecular weight.¹⁴

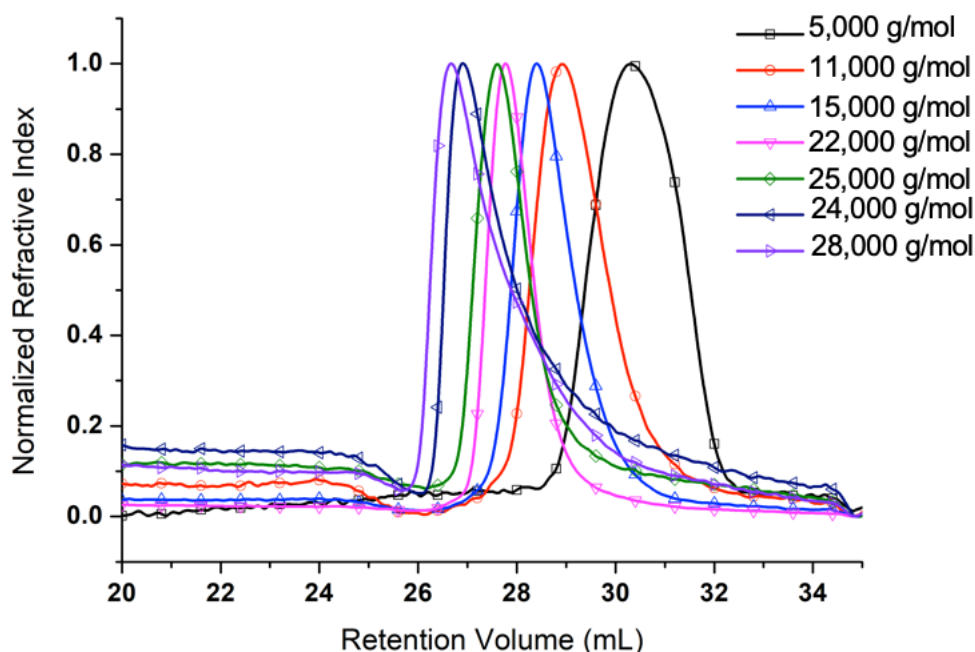


Figure 2.1: GPC plot of Retention Volume and Normalized Refractive Index of P3HT of defined molecular weight ranging from M_n : 5,000 to 28,000 g/mol

Compared to most of the polymers used in OPVs, P3HT is more flexible therefore, molecular weights of synthesized polymers were only marginally overestimated by GPC.

2.2.1.2 Determination of molecular weight and regioregularity of P3HT polymer using ^1H NMR spectroscopy

Molecular weight determination

^1H NMR spectroscopy is a useful technique to determine the M_n of P3HT polymers. In ^1H NMR of P3HT (5,000 g/mol) (Figure 2.4), the relative integration of protons associated with α -carbon of 3-substituent (h, h' and b) can be used to determine molecular weight of P3HT polymer. Due to difference in chemical environment, the protons of α -carbon at the chain end (h and h') resonate at lower chemical shift (δ 2.60 ppm) compared to the proton of α -carbon along the chain (b) resonating slightly higher chemical shift (δ 2.80 ppm) (Figure 2.4).⁶ The α -carbon at the chain end has two protons, therefore, their peak resonances at 2.6 ppm was normalized to value 4. Note that, normalizing peak resonances of α -CH₂ protons as 4 represents an ideal case of P3HT synthesized with 100% H/Br end. The relative integration of aromatic protons (c) was determined to be 28. Since there is only one aromatic proton per repeat unit, therefore, relative integration of these aromatic protons (c) can be used to calculate the number of monomer repeating units which is also known as degree of polymerization (DP_n). To obtain the M_n of P3HT polymer, DP_n was multiplied with the molar mass of monomer unit which is 166.3 g/mol for thiophene monomer, $M_n = 28 \times 166.3 = 4,656$ g/mol or $\sim 4,600$ g/mol. Similarly, DP_n and M_n can be calculated for each of the synthesized P3HT polymers, and the details are listed in Table 2.1.

Table 2.1: Molecular weight and regioregularity of synthesized various molecular weight P3HT

Samples	Target molecular weight (g/mol)	Catalyst/ Regio isomer 3	(GPC)			¹ H NMR	
			M_n (g/mol)	$\bar{D}$	DP _n	M_n (g/mol)	% RR
P3HT	5,000	1/30	5000	1.02	28	4,600	98
	10,000	1/60	11000	1.11	64	10,600	97
	15,000	1/90	15000	1.07	81	13,500	98
	20,000	1/120	22000	1.06	105	17,500	98
	25,000	1/150	25000	1.05	125	21,000	98
	30,000	1/180	24000	1.5	144	24,000	98
	40,000	1/210	28000	1.6	149	24,700	98

Regioregularity determination

¹H NMR experiment helps in determining the regioregularity of P3HT by using the protons on the 4-position of aromatic thiophene ring. If these are the protons of HT-HT triad sequence then they would resonate at chemical shift, δ , of 6.98 ppm. A large signal at this chemical shift is an indication of a nearly perfect regioregular P3HT. However, if these protons belong to other triad sequences such as TT-HT, HH-HT and TT-HH then they are expected to resonate at $\delta = 7.00$ ppm, $\delta = 7.03$ ppm, and TT-HH is at $\delta = 7.05$ ppm respectively.^{2, 15, 16} The relative integration of the HT-HT triad peak with respect to other triad peaks can give the percentage of HT-HT coupling or percent regioregularity (%RR). A representative ¹H-NMR spectrum

(Figure 2.3) of synthesized P3HT (5,000 g/mol) is shown below indicating a highly regioregular P3HT. This observation is in agreement with the fact GRIM method provides highly regioregular P3HT of (H/H) and (H/Br) ends with the unavoidable TT coupling (Scheme 2, compound (c)) occurring at the initial stage of polymerization. Such low level of regio-defect is difficult to be quantified using integration of aromatic protons. To get an approximate of how well-defined a P3HT polymer is (especially the one synthesized from GRIM method), the aliphatic protons present at the side chains of the polymer needs to be integrated.

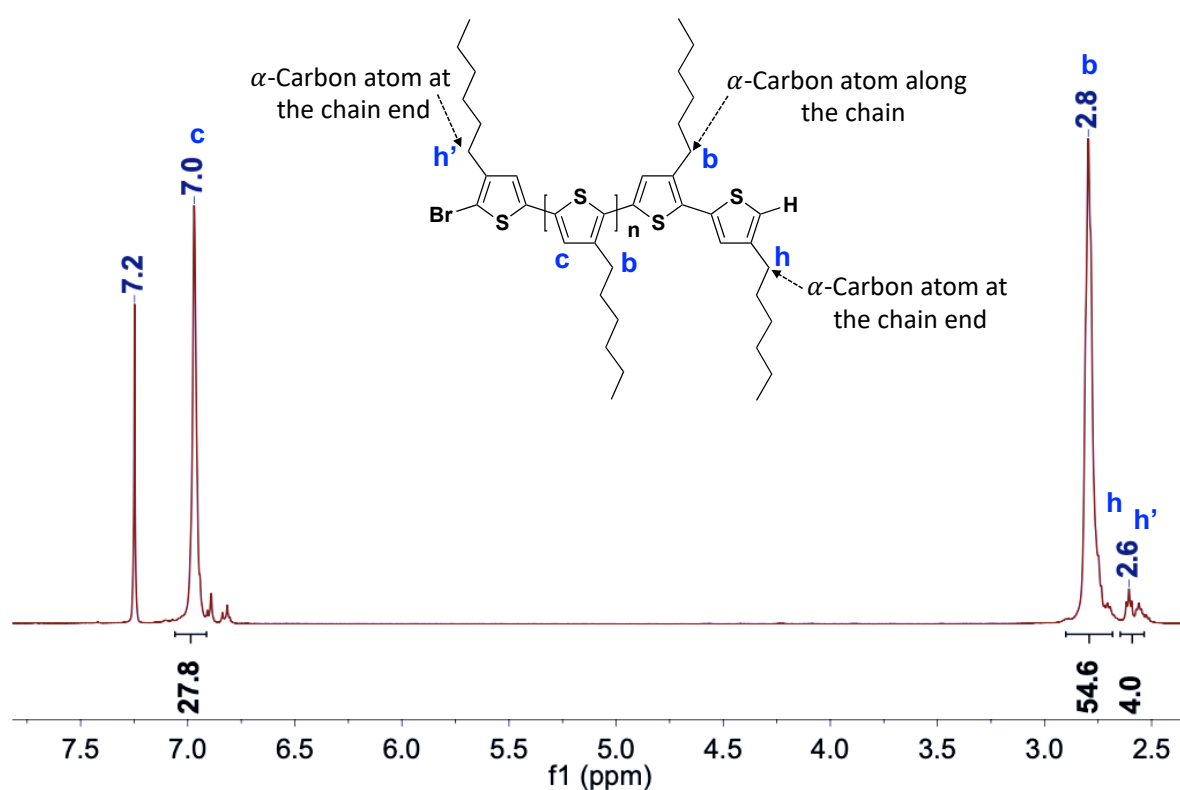


Figure 2.2: Representative expanded ^1H NMR spectrum of P3HT (5,000 g/mol) on a scale of 2.3 to 7.8 ppm. The integration of protons associated with the α -carbon at the chain ends resonate at $\delta \sim 2.60$ ppm were normalized to value 4. The relative integration of aromatic protons of thiophene ring at 7.0 ppm yielded the DP_n as 28 and M_n was calculated as 4,600 g/mol.

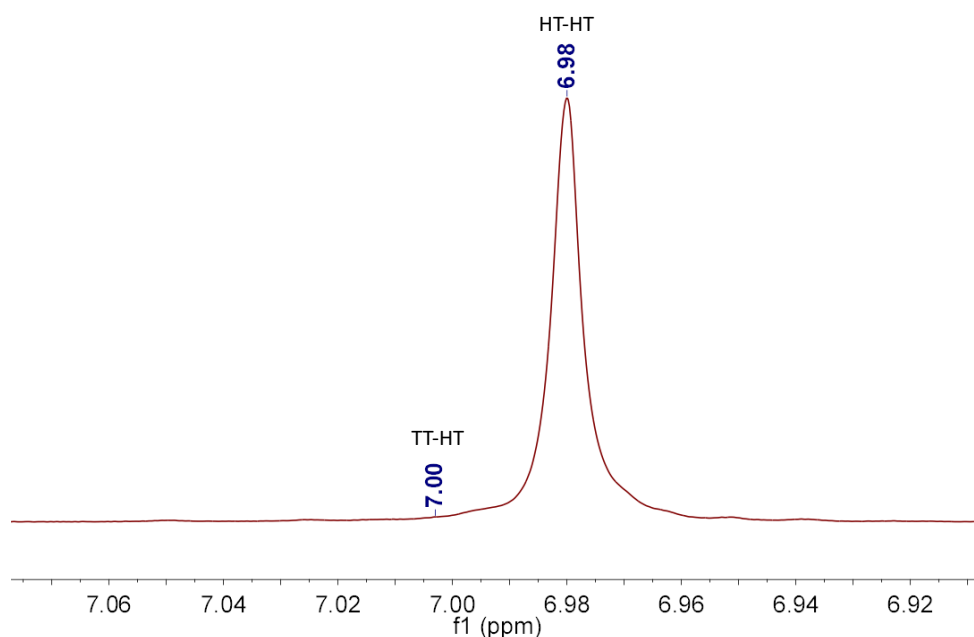


Figure 2.3: Representative expanded ^1H -NMR spectrum of a synthesized P3HT (5,000 g/mol) indicating high regioregularity.

In ^1H NMR spectrum, peak appearing at $\delta \sim 2.80$ ppm belongs to the protons (b) of α -carbon along the chain (HT-HT coupled) of P3HT whereas, the protons of HH arrangement resonate between $\delta \sim 2.5$ to 2.58 ppm.⁶ Considering the integration of protons (b) to be unit 1, the relative integration of protons belonging to HH regiodefect can be estimated. The percent regioregularity (%RR) in this work for defined molecular weight P3HT was calculated using Equation 2.1:

$$\%RR = \frac{\text{integrals of protons (b)}}{\text{integrals of \{protons (b) + protons of HH regio defect\}}} \times 100 \quad (\text{Eq. 2.1})$$

A representative ^1H NMR spectrum of 5,000 g/mol P3HT (Figure 2.4) is shown below indicating 98% regioregular P3HT.

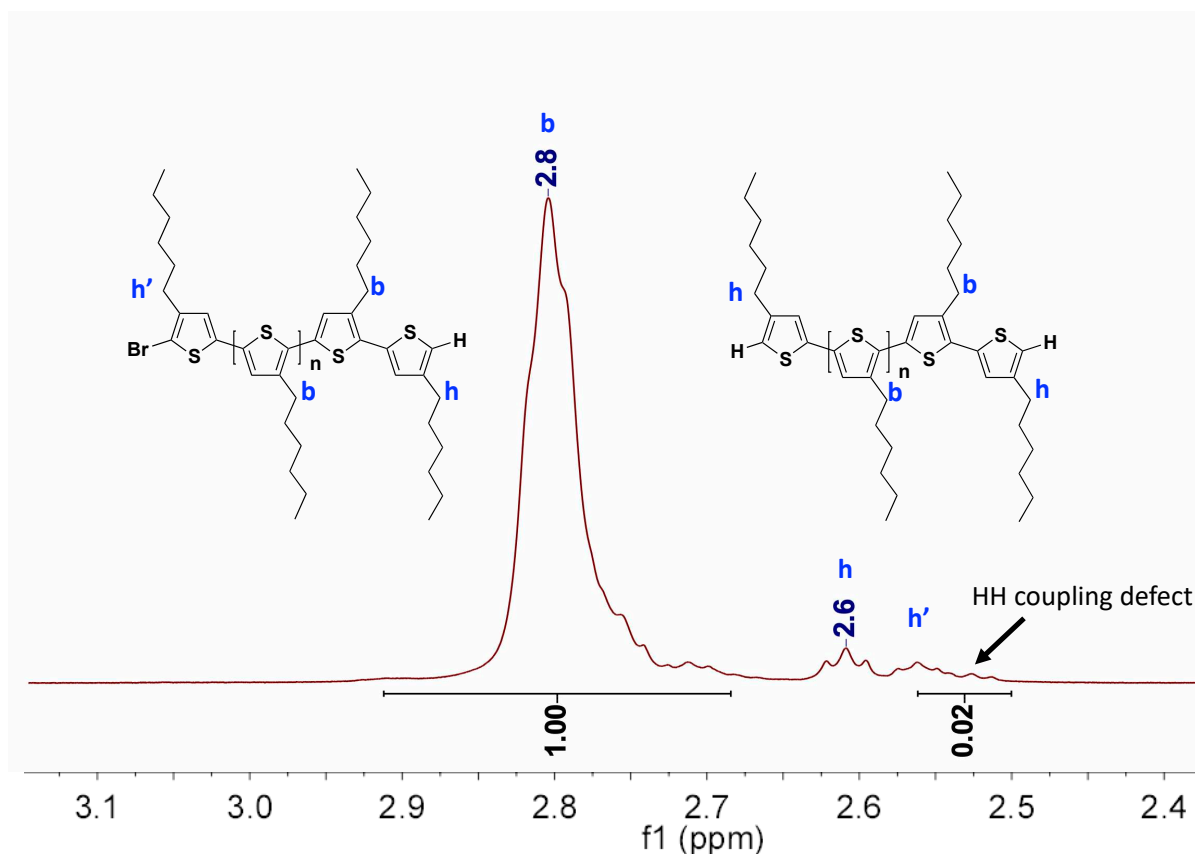


Figure 2.4: An expanded ¹H-NMR spectrum of same P3HT (5,000 g/mol) on a scale of 2.25 to 3.16 ppm indicating 98% regioselectivity.

2.2.2 Photophysical properties of P3HT

The optical properties of synthesized defined molecular weight P3HT polymers were studied through UV-Vis spectroscopy (see experimental section for detailed procedure). In general, regioregular P3HT in a chloroform solution shows absorption maxima at 454 nm whereas, in case of regiorandom P3HT, the peak maxima are blue shifted to 420 nm.^{2, 15, 17} The UV-Vis spectra of P3HT samples (5,000 to 28,000 g/mol) in chloroform solution (Figure 2.5A) exhibited a broad absorption band with peak maxima at 454 nm. The sample preparation for UV measurements is given in experimental section. The thin film spectra of regioregular P3HT samples showed a bathochromic or red shift compared to solution spectra and also exhibited vibronic shoulders in low-energy part of spectrum. This red shift in film absorption spectra is mainly attributed to π -stacked aggregates which results in increased planarity of P3HT

molecules with extended conjugation.⁴ The vibronic features at 610 nm in thin film absorption spectra (Figure 2.5B) for defined molecular weight P3HTs are due to increased crystallinity and $\pi - \pi$ stacking.

These synthesized polymers of well-defined molecular weights (5,000 to 28,000 g/mol) were used to examine the effect of polymer length on nanoparticle formation which will be discussed in Chapter 3.

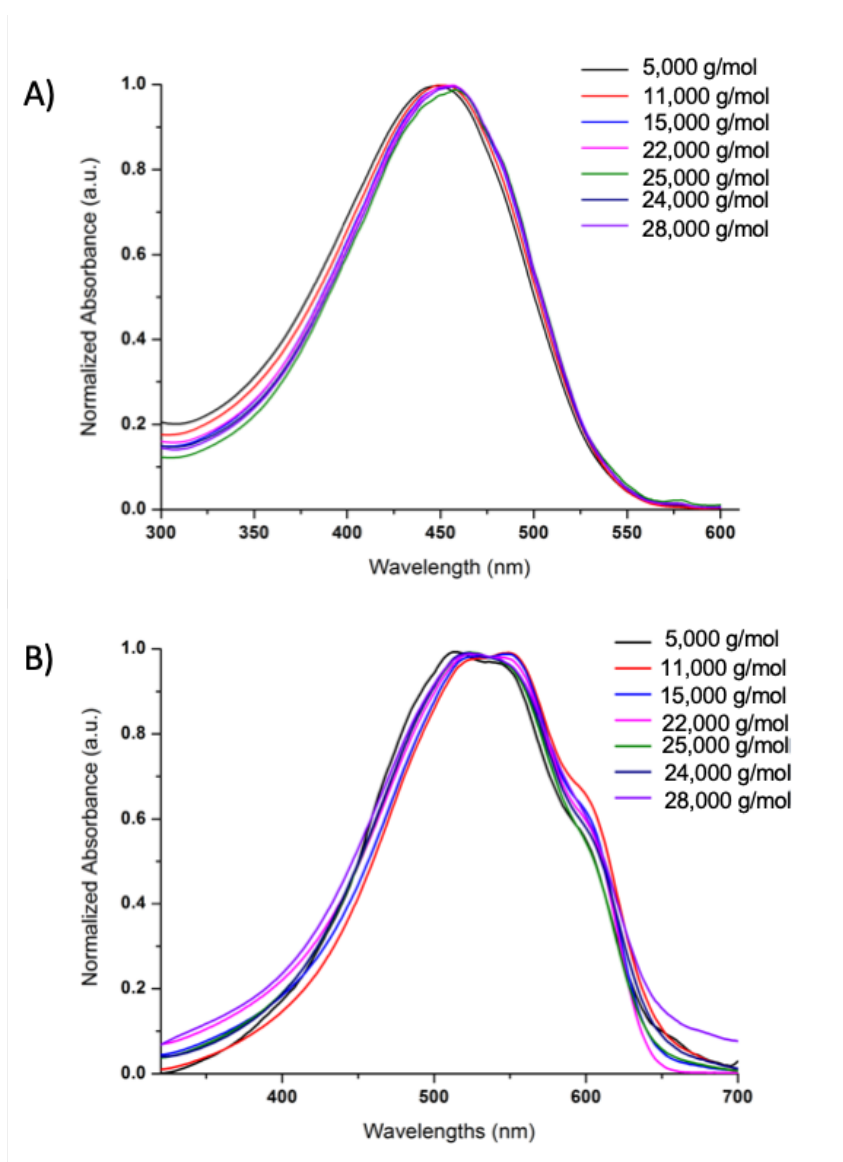


Figure 2.5: UV-Vis spectra of various molecular weights P3HT in A) chloroform solution B) as-cast film

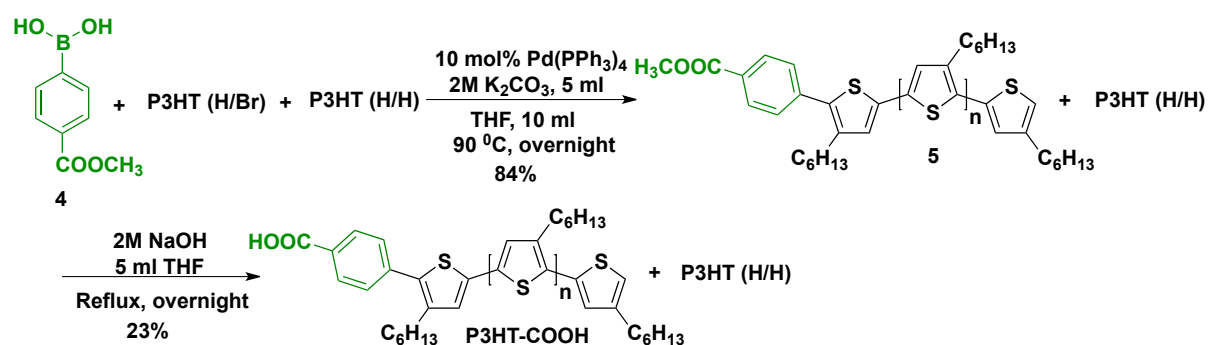
2.3 Suzuki coupling for synthesizing end-capped P3HT: P3HT-COOH and P3HT-Py

Post-polymerization modification of polymers is considered as a powerful strategy for end-group modification of polymer precursors with various functionalities. The Suzuki coupling reaction, which forms new carbon–carbon (C–C) bonds, has shown high efficiency in post-functionalization of precursor polymers.¹⁸ Li et al. reported that poly(3-bromo-4-hexylthiophene) was conveniently end-capped via a Suzuki coupling reaction with high efficiency (>99%) with respect to the Heck coupling reaction (29–51%).¹⁹ In this study, end-capped P3HT with molecular weight of 5000 g/mol were targeted. It was anticipated that a short polymer chain would ease of characterization especially the end-group verification. The P3HT polymer of 5000 g/mol was end-capped by coupling with compound **4** and **6** to obtain P3HT-COOCH₃ and P3HT-Py respectively using Suzuki coupling conditions (Scheme 6 and Scheme 7).

Synthesis of P3HT-COOH

The synthesis of benzoic acid end-capped P3HT (P3HT-COOH) through Suzuki coupling is shown in Scheme 6. It is a palladium catalyzed cross coupling between organoboronic acid (4-methylester of phenyl boronic acid, compound **4**) and halide (P3HT with Br end). The boronic acid was used in excess to attain quantitative conversion of P3HT (Br/H) to P3HT-COOCH₃, however, any P3HT (H/H) remains unreacted. Compound **5** was subjected to preliminary purification steps- 1) liquid-liquid extraction of polymer by washing thoroughly with water to get rid of unwanted salts, 2) filtering through a silica plug to get rid of excess Pd catalyst, and 3) Soxhlet extraction using acetone and petroleum ether to remove oligomers, and chloroform to collect the P3HT-COOCH₃ polymer. After performing basic purification, compound **5** was subjected to base hydrolysis (using 2M NaOH) to obtain the P3HT-COOH. Since P3HT (H/H) is inevitably formed during the polymerization reaction, it is important to remove P3HT (H/H)

to allow accurate quantification of the amount of P3HT-COOH being added for nanoparticle stabilization. Therefore, the polymer was dry loaded onto a basic alumina plug and chromatographed using chloroform as eluent. The P3HT (H/H) was eluted completely with the solvent front while P3HT-COOH stuck to the alumina and could be recovered by elution using a combination of 10% acetic acid, 10% methanol and chloroform (Figure 2.6). The purity of the P3HT-COOH is verified through ^1H NMR spectroscopy as discussed in later section.



Scheme 6: Synthesis of P3HT-COOH using Suzuki coupling conditions

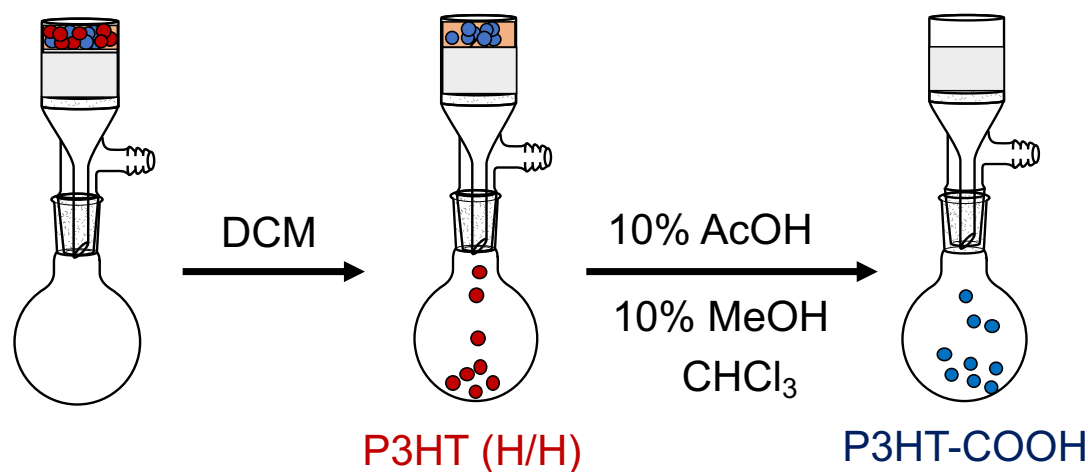
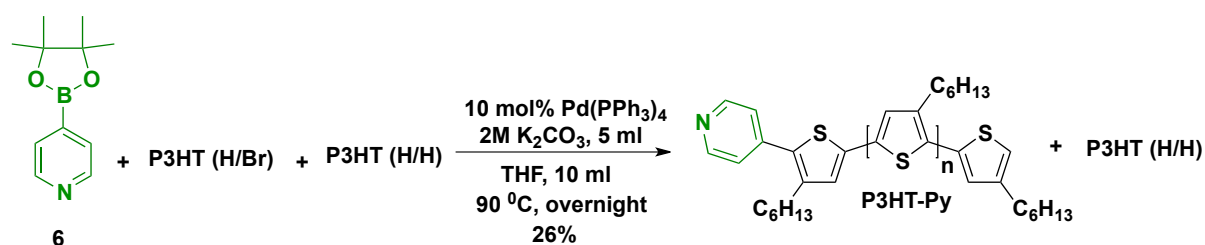


Figure 2.6: Polarity dependent purification of P3HT-COOH to remove P3HT (H/H).

Synthesis of P3HT-Py

Scheme 7 depicts the synthesis of pyridine end-capped P3HT (P3HT-Py). Pyridine boronic acid pinacol ester **6** was used in excess to couple with P3HT (Br/H) in order to maximize the coupling yield. The preliminary purification of polymer involved 1) liquid-liquid extraction of

polymer by washing it thoroughly with water, 2) filtering polymer solution through a silica plug and 3) performing Soxhlet extraction using acetone and petroleum ether to remove oligomers and chloroform to collect polymer. After performing preliminary purification on polymer mixture, the efforts were made to remove unwanted P3HT (H/H). To do so, the polymer was reacted with *p*-toluene sulfonic acid to generate the pyridinium salt of P3HT (P3HT-PyH⁺). Thereafter, the resultant polymer was dry loaded on a silica column and eluted with chloroform. It was expected that the P3HT-PyH⁺ would stick on silica and P3HT (H/H) would elute with the dichloromethane (DCM) solvent front due to the difference in polarities (Figure 2.7).



Scheme 7: Synthesis of P3HT-Py using Suzuki coupling conditions

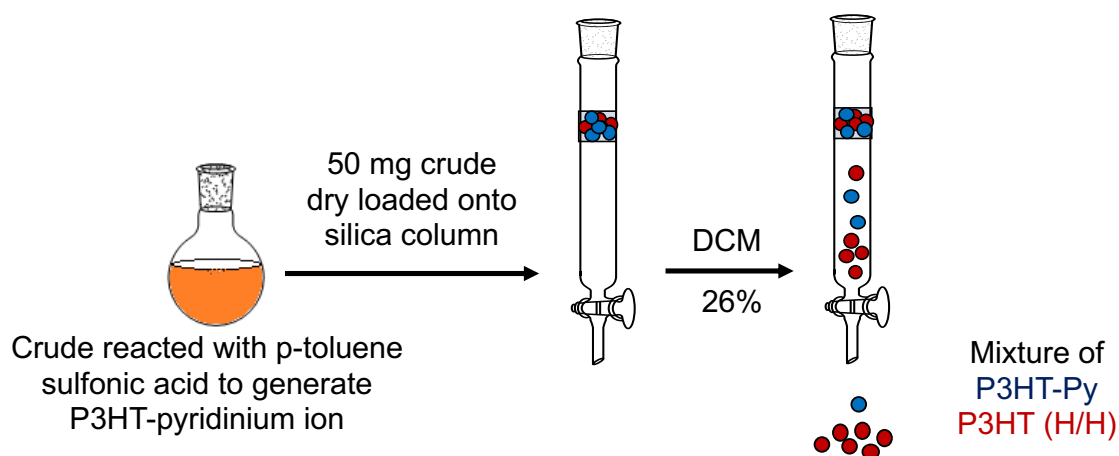


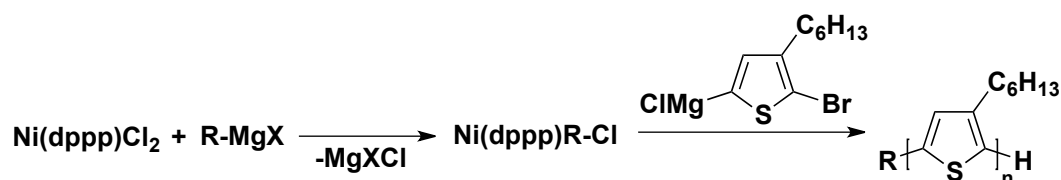
Figure 2.7: Polarity dependent purification of P3HT-Py through flash chromatography using silica as a stationary phase and DCM as a mobile phase.

However, this idea of removing P3HT (H/H) did not work as expected and most of the fractions were the combination of P3HT-PyH⁺ and P3HT (H/H). This may be attributed to the pyridine

being a small functional group at the end of a long P3HT chain creating only slight difference in P3HT-PyH⁺ and P3HT (H/H) polarities. Multiple cycles of purification were required, purifying 50 mg of polymer mixture at a time, while recovering only 25% to 30% of the required polymer in each cycle. The purity of the P3HT-Py is verified through ¹H NMR spectroscopy and mass spectrometry as discussed in later section.

2.4 Synthesis of P3HT-TEG through external initiation of polymerization using GRIM method

External initiation of polymerization can be achieved by using McCullough's approach of GRIM⁷⁻¹¹ (Scheme 8). A nickel initiator is produced ex situ via monotransmetalation of Ni(dppp)Cl₂ catalyst with an appropriate Grignard reagent (R-MgX). Addition of nickel initiator to regioisomer **3** results in P3HT end-capped with desired end functionality by choosing an appropriate R group of Grignard reagent.

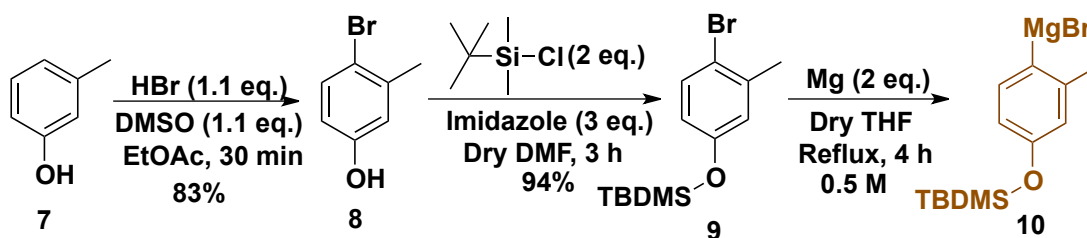


Scheme 8: General route to initiate polymerization using GRIM method

Synthesis of P3HT-TEG

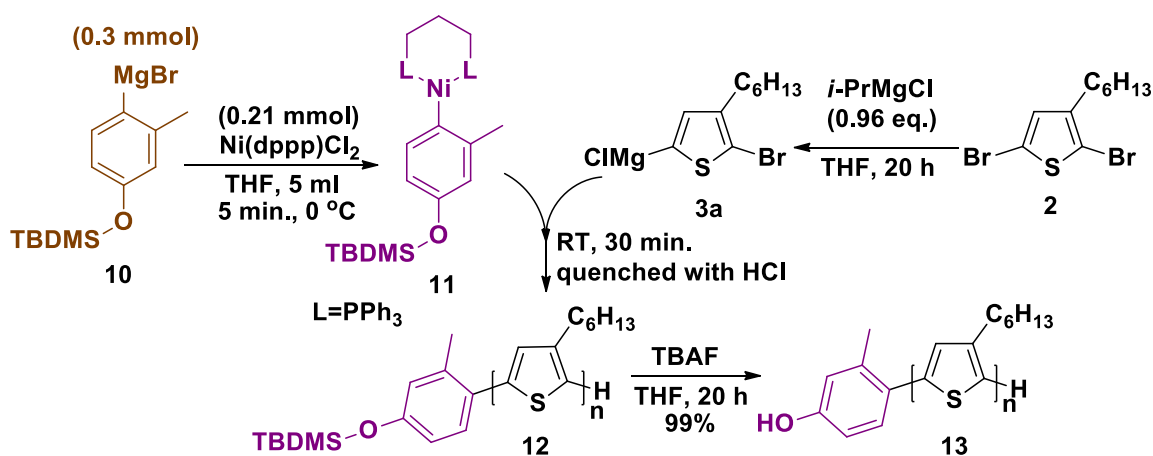
A Grignard reagent **10** (0.5 M) was prepared from silyl protected 4-bromo-*m*-cresol **9** (Scheme 9). The methyl group is easily distinguishable in the ¹H-NMR of the resulting initiated P3HT. To start with the synthesis of Grignard reagent **10**, compound **7** was brominated using hydrobromic acid (HBr, 48 wt.% in H₂O) as a brominating agent to obtain brominated *m*-cresol **8**. Next, the phenol of compound **8** was protected with tert-butyldimethylsilyl chloride (TBDMS-Cl) to synthesize compound **9**. Protection of phenol at this stage is important due to

sensitivity of phenol towards magnesium (Mg) metal which was used in next step to synthesize Grignard reagent **10**.



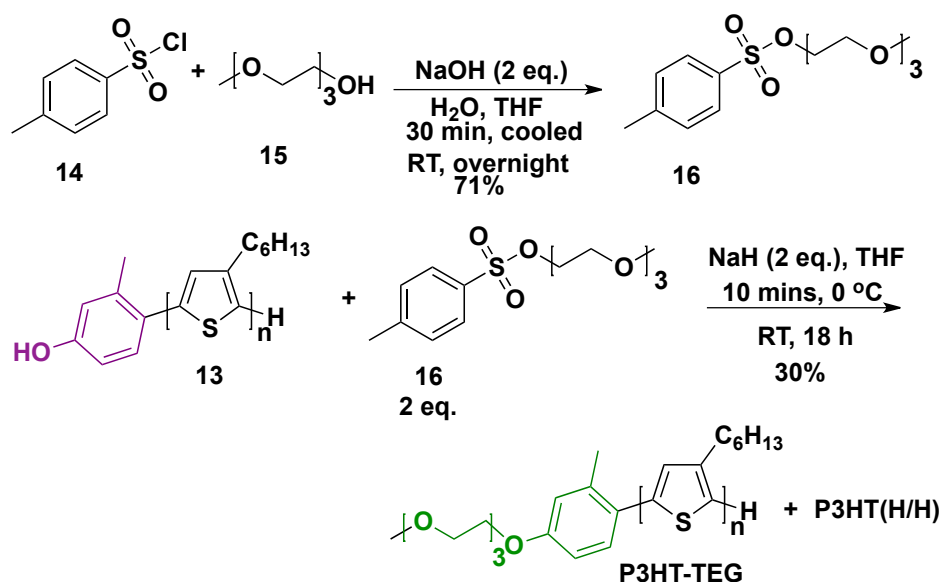
Scheme 9: Synthesis of Grignard reagent to be used for preparing nickel initiator.

Previously synthesized Grignard reagent **10** was added to a solution of Ni(dppp)Cl₂ dissolved in THF, which underwent monotransmetalation to produce nickel initiator **11** (Scheme 10). The polymerization was initiated by adding nickel initiator to regioisomer **3a** which resulted in formation of silyl protected phenol end-capped P3HT **12**. Compound **12** was reacted with tetrabutylammonium fluoride (TBAF) to obtain active phenol end-capped P3HT **14** by deprotecting the alcohol. The resulting polymer was purified by Soxhlet extraction using acetone and petroleum ether as solvents.



Scheme 10: Synthesis of initiated P3HT along with deprotection of phenol to obtain an active phenol end-capped P3HT

The alkylation of compound **13** was performed using with TEG-tosylate **16** to synthesize P3HT-TEG (Scheme 11). Compound **16** was synthesized by reacting compound **14** and **15** under basic conditions.



Scheme 11: Synthesis of P3HT-TEG via alkylation of active phenol end-P3HT with TEG-tosylate.

An excess of compound **16** was used to alkylate compound **13** under strong basic condition of sodium hydride (NaH) to obtain P3HT-TEG. The resultant polymer P3HT-TEG was purified using flash chromatography technique to remove P3HT (H/H).

Note that, TEG was added after the polymerization and not as a part of initiator. Although efforts were made to synthesize Grignard reagent of TEG-monomethyl ether substituted bromo benzene, but they failed possibly due to the sensitivity of magnesium metal towards hydrophilic ethylene glycol chain.

2.5 Structural characterization of end-capped polymers

2.5.1 Gel permeation chromatography of end-capped P3HT polymers

The M_n values obtained from GPC (Table 2.2) for end-capped polymers confirmed that all synthesized polymers have 30 repeating units of thiophene monomer. The observed variability in molecular weights of P3HT-Py and P3HT-COOH with respect to P3HT could be attributed to the chemical interactions between the packing material of GPC columns and the end-groups of P3HT molecules.

Table 2.2: Molecular weight of end-capped P3HT calculated from GPC and ^1H NMR. P3HT-COOH and P3HT-Py were synthesized using same batch of P3HT whereas, P3HT-TEG was synthesized through external initiation of polymerization.

Samples	Theoretical M_n (g/mol)	Catalyst/ monomer	M_n (g/mol) (GPC)	$\bar{D}$	DP_n (^1H NMR)	M_n (g/mol) (^1H NMR)
P3HT	5,000	1/30	5,200	1.2	28	4,600
P3HT-COOH	5,000	1/30	5,000	1.4	29	4,800
P3HT-Py	5,000	1/30	5,600	1.3	28	4,600
P3HT-TEG	5,000	1/30	4,800	1.3	24	3,900

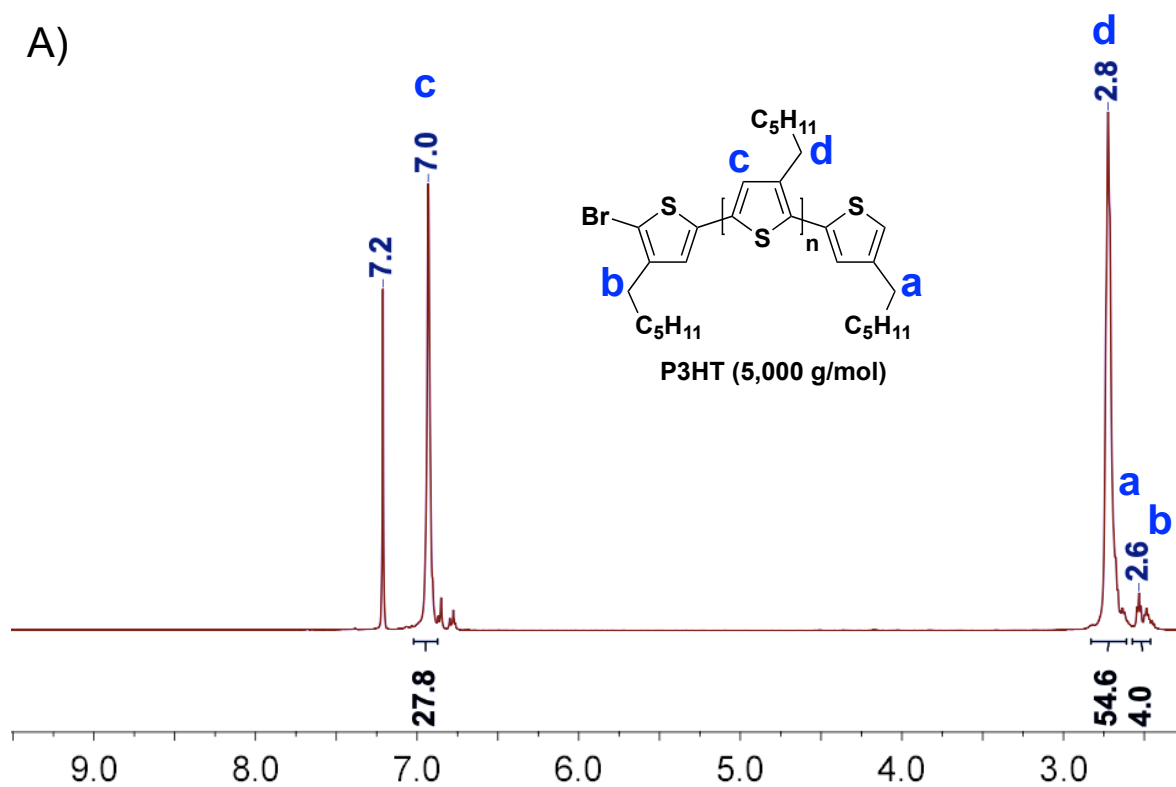
2.5.2 Determination of molecular weight and purity of end-capped P3HT polymer using ^1H NMR spectroscopy

The ^1H NMR spectrum (2.4 to 9.5 ppm range) of end-capped P3HT (P3HT-COOCH₃, P3HT-COOH and P3HT-Py) were compared to P3HT (5,000 g/mol) as they were synthesized using same batch of P3HT polymer.

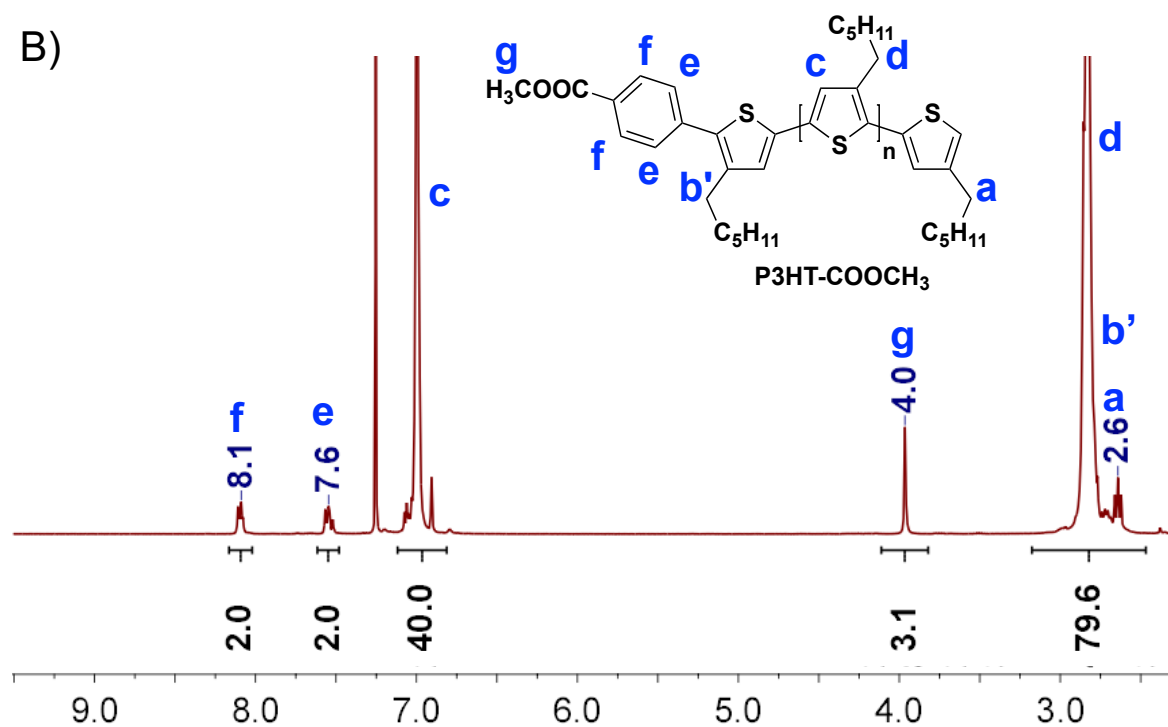
The procedure to determine the molecular weight of P3HT (5,000 g/mol) from ^1H NMR spectrum has been presented in section 2.2.1.2. It can be recalled that peak resonances of $\alpha\text{-CH}_2$ protons was set to unit 4 which represents an ideal case of P3HT with 100% H/Br end. Although there would be some amount of H/H end present in the synthesized P3HT, but its quantification from ^1H NMR of P3HT is difficult. The presence of P3HT (H/H) can be quantified by analyzing ^1H NMR of end-capped P3HTs as discussed in subsequent paragraphs.

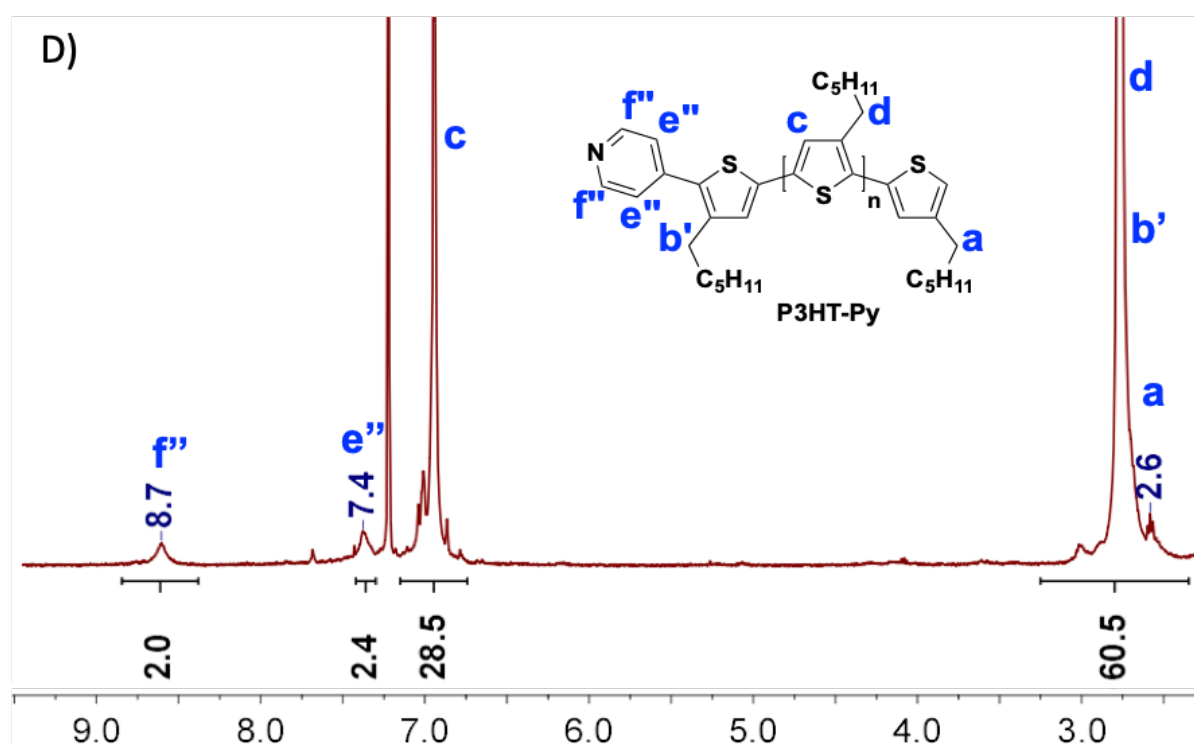
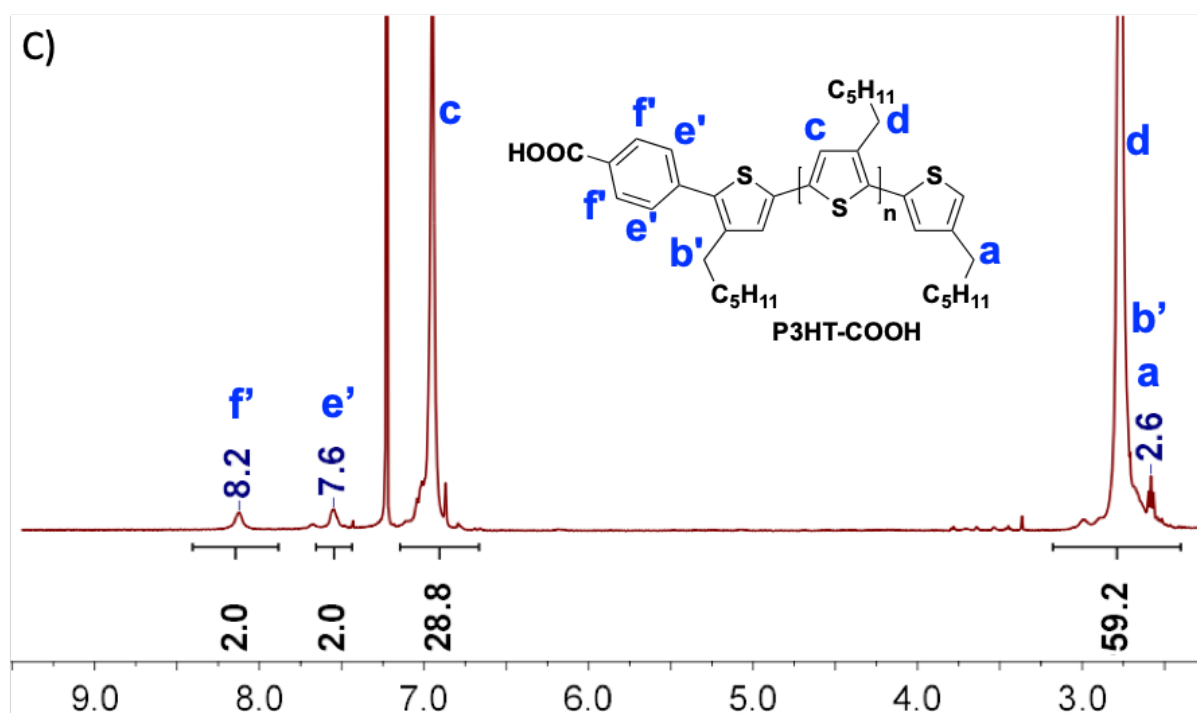
The appearance of methyl ester proton (g) peak at 4 ppm and benzoic ester aromatic proton doublets (e and f) at 7.6 and 8.1 ppm in ^1H NMR spectrum of P3HT-COOCH₃ (Figure 2.8B) confirms the formation of P3HT-COOCH₃. The relative integration of aromatic thiophene protons (c) with respect to the two doublets (e and f) of methyl benzoate group was found to be 40. The difference in DP_n before (Figure 2.8A) and after end-capping of P3HT with benzoic ester group (Figure 2.8B) confirms the presence of ~ 30% P3HT(H/H). P3HT-COOCH₃ was subjected to hydrolysis to synthesize P3HT-COOH. ^1H NMR spectrum of P3HT-COOH (Figure 2.8C) shows the disappearance of methyl ester peak of benzoic ester confirming the complete hydrolysis of P3HT-COOCH₃. It can be recalled from section 2.4 that P3HT-COOH was subjected to polarity dependent purification to remove P3HT (H/H). Therefore, the relative integration of aromatic thiophene protons (c) of purified P3HT-COOH with respect to the doublets of benzoate protons (e' and f') was found to be 29 (DP_n=29) (Figure 2.8C). This integration suggests ~97% pure P3HT-COOH.

A)



B)





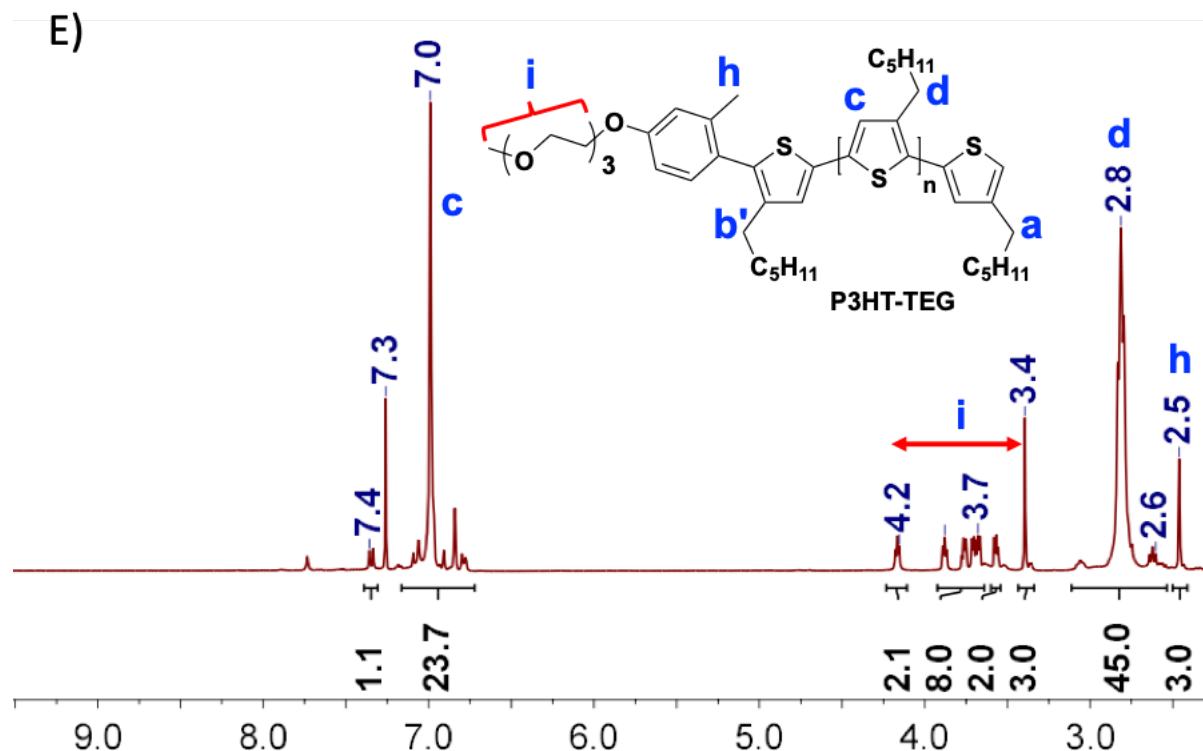


Figure 2.8: ^1H -NMR spectra of pure P3HT and end-capped P3HTs on a scale from 2.4 to 9.5 ppm presenting A) P3HT (5,000 g/mol), B) P3HT-COOCH₃, C) P3HT-COOH, D) P3HT-Py and E) P3HT-TEG.

In case of P3HT-Py (Figure 2.8D), the integration of two doublets (*e''* and *f''*) of pyridine at 7.4 and 8.7 ppm were normalized to 2. The relative integration for aromatic thiophene protons (*c*) was estimated to be 28 ($\text{DP}_n=28$). This confirmed the purification success of P3HT-Py (99% pure) from P3HT (H/H). Lastly, the ^1H NMR spectrum of P3HT-TEG was analyzed (Figure 2.8E). The integration of methyl proton (*h*) was set to the value 3 and consequently the presence of 15 protons (*i*) of TEG methylene groups in alkyl region (3.3-5 ppm) confirms the formation P3HT-TEG. The relative integration of aromatic thiophene protons (*c*) at 7.0 ppm is ~ 24 ($\text{DP}_n=24$) with respect to (*h*) protons. The molecular weights of end-capped polymers were calculated by multiplying DP_n with molecular mass of monomer unit which is 166.3 g/mol in this case.

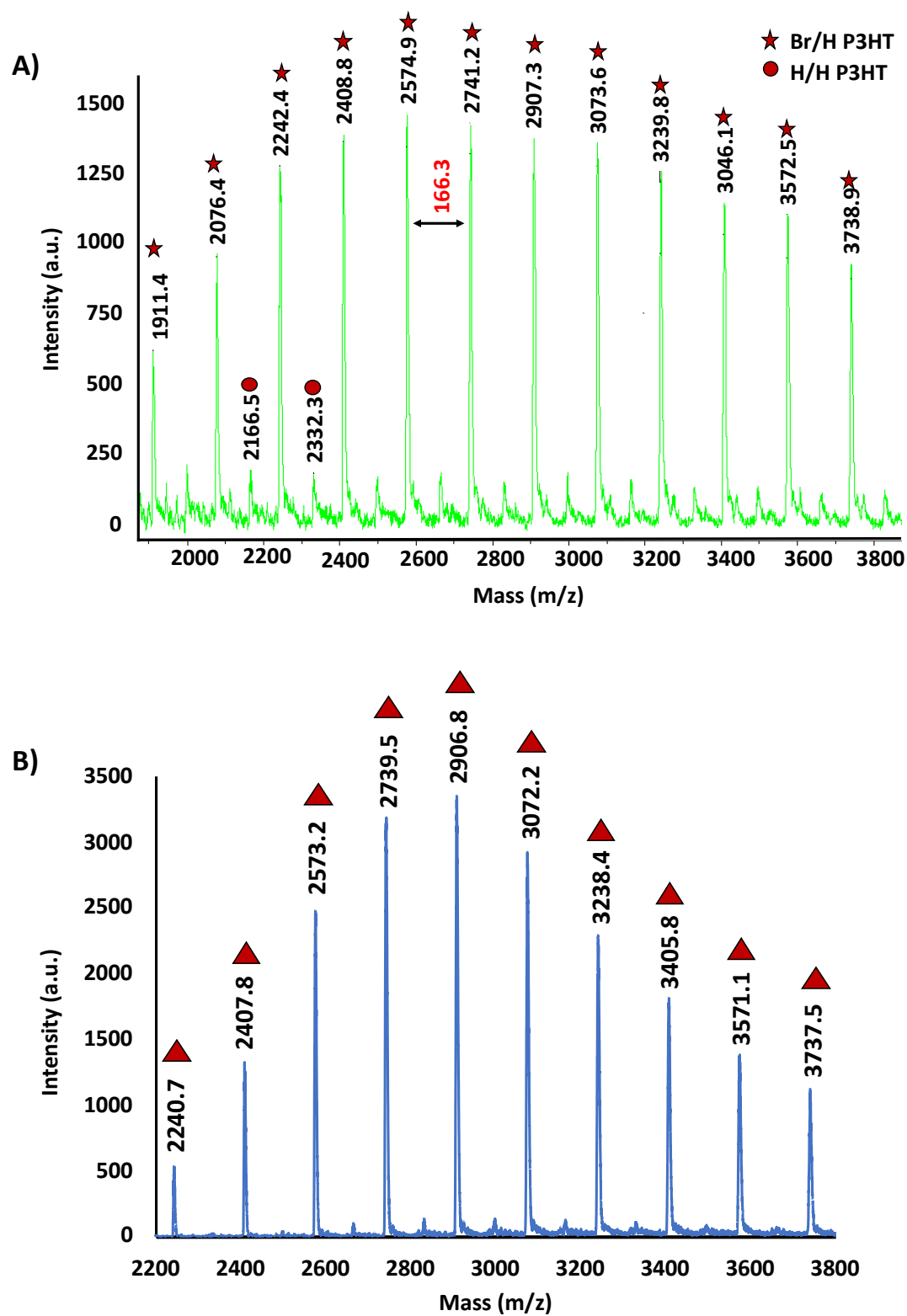
Note that P3HT-Py and P3HT-COOH were synthesized using same batch of P3HT polymer (5,000 g/mol), therefore their M_n determined from ^1H NMR matches closely (Table 2.2). However, the M_n obtained for P3HT-TEG is not comparable with the M_n of other two end-capped P3HTs as P3HT-TEG was synthesized from external initiation of polymerization. The molecular weights obtained from GPC and ^1H NMR are marginally different which is due to the same reason mentioned in section 2.2.1.1.

2.5.3 Matrix assisted laser desorption ionization- time of flight mass spectrometer analysis of synthesized polymers

Matrix assisted laser desorption ionization- time of flight mass spectrometer (MALDI-TOF MS) helps in determining the end-group functionalities of polymers. The MALDI-TOF spectrum of P3HT (5,000 g/mol) shows two different end-groups Br/H and H/H which is expected from ideal GRIM polymerization (Figure 2.9A).

In case of end-capped polymers, the end-group composition can be calculated knowing the repeat unit and end-group molar masses. After confirming the separation of P3HT (H/H) from end-capped P3HTs through ^1H NMR spectroscopy, these polymers were further analyzed through MALDI-TOF spectroscopy. For end-capped P3HT, peaks in a MALDI-TOF spectrum correspond to the sum of molar masses (g/mol) of monomer repeat unit ($166.3n$) + end-group + 1 hydrogen atom. For example, the m/z for purified P3HT-Py is evaluated as $166.3 \times 17 + 78.09 + 1.08 = 2906.3$ for one of the peaks (Figure 2.9B). Similarly, the m/z evaluation for P3HT-COOH and P3HT-TEG from MALDI-TOF spectra (Figure 2.9C and Figure 2.9D) confirmed the end-capping of P3HT with benzoic acid and TEG respectively. The M_n , M_w and D of polymers can be calculated by MALDI-TOF analysis using equations 2.5, 2.6 and 2.7 respectively. The intensity of each peak represents the number of polymer chains (N) at a particular molecular weight (M_i)². The M_n calculated for both P3HT (H/Br) and P3HT (H/H)

were approximately 2900 g/mol. For P3HT-COOH, P3HT-Py and P3HT-TEG, the M_n were estimated to be 4000 g/mol, 3000 g/mol and 2500 g/mol respectively.



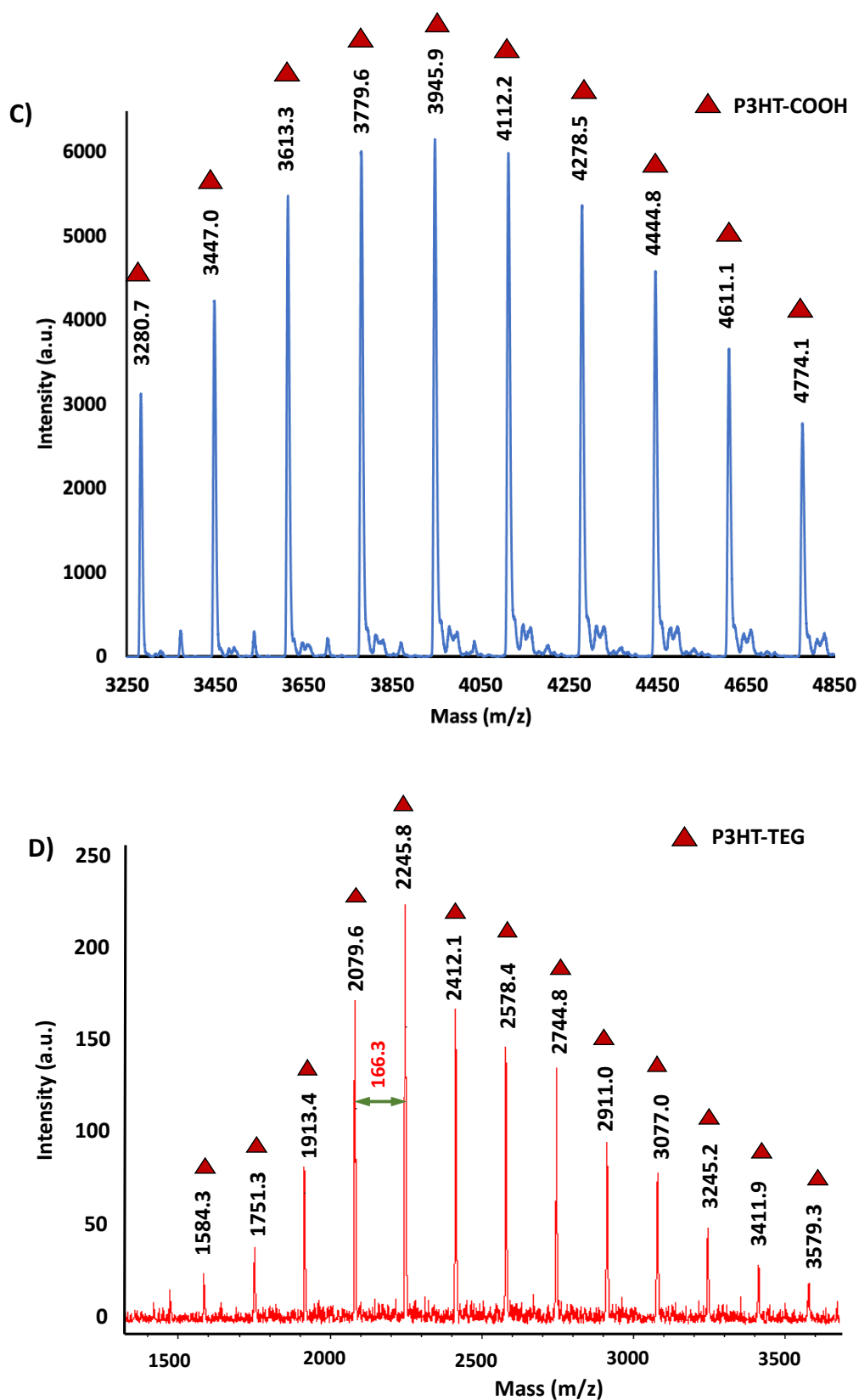


Figure 2.9: MALDI-TOF MS of A) P3HT with Br/H and H/H end-group B) pure P3HT-Py with Py/H end-group, and C) pure P3HT-COOH with COOH/H end group, and D) pure P3HT-TEG with TEG/H end-group

2.5.4 Differential scanning calorimetry measurements of end-capped P3HT polymers

To support the notion that P3HT is a semi-crystalline thermoplastic polymer, thermal properties of end-capped P3HTs vs. P3HT (5,000 g/mol) were determined using a differential scanning calorimetry (DSC) instrument. The analysis was performed under nitrogen atmosphere in the temperature range between 25 °C and 300 °C with a scan rate of 10 °C /min. The 5000 g/mol P3HT was scanned between 25 °C to 250 °C. The DSC data for P3HT and the end-capped P3HT is reported in the experimental section. The melting temperature for these polymers was obtained between 210 °C to 220 °C and the crystallization temperature at 170 °C to 185 °C. The exothermal peak observed confirms that polymers are semi-crystalline in nature, and agrees with the literature.²⁰ It is important to note here that end-capped P3HTs will be used as additives for P3HT:ICBA nanoparticle stabilization and the data matches closely to the bulk P3HT of 5,000 g/mol.

2.5.5 Photophysical and electrochemical properties of end-capped P3HT polymers

The photophysical properties of P3HT (5,000 g/mol) and end-capped P3HTs were studied through UV-Vis spectroscopy. The details regarding sample preparation is given in experimental section. All synthesized polymers exhibited absorption maxima at around 450 nm in solution. The absorption maxima of the as cast films of these polymers showed bathochromic shifts compared to solution spectra (Figure 2.10A and Figure 2.10B). This observation is in agreement with the literature.⁴ The red shift in the wavelength is attributed to the π -stacked aggregates in thin film. The absorption spectrum of P3HT-TEG exhibited less pronounced aggregation (blue-shifted) compared to absorption spectrum of P3HT as-cast film. In fact, the vibronic shoulders in P3HT-TEG spectrum were not well developed indicating a decrease in π -stacked aggregate interaction (Figure 2.10B).

Table 2.3: Wavelengths corresponding to maximum absorption and energy band gap calculated from UV-Vis and CV measurements for synthesized polymers

Polymers (5,000 g/mol)	UV-Vis		CV		
	λ max (nm)		E _g (opt)	HOMO	E _g (CV) (eV)
	Solution	Thin film	(eV)	(eV)	
P3HT-TEG	444	516	1.8	-5.2	2.3
P3HT-Py	452	549	1.8	-5.1	2.3
P3HT-COOH	450	528	1.8	-5.2	2.3
P3HT (5,000 g/mol)	449	553	1.8	-5.2	2.3

The electrochemical properties of end-capped polymers were studied through cyclic voltammetry (CV). The HOMO and LUMO energy levels calculated from the values of oxidation potential onset E_{onset}^{ox} and reduction potential onset E_{onset}^{red} which are calibrated by the redox couple of ferrocene/ferrocenium (Fc/Fc⁺) (5.1 eV below the vacuum level) according to the following Equations 2.2 and 2.3²¹:

$$E(\text{HOMO}) = -((E_{onset}^{ox} - E_{Fc/Fc^+}^{ox}) + 5.1) \text{ [eV]} \quad (Eq. 2.2)$$

$$E(\text{LUMO}) = -((E_{onset}^{red} - E_{Fc/Fc^+}^{ox}) + 5.1) \text{ [eV]} \quad (Eq. 2.3)$$

The optical energy band gap was calculated using Equation 2.4:

$$E_g = |E(\text{HOMO}) - E(\text{LUMO})| \quad (Eq. 2.4)$$

The $(E_{onset}^{ox} - E_{Fc/Fc^+}^{ox})$ for P3HT, P3HT-Py, P3HT-COOH and P3HT-TEG films was estimated to be 0.09, 0.01, 0.1 and 0.07 V respectively. The LUMO value was taken from literature as 2.84 eV.⁴ The energy levels of end-capped polymers were estimated from cyclic voltammetry

(CV) (Table 2.3). The HOMO level of the end-capped P3HT materials were all very similar to P3HT suggesting that the end-groups have little effect on the electronic properties of the parent polymer.

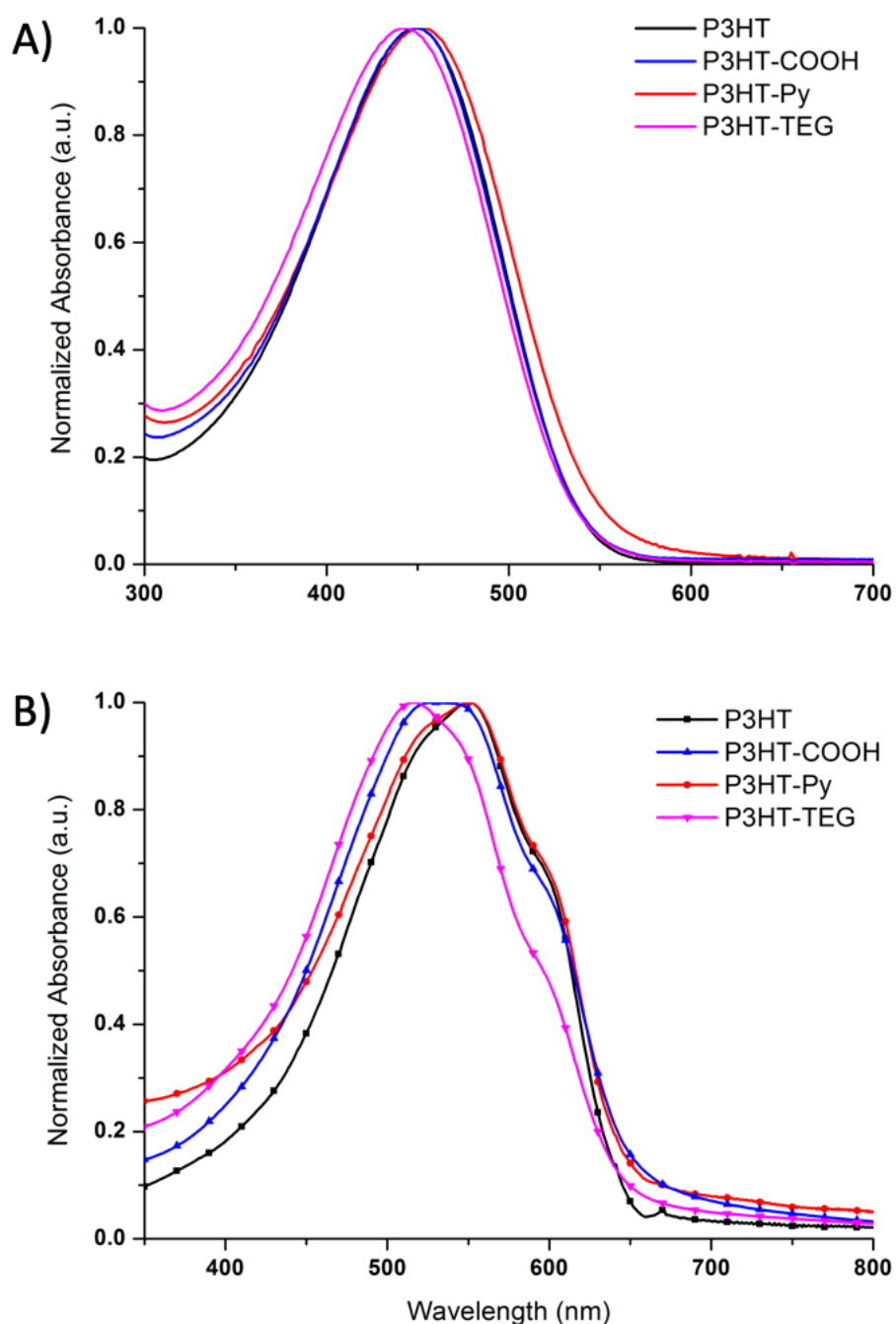


Figure 2.10: UV-Vis spectra of P3HT-COOH, P3HT-Py, P3HT-TEG in comparison with pure P3HT A) solution in chloroform B) as-cast film

2.6 Summary

This chapter discussed the synthesis of P3HT polymer of defined molecular weight (expected range: 5,000 g/mol to 40,000 g/mol). The maximum molecular weight achieved using McCullough approach of GRIM was 28,000 g/mol as estimated by GPC while the target was 40,000 g/mol. GRIM resulted in the synthesis of polymers with high regioregularity and low *D*. The end-capped polymers, P3HT-COOH and P3HT-Py, were synthesized using Suzuki cross-coupling to bromine terminated P3HT (5,000 g/mol) while P3HT-TEG was synthesized through external initiation of polymerization using GRIM. All end-capped polymers were purified to obtain high end-group fidelity as verified by ¹H NMR spectroscopy and MALDI-TOF mass spectrometry analysis.

Next chapter discusses the use of defined molecular weight P3HT polymers to study the impact of polymer length on nanoparticle formulation. The end-capped polymers P3HT-COOH, P3HT-Py and P3HT-TEG were designed to behave as an active surfactant to stabilize nanoparticle dispersions which will be discussed in Chapter 3.

2.7 Materials and methods

Unless otherwise noted, all materials were reagent grade and used as received without further purification. Anhydrous tetrahydrofuran, toluene and dichloromethane were provided by a Pure Processing Technology glass contour solvent purification system.

2.7.1 Gel permeation chromatography

Gel permeation chromatography (GPC) was performed at 25 °C for determining the relative size of polymers using solvent/sample module equipped with a Viscotek VE3580 refractive index detector and a Gilson 159 multiwavelength UV-Vis detector. With the Viscotek, polymers

were passed through three 30 cm 5 μm PL gel mixed C columns and one 30 cm 3 μm PL gel mixed E column in toluene at a flow rate of 0.6 mL/min.

GPC works on basic principle in which different size polymers have different retention times in the column. Polymer with high molecular weight elutes faster than lower molecular weight polymer because small chain polymers have more interactions with the pores of the beads in the column. GPC analysis of polymers is normally reported with three values; number average molecular weight (M_n), weight average molecular weight (M_w) and dispersity ($\mathcal{D}$). The M_n is an average molecular weight of the polymer which can be mathematically expressed as shown in Equation 2.5.

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad (\text{Eq. 2.5})$$

Where, N_i is the number of chains of molecular weight M_i , that is the molecular weight of N_i^{th} polymeric chain. The M_w considers the molecular weight of the polymeric chain which contributes to the molecular weight average. Therefore, longer chains of polymer contribute to more value to M_w as described by Equation 2.6.

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (\text{Eq. 2.6})$$

The broadness of a molecular weight distribution of polymer is defined by $\mathcal{D}$ and can be calculated as described in Equation 2.7.

$$\mathcal{D} = \frac{M_w}{M_n} \quad (\text{Eq. 2.7})$$

A polymer can be considered as monodispersed when all the chain lengths are equal, $M_w/M_n=1$. A step growth polymerization gives $\bar{D}$ around or higher than 2.0, however, a chain growth yields a value between 1.0 to 2.0.

Polymer samples of concentration 2 mg/mL in toluene were run using GPC to determine molecular weights of synthesized polymers relative to narrow polystyrene reference standards.

2.7.2 Nuclear magnetic resonance spectroscopy

Agilent MR400 (400 MHz) or a Varian INOVA 600 (600 MHz) were used to get ^1H or ^{13}C NMR spectra of synthesized polymers. All NMR data was referenced to the chloroform signal and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublets of doublets, m = multiplet, br = broad).

2.7.3 Matrix assisted laser desorption ionization- time of flight mass spectrometer

Matrix assisted laser desorption ionization- time of flight mass spectrometer (MALDI-TOF MS) is a handy tool to analyze polymers, biomolecules and other macromolecules which are vulnerable to fragmentation on ionization by conventional techniques.^{3, 22-24} It involves a matrix which consists of crystalline molecules that transfers the energy from incident laser light to sample molecules required for ionization. Based on the energy required for ionization of samples, different matrices can be employed. In this work, MALDI experiments were performed on Bruker microflex instrument, a very diluted sample in chloroform was spotted on the MALDI plate with trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix to obtain the spectrum.

2.7.4 UV-vis spectroscopy

UV-Vis spectroscopy is type of absorption spectroscopy that uses electromagnetic radiation in ultra-violet (200-400 nm) and visible (400-800 nm) regions.²⁵ Absorption of the ultra-violet

radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the ultra-violet radiation that is absorbed is equal to the energy difference between the ground state and higher energy states. Since this spectroscopy results in transition of electrons, it is also known as electronic spectroscopy. It commonly provides information about π -electron systems, aromatic compounds and conjugated non-bonding electron systems. The basic principle of any UV-Vis spectroscopy is derived from Beer-Lambert law.⁴⁰

To study the photophysical properties of synthesized polymers, absorption measurements were carried out on a JASCO V-670 spectrophotometer. The polymer solution was made in chloroform (50 $\mu\text{g/mL}$) to record absorption spectra in solution. To measure absorption of polymers in thin films, the films were deposited on cleaned microscope slides from 10 mg/mL solution of polymers in chloroform.

2.7.5 Electrochemical cyclic voltammetry

Frontier orbital energy levels of synthesized polymers were estimated by cyclic voltammetry (CV) technique using a potentiostat. The measurement was performed on a Solartron SI1287 and it includes three electrodes set up, a reference electrode (Ag/AgCl), a counter/auxiliary electrode (Pt) and a working electrode (glassy carbon). 0.1 M tetrabutylammonium hexafluorophosphate (0.1 M TBAPF₆) in acetonitrile was used as an electrolyte and ferrocene was used as an external reference. The polymer films were deposited from chloroform solution (1 mg/mL) on working electrode to perform CV. The measurements were done at a scan rate 50 mV/s

2.8 Detailed experiments to synthesize polymers

2.8.1 Synthesis of P3HT

Synthesis of 2,5 dibromo-3-hexylthiophene (Compound 2)²⁶

To a 500 mL oven-dried round bottom flask, under positive N₂ pressure, were added 3-hexylthiophene, compound **1** (15 g, 90 mmol, 1.00 eq.) and glacial acetic acid (150 mL). To this solution, NBS (37.5 g, 210 mmol, 2.3 eq.) was added portion-wise and the mixture was stirred overnight. The reaction was then washed with water and petroleum ether, and the organic layer was dried over anhydrous MgSO₄, and concentrated in vacuum. This crude oil was purified by Kugelrohr distillation to afford the title compound. Colorless oil. Yield 19.59 g, 67%. The reported data is consistent with the literature.²⁶

¹H-NMR (400 MHz; CDCl₃): δ 6.78 (s, 1H), 2.51 (t, J = 7.7 Hz, 2H), 1.58-1.50 (m, 2H), 1.36-1.26 (m, 6H), 0.89 (t, J = 6.7 Hz, 3H).

¹³C NMR (400 MHz; CDCl₃): δ 143.1, 131.1, 110.4, 108.1, 31.7, 29.70, 29.64, 28.9, 22.7, 14.2

Synthesis of P3HT¹²

In a dry Schlenk tube (100 mL), 2,5-dibromo-3-hexylthiophene, compound **2** (2 g, 6.1 mmol) was dissolved in THF (60 mL) and stirred under N₂. Isopropyl magnesium chloride (4.8 mL, 6.1 mmol) was added via syringe, and the mixture was stirred at room temperature for 20 h. After this, a variable amount of Ni(dppp)Cl₂ was added to the bromo-3-hexylthiophene Grignard mixture with respect to molecular weight of the desired polymer. The polymerization was then left for approximately 40 minutes at room temperature and quenched with 5 M HCl and precipitated in methanol. Yields have typically been between 60-80% depending on the success of the workup of the reaction. The polymer was filtered into an extraction thimble and then washed by Soxhlet extraction with methanol, acetone, hexanes, and chloroform. The polymer was isolated from the chloroform extraction. The reported data is consistent with the literature.¹²

¹H-NMR (400 MHz; CDCl₃): δ 7.0 (s, 1H), 2.81 (t, 2H), 1.75-1.68 (m, 2H), 1.45-1.34 (m, 6H), 0.94-0.90 (m, 3H).

GPC: M_n : 5,200 g/mol, M_w : 7,200 g/mol, M_z : 8,100 g/mol, D : 1.2

MS MALDI-TOF; m/z = 1911.4-3738.9 [Gaussian distribution differencing in mass of hexylthiophene monomer, $M \pm 166.3$]

2.8.2 Synthesis of P3HT-COOH

Synthesis of P3HT-COOCH₃

To a dry 100 mL Schlenk tube, 200 mg of P3HT (5000 g/mol, 0.04 mmol), Pd(PPh₃)₄ (10 mole%), 143.9 mg of 4-methoxycarbonylphenyl boronic acid, compound **4** (20 eq, 0.8 mmol) were added and degassed under nitrogen for 30 minutes. Meanwhile, THF and 2 M aq. K₂CO₃ were also degassed for 1 hour in separate RB flasks. After degassing, 10 mL of THF was added into Schlenk tube followed by 4 mL of 2 M K₂CO₃ (8 mmol) and the reaction mixture was heated overnight at 80 °C. The polymer **6** was subjected to preliminary purification steps, 1) liquid-liquid extraction of polymer by washing thoroughly with water to get rid of unwanted salts, 2) filtering through silica to get rid of excess of Pd catalyst, and 3) Soxhlet extraction using acetone and petroleum ether and chloroform. The polymer was precipitated and dried under vacuum (173 mg, 0.034 mmol, 84%).

¹H NMR (400 MHz, CDCl₃): δ [ppm]= 8.1 (d, 2H), 7.6 (d, 2H), 7.0 (s, 40H), 4.0 (s, 3H), 2.6-2.8 (t, 80 H), 1.7-1.4 (m, 325H), 0.9 (m, 117H).

MS MALDI-TOF; m/z = 2465.2-3496.5 [Gaussian distribution differencing in mass of benzoic ester end-cap, $M \pm 135.04$]

Synthesis of P3HT-COOH

The polymer P3HT-COOCH₃ (173 mg, 0.034 mmol) was dissolved in 10 mL of THF in a 50 mL RB flask and hydrolyzed using 1 mL of 2 M aq. NaOH. The reaction was refluxed overnight and quenched with 1 mL of 5 M HCl. The product was washed with water thrice and dried over

anhydrous MgSO_4 . Next, the polymer was precipitated in methanol and filtered. ^1H NMR confirms the complete hydrolysis of ester end-capped P3HT. The H/H fraction of P3HT was removed by dry loading the polymer onto an alumina plug and eluting the non-functionalized P3HT with chloroform. The P3HT-COOH was eluted by using the combination of 10% AcOH, 10% methanol and chloroform (41 mg, 0.008 mmol, 23%).

^1H NMR (400 MHz, CDCl_3): δ [ppm]= 8.2 (d, 2H), 7.6 (d, 2H), 7.0 (s, 29H), 2.6-2.8 (t, 60H), 1.7-1.4 (m, 255H), 0.9 (m, 95H).

GPC: M_n : 5,000 g/mol, M_w : 7,300 g/mol, M_z : 8,000 g/mol, D : 1.4

MS MALDI-TOF; m/z = 3280.7-4774.1 [Gaussian distribution differencing in mass of benzoic ester end-cap, $M \pm 121.04$]

UV-Vis: λ_{max} = 450 nm (solution), 528 nm (as-cast film), E_g = 1.8

CV: $E_{\text{onset}}^{\text{ox}}$ = 0.5 eV

DSC: T_m ($^{\circ}\text{C}$) = 174, T_c ($^{\circ}\text{C}$) = 198

2.8.3 Synthesis of P3HT-Py

To a dry 100 mL Schlenk tube, 200 mg of P3HT (mixture of Br/H and H/H) (5000 g/mol, 0.04 mmol), 10 mole% of $\text{Pd}(\text{PPh}_3)_4$, 164 mg of 4-pyridineboronic acid pinacol ester, compound **6** (20 eq, 0.8 mmol) were added and degassed with nitrogen for 30 minutes. Meanwhile, dry THF and 2 M K_2CO_3 were also degassed in respective round bottom flasks for 1 hour. After degassing, 10 mL of THF was added into Schlenk tube followed by 4 mL of 2 M K_2CO_3 (8 mmol) and the reaction mixture was heated overnight at 80 $^{\circ}\text{C}$. The polymer P3HT-Py was subjected to preliminary purification steps, 1) liquid-liquid extraction of polymer by washing thoroughly with water to get rid of unwanted salts, 2) filtering through silica to get rid of excess

of Pd catalyst, and 3) Soxhlet extraction using acetone and petroleum ether and chloroform. To get rid of P3HT (H/H), the polymer was reacted with *p*-toluene sulfonic acid for 1 hour to generate a pyridinium salt. After this, the resultant polymer was dry loaded to the silica column and eluted with chloroform. Only 26% of the polymer was completely purified from P3HT (H/H) (53.2 mg, 0.01 mmol, 26%).

^1H NMR (400 MHz, CDCl_3): δ [ppm]= 8.7 (d, 2H), 7.4 (d, 2H), 7.0 (s, 28H), 2.6-2.8 (t, 60H), 1.7-1.4 (m, 302H), 1.4-0.9 (m, 112H).

GPC: M_n : 5,600 g/mol, M_w : 7,100 g/mol, M_z : 8,300 g/mol, $\bar{D}$: 1.3

MS MALDI-TOF; m/z = 2074.2-3903.8 [Gaussian distribution differencing in mass of pyridine end-cap, $M \pm 78.03$]

UV-Vis: λ_{max} = 452 nm (solution), 549 nm (as-cast film), E_g = 1.8

CV: $E_{\text{onset}}^{\text{ox}}$ = 0.41 eV

DSC: $T_m(^{\circ}\text{C})$ = 184 , $T_c(^{\circ}\text{C})$ = 214

2.8.4 Synthesis of P3HT-TEG

Synthesis of 4-bromo-3-methylphenol (compound 8)²⁷

To a 500 mL round bottom flask, *m*-cresol, compound 7 (5 g, 45 mmol), DMSO (3.5 mL, 49.5 mmol), and 183 mL of ethyl acetate were stirred until the solid dissolves completely. Later, hydrobromic acid (8.5 g, 49.5 mmol) was added dropwise and the reaction was kept stirring at room temperature for 30 mins. The reaction was quenched by adding 150 mL of petroleum ether and the solvent was evaporated under reduced pressure. The crude was purified by recrystallization using petroleum ether and ethyl acetate to obtain pure product (7.3 g, 83%). The reported data is consistent with the literature.²⁷

^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 8.2$ Hz, 1H), 6.73 (s, 1H), 6.55 (d, $J = 8.2$ Hz, 1H), 4.83 (brs, 1H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.7, 139.2, 133.0, 117.8, 115.5, 114.5, 22.9

Synthesis of (4-bromo-3-methylphenoxy)-tert-butyldimethylsilane (compound 9)²⁸

In a 250 mL round bottom flask, 4-bromo-3-methylphenol, compound **8** (4 g, 21.2 mmol) and imidazole (7.5 g, 108 mmol) were dissolved in 8 mL DMF, and then a 12 mL DMF solution of TBDMS-Cl (4.9 g, 32.8 mmol) was added dropwise with stirring at room temperature. The mixture was stirred for 3 hours under nitrogen atmosphere at room temperature. After confirmation of the disappearance of the starting materials, 100 mL DCM was poured into the reaction mixture. The organic solution was washed with H_2O , 0.1 M NaOH aqueous solution and brine. The organic layer was dried over anhydrous MgSO_4 , filtered and evaporated to afford a colorless oil. This crude product was purified on a silica gel column with 100% petroleum ether to afford colorless oil (6.1 g, 94%). The reported data is consistent with the literature.²⁸

^1H NMR (CDCl_3 , 400 MHz) δ : 0.18 (s, 6H), 0.97 (s, 9H), 2.32 (s, 3H), 6.54 (dd, 1H, $J = 8.6$ Hz, 2.8 Hz), 6.72 (d, 1H, $J = 2.8$ Hz), 7.33 (d, 1H, $J = 8.6$ Hz).

^{13}C NMR (CDCl_3 , 75 MHz) δ : - 4.5, 18.2, 23.0, 25.6, 116.2, 119.1, 122.6, 132.8, 138.8, 154.9

Synthesis of Grignard reagent from 2-bromo-5-(tert-butyldimethylsilyloxy)toluene (Compound 10)

Mg (1.2 g, 0.05 mol) turnings were put into 50 mL 2 necked RB flask (one neck fixed with condenser) and stirred vigorously for 30-60 min under N_2 . Dry THF (15 mL) was added followed by 2-bromo-5-(tert-butyldimethylsilyloxy)toluene, compound **9** (3.32 g, 0.01 mol) drop wise. The reaction mixture was then refluxed for 5 hours. An aliquot from reaction mixture

was titrated against iodine to estimate the concentration of Grignard reagent. The exact concentration of Grignard was found to be 0.5 M.

Synthesis of 2-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}ethyl *p*-Tosylate (Compound 16)²⁹

To a dry Schlenk tube (50 mL), NaOH (2.1 g, 51.9 mmol) and 2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-ethanol, compound **15** (6 g, 36.6 mmol), in a two-phase system of water (8.7 mL) and THF (11.1 mL), was cooled via an ice bath with magnetic stirring. The *p*-Toluenesulfonyl chloride, compound **14** (7.5g, 39.63 mmol) in tetrahydrofuran (7.11 mL) was added dropwise to the mixture, while maintaining the temperature below 5 °C. The solution was stirred at 0 °C for another 3 h and then poured into ice-water (30 mL). The mixture was extracted with methylene chloride, and the combined organic layers were washed with water and brine. After drying over magnesium sulfate, the solvent was evaporated under vacuum to yield the pure compound. Colorless oil, yield 5.97 g, 71%. The reported data is consistent with the literature.²⁹

¹H NMR (400 MHz, CDCl₃) δ = 7.79 (d, 2H), 7.35 (d, 2H), 4.15 (t, 2H), 3.68 (t, 2H), 3.67-3.58 (m, 10H), 3.54 (t, 2H), 3.36 (s, 3H), 2.44 (s, 3H)

¹³C NMR (100 MHz, CDCl₃) δ = 144.6, 132.7, 129.5, 128.0, 71.8, 70.6 (2x), 70.4 (2x), 70.3, 69.1, 68.5, 58.8, 21.4.

Synthesis of P3HT-TEG

2,5-Dibromo-3-hexylthiophene, compound **2** (2.0 g, 6.1 mmol) was dried under high vacuum in a Schlenk tube for 1h. Dry THF (60 mL) was added followed by isopropyl magnesium chloride (3.2 mL, 5.9 mmol, 1.8 M) was added and the mixture was stirred for 20h. This is solution "S".

Ni(dppp)Cl₂ (0.114 g, 0.21 mmol) was placed in an oven dried Schlenk tube under nitrogen gas. 5 mL of dry THF was added and the solution was cooled to 0°C. Grignard initiator, compound **10** (0.6 mL, 0.3 mmol, 0.5M) was added and the mixture was stirred for 5 min at 0°C and then stirred for 30 min. at room temperature. The resulting mixture was added to solution “S” and stirred for 30 min at room temp., after which it was quenched with 5 M HCl/MeOH. The crude product was collected by filtration and washed with MeOH. Drying of the crude product gave 1.13 g of a red compound. The crude product (500 mg) was dissolved in dry THF (500 mL) and TBAF in THF (5 mL) was added followed by stirring the mixture overnight at 24°C. The solvent was evaporated under reduced pressure and then crude was precipitated in MeOH and collected by filtration after washing several times with MeOH. This crude product was further purified by Soxhlet extraction (acetone, chloroform). The chloroform fraction was collected and dried properly for the next step of alkylation.

P3HT-OH, compound **13** (340 mg, 0.1 mmol) was dissolved in dry THF (30 mL) to which 394 mg of NaH was added and the resulting mixture was stirred at 0 °C for 10 min. Next, 238 mg of TEG-Tos, compound **16** was added, and the mixture was stirred at 65°C for 18h. The mixture was quenched with MeOH and the volatiles were evaporated under reduced pressure. The product was dry loaded to silica column using CHCl₃ as an eluent. Successive column purifications were done to remove P3HT (H/H) obtain pure P3HT-TEG, red in color (30%, 52 mg)

¹H NMR (400 MHz, CDCl₃): δ [ppm]= 7.4 (d, 1H), 7.01 (s, 1H) , 7.0 (s, 24H), 6.8 (d, 1H), 3.4 – 4.2 (m, 15H), 2.6-2.8 (t, 45H), 2.5 (t, 3H), 1.7-1.4 (m, 203H), 0.9 (m, 74H).

GPC- *M_n*: 4,800 g/mol, *M_w*: 6,000 g/mol, *M_z*: 7,300 g/mol, *D*: 1.3

MS MALDI-TOF; *m/z* = 1584.3-3579.3 [Gaussian distribution differencing in mass of TEG end-cap, *M* ± 253.14]

UV-Vis: λ_{max} = 444 nm (solution), 516 nm (as-cast film), E_g = 1.8

CV: $E_{\text{onset}}^{\text{ox}}$ = 0.47 eV

DSC: T_m (°C) = 180, T_c (°C) = 210

2.9 References

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Chapter 3 Preparation of P3HT:ICBA Nanoparticles Using Dispersion Method

3.1 Introduction

It can be recalled from section 1.4 that OSCs fabricated from surfactant stabilized dispersions suffer with low device performance due to persistence of electrically inert surfactant in active layer. To combat this issue, surfactant-free NP dispersions were synthesized through dispersion method in the past.^{1,2} Although improved device efficiencies have been reported for surfactant-free dispersions, NP formation was less controlled with indications of higher dependence on experimental parameters such as batch-to-batch variation of the semiconducting polymer. This chapter examines the issue of material dependency by forming NPs using P3HT samples of defined molecular weights synthesized in Chapter 2 as well as commercially available P3HT. It was found that increase in P3HT molecular weight resulted in increase in NP size with some suggestions that polymer dispersity also affected NP formation.

Further, dispersions prepared from surfactant-free approach are of low concentration and also suffers with poor stability and reproducibility (see section 1.4). Clearly, there is need for developing chemical agents, which support NP stability without compromising the device performance. To address this gap, end-capped polymers based on semiconducting material, P3HT (P3HT-Py, P3HT-COOH and P3HT-TEG, Figure 3.1) were synthesized, see Chapter 2,

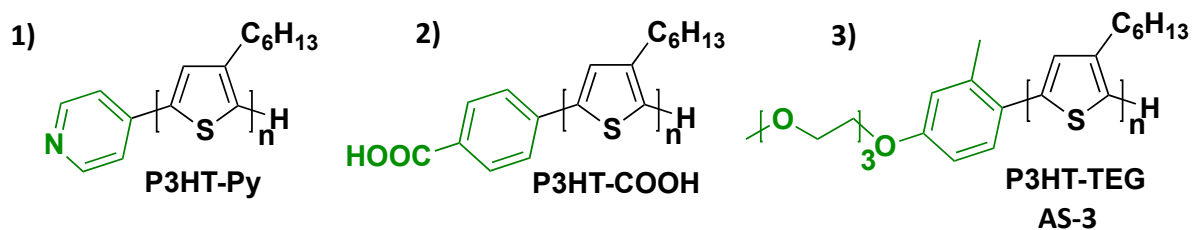
and their use as active surfactant (AS) to stabilize P3HT:ICBA NP dispersions will be assessed in the present chapter. The prime advantage of synthesizing these end-capped polymers is that unlike conventional surfactants, they carry semiconducting properties because they are based on the P3HT unit. Therefore, it can be anticipated that they would have minimal impact on electronic properties in devices.

The underlying mechanisms related to working of each of these end-capped P3HTs is discussed below in detail.

3.2 Rationale behind designing end-capped P3HTs

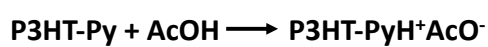
It is well known that the reaction of pyridine with acetic acid to form pyridinium acetate is reversible at modest temperatures (pK_a for AcOH and pyridinium ion (PyH^+) is 4.75 and 5.28). Therefore, we were interested in using this thermally reversible reaction to stabilize organic semiconductor blend NPs. By end-capping a short P3HT chain with pyridine, i.e. P3HT-Py, an active surfactant could be generated on reaction with acetic acid (AcOH). It can be expected that $P3HT-PyH^+AcO^-$ will assemble on the surface of P3HT:ICBA NPs resulting in electric double layer (EDL) formation (Figure 3.1B). The EDL on NP surface should significantly boost NP stability by counteracting the Van der Waal force of attraction with electrostatic repulsion (Figure 3.1B). The phenomenon of NP stabilization via EDL can be observed in any commercial ionic surfactant.³ The advantage of using P3HT-Py over conventional ionic surfactant is the reversibility of the $P3HT-PyH^+AcO^-$ ion pair formation (Figure 3.1C). This concept was then extended to examine a weak acid end-capped benzoic acid end-capped P3HT. The P3HT-COOH can be converted to pyridinium benzoate P3HT ($P3HT-COO^-PyH^+$) in presence of pyridine.

A) Structures of end-capped P3HTs



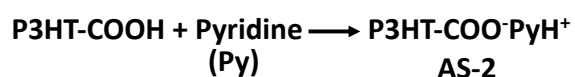
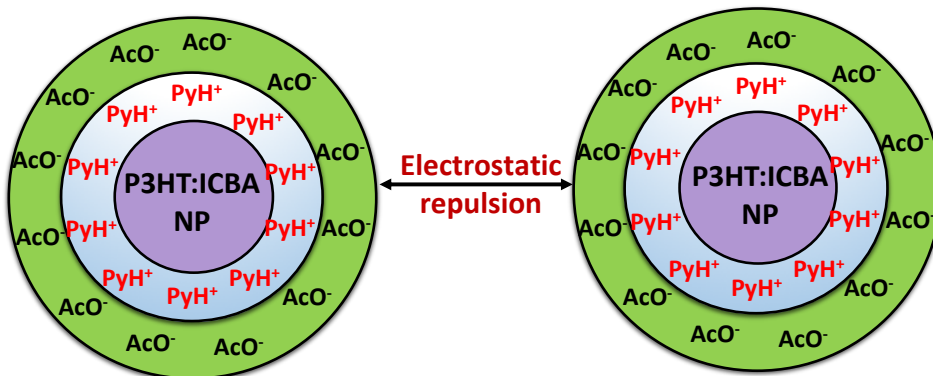
B) During nanoparticle preparation

Ionic pair formation of P3HT-Py and P3HT-COOH



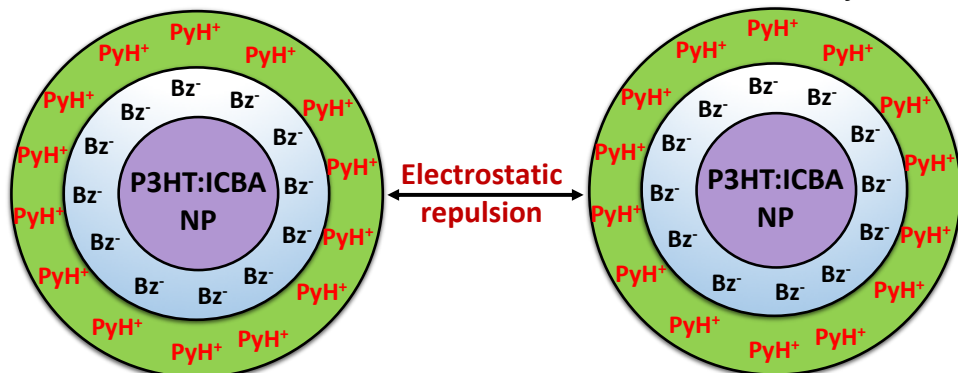
AS-1

NP stabilization via EDL formation



AS-2

NP stabilization via EDL formation



C) During thermal annealing of the nanoparticle film

Reversibility of ionic pair

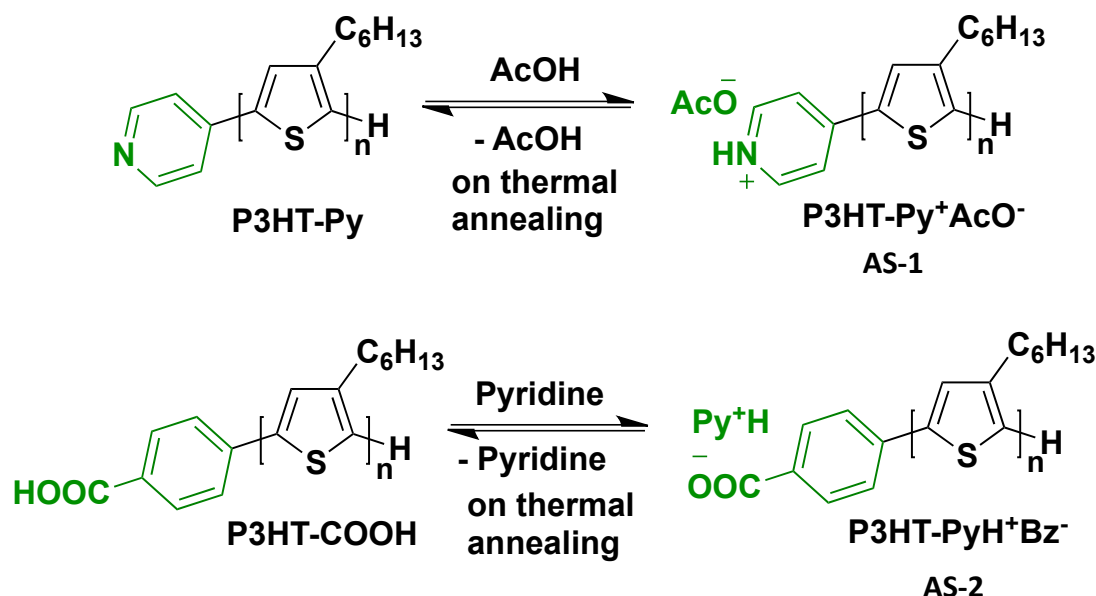


Figure 3.1: Schematic representation of A) structures of three end-capped P3HTs 1) P3HT-Py, 2) P3HT-COOH, and 3) P3HT-TEG, B) conversion of P3HT-Py and P3HT-COOH into P3HT-PyH⁺AcO⁻ and P3HT-COO⁻PyH⁺ on treatment with AcOH and pyridine (Py) respectively to behave as ionic active surfactants (AS-1 and AS-2) to stabilize P3HT:ICBA NP via EDL formation and P3HT-TEG is expected to behave non-ionic active surfactant (AS-3) for NP stabilization, and C) the Dissociation of AS-1 and AS-2 during thermal treatment of NP film to regenerate P3HT-Py and P3HT-COOH with the complete removal of AcOH and pyridine respectively.

This can also behave as an ionic surfactant while forming NP dispersions and can be deactivated after thermal treatment of the NP film (pK_a for benzoic acid and PyH⁺ is 4.20 and 5.28) (Figure 3.1C). P3HT-TEG is expected to behave as non-ionic surfactant and boost the NP stability via steric repulsion.

Hereafter, the combination of P3HT-Py and AcOH (P3HT-PyH⁺AcO⁻), P3HT-COOH and Py (P3HT-COO⁻PyH⁺), and P3HT-TEG will be referred as AS-1, AS-2, and AS-3 respectively.

3.3 Effect of P3HT polymer length on NP dispersions

This section discusses the surfactant-free NP formation of P3HT (synthesized in chapter 2) and ICBA via dispersion method. P3HT polymers of defined molecular weights, ranging from 5,000 to 28,000 g/mol, were synthesized using GRIM polymerization resulting in highly regioregular polymer with low dispersity. These defined molecular weight P3HTs were utilized to examine the effect of polymer length on NP formation and stability, synthesized using the dispersion method.⁴ To formulate these dispersions, P3HT and ICBA (1.25 mg each of P3HT and ICBA, i.e. a wt% ratio of 1:1) were dissolved in chloroform (solvent) to obtain a concentration of 2.5 mg/mL. The chloroform solution was added rapidly into methanol (non-solvent) to form NPs in the mixture of CHCl_3 and MeOH (CHCl_3 :MeOH, 1:4) resulting in dispersions of concentration 0.5 mg/mL. In the end, dispersions were subjected to heating to evaporate mixture of solvent and non-solvent to obtain desired concentration (2.5 mg/mL) (see experimental section for detailed information). This step is critical as it assists in complete removal of CHCl_3 allowing active layer deposition from non-chlorinated solvent.

The initial attempts towards formulating stable NP dispersions using in-house synthesized P3HTs resulted in aggregation and precipitation of material (Figure 3.2).

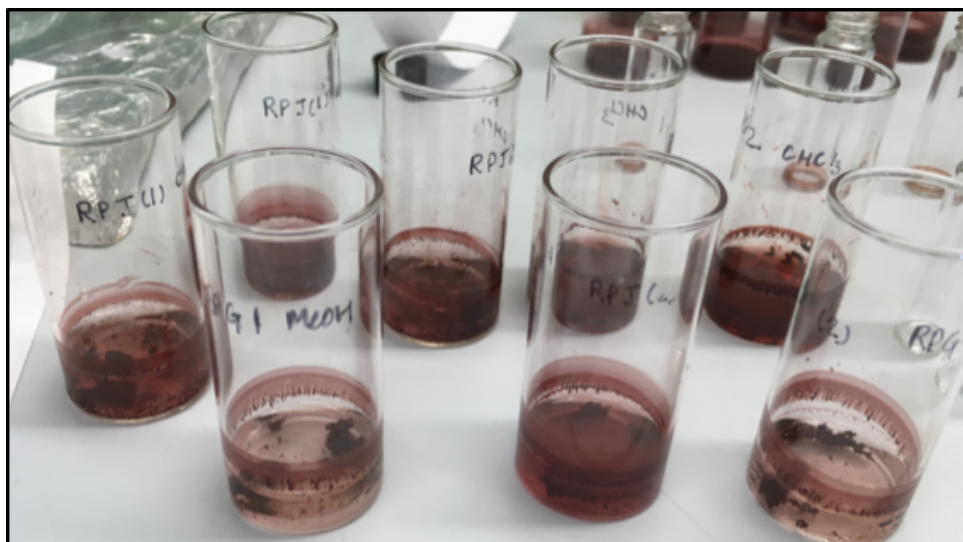


Figure 3.2: Attempts to synthesize defined molecular weight P3HT:ICBA NPs in MeOH (2.5 mg/mL) leading to precipitation of particles

This observation led to a realization that NP formation can be dependent on many physical parameters. Since the dispersion method is a two-step process, that is - a) addition of donor/acceptor blend solution into non-solvent, and b) evaporation of solvent/non-solvent, an immense care should be taken at each step while forming the NP dispersion. Following are the critical parameters that were controlled at first step: choice and temperature of both solvent and non-solvent, the rate of addition of solvent into non-solvent, size and shape of the beakers and stirrer bars, and the rate of mixing of both solvent/non-solvent. For evaporation of solvent/non-solvent in step two, a controlled setup was prepared to heat the dispersions at constant temperature. A brief description to how these parameters were adjusted and controlled is presented in subsequent sections.

3.3.1 Physical parameters affecting first step of dispersion method

3.3.1.1 Temperature of solvent/non-solvent

It should be noted that NP formation through dispersion method is a very fast and complex process. After addition of chloroform solution into methanol, the two sub-processes- splitting of organic solution and counter diffusion of solvent and non-solvent, starts competing with each other leading to different stabilization of NPs (see section 3.3.1.3 for details). Therefore, temperature of both solvent and non-solvent is critical in determining which sub-process out of the two would occur first.

Several trials with varying temperatures were made, for instance, heating solvent at 55 °C and keeping non-solvent at room temperature or vice versa and keeping both at room temperature. The heating temperature of 55 °C was chosen based on the boiling point of chloroform (~61 °C) and methanol (~65 °C). These trials resulted in immediate precipitation of particles which could be attributed to different solubilities of P3HT:ICBA in chloroform/methanol mixtures at different temperatures.

It was observed that prior to addition of chloroform solution of donor/acceptor blend into methanol, both the solvent and the non-solvent must be heated for 10 minutes at same temperature in the range of 45 °C to 55 °C (Figure 3.3). The rapid addition of the heated P3HT:ICBA chloroform solution into the hot methanol, results in nucleation and NP formation.

3.3.1.2 Choice of solvent/non-solvent

Chloroform and THF were used as solvent to dissolve P3HT and ICBA materials whereas, MeOH, EtOH and IPA were used as non-solvent to formulate their NP dispersions. The reported solubilities of P3HT in chloroform and THF are 14 mg/mL and 1 mg/mL respectively⁵ whereas, ICBA has excellent solubility in both chloroform and THF (greater than 90 mg/mL in CHCl₃).⁶ The effect of these solvents and non-solvent on NP stability will be discussed in detail in section 3.4.3 and 3.4.4 respectively.

3.3.1.3 Size and shape of beakers and stirrer bars

One of the key reasons of reproducibility issue in dispersion method is the poor mixing of solvent and non-solvent. The dispersion method proceeds via dispersion of the organic solution into the non-solvent resulting in splitting of organic solution into small droplets. Concurrently, the counter diffusion of solvent and non-solvent results in NP formation.^{7, 8} The two processes “diffusion of solvent and non-solvent” and “organic solution splitting” compete. If the organic solution splits into uniform small droplets prior to diffusion of non-solvent into solvent, then it would allow the formation of uniformly dispersed NPs. If diffusion of non-solvent into solvent occurs rapidly before sufficient splitting of organic solution then NPs of large diameters with broad distribution are expected.⁹ Therefore, it can be anticipated that uniform splitting of solution can be achieved via rapid addition of organic solution into non-solvent in addition to fast mixing of solvent and non-solvent.

While performing NP experiments in this work, the non-solvent (methanol) was continuously stirred at high rate around 700-800 rpm during the addition of chloroform solution of P3HT:ICBA. It was also observed that stable NPs were formed using only 10 mL and 20 mL beakers along with 10 × 20 mm magnetic stirrer bars (Figure 3.4). It can be speculated that this combination of beaker and stirrer bar resulted in appropriate mixing of solvent/non-solvent.

3.3.2 Physical parameters affecting 2nd step of dispersion method

3.3.2.1 Evaporation of solvent/non-solvent

The evaporation of solvent/non-solvent is a key step to prepare stable NP dispersions. The ratio of solvent and non-solvent was kept constant as 1:4 in all the NP experiments performed in this research work. The amounts of P3HT and ICBA were varied in chloroform solution, depending on the required end concentration of dispersion. For example, to prepare 1 mg/mL dispersions, 0.5 mg each of P3HT and ICBA were dissolved in 1 mL chloroform and dispersed in 4 mL methanol to form NPs. At this stage, the concentration of dispersion is 0.2 mg/mL. To obtain the desired concentration (1 mg/mL), the solvent/non-solvent needs to be evaporated. Complete removal of chlorinated solvents at this step would allow the non-chlorinated solution processed thin film deposition of large area OSCs, as the chlorinated solvent can be removed under controlled conditions.

Initial attempts were made to evaporate solvent/non-solvent by applying heat and reducing pressure simultaneously. A set up was made in which a hotplate was coupled with a thermocouple and a pressure controller to control the temperature and pressure respectively (Figure 3.5). It was observed that after placing the beakers containing NP dispersions in this set up, the solvent and non-solvent evaporated in 5 mins at 50 °C and 133 mbar pressure. However, some of the solvent and non-solvent condensed back into the beakers which

promoted aggregation of NPs and eventually precipitation was observed. To overcome the limitation of solvent condensation, another set up was developed in which no reduced pressure was applied, and the water bath covered with a plastic lid was heated to evaporate solvent. Several holes (typically 4 to 6) of beakers' diameter were manually carved in the plastic lid to allow multiple samples to be evaporated at once. The plastic lid also provided full coverage of water bath to prevent the condensation of water into beakers (Figure 3.6). It was anticipated that fast evaporation using high temperature range would allow formation of stable NPs. In this work, all dispersions were heated at 75 °C for 15 mins. to obtain desired concentration of dispersions. Although dispersions were also heated at different temperatures less than 75 °C, such as 60 °C, 65 °C, and 70 °C, which slowed the rate of evaporation, heating at these lower temperatures had no significant effect on NP stability. Heating dispersions at temperature greater than 75 °C resulted in bubbling of solvent and non-solvent leading to deposition of material on the walls of the beaker.

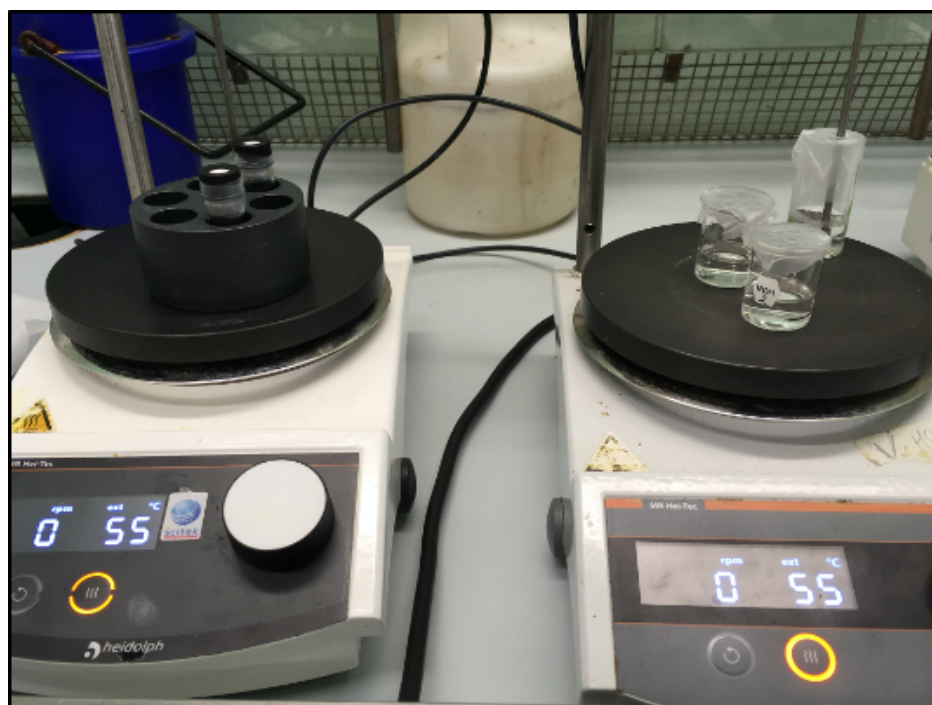


Figure 3.3: Simultaneous heating of P3HT: ICBA solution in chloroform and non-solvent (alcohol) as well at 55 °C for 10 mins. prior to NP formation.

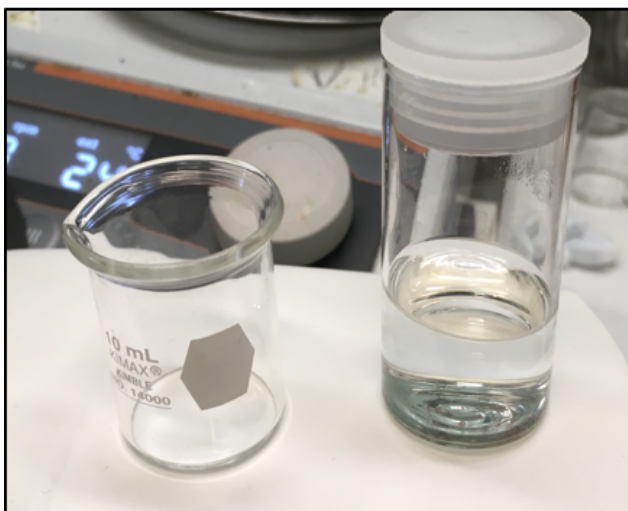


Figure 3.4: Requirement of specific size and shape of the beakers and stirrer bars (10 × 20 mm) to form NP dispersions.



Figure 3.5: Designed set up including a hotplate coupled with a thermocouple and a pressure controller to control the temperature and pressure respectively to evaporate solvent (complete removal)/ non-solvent (up to desired concentration).

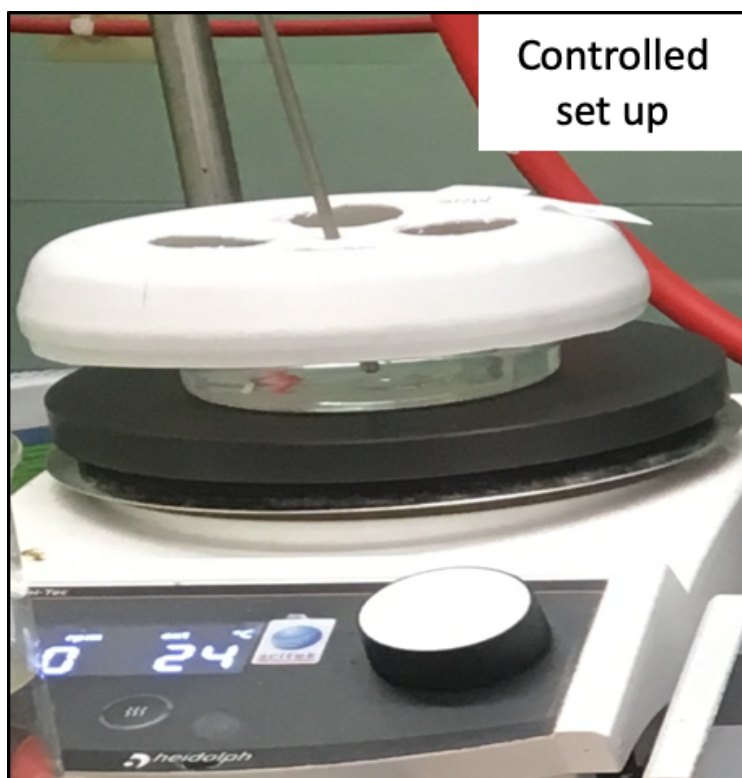


Figure 3.6: A simple set up of heating the solvent/ non-solvent to obtain desired concentration of NP dispersions. This set up includes a water bath with a temperature probe to control the temperature. The plastic lid was cut into 4 holes to hold the beakers intact and it also covers the surface of water bath to prevent the condensation of water into beakers containing dispersions.

After controlling the above-mentioned physical parameters, the next target was to prepare P3HT:ICBA NP dispersions using the series of synthesized P3HTs with well-defined molecular weights to study the impact of polymer length. The NP dispersions (2.5 mg/mL) were prepared in MeOH and they were characterized through dynamic light scattering (DLS) measurements (see experimental section for detailed information).

An increase in NP diameter was observed for P3HT:ICBA NP dispersions with increase in molecular weight of the polymer (Table 3.1). High molecular weight P3HT are expected to show more polymer aggregation than P3HT of low molecular weight, which in turn, causes increased crystallinity in the former. For the same reason, dispersions prepared from P3HT of 28,000 g/mol resulted in precipitation of particles. Also, the observed dispersities of NPs made

from synthesized P3HTs are greater than 0.05 indicating significant distribution in NP size. To differentiate polymer dispersity with nanoparticle dispersity, the dispersity of NP will be denoted as D_{np} .

Table 3.1: Summarized DLS results of defined molecular weight of P3HT: ICBA (1:1) NP dispersions in MeOH (2.5 mg/mL)

GPC data of P3HT polymers				DLS data of P3HT:ICBA NP	
Samples	M_n (g/mol)	D	%RR	Z-avg. (nm)	D_{np}
Synthesized defined molecular weight P3HTs using GRIM	5,000	1.02	92	79 ± 3	0.1
	11,000	1.11	94	138 ± 3	0.08
	22,000	1.06	96	156 ± 2	0.07
	24,000	1.5	97	171 ± 5	0.09
	28,000	1.6	98	Precipitated	
Rieke P3HT, batch 4002-EE	24,000	2.4	91	116 ± 3	0.05

Surfactant-free dispersions of commercial P3HT:ICBA were prepared at a concentration of 10 mg/mL in MeOH and EtOH by Gartner et al.¹⁰ in 2014 and Sankaran et al.¹ in 2015 respectively. The former used Merck P3HT KgaA, $M_n = 38700$, $M_w = 77500$, $D = 2$, % RR = 96 and reported NP diameter of 160 ± 31 nm whereas, the latter used Rieke P3HT, batch 4002-EE, $M_n = 24000$, $M_w = 57000$, $D = 2.4$, % RR = 91 to prepare NP dispersions with Z-avg. 100 nm. In this work, P3HT:ICBA NP dispersions (2.5 mg/mL) using the series of P3HT with

varying molecular weight (M_n = 11,000 to 24,000 g/mol) showed a Z-avg. more than 100 nm. These results suggested that NP formation through the dispersion method depends on specific batch of polymer used. This material dependency was further investigated by using commercially available Rieke P3HT (batch 4002-EE) to prepare P3HT:ICBA NP dispersions in MeOH (2.5 mg/mL). The observed NP diameter of these dispersions was 116 ± 3.2 nm with $\bar{D}_{np}$ = 0.05 (Table 3.1). It should be noted that despite the higher M_n of the Rieke P3HT (24,000 g/mol), the dispersions exhibited smaller Z-avg. than the dispersions formulated using synthesized P3HT (M_n = 11,000 to 24,000 g/mol). The difference in these NP results can be attributed to higher $\bar{D}^{11, 12}$ and lower regioregularity of commercial P3HTs in comparison to the synthesized P3HTs (Table 3.1). In a highly disperse sample, the inherent variation in polymer length is mainly due to greater number of longer and shorter chains rather than fewer chains of average lengths. Therefore, NPs of highly dispersed polymer exhibit small NP diameter due to large number of short polymer chains involved in NP formation compared to the polymers with low $\bar{D}$. Lower regioregularity of polymer indicates greater degree of defects in polymer sample which impacts the planarity of the polymer backbone. As a result, reduction in aggregation and crystallinity of the bulk material is expected which could be a potential reason of forming stable NPs with the polymers of low regioregularity.

These results manifested that surfactant-free NP dispersions made through the dispersion method exhibit a high material dependence, hence accounting for the poor reproducibility and stability at low concentration. Therefore, a potential solution to overcome these issues could be the use of end-capped P3HT polymers as active surfactants (explained in Section 1.4) to produce stable NP dispersions. The synthesis of end-capped P3HT has already been discussed in Chapter 2.

3.4 Stabilization of P3HT:ICBA nanoparticles using AS-1

Section 3.2 discussed that the P3HT-Py can be converted into P3HT-PyH⁺AcO⁻ (AS-1) on chemical treatment with AcOH. The AS-1 is expected to behave as ionic surfactant to stabilize NPs of semiconducting materials via EDL formation. After NP film deposition, thermal treatment of these films the P3HT-PyH⁺AcO⁻ would dissociate into P3HT-Py and AcOH. The migration of active surfactant to the interface during NP formation can be characterized by determining critical micelle concentration of surfactant using a surface tensiometer.¹³ However, this research work does not address the characterization of EDL formation due to time constraints.

The subsequent sections will discuss the use of P3HT-Py for producing stable, concentrated and reproducible NP dispersions along with the dissociation of AS-1.

3.4.1 Concentration optimization

Initial experiments were focused on optimizing the AS-1 concentration required to stabilize P3HT:ICBA NP dispersions. The NP dispersions were prepared using the same procedure discussed as above but with addition of the P3HT-Py in the chloroform solution and AcOH in MeOH (Figure 3.7). Note that preliminary experiments were also performed by adding acetic acid into the chloroform solution of semiconducting materials to understand the impact of changing experimental condition on NP formation. However, the observed NP diameters for both the conditions (addition of AcOH into – a) CHCl₃ solution and b) MeOH) were similar. To maintain the consistency in future experiments, the AcOH was added into methanol.

In these experiments, the wt.% of AS-1 was varied with respect to total weight of commercial P3HT used for NP formation. For example, to prepare 1 mg/mL dispersions of P3HT (0.5 mg):ICBA (0.5 mg) with 3 wt.% AS-1, the P3HT-Py and AcOH (both 3 wt.% of total P3HT i.e. 0.015 mg each) were added into CHCl₃ solution of P3HT:ICBA and MeOH respectively. To add such small amount of AS-1, standard solutions of P3HT-Py and AcOH of concentration

3 mg/mL were prepared in CHCl_3 and MeOH respectively. This required addition of 5 μL from each solution to prepare dispersions with 3 wt.% AS-1. Note that P3HT-Py and AcOH were taken at 1:1 wt. ratio so that acid is present in excess ensuring complete conversion of P3HT-Py into AS-1 ($\text{P3HT-PyH}^+\text{AcO}^-$). The effect of using different wt.% of AS-1 on P3HT:ICBA NP diameter was examined (Table 3.2).

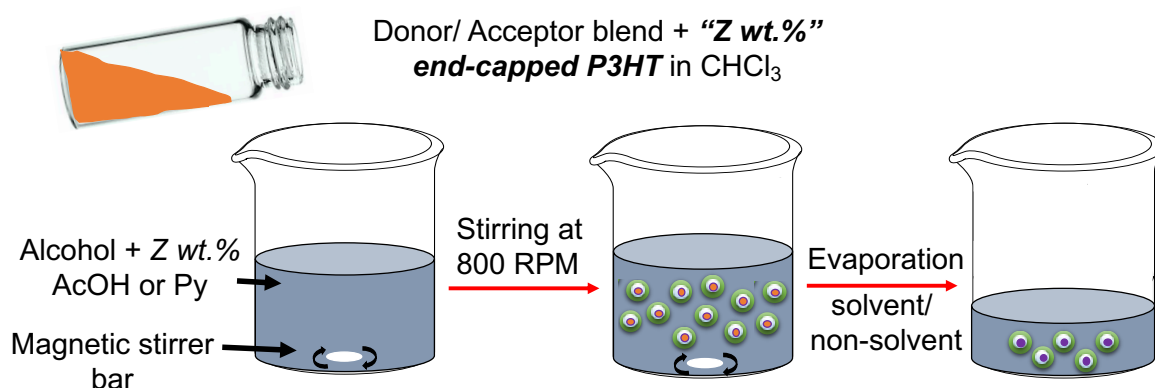


Figure 3.7: Schematic representation of using end-capped P3HT to stabilize P3HT:ICBA NP dispersions through dispersion method.

Table 3.2: Summarized DLS results of optimizing concentration of AS-1 to synthesize NP dispersions of Rieke P3HT: ICBA (1:1) NP dispersions in MeOH (1 mg/mL)

Dispersion	Wt.% of AS-1	$\bar{D}_{np}$	Z-avg. (nm)
P3HT: ICBA/ methanol (1 mg/ml)	0%	0.06	112 ± 3
	2%	0.04	84 ± 2
	3%	0.04	82 ± 2
	4%	0.05	81 ± 1
	5%	0.07	78 ± 2
	6%	0.07	77 ± 1
	7%	0.05	77 ± 1

The average size of the NPs in dilute dispersions (1 mg/mL) was reduced to 77 nm by using 7 wt.% of AS-1 when compared 112 nm for dispersions with no additive. These results confirmed that addition of small amount of AS-1 could aid in reducing NP size.

It will be interesting to know approximately how many P3HT chains would comprise a nanoparticle of size 100 nm for instance. Note that, NPs are considered spherical in shape based on TEM measurements (Figure 3.11). To estimate the number of chains, first the mass of total number of P3HT chains in a 100 nm particle was calculated using the volume of spherical nanoparticles $[(4/3) \times \pi \times (50)^3 = 5.2 \times 10^{-16} \text{ cm}^3]$ and the density of P3HT ($\sim 1 \text{ g/cm}^3$). Next, the number of moles of P3HT within this nanoparticle were determined by dividing the mass of P3HT with its molecular mass. For example, in case of Rieke P3HT (molecular mass $\sim 24,000 \text{ g}$), the number of moles were calculated to be 2.1×10^{-20} . Finally, the number of moles were multiplied with the Avogadro number (1 mole P3HT would have 6.02×10^{23}) to estimate the total number of chains collapsing to form a nanoparticle of 100 nm which comes around ~ 13000 chains. Similarly, an approximate number of P3HT-Py chains covering the nanoparticle surface of Rieke P3HT can be determined. In case of 3 wt.% of P3HT-Py, the volume of P3HT-Py chains can be calculated by taking the 3 wt.% of the volume of spherical nanoparticle $(3 \times 5.2 \times 10^{-16} \text{ cm}^3)/100 = 1.57 \times 10^{-17} \text{ cm}^3$. The mass of P3HT-Py chains was estimated to be $1.57 \times 10^{-17} \text{ g}$ by multiplying the density of P3HT molecule ($\sim 1 \text{ g/cm}^3$) with the volume of 3 wt.% of P3HT-Py chains. The number of moles of P3HT-Py chains were calculated to be 3.14×10^{-21} which was multiplied with the Avogadro number to determine the total number of P3HT-Py chains i.e ~ 1900 chains. Now to find the surface area of nanoparticle occupied per chain of P3HT-Py molecule, the surface area of spherical nanoparticle was divided by the number of chains $[4 \times \pi \times (50)^2]/1900 = 16 \text{ nm}^2$. Number of P3HT-Py chains for 2, 4, 5,6 and 7 wt.% were calculated to be $\sim 1260, 2500, 3200, 3800$ and

4400 chains and the NP surface area occupied by per chain was ~25, 12, 10, 8, 7 nm² respectively.

The next focus of this work was to obtain reproducible NP dispersions using AS-1.

3.4.2 Reproducibility of NP formation

To examine the reproducibility of NP dispersions, three sets of 5 samples each with 0, 3 or 7 wt.% of AS-1 were prepared. In the case of dispersions with no additive, two out of the five samples precipitated immediately. Moreover, the Z-avg. of remaining three dispersions differed by 15 to 20 nm. In comparison, the dispersions formulated with the help of additive exhibited Z-avg. between 70 to 80 nm with good reproducibility, for example the 5 samples with 3 wt% addition of AS-1 vary only between 76 and 80 nm (Table 3.3 Column 4).

One can argue that the NP stabilization could occur due to individual components of AS-1 i.e. P3HT-Py or AcOH, rather than their cumulative influence. For instance, dissociation of acid into free ions could lead up to NP stabilization due to electrostatic repulsion. Similarly, addition of end-capped P3HT to P3HT:ICBA dispersions is expected to broaden the dispersity of this P3HT mixture, which in turn, could stabilize NP dispersions as explained in section 3.3.2.1. To test these speculations, influence of each of the components and AS-1 as a whole on NP formulation was studied. Five dispersions of 1 mg/mL in MeOH were prepared by adding 3 wt.% and 7 wt.% each of AcOH, P3HT-Py and AS-1, and temporal stability of NP dispersions was examined (Table 3.4).

The dispersions with AcOH exhibited NP diameter around 100 nm which was continuously increasing with time. While precipitation of particles was observed in the dispersions with 3 wt.% AcOH after 48 h, the dispersions with 7 wt.% AcOH exhibited increased NP diameter of 129±8 nm. This shows that addition of AcOH in isolation is unable to stabilize NP dispersions

for longer periods of time. For dispersions with P3HT-Py, initial NP diameters were less than 100 nm but with higher standard deviations. Aggregation of NPs was observed in 24 h resulting in larger NPs eventually leading up to precipitation after 48 h. Using 3 and 7 wt.% of AS-1 resulted in formation of reproducible dispersions exhibiting smallest NP diameter and high stability (Table 3.4).

Table 3.3: Reproducibility test of Rieke P3HT: ICBA (1:1) NP dispersions in MeOH (1 mg/mL) using 0, 3 and 7 wt.% of AS-1. Three measurements of 10 runs were performed on each sample using DLS and standard deviation was calculated from the Z-avg. value obtained in 2nd measurement.

Samples	Wt.% Additive					
	0		3		7	
	Z-avg. (nm)	D_{np}	Z-avg. (nm)	D_{np}	Z-avg. (nm)	D_{np}
1 st	precipitated	----	77 ± 1	0.05	72 ± 1	0.08
2 nd	97 ± 3.0	0.09	77 ± 1	0.05	72 ± 1	0.05
3 rd	112 ± 1.0	0.04	77 ± 3	0.05	72 ± 1	0.06
4 th	109 ± 3.0	0.04	76 ± 2	0.03	70 ± 2	0.07
5 th	precipitated	----	80 ± 1	0.06	72 ± 1	0.08

These results indicate that the combination of AcOH and P3HT-Py is the most effective in stabilizing NP dispersions and support our hypothesis of EDL formation on surface of NPs when present together. Attempts were also made to determine surface charge of NPs via zeta

potential measurements. However, inconsistent potential values were obtained for any given sample, therefore, it is not possible to provide supporting evidence of EDL formation.

Table 3.4: Temporal study of stability of P3HT:ICBA NP dispersions (1 mg/mL) formulated using 3 and 7 wt.% of AcOH, P3HT-Py and AS-1. Three measurements of 10 runs were performed on each sample using DLS and standard deviation was calculated from the Z-avg. value obtained in 2nd measurement.

Time (h)	Z-avg. (nm) of P3HT: ICBA NP dispersions					
	Wt.% AcOH		Wt.% P3HT-Py		Wt.% AS-1	
	3	7	3	7	3	7
3	101 ± 2	104 ± 7	84 ± 18	96 ± 11	77 ± 1	72 ± 2
24	125 ± 18	110 ± 7	240 ± 116	205 ± 97	78 ± 2	73 ± 1
48	precipitated	129 ± 8	precipitated	precipitated	78 ± 2	76 ± 5

3.4.3 Effect of solvent on NP dispersions

To eliminate the use of chlorinated solvent completely, this work also examined the use of non-chlorinated solvent for NP formation. The two conditions to form NPs from dispersion method were 1) the miscibility of solvent and non-solvent and 2) the solvent should have the boiling point close to the non-solvent so that it can be evaporated easily. To observe the effect of non-chlorinated solvents on NP dispersions, P3HT and ICBA were dissolved in THF at a conc. of 1 mg/ mL with 3 wt.% of P3HT-Py and dispersed in MeOH containing 3 wt.% AcOH. Five dispersions were prepared to observe the reproducibility of NP experiment. The mean diameter

of NPs was 173 ± 74 nm with $\mathcal{D}_{np} = 0.2 \pm 0.1$. The large standard deviation infers that variations in dispersions made from THF solution are larger compared to the dispersions made from chloroform solution of P3HT:ICBA. The high dispersity of these dispersions indicates the broad distribution of particles' diameter. Some dispersions showed a broad aggregation peak in the DLS plot (Figure 3.8). The observed aggregation and large NP size after replacing chloroform with THF could be attributed to the difference in solubilities of photovoltaic material in THF and chloroform. For instance, the solubility of P3HT in CHCl_3 is 14 times higher than in THF⁵ as mentioned in section 3.3.1.2.

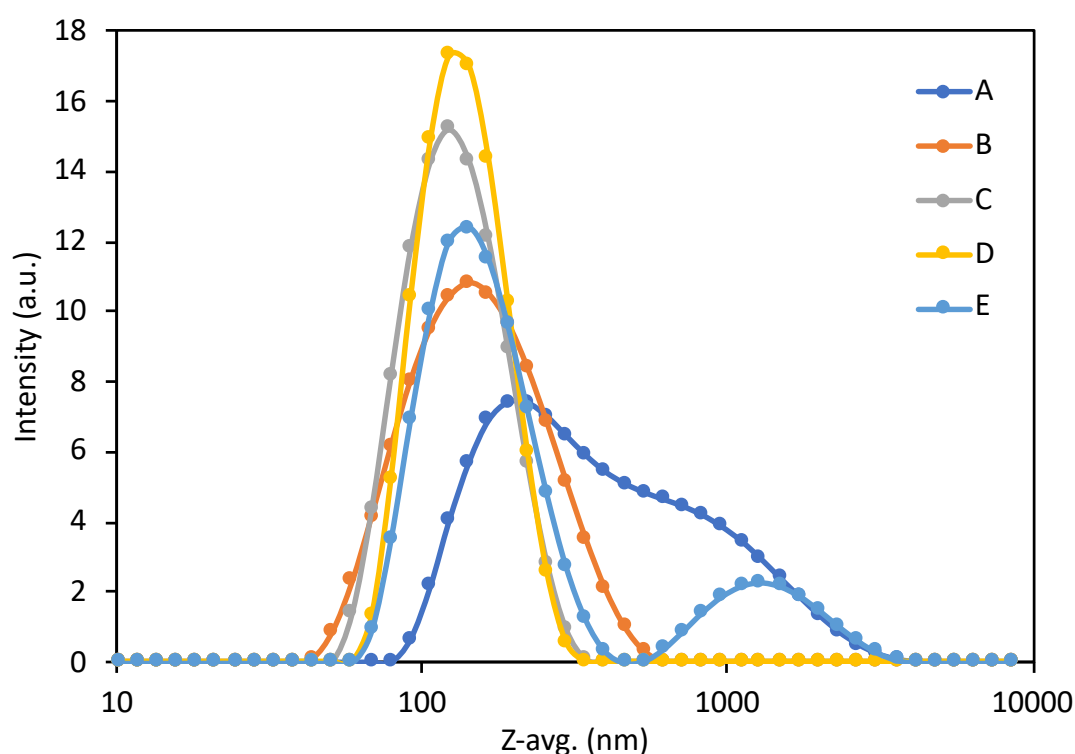


Figure 3.8: DLS plot of five samples (A,B,C,D and E) of Rieke P3HT: ICBA (1:1) NP dispersions in MeOH (1 mg/mL) in which the solvent used was THF to dissolve P3HT: ICBA exhibits inconsistent NP size with large standard deviation. Some dispersions also resulted in broad aggregation peak.

3.4.4 Effect of non-solvents on NP stability

In general, surfactant-free dispersions exhibit low shelf life thus, inhibiting their use in large area devices. The stability data of these dispersions is rarely presented in literature, with only

limited evidence of stable dispersions with respect to time.¹⁴ This section discusses the effect of non-solvents on NP stability.

The interaction of non-solvent with the solvent and its polarity play an important role in determining the quality of NP dispersions. Alcoholic solvents exhibit lower toxicity than most of the solvents such as chloroform, toluene, THF, or chlorobenzene used for OPV processing. They also prevent the de-wetting of substrate which is more commonly observed in water-based inks. Thus, alcohol-based solvents are promising candidates for large scale production of OSCs with minimum environmental impact.

The stability of NP dispersions with 0 and 3 wt.% AS-1 in MeOH, EtOH and IPA was studied using UV-Vis absorption spectroscopy. Although the NP size decreases with an increase in the wt.% of AS-1, we chose to perform the subsequent experiments using only 3 wt.% of AS-1, as- a) it provides NPs with a Z-avg. less than 100 nm, and b) reduces the amount of P3HT-Py in our bulk heterojunction devices, thus, minimizing the risk of residual P3HT-Py affecting device performance.

In this experiment, the total concentration of NPs remaining in dispersion can be estimated by using UV-Vis measurements (Figure 3.9). The initial dispersion becomes the base line, and after set times, the dispersion is filtered to remove precipitated NPs or large NP aggregates and the absorbance measurements were repeated. If the NP dispersion is stable, then little or no change in the baseline will be observed. However, if precipitation or significant aggregation occurs then these residues will be removed by filtering the dispersions through 0.22 μm syringe filter. This would result in decreased absorbance of dispersions due to removal of particles.

Measurements were performed on the dispersions immediately after the formation, referred to as day 1 no filter (base line) (Table 3.5). The absorbance measurements were repeated after filtering the dispersions on day 1, day 15 and day 60 to calculate the % aggregation (Figure

3.9). Dispersions with no additive showed more aggregation in EtOH and IPA compared to MeOH. Although addition of 3 wt.% AS-1 controlled the aggregation in different non-solvents to certain degree, AS-1 worked most effectively in MeOH.

Table 3.5: Calculated percent aggregation of Rieke P3HT: ICBA (1:1) NP dispersions (1 mg/mL) in MeOH, EtOH and IPA with or without 3 wt.% AS-1 (P3HT-Py and AcOH) and 3 wt.% AS-1' (P3HT-Py and TFA) through UV-Vis measurements.

Variations		% Aggregation		
Non-solvents	Samples	Day 1	Day 15	Day 60
MeOH	No additive	4	43	100
	3 wt.% AS-1	6	13	20
	3 wt.% AS-1'	10	11	21
Ethanol	No additive	11	55	100
	3 wt.% AS-1	13	40	81
	3 wt.% AS-1'	5	11	14
IPA	No additive	85	100	-
	3 wt.% AS-1	63	100	-
	3 wt.% AS-1'	61	62	100

This trend of increased % aggregation in longer alkyl chain alcohol could be attributed to the polarity of the non-solvents. Therefore, MeOH has a greater capacity to shield charges due to high dielectric constant resulting in less interaction between charged species. MeOH dispersions after stabilizing with 3 wt.% AS-1 were stable for two months at room temperature showing only 20% aggregation on the 60th day (Table 3.5). Whereas, the MeOH dispersions

with no additive in MeOH showed 43% aggregation on 15th day, eventually leading to complete precipitation as observed on 60th day.

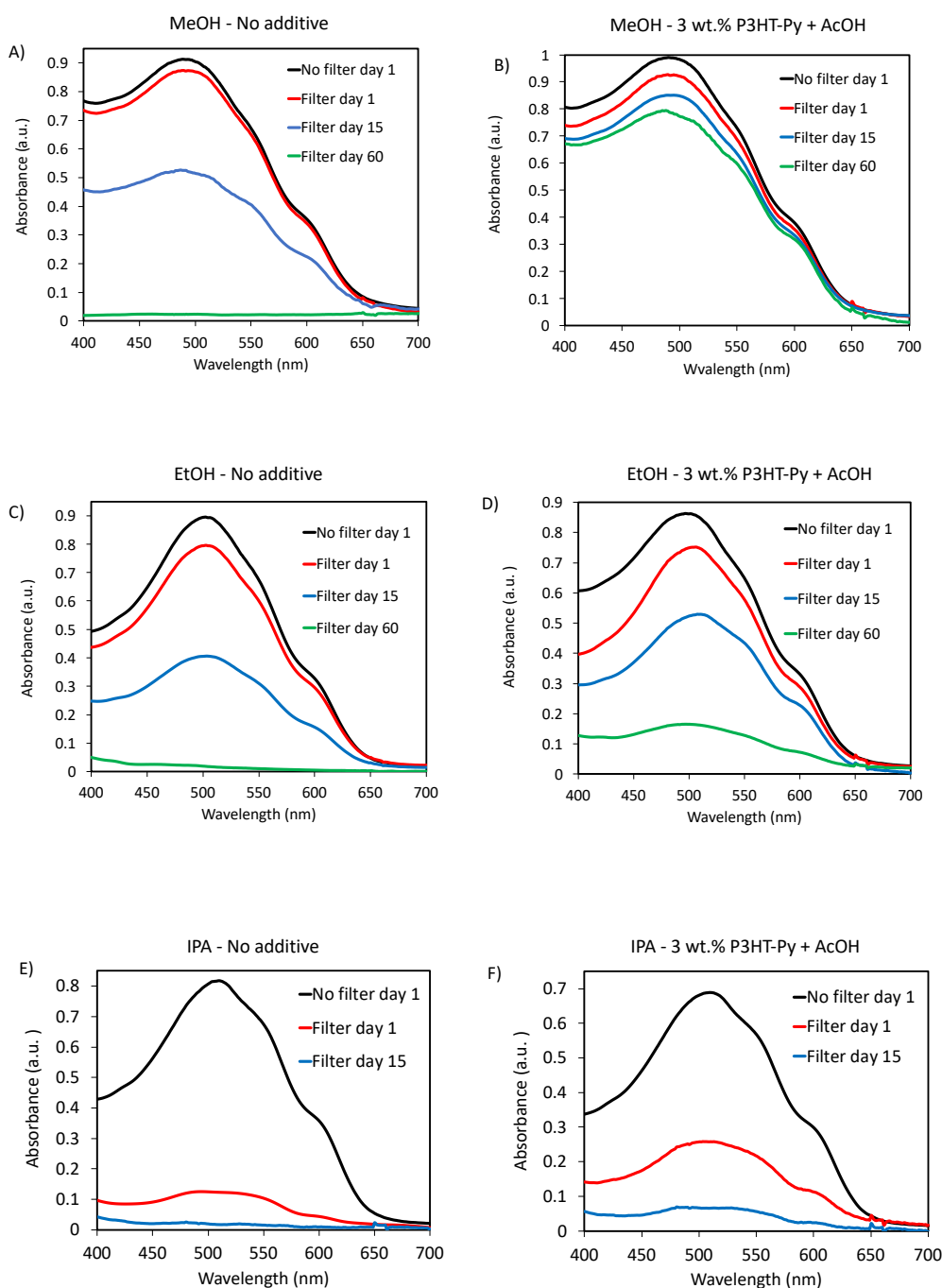


Figure 3.9: UV-Vis absorption spectra of nanoparticle dispersions of Rieke P3HT: ICBA (1:1) (1 mg/mL) in MeOH, EtOH and IPA with no additive (A, C, E) and with 3 wt.% AS-1 (B, D, F) showing that aggregation of particles is controlled after addition of AS-1. The dispersions are more stable in MeOH (up to 60 days) compared to EtOH and IPA.

It can be anticipated that the stability of dispersions in EtOH and IPA can be improved by using stronger acid than AcOH such as trifluoroacetic acid (TFA), however these may impact the temperature required to reverse the reaction. The effect of P3HT-Py and TFA (AS-1') on NP stability was evaluated and it can be seen from Table 3.5 that AS-1' was successful in reducing % aggregation in EtOH. However, the dispersions in IPA still showed 61% aggregation on day 1 and were completely precipitated out on day 60 even after adding AS-1'. Note that, the UV-Vis graphs of dispersions with 3 wt.% AS-1 is shown here for the reader's reference (Figure 3.9). The plots for dispersions with 3 wt.% AS-1' is not shown.

3.4.5 Preparation of concentrated NP dispersions

One of the limitations of the published surfactant free method of dispersion is that it is not possible to produce concentrated NP dispersions. The maximum NP dispersion concentration reported in literature is 10 mg/mL, which subsequently required from six to eight sequential deposition steps to achieve optimum active layer thicknesses in devices. To improve the reproducibility of active layer formation and to reduce the number of deposition steps, attempts were made to increase the concentration of NP dispersions with the addition of P3HT-Py. To do so, the concentration of P3HT:ICBA chloroform solutions containing 3 wt% of P3HT-Py was increased to achieve the pre-defined target concentration of the NP dispersion. For example, to prepare 30 mg/mL dispersion, 15 mg of each P3HT and ICBA were dissolved in 1 mL chloroform along with 3 wt.% of P3HT-Py. This chloroform solution was added rapidly into 4 mL of stirring MeOH containing 3 wt.% AcOH. The total volume of dispersion at this stage was 5 mL which was reduced to 1 mL by evaporating the solvent/non-solvent to achieve 30 mg/mL concentration of dispersion. The NP diameter and D_{np} for 30 mg/mL dispersions was found to be 120 ± 1.2 nm and 0.05 (Table 3.6). Interestingly, DLS plots of 20 and 30 mg/mL NP dispersions of P3HT:ICBA in MeOH did not exhibit any aggregation peak (Figure

3.10). Further, attempts were made to obtain more concentrated dispersions (40 mg/mL) using 3 wt.% AS-1 but Z-avg. of 160 ± 1.2 nm with broad aggregation peak was observed.

Table 3.6: Summarized DLS and TEM results of Rieke P3HT: ICBA (1:1) NP dispersions of 20, 30 and 40 mg/mL in MeOH. Three measurements of 10 runs were performed on each sample using DLS and standard deviation was calculated from the Z-avg. value obtained in 2nd measurement.

Concentration (mg/mL)	DLS		TEM
	Z-avg. (nm)	$\bar{D}_{np}$	Z-avg. (nm)
20	111 ± 2	0.07	98 ± 11
30	120 ± 1	0.05	104 ± 13
40	163 ± 1	0.2	140 ± 11

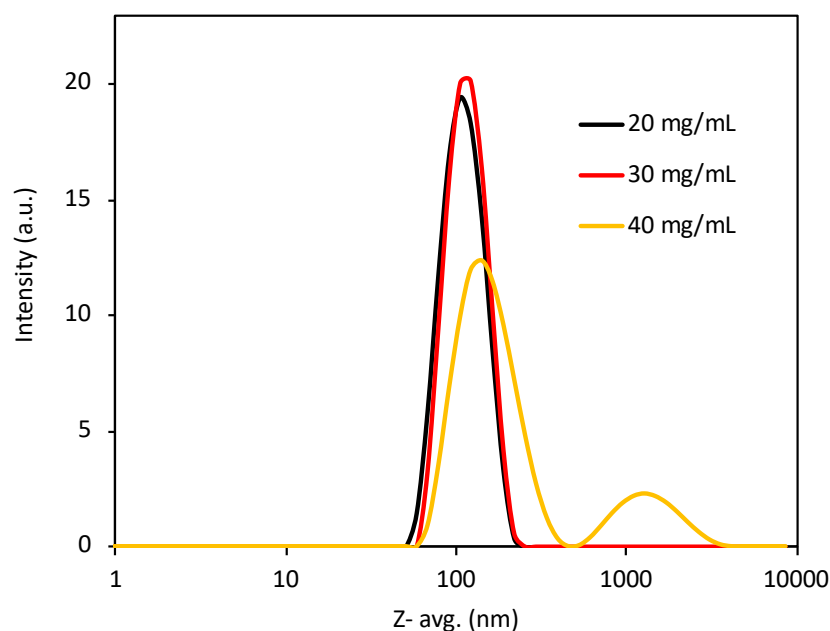


Figure 3.10: DLS plot of 20, 30 and 40 mg/mL NP dispersions of Rieke P3HT:ICBA (1:1) in MeOH formulated with the help of 3 wt.% AS-1, in which, 40 mg/mL dispersion showed broad aggregation peak whereas, other two dispersions exhibited NP diameter between 100 to 120 nm.

Transmission electron microscopy (TEM) was used for further characterization of concentrated NP dispersions. The sample preparation for TEM analysis is discussed in experimental section. TEM measurements help in understanding the morphology of NPs. Previous studies have reported that NPs of P3HT:PCBM and P3HT:ICBA prepared via miniemulsion method exhibit core-shell morphology.¹⁵⁻¹⁷ In this work, the TEM images of films deposited from P3HT:ICBA dispersions showed the presence of amorphous or glass like NPs without core-shell structure. This observation is consistent with the literature.¹⁸ TEM images of films prepared from 20, 30 mg/mL NP dispersions showed discrete and narrow dispersed particles, whereas, the films deposited from 40 mg/mL dispersion showed the presence of aggregated particles (Figure 3.11). The average NP diameters obtained from TEM analysis for 20 , 30 and 40 mg/mL were 98 ± 11 , 104 ± 13 , 140 ± 11 respectively. This trend of NP diameters is consistent with the observations from DLS (Figure 3.10).

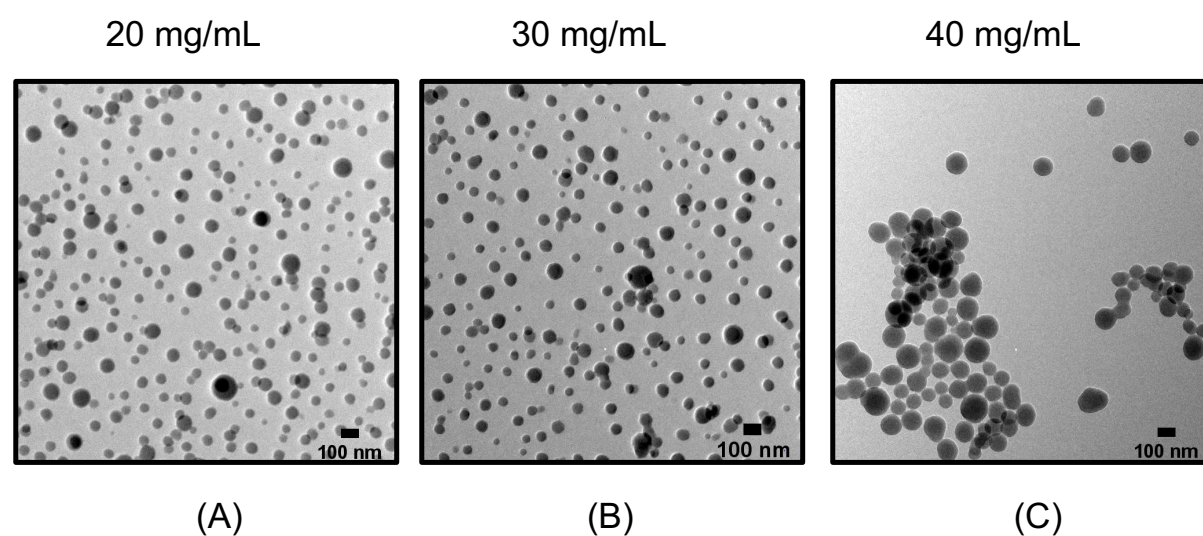


Figure 3.11: TEM analysis of 20, 30 and 40 mg/mL NP dispersions of Rieke P3HT: ICBA (1:1) in MeOH. 20 and 30 mg/mL shows distinct particles whereas the particles in 40 mg/ml dispersions shows some aggregation which is inconsistent with DLS results.

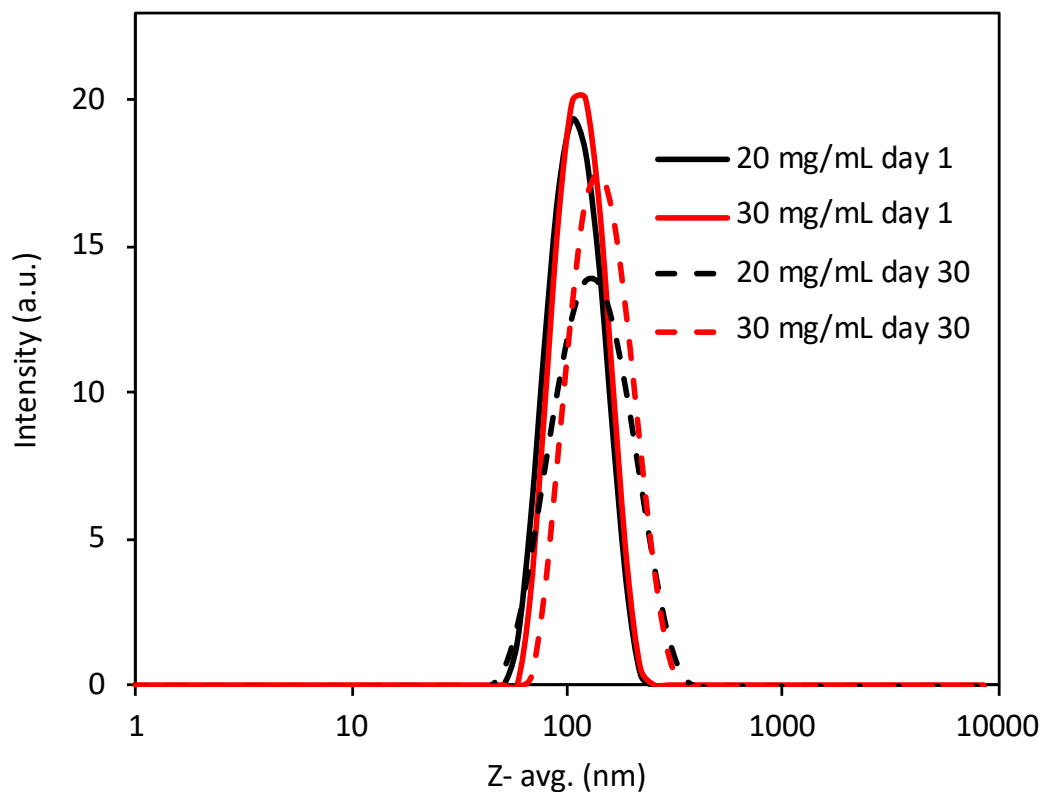


Figure 3.12: DLS plot of 20 and 30 mg/mL NP dispersions of Rieke P3HT: ICBA (1:1) in MeOH formulated with the help of 3 wt.% AS-1, showing dispersions' stability up to 30 days.

The number of coating steps using these concentrated dispersions was optimized to acquire optimum thickness of active layer for efficient devices. The detailed parameters of spin coater along with NP film morphologies will be discussed in next chapter. These dispersions were also sent to the collaborators in Karlsruhe Institute of Technology, KIT, Germany to study their photovoltaic properties. Interestingly, all dispersions survived transportation process and showed no aggregation in DLS measurements even after 1 month (Figure 3.12). Attempts were also made to form concentrated dispersions in EtOH, but only 10 mg/mL concentration was achieved using AS-1. The performance of devices fabricated using MeOH and EtOH dispersions of P3HT:ICBA is discussed in Chapter 4.

3.4.6 Reversibility of ionic pair

As discussed earlier, the design of P3HT-Py is such that it would undergo reversible ion-pair formation on chemical treatment with AcOH. In previous section, it was demonstrated that this ionic pair P3HT-PyH⁺AcO⁻ served as an AS to stabilize NP dispersions. Now, the focus was to examine the thermal dissociation of the pyridinium acetate and subsequent removal of AcOH after film formation. To demonstrate reversibility of pyridinium acetate formation, three films were deposited onto microscope slides using P3HT:ICBA NP dispersions, of which two dispersions were stabilized with 3 wt. % AS-1 and the other dispersion had no additive. One of the films from stabilized dispersions was annealed at 150 °C for 10 mins. The infrared (IR) spectra of all three films were collected, and the carbonyl stretch was monitored as the only carbonyl present was from the acetate. The appearance of C=O stretch at 1770 cm⁻¹ (Figure 3.13A) in the as-cast film containing AS-1 confirms the presence of acetate. The disappearance of C=O vibrational band in case of annealed film confirmed thermal dissociation of the pyridinium acetate and removal of AcOH.

In addition, to examine the impact of using a stronger acid in formation of active surfactants the effect of annealing on films containing AS-1' was examined, and the as cast and annealed NP films of P3HT:ICBA dispersions with 3 wt.% AS-1' were analyzed through IR spectroscopy. The C=O vibrational stretch at 1730 cm⁻¹ disappeared in annealed NP film. It can be inferred from Figure 3.13B that AS-1' dissociated into P3HT-Py and TFA after thermal treatment.

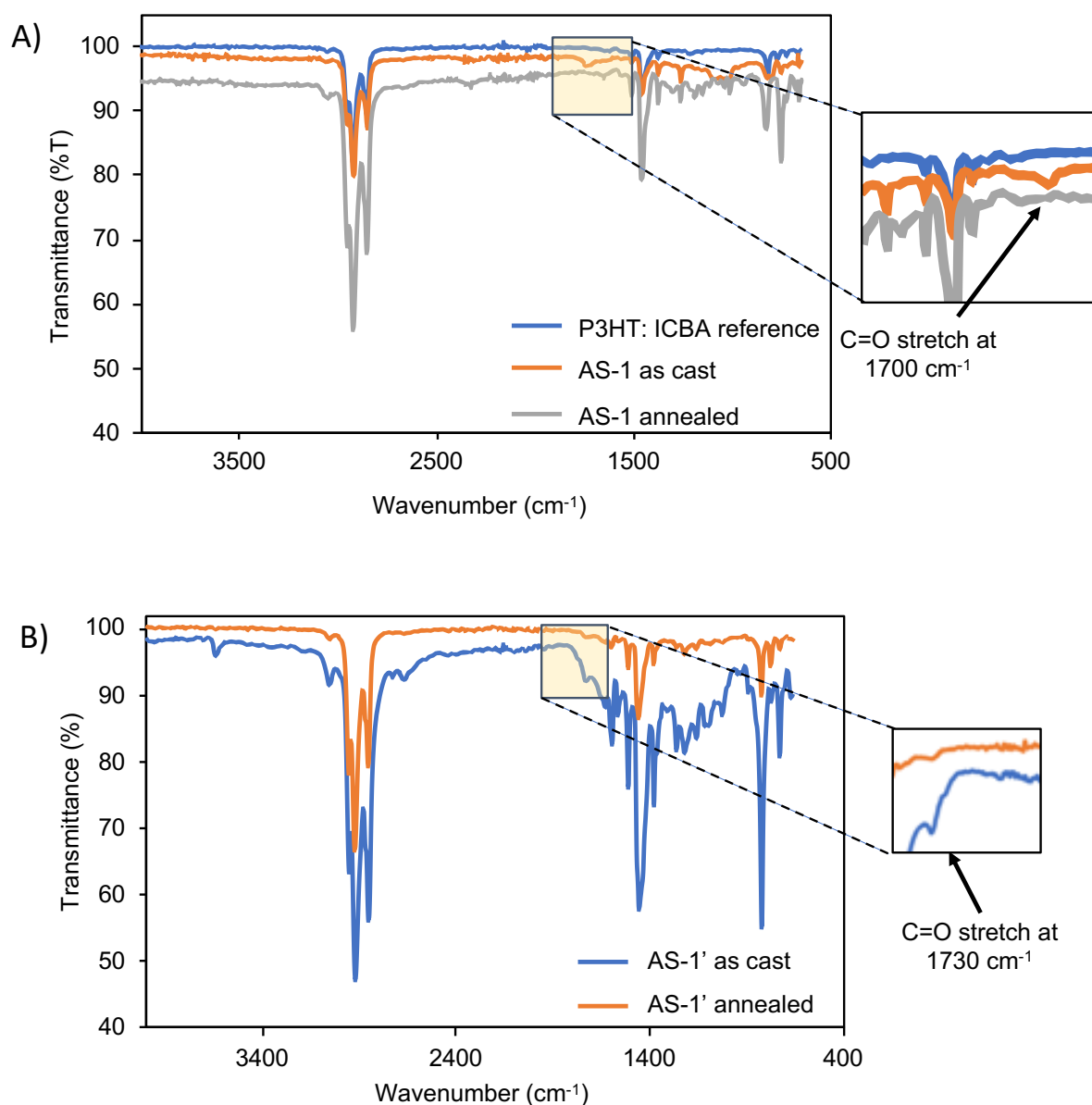


Figure 3.13(A-B): A) An IR spectrum of three NP films; P3HT: ICBA reference, P3HT: ICBA with 3 wt.% of AS-1 as cast and P3HT: ICBA with 3 wt.% of AS-1 annealed at 150 °C for 10 mins. and B) an IR spectrum of two NP films; P3HT: ICBA with 3 wt.% of AS-1' as cast and P3HT: ICBA with 3 wt.% of AS-1' annealed at 150 °C for 10 mins.

3.4.7 Overcoming material dependency

It can be recalled that dispersions formulated through the dispersion method depends on specific batch of polymer used. For instance, the observed NP size for 11,000 g/mol P3HT synthesized using GRIM (chapter 2) was larger than commercial batch of Rieke P3HT of

24,000 g/mol. The difference in NP size can be attributed to higher $\bar{D}$ and lower regioregularity of commercial P3HTs (Table 3.7) in comparison to the synthesized P3HTs (see section 3.3 for reasoning). To overcome material dependency, NP dispersions of a series of defined molecular weights P3HT were formulated using 3 wt.% AS-1. These dispersions showed lower Z-avg. values than dispersions with no additives as displayed in Table 3.7.

Table 3.7: Summarized GPC data of synthesized P3HT and commercial Rieke P3HT along with the DLS results of their NP dispersions in MeOH (2.5 mg/mL) with or without 3 wt.% AS-1. Three measurements of 10 runs were performed on each sample using DLS and standard deviation was calculated from the Z-avg. value obtained in 2nd measurement.

GPC data of P3HT polymers				DLS data of P3HT:ICBA NP			
				0 wt.% AS-1		3 wt.% AS-1	
Samples	M_n (g/mol)	$\bar{D}$	%RR	Z-avg. (nm)	$\bar{D}_{np}$	Z-avg. (nm)	$\bar{D}_{np}$
Synthesized defined molecular weight P3HTs using GRIM.	5,000	1.02	98	80 ± 2	0.1	75 ± 1	0.04
	11,000	1.11	97	140 ± 3	0.08	92 ± 1	0.05
	22,000	1.06	98	155 ± 2	0.07	95 ± 1	0.06
	24,000	1.5	98	170 ± 5	0.09	103 ± 1	0.08
	28,000	1.6	98	Precipitated	-	113 ± 1	0.08
Rieke P3HT, batch 4002-EE	24,000	2.4	98	115 ± 3	0.05	78 ± 2	0.04

In addition, TEM measurements were performed to verify the effectiveness of additive on different molecular weight dispersions. The Z-avg. for 30,000 g/mol P3HT: ICBA NPs with and without additive were determined to be 100 nm and 130 nm respectively from TEM images (Figure 3.14). The images of additive stabilized dispersions showed well separated particles and the obtained Z-avg. values were consistent with DLS measurements.

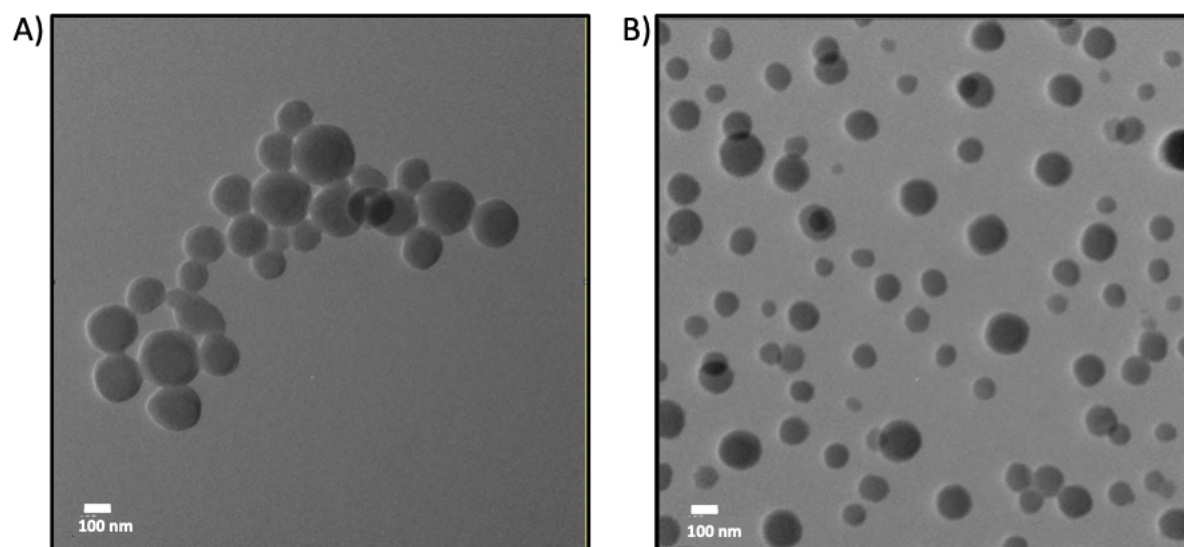


Figure 3.14: TEM image of 30,000 g/mol P3HT: ICBA (1:1) NP dispersions in MeOH A) non-stabilized B) stabilized with 3 wt.% AS-1

3.5 Stabilization of P3HT:ICBA NP using AS-2 (P3HT-COO⁻PyH⁺)

3.5.1 Concentration optimization

Initial experiments to optimize AS-2 addition to P3HT:ICBA NPs targeted 1 mg/mL NP dispersions of P3HT: ICBA in MeOH. In these experiments P3HT-COOH was added to a chloroform solution of P3HT:ICBA, which was then added rapidly into stirring MeOH containing pyridine to form NP dispersions (see experimental section for detailed procedure). No significant difference in NP size was observed between dispersions having up to 2 wt.% addition of AS-2 and dispersions with no additive (Z-avg. ~108 nm) (Table 3.8). However, on addition of 3 wt.% of AS-2, the Z-avg. of NPs increases to 350 nm compared to dispersion with

no additive. The DLS plot also showed a small aggregation peak towards higher Z-avg. values (Figure 3.15). A potential reason for this result could be the formation of a benzoic acid-methanol complex (Figure 15).¹⁹ To confirm this, a ^{13}C NMR study was performed on a solution of benzoic acid and pyridine in MeOH-d^4 (benzoic acid : pyridine, 1:2 eq.) and compared to benzoic acid in CDCl_3 or in MeOH-d^4 (Figure 3.16). The carbon atom **a** of benzoic acid in CDCl_3 shows an upfield shift in MeOH-d^4 due to redistribution of electron density upon formation of intermolecular hydrogen bonds with MeOH. Similar observations were also reported in the literature.¹⁹ One can assume that addition of pyridine base would break the hydrogen bond by forming an ionic pair “pyridinium benzoate”, however, no change was observed in chemical shift value of benzoic acid carbon atom **a** after mixing with pyridine (Figure 3.17). Therefore, it can be concluded that P3HT-COOH undergoes complex formation with MeOH instead of forming $\text{P3HT-COO}^-\text{PyH}^+$ to stabilize nanoparticles with an EDL.

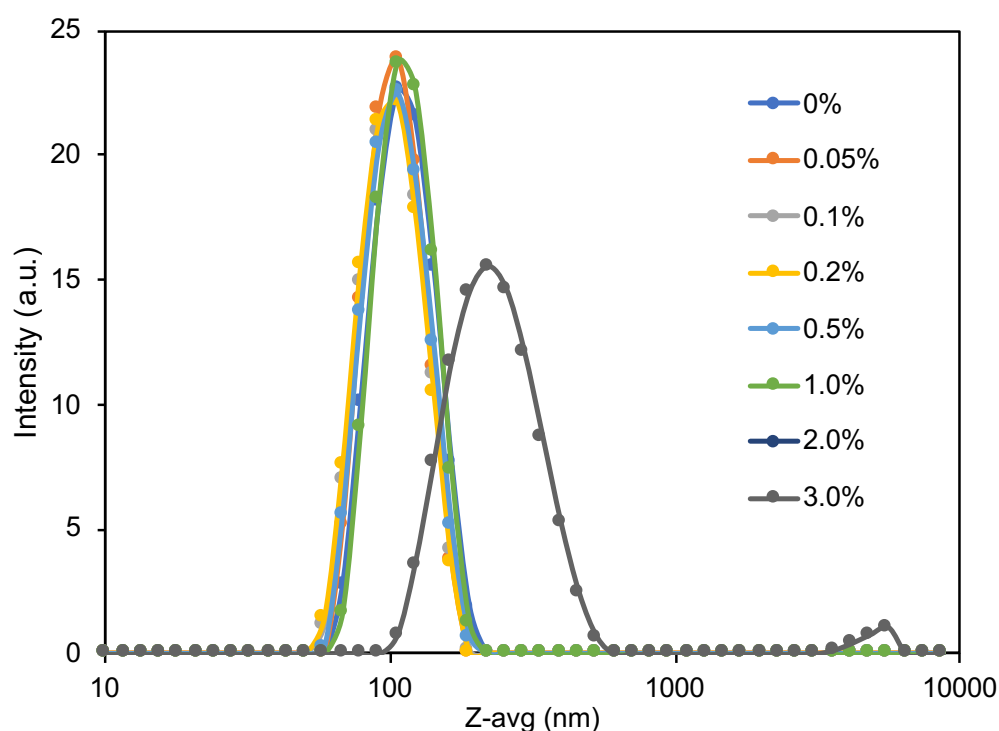
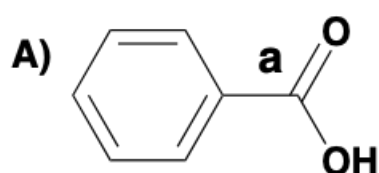


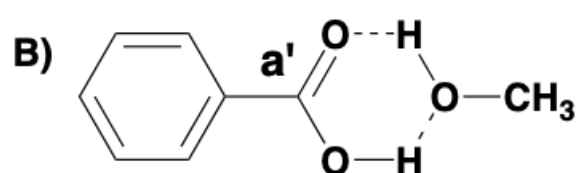
Figure 3.15: Concentration optimization of P3HT-COOH and pyridine for Rieke P3HT: ICBA (1:1) NP dispersions in MeOH (1 mg/mL)

Table 3.8: Summarized DLS results of optimizing concentration of AS-2 to synthesize NP dispersions of Rieke P3HT: ICBA (1:1) NP dispersions in MeOH (1 mg/mL). Three measurements of 10 runs were performed on each sample using DLS and standard deviation was calculated from the Z-avg. value obtained in 2nd measurement.

Sample	Wt.% AS-2	D_{np}	Z-avg. (nm)
1	0	0.04	106 ± 2
2	0.05	0.04	102 ± 1
3	0.1	0.05	99 ± 1
4	0.2	0.05	98 ± 2
5	0.5	0.04	102 ± 8
6	1.0	0.01	108 ± 2
7	2.0	0.04	150 ± 4
8	3.0	0.03	225 ± 6



Benzoic acid



Benzoic acid in methanol

Figure 3.16: Complex formation of benzoic acid in MeOH

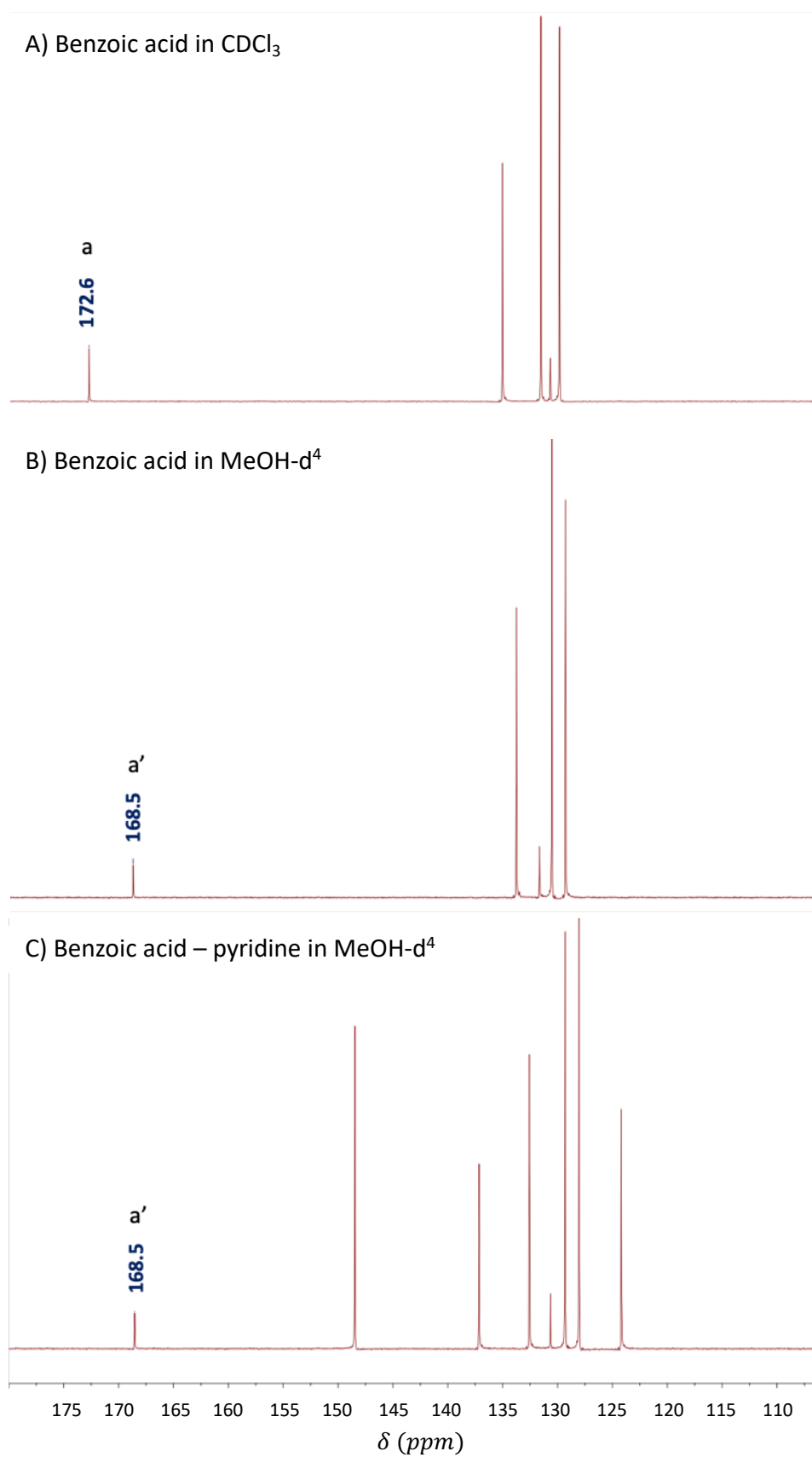


Figure 3.17: ^{13}C NMR of benzoic acid in A) CDCl_3 , B) MeOH-d^4 and C) benzoic acid mixed with 2 eq. of pyridine in MeOH-d^4

3.6 Stabilization of P3HT:ICBA NP using AS-3 (P3HT-TEG)

P3HT-TEG is a type of non-ionic surfactant in which hydrophilic characteristic is contributed to the presence of oxygen atom. In general, oxygen atoms enhance the dissolution of non-ionic surfactants in water through hydrogen bonding. It was anticipated that P3HT-TEG would boost the NP stability of P3HT:ICBA via steric repulsion.

3.6.1 Concentration optimization of AS-3

The NP dispersions of 1 mg/mL concentration were synthesized and the wt.% of AS-3 was varied from 0 to 4 wt.% in P3HT:ICBA chloroform solution as shown in Table 3.9. The respective solutions were added rapidly in MeOH to form NP dispersions.

Table 3.9: Summarized DLS results of optimizing concentration of P3HT-TEG to synthesize NP dispersions of Rieke P3HT: ICBA (1:1) NP dispersions in MeOH (1 mg/mL). Three measurements of 10 runs were performed on each sample using DLS and standard deviation was calculated from the Z-avg. value obtained in 2nd measurement.

Sample	Wt.% AS-3	D_{np}	Z-avg. (nm)
1	0	0.03	118 ± 2
2	0.2	0.07	112 ± 2
3	0.5	0.07	122 ± 1
4	1.0	0.05	134 ± 4
5	2.0	0.05	140 ± 4
6	4.0	0.12	160 ± 2

The Z-avg. of NP dispersions increased with the increase in AS-3 concentration when compared to non-additive dispersions (Table 3.9). Further, addition of 4 wt.% AS-3 resulted in broadly dispersed particles with D_{np} 0.12 which means an uneven distribution of NP size. The increase in Z-average of NP can be attributed to the minimal effect of small hydrophilic TEG chain attached to the long hydrophobic P3HT polymer. The effect of polar group could have been more pronounced if a longer ethylene glycol chain was chosen. It is important to note that not all amphiphiles are surfactants, because amphiphiles with hydrophilic and lipophilic balance (HLB) are likely to migrate to the interface.²⁰

3.7 Summary

The effect of molecular weight of P3HT polymer on P3HT:ICBA NP dispersions was investigated in this chapter. A series of P3HT polymers of well-defined molecular weights (5,000 to 28,000 g/mol) was synthesized in Chapter 2 and were used to form NP dispersions using the dispersion method. The results demonstrated that as the molecular weight of the polymer increases the size of NPs also increases, eventually leading to aggregation and precipitation when a P3HT polymer with a M_n of 28,000 g/mol was used to form P3HT:ICBA dispersions. Contrastingly, NPs of smaller size were obtained for commercial P3HT:ICBA dispersions which is mainly attributed to high $\bar{D}$ and low regioregularity of polymer. This led to a conclusion that surfactant-free NP formation using the dispersion method is dependent on batch of the polymer used and the NP properties are affected by the molecular weight of the polymers if prepared from the same batch of polymer.

This chapter also examined the use of three end-capped P3HTs- P3HT-Py, P3HT-COOH and P3HT-TEG, as active surfactants to formulate NP dispersions of Rieke P3HT:ICBA, so that synthetic reproducibility, NP stability, and ultimate NP concentration could be examined. Out of the three active surfactants only P3HT-Py resulted in a controlled synthesis of NPs. Using 3

wt.% of P3HT-Py and AcOH (AS-1), stable NP dispersions of up to 30 mg/mL in MeOH were obtained. The dispersions were stable up to 2 months at room temperature. Furthermore, controlled NP formation from synthesized P3HT polymer of well-defined molecular weights was also demonstrated highlighting that the advantage of using active surfactant to overcome the limitation associated with batch-to-batch variation in polymers.

3.8 Experimental methods

3.8.1 Dynamic light scattering

DLS is a most common technique to obtain size of the particles dispersed in a solvent lying in the range of 10 and 1000 nm.²¹ These measurements are based on Brownian motion of dispersed particles in which particles move randomly in all direction due to collision with solvent molecules. During the collision, a certain amount of energy is transferred. Since this transfer of energy is constant, it has greater impact on small particles allowing their rapid movement compared to large particles. DLS records the fluctuation in scattering light intensities over a certain time period and a correlation function is generated which is used to measure the translational diffusion coefficient for particles. The hydrodynamic diameter of dispersed particles is calculated using Stoke's Einstein equation (Eq. 3.1):

$$d(H) = \frac{kT}{3\pi\eta D} \quad (Eq. 3.1)$$

where;

$d(H)$ = hydrodynamic diameter

D = translational diffusion coefficient

k = Boltzmann's constant

T = absolute temperature

η = viscosity

DLS also gives the information regarding dispersity of particles which is a measure of broadness of particle size distribution. It can be calculated as the ratio of the quadratic average i.e., average value of squares of measured diameters, $\overline{d^2}$, and square of arithmetic average of measured diameters as expressed in Equation 3.2:

$$D_{np} = \frac{\overline{d^2}}{\bar{d}^2} \quad (Eq. 3.2)$$

Samples were measured using DLS on a Zetasizer Nano ZS (Malvern Instruments) with a 633 nm laser and a backscatter detector angle of 173°. All the measurements were done at room temperature using disposable plastic cuvettes. To measure the particle size, DLS samples were prepared by adding non-solvent (alcohol in this case) for diluting NP dispersions to the concentration of 50 µg/mL.

3.8.2 UV-Vis spectroscopy

To examine the stability of NP dispersions in MeOH, EtOH and IPA their UV measurements were done on 8453 UV-Visible spectrophotometer from Agilent Technologies. The samples were diluted to concentration 50 µg/mL for performing UV measurements

3.8.3 Transmission electron microscopy (TEM)

The TEM is used extensively in fields of medical imaging and material science.²² It uses a high-energy beam of electrons to bombard a thin sample, subsequently producing images based on transmitted electrons through the sample. TEM can be used to study growth of layers, their composition and defects in semiconductors. The working principle of TEM is similar to that of light microscope, except that of using an electron beam rather than a light beam. As the wavelength of electrons is smaller than the light, finer spatial resolution can be achieved.

A beam of electrons from an electron gun is converted into a small and thin coherent beam by the use of condenser lens. This beam is made to strike the sample and transmission of the

electrons through sample is focused by the objective lens on phosphor screen or charged couple device (CCD) camera. Finally, an image is obtained with mix regions of darker and lighter patches. The dark portion in a typical TEM image shows those areas where fewer number of electrons got transmitted, while the lighter areas in image depicts higher transmission through those portions of sample.

To prepare TEM samples, the dispersions of different concentrations 20, 30 and 40 mg/mL in MeOH were diluted to concentration 20 $\mu\text{g/mL}$. The diluted samples were deposited on copper grid (300 mesh $\times$ 83 μm pitch) and dried overnight. TEM analysis was performed on TECNAI F20 which is a high-resolution instrument running at 200 kV.

3.8.4 Infra-red spectroscopy

IR spectroscopy is an analytical technique which measures the infrared intensity versus wavelength (wavenumber) of light. Infrared light can be categorized into three parts based on the wavenumber - far infrared ($4 \sim 400 \text{ cm}^{-1}$), mid infrared ($400 \sim 4,000 \text{ cm}^{-1}$) and near infrared ($4,000 \sim 14,000 \text{ cm}^{-1}$).²³ The interaction of infrared light with the matter results in stretching, contracting and bending of chemical bonds. Due to these changes in chemical bond, a functional group tends to adsorb infrared radiation in a specific wavenumber range. Therefore, the vibration characteristics of chemical functional groups in a sample can be detected through IR spectroscopy regardless of the structure of the rest of the molecule. For example, if a variety of molecules carry carbonyl functional groups then they all can exhibit the C=O stretch for a carbonyl group at around 1700 cm^{-1} . Variables like pressure, temperature, sampling, and molecular structure do not change the position of wavenumber for any functional group.

3.8.5 NP formation using dispersion method

Calculation of amount of P3HT-Py and acid (AcOH and TFA) and P3HT-COOH and base (pyridine) added for NP formation- The wt.% of P3HT-Py and P3HT-COOH were varied in

chloroform solution with respect to total wt. of P3HT used for NP formation. The amount of respective acid (AcOH or TFA) and base (pyridine) added into methanol was similar to the amount of P3HT-Py and P3HT-COOH. For example: To make 1 mg/mL dispersion with 3 wt.% of P3HT-Py and AcOH, 0.5 mg of each P3HT and ICBA along with 0.015 mg $\{(3 \times 0.5)/100\}$ of P3HT-Py were dissolved in chloroform, and similar amount of AcOH (0.015 mg) was added into methanol. To add such small amount of AS-1, standard solutions of P3HT-Py and AcOH of concentration 3 mg/mL were prepared in CHCl_3 and MeOH respectively. This required addition of 5 μL from each solution to prepare dispersions with 3 wt.% AS-1.

Calculation of amount of TEG added for NP formation- The wt.% of P3HT-TEG (AS-3) were varied in chloroform solution with respect to total wt. of P3HT used for NP formation. For example: To make 1 mg/mL dispersion with 1 wt.% of P3HT-TEG, 0.5 mg of each P3HT and ICBA along with 0.015 mg $\{(3 \times 0.5) / 100\}$ of P3HT-TEG were dissolved in chloroform. The standard solution of P3HT-TEG in CHCl_3 (3 mg/mL) was prepared to use 0.015 mg of P3HT-TEG (5 μL) for NP stabilization.

In the case of forming NP dispersions with P3HT-Py and P3HT-COOH, the Rieke P3HT and ICBA (1:1, wt:wt) in combination with P3HT-Py or P3HT-COOH were mixed together in chloroform solution (1 mg/mL) and heated at 56 °C. At the same time, AcOH (in case of P3HT-Py) or pyridine (in case of P3HT-COOH) was added into MeOH (non-solvent). The non-solvent was also heated at 56 °C on a hotplate. The chloroform solution was then added to the methanol (1:4 v:v) to form the NP dispersion with constant stirring (700-800 rpm). Immediately after NP formation, the beaker was removed from hot plate and the stirrer bar was taken out from the beaker to prevent aggregation of NPs. Finally, the volume of the NP dispersion was reduced by evaporating the solvent/non-solvent on a water bath to provide 1

mg/mL concentration of NP dispersions. Different concentrations of dispersions were prepared by varying initial concentration of P3HT: ICBA in chloroform.

In the case of dispersion with P3HT-TEG, the Rieke P3HT and ICBA (1:1, wt:wt) in combination with P3HT-TEG were mixed together in chloroform solution (1 mg/mL) and heated at 56 °C. This solution was added into hot (56 °C) and stirring methanol. Further steps of NP formation are similar as explained above.

3.9 References

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Chapter 4 Nanoparticulate Device Fabrication and Spectroscopic Analysis of Nanoparticle Films

4.1 Introduction

It can be recalled that devices fabricated from surfactant-stabilized nanoparticle (NP) dispersions, synthesized using the mini-emulsion method, exhibit low device efficiencies compared to the devices fabricated using chlorinated solvents¹⁻⁵ (Table 1.1). This has been attributed to the presence of residual surfactant molecules (an insulator) in the active layer which cannot be removed even after extensive dialysis. In general, surfactants such as sodium dodecyl sulfate (SDS) and cetrimonium bromide (CTAB) are used to stabilize NPs via electric double layer (EDL) formation. The mobile surfactant ions present in the film move toward electrode which causes a polarization double layer.⁶ This polarization due to accumulation of mobile charges between the electrode and active layer increases the energy barrier for efficient charge extraction in NP OSCs. Therefore, NP OSCs formulated from surfactant-stabilized dispersions exhibit reduced photocurrent which is one of the potential reasons of obtaining low device efficiency. To overcome this issue, surfactant-free NP dispersions have been formulated which resulted in improved power conversion efficiencies.⁷ However, preparing stable NP dispersions reproducibly, and at high concentrations with a good control on NP formation is challenging in a surfactant-free approach.

The reason for synthesizing end-capped P3HT polymers (Chapter 2) to be used as active surfactants (AS) was two-fold, a) assistance in preparing reproducible, stable and concentrated NP dispersions, and b) the device performance should not be hampered. In Chapter 3, three end-capped P3HT polymers were examined as active surfactants (AS) for NP formation. The combination of P3HT-Py and AcOH (P3HT-PyH⁺AcO⁻ or AS-1) provided good control on P3HT:ICBA NP formation and resulted in stable dispersions of concentration higher than 10 mg/mL. The results suggested that AS-1 behaved as an ionic surfactant to stabilize NP dispersions by forming an electric double layer on the NP surface (Figure 1.15). Chapter 3 also presented the idea of reversibility of ion pair formation in AS-1 (P3HT-PyH⁺AcO⁻) after annealing of NP films to regenerate P3HT-Py. It is hypothesized that the dissociation of the ionic pair would remove all the charges from NP surface and also from NP film if any excess of AS-1 is present. This would minimize the risk of accumulation of charges at the interface of active layer and electrode. It was also supposed that the regenerated P3HT-Py (having semiconducting properties similar to P3HT) would have no significant effect on electronic properties of P3HT:ICBA BHJ, thereby, maintaining device efficiencies similar to chlorinated solvent-processed devices.

In this chapter, the influence of P3HT-Py on OSCs fabricated from P3HT:ICBA NP dispersions of various concentrations in MeOH and EtOH with 0 wt.% and 3 wt.% AS-1 was investigated. The performance of these devices was compared with the devices fabricated using o-dichlorobenzene (DCB) solution of P3HT:ICBA. Thickness of the active layers were characterized using depth profilometer and the root mean square roughness (R_q) of the films was measured using atomic force microscopy (AFM). Optical properties of the films were studied using UV-Vis and photoluminescence spectroscopy. The crystallinity of the films was measured using grazing incident wide angle X-ray (GIWAXS) scattering experiments.

4.2 NP formation for devices

The optimization of NP formation was discussed in Chapter 3. For device fabrication, P3HT:ICBA NP dispersions of different concentrations (with and without AS-1) in EtOH and MeOH were prepared. The 10 mg/mL dispersions were prepared in both EtOH and MeOH using 0 wt.% and 3 wt.% AS-1. NP dispersions with higher concentrations, 20 and 30 mg/mL, were prepared in MeOH using 3 wt.% AS-1. The dispersions were characterized using DLS and the NP diameter were obtained for each variation (Table 4.1). It should be noted that dispersions with concentration higher than 10 mg/mL could not be prepared in EtOH even by using AS-1 and the potential reason for this is discussed in Chapter 3. In MeOH, NP dispersions of concentration higher than 10 mg/mL without AS-1 showed immediate precipitation.

Table 4.1: Summarized DLS data of varying concentration of NP dispersions in MeOH and EtOH (0 wt.% and 3 wt.% AS-1)

Solvent	Concentration (mg/mL)	Wt.% AS-1	Z-avg (nm)	D_{np}
MeOH	10	0	120 ± 2	0.03
	10	3	101 ± 1	0.03
	20	3	111 ± 2	0.07
	30	3	120 ± 1	0.05
EtOH	10	0	130 ± 2	0.03
	10	3	124 ± 2	0.04

4.3 Device fabrication

Devices were fabricated with an inverted device architecture (Figure 4.1) as optimized by our collaborator at Karlsruhe Institute of Technology (KIT), Germany in their earlier work.⁷ It was observed that in a conventional OSC, the deposition of NP dispersions of P3HT:ICBA on hole transport layer (HTL), poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) resulted in uneven distribution of NP film causing the etching of PEDOT:PSS layer. Therefore, devices with an inverted geometry were fabricated by depositing NP dispersions on zinc oxide (ZnO) film, an electron transport layer (ETL) (Figure 4.1). The ZnO NP film was spun cast on cleaned ITO substrate followed by active layer formation using P3HT:ICBA (1:1) dispersions of 10 and 20 mg/mL in MeOH and 10 mg/mL in EtOH. The nanoparticles can be seen clearly in the as-cast devices (see AFM section 4.4.1). Annealing of active layer at 150 °C for 10 min resulted in fusion of the nanoparticles with observed reduction in film thickness and surface roughness. Most of the devices reported in the thesis were made in Alexander Colsmann's (our collaborator) lab at KIT Germany. The annealing temperature used for devices fabricated from P3HT:ICBA NP dispersions varied between 150-200 °C.⁷⁻⁹ Although an improved efficiency has been reported at higher annealing temperature in previous studies, recent experiences from our collaborators reflected that the devices of P3HT:ICBA dispersions do not show significant improvement in performance on increasing the annealing temperature from 150 to 200 °C. The PEDOT:PSS was deposited on top of active layer and annealed at 150 °C for 10 min. This was followed by the vacuum deposition of a silver top electrode (Ag) (see experimental section for details). As a control, a DCB solution of P3HT:ICBA (1:1) (30 mg/mL) was spun cast on top of ZnO for devices processed using chlorinated solvent.

All the dispersions were sent to our collaborator for device fabrication. Due to time constraints, devices from 10 mg/mL dispersions (MeOH and EtOH) were fabricated by the collaborator

and devices from 20 mg/mL dispersions and DCB solution of P3HT:ICBA were built by the candidate with the assistance of Dr. Jegadesan Subbiah at the Bio21 Institute, University of Melbourne. At KIT, the device fabrication and performance measurement were conducted in a glove box placed inside a clean room. For OSCs made by the candidate, the ZnO layer, active layer and PEDOT:PSS were deposited inside the glove box. The devices were taken out of the glove box (exposed to air) and placed in a metal evaporator for vacuum deposition of metal electrode followed by performance measurement in the air.

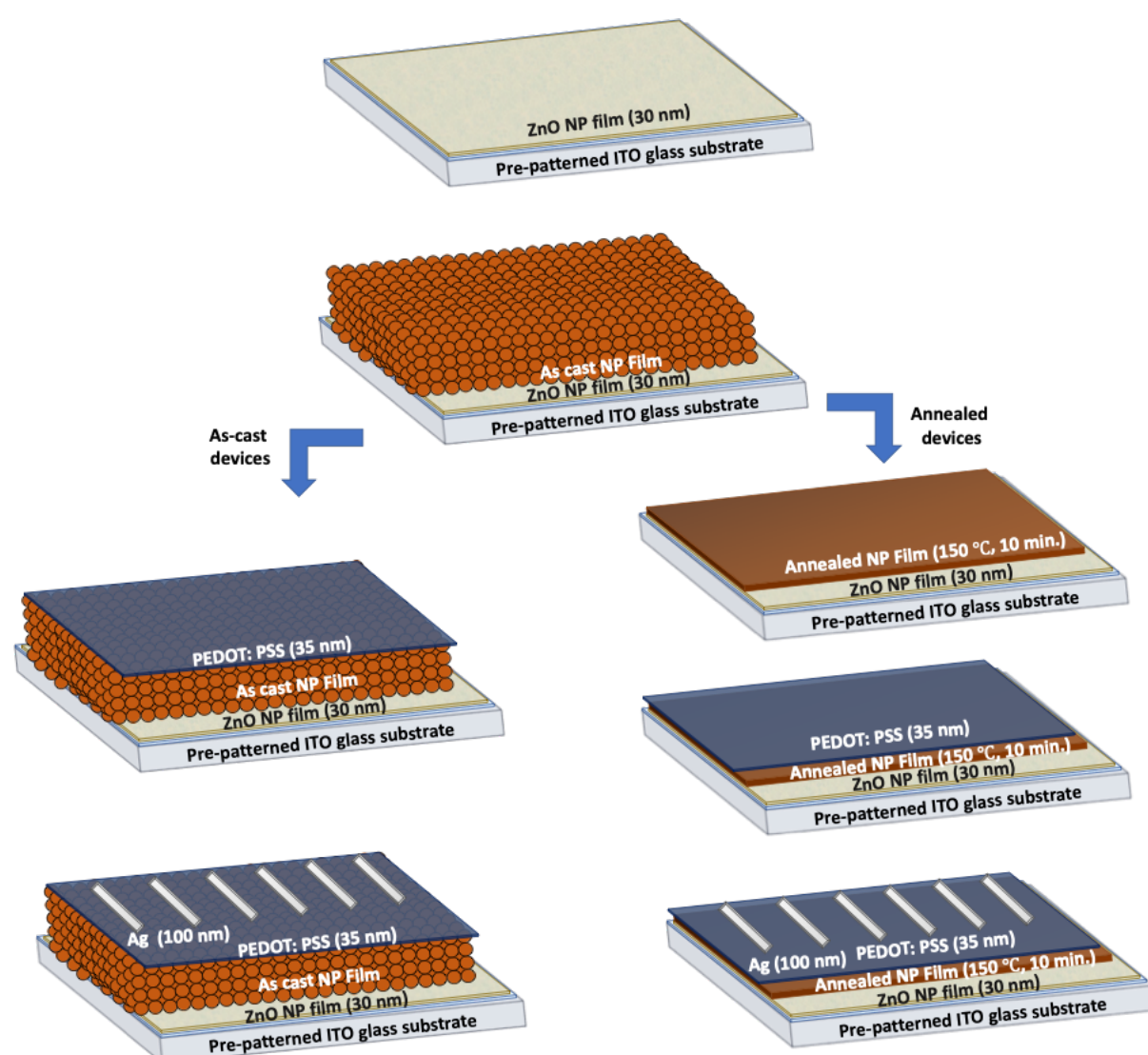


Figure 4.1: Schematic representation of as-cast and annealed devices fabricated with inverted geometry from NP dispersions

4.3.1 Optimization of active layer thickness for efficient devices

It has been demonstrated that obtaining an optimum thickness of the active layer is critical to achieve highly efficient OSCs.¹⁰ In this section, the number of coating steps required to achieve optimally thick NP films from the NP dispersions of different concentrations prepared in EtOH and MeOH is discussed.

To optimize the thickness of the active layer, ZnO was spun cast on ITO coated glass substrates followed by sequential coating of NP dispersions (1000 rpm, 20 s) to obtain the required active layer thickness. The active layers were annealed at 150 °C for 10 min. It should be noted that the subsequent layers were not dried or annealed between the deposition steps. The number of coating steps was varied depending on the concentration of dispersions used for fabricating the active layer of optimum thickness. In this work, successive coatings of the NP dispersions were applied by depositing 50 μ L aliquot from dispersions of a given concentration at an interval of 20 s (see experimental section for detailed procedure) to fabricate the active layer. The thickness of ZnO layer was optimized to be 30 nm and was kept uniform for all the experiments. The active layer thickness was measured using a depth profilometer. The thickness values presented in Table 4.2 are the sum of the thicknesses of ZnO layer and active layer (annealed). For every variation involved in the deposition process of the active layer, eight devices with inverted architecture were fabricated and their efficiencies after annealing at 150 °C for 10 min are reported (Table 4.3-Table 4.5). Note that the as-cast devices were fabricated only with the optimized condition i.e., after identifying the active layer thickness that yielded best device efficiency on annealing.

4.3.1.1 Active layer fabricated from 10 mg/mL dispersions (0 wt.% and 3 wt.% AS-1)

P3HT:ICBA dispersions in MeOH

It has been observed in the previous work that devices formulated from 10 mg/mL P3HT:ICBA dispersions (MeOH) resulted in best device efficiency of 4.1%.⁷ The active layer thickness for these devices after annealing was 250 nm.

In this work, the optimization of active layer thickness was performed by varying the number of coating steps to 4, 6 and 8. The application of 4 coating steps of dispersions with 0 wt.% and 3 wt.% AS-1 on ZnO coated ITO substrate provided thicknesses of active layer as 138 ± 3 nm and 153 ± 11 nm respectively after annealing (Table 4.2). On applying 6 and 8 coatings of these dispersions (0 wt.% and 3 wt.% AS-1), the obtained thickness of active layer was between 200 to 270 nm. It should be noted that the previous highest efficiency of 4.1% (for devices fabricated completely under inert condition) has been reported with NP films of thickness ~ 250 nm (6 coating steps). In the present work, this thickness was obtained using 8 coating steps of NP dispersions with and without AS-1. Therefore, device performance at other active layer thicknesses was not evaluated and all the subsequent devices were formed by applying 8 coating steps with these NP dispersions. The observed efficiencies for as-cast devices fabricated from the dispersions with 0 wt.% and 3 wt.% AS-1 were $\sim 0.5\%$. After annealing the active layer at 150 °C for 10 min, the device efficiency increased to $\sim 3\%$ (Table 4.3). The open circuit voltage (V_{oc}) and fill factor (FF) were only marginally improved after annealing whereas, a significant rise in short current density (J_{sc}) was the main contributor in increased PCE.

P3HT:ICBA dispersions in EtOH

Device efficiencies of 3.5%⁷ and 4.3%⁸ have been reported for surfactant-free NP dispersions of P3HT:ICBA prepared in EtOH with annealed active layers of 220 nm thicknesses (2.8 mg/mL in EtOH, 25 coating steps, 1000 rpm, 20 s), and 170 nm thickness (10 mg/mL in MeOH, 3 coating steps, 1000 rpm, 20 s) respectively. In addition, a thickness of 180 nm has been

reported for the devices fabricated from surfactant-free dispersion of P3HT:PCBM in EtOH (~2 mg/mL, 5 coating steps, 1000 rpm, 30 s).¹¹ Based on these previous observations, the targeted thickness range of active layer deposited from EtOH dispersion was set between 170 to 220 nm.

To perform the thickness optimization of active layer fabricated from dispersions (0 wt.% and 3 wt.% AS-1), number of active layer applications were varied between 4 to 8. The application of 4 coatings of NP dispersions (0 wt.% and 3 wt.% AS-1) provided the thickness of active layer less than 125 nm (Table 4.2). On applying 6 and 8 coating steps from dispersions with 0 wt.% AS-1, the observed thicknesses of active layers were 145 ± 9 nm and 198 ± 3 nm respectively. In the case of films deposited from dispersions with 3 wt.% AS-1, the observed active layer thicknesses using 6 and 8 coating steps were 175 ± 8 nm and 223 ± 15 nm respectively. The device efficiencies were measured for films fabricated using 6 to 8 and 5 to 7 application steps of P3HT:ICBA dispersions with 0 wt.% and 3 wt.% AS-1 respectively.

The as-cast devices fabricated using 6 and 5 coating steps of the NP dispersions with 0 wt.% and 3 wt.% AS-1 exhibited the expected low device performance of ~0.5%. Annealing of active layer at 150 °C for 10 min resulted in improved device efficiencies of 4.3% and 4.1% for devices constructed using dispersions with 0 wt.% and 3 wt.% AS-1 respectively (Table 4.4)

It can be recalled that on annealing NP films deposited from dispersions with 3 wt. % AS-1 dissociation of the ionic pair (P3HT-PyH⁺AcO⁻) is expected, resulting in the regenerating P3HT-Py with the removal of AcOH. Notably, the J_{sc} values of annealed devices fabricated from dispersions with and without AS-1 were similar. This observation suggested that the P3HT-Py had little impact on electronic properties of the bulk-heterojunction.

4.3.1.2 Active layer fabricated from 20 mg/mL dispersions in MeOH (3 wt.% AS-1)

The novelty of this work is that dispersions of concentration greater than 10 mg/mL has been prepared using dispersion method with the help of 3 wt.% AS-1. Now that the concentration of dispersion has been doubled to 20 mg/mL, it was anticipated that the optimum thickness of active layer can be achieved in a fewer number of coating steps (possibly 2-4). The thicknesses of the annealed active layer after 2, 3 and 4 coating steps were 157 ± 4 nm, 260 ± 3 nm, and 340 ± 7 nm respectively (Table 4.2). The as-cast NP devices exhibited an efficiency of 0.3% PCE. Although device efficiency was increased to 1.5% after annealing, but it was comparatively lower than devices fabricated from 10 mg/mL NP dispersions. It can be noted that the J_{sc} of devices fabricated from 20 mg/mL NP dispersions was ~ 1.6 times smaller than the J_{sc} obtained for devices fabricated from 10 mg/mL NP dispersions (MeOH) (Table 4.5).

This could be attributed to rough surface of NP films deposited from 20 mg/mL NP dispersions. Therefore, it was anticipated that performing solvent vapor annealing (SVA) on as-cast film along with thermal annealing (TA) would join the particles resulting in smoothening of the film. The as-cast layer of devices was subjected to SVA with THF (20 sec) followed by TA at 150 °C for 10 min which increased the J_{sc} to 10 mA/cm². As a result, an improved device efficiency of 3.5% was obtained. Therefore, with a slight modification in post deposition treatment, devices could be assembled from concentrated NP dispersion with fewer coating steps but the same device power conversion efficiency.

The performance of devices fabricated from 20 mg/mL NP dispersions were compared with the devices fabricated from DCB solution of P3HT:ICBA (1:1). It can be recalled from section 4.3 that these two devices were fabricated by the candidate using same experimental conditions. Therefore, performance of only these two devices were compared. The efficiencies for as-cast and annealed devices processed from DCB solution were 1.7% and 3.6%

respectively. The device efficiency obtained for devices fabricated from 20 mg/mL dispersions was similar to the devices processed from chlorinated solvent.

Table 4.2: Thickness of annealed active layers fabricated from MeOH and EtOH dispersions by varying the number of application of dispersions depending on the concentration of dispersions. C.S represents the number of coating steps of dispersions.

Solvent	Concentration of P3HT:ICBA (1:1) dispersion (mg/mL)	C.S	Thickness (nm)	
			0 wt.% AS-1	3 wt.% AS-1
EtOH	10	4	102 ± 3	123 ± 6
		6	145 ± 9	175 ± 8
		8	198 ± 3	223 ± 15
MeOH	10	4	138 ± 3	153 ± 11
		6	200 ± 8	210 ± 8
		8	250 ± 5	271 ± 5
	20	2	-	157 ± 4
		3		260 ± 3
		4		340 ± 7
	30	1	-	127 ± 4
		2		220 ± 13
		2.5		287 ± 9
		3		345 ± 6

4.3.1.3 Active layer fabricated from 30 mg/mL dispersions in MeOH (3 wt.% AS-1)

It was expected that the number of coating steps to obtain optimum thickness of active layer should further decrease for 30 mg/mL dispersions, and the depth profile measurements performed on the annealed films indicated the thicknesses of 127 ± 4 nm (1 coating), 220 ± 13 nm (2 coatings), 345 ± 6 nm (3 coatings) (Table 4.2). Since 3 coatings of dispersions were providing a very thick active layer, therefore, another film was deposited using 2 coatings of 50 μ L followed by 1 coating with 25 μ L dispersion. This data is presented as 2.5 coating steps (Table 4.2) which resulted in active layer thickness of 287 ± 9 nm. The device optimization for films fabricated with 2 and 2.5 coating steps were performed, however, inconsistent efficiencies were observed which could be attributed to higher surface roughness of the NP film. Therefore, this work does not include the discussion of devices fabricated from 30 mg/mL dispersions.

Table 4.3: Key performance parameters of inverted OSCs fabricated from P3HT:ICBA (1:1) dispersions in MeOH (10 mg/mL) (0 wt.% and 3 wt.% AS-1) using 8 coating steps (C.S). The average was calculated by considering at least 8 devices. TA denotes to thermal annealing of film at 150 °C for 10 min.

Conditions	Wt.% (AS-1)	C.S	Thickness (nm)	Voc (V)	Jsc (mA/cm ²)	FF	% PCE
As-cast	0	8	350 ± 13	0.7 ± 0.1	2.5 ± 0.3	30 ± 2	0.5 ± 0.1
TA	0	8	250 ± 5	0.8 ± 0.1	7.7 ± 0.2	47 ± 1	3.0 ± 0.1
As-cast	3	8	380 ± 9	0.6 ± 0.3	2.2 ± 0.2	36 ± 3	0.5 ± 0.1
TA	3	8	271 ± 5	0.8 ± 0.1	8.0 ± 0.1	49 ± 2	3.1 ± 0.2

Table 4.4: Key performance parameters of inverted OSCs fabricated from P3HT:ICBA (1:1) dispersions in EtOH (10 mg/mL) with 0 wt.% and 3 wt.% AS-1 by varying the number of coating steps. The average was calculated by considering at least 8 devices. C.S represents the number of coating steps of dispersions. TA refers to thermal annealing of film at 150 °C for 10 min.

Conditions	Wt.% AS-1	C.S	Thickness (nm)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	% PCE
TA	0	8	198 ± 3	9.1 ± 0.1	0.8 ± 0.1	48 ± 1	3.6 ± 0.1
	0	7	170 ± 5	9.3 ± 0.1	0.8 ± 0.1	53 ± 1	4.1 ± 0.1
TA	0	6	145 ± 9	9.0 ± 0.1	0.8 ± 0.1	57 ± 1	4.3 ± 0.1
As-cast	0	6	265 ± 11	2.3 ± 0.2	0.7 ± 0.3	33 ± 2	0.5 ± 0.1
TA	3	7	193 ± 6	9.0 ± 0.1	0.8 ± 0.1	50 ± 1	3.6 ± 0.1
TA	3	6	175 ± 8	8.8 ± 0.1	0.8 ± 0.1	51 ± 1	3.7 ± 0.1
TA	3	5	150 ± 6	9.0 ± 0.1	0.8 ± 0.1	55 ± 1	4.1 ± 0.1
As-cast	3	5	276 ± 12	2.1 ± 0.1	0.7 ± 0.2	34 ± 2	0.4 ± 0.1

Table 4.5: Key performance parameters of inverted OSCs fabricated from P3HT:ICBA (1:1) dispersions in MeOH (20 mg/mL) with 3 wt.% AS-1 by varying the number of coating steps. The device efficiency of optimized active layer thickness fabricated from these dispersions was compared with the efficiency of devices fabricated from DCB solution of P3HT:ICBA (1:1) (30 mg/mL). The average was calculated by considering at least 8 devices. C.S represents the number of coating steps. TA denotes to thermal annealing of film at 150 °C for 10 min.

Condition	C.S	Thickness (nm)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	% PCE
NP OSC, TA	2	157 ± 4	4.7 ± 0.1	0.2 ± 0.1	30 ± 1	0.4 ± 0.1
	4	340 ± 7	4.6 ± 0.1	0.7 ± 0.1	39 ± 1	1.3 ± 0.1
NP OSC, TA	3	260 ± 3	5.2 ± 0.1	0.7 ± 0.1	40 ± 1	1.5 ± 0.1
NP OSC, SVA (20 s) + TA	3	247 ± 11	9.8 ± 0.6	0.76 ± 0.1	46 ± 1	3.5 ± 0.2
NP OSC, as- cast	3	371 ± 14	2.0 ± 0.1	0.5 ± 0.1	35 ± 2	0.3 ± 0.1
DCB, as-cast	1	201 ± 10	6.9 ± 0.2	0.7 ± 0.1	34 ± 3	1.7 ± 0.1
DCB, TA	1	168 ± 16	8.2 ± 0.1	0.7 ± 0.2	64 ± 2	3.6 ± 0.1

To summarize, the observed improvement in efficiencies of devices processed from dispersions (10 mg /mL (MeOH and EtOH), 20 mg/mL (MeOH)) and chlorinated solvent after annealing could be attributed to modification in morphology of these films. In the next sections, the effect of annealing on surface roughness and crystallinity of thin films is discussed.

4.4 Analysis of thin-films

Thin films of P3HT:ICBA prepared from NP dispersions and from DCB solution (as a control) were analyzed through atomic force microscopy (AFM), UV-Vis spectroscopy, photoluminescence (PL) spectroscopy and grazing incidence wide-angle X-ray scattering (GIWAXS) experiments.

4.4.1 Atomic force microscopy

AFM is a mechanical imaging technique in which a probe or tip is moved across the surface of sample to measure the surface height in form of vertical displacement of the tip.¹² The AFM topography images were collected for films fabricated from DCB solutions and NP dispersions before and after annealing (150 °C, 10 min) using tapping mode. A detailed procedure of films preparation for AFM analysis is provided in experimental section. Although images were collected for all the variations (Table 4.6), only images of films deposited from a DCB solution (control) and a 20 mg/mL NP dispersion are shown here (Figure 4.2 and Figure 4.3).

The as-cast P3HT:ICBA films deposited from DCB solution exhibited root mean square roughness (R_q) of ~13 nm whereas, annealed films exhibited R_q ~6 nm (Figure 4.2). These values match closely to the literature.¹³ In case of as-cast NP films deposited from 10 mg/mL dispersions (MeOH and EtOH) with 0 wt.% and 3 wt.% AS-1, the observed R_q was ~40 nm. The as-cast NP layers fabricated from 20 mg/mL dispersions (MeOH) with 3 wt.% AS-1 exhibited R_q ~64 nm (Figure 4.3A). The higher surface roughness of as-cast NP films compared to DCB film is attributed to presence of spherical shape NPs in the former. This observation is consistent with literature.⁷

The surface roughness of all as-cast films was higher than annealed films which could result in poor charge extraction at the electrode, or insufficient surface coverage may simply provide

the opportunity for short circuit pathways. This is one of the potential reasons of obtaining low J_{sc} for all as-cast devices (Table 4.5).

Thermal annealing (150 °C, 10 min) of films reduced the surface roughness which improved the interfacial contact between the electrode and the active layer, thus, resulting in efficient charge extraction and improved device performance.

Table 4.6: Summarized surface roughness (R_q) (nm) for as-cast and annealed films as estimated from AFM analysis. TA denotes to thermal annealing of film at 150 °C for 10 min.

Solvent	Concentration	Wt.% AS-1	RMS roughness (R_q) (nm)		
			As-cast	TA	SVA+TA
DCB	30 mg/mL	0	13	6	
MeOH	10 mg/mL (0 wt.% AS-1)	0	40	28	
	10 mg/mL (3 wt.% AS-1)	3	40	21	
	20 mg/mL (3 wt.% AS-1)	3	64	46	30
EtOH	10 mg/mL (0 wt.% AS-1)	0	40	26	
	10 mg/mL (3 wt.% AS-1)	3	40	20	

The underlying reasons for improved efficiencies after annealing in case of solution and NP dispersions processed devices are different. The donor and acceptor materials in as-cast films deposited from DCB solution were too intimately mixed for efficient charge transport and extraction. Annealing improved the nano-scale phase separation of donor and acceptor blend, and hence the charge percolation pathways. In the case of NP as-cast films, the NPs are not

well connected as they can be distinctly seen in AFM images (Figure 4.3A). Therefore, the free charges generated from dissociation of excitons could not be transported effectively to the respective electrodes as they remain captured in the NPs. Such free charges are susceptible to re-combination, thus, resulting in low J_{sc} of as-cast NP devices. More homogenous films were achieved after annealing which resulted in reduction of voids between the NPs and subsequently a reduction in surface roughness was observed (Table 4.6). The smoothening of the films facilitated better charge extraction at the electrode in annealed NP devices compared to as-cast devices.

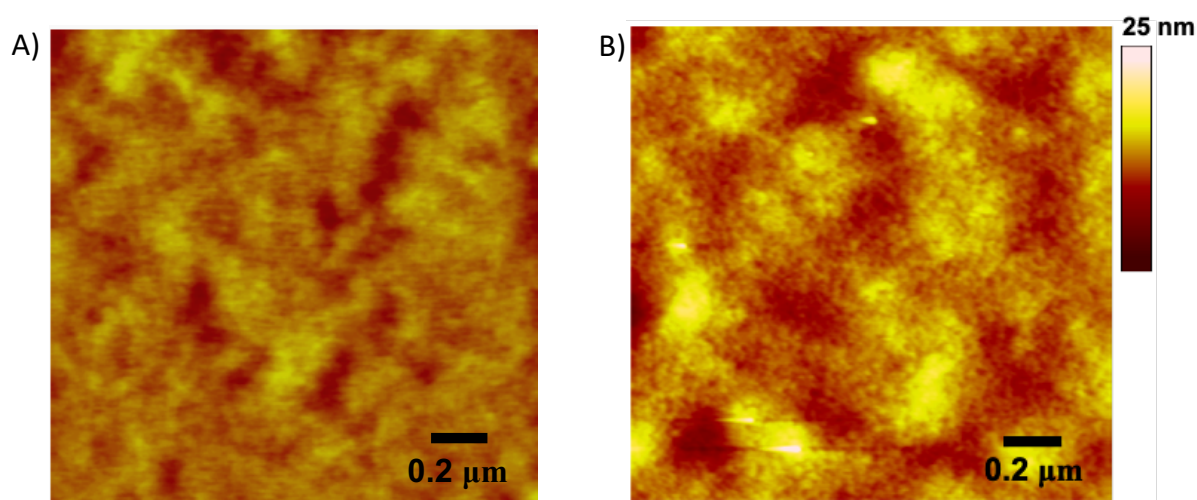


Figure 4.2: $0.2\ \mu\text{m} \times 0.2\ \mu\text{m}$ AFM topography images of active layer spin casted from P3HT:ICBA (1:1) solution in DCB (30 mg/mL) with colour bar of 25 nm displaying A) as-cast film and B) annealed films at 150°C for 10 min. This image was collected by Dr. Jegadesan Subbiah (Jones lab group at the University of Melbourne)

It is important to note that the V_{oc} observed for as-cast NP devices was lower than the annealed NP devices. This observation is consistent with the literature.⁷ The low V_{oc} could be attributed to a greater degree of bimolecular recombination in the rougher as-cast films. However, the relation between surface roughness and bimolecular recombination is not obvious. In a previous study, the greater recombination was observed for as-cast devices compared to annealed devices by performing intensity dependent photo-current density measurements.⁷

They also reported that bimolecular recombination in as-cast devices can be reflected from the low V_{oc} (0.6 V) of the as-cast devices which improved to 0.7 V after annealing as the bimolecular recombination was reduced.

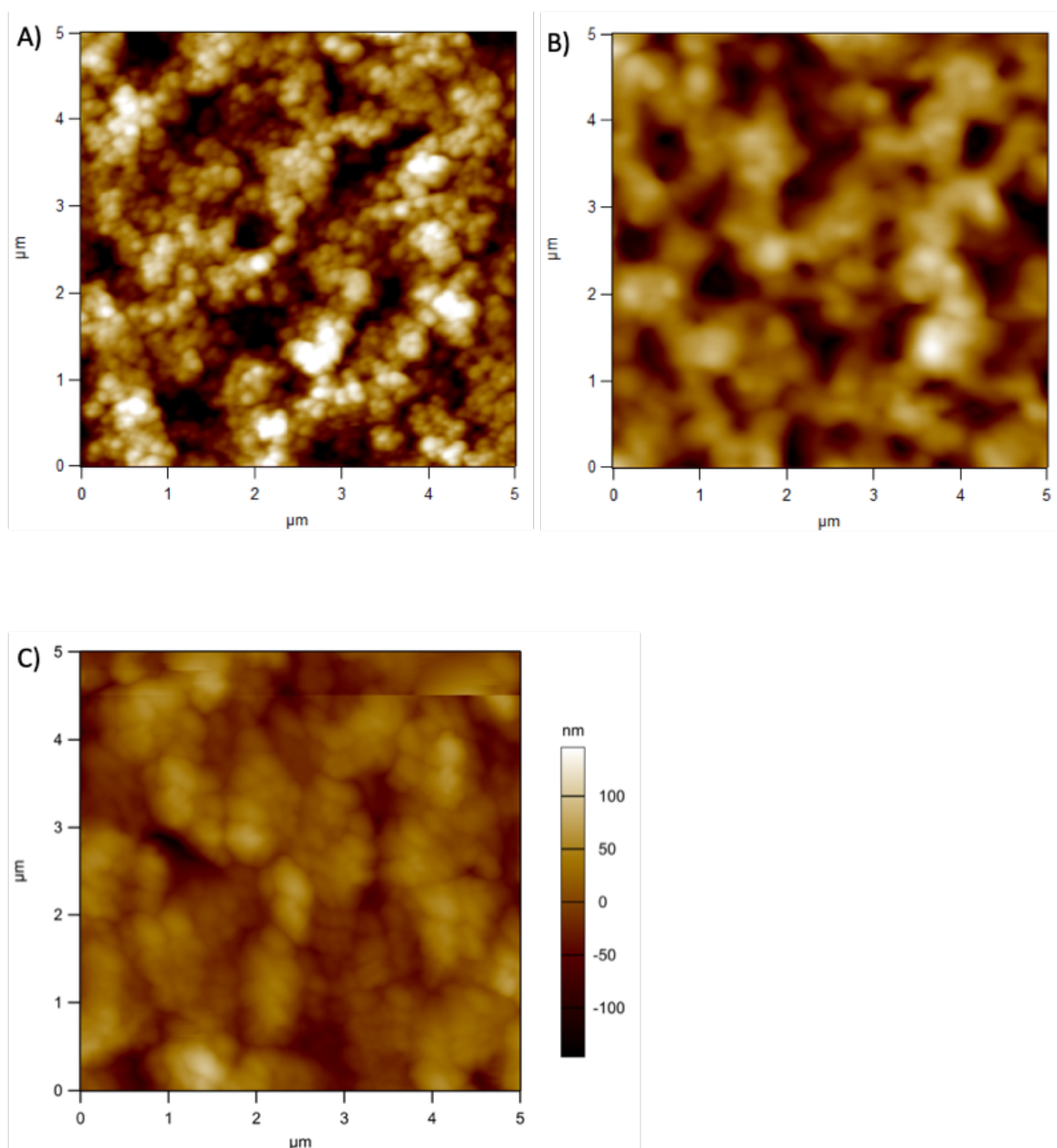


Figure 4.3: $5\mu\text{m} \times 5\mu\text{m}$ AFM topography images of active layer fabricated (3 coating steps) from 20 mg/mL P3HT:ICBA (1:1) dispersions in MeOH using 3 wt.% AS-1 with colour bar of 100 nm displaying A) as-cast film, B) annealed film at 150°C for 10 min., and C) SVA for 20 sec. with THF followed by thermal annealing at 150°C for 10 min.

4.4.2 UV-Vis absorption spectroscopy

UV-Vis absorption spectroscopy was used to study the optical properties of P3HT:ICBA in solution, dispersions and their thin-films. The sample preparation for UV measurements is given in experimental section. The absorption spectra of stabilized and non-stabilized dispersions in EtOH and MeOH were compared with the absorption spectra of P3HT:ICBA DCB solution (Figure 4.4 and Figure 4.5). It is well known that the appearance of peak absorbance at around 500 nm gives an indication of degree of conjugation in P3HT polymer chain.¹⁴ The degree of interchain order can be determined by the relative size of P3HT vibronic shoulder appearing at around 600 nm.¹⁴

The absorption spectra of DCB solution of P3HT:ICBA exhibited absorption maxima at 450 nm which is a typical solution spectrum for P3HT.¹⁵ The absorptions of P3HT in P3HT:ICBA NP dispersions (EtOH and MeOH) were red shifted (Figure 4.4 and Figure 4.5). The red shift indicates aggregation of P3HT which can be expected for NP dispersions. The absorption spectra of NP dispersions exhibited distinct vibronic peaks at wavelengths 510 nm, 560 nm and 610 nm corresponding to 0-2, 0-1 and 0-0 transitions to the vibronic modes of the excited electronic state.¹⁵ These vibronic bands are characteristic of semi-crystalline aggregates.¹⁶ Therefore, it can be inferred that semi-crystalline P3HT domains were already formed inside NPs during NP preparation. This phenomenon has also been observed in other work.^{4, 5, 7, 17}

Next, the effect of annealing was studied on thin-films prepared from NP dispersions and a P3HT:ICBA DCB solution by comparing the absorption spectra of as-cast and annealed films. The thin films were prepared by depositing dispersions of 10 mg/mL (0 wt.% and 3 wt.% AS-1), 20 mg/mL (3 wt.% AS-1) in MeOH, 10 mg/mL (0 wt.% and 3 wt.% AS-1) in EtOH and solution of P3HT:ICBA (30 mg/mL) in DCB. In case of the NP films, annealing did not affect the optical properties of P3HT:ICBA NPs as can be seen in normalized UV-Vis absorption

spectrum (Figure 4.6B and Figure 4.7B). The vibronic features, shape of the spectra and the maximum peak amplitude of annealed NP film spectra matched to the absorption spectra of as-cast NP films. Only a slight enhancement in the vibronic features was observed which can be attributed to enhanced $\pi - \pi$ stacking of P3HT on annealing. Therefore, it can be concluded that the semi-crystallinity of P3HT domains remained stable after film formation which was established during NP preparation. On comparing the absorption spectra of annealed NP film with the film deposited from DCB solution of P3HT:ICBA, the vibronic features of NP films were less pronounced and were slightly blue-shifted. This indicated a lower degree of crystallinity in the annealed NP film as compared to the films prepared from DCB solution of P3HT:ICBA. The NP films deposited from 20 mg/mL dispersions were post-processed through SVA with THF (20 sec) followed by TA (150°C for 10 min). The absorption of these films were slightly red-shifted with enhanced vibronic features and matched closely to the absorption of annealed films fabricated from P3HT:ICBA DCB solution (Figure 4.6B).

The results obtained from thin film UV measurements corroborate the AFM analysis suggesting that reasons for higher device performance in annealed devices compared to as-cast devices are different for both solution and dispersion processed devices. In the former, the thermal treatment increases the crystallinity of the P3HT polymer which is evident from the increase in optical absorption. Due to higher crystallinity in annealed films, a better phase-segregation between donor and acceptor materials could be achieved facilitating improved charge transport and extraction. For NP films, the crystallinity in as-cast and annealed films remained unchanged indicating that the semi-crystalline nature of P3HT was developed during the NP formation process itself. The improvement in device performance for annealed NP films could be due to more intimate contact between the NPs which facilitated enhanced charge extraction.

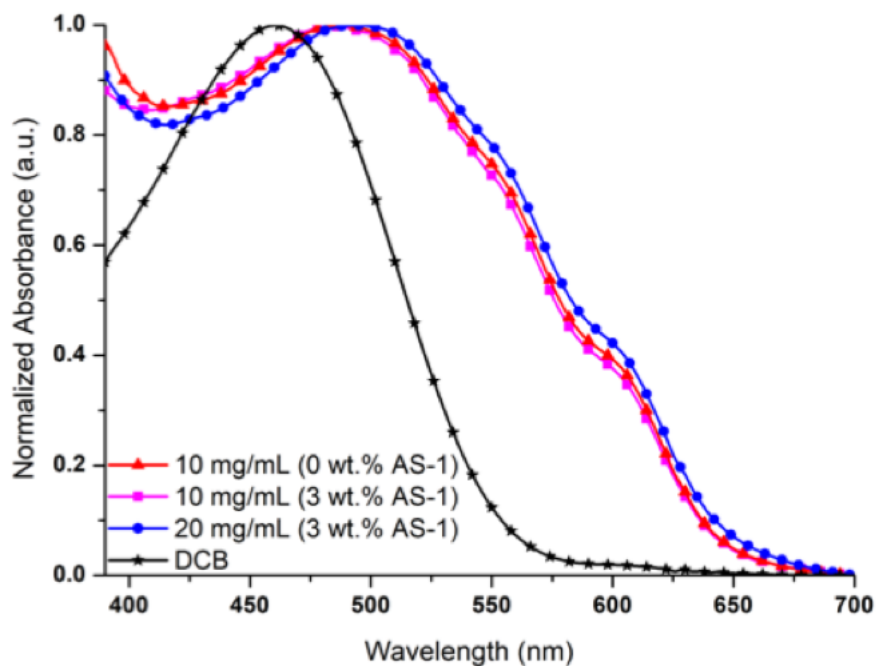


Figure 4.4: Normalized UV-Vis absorption spectra of P3HT:ICBA (1:1) NP dispersions of different concentrations in MeOH; 10 mg/mL (0 wt.% AS-1), 10 mg/mL (3 wt.% AS-1) , 20 mg/mL (3 wt.% AS-1) vs. 30 mg/mL DCB solution of P3HT:ICBA (1:1).

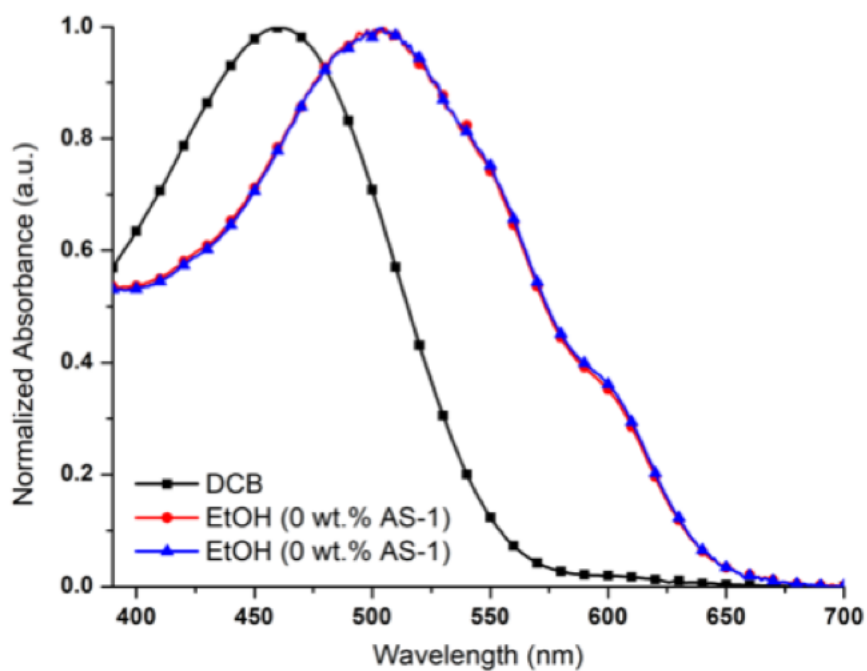


Figure 4.5: Normalized UV-Vis absorption spectra of P3HT:ICBA (1:1) NP dispersions in EtOH (5 mg/mL) with and without AS-1 vs. 30 mg/mL DCB solution of P3HT:ICBA (1:1).

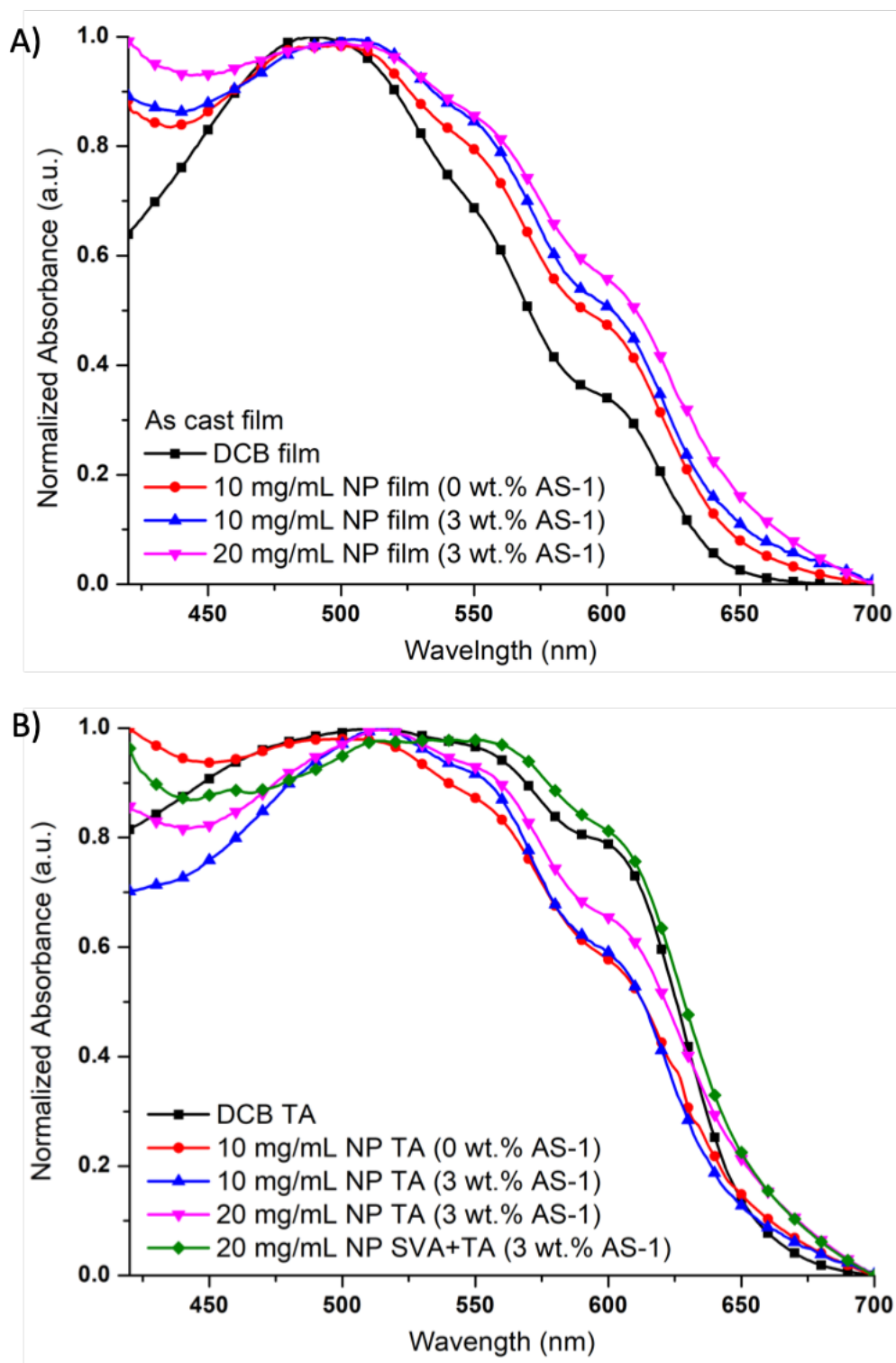


Figure 4.6: Normalized UV-Vis absorption spectra of P3HT:ICBA (1:1) spin coated films from DCB solution and from P3HT:ICBA (1:1) and NP dispersions of different concentrations; 10 mg/mL (0 wt.% AS-1), 10 mg/mL (3 wt.% AS-1) , 20 mg/mL (3 wt.% AS-1) and DCB solution of P3HT:ICBA A) As-cast film B) thermally annealed films (150 °C) for 10 min.

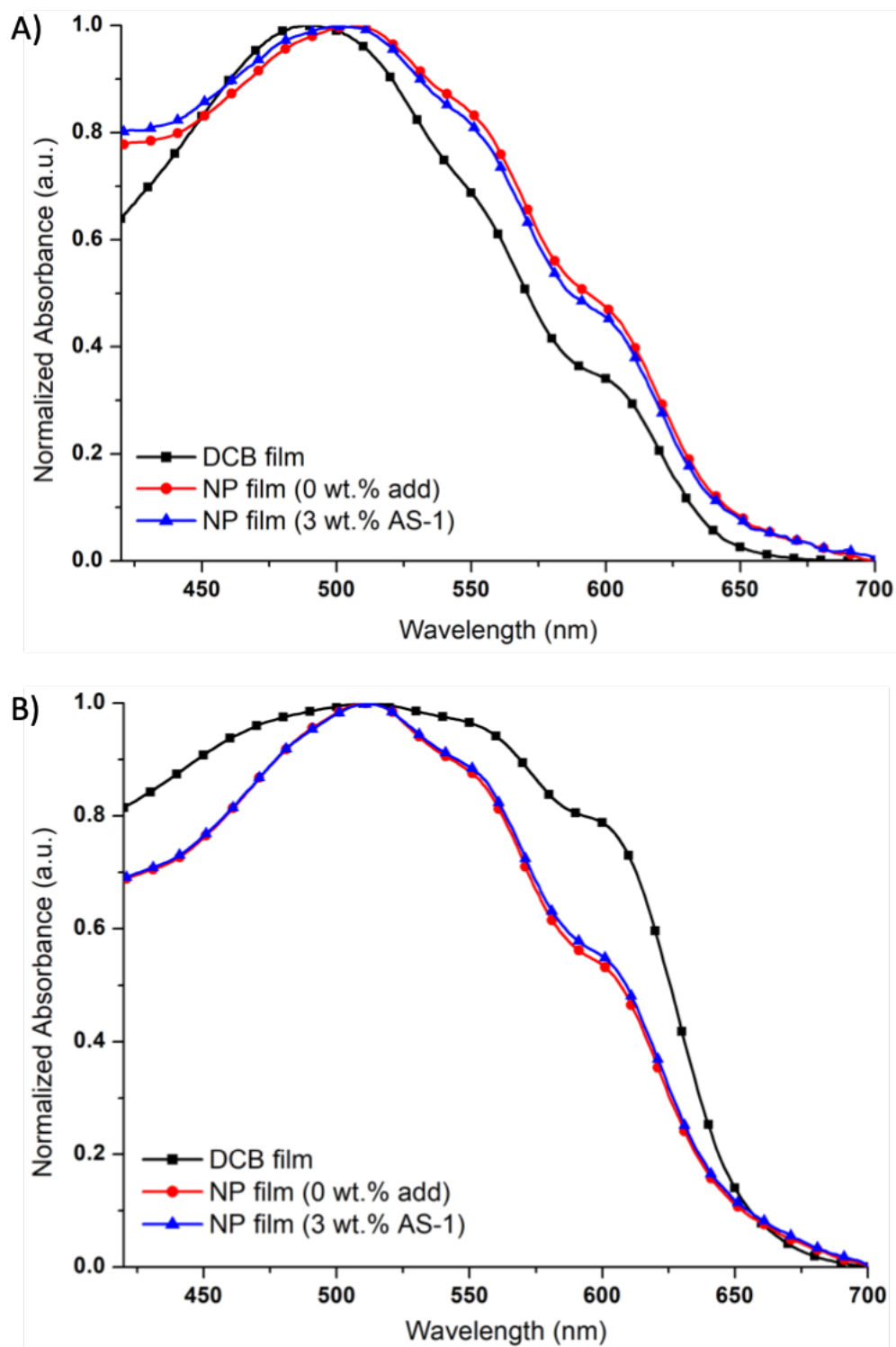


Figure 4.7: Normalized UV-Vis absorption spectra of P3HT:ICBA (1:1) spin coated film from P3HT:ICBA (1:1) NP dispersions of concentration 5 mg/mL with and without AS-1 vs. 30 mg/mL DCB solution of P3HT:ICBA A) as-cast film and B) thermally annealed films (150 °C) for 10 min.

4.4.3 Photoluminescence spectroscopy

The photoluminescence (PL) spectroscopy provides valuable information related to phase segregation and morphology of thin films. Excitons generated due to absorption of light by a semiconducting material re-emit light equal to the material band gap if they do not reach an interface of the donor and acceptor material in their lifetime (~ 10 ns). PL quenching or reduction in PL signal of a donor material by an acceptor material is indicative of effective charge transfer in blend films.¹⁸ An efficient PL quenching is necessary as it provides direct evidence for exciton dissociation¹⁹ which is one of the key parameters that result in efficient OSCs. However, strong PL quenching does not necessarily mean better OPV device performance because too much mixing of donor and acceptor materials will lead to poor percolation pathways for charges to their respective electrodes. This would result in increased bimolecular recombination. In this work, the PL spectra of as-cast and annealed films deposited from 20 mg/mL NP dispersions in MeOH and DCB solution of P3HT:ICBA were recorded (Figure 4.8) to investigate the effect of annealing on phase segregation of films prepared from DCB solution and NP dispersions. The measurements were conducted by exciting the films at a wavelength of 540 nm (see experimental section for detailed procedure).

The PL spectra of annealed DCB film solution exhibit the characteristic P3HT 0-0 and vibronic 0-1 transitions at ~ 640 nm and ~ 700 nm respectively (Figure 4.8A).^{14, 18} The 0-0 and 0-1 peaks are assigned to an intrachain exciton and the interchain exciton arising when electronic excitation in a given chain is coupled with a vibrational excitation in a nearest neighbor chain respectively.²⁰ The as-cast films exhibited highly quenched PL signal (Figure 4.8B) which can be attributed to intimately mixed P3HT:ICBA domains with P3HT existing in less ordered form.²¹ These results are in agreement with previous studies.⁵ Thermal annealing of DCB films resulted in reduced PL quenching (higher 0-0 and vibronic 0-1 peak intensities) due to phase

segregation of P3HT:ICBA in which P3HT became more ordered and expelled the ICBA from the polymer matrix.²²

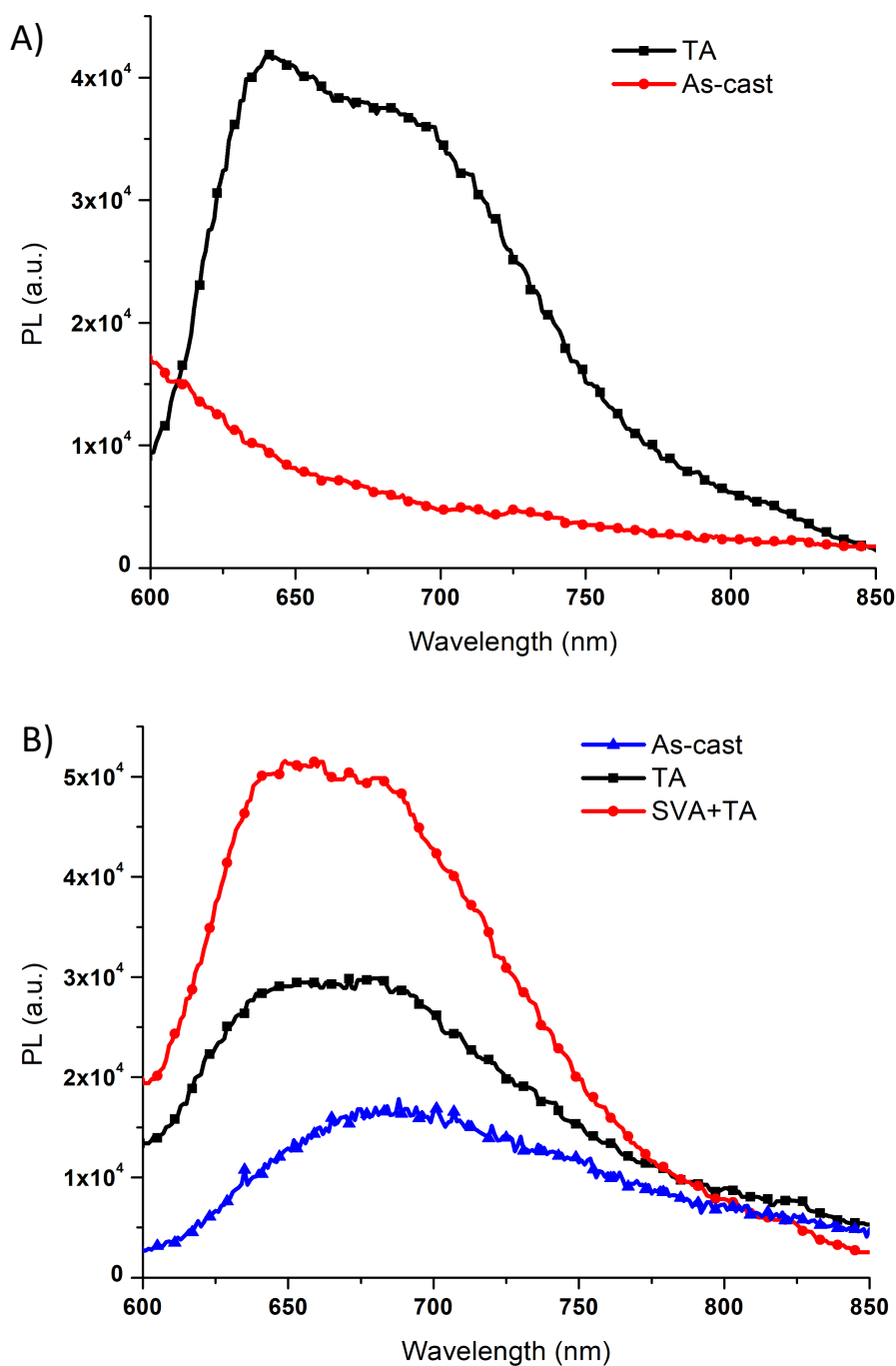


Figure 4.8: PL spectra of as-cast and annealed films prepared from A) DCB P3HT:ICBA (1:1) solution (30 mg/mL) and B) P3HT:ICBA (1:1) NP dispersions with AS-1 in MeOH (20 mg/mL)

The as-cast NP film exhibited higher PL intensities (less quenching) compared to the as-cast DCB films indicating that the former does not possess a well-mixed morphology. This observation is further supported by the UV-Vis data that showed enhanced vibronic features in as-cast NP films compared to as-cast DCB film due to significant phase segregation and interchain ordering of P3HT:ICBA components occurring in as-cast NP films. However, it should be noted that the PL intensities of as-cast NP films were less than the PL intensities of annealed DCB films signifying higher phase segregation in the latter.

Thermal annealing of NP films resulted in increased PL intensities compared to as-cast NP films which could be attributed to attainment of a more crystalline structure by the P3HT component in the annealed NP films. NP films processed with SVA and TA exhibited less PL quenching (high PL intensity) compared to thermally annealed DCB and NP films (Figure 4.8). This observation is consistent with the UV-Vis data, in which, the NP film (SVA+TA) exhibited enhanced vibronic features compared to thermally annealed film.

4.4.4 Grazing incidence wide-angle X-ray scattering analysis

The crystallinity and orientation of the P3HT:ICBA NP films were analyzed by performing GIWAXS measurements at the Australian Synchrotron located in Clayton, Melbourne. The films for GIWAXS measurements were prepared by the author of this thesis and samples were analyzed by Dr. Valerie Mitchell (a member of our lab group (in past) at the University of Melbourne).

In general, a GIWAXS image of P3HT consist of scattering peaks (also known as reflections) in the Q_z (out-of-plane) and Q_{xy} (in-plane) axis (Q denotes the scattering vector in the 3D-reciprocal space) based on which the orientation relative to the substrate (e.g. edge-on or face-on), crystallinity of P3HT polymer and size of crystalline domains are assessed. The edge-on and face-on orientations of P3HT are illustrated in (Figure 4.9). The reflection (100)

corresponds to lamellar stacking (which has a spacing of 16 nm) appear at $Q \sim 4 \text{ nm}^{-1}$ while the reflection (010) corresponds to aromatic or $\pi - \pi$ stacking (which has a spacing of 4 nm) appear at $Q \sim 16 \text{ nm}^{-1}$. For an edge-on orientation, the lamellar and $\pi - \pi$ stackings are expected to be out-of-plane and in-plane respectively. Correspondingly, (100) reflection appear at $Q_z \sim 4 \text{ nm}^{-1}$ and (010) reflection appear at the $Q_{xy} \sim 16 \text{ nm}^{-1}$. Higher order reflections for lamellar stacking i.e., (200) and (300) reflections could also appear on Q_z axis. If the P3HT is oriented face-on, the (100) and (010) reflections would appear on the Q_{xy} and Q_z axis respectively. The presence of the (010) reflection is indicative of crystallinity, and the size of the crystallites can be assessed by the width of the scattering peaks at half-maximum.

The presence of a (100) peak and its higher order reflections in the Q_z axis and (010) reflections in the Q_{xy} axis in GIWAXS profiles of as-cast and annealed samples deposited from DCB solution of P3HT:ICBA suggests a high P3HT crystalline with a predominantly edge-on orientation (Figure 4.10).

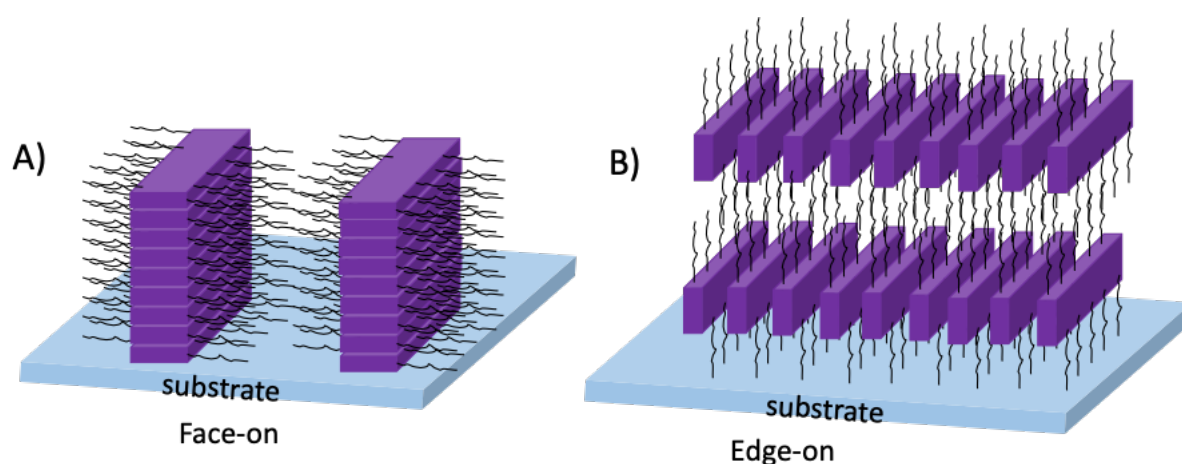


Figure 4.9: Schematic representation of A) face-on and B) edge-on orientation of P3HT in which the purple colour block represents the back-bone of P3HT with the side chain shown in black colour.

For all the as-cast samples deposited from EtOH dispersions, weak Q_z and Q_{xy} reflections were observed which indicated isotropic orientations and low crystallinity of P3HT. The as-cast

samples prepared from EtOH dispersions without AS-1 exhibited the lowest crystallinity (Figure 4.11), while the samples prepared from EtOH dispersions stabilized with AS-1 were slightly more crystalline as evidenced by the appearance of weak (010) reflection (Figure 4.12). The latter also exhibited weak second (200) and third (300) order of (100) reflections. In the GIWAXS profiles of annealed samples (at 150 °C), the series of (100) reflections in Q_z axis and (010) reflection in Q_{xy} axis was observed. This suggested that annealed samples were crystalline and exhibited edge-on orientation.

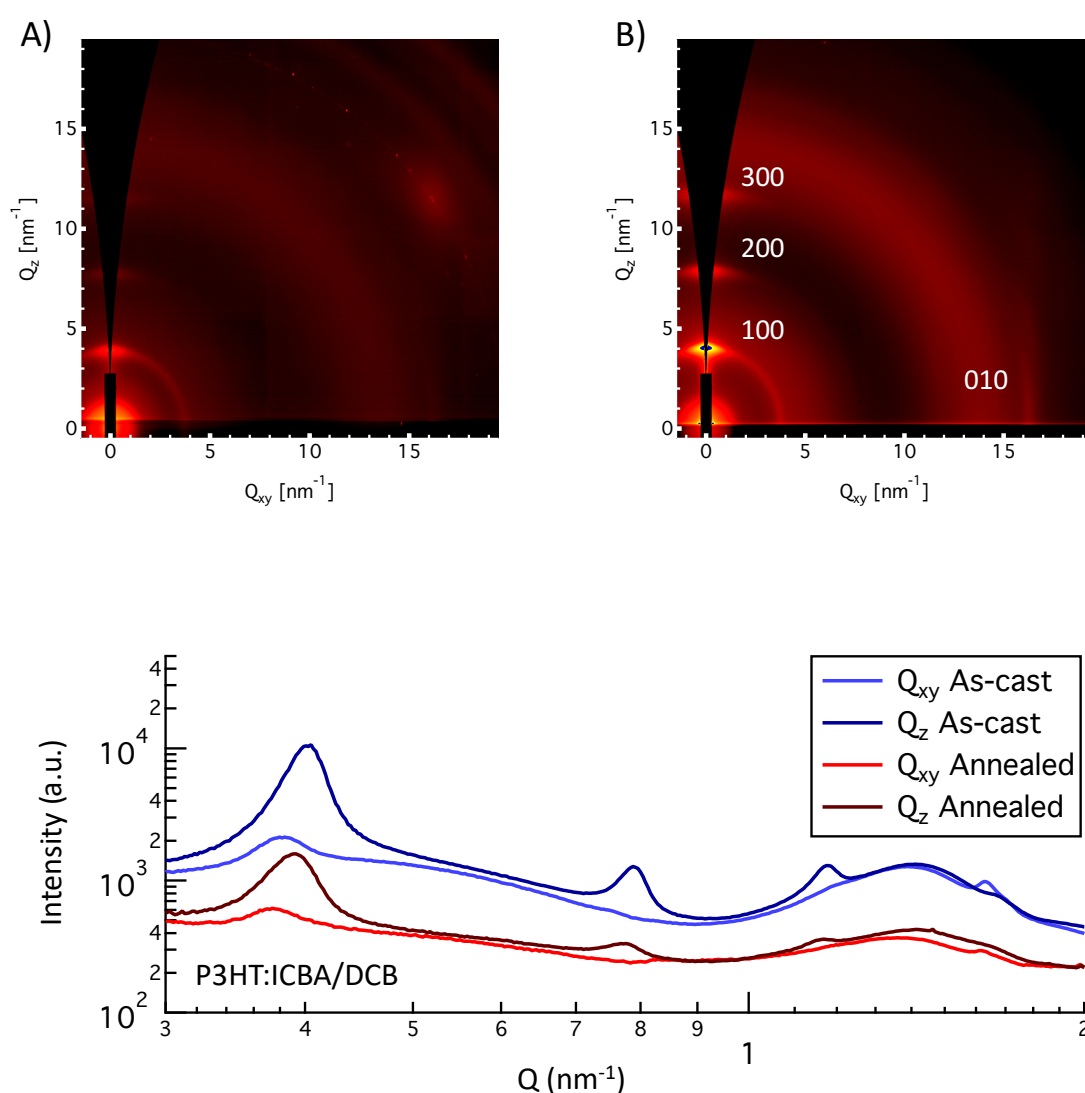


Figure 4.10: GIWAXS diffraction patterns of films deposited from P3HT:ICBA DCB solution a) as-cast and b) annealed at 150 °C for 10 min. and line cuts along the Q_{xy} and Q_z axes.

The annealed samples deposited from EtOH dispersions stabilized with AS-1 showed the strongest $\pi - \pi$ stacking (Figure 4.12). The GIWAXS characterization was also performed for the films prepared from NP dispersions in MeOH. However, the data has not been presented here because all samples exhibited weak intensities. Therefore, measurements will be repeated in future.

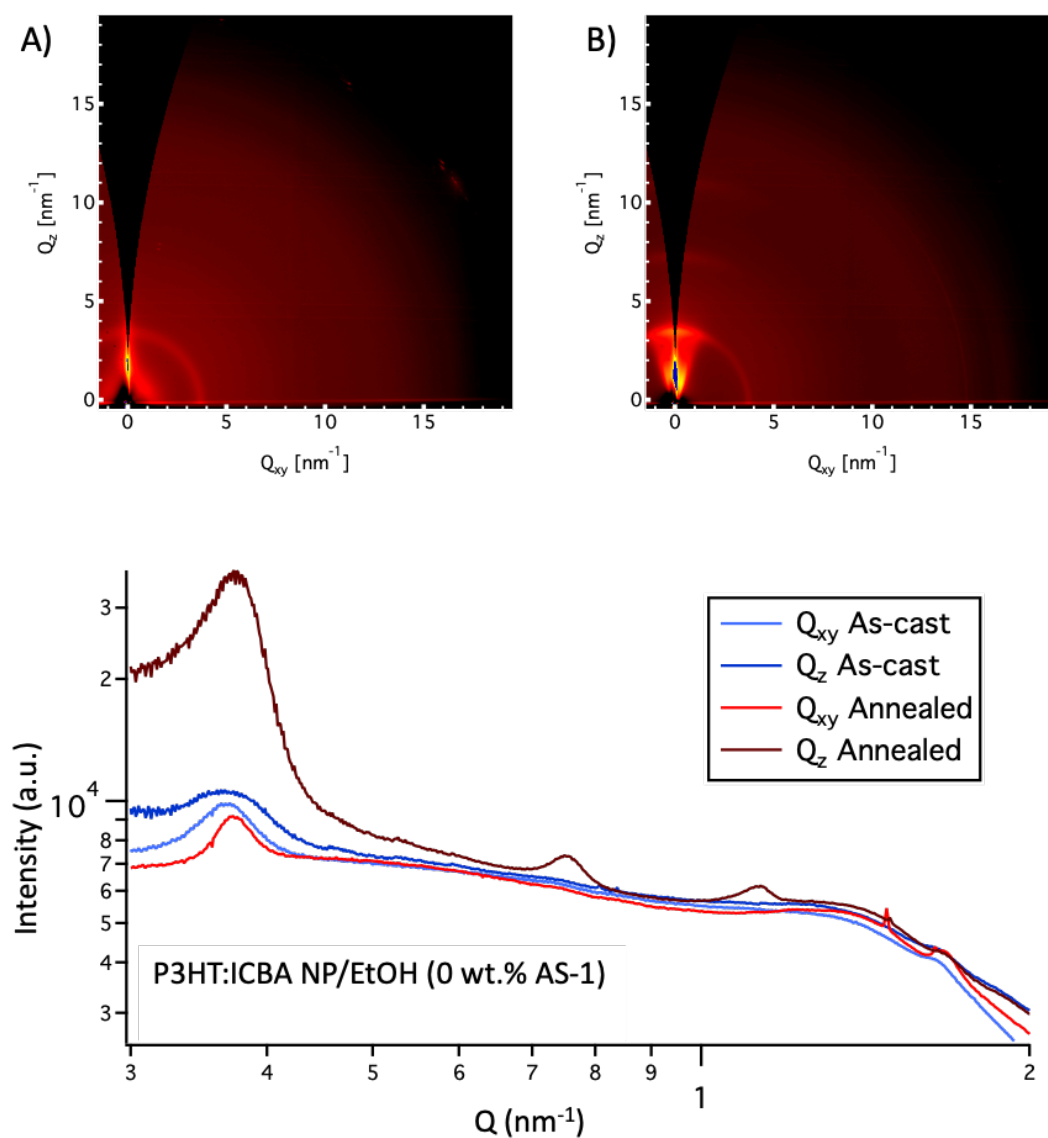


Figure 4.11: GIWAXS diffraction patterns of NP films deposited from P3HT:ICBA dispersions in EtOH with 0 wt.% AS-1 A) as-cast and B) annealed films at 150 °C for 10 min. and line cuts along the Q_{xy} and Q_z axes.

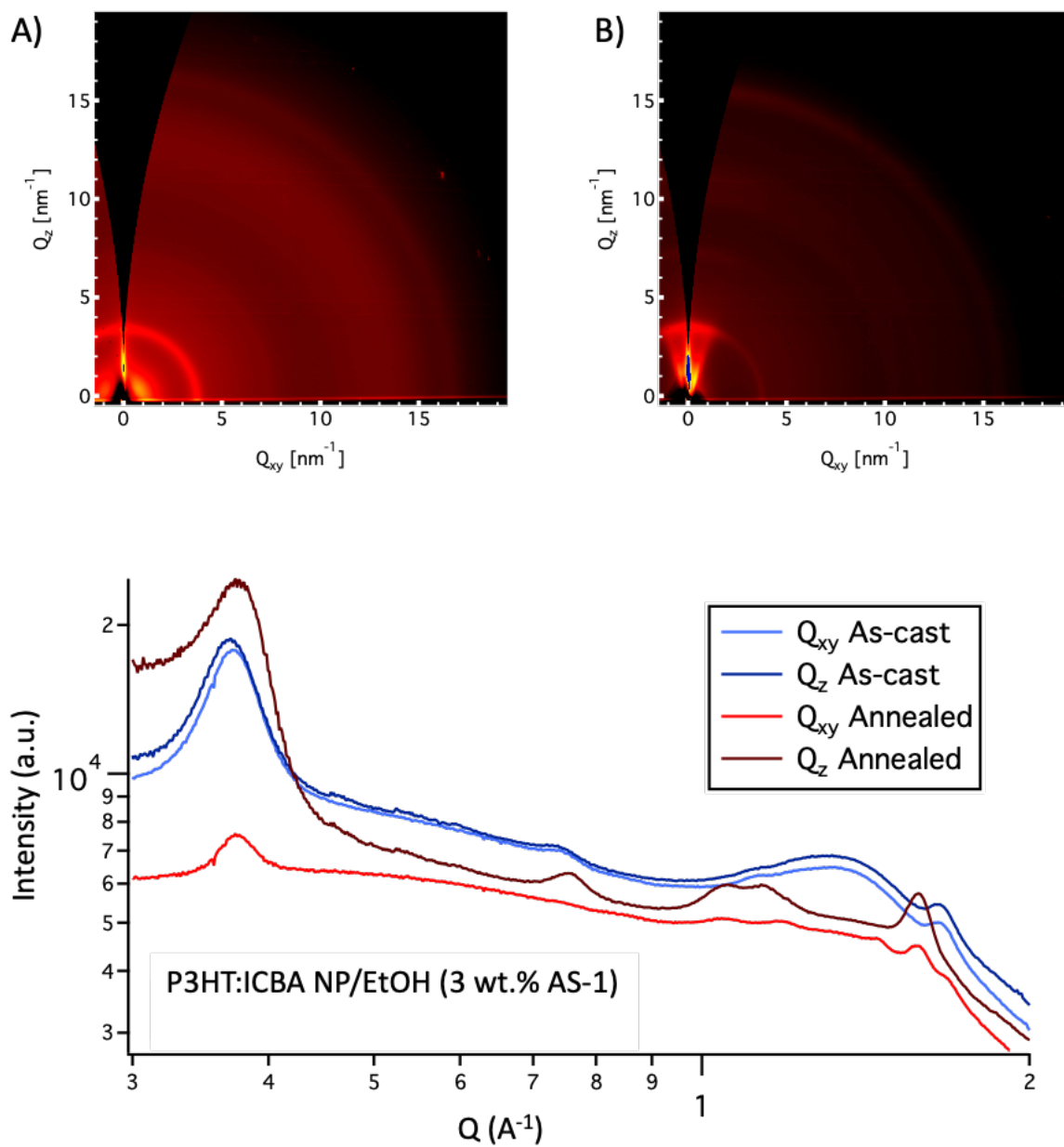


Figure 4.12: GIWAXS diffraction patterns of NP films deposited from P3HT:ICBA dispersions in EtOH with 3 wt.% AS-1 A) as-cast and B) annealed films at 150 °C for 10 min. and line cuts along the Q_{xy} and Q_z axes.

4.5 Summary

In this Chapter, the influence of using AS-1 as active surfactant to stabilize NP dispersions on device performance was investigated. Devices with inverted architecture were fabricated from DCB solution and NP dispersions of P3HT:ICBA in MeOH (10 mg/mL and 20 mg/mL) and EtOH (10 mg/mL) with/without using AS-1. The number of coating steps required to obtain an optimum active layer thickness for each of these dispersions was identified. The influence of post-processing, such as thermal and solvent vapor annealing (in case of devices of 20 mg/mL dispersions), on the device performance and surface morphology of the films was studied. The as-cast devices for all the dispersions exhibited low device efficiencies. The efficiency for annealed NP devices fabricated from the 20 mg/mL dispersions (MeOH) with 3 wt.% AS-1) was similar to efficiency obtained for solution-processed DCB devices. Further, the efficiencies observed for devices fabricated from dispersions (10 mg/mL in MeOH and EtOH) with and without AS-1 were similar. This confirmed that the regenerated P3HT-Py after reversibility of ionic pair ($\text{P3HT-PyH}^+\text{AcO}^-$) on thermal treatment of the NP films has no significant effect on the electronic properties of devices.

The performances of as-cast and annealed devices were correlated with the spectroscopic analysis (UV-Vis and PL quenching) and surface morphology studied using AFM. The spectroscopic analysis revealed that the annealing increased the crystallinity in the thin film deposited from DCB solution which resulted in nano-scale phase separation between the donor and acceptor domains. This is indicative of better charge transport in the active layer of annealed DCB devices. Further, the AFM analysis showed that annealing of films resulted in reduced roughness which could facilitate better charge extraction at the electrode. The spectroscopic analysis on NP dispersions and films deposited from them indicated that the semi-crystalline domains of P3HT were established during NP formation and remained

conserved after film deposition (even after annealing). The AFM analysis suggested that thermal annealing (150°C for 10 min) resulted in more homogenous film with reduced surface roughness due to fusion of NPs. This improved the charge transport in the active layer and charge extraction at the electrode which subsequently resulted in higher efficiencies of annealed devices compared to as-cast devices. The crystalline nature of solution-processed and NP films was further confirmed by conducting GIWAXS analysis.

4.6 Experimental section

4.6.1 Preparation of nanoparticles

NPs were prepared in MeOH and EtOH using dispersion method (see Section 3.8.5 for detailed information).

4.6.2 Sample preparation for analysis

Film preparation and thin film analysis were performed by the candidate unless noted otherwise.

Thin films of DCB solution and NP dispersions of P3HT:ICBA (1:1) were deposited on zinc oxide coated ITO glass substrate (in air). At first, the zinc oxide (ZnO) NP film of thickness 30 nm was spun-cast (3000 rpm, 30 s) on clean indium tin oxide (ITO) coated glass substrates and annealed at 150 °C for 10 min. After that, active layers were deposited using DCB solution and different concentrations of P3HT:ICBA (1:1) dispersions as described below:

Films fabricated from NP dispersions: It can be recalled that a multiple number of coatings are required for NP dispersions to form an active layer of required thickness. In this work, the films were prepared via dynamic coating i.e., the spin coater spun at a constant speed of 1000 rpm and the NP dispersions (50 μ L aliquot) were added sequentially at an interval of 20 s. The MeOH dispersions of 10 mg/mL (0 wt.% and 3 wt.% AS-1) and 20 mg/mL (3 wt.% AS-1) were

coated 8 and 3 times respectively (as optimized in Section 4.2.2). EtOH dispersions with 0 wt.% and 3 wt.% AS-1 were coated 6 and 5 times respective to form the optimally active layer (as optimized in Section 4.2.2).

Films fabricated from DCB solution: The active layer was deposited by spin coating P3HT:ICBA (1:1) solution in DCB (30 mg/mL) at 1000 rpm for 30 s.

For each of the variations, except dispersions of 20 mg/mL (MeOH, 3 wt.% AS-1), two films were prepared in which one served as as-cast and other one as the annealed film. Thin film annealing was performed in air by heating the films at 150 °C for 10 min. In case of 20 mg/mL (MeOH, 3 wt.% AS-1) dispersions, three films were prepared to serve as as-cast, annealed and solvent vapor and thermally annealed. Annealed films were prepared following the above-mentioned procedure for annealed devices. The third film was first subjected to SVA with THF for 20 s followed by annealing at 150 °C for 10 min.

These films were used for thin film analysis using AFM, GIWAXS, UV-Vis and PL measurements.

In case of UV-Vis measurements in solution and dispersions of P3HT:ICBA, the samples were diluted to 50 µg/mL.

4.6.3 Device fabrication and characterization

In this work, devices of 10 mg/mL dispersions (0 wt.% and 3 wt.% AS-1) in MeOH and EtOH were fabricated by Philipp Marlow in KIT, Germany. Although 20 mg/mL dispersions were also sent to Germany for device fabrication, but due to time constraint, the optimization of these devices was performed by the candidate with assistance of Dr. Jegadesan Subbiah at University of Melbourne (UoM). For good comparison, the chlorinated solvent processed devices were also fabricated at Bio21 institute, UoM. It should be noted that devices fabricated

at both KIT and UoM have the same device architecture, but different experimental conditions. At KIT, device fabrication and measurements were conducted in a glove box placed inside clean room. At UoM, the devices were fabricated by depositing ZnO layer, active layer, and PEDOT:PSS inside glove box. Annealing was also performed under N₂ atmosphere. The devices were taken out of the glove box (exposed to air) for metal electrode deposition. Device efficiencies were also recorded in the air.

The OSCs were fabricated with inverted device architecture. The indium tin oxide (ITO) coated glass substrates were cleaned by ultrasonication in acetone and isopropanol (10 min) respectively. The cleaned substrates were exposed to oxygen plasma (10 min) to remove any organic traces. The zinc oxide (ZnO) NP film of thickness 30 nm was spun cast (3000 rpm, 30 s) on cleaned ITO substrate from ZnO NP dispersions and annealed at 150 °C for 10 min. This was used as an electron transport layer. P3HT:ICBA (1:1) dispersions of 10 mg/mL and 20 mg/mL in MeOH were spun cast 8 and 3 times respectively for active layer formation, and again annealed at 150 °C for another 10 min. In case of dispersions in EtOH (10 mg/mL) with 0 wt.% and 3 wt.% AS-1, the active layer was spun cast 6 and 5 times respectively. Then the hole transport layer, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, HTL solar, diluted with H₂O (1:1)) of thickness 35 nm was spin coated in glove box (5 s at 500 rpm, 30 s at 2000 rpm) on top and annealed at 150 °C for 5 min. After that, devices were placed in a sample holder with a mask, allowing deposition of the thin films only in the area needed (0.02 cm²). The sample holder was then placed in a vacuum chamber, and the pressure reduced below 4 x 10⁻⁶ Torr to deposit silver as top electrode (Ag, 100 nm)

Another set of devices from 20 mg/mL dispersions were made using the same conditions except the processing condition of active layer. This time the NP films were SVA instead of thermal annealing using THF for 20 s followed by PEDOT:PSS deposition (in glove box) and then

annealed for another 5 min to ensure the complete drying of PEDOT:PSS. In the end, Ag electrode was vacuum deposited as discussed above.

In case of DCB devices, the active layer of P3HT:ICBA (1:1) solution in DCB was spin coated (1000 rpm, 30 s) on ZnO NP film. The active layer was annealed at 150 °C for 10 min followed by PEDOT:PSS (annealed at 150 °C, 10 min.) and Ag deposition similar to the procedure mentioned above.

Devices were characterized immediately using an AM1.5 G simulator (1 kW, Oriel) controlled by Labview software. The current and voltage in the range of -0.75 V to 1.5 V were recorded, from which the J_{sc} , V_{oc} , PCE, FF were obtained.

4.6.4 Dektak profilometer

A Dektak profilometer is an instrument which is used to measure vertical profile of samples and thickness and morphology of thin films including their roughness. It is based on measurement of vertical displacement of a stylus (typically made of diamond) as it moves physically over the film surface. The vertical displacements of the stylus are recorded as analog signals which are converted into electrical signals and displayed on the computer. A step (scratch) between the film and uncovered substrate is created and the stylus is moved vertically and laterally over a specified region to measure the thickness.²³

4.6.5 Atomic force microscopy

Unlike traditional microscopes, atomic force microscope does not use any light or electron beam to produce an image.¹² An AFM is a mechanical imaging technique in which a probe or tip is moved across the surface of sample. The tip is generally less than 50 nm in size and is attached to a cantilever. As the tip move on surface, it interacts with the force fields associated with the surface. In other words, the nanoscopic tip moves on the surface and the force between

them is measured and subsequently sent to a sensor which creates an image of the surface. Essentially, AFM measures the surface height in form of vertical displacement of the tip. In an output image, the undulation in surface is shown by range of colors, for instance, bright is high and dark as low. Therefore, a multicolor image is typically obtained for viewing and studying the surface morphology.²⁵ The topography images of films were recorded using Asylum Cypher AFM on tapping mode (AC mode) and films preparations for these measurements is discussed in detail in Section 4.5.2.

4.6.6 Photoluminescence or fluorescence spectroscopy

Fluorescence is a phenomenon in which a material (fluorophore) has to emit photons upon absorbing incident photons to return to its ground state.²⁴ In a typical fluorimeter, UV or visible light is used to strike a material which emits longer wavelength light (visible or near-infra red) after absorption. Absorption or emission spectrum can be recorded and used to perform qualitative or quantitative analysis of a compound. The PL spectra in this work were recorded on a Varian Eclipse fluorescence spectrofluorometer at an excitation wavelength of 540 nm with 20 nm excitation slits and 10 nm emission slits at a high detector voltage (600 V). Sample preparation for these measurements is discussed in Section 4.5.2.

4.6.7 Grazing incidence wide-angle X-ray scattering

It is one of an X-ray diffraction method that enables investigation of crystallinity of surfaces and thin films.²⁵ When a beam of X-ray strikes a material, diffraction occurs depending upon its atomic structure. Two important characteristics of diffracted beam are a) angle and b) direction of diffraction. The angle of diffraction aids in identifying crystalline lattice spacing, while the direction of diffraction provides information about orientation of crystal packing. This technique is really helpful to elucidate impacts of side chains in molecular packing. The film for GIWAXS samples were prepared by the candidate with the procedure discussed in

Section 4.5.2. GIWAXS measurements were conducted at the SAXS/WAXS beamline of the Australian Synchrotron by Dr. Valerie Mitchell. The measurements were performed with an X-ray energy of 11 or 15.2 keV and a range of incident angles from $\Omega = 0.025$ –0.5 in 0.01–0.05 increments to allow signal optimization near the critical angle of the polymer film. Data from GIWAXS experiments were analyzed using a customized version of NIKA 2D based in IgorPro.

4.7 References

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Chapter 5 Summary and Conclusion

5.1 Summary and conclusion

The deposition of active layer from NP inks of semiconducting materials processed in an eco-friendly solvent is one of the potential ways to advance towards industrial-scale fabrication of OSCs. In general, the dispersions are formulated using miniemulsion method in which NPs of semiconducting materials are stabilized using commercial surfactants such as sodium dodecyl sulfate (SDS). These surfactants are electrically inert, and their presence in active layer (even in trace amounts) inhibits charge transport and subsequently hampers device performance. To overcome this problem, fabrication of active layer using surfactant-free NP dispersions has been demonstrated. However, there are limitations associated with the surfactant-free approach. The literature review in Chapter 1 suggested that surfactant-free approach provides less control on NP formation, and the properties of NP dispersions (e.g. size of NPs) vary with the batch of P3HT polymer used. Furthermore, this approach yields NP dispersions of low concentrations with poor stability which likely inhibit its application in large-scale fabrication of OSCs.

In this work, P3HT polymer of defined molecular weights (expected range: 5,000 g/mol to 40,000 g/mol) with high regioregularity and low dispersity ($\mathcal{D}$) were synthesized using McCullough's approach of Grignard Metathesis (GRIM) as presented in Chapter 2. The largest M_n achieved was 28000 g/mol. These synthesized P3HT polymers were used to investigate the

effect of molecular weight of P3HT polymer on P3HT:ICBA NP dispersions synthesized using dispersion method (Chapter 3). The results indicated that size of NPs increases with increase in molecular weight of polymer. The P3HT:ICBA dispersions prepared from synthesized polymers with molecular weight >10,000 g/mol exhibited large NP diameters (138-171 nm) and the dispersions with 28,000 g/mol precipitated immediately. In addition to synthesized P3HT polymers, commercially available Rieke P3HT (22,000 g/mol) was used to form P3HT:ICBA dispersions. These dispersions exhibited smaller NP diameter (116 nm) relative to synthesized P3HT polymer which could be attributed to high $\bar{D}$ and regioregularity of the former. This led to a conclusion that surfactant-free NP formation through dispersion method is dependent on the specific batch of the polymer used. If dispersions are prepared using same batch of the polymer, their properties depend on the molecular weight of the polymer.

Given the batch dependence of the surfactant-free process, the idea of active surfactants was explored. Three end-capped P3HT polymers; P3HT-Py, P3HT-COOH and P3HT-TEG were synthesized by using P3HT of molecular weight 5,000 g/mol as base unit to act as active surfactants. The P3HT-Py and P3HT-COOH could be converted into ionic forms on treatment with acid and base respectively, to behave as ionic surfactants while forming NP dispersions. It was anticipated that the activated ionic forms of P3HT-Py and P3HT-COOH would improve NP stability of P3HT:ICBA dispersion via formation of an electric double layer (EDL). Although stabilization of NPs via EDL formation can be expected from any other conventional ionic surfactant, but the advantage of using P3HT-Py and P3HT-COOH is their property of reversibility of ionic pair (deactivation of ionic forms). After NP film deposition, the ionic pair could be dissociated to regenerate P3HT-Py and P3HT-COOH with the removal of acid/base on thermal treatment. The P3HT-TEG was synthesized to act as a neutral or non-ionic active surfactant to stabilize dispersions via steric repulsion.

The synthetic route for these end-capped polymers was presented in Chapter 2. The P3HT-COOH and P3HT-Py end-capped polymers were synthesized by end-capping P3HT using Suzuki coupling conditions. The P3HT-TEG was synthesized through external initiation of polymerization using GRIM. All end-capped polymers were purified to achieve high end-group fidelity as verified by ^1H NMR spectroscopy and MALDI-TOF mass spectrometry analysis.

Chapter 3 demonstrated the application of synthesized end-capped P3HT polymers in achieving reproducible, stable, and concentrated P3HT:ICBA NP dispersions. Amongst the three end-capped polymers, only P3HT-Py resulted in controlled synthesis of NPs. The results indicated that using 3 wt.% of P3HT-Py and AcOH (together referred as AS-1), NP dispersions of Rieke P3HT and ICBA of 30 mg/mL in MeOH were obtained and the dispersions were stable up to 2 months at room temperature. Moreover, controlled NP formation from synthesized P3HT polymer of well-defined molecular weights was achieved using AS-1. This highlighted that the batch-to-batch variation associated with different P3HT polymers could be overcome by using active surfactants.

Finally, Chapter 4 was focused towards assessing the influence of active surfactant on power conversion efficiencies of OSCs. Devices of an inverted architecture were fabricated using NP dispersions of P3HT:ICBA with and without AS-1. All the as-cast devices exhibited low PCE which was largely attributed to poor charge mobility in the active layer and charge extraction at the electrode. The device efficiencies were improved after thermal treatment of active layer at 150 °C for 10 min. The performance of annealed devices fabricated from NP dispersions with and without AS-1 was similar. This confirmed that the P3HT-Py, regenerated from AS-1 after annealing, has no significant effect on electronic properties of donor and acceptor materials. Furthermore, devices fabricated with 20 mg/mL dispersions exhibited similar power conversion efficiency as devices fabricated using state-of-art chlorinated solvents after

annealing. The device performance was correlated to spectroscopic analysis performed using PL quenching and UV-Vis spectroscopy. It was observed that films fabricated from DCB solution of P3HT:ICBA exhibited vibronic features in absorption spectrum indicated increased crystallinity of P3HT after annealing. In case of films deposited from NP dispersions, annealing has no significant effect on crystallinity of P3HT. The vibronic features were appeared in the absorption spectra of dispersions which were enhanced after annealing of NP film. This signified that semiconducting domains were already formed during NP preparation that remained stable after film deposition as also observed in previous work.¹ It can be inferred that AS-1 did not affect the nanostructure of NPs compared to dispersions without AS-1. The surface morphology of the films was studied using AFM which indicated that annealing of the films resulted in reduction of surface roughness which potentially improved charge extraction at the electrode.

To summarize, it can be concluded that active surfactants based on semiconducting materials could be used to form stable and concentrated NP dispersions, without hampering the device performance unlike conventional surfactants. Further, this research highlights that use of active surfactants could eliminate the material dependency associated with the surfactant-free dispersion approach.

5.2 Outlook

5.2.1 Using higher weight% of active surfactant

The 3 wt.% AS-1 has been used to form stable NP dispersions of 20 mg/mL concentration which required 3 coating steps to form thick enough active layer and resulted in device efficiency similar to devices fabricated from DCB solution. It was observed from AFM analysis that surface roughness was higher for the films deposited from dispersions having large NP diameter. There is a possibility of observing small NP diameter with increasing amount of AS-

1. Therefore, it will be interesting to see the effect of 10 wt.% or for that matter 20 wt.% AS-1 on NP formation as a part of the future work. It can be anticipated that use of high loading of AS-1 may assist in preparing dispersions of concentration 40 mg/mL which may require only 1 coating step to form optimally thick active layer with reduced surface roughness.

5.2.2 High-throughput robot-based NP preparation

This research work reported highly reproducible and stable NPs at lab scale by controlling the physical and experimental parameters such as size and shape of stirrer bars and the beakers. With the current set-up, maximum of 8 dispersions could be prepared in 1 hour using the procedure explained in Chapter 3. It will be fascinating if a greater number of dispersions could be produced in a given time with a controlled experimental set up. In a recent study, it was shown that surfactant-free dispersions (10 mg/mL) were formed using high-throughput robot-based approach.² Such process provides greater control on experimental parameters and also carry potential to automate optimization of NP preparation avoiding any risk of human error.

5.2.3 Large area device fabrication

In this work, OSCs with inverted architecture were built using spin coating technique. Previous work has reported the use of doctor blading and ink jet printing to fabricate large area devices (0.105 and 1.1 cm²) from surfactant-free P3HT:ICBA dispersions in ethanol (10 mg/mL).³ The effect of AS-1 on the performance of large area devices can be studied by fabricating devices using doctor blading technique.

5.2.4 Impact of annealing on the diffusion of P3HT-Py

It has been observed in previous work that J_{sc} of devices fabricated from PCDTBT-N and PCBM-N was almost zero.⁴ This was attributed to the amino group which disabled the hole transport ability of BHJ by acting as hole traps. They also fabricated devices using PCDTBT-

N and PCBM-N as electron collection layer and reported improved device performance. It was concluded that hole traps reduce device performance when distributed in the BHJ layer but could enhance device performance when concentrated near the metal electrode. The diffusion mechanism of P3HT-Py after annealing is relevant to this study as it might have a detrimental or positive effect depending on its location. For example; it may be that P3HT-Py migrates to the hole transport layer (HTL) after annealing where it generates a surface dipole aiding charge extraction. The diffusion of P3HT-Py will be investigated in future using the X-ray photoelectron spectroscopy (XPS). XPS is a surface characterization technique that could analyze the elemental composition of a surface and the nature of the chemical bond between the elements. Therefore, vertical distribution of nitrogen atom can be identified to assess if P3HT-Py migrates towards any of the interfacial layers (hole transport or electron transport layer) or remain in the active layer.

5.2.5 A universal active surfactant for any donor and acceptor system

It should be noted that the end-capped P3HT, P3HT-Py, is applicable only in the case of NP formation with P3HT material. For a wider applicability of this approach, such molecules should be synthesized which stabilize NP dispersions of any donor: acceptor system without affecting electronic properties of BHJ. It is proposed that using a pyridine functionalized long chain of hydrocarbon may serve as an active surfactant in presence of acid (Figure 5.1). The hydrocarbon chain would behave as hydrophobic tail of surfactant whereas, the pyridine group in presence of acid would behave as hydrophilic head group. It is anticipated that active surfactants with linear alkyl tail groups may be more favorable than large aromatic tail groups, as they would result in efficient Van der Waals interactions with linear alkyl chains of polymer/ small molecule semiconductors. Moreover, this design would require the optimization of hydrocarbon chain length as it should be long enough to remain undissolved in alcohol (non-solvent phase).

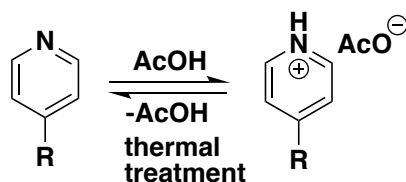


Figure 5.1: Design of active surfactant in which R could be any linear alkyl chain (hydrophobic tail) which is long enough that does not allow the dissolution of surfactant in alcohols. The pyridine group in this surfactant would act as hydrophilic head on treatment with acid such as acetic acid. The surfactant can be deactivated with the dissociation of ionic pair on thermal treatment of NP films.

Overall, this research work presented the idea of using active surfactant to overcome the limitations posed by surfactant-free NP dispersions prepared from dispersion method. Unlike conventional ionic surfactants, these surfactants are based on semiconducting materials and hold the property of reversibility of ionic pair. Early results demonstrated that reproducible and concentrated NP dispersions can be prepared with long-term stability using P3HT based active surfactant. The devices fabricated from these dispersions exhibited efficiencies similar to the devices fabricated from DCB solution. However, these active surfactants are suitable only for those donor and acceptor systems in which P3HT is the donor material. Therefore, future studies need to be directed towards the generalization of the idea of using active surfactant to stabilize NPs of any donor and acceptor systems without hampering device performance.

5.3 References

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