# INVESTIGATING CHARGE TRANSPORT IN CONJUGATED ORGANIC MATERIALS

A Dissertation Presented to The Academic Faculty

by

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## INVESTIGATING CHARGE TRANSPORT IN CONJUGATED ORGANIC MATERIALS

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For a better future

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## LIST OF SYMBOLS AND ABBREVIATIONS

- CB Conduction band
- CV Cyclic voltammetry
- Cp Cyclopentadienyl
- Cp\* Pentamethylcyclopentadienyl
  - DI Deionized water
- DFT Density functional theory
- DSC Differential Scanning Calorimetry
  - EA Electron affinity
  - E<sub>F</sub> Fermi level
- ETM Electron-transporting material
  - eV Electron volt
  - FF Fill factor
- FTO Fluorinated tin oxide
- FWHM Full width at half maximum
  - GPC Gel Permeation Chromatography
    - h Hour
- HOMO Highest occupied molecular orbital
  - IE Ionization energy
  - ITO Indium tin oxide
    - J Current density
    - J<sub>sc</sub> Short-circuit current

- k Boltzmann constant
- Li-TFSI Lithium bis(trifluoromethanesulfonyl)imide
- LUMO Lowest unoccupied molecular orbital
  - mes Mesitylene, (i.e., 1,3,5-trimethylbenzene)
  - min Minute
- MPPT Maximum Power Point Tracking
  - NDI Napthalene diimide
  - NIR Near-infrared
- NMR Nuclear magnetic resonance
- OLEDs Organic light-emitting diodes
  - OPVs Organic photovoltaics
- PMHBCB poly(bicyclo[4.2.0]octa-1(6),2,4-trien-7-yl-hexanoyl methacrylate)
  - PCBM Phenyl-C<sub>60</sub>-butyric methyl ester
    - PCE Power conversion efficiency
    - PDI Perylene diimide
    - PL Photoluminescence
  - PSCs Perovskite solar cells
    - q Absolute value of the charge of an electron
    - s Second

spiro-

**OMeTAD** 

- 2,2',7,7'-Tetrakis(*N*,*N*'-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene
- SPO Stabilized power output
  - T Temperature
- tBP Tert-Butylpyridine
- UHV Ultra-high vacuum

- UV Ultraviolet
- UPS Ultra-violet photoelectron spectroscopy
  - V Voltage
- VB Valence band
- Voc Open-circuit voltage
- XPS X-ray photoelectron spectroscopy
- Vis visible
- vs. Versus

## SUMMARY

The demand for energy has increased dramatically with increase in population and industrialization. However, relying on traditional fossil fuels to meet those demands lead to climate change becoming an existential threat to the livelihood of humanity. Thus, to navigate the challenges of meeting the energy demand, researchers need to investigate pathways to pivot to more benign energy sources as well as discovering sustainable materials for a versatile range of energy applications. Conjugated organic materials have been of great interest for optoelectronic applications for the past 50 years to complement and/or substitute their inorganic counterparts.

This work aims to design and investigate the charge transport properties of conjugated organic materials. This is achieved by providing a diverse toolbox of structure- property studies to further understand the behavior of doped organic materials and guide future development. In addition, this thesis shows an example of how such polymers can used in solar cells to replace an inorganic oxide. Further, a family of dopants along with investigation into their kinetic behavior is presented to be used in the future developments of polymer: dopant systems.

## CHAPTER 1. INTRODUCTION

#### **1.1** Foundations of conjugated materials and charge transport

The electrical properties of conjugated polymers and molecules have attracted considerable interest since the synthesis and subsequent iodine doping of polyacetylene that resulted in a material with a conductivity that could be in excess of 10<sup>5</sup> S/cm.<sup>1</sup> *trans*-polyacetylene was attractive as an original example of an organic polymer achieving metallic-like conductivity values upon oxidation. In addition, the conjugation along the polymeric backbone results in a polymer can be both oxidized and reduced within the window that is accessible to common oxidizing/ reducing agents.<sup>2, 3</sup>

This observation resulted in extensive research on conjugated molecules and polymers in order to uncover their redox properties as well as their charge transport features, conductivity, and enable the utilization of these polymers in different applications and devices such as solar cells,<sup>4</sup> transistors,<sup>5</sup> thermoelectric devices,<sup>6, 7</sup> and/ or bioelectronics.<sup>8</sup> Some of the reasons organic materials are investigated for these applications in a shift from their inorganic counterparts is due to greater control over properties through design as well as low temperature and large scale processing, as well as the potential to match/ exceed the performance of existing inorganic materials.

In order to tune the conductivity for a desired application, one ought to revisit the fundamental equation of conductivity below:

$$\sigma = n. e. \mu \tag{1}$$

Where  $\sigma$  is the conductivity, in S cm<sup>-1</sup>, defined as the ratio of current density in a material to the electric field that causes the flow of current. *n* is the charge carrier density, in cm<sup>-3</sup>, defined as the charge carrier density per unit volume. Last,  $\mu$ , in cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, is the charge carrier mobility, defined as the drift speed of charge carriers in the presence of an electric field. Note that while *n* and  $\mu$  are given as simple constants in equation 1, both may be complex functions of temperature, doping level, among other factors to be discussed in this chapter.

Most conjugated materials, however, do not possess high intrinsic conductivity as they are closedshell materials with band gaps often greater than 2 eV and as such require the use of extrinsic dopants in order to increase the charge carrier density at standard temperatures, and therefore conductivity.<sup>9</sup> To achieve high conductivity, charge carriers need not only be introduced via doping to increase charge carrier density, but should also be mobile from one site another.

Doping, in the case of organic materials can be defined as the introduction of an "impurity" molecule or polymer to modify the electrical properties of the (semi)conductor. Doping can be classified to electrical oxidation or *p*-doping such as when polyacetylene is doped with iodine. On the other hand, when a polymer is electrically reduced by a dopant, the doping is referred to by *n*-doping.<sup>10</sup> The dopant amount added, also called dopant ratio, can be defined as the mole percentage of the dopant added with respect to the monomer. For instance, 10 mol% would mean 0.1 dopants for every monomer. However, this does not necessarily imply that in a single electron transfer dopant, that 0.1 dopants for every monomer will lead to 0.1 electrons per monomer in the polymer chain. The percentage of the dopant added that successfully becomes ionized is defined as the ionization efficiency. To maximize the ionization efficiency of the introduced dopant, the ionization energy of the polymer needs to be lower than the electron affinity of the dopant in the

case of *p*-dopants by ~ 0.1 eV to favor the forward reaction.<sup>10, 11,12</sup> As for *n*-doping, the ionization energy of the dopant needs to be lower than the electron affinity of the polymer.<sup>10, 13</sup> Doping can still occur when electron transfer is an uphill process, with a barrier of ~ 0.1 eV for example, however the forward reaction will be disfavored resulting in a very low ionization efficiency.<sup>14</sup>

Although the backbone conjugation of organic materials can lead to band like energy packets as opposed to filled *vs.* empty frontier orbitals, the presence of structural defects can result in the formation of various localized states.<sup>15, 16</sup> Thus, upon doping, depending on the dominant factor: *i.e.*, an extended wave function *vs.* localized charge transport can occur via a band-like or a hopping regime governing charge transport (*vide infra.*).<sup>16-19</sup>

In a band transport regime, the conjugated polymer is said to exhibit "metallic type" conductivity. This is due to the large inter/intramolecular electronic coupling, and the mobility of the charge carriers being limited by two scattering events: thermally induced vibrations, and charged impurities (*i.e.* the dopant counterion).<sup>20, 21</sup> As such the transport will be thermally deactivated, and higher temperature will lower the charge carrier mobility.<sup>22, 15, 19</sup>

On the other hand, in systems dominated with localized states, low electronic coupling, charge carrier transport is described as hopping from one redox site to the other. In addition, another factor contribution to charge carrier localization is the coulombic attraction between the charge carrier and the dopant counterion leading to its localization. Other factors that can lead to hopping transport include short delocalization segments, structural defects such as chain folding and/or backbone twisting out of coplanarity.<sup>15, 23, 24</sup>

In the hopping regime, the charge carrier is coupled to the geometric relaxations due to charge injections as well as thermally activated molecular vibrations known as phonons. The quasi

particle formed due to the charge carrier interaction with the geometrical changes is known as a polaron. <sup>25-27</sup> The polaron will then hop from one molecular site to the other, pending overcoming the energetic barrier of the potential well.<sup>17, 18, 27, 28</sup> Charge carrier hopping is thermally activated in this case due to the phonon-assisted hopping causing the charge carrier mobility to increase with temperature. Increasing the doping level can result in increasing the spatial and electrostatic overlap between the adjacent molecular cites due to the increase in the polaronic radius, thus lowering the charge-transport barrier.<sup>27</sup>

In brief, the localization/ delocalization of the charge carrier is a tradeoff between the extent of geometric relaxation possible when localizing charge carriers on one redox site (or a combination of redox sites) and the extent of electronic coupling between the two sites.

Assigning a specific charge transport mode *i.e.* hopping *vs.* band to a polymer: dopant system under study is not trivial. Although band transport is explained mainly by band theory, multiple models have been proposed regarding hopping transport. For example, in 1956 Rudolph Marcus presented the Marcus charge transfer model in order to explain the different rates of electron transfer from a donor to an acceptor.<sup>29</sup> His theory takes into consideration the changes in reactants structures, as well as surrounding solvent molecules to calculate the speed of chemical reactions.<sup>29, 30</sup> Multiple other models have been reported including variable range hopping model proposed by Mott in 1969, which describes temperature dependent, localized charge carrier transport in disordered solids arguing that the hopping probability at a given temperature is depending on the spatial separation of two redox sites and their energy difference. However, based on the conductivity dependence on temperature variable range hopping can be distinguished from nearest

neighbor hopping where charge carriers will prefer to reside on the nearest redox site upon successful hopping. <sup>27, 31-35</sup>

#### 1.2 Semi-empirical Kang- Snyder and SLoT models:

Although the earlier models strictly discussed charge transport as band *vs*. hopping transport, polycrystalline organic materials do not necessarily only adhere strictly to one specific model. Thus, Kang and Snyder, utilized the fact that most charge-transport theories can be described through a generalized Boltzmann transport equation:

$$\sigma = \int \sigma_E \left( -\frac{\partial f}{\partial t} \right) dE \tag{1}$$

σ is the conductivity,  $σ_E(E)$ , is an energy dependent transport function, which has units of conductivity but is only equal to conductivity when all mobile carriers have the same energy, whereas the experimentally measured conductivity will constitute carriers with energy with ~4k<sub>B</sub>T around the Fermi level (E<sub>F</sub>). The Fermi level (E<sub>F</sub>) is defined as thermodynamic work required to add one electron to a system, and in a non-metal (such as conjugated materials), this theoretical energy level lies within the bandgap and does not correspond to an actual energy level.<sup>10, 24, 36</sup> The Fermi level position depends on temperature, density of states and extent of doping.<sup>37</sup> Last, the selection function *f* represents a Fermi-Dirac distribution function, which describes identical half spin particle distribution over a series of energy states while obeying the Pauli exclusion principle.<sup>38</sup> The distribution function used in the integral thus samples a range of energies around a considered charge carrier energy. The model requires two experimentally measured values to model a specific system. The first is conductivity and second is the Seebeck coefficient. The

Seebeck coefficient is the voltage generated per Kelvin due to the application of a temperature gradient and can be expressed as:

$$S = \frac{1}{\sigma} \left( \frac{k_B}{e} \right) \int \sigma_E \left( \frac{E - E_F}{k_B T} \right) \left( -\frac{df}{dE} \right) dE \tag{2}$$

The Seebeck coefficient measured across a film, a doped one in the case of organic polymers for example arises due entropy driven diffusion of charge carriers.

Given that, as seen in equations 1 and 2, both the conductivity and Seebeck conductivity stem from the same transport function  $\sigma_E$  Kang- Snyder asserted that the transport function can take two forms based on the energy distribution of charge carriers:

$$\sigma_E = \begin{cases} 0, (E < E_t) \\ \sigma_{E_0} \left(\frac{E - E_t}{k_B T}\right)^s, (E \ge E_t) \end{cases}$$
(3)

In this case the  $\sigma_{E_0}$  represents the density of electronic states, which is an energy independent prefactor. In addition,  $E_t$  is the energy of the transport edge.

Charge carriers above the transport edge contribute to the transport function and display a power law correlation via *s* known as the transport factor. The term  $\left(\frac{E-E_t}{k_BT}\right)^s$  accounts for the increase in electrical conductivity with increasing carrier concentration because, as the system becomes more doped, the energy of the charge carriers *E* moves away from the transport edge. Kang- Snyder and others have utilized this model in order to extract valuable information about the doped system transport phenomena, activation barriers as well as to calculate a weighted charge carrier mobility.

Despite its utility, recent research has shown that the Kang-Snyder model does not account for spatial localization upon doping and proposed a spatial localized model for charge transport, SLoT,

inspired by the Kang-Snyder model.<sup>39</sup> The main modification to the mathematics of the model is modifying the energy independent pre-factor to account for localization effects by adding an exponential term:  $\exp\left(-\frac{W_H}{k_BT}\right)$  where  $W_H$  is the potential energy barrier (well) where the charge carriers are present, which is function of the doping level. The last modification in SLoT model is using a fixed *s* value of *s* =1.



Figure 1.1. Sketch of polymer structure upon doping (a), changes in  $W_H(c)$  vs. doping level (b), comparison of Kang-Snyder and SLoT model fits to electrical data for P3HT doped with FeCl<sub>3</sub>. Reproduced with permission.<sup>39</sup>

#### **1.3** Historic picture of conducting polymers research

In 1976 Alan Heeger, Hideki Shirakawa, and Alan MacDiarmid, reported metallic-like conductivities in *trans*-polyacetylene (10<sup>3</sup> S/cm) upon doping with oxidizing agents,<sup>40</sup> with conductivities up to 10<sup>5</sup> S/cm being achieved in later developments.<sup>1, 41</sup> The three researchers received the Nobel Prize in 2000 in chemistry for the discovery and development of conductive polymers.<sup>42</sup>

In 1979 Allied reported conductivities of  $10^2$  S/cm of poly(p-phenylene).<sup>43</sup> Other conjugated polymers were reported such as poly(pyrrole),<sup>44</sup> and poly(thiophene) (Figure 1.2).<sup>45</sup> Among the challenges in using these polymers, is their insolubility, which would pose difficulties on processing them from solution. As such polyaniline and poly-3-alkyl-thiophenes were reported which were soluble in common organic solvents.<sup>46-48</sup> With the discovery of polyaniline (Figure 1.2), there was another breakthrough which was the concept of acid doping where the polymer can be oxidized via proton exchange.<sup>46</sup> In addition Wudl and Meijer *et al.* in 1986 reported water soluble self-doped polythiophene variant by utilized a butylsulfonate alkyl chain (Figure 1.2).<sup>49, 50</sup> Upon doping, these polymers can be self-compensated through the sulfonate anion already existing in the backbone with no need for the counterion from the dopant to be present. In addition, in the early 2000s Reynolds and coworkers investigated the electrochromic properties of poly(ethylenedioxythiophene) (PEDOT), which has been widely investigated in the literature as a conducting polymer with conductivities exceeding 1000 S cm<sup>-1</sup>.<sup>51-53</sup> This is one example among thousands of other conjugated polymers have been developed and characterized in the literature demonstrating various syntheses, processing techniques, and polymer: dopant combinations.<sup>48, 54-</sup> 56









trans-polyacetylene

Poly(p-phenylene vynilene)

Polypyrolle







Polythiophene



Poly(ethyldioxythiophene)

PEDOT

Poly(3-hexylthiophene) P3HT

Polyaniline PANI

poly-3-(4butanesulfonate)thiophene)

LS~SI>>

p(g42T-TT)

 $C_{12}H_{25}$ 

C<sub>12</sub>H<sub>25</sub>

PdppSe

 $_{10}H_{21}$ 

Poly(3,3'-bis(2-tetraethyleneglycolmonoethylether)[2,2'bithiophen]-5-yl)-5-thieno[3,2-*b*]thiophene) PBTTT



Figure 1.2. Summary of hole transport polymer examples discussed within the context of electrical doping.

As discussed earlier, both the charge carrier mobility and density are not simple constants. Analysis of the current literature of published polymer- dopant- processing combinations allows to classify the research developments into those primarily attempting to improve the charge carrier mobility, density, or strategies that contribute to both. Investigations into the evolution of charge carrier mobility upon doping concluded that the initial introduction of charge carriers introduces trap states due to the tendency of the introduced charges to coulombically interact with the dopant counterion.<sup>57</sup> Upon increasing the charge carrier concentration by increasing the doping level, both the mobility and conductivity increase again. For example, electrochemically doped P3HT shows an initial drop in the charge carrier mobility, which then increases between 0.1% and 10% dopant equivalents and plateau beyond the 10% doping level.<sup>57</sup> One drawback of these investigations is that the doping level used is usually at or below 10% molar ratio of dopant, however in some systems the optimal doping level can go up to 70% (*i.e.* 0.7 electrons/ monomer assuming 100% ionization efficiency). Thus, at a high doping level maintaining a high charge carrier mobility would require the polymer to be able to accommodate the impurity counterion, minimize the number of traps formed due to the columbic charge interactions, or traps formed due to geometric modification in the polymer backbone to accommodate the injected charges, and avoid inhomogeneity/ phase separation in dopant distribution at high dopant loading.



Figure 1.3. Evolution of mobility upon changes in regioregularity of P3HT.<sup>57</sup> Reproduced with permission. Copy right of American Physical Society 2021.

In terms of hole transport materials (Figure 1.2), which can be *p*-doped by oxidation using electron poor compounds (Figure 1.4), conductivities up to  $10^5$  S cm<sup>-1</sup> have been achieved in the case of high temperature rubbed PBTTT (Table 1).<sup>58</sup> Table 1.1 also shows examples of reported high conductivity *p*-doped hole transport materials, as well as the processing method and dopant used.



Figure 1.4. Examples of p-dopants discussed within the context of electrical doping.

Table 1.1. Examples of high conductivity doped hole-transport materials, dopant used, and doping method. Vapor = exposing neat polymer film to dopant vapor. Dipping = dipping of neat polymer film in dopant solution. Blending = blending of both polymer and dopant before casting.

Polymer	σ (S/cm)	Dopant	Method	Reference
PBTTT-C14	604	FTS	Vapor	59
PBTTT-C14	1300	EBSA	Dipping	60
PdppSe	900	FeCl <sub>3</sub>	Dipping	61
Polyacetylene	$6  imes 10^4$	Iodine	Vapor	62
PDPP3T	226	FeCl <sub>3</sub>	Dipping	63
PEDOT	1355	Fe(Tos) <sub>3</sub>	Dipping	64
PCDTBT	160	F4TCNQ	Dipping	65
PCPDTSBT-OC	206	FeCl <sub>3</sub>	Dipping	66
PPDT2FBT-OC	125	FeCl <sub>3</sub>	Dipping	66
РЗНТ	570	FeCl <sub>3</sub>	Dipping	58
C12-PBTTT	$2.7 \times 10^5$	FeCl <sub>3</sub>	Dipping	58

P(g42T-TT)	100	F4TCNQ	Blending	67
C14-PBTTT	320	NOPF <sub>6</sub>	Vapor	68

As for electron transport small molecules and polymers, there is also a variety of aromatic, and conjugated monomers that have been and can be used for that purpose.<sup>69-72</sup> Although multiple efforts have been done to develop more conductive electron transport materials, they still lag behind their hole transport counterparts, likely due to issues of air stability, and miscibility with the dopant, as discussed later in the text.<sup>72, 73</sup>

To date, the highest conductivity reported for an *n*-doped electron transport material is ca. 90 S cm<sup>-1</sup> for a N-DMBI-H doped BDPPV system.<sup>74</sup> Examples of polymers used heavily in the literature can be seen in Figure 1.5, along with the most commonly utilized *n*-dopants in Figure 1.6. Table 1.2 shows a summary of polymers and dopants combinations along with the processing method and the subsequent conductivity values achieved.





 $C_{18}H_{37}$ 

C<sub>18</sub>H<sub>37</sub>

Figure 1.5. Examples of n doped electron transport polymers discussed herein.


Figure 1.6. Examples of commonly used n-dopants discussed herein.

Table 1.2. Summary of electrical conductivities for electron transport conjugated polymers, with the doping method and dopant used. Vapor = exposing neat polymer film to dopant vapor. Dipping = dipping of neat polymer film in dopant solution. Blending = blending of both polymer and dopant before casting.

Polymer	Dopant	Method	σ <sub>max</sub> (S/cm)	Ref.
BBL	TDAE	Vapor	2.4	75
BBL	N-DMBI-H	Dipping	3	76
N2200	TDAE	Vapor	$3 \times 10^{-3}$	75
	N-DMBI-H	Blending	8 × 10 <sup>-3</sup>	77
	N-DPBI-H	Blending	$4 \times 10^{-3}$	77
	2-cyc-DMBI-H	Solution	$0.34 \times 10^{-3}$	78

Table 1.2 continued				
	(2-cyc-DMBI) <sub>2</sub>	Blending	$2.8 \times 10^{-3}$	78
	(2-Fc-DMBI) <sub>2</sub>	Blending	7.6 × 10 <sup>-3</sup>	78
	(2-Rc-DMBI) <sub>2</sub>	Blending	$3.0 \times 10^{-3}$	78
	TAM-H	Blending	$1 \times 10^{-3}$	79
	BV⊷	Dipping	$13.4 \times 10^{-3}$	80
TEG-N2200	N-DMBI-H	Blending	0.17	81
P(NDI2TEG)-2T(OD)	N-DMBI-H	Blending	$0.7 \times 10^{-3}$	82
P[NDI2TEG)-2T(TEG)]	N-DMBI-H	Blending	0.3	83
P(NDI(OD)-2Tz)	TDAE	Vapor	0.1	84
P(NDI2TEG-2Tz(OD)	N-DMBI-H	Blending	1.8	82
P(NDTI(DT)-BBT)	N-DMBI-H	Blending	0.18	85
P(NDTI(DP)-BBT)	N-DMBI-H	Blending	5	85
P(PDI(OD)-2T)	(2-cyc-DMBI) <sub>2</sub>	Blending	$1 \times 10^{-3}$	86
	BV•+	Dipping	0.7 × 10 <sup>-3</sup>	87
P(PDI(OD)-E)	(2-cyc-DMBI) <sub>2</sub>	Blending	2.1 × 10 <sup>-3</sup>	86

P(PDI(OD)-A)	(2-cyc-DMBI) <sub>2</sub>	Blending	0.45	86
P(PDI(OD)-DEBT)	(2-cyc-DMBI) <sub>2</sub>	Blending	$70  imes 10^{-3}$	86
P(TDPP-CT2)	N-DMBI-H	Blending	0.39	88
P(PzDPP)-CT2)	N-DMBI-H	Blending	8.4	88
	N-DMBI-H	Blending	32.1	89
PDPH	N-DMBI-H	Blending	$1 \times 10^{-3}$	90
PDPF	N-DMBI-H	Blending	1.3	90
PDTTzTI	TDAE	Vapor	4.6	91
BDPPV	N-DMBI-H	Blending	0.26	92
FBDPPV	N-DMBI-H	Blending	14	92
	(N-DMBI) <sub>2</sub>	Blending	8	93
	(RuCp*Mes) <sub>2</sub>	Blending	1.6	93
	TAM-H	Blending	21	79
CIBDPPV	N-DMBI-H	Blending	5	92
UFBDPPV	N-DMBI-H	Blending	16	94
	TAM-H	Blending	22	94

LPPV-1	N-DMBI-H	Blending	0.9	94
	ТАМ-Н	Blending	3.7	94
LPPV-2	N-DMBI-H	Blending	0.07	95
2S-trans-N2200	N-DMBI-H	Blending	<b>5.9</b> × 10 <sup>-3</sup>	96
TBDPPV	N-DMBI-H	Blending	92	74
TBDOPV-T	N-DMBI-H	Blending	65	74
TBDOPV-2T	N-DMBI-H	Blending	2.3	74
PCNTI	N-DMBI-H	Blending	0.19	97
PCNDTI	N-DMBI-H	Dipping	0.28	97
PCNI-BTI	N-DMBI-H	Dipping	23.3	97
PCNDTI-BTI	N-DMBI-H	Dipping	0.56	97
PBTI	N-DMBI-H	Dipping	$2 \times 10^{-3}$	97
P(CICITVT)	N-DMBI-H	Blending	16.1	98
P(FCITVT)	N-DMBI-H	Blending	38.3	98

### 1.4 **Charge-carrier mobility:**

1.4.1 Fabrication and doping method:

As evident in tables 1.1 and 1.2 a wide range of conductivities can be achieved based on the choice of polymer-dopant-processing combinations. In some cases, the polymer and dopant can be processed in solution then cast as a film (blending). In this approach, labelled as mixing in the tables above, the redox reaction can either happen in solution, or in the case of NDMBI-H happens after film casting during annealing. High conductivities have been achieved through that method for various hole and electron transport materials. A drawback for this approach is problems with aggregation of the polymer: dopant when doping occurs almost instantaneously in solution followed by precipitation as the doped polymer: dopant ion aggregates are rendered insoluble in the processing solvent. For some systems, this can be solved via solvent modification. For example, P(PzDPP-CT2) conductivity upon doping with N-DMBI-H was improved from ~ 8.4 S cm<sup>-1</sup> when processed with *p*-xylene to exceed 32.4 S cm<sup>-1</sup> when the solvent was switched to (1-chloronaphthalene).<sup>89</sup> The pristine polymer mobility, however, is not affected by the solvent change choice, which arguably means that the 4 fold increase in conductivity is due to the solvent change where the aggregates were better dissolved upon solvent switching before casting the film.



Figure 1.7. (a) Scheme of doped polymer aggregation behavior upon solvent and temperature modification (CN = 1-chloronaphthalene) changes in aggregation upon solvent choice and temperature. (b) plot of conductivity n-doped organic materials vs. year of publication where this work represents P(PzDPP-CT2). (c) conductivity of P(PzDPP-CT2) vs. dopant ratio.<sup>89</sup> Reproduced with permission. Copy right of John Wiley and Sons 2021.

Other strategies call for the avoidance of the issue of aggregation of polymer: dopant altogether via employing sequential doping.<sup>76, 99-102</sup> The process can be seen figure 1.8 where the pristine film of the polymer can be made, annealed if needed, then covered with the dopant solution via dipping or by evaporating the dopant onto the pristine film in a vacuum chamber, then washed by an solvent that dissolves the dopant but not the polymer to remove any excess dopant.<sup>99, 103</sup> An annealing step at this point is also optional. This method avoids the formation of insoluble aggregates that cannot be easily dissolved as in the case of F4TCNQ doped P3HT for example.<sup>60, 100, 104</sup> Multiple reports

comparing P3HT by mixed solution *vs*. sequential doping have illustrated the role of sequential doping in achieving high conductivity.<sup>99, 100</sup>



## Figure 1.8. (a) solution mixing doping. (b) sequential doping in solution. (c) hybrid doping approach.<sup>105</sup> Reproduced with permission. Copy right of John Wiley and Sons 2021.

The neat polymer can be deposited on the substrate via multiple methods including drop casting,<sup>106</sup> spin coating, blade coating, doctor blading, solvent shearing<sup>107, 108</sup>

A third approach to doping is a hybrid doping strategy, which involves mixing the polymer and dopant in solution first, casting the film, then doping the film further sequentially (Figure 1.8). In one study, hybrid doping conductivity was found to be higher than either approach alone. In that case the conductivity of PIDF-BT achieved 630 S cm<sup>-1</sup> when doped using this approach with

F4TCNQ, as opposed to 200 S cm<sup>-1</sup> when doped sequentially and 70 S cm<sup>-1</sup> when doped by blending only.<sup>105</sup>



## Figure 1.9. Plot of a dopant concentration vs. doping method and ionization efficiency (%).<sup>105</sup> Reproduced with permission. Copy right of John Wiley and Sons 2021.

PBTTT (Figure 1.2) also showed an increase in electrical conductivity upon vapor diffusion of F4TCNQ (220 S cm<sup>-1</sup>) *vs.* solution mixing (3.5 S cm<sup>-1</sup>).<sup>60</sup> The in- and out- of plane Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) data showed no substantial changes in the local order of the polymer. However, polarized soft x-ray scattering, which can determine the orientational correlation length (OCL) defined as the average length over which the polymeric backbone drift out of alignment with each other was proven effective in understanding the changes in polymer morphology.<sup>109</sup> For example, in a study of doped PBTTT, more conductive films showed OCL greater than 120 nm whereas the less conductive ones ( $\sigma < 10$  S cm<sup>-1</sup>) had an OCL less than 70 nm. In addition, OCLs have an exponential relationship with the charge-carrier mobility determined for pristine PBTTT in OFETs.<sup>60</sup> As such, the high OCL of the more conductive films can be correlated with the films having a higher charge-carrier mobility. This is

not to say that the local order and packing do not play any role in the charge-carrier mobility and conductivity but to underscore the complexity of the microstructure/ morphology influence on the conductivity.

#### 1.4.2 Inter and intramolecular interactions:

Inter and intramolecular interactions can be divided into polymer: dopant ions interactions, polymer: polymer intermolecular interactions, and polymer intramolecular interactions.

#### 1.4.2.1 Polymer: dopant interactions

Upon doping with an oxidant or reductant, the dopant will become the doped polymer's counterion, and its size, volume, and charge distribution will have a significant effect on the film microstructure, columbic interactions between the opposite charges and ultimately on the conductivity of the film.<sup>110, 111</sup>

Several strategies have been adopted in order to probe the role of the counterion on the conductivity and thermoelectric performance of conjugated polymers.<sup>59, 60, 68, 93, 103, 104</sup> Large and bulky dopants have been used to introduce a large volume anion in order to investigate the influence of the spatial separation between the charges of the polymer and counterion respectively. It was observed that bulkier dodecaborane (DDB) dopants (Figure 11) incorporated into P3HT films, although inducing structural disorder in the packing, the large separation between the anion center and the polaron (on the polymer backbone) (determined to be 15.5 Å) led to the charges observed being more mobile. <sup>112</sup> In addition, AC hall mobility measurements were plotted against the peak location from the near infrared absorption spectra (Figure 11), showing the correlation between the mobility of the charge carrier and the peak position. The IR absorption spectra can be

utilized to determine delocalization from the peak position (a more red shifted peak is considered to originate from a more delocalized polaron) as well as the relative intensity of the peak at ca. 0.15 eV (figure 1.12).<sup>112</sup>



Figure 1.10. Polymer counterion separation in P3HT doped with DDB-F<sub>72</sub>.<sup>112</sup> Reproduced with Permission. Copyright of John Wiley and Sons.



# Figure 1.11. (a) NIR absorbance spectra of P3HT doped different solution concentration of DDB-F<sub>72</sub>. (b) plot of charge carrier mobility of polymer vs. NIR peak location.<sup>112</sup> Reproduced with permission. Copyright of John Wiley and Sons.

However, when investigating F4TCNQ, higher crystallinity of the polymer is associated with more delocalized charges and higher charge carrier mobility.<sup>102, 112</sup> This is due to the fact that F4TCNQ is small in size and thus requires the polymer to have high crystallinity for more mobile polarons.<sup>112</sup> This crystallinity requirement is not a concern in the case of DDB since DDB is bulkier by design and the negative charge is automatically more shielded from the polymer.<sup>112</sup>

Most recently Thomas *et al.*, and Yamashita *et al.* have investigated the effect of exchanging the doped polymer counterion using ionic liquids.<sup>113, 114</sup> First, neat C-14PBTTT films are doped with NOBF<sub>4</sub> vapor, then ionic liquids of a variety of counterions were used to systematically probe the role of counter-ion volume and found that an increase in counterion volume did in fact enhance the performance.<sup>68</sup> The researchers hypothesize that the increased delocalization, conductivity and stability are due to anions of larger diameters enhancing the delocalization of the PBTTT polaronic elements in addition to enhancing the thermal stability of the doped polymer due to the anions themselves being more stable towards heating.<sup>68</sup>



Figure 1.12. UV-vis (a) NIR (b) absorption of PBTTT films doped with NOBF4 vapor upon ion exchange, and (b) ionic diameter vs. NIR peak position and ratio,  $BF_4 =$  tetrafluoroborate,  $PF_6 =$  hexafluorophosphate, TCB = tetracyanoborate, PCF = tris(pentafluoroethyl)trifluorophosphate.<sup>68</sup> Reproduced with permission. Copy right 2020, John Wiley and Sons.

Another strategy used for *n*-doped electron transport materials has been investigating the role of the dopant/ dopant ion size on the conductivity. In the case of BODPV, upon investigating

a series of dopants *i.e.* N-DMBI-H, (N-DMBI)<sub>2</sub> and (RuCp\*Mes)<sub>2</sub> it was shown that although both (RuCp\*Mes)<sub>2</sub> and (N-DMBI)<sub>2</sub> are both strong dopants and their resulting cations have similar volumes (figure 1.14), the relatively more planar and smaller N-DMBI<sup>+</sup> cation can be better accommodated in the BDOPV causing less disruption in the microstructure and that was reflected in conductivity results when BDOPV is doped with (N-DMBI)<sub>2</sub> ( $\sigma_{max} = 8 \text{ S cm}^{-1}$ ) *vs.* when doped with (RuCp\*Mes)<sub>2</sub> ( $\sigma_{max} = 1.75 \text{ S cm}^{-1}$ ) (Figure 1.13).<sup>93</sup> Although N-DMBI-H is expected to result in the same cation as (N-DMBI)<sub>2</sub> and knowing that the latter can provide 2 electrons per dimer *vs.* 1 electron per molecule in N-DMBI-H, it is evident that the conductivity of films doped with N-DMBI-H is lower than those doped with (N-DMBI)<sub>2</sub> even when the N-DMBI-H content is twice that of (N-DMBI)<sub>2</sub>. This demonstrates the complexity electron transfer mechanism of N-DMBI-H *vs.* (N-DMBI)<sub>2</sub>.<sup>93, 115</sup>



Figure 1.13. (a) conductivity and (b) Seebeck coefficient of BDPPV vs. dopant mol % with different dopants. (c) size comparison of (RuCp\*Mes)<sup>+</sup> (orange) and DMBI<sup>+</sup> (blue). (d) Venn diagram of properties among the three dopants considered.<sup>93</sup> Reproduced with permission. Copyright 2018, John Wiley and Sons.

#### 1.4.2.2 Polymer interchain interactions

Inorganic semiconductors are large crystalline materials with some ionic contributions due to defects such as gallium arsenide, meanwhile, conjugated organic small molecules and polymers are anisotropic materials, and mainly interact via the relatively weak Van der Waals forces from the interchain stacking. The distance and thus the resulting  $\pi$ - $\pi$  inter-chain interactions will dictate the spatial overlap between the wavefunction and in turn the electronic coupling between two chains.

This has been studied by modifying the regioregularity of P3HT to probe the effect of the film ordering on the conductivity and thermoelectric properties of the doped films. By investigating the GIWAXS, Raman spectroscopy and resonant soft x-ray scattering, it was concluded that the increase in regioregular content leads to higher crystallinity, long-range connectivity between domains and better charge transport. The existence of the higher crystalline content in this case led to higher doping efficiency and charge carrier mobility. <sup>116</sup> Upon exposure of the films to F4TCNQ vapor under the same conditions (80 °C for 10 minutes), the conductivity could be increased from 0.01 S cm<sup>-1</sup> for regiorandom P3HT to 10 S cm<sup>-1</sup> for 100% regionegular P3HT(figure 1.14).<sup>116</sup> Although the charge carrier density increases linearly with the increase in regioregular content, due to change in steric demands of the chain as well as different regioregular/ regiorandom blends have different ionization energies. The charge-carrier mobility was found to increase from 0.001 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for regiorandom P3HT to 0.8 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for 100% regioregular content in the film (Figure 1.15).<sup>116</sup> The charge carrier mobility in this case was determined from Mott-Schottky measurements which showed that mobility increases non-linearly with the increase in regioregularity reflected in a non-linear increase in conductivity over multiple orders of magnitude.116



Figure 1.14. (a) charge carrier concentration vs. regioregularity of F4TCNQ-doped P3HT films determined from EPR and UV-vis. (b) conductivity vs. regioregularity of P3HT. (c) charge carrier mobility vs. regioregularity of P3HT determined Mott-Schottky measurements.<sup>116</sup> Reproduced with permission. Copyright 2019, John Wiley and Sons.

Another aspect of interchain interactions is the packing of donor-acceptor, (-D-A-)<sub>n</sub> type polymers. These polymers can stack either in "segregated" or "mixed" form. The segregated form would mean that donor units would only stack on top of other donor units whereas the mixed form would mean an alternating or random stacking (Figure 1.15). The charge transfer is enhanced by a higher wavefunction overlap between the consecutive layers as demonstrated in Figure 1.15.<sup>6</sup> For example, theoretical calculations have shown that segregated packing of a poly(benzothiadiazole-cyclopentadithiophene) structure increases the interchain charge transfer integral.<sup>117</sup> Another strategy currently being explored is to synthesize acceptor-acceptor (A-A) architecture polymers to increase the interchain wave function mixing as well as increase the intrachain conjugation (Figure 1.15).



Figure 1.15. (a-c) sketch of polymer stacking based on D-A and A-A building blocks. (d-f) sketch of wavefunction along the x-axis. (g-i) sketch of wavefunction along the y axis.<sup>6</sup> Reproduced with permission. Copy right 2021, Royal Society of Chemistry.

1.3.3 Intrachain interactions: backbone modifications

Along the backbone, torsional twists and kinks in the polymer backbone can disrupt the extended conjugation of the polymer. Extended conjugation is needed for wave function overlap of neighboring (bi)polarons which can enhance the intrachain carrier transport.<sup>26</sup> One strategy used

in modifying one of the co-monomers, introduction of different co-monomer has been proven to improve the charge carrier mobility and conductivity upon reducing the intra-chain strain which induces twists in the backbone where planarizing the backbone is crucial. For example, introduction of a less electron rich bithiazole instead of bithiophene for polymerization with naphthalene diimides which indicated the formation of a more planar backbone. This strategy of "all-acceptor" polymers was shown effective in multiple studies where "typical" donors were swapped by "acceptors" to improve the conductivity. In addition, Naab *et al.* investigated the effect of the removal of the "donor" units where photothermal deflection spectroscopy and UV-vis-NIR spectra established a direct link between the polaron delocalization and the conjugation along the polymer backbone.<sup>86</sup> The conductivity could be increased from 4 mS cm<sup>-1</sup> when they doped N2200 in solution with (Cyc-DMBI)<sub>2</sub> to 0.45 S cm<sup>-1</sup> when P(PDI2OD-A) is doped with the same dopant (figure 1.16).<sup>86</sup>



Figure 1.16. Doping reaction, dopant and polymer structures as well as table representing: delocalization length, polaron absorption energy and maximum conductivity.<sup>86</sup> Adapted with permission. Copyright 2016 John Wiley and Sons.

Second, planarity of the backbone can be achieved via the introduction of intra molecular hydrogen bonding as in the case of the pyrazine flanked diketopyropyrolle polymer (Table 1.2 and Figure 1.7). The polymer structure includes intramolecular hydrogen bonding, which is found to planarize the backbone. The conductivity of the modified polymer upon doping with DMBI-H was found to be 8.4 S/cm.<sup>88</sup>

Third, rigid backbones such as semi-ladder polymers including BBL (Figure 1.15) for example. BBL doped with N-DMBI-H have recently been shown to achieve conductivities of 1.4 S cm<sup>-1</sup> (Table 1.2).<sup>76</sup> One drawback, however, is that BBL is only soluble in acidic solvents and requires  $\sim$  4 hours annealing of the film at 190 °C upon dopant addition to achieve optimal conductivity.<sup>76</sup>

#### 1.3.4 Side chain branching

Many conjugated organic materials rely on the side chains to be solution processable. The properties of these side chains such as their length, polarity, and branching point also play an important role in the resulting performance whether in transistors and/or doped films.<sup>118</sup> For example, charge carrier mobilities have been proven to increase 3 times upon modifying the alkyl chain branching point (Figure 1.18). In fact, Pei and coworkers have shown an "odd-even" effect in the branching point as well as a decrease in the  $\pi$ - $\pi$  distance in the polymer stacking upon increasing the number of carbons between the conjugated backbone and the long alkyl chains (Figure 1.18).<sup>118</sup>



Figure 1.17. Polymer structure, sketch of packing on substrate and plot of  $\pi$ - $\pi$  staking distance and charge carrier mobility vs. branching point position.<sup>118</sup> Reproduced with permission. Copyright 2014, John Wiley and Sons.

Another example is the case of PNDTI-BBT-DT (Figure 1.19), the conductivity and the mobility were increased by 20 and 3 times respectively upon changing the branching point of the alkyl chain where onductivity increases from 0.2 to 5 S cm<sup>-1</sup>.<sup>85</sup> In addition, it is notable that the higher conductivity polymer (PNDTI-BBT-DP) maintains its (100) peak upon doping whereas PNDTI-BBT-DT observes broadening in the peak indicative of disorder.<sup>85</sup> This also highlights the role of the alkyl chain branching in allowing the polymer to accommodate the dopant without significant drawbacks to its structural order.



Figure 1.18. polymer structure, Seebeck coefficient and conductivity plots vs. N-DMBI-H mol % for PNDTI-BBT-DT and PNDTI-BBT-DP as well as XRD patterns for pristine and doped polymer films.<sup>85</sup> Adapted with permission. Copyright 2017, American Chemical Society

However, not all side chain modifications necessarily play a role directly in improving the charge carrier mobility alone. For instance introduction of glycol chains instead of alkyl ones will also be discussed in the context of enhancing the solubility of the polymer: dopant system of choice.<sup>118,</sup>

#### 1.5 **Common factors:**

#### 1.5.1 Polymer- dopant miscibility

The dopant needs to be miscible with the polymer for electron transfer to take place. In solution blending doping, there are two possible scenarios: if the redox reaction is occurring in solution, the miscibility requirement is to ensure that the doped polymer/dopant mixture is not significantly more (or less) soluble than the neutral polymer or phase separate from one another upon casting. However, if the doping occurs after casting the film during the thermal annealing process, miscibility is needed to ensure the dopant and polymer phase do not separate during the annealing process. On the other hand, when sequential doping is used (whether by dipping or vapor exposure) the polymer packing and microstructure need to accommodate the infiltration of the dopant for charge transfer to take place. In addition, the used dopant/ solvent combination need to swell the polymer to yield significant doping that can be observed via conductivity measurements. The miscibility is considered a common factor for both mobility and density because the dopant needs to be in the vicinity of the conjugated backbone for doping to occur and thus increase the charge carrier density. In addition, blending/ phase separation of the dopant/ dopant ion will affect the microstructure of the film affecting the charge carrier mobility.

One of the problematic dopants in terms of its miscibility with the polymer is N-DMBI-H. Despite its wide usage it has been shown that upon doping N2200 with N-DMBI-H only 1% of all added dopants successfully results in doping of N2200.<sup>77</sup> This due to phase separation during the annealing process used to activate the reaction. This is experimentally observed; specifically through aggregate formation at the top of the film upon doping attributed to phase segregation of the polymer-dopant mixture seen by Atomic force microscopy (AFM).<sup>77</sup>

One strategy to improve the miscibility is through introducing glycol side chains. Glycol side chains have been installed on both the polymer and/ or the comonomers yielding TEG-N2200,

PNDI2TTEG-2Tz, or PNDI2C<sub>8</sub>TEG-2Tz (Figure 1.20).<sup>81, 120</sup> In the case of PNDI2TTEG-2Tz, it was shown via molecular dynamics simulation that although the glycol chain can be used to intercalate the dopant ion, placing an alkyl spacer can increase conductivity due to its role in preventing phase separation by intercalating the N-DMBI<sup>+</sup> cations (Figure 1.20).<sup>81</sup> It is notable that in the cases of PNDI2TTEG-2Tz and PNDI2C<sub>8</sub>TEG-2Tz that low amount of dopant is needed to achieve the maximum conductivity observed which is also a factor of the miscibility.<sup>77, 120</sup>



Figure 1.19. (a) structure of polymer and dopants investigated. (b) sketch of alkyl chain design vs. suggested dopant location with respect to the backbone. (c) evolution of conductivity vs. dopant weight percent.<sup>120</sup> Reproduced with permission. Copyright 2020, John Wiley and Sons.

Recently, a new dopant TAM-H with a similar doping mechanism to N-DMBI-H was reported.<sup>79</sup> The main difference has been the shown improved miscibility of TAM-H with n type polymers such as BDPPV. This is due to the ability of TAM<sup>+</sup> cations to remain in the alkyl chains unlike N-

DMBI<sup>+</sup> which phase separate during the annealing process out of the alkyl chains. For instance, upon doping and at equilibrium, TAM<sup>+</sup> ions will reside within the long alkyl chains with the backbone- ion distance mode being ~ 12 angstroms *vs*. 20 angstroms for DMBI<sup>+</sup>. However, although the shorter distances might suggest that the countercharges will be coulombically bound and thus lead to lower conductivity this does not seem to be a significant barrier, presumably due to the cations being already far enough from the doped backbone.



Figure 1.20. (a) Chemical structure of polymer and dopants used in molecular dynamics simulations in sections b-f. (b) sketch of initial supercell dynamics with polymer-TAM<sup>+</sup> configuration. (c-d) equilibrium configurations of n doped FBDDPV by TAM-H and N-DMBIH respectively. (e-f) histograms of anion distribution upon doping and at

## equilibrium. distance = 0 corresponds to 25 Å separation between backbone and alkyl chain.<sup>79</sup> Reproduced from article under creative commons CC BY.

Another strategy to improve compound polymer interaction was demonstrated through anchoring of the dopant to PCBM to prevent the phase segregation in films upon doping. Reiser and coworkers designed a phenylazide version of DMBI-H and covalently anchored it to PCBM which was improves conductivity as well stability of the doped films since the immobilization of dopant results in suppressing the dopant drift.<sup>121</sup> The covalent anchoring approach that Reiser describes is reportedly being investigated for *p*-dopants as well.

#### 1.5.2 Dopant, ions, and doped polymer stability

The stability of precursors as well as the final species in the doped polymer films is integral to sustain performance over time. Sources of instability include be the susceptibility of the polymer (or its doped derivative) to reaction with air/ moisture. Another source is the instability of the dopant or its ion by reacting with air or having the dopant be volatile enough to overcome the intermolecular forces with the polymer and sublime following a reverse electron transfer between the dopant ion and the polymer.

#### 1.5.2.1 Doped polymer stability:

Many of the polymers used for *n*-doping, exhibit air/ moisture sensitivity upon doping. Two strategies have been used in order to increase the stability of the doped film. First, installing electron withdrawing groups to increase the electron affinity of the pristine polymer so that the doped polymer less susceptible to oxidation by air/moisture.<sup>122, 123</sup> However, this is not necessarily always practical if this is used in a layered device where a specific electron affinity is needed.

For instance, upon addition of excess Lawensson's reagent to N2200 (or PNDIT2), 2S-*trans*-PNDIT2 can be formed which displays maximum conductivity of 6 mS cm<sup>-1</sup>, as opposed to 1.2 mS cm<sup>-1</sup> for PNDIT2 (Table 1.2).<sup>96</sup> Notably, 2S-*trans*-PNDIT2 also displays longer air stability than PNDIT2 attributed to the modification of the electrochemically estimated EA of the 2S-*trans*-PNDIT2 to 3.96 eV as opposed to 3.75 eV for PNDIT2 (figure 1.6).<sup>96</sup>



Figure 1.21. conductivity of 2S-trans-PNDTI2 and PNDIT2 vs. doping level. (b) conductivity evolution upon exposure to air.<sup>96</sup> Reproduced with permission. Copyright 2020, American Chemical Society.

A second strategy to enhance the ambient stability of doped polymers is utilization a selfencapsulation approach. A thick film of the polymer is grown so that the few top layers can protect the bulk of the film from being de-doped. This has been successfully applied by growing micrometer thick ClBDPPV films *n*-doped with TBAF where they exhibited enhanced air stability upon doping in comparison to thinner films doped under the same conditions.<sup>124</sup>

#### 1.5.2.2 <u>Neutral and dopant ion stability:</u>

Two main factors can contribute to the dopant instability: dopant or ion reaction with air/ moisture, and volatility of the dopant coupled with reversibility of the electron transfer.

In case of the air instability of the dopants, TDAE doped N2200 films de-doped once polymer films, where removed from the dopant vapor, which can be attributed to the oxidation of the TDAE cation by air as well as the low boiling point TDAE has of 60 °C.<sup>91</sup> Another path would be through a reverse electron transfer to TDAE followed by sublimation. This has been also observed in the case of BBL (Figure 1.5) which displays higher stability when doped with N-DMBI-H *vs.* TDAE (figure 1.22).<sup>76</sup>



Figure 1.22. comparison of conductivity of BBL when doped with N-DMBI-H and TDAE vs. annealing time (a), and exposure to air (b).<sup>76</sup> Reproduced with permission. Copyright 2020, American Chemical Society.

F4TCNQ has also been shown to be volatile yielding to de-doping of the polymer over time due to its ability to escape the film upon back electron transfer. In addition, upon exposure of F4TCNQ doped P3HT films to heat, F4TCNQ radical anion undergoes a side reaction to form HF4TCNQ<sup>-</sup> resulting in a decrease in conductivity upon annealing of the doped films.<sup>125</sup> Moreover, even in the case mentioned earlier regarding PBTTT when different counterions were exchanged, it was indeed proven that enhancing the stability of the counterion *vs*. heating did indeed result in maintaining the high conductivity *vs*. temperature.<sup>68</sup>



Figure 1.23. Normalized absorbance of doped P3HT vs. temperature and evolution of conductivity an absorbance at 1.14 eV as a function of temperature.<sup>125</sup> Adapted with permission. Copyright 2020, American Chemical Society

Another stability factor would be the decomposition of dopants when exposed to air. There are multiple examples of air stable dopants such as (RuCp\*Mes)<sub>2</sub> being moderately air stable.<sup>126, 127</sup> In addition, (DMBI)<sub>2</sub>, its derivatives, and their DMBI-H counterparts have also been shown to be moderately air stable and produce air stable counterions upon doping.<sup>78, 115, 128</sup>

#### 1.6 Charge carrier density

Pristine organic semiconductors, as mentioned earlier, have a very low charge carrier density and although high doping levels may not be necessary to every application, achieving optimal conductivity requires it. This require dopants to increase the charge carrier density via electron transfer which is correlated to increase in conductivity as long as the increase in doping level is not significantly diminishing charge carrier mobility. To achieve and retain high charge carrier density a few requirements need to be met:

#### 1.6.1 Full electron transfer:

This can be achieved by designing dopants, like those *p*- and *n*-dopants shown earlier, while making sure that when doping that the electron affinity of the p-dopant needs to match or exceed the ionization energy of the hole transport material, or vice versa for electron transport materials. This is simple for clean electron transfer dopants such as magic blue, benzyl viologen, (RuCp\*Mes)<sub>2</sub>, (N-DMBI)<sub>2</sub>, TDAE and others. However, for N-DMBI-H or TAM-H this is not as straight forward. N-DMBI-H has a complex mechanism of both hydride/ electron transfer and requires thermal activation over a period of time to achieve proper doping levels and in turn significant conductivities.<sup>115</sup> This is coupled with the earlier mentioned problem of miscibility. Materials such as (N-DMBI)<sub>2</sub> and its derivatives avoid this by being clean electron donors as well as being strong dopants.

In addition, Schwartz and coworkers recently demonstrated that the casting solvent can be used to favor the formation of charge transfer complexes as opposed to integer transport by changing the casting solution of the F4TCNQ doped P3HT films.<sup>129</sup> On the other hand, F4TCNQ was shown to be double reduced to F4TCNQ<sup>2-</sup> upon doping with conjugated polymer P(g42T-TT) (Figure 1.3 and Table 1).<sup>67</sup> Conductivities up to 100 S cm<sup>-1</sup> where achieved in that case. These examples illustrate how dopant behavior can be tuned via molecular design or processing methods which in turn can modify doping level and charge carrier density.

#### 1.7 Thesis chapters synopsis

This thesis includes four research chapters. The first research chapter (chapter 2) the synthesis, doping and conductivity studies on two small molecule naphthalene diimides. A nitrile capped naphthalene diimide dimer (NDI-CN)<sub>2</sub> is shown to exhibit conductivity up to 4 mS cm<sup>-1</sup> upon concomitant doping with (N-DMBI)<sub>2</sub> in solution. The second section of chapter two, a high

mobility naphthalene diimide copolymer referred to as PNBS is synthesized to examine its charge transport properties. A conductivity of 2 mS cm<sup>-1</sup> was achieved in air upon sequential doping. Diffraction patterns, and temperature dependence of conductivity are also reported.

In chapter three, a series of small molecules and a side chain naphthalene diimide polymer are studied for transparent electron transport materials in perovskite solar cell. The performance of the organic materials is studied with  $SnO_2$  as a reference. Solar cells using the polymer exhibited opencircuit voltages of up to 1.02 V, short-circuit currents of over 21 mA cm<sup>-2</sup>, and power conversion efficiencies (PCE) reaching 14% which stabilize at 13.8% upon 90 s of illumination. Meanwhile control  $SnO_2$  devices exhibited PCE of *ca*. 16%, and small-molecule devices gave PCE values less than 10%. The devices employing the polymer exhibited improved long-term stability relative to the  $SnO_2$  control devices under continuous illumination.

Chapter four presents the synthesis and characterization of a series of organic n-dopants based on derivatives of DMBI-H and their dimers. Reactivity studies of the DMBI-H series revealed that our ability to control the reaction kinetics in solution via molecular design. In addition, the dimer reactivity was studied with TIPS-pentacene to probe the role of structure changes on the rate limiting step in the dimer reaction mechanism.

Chapter five investigates the role of the counterion on the reactivity of ferric compounds with polythiophene derivatives. Ferric tosylate and perchlorate afford the lowest and highest conductivities respectively in P3HT, although the doping ratios deduced from X-ray photoelectron spectroscopy (XPS) studies are similar. When a more disordered EDOT derivative  $PE_2$  is employed, both dopants, irrespective the counterion dope the polymer to similar extent and achieved conductivities in excess of 300 S/cm. A spatially localized charge transport model is then used to provide quantitative analysis on the charge transport mechanism in both P3HT and  $PE_2$  with both dopants.

Finally, chapter 6 aims to summarize the research results and provide suggestions inspired

by the content of this thesis and literature analysis done in the introduction, as well as provide

recommendations for future research projects.

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# CHAPTER 2. DOPING OF NAPHTHALENE DIIMIDE SMALL MOLECULES AND POLYMERS

The work described in this chapter benefited from contributions by Shawn Gregory, Samik Jhulki, Maxwell Conte, Hio-Ieng Un and Stephen Barlow. Shawn Gregory, advised by Prof. Shannon Yee, conducted some of the electrical conductivity measurements for the polymer. Hio-Ieng Un performed electrical conductivity measurements of one of the small molecules. Samik Jhulki and Maxwell Conte helped synthesize one of the dopants. The author synthesize, purified and characterized all naphthalene diimide small molecules and polymer, made all the films for optical and electrical measurements except those of (NDI-CN)<sub>2</sub>, measured UV-vis for all the combinations shown in the chapter as well as performed the electrical measurements on (CNNDI<sub>2</sub>-BTT). Parts of this chapter have been published in *Material Advances.*<sup>1</sup>

#### 2.1 Introduction

Electrical doping of organic semiconductors with redox-active molecules is increasingly used to increase conductivity and modify charge-injection/-extraction barriers.<sup>2, 3</sup> Doped films of small-molecule semiconductors are often fabricated by co-evaporation of semiconductor and dopant molecules. For solution-processible molecular and polymeric semiconductors, the dopant and semiconductor are commonly mixed in solution prior to casting the doped film. Recently, sequential doping methods in which the dopant is deposited onto the semiconductor film, either from solution or by evaporation, have increasingly been used.<sup>4, 5</sup> Sequential doping avoids possible complications that arise if the doped material is poorly soluble in the casting solvent and in some cases may allow for the preservation of some of the structural order present in the pristine

semiconductor film. Although widely applied to the *p*-doping of  $P3HT^{6-9}$  and PBTTT,<sup>10, 11</sup> there are only few reports of the sequential *n*-doping of solution-processed polymers.<sup>12</sup>

The air-stability of oxidants, hole-transport materials, and their *p*-doped combinations often allow for easy handling in air. Highly conductive hole-transport materials are achievable in many polymer-dopant systems.<sup>8, 13-17</sup> In contrast, electron transport materials and their corresponding *n*-doped derivatives lag behind *p*-type polymers in terms of both mobility, conductivity and stability.<sup>18-20</sup> One reason is that the dopant-induced polaronic charge carriers tend to be localized on acceptor moieties, and the electronic coupling between adjacent acceptor sites is often poor.<sup>5, 21-24</sup>



# Figure 2.1. Chemical Structures of NDI polymers and n dopants discussed in chapter

2.

A prominent family of electron-transporting semiconducting polymers are conjugated polymers incorporating naphthalene diimides (NDIs), which are reduced at moderate potentials of ca. -1.0 V vs. ferrocene.<sup>23, 25, 26</sup> Although a great diversity of NDI polymers have been reported, most *n*-doping studies have focused on the NDI/bithiophene copolymer, P(NDIOD-T2)/ N2200 (Fig. 1), and materials closely related to it.<sup>25-28</sup> Moreover, few of these studies have employed sequential doping.<sup>12</sup>

In this chapter, two naphthalene diimide dimers (NDI- of moderate electron mobility as well as PNBS (copolymer of an NDI monomer and a selenophene-flanked benzodithiazole (Fig. 1)<sup>29</sup>) are synthesized and doped in order to explore their charge transport behavior and conductivity.

PNBS exhibits a large field-effect electron mobility value of 8.5 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> on par with other recently reported high electron mobility polymers. <sup>30, 31</sup> The two NDI dimers studied here (NDI-CN)<sub>2</sub> and (NDI-CN)<sub>2</sub>-BTT (Figure 1) have reported electron mobility of 0.056 and 0.37 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively. These values raise the hypothesis of obtaining high conductivity values if high charge-carrier densities can be obtained through doping without adversely affecting the mobility. Section 2.3 reports the electrical properties of films obtained through the sequential doping of PNBS with the moderately air-stable *n*-dopants (RuCp\*mes)<sub>2</sub>, (N-DMBI)<sub>2</sub>, and N-DMBI-H (Fig. 1). The doped PNBS films are studied via temperature dependent conductivity measurements determined at different doping levels to investigate carrier transport. In addition, diffraction patterns of the films are reported to understand the impact of doping on film microstructure. Section 2.4 will show the synthesis and electrical properties upon doping of the two NDI dimers with (N-DMBI)<sub>2</sub>.

### 2.2 Materials and Methods

PNBS ( $M_n = 42 \text{ kDa}$ ), (N-DMBI)<sub>2</sub>, N-DMBI-H, and (RuCp\*mes)<sub>2</sub> were synthesized according to modified literature procedures.<sup>29, 32, 33</sup> Other solvents and materials including *n*-butyl acetate, were purchased from Sigma Aldrich and used as received.

Microscope glass slides were sonicated in deionized water, followed by acetone then isopropanol and then dried using nitrogen gas, followed by oxygen plasma treatment for 10 min. The PNBS polymer solution (8 mg mL<sup>-1</sup> in 1,2-dichlorobenzene) was then drop cast on top of the glass slides in air. The films were doped by a (N-DMBI)<sub>2</sub> solution (of the desired concentration, also in air) in *n*-butyl acetate, then spun at 800 rpm for 30 s to remove excess solvent, again in air. Soaking the substrate for longer periods of time (1 min, 2 mins and 5 mins) did not show an impact on conductivity. The same procedure was used for N-DMBI-H and (RuCp\*Mes)<sub>2</sub>.

UV-vis-NIR absorption data were acquired on a Cary 5000 instrument for both the solid and solution spectra. Solution spectra where collected in Schlenk type cuvettes with 1 cm path length

Grazing incidence X-ray diffraction (GIXRD) data were acquired on Panalytical Emperyan XRD instrument with a 1.54 Å Cu K $\alpha$  ( $\lambda$  = 1.5406 Å) source, and by setting the  $\omega$  offset to  $\omega$ = 0.003° in order to fix the penetration depth across measured samples.

Atomic force microscopy (AFM) height images were collected on a Bruker Dimension Icon, with RTESP-150 probes operating in standard tapping mode just below 150 kHz. The scanning rate was fixed to 0.25 Hz across the samples.

DC electrical conductivity and temperature dependent electrical conductivity measurements were performed on a custom-built setup thoroughly described elsewhere.<sup>34</sup> Briefly, thin films were cut into *ca*. 1 cm<sup>2</sup> samples and four platinum contact pads were deposited in a van der Pauw geometry

using a custom-built sputtering chamber and shadow mask. Films were then doped with 250  $\mu$ L of the appropriate dopant solution and permitted to soak for 1 min before excess solvent and dopant were removed via spinning at *ca*. 800 rpm for 30 s. One film was doped at a time and then immediately measured to mitigate any effects on measured electrical properties of dedoping through reaction with atmospheric oxygen or water. As for the doped dimer films the dimer and dopant were blended in solution in a nitrogen filled glovebox then cast on glass slides by spin coating at 500 rpm and measured as discussed earlier.

### 2.3 Investigating charge transport in doped PNBS films



2.3.1 UV-vis of solution and thin films

Figure 2.2. UV-Vis-NIR spectra for PNBS doped with (N-DMBI)<sub>2</sub>. (a) Solution doping in chlorobenzene. (b) Sequential doping of films carried out using n-butyl acetate solutions of (N-DMBI)<sub>2</sub> with the concentrations specified

As discussed above, PNBS<sup>22</sup> was chosen for sequential doping studies owing to the high electron mobility values reported for the pristine polymer. Of the three dopants investigated, N-DMBI-H is the most stable to ambient conditions, but also expected to be the least reactive dopant towards NDI materials,<sup>35, 36</sup> while, in some cases of its use, hydrogenated side products have been observed in addition to the desired N-DMBI<sup>+</sup> dopant ion and the semiconductor radical anion.<sup>32,</sup> <sup>36</sup> Although it has been widely used as an *n*-dopant for NDI polymers including P(NDIOD-T2), both its limited reactivity, likely originating from a slow endergonic hydride-transfer step, and poor miscibility with some polymers<sup>27</sup> have proven obstacles, with thermal annealing often being used to address the former issue.<sup>25, 26, 37</sup> The dimer (RuCp\*mes)<sub>2</sub>, on the other hand, is strongly reducing and reacts cleanly with the loss of two electrons to form two equivalents of RuCp\*mes<sup>+</sup>;<sup>38</sup> it has been previously co-deposited with P(NDIOD-T2) to afford conductivity values up to  $10^{-3}$  S cm<sup>-1</sup>.<sup>39</sup> In addition, other reports demonstrated a DMBI dimer as a more effective dopant for P(NDIOD-T2) than its DMBI-H analogue.<sup>35</sup> Further a recent report demonstrated <sup>33</sup> that the dimeric analogue of N-DMBI-H, (N-DMBI)<sub>2</sub>, leads to higher conductivity values than (RuCp\*mes)<sub>2</sub> in an isoindigo-like polymer, apparently due to the more planar N-DMBI<sup>+</sup> ion leading to less disruption of the polymer ordering than the three-dimensional RuCp\*mes<sup>+</sup> ion.<sup>33</sup> Thus, it was of interest to understand the effects of (N-DMBI)<sub>2</sub> as a dopant on the conductivity and charge transport properties of the polymer and small molecules

First, concomitant doping of PNBS in chlorobenzene solution is examined; however, the utility of this approach was limited by formation of precipitates when  $(N-DMBI)_2$  or  $(RuCp*Mes)_2$  were added to the polymer solution. At low concentrations, where visible precipitates were eliminated (*ca.*  $10^{-4}$  M), UV-Vis-NIR spectroscopy was used to qualitatively assess the extent of doping. Fig. 2a shows the UV-Vis-NIR spectra of PNBS doped with various proportions of  $(N-DMBI)_2$  in

chlorobenzene (where 50 mol% corresponds to one molecule of dimer per two repeat units, *i.e.* potentially one-electron reduction per repeat unit). The weakening and broadening of the low-energy feature (Figure 2a) is similar to what is seen on doping of other NDI conjugated polymers.<sup>28</sup> The growth of the feature at ca. 370 nm peak intensity can be attributed to the presence of N-DMBI<sup>+</sup>. Similar spectral changes, except for the growth of the feature at ca. 370 nm, are seen when doping with (RuCp\*mes)<sub>2</sub>, while N-DMBI-H appears not to react under these conditions, consistent with other room-temperature solution studies of N-DMBI-H with NDI-based polymers,<sup>40</sup> and only to a small extent on brief heating (Figure 3).



Figure 2.3. Solution UV-vis spectra of PNBS doped with N-DMBI-H under different conditions.

An alternate approach to investigate is sequential doping by choosing *n*-butyl acetate as a solvent that dissolves the dopants used in this study, but not PNBS. Absorption spectra for thin films of PNBS immersed for 1 min in various concentrations of dopants in n-butyl acetate show similar trends to the solution experiments (Fig. 3; Fig. 5). In particular, the growth of the feature

at ca. 370 nm indicated incorporation of the dopant counterion, N-DMBI<sup>+</sup>, into the films upon sequential doping.<sup>33</sup>



Figure 2.4. UV-vis-NIR of PNBS film sequentially doped with 5 mM of (N-DMBI)<sub>2</sub> in butyl acetate upon exposure to air.

#### 2.3.2 Microstructural Characterization of Doped Films



Figure 2.5. GIXRD data for pristine and (N-DMBI)<sub>2</sub>-doped PNBS films: (a) diffraction patterns and (b) plots of intensity and full width at half maximum height for the (100) diffraction peaks.

To achieve high electrical conductivity, in addition to high carrier concentration, increasing attention has been given to the dopant ion effect on the polymer film microstructure. To examine PNBS ordering as a function of doping, grazing incidence X-ray diffraction (GIXRD) is done on films of different doping levels (Figure 5). The pristine polymer shows peaks at 5.2 nm<sup>-1</sup> and 7.8 nm<sup>-1</sup> that, as in previous reports of PNBS<sup>22</sup> and of other NDI polymers with similar alkyl substituents,<sup>41</sup> can be assigned to (100) and (200) reflections associated with a lamellar repeat distance of 23 Å. The observation of these two reflections indicates that at least a portion of the polymer chains adopt an "edge-on" orientation relative to the surface. As the (N-DMBI)<sub>2</sub>

concentration used for the sequential doping is increased from 0 to 7.5 mM, the (100) peak intensity increases, while greater dopant concentrations leads to a decrease in the (100). The full width at half maximum (FWHM) for the (100) peak also broadens upon initial doping (2.5 mM), then decreases to a minimum at 7.5 mM, increasing again beyond that. The (100) intensities and FWHM data suggest that the coherence length is maximized and/or lattice disorder is minimized for films doped with 7.5 mM solutions. It is unclear where the dopant ions are located, but the roughly constant *d*-spacing for the (100) reflections suggest that the majority must be located in the  $\pi$ -stacks, in domains with different crystalline orientation to those evident in the GIXRD, or in amorphous regions of the polymer. In contrast, when using concentrations of (RuCp\*Mes)<sub>2</sub> in excess of 1 mM, the (200) peak is not observable and even the (100) peak is barely discernable (Figure 7), presumably indicating that the packing of the polymer is significantly disrupted by the bulky 3D RuCp\*mes<sup>+</sup> cation.<sup>33</sup>



Figure 2.6. GXRD of PNBS films doped with (RuCp\*Mes)<sub>2</sub> sequentially

AFM was used to further examine changes in surface morphology and roughness of doped PNBS films. Figure 7 shows AFM micrographs of pristine and (NDMBI)<sub>2</sub>-doped PNBS films indicating an increase in surface roughness upon doping.



# Figure 2.7. doped films AFM showing increase in surface roughness. Image scale: 4 $\times$ 4 $\mu m$

2.3.3 In-plane DC electrical conductivity and temperature dependence



Figure 2.8. Electrical conductivity as a function of doping and time. (a) PNBS electrical conductivity as a function of (N-DMBI)<sub>2</sub> dopant concentration. Error bars represent sample to sample variation (3 samples). (b) Electrical conductivity of 7.5 mM doped PNBS films as a function of time. Error bars represent imprecision in the measurement of the resistance value at time (t).

The electrical conductivity of doped films was evaluated using a custom built 4-point probe in a van der Pauw configuration.<sup>34</sup> None of the PNBS films sequentially doped with either N-DMBI-H or (RuCp\*mes)<sub>2</sub> exhibited electrical conductivities that could be reliably measured on the conductivity set-up used, suggesting values of  $\sigma$  in either cases being < 10<sup>-5</sup> S cm<sup>-1</sup>. Poor electrical conductivity of PNBS after attempted doping with N-DMBI-H is consistent with the optical data and with some previous reports on concomitant doping that indicate thermal treatments are needed to initiate doping reactions.<sup>27,37</sup>



# Figure 2.9. Temperature dependent PNBS electrical conductivity measurements. (a) Representative electrical conductivities as a function of doping and temperature. Error bars represent measurement error. (b) Activation energies and (c) intrinsic conductivity. as calculated by the Mott Polaron Model. Error bars represent sample to sample errors

In previous reports, (RuCp\*mes)<sub>2</sub> was found to be suitable for concomitant doping of P(NDIOD-T2),<sup>39</sup> but unsuitable for sequentially doping the same polymer, this unsuitability being attributed to the inability of the dopant to enter the ordered (face-on) film.<sup>12</sup> In the present case, the reaction clearly occurs, as shown by optical and GIXRD data; presumably the low conductivity results from the disruption of the film packing. However, PNBS thin films doped with (N-DMBI)<sub>2</sub> sequentially in air exhibit conductivities approaching 2 mS cm<sup>-1</sup> for dopant solution concentration of 7.5 mM (Fig.9a). The dopant level that give the highest conductivity values coincide with those that give the strongest and narrowest (100) reflections in GIXRD measurements (Figs. 6 and 7). However, despite the high charge-carrier mobility reported for pristine PNBS and the apparent

enhancement of ordering on optimal doping, the maximum conductivity values are comparable to other values reported for many NDI polymers, although falling short of those reported for some examples, especially those with oligoether side chains.<sup>23, 29, 32, 42, 43</sup> Fig. 4b shows the electrical conductivity of the optimally (N-DMBI)<sub>2</sub>-doped film as a function of exposure to air and indicates a decrease of *ca*. 20% over 20 minutes exposure, indicating that the exposure necessary for our measurement system does not have a large impact on the conductivity values.

To further characterize charge transport, temperature-dependent electrical conductivities were measured.<sup>34,44</sup> As expected, the conductivity was found to increase exponentially with temperature (Fig. 10a), consistent with the expectation for thermally-activated hopping of carriers.<sup>36,37</sup> The data could accordingly be fit to obtain the theoretical maximum (infinite temperature) electrical conductivity ( $\sigma_0$ ) and the activation energy ( $E_a$ ) using the Mott Polaron Model (Eqn 2, 3)

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_b T}\right) \tag{2}$$

$$\ln(\sigma) = \ln(\sigma_0) + \left(\frac{-E_a}{k_b T}\right)$$
(3)

and analyzed statistically using t-tests with 95% confidence intervals.<sup>21,33,38</sup>

Fig. 10b shows the effective barrier for charge transport,  $E_a$ , for each dopant concentration; it is effectively the same at low doping levels (2.5, 5 mM) but is significantly lower at 7.5 mM (highest conductivity). This is consistent with what is generally seen for trends in  $E_a$  with increasing dopant concentration. In this case, as the dopant concentration is further increased,  $E_a$ increases again.<sup>34</sup> Thus, the lowest  $E_a$  values correspond to the films that GIXRD suggests to be the most ordered. The barriers are similar in size to those reported for other n-doped NDI polymers.<sup>23, 29, 32, 42, 43</sup> Fig. 10c shows  $\sigma_0$  for each dopant system, whereby  $\sigma_0$  is the pre-exponential conductivity that heavily depends on film morphology and hopping distance and represents a maximum electrical conductivity achievable.  $\sigma_0$  is *ca.* 12 S cm<sup>-1</sup> for lightly doped PNBS (2.5 and 5 mM dopant solutions) but decreases to *ca.* 2.5 S cm<sup>-1</sup> for more heavily doped PNBS (7.5, 10 mM dopant solutions). Lastly, it has been reported in many studies that  $\sigma_0$  increases with increased doping until the polymer has become over-doped, *i.e.*,  $\sigma$  decreases with increased doping.<sup>34</sup>

# 2.4 Synthesis and doping of naphthalene diimide small molecules

### 2.4.1 Synthesis of NDI-1 and NDI-2



Figure 2.10. Synthetic scheme for (NDI-CN)2 and (NDI-CN)2-BTT

Naphthalene diimides **1** and **2** can be synthesized upon the bromination and imidization of the dibromo-napthalene-tetracarboxyanhydride with 35% and 65% yield respectively over 2 steps. Then monocyanation of the NDI can be done through Rosenmund-von Braun reaction yielding compounds **3** and **4** in 33% and 30% yields respectively. Stannylation of **3** and **4** yields compounds **5** and **6** in 50% and 40% respectively. (NDI-CN)<sub>2</sub> is synthesized via Stille homocoupling of **5** in 50% yield. On the other hand, Stille coupling of **6** with 3,6-bis(5-bromothiophene)-1,2,4,5-tetrazine to yield (NDI-CN)<sub>2</sub>-BTT in 40% yield. The synthesis of these materials have already been published.<sup>45-47</sup>

#### 2.4.2 Conductivity measurements

Doping of (NDI-CN)<sub>2</sub> was carried out using (N-DMBI)<sub>2</sub> by concomitant doping (Figure 14). The conductivity increases from  $8.3 \times 10^{-6}$  S cm<sup>-1</sup> at 1.2% of dopant added to  $2.0 \times 10^{-4}$  S cm<sup>-1</sup> at 13.9% dopant added. The conductivity increases nearly exponentially between 1.5% and 15% monomer ratio. Once the monomer ratio is increased to 19%, insoluble aggregates that appear in the film as ribbons like aggregates (width = 3 microns) cause an abrupt jump in conductivity to 4 mS cm<sup>-1</sup>. Full conductivity data is tabulated in table 1 below. Data is not collected beyond 19% dopant ratio added due to aggregate formation interfering with film casting.



Figure 2.11. Schematic representation of doping process and evolution of conductivity vs. doping ratio.

Table 2.1. Doping ratio, maximum conductivity (with standard deviation) for NDI-1 films doped with (DMBI)<sub>2</sub> via mixed solution doping.

MR of dopant monomer	1.2%	3.5%	5.8%	9.3%	13.9%	18.6%
$\sigma_{max} (S \text{ cm}^{-1})$	1.4 × 10 <sup>-5</sup>	$3.2 \times 10^{-5}$	6 × 10 <sup>-5</sup>	7.6 × 10 <sup>-5</sup>	3 × 10 <sup>-4</sup>	6 × 10 <sup>-3</sup>
$\sigma_{ m average}( m S~ m cm^{-1})$	$8.3 \times 10^{-6}$	$2.4 \times 10^{-5}$	$4.0 \times 10^{-5}$	$7.8 \times 10^{-5}$	$2.0 \times 10^{-4}$	4.0 × 10 <sup>-3</sup>
	$(\pm 5.0 \times 10^{-6})$	$(\pm 7.1 \times 10^{-6})$	$(\pm 1.2 \times 10^{-5})$	(± 4.3 × 10 <sup>-6</sup> )	$(10^{-5})$	$(\pm 1 \times 10^{-3})$

(N-DMBI)<sub>2</sub> and (NDI-CN)<sub>2</sub>-BTT were mixed in chlorobenzene and the mixture was then heated to 150 °C for 10 minutes to attempt to dissolve some of the aggregates observed immediately upon blending. the doped solution was drop casted when hot, then annealed upon drying at 100 °C for 10 minutes under nitrogen. UV-vis-NIR spectra of the doped films (figure 15B) show a similar trend to solution spectra showing increase in doping.



Figure 2.12. (a) Solution UV-vis-NIR spectra of NDI-2 ( $C = 0.6 \times 10^{-5}$  M) doped with (N-DMBI)<sub>2</sub> in chlorobenzene, in the absence of light, moisture and oxygen. (a) Thin film UV-vis-NIR spectra of mixed solution doped NDI-2 with (N-DMBI)<sub>2</sub> drop casted from 5 mg/mL solutions of mixture in chlorobenzene in an inert atmosphere.

Conductivity of the doped films was measured using a four-point probe in the van der Pauw set up in an inert atmosphere. Upon doping with (N-DMBI)<sub>2</sub>, the conductivities of films doped below 10 mol% were below the instrument and channel length threshold  $(10^{-5} \text{ S cm}^{-1})$ . As dopant molar ratio increases conductivity increased to a maximum of 0.007 S cm<sup>-1</sup> upon adding 43 mol% of dopant. Beyond that value the conductivity decreases where 82 mol% of (N-DMBI)<sub>2</sub> leads to conductivity of 0.0001 S cm<sup>-1</sup> and additional dopant amount causes the films to be less conductive than the instrument threshold.



Figure 2.13. Conductivity of NDI-2 films doped with (N-DMBI)<sub>2</sub>. Error bars represent 1 standard deviation from average.

## 2.5 Conclusion

The high electron mobility polymer (PNBS) has been sequentially doped with several dopants and doping concentration. The recently reported dimer (NDMBI)<sub>2</sub> is more effective dopant for the sequential doping approach of PNBS than either (RuCp\*mes)<sub>2</sub> and N-DMBI-H, because of its ability to *both* successfully dope PNBS and improve structural ordering. (N-DMBI)<sub>2</sub> doping results in a maximum electrical conductivity of *ca.* 2 mS cm<sup>-1</sup>; the doping can be reproducibly carried out in air. The temperature dependent electrical properties provide insight into understanding of structural and energetic contributions to electrical transport. On the other hand, both small molecule NDI dimers can also be doped although interact differently with the dopant ions since films of (NDI-CN)<sub>2</sub> achieve conductivities up to 6 mS cm<sup>-1</sup> at 19 mol%, whereas films of (NDI-CN)<sub>2</sub>-BTT doped with (N-DMBI)<sub>2</sub> can achieve a maximum conductivity of 7 mS cm<sup>-1</sup> at 43 mol% dopant and are only conductive when doped in excess of 10 mol%. In addition (NDI-CN)<sub>2</sub> could only be casted as thin films when doped with less than 19 mol% (N-DMBI)\_2 where conductive

films can be obtained with (NDI-CN)<sub>2</sub>-BBT when doped in excess of 40 mol%. This speaks to the

interplay of aggregation upon doping in the ability to process and characterize the doped thin films.

Last, the conductivity results show that although (NDI-CN)<sub>2</sub>-BTT has one order-of-magnitude

higher charge carrier mobility than (NDI-CN)<sub>2</sub>, they both yield similar conductivities with the

same dopant.

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# CHAPTER 3. A NAPHTHALENE DIIMIDE SIDE-CHAIN POLYMER AS AN ELECTRON-EXTRACTION LAYER FOR STABLE PEROVSKITE SOLAR CELLS

This project was carried out in collaboration with Declan McCarthy who synthesized NDI-1. Sebastian Furer, David McMeekin trained KA on photovoltaic device fabrication, repeated some of the measurements for reproducibility and contributed to data analysis. Stephen Barlow contributed to data analysis discussion. *This work is published in Materials Chemistry Frontiers.*<sup>1</sup>

The author synthesized and characterized all small molecules, fabricated devices with all materials, optimized layer composition, and tested the devices.

#### 3.1 Introduction

Lead-halide perovskite solar cells (PSCs) have received increasing attention since their debut in 2009.<sup>2, 3</sup> In recent years, further optimizations of the various layers and interfaces have allowed the emergence of PSCs with power conversion efficiency (PCE) exceeding 25%.<sup>4</sup> Lead halide perovskites used in this context are 3D crystalline materials, which act as an absorber for sun light to create a hole-electron pair, which then dissociates and subsequently the charge carriers diffuse to the respective transport layers. The unbound holes and electrons are then collected at respective hole and electron collecting electrodes, which have different work functions. Overall the process generates electrical power.<sup>5</sup> The perovskites used in solar cells often have the formula of ABX<sub>3</sub>, where A is either an organic or inorganic cation such as methyl ammonium

(MA<sup>+</sup>), formamidnium (FA<sup>+</sup>), cesium (Cs), rubidium (Rb). B corresponds to the lead which form octahedral structures with the halide in use, X. X is often an iodide (I-) or (Br-). Due to interest in improving long-term stability to enable the rapid commercialization of these devices new strategies have used organic or inorganic additives in attempts to create a more stable, or a perovskite that is more efficient in delivering the charge carries to the charge transport layers. These strategies include adding large organic cations as A site cations such as butylammonium (BA+) which causes the formation of a mixture of 3D/2D perovskite structures, more efficient and more stable devices.<sup>6</sup> On the other hand, incorporation of cesium, rubidium or potassium iodide has been shown to affect the size of perovskite grains in the film and increase the efficiency and stability of the PSCs.<sup>7,8</sup> The performance of a solar cell is measured by measuring the current density as a function of the bias voltage. When no bias is applied (V=0) the current measured is defined as the short circuit current ( $J_{sc}$ ) which is a measure of the maximum current that can be generated from a solar cell due to charge carriers collected at the electrodes upon illumination of the solar cell.<sup>5</sup> When no current is produce (J=0) the voltage is defined as the open circuit voltage  $(V_{oc})$ . The open circuit voltage is a measure of the maximum voltage available to draw out from the solar cell.<sup>5</sup> The open circuit voltage is affected by the recombination of the hole/electron pair, which would not diffuse to the charge transport layer.<sup>5</sup> Two more parameters are used to assess the efficiency of solar cells. The fill factor (FF) is a measure of how "square" the JVcurve is, and its value can be calculated via  $(J_{max} \cdot V_{max}) / (J_{SC} \cdot V_{OC})^{5}$  Last, the power conversion efficiency is a percent measure of the solar cell ability to generate electric

power from sun light and is calculated from the product of open circuit voltage, short circuit current and fill factor to the incident sunlight power.<sup>5</sup>

Hole- and electron-transport materials (HTMs and ETMs, respectively) in PSCs serve not only to transport charges, but can improve the stability of the cells and reduce charge recombination. A variety of organic and inorganic ETMs have been incorporated into socalled n-i-p (negative-intrinsic-positive) and p-i-n (positive-intrinsic-negative) PSCs.<sup>9-12</sup> The "regular" (n-i-p) architecture for PSCs requires the ETM to be deposited prior to the perovskite, and, therefore, for solution-processed cells, to be insoluble in the perovskite precursor solution. Insoluble metal oxides (e.g., SnO<sub>2</sub>, TiO<sub>2</sub>) offer one possible solution.<sup>13-15</sup> Although many approaches require high-temperature (often 450-500 °C for  $TiO_2^{8,9}$ ) sintering subsequent to casting the precursors from solution, limiting compatibility with flexible substrates, recently room-temperature methods for the deposition of efficient low-temperature SnO<sub>2</sub> have been reported.<sup>16</sup> Nevertheless, these oxides can possess trap states that hinder charge extraction and  $TiO_2$  can even act as a photocatalyst. There is also considerable interest in organic ETMs as alternatives that can be processed at low temperature, while also exhibiting good charge-transport abilities and transparency.<sup>17-20</sup> These include both vacuum-processable and solution-processed materials;<sup>21</sup> in some cases solution-processable ETMs have been crosslinked subsequent to deposition to prevent their dissolution during subsequent perovskite deposition.<sup>22, 23</sup> Although fullerenes have been widely used, other non-fullerene electron acceptors with similar reduction potentials may be advantageous in terms of transparency, cost, and/or tunability of reduction potential. Rylene diimides have attracted attention as ETMs for ni-p cells. These include perylene diimides, such as **B** (Fig. 1), and related thermally

evaporable small molecules,<sup>24</sup> solution-processable small molecules,<sup>25</sup> and solutionprocessable polymers.<sup>26</sup> Naphthalene diimide (NDI) derivatives (such as **D** and **E**, Fig. 1) have been used in p-i-n devices,<sup>27-30</sup> but there are few reports of their use in n-i-p devices. However, in one study an insoluble NDI (**A**, Fig. 1) was generated via a hightemperature annealing treatment of soluble solution-cast precursor for use in n-i-p devices.<sup>31</sup> A coronene diimide small molecule (**C**, Fig. 1) has also been used.<sup>32</sup> Unlike their perylene and coronene counterparts, naphthalene diimides (NDI) can exhibit minimal absorption within the visible spectrum.

Since polymeric HTMs such as PEDOT:PSS, P3HT, PTAA, and polyTPD<sup>33-36</sup> have been reported to give impressive performances in PSCs (PCE > 19%), it may be beneficial to examine electron-transporting polymers that are transparent in the visible, with appropriate electron affinities, electron mobility, solvent resistance, and solution processability. Moreover, such polymers may facilitate a "polymer sandwich" architecture in which both transport materials are polymeric, and which may be particularly useful for flexible devices.

This chapter reports the use of a new NDI side-chain polymer (Figure 1), synthesized by Declan McCarthy, which is transparent, solution processable, and thermally stable, in PSCs. The polymer is used to fabricate n-i-p devices with efficiencies up to 14%. The utility of the polymer is illustrated by comparison to NDI small molecules as well as SnO<sub>2</sub> as a reference.



Figure 3.1. Examples of rylene diimide ETMs reported in the literature (A-E) in the context of PSCs and NDI-based ETMs used in this work (NDI 1-4).

# 3.2 Materials and Methods

Commercially available precursors as well as the solvents were purchased form Sigma Aldrich and used without modifications.

FTO coated glass slides  $(1 \text{ cm}^2)$  were cleaned by sonication in 2% Hellmanax in water, followed by deionized water, and ethanol for 15 min each. The slides were then dried and plasma etched for 10 min and used immediately. Organic ETM solutions were prepared by making 1.5 mg mL<sup>-1</sup> solutions in chlorobenzene,<sup>45</sup> which were spun at 2000 rpm for 30 s in air yielding layers of 10 nm thickness. When tin oxide was used as an ETM the layer was prepared by spin coating 10 mg mL<sup>-1</sup> solution in isopropyl alcohol of SnCl<sub>2</sub>.5H<sub>2</sub>O at 2000 rpm for 20 s followed by annealing at 180 °C for 1 h. Plasma

treatment for 1 min was done before  $SnO_2$  nanoparticles were deposited by diluting commercially available precursor in 1:10 DI water then spin coating it at 2000 rpm for 20 s followed by annealing at 180 °C for 1 h. Alumina nanoparticles (< 50 nm) were dispersed in isopropanol in 1:150 vol/vol ratio. 100 µL of this dispersion was then dynamically spun onto the ETL at 3000 rpm for 30 s and then dried at 60 °C for 1 min. The perovskite precursor was prepared by mixing 507.1 mg of PbI<sub>2</sub>, 73.4 mg PbBr<sub>2</sub>, 22.4 mg MABr, 172 mg FAI, with 41  $\mu$ L of 1.5 M CsI solution (in DMSO) and 850  $\mu$ L of a pre-mixed 4:1 dimethylformamide:dimethylsulfoxide (DMF:DMSO). The perovskite was then spun using a two-step program by covering the film with 50  $\mu$ L of the perovskite solution, and spinning that at 1000 rpm for 10 seconds, followed by 6000 rpm for 20 s. When 5 s were left to the end of the program, 260  $\mu$ L of chlorobenzene was dropped to solvent quench the film. The films were rapidly moved to a hot hotplate to be annealed at 100 °C in the dark for 1 h where they turned black immediately. The 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (SpiroOMeTAD) layer was prepared by preparing a 72 mg mL<sup>-1</sup> solution of SpiroOMeTAD in chlorobenzene followed by the addition of a 17.5  $\mu$ L lithium bis(triflouromethanesulfonyl)amide (LiTFSI) solution (52 mg mL<sup>-1</sup> concentration in acetonitrile) and 28.8 µL of 4-*tert*butylpyridine (tBP). The mixed solution was spun dynamically at 2000 rpm for 30 s and devices were exposed to dry air in the dark for doping to take place overnight. Gold electrodes were evaporated using a metal sputtering device, through a shadow mask to fix the area at 0.16 cm<sup>2</sup>, and evaporated at 0.1 nm s<sup>-1</sup> for the first 10 nm and 1 nm s<sup>-1</sup> afterwards.

Devices were measured under 1 sun illumination using a custom-built 16-device set-up in which the devices were light soaked for at least 90 s before measurements to ensure stabilization where the aperture size was fixed at 0.16 cm<sup>2</sup>. Encapsulation was achieved by dispensing UV-curable epoxy resin from Nagase (XNR5516Z-B1) onto the edges of a cover glass with a recess in the middle. The cover glass was then gently pressed on to the solar cell devices and were illuminated from the cover glass side under UV light. UV-vis-NIR measurements were done on a Cary 5000 spectrophotometer. PL spectra were acquired on a Horiba instrument. EQE data were recorded through a Keithley 2400 Source Meter under 300 W xenon lamp irradiation with an Oriel Corner-stone 260<sup>1</sup>/<sub>4</sub> m monochromator. The monochromatic photon flux was quantified through a calibrated silicon cell (Peccell Technologies).<sup>46</sup> Differential scanning calorimetry and thermogravimetric analysis (DSC and TGA) experiments were performed on Mettler-Toledo TA instruments under nitrogen gas atmosphere and at a scan rate of 10 °C min<sup>-1</sup>. Gel Premeation Chromatography (GPC) for polymer samples were performed using a Tosoh EcoSEC HLC 8320GPC system with TSKgel SuperHZ-L columns eluting CHCl<sub>3</sub> containing 0.25% triethylamine at a flow rate of 0.45 mL min<sup>-1</sup>. Number-average molecular weights and dispersity were calculated from refractive index chromatograms using PStQuick Mp-M polystyrene standards. Electrochemical measurements were carried out under nitrogen atmosphere with 0.1 M tetra-n-butylammonium hexafluorophosphate in dry dichloromethane using a CH Instruments CHI620D Electrochemical Workstation CHI620D, and a conventional three-electrode cell with a glassy carbon working electrode, platinum wire counter electrode, and an Ag wire coated with AgCl as the pseudo-reference electrode. Potentials were referenced to
ferrocenium/ferrocene by using ferrocene as an internal standard. Cyclic voltammograms were recorded at a scan rate of 50 mV s<sup>-1</sup>.

### 3.3 **Results and Discussion**

### 3.3.1 Synthesis

A naphthalene diimide polymer is hypothesized to reduce aggregation and crystallization and, thus aid the formation of uniform continuous (*i.e.* pinhole free) thin films with reduced shunt paths between the transparent conducting oxide (TCO) and the perovskite. Although conjugated NDI polymers are well established and have been used in p-i-n cells, many absorb strongly throughout the visible spectrum, which competes with perovskite layer light absorption.<sup>37</sup> Accordingly, NDI-1 which was expected to be a colorless side-chain polymer emerged as a promising candidate (NDI-1, Figure 1 The synthesis of NDI-1 is described in detail with all the purity characterization data elsewhere.<sup>1</sup> Briefly, The polymer synthesis involves four steps, the first of which is an asymmetric imidization of the commercially available naphthalene tetracarboxy-1,8:4,5dianhydride. The second step involves the imidization of N-hexyl-naphthalene-1,8dicaboximide-4,5-di(carboxylic acid) with 5-amino-1-pentanol to afford the asymmetric hydroxyl-functionalized naphthalene diimide. Thirdly, the monomer is produced by esterification using exo-5-norbornenecarboxylic acid. Lastly, the regiorandom polymer NDI-1 (Mn= 13.3 kDa, D= 1.3) is produced via ring-opening metathesis polymerization using the Grubbs first-generation initiator, Ru(=CHPh)(PCy3)2Cl2 (Cy = cyclohexyl).<sup>1</sup>. Several small-molecule NDI molecules (2-4) were synthesized for comparison according

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to published procedures,<sup>38</sup> and were chosen to exhibit a range of reduction potentials (table 1).

## 3.3.2 Characterization of the ETMs



Figure 3.2. Absorption spectra of NDI-1 in solution and thin film (A), TGA (B) and DSC (C) plots of NDI molecules used in this work. TGA and DSC were performed under nitrogen gas at  $10 \,^{\circ}$ C min<sup>-1</sup> scan rate.

Table 3.1. Optical, thermal, and electrical properties of NDI material used. (a) UV-vis is measured in chlorobenzene. (b) Optical bandgap is determined from the onset of the absorption edge. (c) DSC/TGA are done under nitrogen gas at 10 °C/min scan rates, and T<sub>d</sub> is determined at 95% mass being retained. (d)  $E_{1/2 \text{ red}}$  vs. FeCp2<sup>0/+</sup> (CH<sub>2</sub>Cl<sub>2</sub> / 0.1 M NBu<sub>4</sub>PF<sub>6</sub>); data for NDI-1 were acquired using the corresponding monomer.

Compound	$\lambda_{max} (nm)^a$	E <sub>g</sub> (eV) <sup>b</sup>	$T_m$ (°C)	$T_d (^{\circ}C)^c$	$E_{1/2 \text{ red}}(V)^d$
NDI-1	381	3.1	-	384	-1.11
NDI-2	376	3.1	180	328	$-1.14^{38}$
NDI-3	376	3.2	-	274	$-0.88^{38}$
NDI-4	379	3.2	195	305	$-0.96^{38}$

Figure 3A shows absorption spectra for **NDI-1** in solution and in films, while Table 1 gives absorption maxima for NDIs **1-4**. Both solution and films of the NDI derivatives exhibit absorptions onsets at wavelengths shorter and around 400 nm, respectively. The electron affinities of ETMs are critical for efficient charge extraction from the perovskite;

the reduction potentials were measured using cyclic voltammetry (Table 1) and fall into a similar range to other molecular materials successfully used as ETMs in PSCs (such as  $C_{60}$  (-0.98 V *vs*. FeCp<sub>2</sub><sup>+/0</sup>), PCBM (-1.1 V), and a commonly utilized naphthalene diimide-bithiophene copolymer (N2200) (-1.1 V).<sup>37, 39</sup>

The four NDI materials are highly soluble in common organic solvents (chloroform, dichloromethane, toluene), suggesting that they could be readily processed onto perovskite films for p-i-n devices without significant damage to the active layer. They exhibit varying resistance to being dissolved by *N*,*N*-dimethylformamide (DMF, Figure 4).



# Figure 3.3. UV-vis of NDI-1 (A), NDI-2,4 (B) films before and after washing with DMF. Films (1 cm<sup>2</sup>) were drop casted from toluene (5 mg mL<sup>-1</sup>) then washed with DMF (~ 0.4 mL) and dried with nitrogen gas upon spinning off the DMF.

The DMF resistance of NDI-1 is particularly promising for the fabrication of n-i-p device architectures; the small molecules are more easily removed by this solvent, although they are expected to less soluble in concentrated solutions of perovskite

precursors and when protected by an alumina interlayer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) show that the naphthalene diimides examined here exhibit decomposition temperatures above 250 °C and no thermal transitions below 150 °C, which is compatible with temperatures needed for subsequent deposition and annealing of many hybrid perovskites used in PSCs (Figure 3B and 3C).

#### 3.3.3 Device architecture and performance

The materials were incorporated into n-i-p devices (Figure 4). The NDI layers were spincoated from chlorobenzene on fluorinated-tin-oxide (FTO) coated glass (optimally performing layers having thicknesses of *ca*. 10 nm). A thin mesoporous layer of alumina nanoparticles was found to be very helpful in achieving subsequent good coating of the ETM by the perovskite. Although primarily used in the present case to enhance the wettability of the perovskite solution on the NDI films, the alumina nanoparticles may play other roles, as discussed in the literature.<sup>40-42</sup>



Figure 3.4. Schematic representation of device architecture, white dots in active layer represent alumina nanoparticles (A). Reverse Scan J–V plots of optimized devices (B). Box plots of open-circuit voltage (C), short-circuit current (D), fill factor (E), and power conversion efficiency (F) of optimized devices.

For example, at least when used between oxide transport materials and perovskites, a mesoporous alumina layer leads to improved contact between the transport and active layers,<sup>36</sup> and in some cases the use of alumina leads to improved stability for the perovskite.<sup>37</sup> They may also help protect the ETM from dissolution in the perovskite casting solvent (primarily DMF). Figure 5A schematically shows the structure of the resulting solar cell incorporating the insulating alumina scaffold.<sup>43</sup> Our control devices employed a SnO<sub>2</sub> ETL layer instead of the NDI-based material. A mixed-cation perovskite Cs<sub>0.05</sub>FA<sub>0.79</sub>MA<sub>0.16</sub>PbI<sub>2.49</sub>Br<sub>0.51</sub> (FA = formamidinium; MA = methylammonium) using chlorobenzene as an anti-solvent.<sup>7, 44,42</sup> Spiro-OMeTAD, with LiTFSI, and *t*BP as additives, was then deposited on top as the hole transport layer, followed by evaporating 80 nm layer of gold as a counter electrode.

Figure 4B-F show that optimized devices using the polymer were superior to all optimized devices incorporating NDI small molecules, the power conversion efficiencies following the trend NID-1 >> NDI-2 > NDI-4 > NDI-3, with the small molecules all exhibiting lower open-circuit voltage ( $V_{OC}$ ), short-circuit current density ( $J_{SC}$ ), and fill factor (FF) than the polymer. The photovoltaic parameters of the champion and average devices incorporating the small molecules (NDI-2, NDI-3, NDI-4), the polymer (NDI-1), and SnO<sub>2</sub> are summarized in Table 2.

Table 3.2. Photovoltaic parameters of champion and average devices of the various materials employed as electron transport layer in the n-i-p devices studied

Material		V <sub>OC</sub> (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	Fill Factor	PCE (%)
				(%)	
SnO <sub>2</sub>	Champion	1.03	21.0	74	15.6
	Average	0.99 (±0.02)	20.9 (±0.4)	73 (±1.3)	15.0 (±0.5)
NDI-1	Champion	1.02	21.5	65	14.0
	Average	0.98 (±0.02)	21.1 (±0.2)	62 (±2.1)	12.8 (±0.6)
NDI- <b>2</b>	Champion	0.98	18.3	56	9.8
	Average	0.94 (± 0.04)	15.2 (± 2.6)	47 (± 6)	6.7 (± 1.6)
NDI-3	Champion	0.91	11.6	43	4.5
	Average	0.79 (± 0.06)	11.0 (± 2.0)	41 (± 3.7)	3.6 (± 0.7)
NDI-4	Champion	0.84	14.8	46	5.5
	Average	0.79 (± 0.02)	12.6 (± 1.8)	42 (± 2.4)	4.3 (±0.9)

Devices with NDI-1 exhibited comparable  $V_{OC}$  and  $J_{SC}$  to those using tin oxide; however, they fell short in terms of FF and consequently the power conversion efficiency (PCE, Figure 4, 5A). This might be due to higher series resistance of the devices with a polymer ETL, as the conductivity of SnO<sub>2</sub> is likely higher than that of the undoped polymer. Nevertheless, the devices still exhibit a maximum power conversion efficiency of 14%. Both devices with organic and SnO<sub>2</sub> ETMs suffered from non-negligible hysteresis, likely due to the Spiro-OMeTAD/additive HTM. However, a maximum power point tracking test showed a maximum efficiency of 13.8% after 90 s of illumination, representing only a 0.2% decrease from the reverse scan efficiency (Figure 5A). Figure 5B shows external quantum efficiency and integrated current data in order to further characterize the efficiency of the perovskite absorber in the presence of NDI-1 and Figure 5C shows the quenching of PL by the depositing NDI-1 below the perovskite.



Figure 3.5. (A) Box plots of the power conversion efficiency of NDI-1 and SnO<sub>2</sub> devices and (B) and external quantum efficiency (EQE) and integrated shortcircuit current plots for the NDI-1 devices. (C) photoluminescence spectra of perovskite film and perovskite film grown on top of NDI-1.

Since the devices exhibit non-negligible hysteresis forward and reverse scan IV curves are presented in Figure 6A, however upon light illumination it is determined that the PCE over time stabilizes at 13.8% for NDI-1 devices for example, so the reverse scan IV curves are more representative of the device performance (Figure 6B).



Figure 3.6. Forward (dashed) and reversed (solid) JV curves of champion devices with different ETMs (A). (B) evolution of power density with illumination time of NDI-1 devices.

## 3.3.4 Long-term stability



Figure 3.7. long term stability testing of devices employing SnO<sub>2</sub> and NDI-1

Both NDI-1 and SnO<sub>2</sub> based devices showed very small changes in performance over multiple months storage in a dry box (in presence of oxygen and relative humidity < 5%) in the dark, indicating a high shelf life. To compare the stability differences between devices employing NDI-1 to their tin oxide counterparts, full devices are encapsulated (see experimental section) and aged in an environmental chamber at open circuit voltage (*i.e.* at 1 sun illumination)at 60 °C, in air. The study was conducted over 290 hours where the tin oxide device efficiency degraded to <10% of the initial value, whereas that of the devices incorporating the **NDI-1** polymer retained ca. 35% of the original performance, the degradation being dominated by a loss of FF. Figure 5 shows the evolution of PCE over aging time for champion and median devices. Although LiTFSI/tBP-doped Spiro-OMeTAD is the common HTM in both devices here,<sup>43,44</sup> those devices incorporating NDI-1 are more stable over the period of the study.

# 3.4 Conclusions

This chapter reported the use of a side chain NDI polymer that is superior in performance to several NDI small molecules in n-i-p PSCs. Champion devices of undoped NDI-1 achieve a 14% PCE. NDI-1 devices exhibited greater stability than SnO<sub>2</sub>-based control devices when aged under 1 sun conditions for almost 300 hours and 60 °C. This provides a foundation for designing other possible naphthalene diimides or other moieties to be used as dopant-free solution-processable electron-transport materials to replace metal oxide ETMs. This low temperature processing route open new avenues for polymerbased flexible solar cells and the optical transparency for incorporation in tandem devices.

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# CHAPTER 4. INVESTIGATING STRUCTURE- PROPERTY RELATIONSHIPS IN BENZIMIDAZOLE-DERIVED HYDRIDE DONORS AND DIMERS

This project investigates the structural diversity possible in benzimidazole-derived hydride donor and dimeric dopants, reports an improved and facile synthesis of dopants of this type, and investigates their reactivity. This project was performed in collaboration with Swagat Mohapatra, Samik Jhulki, and Maxwell Conte. Dr. Mohapatra synthesized the materials via one of the literature methods used in previous work.<sup>1, 2</sup> Dr. Jhulki successfully demonstrated a simpler and higher yield synthetic approach was possible for the Y-DMBI intermediates discussed in this chapter. Maxwell Conte, an undergraduate student working with the author, replicated and scaled up many of the derivatives that were synthesized by Samik or the author. The author performed scale up of all target compounds, along with their purification and characterization. In addition, the author performed thermal characterization (DSC, TGA), and kinetic studies on all dopants. Characterization data obtained from others and incorporated in this chapter are labelled as such.

# 4.1 Introduction

As discussed in chapter 1, organic electronic devices such as light-emitting diodes (LEDs),<sup>3</sup> field-effect transistors (OFETs),<sup>4</sup> photovoltaics (OPVs),<sup>5-9</sup> and thermoelectrics<sup>10-18</sup> benefit from improved charge transport properties of employed organic semiconductors, which in many cases is achieved via electrical doping using molecular oxidants and reductants.<sup>2, 19-23</sup> Doping experiments are generally performed under inert atmosphere to achieve

maximum performance by avoiding oxygen/air-mediated degradation of doped semiconductors.<sup>24</sup> Although *p*-dopants are generally air-stable, some may yield thermally unstable products or suffer from water-mediated degradation, leading to poor stability. The situation is different for *n*-doping, where many doped polymers can be dedoped by air oxidation, such as the commonly used naphthalene diimide- bithiophene copolymer (N2200) (Figure 1). On the other hand, some dopants such as TDAE (Figure 1), for example can dedope via reverse electron transfer followed by sublimation of the volatile neutral dopant. can be avoided by utilizing air stable, relatively non-volatile dopants such as the organometallic dimer, (RuCp\*mes)<sub>2</sub> (chapter 1 Figure 7), which is a moderately airstable dopant that can be handled in air in the solid state without degradation.<sup>3, 20, 24-26</sup> Although the (RuCp\*mes)<sub>2</sub> dopant can be used with success in doping of electron transport layers for a variety of applications, recent research suggests that a more planar cation such as the 2-Y-1,3-dimethyl-1H-benzoimidazolium cation] formed by 2-Y-2,3-dihydro-1Hbenzimidazoles (Y-DMBI-H), where Y = 4-dimethylaminobenzene for example, and the corresponding dimers may lead to higher conductivity as seen in chapters 1 and 2, as well as in the recent literature.<sup>15, 27-29</sup>



Figure 4.1. Structures of acceptors and dopants referenced in 4.1.

An advantage with the Y-DMBI-H family of dopants is that they can be stored and handled in air for months in the solid state. Moreover, their synthesis involves relatively simple condensation and hydride-reduction chemistry from appropriate precursors. Although reports have indicated that N-DMBI-H derivatives have miscibility problems with polymers, it still has shown great success with doping of polymers. In fact, 90 S cm<sup>-1</sup>, the highest conductivity for an *n* doped polymer to date has been reported when TBDPPV (Figure 1) is doped with N-DMBI-H.<sup>30</sup> In the last decade this family of Y-DMBI-H dopants and their dimers (Y-DMBI)<sub>2</sub> (Figure 2) have gained tremendous attention to use in doping applications.<sup>14, 27, 28, 31-34</sup> Some of these structures and the conductivity values were tabulated and discussed in chapter 1. Examples of Y-DMBI-H and (Y-DMBI)<sub>2</sub> dopants reported in the literature as *n*-dopants as well as this chapter can be seen in Figure

2. The advantages of using Y-DMBI-H dopants can be due to their simpler synthesis, higher air stability than the dimers. Whereas a disadvantage that the dimers solve is the fact that the dimers are clean electron donors without side products due to the hydridic nature of Y-DMBI-Hs.



Figure 4.2. Chemical structure of various (Y-DMBI-H) and (Y-DMBI)<sub>2</sub> reported in the literature as *n*-dopants. Compounds in black are known in the literature, and those in blue are ones which are presented in this work. The numbers next to some of the structures name are used to simplify the name of compounds in the text.<sup>15, 35</sup>

Despite its widespread use in *n*-doping, a disadvantage with (N-DMBI-H) is its hydridic nature that leads to complexity of the mechanism governing their reactivity. A possible

mechanistic route involves a N-DMBI-H transferring a hydride to the acceptor, followed by subsequent loss of hydrogen atom from the semiconductor to yield (N-DMBI)<sup>+</sup> and A<sup>-</sup>.<sup>2, 28, 33</sup> For example, in the case of PCBM (A), the N-DMBI-H (DH) doping proceeds by a hydride transfer, with a second step that yield PCBM<sup>-</sup> so that the overall reaction can be represented as:

$$DH + \left(1 + \frac{1}{x}\right)A \to D^+ + A^{--} + \frac{1}{x}AH_x$$
 (1)

More recently, Jhulki and coworkers investigated the possible mechanisms with nonfullerene acceptors and showed that for strong hydride acceptors, the desired radical anions may not form at all, leading to a persistent H-reduced acceptor. In addition to the desired product, there are H-containing side products such as hydrogen gas from the main reaction. <sup>31</sup> For example, upon doping dicyano-naphthalenediimide with N-DMBI-H, H<sub>2</sub> is speculated to be the side product and the ultimate fate of the H atom of the N-DMBI-H.<sup>31</sup>

Thus to avoid the complexity arising from the hydride involvement in the electron transfer, dimeric versions of these Y-DMBI-H compounds, if synthetically accessible, may be preferred, as the dimers react with the acceptors cleanly and rapidly producing the desired radical anions.<sup>2, 15, 27, 28, 33</sup> Buoyed by these recent findings, and the fact that the generated dopant counterions have profound effects on the doped semiconductor microstructure, this chapter aims to present an expand the library of the Y-DMBI-H and (Y-DMBI)<sub>2</sub> compounds (Figure 1).<sup>15, 36-39</sup> In addition to presenting a simplified synthetic route to obtain the new compounds reported herein, the reactivity of the various Y-DMBI-H and their dimers is investigated and compared to the literature. Lastly, the thermal stability of the

dopant family was investigated in order to gain insight into their potential stability when utilized in organic electronic applications.

## 4.2 Materials and Methods

*General:* All operations were carried out under an atmosphere of nitrogen either using standard Schlenk techniques or in a glove box. Toluene, tetrahydrofuran (THF), and dimethylformamide (DMF) were dried using a solvent purification system from MBraun benzene and hexane were dried over sodium and distilled, and NEt<sub>3</sub> was stored over KOH and distilled prior to use. All solvents were deoxygenated by three 'freeze-pump-thaw' cycle prior to use. All commercially available chemicals were used without further purification unless otherwise noted. Sodium amalgam (1 wt%) was prepared immediately prior to use by addition of small pieces of Na metal to vigorously stirred Hg (electronic grade, 99.99%) against a counter-flow of N<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}

**No table of figures entries found.** NMR spectra were recorded either on Bruker AMX 400 or AVIIIHD 500 MHz spectrometers. Mass spectra were measured on an Applied Biosystems 4700 Proteomics Analyzer using ESI mode. Elemental analyses were carried out by Atlantic Microlabs using a LECO 932 CHNS elemental analyzer. Electrochemical data were acquired using cyclic voltammetry in 0.1 M "Bu<sub>4</sub>NPF<sub>6</sub> in dry THF under nitrogen, using a CHInstruments 620D potentiostat, a glassy carbon working electrode, a platinum wire auxiliary electrode, and, as a pseudo-reference electrode, a silver wire anodized in 1 M aqueous potassium chloride solution. A scan rate of 50 mVs<sup>-1</sup> was used

and ferrocene or decamethylferrocene (- 0.53 V *vs*. FeCp<sub>2</sub> determined experimentally in THF) were used as an internal reference.

*UV-vis-NIR Studies:* UV-vis-NIR kinetic measurements in solution were performed using sealed quartz cuvettes having 1 mm path lengths in a Cary UV-vis-NIR spectrometer. All the stock solutions were prepared in chlorobenzene in a nitrogen filed glovebox. The freshly prepared stock solutions of the respective compounds were mixed in a vial and then transferred to the cuvette for measurements. For the doping experiments involving Y-DMBI-H and PCBM, the concentrations were fixed at 0.4 mM and 2.7 mM, respectively. For the doping studies using the dimers, the concentrations for (Y-DMBI)<sub>2</sub> and PCBM were 0.2 mM and 2.7 mM, respectively. TIPS pentacene (TIPSp) does not react with Y-DMBI-H under the conditions used here. For the studies of reaction between TIPSp and (Y-DMBI)<sub>2</sub>, the concentrations were  $2.6 \times 10^{-5}$  M and  $3.7 \times 10^{-4}$  M, respectively.

*Doping in Thin Films:* Microscope glass slide (1 in<sup>2</sup>) were cleaned by sonication in soapy water, followed by deionized water, and finally ethanol. The clean substrates were then dried in a stream of nitrogen gas and treated with oxygen plasma for 10 minutes. The freshly prepared substrates were immediately used for spin coating of toluene solutions of N2200 (5 mg mL<sup>-1</sup>) at 1000 rpm for 40 seconds. For the Y-DMBI-H doping, Y-DMBI-H solution (chlorobenzene, 3 mg mL<sup>-1</sup>) was added to the N2200 precursor, spun in a glovebox using 1000 rpm for 40 seconds then annealed in the glovebox at 120 °C for 1 h. For the doping using the (Y-DMBI)<sub>2</sub>, sequential doping was followed whereby the dopant solutions in butyl acetate were dropped onto the pristine N2200 films, allowed to react for

30 s, and then the excess solution was spun off at 800 rpm for 30 s and then dried on the hot plate in the glovebox at 60  $^{\circ}$ C for 1 min.

*Thermal Characterization*: Differential Scanning Calorimetry and Thermal Gravimetric Analysis were done on Metler Toledo instruments. The experiments were performed under nitrogen gas with heating/ cooling rate of 10 °C.

# 4.3 Synthesis of benzimidazole compounds:

# Synthetic procedure for imidazole (2\*x):

A mixture of the necessary diamine (46.3 mmol), aldehyde (46.3 mmol) and sodium metabisulfite (46.3 mmol) were added to a flask with 100 mL of dry DMF taken from solvent purification system. The mixture was heated to 100 °C for 12 h. The reaction was then cooled down to room temperature then cooled in an ice water bath. The resulting white powder was collected via vacuum filtration and dried under high vacuum to give the product in quantitative yield.

**2'a:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.52 (s, Ar, 2H), 3.91 (s, OMe, 6H), 2.89 (t, cyc, 1H, *J*<sub>*H*-*H*</sub> = 8 Hz), 2.12 (d, cyc, *J*<sub>*H*-*H*</sub> = 12 Hz, 2H), 1.845 (d, cyc, *J*<sub>*H*-*H*</sub> = 12 Hz, 2H), 1.75-1.58 (m, cyc, 3H), 1.44-1.22 (m, cyc, 3H), N-H signal not observed. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 157.19, 104.34, 101.90, 55.75, 38.51, 31.87, 26.04, 25.98, 25.84. LRMS (ESI): m/z 261.2 (MH<sup>+</sup>)



Figure 4.3. <sup>1</sup>H NMR spectrum of 2'a in CDCl<sub>3</sub>.



Figure 4.4. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2'a in CDCl<sub>3</sub>.

**2b:** <sup>1</sup>H and <sup>13</sup>C spectra are consistent with previous reports.<sup>2, 15, 28</sup>

**2'b:** <sup>1</sup>H NMR (400 MHz, Methanol-*d*<sub>4</sub>): δ 7.98 (d, Ar, 2H, *J*<sub>H-H</sub> = 8 Hz), 6.89 (m, Ar, 4H), 4.00 (s, OMe, 6H), 3.35 (s, NH, 1H), 3.10 (s, NMe, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, Methanol-*d*<sub>4</sub>): δ 154.86, 151.72, 142.61, 130.48, 125.28, 113.07, 110.31, 106.96, 56.83, 40.25. LRMS (ESI): m/z 298.2 (MH<sup>+</sup>)



Figure 4.5. <sup>1</sup>H NMR spectrum for 1'b in CD<sub>3</sub>OD.



Figure 4.6. <sup>13</sup>C{1H} NMR spectrum for 2'b in CD<sub>3</sub>OD.

**2c:** <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):  $\delta$  7.50 (d, thiophene, 1H, *J*<sub>*H*-*H*</sub> = 4 Hz), 7.46 (dd, Ar, 2H, *J*<sub>1</sub> = 5 Hz, *J*<sub>2</sub> = 2.6 Hz), 5.94 (d, thiophene, 1H, *J*<sub>*H*-*H*</sub> = 4 Hz), 3.01 (s, NMe, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, acetone-*d*<sub>6</sub>):  $\delta$  161.66, 184.45, 139.66, 127.25, 121.48, 116.65, 114.02, 102.16, 41.58. HRMS (ESI), Anal. Calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>3</sub>S, theoretical: 244.0903, found m/z 244.0899 [M+H]<sup>+</sup>. Anal. Calcd. For C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>S, C: 64.17, H :5.39, N: 17.27, found: C:63.54, H:5.66, N:17.27.



Figure 4.7. <sup>1</sup>H NMR spectrum of 2c in acetone-d<sub>6</sub>.



Figure 4.8. <sup>13</sup>C{1H} NMR spectrum of 2c in acetone-d<sub>6</sub>.

Synthesis of [NDMBI]<sup>+</sup>I<sup>-</sup> cations:

Benzimidazole (2\*x) (7.58 mmol), iodomethane (MeI) (2.26 g, 15.9 mmol) and K<sub>2</sub>CO<sub>3</sub> (5.5 g, 22.75 mmol) were taken in acetone (75 mL) in a pressure flask. The mixture was stirred at 100 °C for 24 h. Then the acetone was removed using rotary evaporation, and a minimal amount of water was added. The resulting white powder was collected via vacuum filtration and dried under high vacuum. The powder was taken to the next step without further purification.

## Synthesis of PF<sub>6</sub> salts (3\*x):

[Y-DMBI]<sup>+</sup>I<sup>-</sup> (1.25 mmol) was dissolved in a minimum of methanol. To it an excess of NH<sub>4</sub>PF<sub>6</sub> (1 g, 6.1 mmol) was added; the mixture was sonicated for 5 min and then copious amounts of DI water were added. The product was collected via vacuum filtration and dried under high vacuum. The purification of the product can be done by washing with water since unlike the iodide starting material, 3\*x are not water soluble. The product is obtained with quantitative yield.

**3b:** <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$  NMR spectra are consistent with previous reports.<sup>15</sup>

**3'a:** <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ ):  $\delta$  7.07 (s, Ar, 2H), 4.41 (s, OMe, 6H), 4.00 (s, NMe, 6H), 3.67 (m, cyc, 1H), 1.44–1.38 (m, Cyc, 4H), 1.96–1.93 (m, cyc, 2H), 1.81–1.79 (m, cyc, 1H), 1.60–1.58 (m, cyc, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, acetone- $d_6$ ):  $\delta$  155.4, 143.0, 124.0, 108.6, 57.1, 36.5, 36.0, 28.3, 26.7, 25.9. HRMS (ESI) m/z: Anal. Calcd. for C<sub>17</sub>H<sub>25</sub>O<sub>2</sub>N<sub>2</sub> [M-PF<sub>6</sub>]<sup>-</sup> theoretical: 289.1911, found m/z 289.1908. Anal. Calcd. for C<sub>17</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub>PF<sub>6</sub>: C 47.01, H 5.80, N 6.45. Found C 47.29, H 5.60, N 6.63. (NMR data courtesy of Dr. Swagat Mohapatra)



Figure 4.9. <sup>1</sup>H NMR spectrum of 3'a in acetone-d<sub>6</sub>.



Figure 4.10. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3'a in acetone-d<sub>6</sub>.

**3'b:** <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>): δ 7.66 (d, *J*<sub>*H*-*H*</sub> = 9 Hz, Ar, 2H), 7.11 (s, Ar, 2H), 7.03 (d, *J*<sub>*H*-*H*</sub> = 9 Hz, Ar, 2H), 4.10 (s, Me, 6H), 4.02 (s, Me, 6H), 3.14 (s, Me, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, acetone-*d*<sub>6</sub>): δ 154.0, 152.9, 143.1, 132.7, 124.2, 112.7, 108.6, 106.6, 57.2, 40.1, 36.5. LRMS (ESI): m/z 326.2 (M<sup>+</sup>). Anal. Calcd. for C<sub>19</sub>H<sub>24</sub>N<sub>3</sub>O<sub>2</sub>PF<sub>6</sub>: C 48.41, H 5.13, N 8.91. Found C 48.14, H 5.09, N 8.75. (NMR data courtesy of Dr. Swagat Mohapatra)



Figure 4.11. <sup>1</sup>H NMR spectrum of 3'b in acetone-d<sub>6</sub>



Figure 4.12. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3'b in acetone-d<sub>6</sub>

**3c:** <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):  $\delta$  7.98 (dd, Ar, 2H, *J*<sub>*H*-*H*</sub> = 2.4 Hz, *J*<sub>*H*-*H*</sub> = 4 Hz ), 7.82 (d, Th, 1H, *J*<sub>*H*-*H*</sub> = 4 Hz ), 7.72 (dd, Ar, 2H, *J*<sub>*H*-*H*</sub> = 2.4 Hz, *J*<sub>*H*-*H*</sub> = 4 Hz), 6.34 (d, Th, 1H, *J*<sub>*H*-*H*</sub> = 4 Hz), 4.23 (s, Me, 6H), 3.22 (s, Me, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, acetone-*d*<sub>6</sub>):  $\delta$  167.18, 139.13, 132.45, 126.33, 112.40, 103.22, 68.31, 53.79, 41.67, 33.07. HRMS (ESI): Anal. Calcd. for C<sub>15</sub>H<sub>18</sub>SN<sub>3</sub> theoretical: 272.1216, found m/z 272.1215 [M-PF<sub>6</sub>]<sup>+</sup>. Anal. Calcd. for C<sub>15</sub>H<sub>18</sub>F<sub>6</sub>N<sub>3</sub>PS: C 43.17, H 4.35, N 10.07. Found C 43.42, H 4.54, N 10.17.



Figure 4.13. <sup>1</sup>H NMR of 3c in acetone-*d*<sub>6</sub>



# Figure 4.14. <sup>13</sup>C NMR of 3c in acetone-*d*<sub>6</sub>

### Synthesis of [Y-DMBI-H] (4\*xH):

To a solution of N-DMBI<sup>+</sup>PF<sub>6</sub><sup>-</sup> (2.5 mmol) in MeOH (20 mL), solid NaBH<sub>4</sub> (0.114 g, 7.62 mmol) was added in small portions for about 10 min. The solution was stirred at r.t. for 1h. The methanol solution was concentrated, and then minimal distilled water was added to precipitate the desired product. The white solid obtained was filtered, washed with water and dried under high vacuum.

**4'aH:** Yield = 90 mg (60 %).<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.28 (s, Ar, 1H), 3.75 (d, *J*<sub>H-H</sub> = 5Hz, CH, 1H), 3.45 (s, OMe, 6H), 2.91 (s, NMe, 6H), 1.85–1.82 (m, cyc, 2H), 1.70–1.68 (m, cyc, 2H), 1.60 (m, Cyc, 1H), 1.45–144 (m, cyc, 1H), 1.18–1.12 (m, cyc, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  142.9, 133.6, 105.9, 97.5, 55.8, 44.9, 42.1, 27.9, 27.1, 26.7. LRMS (ESI): m/z 259.1 (M<sup>+</sup>–2Me–H). Anal. Calcd. for C<sub>17</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>: C 70.31, H 9.02, N 9.65. Found C 69.73, H 8.80, N 9.60. (NMR data courtesy of Dr. Swagat Mohapatra)



Figure 4.15. <sup>1</sup>H NMR spectrum of 4'aH in C<sub>6</sub>D<sub>6</sub>



Figure 4.16. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4'aH in C<sub>6</sub>D<sub>6</sub>

**4bH**: <sup>1</sup>H and <sup>13</sup>C spectra are consistent with previous reports.<sup>2, 28</sup>

**4'bH:** Yield = 0.3 g (67%). <sup>1</sup>H NMR (400 MHz, benzene- $d_6$ ):  $\delta$  7.58 (d,  $J_{H-H}$ = 8.4 Hz, Ar, 2H), 6.60 (d,  $J_{H-H}$ = 8.8 Hz, Ar, 2H), 6.32 (s, Ar, 2H), 4.66 (s, CH, 1H), 3.42 (s, Me, 6H), 2.95 (s, Me, 6H), 2.48 (s, Me, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, benzene- $d_6$ ):  $\delta$  151.3, 141.7, 131.5, 130.0, 127.2, 112.2, 105.7, 96.4, 56.0, 39.8, 36.2, LRMS (ESI) m/z: 296.1 (M<sup>+</sup>-C<sub>2</sub>H<sub>7</sub>]), Anal. Calcd. for C<sub>19</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>: C 69.70, H 7.70, N 12.88 Found C 69.63, H 7.56, N 12.73. (NMR data courtesy of Dr. Swagat Mohapatra)


Figure 4.17. <sup>1</sup>H NMR spectrum of 4'bH in C<sub>6</sub>D<sub>6</sub>



Figure 4.18. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4'aH in C<sub>6</sub>D<sub>6</sub>

**4cH:** yield = 0.5 g (97%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.90 (d, Th, 1H,  $J_{H-H}$  = 4 Hz), 6.73-6.68 (m, Ar, 2H), 6.46-6.41 (m, Ar, 2H), 5.73 (d, Th, 1H,  $J_{H-H}$  = 4 Hz), 4.92, (s, CH, 1H), 2.93 (s, Me, 6H), 2.64 (s, Me, 6H). <sup>13</sup>C{1H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.70, 141.65, 128.22, 127.10, 119.35, 105.98, 100.13, 90.26, 42.64, 33.12. HRMS (ESI) Anal. Calcd. for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>S, theoretical: 274.1372, found m/z: 274.1372 [M+H]<sup>+</sup>. Anal. Calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>3</sub>S: C 65.90, H 7.01, N 15.37 Found C 65.64, H 6.96, N 15.14.



Figure 4.19. <sup>1</sup>H NMR spectrum of 4cH in CDCl<sub>3</sub>



Figure 4.20. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4cH in CDCl<sub>3</sub>

General procedure for dimer synthesis: the procedure was used following literature procedures.<sup>15</sup> In brief, mercury (195 g) was added to an oven dried Schlenk flask along with a stirrer bar. The flask was cycled with vacuum then nitrogen gas for 3 times. Then, a piece of sodium metal (1.95 g, 0.051 mol), weighed in toluene and shaved with a metal spatula to remove the grey impurities was added to the mercury against a counterflow of nitrogen. The sodium and mercury were stirred gently under nitrogen till the amalgam formed. Then 200 mL of THF were added via a cannula. Then  $[Y-DMBI]^+ PF_6^-$  (7.29) mmol) was added in the solid in one shot against a counterflow of nitrogen. The reaction is allowed to run for  $\sim 90$  mins at room temperature. Then for mercury recycling, THF/ product supernatant is removed via cannula to another Schlenk flask and 20 mL of THF were used to rinse the mercury. The amalgam can then be used to generate more dimer by repeating the THF/ starting material steps. After recycling the mercury a few times, more sodium can be added. The dimer is purified by passing the THF solution over a silica plug (pre-treated with distilled triethyl amine) under nitrogen to remove the  $NaPF_6$  as well as the amide impurity. The THF is then removed on the Schlenk line under vacuum by adding a secondary cold trap.

**5'a2:** Yield = 0.435 g (79 %). <sup>1</sup>H NMR (500 MHz, benzene-*d*<sub>6</sub>):  $\delta$  6.25 (s, Ar, 4H), 3.47 (s, OMe, 12H), 3.44 (s, br, NMe, 12H), 2.16 (m, cyc, 2H), 1.93 (br, cyc, 4H), 1.61–1.58 (m, Cyc, 6H), 1.41–1.38 (m, Cyc, 4H), 1.17–1.05 (br, m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, benzene-*d*<sub>6</sub>):  $\delta$  139.0, 131.6, 105.9, 98.1, 57.5, 47.9, 35.5, 29.9, 28.4, 27.3. LRMS (ESI): m/z 259.1 (M/2<sup>+</sup>–2Me). Anal. Calcd. For C<sub>34</sub>H<sub>50</sub>N<sub>4</sub>O<sub>4</sub>: C 70.56, H 8.71, N 9.68. Found C 70.94, H 8.70, N 9.55. (NMR data courtesy of Dr. Swagat Mohapatra)



Figure 4.21. <sup>1</sup>H NMR spectrum of 5'a<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>



Figure 4.22. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 5'a<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>

**5'b<sub>2</sub>:** Yield = 0.77 g (74%) <sup>1</sup>H NMR (400 MHz, benzene-*d<sub>6</sub>*):  $\delta$  7.81 (d, *J<sub>H-H</sub>* = 6 Hz, Ar, 2H), 6.45-6.32 (br, m, Ar, 8H), 6.20 (d, *J<sub>H-H</sub>* = 8.8 Hz, 2H), 3.48 (s, OMe, 6H), 3.36 (s, OMe, 6H), 3.16 (s, NMe, 6H), 3.14 (s, NMe, 6H), 2.47 (s, NMe, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, benzene-*d<sub>6</sub>*):  $\delta$  149.5, 141.0, 138.9, 134.7, 132.7, 132.2, 125.4, 110.4, 106.4, 103.1, 98.5, 59.6, 56.4, 39.5, 37.9, 36.4. LRMS (ESI): m/z 296.1391 (M/2–2Me<sup>+</sup>). Anal. Calcd. for C<sub>38</sub>H<sub>48</sub>N<sub>6</sub>O<sub>4</sub>: C 69.91, H 7.41, N 12.87. Found C 69.79, H 7.54, N 12.70. (NMR data courtesy of Dr. Swagat Mohapatra)



Figure 4.23. <sup>1</sup>H NMR spectrum of 5'b<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>.



Figure 4.24. <sup>13</sup>C{<sup>1</sup>H} NMR of 5'b<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>.

**5b2:** yield = 75%. <sup>1</sup>H and <sup>13</sup>C NMR are consistent with previous reports.<sup>15</sup>

# 4.4 **Results and Discussion**

# 4.4.1 Synthesis of Y-DMBI-H and (Y-DMBI)<sub>2</sub>.

N-DMBI-H and  $(N-DMBI)_2$  are generally synthesized by reduction of cationic benzimidazole salts. A similar but optimized approach to the literature is used to perform the condensation reactions between the 3,6-X-phenylenedimaine (scheme 1) and the (Y-

CHO) aldehyde in the presence of sodium metabisulfite, an oxidizing agent. First, commercially available *o*-phenylenediamine or 3,6-dimethoxybenzene-1,2-diamine,<sup>40, 41</sup> is condensed with the appropriate carboxaldehydes in the presence of sodium metabisulfite in *N*,*N*-dimethylformaldehyde (DMF) to obtain benzimidazoles.<sup>42</sup>. When treated with methyl iodide, the benzimidazoles 2\*x compounds convert to cationic dimethyl-substituted benzimidazole salts (Y-DMBI<sup>+</sup>I<sup>-</sup>), which can be converted to Y-DMBI<sup>+</sup>PF<sub>6</sub><sup>-</sup> (3\*x) by rapid anion exchange with NH<sub>4</sub>PF<sub>6</sub> followed by precipitation with water, in which the iodide salts are somewhat soluble, but the hexafluorophosphates are not. All Y-DMBI-A (A = I<sup>-</sup>/PF<sub>6</sub>) can react with NaBH<sub>4</sub> to yield the Y-DMBI-H (4\*x) compounds in 65–80% yields. For the synthesis of the dimeric dopants, the Y-DMBI<sup>+</sup>PF<sub>6</sub><sup>-</sup> (3\*x) salts are used for their better solubility compared to Y-DMBI<sup>+</sup>I<sup>-</sup> in tetrahydrofuran (THF). Then, they are reduced by Na(Hg) to obtain the dimeric dopants in moderate to high yields (70-80%).



Scheme 1. Synthetic scheme for Y-DMBI-H and (Y-DMBI)<sub>2</sub> dopants discussed in this chapter.

The synthesis of the dimeric compounds involves stirring a THF solution of Y-DMBI<sup>+</sup>PF $_6^-$  salts over 1% Na(Hg) under inert atmosphere. The mercury in this case was recycled as discussed in the experimental section.

### 4.5 **Electrochemistry:**

D	$D_2$	$E_{red} \left( \mathrm{D}^{+} / \mathrm{D}^{\bullet} \right)$	$E_{ox}$	$E_{ox}$
			(DH*+/DH)	$(D_2^{\bullet+}/D_2)$
J	K	-2.45 <sup>a</sup>	-0.06	-0.64 <sup>a</sup>
4'aH	<b>5'a</b> 2	-2.56	-0.11	-0.92
4bH	5b <sub>2</sub>	-2.38	-0.13	-0.74
4'bH	5'b2	-2.42	-0.22	-0.87
4cH	-	-2.05	-0.22	

Table 4.1. Redox Potentials (V vs. FeCp2<sup>+/0</sup>, THF/0.1 M Bu4NPF6)<sup>*a*</sup> Data from reference <sup>43</sup>. <sup>*b*</sup> Data from reference <sup>26</sup>.

As discussed earlier, the reactivity of the Y-DMBI-H compounds cannot be simply concluded from the redox potentials. However, the redox potential of the DH<sup>\*+</sup>/DH couple can provide insight into the substituent impact on the electronic structure of the relevant molecules as well as the substituent influence on the stability of the different species. For example, the introduction of the methoxy groups in the case of 4'aH and 4'bH renders more easily oxidized than their non-substituted counterparts. On the other hand, a thiophene substituted Y-DMBI-H **4cH** is more easily oxidized electrochemically than N-DMBI-H (**4bH**), which is surprising since the Y substituent *i.e.* thiophene cannot act as a  $\pi$ -donor in the H compound since other studies have shown that the HOMO does extend to the Y substituent.<sup>44</sup> In addition, the values of  $E_{red}$  (D<sup>+</sup>/D<sup>•</sup>) can provide insight into the

impact of the various aryl and Y substituents on stabilizing the monomer cation *vs*. the radical.<sup>2</sup> A more negative reduction potential is seen in the case of **3'a** and **3'b** when methoxy substituents are installed on the compounds. This means that the methoxy substituents stabilize the cation more than the radical. However, the thiophene substituent stabilizes the cation the least since the reduction potential is the least negative. Although one would expect that thiophene is a very good  $\pi$ -donor, it could be the case that the inductive and steric effects outweigh the electron donation of the thiophene substituent.

As for the dimeric compounds, there are two experimentally demonstrated mechanisms by which doping can take place:<sup>2, 44</sup>



### Figure 4.25. Mechanism I and II governing the dimer reaction.<sup>2</sup>

Under the first mechanism, the bond cleavage is generally expected to be rate determining; this mechanism would dominate in dimers where the bond in the dimer is relatively weak (and the barrier to the alternative electron transfer of mechanism II is relatively high). One can gain insight to the strength of the bond from electrochemistry of the  $D^+/D^-$  couple as well as through calculations. In brief, the bond strength is dominated by effect of Y, and X substituents, on the radicals. The relative stabilization of cation *vs*. the radical relates to the  $D^+/D^-$  redox potential.

Under the second mechanism, an electron transfer is the first step and, at least in some cases, rate limiting. The three dimers can be ranked as  $5^{\circ}a_2 > 5^{\circ}b_2 > 5b_2$  in terms of their reducing ability via one electron transfer according to the  $D_2^{*+}/D_2$  redox potential. It is evident that the introduction of methoxy groups leads to the dimer to be easier to oxidize since the oxidation potential becomes more negative. This could mean that when dimer oxidation is rate limiting, the easier dimer to oxidize will have a less endergonic driving force.

These two parameters are of relevance since the overall thermodynamic doping strength is dependent on the ease of monomer ionization as well as the free energy associated with dimer dissociation. The overall doping strength can be expressed via the equation below:

$$E_{eff}(D^+ / 0.5 D_2) = E(D^+ / D^{\bullet}) + \frac{0.5}{F} \Delta G_{diss}(D_2)$$

Where F is Faraday's constant and  $\Delta G_{diss}$  is the free energy of the dimer central C-C bond dissociation, which can be calculated via DFT.<sup>33, 45</sup>

### 4.5.1 Reactivity Studies

### 4.5.1.1 In solution:



Figure 4.26. (A) Evolution of the PCBM radical anion absorption *vs.* time when PCBM is reacted with Y-DMBI-H in chlorobenzene. (B) Evolution of the TIPS<sup>-</sup> absorption *vs.* time when TIPS is reacted with (Y-DMBI)<sub>2</sub> dimers in chlorobenzene.

The various Y-DMBI-H derivatives and dimers reactivity as well as their relative reactivity is of interest in order to understand their behavior when used in organic electronic applications. The kinetic of doping Y-DMBI-H compounds were tested by solution doping of PCBM to determine the rate law for the doping process. The UV-vis-NIR spectra were acquired in chlorobenzene, in air, water and light free environment at 293 K where PCBM is used in excess ([PCBM] = 2.7 mM *vs*. [Y-DMBI-H] = 0.4 mM). Figure 26 A shows the evolution of PCBM<sup>\*-</sup> absorption (1030 nm) *vs*. time. By simply looking at the plot the reactivity of the Y-DMBI-H compounds can be ranked as **4'bH** > **4bH** > **4cH** > **4'aH**. In addition, by assuming that the reaction is first order in *both* the dopant and the acceptor, similar to literature reports,<sup>2, 28, 33</sup> and that this is the case for all Y-DMBI-H discussed in this case, the reaction rate can be expressed as:

$$-\frac{\partial[A]}{\partial t} = k \cdot [A][DH] \quad (2)$$

The kinetic experiments in Figure 26A are done under pseudo first order conditions *i.e.*, the PCBM is in large excess and thus the reaction rate constant can be extracted from the concentration of the radical anion and the dopant. The rate constants are tabulated in Table 2 below confirming the same trend of reactivity seen in the UV-vis spectra.

Compound	Rate constant (M <sup>-1</sup> min <sup>-1</sup> )	
4'aH	0.04	
4'bH	0.48	
4bH	0.26	
4cH	0.13	

Table 4.2. Rate constants of the Y-DMBI-H compounds investigated in this chapter.

In the case of the dimers, the reaction with PCBM is sufficiently fast that by the time the sample is prepared and spectra are obtained, the reaction is has proceeded to completion. That is because PCBM ( $E_{red} = -1.07 \text{ V} vs$ . FeCp<sub>2</sub><sup>+/0</sup>)<sup>33</sup> and as such any of the dimers will react dominantly by electron transfer since PCBM is easily reduced resulting in a reaction that is endergonic by only ~ 0.08 - 0.2 eV.

However, in order to differentiate between the two mechanisms, a less easily reduced acceptor such as TIPS can be used with the dimeric dopants. As such, to further understand the underlying mechanism behind the electron transfer in the dimers, kinetic studies using TIPS  $(E_{red} = -1.45 \text{ V})^2$  as the acceptor were done performed in solution (figure 24). Evidently, by tracking the TIPS radical anion absorption, it seems to plateau in the case of the dimer  $(5'a_2)$  which is consistent with a mechanism whereby electron transfer is rate limiting. The formation of the TIPSp<sup>2-</sup> would not be observed since the second reduction ( $\sim -1.9$  V) would be considerably more endergonic than the first and the TIPS<sup>-</sup> is persistent in solution. In previous work on dimer mechanisms, where the reactivity studies were done under the same conditions employed here, dimer J, which DFT calculations proved to have a relatively stronger C-C central bond exhibits similar behavior to  $5^{\prime}a_{2}$ .<sup>2, 28</sup> This implies that the methoxy substituents do not cause the central bond to be weaker to the extent that the observed mechanism in solution is changed. On the other hand, however, both dimers 5'b<sub>2</sub> and 5b<sub>2</sub>, show evidence of a mechanism where bond cleavage is rate limiting. In that case the reaction is zero order in the acceptor, and one can expect TIPSp<sup>2-</sup> to be formed since the reduction of both TIPS to TIPS<sup>--</sup> and TIPS<sup>--</sup> to TIPS<sup>2-</sup> by D' are both expected to be strongly exergonic and thus rapid and that is what's observed in the UV-vis spectra (Figure 25B, and 26B) and is consistent with literature precedent for reactivity studies on dimers M and O.<sup>2, 28, 44</sup> Figure 25B shows the evolution of the TIPS<sup>-</sup> peak followed by consumption evident of the anion undergoing further reaction at a fairly similar rate. In addition, the fact that the rise of TIPS<sup>--</sup> for the two "weak" bond systems are not exactly straight lines, means that in this experiment, the reaction is not truly zero order in TIPS, implying that both mechanism can be concurrently going on, with both contributing to the formation of TIPS<sup>-</sup> as seen in the literature for other previously reported dimers.<sup>2</sup> The reaction is further reduction to result in TIPS<sup>2-</sup> (Figure 26B, 27B).<sup>2</sup> In addition, it is evident that  $5'b_2$  reacts faster than  $5b_2$ , suggesting that the MeO substitution weakens the central C—C bond, likely primarily by stabilizing the corresponding Y-DMBI' species, however it does not weaken the bond to the extent that the observed reaction proceeds by cleavage rather than electron transfer as seen in  $5'a_2$ .



Figure 4.27. Evolution of UV-vis-NIR spectra of dimers 5'a<sub>2</sub> (A), and 5'b<sub>2</sub> (B) over time when reacted with TIPSp. The peaks at 490, 510, 560, and 810 nm are attributed to TIPSp<sup>2</sup>.<sup>45</sup>



Figure 4.28. Thin film reactivities of N2200 doped with DMBIH derivatives (A), dimer 2<sub>2</sub> (B), and a comparison between the different dimers at the same dopant concentrations (C).

In the solid state:

To further understand the behavior of both the H compounds and the dimers, thin films of each new Y-DMBI-H derivative and dimer reported were used to make N2200 doped films. N2200 is chosen since it's a versatile electron-transport material as discussed in previous chapters (chapter 1 and 2). In the case of Y-DMBI-H derivatives shown here, the doping was done concomitantly in solution then the cast films were annealed at 120 °C for one hour. The observed changes in the UV-vis spectra show different levels of reduction in the peak ~ 700 nm intensity which can be attributed to a higher doping level since the films are of the same thickness (Figure 27A).

As for the dimers, mixed solution doping was made difficult due to the precipitates formed in solution when attempting to dope N2200 with any of the dimers; the reaction occurs rapidly but the doped material was poorly soluble. As such the doping was performed sequentially. According to the UV-vis-NIR data, it is evident that the films are doped without the need to thermally anneal the polymers. The main difference in the doped spectra between the Y-BMDI-H and the dimers is that when doped at high concentrations of dimer solutions, the N2200 film exhibits a new peak ~ 500 nm which is of much lower intensity in the case of Y-DMBI-H compounds. This peak is attributed to the N2200 negative polaron and resembles that seen for other NDI radical anions.<sup>46</sup>

#### Thermal properties of Y-DMBI-H and (Y-DMBI)<sub>2</sub>:

Thermal gravimetric analysis (TGA) of the various Y-DMBI-H and (Y-DMBI)<sub>2</sub> compounds is used to study the thermal stability with 95% mass retained above 150 °C. TGA plots and decomposition temperature ( $T_d$ ) determined at 95% mass retention is tabulated are presented in Figure 29 below. It is worth noting that although the temperature

is referred to as decomposition temperature this does not rule the possibility of sublimation to be the cause of mass loss.



compound	T <sub>d</sub> (°C)		
4'aH	173		
4'bH	240		
4bH	191		
4cH	221		
5'a <sub>2</sub>	170		
5'b <sub>2</sub>	219		
5b <sub>2</sub>	186		

Figure 4.29. TGA plots and Td temperature for Y-DMBI-H and (Y-DMBI)2

Since these dopants are often used in solution processing followed by annealing, it is important to understand their thermal behavior *vs.* temperature. The differential scanning calorimetry (DSC) curves of the dopants discussed in this chapter are seen in Figure 30 below.



# Figure 4.30. DSC graphs of Y-DMBI-H and (Y-DMBI)<sub>2</sub> dopants discussed in this chapter.

The DSC plots of the Y-DMBI-H compounds (Figure 30 A-D) show that in the first heating cycle all compounds exhibit a cold crystallization at T  $\sim$  50 °C which is not seen in the second heating cycle once the compound's thermal history is erased in the first cycle. In addition, all Y-DMBI-H compounds exhibit a melting transition, the melting points of the compounds are tabulated below. In contrast, the (Y-DMBI)<sub>2</sub> dimers do not exhibit any thermal transition which can be due the samples (prepared by drop casting from toluene) are amorphous, or that the melting point is outside the experiment temperature range.

Compound	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	$T_m(^{\circ}C)$
4'aH	-30	23	75
4'ЬН	0	50	150
4bH	0	65	100
4cH	0	25, 125	140

 Table 4.3. Thermal data determined from the DSC plots of Y-DMBI-H compounds.

### 4.6 **CONCLUSION:**

This chapter presents the synthesis of characterization of a family of Y-DMBI-H and (Y-DMBI)<sub>2</sub> compounds. Y-DMBI-H compounds shown in this chapter are air stable for months whereas the dimers as air stable for a few hours in the solid state. The reactivity of the Y-DMBI-H compounds show that the order of reactivity is 4'bH > 4bH > 4cH >4'aH The reactivity of the (Y-DMBI)<sub>2</sub> dimers with TIPSp show that both  $5b_2$  and  $5'b_2$  has dimer cleavage as the dominant mechanism, indicative of a weaker C-C central bond. On the other hand.  $5'a_2$  reacts via an electron transfer rate determining step mechanism similar to what is seen for dimer K. UV-vis spectra of doped films show that these dopants can all dope N2200 upon processing them into thin films. Density functional theory (DFT) calculations can potentially be used to complement this work by studying the hydride donation ability of the Y-DMBI-H as well as the free energy required for dissociation of

the central C-C dimer bond.

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# CHAPTER 5. COMPARING THE EFFECTS OF DIFFERENT IRON(III) DOPANTS ON THE CHARGE-TRANSPORT PROPERTIES OF POLYTHIOPHENE AND POLY(DIALKOXYTHIOPHENE) DERIVATIVES

This project was done in collaboration with Shawn Gregory, Amalie Atassi and Joshua Reinhart where Shawn took the lead on electrical and themoelectrical measurements and their interpretation within the framework of the SLoT model with Amalie and Josh supporting. Riley Hanus also contributed to data analysis of the SLoT model. James Ponder and Austin Jones provided the PEDOT derivative investigated in this study. The author performed all sample preparation and measurements and data analysis for XPS, UV-vis-NIR spectroscopy, and X-ray diffraction. The author and Shawn Gregory are co-first authors on a paper which features parts of this work, where Shawn Gregory significantly contributed to the detailed analysis and the data collection/ modelling in the paper and only a summary of those results/ analyses is shown in this work. Figures made by Shawn Gregory are labelled explicitly as such.

### 5.1 Introduction:

As discussed in chapter 1, and shown throughout the thesis chapters, polymeric semiconductors are incorporated in photovoltaic,<sup>47-50</sup> transistor,<sup>51-53</sup> and thermoelectric devices.<sup>54-56</sup> Systematically designing and evaluating polymer and dopant chemistry is a means to engineer the desired device performance. Poly(thiophene) derivatives such as

poly(3-alkyl thiophenes (P3AT),<sup>21, 57-59</sup> poly(ethylenedioxyhiophene) (PEDOT),<sup>60, 61</sup> and poly[2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT)<sup>62-64</sup>) have received considerable attention due to the tunability of their properties *via* the thiophene backbone, alkyl groups ,and processing techniques, and because, when heavily doped, they can exhibit conductivities and the range of some metals (*i.e.* from 10<sup>2</sup> to 10<sup>5</sup> S cm<sup>-1</sup>).<sup>1</sup> Several thorough transport studies have analyzed P3AT and PBTTT derivatives,<sup>22, 65-69</sup> but fewer studies have examined soluble and solution processible dioxythiophene derivatives (XDOTs).<sup>70-75</sup> These XDOTs have lower ionization energies and oxidation potentials but are typically less ordered in comparison to P3AT or PBTTT derivatives, and these XDOTs can obtain appreciable optical and electrical properties.<sup>52, 76, 77</sup> Overall, XDOTs appear to be promising solution-processible alternatives to PEDOT:PSS for many organic electronic applications,<sup>73-75, 78</sup> making it imperative to contextualize the XDOT's transport properties.

Additionally, there is extensive research on the effects of dopant oxidation potential,<sup>74</sup> size,<sup>39, 71, 79</sup> dopant-polymer-solution miscibility,<sup>29, 58, 80</sup> doping method,<sup>10, 81, 82</sup> and dopant stability on the resulting optical and electronic properties.<sup>83-85</sup> One of the more widely used *p*-type dopants is FeCl<sub>3</sub>,<sup>39, 59, 86</sup> but other iron(III) salts, such as the tosylate, triflate, and perchlorate, are possible alternatives.<sup>69, 80, 86, 87</sup> In the presence of more strongly coordinating ions (*e.g.* chloride or bromide) the iron(III) compound primarily behaves as a complex leaving FeX<sub>4</sub><sup>-</sup> as the charge balancing anion.<sup>88</sup> In contrast, when weakly and non-coordinating ligands (*i.e.* triflate or perchlorate), are present some solvents may substitute some or all of the ligands to yield solvent-separated ions.<sup>83-85</sup> The thermodynamics and kinetics of the solvolysis equilibria<sup>83-85</sup> ultimately influences the doping processes, counterion species in the doped polymer film, and the resulting (thermo)electric

properties.<sup>64, 89, 90</sup> Some studies have examined the extent to which the counterion species affect the resulting transport properties,<sup>86, 90</sup> but this quantification requires additional research.

Polymer-dopant and polymer-counterion interactions affect optical and electronic transport properties, and quantifying these properties with a charge-transport model can lead to deeper physical and mathematical insights. Despite their utility, selecting a charge-transport model consistent with the physics in a polymer-dopant-processing system is non-trivial because several charge-transport models are reported for localized (hopping-like) and delocalized (band-like) transport.<sup>59, 79, 91</sup> Additionally, charge-transport physics in polymers may be highly sensitive to carrier density, electrostatic interactions, structural (dis)order, and processing.<sup>64, 89, 92-94</sup> With these considerations in mind, we utilize the semi-localized transport model (SLoT), discussed in chapter 1, to quantify the changes in transport parameters as a function of the doping level and of the dopant and polymer chemistry. This model accounts for both hopping and band-like contributions to the observable charge-transport properties and adequately captures the anticorrelation between the electrical conductivity and Seebeck coefficient.

Here we report on studies of regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly(3,4-(bis(2-octyldodecyloxymethyl)propane-1,3-dioxy)thiophene-*alt*-bi(3,4-(ethylenedioxy)thiophene) (PE<sub>2</sub>) (**Figure 1**),<sup>72, 75</sup> sequentially doped with solutions of different iron(III) salts at varying molarities with different counterions.



Figure 5.1. Doping reaction scheme of P3HT and PE<sub>2</sub>

### 5.2 Materials and Methods

Material sourcing and synthesis: Regioregular P3HT was purchased from Sigma Aldrich  $(M_n = 27 \text{ kDa}, D: 2)$ . PE<sub>2</sub> was synthesized per literature procedure  $(M_n = 6.2 \text{ kDa}, D: 1.7, D: 2)$ GPC in chloroform vs. polystyrene standards).<sup>72, 75</sup> Specifically, the PE<sub>2</sub> polymers used in this work is PE<sub>2</sub> Batch 3 (b3) from a recent report by Jones, et al.<sup>72</sup> A full set of characterizing data, including GPC, NMR, MALDI, and elemental analysis, was reported.<sup>72</sup> Regarding previously dopants, commercial  $FeCl_3 \cdot 6H_2O$ , FeBr<sub>3</sub>.  $Fe(Tos)_3 \cdot 6H_2O$ ,  $Fe(ClO_4)_3 \cdot 9H_2O$ ,  $Fe(OTf)_3 \cdot 6H_2O$ ,  $Fe(NO_3)_3 \cdot 9H_2O$ were used. Acetonitrile (99.8%) was purchased from Sigma Aldrich. All purchased materials were used as received.

Film preparation and doping procedure: P3HT thin films (*ca.* 300 nm) were spray casted from a 10 mg mL<sup>-1</sup> toluene solution onto precleaned glass slide. P3HT thin films were then annealed at 130 °C for one hour in the dark, under ambient atmosphere. PE<sub>2</sub> thin films (*ca.* 700 nm) were blade coated from 1:1 chlorobenzene/CHCl<sub>3</sub> (30 mg mL<sup>-1</sup>) using a Zehntner Testing Instruments blade coater (equip with a ZUA 2000 blade) under and IR heat lamp (heating the substrate to *ca.* 60 °C) with an absolute blade height of 650 µm (150 µm above the glass substrate) at blade speed of 30 mm/s. Films were then sequentially doped under ambient atmosphere with the selected concentration of iron(III) salts in an acetonitrile solution. 100 µL of the dopant solution was drop casted on the film (*ca.* 1 cm × 1 cm) and allowed to dope for one minute. After one minute, the dopant solution was pipetted off the film, and then the doped film was rinsed with excess acetonitrile to remove

unreacted dopants. Doped films were then dried in a fume hood on a hot plate at ca. 50 °C for one minute to evaporate excess solvent.

**X-ray Photoelectron Spectroscopy** (**XPS**): XPS was conducted with a Thermo Scientific K-Alpha system. A monochromatic Al K $\alpha$  X-ray source (1486.6 eV) was used with a 60° incident angle and a 90° emission collection geometry. During the measurement, an ion flood gun was used. The spot size of the film was fixed at 400 microns. The step size was fixed at 1.0 eV in the survey scan and 0.1 eV for the high-resolution elemental high-resolution spectra. The detection limit of the XPS can go as low as 1% for light elements like silicon, and down to 0.1% for heavier elements. Since films were measured in different XPS sessions, calibration of the XPS spectra is done with respect with the adventitious carbon position at 284.6 eV.

The deconvolution methods employed here have been reported in previous literature.<sup>95-97</sup> The sulfur high resolution XPS spectra (S 2p) were analyzed using the Avantage software after correcting for charge drift if needed. The peak fitting was performed with a Gaussian-Lorentz sum mix with a simplex fitting algorithm. The main assumption upon doping of the poly(thiophenes) is that despite the delocalization of charge carriers, one can still fit the neutral peaks to a doublet with a separation of 1.2 eV and a FWHM of 0.8-1.2 eV. As discussed by Shallcross *et al.* the polaronic sulfur, it has been assigned as in the literature to be separated by *ca.* 0.6 eV from the neutral peak, with the doublet having 1.2 eV separation and similar FWHM to the neutral sulfur peak. As for the multi-polaron peak, it was suggested that their presence is analyzed using the same procedure earlier and their position is at 0.6 eV higher binding energy than the polaronic feature. As for the tosylate
peak, and the sulfoxide when present, the algorithm optimized the FWHM of these peaks to 1.2- 1.3 eV with a 1.2 eV separation.

The doping level was calculated by calculating the ratio of polaronic and multipolaronic sulfur present to the total sulfur content from the polymer, excluding tosylate but not sulfoxide from the calculation.

**UV-vis-NIR Spectroscopy** (**UV-vis-NIR**): A Cary 5000 instrument was used for UV-vis-NIR spectra using films prepared with the same fabrication procedure illustrated above.

**Fourier-Transform Infrared spectroscopy** (**FTIR**): Thin films were measured using ATR mode on a Shimadzu FTIR.

**Thermoelectric measurements:** Pt contact pads were sputtered using a custom-built shadow mask and sputtering chamber onto pristine films. The contact pads are spaced *ca*. 5 mm apart and arranged in a Van der Pauw geometry. The pristine films with contact pads were then doped and immediately measured after doping to mitigate ambient dedoping effects. A custom-built thermoelectric measurement set up was used that has been described in detail elsewhere.<sup>59</sup> In short, electrical conductivity and Seebeck coefficient measurements were performed in increments of 2.5-5 K between *ca*. 283 K and 373 K, depending on the stability of the polymer-dopant system. Exact temperature ranges are found in the charge transport section for specific temperature ranges for each polymer-dopant system. After thermoelectric measurements, film thicknesses were measured using either a Profilm optical profilometer or a Bruker DektakXT mechanical profilometer.



Figure 5.2. GPC of P3HT used in this study in chloroform.



Figure 5.3. Cyclic voltammetry of P3HT films cast on a platinum electrode with 0.1 M NBu<sub>4</sub>PF<sub>6</sub> as an electrolyte in acetonitrile and referenced ferrocene as an internal standard with 50 mV s<sup>-1</sup> as a scan rate. Onset of oxidation is determined to be +0.30 V vs. ferrocenium / ferrocene, consistent with the literature.<sup>86</sup>



Figure 5.4. <sup>1</sup>H NMR spectrum of P3HT in CDCl<sub>3</sub> used in this study. The headto-head content is determined to be 83%, and was calculated from the relative integrations of the methylene group peaks at 2.8 ppm and 2.5-2.6 ppm.<sup>98</sup>

### 5.3 **Results and discussion:**

### 5.3.1 Experimental Approach

First, preliminary spectroscopic and thermoelectric measurements were performed on P3HT sequentially doped at a fixed concentration (12 mM) of varying iron(III) salts, FeX<sub>3</sub>, for X = Cl, Br, CF<sub>3</sub>SO<sub>3</sub> (OTf), CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub> (Tos), and ClO<sub>4</sub>, using doping procedure as shown in Figure 2.



Figure 5.5. Scheme of sequential doping method used in this study.

Second, Fe(Tos)<sub>3</sub> and Fe(ClO<sub>4</sub>)<sub>3</sub> dopants were selected for extensive evaluation because they produced substantially different transport properties for P3HT in the first step. Detailed UV-vis-NIR, X-ray diffraction, and thermoelectric measurements were performed on P3HT films sequentially doped with concentrations of these dopants ranging from 1.5 mM to 100 mM. Similar measurements were performed on PE<sub>2</sub>, which is more is easier to oxidize and more disordered than P3HT, from 0.1 mM to 12 mM. This comparison quantifies to what extent polymer ordering and ease of oxidation may affect doping susceptibility and transport properties. Third, the transport properties for all four P3HT and PE<sub>2</sub> polymer-dopant combinations were analyzed within the SLoT model. The fundamental parameters extracted from the SLoT model were then related to the spectroscopic and structural measurements to better understand the governing physics and to provide guidance for future studies. **Table 1:** Coordination ability and volume of various anions and solvents used. <sup>99 100</sup> coordination ability is experimentally determined from literature complexes where the species behaved as a complex vs. as a free anion.

Species	Coordination ability	Volume (Å <sup>3</sup> )	Anion 3D shape
Chloride	1.3	61	•
Bromide	1.0	66	
Nitrate	0.1	40	~
Water	-0.1	30	
Acetonitrile	-0.2	66	•
Tosylate	-0.2	154	* <b>\``</b>
Triflate	-0.4	86	<b>~~</b> ~~
Perchlorate	-0.6	86	×

# 5.3.2 Initial survey on the effects of various iron (III) dopants on (thermo)electrical properties

Dopant counterions play an important role in the doping kinetics, thermodynamics, and charge transport properties.<sup>39, 90</sup> Isolating the counterions' role in each of these processes is difficult because the observable spectroscopic and thermoelectric properties result from their convolution. Five iron(III) compounds were screened to probe their impact on the carrier ratio, electrical conductivity, and Seebeck coefficient. For an initial evaluation, P3HT films were sequentially doped with 12 mM acetonitrile solutions of iron(III) chloride, bromide, triflate, tosylate, and perchlorate (Figure 2).

First, the electrical conductivity and Seebeck coefficient of these P3HT films is assessed (**Figure 3**). Electrical conductivities of P3HT films sequentially doped with 12 mM solutions of iron(III) salts show that the P3HT doped with Fe(ClO<sub>4</sub>)<sub>3</sub> is the most conductive (55 S cm<sup>-1</sup>) whereas the P3HT films doped with Fe(Tos)<sub>3</sub> are the least conductive (5 S cm<sup>-1</sup>) (**Figure 3a**). Consistent with this trend, Fe(ClO<sub>4</sub>)<sub>3</sub>-doped films have the lowest Seebeck coefficients (+31  $\mu$ VK<sup>-1</sup>), whereas Fe(Tos)<sub>3</sub>-doped films have the highest Seebeck coefficients (+82  $\mu$ VK<sup>-1</sup>) (**Figure 3b**). These trends in thermoelectric properties are commensurate with the optical absorbance spectra (**Figure 3c**) that also suggest that under these conditions P3HT is likely doped to a greater extent by Fe(ClO<sub>4</sub>)<sub>3</sub> than by Fe(Tos)<sub>3</sub>, evident by the larger polaronic absorption for the first. Lastly, these observations are consistent with a similar comparison of P3HT doping by FeCl<sub>3</sub>, Fe(OTf)<sub>3</sub>, and Fe(Tos)<sub>3</sub> reported by Wu *et al.* while this thesis was under preparation.<sup>86</sup>

X-ray photoelectron spectroscopy (XPS) is used to quantify the extent of doping in the polythiophene films. Deconvolutions of S-2p spectra were used to calculate the ratio of "polaronic" sulfur signals to total sulfur signal,  $^{48,95,101}$  as a measure of the carrier ratio (c)<sup>65</sup> and, therefore, the carrier density (n).<sup>71</sup> Although spectroscopic and thermoelectric measurements suggest that P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> has a greater number of charge carriers than P3HT-Fe(Tos)<sub>3</sub>, XPS calculated carrier ratios are within error for these two salts, and the data for the whole series of salts vary little, giving carrier ratios of ca. 0.22-0.30 (corresponding to 1 carrier for every 3.3-4.5 thiophene rings) independent of the dopant used (including iron(III) triflate, bromide, and chloride) (See Note S5). Although the carrier ratios are nearly comparable, there are several differences amongst these dopant systems. Notably, P3HT films doped with Fe(ClO<sub>4</sub>)<sub>3</sub> showed the formation of thiophene-S-oxides via an oxygen transfer reaction. Additionally, no iron was detected by XPS in films doped with  $Fe(ClO_4)_3$  and  $Fe(OTf)_3$ , likely because both salts contain weakly coordinating anions. Examples of elemental composition of doped films can be seen in table 2 below.

System	С	S	0	Х	Fe	
РЗНТ						
100 mM Fe(Tos) <sub>3</sub>	70.65	20.62	5.62	-	3.09	
100 mM Fe(ClO <sub>4</sub> ) <sub>3</sub>	84.46	7.66	4.29	1.51(Cl)	2.07	
12 mM Fe(Tos) <sub>3</sub>	85.91	7.22	2.5	-	4.36	
12 mM Fe(ClO <sub>4</sub> ) <sub>3</sub>	83.71	7.35	7.53	1.41 (Cl)	-	
12 mM FeCl <sub>3</sub>	61.69	4.78	7.24	15 (Cl)	8.88	
12 mM Fe(OTf) <sub>3</sub>	73.67	3.89	15.29	4.13 (F)	-	
12 mM FeBr <sub>3</sub>	74.66	3.07	20.02	1 (Br)	1.3	

 Table 5.1. Elemental composition tables of pristine and doped films of P3HT and PE2.

# Table 5.1 continued

Pristine	92	8	-	-	-
$\mathbf{PE}_2$					
12 mM Fe(Tos) <sub>3</sub>	82.08	4.79	4.82	-	3.51
12 mM Fe(ClO <sub>4</sub> ) <sub>3</sub>	81.34	4.39	11.82	1.63	-
1.5 mM Fe(Tos) <sub>3</sub>	74	4.71	18.39	-	2.9
1.5 mM Fe(ClO <sub>4</sub> ) <sub>3</sub>	84.72	4.57	9.2	1.05	-
0.1 mM Fe(Tos) <sub>3</sub>	88.58	5.15	4.86		1.42
0.1 mM Fe(ClO <sub>4</sub> ) <sub>3</sub>	86.39	4.39	7.6	0.32	1.3
Pristine	90.39	4.79	4.82	-	-

Ultimately, that the counterion substantially affects the electrical conductivity and Seebeck coefficients, and this is especially apparent between P3HT-Fe(Tos)<sub>3</sub> and P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub>. These two systems have approximately an  $11 \times$  and  $3 \times$  difference in electrical conductivity and Seebeck coefficient, respectively, that cannot be explained solely by the small differences in carrier densities. Therefore, the varying dopant counterion coordination ability, counterion size, and polymer-counterion interactions affect additional optical and charge transport properties that are not commonly nor easily evaluated (*e.g.* optical absorptivity, carrier mobility, localization, and carrier effective masses).<sup>17, 102, 103</sup> Thus it is highly needed to find a reliable method to quantify the relationship between polymer chemistry, dopant chemistry, and their interactions with the observable optical, structural, and charge transport properties, which is attempted in this work.



Figure 5.6. (a) UV-vis-NIR spectra (b) electrical and (c) thermoelectric and (c) XPS spectra of P3HT films doped with different iron(III) salts.

### 5.3.3 Spectroscopic analysis of P3HT and $PE_2$ doped with $Fe(Tos)_3$ and $Fe(ClO_4)_3$

To better understand how and to what extent the nature of the counterion affects transport properties, sequentially doped P3HT and  $PE_2$  with  $Fe(Tos)_3$  and  $Fe(ClO_4)_3$  over a wide range of concentrations are examined. Fe<sup>3+</sup> solution molarities are varied from 1.5 mM to 100 mM for P3HT, and from 0.1 mM to 12 mM for PE<sub>2</sub>. The extent of doping was first qualitatively monitored by UV-Vis-NIR spectroscopy (Figure 7). By comparing the evolution of the polaronic absorption and the disappearance of neutral absorption, optical spectra show that  $PE_2$  is more susceptible to  $Fe(Tos)_3$  and  $Fe(ClO_4)_3$  doping than P3HT (Figure 7). Explicitly, PE<sub>2</sub> pristine  $\pi$ - $\pi^*$  absorbances bleach near 3 mM Fe(Tos)<sub>3</sub> or Fe(ClO<sub>4</sub>)<sub>3</sub> and remains bleached through 12 mM. In contrast, P3HT pristine  $\pi$ - $\pi$ <sup>\*</sup> bleaching requires at least 25 mM Fe(ClO<sub>4</sub>)<sub>3</sub>, and Fe(Tos)<sub>3</sub> cannot effectively bleach the pristine  $\pi$ - $\pi^*$  peak. The ability of less concentrated solutions to bleach the pristine  $\pi$ - $\pi^*$  absorption of  $PE_2$  is consistent with its less positive oxidation potential (onsets of oxidation are 0.3 V and -0.5 V vs. ferrocene for P3HT and PE2).72,86,104 Additionally, the significant differences in the P3HT-Fe(Tos)<sub>3</sub> and P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> UV-Vis-NIR spectra suggest that the doped P3HT changes in optical absorptions is heavily influeced by dopant counterion while PE2 is rather agnostic to the counterion.



Figure 5.7. UV-vis-NIR spectra of doped (a-b) P3HT , and (c-d) PE2.

To quantify the extent of doping, the carrier ratio, and the doping mechanisms in P3HT and PE<sub>2</sub> films, XPS is used.. **Figure 8a-c** shows representative deconvoluted spectra for pristine and 12 mM doped P3HT films, and **Figure 8d-f** shows representative deconvoluted spectra for the pristine and 12 mM doped PE<sub>2</sub> films.

Regarding the P3HT spectra (**Figure 3a-c**), pristine and neutral thiophene peaks occur between *ca*. 163 and 164.5 eV, electrically oxidized thiophene (polaronic) peaks occur between *ca*. 164.5 and 166 eV, and sulfonate peaks (from tosylate or sulfones) occur between *ca*. 167 and 170 eV. Notably, find  $Fe(ClO_4)_3$  results in the formation of sulfur

species with binding energies at *ca*. 167 eV as well as electrically oxidizing, *i.e.* doping, to form polaronic carriers. The 167 eV binding energy is assigned to the formation of thiophene oxides; this observation is further confirmed with FTIR measurements, has been previously reported in literature, and will be discussed in detail in the next section.<sup>105, 106</sup> To approximate the carrier ratio, the thiophene S-2p feature is deconvoluted into neutral sulfur contributions and polaronic sulfur (denoted as S\*) contributions, where the ratio of the S\* peak area to the total thiophene (and thiophene oxide, where applicable) peak area is taken to be equal to the number of holes per thiophene unit, as previously demonstrated using XPS studies of electrochemically oxidized films.<sup>48, 95, 101, 107</sup> Additionally, for Fe(Tos)<sub>3</sub>-doped films, the extent of oxidation was also quantified using the abundance ratio of tosylate counterions (using the sulfoxide doublet at *ca*. 168 eV for Fe(Tos)<sub>3</sub> doped films) with respect to thiophene.<sup>76</sup> Lastly, for P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> films, the extent of oxidation was also calculated by deconvoluting the C-1s spectra of  $Fe(ClO_4)_3$ -doped P3HT (Figure 10). The pristine  $sp^3$  and  $sp^2$  carbon fall under one peak at 284.6 eV, and as the doping level increases a new peak 286.2 eV emerges, increases, and is attributed to oxidized aromatic carbons from the polymer main chain.<sup>108, 109</sup>

PE<sub>2</sub> spectra (**Figure 8d-f**) show similar features to the P3HT spectra, but the doped PE<sub>2</sub> films show additional features at binding energies between 166 and 167.5 eV (denoted S\*\* in **Figure 8**) when doped with either Fe(Tos)<sub>3</sub> or Fe(ClO<sub>4</sub>)<sub>3</sub>. Previous studies on PEDOT and P3HT have attributed the S-2p energies near 166 eV to multi-polaronic charge carriers, but the exact assignment is not clear.<sup>48, 77, 101, 110, 111</sup> For example, Wegner *et al.* correlated the presence of higher binding energies in P3HT doped using [B(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with EPR measurements, and they assigned features at *ca.* 166 eV to bipolaron formation.<sup>22</sup> In contrast, Marrikar *et al.* assigned binding energies near 166-168 eV to heterogeneously doped and oxidized regions in PEDOT films.<sup>107</sup> Lastly, we note that pristine PE<sub>2</sub> is susceptible to air oxidation and doping; this is observed in **Figure 8d** with peaks intensities at higher binding energies (166 eV). This air doping can result in electrically conductive PE<sub>2</sub> thin films (*ca.* 15 S cm<sup>-1</sup> at 35 nm)<sup>72</sup> and is notably evident in the S-2p spectra because XPS is a surface-sensitive technique; however, thicker PE<sub>2</sub> films show low electrical conductivities (*ca.* 10<sup>-4</sup> S cm<sup>-1</sup> at 150 nm),<sup>72</sup> and the undoped PE<sub>2</sub> films in this study (*ca.* 700 nm thick) do not have an observable electrical conductivity.



Figure 5.8. Representative XPS S 2p spectra for P3HT and PE<sub>2</sub>. (a) pristine P3HT. (b) P3HT doped with 12 mM Fe(OTs)<sub>3</sub>. (c) P3HT doped with 12 mM Fe(ClO<sub>4</sub>)<sub>3</sub>. (d) pristine PE<sub>2</sub>. (e) PE<sub>2</sub> doped with 12 mM Fe(OTs)<sub>3</sub>. (f) PE<sub>2</sub> doped with 12 mM Fe(ClO<sub>4</sub>)<sub>3</sub>.

For each polymer-dopant chemistry-dopant molarity combination, the carrier ratio and the extent of thiophene oxide formation is calculated. The carrier ratio is quantified using the previously described methods: (1) the ratio of S\* and S\*\* to total thiophene abundance, (2) the ratio of tosylate to total thiophene abundance, and (3) the ratio of oxidized aromatic carbons to aromatic carbons, as calculated from the ratio of aromatic carbons to aliphatic carbons. Figure 5 shows the changes in the XPS S 2p spectra when P3HT and PE2 are doped at varying dopant molarity.



Figure 5.9. S 2p XPS spectra of doped P3HT (a-b), and (c-d) PE2

For P3HT (Figure 11a), as the dopant concentration increases, the extent of electrical oxidation and the polaronic abundance increases. Specifically, at high doping

levels (> 25 mM), the average extent of electrical oxidation begins to saturate at *ca*. 0.35 (*i.e.* corresponding to ca. one charge carrier for every three rings). This extent of electrical oxidation is consistent with previously reported spectroscopic and electrochemical P3HT doping studies.<sup>53, 95, 112</sup> Additionally, **Figure 11a** shows that at most dopant concentrations, P3HT films doped by  $Fe(Tos)_3$  or  $Fe(ClO_4)_3$  have similar S\* carrier concentrations, consistent with the initial analysis in **Figure 2**. Lastly, in the case of  $Fe(ClO_4)_3$ -doped P3HT- films, there is an increasing amount of chemically oxidized sulfoxide rings present, and this begins to saturate near 35% as well.



# Figure 5.10. C 1s deconvoluted spectra of (a) P3HT and (b) $PE_2$ doped with $Fe(ClO_4)_3$

Figure 11b shows that with increasing solution molarity, the  $PE_2$  films, like P3HT films, become increasingly doped; however, doping saturates at a greater carrier ratio of *ca*. 0.5, or one charge carrier per two thiophene rings. This carrier ratio is consistent with

previous PEDOT reports.<sup>52, 76, 111</sup> The thiophenes in PE<sub>2</sub> are less susceptible to chemical oxidation to sulfoxide by  $Fe(ClO_4)_3$  than P3HT (reaching a maximum level of *ca.* 10% *vs.* 35%). It is possible that the S---O interaction in the PE<sub>2</sub> backbone could contribute to the kinetic barrier for the oxygen-transfer reaction, while higher levels of electrical doping may also hinder oxygen-transfer oxidation because with a greater extent of doping on the PE<sub>2</sub> relative to P3HT, the increased positive charge per thiophene repeat unit may make the sulfur more to difficult to chemically oxidize. Similar to P3HT, Fe(Tos)<sub>3</sub> and Fe(ClO<sub>4</sub>)<sub>3</sub> result in roughly the same carrier ratio in PE<sub>2</sub> when used as the same molarity.



Figure 5.11. Relative ratio of doping calculated from XPS spectra as a function of solution concentration for (a) P3HT. (b) PE<sub>2</sub>.  $S^* + S^{**} = (multi)$ polaronic sulfur, S=O sulfoxide, Tos = tosylate, C\* = doped carbon ratio from C 1s spectra. Note that data are presented on a logarithmic x-axis for clarity.

### 5.3.4 FTIR Spectra of P3HT doped with Fe(ClO<sub>4</sub>)<sub>3</sub>

P3HT and PE<sub>2</sub> films doped with  $Fe(ClO_4)_3$  show high-binding energy S 2p peaks in the XPS spectra (**Figure 8**), suggesting the formation of S–O bonds, although the amount as seen in figure X is much lower in PE<sub>2</sub>. These high-binding energy peaks are not observed with other Fe<sup>3+</sup> salts. To confirm the presence of S-O bonds, FTIR spectroscopy of doped

and dedoped films is used. Sulfoxides ( $R_2S=O$ ) typically show IR absorptions in the 1030-1070 cm<sup>-1</sup> range, whereas sulfones ( $R_2S(=O)_2$ ) absorb at *ca*. 1200 cm<sup>-1</sup>. **Figure 12** clearly shows that P3HT films doped with Fe(ClO<sub>4</sub>)<sub>3</sub> and subsequently dedoped with hydrazine exhibit IR spectra that are most consistent with the formation of sulfoxides. In contrast, P3HT doped with FeCl<sub>3</sub> and then dedoped with hydrazine do not show the S=O absorbance. This suggests that a strong oxidizing counterion is needed for an observable level of sulfuroxygen bond formation. Lastly, the peak at 1650 cm<sup>-1</sup> is characteristic of the perchlorate ion,<sup>113</sup> and this peak is only evident in P3HT when doped with Fe(ClO<sub>4</sub>)<sub>3</sub>.

Although initial XPS and FTIR evidence indicate the sulfoxide formation, we explore other hypotheses to determine the conditions leading to the sulfoxide formation. First, **Figure 12, 15** indicates no reaction between hydrazine and P3HT. Additionally, doping of P3HT films with FeCl<sub>3</sub> then dedoping them with hydrazine resembles IR of neat P3HT films. Notably, the sulfoxide formation is indeed dependent on the concentration of the dopant solution used as evident in **Figure 14** where the intensity of both S=O and Cl=O peaks increase with increase in dopant solution concentration.

The role of oxygen is examined next. FTIR spectra of P3HT films doped using iron(III) perchlorate in air, show the formation of S=O whereas that doped under an inert atmosphere show no presence of S=O (**Figure 13**). This negates the hypothesis that the new peaks are only due to the perchlorate anion and suggests that air, and doping with iron(III) perchlorate are needed for the formation of S=ONext, the role of dedoping is investigated. Although a doped film without the exposure to air does not show formation of S=O, when doped and dedoped under nitrogen gas, when exposed to air to be dedoped

with hydrazine vapor, the S=O is observed (**Figure 14**). This suggests that the presence of the perchlorate anion in the P3HT film leads to the formation of S=O on air exposure



Figure 5.12. FTIR spectra of P3HT films doped, then dedoped by exposure to hydrazine vapor. The films are washed with acetonitrile. The gray spectrum represents P3HT film exposed to hydrazine vapor only then washed with acetonitrile as a control. The blue spectrum represents a neat P3HT film.



Figure 5.13. Comparison of P3HT IR doped under air vs. under inert atmosphere to understand role of oxygen in formation of S=O



Figure 5.14. FTIR of P3HT films doped with various solution molarities of Fe(ClO<sub>4</sub>)<sub>3</sub>, in air, then dedoped with hydrazine vapor, and washed with acetonitrile. The gray spectrum represents a neat P3HT film.



Figure 5.15. FTIR spectra of neat P3HT films (blue), doped/dedoped in air (red), doped and dedoped under nitrogen atmosphere then exposed to air (gray).

5.3.5 Structural analysis of P3HT and  $PE_2$  doped with  $Fe(Tos)_3$  and  $Fe(ClO_4)_3$ 

To investigate the structural impact of doping, XRD patterns of pristine and increasingly doped films are examined (**Figure 5**). For P3HT films doped with Fe(Tos)<sub>3</sub> (**Figure 5a**), increasing the molarity shifts the (100) peaks to a lower angle, indicative of increasing the lamellar stacking distance between adjacent polymer chains. This increase is consistent with incorporation of dopant species between the alkyl side chains. Additionally, there is a consistent decrease in peak intensity with increase in doping level, suggesting that some of the crystallites are being interrupted by the tosylate anion. Notably, the peak width is not significantly impacted, indicating that the size of some crystallites is constant throughout the doping process in some areas while other areas have large amounts

of tosylate ions and are no longer crystalline. Ultimately, we believe that the tosylate ions are inhomogeneously distributed and reduces the ordering in the P3HT-Fe(Tos)<sub>3</sub> films.

For Fe(ClO<sub>4</sub>)<sub>3</sub>-doped P3HT films, increasing the molarity shifts the (100) peaks to a lower angle and increases the distance between lamellar stacks, similar to what is seen for Fe(Tos)<sub>3</sub>. In contrast, however, the P3HT-ClO<sub>4</sub> (100) peak intensity remains nearly constant, suggesting that the perchlorate anions, which are around half the size of tosylate ions, intercalate with the alkyl chains of the P3HT polymer with little disruption to the microstructure.<sup>114</sup> Interestingly, the formation of the sulfoxide by chemical oxidation does not seem to significantly alter crystallinity, which could be indicative of the oxidation mostly occurring in the amorphous regions of the films. Overall, these observations are consistent with those reported by Wu *et al.*, who used GIWAXS measurements to study how different iron(III) salts affect the microstructure; similarly, they found that Fe(Tos)<sub>3</sub>

Lastly, GIXRD patterns for  $PE_2$  show no discernable diffraction peaks, under the same conditions used for P3HT, consistent with previously reported GIWAXS measurements indicating this material is considerably more disordered than P3HT.<sup>72</sup>



Figure 5. Grazing Incidence X-ray Diffraction (GIXRD) patterns for doped P3HT films with (a) Fe(ClO<sub>4</sub>)<sub>3</sub> and (b) Fe(Tos)<sub>3</sub>

The full width at half maximum of the (100) peaks of the P3HT films doped with iron (III) tosylate or iron (III) perchlorate have been calculated and are tabulated below. Note that the FWHM did not substantially change as a function of dopant chemistry or concentration, indicating that the size of the crystalline domains did not substantially change and appear to be independent of doping chemistry and concentration.

# Table 5.2. FWHM of (100) peaks (in degrees) for doped P3HT films

Concentration	<b>FeCl</b> <sub>3</sub>	Fe(Tos)3	Fe(ClO <sub>4</sub> )3
0 mM	0.75	0.74	0.74
1.5 mM	0.79	0.65	0.73
6 mM	0.85	0.64	0.72
25 mM	0.74	0.66	0.67
100 mM	0.77	0.74	0.73

5.3.6 Effect of dopant selection on P3HT and PE<sub>2</sub> fundamental transport parameters, analyzed through the SLoT model

To better understand the different transport properties of P3HT and PE<sub>2</sub> doped with  $Fe(Tos)_3$  and  $Fe(ClO_4)_3$ , the temperature dependent Seebeck coefficients, electrical conductivities, and carrier ratios are analyzed within the Semi-localized transport (SLoT) model. As discussed in chapter 1, The SLoT model isolates energy dependent contributions to charge transport and energy independent contributions to charge transport using a metal-like Boltzmann transport formalism<sup>17, 115</sup> with a hopping-like thermal activation prefactor.<sup>91</sup>

Figure 16a plots the  $\eta(c)$  relationship for Fe(Tos)<sub>3</sub>- and Fe(ClO<sub>4</sub>)<sub>3</sub>-doped P3HT. Figure 16a shows that the  $\eta(c)$  relationships P3HT-Fe(Tos)<sub>3</sub> and P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> are significantly different, suggesting that the dopant selection alters the  $\eta(c)$  curve and therefore the filling and the formation of electronic states. The x-intercept of the  $\eta(c)$  vs. c plot can be used to quantitatively compare the  $\eta(c)$  curves for the different system combinations.

The x-intercept is indicative of the minimum carrier ratio (density) needed for the Fermi energy level to enter the "band", and this value is labelled as  $c_t$ . From experimental observations,  $c_t$  for P3HT-Fe(Tos)<sub>3</sub> is 0.02, which is similar to the observed  $c_t$  for P3HT-FeCl<sub>3</sub> in the original SLoT study and P3HT-NOPF<sub>6</sub>. In contrast,  $c_t$  for P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> is 0.18, which indicates that P3HT doped with Fe(ClO<sub>4</sub>)<sub>3</sub> requires *ca*. 9′ more carriers for  $E_F > E_t$  in comparison to P3HT-Fe(Tos)<sub>3</sub>. Although  $c_t$  is larger for P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub>, **Figure 16a** shows that P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> has a steeper (larger slope)  $\eta(c)$  curve in comparison to P3HT-Fe(Tos)<sub>3</sub>. In this case, the larger slope is correlated with a steeper increase in electrical conductivity. Notably, at similar carrier ratios (*ca*. 0.33),  $\eta$  is *ca*. 6 and 14 for P3HT-Fe(Tos)<sub>3</sub> and P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub>, respectively. At the carrier ratio of 0.33, P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> has the higher  $\eta$  value, so its charge carriers occupy higher energy levels, and lead to higher electrical conductivities (107 *vs*. 44 S cm<sup>-1</sup>). These carrier densities, conductivities, and qualitative trends are consistent with those reported by Wu *et al.* for Fe(Tos)<sub>3</sub> and Fe(OTf)<sub>3</sub> doped P3HT, where they employed AC Hall effect measurements.<sup>116</sup>

Next,  $W_{\rm H}(c)$  represent the depth of the potential wells that localizes charge carriers.  $W_{\rm H}$  is calculated from temperature-dependent electrical conductivity and Seebeck coefficient measurements. **Figure 16b** plots the  $W_{\rm H}(c)$  experimental data, and P3HT-Fe(Tos)<sub>3</sub> and P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> have different  $W_{\rm H}(c)$  relationships.  $W_{\rm H}(c)$  models are used for quantitative comparison and this model's mathematical expression is built upon Mott's work for disordered inorganic semiconductors.<sup>91</sup>

 $W_{\rm H}(c) = W_{\rm H,max}$  when c = 0, and it is the y-intercept in **Figure 16b**. In this study,  $W_{\rm H,max}$  for P3HT-Fe(Tos)<sub>3</sub> is *ca*. 290 meV, which is similar to  $W_{\rm H,max}$  for P3HT-FeCl<sub>3</sub> and P3HT-NOPF<sub>6</sub> systems previously reported. In contrast,  $W_{\rm H,max}$  for Fe(ClO<sub>4</sub>)<sub>3</sub> doped P3HT is *ca*. 690 meV, which is within error of the value obtained for oxidatively polymerized PEDOT.<sup>76</sup> A large  $W_{\rm H,max}$  indicates that carriers at low doping levels are localized in potential wells. From a chemical perspective, it is likely that P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> has a large  $W_{\rm H,max}$  due to the sulfoxide formation.  $W_{\rm H,slope}$  is indicative of how quickly localization diminishes with increasing carrier concentration; as  $W_{\rm H,slope}$  increases,  $W_{\rm H}$  approaches zero faster.  $W_{\rm H,slope}$  for P3HT-Fe(Tos)<sub>3</sub> is *ca*. 350 meV where in contrast,  $W_{\rm H,slope}$  for Fe(ClO<sub>4</sub>)<sub>3</sub>-doped P3HT is *ca*. 970 meV, which is quite large and similar to values for oxidatively polymerized PEDOT and poly(acetylene).

 $W_{\rm H,slope}$  and  $W_{\rm H,max}$  will determine the critical carrier ratio where  $W_{\rm H}(c) = 0$  and delocalized (degenerate and metal-like) transport behavior is expected to become dominant.  $c_d$  for P3HT-ClO<sub>4</sub> is *ca*. 0.33, while  $c_d$  for P3HT-Tos is not observed. The electrical conductivities of several P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> films showed little thermal activation energy and some demonstrated thermal deactivation (metal-like temperature dependence) near 300 K.

Next is  $\sigma_0$ , which is the transport function prefactor, and it is independent of doping level.  $\sigma_0$  is most easily calculated from the  $S - \sigma$  curve in the degenerate regime (**Figure 16c**). In general, polymer-dopant-processing systems with larger  $\sigma_0$  values will have larger electrical conductivities at a fixed Seebeck coefficient. Additionally, the SLoT curves begin to coincide with degenerate transport model curves (Kang-Snyder *s* =1 model) when  $W_{\rm H}(c) < k_{\rm B}T$ . Data points at electrical conductivities lower than this intersection are dominated by localized contributions, while data points at electrical conductivities greater than this intersection are dominated by delocalized contributions.

**Figure 16c** shows that at a fixed Seebeck coefficient, the P3HT-Fe(Tos)<sub>3</sub> data points are at a higher electrical conductivity (right-shifted) with respect to the P3HT- $Fe(ClO_4)_3$  data points. This right shifting could be because either P3HT-Fe(Tos)<sub>3</sub> has less localized charge carriers or because P3HT-Fe(Tos)<sub>3</sub> has a larger  $\sigma_0$  value. In addition, P3HT-Fe(Tos)<sub>3</sub> charge carriers are always localized while P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> charge carriers eventually achieve delocalized transport (**Figure 16b**). Lastly, P3HT-Fe(Tos)<sub>3</sub> data points and the SLoT model curve do not coincide with their metal-like transport curve because  $W_{\rm H}(c) > k_{\rm B}T$  at all doping levels; the lowest  $W_{\rm H}$  values for P3HT-Fe(Tos)<sub>3</sub> were on the order of 40 meV. In contrast, the P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> system achieves low localization energies, and a metal-like  $S - \sigma$  curve. Ultimately, from **Figure 16c**  $\sigma_0$  is 30 S cm<sup>-1</sup> for P3HT-Fe(Tos)<sub>3</sub> and 7 S cm<sup>-1</sup> for P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub>.

Although the values of  $\sigma_0$  may seem counterintuitive, recall that  $\sigma_0$  is (ideally) independent of the doping level, Fermi energy level, and the localization energy.<sup>17</sup> Instead,  $\sigma_0$  is a function of the energy-independent and characteristic charge-carrier mobilities, relaxation times, and electronic band curvatures (in an ideal parabolic system).<sup>102</sup> In these ideal cases and in absence of localization effects,  $\sigma_0$  increases as the number of electronic states per energy level increases.<sup>17, 102</sup> On the other hand,  $PE_2$  is less crystalline and more susceptible to oxidation.<sup>75, 117, 118</sup> Figure 16d shows the calculated reduced Fermi energy level as a function of the carrier ratio for PE<sub>2</sub> doped with Fe(Tos)<sub>3</sub> and Fe(ClO<sub>4</sub>)<sub>3</sub>. In comparison to P3HT (Figure 16a), PE<sub>2</sub> exhibits much higher  $\eta$  values (*ca.* 50 vs. 14), lower Seebeck coefficients (ca. 7 vs. 20  $\mu$ V K<sup>-1</sup>), and higher maximum extents of oxidation (ca. 0.5 vs. 0.35). PE<sub>2</sub> has an  $\eta(c)$  relationship that is more independent of dopant selection in comparison to P3HT, with subtle differences between PE<sub>2</sub>-Fe(Tos)<sub>3</sub> and PE<sub>2</sub>-Fe(ClO<sub>4</sub>)<sub>3</sub>. For example, PE<sub>2</sub>-Fe(Tos)<sub>3</sub> has a  $c_t$  value closer to 0.12, similar to that seen in a PEDOT:PSS electrochemical transistor study.<sup>52</sup> In contrast, PE<sub>2</sub>-Fe(ClO<sub>4</sub>)<sub>3</sub> has a  $c_t$  values closer to 0.23, closer to that seen in a PEDOT-Fe(Tos)<sub>3</sub> study.<sup>76</sup> In this lightly doped and low  $\eta$  regime, Fe(ClO<sub>4</sub>)<sub>3</sub> chemically oxidizes PE<sub>2</sub> to form some sulfur-oxide moieties which may trap some carriers, similar to what is seen in the P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> system. Lastly, in general, the  $\eta(c)$  curves for PE<sub>2</sub> are right-shifted in comparison to the P3HT  $\eta(c)$ curves suggesting that PE<sub>2</sub> generally has a greater ratio of carriers below  $c_t$  in comparison to P3HT.

Both PE<sub>2</sub> data sets have similar  $W_{\rm H}(c)$  curves, with  $W_{\rm H,max}$  values of ca. 600 meV and  $W_{H,slope}$  values of ca. 850 meV. Notably, PE<sub>2</sub> has a larger  $W_{H,max}$  in comparison to most P3HT systems (Fe(Tos)<sub>3</sub>, FeCl<sub>3</sub>, NOPF<sub>6</sub>), and this may be because pristine PE<sub>2</sub> is more disordered than pristine P3HT. PE<sub>2</sub> also has a larger  $W_{H,slope}$  in comparison to most P3HT systems, and this may be because the XDOT backbone is substituted with alkoxy groups with more possible resonance structures to delocalize the positive charges in comparison to P3HT. Nonetheless, using the SLoT model provides quantitative comparisons for understanding to what extent are the charge carriers localized and to what extent does that localization decrease with increasing carrier ratio. cd for the PE<sub>2</sub> systems is ca. 0.35, which is greater than that for previously reported PEDOT-Fe(Tos)<sub>3</sub> (ca. 0.2). This large difference in  $c_d$  may be due to electrically insulating side chains in PE<sub>2</sub>, which are not found in the previously reported oxidatively polymerized PEDOT. This demonstrates that increasing  $c_{\text{max}}$  (without significantly increasing scattering events or deleteriously disrupting the microstructure) and decreasing the ratio of  $c_d/c_{max}$  appears to be a strategy to improve the macroscopic and observable electrical conductivities and mobilities.

**Figure 16f** shows the  $S - \sigma$  plot for PE<sub>2</sub>, the degenerate s = 1 curve, and the SLoT model curve with no freely adjustable parameters. Overall, the SLoT model better captures the curvatures, slopes, and nominal coordinates better than the leading degenerate model. Additionally, both PE<sub>2</sub> doped with Fe(Tos)<sub>3</sub> and Fe(ClO<sub>4</sub>)<sub>3</sub> have similar curvatures, slopes, and coordinates, so the same SLoT model curve with the same conductivity prefactor ( $\sigma_0$  = 9 S cm<sup>-1</sup>) is used to model both data sets.

Lastly, PE<sub>2</sub> achieves electrical conductivities 3-5 × larger than P3HT with the same dopant species at lower solution molarities (12 mM *vs.* 100 mM). At a common *c*, *e.g.* 0.35, both P3HT and PE<sub>2</sub> have an  $\eta$  near 14 (**Figure 16a, d**). This means that both systems have carriers with roughly the same energetic contribution to the Seebeck coefficient and electrical conductivity. This holds true for most *c* values greater than *c*<sub>t</sub> in both systems. Therefore, the energy-dependent contribution to electrical conductivity does not explain this difference in maximum electrical conductivity. Similarly, at this carrier ratio, both systems have similar localization energies ( $W_{\rm H} < k_{\rm B}$ T) and ultimately electrical conductivities (*ca.* 100 S cm<sup>-1</sup>). From these observations and the fact that both systems have the same  $\sigma_0$  (within error), PE<sub>2</sub> and P3HT doped with Fe(ClO<sub>4</sub>)<sub>3</sub> have nearly identical transport properties in this study. Therefore, PE<sub>2</sub>-Fe(ClO<sub>4</sub>)<sub>3</sub> obtains significantly higher electrical conductivities than P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> largely because PE<sub>2</sub> obtains higher carrier ratios and reduced Fermi energy levels that are not accessible to P3HT (**Figure 16a,c**).



Figure 5.16. SLoT transport property analysis of P3HT and PE<sub>2</sub> doped with Fe(Tos)<sub>3</sub> and Fe(ClO<sub>4</sub>)<sub>3</sub> at varying molarities. (a) P3HT and (d) PE<sub>2</sub> reduced Fermi energy level as a function of the carrier concentration. (b) P3HT and (e) PE<sub>2</sub> activation energies as a function of the carrier concentration ratio. (c) P3HT and (f) PE<sub>2</sub> S- $\sigma$  plots. Individual data points are represented by open data points, and doping level averages are represented by filled data points with sample to sample standard deviation error bars. Dashed lines represent a nominal Kang-Snyder s = 1 curve, and solid lines represent SLoT model curves, calculated with no freely adjustable paramters. Figure is courtesy of Shawn Gregory.

#### 5.4 **Conclusion and Perspective:**

This study examined the doping susceptibility and transport properties of two poly(thiophene) derivatives, P3HT and PE<sub>2</sub>, with a variety of different iron(III) salts at different concentrations. Among the salts studied,  $Fe(ClO_4)_3$  imparted P3HT with the highest electrical conductivities, lowest Seebeck coefficients, and most strongly absorbing polaronic absorptions while  $Fe(Tos)_3$  yielded the lowest electrical conductivities, highest Seebeck coefficients, and weakest polaronic absorptions, despite comparable charge

carrier densities suggested by XPS measurements and deconvolution calculations. This indicates that the choice of salt significantly affects charge-transport properties. For  $PE_2$ , which is more disordered, easier to oxidize, and can support a higher carrier ratio compared to P3HT, the differences between Fe(Tos)<sub>3</sub> and Fe(ClO<sub>4</sub>)<sub>3</sub> are less evident.

The SLoT model is used to quantify how the charge carriers contributed to the observable transport properties. P3HT-  $Fe(ClO_4)_3$  has a larger number of charge carriers "trapped" below the transport edge in comparison to P3HT- Fe(Tos)<sub>3</sub>, likely due to the thiophene oxide formation. In contrast, at high doping levels,  $P3HT-Fe(ClO_4)_3$  exhibits delocalized transport while P3HT-Fe(Tos)<sub>3</sub> does not, likely because Fe(Tos)<sub>3</sub> disrupts the microstructure to a greater extent. Ultimately P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub>achieves larger electrical conductivities and lower Seebeck coefficients in the highly doped limit (*ca.* 107 S cm<sup>-1</sup> and +20  $\mu$ V K<sup>-1</sup> at 100 mM). In contrast, PE<sub>2</sub> doped with either Fe(Tos)<sub>3</sub> or Fe(ClO<sub>4</sub>)<sub>3</sub> achieves similar transport properties and can be modeled sufficiently well using the same curve on the S- $\sigma$  plot. This further confirms the earlier conclusion that PE<sub>2</sub> is less sensitive to the choice of iron salt. At the high doping limit, PE<sub>2</sub>-Fe(ClO<sub>4</sub>)<sub>3</sub> achieves transport properties of 313 S cm<sup>-1</sup> and  $+7.3 \mu$ V K<sup>-1</sup> at 12 mM, which is 10 × more dilute than that used in P3HT. A thorough transport analysis suggests that  $PE_2$ -Fe(ClO<sub>4</sub>)<sub>3</sub> achieves higher electrical conductivities and lower Seebeck coefficients than P3HT-Fe(ClO<sub>4</sub>)<sub>3</sub> because the PE<sub>2</sub>- $Fe(ClO_4)_3$  system can achieve higher extents of electrical oxidation (*i.e.* more charge carriers) and higher reduced Fermi energy levels.

For future studies, it should be noted that the chemistry of different iron(III) salts can significantly alter the resulting transport properties. Additionally, increasing the extent

of oxidation and/or the extent of ordering does not necessarily guarantee an increase in the electrical conductivity, but increasing these parameters are likely good approaches towards high electrical conductivities. Lastly, the SLoT model provides a quantitative framework for understanding the effects of dopant and polymer selection on the observable transport properties (*e.g.*, *S*,  $\sigma$ ) and the fundamental transport parameters (*e.g.*,  $c_t$ ,  $c_d$ ,  $W_H(c)$ ,  $\eta(c)$ ,  $\sigma_0$ ) and for relating these effects to changes in electronic and structural properties.

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#### CHAPTER 6. SUMMARY AND FUTURE WORK

This chapter aims to summarize the results described in chapters 2-5, and their key contributions to the field of organic semiconductors and their doping, and suggest future avenues for research based on the work in this thesis. This thesis have provided contributions to the field of organic electronics by doping of conjugated materials for electron transport materials (chapter 2), developing stable perovskite solar cells using naphthalene diimide transport layers (chapter 3). In addition, a family of dopants along with their reactivity studies were investigated in chapter 4. Chapter 5 investigated the impact of iron(III) salt choice on the charge transport properties of polythiophene derivatives.

#### 6.1 Strategies to improve the conductivity of electron transport materials

Chapter 1 presented strategies documented in the literature to improve the electrical conductivity of doped polymers. Since the charge carrier mobilities and conductivities of electron transport materials and their doped derivatives are generally lower than those reported for doped hole transport materials, these were a focus of the work reviewed in chapter 1. The strategies used in the literature to improve the conductivity are categorized in table 1 below.

## Table 6.1. Summary of strategies to improve conductivity discussed in chapter1.

Charge carrier mobility	Common factors	Charge carrier density
Polymer: dopant interactions	Polymer- dopant miscibility	Full electron transfer
Polymer inter/ intramolecular interactions	Dopant (ion) and (doped) polymer stability	
Fabrication and doping method		
Side chain branching		

Other approaches have recently emerged in the literature in order to improve the conductivity of electron transport polymers. These strategies are gaining more traction as more publications documenting their success get published. A notable development is the usage of nickel based organic-inorganic polymers to obtain highly conducting n type polymers, often without the need for additional dopants due to the manner of their synthesis, which affords directly partially doped material.<sup>1-3</sup> Structures of one such class of polymers (figure 1) and examples of the highest conductivity values reported in the literature are shown in table 6.2. One drawback of these polymers is, however, that they are not readily soluble in common organic solvents and, therefore, cannot be processed by many of the methods applicable to typical polymers, often requiring dispersion in polymer

matrices.<sup>1</sup> As such a promising strategy could be the investigation of similar analogues to this polymer due to the high conductivity values already reported as seen in a recent review.<sup>1</sup> In addition, recent reports have shown utility for using inorganic co-monomers with organic polymers to improve their conductivity. For example Liu and coworkers reported the incorporation of platinum(II) acetylide inside in polythiophene to form a block polymer where the conductivity ca be improved from 55 to 76 S cm<sup>-1</sup> when the platinum(II) acetylide comonomer is incorporated in 1% ratio.<sup>4</sup>



Figure 6.1. Structures of NiTTO and A[NiETT].

Table 6.2. Examples of conductivities of nickel based polymers

Polymer	$\sigma$ (S cm <sup>-1</sup> )	Processing	Reference
Na[NiETT]	52	Drop cast from ethylene	3
		glycol	
NiETT	220	Electrochemical deposition	2
K[NiETT]	44	Pellet	5
NiTTO	31	Pellet	6

A third is the p doping of hole transport materials where high level of doping can lead to electrons being the dominant transported carriers as opposed to holes. Although this might not be optimal for an electron injecting electrode application for example, since the heavily doped p-doped material will have a high electron affinity, they are being investigated towards thermoelectric applications.<sup>7</sup>

Recall that the Seebeck effect originates from carrier diffusion across a polymer sample. In doped organic polymers, a positive Seebeck coefficient is associated with hole transport whereas a negative one is associated with electron transport. The literature shows that this is merely inferred from the experiment conducted *i.e.* when an electron transport polymer is *n*-doped rather than a universal phenomenon. This is due to the fact that Seebeck sign have been shown to flip in polyaniline for instance upon modifying the pH, crystallinity, direction of alignment, as well as contributions from metallic relative to hopping transport in doped polymers.<sup>8-18</sup>

From a physics standpoint, the Seebeck coefficient is defined via equation 1 below. In equation 1  $k_B$  is Boltzmann constant, T is the temperature, and q is the elementary charge. From equation 1, it is evident that the position of the Fermi level with respect to carrier energy (E) can influence the sign. Figure 6.2 shows a sketch of the Fermi level with respect to the density of states in a typical *n*- and *p*-doped semiconductors. In addition, it is worth noting that the picture is not as straightforward in organic polymers which can have energetic disorder, and a mixture of hopping and metallic transport regimes.<sup>10, 18-20</sup> It is possible to flip the sign with sufficient electrical doping or processing modifications in a system so that the Fermi level is pushed to lie near the middle of a band of electronic states.<sup>8, 12, 16, 17, 21</sup>

$$\alpha = -\frac{k_B}{q} \int \left(\frac{E - E_F}{k_B T}\right) \frac{\sigma(E)}{\sigma} dE \quad (1)$$

In metals, for instance, a large number of mobile electrons can reside near the Fermi energy level leading to a positive Seebeck coefficient to be observed. In organic materials



Figure 6.2. Sketch of density of states of n and p doped semiconductors.

however, a sign flip cannot be the only evidence to claim a change in the nature of the charge transport but rather need to be coupled with other spectroscopic and electrical techniques.

Recently, Liang and coworkers demonstrated a negative Seebeck coefficient along with direct evidence for electron transport through hall effect measurements are possible with heavily doped hole-transport polymers.<sup>7</sup> In the case of FeCl<sub>3</sub>-doped diketopyropyrolle-thiophene copolymers, increase in electrical doping led to diminishing the transport gap, observed experimentally via ultra-violet and inverse photoelectron spectroscopy and the

Fermi energy level then lies at the intersection of two bands. To further prove that the charge transport can be unequivocally be ascribed to electrons AC Hall effect measurements were used as well.

In addition, Zeng and coworkers demonstrated the same phenomena in oriented diketopyropyrrole polymers fabricated by high temperature rubbing also doped with FeCl<sub>3</sub>.<sup>22</sup> The researchers further confirmed the role of the density of states by establishing a direct correlation between the molecular weight of the polymer, that affects the density of states mainly impacting the polarity switching between *p* to *n* type conductivity.<sup>22</sup>

In the near future, it is plausible that the research focus in advancing the conductivity of electron transport materials could either focus on improving the conductivity of existing polymers such as those by Pei and coworkers through dopant: polymer: processing manipulations or shift towards investigating electron transport in heavily doped hole transport polymers.

#### 6.2 **Doping of electron transport small molecules and polymers**

Doping of PNBS sequentially with (DMBI)<sub>2</sub> produced conductivities up to 2 mS cm<sup>-1</sup> and conductive films that were stable in air up to one hour. In addition, doping of two small-molecule naphthalene diimide dimers produced conductivities up to 7 mS cm<sup>-1</sup> with the same dopant.

A future project could be the utilization of pyridine rings. Although the heterocycle is not expected to contribute to the electronic structure of the LUMO in the polymer the nitrogen can be used in order to be alkylated (figure 6.3). However, alkylation of the pyridine ring

can lower the LUMO of the ring, making it a better mediator for NDI-NDI intrachain coupling. Once alkylated the cationic nature of the nitrogen can be used to generate a self-compensated polymer once doped. Upon doping the dopant cation  $D^+$  could be washed away with the counterion of the ammonium ion (X<sup>-</sup>) (figure 6.3). It is worth noting, that this will only apply for NDI units reduced, so when the polymer is doped at 50 mol% for example, X<sup>-</sup> can still be present for balancing the pyridinium positive charge.



#### Figure 6.3. Structure of NDI py polymer and possible doping reaction.

### 6.3 Naphthalene diimides small molecules and polymer as electron transport materials in perovskite solar cells

Chapter 3 reported the utilization of various small molecules and a side chain polymer in n-*i*-p perovskite solar cells. The side chain NDI polymer exhibited solvent resistance against DMF-DMSO and perovskite solar cells incorporating this polymer power conversion efficiency (PCE) up to 14%, superior to that of several small molecules

examined, and comparable to those of cells using  $SnO_2$ . Although we demonstrated the utility of the NDI polymer as a transparent layer producing stable devices, there are several future projects that can stem from the observations seen during this study.

First, the wettability of the side-chain polymer by the active perovskite layer precursor solution can be improved. Although the wettability of the polymer was improved by using a mesoporous alumina layer that allowed for deposition of the perovskite layer was used in chapter 3, it is worth investigating approaches to remove the need for an interlayer all together. In order to improve the wettability one can think of modifying the solubilizing alkyl chain on the polymer by introducing a more polar side chain by on the naphthalene diimide molecules. This is inspired from recent work done to improve perovskite wettability on top of PCBM in *n-i-p* devices by using polyethylene glycol as an additive.<sup>23</sup> Example structures of polymers can be seen in figure 6.4 below. The rationalization in case of polymer 1 and its variants, for example, is to optimize the wettability by varying the length of the ethylene glycol chain. This can be done to make either one or both side chain based on ethylene glycol, *i.e.* polymer 2.



Figure 6.4. Structures of potential target polymers.

Second, the impact of UV light on ND1-1 and the subsequent device performance needs to be investigated. This is because NDI-1absorbs in the UV region and upon probing the effect of light on performance the initial results below show a clear effect of light on device performance. Upon aging NDI-1 films under 1 sun at 60 °C in air, for 3 days the device performance diminished in comparison to aging the films in absence of light at the same conditions. UV-vis-NIR and PL spectra of aged films can be seen in figure 6.5 as well as the PCE of devices fabricated from fresh vs. aged films. These results show the impact of the light interaction with NDI-1. Although the UV-vis spectrum does not show significant changes, the diminishing in the PL intensity could indicate a change in the aggregation/ self-assembly in the solid state as seen in previous reports. It would be then of interest to investigate the role of UV light (since NDI-1 absorbs between 350 - 400 nm) on the performance of devices both in the short and long term.



Figure 6.5. PL spectrum (A), PCE (B), and UV-vis (C) spectra of NDI-1 films that are fresh or aged under 1 sun, in air at 60 °C.

#### 6.4 Organic Dopants based on Y-DMBI-H and their dimers

Chapter 4 reported the synthesis of various Y-DMBI-H compounds and their dimers. In addition to reporting multigram synthesis with high yields, the chapter discussed the impact of the Y substituent on the redox and reactivity with common acceptors in solution. In addition to the dopants shown in chapter 4 other substituents have been investigated but were not successful on first attempt in synthesis of the hydride and/ or dimer compounds. The structures of these compounds can be seen in the figure below. Future dopant design studies can also investigate the usage of stronger  $\pi$  donors at the Y position or on the benzoimidazole 6-membered ring. Some suggested dopant structures and substituents to investigate are shown in figure 6.6 below.



Figure 6.6. Structures of future Y-DMBI-H and (Y-DMBI)<sub>2</sub> to investigate.

In addition, the MeO-substituted hydride donors (**4'aH** and **4'bH** in chapter 4) can be used to probe whether they can react with acceptors N-DMBI-H does not dope.

Another potential future direction is to compare the utilization of the various Y-DMBI-H and their dimers from chapter 4 on the conductivity of common electron-transporting polymers to differentiate between their performance in terms of target organic electronic applications. The variables in this case would be the resulting cations size and shape. In addition, once the solid state phase separation *vs*. miscibility of the various dopants can be investigated as well.

In addition, DFT calculations can be used in combination with the results shown in chapter 4 to provide a more comprehensive understanding of the relation between the chemical structure of the Y-DMBI dopants shown in the chapter and their reactivity.

A fourth potential avenue for future work would be direct comparison of the impact of doping mechanism kinetics *i.e.* Y-DMBI-H *vs.* (Y-DMBI)<sub>2</sub> on the conductivity of electron transport polymer. Y-DMBI-Hs are attractive since they are air stable in the solid state, provide air stable cations but on the downside need to be heated for extended periods of times to thermally activate the reaction along with their complex mechanism of hydride transfer. On the other hand, (Y-DMBI)<sub>2</sub> dopants are clean electron donors, produce the same cations as Y-DMBI-H, and do not require heating. A downside for these is that since they can react so quickly they will result in forming the doped polymer, which is often air sensitive, almost instantaneously. An example study could be that with BDPPV, which can achieve up to 90 S cm<sup>-1</sup> when doped with Y-DMBI-H.<sup>25</sup>This can provide insight into the role of doping kinetics and reactions complexity, or lack thereof, on electrical performance. The overarching picture would be investigating the role of doing kinetics on the processing and ultimately the conductivity of the polymer used.

# 6.5 Investigating doping of electron rich polymers polythiophenes doping with iron(III) salts

Chapter 5 presented doping studies of P3HT and PE<sub>2</sub> with various  $Fe^{3+}$  compounds to illustrate the impact of various counterion on doping level, conductivity, and thermoelectric performance. Ultimately P3HT doped with  $Fe(ClO_4)_3$  was 33% doped with 107 S cm<sup>-1</sup> conductivity while PE<sub>2</sub> could be doped up to 50% with conductivities up to 300 S cm<sup>-1</sup>. The study also utilized the SLoT model in order to investigate the impact of dopant-polymer-processing system on fundamental charge transport properties.

A potential future direction would be to utilize the same approach studied in chapter 5 in other common hole transport materials, like those discussed in chapter 1 that show high conductivity upon high temperature rubbing for example. In addition, the SLoT analysis can be used in those systems to also provide quantitative insights to the charge transport properties of the polymer : dopant system.

Another approach would be to investigate the easily doped polymer  $PE_2$ , upon heavy doping, and whether one can switch its Seebeck coefficient and identify whether or not the charge carrier transport can be switched from holes to electrons.

In brief, this thesis have presented multiple projects to investigate charge transport properties of conjugated materials along with their dopants to inspire the design of future organic materials. In addition, the future directions outlined in this chapter can be used to build upon the findings of this thesis.

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