

UCLA

UCLA Electronic Theses and Dissertations

Title

Understanding Charge Transport in Chemically Doped Conjugated Polymers: The Roles of the Dielectric Environment, Ambient Stability, Counterion Interactions, and Microstructure

Permalink

<https://escholarship.org/uc/item/8jr7v2np>

ISBN

9798191649603

Author

Garcia Vidales, Diego

Publication Date

2026-09-18

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA

Los Angeles

Understanding Charge Transport in Chemically Doped Conjugated Polymers:
The Roles of the Dielectric Environment, Ambient Stability, Counterion Interactions, and
Microstructure

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Chemistry

by

Diego Garcia Vidales

2026

© Copyright by

Diego Garcia Vidales

2026

ABSTRACT OF THE DISSERTATION

Understanding Charge Transport in Chemically Doped Conjugated Polymers:
The Roles of the Dielectric Environment, Ambient Stability, Counterion Interactions, and
Microstructure

by

Diego Garcia Vidales

Doctor of Philosophy in Chemistry

University of California, Los Angeles, 2026

Professor Benjamin J. Schwartz, Chair

Conjugated polymers are organic semiconductors with extended π -electron systems that enable charge transport in these lightweight, flexible, and solution-processable materials. Their low thermal conductivity and relatively high Seebeck coefficients make them promising candidates for soft thermoelectric devices. However, pristine conjugated polymers possess low electrical conductivity due to their wide bandgaps and limited free carrier density at room temperature. Improving their performance therefore requires strategies that increase carrier density while supporting efficient charge delocalization.

This dissertation investigates chemical doping as a route to enhance the electrical and thermoelectric properties of semiconducting polymer films, with a focus on understanding how the dielectric environment, environmental stability, dopant identity, doping method, and pristine microstructure shape charge transport. A combination of four-point probe conductivity, Seebeck coefficient, Hall effect, temperature-dependent conductivity, and X-ray scattering measurements, as well as steady-state and time-resolved spectroscopies, is used to develop a multiscale picture of transport in doped semiconducting polymer systems.

The first half of this dissertation focuses on understanding anion-exchange doping, a doping method that has been shown to boost the doping levels achieved with relatively weak molecular dopants while allowing precise control over the counterion that intercalates into the polymer film. Chapter 2 examines the origin of the enhanced carrier generation observed during anion-exchange doping. By separating the initial molecular doping step from subsequent electrolyte exposure, we show that the high-dielectric electrolyte environment can increase the effective oxidizing power of an already-reduced dopant anion, enabling a second electron-transfer event with the polymer backbone. This double-doping process nearly doubles the carrier density, demonstrating that the dielectric environment plays a central role in the enhanced doping efficiency associated with anion-exchange doping.

Chapter 3 builds on this mechanistic understanding by examining how the choice of counterion affects electrical conductivity and environmental stability under ambient conditions. Although anion-exchange doping enables control over the choice of counterion, many electrolyte salts used for this process are hygroscopic and can introduce counterion-dependent ambient stability limitations. We demonstrate that hygroscopic counterions incorporated during anion exchange can draw ambient water into the polymer, leading to strong reductions in electrical

conductivity. Hall effect and optical measurements reveal that humidity primarily suppresses carrier mobility rather than carrier density, indicating that absorbed water introduces additional trapping sites that localize polarons.

Chapter 4 investigates how dopant identity and doping method influence the Seebeck–conductivity relationship and charge transport in doped poly(3-hexylthiophene-2,5-diyl) (P3HT). By comparing the classic dopant 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ), two large (~2-nm diameter) dodecaborane-based dopants, and anion-exchange doping, we show that different dopants modulate carrier transport through distinct mechanisms. Large counterions reduce Coulomb trapping and lower hopping barriers, while anion-exchange doping enhances mesoscale connectivity by enabling doping of amorphous regions. Using temperature-dependent conductivity and the Semi-Localized Transport (SLoT) model, we show that both routes can improve the thermoelectric performance depending on how they reshape the energetic and structural landscape of the doped film.

Chapter 5 explores how the microstructure of pristine P3HT governs carrier transport after doping. By systematically varying the polymer regioregularity, we can tune crystallinity and domain connectivity before introducing carriers through anion-exchange doping. UV–vis–NIR and transient absorption spectroscopy show that higher-crystallinity polymers support greater intradomain delocalization. Surprisingly, Hall effect and temperature-dependent conductivity measurements reveal that at low doping levels, less crystalline P3HT samples exhibit higher macroscopic carrier mobility due to superior mesoscale connectivity. At higher doping levels, these mesoscale-connectivity-driven mobility differences become less dominant, and the higher-regioregularity, more crystalline P3HT films exhibit more favorable charge transport. These results

highlight the interplay between local order and long-range domain connectivity in determining charge transport.

Collectively, this dissertation establishes how the carrier environment—whether altered by the dielectric constant of a doping solution, relative humidity, dopant–counterion interactions, or the intrinsic polymer structure—governs carrier delocalization and mobility in doped conjugated polymers. Understanding these multiscale relationships provides a foundation for designing higher-performance thermoelectric materials and, more broadly, for controlling charge transport in soft electronic systems.

The dissertation of Diego Garcia Vidales is approved.

William M. Gelbart

Richard B. Kaner

Daniel Neuhauser

Benjamin J. Schwartz, Committee Chair

University of California, Los Angeles

2026

TABLE OF CONTENTS

LIST OF FIGURES	xi
LIST OF TABLES	xxii
Acknowledgements.....	xxiii
Publications and Contributions	xxvi
VITA	xxix
CHAPTER 1 Introduction	1
1.1 Semiconducting Conjugated Polymers	1
1.2 Chemical Doping: Introducing Carriers While Preserving Structure	3
1.2.1 Fundamentals of p-Type Doping and Polaron Formation.....	3
1.2.2 Solution (Blend) Doping and Its Limitations.....	4
1.2.3 Sequential Processing: A Morphology-Preserving Alternative.....	5
1.2.4 Anion-Exchange Doping: Expanding the Design Landscape	6
1.3 Charge Transport in Conjugated Polymers	7
1.3.1 Structural Disorder in Semicrystalline Polymers.....	7
1.3.2 Energetic Disorder and Coulomb Trapping	8
1.4 Dissertation Overview and Goals	9
1.4.1 Chapter 2: Dielectric Enhancement of Doping Ability in Semicrystalline Conjugated Polymers	10
1.4.2 Chapter 3: Humidity and Environmental Stability in Anion-Exchange-Doped P3HT	11
1.4.3 Chapter 4: Dopant Identity, Coulomb Interactions, and the S– σ Relationship.....	12
1.4.4 Chapter 5: Pristine Microstructure and Its Influence on Delocalization After Doping	14
1.5 References.....	15
CHAPTER 2 Double Doping of Conjugated Polymers Can Be Induced by the High-Dielectric Environment Present During Anion-Exchange Doping	20
Abstract	21
2.1 Introduction.....	22
2.2 Results and Discussion	26
2.2.1 Anion Exchange Enables Double Doping in a High-Dielectric Environment.....	29
2.2.2 Structural Changes in Double-Doped PBTTT Films	35
2.2.3 Estimating the Magnitude of the High-Dielectric Doping Boost	37
2.3 Conclusions.....	40
2.4 Experimental Section	41
2.4.1 Materials	41
2.4.2 Film Preparation.....	41

2.4.3 Optical and Electrical Characterization	43
2.4.4 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) Measurements	43
2.4.5 Cyclic Voltammetry (CV) Measurements.....	43
2.5 References.....	44
CHAPTER 3 The Effects of Humidity on the Electrical Properties and Carrier Mobility of Semiconducting Polymers Anion-Exchange Doped with Hygroscopic Salts	49
Abstract	50
3.1 Introduction.....	51
3.2 Results and Discussion	54
3.2.1 Device Fabrication for Doped Semiconducting Polymer Thin Films	54
3.2.2 Methods for Measuring Electrical Conductivity and Hall Effect	54
3.2.3 Electrical Conductivity and Hall Effect Results	55
3.2.4 Near-IR Spectroscopy of the Polaronic P1 Peak	58
3.2.5 Probing Electrical Conductivity as a Function of Controlled Relative Humidity	61
3.3 Conclusion	63
3.4 References.....	64
CHAPTER 4 How the Carrier Mobility and Seebeck Coefficient of Doped Semiconducting Polymers Are Controlled by Counterion Interactions and Mesoscale Order	67
Abstract	68
4.1 Introduction.....	69
4.2 Results and Discussion	76
4.2.1 UV–Vis–NIR Spectroscopy	77
4.2.2 Probing Film Morphology Using Grazing-Incidence Wide- and Small-Angle X-ray Scattering	80
4.2.3 Seebeck Coefficient–Electrical Conductivity Relationship.....	86
4.2.4 Hall Effect Measurements.....	88
4.2.5 Probing the Activation Energy, W_H , via Temperature-Dependent Conductivity	90
4.2.6 Semi-Localized Transport (SLoT) Model.....	93
4.3 Conclusions.....	96
4.4 Experimental	97
4.4.1 Device Preparation.....	97
4.4.2 Film Characterization.....	98
4.5 References.....	99
CHAPTER 5 The Role of Microstructural Disorder in the Charge Transport Characteristics of Doped Semiconducting Polymers.....	106
Abstract	107
5.1 Introduction.....	108
5.2 Results and Discussion	111

5.2.1 Macroscopic Conductivity and Seebeck Coefficient Measurements in Different Semicrystalline P3HT Films Doped via Anion Exchange	111
5.2.2 Probing Film Morphology of Semicrystalline P3HT Films	114
5.2.3 Probing the Microscale Charge-Transport Characteristics of Anion-Exchange-Doped P3HT with Different Regioregularities.....	120
5.2.4 Macroscopic Length-Scale Charge Transport – Hall and Activation Energy of Anion-Exchange-Doped P3HT	127
5.2.5 Thermoelectric Performance of Different Anion-Exchange-Doped P3HT Polymers	132
5.3 Conclusions.....	137
5.4 Experimental Section/Methods	138
5.4.1 Materials	138
5.4.2 Sample Preparation	139
5.4.3 Film Characterization.....	140
5.5 References.....	142
Appendix A Supporting Information for Chapter 2: Double Doping of Conjugated Polymers Can Be Induced by the High-Dielectric Environment Present During Anion-Exchange Doping	150
A.1 UV–Vis–NIR Spectroscopy	151
A.1.1 Solvent Washing.....	151
A.1.2 Polaronic Peak Location Indicates Successful DDB-F ₆₀ [–] Exchange for TFSI [–]	154
A.1.3 Oscillator-Strength-Weighted P1 Peak Areas	156
A.2 Electrical Conductivity and Hall Effect Measurements.....	159
A.3 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS).....	160
A.4 Cyclic Voltammetry (CV) of PBTTT and DDB-F ₆₀	167
A.5 References	169
Appendix B Supporting Information for Chapter 3: The Effects of Humidity on the Electrical Properties and Carrier Mobility of Semiconducting Polymers Anion-Exchange Doped with Hygroscopic Salts	172
B.1 Materials.....	173
B.2 Film Fabrication and Doping	173
B.3 Conductivity and Hall Measurements	173
B.4 UV–Vis–NIR Spectroscopy	177
B.5 Humidity-Sensing Measurement.....	178
Appendix C Supporting Information for Chapter 4: How the Carrier Mobility and Seebeck Coefficient of Doped Semiconducting Polymers Are Controlled by Counterion Interactions and Mesoscale Order	179
C.1 Materials.....	180
C.2 UV–Vis–NIR Spectroscopy	180

C.3 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS).....	181
C.4 Grazing-Incidence Small-Angle X-ray Scattering (GISAXS).....	188
C.5 Electrical Conductivity Measurements	191
C.6 Seebeck Coefficient Measurements	193
C.7 Hall Effect Measurements	195
C.8 Measurements of the Activation Energy, W_H	198
C.9. The Transport Function, σ_E , and the Semi-Localized Transport (SLoT) Model	199
C.10 References	201
Appendix D Supporting Information for Chapter 5: The Role of Microstructural Disorder in the Charge Transport Characteristics of Doped Semiconducting Polymers	204
D.1 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS).....	205
D.2 Grazing-Incidence Small-Angle X-ray Scattering (GISAXS).....	210
D.3 UV–Vis–NIR Spectroscopy	214
D.4 Transient Absorption Spectroscopy	218
D.5 Electrical Conductivity Measurements	220
D.6 Hall Effect Measurements and P1-Correlated Carrier Density	221
D.7 Seebeck Coefficient	229
D.8 Activation Energy Measurements via Temperature-Dependent Conductivity.....	230
D.9 S – σ Relation and the Semi-Localized Transport (SLoT) Model.....	231
D.10 References	234

LIST OF FIGURES

Figure 1.1. (a) Schematic of a thermoelectric device. (b) Seebeck coefficient (S), electrical conductivity (σ) and figure of merit plotted as a function of carrier density, showing the inverse relationship between S and σ as the carrier concentration is increased. This trade-off between S and σ results in a “sweet spot” in carrier concentration for optimizing the ZT of a thermoelectric device.	2
Figure 1.2. Neutral P3HT polymer backbone before the charge transfer process with a molecular dopant. Chemical doping creates a radical cation, resulting in backbone reorganization from an aromatic to a quinoid structure. The lattice distortion, along with the radical cation, is referred to as a polaron (purple shading). This structural reorientation also changes the electronic structure of the polymer, creating two new intragap energy states between the bandgap (BG) transition. These new energy levels give rise to two new optically allowed polaronic transitions, labeled P1 and P2. The blue circle represents the dopant counterion that remains inside the polymer film after the doping process is complete.	4
Figure 1.3. Overview of the sequential processing (SqP) method and representative materials used throughout this dissertation. (a) In sequential processing, a pristine polymer film is first deposited from solution and then exposed to a dopant-containing solution, allowing dopants and/or electrolyte ions to enter the pre-formed film without dissolving the polymer. (b–d) Chemical structures of representative semiconducting polymers, anion-exchange electrolyte salts, and molecular dopants used to control carrier density, counterion identity, and charge transport in doped conjugated polymer films.	6
Figure 1.4. Energetic schematic depicting charge carriers (blue circles) moving through a disordered energy landscape by hopping between localized states. The right cartoon shows a semicrystalline polymer film with both ordered domains (darker purple) and amorphous regions, where chain bends, kinks, grain boundaries, and disrupted packing create structural and energetic disorder. The zoomed-in circle shows polarons (blue ovals) experiencing Coulomb interactions with dopant counterions (orange circles).	8
Figure 2.1. (a) Structures of the polymers, dopant, and electrolyte used for investigating the extra oxidizing power achieved by anion-exchange doping in this work. (b) Energy level diagram for the conjugated polymers, PBTTT-C14, regioregular (RR) and regiorandom (RRa) P3HT, as well as the dodecaborane cluster (DDB-F ₆₀) in the presence and absence of electrolyte (LiTFSI). The idea is that the electrolyte increases the dielectric constant of the dopant solution, which in turn increases the dielectric constant of the solvent-swollen polymer film, allowing dopants to more easily remove electrons from conjugated polymers. Here, we focus on the example where the dielectric enhancement of anion exchange allows the DDB-F ₆₀ [−] anion to dope PBTTT, something that is not possible with conventional doping. The HOMO levels for PBTTT and RR P3HT were obtained from Refs. [27–29] and Refs. [30,31], respectively. The energy level offset between RR and RRa P3HT was obtained from Refs. [32–34].	24
Figure 2.2. UV–vis–NIR absorption spectra for (a) PBTTT doped conventionally with 1 mM DDB-F ₆₀ and PBTTT doped with 1 mM DDB-F ₆₀ and then subjected to 2-pot AED with different LiTFSI concentrations. The intensities of the P1 and P2 polaronic bands increase with increasing electrolyte concentration, as denoted by the gray arrows, indicating that the high-dielectric environment with 2-pot AED can achieve double doping of PBTTT. (b) Absorption spectra of	

PBTTT films doped with both 1 mM (solid curves) and 2 mM (dashed curves) DDB-F₆₀ solutions using both the conventional (red curves) and 2-pot AED (blue curves) methods, where the LiTFSI concentration was fixed at 104 mM. Panel (c) displays a zoomed-in view of the P1 polaron absorption peak for PBTTT doped with 1 mM DDB-F₆₀ and the same sample following 2-pot AED with 104 mM LiTFSI. The shaded areas indicate the spectral regions used to calculate the oscillator-strength-weighted integrated P1 areas in panel (d). Panel (d) compares the normalized oscillator-strength-weighted P1 areas (solid bars) and Hall carrier densities (striped bars) for the doped PBTTT samples shown in panel (c). Both the P1 areas and Hall carrier densities increase by ~2× following 2-pot AED at high electrolyte concentrations, verifying double doping. 30

Figure 2.3. Integrated GIWAXS diffractograms of pristine PBTTT (purple curves), PBTTT doped conventionally with DDB-F₆₀ (red curves), PBTTT doped by the traditional 1-pot anion-exchange method with DDB-F₆₀ and LiTFSI (green curves), and PBTTT doped via 2-pot AED (blue curves). (a) The out-of-plane integrations show that doping PBTTT with DDB-F₆₀ results in a PBTTT structure with a highly expanded lamellar spacing, with scattering peaks denoted by the red (*h*00)' labels. As the large DDB-F₆₀⁻ anion is exchanged with the smaller TFSI⁻ anion via 2-pot AED, a shift of the lamellar scattering peaks back to higher *q*-spacing values is observed, indicating that the 2-pot exchange was successful. The lamellar peak positions are at identical *q*-spacing values following both 1-pot and 2-pot anion exchange, indicating that the same doped final structure is reached independent of how the anion exchange was accomplished. Panel (b) shows the in-plane integrated diffractograms, which again verify that the two anion-exchange processes lead to the same final PBTTT structure. 36

Figure 2.4. UV-vis-NIR spectroscopy of (a) regioregular (RR) P3HT (green curve) and (b) regiorandom (RRa) P3HT (yellow curve), demonstrating that double doping using 2-pot AED with DDB-F₆₀ followed by LiTFSI (blue curves) does not occur for polymers with deeper HOMO levels than PBTTT. The spectra show a blue shift of the P1 band as the counterion is exchanged from the DDB-F₆₀⁻ anion to the TFSI⁻ anion, as expected for the smaller counterion size.^[21–23] (c) Oscillator-strength-weighted P1 peak areas of the conventionally doped and 2-pot AED-doped samples, showing that for the P3HT polymers with their deeper HOMOs, the 2-pot AED process leads to no change in overall doping levels. 39

Figure 3.1. Near-IR spectra of 0.1 mg/mL F₄TCNQ + 30 mg/mL LiTFSI (AE) and 0.5 mg/mL F₄TCNQ (Conv) samples. The blue side of the P1 polaron absorption, which is associated with trapped carriers, for (a) an anion-exchange-doped P3HT film and (b) a conventionally-doped P3HT film that had been exposed to ambient conditions as a function of time after purging with dry N₂. Purging clearly decreases the blue P1 absorption for the anion-exchange-doped sample while having no effect on the conventionally-doped sample, consistent with the idea that humidity lowers the mobility of carriers in the anion-exchange-doped films. The inset in **Figure 3.1a,b** shows the same spectra extended deeper into the IR region, including the absorption of the water O–H stretch near 2700 nm (this absorption appears to go in opposite directions in the two panels because of the way the spectra were base-lined; see text). 60

Figure 3.2. Electrical conductivity of conventionally- (0.5 mg/mL F₄TCNQ, red circles) and anion-exchange-doped (0.1 mg/mL F₄TCNQ with 30 mg/mL LiTFSI, green squares, and 0.1 mg/mL F₄TCNQ with 5 mg/mL LiPF₆, purple triangles) P3HT films as a function of percent relative humidity in air. The ordinate plots the relative change in conductivity compared to that measured at 15% RH, the lowest we could obtain with this setup. The conductivity change is

highly linear down to ~20% RH, suggesting that the doped polymer films anion-exchanged with LiTFSI could possibly be used as resistance-based humidity sensors..... 63

Figure 4.1. Chemical structures of P3HT and the various dopants used in this study. Two doping methods are used in this study: conventional and anion-exchange. For the conventional doping method, we utilize three dopants: F₄TCNQ, DDB-F₃₆, and DDB-F₇₂, which vary in oxidizing power from weakest to strongest, respectively. The weakest dopant, F₄TCNQ, is primarily able to dope only crystalline regions of P3HT. The two boron cluster dopants are stronger oxidants, and although the oxidation power difference between the DDB-F₃₆ and DDB-F₇₂ dopants is ~200 mV, their equally large counterions reside in the lamellae in the polymer lattice upon doping. For the anion-exchange method, the dopant is F₄TCNQ and the electrolyte is LiTFSI. The anion-exchange doping method allows for control over the nature of the dopant's counterion, and the presence of the electrolyte provides an extra oxidative boost allowing doping of both amorphous and crystalline regions in the polymer matrix. 73

Figure 4.2. UV–vis–NIR spectra of doped P3HT films using different dopants/methods: (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, and (d) anion exchange (AE) at various doping levels. All four doping methods produce the P1 and P2 absorption bands characteristic of polarons, as well as decrease the absorption intensity of the P3HT bandgap. The bandgap bleach is less apparent for the two DDB dopants because the DDB anions absorb near 2.4 eV, overlapping the P3HT bandgap transition. The vibronic structure near 1.5 eV and the peak near 3.0 eV in panel (c) come from the F₄TCNQ anion. The legend in the anion exchange samples shows the final F₄TCNQ concentrations. The LiTFSI concentration was kept constant at 104.5 mM. 78

Figure 4.3. Out-of-plane (panel a) and in-plane (panel b) integrated GIWAXS data for pristine P3HT (black curve) and for the most highly-doped P3HT samples for each dopant shown in **Figure 4.2**. Specific dopant concentrations were 1 mM DDB-F₃₆, 3.62 mM F₄TCNQ, and 3.62 mM F₄TCNQ combined with 104.5 mM LiTFSI for the anion exchange sample. For P3HT doped using DDB-F₇₂, the data shown correspond to the second-highest concentration (0.3 mM), because there is a drop in the electrical conductivity and Hall carrier mobility due to amorphization of the film at the highest doping concentration. 81

Figure 4.4. Seebeck coefficient–conductivity (S – σ) relationship for P3HT doped at different levels with various dopants/counterions. The dashed curves are fits to the SLoT model (**Equations (4.2–4.4)**), with parameters summarized in **Table 4.1** and in Appendix C. Both the DDB-based dopants and anion-exchange doping show significantly higher Seebeck coefficients for the same electrical conductivity compared to F₄TCNQ-doped P3HT samples..... 87

Figure 4.5. (a) Hall effect measurements for P3HT films doped at different levels with various dopants. The x-axis is the Hall carrier density (rather than dopant concentration) since the different dopants and methods have different doping efficiencies. The DDB-based dopants and anion-exchange method show significantly higher Hall mobility at a given carrier density than the samples doped using F₄TCNQ. Panel (b) shows how the R_g obtained from GISAXS changes as a function of the Hall carrier density when P3HT (pristine, black circle) is doped using DDB-F₇₂, DDB-F₃₆, F₄TCNQ, and via anion exchange. **Table 4.1** summarizes the R_g values for samples doped at a carrier density of $\sim 5 \times 10^{20} \text{ cm}^{-3}$. Most dopants produced smaller domains upon doping, but anion-exchanged samples show larger domains because of doping-induced crystallization of the amorphous parts of the film. 89

Figure 4.6. (a) The experimentally measured activation energy, W_H , for P3HT films doped with different dopants as a function of Hall carrier density. The W_H values are obtained using temperature-dependent conductivity measurements and fitting to the Arrhenius equation. The DDB-based dopants show the fastest drop in W_H upon doping (largest slope) compared to anion-exchange doping or doping with F4TCNQ. (b) The (general lack of) relation between W_H and R_g from GISAXS. 92

Figure 4.7. Relationship between σ_0 , obtained from SLoT fitting of electrical and thermal measurements, and R_g values, obtained from GISAXS, at all measured carrier densities. The trend indicates that as the domain length increases, the intrinsic conductivity improves proportionally, regardless of the doping level for each dopant. The orange curve is to help guide the eye. 94

Figure 5.1. Electrical conductivity (left axes) and Seebeck coefficient (right axes) for (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT samples doped via anion exchange with different concentrations of F4TCNQ along with a constant LiTFSI electrolyte concentration of 30 mg/mL. For all four P3HT polymers, the typical inverse relationship between electrical conductivity and Seebeck coefficient was observed with increasing doping levels. The arrows point toward the appropriate y-axis for each data set. Note that the x-axes have different values as the dopant concentrations were chosen to give a similar range of conductivity values for each material. 113

Figure 5.2. Out-of-plane (a) and in-plane (b) GIWAXS integrations for pristine P3HT samples (dashed curves): 99% RR P3HT (red), 97% RR P3HT (blue), 93% RR P3HT (green), and RRa P3HT (yellow). Out-of-plane (c) and in-plane (d) GIWAXS integrations for the highest anion-exchange-doped samples for each P3HT regioregularity are shown as solid curves, with the same colors as in (a) and (b). Insets in the out-of-plane panels show the lamellar overtones normalized to the height of the (200) peak for pristine samples and the (300) peak for doped samples. Peaks labeled with an asterisk (*) in the doped P3HT films are due to scattering from excess LiTFSI. 116

Figure 5.3. (a) UV-vis-NIR spectra of pristine P3HT films with different regioregularities (99% RR, 97% RR, 93% RR, and RRa P3HT). Inset: Energy-level diagram showing the bandgap (BG) and polaronic transitions of doped conjugated polymers. Exciting the P1 transition leads to an increase in P2 absorption. (b) Normalized P1 absorption region of anion-exchange-doped P3HT films for representative samples (99% RR Low, 97% RR High, 93% RR High, and RRa Low) doped using different F4TCNQ concentrations (0.05, 0.5, 1, and 1 mg/mL, respectively) while maintaining a constant LiTFSI electrolyte concentration of 30 mg/mL. These doping conditions were chosen to match carrier densities in the different samples (see **Figure D6**). (c) P1 peak energy versus maximum P1 absorption intensity, obtained by Gaussian fitting (see **Figure D8** in Appendix D), for all four P3HT polymers for different doping concentrations (see **Figure D6**). Circles indicate the samples selected for ultrafast transient (TA) absorption measurements. Colored blocks are used as visual guides for polymers with different regioregularities. (d) Slower induced P2 decay times extracted from TA measurements for the circled samples in **Figure 5.3c** (dashed bars), plotted alongside their corresponding steady-state P1 peak positions (solid bars). The TA decay times, which are a measure of the local carrier mobility, follow the same trend as the P1 peak positions, with doped 99% RR and 97% RR P3HT samples exhibiting faster decay dynamics than 93% RR and RRa P3HT. 122

Figure 5.4. (a) Relation between carrier mobility and carrier density for the four different doped P3HT samples. Carrier mobility and density values for the 99% RR P3HT (red), 97% RR P3HT (blue), and 93% RR P3HT (green) samples were measured via Hall effect measurements. For RRa P3HT (yellow), carrier density was estimated from the oscillator-strength-weighted P1 peak area (calibrated using the 97% RR and 93% RR P3HT samples; see **Figure D12** in Appendix D). The circled data points correspond to the same samples whose P1 peaks and TA dynamics are highlighted in **Figure 5.3c,d**. (b) Radius of gyration, R_g , obtained from GISAXS (see Appendix D), as a function of carrier density for pristine and doped P3HT films with different regioregularities. The fact that the RR samples' mobility inverts between the blue and white regions corresponds directly to when the R_g values of the different samples become similar. (c) Activation energy (E_a) as a function of carrier density for the different doped P3HT samples. E_a values were obtained as the slope of Arrhenius fits to the temperature-dependent conductivity versus $(k_B T)^{-1}$, shown in **Figure D15** in Appendix D. 131

Figure 5.5. Thermoelectric properties of 99% RR, 97% RR, 93% RR, and RRa P3HT films doped via anion exchange, including (a) the Seebeck coefficient–conductivity (S – σ) relation and (b) the power factor (PF). The dashed curves in **Figure 5.5a** represent fits to the SLoT model, with parameters presented in **Table 5.1**. The higher-RR P3HT samples exhibit better thermoelectric performance than the lower-RR P3HT samples, whose properties are more strongly limited by local disorder and reduced mesoscale connectivity. 134

Figure 5.6. Behavior of σ_0 , the intrinsic conductivity in the SLoT model, as a function of relative crystallinity (out-of-plane lamellar (100) peak area) for the most-doped P3HT samples. The more crystalline 99% RR and 97% RR P3HT samples exhibit higher intrinsic conductivities than the lower-crystallinity 93% RR and RRa P3HT samples. 136

Figure A1. UV–vis absorption spectra of polystyrene films under various conditions. The black curve shows the spectrum of pristine PS. The red and blue curves show the same film after soaking in a 1 mM DDB-F₆₀ solution before and after washing with ACN, respectively. The green and yellow vertical dashed lines show the energies where the DDB-F₆₀[−] anion and neutral DDB-F₆₀ species absorb, respectively, indicating the removal of both species upon the ACN wash. 152

Figure A2. UV–vis spectra of ACN-washed (red curves) and unwashed (blue curves) (a) pristine PBTTT and (b) PBTTT doped with 1 mM DDB-F₆₀. The yellow dashed line indicates the absorption maximum of the neutral DDB-F₆₀ molecule (near 2.7 eV). The shoulder in the unwashed (blue curve) sample disappears upon ACN washing, indicating the removal of all neutral DDB-F₆₀ molecules in our films prior to 2-pot AED. 153

Figure A3. UV–vis–NIR spectra of doped conjugated polymer films before and after *n*-BA solvent washing. (a,b) PBTTT and (c,d) RRa-P3HT samples doped using 1 mM DDB-F₆₀ (a,c) and 1 mM DDB-F₆₀ followed by 2-pot AED (b,d). Spectra were collected after the initial doping step and subsequent *n*-BA washing for the 1 mM DDB-F₆₀-doped samples. The 2-pot AED samples were exchanged with LiTFSI solution followed by an *n*-BA wash to remove any salt left on the surface of the films. Minimal changes in the absorption features before and after the first or second *n*-BA wash indicate limited dedoping, demonstrating the robustness of both doping methods against solvent washing. 154

Figure A4. Normalized P1 peaks for PBTTT doped with 1 mM DDB-F₆₀ and PBTTT subjected to 2-pot AED with different LiTFSI concentrations of 3.5, 17, and 104 mM. These are the same samples shown in **Figure 2.2a** in the main text. 155

Figure A5. NIR P1 absorption peaks for P3HT polymers doped both conventionally with 1 mM DDB-F₆₀ and following 2-pot AED with 104 mM LiTFSI. Panels (a,b) show spectra for regioregular (RR) P3HT, while panels (c,d) correspond to regiorandom (RRa) P3HT. Shaded regions indicate the range used in the frequency-weighted integrated P1 area calculations. 157

Figure A6. (a–c) UV–vis–NIR spectra of PBTTT thin films (purple curves) conventionally SqP-doped with 0.3, 1, and 2 mM DDB-F₆₀, respectively (red curves), and subsequently subjected to 2-pot AED using a 104 mM LiTFSI solution (blue curves), showing an increase in the signature polaron peak intensities (P1 and P2). These spectra demonstrate the extra doping gained upon exposure to the high-dielectric environment of the LiTFSI solution at different initial dopant concentrations. 158

Figure A7. Doping level-matched UV–vis–NIR spectra of PBTTT thin films doped via the 2-pot (blue curve) and 1-pot (green curve) AED methods. The 1-pot method requires a lower dopant concentration (0.3 mM) to reach similar doping levels as the 2-pot method (1 mM), as indicated by the comparable bandgap-to-P1 absorption ratios. The absorbance was thickness normalized to clearly show the matched P1/BG ratios in both films. This matching allows us to confidently comment on the structural similarities between the 1-pot and 2-pot AED samples in **Figure 2.3** in the main text. 159

Figure A8. 2D GIWAXS diffractograms of (a) pristine PBTTT, (b) PBTTT doped with 1 mM DDB-F₆₀, and (c) PBTTT doped via 2-pot AED with a 104 mM LiTFSI solution. We obtained the 1D integrations along the OOP (q_z) and along the IP (q_{xy}) directions shown in **Figure 2.3** in the main text. 161

Figure A9. 2D GIWAXS diffractograms for ACN-washed (a) pristine RR P3HT, (b) RR P3HT conventionally doped with 1 mM DDB-F₆₀, and (c) RR P3HT doped via 2-pot AED with 104 mM LiTFSI. 1D integrations in OOP and IP directions are shown in **Figure A10**. 161

Figure A10. 1D integrations (a) out-of-plane and (b) in-plane for ACN-washed pristine RR P3HT, RR P3HT doped with 1 mM DDB-F₆₀, and RR P3HT doped via the 2-pot AED method. Panels (c,d) represent the out-of-plane and in-plane integrations, respectively, for the unwashed RR samples. The similarity between ACN-washed samples in panels (a,b) and the unwashed samples in panels (c,d) indicates that solvent washing did not affect the structure of the RR P3HT samples. 163

Figure A11. 2D GIWAXS diffractograms of washed (a) RRa P3HT, (b) RRa P3HT conventionally doped using a 1 mM DDB-F₆₀ solution, and (c) the same doped RRa P3HT subjected to 2-pot AED with 104 mM LiTFSI. Doping induces an increase in crystallinity in the originally amorphous RRa P3HT polymer films, as seen in prior studies. 164

Figure A12. Radially integrated out-of-plane (a) and in-plane (b) GIWAXS patterns for washed RRa P3HT films doped with DDB-F₆₀ and films subjected to 2-pot AED. Doped RRa P3HT shows a large doping-induced crystallization, as indicated by the formation of ($h00$) and (020) peaks compared to the pristine film. Panels (c,d) show the unwashed 1D integrations along the out-of-

plane and in-plane directions, respectively, and indicate no major structural changes due to solvent washing. 166

Figure A13. 1D integrated out-of-plane and in-plane GIWAXS patterns for (a,b) PBTTT and (c,d) P3HT doped via the 2-pot AED method with 17 mM (pink curves) and 104 mM (blue curves) LiTFSI. Both PBTTT and P3HT doped via the 2-pot AED method show similar q -spacing values along the out-of-plane (lamellar spacing) and in-plane (π -stacking spacing) directions at low and high electrolyte concentrations, indicating they have similar structures and that anion exchange has gone to completion even at lower dopant-to-electrolyte ratios. 167

Figure A14. Cyclic voltammograms of PBTTT and DDB-F₆₀ measured in a 100 mM TBAPF₆ electrolyte solution in ACN using a three-electrode cell. The PBTTT CV was collected using ITO as the working electrode, a Pt sheet as the counter electrode, and a nonaqueous Ag/Ag⁺ reference electrode consisting of an Ag wire in 1 mM AgNO₃/100 mM TBAPF₆ in ACN separated by a glass frit. The CV for DDB-F₆₀ was measured by dissolving 1 mM DDB-F₆₀ in the electrolyte and using a Pt sheet as the counter electrode, a glassy carbon electrode (GCE) as the working electrode, and the same nonaqueous Ag/Ag⁺ reference electrode described above. All potentials were referenced to the Fc/Fc⁺ redox couple measured under identical conditions. 168

Figure B1. (a) Conductivity values for higher concentrations of dopants for conventional (1 mg/mL F₄TCNQ) and anion-exchange (0.5 mg/mL F₄TCNQ + 30 mg/mL LiTFSI and 0.5 mg/mL F₄TCNQ + 5 mg/mL LiPF₆)-doped 97% RR P3HT in three different environments. Similar to the result shown in **Table 3.1**, only samples doped with hygroscopic salts (LiTFSI and LiPF₆) show a drop in conductivity when exposed to the ambient environment. The sample doped with the conventional method (F₄TCNQ) remains unchanged within measurement error. (b) Conductivity of various P3HT regioregularities (99% RR and 93% RR) doped with 0.5 mg/mL F₄TCNQ + 30 mg/mL LiTFSI. Like the case for 97% RR P3HT, when 99% RR and 93% RR P3HT are doped with anion exchange, the electrical conductivity drops roughly by a factor of 2 for all regioregularities and doping concentrations once the samples are exposed to ambient air, indicating that LiTFSI absorbs water independently of the polymer. 175

Figure B2. Conductivity values for the 97% RR P3HT doped with 0.1 mg/mL F₄TCNQ + 30 mg/mL LiTFSI via anion exchange (AE) were measured inside an argon glovebox, exposed to ambient air for 5 minutes, and subjected to four 5-minute vacuum/Ar-purge cycles in a chamber. 176

Figure B3. UV-vis-NIR spectra of P3HT samples doped with 0.5 mg/mL F₄TCNQ (red), 0.1 mg/mL F₄TCNQ anion-exchanged with 30 mg/mL LiTFSI (green), and 0.1 mg/mL F₄TCNQ anion-exchanged with 5 mg/mL LiPF₆ (purple) taken in ambient air. 177

Figure C1. 2D GIWAXS diffractograms for P3HT doped with (a) 0.3 mM DDB-F₇₂, (b) 1 mM DDB-F₃₆, (c) 3.62 mM F₄TCNQ, and (d) 3.62 mM F₄TCNQ plus 104.5 mM LiTFSI via anion exchange. 182

Figure C2. GIWAXS out-of-plane 1D integrations for P3HT doped with (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, (d) F₄TCNQ plus LiTFSI via anion exchange (AE). For anion-exchange-doped (AE) samples, the concentrations are reported based on the amount of F₄TCNQ added, plus 104.5 mM LiTFSI. The black (100) curve indicates the primary lamellar scattering for pristine P3HT, while the rainbow-colored ($h00$) curves are for the various doped P3HT samples. Peaks labeled

with an asterisk (*) are from excess LiTFSI salt crystals on the surface of the anion-exchange-doped films..... 183

Figure C3. GIWAXS in-plane 1D integrations for P3HT doped at various levels with: (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, (d) F₄TCNQ plus LiTFSI via anion exchange (AE). For anion-exchange-doped samples, the concentrations reported in the legend are based on the amount of F₄TCNQ added plus a constant concentration of 104.5 mM LiTFSI. Peaks labeled with an asterisk (*) are from excess LiTFSI salt crystals on the surface of the anion-exchange-doped films. 185

Figure C4. In-plane GIWAXS integrations for pristine P3HT (black curves) and P3HT doped with F₄TCNQ at 0.36 mM (red curves) and 3.62 mM (blue curves) using (a) DCM and (b) *n*-BA as the doping solvent. The diffraction patterns are almost identical for both solvents, indicating that the solvent choice alone is not important for determining structural change. These data serve as a control for the anion-exchange-doped samples, which show the appearance of a pronounced scattering peak near 1.4 Å⁻¹ that is associated with scattering from a disordered π -stacking region. Because the F₄TCNQ-doped P3HT films do not exhibit the strong scattering feature near 1.4 Å⁻¹ upon doping from either solvent, these data suggest that the additional scattering from the disordered π -stacking feature observed in the AE-doped samples is indeed associated with AE-induced ordering of the less ordered/amorphous fraction and is not due to the use of *n*-BA as the doping solvent. 186

Figure C5. Paracrystallinity ($g_{(h00)}$ (%)) from GIWAXS versus carrier density for P3HT doped with DDB-F₇₂ (brown triangles), DDB-F₃₆ (blue squares), F₄TCNQ (pink circles), and F₄TCNQ plus LiTFSI via anion exchange (green circles). 187

Figure C6. Horizontal 1D integrations of GISAXS data for all concentrations of P3HT doped with: (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, and (d) via anion exchange (F₄TCNQ with 104.5 mM LiTFSI). The scattering from pristine P3HT (black curves) is also plotted in all panels for reference. 188

Figure C7. Representative Unified Fit modeling of doped P3HT using (a) 0.3 mM DDB-F₇₂, (b) 1 mM DDB-F₃₆, (c) 3.62 mM F₄TCNQ, and (d) 3.62 mM F₄TCNQ anion-exchanged with 104.5 mM LiTFSI. 190

Figure C8. Electrical conductivity (σ) and Seebeck coefficient (S) of P3HT plotted as a function of dopant concentration for the four dopants used in this study. All doping cases demonstrate an inverse relationship between the conductivity and Seebeck coefficient: higher doping levels increase conductivity while decreasing the Seebeck coefficient. For anion-exchange-doped (AE) samples, the concentrations are reported based on the amount of F₄TCNQ, all with 104.5 mM LiTFSI added. 193

Figure C9. Thermovoltages versus the applied temperature difference for P3HT films doped with different concentrations of (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, and (d) F₄TCNQ plus 104.5 mM LiTFSI via anion exchange. The slopes of the ΔV versus ΔT plots were used to calculate the Seebeck coefficients in **Figure C8** and the main text. For the AE samples, the legend shows the F₄TCNQ concentration with 104.5 mM LiTFSI for all samples. 195

Figure C10. Hall carrier density and mobilities for P3HT doped with (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, and (d) via anion exchange (AE) as a function of dopant concentration. For the AE samples, the legend represents the F₄TCNQ concentration with 104.5 mM LiTFSI. 196

Figure C11. UV–vis–NIR oscillator-strength-weighted P1 peak area plotted versus Hall carrier density for F₄TCNQ- and anion-exchange-doped P3HT shows a linear relation..... 197

Figure C12. $\ln(\sigma(T))$ versus $(k_B T)^{-1}$ plots for P3HT doped with (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, and (d) via anion exchange (AE) at various doping concentrations. For the AE samples, the legend represents the F₄TCNQ concentration with 104.5 mM LiTFSI. 199

Figure D1. GIWAXS out-of-plane integrations for pristine and anion-exchange-doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT films. The sharp peaks labeled with an asterisk (*) in the doped P3HT films are due to scattering from excess LiTFSI. 205

Figure D2. GIWAXS in-plane integrations for pristine and doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT films. The intensity of each integration is normalized to the corresponding film thickness. Peaks labeled with an asterisk (*) in the doped P3HT films are due to scattering from excess LiTFSI. 208

Figure D3. Edge-on to face-on texture analysis of P3HT films. (a) Representative 2D GIWAXS diffractogram of a pristine 93% RR P3HT sample, with the (100) diffraction integrated along the azimuthal angle (χ) over a q range of 0.3–0.5 Å⁻¹. χ -dependent intensity profiles of the (100) diffraction for (b) pristine P3HT samples (q range integrated 0.3–0.5 Å⁻¹) with varying regioregularity and (c) the most-doped P3HT samples (q range integrated 0.25–0.45 Å⁻¹) prepared via anion exchange and presented in **Figure 5.2** of the main text. 209

Figure D4. Horizontal 1D GISAXS integrations near the Yoneda band for pristine and doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT polymers. Legends indicate the F₄TCNQ concentration; the LiTFSI concentration was fixed at 30 mg/mL for all doped samples..... 211

Figure D5. Representative Unified fits of the most-doped P3HT samples for (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT via the anion-exchange method using the F₄TCNQ concentration indicated in the legend with 30 mg/mL LiTFSI. The green and blue lines represent the Level 1 and Level 2 fits that give rise to the calculated intensity (black curves), which closely match the measured intensities. 212

Figure D6. UV–vis–NIR spectra of: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT pristine films (black curves) and anion-exchange-doped films (various colored curves) at various F₄TCNQ dopant concentrations, where thicker colored lines indicate higher doping concentrations. The LiTFSI electrolyte concentration was kept constant at 30 mg/mL for all of the anion-exchange doped samples. The spectra confirm successful chemical doping of the P3HT films through the appearance of the polaronic P1 and P2 peaks at ~0.4–0.6 and ~1.2–1.6 eV, respectively, and through the depletion of the bandgap absorption at ~2.3–3.3 eV. The lack of F₄TCNQ anion absorption at ~1.5 and ~3.0 eV confirms that the exchange process was successful. 214

Figure D7. Normalized polaronic P1 peaks for the doped samples of: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT. P1 peaks were normalized to the maximum absorbance in the IR region 0.38–0.8 eV. The curves highlight the red-shifted P1 peak positions of the doped 99% RR and 97% RR P3HT polymers compared to the doped 93% RR and RRa polymers..... 216

Figure D8. Representative Gaussian fits (green dashed lines) of the P1 peak for: (a) 99% RR P3HT (1 mg/mL F₄TCNQ with 30 mg/mL LiTFSI), (b) 97% RR P3HT (1 mg/mL F₄TCNQ with 30 mg/mL LiTFSI), (c) 93% RR P3HT (3 mg/mL F₄TCNQ with 30 mg/mL LiTFSI), and (d) RRa P3HT (9 mg/mL F₄TCNQ with 30 mg/mL LiTFSI). Only the highest dopant concentrations are shown for clarity. 218

Figure D9. Normalized transient P2 peak integrated area as a function of time for the doped 99% RR P3HT, 97% RR P3HT, 93% RR P3HT, and RRa P3HT polymers following excitation at 1400 nm. The more regioregular 99% RR and 97% RR P3HT films exhibit faster decay dynamics relative to the less ordered 93% RR and RRa P3HT samples, indicating higher local carrier mobility. 220

Figure D10. Hall effect measurements for doped: (a) 99% RR P3HT, (b) 97% RR P3HT, and (c) 93% RR P3HT doped via the anion-exchange method at various doping levels. The arrows for the solid (mobility) and dashed (carrier density) lines point toward the corresponding y-axis. The doped RRa samples were unable to give reproducible results and thus are not shown here. The x-axis is the F₄TCNQ concentration (with 30 mg/mL LiTFSI). 222

Figure D11. Full P1 peaks for the: (a) 97% RR, (b) 93% RR and (c) RRa P3HT samples used to create the P1–Hall correlation plots in **Figures D12 and D13**. The spectra of the 97% RR and RRa P3HT polymers show a bipolaron shoulder at high doping levels. 224

Figure D12. (a) Hall carrier density plotted against frequency-weighted oscillator-strength P1 peak area (A_{P1}) for doped 97% RR and 93% RR P3HT. The A_{P1} values were integrated over 90% of the peak maximum on each side to avoid the bipolaron blue shoulder (see **Figure D11**). The linear regression yields $n_{P1} = 2.5 \times 10^{25} A_{P1} - 1.0 \times 10^{20}$, which was used to convert the A_{P1} values for the doped RRa samples into carrier density. (b) Carrier densities obtained from the calibration line in (a), plotted alongside the carrier mobility calculated using the conductivity values and the n_{P1} values. Comparison of Hall carrier density (solid lines) and P1-derived carrier density (dashed lines) for the doped: (c) 97% RR and (d) 93% RR samples, respectively. Carrier mobility versus carrier density for: (e) 97% RR and (f) 93% RR P3HT, using both Hall and P1-derived carrier densities, showing consistent overall trends except at low and high doping levels. 227

Figure D13. Same analysis as **Figure D12** but using an asymmetric integration energy window defined as 85% of the peak maximum on the low-energy side to 50% of the maximum on the high-energy side. (a) Hall carrier density plotted against frequency-weighted oscillator-strength P1 peak area (A_{P1}) for doped 97% RR and 93% RR P3HT, yielding a calibration curve of $n_{P1} = 1.59 \times 10^{25} A_{P1} - 1.11 \times 10^{20}$. (b) P1-derived carrier density and mobility for RRa P3HT obtained from the calibration curve in (a). Comparison of Hall and P1 carrier density versus dopant concentration for doped: (c) 97% RR and (d) 93% RR samples. Carrier mobility versus carrier density for: (e) 97% RR and (f) 93% RR P3HT using both Hall and P1-derived values. Similar to **Figure D12**, n_{Hall} and n_{P1} agree well across most of the doping range. 228

Figure D14. Linear relation between the induced voltage difference (ΔV) and the applied temperature difference (ΔT) for doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT. The Seebeck coefficient for each doping concentration was obtained from the slope of the ΔV – ΔT line. Legends indicate the F₄TCNQ concentration with 30 mg/mL LiTFSI for the anion-exchange method. 229

Figure D15. Temperature-dependent conductivity measurements for anion-exchange-doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT. Conductivity was measured using the van der Pauw geometry, and the activation energy, E_a , was calculated using the Arrhenius equation $\sigma(T) = \sigma_0 \exp(-E_a/k_B T)$. The legends report the F₄TCNQ doping concentrations. All doping solutions contained 30 mg/mL LiTFSI..... 231

Figure D16. Power factor (PF) plotted versus carrier density, n , for the doped P3HT polymers. The more crystalline polymers exhibit an optimum in the PF at lower n indicating that their enhanced TE performance comes from a higher carrier mobility..... 233

Figure D17. σ_0 plotted versus the change in R_g (ΔR_g) in the highest-doped samples for each polymer. ΔR_g was calculated by taking the difference of the doped R_g and the corresponding pristine R_g values. The monotonic trend between increased σ_0 in higher-regioregularity P3HT and increased domain correlation length R_g suggests that mesoscale ordering contributes to the enhanced TE performance in those systems. 233

LIST OF TABLES

Table 3.1. Electrical conductivities of anion-exchange- (AE) and conventionally- (Conv) doped P3HT films measured under different environmental conditions. The dopant concentrations for AE were 0.1 mg/mL F ₄ TCNQ + 30 mg/mL LiTFSI and 0.1 mg/mL F ₄ TCNQ + 5 mg/mL LiPF ₆ , while the conventionally-doped samples used 0.5 mg/mL F ₄ TCNQ. Exposure to humidity dramatically lowers the conductivity of anion-exchange-doped samples, whereas conventionally-doped samples show no conductivity change within error. Hall mobility and carrier densities were all obtained on the same set of samples. Unfortunately, due to logistical constraints, we are unable to perform Hall measurements inside the Ar glovebox.....	57
Table 4.1. Radius of gyration (R_g) obtained from GISAXS for P3HT samples doped at similar Hall carrier densities of $\sim 5 \times 10^{20} \text{ cm}^{-3}$ with different dopants (cf. Figure 4.5b). The dopant concentrations needed to achieve carrier densities around this level are 0.3 mM DDB-F ₇₂ , 1 mM DDB-F ₃₆ , 0.18 mM F ₄ TCNQ, and 1.81 mM/104.5 mM anion exchange (F ₄ TCNQ/LiTFSI). The R_g values for all four dopants at all the dopant concentrations studied are presented in Table C1 . The R_g values were obtained using the Unified Fit model (see Appendix C for fitting details). Also presented are the σ_0 and $W_{H,\text{slope}}$ parameters from the SLoT model fits to the Seebeck coefficient–conductivity data in Figure 4.4	84
Table 5.1. Relative integrated GIWAXS (100) peak areas representing the relative crystallinity of pristine and most-doped 99% RR, 97% RR, 93% RR, and RRa P3HT samples, normalized to the corresponding 99% RR P3HT sample. The most-doped samples were prepared using 1, 1, 3, and 9 mg/mL F ₄ TCNQ, respectively, with 30 mg/mL LiTFSI. Also shown are the effective domain sizes, R_g , from GISAXS measurements for these same samples, as well as key SLoT parameters (σ_0 and $W_{H,\text{slope}}$), obtained from the fits shown in Figure 5.5	119
Table A1. Electrical conductivity, Hall mobility, and carrier density measurements for PBTTT doped conventionally with DDB-F ₆₀ at two different doping levels, and again following 2-pot AED with 104 mM LiTFSI. The data show that double doping occurs, as there is no alternative explanation that accounts for the significantly increased carrier density in the 2-pot AED samples. The decreased Hall mobilities following 2-pot AED are also consistent with the blue-shifted P1 peaks seen in these samples, indicating that the carriers are Coulombically trapped by the TFSI [−] counterion.	160
Table C1. R_g values obtained from Unified Fit modeling of P3HT films doped with F ₄ TCNQ, via anion exchange (AE), and with DDB-F ₇₂ and DDB-F ₃₆ at all doping levels used in this study. Shaded columns give the dopant concentrations for reference. For comparison, P3HT doped with 3.62 mM F ₄ TCNQ from <i>n</i> -BA gives an R_g value similar to that obtained for F ₄ TCNQ doping from DCM, indicating that the larger R_g values observed for AE-doped samples are not produced by changing the solvent from DCM to <i>n</i> -BA, but instead result from doping-induced crystallization of originally disordered regions.	191
Table C2. Parameters obtained from the SLoT fits performed for P3HT doped with F ₄ TCNQ, DDB-F ₇₂ , DDB-F ₃₆ , and via anion exchange (AE).....	201

Acknowledgements

I write this with deep gratitude for the people in my life who have transformed me into the person I am today. I want to thank my friends Trejo, Lui, and Angel, who have been there almost my entire life. I would also like to thank my college friends, Uli, Malik, Ivan, Wendi, Gemma, and many others, who taught me what it means to be part of a community. My family has always played a vital role in my life, and I would not be here today if it were not, in part, for their great sense of humor and unconditional support. Thank you, Joco (Lily and Tony), Mago (A.B.), and Rodolfo, for being in my life. I want to thank Benjamin for being the father figure in my life. Thank you for choosing to stay and support us, even when it was not your responsibility. I want to take the time to thank Saul Delgado (Bui) for being there for my mother when no one else was; for feeding my siblings and me when we were hungry, even if it was *Roles con leche*. I will always remember you. Until we see each other again.

Nineteen years ago, we crossed the border to come to the USA in search of a better life. Today, I can confidently say that I am, indeed, living a better life, and that is all thanks to the most selfless person I know: the person who left everything and everyone she had ever known behind so we could have meals every day; the only person I can confidently say would give her entire life so I can live mine—my mother. I vividly remember you telling me that you were so proud of me when I went to college, but little did you know that it has been me who has been so proud of you all these years. Everything I have accomplished is a reflection of your sacrifice, strength, and love. This is for us. *Te quiero mucho, Jefa*.

Throughout my scientific and professional career, I've had the pleasure of meeting and working with wonderful individuals who opened doors for me long before I knew how to open them myself. First, I would like to deeply thank Dr. Armando Contreras and Dr. Rocio Mendoza

for believing in that little kid back in his high school days and, despite systemic barriers, giving me a space where I was able to grow and learn more about higher education opportunities. I would also like to thank my English teacher, Mr. Dean, for believing in that sophomore student who could barely read English at a second-grade level. Lastly, I would like to thank my undergraduate research mentor, Dr. Michael Roders, who took me in after I had received many rejections from other PIs. I would not be here if you had never replied to my email.

During my time at UCLA, I've worked and shared moments with great colleagues and now dear friends. First and foremost, I want to thank Dr. Quynh Duong, who honestly made my PhD journey enjoyable and greatly facilitated my transition into research. His mentorship and vast knowledge in problem solving made me grow exponentially during this journey and allowed me to become an independent thinker. Thank you for having made my life much easier. I also want to express my appreciation to Dr. Eric Wu (and Luke) for his enormous contributions during our discussions and, overall, for being a very supportive figure in my life.

Other collaborators and dear friends—Dr. Charlene Salamat, Dr. Will Borelli (and family), Kajsa Williams and the “Holy Spirit” chat—thank you for your constant joy, support, and most importantly, community. I want to extend my thanks to previous and current graduate students: Alex L., Reid W., Sanghyun P., Jose G., Xiaoyan L., Kimberly S., Jack KF, and Stephanie J. Thank you for the conversations, support, troubleshooting, shared frustrations, and small moments that made graduate school feel less isolating. I'd like to thank some of the amazing undergraduate students I met throughout the years at UCLA: Brandon F., Angela T., Juan J., Angel S., and especially Isabella T., for allowing me to grow as an educator, or at the very least, as a comedian. I would also like to thank the members of my doctoral committee: Prof. Daniel Neuhauser, Prof. Benjamin J. Schwartz, Prof. William M. Gelbart, and Prof. Richard B. Kaner.

Finally, I want to thank Xinyu Liu especially, who is the hardest-working and most collaborative individual I know. Thank you for being yourself and allowing me to get to know you as a colleague, friend, and human. I cannot wait until you become a great PI. I will certainly be the first to read any future work you publish. You deserve this more than anyone I know and I smile at every thought of you becoming an amazing professor doing amazing research. I will cherish every second, every minute, and every hour I got to know you. Despite having an awful time in the lab, you made it worthwhile. I'd choose it all over again if it meant spending one minute working with you. You made me a better scientist; a better thinker; but most importantly, a more loving human. I would not be the person I am today without you; *cada mañana me regalas la vida*.

Publications and Contributions

Chapter 2 is a version of Dr. A. León Ruiz*, D. Garcia Vidales*, X. Liu, Dr. A. F. Simafranca, H. A. Khunaizi, N. Akmanşen-Kalayci, Dr. E. A. Doud, Dr. E. C. Wu, Dr. Z. Mehmedović, Prof. A. M. Spokoyny, Prof. S. H. Tolbert, and Prof. B. J. Schwartz, “Double Doping of Conjugated Polymers Can Be Induced by the High-Dielectric Environment Present During Anion-Exchange Doping.” Dr. A. León Ruiz and D. Garcia Vidales contributed equally to this work. Dr. A. León Ruiz and D. Garcia Vidales collected and analyzed the optical spectroscopy and electrical measurements. X. Liu, N. Akmanşen-Kalayci, and Dr. A. F. Simafranca collected the grazing-incidence wide-angle scattering (GIWAXS) data under the supervision of Prof. S. H. Tolbert. X. Liu processed and analyzed the GIWAXS data and performed cyclic voltammetry measurements. Dr. E. A. Doud and H. A. Khunaizi synthesized the DDB-based dopant used in this study under the supervision of Prof. A. M. Spokoyny. Dr. A. León Ruiz and D. Garcia Vidales wrote the manuscript under the supervision of Prof. B. J. Schwartz. Prof. A. M. Spokoyny, Prof. S. H. Tolbert, and Prof. B. J. Schwartz are the PIs and/or project directors for the project. This manuscript has been ready for submission to Matter for over a year and a half and counting.

Chapter 3 is a version of Dr. Q. M. Duong*, D. Garcia Vidales*, and Prof. B. J. Schwartz, “The Effects of Humidity on the Electrical Properties and Carrier Mobility of Semiconducting Polymers Anion-Exchange Doped with Hygroscopic Salts.” Both Dr. Q. M. Duong and D. Garcia Vidales contributed equally to the data collection and manuscript preparation. Prof. B. J. Schwartz was the PI and/or project director for the project. The manuscript was published in Applied Physics Letters, 2023, 123 (20), 202101. DOI: [10.1063/5.0169905](https://doi.org/10.1063/5.0169905).

Chapter 4 is a version of the published work by Dr. Q. M. Duong*, D. Garcia Vidales*, X. Liu, Dr. C. Z. Salamat, Dr. A. Ready, H. A. Khunaizi, M. Matsumoto, Prof. A. M. Spokoyny,

Prof. S. H. Tolbert, and Prof. B. J. Schwartz, “How the Carrier Mobility and Seebeck Coefficient of Doped Semiconducting Polymers Are Controlled by Counterion Interactions and Mesoscale Order.” Both Dr. Q. M. Duong and D. Garcia Vidales contributed equally to the data collection. Dr. Q. M. Duong collected and analyzed electrical, thermoelectric, and optical data; D. Garcia Vidales collected and analyzed electrical, thermoelectric, and optical data; X. Liu collected and analyzed grazing-incidence wide- and small-angle X-ray scattering data (GIWAXS and GISAXS); Dr. C. Z. Salamat collected GIWAXS data; all GIWAXS and GISAXS measurements were performed under the supervision of Prof. S. H. Tolbert. Dr. A. Ready, H. A. Khunaizi, and M. Matsumoto synthesized the dodecaborane clusters under the supervision of Prof. A. M. Spokoyny. Prof. A. M. Spokoyny, Prof. S. H. Tolbert, and Prof. B. J. Schwartz were the PIs and/or project directors for the project. The manuscript has been published in *Advanced Functional Materials*, 2026, DOI: [10.1002/adfm.75510](https://doi.org/10.1002/adfm.75510).

Chapter 5 is a version of D. Garcia Vidales*, Dr. Q. M. Duong*, X. Liu, Dr. E. C. Wu, Dr. C. Z. Salamat, J. Kelleher-Ferguson, K. Sung, R. Tagawa, Prof. S. H. Tolbert, and Prof. B. J. Schwartz, “The Role of Microstructural Disorder in Charge Transport Characteristics of Doped Semiconducting Polymers.” Both D. Garcia Vidales and Dr. Q. M. Duong contributed equally to this work in data collection, analysis, and manuscript preparation. X. Liu collected and analyzed GIWAXS data; Dr. C. Z. Salamat analyzed GIWAXS data; Dr. E. C. Wu collected and analyzed transient absorption experiments; J. Kelleher-Ferguson and K. Sung provided optical measurements; R. Tagawa provided thermoelectric measurements. Prof. B. J. Schwartz and Prof. S. H. Tolbert are the PIs and/or project directors for the project. The manuscript has been ready for submission to *Advanced Energy Materials* for over five months and counting.

The research presented in this dissertation was supported by multiple funding sources from the National Science Foundation under grants DMR-2513790 and CHE-2305152. Dr. Quynh Duong and I also contributed personal funds to build lab setups used for these measurements. I acknowledge personal support from the UCLA Graduate Division Cota-Robles Fellowship and the UCLA Chemistry and Biochemistry Department, which supported much of my PhD studies through fellowships and/or teaching positions. All grazing-incidence wide- and small-angle X-ray scattering data presented in this dissertation were collected at the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory. Use of the Stanford Synchrotron Radiation Lightsource is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. The authors thank Dr. Sarah A. Hesse, Dr. Nicholas A. Strange, Dr. Olga Kraynis, and Dr. Partha P. Paul for help with beamline setup.

VITA

Experience

- 2017 – B.S. Chemistry, UNIVERSITY OF CALIFORNIA, Santa Cruz (UCSC).
2019 – Hispanic-Serving Institution (HSI) Program Coordinator, UCSC.
2021 – Learning Skill Advisor, Academic Excellence Program, UCSC.
2021–2025 – Eugene V. Cota-Robles Fellowship, UNIVERSITY OF CALIFORNIA, Los Angeles Graduate Division.
2023 – M.S. Chemistry, UCLA.
2024 – Jim and Barbara Tsay Excellence in Research Award, UCLA.
2025 – Michael E. Jung Excellence in Teaching Award, UCLA.
2025 – Immanuel Wilk Award for Mentorship, Inclusion, and Service, UCLA.
2026 – Ralph and Charlene Bauer Graduate Award, UCLA.

Publications

1. Q. M. Duong[†], D. Garcia Vidales[†], C. Z. Salamat, S. H. Tolbert, and B. J. Schwartz, *Phys. Rev. Appl.* 21, 024006, 1–10 (2024).
2. Q. M. Duong[†], D. Garcia Vidales[†], and B. J. Schwartz, *Appl. Phys. Lett.* 13 November 2023, 123 (20), 202101.
3. Q. M. Duong[†], D. Garcia Vidales[†], C. Z. Salamat, X. Liu, A. Ready, H. A. Khunaizi, A. M. Spokoyny, S. H. Tolbert, and B. J. Schwartz, *Adv. Funct. Mater.* (2026): e75510.
4. E. C. Wu, D. Garcia Vidales, C. Z. Salamat, Q. M. Duong, A. O. León Ruiz, A. Ready, Z. Mehmedović, D. A. Stanfield, A. M. Spokoyny, S. H. Tolbert, and B. J. Schwartz, *Adv. Funct. Mater.* 35, no. 51 (2025): e07480.
5. Z. Mehmedović, A. León Ruiz, A. N. Nguyen, K. Lo, D. Garcia Vidales, X. Liu, C. Z. Salamat, E. Doud, A. M. Spokoyny, S. H. Tolbert, and B. J. Schwartz, *J. Phys. Chem. C* 2025, 129, 35, 15771–15781.
6. K. J. Winchell, P. Y. Yee, Y. L. Li, A. F. Simafranca, J. Chang, C. Beren, X. Liu, D. Garcia Vidales, R. J. Thompson, C. Z. Salamat, Q. M. Duong, R. S. Jordan, B. J. Schwartz, W. M. Gelbart, Y. Rubin, and S. H. Tolbert, *Macromolecules* 2023, 56, 8, 3160–3170.
7. X. Liu, A. F. Simafranca, J. Chang, D. Garcia Vidales, K. Lo, Y. Wu, B. J. Schwartz, Y. Rubin, and S. H. Tolbert, *ACS Appl. Mater. Interfaces* 2026, 18, 7, 11795–11808.
8. M. Roders, G. M. Pitch, D. Garcia Vidales, and A. L. Ayzner, *J. Phys. Chem. C* 2018, 122, 7, 3700–3708.
9. R. W. Wilson, X. Shi, D. Garcia Vidales, A. Slimp, Z. Mehmedović, E. C. Wu, S. H. Tolbert, R. B. Wilson, and B. J. Schwartz, *Adv. Funct. Mater.* (2026): e76788.

[†] = Authors contributed equally.

CHAPTER 1

Introduction

1.1 Semiconducting Conjugated Polymers

Conjugated polymers are a class of organic semiconductors defined by alternating single and double bonds along their backbones, which create a delocalized π -electron system capable of supporting charge transport. These materials show a unique combination of semiconducting behavior, solution processability,^[1] mechanical flexibility, and compatibility with room-temperature fabrication, which has established them as leading candidates for next-generation electronic materials. Conjugated polymers can be processed by simple, scalable techniques—such as spin-coating,^[1] blade-coating,^[2] or inkjet printing^[3]—enabling inexpensive, large-area fabrication of lightweight, flexible devices. As a result, they underpin technologies ranging from organic photovoltaics (OPVs) and organic field-effect transistors (OFETs) to light-emitting diodes (OLEDs), bioelectronic interfaces, and sensors.^[4]

In addition to their successes in optoelectronics, conjugated polymers are increasingly recognized as promising materials for thermoelectric (TE) energy harvesting, where TE devices convert waste heat into reusable electricity.^[5–10] Thermoelectric devices operate based on the Seebeck effect, in which a temperature gradient across a material generates a voltage, as depicted in **Figure 1.1a**. Semiconducting polymers' inherently low thermal conductivities (κ)^[7,8,11–13] and relatively large Seebeck coefficients (S)^[7,14] provide a favorable foundation for converting small temperature gradients into electrical power—particularly for low-grade heat and wearable applications.^[7–10,14] The thermoelectric efficiency can be quantified using the figure of merit ZT , given by:

$$ZT = \frac{S^2 \sigma}{\kappa} T, \quad (1.1)$$

where σ is the electrical conductivity, κ is the thermal conductivity, S is the Seebeck coefficient, and T is the absolute temperature, included to make ZT dimensionless. Because κ is intrinsically low in conjugated polymers, improving ZT relies primarily on controlling S and σ .

Electrical conductivity in a semiconductor is dictated by **Equation (1.2)**:

$$\sigma = n \mu e, \quad (1.2)$$

where n is the carrier density, e is the elementary charge, and μ is the carrier mobility. From this expression, it is clear that one can enhance the electrical properties of conjugated polymers by increasing the number of carriers via doping and/or by improving the conductive pathways that determine μ .^[8,15–18]

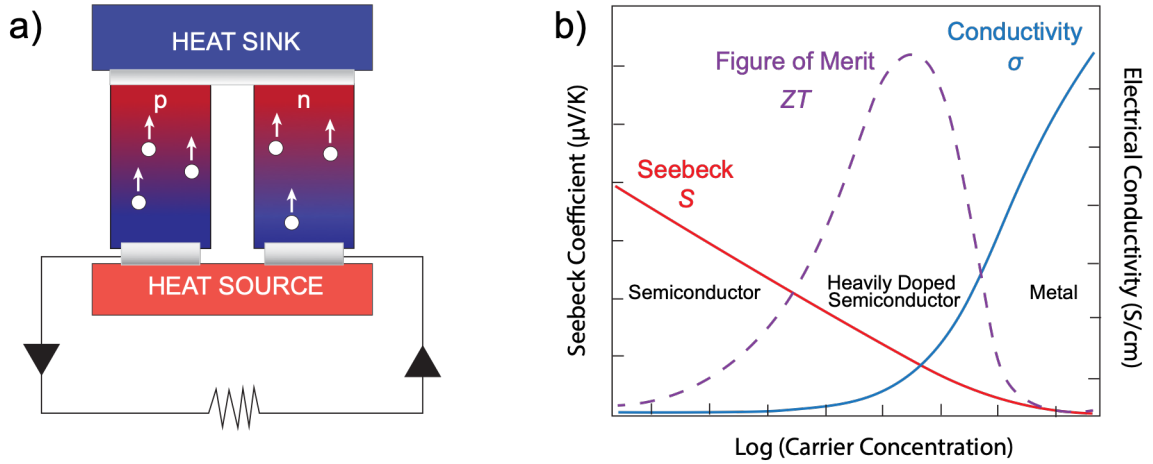


Figure 1.1. (a) Schematic of a thermoelectric device. (b) Seebeck coefficient (S), electrical conductivity (σ) and figure of merit plotted as a function of carrier density, showing the inverse relationship between S and σ as the carrier concentration is increased. This trade-off between S and σ results in a “sweet spot” in carrier concentration for optimizing the ZT of a thermoelectric device.

Introducing additional carriers through doping is an intuitive strategy for increasing σ . However, maximizing thermoelectric performance requires careful consideration of the intrinsic trade-off between the Seebeck coefficient and electrical conductivity with increasing carrier concentration.^[19–22] As **Figure 1.1b** illustrates schematically, increasing n increases σ but lowers S . This results in an inverse S – σ relation that produces a characteristic “sweet spot” in doping level where ZT is optimized. Therefore, a successful doping strategy must introduce carriers while enhancing carrier mobility and minimizing the drop in S .

1.2 Chemical Doping: Introducing Carriers While Preserving Structure

1.2.1 Fundamentals of *p*-Type Doping and Polaron Formation

A common method utilized to introduce carriers into conjugated polymer films is chemical doping. In a typical *p*-doping process, an electron is transferred from the polymer’s highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of an electron-accepting dopant molecule. This oxidation event produces a positively-charged radical cation on the polymer chain. To stabilize this electronic excitation, the polymer backbone undergoes a transformation from an aromatic structure to a more quinoidal form.^[23–25] The resulting stabilized radical cation, along with the lattice distortion, is known as a polaron. **Figure 1.2** shows the Lewis structures of a neutral polymer chain and the same polymer chain after chemical doping has occurred with the creation of the polaron (purple oval shading); also shown is the dopant anion that serves as a counterion to maintain charge neutrality in the polymer film.

In addition to structural changes in the backbone conformation, chemical doping also changes the electronic structure of the polymer, giving rise to two new electronic states within the bandgap. **Figure 1.2** depicts these changes in the electronic structure of the conjugated polymer after chemical doping. The two doping-induced midgap states result in two new optically-allowed

transitions, labeled P1 and P2, which appear as absorption features in the UV–vis–NIR spectra. The P1 transition, occurring near ~ 0.5 eV in an otherwise spectrally quiet region, is frequently used as an indicator of polaron formation, doping level, and carrier delocalization.^[26–31]

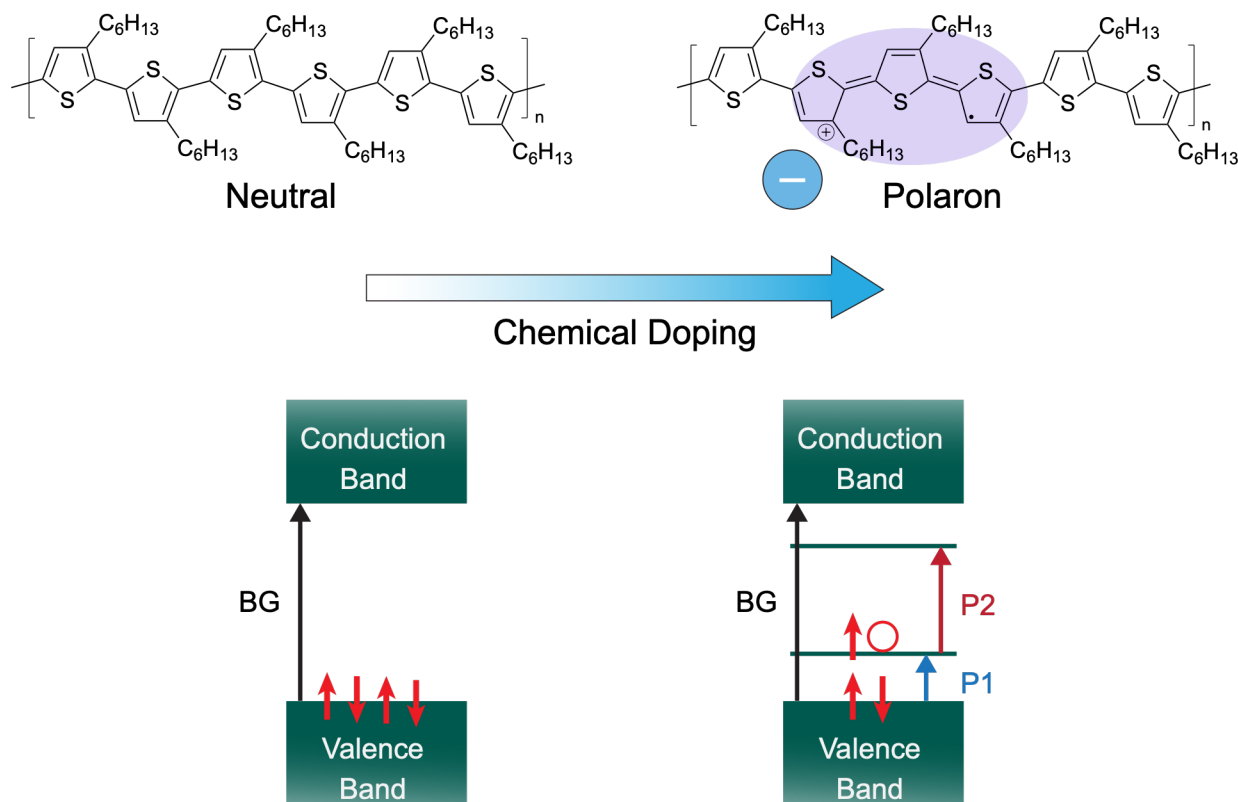


Figure 1.2. Neutral P3HT polymer backbone before the charge transfer process with a molecular dopant. Chemical doping creates a radical cation, resulting in backbone reorganization from an aromatic to a quinoid structure. The lattice distortion, along with the radical cation, is referred to as a polaron (purple shading). This structural reorientation also changes the electronic structure of the polymer, creating two new intragap energy states between the bandgap (BG) transition. These new energy levels give rise to two new optically allowed polaronic transitions, labeled P1 and P2. The blue circle represents the dopant counterion that remains inside the polymer film after the doping process is complete.

1.2.2 Solution (Blend) Doping and Its Limitations

One of the earliest approaches to molecularly dope conjugated polymers was to co-dissolve the polymer and dopant in a common casting solvent (“blend doping”).^[32–36] In this method, the dopant oxidizes the polymer while both are still in solution. As the polymer becomes charged,

however, its solubility in the nonpolar solvents typically used for conjugated polymers drops sharply. The charged doped chains then tend to aggregate and phase-separate from the solution, so that the morphology of the resulting cast film is governed largely by aggregation rather than by the microstructure of the original neutral polymer. The films produced in this way often exhibit poor uniformity, increased structural disorder, and reduced charge-carrier mobility.^[33,35,36] For thermoelectric applications, where high conductivity and controlled microstructure are essential, these limitations make blend doping less attractive than post-deposition methods that introduce dopants into a pre-formed polymer film.

1.2.3 Sequential Processing: A Morphology-Preserving Alternative

To mitigate these solution-processing difficulties and to better preserve the microstructure of the undoped film, our group developed sequential processing (SqP) methods.^[33,37–40] In the SqP approach, a high-quality pristine polymer film is first cast under conditions optimized for structural order (see **Figure 1.3a**). This film is then exposed to a dopant solution prepared in a semi-orthogonal solvent that swells the pre-cast polymer but does not dissolve it. Swelling allows dopant molecules to intercalate into the polymer film, and mass action drives the charge-transfer process between the polymer and dopant. Because the polymer crystallites remain largely intact and the film does not redissolve, the morphology of the pristine film is largely preserved even after substantial levels of doping. Sequential processing thus provides a way to increase n while maintaining, or in some cases, even enhancing μ , yielding more uniformly-doped polymer films with better-preserved conductive pathways.

creating polarons and leaving behind F_4TCNQ^- as the counterion, and then mass action drives an exchange in which this counterion is replaced by the electrolyte anion, for example, $TFSI^-$ or PF_6^- . The net result is that the polymer remains oxidized but now is associated with a different counterion than the one supplied by the molecular dopant. This method thus allows for precise control over the choice of counterion that remains in the doped polymer films.^[29,41–43] It can also achieve much higher doping levels than conventional methods in which only molecular dopants are introduced by the SqP method, leading to a much higher σ than achieved by the same dopant when no electrolyte is present in solution.

1.3 Charge Transport in Conjugated Polymers

Although chemical doping mitigates the low electrical conductivity in conjugated polymers by increasing n , carrier mobility is limited both by the disordered nature of conjugated polymer films and by electrostatic polaron–counterion interactions. Unlike crystalline inorganic semiconductors, where charge transport occurs through extended Bloch states, charge transport in conjugated polymers is usually described as a hopping process between localized states. As shown in **Figure 1.4**, carriers hop from one localized site to another, and their ability to move over long distances depends on both structural and energetic disorder.

1.3.1 Structural Disorder in Semicrystalline Polymers

Conjugated polymers are typically semicrystalline, with both ordered crystalline domains and amorphous regions (**Figure 1.4**). Carriers can move relatively easily within the crystalline domains, exhibiting band-like transport characteristics. However, to achieve long-range transport, carriers must cross grain boundaries and amorphous regions where the chains are more twisted, the packing is less regular, and the energetic landscape is more disordered. These structural defects introduce energetic barriers between localized states. If these barriers exceed the available thermal

energy, hopping becomes inefficient and carriers become trapped, leading to reduced mobility.^[44–46] Thus, both local structural disorder (within domains) and mesoscale disorder (grain boundaries, disconnected crystallites, and poorly connected domains) play critical roles in determining the microscopic and macroscopic transport properties of doped conjugated polymers.^[46–51]

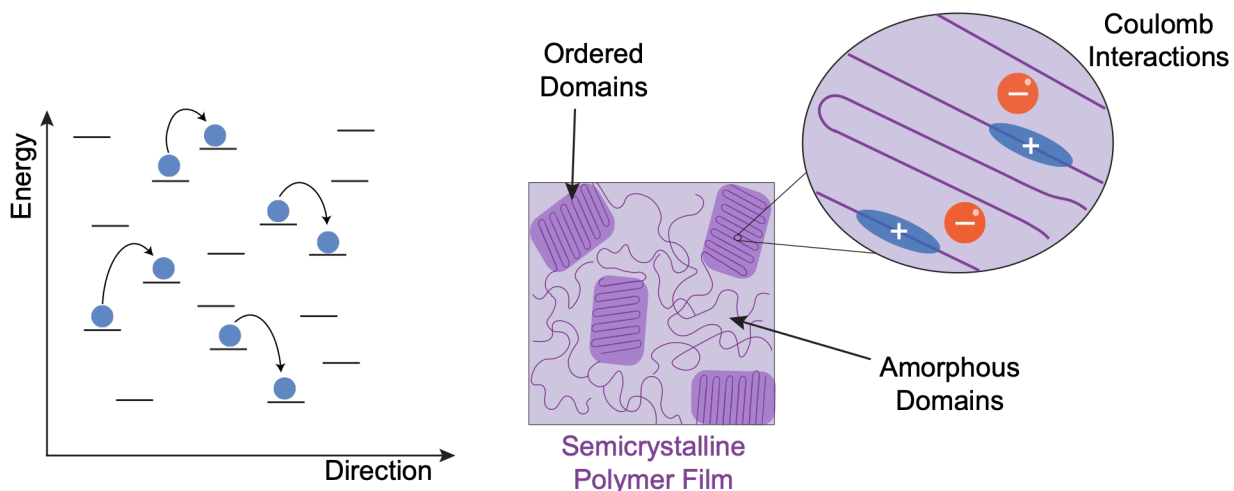


Figure 1.4. Energetic schematic depicting charge carriers (blue circles) moving through a disordered energy landscape by hopping between localized states. The right cartoon shows a semicrystalline polymer film with both ordered domains (darker purple) and amorphous regions, where chain bends, kinks, grain boundaries, and disrupted packing create structural and energetic disorder. The zoomed-in circle shows polarons (blue ovals) experiencing Coulomb interactions with dopant counterions (orange circles).

1.3.2 Energetic Disorder and Coulomb Trapping

In addition to structural disorder, a key source of energetic disorder arises directly from the presence of dopant counterions. When a polymer is doped, each polaron is stabilized by a nearby anion that remains in the film after the charge transfer is complete. Because the polaron and its counterion carry opposite charge, they attract each other via Coulomb's law, with an interaction strength that is inversely proportional to the distance between them (**Figure 1.4**).^[30,31,52,53] When the counterion is small and closely associated with the polymer backbone, this attraction creates a Coulomb trap that localizes the polaron and increases the energetic barrier for hopping to

neighboring sites, hindering carrier mobility.^[30,31,52,53] Larger or more diffuse anions distribute their charge over a larger volume, reducing the depth of the Coulomb well and allowing the polaron to delocalize over additional repeat units. In this way, the identity, size, and spatial distribution of the counterions directly control the energetic landscape that carriers experience.

Taken together, these considerations highlight the complexity of designing high-performance thermoelectric devices based on conjugated polymers. Increasing the carrier density through chemical doping is necessary to raise σ , but the same dopants that create charge carriers also introduce counterions and can modify the microstructure in ways that affect μ . The resulting transport is governed by an intertwined set of factors: the strength of Coulomb interactions between polarons and counterions, the degree and nature of structural disorder, the connectivity of ordered domains, and the susceptibility of the doped film to environmental perturbations such as humidity. Understanding how these factors work together to control hopping transport and the S – σ relationship is the central theme of this dissertation.

1.4 Dissertation Overview and Goals

The goal of this dissertation is to understand and deconvolute how the dielectric environment, ambient humidity, dopant identity, and pristine polymer microstructure influence charge transport in conjugated polymer films. Across four major projects, we use the workhorse polymers poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly[2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT-C14) (see **Figure 1.3** for chemical structures) as our main systems and chemically dope them using different molecular dopants and anion-exchange doping. These studies are united by a common theme: decoupling the factors that determine carrier delocalization and mobility, including electrostatic interactions with counterions, structural connectivity across length scales, and environmental perturbations such as humidity. By

combining spectroscopy, electrical measurements, and X-ray scattering, we build a comprehensive framework linking microscopic disorder to macroscopic transport behavior.

1.4.1 Chapter 2: Dielectric Enhancement of Doping Ability in Semicrystalline Conjugated Polymers

Chapter 2 examines the role of the dielectric environment in the enhanced carrier generation observed during anion-exchange doping. Although anion-exchange doping has been shown to increase carrier density and improve the performance of doped polymer films, the physical origin of this enhancement remains under discussion. Previous explanations have emphasized mass action, counterion exchange, and favorable ion-pairing effects, but less emphasis has been placed on the role of the dielectric constant of the doping environment.

In this Chapter, we aim to understand the origin of this enhanced doping efficiency and the role that the dielectric environment plays in it. To isolate the role of the dielectric environment, this Chapter uses a two-step anion-exchange-doping process that separates the initial chemical doping step from the subsequent electrolyte exposure step. By first doping PBTTT with the dodecaborane-based dopant DDB-F₆₀ (see **Figure 1.3** for chemical structure) and then exposing the doped film to a LiTFSI solution, we show that the high-dielectric electrolyte environment enables an already-reduced dopant anion to oxidize the polymer backbone a second time. We find that in order for a second electron-transfer event to occur between the DDB-F₆₀⁻ anion and PBTTT, the effective oxidizing power of the dopant anion must be increased by ~200 mV. UV-vis-NIR spectroscopy and Hall effect measurements confirm that this process nearly doubles the carrier density, supporting the double-doping process. These results demonstrate that the dielectric environment plays a central role in the enhanced doping efficiency observed in anion-exchange doping.

The work presented in this chapter was completed in collaboration with Dr. A. León Ruiz, D. Garcia Vidales, X. Liu, Dr. A. F. Simafranca, H. A. Khunaizi, N. Akmanşen-Kalayci, Dr. E. Doud, Dr. E. C. Wu, Z. Mehmedović, Professor A. M. Spokoyny, Professor S. H. Tolbert, and Professor B. J. Schwartz.

1.4.2 Chapter 3: Humidity and Environmental Stability in Anion-Exchange-Doped P3HT

Chapter 3 builds on Chapter 2 by examining the environmental stability of anion-exchange-doped samples in ambient air. Given that this doping method greatly enhances carrier generation and allows control over counterion identity, it provides an important advance for thermoelectric applications. However, most of these applications are carried out in ambient conditions and thus require that the doped films remain stable in ambient environments.

This work finds that although anion-exchange doping enhances doping efficiency, the electrolytes used during the doping process, such as LiTFSI, are highly hygroscopic. Despite this, there had been no reports on the impact of humidity on semiconducting polymer films doped using the anion-exchange method. We showed that the electrical conductivity of anion-exchange-doped P3HT samples drops significantly with increasing relative humidity when the hygroscopic LiTFSI salt is used. From Hall effect measurements, we saw that the drop in conductivity results from a drop in carrier mobility and not from a dedoping process that lowers the carrier density. From UV–vis–NIR spectroscopy, we showed that the humidity affects the carrier mobility by introducing water-related traps, leading to more localized polarons in high-humidity environments.

This chapter was reprinted with permission from Duong, Q. M.; Garcia Vidales, D.; Schwartz, B. J.; and AIP Publishing. “The Effects of Humidity on the Electrical Properties and Carrier Mobility of Semiconducting Polymers Anion-Exchange Doped with Hygroscopic Salts,” *Appl. Phys. Lett.* **123**, 202101, 1–6 (2023); DOI: 10.1063/5.0169905.

1.4.3 Chapter 4: Dopant Identity, Coulomb Interactions, and the S – σ Relationship

Chapter 4 aims to understand and deconvolute how dopant identity and counterion–polaron interactions influence the transport characteristics and S – σ relation in doped P3HT. We compare four distinct doping systems designed to decouple the roles of redox strength, dopant size, and dopant-induced structural changes. We use the SqP method to chemically dope P3HT with three molecular dopants. First, we choose F₄TCNQ, which serves as our control system since it is commonly used as a dopant in the literature. Due to its lower redox strength, F₄TCNQ is only able to dope crystalline regions in P3HT. Furthermore, carriers are expected to have strong Coulomb interactions with the smaller F₄TCNQ[−] counterion.

Next, we chemically dope P3HT with two large dodecaborane-based dopants, DDB-F₇₂ and DDB-F₃₆ (see **Figure 1.3** for chemical structures of the dodecaborane-based dopants and other materials used in this dissertation), which mitigate Coulomb interactions with the polaron. Due to the stronger redox strength of DDB-F₇₂, it can dope both crystalline and amorphous regions in P3HT, while DDB-F₃₆ is only able to dope crystalline domains. Lastly, we compare these doped P3HT systems to P3HT doped via the anion-exchange-doping method using F₄TCNQ as the dopant and LiTFSI as the electrolyte. We examine the S – σ relation curves for these four doped P3HT systems across different doping levels and show that the F₄TCNQ-doped P3HT system has the lowest thermoelectric performance and poorest charge transport. Using temperature-dependent conductivity measurements, we extract the hopping barriers of these doped systems and find that the carriers in the DDB-based doped P3HT systems experience lower hopping barriers due to mitigated Coulomb interactions between the large counterions and polarons, thus enhancing the S – σ relation in these doped systems. In contrast, F₄TCNQ and anion-exchange-doped P3HT

samples show larger hopping barriers, suggesting stronger electrostatic interactions that localize the polarons.

We also probe the macroscopic carrier mobility via Hall effect measurements and show that the carriers in the DDB-based doped P3HT films have higher carrier mobilities than carriers in the F₄TCNQ-doped P3HT films at a given carrier density. Remarkably, the charge carriers in the anion-exchange-doped P3HT films exhibit similarly high Hall carrier mobilities, comparable to the DDB-based doped P3HT films, despite experiencing larger hopping barriers, indicating that a distinct mechanism must be contributing to the high macroscopic carrier mobility.

To understand the enhanced macroscopic carrier mobility in anion-exchange-doped samples, we employ grazing-incidence small-angle X-ray scattering (GISAXS). We find that the enhanced carrier mobility originates from increased long-range structural ordering that improves mesoscale connectivity between ordered domains, improving macroscopic transport.

To quantitatively connect microscopic disorder to macroscopic transport, we fit the Seebeck and conductivity data using the Semi-Localized Transport (SLoT) model,^[54] which is described in Section 4.2.6; the full SLoT fits and fitting parameters are presented below in **Figure 4.4** and **Table 4.1**, respectively. These fits reveal that the intrinsic conductivity parameter, σ_0 , is significantly larger in anion-exchange-doped films, consistent with long-range structural improvements, while DDB dopants reduce energetic disorder primarily through Coulombic effects. Together, these findings demonstrate that dopant choice can influence transport through two fundamentally different mechanisms: Coulomb-trapping mitigation and mesoscale structural ordering.

This chapter was reprinted with permission from Q. M. Duong; D. Garcia Vidales; X. Liu; C. Z. Salamat; A. Ready; H. A. Khunaizi; M. Matsumoto; A. M. Spokoyny; S. H. Tolbert; B. J.

Schwartz; and Wiley-VCH. “How the Carrier Mobility and Seebeck Coefficient of Doped Semiconducting Polymers Are Controlled by Counterion Interactions and Mesoscale Order,” *Adv. Funct. Mater.* 2026, DOI: 10.1002/adfm.75510.

1.4.4 Chapter 5: Pristine Microstructure and Its Influence on Delocalization After Doping

Chapter 5 explores how the initial microstructure of the polymer influences carrier delocalization, mobility, and thermoelectric performance after chemical doping. To tune the microstructure of P3HT, we use P3HT samples with different regioregularities: regiorandom P3HT (RRa), 93% regioregular P3HT (RR), 97% RR P3HT, and 99% RR P3HT. By varying the P3HT regioregularity, we can systematically tune the degree of crystallinity and thus determine how the microstructure affects charge transport using the anion-exchange-doping method.

First, we characterized the molecular packing and intradomain morphology in the four P3HT polymers with different regioregularities via grazing-incidence wide-angle X-ray scattering (GIWAXS). We find that the crystalline fraction increases substantially as the polymer regioregularity is increased. UV–vis–NIR and transient absorption (TA) spectroscopy show that more crystalline polymers yield more delocalized polarons after doping, consistent with longer effective conjugation lengths and improved intradomain crystallinity.

We probe the macroscopic charge transport in these doped microstructures via Hall and temperature-dependent conductivity measurements. Surprisingly, Hall effect measurements show that at low doping levels, the 93% RR polymer exhibits the highest macroscopic mobility, exceeding even the 97% RR and 99% RR P3HT samples. Temperature-dependent conductivity show that this mobility inversion is accompanied by lower hopping barriers in the doped 93% RR sample at low carrier densities. These behaviors appear to contradict the intradomain trends observed via our spectroscopy and GIWAXS measurements.

GISAXS measurements were able to resolve this apparent inconsistency. At low doping levels, the 93% RR films exhibit the largest mesoscale correlation length, indicating that their domains are better connected across longer distances. This enhanced mesoscale connectivity allows carriers to traverse fewer grain boundaries early in the doping process, boosting the macroscopic carrier mobility. As doping increases, the mesoscale connectivity between ordered domains converges across all the different films, and the mobility hierarchy reverts to the expected trend: more crystalline polymers (97% RR and 99% RR P3HT) dominate once mesoscale limitations are lifted.

By applying SLoT model fitting, we find that the intrinsic conductivity, σ_0 , correlates strongly with crystallinity, highlighting that the pristine microstructure fundamentally sets the transport ceiling, even though mesoscale effects dominate at low doping levels.

The work presented in this chapter was completed in collaboration with D. G. Vidales, Dr. Q. M. Duong, X. Liu, Dr. E. C. Wu, Dr. C. Z. Salamat, J. Kelleher-Ferguson, K. Sung, R. Tagawa, Professor S. H. Tolbert, and Professor B. J. Schwartz.

1.5 References

- [1] J. A. Rogers, Z. Bao, A. Makhija, P. Braun, *Advanced Materials* **1999**, *11*, 741.
- [2] X. Gu, H. Yan, T. Kurosawa, B. C. Schroeder, K. L. Gu, Y. Zhou, J. W. F. To, S. D. Oosterhout, V. Savikhin, F. Molina-Lopez, C. J. Tassone, S. C. B. Mannsfeld, C. Wang, M. F. Toney, Z. Bao, *Advanced Energy Materials* **2016**, *6*, 1601225.
- [3] D. Pede, G. Serra, D. De Rossi, *Materials Science and Engineering: C* **1998**, *5*, 289.
- [4] B. D. Fahlman, In *Materials Chemistry* (Ed.: Fahlman, B. D.), Springer Netherlands, Dordrecht, **2011**, pp. 239–347.
- [5] L. E. Bell, *Science* **2008**, *321*, 1457.
- [6] J. Sharp, J. Bierschenk, H. B. Lyon, *Proceedings of the IEEE* **2006**, *94*, 1602.

- [7] N. Dubey, M. Leclerc, *Journal of Polymer Science Part B: Polymer Physics* **2011**, 49, 467.
- [8] G.-H. Kim, L. Shao, K. Zhang, K. P. Pipe, *Nature Mater* **2013**, 12, 719.
- [9] M. Culebras, C. M. Gómez, A. Cantarero, *Materials* **2014**, 7, 6701.
- [10] M. He, F. Qiu, Z. Lin, *Energy & Environmental Science* **2013**, 6, 1352.
- [11] M. Martín-González, O. Caballero-Calero, P. Díaz-Chao, *Renewable and Sustainable Energy Reviews* **2013**, 24, 288.
- [12] A. Lodha, R. Singh, *IEEE Transactions on Semiconductor Manufacturing* **2001**, 14, 281.
- [13] J. Liu, X. Wang, D. Li, N. E. Coates, R. A. Segalman, D. G. Cahill, *Macromolecules* **2015**, 48, 585.
- [14] R. Zuzok, A. B. Kaiser, W. Pukacki, S. Roth, *J. Chem. Phys.* **1991**, 95, 1270.
- [15] C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.* **1977**, 39, 1098.
- [16] V. Untilova, J. Hynynen, A. I. Hofmann, D. Scheunemann, Y. Zhang, S. Barlow, M. Kemerink, S. R. Marder, L. Biniek, C. Müller, M. Brinkmann, *Macromolecules* **2020**, 53, 6314.
- [17] H. T. Nicolai, M. Kuik, G. a. H. Wetzelaer, B. de Boer, C. Campbell, C. Risko, J. L. Brédas, P. W. M. Blom, *Nature Mater* **2012**, 11, 882.
- [18] I. E. Jacobs, A. J. Moulé, *Advanced Materials* **2017**, 29, 1703063.
- [19] J. Sun, M.-L. Yeh, B. J. Jung, B. Zhang, J. Feser, A. Majumdar, H. E. Katz, *Macromolecules* **2010**, 43, 2897.
- [20] Y. Xuan, X. Liu, S. Desbief, P. Leclère, M. Fahlman, R. Lazzaroni, M. Berggren, J. Cornil, D. Emin, X. Crispin, *Phys. Rev. B* **2010**, 82, 115454.
- [21] O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren, X. Crispin, *Nature Mater* **2011**, 10, 429.
- [22] S. D. Kang, G. J. Snyder, *Nature Mater* **2017**, 16, 252.
- [23] M. G. Voss, D. T. Scholes, J. R. Challa, B. J. Schwartz, *Faraday Discuss.* **2019**, 216, 339.

- [24] B. Xu, S.-A. Gopalan, A.-I. Gopalan, N. Muthuchamy, K.-P. Lee, J.-S. Lee, Y. Jiang, S.-W. Lee, S.-W. Kim, J.-S. Kim, H.-M. Jeong, J.-B. Kwon, J.-H. Bae, S.-W. Kang, *Sci Rep* **2017**, *7*, 45079.
- [25] E. C. Wu, D. G. Vidales, C. Z. Salamat, Q. M. Duong, A. León Ruiz, A. D. Ready, Z. Mehmedović, D. A. Stanfield, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Advanced Functional Materials* **2025**, *35*, e07480.
- [26] R. Österbacka, C. P. An, X. M. Jiang, Z. V. Vardeny, *Science* **2000**, *287*, 839.
- [27] C. Wang, D. T. Duong, K. Vandewal, J. Rivnay, A. Salleo, *Phys. Rev. B* **2015**, *91*, 085205.
- [28] I. Salzmann, G. Heimel, M. Oehzelt, S. Winkler, N. Koch, *Acc. Chem. Res.* **2016**, *49*, 370.
- [29] T. L. Murrey, M. A. Riley, G. Gonel, D. D. Antonio, L. Filardi, N. Shevchenko, M. Mascal, A. J. Moulé, *J. Phys. Chem. Lett.* **2021**, *12*, 1284.
- [30] T. J. Aubry, K. J. Winchell, C. Z. Salamat, V. M. Basile, J. R. Lindemuth, J. M. Stauber, J. C. Axtell, R. M. Kubena, M. D. Phan, M. J. Bird, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2020**, *30*, 2001800.
- [31] T. J. Aubry, J. C. Axtell, V. M. Basile, K. J. Winchell, J. R. Lindemuth, T. M. Porter, J.-Y. Liu, A. N. Alexandrova, C. P. Kubiak, S. H. Tolbert, A. M. Spokoyny, B. J. Schwartz, *Advanced Materials* **2019**, *31*, 1805647.
- [32] L. Müller, D. Nanova, T. Glaser, S. Beck, A. Pucci, A. K. Kast, R. R. Schröder, E. Mankel, P. Pingel, D. Neher, W. Kowalsky, R. Lovrincic, *Chem. Mater.* **2016**, *28*, 4432.
- [33] P. Pingel, D. Neher, *Phys. Rev. B* **2013**, *87*, 115209.
- [34] J. Gao, E. T. Niles, J. K. Grey, *J. Phys. Chem. Lett.* **2013**, *4*, 2953.
- [35] J. Gao, J. D. Roehling, Y. Li, H. Guo, A. J. Moulé, J. K. Grey, *Journal of Materials Chemistry C* **2013**, *1*, 5638.
- [36] I. E. Jacobs, E. W. Aasen, J. L. Oliveira, T. N. Fonseca, J. D. Roehling, J. Li, G. Zhang, M. P. Augustine, M. Mascal, A. J. Moulé, *J. Mater. Chem. C* **2016**, *4*, 3454.
- [37] A. L. Ayzner, C. J. Tassone, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2009**, *113*, 20050.
- [38] J. C. Aguirre, S. A. Hawks, A. S. Ferreira, P. Yee, S. Subramaniyan, S. A. Jenekhe, S. H. Tolbert, B. J. Schwartz, *Adv. Energy Mater.* **2015**, *5*, 1402020.

- [39] G. Zhang, R. C. Huber, A. S. Ferreira, S. D. Boyd, C. K. Luscombe, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2014**, *118*, 18424.
- [40] S. A. Hawks, J. C. Aguirre, L. T. Schelhas, R. J. Thompson, R. C. Huber, A. S. Ferreira, G. Zhang, A. A. Herzing, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2014**, *118*, 17413.
- [41] Y. Yamashita, J. Tsurumi, M. Ohno, R. Fujimoto, S. Kumagai, T. Kurosawa, T. Okamoto, J. Takeya, S. Watanabe, *Nature* **2019**, *572*, 634.
- [42] I. E. Jacobs, Y. Lin, Y. Huang, X. Ren, D. Simatos, C. Chen, D. Tjhe, M. Statz, L. Lai, P. A. Finn, W. G. Neal, G. D'Avino, V. Lemaire, S. Fratini, D. Beljonne, J. Strzalka, C. B. Nielsen, S. Barlow, S. R. Marder, I. McCulloch, H. Sirringhaus, *Advanced Materials* **2022**, *34*, 2102988.
- [43] C. Chen, I. E. Jacobs, K. Kang, Y. Lin, C. Jellett, B. Kang, S. B. Lee, Y. Huang, M. BaloochQarai, R. Ghosh, M. Statz, W. Wood, X. Ren, D. Tjhe, Y. Sun, X. She, Y. Hu, L. Jiang, F. C. Spano, I. McCulloch, H. Sirringhaus, *Advanced Energy Materials* **2023**, *13*, 2202797.
- [44] N. Lu, L. Li, M. Liu, *Physical Chemistry Chemical Physics* **2016**, *18*, 19503.
- [45] M. Upadhyaya, C. J. Boyle, D. Venkataraman, Z. Aksamija, *Scientific Reports* **2019**, *9*, 5820.
- [46] H. Bässler, *Philosophical Magazine B* **1984**, *50*, 347.
- [47] D. T. Scholes, P. Y. Yee, J. R. Lindemuth, H. Kang, J. Onorato, R. Ghosh, C. K. Luscombe, F. C. Spano, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2017**, *27*, 1702654.
- [48] K. Lu, C. Chen, J.-L. Cheng, I. E. Jacobs, B. Yue, P. Huang, L.-W. Feng, Y. Lin, *ACS Materials Lett.* **2024**, *6*, 4351.
- [49] F. P. V. Koch, J. Rivnay, S. Foster, C. Müller, J. M. Downing, E. Buchaca-Domingo, P. Westacott, L. Yu, M. Yuan, M. Baklar, Z. Fei, C. Luscombe, M. A. McLachlan, M. Heeney, G. Rumbles, C. Silva, A. Salleo, J. Nelson, P. Smith, N. Stingelin, *Progress in Polymer Science* **2013**, *38*, 1978.
- [50] S. Himmelberger, J. Dacuña, J. Rivnay, L. H. Jimison, T. McCarthy-Ward, M. Heeney, I. McCulloch, M. F. Toney, A. Salleo, *Advanced Functional Materials* **2013**, *23*, 2091.
- [51] A. R. Chew, R. Ghosh, Z. Shang, F. C. Spano, A. Salleo, *J. Phys. Chem. Lett.* **2017**, *8*, 4974.

- [52] J. Liu, Y. Shi, J. Dong, M. I. Nugraha, X. Qiu, M. Su, R. C. Chiechi, D. Baran, G. Portale, X. Guo, L. J. A. Koster, *ACS Energy Lett.* **2019**, *4*, 1556.
- [53] B. A. Gregg, S.-G. Chen, R. A. Cormier, *Chem. Mater.* **2004**, *16*, 4586.
- [54] S. A. Gregory, R. Hanus, A. Atassi, J. M. Rinehart, J. P. Wooding, A. K. Menon, M. D. Losego, G. J. Snyder, S. K. Yee, *Nat. Mater.* **2021**, *20*, 1414.

CHAPTER 2

Double Doping of Conjugated Polymers Can Be Induced by the High-Dielectric Environment Present During Anion-Exchange Doping

Chapter 2 examines how the dielectric environment influences chemical doping in conjugated polymers. By separating the initial doping step from the electrolyte exposure step, this chapter shows that high-dielectric electrolyte solutions can enhance the effective oxidizing power of dopants and enable double doping, where an already-reduced dopant anion oxidizes the polymer backbone a second time. These results highlight the dielectric environment as a key factor controlling the enhanced doping efficiency observed during anion-exchange doping.

Supporting Information is given in Appendix A.

Abstract

Anion-exchange doping (AED) enhances the efficiency of chemical doping in conjugated polymers by incorporating an electrolyte into the dopant solution; however, the mechanism by which this improvement occurs relative to conventional doping without an electrolyte remains unclear. Here, we investigate the role of the electrolyte using a multistep variant of AED, denoted “2-pot AED”, in which the polymer film is first conventionally doped and then exposed to an electrolyte solution in a separate step. We compare conventional doping and 2-pot AED using poly(3-hexylthiophene-2,5-diyl), poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT), the dopant (2,3,4,5,6-pentafluoro)benzyloxy-substituted icosahedral dodecaborane (DDB-F₆₀), and the electrolyte lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Using UV–vis–NIR spectroscopy and Hall effect measurements, we show that, when a sufficiently strong dopant is used, exposure to the electrolyte enables the already-present dopant anions to oxidize the polymer a second time, nearly doubling the carrier density. Through a series of control experiments, we attribute these additional carriers to dielectric-enhanced double doping. By decoupling the high-dielectric environment from the initial doping step, we show that the increased dielectric constant of the electrolyte-swollen polymer film is the key contributor to the enhanced carrier generation observed with AED.

2.1 Introduction

Semiconducting polymers have garnered significant interest for use in electronic and energy applications due to their solution-processability, mechanical flexibility, and chemical tunability.^[1–3] One of the primary challenges for using semiconducting polymers in different applications is their intrinsically low electrical conductivity (σ), which arises from their wide bandgaps and low density of intrinsic charge carriers. Chemical doping has become a central strategy for enhancing the charge carrier density of semiconducting polymers.^[4–8] In particular, sequential processing (SqP) has emerged as a powerful and widely adopted doping method. In this method, a dopant solution, made using a solvent chosen to swell but not dissolve the polymer, is spin-coated onto a pre-cast polymer film; mass action then drives the dopant into the swollen film, allowing for the preservation of the structure of the original undoped polymer matrix and the production of high-performance doped polymer films.^[9,10]

In the case of *p*-type semiconducting polymers, doping occurs via electron transfer from the polymer backbone to the dopant molecule, generating positively charged carriers (holes).^[11–15] This means that efficient *p*-type doping requires a dopant with sufficient oxidizing power to remove electrons from energy levels at and below the polymer's highest occupied molecular orbital (HOMO), or valence band. When an electron is removed from the HOMO of a conjugated polymer, the polymer backbone undergoes a local structural change from an aromatic to a quinoidal configuration.^[16] This transformation gives rise to a polaron, which consists of the unpaired electron, positive charge, and the accompanying distortion of the polymer chain. Polaron formation on semiconducting polymers introduces two new electronic states within the polymer bandgap, enabling two new optically allowed transitions in addition to the bandgap transition. The new polaron absorption peaks can be observed through UV–vis–NIR spectroscopy and are usually

denoted as P1, which occurs in the mid-infrared near ~ 0.5 eV, and P2, which is usually seen in the near-infrared at ~ 1.5 eV. Since the P1 transition occurs in an otherwise spectrally quiet region, one can use its oscillator-strength-weighted integrated area to roughly estimate the number of carriers on a doped conjugated polymer.^[17–19]

Previous work by our groups demonstrated the use of a series of functionalized dodecaborane (DDB) cluster-based dopants for the chemical doping of conjugated polymers like poly(3-hexylthiophene-2,5-diyl) (P3HT) (see **Figure 2.1a** for chemical structure).^[20–23] The DDB dopants share a common dodecaborane cage core structure, and their periphery can be readily functionalized to tune their redox potentials.^[20] Due to their high doping efficiency and large molecular size, typically ~ 2 nm in diameter,^[21] DDB-based dopants are particularly effective in minimizing Coulombic interactions between the generated polarons and the dopant counterions, resulting in enhanced carrier delocalization as seen by high Hall carrier mobilities and a red-shift of the P1 absorption band. As a result, chemical doping of conjugated polymers with DDB clusters leads to significant improvements in σ , attributable to both increased carrier density and mobility.^[20–22]

Recently, a new variation of sequential doping for conjugated polymers, the anion-exchange method, has been introduced by Yamashita *et al.*^[24] In this method, pre-cast polymer films are immersed in a solution containing both a molecular dopant and a high concentration of an electrolyte, such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The doping occurs in two steps where the dopant oxidizes the polymer, and then mass action causes the dopant's counterion to be replaced by the electrolyte anion. This method allows for precise control over the choice of counterion that remains in the doped polymer films. It can also achieve much higher doping levels than conventional methods in which only molecular dopants are introduced by the

SqP method, leading to much higher σ than achieved by the same dopant when no electrolyte is present in solution.^[24–26]

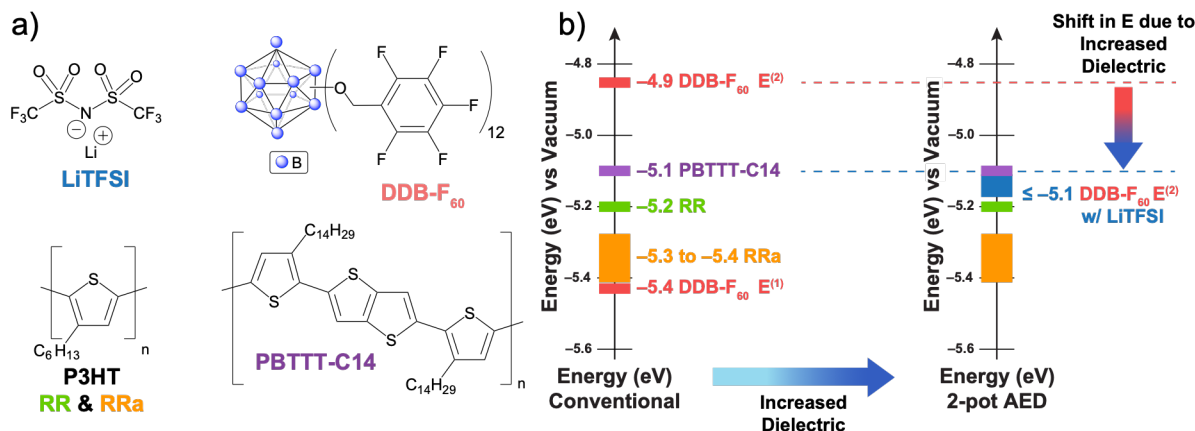


Figure 2.1. (a) Structures of the polymers, dopant, and electrolyte used for investigating the extra oxidizing power achieved by anion-exchange doping in this work. (b) Energy level diagram for the conjugated polymers, PBTTT-C14, regioregular (RR) and regiorandom (RRa) P3HT, as well as the dodecaborane cluster (DDB-F₆₀) in the presence and absence of electrolyte (LiTFSI). The idea is that the electrolyte increases the dielectric constant of the dopant solution, which in turn increases the dielectric constant of the solvent-swollen polymer film, allowing dopants to more easily remove electrons from conjugated polymers. Here, we focus on the example where the dielectric enhancement of anion exchange allows the DDB-F₆₀[−] anion to dope PBTTT, something that is not possible with conventional doping. The HOMO levels for PBTTT and RR P3HT were obtained from Refs. [27–29] and Refs. [30,31], respectively. The energy level offset between RR and RRa P3HT was obtained from Refs. [32–34].

Although anion exchange provides a significant enhancement in doping efficiency, there is not a detailed mechanistic understanding of why this enhancement occurs. Murrey *et al.* developed a thermodynamic model—termed the Generalized Anion Exchange Isotherm (GAEI)—in an attempt to understand and predict the way anion-exchange doping enhances carrier creation in semiconducting polymers.^[26] According to the model, which is based on the Langmuir adsorption isotherm, anion-exchange doping is more thermodynamically favored than conventional doping when the electrolyte counterion forms a weaker ion pair with the polymer cation (polaron) than with the original dopant counterion. The model does predict an enhanced driving force for

exchange at higher salt concentrations, but is unable to explain experimental results showing that anion-exchange doping still proceeds efficiently at relatively low salt concentrations.^[26] This suggests that other factors must play a critical role in producing the effective extra oxidizing power associated with anion-exchange doping.

Here, we propose an alternative mechanism to explain the enhanced doping observed in the anion-exchange doping process. Our idea is based on the fact that the concentrated electrolyte solutions used in anion-exchange doping have very high dielectric constants (ϵ), so that they also raise the dielectric constant inside the swollen polymer film when doping via SqP. Given that the typical ϵ of conjugated polymers is ~ 3 while that of a salt solution can easily exceed ~ 100 ,^[35] the elevated dielectric environment of an electrolyte-swollen conjugated polymer could reduce the energetic cost of charge transfer from the polymer backbone to the dopant during chemical doping.

To test this idea that anion-exchange doping depends on the local dielectric environment, in this work we make use of a two-step sequential doping process, which we refer to as “2-pot anion-exchange doping (AED)”, where we first conventionally dope a polymer film and then spin-coat a plain electrolyte solution without any redox-active chemicals onto the pre-doped film in a second processing step. Our goal is to build on work from Kiefer *et al.*^[36] and Järsvall *et al.*,^[37] who demonstrated that “double doping” of conjugated polymers can occur when both the neutral dopant and its reduced anion possess sufficient redox strength to oxidize a polymer backbone; in other words, with strong dopants and easily oxidized polymers, each dopant can create two charge carriers. Here, we chose a dopant that is not able to double-dope a conjugated polymer film on its own, but show that this dopant becomes able to double-dope when the pre-doped film is swollen in the presence of a high-dielectric electrolyte solution during 2-pot AED. Since we have decoupled the doping and exchange steps using 2-pot AED, we are thus able to show that it is the

enhanced dielectric constant, not the entropy of counterion release as in the GAEI model,^[26] that is the primary factor leading to the enhanced doping efficiency associated with anion-exchange doping.

For our main experiments, we use poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene) (PBTTT-C14; see **Figure 2.1a** for chemical structure), a well-characterized semiconducting polymer known for its high crystallinity and elevated HOMO level (-5.1 eV),^[27,28] which facilitates efficient *p*-type doping. For our dopant, we choose a dodecaborane-based cluster functionalized with sixty peripheral fluorine atoms (DDB-F₆₀; also see **Figure 2.1a** for chemical structure), which is easily capable of doping PBTTT but whose anion has a redox potential roughly 200 mV too low to dope this polymer a second time,^[38–41] as summarized in **Figure 2.1b**. We show that by immersing a DDB-F₆₀-doped PBTTT film in an electrolyte solution containing LiTFSI (also see **Figure 2.1a** for chemical structure), we can raise the dielectric of the swollen film enough for the DDB-F₆₀[−] anion to be able to oxidize the polymer again, leading to double doping of PBTTT. We verify that double doping takes place using both UV–vis–NIR spectroscopy and Hall effect measurements, which show that the 2-pot AED process indeed doubles the number of carriers compared to the conventional single-doping process. Control experiments with different polymers, dopants, and salt concentrations all help to verify that the increased dielectric constant is what is responsible for the enhanced doping efficiency of anion-exchange doping.

2.2 Results and Discussion

To investigate the ability of the enhanced dielectric constant associated with 2-pot AED to double dope conjugated polymers, we examine 2-pot AED not only with PBTTT but also with two different regioregularities (RR, regioregular, and RRa, regiorandom) of poly(3-hexylthiophene-2,5-diyl) (P3HT). **Figure 2.1b** shows an energy level diagram depicting the P3HT HOMO levels

(-5.2 eV RR^[30,31] and -5.3 to -5.4 eV RRa^[32–34]) as well as the doping ability for the first and second reduction of DDB-F₆₀, as measured by cyclic voltammetry (CV) (see Appendix A **Figure A14**). As is well documented in the literature, PBTTT is ~ 100 mV easier to oxidize than RR-P3HT and ~ 300 mV easier to oxidize than RRa-P3HT. Thus, we can make use of the energy level differences between these polymers to evaluate when the anion-exchange process can induce double doping via the 2-pot AED method. The energy level diagram in **Figure 2.1b** shows that the DDB-F₆₀[−] anion must effectively gain ~ 200 mV of oxidizing power to double dope PBTTT, as confirmed by the CV scans in Appendix A **Figure A14**, but would need to become ~ 300 mV more oxidizing to undergo efficient second-charge transfer with RR-P3HT and ~ 400 – 500 mV more oxidizing to double-dope RRa-P3HT.

We prepared our PBTTT thin films by spin-casting a hot (120 °C) 1% w/v solution in a 1:1 mixture of *o*-dichlorobenzene (*o*-DCB) and chlorobenzene (CB) followed by a thermal annealing step at 180 °C for 10 minutes under an inert atmosphere.^[42] The annealed films were then sequentially doped by soaking them in a solution of 1 mM DDB-F₆₀ in dichloromethane (DCM) followed by a solvent washing step with pure acetonitrile (ACN) to remove any unreacted neutral dopants, as described further below. P3HT films were spin-cast from a 2% w/v (20 mg/mL) *o*-DCB solution and left to rest under an inert atmosphere before the doping and washing steps mentioned above. Finally, the doped and washed polymer films were soaked in an *n*-butyl acetate (*n*-BA) solution containing 3.5, 17, or 104 mM LiTFSI to perform the 2-pot AED process, followed by a final ACN washing step to remove any extra electrolyte (see Appendix A **Figures A2 and A3** for solvent washing comparisons between ACN and *n*-BA washes). For additional sample and device fabrication details, please see Appendix A.

To confirm that 2-pot AED causes double doping from the DDB-F₆₀[−] anions in the film rather than any conventional doping from leftover neutral DDB-F₆₀ molecules that might have remained on the film’s surface, we conducted rigorous solvent-washing experiments using ACN, a solvent that dissolves the neutral DDB-F₆₀ dopant but not the polymer. We note that it is challenging to use UV–vis spectroscopy to determine the relative amounts of DDB-F₆₀[−] anion and any potential neutral DDB-F₆₀ dopant in conjugated polymer films because they have their primary electronic absorptions at ~2.3 eV and ~2.7 eV, respectively, which directly overlap the polymer bandgap absorption.^[38,41] Thus, to verify that washing with ACN does effectively remove any remaining neutral DDB-F₆₀ from the doped polymer films, we tested the washing process on films of the neutral DDB-F₆₀ dopant in polystyrene (PS), as shown in Appendix A **Figure A1**. The PS films were spin-coated and subsequently soaked in a 1 mM DDB-F₆₀ solution, after which an absorption peak at ~2.7 eV showed significant uptake of the neutral dopant. When we then washed these DDB-F₆₀-infiltrated PS films with ACN, we found that the DDB-F₆₀ absorption vanished, verifying that the solvent wash was effective at removing the neutral dopant (see Appendix A **Figure A1**).

We used this same ACN washing procedure on DDB-F₆₀-doped conjugated polymer films to ensure that there was no unreacted neutral dopant in the films that could become activated in the presence of the 2-pot AED electrolyte solution and thus cause additional doping. We found that the washing step did not change the UV–vis absorption spectrum of the doped polymer films (see Appendix A **Figure A2**), verifying that washing did not affect the initial doping process. We also found that the washing step made almost no difference in the subsequent 2-pot AED step, verifying that any additional charge carriers produced must have come from double doping by the DDB-F₆₀[−] anion and not from unreacted neutral dopant in the film.

2.2.1 Anion Exchange Enables Double Doping in a High-Dielectric Environment

We first investigate how the introduction of an electrolyte increases the dielectric constant of the environment in a doped polymer film by demonstrating that 2-pot AED results in the double doping of PBTtT. To evaluate the 2-pot AED doping enhancement, we start with UV–vis–NIR spectroscopy; as mentioned above, this technique provides a method for assessing the degree of doping of conjugated polymers by probing the amount of polaronic absorption. We proceeded by doping PBTtT with 1 mM DDB-F₆₀ in DCM and then performing 2-pot AED with LiTFSI solutions of different concentrations (3.5, 17, and 104 mM) in *n*-BA; the results are shown in **Figure 2.2a**.

The data in **Figure 2.2a** show that undoped PBTtT (purple curve) has its characteristic bandgap (BG) absorption peaking near 2.3 eV. Upon SqP doping with DDB-F₆₀ (red curve), we see a small depletion of the BG absorption plus creation of the characteristic P2 and P1 polaronic absorption peaks near ~1.5 eV and ≤0.5 eV, respectively, which indicate the formation of charge carriers. Interestingly, similar to what was observed in our control experiments using PS films (see Appendix A **Figure A1**), the lack of any observable absorption shoulder near 2.7 eV provides a strong indication that there is no neutral DDB-F₆₀ present in the doped PBTtT film, demonstrating that the solvent wash step (ACN) before the 2-pot AED step effectively removed any residual neutral DDB-F₆₀ from this film (see Appendix A **Figure A2**). We note that the BG bleach of the doped PBTtT films appears smaller than that observed with other dopants because the DDB-F₆₀[−] anion absorbs near 2.3 eV, overlapping the polymer BG absorption.^[38,41]

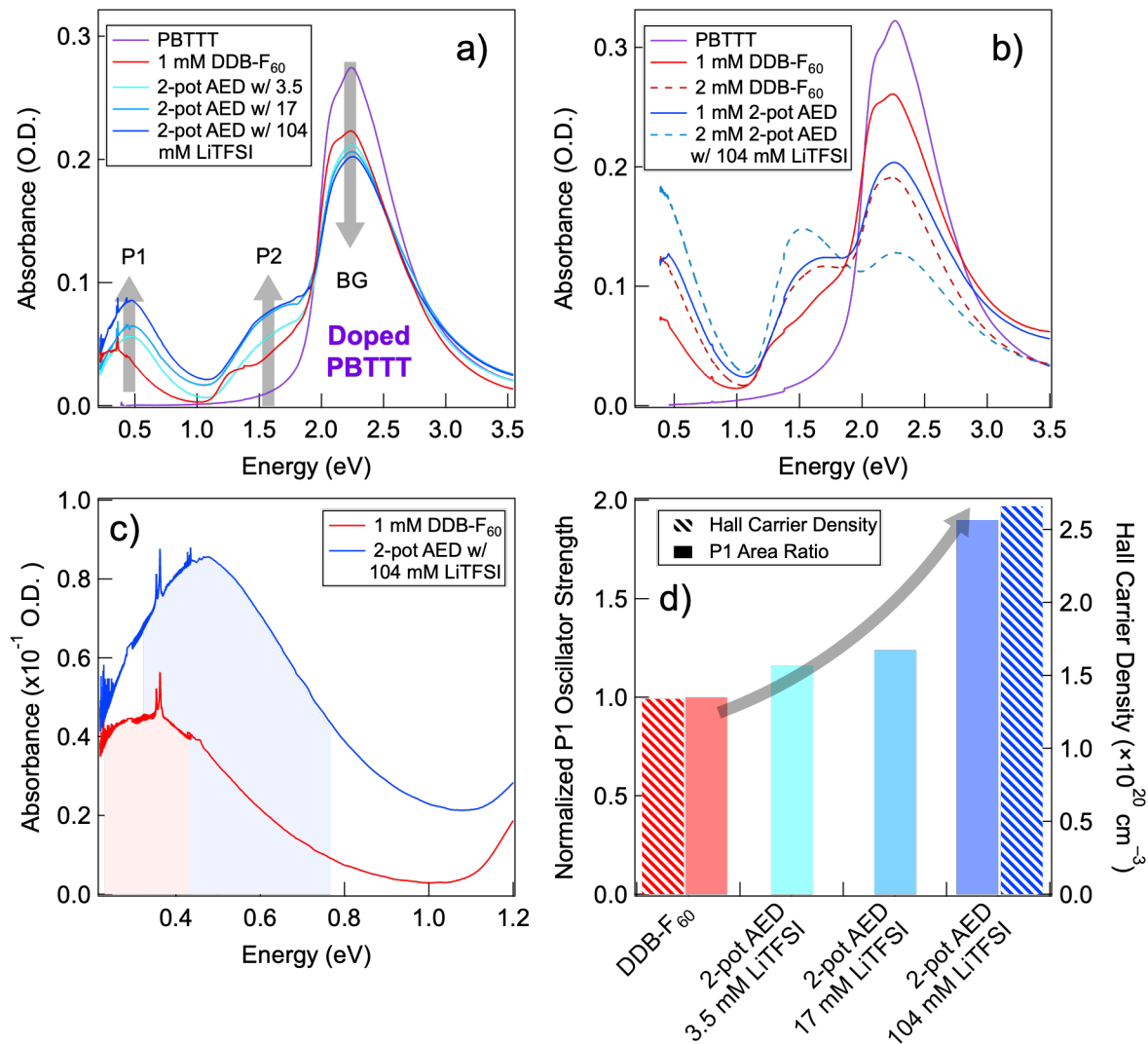


Figure 2.2. UV-vis-NIR absorption spectra for (a) PBTtT doped conventionally with 1 mM DDB-F₆₀ and PBTtT doped with 1 mM DDB-F₆₀ and then subjected to 2-pot AED with different LiTFSI concentrations. The intensities of the P1 and P2 polaronic bands increase with increasing electrolyte concentration, as denoted by the gray arrows, indicating that the high-dielectric environment with 2-pot AED can achieve double doping of PBTtT. (b) Absorption spectra of PBTtT films doped with both 1 mM (solid curves) and 2 mM (dashed curves) DDB-F₆₀ solutions using both the conventional (red curves) and 2-pot AED (blue curves) methods, where the LiTFSI concentration was fixed at 104 mM. Panel (c) displays a zoomed-in view of the P1 polaron absorption peak for PBTtT doped with 1 mM DDB-F₆₀ and the same sample following 2-pot AED with 104 mM LiTFSI. The shaded areas indicate the spectral regions used to calculate the oscillator-strength-weighted integrated P1 areas in panel (d). Panel (d) compares the normalized oscillator-strength-weighted P1 areas (solid bars) and Hall carrier densities (striped bars) for the doped PBTtT samples shown in panel (c). Both the P1 areas and Hall carrier densities increase by $\sim 2\times$ following 2-pot AED at high electrolyte concentrations, verifying double doping.

The blue curves in **Figure 2.2a** show that the P1 and P2 absorption bands increase in intensity with increasing electrolyte concentration following 2-pot AED (as indicated by the gray arrows); the absorption in the BG region also decreases, both due to additional doping and to exchange of the DDB-F₆₀⁻ anion for the TFSI⁻ anion, which does not absorb at 2.3 eV (we verify that the anion-exchange process indeed goes to completion below using grazing-incidence wide-angle X-ray scattering (GIWAXS)). These data directly show that the amount of salt in the 2-pot AED solution influences the number of carriers in the doped film. Since the only way new carriers could be created is via doping from the DDB-F₆₀⁻ anion, this means that higher electrolyte content facilitates double doping through electron transfer from the polymer backbone to DDB-F₆₀⁻ anions. We believe that this observation points to a key role played by the dielectric environment: as LiTFSI is added to the 2-pot AED solution, the dielectric constant (ϵ) of the swollen doped polymer film increases, effectively increasing the oxidizing power of the already-present DDB-F₆₀⁻ anions.

One of the key advantages of using DDB-F₆₀ to understand how anion exchange increases doping efficiency is that this dopant minimizes ion pairing effects. This is because the polarons formed by doping with DDB-F₆₀ are highly delocalized, as seen by the red-shifted P1 peak location in **Figure 2.2c**, due to the large size of the counterion that minimizes Coulombic interactions with the polaron.^[21,22,40] In contrast, TFSI⁻ anions form more Coulombically trapped polarons, as indicated by the blue shift of the P1 peak location after the 2-pot AED step.^[17–19,21,22,40] The fact that increased doping occurs even in the presence of stronger polaron–counterion pairing following 2-pot AED further underscores that dielectric enhancement, rather than entropic effects like ion pairing or mass action alone, is primarily responsible for facilitating the second charge transfer and counterion exchange in the double doping process.

We also note that in solution, highly polarizable anions tend to form weak ion pairs with smaller cations, like Li^+ . The TFSI^- anion is known to form relatively weak ion pairs with Li^+ due to its poor affinity for Li^+ ,^[24,43] and we expect the DDB-F_{60}^- anion to form even weaker ion pairs with Li^+ because of its larger size and delocalized negative charge. This implies that the observed anion exchange from DDB-F_{60}^- to TFSI^- is not primarily driven by the dissociation or formation of strong Li^+ -anion pairs but rather is facilitated by the dielectric increase in the swollen polymer matrix, which screens electrostatic interactions and allows anions to exchange more freely. This supports the idea that dielectric screening, rather than ion-pairing enthalpy or entropic considerations alone, is the dominant factor enabling continued charge transfer and counterion exchange during the double doping process.^[24,26,44]

The largest increase in the P1 absorption intensity observed in **Figure 2.2a** occurred for the PBTTT sample doped with 1 mM DDB-F_{60} followed by 2-pot AED with 104 mM LiTFSI . We can quantify the extent of 2-pot AED-induced double doping in two ways, first by using the intensity of the P1 band of the polarons created by doping. Although there are changes in peak position and shape following 2-pot AED, the integrated oscillator strength in the P1 band should be proportional to the number of carriers that are present.^[20,25,26,45,46] Thus, one way we can determine the relative amount of additional doping induced by 2-pot AED is by examining the changes in the integrated P1 oscillator strength.

Figure 2.2c shows the NIR P1 spectra of PBTTT doped with 1 mM DDB-F_{60} and the corresponding 2-pot AED sample (1 mM DDB-F_{60} followed by 104 mM LiTFSI). The shaded regions, chosen as 80% of the peak height on the low-energy side and 50% of the peak height on the high-energy side, represent the energy range over which we chose to integrate the peak areas. More information about the P1 area integrations is given in Appendix A. The oscillator-strength-

weighted integrated P1 peak areas are compared in **Figure 2.2d**, where we normalize the integrated area for the conventionally doped sample to 1 and express the integrated areas of the 2-pot AED samples relative to this value. Interestingly, we observe the P1 area increase as the salt concentration increases until the area exactly doubles, within error, following the 2-pot processing step at a 104 mM salt concentration. This suggests that the use of the 1:104 dopant-to-electrolyte ratio achieves ~100% double doping efficiency.

Even at low dopant-to-electrolyte ratios (1:3.5 and 1:17), we observe both an increase in integrated P1 area (**Figure 2.2d**) and a blue shift in P1 peak location (**Figure 2.2a**; see Appendix A **Figure A4** for normalized P1 peaks). These spectral changes indicate that double doping and efficient anion exchange, respectively, occur even in low dopant-to-electrolyte ratios where entropic effects like mass action and ion pairing are expected to be minimal. This observation is further supported by the structural measurements (described further below in conjunction with **Figure 2.3**) shown in Appendix A **Figure A13**, which show that high and low dopant-to-electrolyte ratio 2-pot AED-doped samples have similar structures, indicating that anion exchange of the large DDB-F₆₀⁻ anion with the smaller TFSI⁻ anion was successful in both cases. The fact that anion exchange takes place fully at different 2-pot AED electrolyte concentrations shows clearly that the extra driving force for doping is not coming from mass action or changes in ion pairing.

As another route to verify the extent of double doping induced by 2-pot AED, we performed Hall effect measurements, details of which are provided in Appendix A, on our DDB-F₆₀-doped PBTTT films both before and after 2-pot AED using 104 mM LiTFSI. The results are summarized by the dashed bars in **Figure 2.2d**. In agreement with the oscillator-strength-weighted P1 peak area integration, we find that the carrier density doubles from $1.3 \times 10^{20} \text{ cm}^{-3}$ for the 1 mM DDB-F₆₀-doped PBTTT film to $2.7 \times 10^{20} \text{ cm}^{-3}$ for the same film after 2-pot AED with

104 mM LiTFSI. This agreement confirms that the high-dielectric environment created by swelling with the salt solution allows for high-efficiency double doping of PBTTT by DDB-F₆₀.

This idea of dielectric-induced double doping is depicted in the energy level diagram in **Figure 2.1b**: the second electron affinity (EA) of DDB-F₆₀ at -4.9 eV effectively drops when the doped film is swollen with a high-dielectric solution; the amount of the effective EA drop depends on the local dielectric constant, which in turn varies with the amount of LiTFSI in the swelling solution. At the highest salt concentration (104 mM), the fact that we observe complete double doping of PBTTT with DDB-F₆₀[−] anions suggests that the enhanced dielectric environment in the swollen polymer film is equivalent to ~ 200 mV of additional oxidizing power for the dopant anion to fully dope PBTTT based on its reported HOMO level.

To further understand the role that the dielectric effect plays in enabling double doping, we varied the concentration of DDB-F₆₀ used in the initial doping step prior to the 2-pot anion-exchange step, as shown in **Figure 2.2b**. By keeping the LiTFSI concentration constant while changing the dopant concentration, we fixed the dielectric environment of the swollen film while varying the electrolyte-to-dopant ratio. Similar to the results in panel (a), we observe increases in the P1 and P2 polaron absorption bands when PBTTT is doped with both 1 mM and 2 mM DDB-F₆₀ solutions and then subsequently subjected to 2-pot AED with a 104 mM LiTFSI solution. Hall carrier densities, shown in Appendix A **Table A1**, and UV–vis–NIR spectra, shown in **Figure A6**, confirm that double doping takes place even at higher dopant concentrations where the electrolyte-to-dopant ratios are lower.

2.2.2 Structural Changes in Double-Doped PBTTT Films

To verify that the 2-pot AED method allows for full exchange of the DDB-F₆₀[−] anions for TFSI[−] anions from the electrolyte, we performed grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements (see Appendix A **Figure A8** for the full 2D diffractograms) on pristine PBTTT films (purple curves), films conventionally doped with DDB-F₆₀ (red curves), and the same films subjected to 2-pot AED with a LiTFSI solution (blue curves), all of which are shown in **Figure 2.3**. Due to the preferential edge-on orientation of PBTTT, the out-of-plane integration (panel (a)) shows the scattering from the lamellar (*h*00) structure of PBTTT, while the in-plane integration (panel (b)) emphasizes scattering from the polymer π -stacking (0*k*0). For the undoped polymer (purple curves), the lamellar (*h*00) peaks appear at *q*-spacing values of multiples of $\sim 0.29 \text{ \AA}^{-1}$, corresponding to a lamellar spacing of $\sim 21.6 \text{ \AA}$, which agrees with other reports for PBTTT in the literature.^[47–50]

Previous work by our groups has demonstrated that bulky dodecaborane-based dopants like DDB-F₆₀ intercalate into the lamellar region of conjugated polymer crystallites between the side chains,^[21,22,40] given the very large size of these dopants ($\sim 2 \text{ nm}$ diameter),^[21] this forces a significant expansion of the lattice in the lamellar direction.^[20] Similarly, for our samples of PBTTT doped with DDB-F₆₀, the red curve in **Figure 2.3a** shows an expansion in the lamellar spacing of the polymer (peaks labeled by (*h*00)') to $\sim 28.8 \text{ \AA}$, verifying the intercalation of this large dopant's counterions.

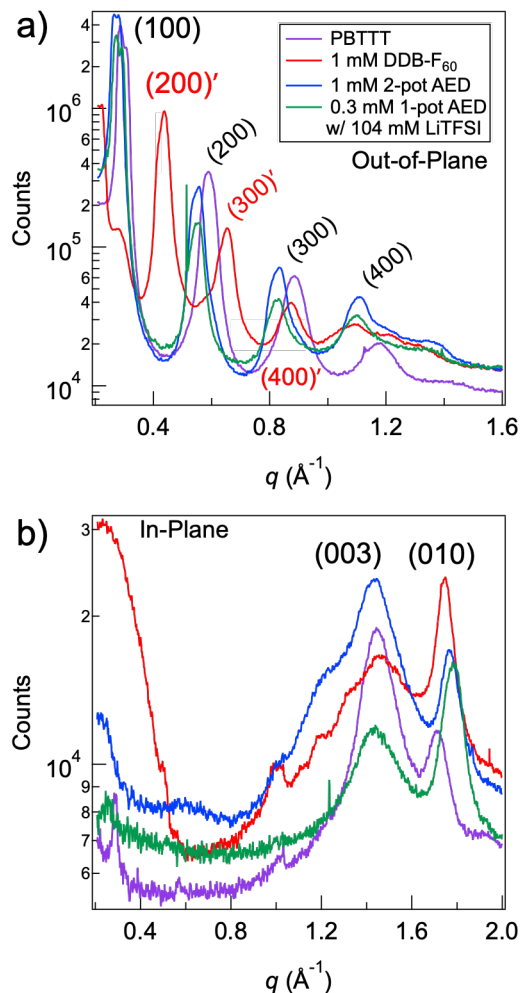


Figure 2.3. Integrated GIWAXS diffractograms of pristine PBTBT (purple curves), PBTBT doped conventionally with DDB- F_{60} (red curves), PBTBT doped by the traditional 1-pot anion-exchange method with DDB- F_{60} and LiTFSI (green curves), and PBTBT doped via 2-pot AED (blue curves). (a) The out-of-plane integrations show that doping PBTBT with DDB- F_{60} results in a PBTBT structure with a highly expanded lamellar spacing, with scattering peaks denoted by the red ($h00$)' labels. As the large DDB- F_{60}^- anion is exchanged with the smaller TFSI $^-$ anion via 2-pot AED, a shift of the lamellar scattering peaks back to higher q -spacing values is observed, indicating that the 2-pot exchange was successful. The lamellar peak positions are at identical q -spacing values following both 1-pot and 2-pot anion exchange, indicating that the same doped final structure is reached independent of how the anion exchange was accomplished. Panel (b) shows the in-plane integrated diffractograms, which again verify that the two anion-exchange processes lead to the same final PBTBT structure.

Figure 2.3a also shows that following the 2-pot AED step (blue curve), there is a shift of the lamellar scattering peaks back to higher q -spacing values, corresponding to a lamellar spacing of ~ 23.0 $\text{\AA}$, indicating a significant contraction in the lamellar spacing. The q -spacing values

obtained after the 2-pot step match those seen with the traditional 1-pot AED method^[24] using 0.3 mM DDB-F₆₀ and 104 mM LiTFSI (green curve), a doping condition that produces a similar overall doping level as our 2-pot AED samples (see Appendix A **Figure A7** for details). The fact that both the traditional and 2-pot anion-exchange processes produce the same final doped and exchanged structures provides additional verification that the 2-pot AED method used here successfully exchanges DDB-F₆₀⁻ anions for TFSI⁻ anions. Moreover, it shows that the enhanced dielectric environment during 2-pot AED not only enables DDB-F₆₀ to double dope the polymer, but that each DDB-F₆₀ dianion is then exchanged for two TFSI⁻ anions that maintain charge neutrality.

Figure 2.3b displays the in-plane GIWAXS integrations for the same set of samples, showing the doping-induced changes in the polymer π -stacking peak, indexed as (010). Although the changes are more subtle than with the lamellar peaks, we see again that the 2-pot and 1-pot AED doping methods lead to a similar final structure, one that is consistent with previous reports for PBTTT doped via conventional anion exchange with the TFSI⁻ anion.^[25,47,48] A more detailed GIWAXS analysis is provided in Appendix A.

2.2.3 Estimating the Magnitude of the High-Dielectric Doping Boost

The fact that our 2-pot AED experiments were able to induce double doping in PBTTT by DDB-F₆₀ suggests that the enhanced dielectric environment provided by the electrolyte solution raises the effective doping power by at least ~200 mV. To better understand the magnitude of the dielectric boost to anion-exchange doping efficiency, we also studied 2-pot AED with both regioregular (RR) and regiorandom (RRa) P3HT, polymers that have HOMO levels that are ~100 and ~200–300 mV deeper than PBTTT, respectively (see **Figure 2.1b**).

Figure 2.4a,b shows the absorption spectra of RR and RRa P3HT films (green and yellow curves, respectively). As in our previous experiments, we doped our two different P3HT materials with 1 mM DDB-F₆₀ (red curves), followed by 2-pot anion exchange with a 104 mM LiTFSI solution (blue curves). The UV–vis–NIR spectra show that, for these two materials, 2-pot AED does not produce an additional increase in the P1 or P2 transition peaks, but only a blue shift in the P1 peak position. This indicates that exposure of the DDB-F₆₀-doped P3HT films to the electrolyte solution does not generate additional carriers but only exchanges the counterions; this exchange is supported by GIWAXS results in Appendix A **Figures A10 and A12**. To quantify the lack of additional doping, we calculate oscillator-strength-weighted P1 peak areas using the same approach applied for PBTTT. **Figure 2.4c** shows that the weighted P1 areas for both P3HT polymers do not increase once the DDB-F₆₀-doped P3HT films are subjected to 2-pot AED with the LiTFSI solution. The integration regions used to calculate the P1 areas are shown in **Figure A5**. Based on the energy level schematic shown in **Figure 2.1b**, the enhanced dielectric environment during 2-pot AED would need to provide ~300 mV of additional oxidizing power for RR-P3HT and ~400–500 mV for RRa-P3HT to enable double doping. This indicates that the additional doping power provided by exposure to the ~104 mM LiTFSI solution is at least 200 but less than 300 mV. As a result, the 2-pot AED double-doping effect is only readily observed when using very strong dopants, such as DDB-F₆₀, and easily oxidized conjugated polymers, such as PBTTT.

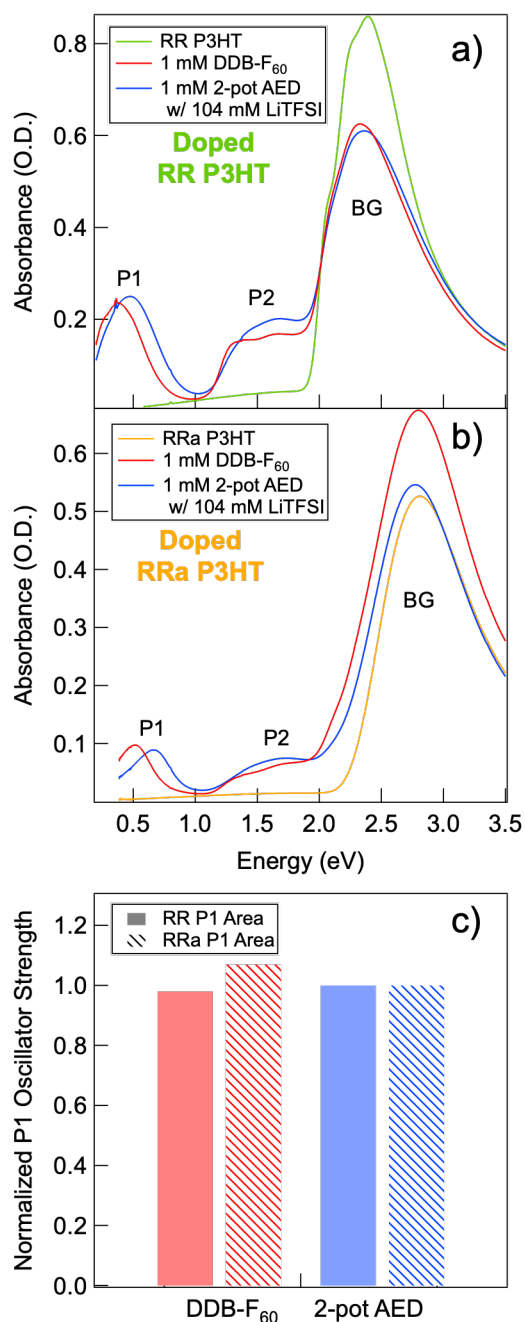


Figure 2.4. UV-vis-NIR spectroscopy of (a) regioregular (RR) P3HT (green curve) and (b) regiorandom (RRa) P3HT (yellow curve), demonstrating that double doping using 2-pot AED with DDB-F₆₀ followed by LiTFSI (blue curves) does not occur for polymers with deeper HOMO levels than PBTBT. The spectra show a blue shift of the P1 band as the counterion is exchanged from the DDB-F₆₀⁻ anion to the TFSI⁻ anion, as expected for the smaller counterion size.^[21–23] (c) Oscillator-strength-weighted P1 peak areas of the conventionally doped and 2-pot AED-doped samples, showing that for the P3HT polymers with their deeper HOMOs, the 2-pot AED process leads to no change in overall doping levels.

2.3 Conclusions

In summary, we have shown that the presence of an electrolyte in the dopant solutions used for anion-exchange doping increases the ability of a dopant to oxidize the conjugated polymer backbone by increasing the dielectric constant in the solvent-swollen polymer film. Interactions between the anions and cations of the electrolyte and the counterions and polarons in the doped polymer, as suggested by the GAEI model,^[26] do not play a significant role in the doping enhancement provided by AED, a conclusion we reached by choosing ions with weak ion-pairing interactions (DDB-F₆₀ and LiTFSI) and by demonstrating that 2-pot anion exchange could induce double doping in PBTTT films doped with DDB-F₆₀. We verified that double doping took place using both UV–vis–NIR spectroscopy and Hall effect measurements, and we showed that 2-pot AED goes to completion using GIWAXS.

In addition, using two types of P3HT with different regioregularities, we showed that the effective increase in oxidation potential provided by swelling a conjugated polymer film with a high-dielectric salt solution is between ~200 and ~300 mV. This value is consistent with the original AED work of Yamashita *et al.*,^[24] which showed that the redox potential of molecular dopants can be significantly enhanced by adding an electrolyte to the dopant solution.^[51–53] In particular, our work also explains Yamashita's observation that different salts produce different degrees of oxidative enhancement:^[24] the dielectric constant of a salt solution depends on the identity of the electrolyte and the degree of ion pairing in the solution, so that the use of different salts results in different extents of dielectric stabilization and thus different effective shifts in oxidation potential.

Fundamentally, double doping through 2-pot AED highlights the role of the dielectric effect as the key factor behind the increase in doping efficiency and doping ability observed in AED.^[24,25]

Understanding the effects that comprise molecular doping techniques, such as AED, can help us improve our control over the dopant–polymer interactions and thus enhance high-efficiency polaron creation. Finally, our work shows that anion exchange has the potential to allow for double doping by changing the dielectric environment of the system, an observation similar to that of Kiefer *et al.*,^[36] who enabled double doping by increasing the polymer’s dielectric constant through the incorporation of glycol side chains. With a deeper understanding of these mechanisms, it should be possible to further advance molecular doping strategies and enhance the performance of conjugated polymers in applications, including thermoelectric and other electronic devices.

2.4 Experimental Section

2.4.1 Materials

Poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene) (PBTTC14) was purchased from Sigma-Aldrich. Poly(3-hexylthiophene-2,5-diyl) (P3HT), including a 93% regioregularity and a regiorandom (RRa) version, was obtained from Rieke Metals, Inc. Polystyrene (PS) was purchased from Sigma-Aldrich. Chlorobenzene (CB, anhydrous, 99%), 1,2-dichlorobenzene (*o*-DCB, anhydrous, 99%), *n*-butyl acetate (*n*-BA, anhydrous, >99%), acetonitrile (ACN, anhydrous, >99%), dichloromethane (DCM, anhydrous, >99%), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Sigma-Aldrich. All chemicals and reagents were used as received. The DDB-based dopant, DDB-F₆₀, was synthesized in-house following previously reported procedures.^[38,54]

2.4.2 Film Preparation

Sample fabrication was carried out on different substrates depending on the application: pre-cleaned sapphire substrates for UV–vis–NIR measurements, glass substrates for electrical

measurements, and pre-cleaned silicon wafers for GIWAXS measurements. Glass substrates were cut into 1.1×1.1 cm pieces. Si substrates were cut into 1.5×1.5 cm pieces. Sapphire substrates were used as purchased/received. All substrates were cleaned sequentially with Alconox detergent, deionized water, and acetone. After drying under nitrogen gas, they were plasma-etched for approximately 15 minutes, then transferred to a nitrogen glovebox for spin coating of polymers and/or dopants. All casting and doping procedures were conducted inside the N₂ glovebox.

A 1 wt% (10 mg/mL) solution of PBTtT in a 1:1 CB:*o*-DCB mixture was stirred at 80 °C until fully dissolved. PBTtT films were spin-coated from this solution at 120 °C, first at 1000 rpm for 60 seconds, followed by a spinning step at 4000 rpm for 5 seconds. The films were subsequently annealed at 180 °C^[42,55] for 10 minutes and allowed to cool to room temperature overnight in the nitrogen glovebox.

For P3HT, 2% w/v (20 mg/mL) solutions of both 93% regioregular (RR) and regiorandom (RRa) P3HT in *o*-DCB were stirred at room temperature for approximately 6 hours until fully dissolved. These solutions were spin-coated onto substrates at 1000 rpm for 60 seconds, followed by 4000 rpm for 5 seconds. The films were stored in the glovebox overnight prior to doping.

Sequential doping was carried out by exposing the pre-cast pristine polymer films to a DDB-F₆₀ dopant solution for 10 seconds, followed by spin coating at 4000 rpm for 10 seconds to remove residual dopant and dry the films. DDB-F₆₀ solutions were prepared by dissolving the dopant in DCM at the specified concentrations.

All doped films were subsequently solvent-washed with 0.5 mL ACN by spin-coating at 4000 rpm for 10 seconds. For 2-pot AED samples, the doped and washed films were further exposed to different concentrations of LiTFSI solutions in *n*-BA by soaking for 80 seconds, followed by a spin coating step at 4000 rpm.

2.4.3 Optical and Electrical Characterization

UV–vis–NIR spectroscopy was performed on films cast on sapphire substrates using a JASCO V-770 spectrometer. Fourier transform infrared (FTIR) measurements were performed on the same sapphire samples using an Agilent Cary 600 series FTIR spectrometer.

Four-point probe conductivity and Hall effect measurements were performed on films deposited on glass substrates. Measurements were carried out using a Lake Shore MeasureReady M91 FastHall instrument in the van der Pauw configuration with square sample geometry. For conductivity and Hall effect measurements, 45-nm-thick gold electrodes were thermally evaporated through a shadow mask onto the doped films using an Angstrom Engineering Nexdep evaporator at pressures below 1×10^{-6} torr and a deposition rate of 0.5 Å/s. Film thicknesses were measured using a Dektak 150 stylus profilometer. At least three independently prepared samples were measured for each condition to ensure reproducibility.

2.4.4 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) Measurements

GIWAXS measurements were performed on silicon substrates at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11-3 using an incident X-ray energy of 12.7 keV and an incidence angle of 0.12°. The 2D GIWAXS patterns were calibrated in Igor Pro using the Nika and Irena packages, and the data were reduced using Nika, Irena, and WAXStools. Measurements were carried out on triplicate samples to ensure reproducibility. Additional experimental and analysis details are provided in Appendix A.

2.4.5 Cyclic Voltammetry (CV) Measurements

All cyclic voltammetry (CV) experiments were performed in an Ar glovebox with O₂ and H₂O levels below 0.2 ppm using a BioLogic VMP3 potentiostat. Measurements were carried out in a three-electrode configuration with a Pt sheet counter electrode, a nonaqueous Ag/Ag⁺

reference electrode (Ag wire in 1 mM AgNO₃/100 mM TBAPF₆ in ACN, separated by a glass frit), and 100 mM TBAPF₆ in ACN as the electrolyte. PBTtT films spin-coated onto indium tin oxide (ITO) substrates were used as the working electrode for the polymer measurements, while a glassy carbon electrode (GCE) was used as the working electrode for the DDB-F₆₀ measurements. 1 mM DDB-F₆₀ was dissolved in the electrolyte prior to collecting the CV scans. All scans were collected at a scan rate of 10 mV s⁻¹, and all potentials were referenced internally to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple.

2.5 References

- [1] A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, A. Salleo, *Chem. Rev.* **2010**, *110*, 3.
- [2] B. Lüssem, M. Riede, K. Leo, *physica status solidi (a)* **2013**, *210*, 9.
- [3] Y. Zhang, H. Zhou, J. Seifter, L. Ying, A. Mikhailovsky, A. J. Heeger, G. C. Bazan, T.-Q. Nguyen, *Advanced Materials* **2013**, *25*, 7038.
- [4] Y. Xu, H. Sun, A. Liu, H.-H. Zhu, W. Li, Y.-F. Lin, Y.-Y. Noh, *Advanced Materials* **2018**, *30*, 1801830.
- [5] Y. Lu, J.-Y. Wang, J. Pei, *Acc. Chem. Res.* **2021**, *54*, 2871.
- [6] B. Yurash, D. X. Cao, V. V. Brus, D. Leifert, M. Wang, A. Dixon, M. Seifrid, A. E. Mansour, D. Lungwitz, T. Liu, P. J. Santiago, K. R. Graham, N. Koch, G. C. Bazan, T.-Q. Nguyen, *Nat. Mater.* **2019**, *18*, 1327.
- [7] Z.-D. Yu, Y. Lu, Z.-Y. Wang, H.-I. Un, S. J. Zelewski, Y. Cui, H.-Y. You, Y. Liu, K.-F. Xie, Z.-F. Yao, Y.-C. He, J.-Y. Wang, W.-B. Hu, H. Sirringhaus, J. Pei, *Science Advances* **2023**, *9*, eadf3495.
- [8] H. Guo, C.-Y. Yang, X. Zhang, A. Motta, K. Feng, Y. Xia, Y. Shi, Z. Wu, K. Yang, J. Chen, Q. Liao, Y. Tang, H. Sun, H. Y. Woo, S. Fabiano, A. Facchetti, X. Guo, *Nature* **2021**, *599*, 67.
- [9] P. Pingel, D. Neher, *Phys. Rev. B* **2013**, *87*, 115209.
- [10] T. J. Aubry, A. S. Ferreira, P. Y. Yee, J. C. Aguirre, S. A. Hawks, M. T. Fontana, B. J. Schwartz, S. H. Tolbert, *J. Phys. Chem. C* **2018**, *122*, 15078.

- [11] J. Li, G. Zhang, D. M. Holm, I. E. Jacobs, B. Yin, P. Stroeve, M. Mascal, A. J. Moulé, *Chem. Mater.* **2015**, *27*, 5765.
- [12] I. E. Jacobs, E. W. Aasen, J. L. Oliveira, T. N. Fonseca, J. D. Roehling, J. Li, G. Zhang, M. P. Augustine, M. Mascal, A. J. Moulé, *J. Mater. Chem. C* **2016**, *4*, 3454.
- [13] R. Ghosh, F. C. Spano, *Acc. Chem. Res.* **2020**, *53*, 2201.
- [14] J. L. Bredas, G. B. Street, *Acc. Chem. Res.* **1985**, *18*, 309.
- [15] R. Tautz, E. Da Como, T. Limmer, J. Feldmann, H.-J. Egelhaaf, E. von Hauff, V. Lemaure, D. Beljonne, S. Yilmaz, I. Dumsch, S. Allard, U. Scherf, *Nat Commun* **2012**, *3*, 970.
- [16] E. C. Wu, C. Z. Salamat, O. L. Ruiz, T. Qu, A. Kim, S. H. Tolbert, B. J. Schwartz, *Advanced Functional Materials* **2023**, *33*, 2213652.
- [17] R. Ghosh, C. M. Pochas, F. C. Spano, *J. Phys. Chem. C* **2016**, *120*, 11394.
- [18] R. Ghosh, A. R. Chew, J. Onorato, V. Pakhnyuk, C. K. Luscombe, A. Salleo, F. C. Spano, *J. Phys. Chem. C* **2018**, *122*, 18048.
- [19] D. T. Scholes, P. Y. Yee, J. R. Lindemuth, H. Kang, J. Onorato, R. Ghosh, C. K. Luscombe, F. C. Spano, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2017**, *27*, 1702654.
- [20] T. J. Aubry, K. J. Winchell, C. Z. Salamat, V. M. Basile, J. R. Lindemuth, J. M. Stauber, J. C. Axtell, R. M. Kubena, M. D. Phan, M. J. Bird, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2020**, *30*, 2001800.
- [21] T. J. Aubry, J. C. Axtell, V. M. Basile, K. J. Winchell, J. R. Lindemuth, T. M. Porter, J.-Y. Liu, A. N. Alexandrova, C. P. Kubiak, S. H. Tolbert, A. M. Spokoyny, B. J. Schwartz, *Advanced Materials* **2019**, *31*, 1805647.
- [22] Y. Wu, C. Z. Salamat, A. León Ruiz, A. F. Simafranca, N. Akmanşen-Kalayci, E. C. Wu, E. Doud, Z. Mehmedović, J. R. Lindemuth, M. D. Phan, A. M. Spokoyny, B. J. Schwartz, S. H. Tolbert, *Chem. Mater.* **2024**, *36*, 5552.
- [23] E. C. Wu, D. G. Vidales, C. Z. Salamat, Q. M. Duong, A. León Ruiz, A. D. Ready, Z. Mehmedović, D. A. Stanfield, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Advanced Functional Materials* *n/a*, e07480.
- [24] Y. Yamashita, J. Tsurumi, M. Ohno, R. Fujimoto, S. Kumagai, T. Kurosawa, T. Okamoto, J. Takeya, S. Watanabe, *Nature* **2019**, *572*, 634.

- [25] I. E. Jacobs, Y. Lin, Y. Huang, X. Ren, D. Simatos, C. Chen, D. Tjhe, M. Statz, L. Lai, P. A. Finn, W. G. Neal, G. D'Avino, V. Lemaure, S. Fratini, D. Beljonne, J. Strzalka, C. B. Nielsen, S. Barlow, S. R. Marder, I. McCulloch, H. Sirringhaus, *Advanced Materials* **2022**, *34*, 2102988.
- [26] T. L. Murrey, M. A. Riley, G. Gonel, D. D. Antonio, L. Filardi, N. Shevchenko, M. Mascal, A. J. Moulé, *J. Phys. Chem. Lett.* **2021**, *12*, 1284.
- [27] A. K. Singh, A. Pandey, P. Chakrabarti, *Organic Electronics* **2019**, *75*, 105424.
- [28] J. E. Cochran, M. J. N. Junk, A. M. Glauddell, P. L. Miller, J. S. Cowart, M. F. Toney, C. J. Hawker, B. F. Chmelka, M. L. Chabinyc, *Macromolecules* **2014**, *47*, 6836.
- [29] I. McCulloch, M. Heeney, M. L. Chabinyc, D. DeLongchamp, R. J. Kline, M. Cölle, W. Duffy, D. Fischer, D. Gundlach, B. Hamadani, R. Hamilton, L. Richter, A. Salleo, M. Shkunov, D. Sparrowe, S. Tierney, W. Zhang, *Advanced Materials* **2009**, *21*, 1091.
- [30] K. Bruchlos, D. Trefz, A. Hamidi-Sakr, M. Brinkmann, J. Heinze, A. Ruff, S. Ludwigs, *Electrochimica Acta* **2018**, *269*, 299.
- [31] P. Acevedo-Peña, A. Baray-Calderón, H. Hu, I. González, V. M. Ugalde-Saldivar, *J Solid State Electrochem* **2017**, *21*, 2407.
- [32] K. N. Baustert, A. Abtahi, A. N. Ayyash, K. R. Graham, *Journal of Polymer Science* **2022**, *60*, 602.
- [33] Y. Lee, A. Mongare, A. Plant, D. Ryu, *Polymers* **2021**, *13*, 935.
- [34] W. C. Tsoi, S. J. Spencer, L. Yang, A. M. Ballantyne, P. G. Nicholson, A. Turnbull, A. G. Shard, C. E. Murphy, D. D. C. Bradley, J. Nelson, J.-S. Kim, *Macromolecules* **2011**, *44*, 2944.
- [35] J. Brebels, J. V. Manca, L. Lutsen, D. Vanderzande, W. Maes, *J. Mater. Chem. A* **2017**, *5*, 24037.
- [36] D. Kiefer, R. Kroon, A. I. Hofmann, H. Sun, X. Liu, A. Giovannitti, D. Stegerer, A. Cano, J. Hynynen, L. Yu, Y. Zhang, D. Nai, T. F. Harrelson, M. Sommer, A. J. Moulé, M. Kemerink, S. R. Marder, I. McCulloch, M. Fahlman, S. Fabiano, C. Müller, *Nature Mater* **2019**, *18*, 149.
- [37] E. Järsvall, T. Biskup, Y. Zhang, R. Kroon, S. Barlow, S. R. Marder, C. Müller, *Chem. Mater.* **2022**, *34*, 5673.

- [38] A. D. Ready, Y. A. Nelson, D. F. Torres Pomares, A. M. Spokoyny, *Acc. Chem. Res.* **2024**, *57*, 1310.
- [39] A. I. Wixtrom, Z. A. Parvez, M. D. Savage, E. A. Qian, D. Jung, S. I. Khan, A. L. Rheingold, A. M. Spokoyny, *Chemical Communications* **2018**, *54*, 5867.
- [40] T. L. Murrey, T. J. Aubry, O. L. Ruiz, K. A. Thurman, K. H. Eckstein, E. A. Doud, J. M. Stauber, A. M. Spokoyny, B. J. Schwartz, T. Hertel, J. L. Blackburn, A. J. Ferguson, *Cell Reports Physical Science* **2023**, *4*, 101407.
- [41] M. S. Messina, J. C. Axtell, Y. Wang, P. Chong, A. I. Wixtrom, K. O. Kirlikovali, B. M. Upton, B. M. Hunter, O. S. Shafaat, S. I. Khan, J. R. Winkler, H. B. Gray, A. N. Alexandrova, H. D. Maynard, A. M. Spokoyny, *J. Am. Chem. Soc.* **2016**, *138*, 6952.
- [42] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, M. F. Toney, *Nature Mater* **2006**, *5*, 328.
- [43] R. G. Pearson, *Coordination Chemistry Reviews* **1990**, *100*, 403.
- [44] Y. Yamashita, J. Tsurumi, T. Kurosawa, K. Ueji, Y. Tsuneda, S. Kohno, H. Kempe, S. Kumagai, T. Okamoto, J. Takeya, S. Watanabe, *Commun Mater* **2021**, *2*, 45.
- [45] A. R. Umar, A. L. Dorris, C. Grieco, *Advanced Functional Materials* **2024**, *34*, 2407181.
- [46] C. Wang, D. T. Duong, K. Vandewal, J. Rivnay, A. Salleo, *Phys. Rev. B* **2015**, *91*, 085205.
- [47] S. A. Gregory, A. Atassi, J. F. Jr. Ponder, G. Freychet, G. M. Su, J. R. Reynolds, M. D. Losego, S. K. Yee, *J. Phys. Chem. C* **2023**, *127*, 12206.
- [48] Y. Fan, J. Liu, P.-A. Chen, D. Xia, J. Wang, Y. Hu, Z. Liu, Y. Liu, L. Jiang, *Cell Reports Physical Science* **2024**, *5*, 102197.
- [49] W. Jin, C.-Y. Yang, R. Pau, Q. Wang, E. K. Tekelenburg, H.-Y. Wu, Z. Wu, S. Y. Jeong, F. Pitzalis, T. Liu, Q. He, Q. Li, J.-D. Huang, R. Kroon, M. Heeney, H. Y. Woo, A. Mura, A. Motta, A. Facchetti, M. Fahlman, M. A. Loi, S. Fabiano, *Nature* **2024**, *630*, 96.
- [50] J. Kim, D. Ju, S. Kim, K. Cho, *Advanced Functional Materials* **2024**, *34*, 2309156.
- [51] M. J. Bird, T. Iyoda, N. Bonura, J. Bakalis, A. J. Ledbetter, J. R. Miller, *Journal of Electroanalytical Chemistry* **2017**, *804*, 107.
- [52] M. J. Bird, M. A. Pearson, S. Asaoka, J. R. Miller, *J. Phys. Chem. A* **2020**, *124*, 5487.

- [53] J. R. Miller, M. J. Bird, J. R. Miller, M. J. Bird, In *Redox Chemistry - From Molecules to Energy Storage*, IntechOpen, **2022**.
- [54] M. S. Messina, J. C. Axtell, Y. Wang, P. Chong, A. I. Wixtrom, K. O. Kirlikovali, B. M. Upton, B. M. Hunter, O. S. Shafaat, S. I. Khan, J. R. Winkler, H. B. Gray, A. N. Alexandrova, H. D. Maynard, A. M. Spokoyny, *J. Am. Chem. Soc.* **2016**, *138*, 6952.
- [55] M. L. Chabinyc, M. F. Toney, R. J. Kline, I. McCulloch, M. Heeney, *J. Am. Chem. Soc.* **2007**, *129*, 3226.

CHAPTER 3

The Effects of Humidity on the Electrical Properties and Carrier Mobility of Semiconducting Polymers Anion-Exchange Doped with Hygroscopic Salts

Chapter 3 explores the effects of humidity on the electrical properties of anion-exchange-doped conjugated polymers. Given that the anion-exchange-doping method requires hygroscopic salts, this study shows that water absorption into the doped film significantly decreases the electrical conductivity. Using UV–vis–NIR spectroscopy and Hall effect measurements, we show that the drop in conductivity is due to a drop in carrier mobility.

Chapter 3 was reprinted with permission from Duong, Q. M.; Garcia Vidales, D.; Schwartz, B. J.; and AIP Publishing. “The Effects of Humidity on the Electrical Properties and Carrier Mobility of Semiconducting Polymers Anion-Exchange Doped with Hygroscopic Salts,” *Appl. Phys. Lett.* **123**, 202101, 1–6 (2023); DOI: 10.1063/5.0169905.

A reprint of the Supporting Information is given in Appendix B.

Abstract

To improve their electrical conductivity for various applications, semiconducting polymer films are often chemically doped to increase their equilibrium charge carrier density. Recently, a novel doping method involving anion exchange has provided control over the identity of the counterions that reside in such films, leading to increased stability under ambient conditions. In this work, however, we show that by ion-exchanging 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ)-doped poly(3-hexylthiophene-2,5-diyl) (P3HT) films with hygroscopic salts like lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) or lithium hexafluorophosphate (LiPF₆), the doped film's electrical conductivity drops significantly when exposed to ambient humidity. The change in electrical conductivity depends directly on the degree of hygroscopicity of the counterion and can be over 50% with relatively modest changes in relative humidity (RH), and up to a factor of four between ambient and completely dry conditions. The film's humidity response is entirely reversible when adsorbed water is removed, potentially allowing the doped semiconducting polymer films to function as humidity sensors. Hall effect measurements show that the cause of the drop in conductivity with increasing RH is due to a decrease in carrier mobility and not due to dedoping. Our results emphasize that it is important to control the sample environment when making electrical measurements on doped semiconducting polymer films.

3.1 Introduction

Thanks to their ease of processing, structural tunability, low intrinsic thermal conductivity, and biocompatibility, interest in using semiconducting polymers for applications such as biosensors or thermoelectric generators has grown steadily.^[1-3] Due to their intrinsically low carrier density, conjugated polymers need to be electrically doped to meet the performance standards demanded by many applications. The most common way to do this is through chemical doping, a process that introduces a small molecule that can undergo a charge transfer reaction with the semiconducting polymer; since most conjugated polymers are *p*-type materials, oxidizing agents are chosen to create mobile hole charge carriers.^[4-6] The extent of chemical doping depends mainly on the polymer's ionization energy and the dopant's electron affinity,^[7] as well as the concentration of the dopant that is used.^[8]

Recently, Yamashita *et al.* introduced a novel method referred to as anion-exchange doping,^[9] which provides several advantages over conventional chemical doping. The method involves exposing a conjugated polymer film to a solution containing both a chemical dopant and a high concentration of electrolyte. The dopant oxidizes the polymer, and the dopant counterion is then exchanged out by mass action for the electrolyte anion from solution. This method not only provides control over the choice of counterion in doped semiconducting polymer films, but it also can achieve doping levels much higher than those reached via conventional doping: for example, Yamashita *et al.* were able to obtain nearly one carrier per monomer unit for the polymer poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) and the dopant 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) in the presence of different electrolytes.^[9] The ability to choose the counterion inside the doped film can make doped films more stable under ambient conditions,^[9] and also can help tune the effect of Coulomb interaction

between the free carriers on the polymer backbone and its compensating charge, which is important for controlling carrier mobility.^[9,10]

Because of all its advantages, multiple groups are now employing anion-exchange doping when using semiconducting polymers in different applications. In the course of our exploration of anion-exchange doping, however, we have discovered one potentially serious drawback: the typical electrolyte salts used in anion-exchange doping, such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), are generally highly hygroscopic, which means that the electrical behavior of anion-exchange-doped polymer films can be highly sensitive to the ambient humidity. In this work, we show that exposure of anion-exchange-doped polymer films to even moderate humidity can decrease the carrier mobility by over a factor of 3. This means that workers who study the properties of such films need to make sure they do so in a humidity-controlled environment.

There are of course previous studies on the influence of moisture on trap formation in semiconducting polymers.^[11–17] Zuo *et al.* reported that the dielectric effect of water in nanovoids of semiconducting polymer thin films can create carrier traps that can be ~0.3–0.5 eV deep.^[14] These traps can be mitigated by solvent annealing to reduce the number of nanovoids^[14] or by filling the nanovoids with dopants that displace the water.^[11,13,18] Another approach to mitigate the effects of water inhabiting nanovoids is to use conjugated polymers with denser side chain placement, such as regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT),^[17] which is a workhorse material in the field.

The aforementioned moisture studies were done on pristine or very lightly-doped semiconducting polymer films used in either organic field-effect transistors or solar cells, and none of these studies examined the film's electrical conductivity or the effects of different doping

methods. Here, we investigate the effect of humidity on the electrical conductivity, carrier density, and carrier mobility of both conventionally-doped and anion-exchange-doped P3HT films. In particular, we study the effects of moisture on P3HT films doped via the anion-exchange method using LiTFSI, and find a dramatic drop in electrical conductivity with increasing ambient humidity. We then use Hall effect measurements to show that the drop in conductivity with increasing humidity is primarily due to changes in carrier mobility and not due to dedoping. We also show that the effect of humidity on charge transport is quasi-reversible, and that the electrical conductivity changes almost linearly with humidity. Thus, not only is care needed to control the humidity when studying these materials, but anion-exchange-doped conjugated polymer films also could possibly serve a role as resistance-based humidity sensors.

In addition to exploring the effects of humidity on anion-exchange-doped P3HT films, we also demonstrate that the salt's hygroscopicity is key to the drop in electrical conductivity by comparing the properties of anion-exchange-doped P3HT films with LiTFSI to those exchanged with a less hygroscopic salt, lithium hexafluorophosphate (LiPF_6).^[19–22] It is worth noting that determining which of the anions is more hygroscopic depends on the conditions being explored. For example, under conditions close to vacuum dry, the distinction of which ion is more hygroscopic may not be clear, as seen in the ionic liquid literature.^[23,24] But under typical ambient relative humidity conditions such as those studied here, it is generally well accepted that TFSI^- is more hygroscopic than PF_6^- ,^[19–22] and indeed, we will show below that there are stronger humidity effects on the electrical properties of doped P3HT films with TFSI^- than PF_6^- .

3.2 Results and Discussion

3.2.1 Device Fabrication for Doped Semiconducting Polymer Thin Films

The overall goal of this study is to investigate the impact of humidity on conjugated polymer films doped both conventionally and with anion-exchange doping. To conduct this comparison, we start with 112-nm-thick P3HT films spin-cast from a 2% w/v solution in *o*-dichlorobenzene (*o*-DCB). For the conventional doping method, we sequentially dope the P3HT films using different concentrations of F₄TCNQ dissolved in *n*-butyl acetate (*n*-BA). For the anion-exchange doping process, we follow the same procedure as for the conventional doping method, but with the addition of a high concentration of LiTFSI (30 mg/mL) or LiPF₆ (5 mg/mL) dissolved in the same solution as the F₄TCNQ. All of the processing steps were carried out in the inert atmosphere of a glovebox with effectively 0% relative humidity (RH). Details of the materials we use and the casting and doping conditions are given in Appendix B.

3.2.2 Methods for Measuring Electrical Conductivity and Hall Effect

To investigate the effect that humidity plays on the electrical properties of doped conjugated polymer films, we chose dopant concentrations that resulted in similar electrical conductivity values with the two different doping methods (and thus with counterions with different degrees of hygroscopicity). The concentrations we focus on for anion-exchange (AE) and conventional (Conv) doping were 0.1 mg/mL F₄TCNQ + 30 mg/mL LiTFSI, 0.1 mg/mL F₄TCNQ + 5 mg/mL LiPF₆, and 0.5 mg/mL F₄TCNQ, respectively; results with additional doping concentrations are given in Appendix B. We note that the F₄TCNQ concentrations we use are low enough that there is no neutral F₄TCNQ present in the doped films, as confirmed by UV–vis–NIR spectroscopy in **Figure B3** in Appendix B.

After preparing doped P3HT films with these different processing conditions, we measured the films' electrical conductivities in three different environments with different RH levels. First, the conductivity was measured in the inert atmosphere of an Ar-filled glovebox (labeled as Ar Glovebox) with effectively 0% humidity. The samples were then transferred out of the Ar glovebox and exposed to ambient air for roughly 5 minutes before the conductivity was re-measured (labeled as Ambient Air). The air-exposed samples were then purged with Ar for 5 minutes prior to measuring the conductivity for a third time (labeled as Ar Purged). We chose a 5-minute purge because the electrical conductivity of the samples no longer changed past that time.

3.2.3 Electrical Conductivity and Hall Effect Results

Table 3.1 shows the electrical conductivities, measured via the van der Pauw 4-point-probe method with electrodes placed at the corners of our 1.5×1.5 cm samples, of 97% regioregular P3HT films doped using the conventional and anion-exchange methods in environments with different RHs. The conventionally-doped samples have the same electrical conductivity in all three different environments within error. The anion-exchange-doped samples with both salts, however, show a significant drop in conductivity when taken from the inert, 0% RH environment of the Ar Glovebox and introduced to the ambient environment ($\sim 36\%$ and $\sim 40\%$ RH for LiTFSI and LiPF₆, respectively). The drop in conductivity upon exposure to ambient humidity is quite significant, with the LiTFSI anion-exchanged sample showing a conductivity loss of nearly a factor of four. The samples anion-exchanged using LiPF₆ also exhibit a considerable reduction in conductivity, but the decrease is only about a factor of 2. This difference in the humidity-induced conductivity drop between LiPF₆ and LiTFSI makes sense in light of the fact that LiPF₆ is less hygroscopic,^[19–22] indicating that the hygroscopicity of the anion plays a key role in the humidity-dependent electrical behavior. We also saw very similar results for P3HT samples created using different

dopant concentrations and P3HT regioregularities, as demonstrated in **Figure B1** and elsewhere in Appendix B, indicating that the humidity effect is not system specific.

The fact that the drop in conductivity is seen only with the anion-exchange doping method and not with conventional doping also lends support to our conclusion that the humidity effect involves the hygroscopic anions that were exchanged into the doped films. The hygroscopic nature of LiTFSI and its effect on electronic transport is well-documented in the mixed organic/inorganic perovskite solar cell community, where LiTFSI is often employed as an additive to enhance the *p*-doping of 2,2',7,7'-tetrakis-(N,N-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD).^[21,25–28] However, in the case of perovskite materials, the consequence of using LiTFSI is more severe than just the introduction of carrier traps, as adsorbed water can actually dissolve the material.^[29]

To verify that it is water in the ambient environment that causes the large drop in conductivity for the anion-exchange-doped P3HT films, we attempted to restore the conductivity by flowing either dry air or argon gas into our ambient conductivity measurement setup; **Table 3.1** shows that doing so yielded partial recovery of the conductivity. However, we were able to fully recover the original conductivity measured in the Ar glovebox by subjecting the films to a vacuum/purging process. This process involved 4 cycles where the films were placed under rough-pump vacuum for 5 minutes, followed by an Ar-gas refill (the green X in **Figure B2** in Appendix B shows the fully-recovered conductivity value for the 0.1 mg/mL LiTFSI-anion-exchanged sample after undergoing this process). All of this is consistent with the idea that an initially “dry” anion-exchange-doped sample readily absorbs water due to hygroscopic counterions upon exposure to moist air. Surface-level adsorbed water can easily be removed simply by purging with dry gas, resulting in partial restoration of the electrical conductivity. However, exposing the

samples to the vacuum/purging process enables the complete removal of water from deeper within the films, leading to full recovery of the electrical conductivity.

Table 3.1. Electrical conductivities of anion-exchange- (AE) and conventionally- (Conv) doped P3HT films measured under different environmental conditions. The dopant concentrations for AE were 0.1 mg/mL F₄TCNQ + 30 mg/mL LiTFSI and 0.1 mg/mL F₄TCNQ + 5 mg/mL LiPF₆, while the conventionally-doped samples used 0.5 mg/mL F₄TCNQ. Exposure to humidity dramatically lowers the conductivity of anion-exchange-doped samples, whereas conventionally-doped samples show no conductivity change within error. Hall mobility and carrier densities were all obtained on the same set of samples. Unfortunately, due to logistical constraints, we are unable to perform Hall measurements inside the Ar glovebox.

	Environment	Conductivity (S cm ⁻¹)	Hall Mobility (cm ² V ⁻¹ s ⁻¹)	Hall Carrier Density (×10 ²⁰ cm ⁻³)
0.5 mg/mL Conventional	Ambient	3.03 ± 0.20	0.029 ± 0.006	6.4 ± 0.94
	Ar Purged	2.98 ± 0.20	0.029 ± 0.005	6.3 ± 0.84
	Ar Glovebox	3.18 ± 0.16	N/A	N/A
0.1 mg/mL AE (LiTFSI)	Ambient	0.75 ± 0.15	0.014 ± 0.0004	3.3 ± 0.74
	Ar Purged	1.65 ± 0.14	0.042 ± 0.005	2.5 ± 0.51
	Ar Glovebox	2.88 ± 0.55	N/A	N/A
0.1 mg/mL AE (LiPF ₆)	Ambient	3.66 ± 0.28	0.037 ± 0.003	6.1 ± 0.63
	Ar Purged	3.89 ± 0.24	0.040 ± 0.004	6.1 ± 0.65
	Ar Glovebox	6.74 ± 0.59	N/A	N/A

It may not be surprising that for conventionally-doped P3HT films, the non-hygroscopic F₄TCNQ dopants are not affected by humidity, but we were still intrigued to observe no moisture-related trap effects induced by water adsorption into nanovoids in these films.^[17] We believe that this could be due to a combination of our use of 97% regioregular P3HT, which has densely-packed side-chains, combined with the space-filling properties of the non-hygroscopic F₄TCNQ dopants,^[11,17] which together mitigate water-related traps and their influence on electrical conductivity. Another possibility for the insensitivity of the conventionally-doped samples to humidity could be due to leftover neutral F₄TCNQ in the polymer films, as previous studies have

indicated that neutral additives with strong electron-withdrawing nitrile groups can bind with water molecules and thus hinder the formation of water-induced traps.^[30] As mentioned above, however, the relatively low doping concentration used in our experiments, along with the UV-vis-NIR spectrum shown in Appendix B (**Figure B3**), confirm that our films do not contain neutral F₄TCNQ. As a result, we believe that the humidity-independent behavior of our conventionally-doped films is most likely due to void-filling repulsion of water by the counterions.

To understand the molecular-level causes of the conductivity decrease of anion-exchange-doped P3HT samples upon exposure to humidity, we also conducted Hall effect measurements on the same set of samples. **Table 3.1** shows the Hall carrier mobilities and densities obtained both in ambient air and after argon purging; unfortunately, logistical constraints prevented us from placing our Hall effect setup in the Ar glovebox where the samples were fabricated. The results indicate that the mobile carrier density remains unaffected within error by ambient humidity for both the anion-exchange- and conventionally-doped samples; in other words, humidity does not cause dedoping. Indeed, the TFSI⁻ and PF₆⁻ anions are quite stable and thus not expected to react chemically or undergo any redox reactions in the presence of moisture.^[9,31–34] Instead, the drop in electrical conductivity observed in the anion-exchange-doped samples upon exposure to humid environments primarily stems from a decline in carrier mobility. This agrees with previous studies suggesting that water can act as shallow traps in semiconducting polymer films.^[11–17]

3.2.4 Near-IR Spectroscopy of the Polaronic P1 Peak

To further investigate the idea that the primary effect of humidity on anion-exchange-doped films is to reduce the carrier mobility, we utilized near-IR spectroscopy to investigate the trapping of carriers that results from humidity exposure. It is well-established in the literature that the degree of carrier delocalization and thus carrier mobility is reflected in the position of the so-called

P1 polaron absorption band in the near-IR: less trapped or more delocalized polarons show a red-shifted P1 band, while trapped polarons that are more localized and have lower mobilities are associated with more blue-shifted P1 bands.^[10,35–37] Thus, we took the 0.1 mg/mL anion-exchange-doped (LiTFSI) and 0.5 mg/mL conventionally-doped samples that had been exposed to ambient conditions and monitored their near-IR absorption as a function of time as the samples were purged with dry N₂ gas.

Figure 3.1a shows the results of this experiment, plotting the evolution of the blue side of the P1 absorption as the N₂ purging time increases for the humidity-exposed anion-exchange-doped P3HT sample; we chose to focus on the blue side because it better reflects the presence of more highly trapped polarons in the films,^[10,35–37] and because the red side of the P1 band overlaps with the water O–H stretch near 2700 nm (see inset), making it hard to disentangle competing effects. The data show that with longer N₂ purging times, the intensity of the blue side of the P1 absorption diminishes, indicating a drop in the number of trapped polarons in the film. Moreover, despite the complication arising from the water O–H stretch, there is an observable isobestic point near 2900 nm (see inset) where the redder side of the P1 band increases with purging time. This shows that purging with dry gas causes the conversion of trapped polarons into more mobile polarons via the removal of moisture.

In contrast, for the conventionally-doped P3HT sample, shown in **Figure 3.1b**, there are no changes in the intensity of the P1 band with purging time, indicating that changing the humidity does not alter the trapping of polarons in conventionally-doped P3HT films; both results are consistent with the way the carrier mobility changes in response to humidity, as shown in **Table 3.1**. We note that because of the way we performed the baseline (either under ambient conditions for the anion-exchange-doped sample or after N₂ purging for the conventionally-doped sample),

the water absorption feature near 2700 nm appears to go in opposite directions in the two panels of **Figure 3.1**.

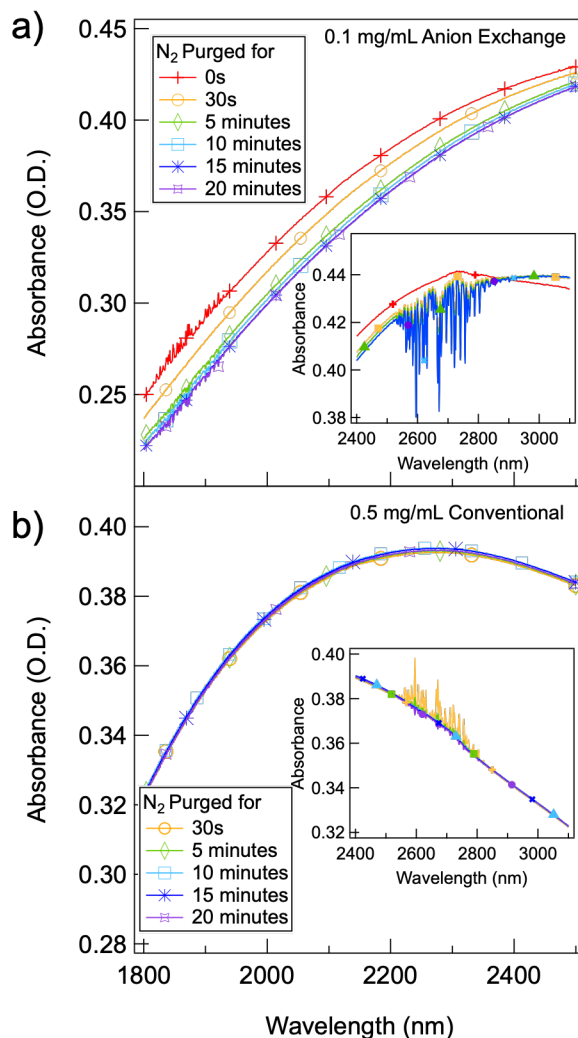


Figure 3.1. Near-IR spectra of 0.1 mg/mL F₄TCNQ + 30 mg/mL LiTFSI (AE) and 0.5 mg/mL F₄TCNQ (Conv) samples. The blue side of the P1 polaron absorption, which is associated with trapped carriers, for (a) an anion-exchange-doped P3HT film and (b) a conventionally-doped P3HT film that had been exposed to ambient conditions as a function of time after purging with dry N₂. Purging clearly decreases the blue P1 absorption for the anion-exchange-doped sample while having no effect on the conventionally-doped sample, consistent with the idea that humidity lowers the mobility of carriers in the anion-exchange-doped films. The inset in **Figure 3.1a,b** shows the same spectra extended deeper into the IR region, including the absorption of the water O–H stretch near 2700 nm (this absorption appears to go in opposite directions in the two panels because of the way the spectra were base-lined; see text).

3.2.5 Probing Electrical Conductivity as a Function of Controlled Relative Humidity

Finally, to verify that the decrease in conductivity in anion-exchange-doped P3HT samples is specifically caused by humidity rather than other ambient gases such as O_2 , we performed a set of measurements in ambient conditions under controlled RH. This was accomplished by placing 0.1 mg/mL anion-exchange-doped samples using both LiTFSI and $LiPF_6$ inside an air-filled desiccator containing Drierite to control the humidity, and then measuring the electrical conductivity as a function of RH. The results are presented in **Figure 3.2**, which shows a remarkably linear relationship between the change in electrical conductivity (relative to that measured at 15% RH, the lowest we could achieve with this setup) and relative humidity for the air-exposed anion-exchange-doped films. We note that for RH lower than $\sim 20\%$, the linear relationship between conductivity and RH appears to lessen relative to what is observed at higher RH. This is because, as with the purging experiments described above, Drierite is not capable of removing water from deep within the film. However, even with some trapped water, the nearly linear relationship between RH and conductivity depicted in **Figure 3.2** suggests that anion-exchange-doped films employing hygroscopic salts can possibly serve as viable materials for resistance-based humidity-sensing applications.

It is worth mentioning that the trend observed in **Figure 3.2** is similar to that seen in humidity sensors based on organic field-effect transistors (OFETs).^[38,39] Even though OFET-based humidity sensors typically utilize pristine conjugated polymers rather than doped ones, the underlying sensing mechanism is basically the same in that adsorbed water acts as a trap leading to a decrease in charge carrier mobility. We note that although our doped films may be slightly less sensitive to humidity than OFETs, our resistance-based humidity-sensing approach offers a significant advantage in terms of simplicity of production.

The data in **Figure 3.2** also show that the slope of the relative change in conductivity versus RH for LiTFSI-exchanged samples (green squares) is considerably higher than that of LiPF₆-exchanged samples (purple triangles), consistent with the idea that TFSI⁻ is a more hygroscopic anion than PF₆⁻.^[19–22] The conventionally-doped samples (red circles) show no response to changes in humidity within error, as discussed above, consistent with the idea that hydrophobic F₄TCNQ prevents water from interacting with the charge carriers in doped P3HT.^[21,28] These observations further confirm our hypothesis that exposure of the anions to water vapor is what is responsible for the observed decline in conductivity, rather than the infiltration of water into the void spaces of the film.

Although ions like TFSI⁻ and PF₆⁻ are generally chosen for their electrochemical stability, the fact that they are hygroscopic is often overlooked. The hygroscopicity of these ions depends on how water molecules bind around them, a factor defined as water sorption capacity per ion pair.^[40] Several studies have demonstrated that under ambient temperature and humidity conditions, TFSI⁻ possesses a higher capacity to absorb water than the PF₆⁻ anion.^[19–22] The extent of water absorption by different ions also is connected to both the relative basicity of the anions and the ratio of hydrophobic F atoms to the total number of atoms within the anions.^[19,21,22] In combination, doped P3HT films with TFSI⁻ not only have a stronger affinity for water but also tend to accommodate more water, explaining why these films show a more significant humidity-induced drop in conductivity than films containing PF₆⁻.

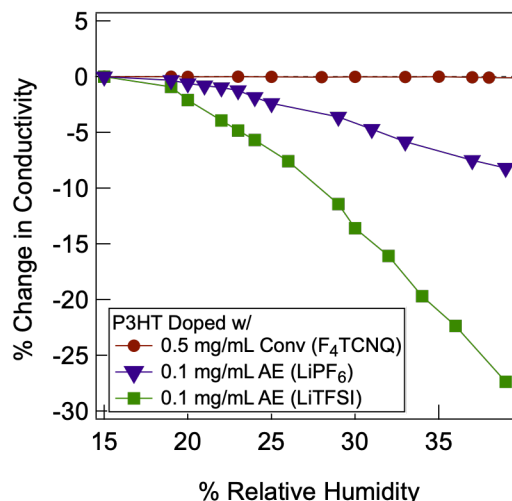


Figure 3.2. Electrical conductivity of conventionally- (0.5 mg/mL F₄TCNQ, red circles) and anion-exchange-doped (0.1 mg/mL F₄TCNQ with 30 mg/mL LiTFSI, green squares, and 0.1 mg/mL F₄TCNQ with 5 mg/mL LiPF₆, purple triangles) P3HT films as a function of percent relative humidity in air. The ordinate plots the relative change in conductivity compared to that measured at 15% RH, the lowest we could obtain with this setup. The conductivity change is highly linear down to ~20% RH, suggesting that the doped polymer films anion-exchanged with LiTFSI could possibly be used as resistance-based humidity sensors.

3.3 Conclusion

In summary, our study has demonstrated a high sensitivity of the electrical properties of conjugated polymer films anion-exchange-doped with hygroscopic salts, such as LiTFSI, to humidity. Given that one of the advantages of anion-exchange doping is that it creates more air-stable samples, our results show that it is crucial to consider the impact of the environment, and particularly RH, to make accurate measurements and interpretations. We verified that it is the hygroscopic nature of anions like TFSI⁻ that is responsible for the change in electrical behavior with RH by showing that less hygroscopic anions like PF₆⁻ show a smaller conductivity change with RH, and that non-hygroscopic dopants like F₄TCNQ show no changes with RH at all. Through Hall effect measurements and near-IR spectroscopy, we established that the decrease in electrical conductivity caused by humidity is a result of water-induced trapping affecting the transport of charge carriers; exposure to moisture does not appear to affect the doped carrier

density. The effects of humidity on the conductivity of anion-exchange-doped films are reversible, as long as sufficient efforts are made to remove deeply trapped water from within the doped films by using a combination of vacuum and humidity-free gas purging. Finally, it appears that the decrease in electrical conductivity shows a roughly linear relationship with relative humidity, suggesting that anion-exchange-doped conjugated polymers hold potential for humidity-sensing applications.

3.4 References

- [1] T. M. Swager, *Macromolecules* **2017**, *50*, 4867.
- [2] J. Mei, *Journal of Polymer Science* **2022**, *60*, 287.
- [3] I. B. Dimov, M. Moser, G. G. Malliaras, I. McCulloch, *Chem. Rev.* **2022**, *122*, 4356.
- [4] B. Lüssem, C.-M. Keum, D. Kasemann, B. Naab, Z. Bao, K. Leo, *Chem. Rev.* **2016**, *116*, 13714.
- [5] H. Sun, X. Guo, A. Facchetti, *Chem* **2020**, *6*, 1310.
- [6] A. D. Scaccabarozzi, A. Basu, F. Aniés, J. Liu, O. Zapata-Arteaga, R. Warren, Y. Firdaus, M. I. Nugraha, Y. Lin, M. Campoy-Quiles, N. Koch, C. Müller, L. Tsetseris, M. Heeney, T. D. Anthopoulos, *Chem. Rev.* **2022**, *122*, 4420.
- [7] I. E. Jacobs, A. J. Moulé, *Advanced Materials* **2017**, *29*, 1703063.
- [8] M. T. Fontana, D. A. Stanfield, D. T. Scholes, K. J. Winchell, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2019**, *123*, 22711.
- [9] Y. Yamashita, J. Tsurumi, M. Ohno, R. Fujimoto, S. Kumagai, T. Kurosawa, T. Okamoto, J. Takeya, S. Watanabe, *Nature* **2019**, *572*, 634.
- [10] T. J. Aubry, K. J. Winchell, C. Z. Salamat, V. M. Basile, J. R. Lindemuth, J. M. Stauber, J. C. Axtell, R. M. Kubena, M. D. Phan, M. J. Bird, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2020**, *30*, 2001800.
- [11] H. F. Haneef, A. M. Zeidell, O. D. Jurchescu, *J. Mater. Chem. C* **2020**, *8*, 759.

- [12] M. Nikolka, I. Nasrallah, B. Rose, M. K. Ravva, K. Broch, A. Sadhanala, D. Harkin, J. Charmet, M. Hurhangee, A. Brown, S. Illig, P. Too, J. Jongman, I. McCulloch, J.-L. Bredas, H. Sirringhaus, *Nature Mater* **2017**, *16*, 356.
- [13] G. Zuo, Z. Li, O. Andersson, H. Abdalla, E. Wang, M. Kemerink, *J. Phys. Chem. C* **2017**, *121*, 7767.
- [14] G. Zuo, M. Linares, T. Upreti, M. Kemerink, *Nat. Mater.* **2019**, *18*, 588.
- [15] N. B. Kotadiya, A. Mondal, P. W. M. Blom, D. Andrienko, G.-J. A. H. Wetzelaer, *Nat. Mater.* **2019**, *18*, 1182.
- [16] H. F. Iqbal, M. Waldrip, H. Chen, I. McCulloch, O. D. Jurchescu, *Advanced Electronic Materials* **2021**, *7*, 2100393.
- [17] D. J. Yaron, T. Kowalewski, *Nat. Mater.* **2019**, *18*, 1154.
- [18] M. P. Hein, A. A. Zakhidov, B. Lüssem, J. Jankowski, M. L. Tietze, M. K. Riede, K. Leo, *Applied Physics Letters* **2014**, *104*, 013507.
- [19] T. Wu, R. Zhuang, R. Zhao, R. Zhao, L. Zhu, G. Liu, R. Wang, K. Zhao, Y. Hua, *ACS Energy Lett.* **2021**, *6*, 2218.
- [20] Y. Cao, Y. Chen, X. Sun, Z. Zhang, T. Mu, *Phys. Chem. Chem. Phys.* **2012**, *14*, 12252.
- [21] S. Goh, G. Jang, S. Ma, J. Park, H. Ban, C. U. Lee, J. Lee, J. Moon, *ACS Sustainable Chem. Eng.* **2021**, *9*, 16730.
- [22] L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Physical Chemistry Chemical Physics* **2001**, *3*, 5192.
- [23] J. G. McDaniel, A. Verma, *J. Phys. Chem. B* **2019**, *123*, 5343.
- [24] A. M. O'Mahony, D. S. Silvester, L. Aldous, C. Hardacre, R. G. Compton, *J. Chem. Eng. Data* **2008**, *53*, 2884.
- [25] U. B. Cappel, T. Daeneke, U. Bach, *Nano Lett.* **2012**, *12*, 4925.
- [26] J. Lu, A. D. Scully, J. Sun, B. Tan, A. S. R. Chesman, S. Ruiz Raga, L. Jiang, X. Lin, N. Pai, W. Huang, Y.-B. Cheng, U. Bach, A. N. Simonov, *J. Phys. Chem. Lett.* **2019**, *10*, 4675.
- [27] L. Huang, Z. Hu, J. Xu, K. Zhang, J. Zhang, J. Zhang, Y. Zhu, *Electrochimica Acta* **2016**, *196*, 328.

- [28] H. Kwon, J. Won Lim, J. Han, L. Na Quan, D. Kim, E.-S. Shin, E. Kim, D.-W. Kim, Y.-Y. Noh, I. Chung, D. Ha Kim, *Nanoscale* **2019**, *11*, 19586.
- [29] Q. Fu, X. Tang, B. Huang, T. Hu, L. Tan, L. Chen, Y. Chen, *Advanced Science* **2018**, *5*, 1700387.
- [30] M. Nikolka, G. Schweicher, J. Armitage, I. Nasrallah, C. Jellett, Z. Guo, M. Hurhangee, A. Sadhanala, I. McCulloch, C. B. Nielsen, H. Sirringhaus, *Advanced Materials* **2018**, *30*, 1801874.
- [31] S. F. Lux, L. Terborg, O. Hachmöller, T. Placke, H.-W. Meyer, S. Passerini, M. Winter, S. Nowak, *J. Electrochem. Soc.* **2013**, *160*, A1694.
- [32] J. Kalhoff, G. G. Eshetu, D. Bresser, S. Passerini, *ChemSusChem* **2015**, *8*, 2154.
- [33] M. Liu, J. Vatamanu, X. Chen, L. Xing, K. Xu, W. Li, *ACS Energy Lett.* **2021**, *6*, 2096.
- [34] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, *Science* **2015**, *350*, 938.
- [35] D. T. Scholes, P. Y. Yee, J. R. Lindemuth, H. Kang, J. Onorato, R. Ghosh, C. K. Luscombe, F. C. Spano, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2017**, *27*, 1702654.
- [36] T. J. Aubry, J. C. Axtell, V. M. Basile, K. J. Winchell, J. R. Lindemuth, T. M. Porter, J.-Y. Liu, A. N. Alexandrova, C. P. Kubiak, S. H. Tolbert, A. M. Spokoyny, B. J. Schwartz, *Advanced Materials* **2019**, *31*, 1805647.
- [37] M. G. Voss, D. T. Scholes, J. R. Challa, B. J. Schwartz, *Faraday Discuss.* **2019**, *216*, 339.
- [38] S. Wu, G. Wang, Z. Xue, F. Ge, G. Zhang, H. Lu, L. Qiu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 14974.
- [39] Y. Zhu, Y. Zhang, J. Yu, C. Zhou, C. Yang, L. Wang, L. Wang, L. Ma, L. J. Wang, *Sensors and Actuators B: Chemical* **2023**, *374*, 132815.
- [40] C. G. Tang, M. N. Syafiqah, Q.-M. Koh, M. C.-Y. Ang, K.-K. Choo, M.-M. Sun, M. Callsen, Y.-P. Feng, L.-L. Chua, R.-Q. Png, P. K. H. Ho, *Nat Commun* **2023**, *14*, 3978.

CHAPTER 4

How the Carrier Mobility and Seebeck Coefficient of Doped Semiconducting Polymers Are Controlled by Counterion Interactions and Mesoscale Order

Chapter 4 explores how counterion interactions and mesoscale order control carrier mobility and the Seebeck coefficient in doped semiconducting polymers. By comparing conventional molecular dopants, large dodecaborane-based dopants, and anion-exchange doping, this chapter shows that charge transport can be improved either by weakening Coulomb interactions between polarons and counterions or by increasing mesoscale ordering within the doped film. Together, these results demonstrate that both energetic interactions and doping-induced structural changes must be considered when designing doped conjugated polymers with improved thermoelectric performance.

Chapter 4 was reprinted with permission from Q. M. Duong; D. Garcia Vidales; X. Liu; C. Z. Salamat; A. Ready; H. A. Khunaizi; M. Matsumoto; A. M. Spokoyny; S. H. Tolbert; B. J. Schwartz; and Wiley-VCH. “How the Carrier Mobility and Seebeck Coefficient of Doped Semiconducting Polymers Are Controlled by Counterion Interactions and Mesoscale Order,” *Adv. Funct. Mater.* 2026, DOI: 10.1002/adfm.75510.

A reprint of the Supporting Information is given in Appendix C.

Abstract

Charge transport–structure relationships in chemically-doped poly(3-hexylthiophene-2,5-diyl) (P3HT) films are explored using four different dopants: the classic 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) as well as two large dodecaborane (DDB) cluster-based dopants that minimize counterion Coulomb interactions with carriers on the polymer backbone. Anion-exchange doping with F₄TCNQ and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was also used to put TFSI[−] counterions into the doped polymer. The Seebeck coefficient (S) and conductivity (σ) were measured as a function of doping level, along with temperature-dependent conductivity, wide- and small-angle X-ray scattering, optical spectroscopy, and Hall effect mobility. The results indicate that large DDB-based counterions produce lower carrier transport activation energies and thus more favorable S – σ relationships than F₄TCNQ. Anion-exchange doping leads to higher activation energies but still produces a favorable S – σ relationship. Analysis using the semi-localized transport (SLoT) model indicates that anion exchange doping produces films with the highest intrinsic conductivities, which results from doping-induced crystallization of originally amorphous regions of the film. Such crystallization leads to increased mesoscale domain sizes, as observed by small-angle X-ray scattering. Together, the results indicate that transport in doped conjugated polymers can be equivalently improved either by reducing the Coulomb interaction of carriers with counterions or by structurally improving mesoscale conductivity pathways.

4.1 Introduction

Doped semiconducting polymers have great promise for thermoelectric applications due to their ease of processing, chemical tunability, and inherently low thermal conductivity.^[1–4] Interest in these materials has increased in recent years with the development of new polymers, dopants, and doping methods.^[5–10] Most of the work in this field focuses on improving the electrical conductivity of semiconducting polymers by overcoming their intrinsically low carrier mobility and density via doping, which creates mobile carriers on the polymer backbone. For thermoelectric devices, it is also crucial to consider the Seebeck coefficient, which is the voltage difference generated in response to a temperature gradient across a material. This voltage facilitates the flow of charge carriers, enabling the direct conversion of waste heat into electrical energy.

The efficiency of the thermoelectric conversion process is described by the figure of merit, ZT :

$$ZT = \frac{\sigma S^2}{\kappa} T, \quad (4.1)$$

which depends on the electrical conductivity (σ), Seebeck coefficient (S), and thermal conductivity (κ). The temperature (T) is included to make the quantity dimensionless. Although it is desirable to maximize both the electrical conductivity and the Seebeck coefficient to achieve higher ZT , increasing the electrical conductivity through doping generally results in a decrease in the Seebeck coefficient. This leads to a sweet spot in choosing the doping level to maximize the numerator of **Equation (4.1)**, which is also referred to as the power factor.

The inverse relationship between σ and S can be understood using the Boltzmann transport formalism. In the version developed by Kang *et al.*, these factors are described in terms of a transport function, σ_E , which is related to the carrier mobility:^[11]

$$\sigma = \int \sigma_E \left(-\frac{\partial f}{\partial E} \right) dE \quad (4.2)$$

$$S = -\frac{k_B}{q} \int \left(\frac{E - E_F}{k_B T} \right) \left(\frac{\sigma_E}{\sigma} \right) \left(-\frac{\partial f}{\partial E} \right) dE, \quad (4.3)$$

where k_B is the Boltzmann constant, E is the energy of the charge carrier, q is the fundamental charge, E_F is the Fermi level, and $f(E)$ is the Fermi–Dirac distribution. Although not explicit in these equations, increasing the conductivity by increasing the carrier density shifts the Fermi level into the band, thereby reducing the asymmetry in σ_E about E_F and lowering the average value of $(E - E_F)$ for the carriers that contribute to the Seebeck coefficient.^[11] This explains why the Seebeck coefficient decreases when the electrical conductivity increases at higher doping levels.^[12–16]

The electrical conductivity of a doped conjugated polymer depends not only on the number density of carriers but also on the carrier mobility: higher carrier mobility results in higher conductivity at the same carrier density. **Equations (4.2 and 4.3)** indicate that doped semiconducting polymers that have higher carrier mobilities also will have higher Seebeck coefficients relative to their electrical conductivity,^[17,18] thus leading to an improved power factor and ZT .

Charge transport in doped semiconducting polymer films is typically understood as a hopping process, where carriers must thermally surmount a barrier in order to move. This process is influenced by several factors, including structural disorder and the Coulomb interactions between polarons and their counterions, both of which create barriers that trap charge carriers at specific locations. Temperature also plays a key role in this transport: at higher temperatures, polarons gain enough thermal energy to surmount these energy barriers. In order to improve the

carrier mobility in doped semiconducting polymers, it is necessary to understand how the interplay of all of these factors contributes to charge transport.^[8,9,12,16,19–22]

Recently, Gregory *et al.*^[17,18] expanded on the transport model developed by Kang *et al.*^[11] by proposing that the charge transport function takes the following form:

$$\sigma_E(E, T, c) = \sigma_0 \exp\left(-\frac{W_H(c)}{k_B T}\right) \times \left(\frac{E - E_t}{k_B T}\right). \quad (4.4)$$

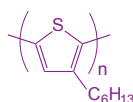
This expression for the transport function is termed the semi-localized transport (SLoT) model, which introduces three components: σ_0 , the prefactor or intrinsic conductivity in the absence of localization effects; $W_H(c)$, a localization energy that depends on the carrier density (c), which represents the energy that carriers must overcome to hop between sites; and an energy-dependent term, $\left(\frac{E - E_t}{k_B T}\right)$. By assuming that the material is homogeneous throughout its volume, $W_H(c)$ can further be broken down into a maximum localization energy ($W_{H,\max}$) and the (presumed linear) rate at which the localization energy decreases with increasing carrier density ($W_{H,\text{slope}}$). Thus, by using temperature-dependent conductivity measurements to extract the activation energy, in combination with **Equation (4.4)**, one can determine whether charge transport is primarily influenced by σ_0 or by $W_H(c)$ upon doping. Our goal in this work is to determine how these factors depend on both the microscopic and mesoscopic morphology of the doped polymer films.

Different dopants and doping methods are well known to significantly influence the morphology of doped polymer films.^[8,9,12,16,19–30] These morphological changes can occur on microscopic length scales, such as changes in crystallite structure, as well as on mesoscopic scales, leading to variations in domain length.^[8,9,12,16,19–25,27,30] Such structural variations can lead to significant differences in the charge transport properties of doped semiconducting polymer films. In this study, we explore how different dopants and doping methods affect morphology and thus

charge transport in doped semiconducting polymers. Specifically, we measure the electrical conductivity, Seebeck coefficient, and activation energy (W_H) and then use the SLoT model to analyze charge transport in terms of parameters such as σ_0 and $W_H(c)$. We then interpret the results using both small- and wide-angle X-ray scattering experiments to reveal how the morphology induced by different doping methods affects the S - σ relationship.

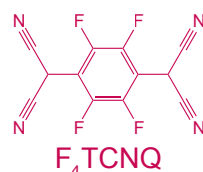
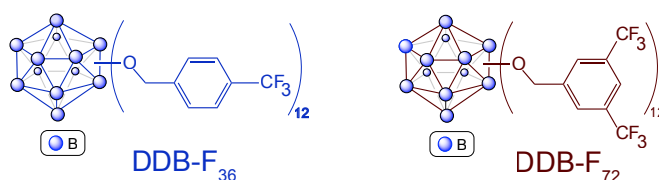
To investigate how different dopants and doping methods influence charge transport and the S - σ relationship, we focus on the workhorse semiconducting polymer poly(3-hexylthiophene-2,5-diyl) (P3HT).^[20,31–39] P3HT is a semicrystalline polymer containing both crystalline and amorphous regions. The lack of order in the amorphous regions leads to shorter average conjugation lengths and thus higher oxidation potentials; in other words, amorphous regions can be up to a few hundred meV harder to dope than crystalline regions.^[40] We then choose dopants and doping methods that have different effects on film morphology, including: where the counterion sits in the polymer crystal structure, whether or not the method enhances or destroys overall crystallinity, and whether or not the dopant can create carriers only in the crystalline regions or in both the crystalline and amorphous regions. **Figure 4.1** shows the chemical structures of the semiconducting polymer and dopants used in this study.

Semiconducting Polymer



P3HT

Conventional Doping Method



Anion Exchange Method

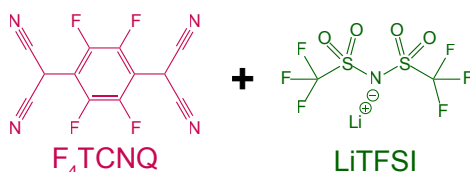


Figure 4.1. Chemical structures of P3HT and the various dopants used in this study. Two doping methods are used in this study: conventional and anion-exchange. For the conventional doping method, we utilize three dopants: F₄TCNQ, DDB-F₃₆, and DDB-F₇₂, which vary in oxidizing power from weakest to strongest, respectively. The weakest dopant, F₄TCNQ, is primarily able to dope only crystalline regions of P3HT. The two boron cluster dopants are stronger oxidants, and although the oxidation power difference between the DDB-F₃₆ and DDB-F₇₂ dopants is ~200 mV, their equally large counterions reside in the lamellae in the polymer lattice upon doping. For the anion-exchange method, the dopant is F₄TCNQ and the electrolyte is LiTFSI. The anion-exchange doping method allows for control over the nature of the dopant's counterion, and the presence of the electrolyte provides an extra oxidative boost allowing doping of both amorphous and crystalline regions in the polymer matrix.

For our initial dopant, we chose 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) because it is widely used in studies of doped semiconducting polymers.^[9,16,41–45] The doping efficiency and the regions of polymer films that can be doped by F₄TCNQ depend strongly on the doping procedure, the choice of solvent used for doping, and the dopant

concentration.^[8,21,22,43,46–48] Under sequential doping conditions at high-doping concentrations in relatively high-swelling solvents like dichloromethane (DCM), which is what we will use in this work, F₄TCNQ has sufficient oxidizing power to dope the crystalline regions of P3HT without significantly doping the amorphous regions.^[8,21,22,43,48]

When doping P3HT with F₄TCNQ, which occurs via integer charge transfer (ICT), the F₄TCNQ[−] counterions typically reside in the lamellar regions of the P3HT crystallites, nestled among the hexyl side chains. With some processing conditions, the addition of F₄TCNQ to P3HT can produce charge-transfer complexes (CTCs), where the F₄TCNQ[−] anion π -stacks with the P3HT backbone; CTCs have only partial charge transfer and thus are not associated with mobile carrier formation.^[48,49] Even when creating carriers via ICT, however, the relatively strong Coulomb interactions between polarons and the F₄TCNQ[−] counterions in the crystalline lamellae promote carrier localization,^[20] resulting in a substantial population of trapped charge carriers.^[9,20,50]

In addition to F₄TCNQ, we also explore using dodecaborane (DDB) cluster-based dopants, whose large ~2-nm-diameter size leads to reduced Coulomb interactions, resulting in more mobile charge carriers.^[8,9,51] DDBs can be modified with different substituents to change their oxidation power.^[8,9,51] The two dopants we use in this work, DDB-F₇₂ and DDB-F₃₆, are named based on the total number of fluorine atoms on each cluster. Although both DDB-based dopants help minimize Coulomb trapping, DDB-F₇₂ can dope amorphous regions of P3HT films more effectively than DDB-F₃₆ due to its ~200 mV stronger oxidizing power. The large size and strong oxidizing power of DDB-F₇₂, however, play a direct role in the P3HT film's morphology: our previous work has shown that the intercalation of DDB-F₇₂ dopant in the P3HT film disrupts the film's crystallinity at high doping concentrations. This is not the case when DDB-F₃₆ is used to dope P3HT, where we have shown that doped films retain their degree of crystallinity but with a crystal structure that

has a significantly expanded lamellar distance.^[9,51] By employing both dopants, we are thus able to keep local counterion-polaron Coulomb interactions constant, giving us a direct handle to understand the trade-off between doping-induced structural disorder and dopant accessibility to different regions of the film, and how these factors influence charge transport characteristics.

Recently, Yamashita *et al.* developed a new technique called anion-exchange (AE) doping, which offers several benefits over traditional chemical doping methods.^[6] The AE approach involves immersing a conjugated polymer film into a solution containing both a chemical dopant and a high concentration of an electrolyte in a semi-orthogonal solvent, which swells the polymer film without dissolving it, thereby facilitating intercalation of the dopant and electrolyte ions into the polymer. Anion-exchange doping proceeds through a two-step process: first, the dopant oxidizes the polymer, and second, the dopant counterion is replaced by the electrolyte anion through mass action. This method not only allows for control over the choice of counterion in doped polymer films, but it also boosts the doping power by ~200 mV, thereby enabling higher doping levels than conventional methods.^[6] In this study, we take advantage of this oxidative boost by using F₄TCNQ, which predominantly dopes crystalline regions, together with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as the electrolyte salt, to dope both the crystalline and amorphous regions in P3HT films. Since doping the amorphous regions can lead to significant structural changes, we can then investigate how these structural changes relate to charge transport and the S - σ relationship.

Thus, in this study, we examine how different dopants (F₄TCNQ, DDB-F₇₂, and DDB-F₃₆) and different doping methods (conventional and anion exchange) affect the morphology, charge transport, Seebeck coefficient, and electrical conductivity of doped P3HT. Our findings show that charge transport, and thus the Seebeck coefficient–electrical conductivity (S - σ) relationship, can

be improved either by reducing Coulomb trapping or by increasing mesoscale ordering through the crystallization of formerly amorphous regions. Using a combination of temperature-dependent conductivity and Hall effect measurements, along with UV–vis–NIR spectroscopy, we demonstrate that P3HT films doped with DDB-based dopants exhibit much less carrier localization compared to those doped with F₄TCNQ or via the anion-exchange method due to the reduced counterion-polaron interaction. Additionally, using the SLoT model, we find that doping by anion exchange produces a significantly higher σ_0 than conventional doping, allowing charge carriers to overcome their increased localization and achieve charge transport and Seebeck coefficient–electrical conductivity relationships that are similar to those of DDB-doped films, where the carriers have much lower activation energy. Furthermore, grazing-incidence wide- and small-angle X-ray scattering (GIWAXS and GISAXS) analyses reveal that the high σ_0 observed in anion-exchange-doped films is due to an increase in mesoscale domain length that results from doping and ordering of the amorphous regions. Overall, our work emphasizes the key role that dopants and doping methods play in the thermoelectric efficiency of doped conjugated polymers: by controlling key factors such as dopant size and oxidizing power, we can deconvolute the different doping-induced structural and energetic disorder governing the charge transport characteristics of doped conjugated polymers.

4.2 Results and Discussion

As mentioned above, the goal of this study is to examine dopant-induced structural changes in P3HT to better understand the relationship between morphology and charge transport characteristics in doped semiconducting polymer systems. To deconvolute the role of morphology in the charge transport characteristics of doped P3HT, we control not only the dopant size and shape, but also the oxidizing power that determines which regions of the polymer film can be

doped. To fabricate the doped semiconducting polymer P3HT films for this study, we used the sequential processing (SqP) method.^[52–55] First, P3HT films were spin-coated onto glass substrates. After the films dried, this was followed by a second spin-coating step with solutions of different dopants, including F₄TCNQ, DDB-F₇₂, and DDB-F₃₆. For anion-exchange doping, we used a dopant solution containing F₄TCNQ as well as 104.5 mM LiTFSI. Additional details on the materials used, film fabrication techniques, and doping processes can be found in the Experimental Section.

4.2.1 UV–Vis–NIR Spectroscopy

We start our investigation by performing UV–vis–NIR spectroscopy on P3HT films doped using DDB-F₇₂, DDB-F₃₆, F₄TCNQ, and via anion exchange (AE) at various doping concentrations (**Figure 4.2**). For all of the doped samples, we observe an absorption increase at ~ 1.5 eV and ~ 0.5 eV, the so-called P2 and P1 peaks, respectively, which are associated with the presence of polaronic charge carriers. All of the doped films also show a depletion of the bandgap transition of the neutral polymer near ~ 2.3 eV. Both the DDB-F₇₂- and DDB-F₃₆-doped films exhibit a third polaron transition (P3) at ~ 1.6 eV that disappears at higher doping levels.^[8,9] The P2 region in F₄TCNQ-doped samples and the bandgap region in the DDB-doped samples also have overlapping absorptions from the dopant anions.^[8,45,51,55–57] Despite the peak overlaps, we see that with increasing dopant concentration, both the P1 and P2 intensities rise, indicating the creation of more polarons. In the case of the anion exchange doping method, we also see no absorption signatures of F₄TCNQ[−] in the P2 region, indicating that anion exchange occurred.

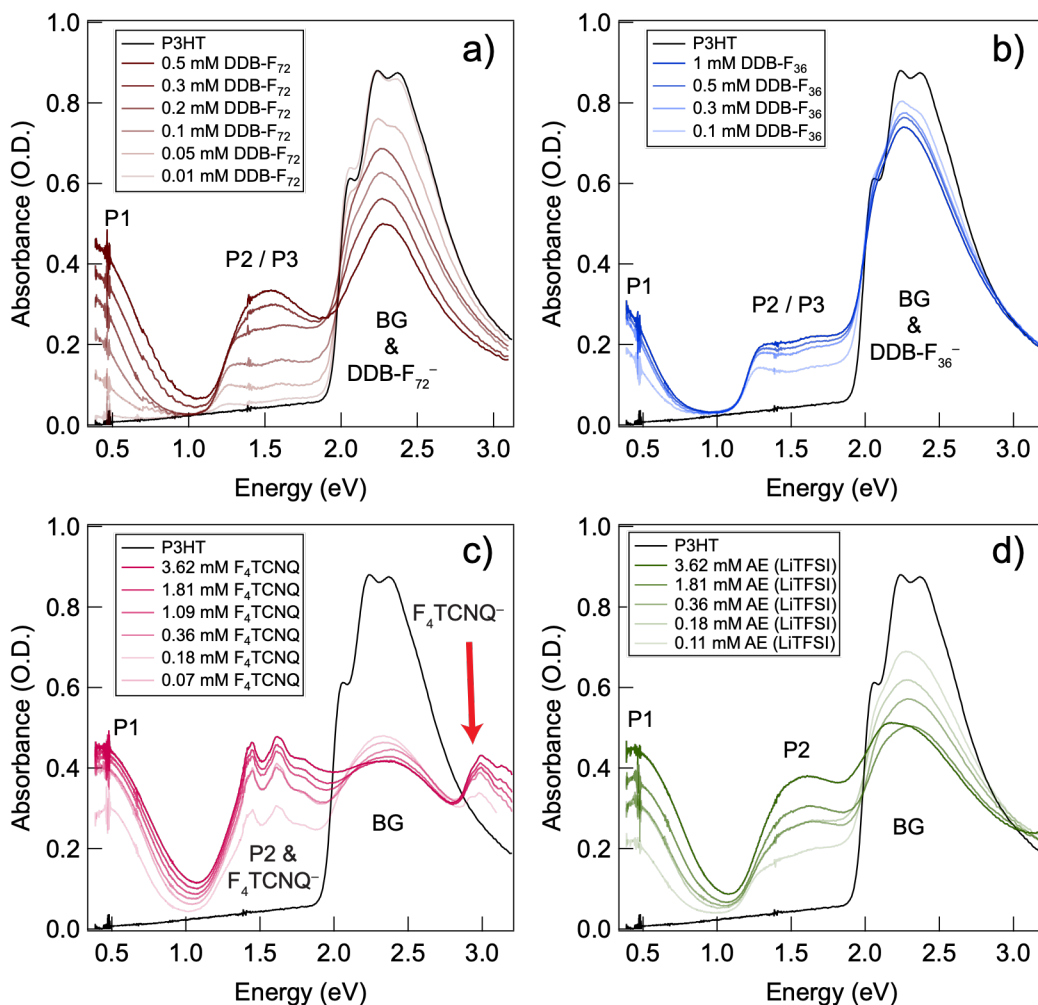


Figure 4.2. UV-vis-NIR spectra of doped P3HT films using different dopants/methods: (a) DDB- F_{72} , (b) DDB- F_{36} , (c) F_4 TCNQ, and (d) anion exchange (AE) at various doping levels. All four doping methods produce the P1 and P2 absorption bands characteristic of polarons, as well as decrease the absorption intensity of the P3HT bandgap. The bandgap bleach is less apparent for the two DDB dopants because the DDB anions absorb near 2.4 eV, overlapping the P3HT bandgap transition. The vibronic structure near 1.5 eV and the peak near 3.0 eV in panel (c) come from the F_4 TCNQ anion. The legend in the anion exchange samples shows the final F_4 TCNQ concentrations. The LiTFSI concentration was kept constant at 104.5 mM.

Based on their similar P1 absorption intensities, which are in a region free of spectral overlap, the F_4 TCNQ, DDB- F_{72} , and anion-exchange (F_4 TCNQ with LiTFSI)-doped P3HT films have similar doping levels at dopant concentrations of 3.62 mM, 0.5 mM, and 3.62 mM with 104.5 mM LiTFSI, respectively. DDB- F_{72} is clearly more efficient at doping, as it reaches the same level of doping at a solution concentration ~ 7 times lower than that of the other dopants. In contrast,

DDB-F₃₆ is less effective at doping P3HT than DDB-F₇₂, showing a much lower P1 intensity even at twice the doping concentration; it also appears slightly less effective at doping P3HT than F₄TCNQ.

Based on cyclic voltammetry, DDB-F₃₆ is slightly more oxidizing than F₄TCNQ,^[8] which would typically suggest a higher doping efficiency. However, solution-phase redox potentials may not necessarily translate directly to doping efficiency, where ion pairing effects, the local dielectric environment of the solvent-swollen film, and dopant intercalation can strongly influence charge transfer and stabilization of the resulting ionized species and thus the doping levels achieved. In the case of DDB-F₃₆, its large size likely makes it more difficult to intercalate into the polymer lattice during SqP, even in high-swelling solvents like DCM, leading to a lower doping level.

In addition to providing qualitative insights into doping level, the spectral position of the P1 absorption also reveals important details about charge carrier delocalization. Although a detailed assignment of the P1 transition is still the subject of discussion in the literature, recent experimental and theoretical work from our group and others supports a description in which the P1 transition corresponds to excitation from the valence band into a partially-filled polaronic intragap state in doped P3HT.^[19,58–63] Theoretical work by Spano and co-workers has argued that a red-shifted P1 transition is associated with greater carrier delocalization, whereas a blue-shifted P1 indicates stronger localization.^[8,9,21,64] We have argued previously that there is a correlation between the molecular-level degree of localization and the macroscopic carrier mobility,^[8,9] but others have pointed out that this correlation is not perfect,^[28,30] and one of the purposes of this paper is to explore carrier transport on length scales between the molecular and macroscopic.

The observation that the position of the P1 absorption band reflects localization of the polaron due to Coulomb interactions with the dopant counterion explains why P3HT films doped

with DDB-F₇₂ and DDB-F₃₆ exhibit a significant P1 redshift compared to those doped with F₄TCNQ or via AE. This is because the larger size of the DDB dopants forces the charge of the counterion to be positioned further from the polymer backbone than is the case for smaller counterions, such as TFSI⁻ or F₄TCNQ⁻.^[8] This increased distance weakens the Coulomb interaction, leading to more delocalized carriers and thus a red-shifted P1 band.^[50] In contrast, the P1 transition for films doped with the anion-exchange method is at a similar position to that of F₄TCNQ-doped films, with both showing a bluer P1 transition. This similarity in P1 peak position suggests that the counterion Coulomb interactions, and thus the degree of carrier localization, in anion-exchange-doped P3HT films are comparable to those in F₄TCNQ-doped films.

4.2.2 Probing Film Morphology Using Grazing-Incidence Wide- and Small-Angle X-ray Scattering

To investigate the different morphologies that result from the various dopants and doping methods used in this study, we structurally characterized the doped semiconducting P3HT polymer films using grazing-incidence wide- and small-angle X-ray scattering (GIWAXS and GISAXS). All films retain their crystallinity upon doping and show the expected edge-on orientation with respect to the substrate, as seen in the raw 2D scattering data (**Figure C1**). **Figure 4.3a,b** displays integrations of the GIWAXS diffraction patterns for the most highly-doped samples shown in **Figure 4.2**, with integrations in the out-of-plane and in-plane directions plotted separately. The one exception is the DDB-F₇₂-doped film, which is shown for the second-highest doping level, 0.3 mM, because of increased disorder that occurs at the highest doping level. Out-of-plane and in-plane integrations can be found for P3HT doped with all four dopants at all doping levels in **Figures C2 and C3**.

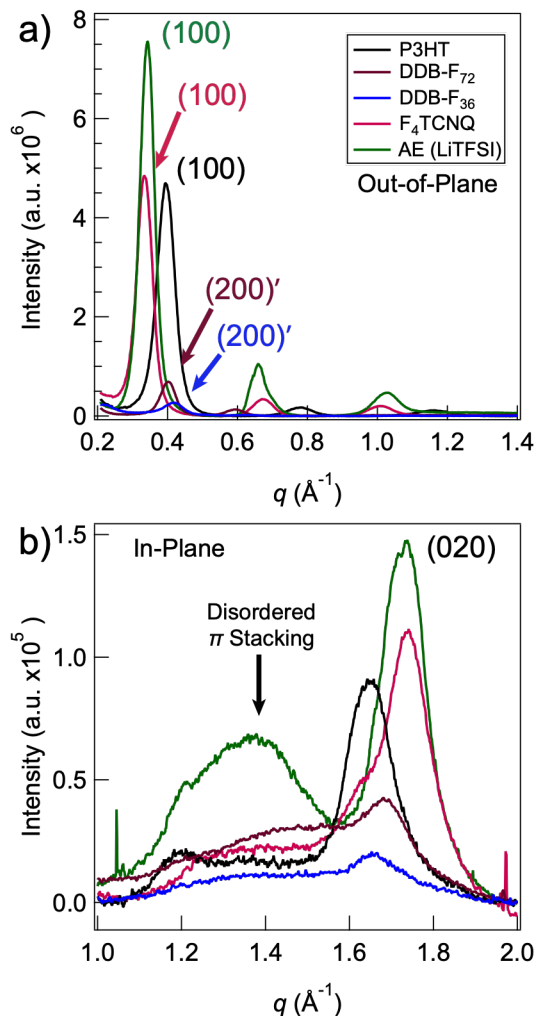


Figure 4.3. Out-of-plane (panel a) and in-plane (panel b) integrated GIWAXS data for pristine P3HT (black curve) and for the most highly-doped P3HT samples for each dopant shown in **Figure 4.2**. Specific dopant concentrations were 1 mM DDB-F₃₆, 3.62 mM F₄TCNQ, and 3.62 mM F₄TCNQ combined with 104.5 mM LiTFSI for the anion exchange sample. For P3HT doped using DDB-F₇₂, the data shown correspond to the second-highest concentration (0.3 mM), because there is a drop in the electrical conductivity and Hall carrier mobility due to amorphization of the film at the highest doping concentration.

For the case of F₄TCNQ (red curve, **Figure 4.3a**), the data show a shift of the (100) peak, which corresponds to the lamellar spacing of the P3HT crystallites, from approximately $0.39 \text{ \AA}^{-1}$ to a lower q -spacing of about $0.35 \text{ \AA}^{-1}$ upon doping. This shift, which has been noted in several studies, indicates that the lamellar region of P3HT is expanding to accommodate the F₄TCNQ anion within the polymer crystal structure.^[20,21,51] **Figure 4.3b** shows that F₄TCNQ doping also

causes a shift of the (020) π -stacking peak: this peak moves from approximately $1.65 \text{ \AA}^{-1}$ to a higher q around $1.70 \text{ \AA}^{-1}$, indicating a reduction in the π -stacking distance. This shift has been attributed to a reorientation of the π -stacking direction with respect to the unit cell axis, a change that modifies the tilt-angle of the hexyl side chains to make more room for intercalation of counterions into the lamellar region.^[20,21,51]

In the out-of-plane GIWAXS integration in **Figure 4.3a**, the anion-exchange-doped (green curve) films show a shift in the (100) lamellar peak to approximately $0.35 \text{ \AA}^{-1}$,^[27] resulting in a lamellar spacing similar to that of the F₄TCNQ-doped samples. In the in-plane integration in **Figure 4.3b**, the (020) π -stacking peak shifts to a q -spacing of $\sim 1.75 \text{ \AA}^{-1}$, a value that is only slightly larger than that observed for the F₄TCNQ-doped materials. The similarity in changes to both the (100) and (020) peaks between anion-exchange-doped films and F₄TCNQ-doped films suggests that these similarly-sized counterions distort the P3HT crystal lattice in a comparable fashion and that both sit within the lamellar region. Therefore, the hypothesis of roughly similar Coulomb interactions between polarons and each of these anions is consistent with the similar P1 peak positions seen in **Figure 4.2**.

Additionally, **Figure 4.3b** shows that the anion-exchange-doped P3HT samples have a broad scattering peak centered around $\sim 1.4\text{--}1.5 \text{ \AA}^{-1}$. Scattering in this region has been previously attributed to partly-ordered π -stacking associated with semi-amorphous regions of doped polymer films.^[8,51] When amorphous polymer regions are doped, they become more ordered, but they are not always able to fully crystallize. Therefore, the presence of this peak suggests that anion-exchange doping is affecting the amorphous regions of the P3HT film and increasing their degree of order to the point where they contribute to the scattering pattern. We note that the AE films were doped using *n*-butyl acetate (*n*-BA) as the solvent while the other films were doped using

dichloromethane (DCM) as the solvent. Thus, to test whether this disordered π -stacking peak was related to the AE doping method or the use of *n*-BA, we performed a series of control experiments where we doped P3HT films with F₄TCNQ from both *n*-BA and DCM. The results are shown in **Figure C4**, and they make clear that F₄TCNQ-doped P3HT films do not show significant scattering in the disordered π -stacking region upon doping from either solvent (see Appendix C), indicating that the $\sim 1.4\text{--}1.5\text{ \AA}^{-1}$ feature observed in the anion-exchange-doped samples is not caused by the solvent alone.

Unlike the F₄TCNQ- and anion-exchange-doped samples, the out-of-plane integrations for the DDB-doped samples in **Figure 4.3a** (brown and blue curves) show a significant shift of the (*h*00) peaks to a much lower *q*-spacing, so low that only the (200) lamellar peak of the doped structure [labeled (200)'] can be observed outside of the beamstop used in the experiment.^[8] This expansion is driven by the large size ($\sim 2\text{ nm}$ diameter) of the DDB-based counterions, which greatly expand the lattice in the lamellar direction in order to create a larger space into which they can fit. This expansion is what causes the DDB anions to have weaker Coulomb interactions with polarons due to their increased distance from the polymer backbone.^[9]

In contrast to the significant expansion of the lamellae, the in-plane integration in **Figure 4.3b** reveals that the (020) π -stacking peaks for both DDB-F₇₂- and DDB-F₃₆-doped P3HT films show minimal change from the pristine value, suggesting that the original π -stacking morphology is largely preserved; the DDB clusters are so large that they cannot intercalate within the hexyl side chains, as with the F₄TCNQ- and anion-exchange-doped samples, so they instead sit as an independent layer between the hexyl moieties.^[8] Although the two DDB-based dopants have largely similar molecular structures, a broad shoulder centered near $1.4\text{--}1.5\text{ \AA}^{-1}$ appears below the (020) π -stacking peak in DDB-F₇₂-doped films, which is much less pronounced in the DDB-F₃₆-

doped films. This broad shoulder could be either a signature of partial doping-induced crystallization of amorphous regions, as mentioned above, or it could correspond to a loss of some of the originally crystalline regions of the film.^[8,51] Since DDB-F₇₂ is highly oxidizing, it should dope the amorphous regions, making them more ordered, and heavily dope the crystalline regions to the point where the crystal structure could be partly disrupted due to the large number of DDB clusters that must be inserted into the crystalline lattice. The smaller shoulder at 1.4–1.5 Å⁻¹ in the DDB-F₃₆-doped films indicates that this less oxidizing dopant does not dope strongly enough to disrupt the crystallites or significantly re-order amorphous regions.

Table 4.1. Radius of gyration (R_g) obtained from GISAXS for P3HT samples doped at similar Hall carrier densities of $\sim 5 \times 10^{20} \text{ cm}^{-3}$ with different dopants (cf. **Figure 4.5b**). The dopant concentrations needed to achieve carrier densities around this level are 0.3 mM DDB-F₇₂, 1 mM DDB-F₃₆, 0.18 mM F₄TCNQ, and 1.81 mM/104.5 mM anion exchange (F₄TCNQ/LiTFSI). The R_g values for all four dopants at all the dopant concentrations studied are presented in **Table C1**. The R_g values were obtained using the Unified Fit model (see Appendix C for fitting details). Also presented are the σ_0 and $W_{\text{H,slope}}$ parameters from the SLoT model fits to the Seebeck coefficient–conductivity data in **Figure 4.4**.

	P3HT Pristine	F ₄ TCNQ	AE (LiTFSI)	DDB-F ₇₂	DDB-F ₃₆
R_g (Å)	80	57	99	39	58
Hall Carrier Density ($\times 10^{20} \text{ cm}^{-3}$)	–	5.2	4.8	5.1	3.6
σ_0 (S cm ⁻¹)	–	10	125	25	35
$W_{\text{H,slope}}$ (meV)	–	310	350	1000	1550

In addition to changes in the local crystal structure, doping also causes changes on larger length scales, which we probe using GISAXS.^[65–71] **Table 4.1** provides the domain size, or radius of gyration (R_g) correlation length, extracted from GISAXS for P3HT thin films doped at a Hall carrier density of $\sim 5 \times 10^{20} \text{ cm}^{-3}$ for all four dopants (see **Figures C6 and C7** for the GISAXS integrations and fits used to obtain R_g for each dopant). A larger R_g is associated with doped

domains that persist over a greater distance, likely indicating greater continuity of the conductive pathways within those films.^[72,73]

Our GISAXS results reveal that the initial pristine P3HT film has $R_g = 80 \text{ \AA}$, a value that likely corresponds to the crystalline domain sizes within the film. Upon doping with F₄TCNQ, R_g decreases to $57 \text{ \AA}$, indicating that the doped domains may be smaller than the original polymer crystallites.^[12,29,74] Interestingly, both DDB-F₇₂- and DDB-F₃₆-doped films exhibit still lower R_g values, $39 \text{ \AA}$ and $58 \text{ \AA}$, respectively. The decrease in R_g in the DDB-based P3HT samples can be attributed to the dopant's large size, which should cause significant strain within the polymer network, causing single polymer domains to break up into multiple smaller domains upon doping. Doping-induced crystallization may also result in the formation of new, small, doped polymer domains. The much lower R_g value observed in the DDB-F₇₂-doped P3HT films is likely caused by this latter effect. The less oxidizing DDB-F₃₆ dopant has only enough oxidizing power to dope P3HT but not to crystallize the amorphous regions, leading to a smaller change in domain size from the pristine P3HT. In contrast to both the F₄TCNQ- and DDB-doped P3HT films, the GISAXS data show two different correlation lengths for the anion-exchange-doped samples at the highest concentration, with R_g values of $51 \text{ \AA}$ and $107 \text{ \AA}$; additionally, all anion-exchange-doped samples show an increase in R_g . The higher R_g value of $107 \text{ \AA}$, which exceeds that of the pristine film, likely corresponds to growth of the original domains through the same process of doping-induced crystallization. The smaller R_g signal may arise from new crystalline domains formed through doping-induced crystallization of amorphous regions where the new domains were not able to grow epitaxially onto existing domains and instead nucleated independently.

Finally, to fully understand the doping-induced structural changes, we also evaluated the paracrystallinity, $g_{(h00)}$, of these samples, shown in **Figure C5** of Appendix C. We found little

overall change in $g_{(h00)}$ upon doping, a result that indicates that $g_{(h00)}$ values do not follow the same trend as R_g . This is because paracrystallinity reflects lattice disorder within the crystallites,^[75–77] whereas R_g reflects the larger-scale domain size within the doped films.^[72,73] As domains grow or fracture upon doping, they may do so with retention of crystalline order, or with increased disorder, but grain growth and disorder are not intrinsically coupled.

With this understanding of the P3HT structural changes induced by different dopants, we turn next to address the question: how do these doping-induced morphological changes influence the charge transport characteristics in doped P3HT systems?

4.2.3 Seebeck Coefficient–Electrical Conductivity Relationship

Having investigated the local and mesoscopic structure of P3HT doped with DDB-F₇₂, DDB-F₃₆, F₄TCNQ, and via anion exchange, we now turn to investigating how the different doped polymer morphologies affect macroscopic thermoelectric properties such as the Seebeck coefficient and electrical conductivity. To measure the Seebeck coefficient, we deposited two parallel line electrodes onto the film and created a temperature gradient to measure the resulting voltage; the corresponding ΔV versus ΔT data used to extract the Seebeck coefficients are shown in **Figure C9**. Electrical conductivity was assessed using the van der Pauw method, with electrodes placed at the four corners of square film samples. More details of how the Seebeck coefficient and electrical conductivity are measured can be found in the Experimental Section, and the full conductivity and Seebeck coefficient data as a function of dopant concentration are shown in **Figure C8**. **Figure 4.4** shows the measured Seebeck coefficient and the electrical conductivity of P3HT doped with all four dopants across various doping levels (the same samples whose absorption spectra are presented in **Figure 4.2**). We note that some of the lowest-concentration-

doped samples, even though they showed evidence of doping via UV–vis–NIR spectroscopy, had electrical conductivities too low to be accurately measured.

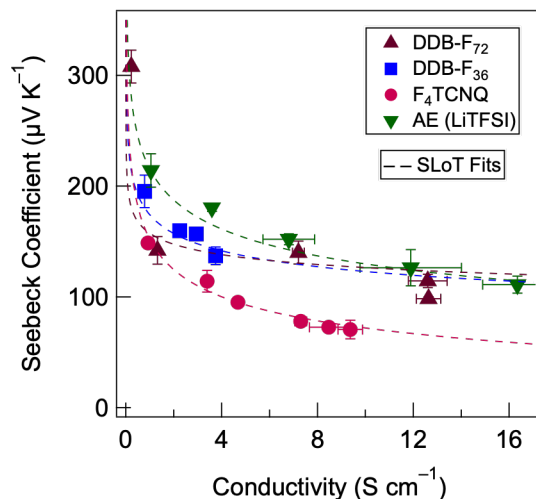


Figure 4.4. Seebeck coefficient–conductivity (S – σ) relationship for P3HT doped at different levels with various dopants/counterions. The dashed curves are fits to the SLot model (**Equations (4.2–4.4)**), with parameters summarized in **Table 4.1** and in Appendix C. Both the DDB-based dopants and anion-exchange doping show significantly higher Seebeck coefficients for the same electrical conductivity compared to F₄TCNQ-doped P3HT samples.

For all of the doped P3HT samples, increased doping improves the conductivity but also shifts the Fermi level deeper into the band, reducing the asymmetry of the transport distribution around E_F and lowering the average excess energy of the carriers contributing to the transport. As a result, the Seebeck coefficient decreases with increasing doping level, as described by **Equation (4.3)**. P3HT films doped with F₄TCNQ exhibit the lowest Seebeck coefficient for a given conductivity compared to films doped with the other oxidants. The films doped with DDB-F₇₂, DDB-F₃₆, and via anion exchange all show a similar (and more favorable) S – σ trend over the measured conductivity range. This indicates that the charge transport efficiency of P3HT films doped with DDBs and via anion exchange is better than that doped using F₄TCNQ.

Figure 4.4 also displays fits of the S – σ results to the SLoT model (**Equations (4.2–4.4)**); a detailed discussion of these fits and the model is given in Appendix C as well as further below. We reiterate that this model assigns charge transport as resulting from an intrinsic conductivity (σ_0) and a carrier-density-dependent localization energy ($W_H(c)$). Although **Equation (4.4)** doesn't specify whether σ_0 or $W_H(c)$ has a greater impact on the Seebeck coefficient–conductivity relationship, it is clear that having a higher Seebeck coefficient for a given conductivity level indicates a more favorable doping method.

4.2.4 Hall Effect Measurements

To further understand the factors contributing to the S – σ relationship in P3HT doped in different ways, including the carrier mobility, we conducted Hall effect measurements on the same set of samples used for the SLoT fits in **Figure 4.4**. A more detailed discussion of the Hall measurements can be found in Appendix C; the Hall carrier density and mobility as a function of dopant concentration are shown in **Figure C10**, and an additional comparison supporting the consistency of the Hall-derived carrier densities is shown in **Figure C11**. **Figure 4.5a** shows the measured Hall mobility as a function of the measured Hall carrier density for P3HT films doped with the four different methods. As expected, the Hall carrier mobility generally increases with increasing carrier density due to trap filling and screening effects.^[17,18,78–80] However, for P3HT films doped with DDB-F₇₂ at very high concentrations, the loss of crystallinity leads to a decrease in carrier mobility, as we have noted above and in previous work.^[8]

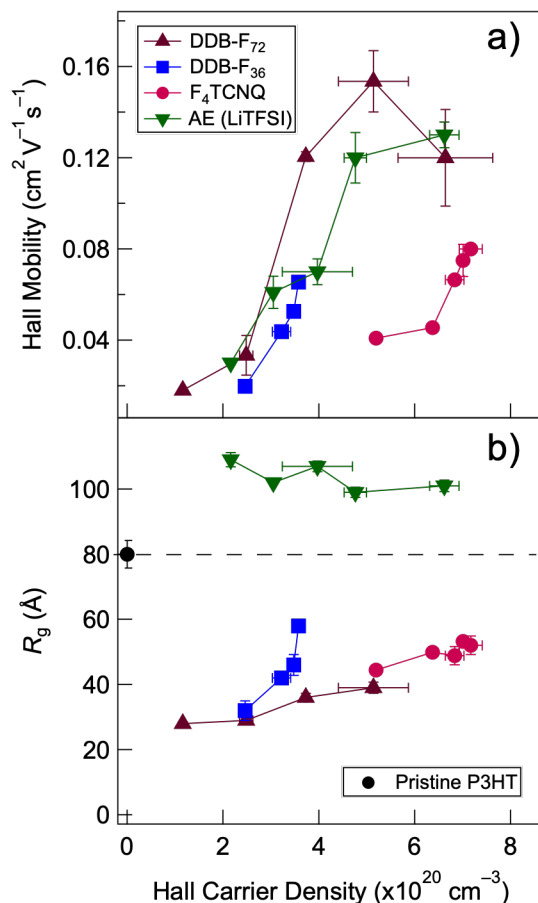


Figure 4.5. (a) Hall effect measurements for P3HT films doped at different levels with various dopants. The x-axis is the Hall carrier density (rather than dopant concentration) since the different dopants and methods have different doping efficiencies. The DDB-based dopants and anion-exchange method show significantly higher Hall mobility at a given carrier density than the samples doped using F_4TCNQ . Panel (b) shows how the R_g obtained from GISAXS changes as a function of the Hall carrier density when P3HT (pristine, black circle) is doped using DDB- F_{72} , DDB- F_{36} , F_4TCNQ , and via anion exchange. **Table 4.1** summarizes the R_g values for samples doped at a carrier density of $\sim 5 \times 10^{20} \text{ cm}^{-3}$. Most dopants produced smaller domains upon doping, but anion-exchanged samples show larger domains because of doping-induced crystallization of the amorphous parts of the film.

Figure 4.5a also shows that the DDB- F_{72} -, DDB- F_{36} -, and anion-exchange-doped P3HT samples have similar carrier mobilities at the same carrier density. In contrast, the F_4TCNQ -doped samples exhibit significantly lower mobility at equivalent carrier densities. This fits with the S - σ relationships seen in **Figure 4.4**, which indicate that the DDB- and anion-exchange-doped films have better charge transport compared to F_4TCNQ -doped samples. However, this finding poses an

interesting question: given that the DDB-based dopants experience reduced Coulomb interactions with the carriers, as indicated by their red-shifted P1 absorption, and high Hall carrier mobility, why do the anion-exchange-doped P3HT films also exhibit high Hall carrier mobility despite having a bluer P1 peak and thus more localized carriers? Although we previously have argued that a dopant's size, the location of the P1 absorption, and Hall carrier mobility are directly correlated,^[8,9] it appears that this is not the case for anion-exchange-doped P3HT.^[28,30] This suggests that other factors, presumably related to the local crystalline and mesoscale morphology, are important for determining the carrier mobility in anion-exchange-doped systems.

One factor that could explain this observation is how different the R_g values are for each dopant, as summarized in **Figure 4.5b**. As mentioned above, the larger R_g values for anion exchange likely result from the ability of this method to dope amorphous regions without the large strains associated with DDB insertion into the lattice, leading to the formation of larger, more connected domains. Thus, **Figure 4.5** suggests that the macroscopic charge transport characteristics of P3HT doped with different dopants may be related to the long-range structural ordering in these films, an idea that we explore further below.

4.2.5 Probing the Activation Energy, W_H , via Temperature-Dependent Conductivity

Having established the role of dopant-dependent morphology and its impact on Hall carrier mobility, we now turn to temperature-dependent conductivity measurements to examine the energetic landscape of charge transport. Charge transport in semiconducting polymers is often described as hopping between localized states, which requires thermal energy to overcome the barriers between them.^[18,81–85] By measuring the electrical conductivity as a function of temperature ($\sigma(T)$) and fitting the data to the Arrhenius equation, we extract the activation energy, W_H , from the slope of the linear $\ln(\sigma(T))$ versus $(k_B T)^{-1}$ plot to determine how this energy changes

with carrier density.^[82] Details of the measurement methods and Arrhenius fits are given in the Experimental Section (see also **Figure C12**). The results are shown in **Figure 4.6a,b**.

Figure 4.6a shows that both DDB-F₇₂- and DDB-F₃₆-doped P3HT films initially experience a sharp decrease in W_H as the Hall carrier density increases. This sharp drop suggests that DDB-doped films have highly delocalized carriers, consistent with the large counterion having reduced Coulomb interaction with the carriers, as evidenced by the red-shifted P1 absorption transition seen in **Figure 4.2**. One of the key advantages of using DDB-F₇₂ as a dopant, in comparison to DDB-F₃₆, is its strong oxidizing power and higher doping efficiency, which allows us to study the barrier height at very low doping levels. The data suggest that at low doping levels, carriers in DDB-F₇₂-doped P3HT films still experience significant localization despite the weaker Coulomb interactions between the polaron and the dopant counterion. This localization can be understood by the increased distance between doping sites at low doping levels, leading to poorer overlap between potential wells and thus a higher W_H .^[18] Given that the Coulomb interaction with charge carriers is already low in DDB-doped samples, this explains why the decrease in W_H with increasing carrier density is more rapid than with F₄TCNQ doping and anion-exchange doping, where the local Coulomb attraction between carriers and counterions is stronger.

Perhaps the most striking result in **Figure 4.6a**, however, is that although the anion-exchange-doped samples have relatively high Hall carrier mobilities (**Figure 4.5a**) and a favorable Seebeck coefficient–conductivity relationship (**Figure 4.4**), they show similar activation energy to the F₄TCNQ-doped samples at the same carrier density. This relatively large W_H , along with the blue-shifted P1 peaks for the AE-doped samples, indicates that the polarons still experience relatively strong Coulomb interactions with the TFSI[−] counterions. This again raises the question: why do these samples have high carrier mobilities despite having high activation energies?

Normally, a large activation energy would suggest poor carrier mobility, so the better mobility and charge transport must be due to another factor that compensates for the large activation energy.

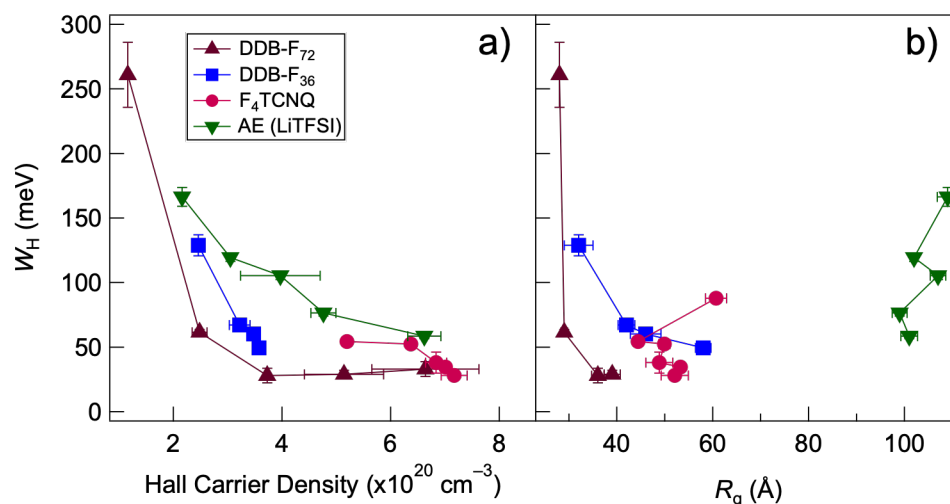


Figure 4.6. (a) The experimentally measured activation energy, W_H , for P3HT films doped with different dopants as a function of Hall carrier density. The W_H values are obtained using temperature-dependent conductivity measurements and fitting to the Arrhenius equation. The DDB-based dopants show the fastest drop in W_H upon doping (largest slope) compared to anion-exchange doping or doping with F₄TCNQ. (b) The (general lack of) relation between W_H and R_g from GISAXS.

As mentioned above, we believe that this other factor is related to the mesoscale domain ordering, as quantified by R_g . **Figure 4.6b** shows that DDB-F₇₂- and DDB-F₃₆-doped P3HT experience similar W_H barriers, despite having much smaller R_g values compared to F₄TCNQ- and anion-exchange-doped P3HT. This suggests that, for the DDB-doped systems, favorable charge transport is driven primarily by the reduced Coulomb trapping rather than by favorable longer-range morphological effects. The one exception to this trend is the most highly-doped DDB-F₇₂ sample, which shows a very large domain size and a slightly increased W_H barrier. As discussed above, this overdoped sample is starting to amorphize due to an excess of DDB clusters in the lattice, resulting in reduced domain contrast and thus a larger R_g . In contrast, the anion-exchange-

doped P3HT samples exhibit larger R_g values across doping levels, indicating that improved mesoscale connectivity contributes importantly to their favorable long-range transport. These observations therefore suggest that activation energy alone does not fully determine macroscopic transport. This motivates an analysis of σ_0 , the intrinsic conductivity, in **Equation (4.4)**, which we discuss below.

4.2.6 Semi-Localized Transport (SLoT) Model

To better understand the enhanced carrier mobilities and S - σ relation in the AE-doped samples, we next examine the SLoT fits, focusing particularly on the extracted σ_0 values. Within the SLoT framework, σ_0 is the transport prefactor in the absence of localization effects and thus sets the intrinsic conductivity scale of a system. As a result, larger σ_0 values correspond to systems that can achieve higher conductivities with a given Seebeck coefficient, even if localization effects are present. The parameters used to fit the SLoT model (**Equations (4.2–4.4)**) to the S - σ relationship for the P3HT samples doped at different concentrations with different dopants, shown by the dashed curves in **Figure 4.4**, are summarized in **Table 4.1** (see also **Table C2**).

From these SLoT parameters, we see that P3HT samples doped with DDB-F₇₂ and DDB-F₃₆ have similar σ_0 values (25 S cm⁻¹ and 35 S cm⁻¹, respectively) and similar rates of change of the localization energy with carrier density ($W_{H,\text{slope}} = 1000$ meV and 1550 meV, respectively). In contrast, the SLoT model fits for the F₄TCNQ- and anion-exchange-doped P3HT samples have much smaller $W_{H,\text{slope}}$ values (310 meV and 350 meV, respectively), as seen in **Figure 4.6**. Additionally, σ_0 increases substantially from 10 S cm⁻¹ for the F₄TCNQ-doped samples to 125 S cm⁻¹ for the AE-doped samples; the latter value is 3–4 times higher than the σ_0 values for P3HT doped with the DDB clusters. This suggests that the enhanced charge transport characteristics in the DDB-based doped samples result from both a moderately high σ_0 and a reduced localization

energy, while the favorable charge transport characteristics of the anion-exchange-doped samples result from a σ_0 that is so high that it can overcome fairly high localization effects and high activation energies from strong Coulomb interactions.

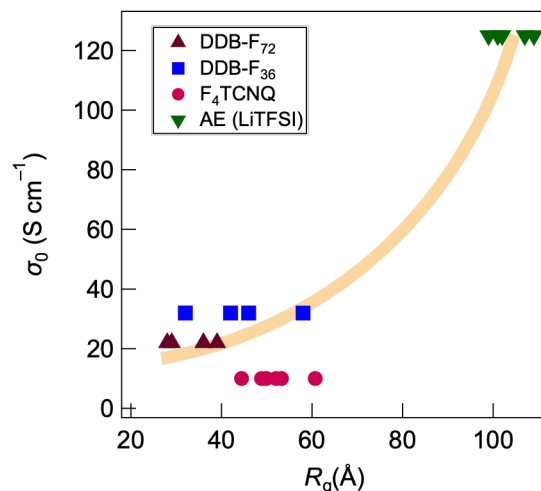


Figure 4.7. Relationship between σ_0 , obtained from SLoT fitting of electrical and thermal measurements, and R_g values, obtained from GISAXS, at all measured carrier densities. The trend indicates that as the domain length increases, the intrinsic conductivity improves proportionally, regardless of the doping level for each dopant. The orange curve is to help guide the eye.

Given that all the samples we studied in this work are based on the same semiconducting polymer, P3HT, this leads to the question: how can the same doped polymer have such dramatically different intrinsic conductivities simply by changing the dopant or doping method? We find that there is a correlation between the σ_0 parameter obtained from fitting the SLoT model and the mesoscopic degree of order, R_g , obtained from GISAXS, as highlighted in **Table 4.1** and **Figure 4.7**. This suggests that the dopant's identity, which determines its ability to dope and crystallize certain regions within the P3HT films, thus determining the mesoscale morphology of the doped films, directly influences the charge transport characteristics.

Table 4.1 and **Figure 4.7** show that although the DDB-based dopants have moderately large values of σ_0 , they have smaller R_g values compared to anion-exchange-doped samples. These

very small R_g values can be attributed to these dopants' large size, which disrupts the polymer lattice, as seen in **Figure 4.3**, leading to shorter long-range structural connectivity between domains. The differences in the σ_0 and R_g values between DDB-F₇₂-doped and DDB-F₃₆-doped P3HT can be explained by the difference in these dopants' oxidizing power. Although DDB-F₇₂ can readily dope both crystalline and amorphous regions, its high oxidizing power and large size cause it to overdope the crystalline domains, disrupting the periodicity and resulting in a lower R_g and σ_0 . On the other hand, DDB-F₃₆, which is less oxidizing but has an equally large counterion, breaks up the domains less, resulting in better connectivity between crystalline domains and slightly improved long-range charge transport.

In the case of F₄TCNQ-doped P3HT samples, we attribute the low values of σ_0 and R_g seen in **Figures 4.5b and 4.7** to the fact that under these conditions, F₄TCNQ predominantly dopes the crystalline regions of P3HT films, creating smaller isolated doped crystalline domains with poorer interdomain transport. In contrast, the anion-exchange-doped P3HT samples exhibit a larger R_g value due to doping-induced crystallization of the amorphous regions without the large lattice strain seen with the DDB clusters, which expands the connectivity between doped domains and provides improved long-range charge transport pathways. The large increase in σ_0 observed for the AE-doped samples occurs together with a substantial increase in R_g , suggesting that improved mesoscale ordering and connectivity contribute to the enhanced intrinsic transport scale captured by σ_0 . This correlation indicates that the structural reorganization induced by anion exchange favorably modifies the transport landscape of the doped film.

This interpretation is consistent with prior work from both Yamashita *et al.*, who observed enhanced doping levels together with reduced lattice/structural disorder,^[6,86] and also Chen *et al.*, who similarly linked charge-transport enhancement with doping-induced ordering of previously

less-ordered regions.^[30] It is important to note that the SLoT model parameters, including σ_0 , are determined entirely from electrical and thermal measurements, while the GISAXS parameters are entirely structurally based, so our results provide perhaps the strongest link to date between the mesoscale morphology of doped conjugated polymers and thermoelectric properties. From **Figure 4.7**, we see that the dopant size, redox potential, and propensity to drive doping-induced crystallization of the amorphous polymer regions are all important for controlling electrical conductivity, since the local and mesoscale structures both directly influence the charge transport characteristics of doped organic semiconducting polymers.

4.3 Conclusions

In summary, we explored using four different dopants/doping methods to create doped P3HT films with different morphologies and thus different charge transport characteristics. Hall effect measurements demonstrate that DDB-based dopants and anion-exchange doping provide better charge transport compared to F₄TCNQ, resulting in a better S – σ relationship. The enhanced charge transport observed with DDB-based dopants is attributed to reduced Coulomb interactions and lower activation energy, while anion-exchange-doped films and those doped with F₄TCNQ experience strong localization effects and higher activation energy. Hall effect, temperature-dependent conductivity, and UV–vis–NIR spectroscopy measurements all show that Coulomb interactions between the dopant counterions and the charge carriers are the dominant factor influencing carrier localization and activation energy in these samples.

Further analysis using the SLoT model indicates that the improvement in charge transport for anion-exchange doping is primarily due to a much higher intrinsic conductivity σ_0 that can compensate for the accompanying higher carrier localization energy ($W_H(c)$). Our structural measurements show that this improvement in the intrinsic conductivity is linked to the doping and

ordering of the amorphous regions, improving the R_g and thus the mesoscale charge transport connectivity. All of the results indicate that it is a combination of the local molecular Coulomb interaction, the degree of doping-induced crystallization, and ordering on the mesoscale that controls overall charge transport in doped conjugated polymer films. Clearly, it is possible to use mesoscale ordering to achieve similar charge transport characteristics even in the presence of strong localization effects, indicating that further research on how to enhance ordering on this length scale is warranted for improving the thermoelectric properties of doped conjugated polymers.

4.4 Experimental

4.4.1 Device Preparation

Device fabrication was performed on pre-cleaned glass substrates for thermoelectric, electrical, and spectroscopy samples, and on pre-cleaned silicon wafer substrates for GIWAXS and GISAXS samples. The cleaning process involved cutting the substrates into 1.2×1.2 cm pieces, followed by sequential washes with Alconox detergent, deionized water, and acetone. After drying with nitrogen gas, the substrates were plasma-etched for approximately 10 minutes. Substrates were transferred to a nitrogen glovebox for spin coating and doping.

P3HT was dissolved in *o*-dichlorobenzene (*o*-DCB, 20 mg/mL) and stirred until fully dissolved. Pristine polymer films were deposited by spin coating at 1000 rpm, followed by a brief high-speed spin step to remove residual solvent. Before doping, films were allowed to crystallize overnight under an inert nitrogen atmosphere. For the sequential doping procedure, the pristine P3HT polymer films were exposed to a dopant solution for a set time period before spin coating at 4000 rpm for 10 seconds to remove any residual dopant solution. For F₄TCNQ, DDB-F₇₂, and DDB-F₃₆, the dopants were dissolved in dichloromethane (DCM) at the specified concentrations,

and the polymer films were then exposed to the corresponding solution for 10 seconds before spin coating. For anion-exchange-doped samples, various concentrations of F₄TCNQ were dissolved in *n*-butyl acetate (*n*-BA) and mixed with an equal volume of 209.0 mM LiTFSI solution (in *n*-BA) to obtain anion-exchange solutions with varying F₄TCNQ concentrations while keeping the LiTFSI concentration constant (104.5 mM). The polymer films were exposed to the dopant solution for 80 seconds before spin coating.

4.4.2 Film Characterization

GIWAXS measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11-3 using an X-ray energy of 12.7 keV at an incidence angle of 0.12°. Diffraction patterns were collected in a helium chamber to increase signal-to-noise ratio with a sample-to-detector distance of 250 mm and a spot size of ~150 µm on the image plate. The Igor macro Nika was used to calibrate the 2D spectra. WAXStools and Nika were used to reduce the raw data. To ensure reproducibility, all samples were made and measured in triplicate.

GISAXS was collected at the Stanford Synchrotron Radiation Lightsource using beamline 1-5. The scattering X-rays with an incident energy set at 12 keV were collected using a 2D detector at a sample-to-detector distance of 3 meters. The incident angle was set to 0.12°. The 1D integrations were obtained by horizontally integrating near the Yoneda band and were fit using the Unified Fit method from the Irena and Nika package in Igor software. To ensure reproducibility, all samples were made and measured in triplicate.

Conductivity, Hall effect, temperature-dependent conductivity, and UV-vis-NIR spectroscopy measurements were all performed on the same samples. Conductivity was measured by determining the sheet resistance using a Lake Shore MeasureReady M91 FastHall instrument. Film thicknesses were measured with a Dektak 150 stylus profilometer. The samples had 1 × 1

mm square Au electrodes, 50 nm thick, thermally evaporated onto the corners using a 3D-printed shadow mask in an Angstrom Engineering Nexdep thermal evaporator. To ensure reproducibility, all conductivity measurements were conducted on three independent samples.

Hall effect measurements were performed using the same Lakeshore instrument, with a source current of 10 μ A and a magnetic field of 1.0236 T; these measurements were conducted on at least three independent samples for reproducibility. Temperature-dependent conductivity was determined by measuring the sample sheet resistance as a function of temperature in a custom-built van der Pauw setup using a Keithley 2400 Sourcemeter controlled by LabVIEW software. A Peltier plate controlled the sample temperature, which was measured by an RTD sensor. UV–vis–NIR spectra were obtained using a JASCO V-770 spectrophotometer.

The Seebeck coefficient was measured on a separate device with a different electrode geometry, consisting of electrodes made from two parallel gold rectangles (10×1 mm, 45 nm thick) spaced 10 mm apart. Measurements were performed using a custom-built setup with two Peltier plates to generate a temperature gradient, and the films' temperature gradient was monitored with two RTD sensors. Samples for Seebeck measurements were prepared with the same solutions and at the same time as those used for sheet resistance/Hall/temperature-dependent conductivity/UV–vis–NIR measurements to ensure that all samples were as identical as possible. All Seebeck measurements were conducted on at least three separate samples to ensure reproducibility.

4.5 References

- [1] T. M. Swager, *Macromolecules* **2017**, *50*, 4867.
- [2] N. Dubey, M. Leclerc, *J. Polym. Sci. Part B Polym. Phys.* **2011**, *49*, 467.
- [3] G.-H. Kim, L. Shao, K. Zhang, K. P. Pipe, *Nat. Mater.* **2013**, *12*, 719.

- [4] J. Tang, Y.-H. Pai, Z. Liang, *ACS Energy Lett.* **2022**, 7, 4299.
- [5] E. E. Havinga, W. ten Hoeve, H. Wynberg, *Polym. Bull.* **1992**, 29, 119.
- [6] Y. Yamashita, J. Tsurumi, M. Ohno, R. Fujimoto, S. Kumagai, T. Kurosawa, T. Okamoto, J. Takeya, S. Watanabe, *Nature* **2019**, 572, 634.
- [7] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, M. F. Toney, *Nat. Mater.* **2006**, 5, 328.
- [8] T. J. Aubry, K. J. Winchell, C. Z. Salamat, V. M. Basile, J. R. Lindemuth, J. M. Stauber, J. C. Axtell, R. M. Kubena, M. D. Phan, M. J. Bird, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2020**, 30, 2001800.
- [9] T. J. Aubry, J. C. Axtell, V. M. Basile, K. J. Winchell, J. R. Lindemuth, T. M. Porter, J.-Y. Liu, A. N. Alexandrova, C. P. Kubiak, S. H. Tolbert, A. M. Spokoyny, B. J. Schwartz, *Adv. Mater.* **2019**, 31, 1805647.
- [10] B. Lüssem, C.-M. Keum, D. Kasemann, B. Naab, Z. Bao, K. Leo, *Chem. Rev.* **2016**, 116, 13714.
- [11] S. D. Kang, G. J. Snyder, *Nat. Mater.* **2017**, 16, 252.
- [12] V. Untilova, J. Hynynen, A. I. Hofmann, D. Scheunemann, Y. Zhang, S. Barlow, M. Kemerink, S. R. Marder, L. Biniek, C. Müller, M. Brinkmann, *Macromolecules* **2020**, 53, 6314.
- [13] Y. Xuan, X. Liu, S. Desbief, P. Leclère, M. Fahlman, R. Lazzaroni, M. Berggren, J. Cornil, D. Emin, X. Crispin, *Phys. Rev. B* **2010**, 82, 115454.
- [14] M. Statz, D. Venkateshvaran, X. Jiao, S. Schott, C. R. McNeill, D. Emin, H. Sirringhaus, R. Di Pietro, *Commun. Phys.* **2018**, 1, 1.
- [15] O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren, X. Crispin, *Nat. Mater.* **2011**, 10, 429.
- [16] Y. Zhong, V. Untilova, D. Muller, S. Guchait, C. Kiefer, L. Herrmann, N. Zimmermann, M. Brosset, T. Heiser, M. Brinkmann, *Adv. Funct. Mater.* **2022**, 32, 2202075.
- [17] S. A. Gregory, A. Atassi, J. F. Jr. Ponder, G. Freychet, G. M. Su, J. R. Reynolds, M. D. Losego, S. K. Yee, *J. Phys. Chem. C* **2023**, 127, 12206.

- [18] S. A. Gregory, R. Hanus, A. Atassi, J. M. Rinehart, J. P. Wooding, A. K. Menon, M. D. Losego, G. J. Snyder, S. K. Yee, *Nat. Mater.* **2021**, *20*, 1414.
- [19] M. G. Voss, D. T. Scholes, J. R. Challa, B. J. Schwartz, *Faraday Discuss.* **2019**, *216*, 339.
- [20] D. T. Scholes, P. Y. Yee, J. R. Lindemuth, H. Kang, J. Onorato, R. Ghosh, C. K. Luscombe, F. C. Spano, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2017**, *27*, 1702654.
- [21] D. T. Scholes, P. Y. Yee, G. R. McKeown, S. Li, H. Kang, J. R. Lindemuth, X. Xia, S. C. King, D. S. Seferos, S. H. Tolbert, B. J. Schwartz, *Chem. Mater.* **2019**, *31*, 73.
- [22] V. Untilova, T. Biskup, L. Biniek, V. Vijayakumar, M. Brinkmann, *Macromolecules* **2020**, *53*, 2441.
- [23] Y.-J. Heo, H.-G. Jeong, J. Kim, B. Lim, J. Kim, Y. Kim, B. Kang, J.-M. Yun, K. Cho, D.-Y. Kim, *ACS Appl. Mater. Interfaces* **2020**, *12*, 49886.
- [24] Y.-J. Kim, N.-K. Kim, W.-T. Park, C. Liu, Y.-Y. Noh, D.-Y. Kim, *Adv. Funct. Mater.* **2019**, *29*, 1807786.
- [25] J. Mei, D. H. Kim, A. L. Ayzner, M. F. Toney, Z. Bao, *J. Am. Chem. Soc.* **2011**, *133*, 20130.
- [26] Z. Liang, Y. Zhang, M. Souri, X. Luo, A. M. Boehm, R. Li, Y. Zhang, T. Wang, D.-Y. Kim, J. Mei, S. R. Marder, K. R. Graham, *J. Mater. Chem. A* **2018**, *6*, 16495.
- [27] I. E. Jacobs, G. D'Avino, V. Lemaire, Y. Lin, Y. Huang, C. Chen, T. F. Harrelson, W. Wood, L. J. Spalek, T. Mustafa, C. A. O'Keefe, X. Ren, D. Simatos, D. Tjhe, M. Statz, J. W. Strzalka, J.-K. Lee, I. McCulloch, S. Fratini, D. Beljonne, H. Sirringhaus, *J. Am. Chem. Soc.* **2022**, *144*, 3005.
- [28] E. M. Thomas, K. A. Peterson, A. H. Balzer, D. Rawlings, N. Stingelin, R. A. Segalman, M. L. Chabinyc, *Adv. Electron. Mater.* **2020**, *6*, 2000595.
- [29] M. Lu-Díaz, M. Duhandžić, S. Harrity, S. Samanta, Z. Akšamija, D. Venkataraman, *J. Phys. Chem. C* **2024**, *128*, 5996.
- [30] C. Chen, I. E. Jacobs, K. Kang, Y. Lin, C. Jellett, B. Kang, S. B. Lee, Y. Huang, M. BaloochQarai, R. Ghosh, M. Statz, W. Wood, X. Ren, D. Tjhe, Y. Sun, X. She, Y. Hu, L. Jiang, F. C. Spano, I. McCulloch, H. Sirringhaus, *Adv. Energy Mater.* **2023**, *13*, 2202797.
- [31] K.-H. Yim, G. L. Whiting, C. E. Murphy, J. J. M. Halls, J. H. Burroughes, R. H. Friend, J.-S. Kim, *Adv. Mater.* **2008**, *20*, 3319.

- [32] C. Y. Kao, B. Lee, L. S. Wielunski, M. Heeney, I. McCulloch, E. Garfunkel, L. C. Feldman, V. Podzorov, *Adv. Funct. Mater.* **2009**, *19*, 1906.
- [33] J. Yamamoto, Y. Furukawa, *J. Phys. Chem. B* **2015**, *119*, 4788.
- [34] V. A. Kolesov, C. Fuentes-Hernandez, W.-F. Chou, N. Aizawa, F. A. Larrain, M. Wang, A. Perrotta, S. Choi, S. Graham, G. C. Bazan, T.-Q. Nguyen, S. R. Marder, B. Kippelen, *Nat. Mater.* **2017**, *16*, 474.
- [35] G. Lu, J. Blakesley, S. Himmelberger, P. Pingel, J. Frisch, I. Lieberwirth, I. Salzmann, M. Oehzelt, R. Di Pietro, A. Salleo, N. Koch, D. Neher, *Nat. Commun.* **2013**, *4*, 1588.
- [36] A. M. Glaudell, J. E. Cochran, S. N. Patel, M. L. Chabinyc, *Adv. Energy Mater.* **2015**, *5*, 1401072.
- [37] O. Khatib, B. Lee, J. Yuen, Z. Q. Li, M. Di Ventra, A. J. Heeger, V. Podzorov, D. N. Basov, *J. Appl. Phys.* **2010**, *107*, 123702.
- [38] S. Himmelberger, D. T. Duong, J. E. Northrup, J. Rivnay, F. P. V. Koch, B. S. Beckingham, N. Stingelin, R. A. Segalman, S. C. B. Mannsfeld, A. Salleo, *Adv. Funct. Mater.* **2015**, *25*, 2616.
- [39] A. Hamidi-Sakr, L. Biniek, J.-L. Bantignies, D. Maurin, L. Herrmann, N. Leclerc, P. Lévêque, V. Vijayakumar, N. Zimmermann, M. Brinkmann, *Adv. Funct. Mater.* **2017**, *27*, 1700173.
- [40] D. Neusser, C. Malacrida, M. Kern, Y. M. Gross, J. van Slageren, S. Ludwigs, *Chem. Mater.* **2020**, *32*, 6003.
- [41] Y. Wu, Q. M. Duong, A. F. Simafranca, C. Z. Salamat, B. J. Schwartz, S. H. Tolbert, *ACS Mater. Lett.* **2024**, *6*, 489.
- [42] K. E. Watts, B. Neelamraju, E. L. Ratcliff, J. E. Pemberton, *Chem. Mater.* **2019**, *31*, 6986.
- [43] V. Untilova, H. Zeng, P. Durand, L. Herrmann, N. Leclerc, M. Brinkmann, *Macromolecules* **2021**, *54*, 6073.
- [44] J. Hynynen, D. Kiefer, C. Müller, *RSC Adv.* **2018**, *8*, 1593.
- [45] P. Pingel, D. Neher, *Phys. Rev. B* **2013**, *87*, 115209.
- [46] A. R. Chew, R. Ghosh, Z. Shang, F. C. Spano, A. Salleo, *J. Phys. Chem. Lett.* **2017**, *8*, 4974.

- [47] I. E. Jacobs, E. W. Aasen, J. L. Oliveira, T. N. Fonseca, J. D. Roehling, J. Li, G. Zhang, M. P. Augustine, M. Mascal, A. J. Moulé, *J. Mater. Chem. C* **2016**, *4*, 3454.
- [48] D. A. Stanfield, Y. Wu, S. H. Tolbert, B. J. Schwartz, *Chem. Mater.* **2021**, *33*, 2343.
- [49] E. C.-K. Wu, C. Z. Salamat, S. H. Tolbert, B. J. Schwartz, *ACS Appl. Mater. Interfaces* **2022**, *14*, 26988.
- [50] D. A. Stanfield, Z. Mehmedović, B. J. Schwartz, *Chem. Mater.* **2021**, *33*, 8489.
- [51] Y. Wu, C. Z. Salamat, A. León Ruiz, A. F. Simafranca, N. Akmanşen-Kalayci, E. C. Wu, E. Doud, Z. Mehmedović, J. R. Lindemuth, M. D. Phan, A. M. Spokoyny, B. J. Schwartz, S. H. Tolbert, *Chem. Mater.* **2024**, *36*, 5552.
- [52] A. L. Ayzner, C. J. Tassone, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2009**, *113*, 20050.
- [53] S. A. Hawks, J. C. Aguirre, L. T. Schelhas, R. J. Thompson, R. C. Huber, A. S. Ferreira, G. Zhang, A. A. Herzing, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2014**, *118*, 17413.
- [54] J. C. Aguirre, S. A. Hawks, A. S. Ferreira, P. Yee, S. Subramaniyan, S. A. Jenekhe, S. H. Tolbert, B. J. Schwartz, *Adv. Energy Mater.* **2015**, *5*, 1402020.
- [55] D. T. Scholes, S. A. Hawks, P. Y. Yee, H. Wu, J. R. Lindemuth, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. Lett.* **2015**, *6*, 4786.
- [56] T. H. Le, A. Nafady, X. Qu, L. L. Martin, A. M. Bond, *Anal. Chem.* **2011**, *83*, 6731.
- [57] Q. M. Duong, D. Garcia Vidales, C. Z. Salamat, S. H. Tolbert, B. J. Schwartz, *Phys. Rev. Appl.* **2024**, *21*, 024006.
- [58] E. C. Wu, D. G. Vidales, C. Z. Salamat, Q. M. Duong, A. León Ruiz, A. D. Ready, Z. Mehmedović, D. A. Stanfield, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2025**, *35*, e07480.
- [59] E. C. Wu, B. J. Schwartz, *J. Chem. Theory Comput.* **2023**, *19*, 6761.
- [60] E. C. Wu, B. J. Schwartz, *J. Chem. Theory Comput.* **2024**, *20*, 10059.
- [61] A. R. Umar, C. Grieco, *J. Chem. Phys.* **2025**, *162*, 054720.
- [62] A. R. Umar, A. L. Dorris, C. Grieco, *Adv. Funct. Mater.* **2024**, *34*, 2407181.

- [63] A. R. Umar, A. L. Dorris, N. B. Kotadiya, N. C. Giebink, G. S. Collier, C. Grieco, *J. Phys. Chem. C* **2023**, *127*, 9498.
- [64] R. Ghosh, C. M. Pochas, F. C. Spano, *J. Phys. Chem. C* **2016**, *120*, 11394.
- [65] P. Walter, M. Ilchen, J. Roeh, W. Ohm, C. B. Zeuthen, U. Klemradt, *Appl. Sci.* **2021**, *11*, 8970.
- [66] H. V. Sureka, A. C. Obermeyer, R. J. Flores, B. D. Olsen, *ACS Appl. Mater. Interfaces* **2019**, *11*, 32354.
- [67] G. Freychet, M. Maret, M. Fernandez-Regulez, R. Tiron, A. Gharbi, C. Nicolet, P. Gergaud, *J. Polym. Sci.* **2020**, *58*, 2041.
- [68] C. Darko, I. Botiz, G. Reiter, D. W. Breiby, J. W. Andreasen, S. V. Roth, D.-M. Smilgies, E. Metwalli, C. M. Papadakis, *Phys. Rev. E* **2009**, *79*, 041802.
- [69] Y. She, J. Lee, B. T. Diroll, B. Lee, S. Aouadi, E. V. Shevchenko, D. Berman, *ACS Omega* **2017**, *2*, 7812.
- [70] D.-M. Smilgies, *J. Polym. Sci.* **2022**, *60*, 1023.
- [71] G. Santoro, S. Yu, In *X-ray Scattering*, IntechOpen, **2017**.
- [72] G. Beaucage, *J. Appl. Crystallogr.* **1995**, *28*, 717.
- [73] S. Lenz, M. Bonini, S. K. Nett, M. C. Lechmann, S. G. J. Emmerling, R. S. Kappes, M. Memesa, A. Timmann, S. V. Roth, J. S. Gutmann, *Eur. Phys. J. Appl. Phys.* **2010**, *51*, 10601.
- [74] X. Yan, M. Xiong, X.-Y. Deng, K.-K. Liu, J.-T. Li, X.-Q. Wang, S. Zhang, N. Prine, Z. Zhang, W. Huang, Y. Wang, J.-Y. Wang, X. Gu, S. K. So, J. Zhu, T. Lei, *Nat. Commun.* **2021**, *12*, 5723.
- [75] J. Rivnay, R. Noriega, R. J. Kline, A. Salleo, M. F. Toney, *Phys. Rev. B* **2011**, *84*, 045203.
- [76] Z. Peng, L. Ye, H. Ade, *Mater. Horiz.* **2022**, *9*, 577.
- [77] X. Jiao, M. Statz, L. Lai, S. Schott, C. Jellett, I. McCulloch, H. Sirringhaus, C. R. McNeill, *J. Phys. Chem. B* **2020**, *124*, 10529.
- [78] R. Warren, P. W. M. Blom, N. Koch, *Appl. Phys. Lett.* **2023**, *122*, 152108.

- [79] S. P. Schießl, X. de Vries, M. Rother, A. Massé, M. Brohmann, P. A. Bobbert, J. Zaumseil, *Phys. Rev. Mater.* **2017**, *1*, 046003.
- [80] K. N. Baustert, J. H. Bombile, M. T. Rahman, A. O. Yusuf, R. Li, A. J. Huckaba, C. Risko, K. R. Graham, *Adv. Mater.* **2024**, *36*, 2313863.
- [81] O. Bubnova, X. Crispin, *Energy Environ. Sci.* **2012**, *5*, 9345.
- [82] M. Schwarze, C. Gaul, R. Scholz, F. Bussolotti, A. Hofacker, K. S. Schellhammer, B. Nell, B. D. Naab, Z. Bao, D. Spoltore, K. Vandewal, J. Widmer, S. Kera, N. Ueno, F. Ortman, K. Leo, *Nat. Mater.* **2019**, *18*, 242.
- [83] B. A. Gregg, S.-G. Chen, R. A. Cormier, *Chem. Mater.* **2004**, *16*, 4586.
- [84] R. Noriega, J. Rivnay, K. Vandewal, F. P. V. Koch, N. Stingelin, P. Smith, M. F. Toney, A. Salleo, *Nat. Mater.* **2013**, *12*, 1038.
- [85] S. Ihnatsenka, X. Crispin, I. V. Zozoulenko, *Phys. Rev. B* **2015**, *92*, 035201.
- [86] Y. Yamashita, J. Tsurumi, T. Kurosawa, K. Ueji, Y. Tsuneda, S. Kohno, H. Kempe, S. Kumagai, T. Okamoto, J. Takeya, S. Watanabe, *Commun. Mater.* **2021**, *2*, 45.

CHAPTER 5

The Role of Microstructural Disorder in the Charge Transport Characteristics of Doped Semiconducting Polymers

Chapter 5 examines how the pristine microstructure of conjugated polymer films influences charge transport after chemical doping. Using P3HT as a model system, this chapter explores how differences in polymer regioregularity, crystallinity, and mesoscale ordering affect carrier mobility and thermoelectric performance. By combining spectroscopic, electrical, and X-ray scattering measurements, this work shows that charge transport in doped semiconducting polymers is governed not only by local molecular order, but also by how ordered domains are connected across longer length scales.

Supporting Information is given in Appendix D.

Abstract

We investigate how the microstructure of poly(3-hexylthiophene-2,5-diyl) (P3HT) governs charge transport and thermoelectric performance following anion-exchange doping. We systematically vary the P3HT regioregularity (RR) from 99% to 97% to 93% to regiorandom (RRa) to tune both the local crystallinity and mesoscale ordering. Grazing-incidence wide-angle X-ray scattering shows that the relative degree of crystallinity of the pristine P3HT materials is largely maintained after doping. Using UV–vis–NIR and ultrafast transient absorption spectroscopies, we show that the more crystalline 99% RR and 97% RR P3HT films have more delocalized polarons and better intradomain charge transport. However, Hall effect and temperature-dependent conductivity measurements show that these materials exhibit lower macroscopic mobility at low doping levels. Small-angle X-ray scattering reveals that this limitation arises from reduced mesoscale connectivity between ordered domains. At higher doping levels, doping-induced changes in domain size in the higher-RR P3HT films lower the activation energy for transport and increase carrier mobility. Despite their reduced mobility at low doping levels, these polymers exhibit more favorable Seebeck coefficient–conductivity relationships and higher power factors across the full doping range. Using the semi-localized transport (SLoT) model, we attribute this enhanced thermoelectric performance to a higher intrinsic conductivity, σ_0 , and a more efficient suppression of localization barriers, $W_{\text{H,slope}}$, with doping.

5.1 Introduction

Organic semiconducting polymers have emerged as promising candidates for thermoelectric (TE) energy conversion due to their solution processability, mechanical flexibility, chemical tunability, and potential for low-cost, large-area device fabrication.^[1–5] In addition to these processing advantages, organic semiconducting polymers exhibit inherently low thermal conductivities (κ)^[6–11] and relatively high Seebeck coefficients (S),^[8,12,13] making them attractive for TE applications.^[6,14–17] TE device performance can be quantified by the dimensionless figure of merit, ZT :^[2,3,5–7]

$$ZT = \frac{\sigma S^2}{\kappa} T, \quad (5.1)$$

where σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity, and T is the absolute temperature. Because the low κ of organic semiconducting polymers is challenging to measure, their TE performance is often described by the power factor (PF), σS^2 , which is the numerator of **Equation (5.1)**.

Despite their relatively low κ and high S values, a persistent challenge for organic semiconducting polymers in thermoelectric applications is their low σ , which is given by $\sigma = ne\mu$, where n is the “free” charge carrier density, μ is the carrier mobility, and e is the elementary charge. As intrinsic wide-bandgap semiconductors, n is near zero in pristine polymer films, and the most widely used strategy to increase n is through chemical doping of organic semiconducting polymers, a process in which a small-molecule dopant removes (for p -type doping) an electron from the polymer backbone via a charge transfer reaction.^[18–25] This charge transfer induces an aromatic-to-quinoidal structural distortion of the polymer backbone, and the positively charged carrier and structural distortion are together known as a polaron.^[26–28] Although chemical doping enhances the

electrical conductivity of conjugated polymers, there is an inverse relationship between n and the Seebeck coefficient S ,^[7,14,17,29–34] therefore, thermoelectric performance is maximized by tuning n and μ to balance the increase in σ with the accompanying decrease in S .

More specifically, increasing μ allows higher electrical conductivity to be achieved at lower n , which helps maintain a larger S and thereby improves the PF. Unfortunately, achieving high μ in doped conjugated polymers remains challenging because charge transport generally relies on hopping, where carriers must overcome energetic barriers to move.^[6,35–38] This hopping process is influenced by both energetic disorder, involving Coulomb interactions between the polarons and dopant counterions,^[39–42] as well as structural disorder, caused by the semicrystalline morphology of most conjugated polymers.^[37,43,44] In semicrystalline polymers, ordered domains generally support efficient charge transport.^[37,45] However, macroscopic transport also requires carriers to move between ordered regions through more disordered amorphous domains, where structural defects and greater energetic disorder can localize carriers and hinder transport. As a result, both short-range intradomain transport and longer-range interdomain connectivity must be considered to optimize the charge transport and thus the TE performance of doped conjugated polymers.

Prior studies have shown that both local crystallinity and longer-range connectivity can strongly influence charge transport in doped conjugated polymers.^[44,46–48] In particular, increased P3HT crystallinity and structural order have often been correlated with higher charge-carrier mobility or conductivity, including in field-effect transistors and doped thermoelectric devices.^[43,44,49–52] Building on this framework, Scholes *et al.*^[44] found that carriers in more doped crystalline, regioregular polymers have larger macroscopic carrier mobilities than those in less crystalline, regiorandom materials. Their work, however, only investigated carrier properties at

moderate doping levels, so the question of how polymer regioregularity, crystallinity and longer-range structural ordering affect carrier transport across doping levels is still less explored.

In previous work, we systematically investigated how different dopants and doping methods influence charge transport in semicrystalline poly(3-hexylthiophene-2,5-diyl) (P3HT) films.^[22,40,41,53] We found that there are two distinct approaches for enhancing carrier transport. First, we showed that the use of large dopants that have weakly interacting counterions can reduce the Coulomb trapping of polarons and lower the activation energy for hopping, thus improving polaron delocalization.^[22,40,41,53] Second, we used anion exchange,^[20] a doping method that can strongly dope the amorphous regions of semicrystalline polymer films, and found that extended mesoscale domain connectivity facilitates longer-range charge delocalization, even with a stronger Coulombic interaction between the polarons and their counterions. Our findings thus showed that the carrier mobility of doped conjugated polymers can be improved both by minimizing local electrostatic interactions and by structurally enhancing the doped polymer's mesoscale connectivity.

One question that has not yet been explored in detail is the role of the initial polymer degree of crystallinity and how crystallinity changes with doping. In this paper, we ask specifically: how do the degree of crystallinity and longer-range connectivity of the pristine polymer structure determine the efficiency with which doping generates mobile carriers and forms mesoscale conductive networks? We address this question using P3HT as a model system, since its initial morphology can be systematically tuned through regioregularity via synthetic approaches.^[54]

In particular, we study four P3HT samples that are 99% regioregular (RR), 97% RR, 93% RR, and regiorandom (RRa), doping all of them to different extents via the anion-exchange method^[20] using the widely used *p*-type dopant 2,3,5,6-tetrafluoro-7,7,8,8-

tetracyanoquinodimethane (F₄TCNQ) and the commonly used electrolyte lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Because anion exchange is a sequential doping approach, it largely preserves the relative degree of the polymer crystallinity while enabling high doping levels.^[20,55] By combining grazing-incidence wide- and small-angle X-ray scattering (GIWAXS and GISAXS) with UV–visible–near IR (NIR), ultrafast transient absorption, Hall effect, temperature-dependent conductivity, and thermoelectric measurements, we separately probe crystal structure, mesoscale ordering, local charge delocalization, macroscopic charge transport, and the S – σ relation across doping levels. We find that the more crystalline 99% RR and 97% RR P3HT samples exhibit more delocalized polarons and more efficient local transport than 93% RR P3HT, but unexpectedly lower macroscopic carrier mobilities at low doping than 93% RR P3HT because of limited longer-range mesoscale connectivity. At intermediate and high doping levels, however, domain connectivity improves in these high-RR polymers, leading to higher macroscopic mobility. Despite their lower low-doping carrier mobility, the more crystalline polymers exhibit more favorable S – σ relations and higher power factors across the full doping range. Analysis with the semi-localized transport (SLoT) model^[56] shows that these behaviors arise from both higher intrinsic conductivity and more efficient suppression of localization effects with doping.

5.2 Results and Discussion

5.2.1 Macroscopic Conductivity and Seebeck Coefficient Measurements in Different

Semicrystalline P3HT Films Doped via Anion Exchange

To examine how both microstructure and macrostructure influence charge transport and the S – σ relation in doped conjugated polymers, we doped P3HT films of varying regioregularity using the anion-exchange method.^[20] Films of 99% RR, 97% RR, 93% RR, and regiorandom

(RRa) P3HT were spin-coated from 2% w/v (20 mg/mL) solutions in *o*-dichlorobenzene (*o*-DCB) and subsequently doped by the sequential-processing (SqP) method using F₄TCNQ^[57–60] as the dopant and LiTFSI as the electrolyte co-dissolved in *n*-butyl acetate (*n*-BA). The F₄TCNQ concentration was systematically varied while the LiTFSI concentration was held fixed at 30 mg/mL, allowing us to study transport behavior as a function of doping level (see the Experimental Section for additional sample fabrication details).

Figure 5.1 plots the electrical conductivity (circles, solid lines) and Seebeck coefficient (triangles, dashed lines) versus the concentration of F₄TCNQ in the anion-exchange doping solution with 30 mg/mL LiTFSI for doped 99% RR, 97% RR, 93% RR, and RRa P3HT films (**Figure 5.1a–d**, respectively); the arrows in each panel point to the corresponding *y*-axis. We chose the dopant concentrations to roughly match the range of electrical conductivities across all four polymers. The most crystalline 99% RR and 97% RR P3HT polymers reached conductivities of $\sim 16 \text{ S cm}^{-1}$ with only 1 mg/mL F₄TCNQ (along with 30 mg/mL LiTFSI), whereas the 93% RR P3HT polymer needed a dopant concentration that was three times higher (3 mg/mL F₄TCNQ along with 30 mg/mL LiTFSI), while amorphous RRa P3HT needed nine times more dopant (9 mg/mL F₄TCNQ with 30 mg/mL LiTFSI) to achieve comparable conductivity values.

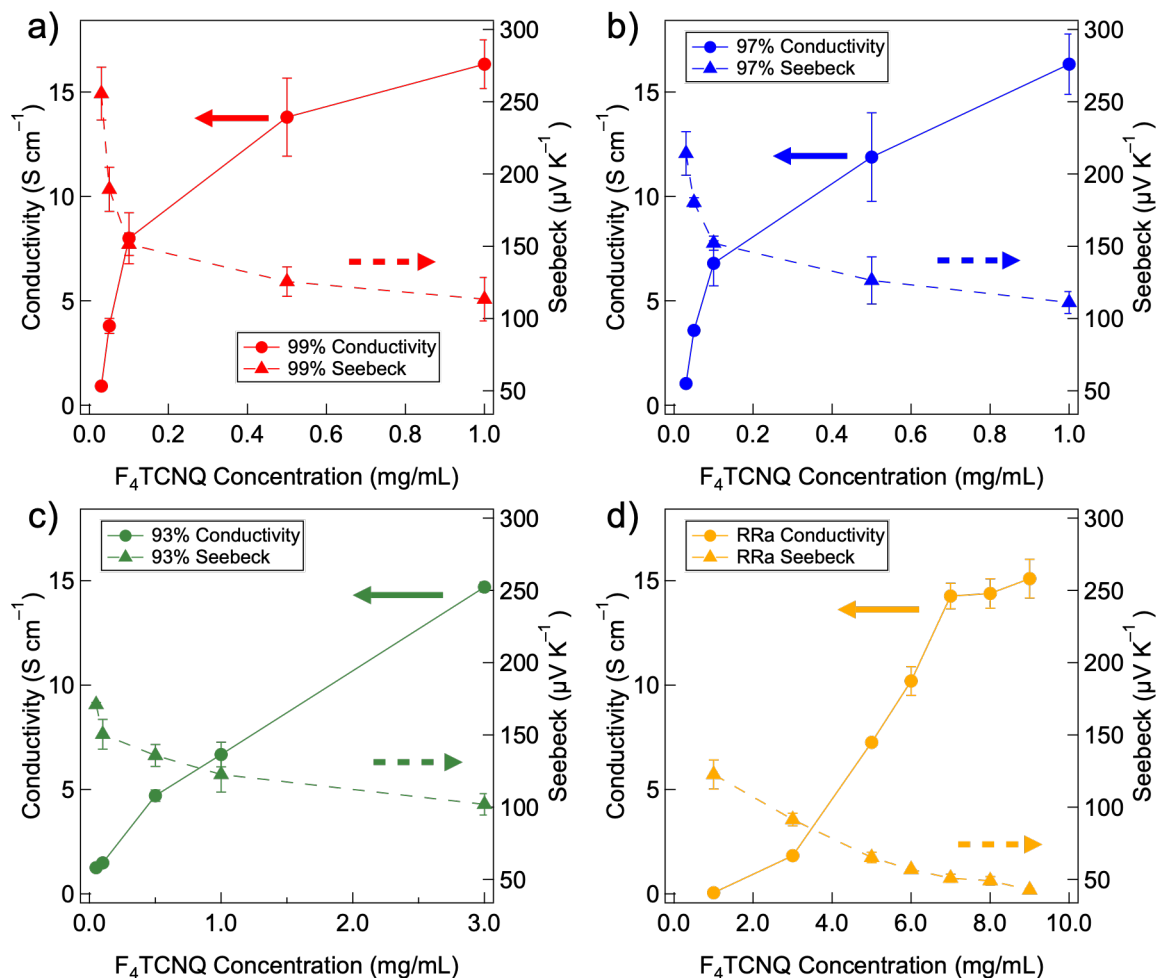


Figure 5.1. Electrical conductivity (left axes) and Seebeck coefficient (right axes) for (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT samples doped via anion exchange with different concentrations of F_4TCNQ along with a constant LiTFSI electrolyte concentration of 30 mg/mL. For all four P3HT polymers, the typical inverse relationship between electrical conductivity and Seebeck coefficient was observed with increasing doping levels. The arrows point toward the appropriate y-axis for each data set. Note that the x-axes have different values as the dopant concentrations were chosen to give a similar range of conductivity values for each material.

Figure 5.1 shows the typical inverse relationship between the electrical conductivity and the Seebeck coefficient with increasing doping level for all four P3HT polymers. The 99% RR and 97% RR P3HT polymers (**Figure 5.1a,b**) show a more pronounced drop in S with increasing doping compared to the less semicrystalline, 93% RR and regiorandom P3HT materials (**Figure 5.1c,d**). This behavior is consistent with a more ordered microstructure in the higher-RR polymers

that enhances interchain electronic coupling and reduces energetic disorder, leading to a narrower density of states near the Fermi level.^[37,61–64] In organic semiconductor systems with a narrower density of states near the Fermi level due to stronger π – π coupling, the mobility edge is sharper, making S more sensitive to shifts in the Fermi level and causing it to more rapidly decrease as doping increases for higher-RR P3HT.^[62,64] Importantly, despite this stronger decline with increased doping, the more crystalline P3HT polymers maintain higher Seebeck coefficients across the entire doping range. Although these trends in conductivity and Seebeck coefficient indicate that varying the P3HT regioregularity directly impacts thermoelectric performance, they do not directly provide information on how morphology influences charge transport in these different P3HT polymers, which we turn to in the next section.

5.2.2 Probing Film Morphology of Semicrystalline P3HT Films

5.2.2.1 Investigating the Microstructure of Different P3HT Films Using Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS)

To understand how microstructure—i.e., intradomain order within crystallites—influences charge transport across different P3HT regioregularities, we performed grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements on both pristine and anion-exchange-doped P3HT films. **Figure 5.2** shows out-of-plane and in-plane integrated GIWAXS patterns for the four different pristine P3HT films with varying regioregularity (**Figure 5.2a,b**) and their corresponding most-doped samples: 99% RR P3HT (1 mg/mL F₄TCNQ + 30 mg/mL LiTFSI), 97% RR P3HT (1 mg/mL F₄TCNQ + 30 mg/mL LiTFSI), 93% RR P3HT (3 mg/mL F₄TCNQ + 30 mg/mL LiTFSI), and RRa P3HT (9 mg/mL F₄TCNQ + 30 mg/mL LiTFSI) (**Figure 5.2c,d**).

As expected, the pristine, semicrystalline regioregular polymers (99% RR, 97% RR, and 93% RR P3HT) exhibit a pronounced edge-on texture, evidenced by sharp lamellar (100) peaks at

a q -spacing of $\sim 0.39 \text{ \AA}^{-1}$ in the out-of-plane direction and π - π stacking (020) peaks at a q -spacing of $\sim 1.65 \text{ \AA}^{-1}$ in the in-plane direction.^[65–68] Higher-order ($h00$) overtones, shown in the inset, appear at positions consistent with the known lamellar spacing of P3HT.^[65–68] The nearly identical (100) and (020) q -spacing values across the regioregular pristine P3HT polymers indicate that the unit-cell geometry of RR P3HT is conserved independent of the degree of regioregularity. In contrast, amorphous RRa P3HT lacks distinct lamellar features and displays only a broad scattering peak at a q -spacing of $\sim 1.4 \text{ \AA}^{-1}$, which has been previously associated with scattering of poorly ordered, partially π -stacked regions.^[40,69]

Although the crystal-packing motif of the regioregular P3HT polymers is the same, their relative degrees of crystallinity and texture differ significantly. The relative crystallinity can be quantified by integration of the thickness-normalized (100) peak area, which shows that the higher the %RR, the greater the degree of crystallinity, with RRa P3HT being essentially completely amorphous. **Table 5.1** reports the integrated (100) areas for the different pristine and most-doped P3HT films normalized to the area of the corresponding 99% RR sample. Similarly, the fraction of edge-on-oriented crystallites (texture), quantified by the ratio of the out-of-plane (100) intensity relative to that in the in-plane direction, follows the same order with %RR (see Appendix D **Figure D3** for texture analysis).^[44,65–68] Because charge transport in conjugated polymer films benefits from ordered domains and is morphology-dependent, differences in crystallinity and texture are expected to influence how efficiently carriers move through the film and, ultimately, their thermoelectric performance.^[44,46,70]

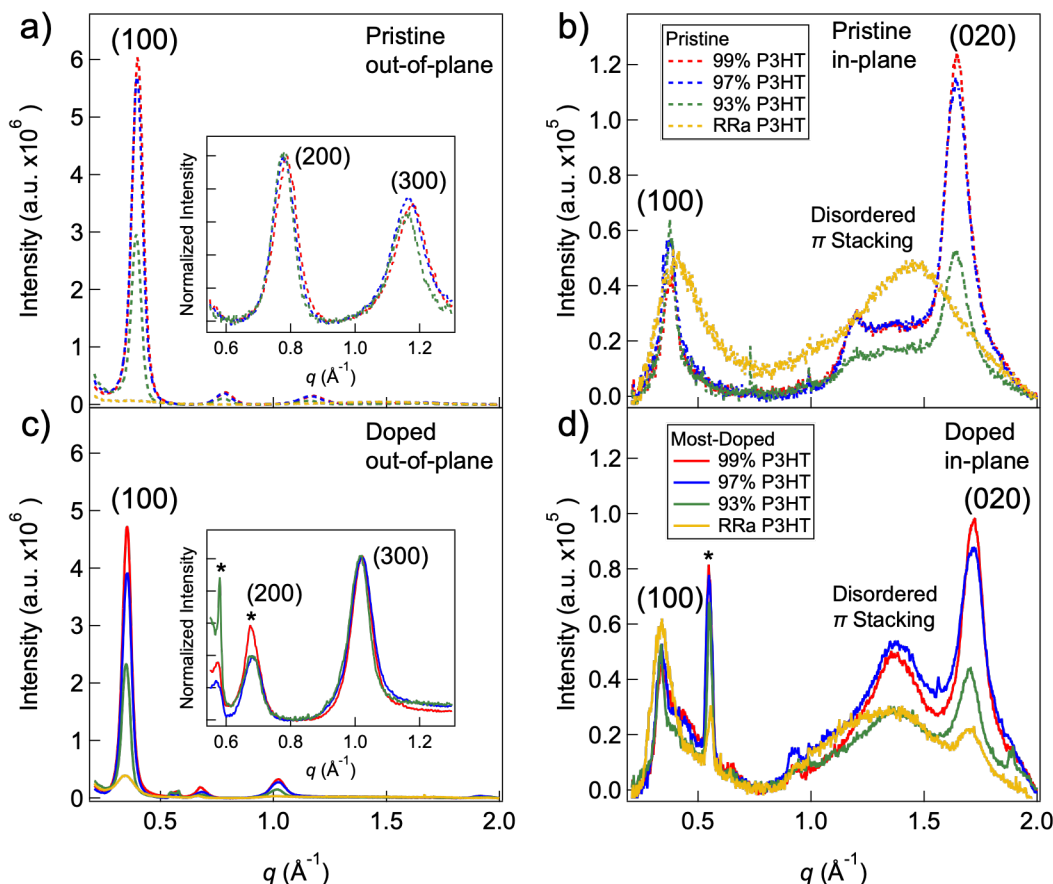


Figure 5.2. Out-of-plane (a) and in-plane (b) GIWAXS integrations for pristine P3HT samples (dashed curves): 99% RR P3HT (red), 97% RR P3HT (blue), 93% RR P3HT (green), and RRa P3HT (yellow). Out-of-plane (c) and in-plane (d) GIWAXS integrations for the highest anion-exchange-doped samples for each P3HT regioregularity are shown as solid curves, with the same colors as in (a) and (b). Insets in the out-of-plane panels show the lamellar overtones normalized to the height of the (200) peak for pristine samples and the (300) peak for doped samples. Peaks labeled with an asterisk (*) in the doped P3HT films are due to scattering from excess LiTFSI.

Upon anion-exchange doping, the ($h00$) peaks of the regioregular P3HT polymers shift to lower q -spacing values, reflecting an expansion of the lamellar spacing consistent with the intercalation of the TFSI⁻ counterions into the lamellar region of the crystallites (**Figure 5.2c**).^[20,33,47,48,53,55] Simultaneously, the π - π stacking (020) peaks shift to higher q -spacing, indicating a change in tilt of the unit cell (**Figure 5.2d**).^[20,33,47,48,55,68] These shifts in q -spacing in the (100) and (020) are observed across all the different doping levels for all P3HT polymers (see **Figures D1 and D2** in Appendix D). In the RRa P3HT film, doping creates distinct (100) and

(020) peaks from the originally amorphous pristine material, signifying doping-induced crystallization.^[40,69] All of the doped films have nearly identical (100) and (020) peak positions, confirming that all four of the doped P3HT polymers share the same crystal packing after the anion-exchange doping process. However, we note that similar *d*-spacings do not necessarily imply identical microstructural order, as variations in crystallinity, edge-on fraction, and other local disorder may still be present. For example, the relative trends of crystallinity (**Table 5.1**) and texture (**Figure D3**) observed in the pristine polymers persist in the doped structures, with doped 99% RR P3HT being the most crystalline and having the largest edge-on crystallite fraction, followed by doped 97% RR and 93% RR P3HT, and finally doped RRa P3HT.

The inset in **Figure 5.2c** shows the (*h*00) lamellar scattering overtones of the doped RR polymers normalized to the intensity of the (300) peak. Previous studies have shown that the introduction of counterions modifies the electron-density distribution within the lamellae and alters the envelope function governing the lamellar scattering, leading to suppression of some of the higher-order lamellar overtones.^[47,55,71] Thus, such suppression provides information about the positions of the counterions within the polymer lattice. Here, we observe that the most-doped RR P3HT films all show a similar suppression of the (200) peak relative to the (300) overtone. This similarity suggests that the TFSI[−] counterions occupy comparable positions within the crystalline lamellae of all four P3HT polymers. This suggests that the Coulomb interactions between polarons and their counterions should be comparable across the samples, so that using different P3HT regioregularities allows us to isolate the effects of polymer crystallinity on charge transport. We note that the (200)-to-(300) peak ratio is hard to discern in the highest-doped RRa sample (and also the 99% RR sample) because of overlapping scattering from excess LiTFSI, labeled with an

asterisk (*). However, a similar suppression of the (200) peak is evident in lower-doped samples, as shown in Appendix D **Figure D1**.

5.2.2.2 Probing Longer-Range Structural Differences of Pristine and Anion-Exchange-Doped P3HT Polymers via Grazing-Incidence Small-Angle X-ray Scattering (GISAXS)

Although GIWAXS allows us to study the local structure within the crystallites of the different pristine and doped P3HT polymers, it does not capture how these ordered domains are organized on longer (mesoscale) length scales. Here, we argue that this type of information is critical for understanding how both micro- and mesoscale structure collectively determine charge transport in doped conjugated polymers.^[47,53,71] To probe longer-range morphology in our samples, we performed grazing-incidence small-angle X-ray scattering (GISAXS).^[53,72–76] We then fit the radial integrations to the Unified fit model^[77,78] to extract the radius of gyration, R_g (see **Figures D4 and D5** in Appendix D for GISAXS integrations and Unified fits). Because features in GISAXS data arise from electron-density differences between different domains in the film (e.g., crystalline and amorphous regions), R_g can be interpreted as an effective domain size.^[77,78]

In previous work, we demonstrated that for anion-exchange-doped P3HT films, the change in a pristine film's R_g upon doping, denoted as ΔR_g , correlates with the thermoelectric properties of doped P3HT films: positive values of ΔR_g , which indicate the doping-induced formation of larger, more connected domains, were associated with higher carrier mobilities and improved Seebeck coefficient–conductivity relationships and vice versa.^[53] Here, we examine the role of the initial polymer crystallinity in anion-exchange-doping-induced long-range ordering effects.

Table 5.1. Relative integrated GIWAXS (100) peak areas representing the relative crystallinity of pristine and most-doped 99% RR, 97% RR, 93% RR, and RRa P3HT samples, normalized to the corresponding 99% RR P3HT sample. The most-doped samples were prepared using 1, 1, 3, and 9 mg/mL F₄TCNQ, respectively, with 30 mg/mL LiTFSI. Also shown are the effective domain sizes, R_g , from GISAXS measurements for these same samples, as well as key SLoT parameters (σ_0 and $W_{H,slope}$), obtained from the fits shown in **Figure 5.5**.

	99% RR P3HT	97% RR P3HT	93% RR P3HT	RRa P3HT
Pristine Relative Crystallinity	1	0.93	0.44	0.04
Doped Relative Crystallinity	1	0.81	0.46	0.12
Pristine R_g (Å)	75	80	137	342
Most-Doped R_g (Å)	104	101	105	58
σ_0 (S cm ⁻¹)	140	120	70	10
$W_{H,slope}$ (meV)	425	350	265	125

Table 5.1 summarizes the R_g values of the different pristine and most-doped P3HT samples. In the pristine state, the more crystalline 99% and 97% RR P3HT films exhibit smaller R_g values than the less-ordered 93% RR and amorphous RRa P3HT samples. The smaller R_g values observed in the more crystalline polymers reflect an electron-density contrast between well-defined crystallites and their more amorphous surroundings (see **Figure D4** in Appendix D). In contrast, 93% RR P3HT exhibits weaker electron-density contrast between its more crystalline and more amorphous regions. This suggests that structural defects and reduced crystallinity lead to less well-defined domains, allowing partially ordered regions to blend more gradually into the surrounding amorphous matrix, resulting in larger effective domain sizes (larger R_g). In the case of RRa P3HT, the lack of any distinctive electron-density contrast due to the isotropic, amorphous morphology results in a very large R_g value.

Table 5.1 also shows that R_g values of the different P3HT polymers change upon doping. For the two most crystalline polymers, 99% RR and 97% RR P3HT, R_g increases upon doping and plateaus near ~ 100 Å. In contrast, the less semicrystalline 93% RR P3HT exhibits a decrease in R_g

upon doping, also converging to ~ 100 Å, while the initially amorphous RRa P3HT shows a significant decrease from ~ 340 to ~ 60 Å. These distinct R_g responses can be understood in terms of the fact that anion-exchange doping provides sufficient oxidative strength to dope originally amorphous domains and induce crystallization,^[40,53,69,71] as evidenced here by the appearance of new crystalline scattering peaks in doped RRa P3HT in **Figure 5.2c,d**. In the more crystalline 99% RR and 97% RR P3HT samples, this doping-induced crystallization of amorphous regions creates new ordered connections between previously separated crystallites, thus increasing R_g . In contrast, the R_g of 93% RR P3HT decreases gradually with increasing dopant concentration, suggesting that crystallization of the amorphous surroundings proceeds slowly until it reaches a domain size similar to that of the 99% and 97% RR P3HT samples. Finally, in originally amorphous RRa P3HT, doping induces crystallization, generating numerous small, isolated doped crystallites.^[40,69] These domains produce strong local electron-density contrast with limited spatial correlation, leading to a pronounced reduction of R_g .

In Section 5.2.4 below, we tie this evolution of the mesoscale organization directly to macroscopic charge transport characteristics of the doped polymer films measured via the Hall effect and temperature-dependent conductivity.

5.2.3 Probing the Microscale Charge-Transport Characteristics of Anion-Exchange-Doped P3HT with Different Regioregularities

5.2.3.1 Optical Properties of Pristine P3HT Films via UV–Vis–NIR Spectroscopy

Having established the structural differences among the four polymers using GIWAXS and GISAXS, we next examine their optical properties using UV–vis–NIR spectroscopy. **Figure 5.3a** shows the normalized absorption spectra of the pristine P3HT films. The more regioregular polymers exhibit increasingly pronounced vibronic structure in the bandgap (BG) absorption

(black arrow in **Figure 5.3a** inset). This makes sense within the theoretical framework developed by Spano and co-workers,^[79,80] who showed that P3HT films with greater structural order exhibit stronger H - J aggregate coupling and thus sharper vibronic features, whereas disordered films display broadened spectra with diminished vibronic structure.^[44,81–83] In addition, the main π - π^* absorption band shifts progressively to lower energy with increasing regioregularity, with 99% RR and 97% RR P3HT exhibiting the most red-shifted bandgap transitions, followed by 93% RR and RRa P3HT. This observation is consistent with the idea that more-ordered polymers have more delocalized excitons. Both the spectral shifts and vibronic structure are consistent with the crystallinity differences identified by GIWAXS above.

5.2.3.2 P1 Peak Position of Doped P3HT Films Probes Local Polaron Localization Effects

In addition to changes in the excitonic absorption of pristine P3HT with polymer structure, it is well established that polarons on doped polymers become increasingly delocalized as the degree of crystallinity increases.^[44,84] To probe how polymer crystallinity influences electronic structure, we measured the UV–vis–NIR spectra of the four P3HT polymers across a range of doping concentrations (full spectra are shown in **Figure D6** in Appendix D).

All four doped P3HT films exhibit the characteristic spectroscopic signatures of polaron formation, including the growth of the P1 (~ 0.4 – 0.5 eV) and P2 (~ 1.2 – 1.6 eV) absorption bands and the bleaching of the neutral polymer bandgap transition (~ 2.3 – 3.3 eV) as the dopant concentration increases (see **Figure D6** in Appendix D). These features arise from optical transitions involving the partially occupied polaronic mid-gap state, as illustrated in the energy-level diagram in **Figure 5.3a** inset (blue arrow for P1 and red arrow for P2).^[22,28,41,44,85,86] Furthermore, the absence of absorption features from the F₄TCNQ anion that would appear near ~ 1.5 eV and ~ 3.0 eV confirms that anion exchange was successful in all doped films.^[20,55,87–89]

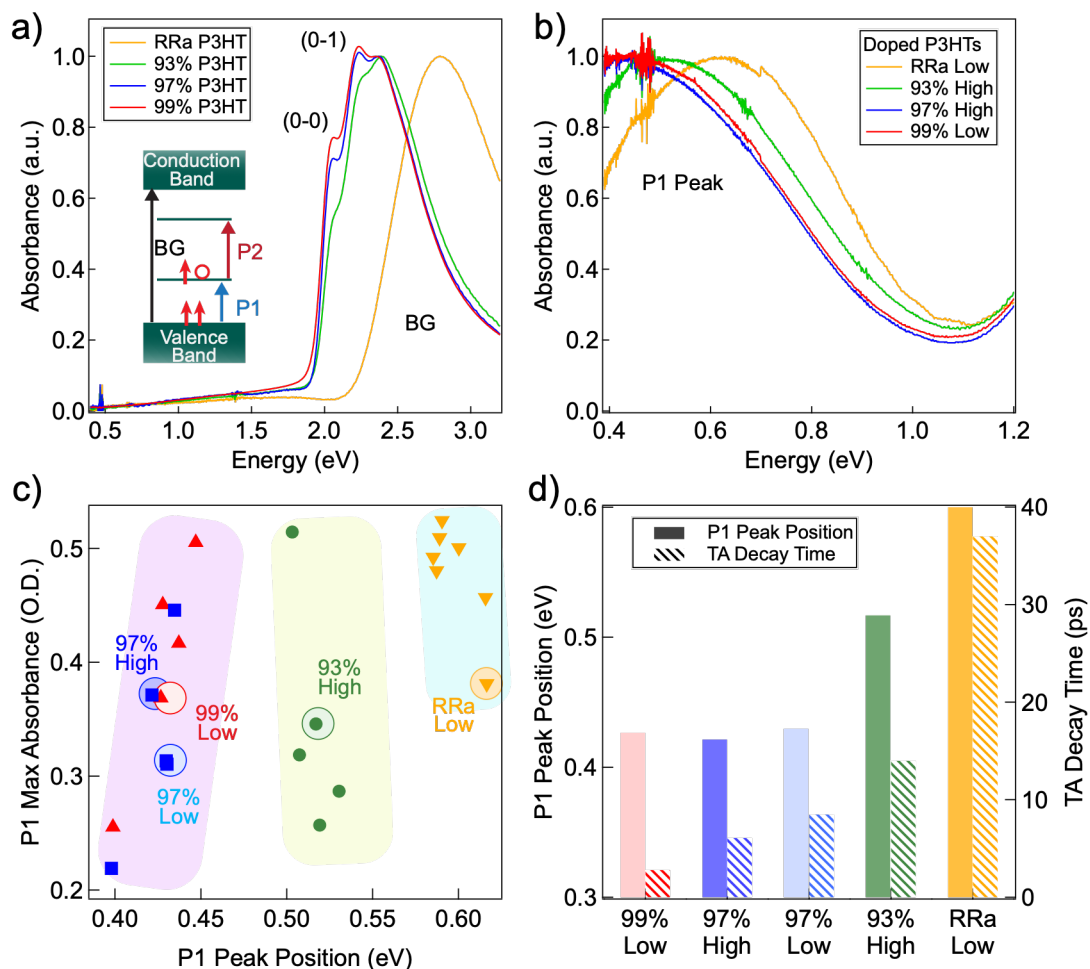


Figure 5.3. (a) UV-vis-NIR spectra of pristine P3HT films with different regioregularities (99% RR, 97% RR, 93% RR, and RRa P3HT). Inset: Energy-level diagram showing the bandgap (BG) and polaronic transitions of doped conjugated polymers. Exciting the P1 transition leads to an increase in P2 absorption. (b) Normalized P1 absorption region of anion-exchange-doped P3HT films for representative samples (99% RR Low, 97% RR High, 93% RR High, and RRa Low) doped using different F_4TCNQ concentrations (0.05, 0.5, 1, and 1 mg/mL, respectively) while maintaining a constant LiTFSI electrolyte concentration of 30 mg/mL. These doping conditions were chosen to match carrier densities in the different samples (see **Figure D6**). (c) P1 peak energy versus maximum P1 absorption intensity, obtained by Gaussian fitting (see **Figure D8** in Appendix D), for all four P3HT polymers for different doping concentrations (see **Figure D6**). Circles indicate the samples selected for ultrafast transient (TA) absorption measurements. Colored blocks are used as visual guides for polymers with different regioregularities. (d) Slower induced P2 decay times extracted from TA measurements for the circled samples in **Figure 5.3c** (dashed bars), plotted alongside their corresponding steady-state P1 peak positions (solid bars). The TA decay times, which are a measure of the local carrier mobility, follow the same trend as the P1 peak positions, with doped 99% RR and 97% RR P3HT samples exhibiting faster decay dynamics than 93% RR and RRa P3HT.

Figure 5.3b shows the normalized P1 absorption spectra for four representative doped P3HT samples, labeled as 99% Low (0.05 mg/mL F₄TCNQ with 30 mg/mL LiTFSI), 97% High (0.5 mg/mL F₄TCNQ with 30 mg/mL LiTFSI), 93% High (1 mg/mL F₄TCNQ with 30 mg/mL LiTFSI), and RRa Low (1 mg/mL F₄TCNQ with 30 mg/mL LiTFSI). We selected these samples because of their similar doping levels, as indicated by their comparable P1 absorption intensities and confirmed by Hall effect measurements, discussed below. These spectra thus allow differences in the P1 peak position to be compared without complications arising from variations in carrier concentration. A clear systematic red shift of the P1 transition is observed with increasing polymer regioregularity. Within the framework developed by Spano and co-workers,^[85,90] the energetic position of the P1 transition directly reflects the spatial extent of the polaron wavefunction: more delocalized polarons exhibit red-shifted P1 transitions, whereas localized polarons display blue-shifted P1 peaks. This indicates that the doped samples with higher regioregularity have a higher degree of carrier delocalization at this doping level.

To quantify the trends in the P1 peak positions across doping levels, we fit the P1 peaks with Gaussian functions to extract both their maximum optical densities and peak positions (see **Figures D6 and D8** in Appendix D). The extracted optical densities are plotted against the peak energies in **Figure 5.3c**. Across the entire doping range investigated here, the more crystalline 99% RR and 97% RR P3HT films consistently exhibit lower-energy (red-shifted) P1 transitions than the less ordered 93% RR and RRa P3HT polymers. This indicates that polarons are more delocalized in the more crystalline materials regardless of the doping level. The similarity in P1 energies between the 99% RR and 97% RR samples suggests that increasing regioregularity beyond ~97% RR provides little additional enhancement in local polaron delocalization, whereas the increase from 93% RR to 97% RR produces a much larger change.

Because our GIWAXS analysis showed that all four doped P3HT samples possess similar crystalline packing and counterion positions (Section 5.2.2.1), the Coulomb interactions between polarons and counterions are expected to be comparable across the regioregularity series. The observed P1 shifts, therefore, reflect differences in polymer microstructure rather than variations in dopant–polymer electrostatic interactions governing polaron localization. Thus, **Figure 5.3c** demonstrates that increasing polymer regioregularity, and the associated increase in crystallinity, directly enhances local polaron delocalization.

Interestingly, the evolution of the P1 peak with increasing doping level differs between the polymers. The more crystalline 99% RR and 97% RR P3HT samples exhibit a slight blue shift of the P1 transition at higher optical densities, whereas the less ordered 93% RR and RRa P3HT polymers show a gradual red shift (see **Figure D7** for the normalized P1 peaks). Because the P1 energy reflects the spatial extent of the polaron delocalization,^[22,28,41,44,85,86] these trends indicate that increasing the doping level modifies the local polaron environment differently in initially ordered and disordered films. In the more crystalline polymers, the slight blue shift in P1 suggests that increasing the doping level does not further increase local polaron delocalization and may instead modestly perturb the local electronic environment of the polarons. In contrast, in the more disordered polymers, the gradual red shift suggests that increasing doping produces a modest increase in the local polaron delocalization, potentially through doping-induced ordering within initially disordered regions.^[40,69] Notably, as the doping level increases, the P1 energies of the different regioregular polymers begin to converge, suggesting that the local electronic environments of the polarons become increasingly similar at higher doping levels.

5.2.3.3 Probing Local Carrier Delocalization via Transient Absorption (TA) Spectroscopy

Although P1 peak position reveals insights about the localization effects hindering polaron delocalization, it is not clear how precisely to correlate polaron delocalization with the local carrier mobility. The local mobility of polarons, however, can be indirectly revealed using ultrafast transient absorption (TA) spectroscopy.^[26,27,91–94] Excitation of the P1 transition creates a transient absorption feature of P2 (**Figure 5.3a** inset),^[95,96] and the kinetics of the induced P2 decay are different for free and more trapped carriers.^[26,27,91] We pumped different doped polymer samples at multiple wavelengths spanning the P1 transition and then recorded the dynamics of the resulting induced P2 TA; details are given in the Transient Absorption Spectroscopy section in the Supporting Information. Singular value decomposition (SVD) allows deconvolution of the induced P2 TA signals into a fast (≤ 1 ps) component, which results from the rapid relaxation of newly created “hot” polarons, and a slower (1–10 ps) component, which arises due to the migration of trapped polarons back to their original equilibrium positions.^[26,27,91] It is worth noting that this slower TA process probes carrier dynamics over short length scales within local domains (i.e., within or between neighboring chains inside a crystallite),^[26,27,91] similar to short-range transport probed by terahertz conductivity measurements,^[97,98] rather than macroscopic longer-range transport across multiple domains. Thus, the relaxation rate of the slow component in the TA signals provides direct information about the polarons’ local delocalization.^[26,27,91]

We chose to focus our TA measurements on the four representative samples shown in **Figure 5.3b**, plus an additional 97% RR sample doped at a lower carrier density (97% Low; 0.1 mg/mL F₄TCNQ with 30 mg/mL LiTFSI) than the 97% High sample, as labeled in **Figure 5.3c**. The matched-carrier-density samples from **Figure 5.3b** allow us to explore the role of crystallinity

from samples that all have the same carrier concentration, while the additional 97% RR Low sample provides a way to explore the effects of carrier density at fixed crystallinity.

The SVD-extracted slow-component decay times for the different doped P3HT samples are plotted in **Figure 5.3d**, while the corresponding TA traces are shown in **Figure D9**. The extracted decay times reveal a clear dependence on polymer regioregularity. The 99% Low sample exhibits the fastest decay, followed by 97% High and then 97% Low; 93% High and RRa Low show the slowest decay dynamics. Faster decay times reflect more rapid carrier transport, indicating that increased local crystallinity leads to improved local carrier mobility.^[26,27,91–94] The more doped 97% High sample also exhibits a faster decay than 97% Low, indicating that the local carrier mobility and delocalization increase with doping level at fixed crystallinity.^[56] Notably, the trends in TA decay time seen in **Figure 5.3d** closely follow the P1 peak positions shown in **Figure 5.3c**: the more crystalline samples exhibit red-shifted P1 absorption and faster decay dynamics, whereas the less ordered samples show blue-shifted P1 and slower decays regardless of doping level. Because the TA slow-component decay directly reflects the local carrier mobility, this correlation demonstrates that the P1 peak position probes both the degree of local polaron delocalization and the associated short-range carrier mobility.

This correlation between TA decay time and P1 peak position in **Figure 5.3d** serves to clarify previous reports in which the P1 peak position did not appear to directly correlate with counterion size or macroscopic carrier mobilities measured via the Hall effect or other methods.^[22,47,71,99] Our TA measurements thus indicate that there is an important distinction between local and more macroscopic mobilities in doped conjugated polymers: P1 (and ultrafast TA) probes the local carrier delocalization and mobility but does not see barriers on longer length

scales, such as grain boundaries, that can affect Hall measurements where the electrodes are a macroscopic distance apart. We elaborate on this idea in the following sections.

5.2.4 Macroscopic Length-Scale Charge Transport – Hall and Activation Energy of Anion-Exchange-Doped P3HT

5.2.4.1 Probing Macroscopic Mobility via Hall Effect Measurements

Having established how polymer crystallinity influences local carrier delocalization and mobility within crystallites using GIWAXS, UV–vis–NIR, and TA spectroscopy (**Figures 5.2 and 5.3**), we next examine macroscopic charge transport in our doped P3HT films. In contrast to the spectroscopic probes discussed above, electrical conductivity and Seebeck measurements (**Figure 5.1**) reflect carrier motion on macroscopic length scales across many crystallites and grain boundaries. To understand how the polymer structure influences macroscopic transport, we obtain the carrier mobility, μ , and carrier density, n , of the doped P3HT films via Hall effect measurements.

We were able to obtain reliable Hall signals for all of the doped regioregular P3HT samples. In contrast, the doped RRa P3HT films exhibited unphysical Hall responses, consistent with doped semiconducting polymer systems in which a substantial hopping transport contribution can partially compensate the measured Hall voltages.^[100] For these samples, we estimated the carrier density by integrating the oscillator-strength-weighted P1 absorption^[101,102] and calibrating this value against the Hall-measured carrier densities of the regioregular polymers (see **Figures D10–D13** in the Hall Effect Measurements and P1-Correlated Carrier Density section of Appendix D for a detailed discussion). Once the carrier density was measured by Hall or determined by integrating the P1 peak area, the carrier mobility in our doped P3HT samples was then obtained from the measured four-point-probe conductivity using $\sigma = ne\mu$.

Figure 5.4a shows μ as a function of n for the four different doped P3HT polymers. As expected, carrier mobility increases with carrier density for all doped samples.^[56] Similar trends are observed with increasing dopant concentration in **Figure D10**. The RR P3HT polymers exhibit higher mobilities than RRa P3HT, consistent with the stronger polaron localization and slower TA decay dynamics observed for the initially more amorphous polymer. Interestingly, however, the order of the macroscopic carrier mobility for the doped RR polymers depends on carrier density. In the low-doping regime (blue shaded region), 93% RR P3HT exhibits the highest carrier mobility. At intermediate carrier densities ($\sim 4.2 \times 10^{20} \text{ cm}^{-3}$), this ordering reverses, and the carrier mobilities of the doped 99% RR and 97% RR P3HT samples surpass that of the 93% RR polymer.

This inversion of the macroscopic mobility contrasts with the microscopic trends revealed by the spectroscopic probes in **Figure 5.3**. Both the P1 peak positions and TA decay dynamics showed that the more crystalline 99% RR and 97% RR P3HT samples have greater local carrier mobility than the 93% RR polymer across all doping levels. Thus, the origin of the macroscopic mobility reversal must arise from structural effects occurring on larger length scales than those probed spectroscopically and locally, such as transport across the grain boundaries separating neighboring domains.

To understand the structural origin of the macroscopic mobility trends observed in **Figure 5.4a**, we return to the mesoscale structural information obtained from GISAXS. As discussed above in Section 5.2.2.2, the different P3HT polymers exhibit different mesoscale domain correlations characterized by the radius of gyration (R_g). **Figure 5.4b** plots the extracted R_g values as a function of carrier density for the doped P3HT films. Interestingly, the evolution of mesoscale ordering follows a similar trend as the macroscopic carrier mobility. At low doping levels, the 93% RR P3HT films exhibit larger mesoscale correlation lengths (R_g), suggesting more extended

structural organization. Such morphology may facilitate carrier transport between neighboring domains, enabling higher macroscopic mobility despite the lower overall crystallinity of this polymer. In contrast, the more crystalline 99% RR and 97% RR P3HT polymers initially exhibit smaller mesoscale correlation lengths, which indicates the presence of additional barriers in interdomain transport. The strong correlation between R_g and macroscopic carrier mobility suggests that mesoscale connectivity has an important influence on long-range charge transport.

As the carrier density increases, anion-exchange doping promotes crystallization of the surrounding amorphous regions, increasing the mesoscale connectivity of the more crystalline polymers. As a result, the R_g values of the three RR polymers converge at higher carrier densities. Once the mesoscale connectivity becomes comparable across the polymers, the intrinsic microscopic advantage of higher crystallinity and greater polaron delocalization in the 99% and 97% RR samples dominates the carrier mobility, leading to the observed mobility inversion. In contrast, doped RRa P3HT exhibits both weak microscopic ordering and poor mesoscale connectivity, resulting in consistently low carrier mobilities.

The mobility inversion, therefore, highlights the importance of mesoscale connectivity in determining macroscopic charge transport in doped conjugated polymers. Although microscopic crystallinity governs the intrinsic carrier mobility within individual domains, the mesoscale arrangement and connectivity of these domains ultimately determine the efficiency of long-range macroscopic charge transport across the film.

5.2.4.2 Probing Macroscopic Activation Energy in Anion-Exchange-Doped P3HT Polymers

To further understand the doping-level-dependent trends in the macroscopic carrier mobility for the different P3HT samples, we extracted the activation energy (E_a) for carrier transport from temperature-dependent conductivity measurements. In doped semiconducting

polymers, charge transport proceeds via thermally activated hopping over barriers between localized sites;^[6,35–38] thus, E_a is determined from the slope of a $\ln(\sigma(T))$ versus $(k_B T)^{-1}$ plot (see **Figure D15** in Appendix D). **Figure 5.4c** shows the extracted E_a values as a function of n for the different doped P3HT films. As expected, E_a decreases with increasing n for all samples, reflecting enhanced overlap between dopant-induced potential wells as the doping level increases.^[56]

More importantly, the E_a trends follow behavior similar to the mesoscale ordering and macroscopic mobility results discussed above. At low doping levels (blue-shaded region), the 93% RR P3HT samples exhibit lower E_a values than the 99% RR and 97% RR P3HT films. This observation suggests that the more extended mesoscale correlations in the 93% RR polymer, reflected in its larger R_g values, facilitate carrier transport between neighboring domains and thus lower activation energies when the carrier density is low. In contrast, the smaller R_g values observed in the more crystalline 99% RR and 97% RR P3HT polymers indicate more sharply defined structural boundaries between ordered regions, which likely increase the activation energy for carriers moving between domains.

As the carrier density increases to $\sim 4.2 \times 10^{20} \text{ cm}^{-3}$, the E_a values of the three regioregular polymers converge, consistent with the mobility inversion observed in **Figure 5.4a** and the convergence of R_g in **Figure 5.4b**. These converging trends suggest that the activation energies associated with transport between crystalline domains become comparable across the RR polymers at higher carrier densities. Once these mesoscale barriers no longer limit transport in the more crystalline samples, the intrinsic advantage of greater polaron delocalization in the 99% RR and 97% RR P3HT polymers becomes apparent, resulting in higher macroscopic mobility.

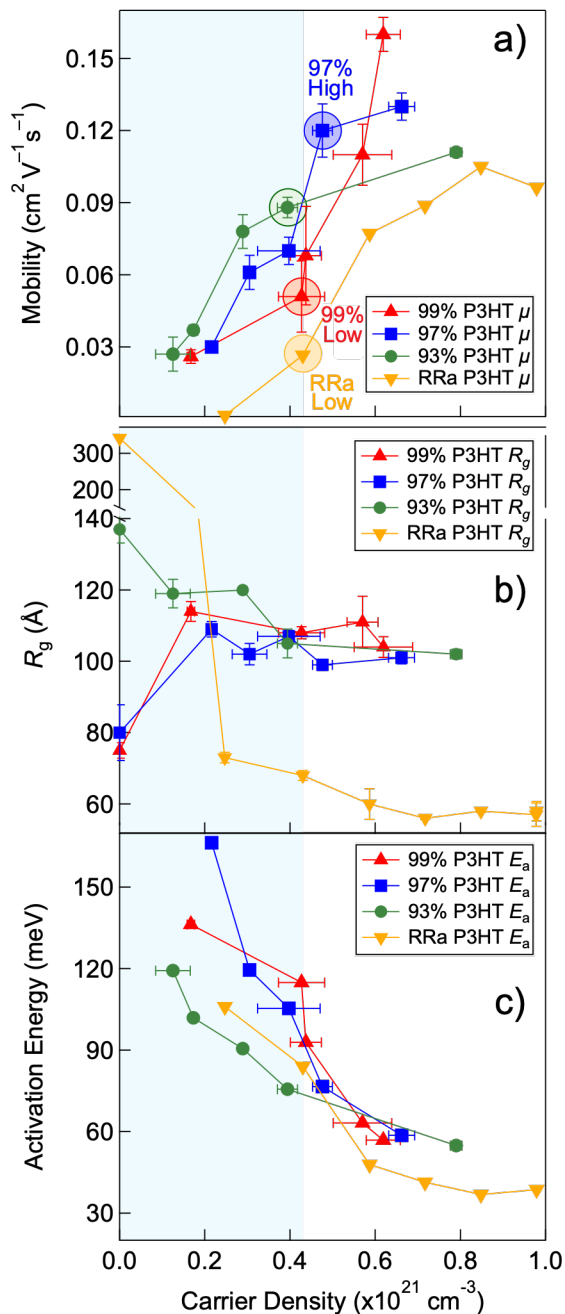


Figure 5.4. (a) Relation between carrier mobility and carrier density for the four different doped P3HT samples. Carrier mobility and density values for the 99% RR P3HT (red), 97% RR P3HT (blue), and 93% RR P3HT (green) samples were measured via Hall effect measurements. For RRa P3HT (yellow), carrier density was estimated from the oscillator-strength-weighted P1 peak area (calibrated using the 97% RR and 93% RR P3HT samples; see **Figure D12** in Appendix D). The circled data points correspond to the same samples whose P1 peaks and TA dynamics are highlighted in **Figure 5.3c,d**. (b) Radius of gyration, R_g , obtained from GISAXS (see Appendix D), as a function of carrier density for pristine and doped P3HT films with different regioregularities. The fact that the RR samples' mobility inverts between the blue and white regions corresponds directly to when the R_g values of the different samples become similar. (c) Activation energy (E_a) as a function of carrier density for the different doped P3HT samples. E_a values were

obtained as the slope of Arrhenius fits to the temperature-dependent conductivity versus $(k_B T)^{-1}$, shown in **Figure D15** in Appendix D.

Interestingly, the RRa P3HT samples exhibit the lowest E_a values across all doping levels despite also having the lowest macroscopic carrier mobility. This indicates that the activation energy does not directly track the overall mobility in these highly amorphous films. We attribute this behavior to the absence of semicrystalline grain boundaries in RRa P3HT: because transport occurs through a more uniformly disordered morphology, there may be fewer distinct high-barrier interdomain hopping events contributing to E_a in the doped RRa samples. Concurrently, the strong local energetic and structural disorder of amorphous RRa P3HT films severely limits carrier delocalization and suppresses transport, resulting in low overall mobility despite the relatively small E_a values.

Together, these results suggest that the activation energies extracted from temperature-dependent conductivity measurements are associated with transport across mesoscale structural boundaries that are probed by GISAXS. Although the microscopic degree of crystallinity governs carrier delocalization and local mobility within individual domains, the mesoscale connectivity between domains ultimately determines the activation energy associated with longer-range charge transport in doped P3HT films.

5.2.5 Thermoelectric Performance of Different Anion-Exchange-Doped P3HT Polymers

5.2.5.1 Linking Local and Mesoscale Transport to the S - σ Relation

Having established how microscopic (intradomain) and macroscopic (interdomain) charge transport evolve in different anion-exchange-doped P3HT polymers, we now evaluate how these structure–transport relationships affect thermoelectric performance. **Figure 5.5** shows the Seebeck coefficient–conductivity (S - σ) relation and power factor (PF) for the four anion-exchange-doped

P3HT polymers. The dashed curves represent fits to the SLoT model,^[56] which is discussed in more detail in the next section. Across the measured conductivity range, the doped 99% RR and 97% RR P3HT samples exhibit higher Seebeck coefficients and PF values at a given conductivity than the doped 93% RR and RRa P3HT samples, indicating superior thermoelectric performance. These improved thermoelectric properties indicate that local crystallinity plays an important role in enhancing the macroscopic S - σ relation, as the 99% RR and 97% RR P3HT samples also show more favorable local transport characteristics, including their red-shifted P1 peaks, faster TA decay times, and higher long-range carrier mobilities at high doping levels (**Figures 5.3c,d and 5.4a**).

The PF versus conductivity relation (**Figure 5.5b**) further shows that the PF maximum for the doped RR P3HT polymers occurs at a similar conductivity, $\sim 15 \text{ S cm}^{-1}$. Because conductivity depends on both μ and n , a similar σ can be achieved either by increasing mobility or by increasing carrier density. In the 99% RR and 97% RR P3HT polymers, this conductivity is reached at comparatively lower carrier densities because the higher local crystallinity supports greater carrier delocalization and higher mobility.^[37,64] As a result, these polymers maintain relatively large Seebeck coefficients while still achieving high σ values, resulting in enhanced PF values.^[62] In contrast, the 93% RR and RRa P3HT polymers require heavier doping to reach similar conductivities because of their lower carrier mobilities. The resulting need for increased carrier density shifts the Fermi level closer to the transport edge, which reduces S and suppresses the PF.^[37,62] This trend is also evident when examining how the PF changes with n (**Figure D16** in Appendix D).

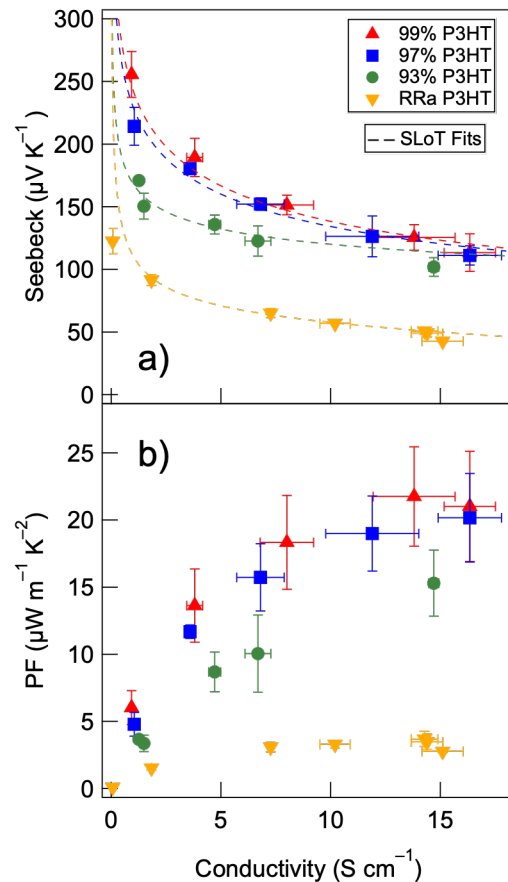


Figure 5.5. Thermoelectric properties of 99% RR, 97% RR, 93% RR, and RRa P3HT films doped via anion exchange, including (a) the Seebeck coefficient–conductivity (S – σ) relation and (b) the power factor (PF). The dashed curves in **Figure 5.5a** represent fits to the SLoT model, with parameters presented in **Table 5.1**. The higher-RR P3HT samples exhibit better thermoelectric performance than the lower-RR P3HT samples, whose properties are more strongly limited by local disorder and reduced mesoscale connectivity.

Notably, although the most favorable S – σ relationships and higher PF values of the 99% RR and 97% RR P3HT polymers indicate that higher local crystallinity plays a dominant role in improving thermoelectric performance, these polymers also exhibit a more pronounced decrease in S in the low-to-mid σ region, suggesting that the thermoelectric performance is also influenced by the mesoscale connectivity of these polymers. Specifically, the 99% RR and 97% RR P3HT samples exhibit lower macroscopic mobilities and poorer mesoscale connectivity at low doping levels, which partially limits thermoelectric performance. Importantly, this mesoscale limitation

does not overcome the benefits of higher local crystallinity, as the higher-RR polymers still maintain improved S - σ relationships and higher PF values across the measured conductivity range. Consequently, these trends indicate that the macroscopic thermoelectric performance is governed by both local crystalline order, which enhances intradomain transport, and longer-range connectivity between polymer domains. These findings suggest that improving long-range mesoscale connectivity and maintaining high local crystallinity are needed to enhance the thermoelectric performance of doped conjugated polymers.

5.2.5.2 Relating Macroscopic S - σ Relation to Microscopic Charge Transport Characteristics

Using the SLoT Model

Although the S - σ and PF trends highlight that structural changes strongly influence charge transport in anion-exchange-doped P3HT, these measurements alone do not reveal precisely what factors govern this behavior. To quantitatively evaluate the energetic landscape experienced by charge carriers, we fit the experimental S - σ relations using the Semi-Localized Transport (SLoT) model.^[56]

The SLoT model uses the Boltzmann transport formalism originally developed in the Kang-Snyder model^[103] and later extended by Gregory *et al.* by incorporating a carrier-density-dependent localization energy ($W_H(c)$), thereby capturing the transition from localized hopping-like transport to more delocalized, metal-like behavior.^[56] Within this framework, the transport function is expressed as:

$$\sigma_E(E, T, c) = \sigma_0 \exp\left(-\frac{W_H(c)}{k_B T}\right) \times \left(\frac{E - E_t}{k_B T}\right), \quad (5.2)$$

where σ_0 is the intrinsic conductivity, E_t is the energy of the transport edge, k_B is the Boltzmann constant, T is the absolute temperature, and $W_H(c)$ is the localization energy, which is a function

of doping level, c . Within this framework, $W_H(c)$ is expressed using the maximum localization energy at low doping ($W_{H,\text{max}}$) and the slope of how this energy decreases as carrier density increases ($W_{H,\text{slope}}$). Thus, the SLoT model allows us to independently assess both the intrinsic conductivity of different doped P3HT polymers (σ_0) and how efficiently doping suppresses localization effects, $W_H(c)$.

Figure 5.5a shows the SLoT fits (dashed curves) to the measured S - σ data; the key extracted fit parameters, $W_{H,\text{slope}}$ and σ_0 , are summarized in **Table 5.1**. Notably, σ_0 increases monotonically with polymer regioregularity, with 99% RR and 97% RR P3HT exhibiting the highest intrinsic conductivities (**Table 5.1** and **Figure 5.6**). Because σ_0 is a doping-level-independent parameter extracted from the entire S - σ curve, it reflects the inherent ability of the polymer to transport charge in the absence of localization effects. In our case, σ_0 scales both with increasing doped polymer crystallinity (**Table 5.1** and **Figure 5.6**) and with the increase in domain correlation length upon doping, ΔR_g (**Table 5.1** and **Figure D17**).

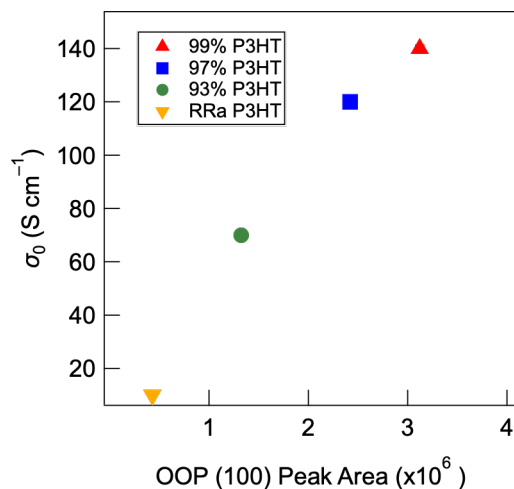


Figure 5.6. Behavior of σ_0 , the intrinsic conductivity in the SLoT model, as a function of relative crystallinity (out-of-plane lamellar (100) peak area) for the most-doped P3HT samples. The more crystalline 99% RR and 97% RR P3HT samples exhibit higher intrinsic conductivities than the lower-crystallinity 93% RR and RRa P3HT samples.

The SLoT fits also yield $W_{H,slope}$, which quantifies how rapidly localization energy decreases with increased doping (**Table 5.1**). The larger $W_{H,slope}$ values observed for the RR polymers indicate that doping suppresses the localization energy more efficiently in these materials. As a result, carriers in the 99% RR and 97% RR P3HT films can more readily access less-localized transport states as the doping level increases, leading to improved charge transport. This observation is consistent with the red-shifted P1 peaks, which independently indicate greater polaron delocalization. Together with their larger σ_0 values, this shows that the superior transport of the 99% RR and 97% RR P3HT polymers arises from both stronger intrinsic transport within crystalline domains and more efficient reduction of localization effects upon doping. In contrast, the smaller σ_0 and $W_{H,slope}$ values of the 93% RR and RRa P3HT polymers indicate that charge transport remains more strongly limited by the lower crystallinity and greater structural disorder in these less-ordered materials. Thus, the SLoT analysis provides a microscopic interpretation of the macroscopic S - σ relation, showing that it reflects both the local crystalline structure and mesoscale connectivity of the different films.

5.3 Conclusions

In this work, we investigated how the morphology of a pristine conjugated polymer influences charge transport and TE performance upon doping via anion exchange. We systematically changed the regioregularity of the polymer, tuning both the polymer microstructure and mesoscale connectivity, and found that anion-exchange doping via the SqP method largely preserves the original local crystalline morphology after doping. The enhanced local crystallinity of doped 99% RR and 97% RR P3HT greatly enhances local charge transport, as indicated by red-shifted P1 peak positions and faster ultrafast TA decay times compared to the less crystalline doped 93% RR and RRa P3HT polymers.

Our Hall effect and temperature-dependent conductivity measurements showed that the more crystalline P3HT polymers surprisingly exhibited lower macroscopic carrier mobilities and higher activation energies at low doping levels. GISAXS measurements, which probe the mesoscale domain connectivity, indicate that the lower mobilities and higher activation energies for macroscopic transport at low n result from poor longer-range domain connectivity, as shown by smaller R_g values in the higher-RR samples. At intermediate doping levels, however, anion-exchange doping induces longer-range mesoscale ordering in 99% RR and 97% RR P3HT, resulting in higher macroscopic mobilities and lower activation energies compared to doped 93% RR and RRa P3HT.

Despite the lack of longer-range ordering at low doping levels, the doped 99% RR and 97% RR P3HT polymers still show better S – σ relations and higher PFs across all doping levels, indicating that intradomain transport dominates the thermoelectric properties of these doped polymer systems. Further analysis using the SLoT model indicates that the enhanced TE performance in these highly crystalline polymers arises from a steeper $W_{H,slope}$ and higher σ_0 . Overall, these results show that optimizing thermoelectric performance of doped conjugated polymers requires consideration of morphology on multiple length scales. High local crystallinity promotes intrinsically favorable intradomain charge transport, while longer-range mesoscale ordering controls how effectively this local transport advantage is translated into macroscopic conductivity upon doping.

5.4 Experimental Section/Methods

5.4.1 Materials

Poly(3-hexylthiophene-2,5-diyl) (P3HT) samples with different regioregularities were used in this work. The 99% regioregular P3HT was purchased from TCI ($M_n = 27$ –45 kDa). The

97.6% regioregular P3HT ($M_w = 60.15$ kDa) was purchased from Ossila. The 93% regioregular P3HT ($M_w = 50\text{--}70$ kDa) and regiorandom P3HT (RRa; $M_w = 60\text{--}95$ kDa) were purchased from Rieke Metals, Inc. 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ ; purity > 99.0%) was purchased from Ossila. 1,2-Dichlorobenzene (*o*-DCB, anhydrous, 99%), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and *n*-butyl acetate (*n*-BA, anhydrous, >99%) were purchased from Sigma-Aldrich. All chemicals and reagents were used as received.

5.4.2 Sample Preparation

Devices for thermoelectric, electrical conductivity, Hall effect, and spectroscopy measurements (UV–vis–NIR and TA) were cast on pre-cleaned glass substrates. GIWAXS and GISAXS samples were cast on silicon wafers. FTIR spectra were acquired on samples cast onto pre-cleaned sapphire substrates. Glass substrates were cut into 1.2×1.2 cm squares, and silicon substrates were cut into 1.5×1.5 cm squares; the substrates were pre-cleaned by sequential washing and sonication with Alconox detergent, deionized water, and acetone. The substrates were dried using nitrogen gas and plasma etched for ~15 min and transferred into a nitrogen glovebox for spin coating and doping.

All P3HT films were cast using 2% w/v (20 mg/mL) solutions in *o*-dichlorobenzene (*o*-DCB). The polymer solutions were stirred until fully dissolved (~8 hours) with constant stirring (300 rpm). The 2% w/v P3HT solutions were spin-coated onto the substrates at 1000 rpm for 60 seconds, followed by a drying step at 4000 rpm for 5 seconds. The polymer films were left in the nitrogen glovebox overnight to fully dry. For doping, the pristine P3HT polymer films were exposed to a dopant/electrolyte solution for 80 seconds before spin coating at 4000 rpm for 10 seconds to remove any residual solution. Doping solutions were made by mixing varying amounts of F_4TCNQ with a fixed volume of a LiTFSI stock solution (60 mg/mL) in *n*-butyl acetate (*n*-BA),

yielding the F₄TCNQ concentrations reported in the legends while maintaining a constant LiTFSI concentration of 30 mg/mL.

5.4.3 Film Characterization

Electrical conductivity, Hall effect, temperature-dependent conductivity, UV–vis–NIR spectroscopy, and TA spectroscopy measurements were all performed on the same device. Sheet resistance was measured using a Lake Shore MeasureReady M91 FastHall instrument with electrodes placed in the van der Pauw geometry. Gold contacts (1 × 1 mm square, 45 nm thick) were thermally evaporated onto the sample corners using a 3D-printed shadow mask in an Angstrom Engineering Nexdep thermal evaporator. Film thicknesses were measured with a Dektak 150 stylus profilometer. Electrical conductivity measurements were repeated on at least three independent prepared samples.

Hall effect measurements used the same M91 instrument with a source current of 10 μ A and a magnetic field of 1.0236 T; at least three triplicate samples were measured for reproducibility. Temperature-dependent conductivity was obtained by measuring the sample sheet resistance as a function of temperature in a custom-built van der Pauw setup using a Keithley 2400 Sourcemeter controlled by LabVIEW software. A Peltier plate controlled the sample temperature, which was measured by an RTD sensor. UV–vis–NIR spectra were obtained using a JASCO V-770 spectrophotometer.

TA spectroscopy was measured and analyzed via singular value decomposition (SVD) similarly to our previous work.^[26,27,91] The amplified Ti:sapphire laser, Coherent Legend, delivered ~3 mJ, ~50 fs pulses at 800 nm with a 1 kHz repetition rate. The 800-nm output was split, with one portion pumping an optical parametric amplifier (TOPAS, Coherent) to generate ~100 μ J pump pulses at 1800, 2000, or 2200 nm; the other portion passed through a CaF₂ plate to produce a white-

light continuum used to probe over the 900–1300 nm range. Transient absorption signals were recorded with a Helios spectrometer (Ultrafast Systems). At the spatial overlap, the pump exhibited a Gaussian profile with an ~ 8 mm FWHM, while the probe was focused to a diffraction-limited spot. Measurements were carried out under an argon atmosphere with multiple scans collected to ensure that the samples did not de-dope or otherwise degrade during the measurement.

The temporal and spectral components in the TA spectra were deconvolved using SVD.^[26,27,91,104] The TA spectrum of each individual component was fit to a kinetic model that decays exponentially to extract the TA decay times. For all of our data, SVD indicates that there are only two principal components, one for free polarons and one for Coulomb-trapped polarons.^[26,27,91]

Seebeck coefficients were measured using devices fabricated separately from those used for sheet resistance, Hall effect, and temperature-dependent conductivity measurements. The Seebeck devices consisted of two parallel gold rectangular electrodes, each measuring 10×1 mm and 45 nm in thickness, separated by a 10 mm gap. A home-built measurement setup equipped with two Peltier plates was used to generate a temperature gradient across the film, while two RTDs monitored the temperature at each electrode. To minimize sample-to-sample variation, Seebeck devices were prepared from the same solutions and at the same time as the samples used for sheet resistance, Hall effect, and temperature-dependent conductivity measurements. Measurements were collected from three independent samples.

GIWAXS measurements were conducted at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11-3 using 12.7 keV X-rays at an incidence angle of 0.12° . Scattering patterns were collected in a helium environment to improve the signal-to-noise ratio, with a sample-to-detector distance of 250 mm and a spot size of ~ 150 μm on the image plate. The

2D GIWAXS images were calibrated in Igor Pro using the Nika package, and subsequent data reduction was performed using Nika and WAXStools. All samples were prepared and measured in triplicate.

GISAXS measurements were performed at SSRL beamline 1-5 using an X-ray energy of 12 keV, an incident angle of 0.12° and a two-dimensional detector placed 3 m from the sample. 1D integrations were generated by horizontally integrating the intensity near the Yoneda band. The resulting profiles were fit using the Unified Fit method implemented in the Irena and Nika packages in Igor Pro. All samples were prepared and measured in triplicate.

5.5 References

- [1] M. Berggren, D. Nilsson, N. D. Robinson, *Nature Mater* **2007**, 6, 3.
- [2] E. Yvenou, M. Sandroni, A. Carella, M. N. Gueye, J. Faure-Vincent, S. Pouget, R. Demadrille, J.-P. Simonato, *Materials Chemistry Frontiers* **2020**, 4, 2054.
- [3] M. Sharafat Hossain, T. Li, Y. Yu, J. Yong, J.-H. Bahk, E. Skafidas, *RSC Advances* **2020**, 10, 8421.
- [4] G. Prunet, F. Pawula, G. Fleury, E. Cloutet, A. J. Robinson, G. Hadziioannou, A. Pakdel, *Materials Today Physics* **2021**, 18, 100402.
- [5] Y. Wang, L. Yang, X.-L. Shi, X. Shi, L. Chen, M. S. Dargusch, J. Zou, Z.-G. Chen, *Advanced Materials* **2019**, 31, 1807916.
- [6] O. Bubnova, X. Crispin, *Energy Environ. Sci.* **2012**, 5, 9345.
- [7] G. J. Snyder, E. S. Toberer, *Nature Mater* **2008**, 7, 105.
- [8] N. Dubey, M. Leclerc, *Journal of Polymer Science Part B: Polymer Physics* **2011**, 49, 467.
- [9] G.-H. Kim, L. Shao, K. Zhang, K. P. Pipe, *Nature Mater* **2013**, 12, 719.
- [10] M. Martín-González, O. Caballero-Calero, P. Díaz-Chao, *Renewable and Sustainable Energy Reviews* **2013**, 24, 288.

- [11] J. Liu, X. Wang, D. Li, N. E. Coates, R. A. Segalman, D. G. Cahill, *Macromolecules* **2015**, *48*, 585.
- [12] R. Zuzok, A. B. Kaiser, W. Pukacki, S. Roth, *J. Chem. Phys.* **1991**, *95*, 1270.
- [13] G. Zuo, X. Liu, M. Fahlman, M. Kemerink, *Advanced Functional Materials* **2018**, *28*, 1703280.
- [14] W. Zhao, J. Ding, Y. Zou, C. Di, D. Zhu, *Chemical Society Reviews* **2020**, *49*, 7210.
- [15] B. Russ, A. Glaudell, J. J. Urban, M. L. Chabinyc, R. A. Segalman, *Nat Rev Mater* **2016**, *1*, 16050.
- [16] R. Kroon, D. Alemu Mengistie, D. Kiefer, J. Hynynen, J. D. Ryan, L. Yu, C. Müller, *Chemical Society Reviews* **2016**, *45*, 6147.
- [17] O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren, X. Crispin, *Nature Mater* **2011**, *10*, 429.
- [18] Y. Huang, D. H. Lukito Tjhe, I. E. Jacobs, X. Jiao, Q. He, M. Statz, X. Ren, X. Huang, I. McCulloch, M. Heeney, C. McNeill, H. Sirringhaus, *Appl. Phys. Lett.* **2021**, *119*, 111903.
- [19] E. E. Havinga, W. ten Hoeve, H. Wynberg, *Polymer Bulletin* **1992**, *29*, 119.
- [20] Y. Yamashita, J. Tsurumi, M. Ohno, R. Fujimoto, S. Kumagai, T. Kurosawa, T. Okamoto, J. Takeya, S. Watanabe, *Nature* **2019**, *572*, 634.
- [21] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, M. F. Toney, *Nature Mater* **2006**, *5*, 328.
- [22] T. J. Aubry, K. J. Winchell, C. Z. Salamat, V. M. Basile, J. R. Lindemuth, J. M. Stauber, J. C. Axtell, R. M. Kubena, M. D. Phan, M. J. Bird, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2020**, *30*, 2001800.
- [23] B. Lüssem, C.-M. Keum, D. Kasemann, B. Naab, Z. Bao, K. Leo, *Chem. Rev.* **2016**, *116*, 13714.
- [24] M. Jha, J. Mogollon Santiana, A. A. Jacob, K. Light, M. L. Hong, M. R. Lau, L. R. Filardi, H. Miao, S. M. Gurses, C. X. Kronawitter, M. Mascal, A. J. Moulé, *J. Phys. Chem. C* **2024**, *128*, 1258.

- [25] A. J. Moulé, G. Gonel, T. L. Murrey, R. Ghosh, J. Saska, N. E. Shevchenko, I. Denti, A. S. Ferguson, R. M. Talbot, N. L. Yacoub, M. Mascal, A. Salleo, F. C. Spano, *Advanced Electronic Materials* **2022**, 8, 2100888.
- [26] E. C. Wu, D. G. Vidales, C. Z. Salamat, Q. M. Duong, A. León Ruiz, A. D. Ready, Z. Mehmedović, D. A. Stanfield, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Advanced Functional Materials* **2025**, 35, e07480.
- [27] M. G. Voss, D. T. Scholes, J. R. Challa, B. J. Schwartz, *Faraday Discuss.* **2019**, 216, 339.
- [28] E. C. Wu, C. Z. Salamat, O. L. Ruiz, T. Qu, A. Kim, S. H. Tolbert, B. J. Schwartz, *Adv Funct Materials* **2023**, 33, 2213652.
- [29] V. Untilova, J. Hynynen, A. I. Hofmann, D. Scheunemann, Y. Zhang, S. Barlow, M. Kemerink, S. R. Marder, L. Biniek, C. Müller, M. Brinkmann, *Macromolecules* **2020**, 53, 6314.
- [30] Y. Xuan, X. Liu, S. Desbief, P. Leclère, M. Fahlman, R. Lazzaroni, M. Berggren, J. Cornil, D. Emin, X. Crispin, *Phys. Rev. B* **2010**, 82, 115454.
- [31] M. Statz, D. Venkateshvaran, X. Jiao, S. Schott, C. R. McNeill, D. Emin, H. Sirringhaus, R. Di Pietro, *Commun Phys* **2018**, 1, 1.
- [32] Y. Zhong, V. Untilova, D. Muller, S. Guchait, C. Kiefer, L. Herrmann, N. Zimmermann, M. Brosset, T. Heiser, M. Brinkmann, *Advanced Functional Materials* **2022**, 32, 2202075.
- [33] B. J. Kim, S. Chung, S. Sim, H. Lee, J. Lee, K. Cho, *Nano Energy* **2025**, 146, 111547.
- [34] S. H. Kim, H. Yook, W. Sung, J. Choi, H. Lim, S. Chung, J. W. Han, K. Cho, *Advanced Materials* **2023**, 35, 2207320.
- [35] M. Schwarze, C. Gaul, R. Scholz, F. Bussolotti, A. Hofacker, K. S. Schellhammer, B. Nell, B. D. Naab, Z. Bao, D. Spoltore, K. Vandewal, J. Widmer, S. Kera, N. Ueno, F. Ortmann, K. Leo, *Nature Mater* **2019**, 18, 242.
- [36] B. A. Gregg, S.-G. Chen, R. A. Cormier, *Chem. Mater.* **2004**, 16, 4586.
- [37] R. Noriega, J. Rivnay, K. Vandewal, F. P. V. Koch, N. Stingelin, P. Smith, M. F. Toney, A. Salleo, *Nature Materials* **2013**, 12, 1038.
- [38] S. Ihnatsenka, X. Crispin, I. V. Zozoulenko, *Phys. Rev. B* **2015**, 92, 035201.
- [39] J. Kim, H. Lee, S. H. Kim, S. H. Kim, S. Chung, E. Ok, K. Cho, *ACS Nano* **2025**, 19, 38255.

- [40] Y. Wu, C. Z. Salamat, A. León Ruiz, A. F. Simafranca, N. Akmanşen-Kalayci, E. C. Wu, E. Doud, Z. Mehmedović, J. R. Lindemuth, M. D. Phan, A. M. Spokoyny, B. J. Schwartz, S. H. Tolbert, *Chem. Mater.* **2024**, *36*, 5552.
- [41] T. J. Aubry, J. C. Axtell, V. M. Basile, K. J. Winchell, J. R. Lindemuth, T. M. Porter, J.-Y. Liu, A. N. Alexandrova, C. P. Kubiak, S. H. Tolbert, A. M. Spokoyny, B. J. Schwartz, *Advanced Materials* **2019**, *31*, 1805647.
- [42] S. H. Kim, S. Kang, M. Jeong, J. Park, S. Jeong, H. Lee, C. Y. Son, K. Cho, *ACS Nano* **2025**, *19*, 29265.
- [43] J. Hynynen, D. Kiefer, C. Müller, *RSC Adv.* **2018**, *8*, 1593.
- [44] D. T. Scholes, P. Y. Yee, J. R. Lindemuth, H. Kang, J. Onorato, R. Ghosh, C. K. Luscombe, F. C. Spano, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2017**, *27*, 1702654.
- [45] A. Troisi, *Organic Electronics* **2011**, *12*, 1988.
- [46] K. Lu, C. Chen, J.-L. Cheng, I. E. Jacobs, B. Yue, P. Huang, L.-W. Feng, Y. Lin, *ACS Materials Lett.* **2024**, *6*, 4351.
- [47] I. E. Jacobs, G. D’Avino, V. Lemaure, Y. Lin, Y. Huang, C. Chen, T. F. Harrelson, W. Wood, L. J. Spalek, T. Mustafa, C. A. O’Keefe, X. Ren, D. Simatos, D. Tjhe, M. Statz, J. W. Strzalka, J.-K. Lee, I. McCulloch, S. Fratini, D. Beljonne, H. Sirringhaus, *J. Am. Chem. Soc.* **2022**, *144*, 3005.
- [48] I. E. Jacobs, Y. Lin, Y. Huang, X. Ren, D. Simatos, C. Chen, D. Tjhe, M. Statz, L. Lai, P. A. Finn, W. G. Neal, G. D’Avino, V. Lemaure, S. Fratini, D. Beljonne, J. Strzalka, C. B. Nielsen, S. Barlow, S. R. Marder, I. McCulloch, H. Sirringhaus, *Advanced Materials* **2022**, *34*, 2102988.
- [49] R. Zhang, B. Li, M. C. Iovu, M. Jeffries-EL, G. Sauvé, J. Cooper, S. Jia, S. Tristram-Nagle, D. M. Smilgies, D. N. Lambeth, R. D. McCullough, T. Kowalewski, *J. Am. Chem. Soc.* **2006**, *128*, 3480.
- [50] C. H. Woo, C. Piliego, T. W. Holcombe, M. F. Toney, J. M. J. Fréchet, *Macromolecules* **2012**, *45*, 3057.
- [51] K. A. Mazzio, A. H. Rice, M. M. Durban, C. K. Luscombe, *J. Phys. Chem. C* **2015**, *119*, 14911.
- [52] M. F. DiTusa, G. L. Grocke, T. Ma, S. N. Patel, *Mol. Syst. Des. Eng.* **2022**, *7*, 788.

- [53] Q. M. Duong, D. G. Vidales, X. Liu, C. Z. Salamat, A. Ready, H. A. Khunaizi, M. Matsumoto, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Advanced Functional Materials* **2026**, e75510.
- [54] J.-S. Kim, J.-H. Kim, W. Lee, H. Yu, H. J. Kim, I. Song, M. Shin, J. H. Oh, U. Jeong, T.-S. Kim, B. J. Kim, *Macromolecules* **2015**, 48, 4339.
- [55] Y. Yamashita, J. Tsurumi, T. Kurosawa, K. Ueji, Y. Tsuneda, S. Kohno, H. Kempe, S. Kumagai, T. Okamoto, J. Takeya, S. Watanabe, *Commun Mater* **2021**, 2, 45.
- [56] S. A. Gregory, R. Hanus, A. Atassi, J. M. Rinehart, J. P. Wooding, A. K. Menon, M. D. Losego, G. J. Snyder, S. K. Yee, *Nat. Mater.* **2021**, 20, 1414.
- [57] P. Pingel, D. Neher, *Phys. Rev. B* **2013**, 87, 115209.
- [58] A. L. Ayzner, C. J. Tassone, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2009**, 113, 20050.
- [59] J. C. Aguirre, S. A. Hawks, A. S. Ferreira, P. Yee, S. Subramaniyan, S. A. Jenekhe, S. H. Tolbert, B. J. Schwartz, *Adv. Energy Mater.* **2015**, 5, 1402020.
- [60] S. A. Hawks, J. C. Aguirre, L. T. Schelhas, R. J. Thompson, R. C. Huber, A. S. Ferreira, G. Zhang, A. A. Herzing, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2014**, 118, 17413.
- [61] V. Vijayakumar, P. Durand, H. Zeng, V. Untilova, L. Herrmann, P. Algayer, N. Leclerc, M. Brinkmann, *J. Mater. Chem. C* **2020**, 8, 16470.
- [62] D. Venkateshvaran, M. Nikolka, A. Sadhanala, V. Lemaure, M. Zelazny, M. Kepa, M. Hurhangee, A. J. Kronemeijer, V. Pecunia, I. Nasrallah, I. Romanov, K. Broch, I. McCulloch, D. Emin, Y. Olivier, J. Cornil, D. Beljonne, H. Sirringhaus, *Nature* **2014**, 515, 384.
- [63] C. Chen, H. Ma, K. Lu, X. Zhang, B. Yue, C. Song, P. Huang, H. Cheng, Y. Lin, *Advanced Materials* **2025**, 37, 2417594.
- [64] O. Bubnova, Z. U. Khan, H. Wang, S. Braun, D. R. Evans, M. Fabretto, P. Hojati-Talemi, D. Dagnelund, J.-B. Arlin, Y. H. Geerts, S. Desbief, D. W. Breiby, J. W. Andreasen, R. Lazzaroni, W. M. Chen, I. Zozoulenko, M. Fahlman, P. J. Murphy, M. Berggren, X. Crispin, *Nature Mater* **2014**, 13, 190.
- [65] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. a. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, 401, 685.

- [66] R. Joseph Kline, M. D. McGehee, M. F. Toney, *Nature Mater* **2006**, 5, 222.
- [67] A. Zen, M. Saphiannikova, D. Neher, J. Grenzer, S. Grigorian, U. Pietsch, U. Asawapirom, S. Janietz, U. Scherf, I. Lieberwirth, G. Wegner, *Macromolecules* **2006**, 39, 2162.
- [68] M. Brinkmann, *Journal of Polymer Science Part B: Polymer Physics* **2011**, 49, 1218.
- [69] P. Y. Yee, D. T. Scholes, B. J. Schwartz, S. H. Tolbert, *J. Phys. Chem. Lett.* **2019**, 10, 4929.
- [70] D. Rosas Villalva, D. Derewjanko, Y. Zhang, Y. Liu, A. Bates, A. Sharma, J. Han, M. Gibert-Roca, O. Z. Arteaga, S. Jang, S. Moro, G. Costantini, X. Gu, M. Kemerink, D. Baran, *Nat. Mater.* **2025**, 24, 1236.
- [71] C. Chen, I. E. Jacobs, K. Kang, Y. Lin, C. Jellett, B. Kang, S. B. Lee, Y. Huang, M. BaloochQarai, R. Ghosh, M. Statz, W. Wood, X. Ren, D. Tjhe, Y. Sun, X. She, Y. Hu, L. Jiang, F. C. Spano, I. McCulloch, H. Sirringhaus, *Advanced Energy Materials* **2023**, 13, 2202797.
- [72] P. Walter, M. Ilchen, J. Roeh, W. Ohm, C. B. Zeuthen, U. Klemradt, *Applied Sciences* **2021**, 11, 8970.
- [73] H. V. Sureka, A. C. Obermeyer, R. J. Flores, B. D. Olsen, *ACS Appl. Mater. Interfaces* **2019**, 11, 32354.
- [74] G. Freychet, M. Maret, M. Fernandez-Regulez, R. Tiron, A. Gharbi, C. Nicolet, P. Gergaud, *Journal of Polymer Science* **2020**, 58, 2041.
- [75] C. Darko, I. Botiz, G. Reiter, D. W. Breiby, J. W. Andreasen, S. V. Roth, D.-M. Smilgies, E. Metwalli, C. M. Papadakis, *Phys. Rev. E* **2009**, 79, 041802.
- [76] D.-M. Smilgies, *Journal of Polymer Science* **2022**, 60, 1023.
- [77] S. Lenz, M. Bonini, S. K. Nett, M. C. Lechmann, S. G. J. Emmerling, R. S. Kappes, M. Memesa, A. Timmann, S. V. Roth, J. S. Gutmann, *Eur. Phys. J. Appl. Phys.* **2010**, 51, 10601.
- [78] G. Beaucage, *Journal of Applied Crystallography* **1995**, 28, 717.
- [79] F. C. Spano, C. Silva, *Annual Review of Physical Chemistry* **2014**, 65, 477.
- [80] N. J. Hestand, F. C. Spano, *Chem. Rev.* **2018**, 118, 7069.
- [81] P. J. Brown, D. S. Thomas, A. Köhler, J. S. Wilson, J.-S. Kim, C. M. Ramsdale, H. Sirringhaus, R. H. Friend, *Phys. Rev. B* **2003**, 67, 064203.

- [82] P. Ehrenreich, S. T. Birkhold, E. Zimmermann, H. Hu, K.-D. Kim, J. Weickert, T. Pfadler, L. Schmidt-Mende, *Sci Rep* **2016**, *6*, 32434.
- [83] K. Rahimi, I. Botiz, J. O. Agumba, S. Motamen, N. Stingelin, G. Reiter, *RSC Advances* **2014**, *4*, 11121.
- [84] M. Wohlgenannt, X. M. Jiang, Z. V. Vardeny, *Phys. Rev. B* **2004**, *69*, 241204.
- [85] R. Ghosh, C. M. Pochas, F. C. Spano, *J. Phys. Chem. C* **2016**, *120*, 11394.
- [86] D. A. Stanfield, Z. Mehmedović, B. J. Schwartz, *Chem. Mater.* **2021**, *33*, 8489.
- [87] D. Kiefer, R. Kroon, A. I. Hofmann, H. Sun, X. Liu, A. Giovannitti, D. Stegerer, A. Cano, J. Hynynen, L. Yu, Y. Zhang, D. Nai, T. F. Harrelson, M. Sommer, A. J. Moulé, M. Kemerink, S. R. Marder, I. McCulloch, M. Fahlman, S. Fabiano, C. Müller, *Nature Mater* **2019**, *18*, 149.
- [88] J. E. Cochran, M. J. N. Junk, A. M. Glaudell, P. L. Miller, J. S. Cowart, M. F. Toney, C. J. Hawker, B. F. Chmelka, M. L. Chabinyc, *Macromolecules* **2014**, *47*, 6836.
- [89] M. T. Fontana, D. A. Stanfield, D. T. Scholes, K. J. Winchell, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2019**, *123*, 22711.
- [90] C. M. Pochas, F. C. Spano, *J. Chem. Phys.* **2014**, *140*, 244902.
- [91] M. G. Voss, J. R. Challa, D. T. Scholes, P. Y. Yee, E. C. Wu, X. Liu, S. J. Park, O. León Ruiz, S. Subramanian, M. Chen, S. A. Jenekhe, X. Wang, S. H. Tolbert, B. J. Schwartz, *Advanced Materials* **2021**, *33*, 2000228.
- [92] A. R. Umar, A. L. Dorris, N. B. Kotadiya, N. C. Giebink, G. S. Collier, C. Grieco, *J. Phys. Chem. C* **2023**, *127*, 9498.
- [93] A. R. Umar, C. Grieco, *J. Chem. Phys.* **2025**, *162*, 054720.
- [94] A. R. Umar, A. L. Dorris, C. Grieco, *Advanced Functional Materials* **2024**, *34*, 2407181.
- [95] E. C. Wu, B. J. Schwartz, *J. Chem. Theory Comput.* **2024**, *20*, 10059.
- [96] E. C. Wu, B. J. Schwartz, *J. Chem. Theory Comput.* **2023**, *19*, 6761.
- [97] E. Röck, D. Tsokkou, B. Hunger, M. M. Horn, S. Zokaei, R. Kroon, J. Asatryan, J. Martín, C. Müller, M. Kemerink, N. Banerji, *Materials Horizons* **2025**, *12*, 10827.

- [98] B. Hunger, M. M. Horn, E. Röck, D. R. Villalva, L. Bynens, J. Vanderspikken, C. Kousseff, S. Gobeil, O. Bardagot, N. Akmanşen-Kalayci, S. H. Tolbert, I. McCulloch, W. Maes, D. Tsokkou, N. Banerji, *Advanced Materials* **2026**, e23635.
- [99] E. M. Thomas, K. A. Peterson, A. H. Balzer, D. Rawlings, N. Stingelin, R. A. Segalman, M. L. Chabinyc, *Advanced Electronic Materials* **2020**, 6, 2000595.
- [100] H. T. Yi, Y. N. Gartstein, V. Podzorov, *Sci Rep* **2016**, 6, 23650.
- [101] O. Khatib, B. Lee, J. Yuen, Z. Q. Li, M. Di Ventra, A. J. Heeger, V. Podzorov, D. N. Basov, *Journal of Applied Physics* **2010**, 107, 123702.
- [102] Z. Q. Li, G. M. Wang, N. Sai, D. Moses, M. C. Martin, M. Di Ventra, A. J. Heeger, D. N. Basov, *Nano Lett.* **2006**, 6, 224.
- [103] S. D. Kang, G. J. Snyder, *Nature Mater* **2017**, 16, 252.
- [104] R. W. Hendler, R. I. Shrager, *Journal of Biochemical and Biophysical Methods* **1994**, 28, 1.

Appendix A

Supporting Information for Chapter 2: Double Doping of Conjugated Polymers Can Be Induced by the High-Dielectric Environment Present During Anion-Exchange Doping

A.1 UV–Vis–NIR Spectroscopy

A.1.1 Solvent Washing

To investigate the effects of the double-doping process in PBTTT using DDB-F₆₀ followed by LiTFSI (i.e., the 2-pot AED method), we performed near-infrared (NIR) and UV–vis–NIR spectroscopy measurements. However, to rely on spectroscopy as an indicator of double doping, it was essential to confirm that any additional doping during 2-pot AED resulted from the double-doping mechanism—specifically from DDB-F₆₀[−] anions introduced during the initial doping step—rather than from residual neutral dopant left on the film surface that was then able to dope for the first time upon application of the electrolyte solution.

To ensure the complete removal of neutral DDB-F₆₀ prior to LiTFSI treatment with 2-pot AED, rigorous washing procedures were implemented. However, because both the anionic and neutral forms of DDB-F₆₀ absorb under the bandgaps of PBTTT and P3HT (~2.3 eV and ~2.7 eV, respectively),^[1,2] it is difficult to definitively verify washing efficacy in those polymer matrices using UV–vis spectroscopy alone. To address this, polystyrene (PS), which does not absorb in the UV–vis region, was selected as an inert polymer matrix to test the efficacy of the washing process. A PS film was cast using a 20 mg/mL PS solution in *o*-DCB. After drying, the film was soaked in a 1 mM DDB-F₆₀ solution for 80 seconds, followed by spin coating at 4000 rpm for 10 seconds. The red curve in **Figure A1** shows the characteristic absorptions of the neutral DDB-F₆₀ species in these films at approximately 2.7 eV; a small amount of the DDB-F₆₀[−] anion, which absorbs at ~2.3 eV, is also present due to the dopant oxidizing impurities in the PS film.

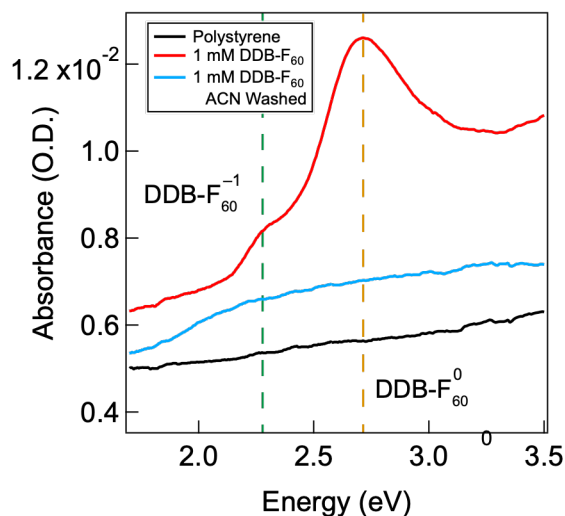


Figure A1. UV-vis absorption spectra of polystyrene films under various conditions. The black curve shows the spectrum of pristine PS. The red and blue curves show the same film after soaking in a 1 mM DDB-F₆₀ solution before and after washing with ACN, respectively. The green and yellow vertical dashed lines show the energies where the DDB-F₆₀⁻ anion and neutral DDB-F₆₀ species absorb, respectively, indicating the removal of both species upon the ACN wash.

These “doped” PS films were then solvent-washed with 0.5 mL of ACN, followed by spin coating for 10 seconds at 4000 rpm. After washing, the characteristic absorptions of both the neutral and anionic DDB-F₆₀ species disappeared, indicating that the washing procedure effectively removes neutral dopant molecules (and the minor amount of anions) from the film. This result supports the conclusion that the increased doping levels observed after 2-pot AED in the washed PBTtT films (as discussed in the main text) primarily originate from double doping by the DDB-F₆₀⁻ anions during the 2-pot AED process, rather than from newly induced doping from any residual neutral species.

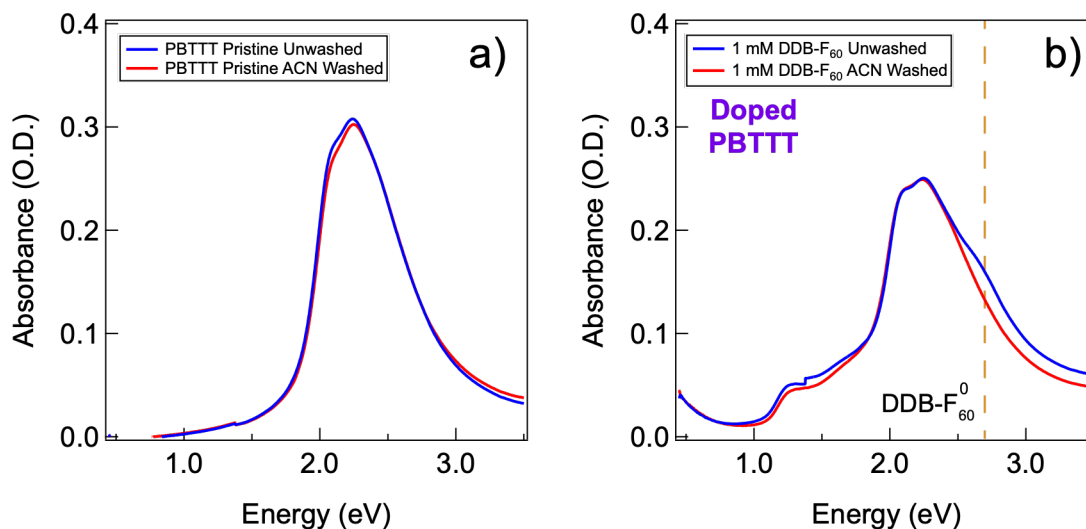


Figure A2. UV-vis spectra of ACN-washed (red curves) and unwashed (blue curves) (a) pristine PBTBT and (b) PBTBT doped with 1 mM DDB-F₆₀. The yellow dashed line indicates the absorption maximum of the neutral DDB-F₆₀ molecule (near 2.7 eV). The shoulder in the unwashed (blue curve) sample disappears upon ACN washing, indicating the removal of all neutral DDB-F₆₀ molecules in our films prior to 2-pot AED.

With the ACN washing step well-characterized using PS films, we performed the same washing step with our PBTBT films doped with DDB-F₆₀. Although less noticeable than in the case of PS, washing PBTBT doped with DDB-F₆₀ also leads to the disappearance of the small amount of neutral DDB-F₆₀ absorption (yellow dashed line), as shown in **Figure A2**. It is worth noting that washing doped conjugated polymer films often leads to dedoping. In our case, however, the amount of dedoping following the washing step was minimal, as also seen in **Figure A2**. We also see relatively minimal dedoping even when a more strongly swelling solvent, *n*-BA, is used for the washing step, as shown in **Figure A3**.

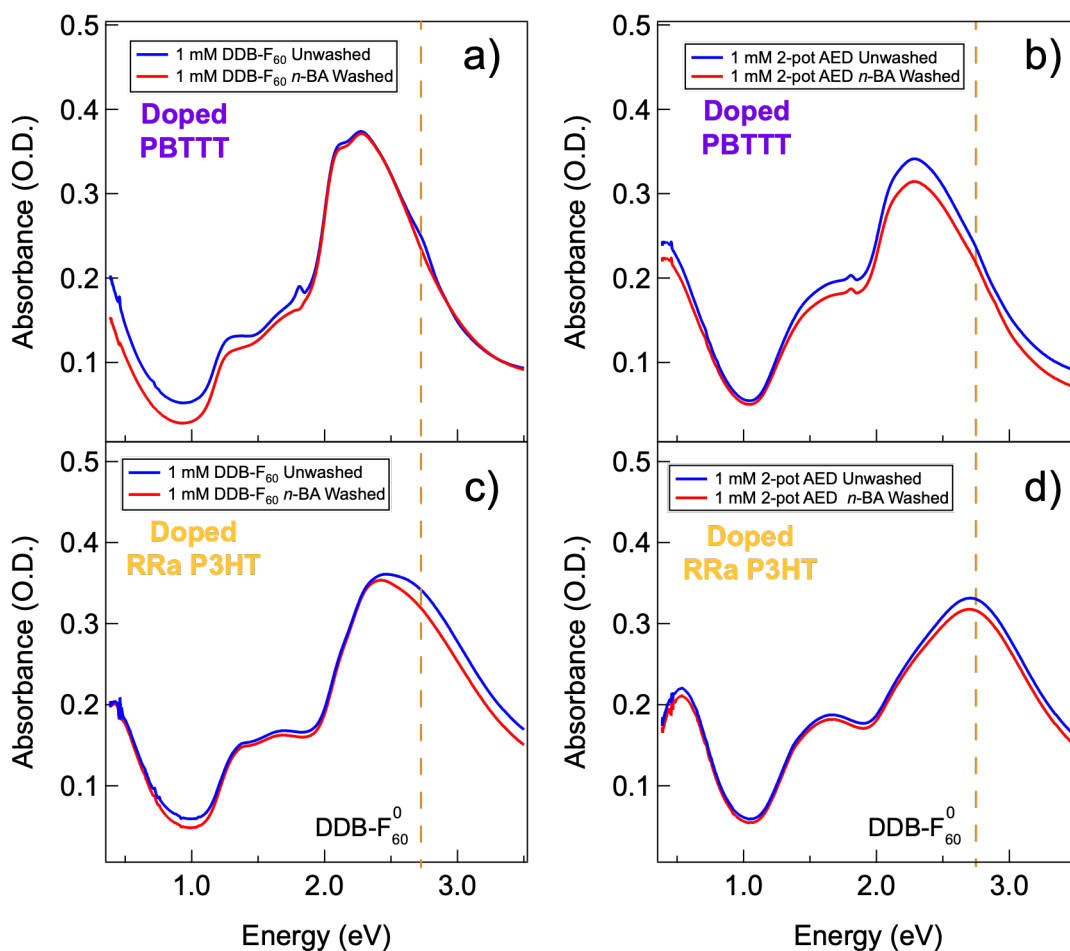


Figure A3. UV-vis-NIR spectra of doped conjugated polymer films before and after *n*-BA solvent washing. (a,b) PBTtT and (c,d) RRa-P3HT samples doped using 1 mM DDB-F₆₀ (a,c) and 1 mM DDB-F₆₀ followed by 2-pot AED (b,d). Spectra were collected after the initial doping step and subsequent *n*-BA washing for the 1 mM DDB-F₆₀-doped samples. The 2-pot AED samples were exchanged with LiTFSI solution followed by an *n*-BA wash to remove any salt left on the surface of the films. Minimal changes in the absorption features before and after the first or second *n*-BA wash indicate limited dedoping, demonstrating the robustness of both doping methods against solvent washing.

A.1.2 Polaronic Peak Location Indicates Successful DDB-F₆₀⁻ Exchange for TFSI⁻

Previous studies have shown that DDB-based dopants create highly delocalized polarons in P3HT, as evidenced by high Hall mobility measurements and a red-shifted P1 peak location.^{[3–}

^{6]} This behavior has been attributed to the large size of the DDB-based dopant anions,^[3] which minimizes Coulomb interactions between the dopant counterion and the hole on the polymer

backbone. In contrast, smaller counterions like $F_4TCNQ^{-[3]}$ or $TFSI^-$ lead to blue-shifted P1 peak locations, suggesting stronger Coulombic interactions between the counterion and the hole.

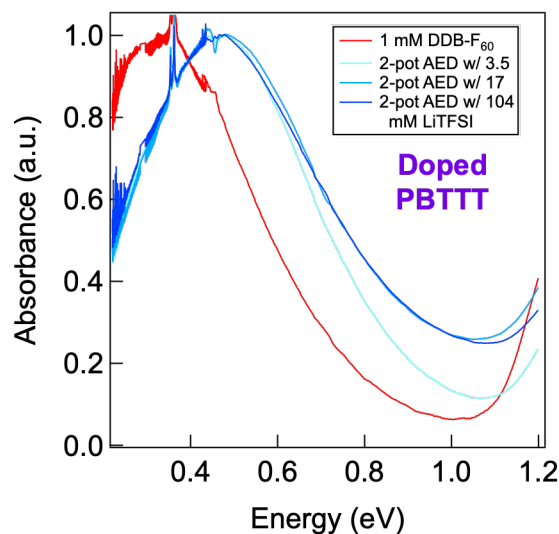


Figure A4. Normalized P1 peaks for PBTtT doped with 1 mM DDB- F_{60} and PBTtT subjected to 2-pot AED with different LiTFSI concentrations of 3.5, 17, and 104 mM. These are the same samples shown in **Figure 2.2a** in the main text.

Figure A4 shows the normalized P1 peaks for PBTtT doped with 1 mM DDB- F_{60} and subsequently subjected to the 2-pot AED step using different electrolyte concentrations. The 2-pot exchanged samples exhibit a significantly blue-shifted P1 peak compared to the initial DDB- F_{60} -doped film, indicating successful exchange of the bulky DDB- F_{60}^- anion with the smaller $TFSI^-$ anion. Notably, the P1 peak position and shape remain nearly unchanged across all 2-pot electrolyte concentrations, suggesting that efficient anion exchange occurs even at relatively low dopant-to-electrolyte ratios, where entropic effects such as mass action would suggest that anion exchange is unfavorable.^[7] This observation is further supported by GIWAXS data (see **Figure A13**, below), which show similar q -spacing values in both the out-of-plane (lamellar stacking) and in-plane (π -stacking) directions for the 2-pot AED samples treated with 17 mM and 104 mM

LiTFSI. These results are consistent with the formation of similar polymer structures following complete anion exchange.

A.1.3 Oscillator-Strength-Weighted P1 Peak Areas

To compare the intensities of the P1 absorption bands, which should be related to the doped carrier density, we use the integrated oscillator-strength-weighted NIR P1 peak area. This was calculated by weighting the absorption spectrum by frequency (in wavenumbers) prior to integration. Due to strong absorption by the sapphire substrates below 0.18 eV, the red side of the P1 peak could not be accurately measured. To address this limitation and ensure consistent comparison of relative polaron populations, we defined an asymmetric integration window from the point on the red side of the peak where the absorption reached 80% of the maximum intensity, extending to the full width at half maximum (FWHM) point on the blue side. This constrained integration range minimizes errors from spectral truncation while preserving the comparative integrity of the peak area analysis. The selected regions are highlighted by the shaded areas in **Figure 2.2c** of the main text for PBTTT and in **Figure A5** for doped RR and RRa P3HT films.

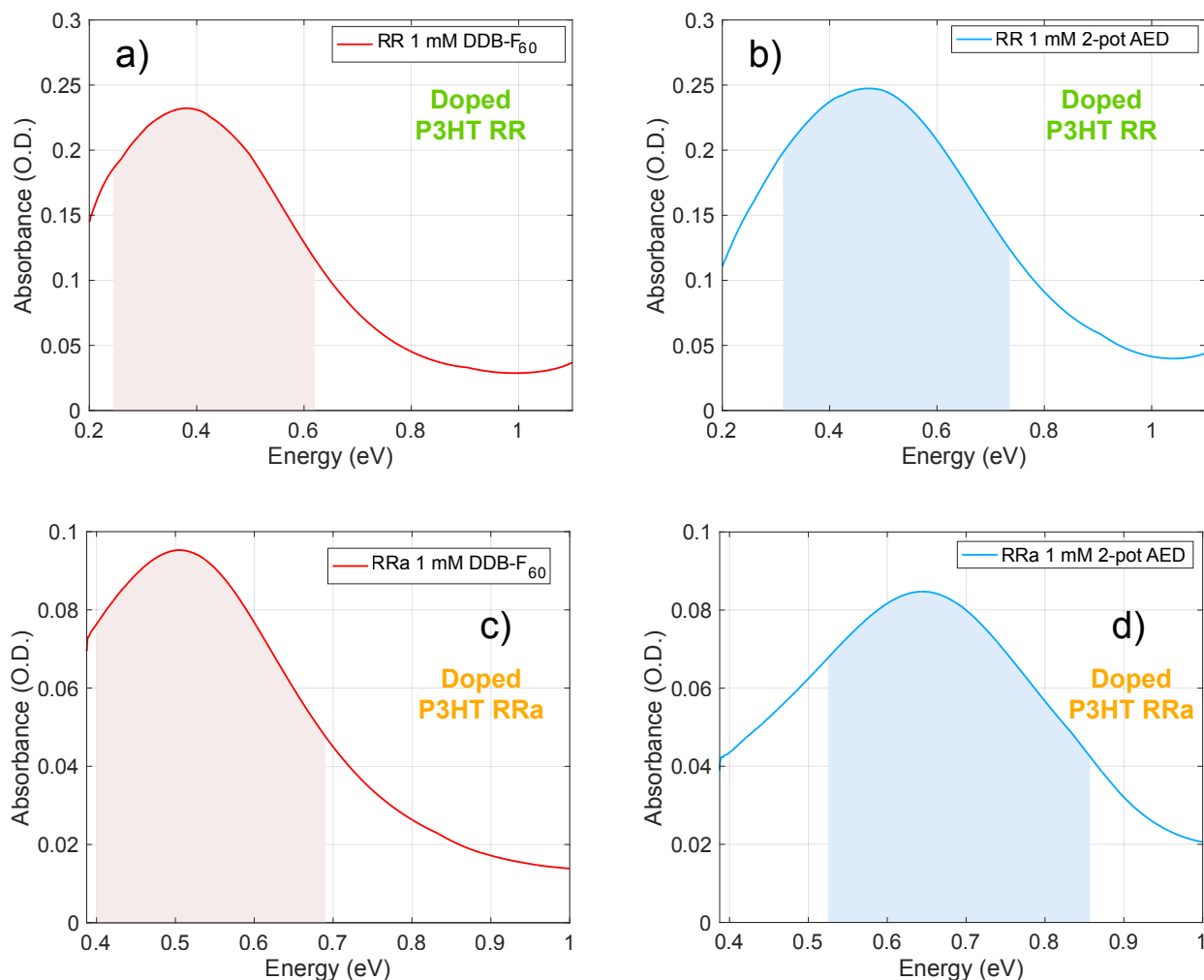


Figure A5. NIR P1 absorption peaks for P3HT polymers doped both conventionally with 1 mM DDB-F₆₀ and following 2-pot AED with 104 mM LiTFSI. Panels (a,b) show spectra for regioregular (RR) P3HT, while panels (c,d) correspond to regiorandom (RRa) P3HT. Shaded regions indicate the range used in the frequency-weighted integrated P1 area calculations.

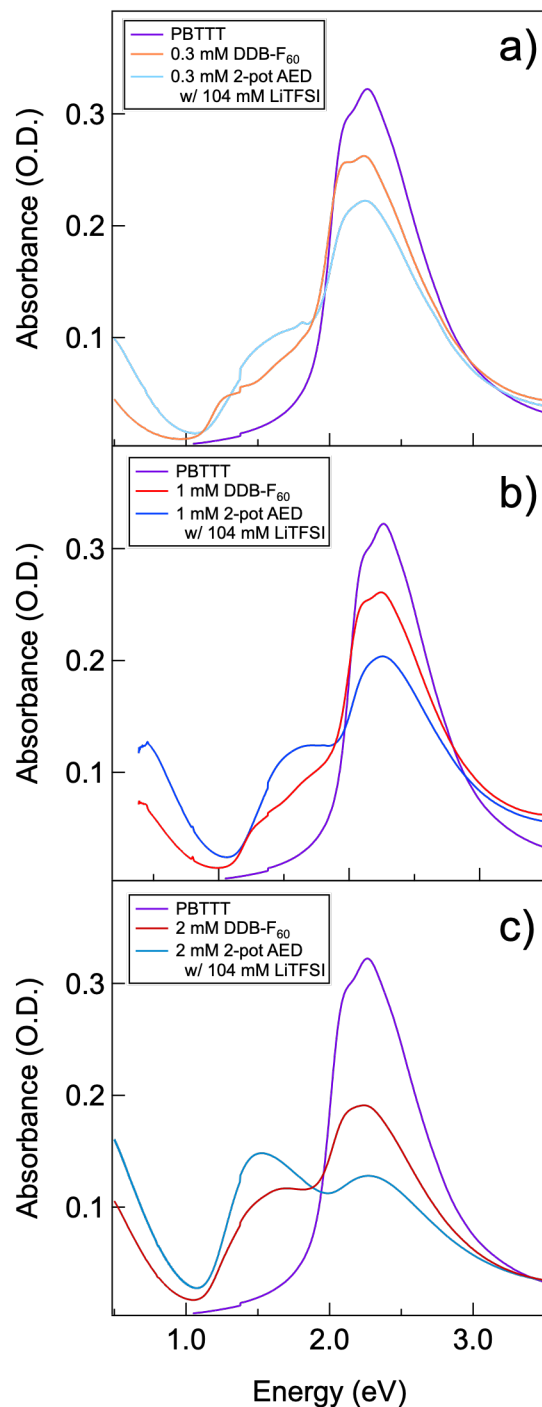


Figure A6. (a–c) UV–vis–NIR spectra of PBTtT thin films (purple curves) conventionally SqP-doped with 0.3, 1, and 2 mM DDB-F₆₀, respectively (red curves), and subsequently subjected to 2-pot AED using a 104 mM LiTFSI solution (blue curves), showing an increase in the signature polaron peak intensities (P1 and P2). These spectra demonstrate the extra doping gained upon exposure to the high-dielectric environment of the LiTFSI solution at different initial dopant concentrations.

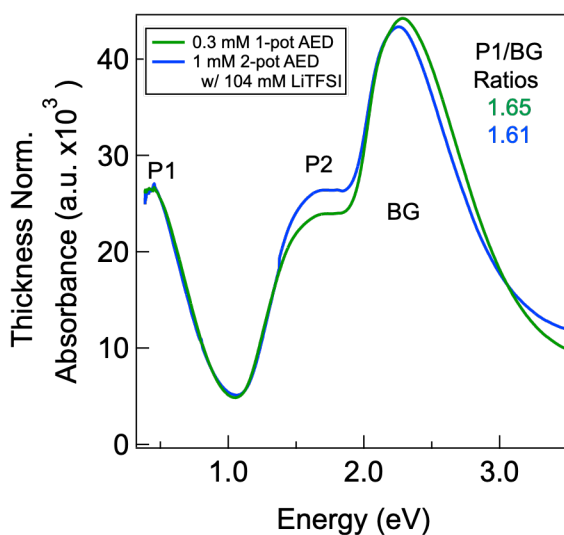


Figure A7. Doping level-matched UV–vis–NIR spectra of PBTTT thin films doped via the 2-pot (blue curve) and 1-pot (green curve) AED methods. The 1-pot method requires a lower dopant concentration (0.3 mM) to reach similar doping levels as the 2-pot method (1 mM), as indicated by the comparable bandgap-to-P1 absorption ratios. The absorbance was thickness normalized to clearly show the matched P1/BG ratios in both films. This matching allows us to confidently comment on the structural similarities between the 1-pot and 2-pot AED samples in **Figure 2.3** in the main text.

A.2 Electrical Conductivity and Hall Effect Measurements

Multifunctional samples for UV–vis–NIR spectroscopy, electrical conductivity, and Hall effect measurements were fabricated on 1.1×1.1 cm pre-cleaned substrates via sequential processing (SqP) followed by the 2-pot step with LiTFSI. All three measurements were performed on the same sample. Gold contact electrodes were evaporated on the corners of the samples. The van der Pauw method with square geometry was used to measure the electrical conductivity and Hall effect. The conductivity and Hall effect measurements on the doped samples were performed using a Lake Shore MeasureReady M91 FastHall instrument, with a source current of 10 μ A.

Hall measurements provide an accurate way of determining the carrier density (n) by measuring a potential difference, also known as the Hall voltage (V_H), when an electrical current (I_x) is applied perpendicular to the voltage measurement and a magnetic field (B_z) is applied

orthogonal to both the voltage and the current (see **Equation (A1)**). The Hall voltage, V_H , for a sample with known thickness, t , is given by:

$$V_H = \frac{I_x B_z}{nte}, \quad (\text{A1})$$

The magnetic field used for our Hall measurements was 1.0236 T. All reported values were measured and averaged over at least three independent samples. The results are summarized in

Table A1.

Table A1. Electrical conductivity, Hall mobility, and carrier density measurements for PBTTT doped conventionally with DDB-F₆₀ at two different doping levels, and again following 2-pot AED with 104 mM LiTFSI. The data show that double doping occurs, as there is no alternative explanation that accounts for the significantly increased carrier density in the 2-pot AED samples. The decreased Hall mobilities following 2-pot AED are also consistent with the blue-shifted P1 peaks seen in these samples, indicating that the carriers are Coulombically trapped by the TFSI[−] counterion.

PBTTT	Conductivity (S cm ^{−1})	Hall Mobility (cm ² V ^{−1} s ^{−1})	Hall Carrier Density (10 ^{×20} cm ^{−3})
1 mM DDB-F ₆₀	5.9	0.29	1.3
1 mM 2-pot AED	5.7	0.13	2.7
2 mM DDB-F ₆₀	4.7	0.32	2.0
2 mM 2-pot AED	6.9	0.14	3.0

A.3 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS)

GIWAXS measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11-3 using an X-ray energy of 12.7 keV at an incidence angle of 0.12°. The Igor Pro packages Nika and Irena were used to calibrate the GIWAXS 2D data. Nika, Irena, and WAXStools were used to reduce the data. For 2D diffractograms, integrations of a narrow wedge (80°–89°) along the y -axis (q_z in **Figures A8, A9, and A11**) provide information

about scattering in the direction perpendicular to the plane of the substrate (out-of-plane, OOP), and integrations of a pie wedge (0° – 10°) oriented along the x -axis (q_{xy} in **Figures A8, A9, and A11**) provide information about scattering in the in-plane (IP) direction.

Figure A8 shows the 2D diffractograms of pristine PBTTT, PBTTT doped with 1 mM DDB-F₆₀ and with 1 mM DDB-F₆₀ followed by 2-pot AED. These diffraction patterns in **Figure A8** were used to plot the 1D in- and out-of-plane integrations shown in **Figure 2.3** of the main text.

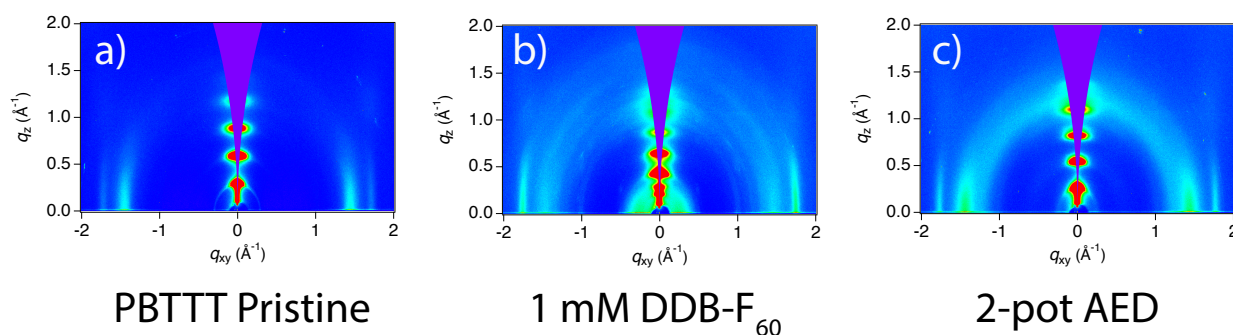


Figure A8. 2D GIWAXS diffractograms of (a) pristine PBTTT, (b) PBTTT doped with 1 mM DDB-F₆₀, and (c) PBTTT doped via 2-pot AED with a 104 mM LiTFSI solution. We obtained the 1D integrations along the OOP (q_z) and along the IP (q_{xy}) directions shown in **Figure 2.3** in the main text.

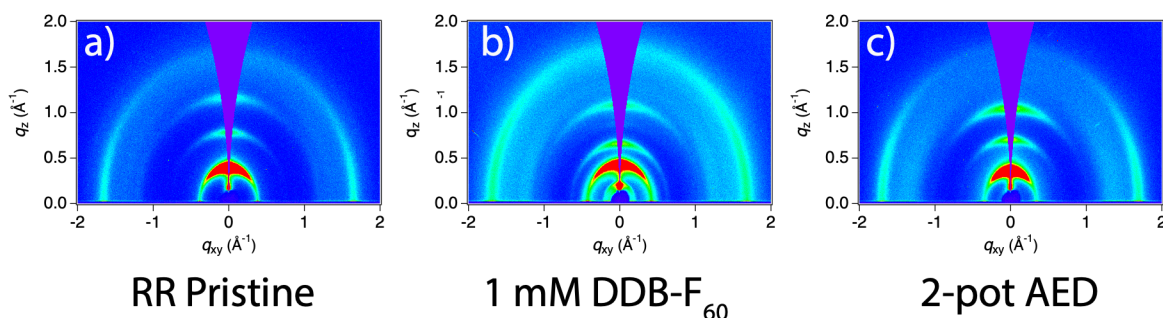


Figure A9. 2D GIWAXS diffractograms for ACN-washed (a) pristine RR P3HT, (b) RR P3HT conventionally doped with 1 mM DDB-F₆₀, and (c) RR P3HT doped via 2-pot AED with 104 mM LiTFSI. 1D integrations in OOP and IP directions are shown in **Figure A10**.

As mentioned in the main text, we also studied the structural changes in RR P3HT doped with DDB-F₆₀ and followed by 2-pot AED with LiTFSI. Like the PBTTT samples, the P3HT samples doped via both methods did not show noticeable signs of dedoping after solvent washing. **Figure A9** shows the 2D diffractograms of the ACN-washed pristine, DDB-F₆₀-doped, and 2-pot AED-doped RR P3HT films. The corresponding 1D patterns produced by radial integration along the q_{xy} - and q_z -axes (in-plane and out-of-plane directions, respectively) are plotted in **Figure A10a,b**. Panels (c,d) show the 1D OOP and IP integrations for the unwashed samples.

Figure A10 shows how the lamellar ($(h00)$, out-of-plane) and π -stacking ((020) , in-plane) structure of RR P3HT changes after doping with 1 mM DDB-F₆₀ and again after 2-pot AED. The structural changes we observed are qualitatively similar to those reported in the main text for PBTTT. The pristine RR P3HT (100) peak and its corresponding overtones appear at distances representing a lamellar spacing of 16 Å, as previously reported.^[3,4,8–10] As the pristine polymer is doped with the bulky DDB-F₆₀ dopant, the pristine structure undergoes a large expansion, creating a new, highly expanded lamellar structure, with peaks denoted by $(h00)'$, in agreement with previous studies.^[3,4] Due to the large expansion, the $(100)'$ peak is not visible, as it falls within the low- q region blocked by the beam. We note that when doping with a 1 mM DDB-F₆₀ solution, all of the lamellar peaks of the pristine structure have entirely disappeared, leaving only the overtones of the doped structure, indicating a complete transformation of the P3HT crystal lattice.

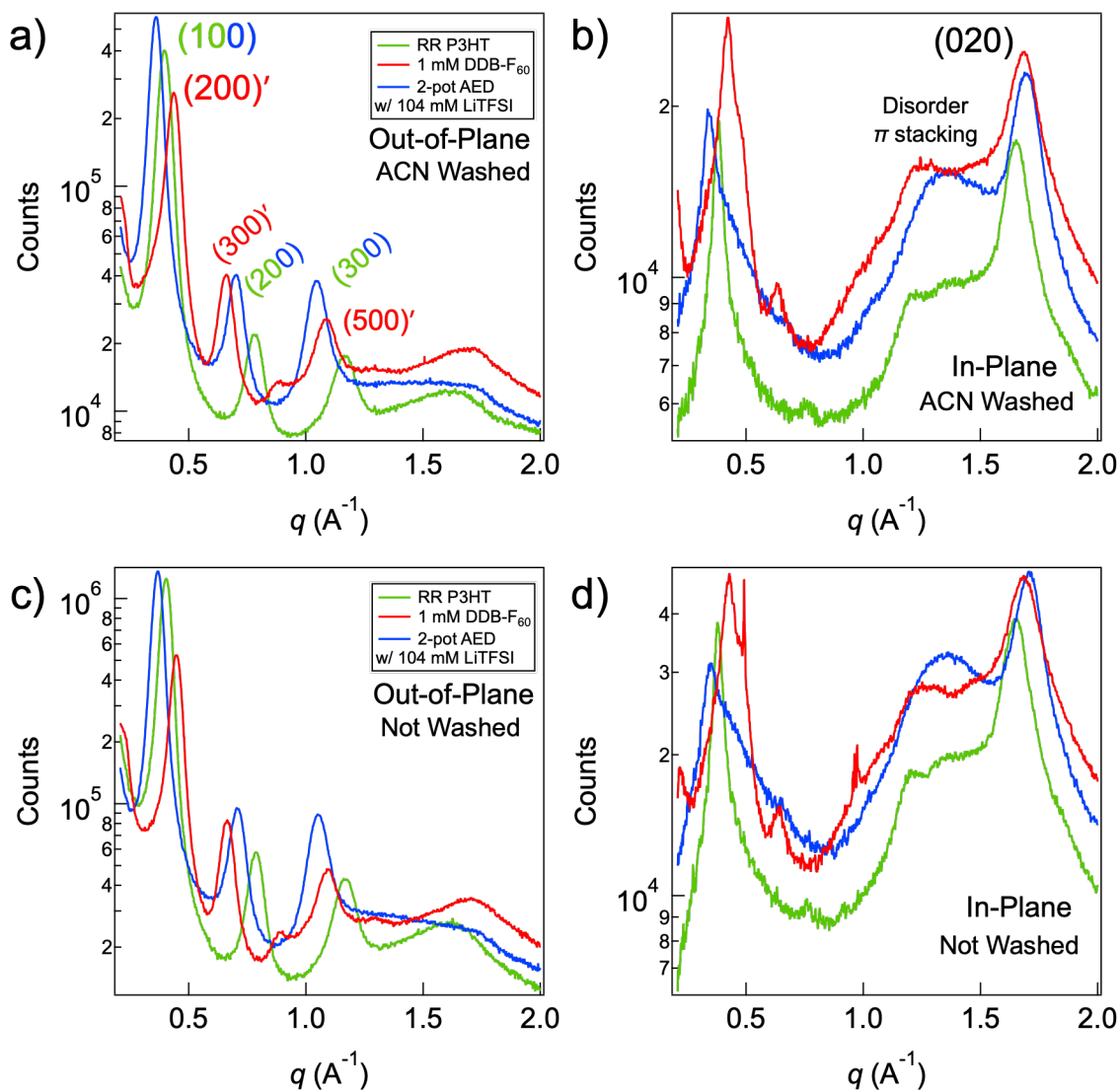


Figure A10. 1D integrations (a) out-of-plane and (b) in-plane for ACN-washed pristine RR P3HT, RR P3HT doped with 1 mM DDB- F_{60} , and RR P3HT doped via the 2-pot AED method. Panels (c,d) represent the out-of-plane and in-plane integrations, respectively, for the unwashed RR samples. The similarity between ACN-washed samples in panels (a,b) and the unwashed samples in panels (c,d) indicates that solvent washing did not affect the structure of the RR P3HT samples.

In the case of the 2-pot AED-doped RR P3HT samples, we see a much smaller shift in the q -spacing values relative to the pristine P3HT samples. As discussed in the main text, this verifies that the 2-pot AED process achieved full anion exchange, as the smaller TFSI $^{-}$ anions only lead to a slight expansion of the lamellar spacing relative to the large expansion caused by the bulky DDB-

F_{60}^- anion. This reversal of the DDB- F_{60} -induced lattice expansion indicates that anion exchange alleviates some of the structural disorder caused by the initial doping process.

In the in-plane integration, we only see a slight shift in q -spacing values of the (020) upon doping with DDB- F_{60} , indicating that the original π -stacking of the pristine polymer is largely preserved; we believe that this is because the lamellar expansion is so large that the P3HT backbones do not need to un-tilt or otherwise move to accommodate the large dopant counterion. Upon 2-pot AED, the (020) shifts to higher q -spacing values, consistent with the reorientation of the unit cell needed to accommodate the smaller TFSI $^-$ anion between the polymer side chains.

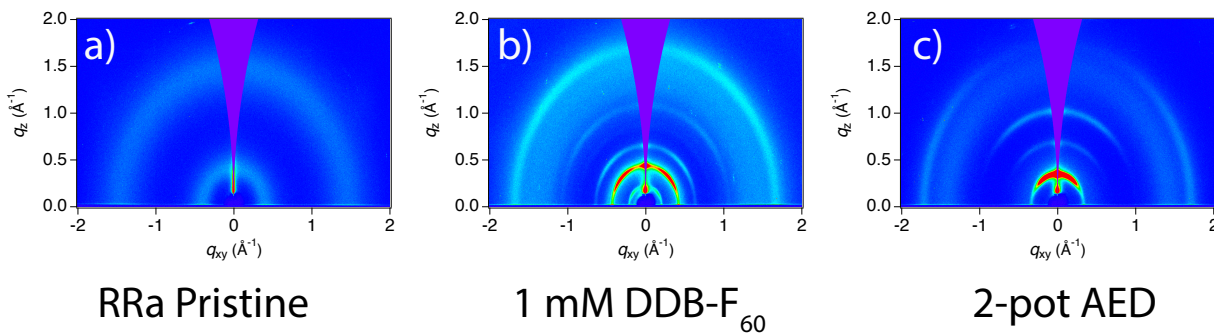


Figure A11. 2D GIWAXS diffractograms of washed (a) RRa P3HT, (b) RRa P3HT conventionally doped using a 1 mM DDB- F_{60} solution, and (c) the same doped RRa P3HT subjected to 2-pot AED with 104 mM LiTFSI. Doping induces an increase in crystallinity in the originally amorphous RRa P3HT polymer films, as seen in prior studies.

Figure A11 shows 2D GIWAXS diffractograms for washed pristine RRa P3HT and RRa P3HT doped both conventionally with DDB- F_{60} and subsequently subjected to 2-pot AED. Pristine RRa P3HT shows only two very diffuse and broad isotropic scattering rings, one corresponding to the lamellar spacing and the other to an amorphous π -stacking distance, indicating the absence of long-range crystalline domains. The isotropic rings indicate a lack of preferred crystallite orientation relative to the substrate.

Upon doping RRa P3HT with 1 mM DDB-F₆₀ and then via 2-pot AED, we see a large increase in ordering, as indicated by the appearance of distinct lamellar and π -stacking peaks (**Figures A11 and A12**). Doping-induced crystallization has been reported previously in RRa P3HT doped with F₄TCNQ and other DDB-based dopants,^[5] so it is no surprise that we see a dramatic increase in structural ordering when doping using DDB-F₆₀ and via the 2-pot AED method.

For RRa P3HT doped with 1 mM DDB-F₆₀, we see the appearance of new crystallites with a highly expanded lamellar spacing (indexed as (*h*00)') with a fundamental scattering peak at $\sim 0.2 \text{ \AA}^{-1}$. This indicates successful intercalation of the large DDB-F₆₀⁻ anions into the polymer matrix, which induces ordering in it. The in-plane integration also shows the formation of a sharp (020) peak near $q_{xy} \sim 1.70 \text{ \AA}^{-1}$. Upon 2-pot AED, these peaks shift to values expected for P3HT doped with TFSI⁻ anions, mirroring the behavior seen with RR P3HT and PBTTT. We note that doping RRa P3HT via both methods still shows scattering at $1.4 \text{ \AA}^{-1}$, which is associated with amorphous π -stacking, indicating that although RRa P3HT undergoes doping-induced crystallization,^[5,11] the crystallites are much less ordered than those in RR P3HT or PBTTT.

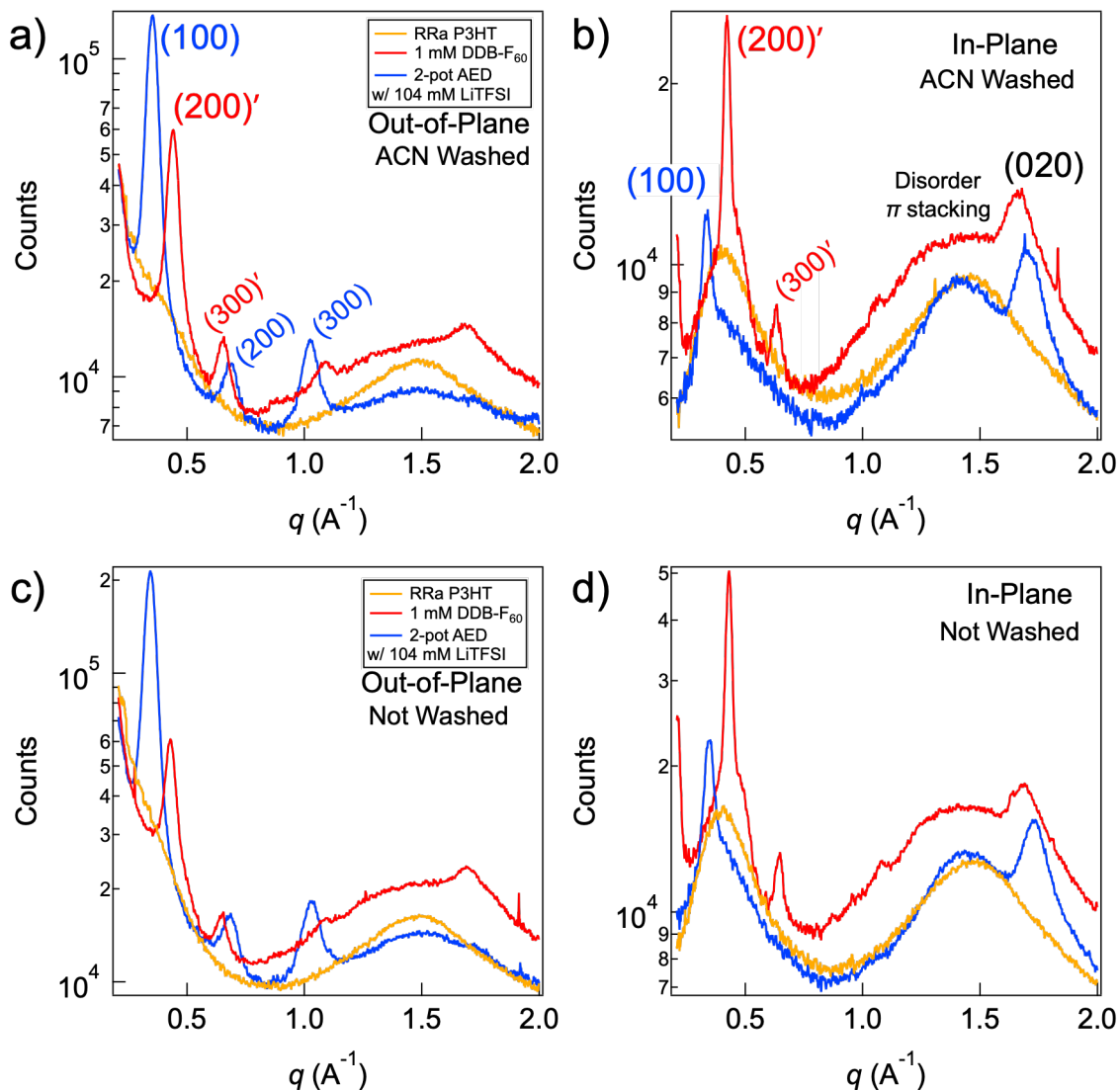


Figure A12. Radially integrated out-of-plane (a) and in-plane (b) GIWAXS patterns for washed RRa P3HT films doped with DDB- F_{60} and films subjected to 2-pot AED. Doped RRa P3HT shows a large doping-induced crystallization, as indicated by the formation of ($h00$) and (020) peaks compared to the pristine film. Panels (c,d) show the unwashed 1D integrations along the out-of-plane and in-plane directions, respectively, and indicate no major structural changes due to solvent washing.

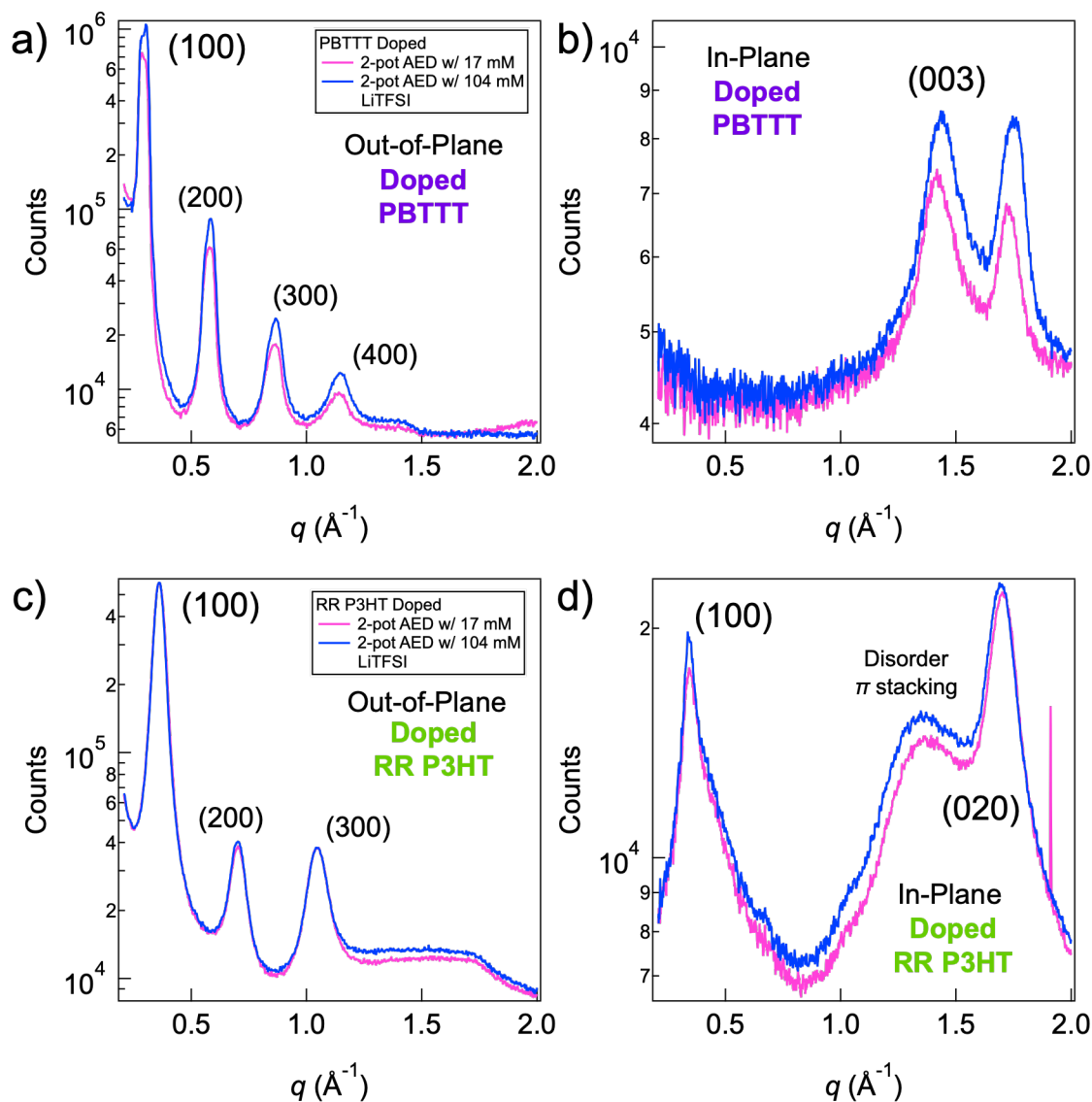


Figure A13. 1D integrated out-of-plane and in-plane GIWAXS patterns for (a,b) PBTtT and (c,d) P3HT doped via the 2-pot AED method with 17 mM (pink curves) and 104 mM (blue curves) LiTFSI. Both PBTtT and P3HT doped via the 2-pot AED method show similar q -spacing values along the out-of-plane (lamellar spacing) and in-plane (π -stacking spacing) directions at low and high electrolyte concentrations, indicating they have similar structures and that anion exchange has gone to completion even at lower dopant-to-electrolyte ratios.

A.4 Cyclic Voltammetry (CV) of PBTtT and DDB-F₆₀

Cyclic voltammetry (CV) measurements were performed to estimate the doping boost required to see double doping from the DDB-F₆₀[−] anion in PBTtT. CV scans were measured in a three-electrode cell using an electrolyte composed of 100 mM TBAPF₆ in ACN. For the PBTtT

CV, a polymer film was cast onto a pre-cleaned ITO substrate, which served as the working electrode (WE). A Pt sheet was used as the counter electrode (CE), and the reference electrode was a nonaqueous Ag/Ag⁺ electrode consisting of an Ag wire immersed in 1 mM AgNO₃ in 100 mM TBAPF₆ in ACN, separated by a glass frit. The DDB-F₆₀ CV was measured by dissolving 1 mM DDB-F₆₀ in the electrolyte, using a Pt sheet as the CE, a glassy carbon electrode (GCE) as the WE, and the same nonaqueous Ag/Ag⁺ reference electrode. Both CV scans were collected at a scan rate of 10 mV s⁻¹. The CV plots shown here are the first scan. All potentials were referenced internally to the Fc/Fc⁺ redox couple.

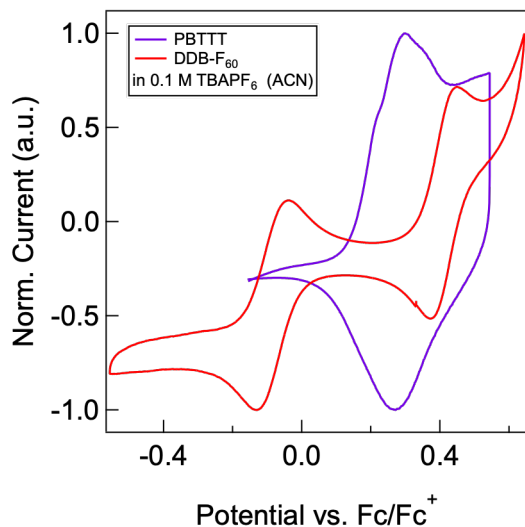


Figure A14. Cyclic voltammograms of PBTtT and DDB-F₆₀ measured in a 100 mM TBAPF₆ electrolyte solution in ACN using a three-electrode cell. The PBTtT CV was collected using ITO as the working electrode, a Pt sheet as the counter electrode, and a nonaqueous Ag/Ag⁺ reference electrode consisting of an Ag wire in 1 mM AgNO₃/100 mM TBAPF₆ in ACN separated by a glass frit. The CV for DDB-F₆₀ was measured by dissolving 1 mM DDB-F₆₀ in the electrolyte and using a Pt sheet as the counter electrode, a glassy carbon electrode (GCE) as the working electrode, and the same nonaqueous Ag/Ag⁺ reference electrode described above. All potentials were referenced to the Fc/Fc⁺ redox couple measured under identical conditions.

Figure A14 shows the cyclic voltammograms of PBTtT (purple curve) and DDB-F₆₀ (red curve). Previous studies have used the oxidation onset potential, $E_{\text{onset}}^{\text{ox}}$, as an estimate of the

polymer HOMO level.^[12–15] $E_{\text{onset}}^{\text{ox}}$ was determined from the first oxidation feature (~ 0.5 V) by taking the intersection of the baseline at low potential with a tangent line drawn to the rising portion of the current. This analysis gives $E_{\text{onset}}^{\text{ox}} = +0.127$ V versus Fc/Fc⁺.

For DDB-F₆₀, prior studies have shown that the redox potential measured by CV can serve as a useful proxy for dopant electron affinity and, more generally, for its oxidizing strength toward a polymer.^[7,16,17] We therefore use the measured half-wave potential, approximated as the average of the oxidation and reduction peak potentials, $E_{1/2}$, as a proxy for the doping ability of DDB-F₆₀ and its anion. DDB-F₆₀ exhibits a first redox couple with $E_{1/2}^{(0/-1)} = +0.415$ V versus Fc/Fc⁺, followed by a second redox couple $E_{1/2}^{(-1/-2)} = -0.082$ V versus Fc/Fc⁺. As shown in **Figure A14**, the DDB-F₆₀[−] anion is not expected to further oxidize PBTTT, since $E_{1/2}^{(-1/-2)}$ lies at a lower potential than the PBTTT $E_{\text{onset}}^{\text{ox}}$.

To obtain the values reported in **Figure 2.1** of the main text, the measured potentials were shifted onto the vacuum scale by pinning the PBTTT HOMO to the widely reported value of -5.1 eV versus vacuum^[18–20] and offsetting the measured $E_{\text{onset}}^{\text{ox}}$ versus Fc/Fc⁺ accordingly, which gives an offset of 4.97 eV. Applying this same offset to the two DDB-F₆₀ redox potentials gives energies of approximately $E_{1/2}^{(0/-1)} \sim -5.4$ eV and $E_{1/2}^{(-1/-2)} \sim -4.9$ eV versus vacuum.

A.5 References

- [1] M. S. Messina, J. C. Axtell, Y. Wang, P. Chong, A. I. Wixtrom, K. O. Kirlikovali, B. M. Upton, B. M. Hunter, O. S. Shafaat, S. I. Khan, J. R. Winkler, H. B. Gray, A. N. Alexandrova, H. D. Maynard, A. M. Spokoyny, *J. Am. Chem. Soc.* **2016**, *138*, 6952.
- [2] A. D. Ready, Y. A. Nelson, D. F. Torres Pomares, A. M. Spokoyny, *Acc. Chem. Res.* **2024**, *57*, 1310.

- [3] T. J. Aubry, J. C. Axtell, V. M. Basile, K. J. Winchell, J. R. Lindemuth, T. M. Porter, J.-Y. Liu, A. N. Alexandrova, C. P. Kubiak, S. H. Tolbert, A. M. Spokoyny, B. J. Schwartz, *Advanced Materials* **2019**, *31*, 1805647.
- [4] T. J. Aubry, K. J. Winchell, C. Z. Salamat, V. M. Basile, J. R. Lindemuth, J. M. Stauber, J. C. Axtell, R. M. Kubena, M. D. Phan, M. J. Bird, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2020**, *30*, 2001800.
- [5] Y. Wu, C. Z. Salamat, A. León Ruiz, A. F. Simafranca, N. Akmanşen-Kalayci, E. C. Wu, E. Doud, Z. Mehmedović, J. R. Lindemuth, M. D. Phan, A. M. Spokoyny, B. J. Schwartz, S. H. Tolbert, *Chem. Mater.* **2024**, *36*, 5552.
- [6] E. C. Wu, D. G. Vidales, C. Z. Salamat, Q. M. Duong, A. León Ruiz, A. D. Ready, Z. Mehmedović, D. A. Stanfield, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Advanced Functional Materials* *n/a*, e07480.
- [7] I. E. Jacobs, Y. Lin, Y. Huang, X. Ren, D. Simatos, C. Chen, D. Tjhe, M. Statz, L. Lai, P. A. Finn, W. G. Neal, G. D’Avino, V. Lemaure, S. Fratini, D. Beljonne, J. Strzalka, C. B. Nielsen, S. Barlow, S. R. Marder, I. McCulloch, H. Sirringhaus, *Advanced Materials* **2022**, *34*, 2102988.
- [8] P. A. Finn, I. E. Jacobs, J. Armitage, R. Wu, B. D. Paulsen, M. Freeley, M. Palma, J. Rivnay, H. Sirringhaus, C. B. Nielsen, *Journal of Materials Chemistry C* **2020**, *8*, 16216.
- [9] M. Brinkmann, *Journal of Polymer Science Part B: Polymer Physics* **2011**, *49*, 1218.
- [10] Y. Wu, Q. M. Duong, A. F. Simafranca, C. Z. Salamat, B. J. Schwartz, S. H. Tolbert, *ACS Materials Lett.* **2024**, *6*, 489.
- [11] P. Y. Yee, D. T. Scholes, B. J. Schwartz, S. H. Tolbert, *J. Phys. Chem. Lett.* **2019**, *10*, 4929.
- [12] J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li, Y. Yang, *Macromolecules* **2008**, *41*, 6012.
- [13] M. Al-Ibrahim, H.-K. Roth, M. Schroedner, A. Konkin, U. Zhokhavets, G. Gobsch, P. Scharff, S. Sensfuss, *Organic Electronics* **2005**, *6*, 65.
- [14] D. Giri, S. K. Saha, I. Anderson, A. Chakraborty, J. Kala, J. S. Müller, J. Nelson, R. K. Canjeevaram Balasubramanyam, S. Patil, *Advanced Functional Materials* **2025**, *35*, 2410815.
- [15] M. Segantini, A. Ballesio, G. Palmara, P. Zaccagnini, F. Frascella, G. Garzone, S. L. Marasso, M. Cocuzza, M. Parmeggiani, *Advanced Electronic Materials* **2022**, *8*, 2101332.

- [16] J. Li, I. Duchemin, O. M. Roscioni, P. Friederich, M. Anderson, E. D. Como, G. Kociok-Köhn, W. Wenzel, C. Zannoni, D. Beljonne, X. Blase, G. D'Avino, *Mater. Horiz.* **2019**, *6*, 107.
- [17] B. Wegner, L. Grubert, C. Dennis, A. Opitz, A. Röttger, Y. Zhang, S. Barlow, S. R. Marder, S. Hecht, K. Müllen, N. Koch, *J. Mater. Chem. C* **2019**, *7*, 13839.
- [18] I. McCulloch, M. Heeney, M. L. Chabinyc, D. DeLongchamp, R. J. Kline, M. Cölle, W. Duffy, D. Fischer, D. Gundlach, B. Hamadani, R. Hamilton, L. Richter, A. Salleo, M. Shkunov, D. Sparrowe, S. Tierney, W. Zhang, *Advanced Materials* **2009**, *21*, 1091.
- [19] J. E. Cochran, M. J. N. Junk, A. M. Glaudell, P. L. Miller, J. S. Cowart, M. F. Toney, C. J. Hawker, B. F. Chmelka, M. L. Chabinyc, *Macromolecules* **2014**, *47*, 6836.
- [20] A. K. Singh, A. Pandey, P. Chakrabarti, *Organic Electronics* **2019**, *75*, 105424.

Appendix B

Supporting Information for Chapter 3: The Effects of Humidity on the Electrical Properties and Carrier Mobility of Semiconducting Polymers Anion-Exchange Doped with Hygroscopic Salts

B.1 Materials

Poly(3-hexylthiophene-2,5-diyl) (P3HT; regioregularity 97.6%; $M_w = 60.15$ kDa) and F₄TCNQ (purity >99%) were purchased from Ossila. 1,2-dichlorobenzene (*o*-DCB, anhydrous, 99%), *n*-butyl acetate (*n*-BA, anhydrous, >99%), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and lithium hexafluorophosphate (LiPF₆) were purchased from Sigma-Aldrich. The 99% regioregular P3HT was purchased from TCI ($M_n = 27\text{--}45$ kDa), and the 93% regioregular P3HT ($M_w = 50\text{--}70$ kDa) was purchased from Rieke Metals.

B.2 Film Fabrication and Doping

Prior to spin-coating the polymer, the glass substrates underwent several steps. First, they were cut into 1.3×1.3 cm pieces and then sequentially cleaned using Alconox detergent, DI water, and acetone. Next, the glass substrates were plasma-etched for approximately 15 minutes. The samples were then transferred to a nitrogen glovebox for spin coating. A 2% w/v (20 mg/mL) P3HT solution in *o*-DCB was then spin-coated onto the substrate at 1000 rpm for 60 seconds, followed by 4000 rpm for 10 seconds. After spin-coating, the films were left to dry for approximately 30 minutes before the doping process. For doping, the films were exposed to a doping solution for 80 seconds and subsequently spin-coated at 4000 rpm for 10 seconds to eliminate any residual doping solution.

B.3 Conductivity and Hall Measurements

Before conducting the conductivity measurement, a 45-nm-thick layer of gold was deposited onto the doped films. This deposition process was carried out using the Angstrom Engineering Nexdep thermal evaporator at pressures below 1×10^{-6} torr and a deposition rate of 0.5 Å/s.

The conductivity measurement was initially performed within an argon glovebox. A Keithley 2400 Sourcemeter, controlled by LabVIEW software, was utilized for this purpose. The source currents were maintained below a total power of 1 mW. Following the measurement inside the argon glovebox, the samples were transferred to the ambient air environment. Subsequently, both conductivity and DC Hall measurements were conducted using a Lake Shore MeasureReady M91 FastHall instrument. In these measurements, a source current of 10 μA was employed. For the DC Hall measurements, a magnetic field strength of 1.0623 T was applied. To obtain the argon purge samples reported in the main text, argon gas was flowed into the MeasureReady M91 FastHall sample compartment for roughly 5 minutes prior to conducting the measurement.

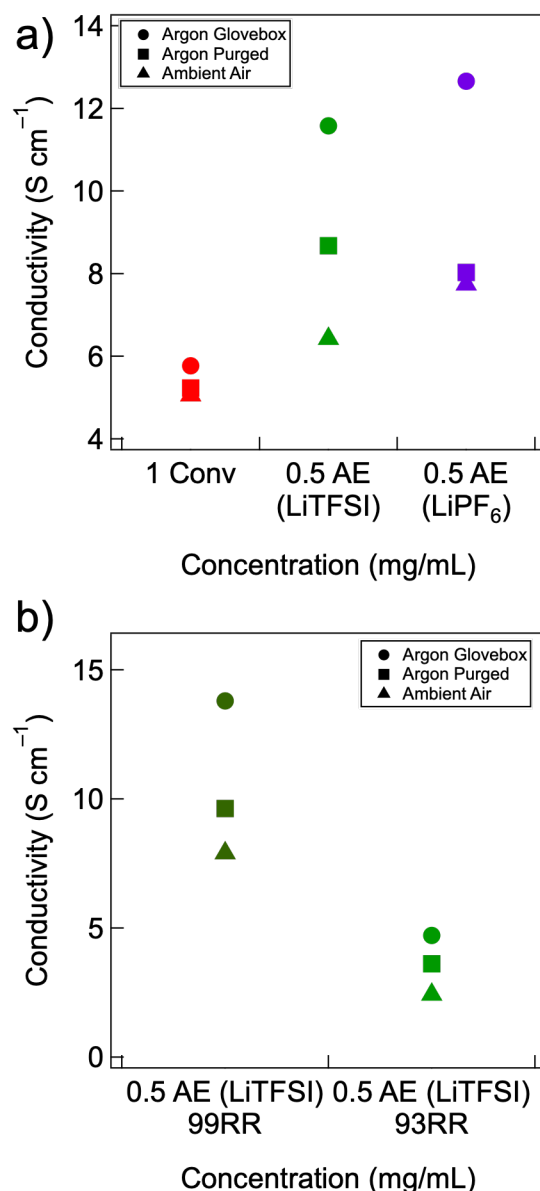


Figure B1. (a) Conductivity values for higher concentrations of dopants for conventional (1 mg/mL F₄TCNQ) and anion-exchange (0.5 mg/mL F₄TCNQ + 30 mg/mL LiTFSI and 0.5 mg/mL F₄TCNQ + 5 mg/mL LiPF₆)-doped 97% RR P3HT in three different environments. Similar to the result shown in **Table 3.1**, only samples doped with hygroscopic salts (LiTFSI and LiPF₆) show a drop in conductivity when exposed to the ambient environment. The sample doped with the conventional method (F₄TCNQ) remains unchanged within measurement error. (b) Conductivity of various P3HT regioregularities (99% RR and 93% RR) doped with 0.5 mg/mL F₄TCNQ + 30 mg/mL LiTFSI. Like the case for 97% RR P3HT, when 99% RR and 93% RR P3HT are doped with anion exchange, the electrical conductivity drops roughly by a factor of 2 for all regioregularities and doping concentrations once the samples are exposed to ambient air, indicating that LiTFSI absorbs water independently of the polymer.

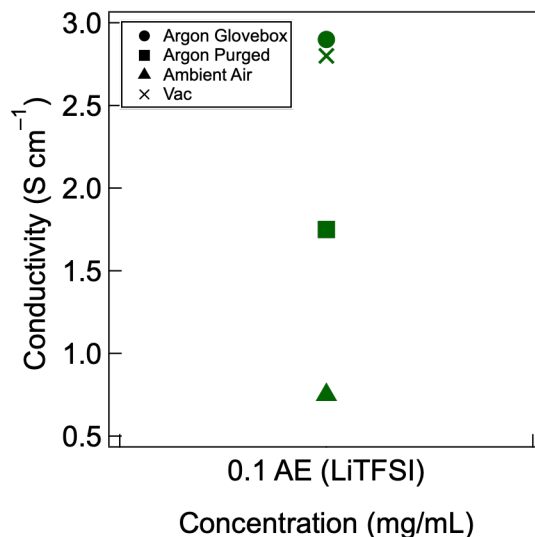


Figure B2. Conductivity values for the 97% RR P3HT doped with 0.1 mg/mL F₄TCNQ + 30 mg/mL LiTFSI via anion exchange (AE) were measured inside an argon glovebox, exposed to ambient air for 5 minutes, and subjected to four 5-minute vacuum/Ar-purge cycles in a chamber.

The electrical conductivity for 97% RR P3HT doped with 0.1 mg/mL F₄TCNQ + 30 mg/mL LiTFSI via anion exchange is shown in **Figure B2**. The conductivity is first measured in an inert Ar atmosphere, followed by air exposure, leading to a drop in the electrical conductivity. Purging the sample with Ar yields some of the conductivity back. Loading the sample into an antechamber and performing four 5-minute cycles of vacuum followed by Ar gas refill and remeasuring the conductivity using the same setup as in the “Ar Box” configuration recovers ~97% of the conductivity in the same sample (black × “Vac”). It is worth mentioning that the slightly higher conductivity observed in the argon glovebox can be attributed to the elevated temperature within the box compared to the ambient room temperature. Since transport in semiconducting polymer films is predominantly governed by hopping transport, higher temperatures lead to increased conductivity.

B.4 UV–Vis–NIR Spectroscopy

The Agilent Cary 600 Series FTIR Spectrometer was employed to measure the near-IR absorption spectra. The spectra were captured within the range of 1666–2500 nm to prevent any overlap with water stretches in the longer wavelength region. In order to investigate the impact of water on the P1 transition, the sample compartment of the FTIR spectrometer was subjected to dry N₂ gas flow for various durations, as mentioned in the main text.

Additionally, a Shimadzu UV3101PC Scanning Spectrophotometer was utilized for UV–vis–NIR spectroscopy. The slit width was set at 1 nm, and a sampling interval of 1 nm was employed. To ensure the UV–vis beam was accurately centered on the sample, a small 3D-printed aperture was utilized.

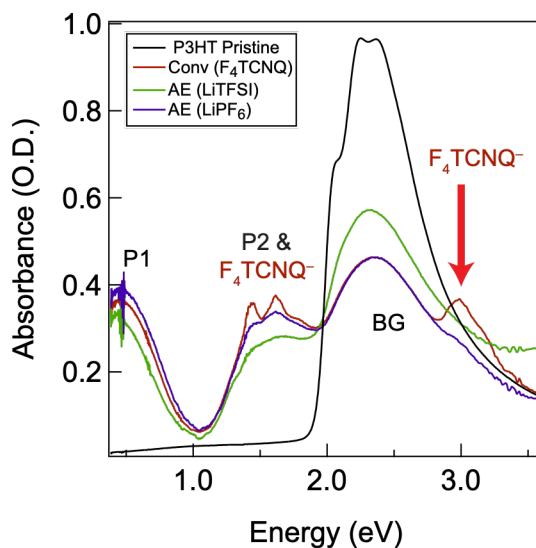


Figure B3. UV–vis–NIR spectra of P3HT samples doped with 0.5 mg/mL F₄TCNQ (red), 0.1 mg/mL F₄TCNQ anion-exchanged with 30 mg/mL LiTFSI (green), and 0.1 mg/mL F₄TCNQ anion-exchanged with 5 mg/mL LiPF₆ (purple) taken in ambient air.

Doping P3HT polymer films leads to the emergence of two polaronic transitions referred to as P1 and P2, which are centered around approximately 0.5 eV and 1.7 eV, respectively. In the

case of the sample doped solely with F₄TCNQ, the P2 transition overlaps with the F₄TCNQ anion vibronic transition, resulting in the observed peaks in the ~1.7 eV region. It is important to note that at a concentration of 0.5 mg/mL of F₄TCNQ, we primarily observe only the F₄TCNQ anions (~3.0 eV) rather than the neutral form (~3.2 eV). This suggests that the F₄TCNQ present in the films is likely, if not entirely, engaged in doping the polymers. However, for anion-exchange-doped P3HT films, the F₄TCNQ is substituted with the salt anion used, causing most of the F₄TCNQ vibronic features to be absent, as depicted in the green and purple traces.

B.5 Humidity-Sensing Measurement

A homemade setup was used to measure conductivity as a function of humidity. To prevent additional moisture from entering, the setup was carefully sealed using vacuum grease. Gradual moisture removal was facilitated by using Drierite within the setup. A digital hygrometer was then used to track the humidity, while conductivity was measured using a Keithley 2400 Sourcemeeter.

Appendix C

Supporting Information for Chapter 4: How the Carrier Mobility and Seebeck Coefficient of Doped Semiconducting Polymers Are Controlled by Counterion Interactions and Mesoscale Order

C.1 Materials

Poly(3-hexylthiophene-2,5-diyl) (P3HT; regioregularity 97.6%, $M_w = 60,150$ g/mol) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ; purity >99.0%) were purchased from Ossila. 1,2-dichlorobenzene (*o*-DCB, anhydrous, 99.0%), *n*-butyl acetate (*n*-BA, anhydrous, >99%), dichloromethane (DCM, anhydrous, 99.8%), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Sigma-Aldrich. All chemicals were used as received. The DDB-based dopants DDB-F₇₂ and DDB-F₃₆ were synthesized according to a previously reported procedure.^[1,2]

C.2 UV–Vis–NIR Spectroscopy

As mentioned in the main text, the anion-exchange method is more efficient at doping compared to conventional F₄TCNQ doping.^[3] However, the P1 polaron absorption intensity at the highest doping concentration is nearly identical for both methods, suggesting a similar doping efficiency. The difference in solvents used for doping explains this outcome. Our F₄TCNQ doping used dichloromethane (DCM), a more effective swelling solvent for P3HT, whereas our anion-exchange doping employs *n*-butyl acetate (*n*-BA), chosen for its high solubility for LiTFSI. Because DCM swells the polymer more, its use allows F₄TCNQ to intercalate into and thus dope the P3HT film more thoroughly. Despite this swelling advantage, F₄TCNQ doping from DCM appears to be reaching its limit in doping power, as indicated by a slower increase in P1 intensity with each successive concentration. In contrast, the anion-exchange method has further doping potential if the dopant concentration were to be further increased.

A similar pattern as to how the P1 intensity changes with dopant concentration is seen in films doped with DDB-F₇₂ and DDB-F₃₆. DDB-F₇₂ continues to increase doping level with increasing dopant concentration, while DDB-F₃₆ reaches a doping limit as the concentration is

increased. This is consistent with DDB-F₇₂'s stronger oxidizing power, which as shown by Aubry *et al.*,^[4] can not only dope the amorphous regions but also further dope the crystalline regions to the point of causing structural disorder. On the other hand, although DDB-F₃₆ is slightly more oxidizing than F₄TCNQ and can likely dope the amorphous regions to some extent, it lacks the ability to further dope and disrupt the structure to the same extent as DDB-F₇₂.^[4]

C.3 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS)

GIWAXS measurements were performed on P3HT films deposited on Si substrates at the Stanford Synchrotron Radiation Lightsource (SSRL, beamline 11-3) using an X-ray energy of 12.7 keV and an incidence angle of 0.12°. Films were prepared under the same conditions and doping concentrations described in the main text. Substrates were cleaned and plasma treated prior to film deposition, after which samples were handled under inert atmosphere. GIWAXS samples were prepared at the same doping concentrations and spinning parameters listed in the experimental section of the main text.

The GIWAXS 2D data were calibrated using the Igor macro Nika. Nika and WAXStools were used to reduce the data. For a 2D diffractogram, integrations along the q_z direction in **Figure C1** provide information about periodicity along the out-of-plane (OOP), and integrations along the q_{xy} direction in **Figure C1** provide information about in-plane (IP) periodicity. **Figure C1** shows the 2D diffractograms for the highest-doped P3HT samples for each dopant used in this study. These are the same samples from **Figure 4.3** in the main text.

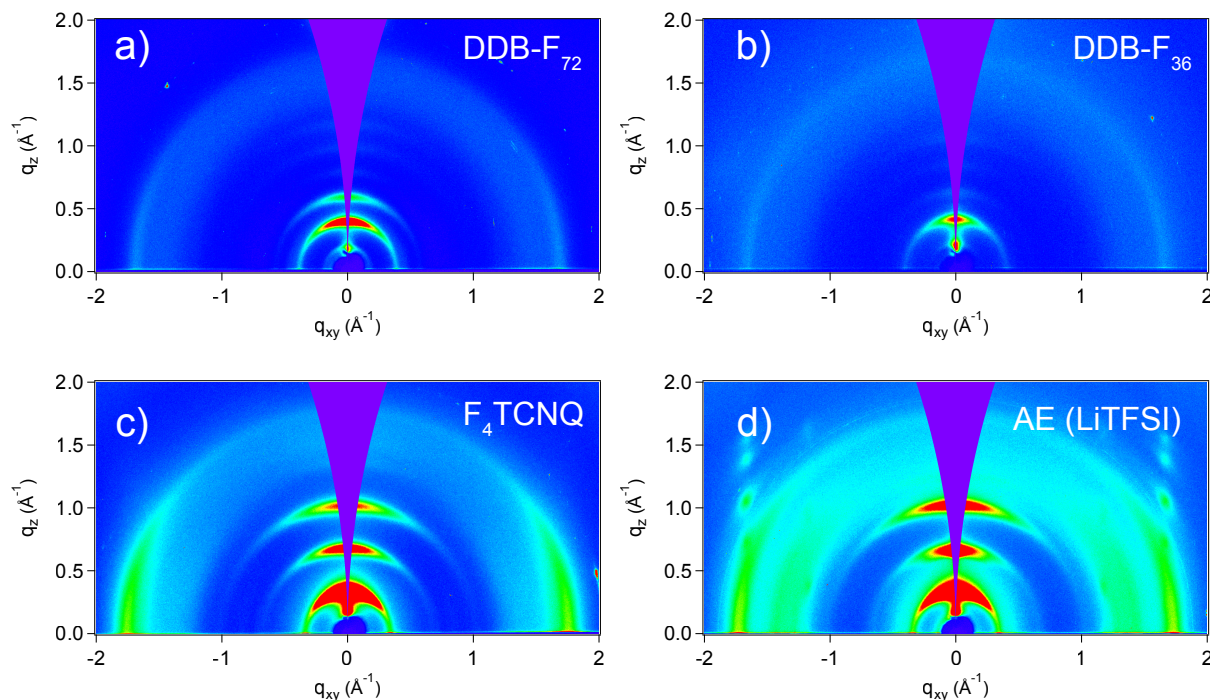


Figure C1. 2D GIWAXS diffractograms for P3HT doped with (a) 0.3 mM DDB-F₇₂, (b) 1 mM DDB-F₃₆, (c) 3.62 mM F₄TCNQ, and (d) 3.62 mM F₄TCNQ plus 104.5 mM LiTFSI via anion exchange.

Figures C2 and C3 show the OOP and IP integrations of the 2D diffractograms as a function of dopant concentration, stacked into a single plot. For the DDB-based dopants, we see similar structural changes upon doping with the large DDB dopants as in previous work.^[2,4] This includes a shift of the lamellar spacing to a much larger distance in the OOP direction (**Figure C2a,b**). So large, in fact, that the (100) peak is lost under the beamstop, and only the higher-order lamellar overtones are observed. In the IP direction (**Figure C3a,b**), the appearance of a broad peak around 1.4 Å⁻¹ indicates some disordering of polymer crystallites, likely due to the large size of the counterion that is inserted into the polymer network. This disordering becomes even more obvious at higher concentrations that we did not include the 1 mM DDB-F₇₂ samples in this study.

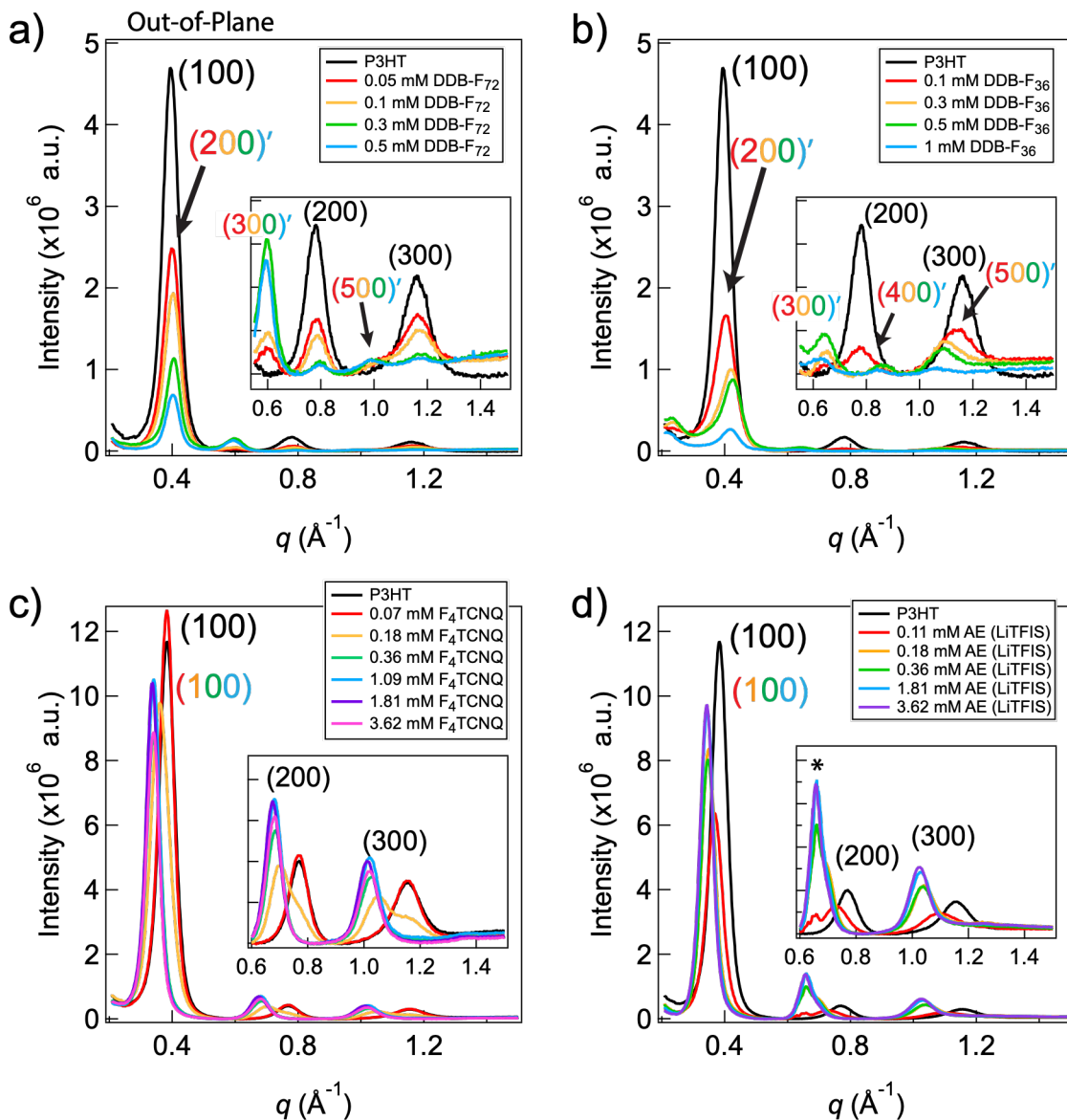


Figure C2. GIWAXS out-of-plane 1D integrations for P3HT doped with (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, (d) F₄TCNQ plus LiTFSI via anion exchange (AE). For anion-exchange-doped (AE) samples, the concentrations are reported based on the amount of F₄TCNQ added, plus 104.5 mM LiTFSI. The black (100) curve indicates the primary lamellar scattering for pristine P3HT, while the rainbow-colored (*h*00) curves are for the various doped P3HT samples. Peaks labeled with an asterisk (*) are from excess LiTFSI salt crystals on the surface of the anion-exchange-doped films.

In contrast to the DDB-based dopants, which show two-phase coexistence between the doped and undoped structures across a broad range of dopant concentrations, the phase transition

behavior in the F₄TCNQ sample occurs at very low doping levels, and all samples show effectively the same crystal structure after the initial first-order phase transition, regardless of doping level (**Figures C2c and C3c**). The anion-exchange-doped samples in **Figures C2d and C3d** show similar behavior to the F₄TCNQ-doped material, with one difference. Although clear two-phase coexistence is observed at the phase transition concentration of 0.18 mM in **Figure C3c**, indicative of a first-order, discontinuous phase transition, **Figure C3d** shows a gradual shift in peak position across the phase transition. Once transformed, however, the structure in the anion-exchange-doped samples remains fixed, regardless of doping level.

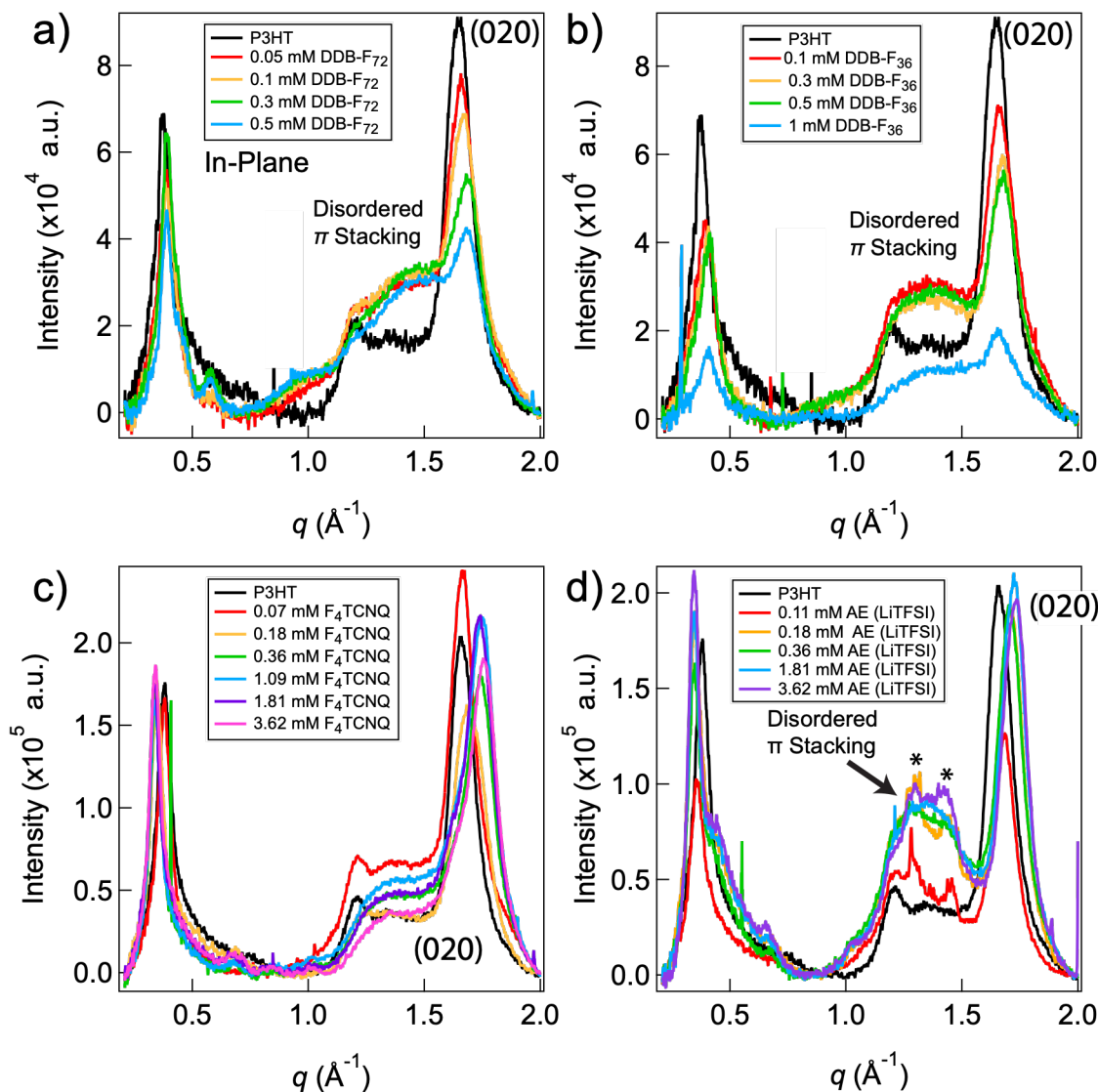


Figure C3. GIWAXS in-plane 1D integrations for P3HT doped at various levels with: (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, (d) F₄TCNQ plus LiTFSI via anion exchange (AE). For anion-exchange-doped samples, the concentrations reported in the legend are based on the amount of F₄TCNQ added plus a constant concentration of 104.5 mM LiTFSI. Peaks labeled with an asterisk (*) are from excess LiTFSI salt crystals on the surface of the anion-exchange-doped films.

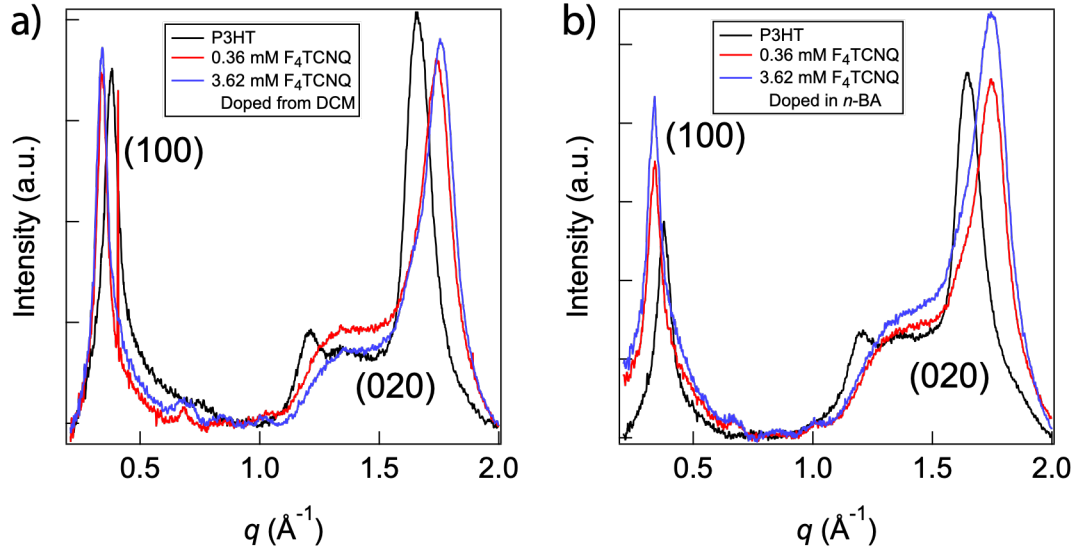


Figure C4. In-plane GIWAXS integrations for pristine P3HT (black curves) and P3HT doped with F₄TCNQ at 0.36 mM (red curves) and 3.62 mM (blue curves) using (a) DCM and (b) *n*-BA as the doping solvent. The diffraction patterns are almost identical for both solvents, indicating that the solvent choice alone is not important for determining structural change. These data serve as a control for the anion-exchange-doped samples, which show the appearance of a pronounced scattering peak near 1.4 Å⁻¹ that is associated with scattering from a disordered π -stacking region. Because the F₄TCNQ-doped P3HT films do not exhibit the strong scattering feature near 1.4 Å⁻¹ upon doping from either solvent, these data suggest that the additional scattering from the disordered π -stacking feature observed in the AE-doped samples is indeed associated with AE-induced ordering of the less ordered/amorphous fraction and is not due to the use of *n*-BA as the doping solvent.

Paracrystallinity ($g_{(h00)}$ (%)) was extracted from the GIWAXS data using **Equation (C1)** based on Williamson–Hall (W–H) analysis:^[5–7]

$$\text{FWHM}_{(h00)} \propto \frac{\pi^2 g_{(h00)}^2}{d_{(h00)}} m^2, \quad (\text{C1})$$

where $d_{(h00)}$ is the lamellar spacing and m is the diffraction order. The $d_{(h00)}$ spacing and full width at half maximum (FWHM) of the ($h00$) reflections were obtained by Voigt fitting in reciprocal space. The FWHM values were then plotted as a function of m^2 , and the slope of the linear fit is proportional to $g_{(h00)}^2$. The extracted $g_{(h00)}$ (%) values were then plotted as a function of carrier

density in **Figure C5** for all of the samples in this study. The $g_{(h00)}$ values for P3HT doped with either DDB-F₇₂ or F₄TCNQ remain similar to that of the pristine sample. Similarly, the anion-exchange-doped sample showed some variation in paracrystallinity, first increasing in the partly filled lattice and then decreasing again at higher doping levels, but no systematic trends in the value were observed. In the case of P3HT doped with DDB-F₃₆, $g_{(h00)}$ increases upon doping to about 15%, indicating doping-induced lattice disorder. Overall, except perhaps for DDB-F₃₆, the paracrystallinity does not show a strong systematic dependence on carrier density, with most values remaining close to the ~10% observed for pristine P3HT. Because paracrystallinity reflects local lattice disorder within crystalline domains, rather than the larger-scale domain size evolution, it is not expected to follow the same trend as the GISAXS-derived domain size (R_g) discussed in the main text.

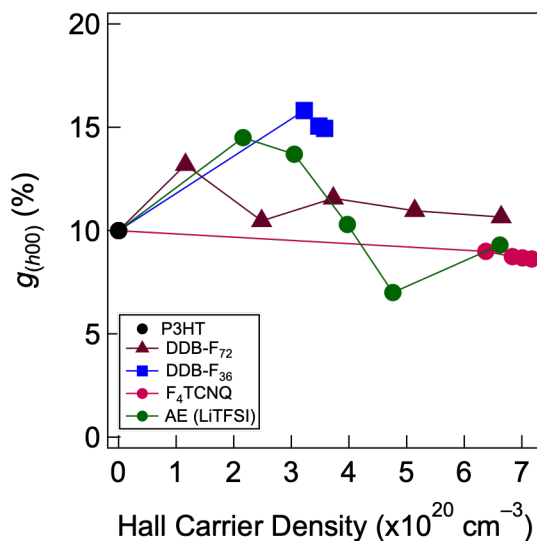


Figure C5. Paracrystallinity ($g_{(h00)}$ (%)) from GIWAXS versus carrier density for P3HT doped with DDB-F₇₂ (brown triangles), DDB-F₃₆ (blue squares), F₄TCNQ (pink circles), and F₄TCNQ plus LiTFSI via anion exchange (green circles).

C.4 Grazing-Incidence Small-Angle X-ray Scattering (GISAXS)

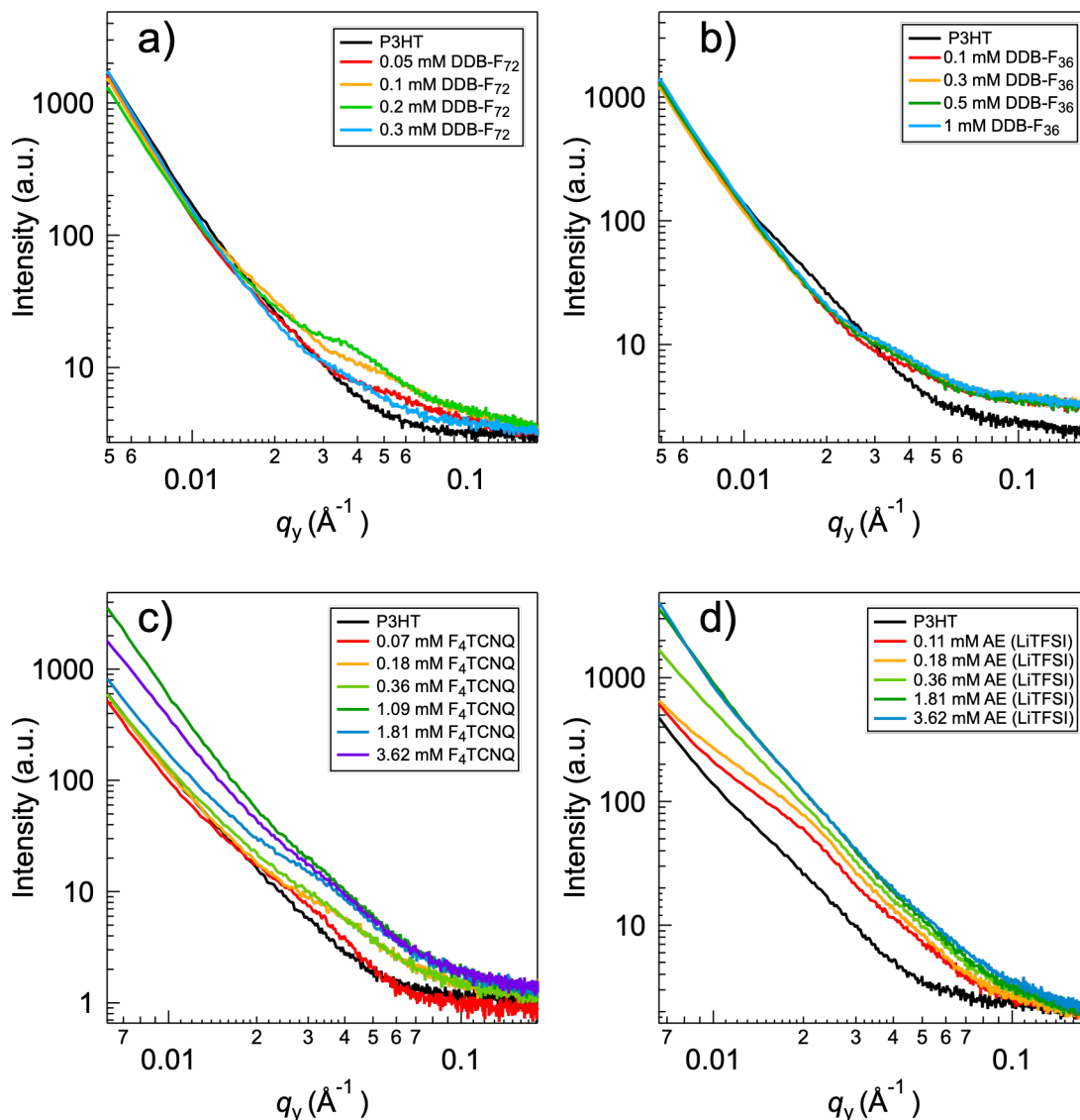


Figure C6. Horizontal 1D integrations of GISAXS data for all concentrations of P3HT doped with: (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, and (d) via anion exchange (F₄TCNQ with 104.5 mM LiTFSI). The scattering from pristine P3HT (black curves) is also plotted in all panels for reference.

GISAXS measurements were performed on the same GIWAXS films described above.

Figure C6 shows the horizontal integrations of the 2D GISAXS data near the Yoneda band for P3HT doped at the various concentrations of the different dopants presented in the main text. The

1D integrations for P3HT doped with DDB-F₇₂ show a well-defined peak, particularly at intermediate doping levels, while the peaks in the DDB-F₃₆-doped materials are smaller, suggesting less sharp density differences. P3HT doped using F₄TCNQ and via anion exchange also shows clear peaks, especially at the low and mid doping concentrations.

To be able to extract the domain sizes from the GISAXS data of our doped P3HT films, we carried out fits for the 1D integrated GISAXS traces using the Unified Fit method,^[8,9] which has been shown to be an accurate fitting model for weakly correlated films with diffuse, non-specular scattering.^[8,10] For a system with multilevel structures, the total scattering can be expressed as

Equation (C2):

$$I(q) = \sum_{i=1}^n \left[G_i \exp\left(\frac{-q^2 R_{g,i}^2}{3}\right) + B_i (q_i^*)^{-P_i} \exp\left(\frac{-q^2 R_{g,i-1}^2}{3}\right) \right], \quad (\text{C2})$$

where $q_i^* = q[\text{erf}(\frac{kqR_{g,i}}{\sqrt{6}})]^{-3}$. For a level i , the first term gives the Guinier scattering regime with a prefactor, G_i and a characteristic size given by $R_{g,i}$. The second term represents the power-law Porod scattering regime with prefactor B_i , and structure P_i .^[9]

Other than the anion-exchange-doped samples, which exhibit two distinct shoulders, we observe only one characteristic shoulder in the 1D GISAXS traces for all of the other dopants. The level 1 Unified Fit was utilized to capture the characteristic Guinier size, while the $R_{g,2}$ of level 2 was set to an arbitrarily large value (1×10^{10} with volume $G_2 = 0$) so that only P_2 shows up in the observable q range and compensates for the scattering intensity from even larger domains and other background scattering. The reported R_g values were averaged among triplicate samples. **Figure C7** shows the GISAXS Unified Fits for P3HT doped at the highest concentration for each dopant; the one exception is the DDB-F₇₂-doped samples, where the second-highest concentration is shown due to disordering at the highest concentration.

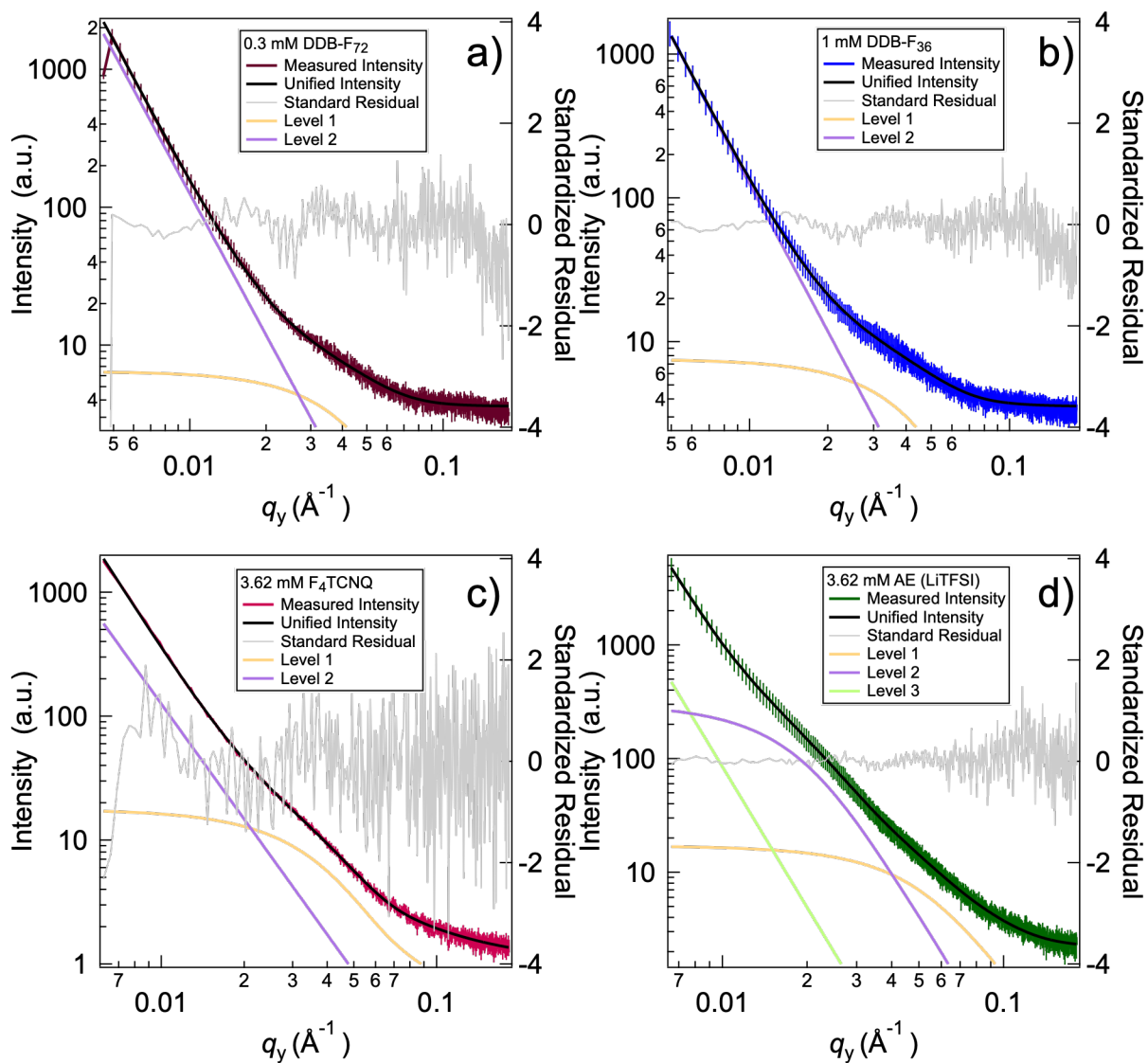


Figure C7. Representative Unified Fit modeling of doped P3HT using (a) 0.3 mM DDB-F₇₂, (b) 1 mM DDB-F₃₆, (c) 3.62 mM F₄TCNQ, and (d) 3.62 mM F₄TCNQ anion-exchanged with 104.5 mM LiTFSI.

Table C1. R_g values obtained from Unified Fit modeling of P3HT films doped with F₄TCNQ, via anion exchange (AE), and with DDB-F₇₂ and DDB-F₃₆ at all doping levels used in this study. Shaded columns give the dopant concentrations for reference. For comparison, P3HT doped with 3.62 mM F₄TCNQ from *n*-BA gives an R_g value similar to that obtained for F₄TCNQ doping from DCM, indicating that the larger R_g values observed for AE-doped samples are not produced by changing the solvent from DCM to *n*-BA, but instead result from doping-induced crystallization of originally disordered regions.

F ₄ TCNQ (DCM)	3.62 mM	1.81 mM	1.09 mM	0.36 mM	0.18 mM	0.07 mM
R_g (Å)	52	53	49	50	57	61
F ₄ TCNQ (<i>n</i> -BA)	3.62 mM	–	–	–	–	–
R_g (Å)	58	–	–	–	–	–
AE (LiTFSI) (<i>n</i> -BA)	3.62 mM	1.81 mM	0.36 mM	0.18 mM	0.11 mM	–
R_g (Å)	107/51	99	107	102	109	–
DDB-F ₇₂ (DCM)	0.5 mM	0.3 mM	0.2 mM	0.1 mM	0.05 mM	–
R_g (Å)	88	39	36	29	28	–
DDB-F ₃₆ (DCM)	1 mM	0.5 mM	0.3 mM	0.1 mM	–	–
R_g (Å)	58	46	42	32	–	–

C.5 Electrical Conductivity Measurements

Multifunctional devices for conductivity, Hall effect, and UV–vis–NIR spectroscopy were fabricated on 1.2×1.2 cm pre-cleaned glass substrates via sequential processing (SqP). Gold contact electrodes (1 mm square) were evaporated onto the corners of the samples. The van der Pauw method was used to measure the conductivities reported in the main text. The conductivities of the doped samples were measured using a Lake Shore MeasureReady M91 FastHall instrument, with a source current of 10 μ A. Given the high hygroscopicity of the anion-exchange-doped samples,^[11] the sample compartment of the MeasureReady M91 FastHall was argon-purged for 4

minutes before each measurement of these samples. In contrast, the samples doped with F₄TCNQ, DDB-F₇₂, and DDB-F₃₆ showed no significant humidity dependence; thus, purging was not necessary. All reported values were measured and averaged over at least three independent samples. All Hall effect, conductivity, temperature-dependent conductivity, and UV–vis–NIR spectroscopy measurements were performed on the exact same devices.

Figure C8 displays the electrical conductivity as a function of dopant concentration for the DDB-F₇₂, DDB-F₃₆, F₄TCNQ, and anion-exchange-doped P3HT samples. To facilitate comparison of charge transport characteristics across these doped systems, we aimed to maintain similar conductivity ranges (0–18 S cm⁻¹). In the case of P3HT doped using DDB-F₇₂, the dopant concentrations that gave conductivity values in this range were 0.05, 0.1, 0.2, 0.3, and 0.5 mM with DCM as the SqP doping solvent. For P3HT doped with DDB-F₃₆, we were able to obtain conductivity values in this range using 0.1, 0.3, 0.5, and 1 mM solutions in DCM. F₄TCNQ-doped P3HT gave conductivity values within this range at F₄TCNQ concentrations of 0.07, 0.18, 0.36, 1.09, 1.81, and 3.62 mM in DCM. Lastly, the conductivities of doped P3HT using the anion-exchange doping solutions were obtained at final concentrations of 0.11, 0.18, 0.36, 1.81, and 3.62 mM F₄TCNQ, with all solutions containing 104.5 mM LiTFSI in *n*-BA.

As shown in **Figure C8**, all dopants led to an increase in electrical conductivity with higher doping levels, consistent with the expected relationship:

$$\sigma = en\mu, \quad (\text{C3})$$

where σ is the conductivity, e is the elementary charge, n is the carrier density, and μ is the carrier mobility.

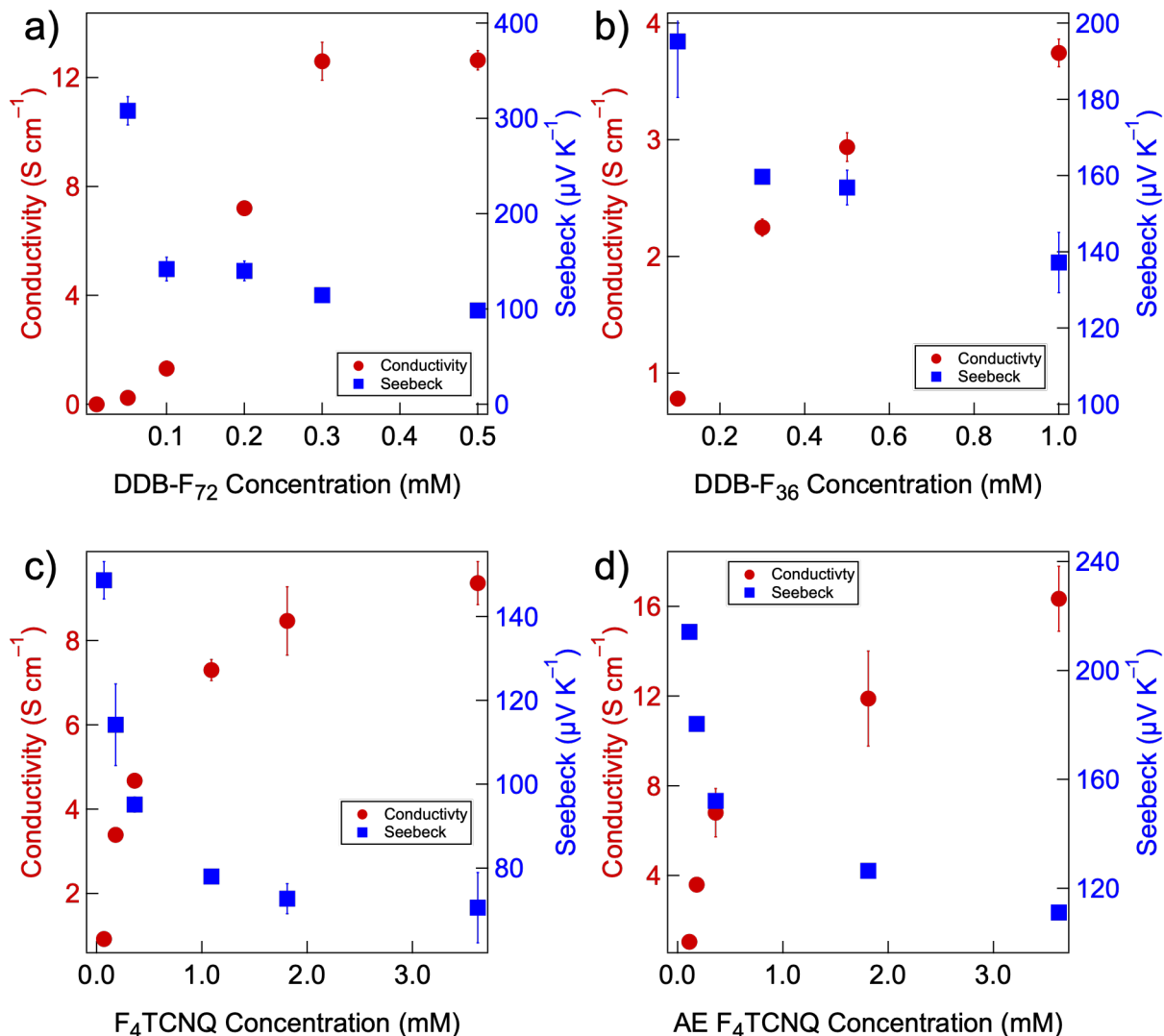


Figure C8. Electrical conductivity (σ) and Seebeck coefficient (S) of P3HT plotted as a function of dopant concentration for the four dopants used in this study. All doping cases demonstrate an inverse relationship between the conductivity and Seebeck coefficient: higher doping levels increase conductivity while decreasing the Seebeck coefficient. For anion-exchange-doped (AE) samples, the concentrations are reported based on the amount of F₄TCNQ, all with 104.5 mM LiTFSI added.

C.6 Seebeck Coefficient Measurements

The Seebeck coefficient measurements were conducted on separate pre-cleaned substrates with dimensions of 1.2×1.2 cm, using the SqP process. Gold contact electrodes, 1×10 mm in size, were evaporated onto the doped samples. Due to differences in the required electrode

geometry, it was not possible to measure both electrical conductivity and the Seebeck coefficient on the same device. Therefore, for each doping level, separate devices were prepared for measuring the Seebeck coefficient and electrical conductivity. These devices were fabricated and measured in parallel to ensure that they were fabricated and tested under the same environmental conditions. The Seebeck coefficient was measured at the same doping concentrations for each dopant as those described in the conductivity section and shown in **Figure C8**.

The Seebeck coefficient was obtained from the slope of a linear fit of the induced voltage due to a temperature gradient (ΔV) and the temperature difference between the hot side and the cold side ($\Delta T = T_{\text{hot}} - T_{\text{cold}}$). The Seebeck relation is given by **Equation (C4)**:

$$S = -\frac{\Delta V}{\Delta T}, \quad (\text{C4})$$

Figure C9 shows a linear relation between the voltages measured versus the applied temperature difference for P3HT doped with DDB-F₇₂, DDB-F₃₆, F₄TCNQ, and via anion exchange at various doping concentrations. We use the slopes from these lines to calculate the Seebeck coefficient values presented in **Figure C8** and in the main text.

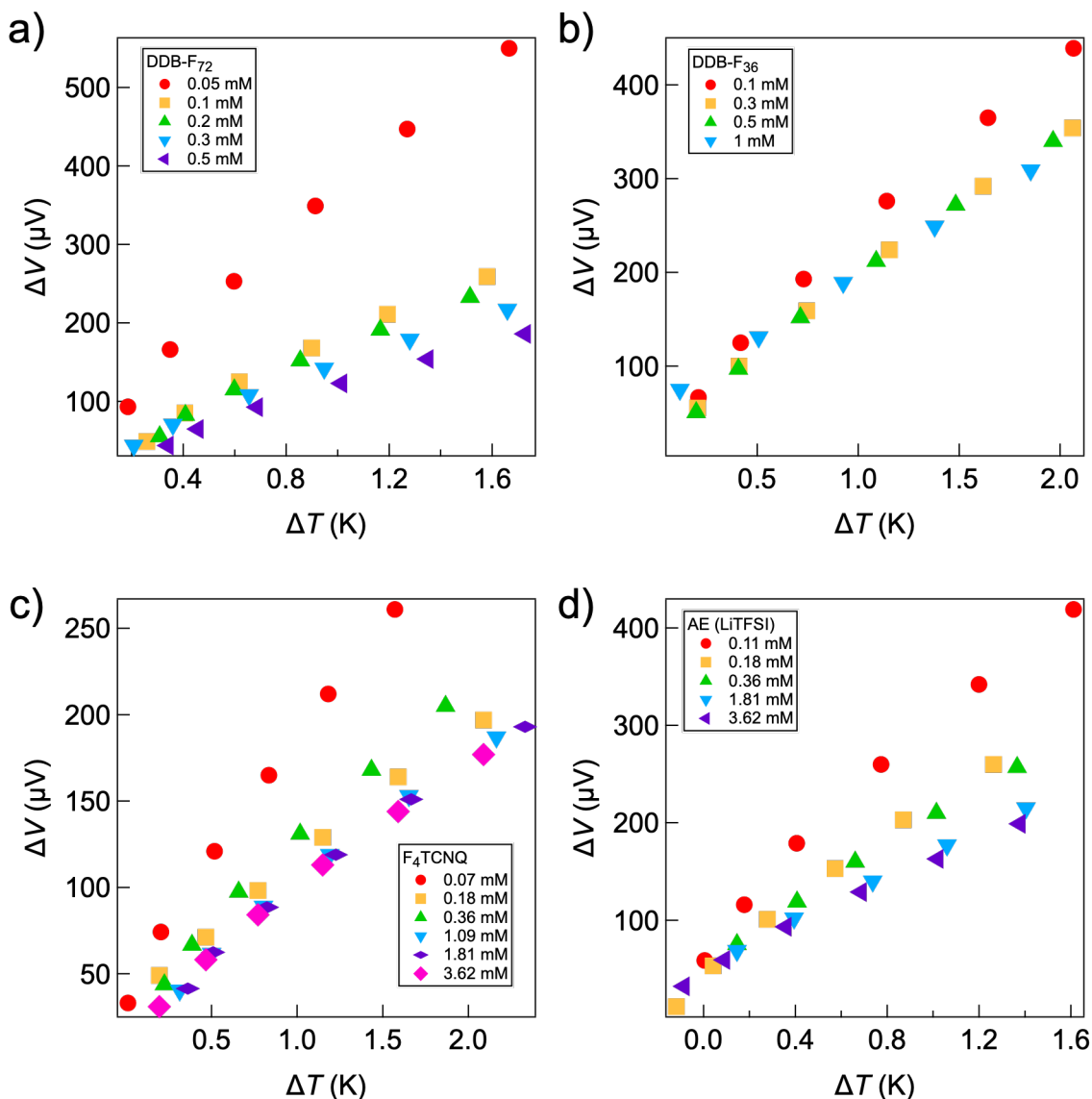


Figure C9. Thermovoltages versus the applied temperature difference for P3HT films doped with different concentrations of (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, and (d) F₄TCNQ plus 104.5 mM LiTFSI via anion exchange. The slopes of the ΔV versus ΔT plots were used to calculate the Seebeck coefficients in **Figure C8** and the main text. For the AE samples, the legend shows the F₄TCNQ concentration with 104.5 mM LiTFSI for all samples.

C.7 Hall Effect Measurements

Hall effect measurements were carried out on the multifunctional devices mentioned in the electrical conductivity section. Hall values reported were taken and averaged over at least three samples. The Hall effect results are plotted for P3HT doped with DDB-F₇₂, DDB-F₃₆, F₄TCNQ,

and via anion exchange in **Figure C10**. Due to the low doping level observed in the 0.07 mM F₄TCNQ-doped P3HT sample, we were unable to obtain reliable Hall carrier density and mobility values. Thus, we have omitted this point from the Hall analysis.

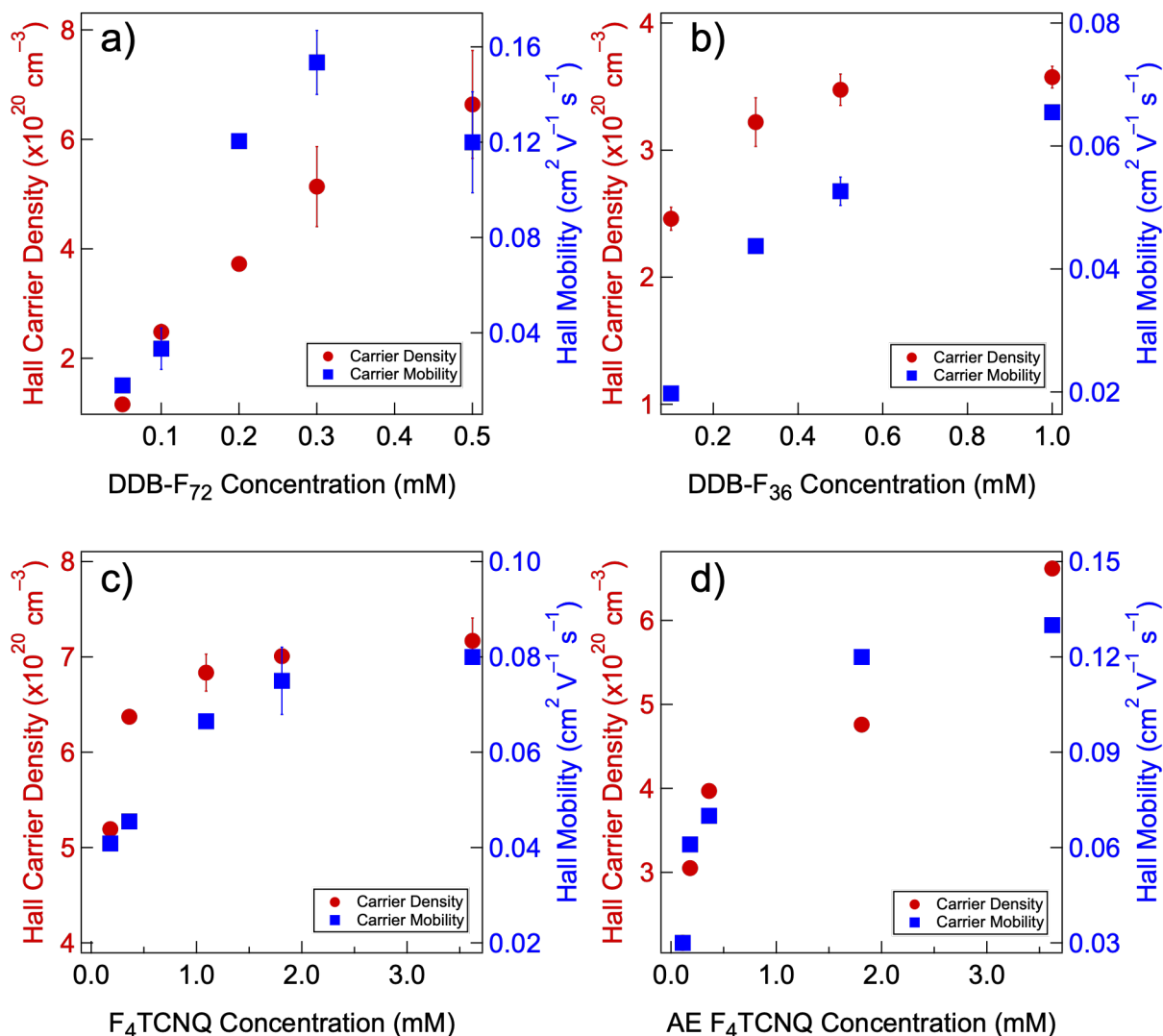


Figure C10. Hall carrier density and mobilities for P3HT doped with (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, and (d) via anion exchange (AE) as a function of dopant concentration. For the AE samples, the legend represents the F₄TCNQ concentration with 104.5 mM LiTFSI.

Hall effect measurements in doped semiconducting polymer films are challenging to obtain due to the low carrier mobilities, which lead to small Hall voltages that can be obscured by

thermoelectric and offset contributions.^[12–14] To address these challenges, we employ DC Hall measurements with systematic current and magnetic field reversals, a protocol that has been shown to reliably extract carrier density and mobility in low-mobility doped polymer systems.^[11,15] Consistent with prior reports using AC Hall measurements on similarly doped P3HT films, the mobilities obtained in this work fall within the expected range.^[4]

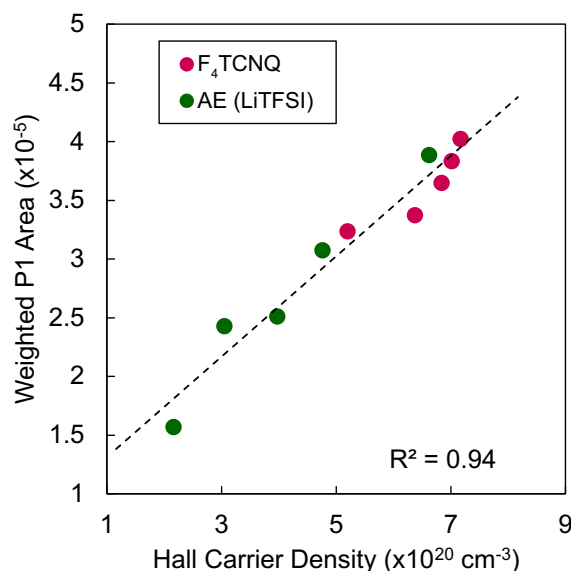


Figure C11. UV–vis–NIR oscillator-strength-weighted P1 peak area plotted versus Hall carrier density for F₄TCNQ- and anion-exchange-doped P3HT shows a linear relation.

To further support the carrier densities obtained in our Hall effect measurements, we compare the oscillator-strength-weighted integrated UV–vis–NIR P1 peak areas, from **Figure 4.2** in the main text, with the Hall carrier densities of the F₄TCNQ and anion-exchange-doped samples. Plotting the integrated P1 peak area versus Hall carrier density for P3HT samples doped at various levels with F₄TCNQ and via anion exchange, shown in **Figure C11**, gives a linear relationship. This gives us confidence that the Hall measurements are providing carrier density values that are accurate.

C.8 Measurements of the Activation Energy, W_H

Carrier activation energies in doped P3HT films were determined from temperature-dependent electrical conductivity measurements using an Arrhenius analysis. For each sample, the temperature-dependent conductivity was fit using:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{W_H}{k_B T}\right), \quad (C5)$$

where $\sigma(T)$ is the electrical conductivity at different temperatures, σ_0 is the temperature-independent pre-exponential factor, and W_H is the activation energy for carrier transport.^[2,4,15–19] W_H values were obtained from the slope of $\ln(\sigma(T))$ versus $(k_B T)^{-1}$.

Figure C12 shows $\ln(\sigma)$ versus $(k_B T)^{-1}$ at various temperatures for P3HT doped with DDB-F₇₂, DDB-F₃₆, F₄TCNQ, and via anion exchange. All temperature-dependent conductivities were measured on the same multifunctional devices described in the conductivity section above. All fits produced a linear relation between $\ln(\sigma)$ and $(k_B T)^{-1}$, with R^2 values of 0.99 or higher, indicating that the Arrhenius model describes the measured data well. The W_H values plotted in **Figure 4.6a** of the main text were obtained from these linear fits.

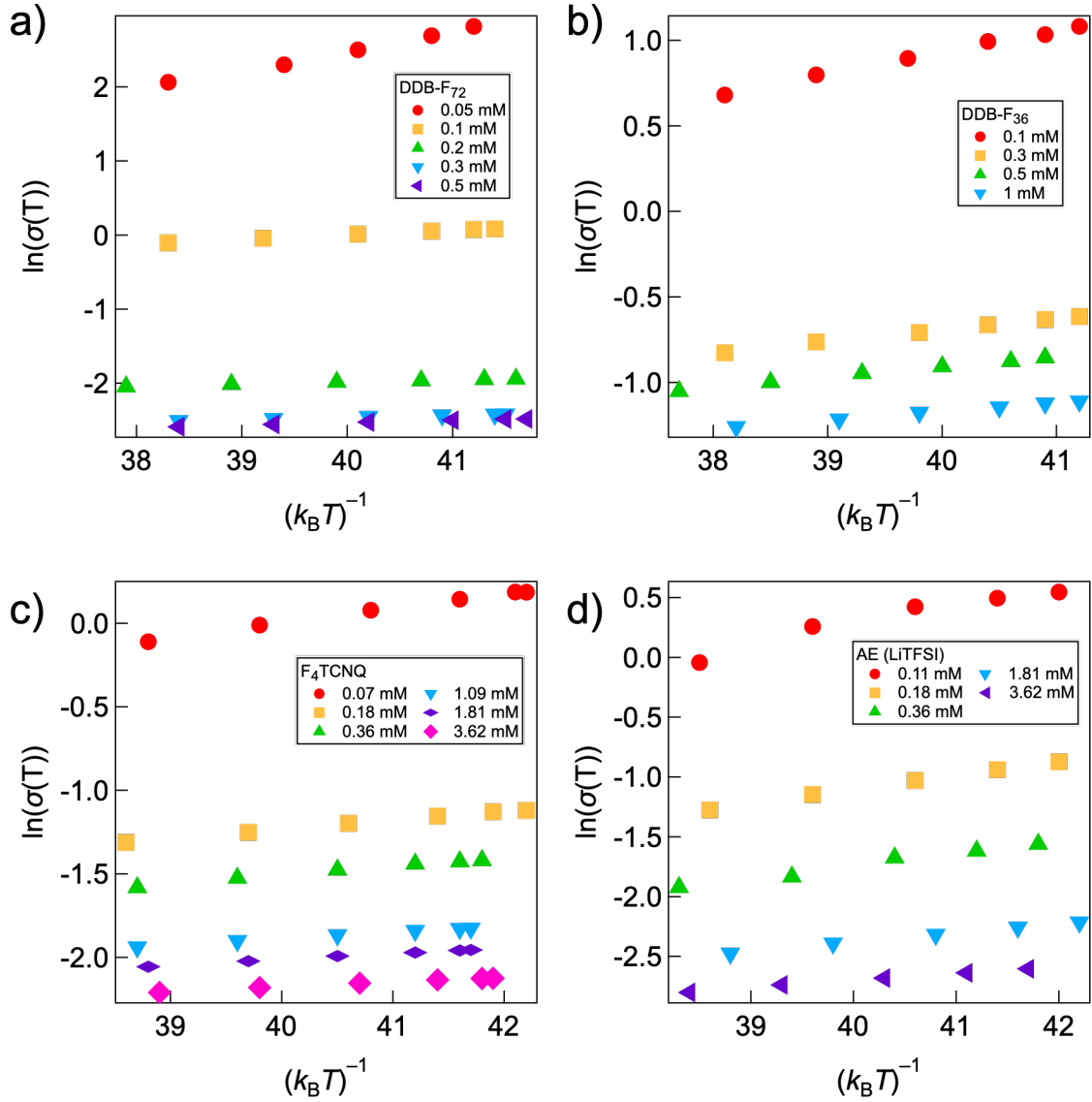


Figure C12. $\ln(\sigma(T))$ versus $(k_B T)^{-1}$ plots for P3HT doped with (a) DDB-F₇₂, (b) DDB-F₃₆, (c) F₄TCNQ, and (d) via anion exchange (AE) at various doping concentrations. For the AE samples, the legend represents the F₄TCNQ concentration with 104.5 mM LiTFSI.

C.9. The Transport Function, σ_E , and the Semi-Localized Transport (SLoT) Model

To provide a physical basis for the transport equations used in the main text, we define the transport function σ_E (Equations (4.2 and 4.3) of the main text) as the energy-resolved conductivity. Within the Boltzmann transport formalism under the relaxation-time approximation, the transport function can be expressed as:

$$\sigma_E(E) = \frac{e^2}{3} \cdot N(E) \cdot v^2(E) \cdot \tau(E), \quad (\text{C6})$$

where e is the elementary charge, $N(E)$ is the electronic density of states, $v(E)$ is the carrier velocity, and $\tau(E)$ is the energy-dependent relaxation time. Using $\tau(E) = \frac{m^*(E) \cdot \mu(E)}{e}$, this expression can equivalently be rewritten as:^[20]

$$\sigma_E(E) = \frac{e}{3} \cdot N(E) \cdot v^2(E) \cdot m^*(E) \cdot \mu(E), \quad (\text{C7})$$

which makes explicit that σ_E contains the energy dependence of carrier mobility, $\mu(E)$. This expression describes both how many electronic states are available at a given energy and how effectively carriers at that energy contribute to transport.

The semi-localized transport (SLoT) model explicitly defines the form of the transport function, σ_E , for doped conjugated polymer systems. In this framework, the transport function is recast into the phenomenological form given in **Equation (4.4)** of the main text, where the localization-energy term $W_H(c)$ acts as a damping term on the intrinsic conductivity σ_0 .

The SLoT model was implemented in our study to analyze how the experimentally extracted activation energies vary with doping level, c , for P3HT doped with DDB-F₇₂, DDB-F₃₆, F₄TCNQ, and via anion exchange. Thus, the W_H values obtained from the Arrhenius fits above serve as the experimental activation energies that are compared with the SLoT model.

The five SLoT parameters used to describe the charge transport of the systems studied in this work are listed in **Table C2**. As described in the main text, σ_0 is related to the intrinsic conductivity when there are no localization effects present; $W_{H,\text{max}}$ represents the localization energy in the low doping regime; and $W_{H,\text{slope}}$ represents how rapidly the localization energy

decreases with increasing doping level.^[16] In other words, $W_{H,max}$ and $W_{H,slope}$ are model parameters that describe the doping dependence of the experimentally measured W_H from **Figure 4.6a** of the main text.

Following Gregory *et al.*, the doping level c is described as a function of the reduced Fermi energy level, η , as follows:^[16]

$$c = \frac{c_{max}}{\exp[A_0(A_1 - \eta)] + 1}, \quad (C8)$$

where c_{max} is the maximum doping level within the model. The parameters A_0 and A_1 are phenomenological fitting parameters that determine the shape of the $c(\eta)$ relation.

Table C2. Parameters obtained from the SLoT fits performed for P3HT doped with F₄TCNQ, DDB-F₇₂, DDB-F₃₆, and via anion exchange (AE).

Parameters	F ₄ TCNQ	AE (LiTFSI)	DDB-F ₇₂	DDB-F ₃₆
σ_0 (S cm ⁻¹)	10	125	25	35
$W_{H,max}$ (meV)	210	275	500	750
$W_{H,slope}$ (meV)	310	350	1000	1550
c_{max}	0.25	0.4	0.33	0.30
A_0	0.5	0.5	1	0.25
A_1	1.8	2	2	3.8

C.10 References

- [1] A. I. Wixtrom, Y. Shao, D. Jung, C. W. Machan, S. N. Kevork, E. A. Qian, J. C. Axtell, S. I. Khan, C. P. Kubiak, A. M. Spokoyny, *Inorg. Chem. Front.* **2016**, 3, 711.
- [2] T. J. Aubry, J. C. Axtell, V. M. Basile, K. J. Winchell, J. R. Lindemuth, T. M. Porter, J.-Y. Liu, A. N. Alexandrova, C. P. Kubiak, S. H. Tolbert, A. M. Spokoyny, B. J. Schwartz, *Adv. Mater.* **2019**, 31, 1805647.

- [3] Y. Yamashita, J. Tsurumi, M. Ohno, R. Fujimoto, S. Kumagai, T. Kurosawa, T. Okamoto, J. Takeya, S. Watanabe, *Nature* **2019**, 572, 634.
- [4] T. J. Aubry, K. J. Winchell, C. Z. Salamat, V. M. Basile, J. R. Lindemuth, J. M. Stauber, J. C. Axtell, R. M. Kubena, M. D. Phan, M. J. Bird, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2020**, 30, 2001800.
- [5] X. Jiao, M. Statz, L. Lai, S. Schott, C. Jellett, I. McCulloch, H. Sirringhaus, C. R. McNeill, *J. Phys. Chem. B* **2020**, 124, 10529.
- [6] Z. Peng, L. Ye, H. Ade, *Mater. Horiz.* **2022**, 9, 577.
- [7] J. Rivnay, R. Noriega, R. J. Kline, A. Salleo, M. F. Toney, *Phys. Rev. B* **2011**, 84, 045203.
- [8] S. Lenz, M. Bonini, S. K. Nett, M. C. Lechmann, S. G. J. Emmerling, R. S. Kappes, M. Memesa, A. Timmann, S. V. Roth, J. S. Gutmann, *Eur. Phys. J. Appl. Phys.* **2010**, 51, 10601.
- [9] G. Beaucage, *J. Appl. Crystallogr.* **1995**, 28, 717.
- [10] N. C. Buggy, Y. Du, M.-C. Kuo, S. Seifert, R. J. Gasvoda, S. Agarwal, E. B. Coughlin, A. M. Herring, *J. Phys. Chem. C* **2021**, 125, 20592.
- [11] Q. M. Duong, D. Garcia Vidales, B. J. Schwartz, *Appl. Phys. Lett.* **2023**, 123, 202101.
- [12] J. Lindemuth, S.-I. Mizuta, In *Thin Film Solar Technology III*, SPIE, **2011**, pp. 65–71.
- [13] Y. Chen, H. T. Yi, V. Podzorov, *Phys. Rev. Appl.* **2016**, 5, 034008.
- [14] F. Werner, *J. Appl. Phys.* **2017**, 122, 135306.
- [15] Q. M. Duong, D. Garcia Vidales, C. Z. Salamat, S. H. Tolbert, B. J. Schwartz, *Phys. Rev. Appl.* **2024**, 21, 024006.
- [16] S. A. Gregory, R. Hanus, A. Atassi, J. M. Rinehart, J. P. Wooding, A. K. Menon, M. D. Losego, G. J. Snyder, S. K. Yee, *Nat. Mater.* **2021**, 20, 1414.
- [17] A. I. Hofmann, R. Kroon, S. Zokaei, E. Järsvall, C. Malacrida, S. Ludwigs, T. Biskup, C. Müller, *Adv. Electron. Mater.* **2020**, 6, 2000249.
- [18] D. Neusser, C. Malacrida, M. Kern, Y. M. Gross, J. van Slageren, S. Ludwigs, *Chem. Mater.* **2020**, 32, 6003.

- [19] V. Untilova, T. Biskup, L. Biniek, V. Vijayakumar, M. Brinkmann, *Macromolecules* **2020**, 53, 2441.
- [20] V. I. Fistul', *Heavily Doped Semiconductors*, Springer New York, Boston, MA, **1995**.

Appendix D

Supporting Information for Chapter 5: The Role of Microstructural Disorder in the Charge Transport Characteristics of Doped Semiconducting Polymers

D.1 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS)

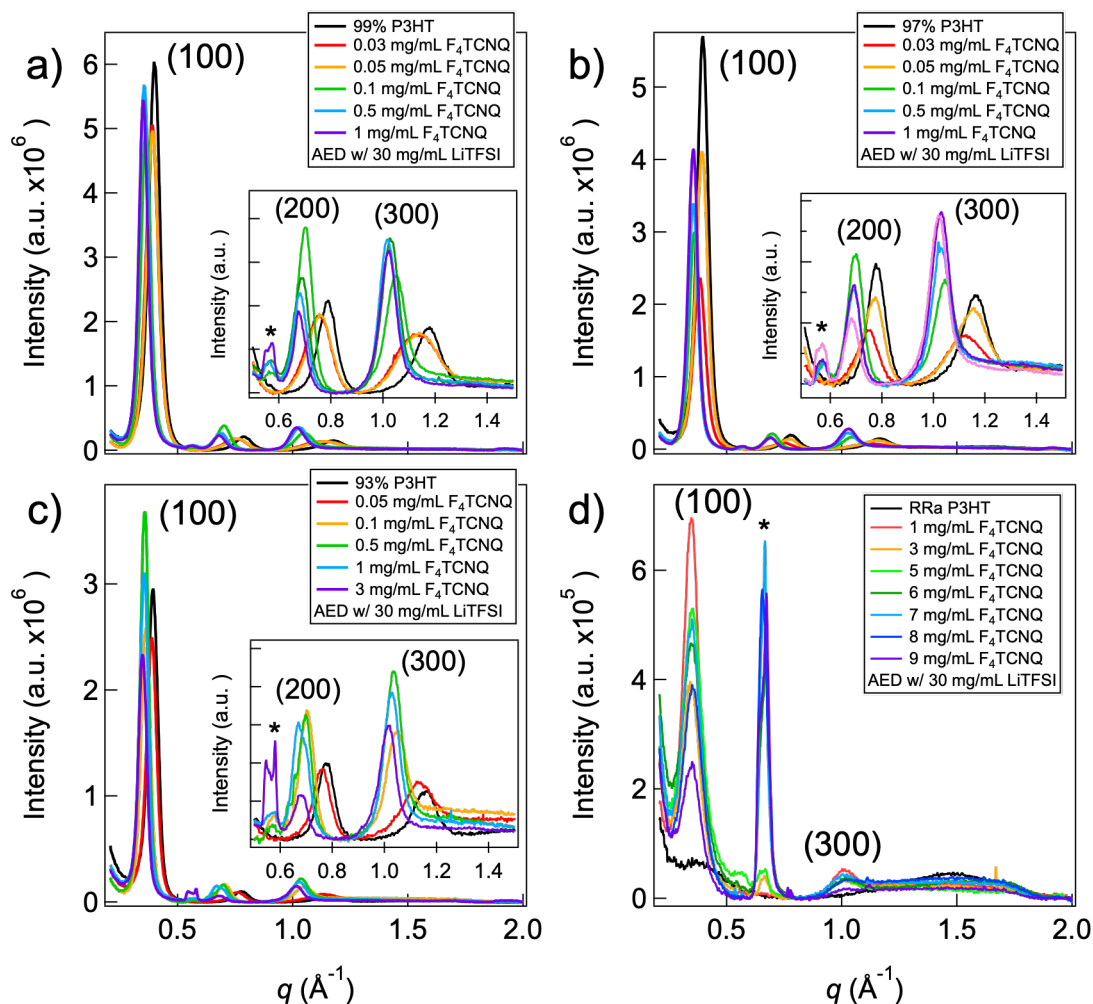


Figure D1. GIWAXS out-of-plane integrations for pristine and anion-exchange-doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT films. The sharp peaks labeled with an asterisk (*) in the doped P3HT films are due to scattering from excess LiTFSI.

GIWAXS and grazing-incidence small-angle X-ray scattering (GISAXS) samples were prepared by spin-coating the polymer solution and subsequently the dopant solution onto 1.5×1.5 cm Si substrates with a (100) orientation. Films were cast and doped using the same doping concentrations and spinning parameters described in the Experimental Section. The substrates were cleaned sequentially in an Alconox/water solution, isopropanol, and acetone, followed by

plasma etching prior to use. GIWAXS measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on BL 11-3 using an X-ray energy of 12.7 keV at an incidence angle of 0.12°. The Igor Pro macro Nika was used to calibrate the GIWAXS 2D data. Nika and WAXStools were used to reduce the data. Measurements were performed in triplicate.

Figure 5.2 in the main text and **Figures D1 and D2** show the out-of-plane and in-plane GIWAXS integrations, respectively, for both the pristine and doped P3HT polymer films. In the pristine polymers, the strong out-of-plane lamellar (100) scattering (**Figure D1**) confirms that the crystallites in these samples have an edge-on orientation. Upon doping, the (100) lamellar peak shifts to lower q , corresponding to a larger d -spacing, consistent with the intercalation of TFSI[−] anions into the polymer lattice.^[1–4] Importantly, the strong lamellar (100) scattering in the out-of-plane integrations in the doped samples shows that the edge-on orientation is preserved after doping. Additionally, the similar d -spacings of lamellar ($h00$) peaks in the pristine samples (99% RR P3HT, $d \sim 16.0$ Å; 97% RR P3HT, $d \sim 16.1$ Å; and 93% RR P3HT, $d \sim 16.2$ Å) and highest-doped samples (99% RR P3HT, $d \sim 18.5$ Å; 97% RR P3HT, $d \sim 18.5$ Å; 93% RR P3HT, $d \sim 18.5$ Å; and RRa P3HT, $d \sim 18.2$ Å) indicate similar crystal packing within the pristine films and within the doped films despite the different regioregularities.

In addition, doping produces a clear suppression in the intensity ratio of the (200) relative to the (300) lamellar overtones, particularly in the regioregular polymers. Prior studies have associated the suppression of lamellar overtones with an off-center spatial location of the counterions in the lattice.^[1,2,4] We note that changes in doping level may also contribute to the attenuation of higher-order peaks; however, the similar suppression trends observed across all the doped P3HT films, especially at high doping levels, suggest that TFSI[−] anions occupy equivalent positions relative to the polymer backbone regardless of regioregularity.

Figure D2 shows in-plane GIWAXS integrations of the pristine and doped P3HT polymers. The π - π stacking (020) peak shifts systematically to higher q -spacing values (smaller d -spacing) upon anion-exchange doping. This indicates that the pristine π - π stacking changes due to a reorientation of the unit cell upon intercalation of TFSI⁻ anions between the polymer sidechains.^[2-7] In the case of pristine RRa P3HT, its highly amorphous nature and strong scattering from an isotropic disordered structure ($\sim 1.5 \text{ \AA}^{-1}$) prevent the identification of a clear (020) peak in the in-plane direction.

Moreover, the similar (020) distances in pristine samples (99% RR P3HT, $d \sim 3.83 \text{ \AA}$; 97% RR P3HT, $d \sim 3.81 \text{ \AA}$; and 93% RR P3HT, $d \sim 3.82 \text{ \AA}$) confirm that the pristine polymers have nearly identical π - π stacking distances, consistent with the similar lamellar spacings observed in the out-of-plane data. Upon doping, the (020) spacings also converge to similar values (99% RR P3HT, $d \sim 3.67 \text{ \AA}$; 97% RR P3HT, $d \sim 3.67 \text{ \AA}$; 93% RR P3HT, $d \sim 3.70 \text{ \AA}$; and RRa P3HT, $d \sim 3.73 \text{ \AA}$), supporting the conclusion from the out-of-plane data that all of the doped P3HT polymers adopt comparable crystal packing. All pristine and doped samples exhibit only weak scattering from the lamellar (100) peak in the in-plane direction, further supporting a preferential edge-on orientation. The sharp features labeled with an asterisk (*) at $q \sim 0.55 \text{ \AA}^{-1}$ arise from LiTFSI salt at the film surface.

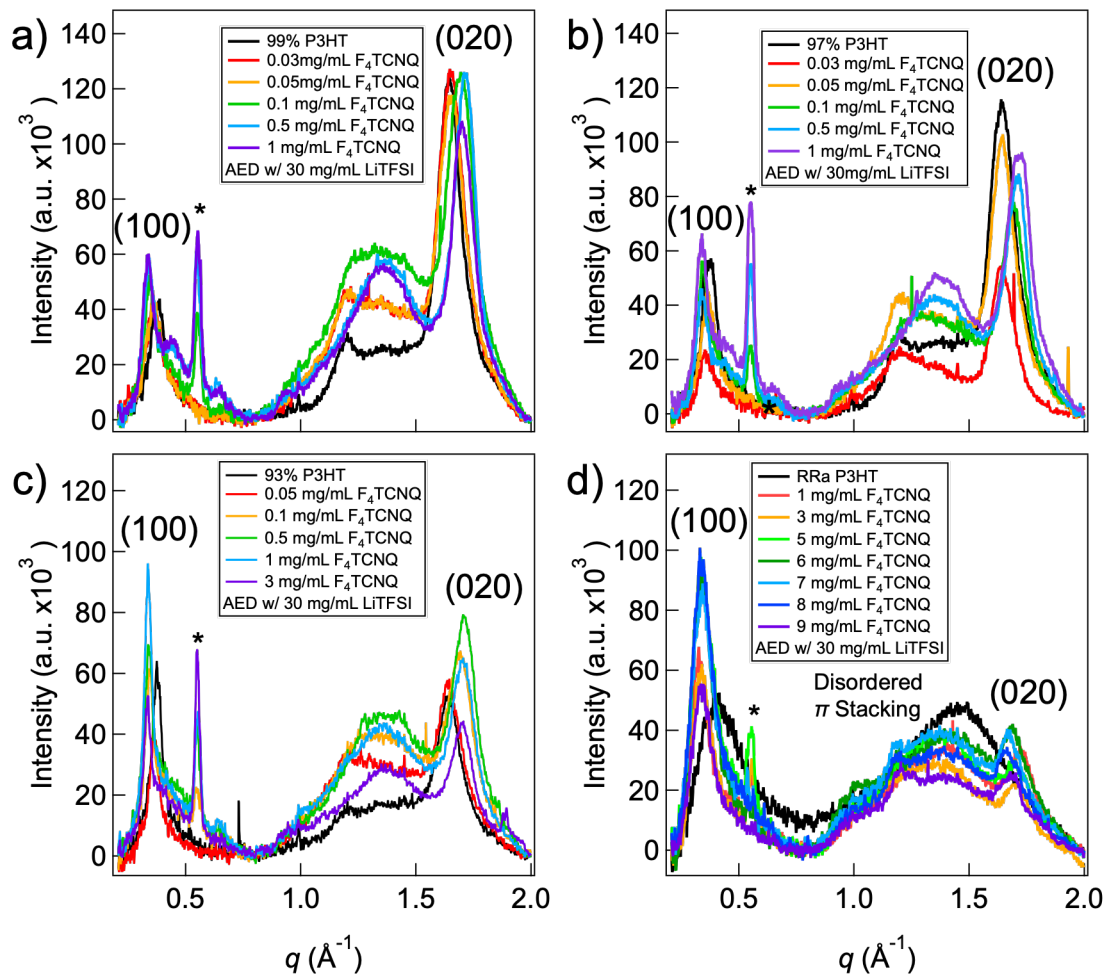


Figure D2. GIWAXS in-plane integrations for pristine and doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT films. The intensity of each integration is normalized to the corresponding film thickness. Peaks labeled with an asterisk (*) in the doped P3HT films are due to scattering from excess LiTFSI.

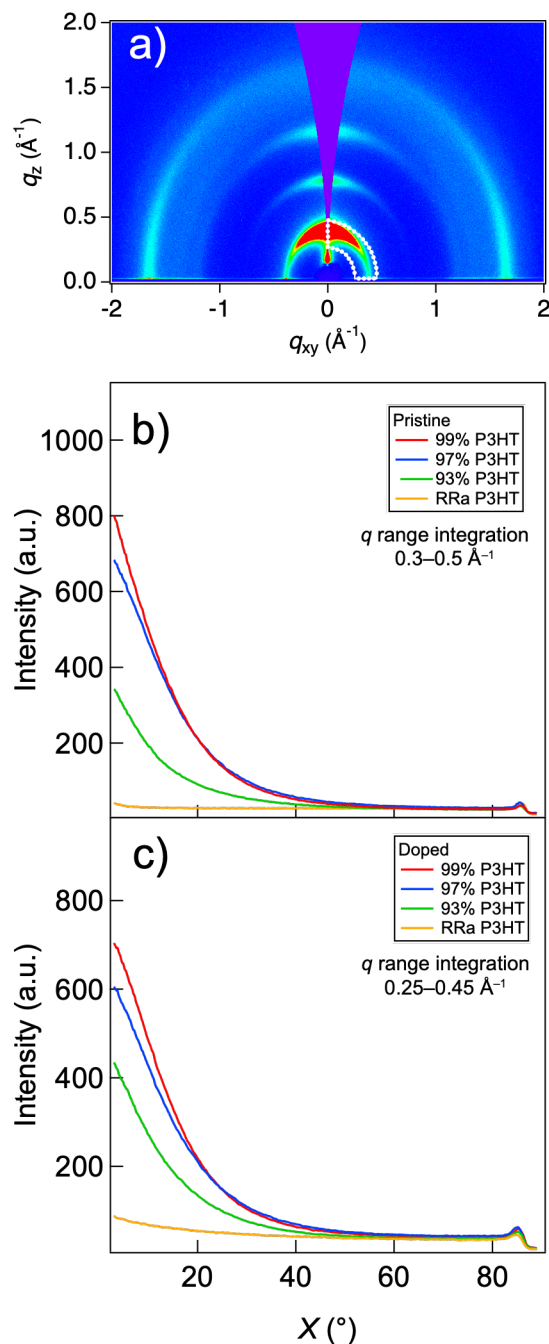


Figure D3. Edge-on to face-on texture analysis of P3HT films. (a) Representative 2D GIWAXS diffractogram of a pristine 93% RR P3HT sample, with the (100) diffraction integrated along the azimuthal angle (χ) over a q range of 0.3–0.5 Å⁻¹. χ -dependent intensity profiles of the (100) diffraction for (b) pristine P3HT samples (q range integrated 0.3–0.5 Å⁻¹) with varying regioregularity and (c) the most-doped P3HT samples (q range integrated 0.25–0.45 Å⁻¹) prepared via anion exchange and presented in **Figure 5.2** of the main text.

The (100) diffraction intensity distribution along the azimuthal angle (χ) was extracted from the 2D GIWAXS patterns by integrating over the specified q range (**Figure D3a**). For pristine samples, a q range of 0.3–0.5 Å⁻¹ was used to capture the full (100) diffraction, while for doped samples, the integration range was adjusted to 0.25–0.45 Å⁻¹ to account for the shift of the (100) peak to lower q -spacing upon doping. The resulting χ profiles serve as a measure of the edge-on to face-on orientation distribution. In **Figure D3b**, $\chi = 0^\circ$ corresponds to the out-of-plane direction; however, this region overlaps with the specular beam reflection and is thus omitted for clarity. Samples with higher regioregularity exhibit increased intensity near $\chi \sim 0^\circ$, indicating enhanced crystallinity and a higher fraction of crystallite edge-on orientation. After doping, this trend is preserved, as shown in **Figure D3c**, suggesting that the initial crystallinity and orientational distribution remain largely intact upon doping.

D.2 Grazing-Incidence Small-Angle X-ray Scattering (GISAXS)

GISAXS measurements were performed in parallel with the GIWAXS measurements at the Stanford Synchrotron Radiation Lightsource using beamline 1-5. The scattered X-rays with an energy of 12 keV were collected using a 2D detector at a sample-to-detector distance of 3 m. The incident angle was set to 0.12°. The 1D integrations were obtained by horizontally integrating near the Yoneda band and were fit using the Unified Fit method from the Irena and Nika packages in Igor Pro. All samples were prepared and measured in triplicate to ensure reproducibility.

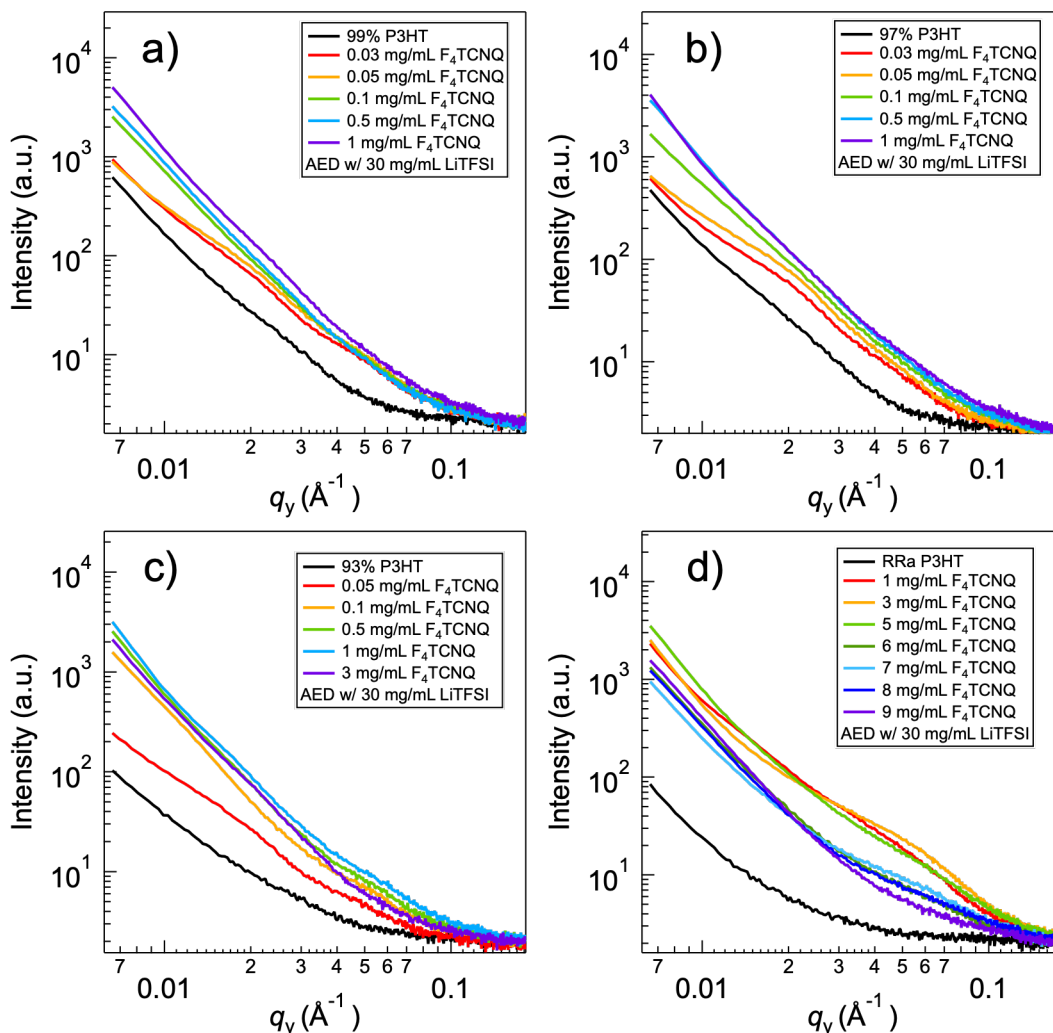


Figure D4. Horizontal 1D GISAXS integrations near the Yoneda band for pristine and doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT polymers. Legends indicate the F₄TCNQ concentration; the LiTFSI concentration was fixed at 30 mg/mL for all doped samples.

Figure D4 shows horizontal GISAXS integrations near the Yoneda band for the different pristine and doped P3HT polymers. Legends indicate the F₄TCNQ concentration used for each sample, along with 30 mg/mL LiTFSI. For the 99% RR and 97% RR P3HT samples, doping induces a pronounced increase in scattering intensity and the appearance of a shoulder in the mid- q_y region relative to the pristine films. In contrast, the doped RRa P3HT samples exhibit shoulders at higher q_y , particularly at the highest doping concentrations.

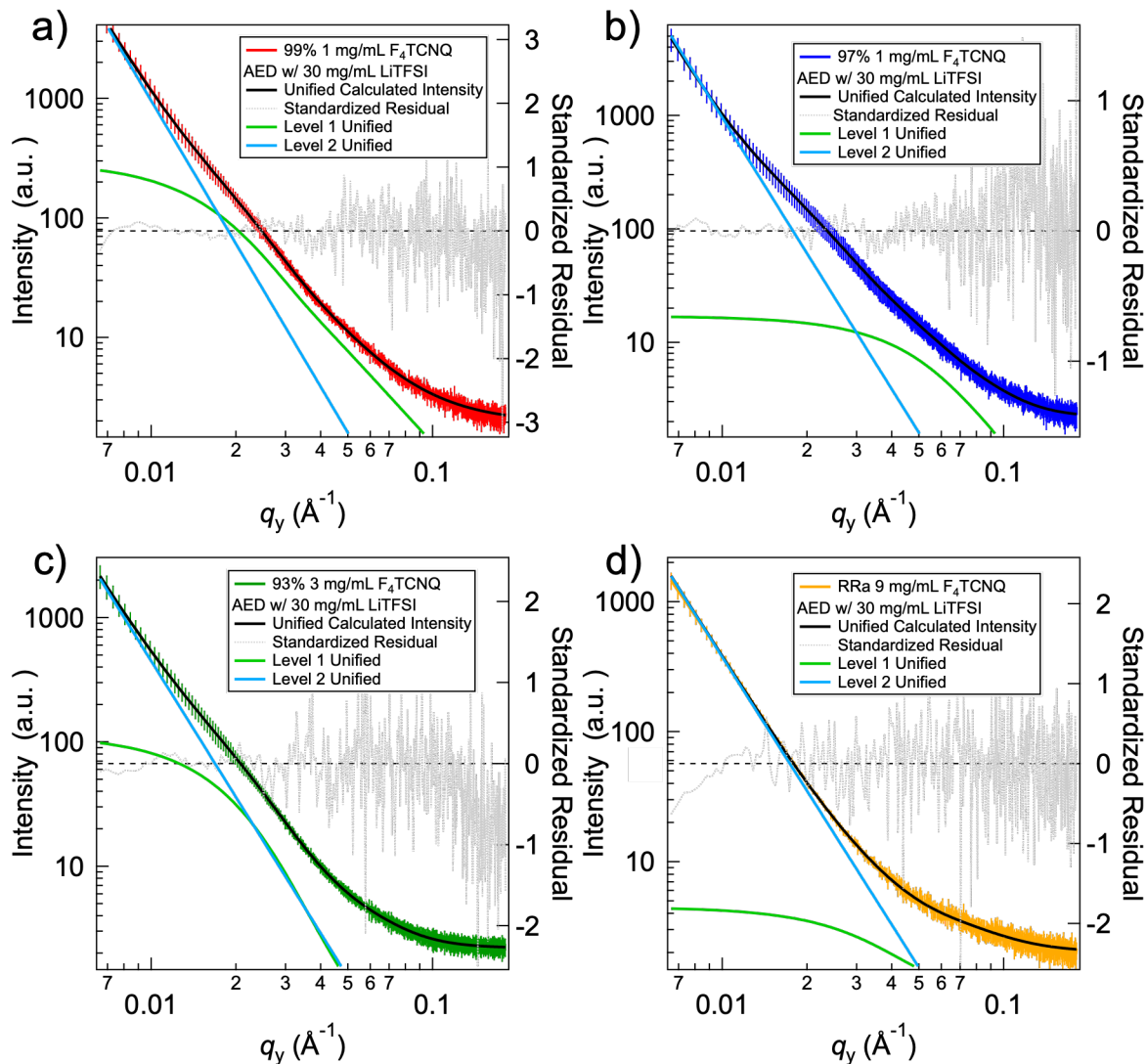


Figure D5. Representative Unified fits of the most-doped P3HT samples for (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT via the anion-exchange method using the F₄TCNQ concentration indicated in the legend with 30 mg/mL LiTFSI. The green and blue lines represent the Level 1 and Level 2 fits that give rise to the calculated intensity (black curves), which closely match the measured intensities.

To quantify mesoscale structural features, the 1D GISAXS profiles were analyzed using the Unified Guinier–Porod model, which has been demonstrated to accurately describe weakly correlated polymer films that exhibit diffuse, non-specular scattering.^[8,9] This approach captures hierarchical scattering contributions by representing the total intensity as a sum of Guinier (low- q_y) and power-law (high- q_y) regimes associated with different structural length scales. In this

framework, each “level” corresponds to a distinct characteristic size regime contributing to the scattering profile.

Figure D5 shows Unified Fit analysis of representative doped samples for each P3HT regioregularity: 99% RR, 97% RR, 93% RR, and RRa P3HT (**Figure D5a–d**, respectively). The Level 1 Unified Fit (green curve) describes the Guinier regime at high q_y and provides the R_g values that correspond to the primary mesoscale domain size. To account for background scattering, such as scattering from large particles beyond the primary domains and beam reflection, we implemented an extra level, where the Guinier contribution was set to zero so that only the Porod slope appears in the range of interest. The total Unified fit is shown in black, with experimental data in red, deep blue, deep green, and orange, respectively, and the residuals in gray plotted below each dataset. The more crystalline polymers (99% RR and 97% RR P3HT) are well described by a Level 1 Guinier–Porod contribution and a Level 2 Porod contribution, while the less ordered polymers (93% RR and RRa P3HT) often require an additional Level 2 Guinier–Porod contribution, consistent with increased structural heterogeneity at larger length scales.

D.3 UV–Vis–NIR Spectroscopy

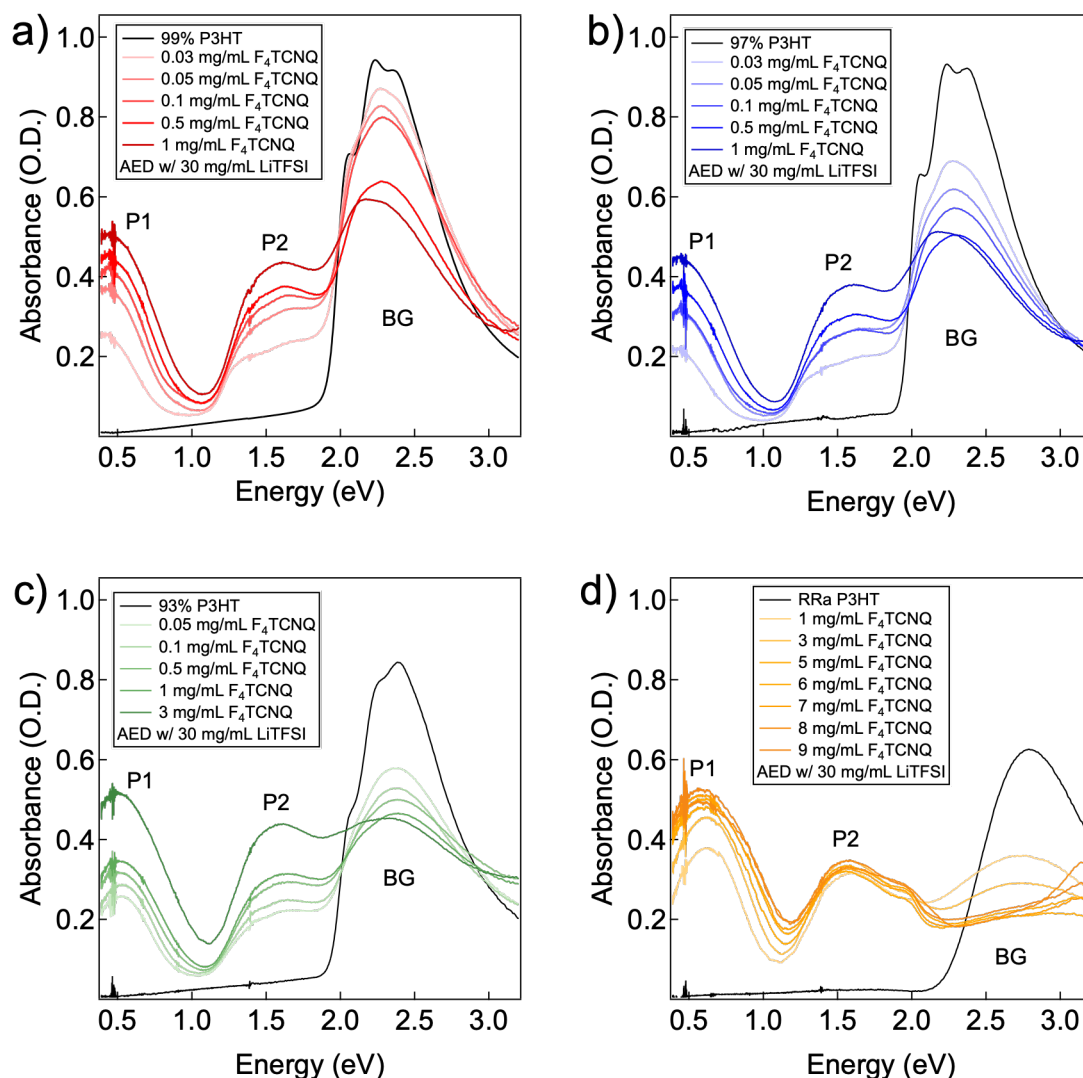


Figure D6. UV–vis–NIR spectra of: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT pristine films (black curves) and anion-exchange-doped films (various colored curves) at various F₄TCNQ dopant concentrations, where thicker colored lines indicate higher doping concentrations. The LiTFSI electrolyte concentration was kept constant at 30 mg/mL for all of the anion-exchange doped samples. The spectra confirm successful chemical doping of the P3HT films through the appearance of the polaronic P1 and P2 peaks at ~0.4–0.6 and ~1.2–1.6 eV, respectively, and through the depletion of the bandgap absorption at ~2.3–3.3 eV. The lack of F₄TCNQ anion absorption at ~1.5 and ~3.0 eV confirms that the exchange process was successful.

The data in **Figure D6** tracks the progression of anion-exchange doping in the different P3HT films via UV–vis–NIR spectroscopy. All doped P3HT films show an increase in the P1

(~0.4–0.6 eV) and P2 (~1.2–1.6 eV) polaronic absorption bands, as well as a bleach of the bandgap transition (~2.3–3.3 eV) as the dopant concentration is increased, indicating the formation of polarons. Furthermore, the absence of absorption signatures from the F₄TCNQ anion at ~1.5 and ~3.0 eV confirms that anion exchange was successful in all doped films.^[2,3,7,10]

Because the magnitude of the P1 absorption band is proportional to the number of polarons, we can easily see that increasing the doping concentration increases the polaron population in all four P3HT regioregularities to similar optical density values, indicating that our concentration series captures a comparably wide doping range. This observation corroborates the electrical conductivity data in **Figure 5.1** of the main text, showing that the chosen dopant concentrations effectively capture similar doping levels and thermoelectric performance regimes across the different P3HT regioregularities. Notably, the most crystalline 99% RR and 97% RR P3HT polymers require much lower dopant concentrations to reach similar P1 optical densities than the less ordered 93% RR P3HT and amorphous RRa P3HT. For RRa P3HT, the P1 peak intensity exhibits a plateau at high concentrations, and the bandgap is nearly fully bleached.

UV–vis–NIR spectroscopy was used to characterize the anion-exchange-doped P3HT polymers. We focus on the position of the polaronic P1 peak as a marker for carrier delocalization. **Figure D7** shows the normalized P1 peaks for all of the doped samples presented in **Figure D6a–d**. Normalization allows for a clearer comparison of the peak positions: doped 99% RR and 97% RR P3HT samples exhibit the most red-shifted P1 peaks, followed by 93% RR and RRa P3HT samples. Since the samples were cast and doped on glass substrates, the full P1 peak could not be obtained due to strong absorption from the glass.

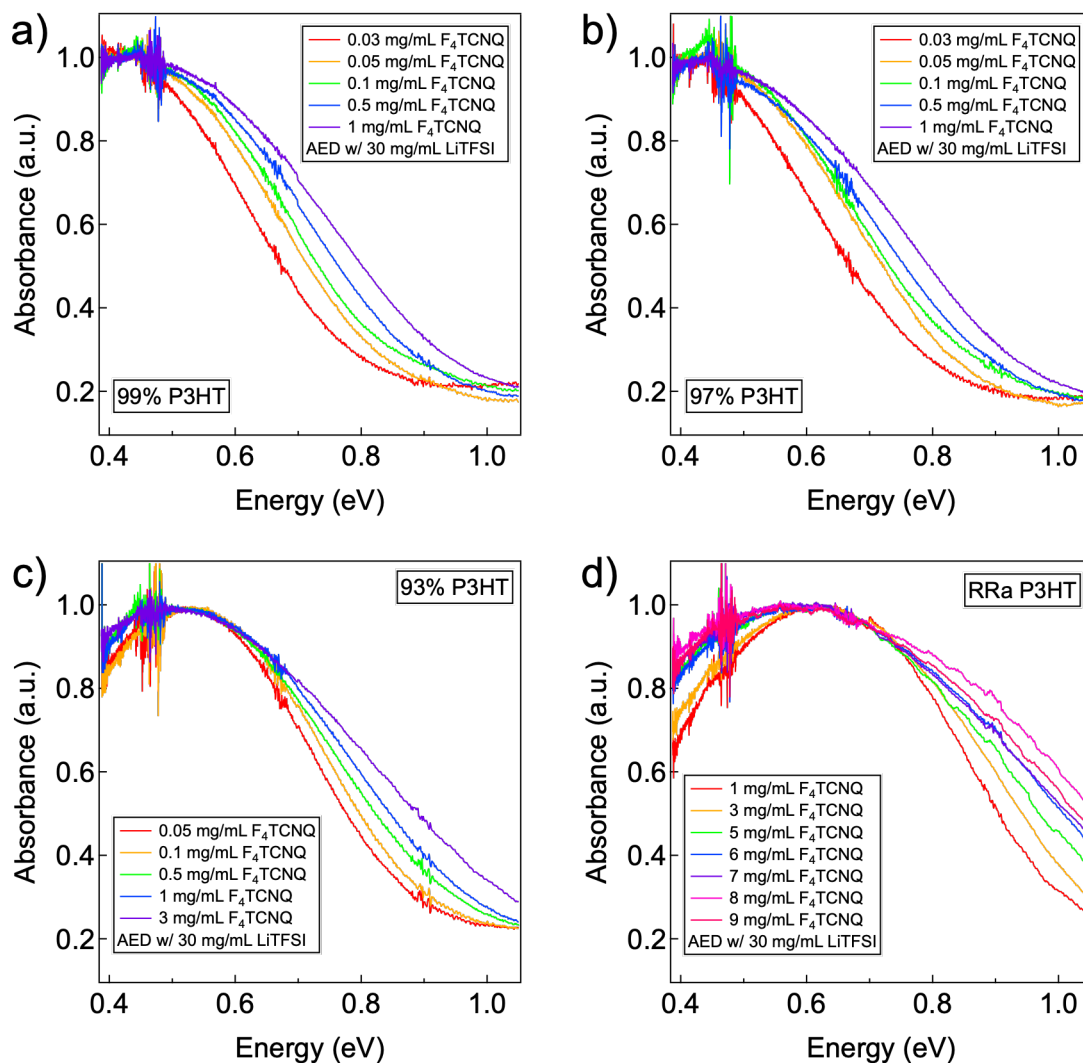


Figure D7. Normalized polaronic P1 peaks for the doped samples of: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT. P1 peaks were normalized to the maximum absorbance in the IR region 0.38–0.8 eV. The curves highlight the red-shifted P1 peak positions of the doped 99% RR and 97% RR P3HT polymers compared to the doped 93% RR and RRa polymers.

The data in **Figure D7** also shows a shoulder on the high-energy side of the P1 peak, associated with bipolaron formation, at high doping levels.^[11–13] P1 peak broadening is a well-established phenomenon in doped conjugated polymers, typically arising from inhomogeneous carrier populations (trapped and “free”).^[13,14] In the case of RRa P3HT, this inhomogeneous broadening is accompanied by a pronounced red shift of the peak location, indicating changes in

carrier delocalization at moderate and high doping levels. This observation is consistent with previous studies of doping-induced structural ordering in RRa P3HT.^[15,16]

We extracted the P1 peak positions and maximum absorbances plotted in **Figure 5.3c** of the main text by fitting the peaks with a Gaussian function:

$$g(x; A, \sigma, \mu) = \frac{A}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}, \quad (\text{D1})$$

where A is the amplitude, μ is the peak center, and σ is the peak width. All P1 peak fittings were performed in MATLAB using the `gaussmf` function. **Figure D8** shows the fits (green dashed lines) for the most-doped samples for each regioregularity.

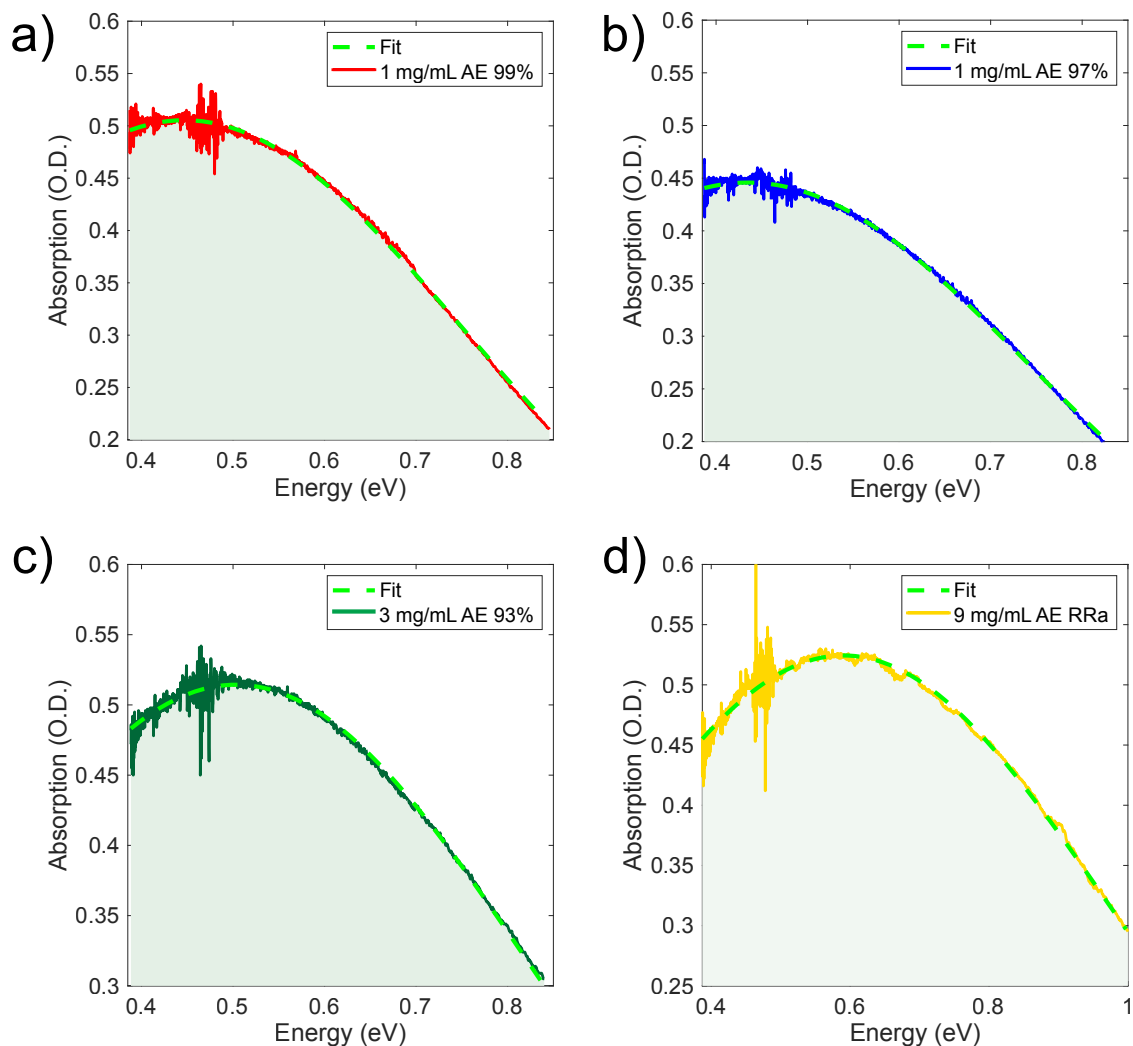


Figure D8. Representative Gaussian fits (green dashed lines) of the P1 peak for: (a) 99% RR P3HT (1 mg/mL F₄TCNQ with 30 mg/mL LiTFSI), (b) 97% RR P3HT (1 mg/mL F₄TCNQ with 30 mg/mL LiTFSI), (c) 93% RR P3HT (3 mg/mL F₄TCNQ with 30 mg/mL LiTFSI), and (d) RRa P3HT (9 mg/mL F₄TCNQ with 30 mg/mL LiTFSI). Only the highest dopant concentrations are shown for clarity.

D.4 Transient Absorption Spectroscopy

To extract the overlapping spectral and temporal components in the ultrafast transient absorption measurements, we applied singular value decomposition (SVD),^[17,18] similar to our previous work.^[19–21] SVD factorizes the data matrix into orthogonal basis sets that capture its significant components. In our application, the data are stored in a matrix, *TA Data*, with

wavelength in the column space and the temporal component in the row space. The decomposition of this matrix can be expressed by **Equations (D2 and D3)**:

$$TA\ Data = USV^T = DF^T \quad (D2)$$

$$D = US(V^T F^{T+}) \quad (D3)$$

where U contains the column-space (spectral) eigenvectors, transpose V^T contains the row-space (temporal) eigenvectors, and S contains the singular values used to deconvolve the important spectral and temporal components in our TA signal.

We can further relate the *TA Data* matrix to a matrix D (**Equation (D3)**), which contains the transient absorption spectrum of each individual component, and a matrix F , which contains a fitted kinetic model that describes the temporal dynamics of each individual component. For our model, F was constructed as a two-column matrix representing two independent exponential decays. Each row of F corresponds to one component (fast and slow), parameterized by decay constants τ_1 and τ_2 , as well as their initial amplitudes (a_i) under different pump/probe conditions. The columns of F run over time steps (t_n) ranging from 0.25–10 ps, describing the exponential decay of each component as a function of its amplitude and lifetime.

The important temporal components in V^T are linear combinations of the columns in F ; therefore, the decay constants were obtained by fitting the important temporal components of V^T using a least-squares approach. Then, the relative amplitudes and spectral shapes can be obtained using **Equation (D3)**.

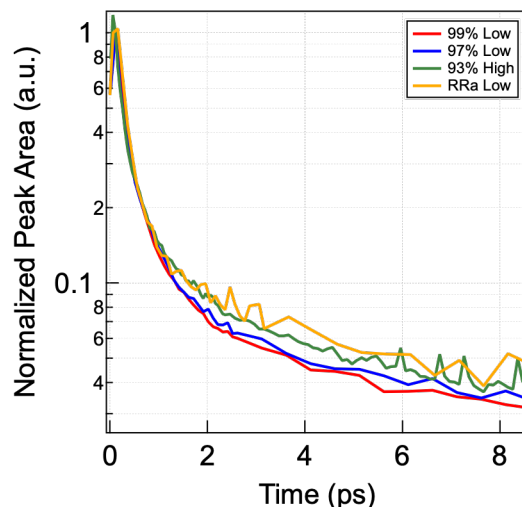


Figure D9. Normalized transient P2 peak integrated area as a function of time for the doped 99% RR P3HT, 97% RR P3HT, 93% RR P3HT, and RRa P3HT polymers following excitation at 1400 nm. The more regioregular 99% RR and 97% RR P3HT films exhibit faster decay dynamics relative to the less ordered 93% RR and RRa P3HT samples, indicating higher local carrier mobility.

D.5 Electrical Conductivity Measurements

Multifunctional devices were fabricated to probe UV–vis–NIR spectroscopy, electrical conductivity, Hall effect, temperature-dependent conductivity, and transient absorption spectroscopy measurements. The electrical conductivity measurements presented in **Figures 5.1 and 5.5** in the main text were collected on the pre-cleaned glass substrates (1.1×1.1 cm) with gold corner electrodes (1 mm squares deposited via an Angstrom Engineering Nexdep thermal evaporator). Conductivities (σ) were measured using the van der Pauw method. Sheet resistance was measured using a home-built conductivity setup equipped with a Keithley 2400 Sourcemeter and controlled via LabVIEW software. All measurements were performed inside an argon glovebox to avoid humidity issues in anion-exchange-doped samples.^[22] Film thickness was measured using a Dektak 150 stylus profilometer.

D.6 Hall Effect Measurements and P1-Correlated Carrier Density

We probed carrier mobility in the multifunctional devices using the Hall effect. Hall voltages were measured with a Lake Shore MeasureReady M91 FastHall instrument with a source current of 10 μA and a fixed magnetic field of 1.023 T. Because the anion-exchange-doped samples are highly hygroscopic, the FastHall chamber was purged with argon for 2 minutes prior to each measurement.^[22] The conductivities obtained from FastHall matched those measured inside the argon glovebox, confirming that the Hall results reliably represent the charge transport behavior associated with the Seebeck and conductivity measurements in an inert atmosphere.

Hall voltages (V_{Hall}) were measured for the doped P3HT films to probe the carrier delocalization and charge-transport characteristics. **Figure D10** shows the Hall mobility and carrier density values for the doped 99% RR, 97% RR, and 93% RR P3HT polymers as a function of F₄TCNQ concentration (with 30 mg/mL LiTFSI). As expected, both carrier mobility (solid lines, circles) and carrier density (dashed lines, triangles) increase as the doping concentration increases. The arrows in each panel indicate the corresponding y-axis.

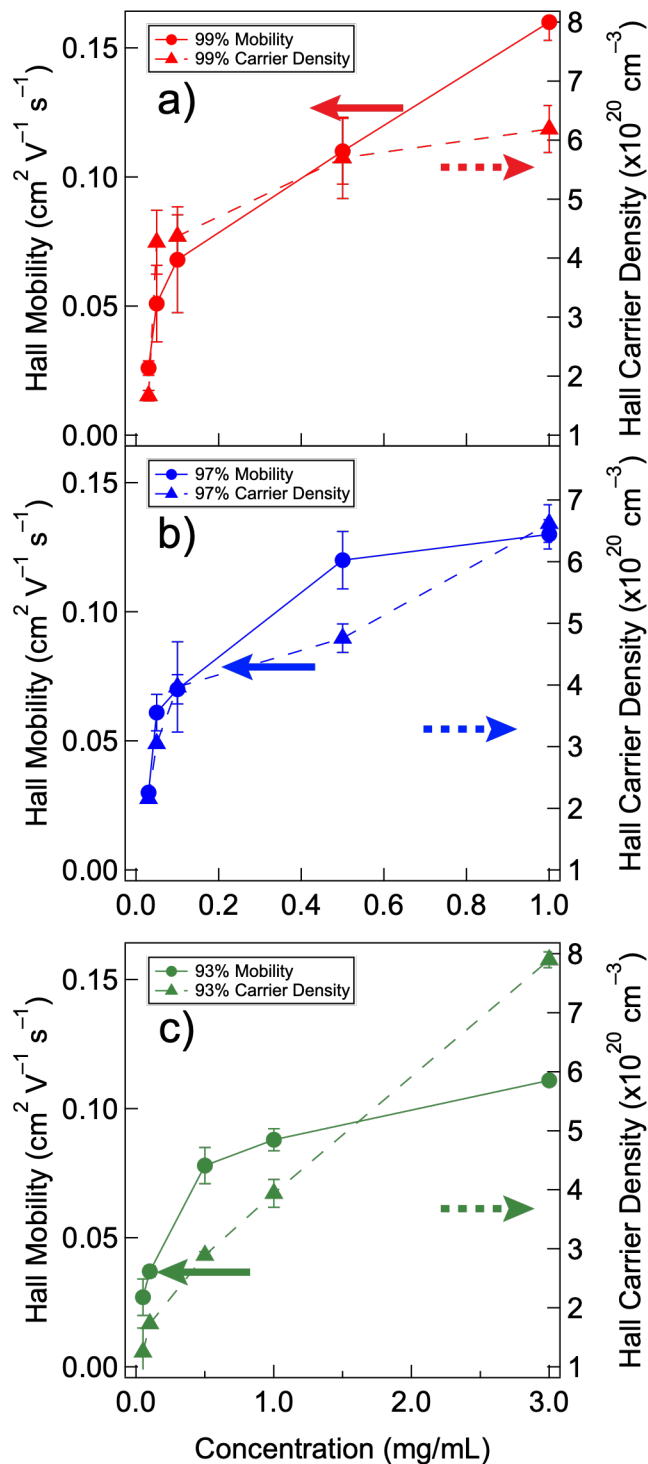


Figure D10. Hall effect measurements for doped: (a) 99% RR P3HT, (b) 97% RR P3HT, and (c) 93% RR P3HT doped via the anion-exchange method at various doping levels. The arrows for the solid (mobility) and dashed (carrier density) lines point toward the corresponding y-axis. The doped RRa samples were unable to give reproducible results and thus are not shown here. The x-axis is the F₄TCNQ concentration (with 30 mg/mL LiTFSI).

The Hall effect provides a direct route to determining carrier mobility and carrier density; however, these measurements are less reliable in low-mobility systems with hopping-like transport, such as doped conjugated polymers.^[23–27] Since the Hall voltage can be screened by localized carriers, Hall effect measurements often result in an overestimation of carriers compared to other methods like X-ray photoelectron spectroscopy (XPS).^[28] To minimize screening effects and offset voltages, we implemented both current and magnetic-field reversal to cancel out the offset voltages created by the hopping carriers in the doped P3HT films. Given that our 99% RR, 97% RR, and 93% RR P3HT samples are semicrystalline (relatively high mobility compared to other polymers) and doped at intermediate doping levels, we were able to obtain reliable measurements across triplicate samples. Furthermore, the carrier mobilities and densities obtained are within the range of values previously reported for doped P3HT in other work using DC Hall^[22] and AC Hall techniques.^[29,30] In contrast, the doped RRa samples produced intrinsically small Hall voltages due to stronger carrier localization and screening, yielding unreliable Hall carrier density values.

To overcome the limitations of Hall measurements in the doped RRa samples, we used the P1 absorption peak as a proxy for carrier density. The P1 band occurs in a spectroscopically quiet IR region, with minimal interference from other transitions, and thus its oscillator-strength area scales with the number of absorbers (polarons), with the assumption that the oscillator strength per polaron is comparable across these systems.^[31,32] We integrated the frequency-weighted absorbance over a defined energy window to obtain oscillator-strength areas (A_{P1}) proportional to the polaron population. A_{P1} values for doped 97% RR, 93% RR, and RRa P3HT samples were calculated by weighting their absorption spectra by frequency (in wavenumbers), followed by integration.

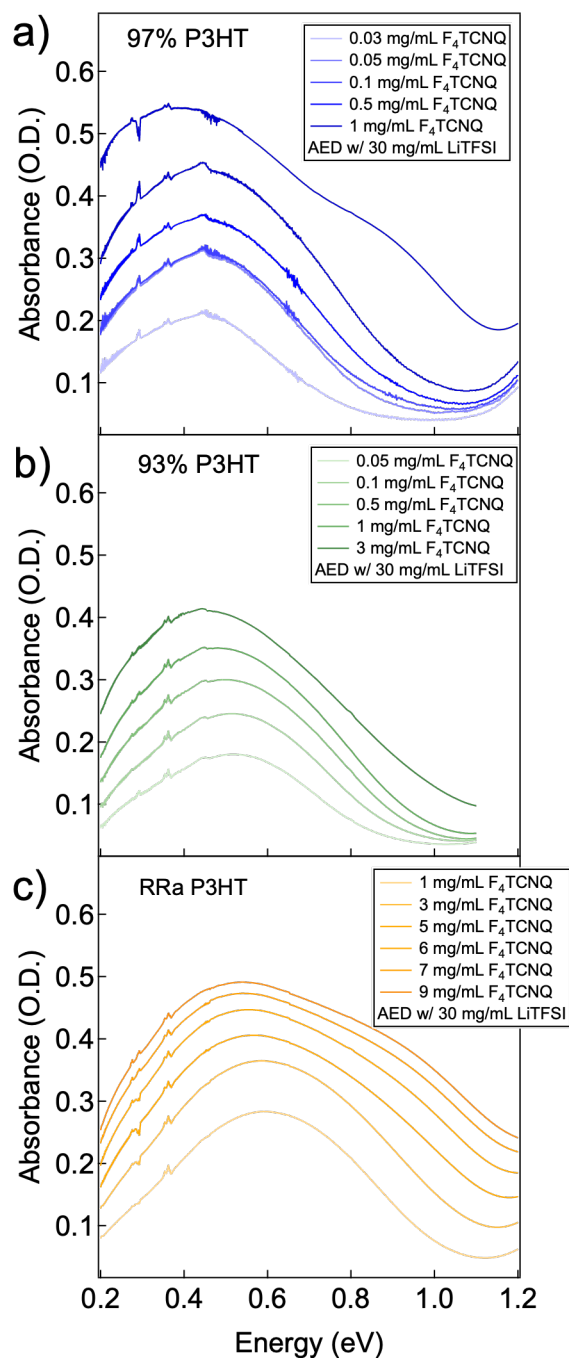


Figure D11. Full P1 peaks for the: (a) 97% RR, (b) 93% RR and (c) RRa P3HT samples used to create the P1–Hall correlation plots in **Figures D12 and D13**. The spectra of the 97% RR and RRa P3HT polymers show a bipolaron shoulder at high doping levels.

To construct a calibration line that maps the A_{P1} values of the doped RRa samples to carrier density, we used the reliable Hall carrier density values for the doped 97% RR and 93% RR

samples with their frequency-weighted oscillator-strength integrated P1 peak areas. Since the P1 peak positions of the doped 97% RR, 93% RR, and RRa samples occur at different energies, we used a symmetric integration window around each peak center. Specifically, we integrated from 90% of the peak maximum on both sides to ensure a consistent comparison of the relative polaron populations. Furthermore, this range excludes the bipolaron shoulder on the blue side of the P1 band at high doping levels (**Figure D11**). **Figure D11** shows the full P1 peaks for all the 97% RR, 93% RR, and RRa P3HT doped samples included in this analysis. Those samples were doped following the same procedure described in the Experimental Section in the main text. To ensure we captured a wider doping range in the correlation line, we extended the doping concentrations of the 97% RR P3HT to 6 mg/mL F4TCNQ with 30 mg/mL LiTFSI, which is known to heavily dope the 97% RR P3HT polymer.^[33] All films used for P1 analysis were cast onto sapphire substrates to eliminate the strong IR absorption of glass.

Figure D12a shows the obtained relation between the Hall carrier density and frequency-weighted oscillator-strength P1 peak areas for the doped 97% RR and 93% RR samples, giving the relation:

$$n_{P1} = 2.5 \times 10^{25} A_{P1} - 1.0 \times 10^{20}, \quad (\text{D4})$$

where n_{P1} is the P1-derived carrier density and A_{P1} is the oscillator-strength P1 area. **Figure D12b** shows the corresponding n_{P1} values and calculated carrier mobility for the doped RRa samples. Carrier mobility values were calculated using the electrical conductivity and the derived n_{P1} values. The resulting carrier densities fall within the range of highly doped polymer systems and are below the maximum site density of P3HT.^[29,34–38] Moreover, the UV–vis–NIR spectra of RRa P3HT (**Figure D6**) show significant bandgap depletion at high doping, consistent with the elevated n_{P1} values.

Because the P1 band is broadened by morphological and energetic disorder,^[13,14] it was important to test whether the correlation built from the 97% RR and 93% RR semicrystalline samples was valid for estimating carrier density in the amorphous RRa. To do so, we compared the Hall carrier densities (n_{Hall}) with the P1-derived carrier densities (n_{P1}) for the 97% RR and 93% RR polymers using the same calibration line. **Figure D12c,d** shows that there is strong agreement between n_{Hall} and n_{P1} with dopant concentration, particularly in the doped 97% samples. Likewise, mobility-carrier density trends obtained from both methods (**Figure D12e,f**) were consistent, with deviations only at the low- and high-doping extremes of the 93% RR polymer, where Hall sensitivity is most limited.

Finally, we tested the influence of the integration energy window by expanding the range asymmetrically, from 85% of the peak maximum on the low-energy side to 50% on the high-energy side, where bipolaron absorption is captured in the integration energy window. As shown in **Figure D13**, this alternative integration produced no significant changes in the correlations, confirming the robustness of the method.

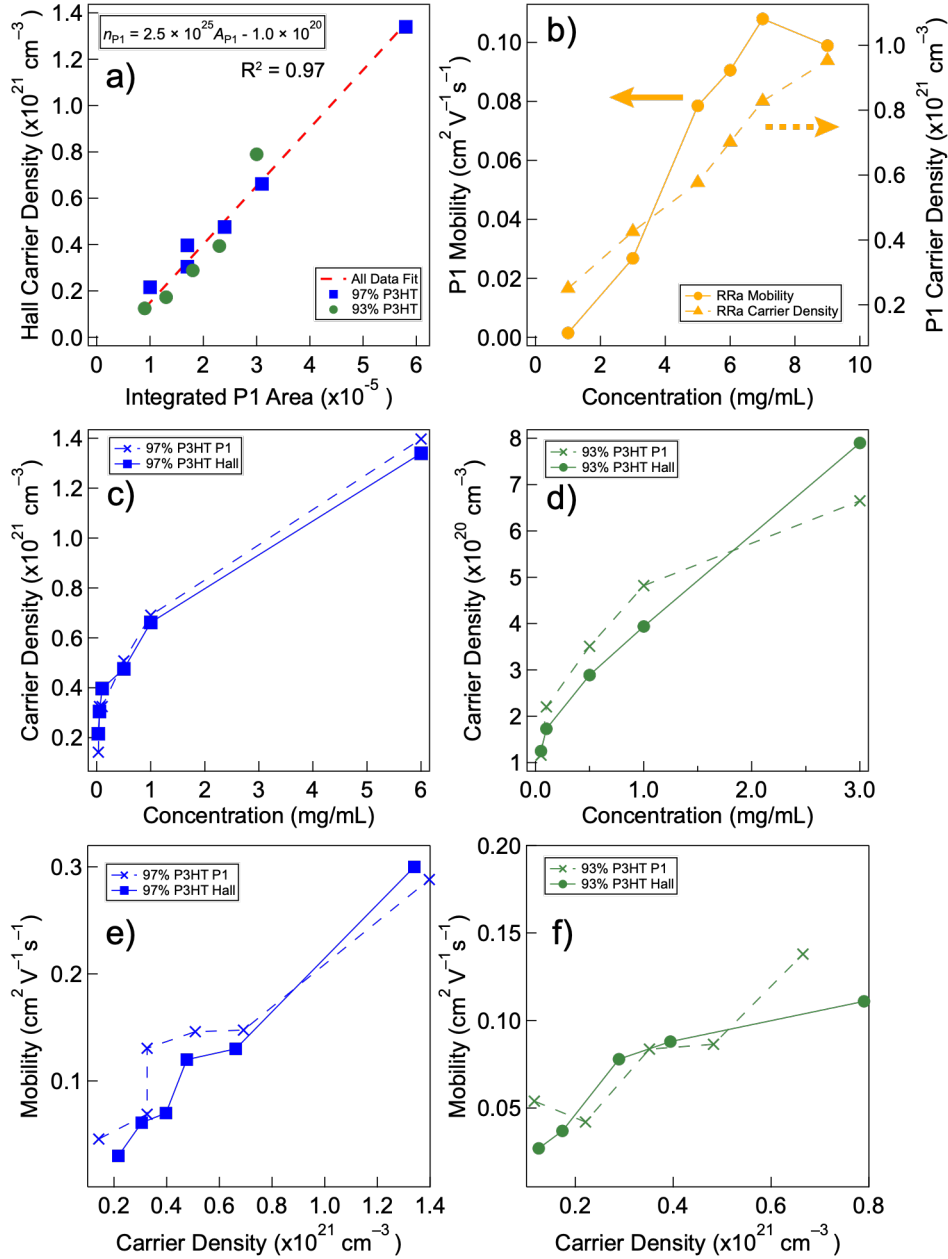


Figure D12. (a) Hall carrier density plotted against frequency-weighted oscillator-strength P1 peak area (A_{P1}) for doped 97% RR and 93% RR P3HT. The A_{P1} values were integrated over 90% of the peak maximum on each side to avoid the bipolaron blue shoulder (see **Figure D11**). The linear regression yields $n_{P1} = 2.5 \times 10^{25} A_{P1} - 1.0 \times 10^{20}$, which was used to convert the A_{P1} values for the doped RRa samples into carrier density. (b) Carrier densities obtained from the calibration line in (a), plotted alongside the carrier mobility calculated using the conductivity values and the n_{P1} values. Comparison of Hall carrier density (solid lines) and P1-derived carrier density (dashed lines) for the doped: (c) 97% RR and (d) 93% RR samples, respectively. Carrier mobility versus carrier density for: (e) 97% RR and (f) 93% RR P3HT, using both Hall and P1-derived carrier densities, showing consistent overall trends except at low and high doping levels.

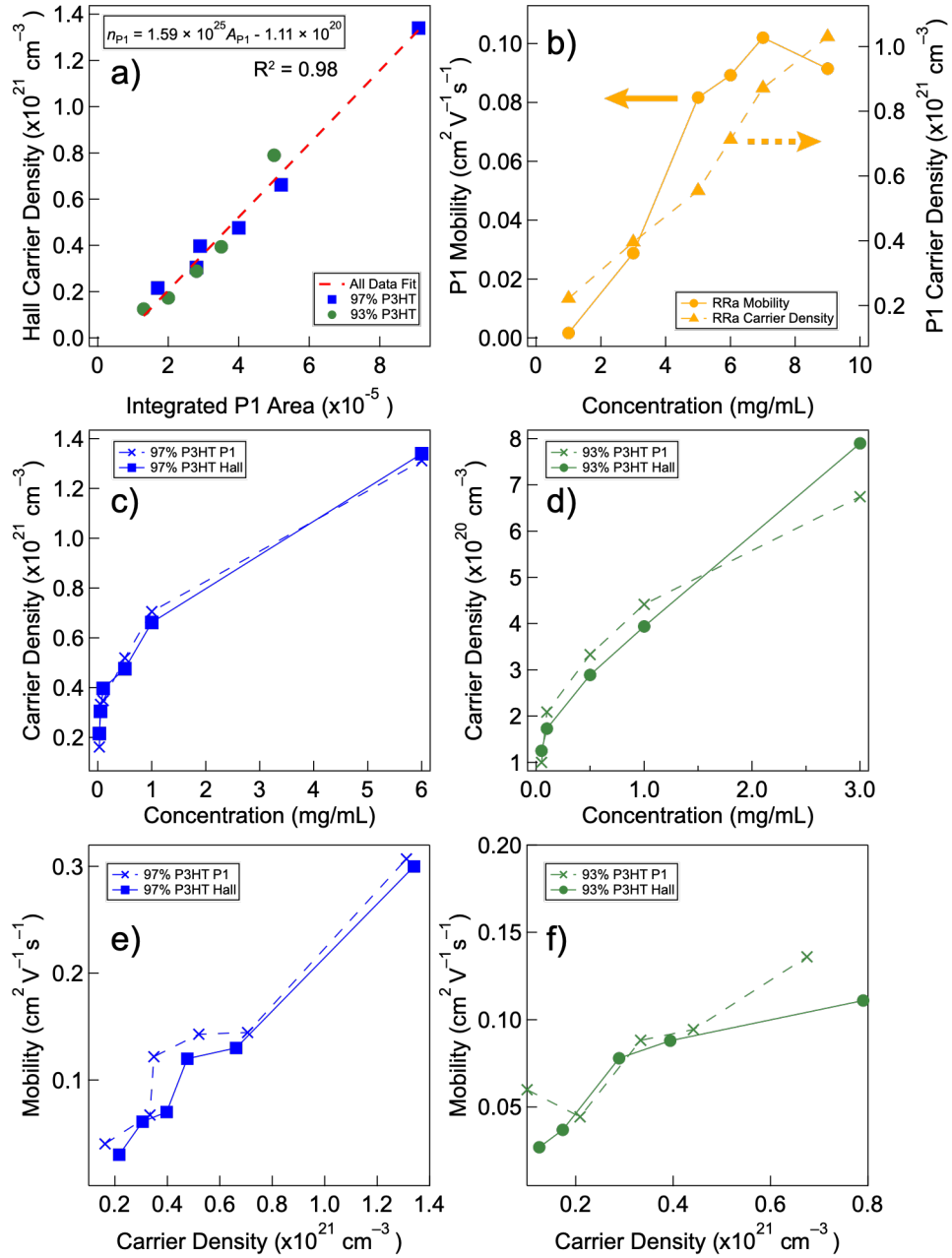


Figure D13. Same analysis as **Figure D12** but using an asymmetric integration energy window defined as 85% of the peak maximum on the low-energy side to 50% of the maximum on the high-energy side. (a) Hall carrier density plotted against frequency-weighted oscillator-strength P1 peak area (A_{P1}) for doped 97% RR and 93% RR P3HT, yielding a calibration curve of $n_{P1} = 1.59 \times 10^{25} A_{P1} - 1.11 \times 10^{20}$. (b) P1-derived carrier density and mobility for RRa P3HT obtained from the calibration curve in (a). Comparison of Hall and P1 carrier density versus dopant concentration for doped: (c) 97% RR and (d) 93% RR samples. Carrier mobility versus carrier density for: (e) 97% RR and (f) 93% RR P3HT using both Hall and P1-derived values. Similar to **Figure D12**, n_{Hall} and n_{P1} agree well across most of the doping range.

D.7 Seebeck Coefficient

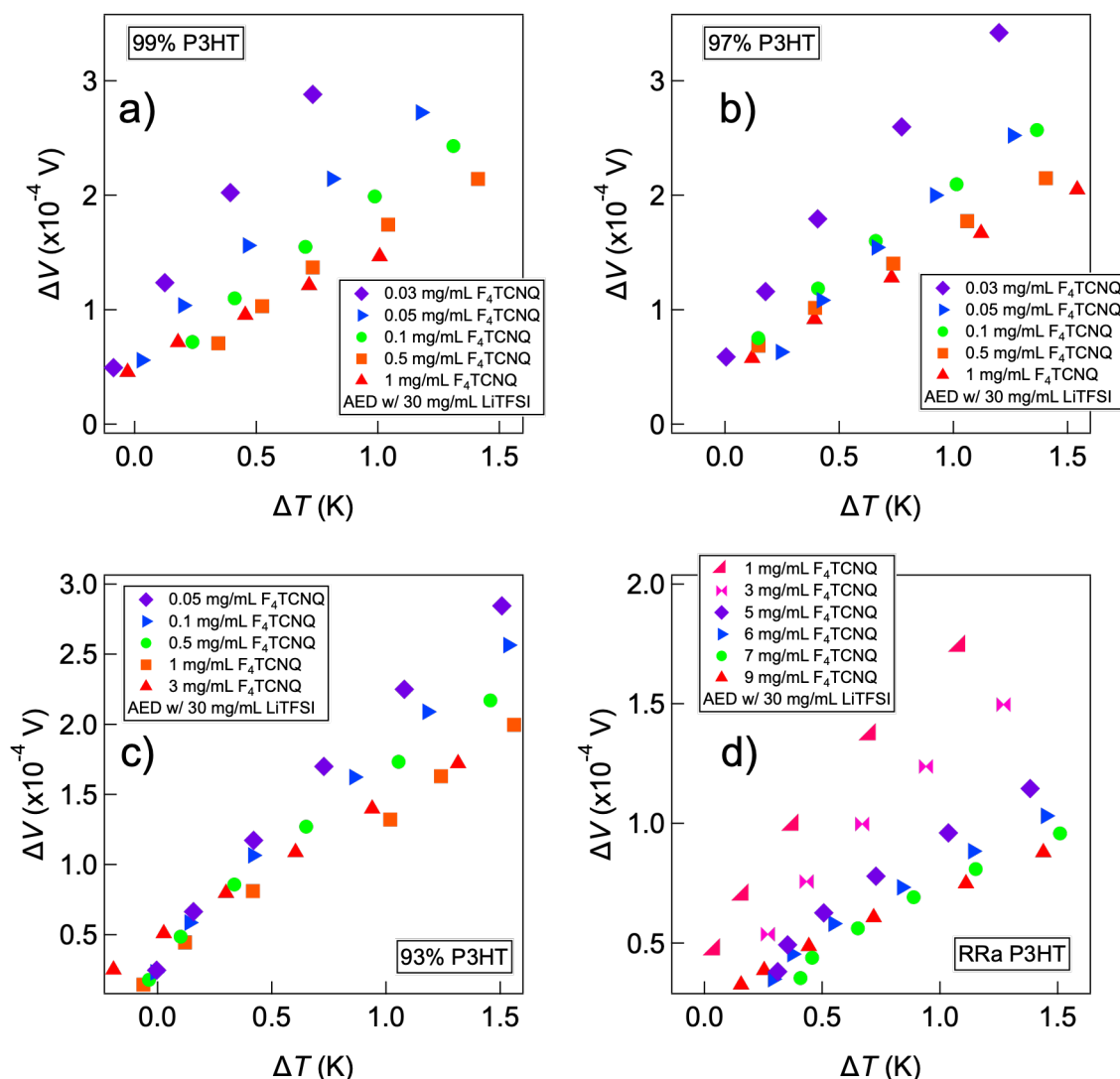


Figure D14. Linear relation between the induced voltage difference (ΔV) and the applied temperature difference (ΔT) for doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT. The Seebeck coefficient for each doping concentration was obtained from the slope of the ΔV – ΔT line. Legends indicate the F₄TCNQ concentration with 30 mg/mL LiTFSI for the anion-exchange method.

The Seebeck coefficient was measured on separate devices because the electrode geometry differs from that used for conductivity and Hall. Devices were prepared by casting and doping the polymer films onto pre-cleaned glass substrates (1.2×1.2 cm). The electrodes consisted of two

parallel gold bars (10×1 mm, 45 nm thick) separated by 10 mm. Seebeck measurements were carried out using a custom-built system in which two Peltier plates generated a controlled temperature gradient across the film, and the resulting temperature difference was monitored with two RTD sensors placed in contact with the device. To ensure that Seebeck and conductivity measurements reflected equivalent doping levels, both types of devices were fabricated and doped simultaneously under identical conditions.

The Seebeck coefficient of each doped sample was determined from the slope of the induced voltage difference (ΔV) versus the temperature difference between the hot and cold sides (ΔT). **Figure D14** shows the linear relation between ΔV and ΔT for the doped 99% RR, 97% RR, 93% RR, and RRa P3HT samples.

D.8 Activation Energy Measurements via Temperature-Dependent Conductivity

We used temperature-dependent conductivity to investigate the thermal activation energy (E_a) of the doped P3HT samples. Activation energies were extracted from linear fits of the Arrhenius equation $\sigma(T) = \sigma_0 \exp(-E_a/k_B T)$ where σ_0 is the temperature-independent prefactor and E_a is the thermal activation energy.^[39] **Figure D15** shows $-\ln(\sigma)$ versus $(k_B T)^{-1}$ at various temperatures for all four P3HT polymers doped via the anion-exchange method. All fits produced a linear relation with $R^2 \geq 0.99$, confirming that the Arrhenius equation accurately describes the thermally activated transport in the measured temperature ranges. All temperature-dependent conductivity values were measured on the same multifunctional devices described in the conductivity section above.

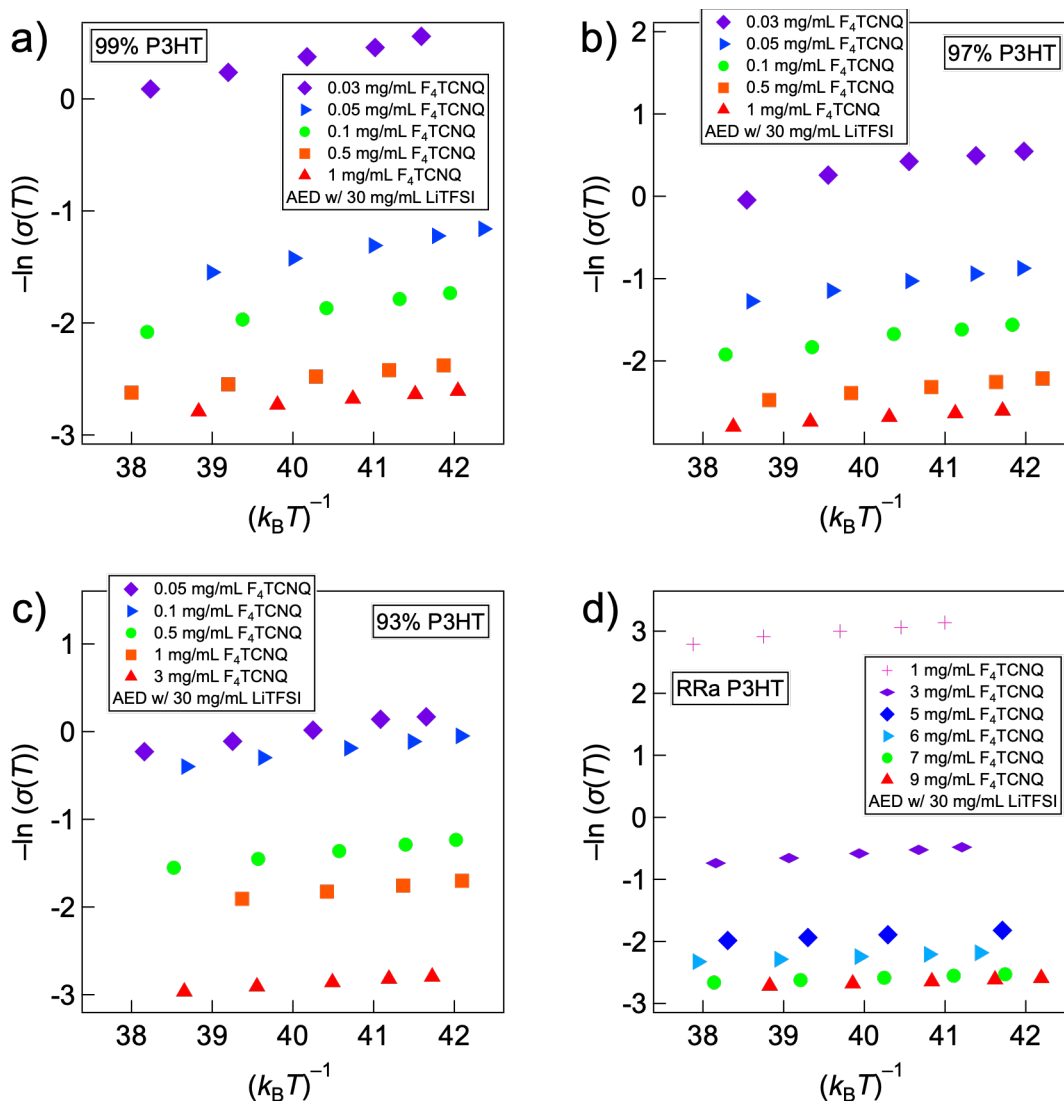


Figure D15. Temperature-dependent conductivity measurements for anion-exchange-doped: (a) 99% RR P3HT, (b) 97% RR P3HT, (c) 93% RR P3HT, and (d) RRa P3HT. Conductivity was measured using the van der Pauw geometry, and the activation energy, E_a , was calculated using the Arrhenius equation $\sigma(T) = \sigma_0 \exp(-E_a/k_B T)$. The legends report the F_4TCNQ doping concentrations. All doping solutions contained 30 mg/mL LiTFSI.

D.9 S - σ Relation and the Semi-Localized Transport (SLoT) Model

The electrical conductivity, σ , and Seebeck coefficient, S , are evaluated using the generalized Boltzmann transport **Equations (D5 and D6)**:

$$\sigma = \int \sigma_E \left(-\frac{\partial f}{\partial E} \right) dE \quad (\text{D5})$$

$$S = -\frac{k_B}{q} \int \left(\frac{E - E_F}{k_B T} \right) \left(\frac{\sigma_E}{\sigma} \right) \left(-\frac{\partial f}{\partial E} \right) dE, \quad (\text{D6})$$

where k_B is the Boltzmann constant, E is the energy of the charge carrier, q is the fundamental charge, E_F is the Fermi level, $f(E)$ is the Fermi–Dirac distribution, and σ_E is the transport function describing the carrier mobility.

Gregory *et al.* ^[28] expanded on the charge transport model developed by Kang and Snyder^[40] by proposing that the transport function also depends on doping level, c . In this framework, $\sigma_E(E, T, c)$ takes on the form in **Equation (D7)** for $E > E_t$ values:

$$\sigma_E(E, T, c) = \sigma_0 \exp \left(-\frac{W_H(c)}{k_B T} \right) \times \left(\frac{E - E_t}{k_B T} \right), \quad (\text{D7})$$

where the components are σ_0 , the prefactor or “intrinsic” conductivity in the absence of localization effects; W_H , a localization energy that depends on the carrier density c ; and an energy-dependent term, $\left(\frac{E - E_t}{k_B T} \right)$. This formalism is referred to as the semi-localized transport (SLoT) model.

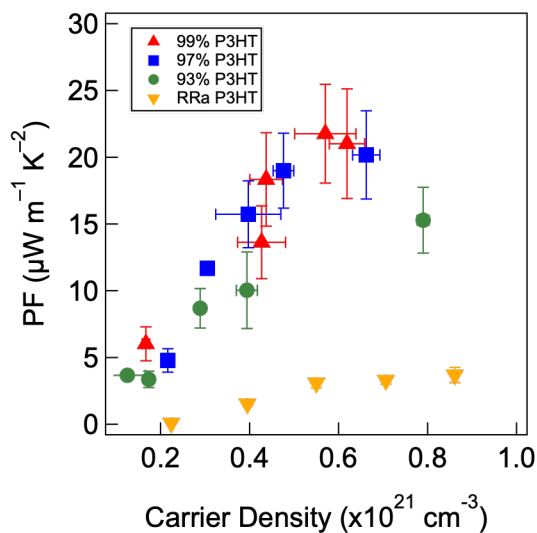


Figure D16. Power factor (PF) plotted versus carrier density, n , for the doped P3HT polymers. The more crystalline polymers exhibit an optimum in the PF at lower n indicating that their enhanced TE performance comes from a higher carrier mobility.

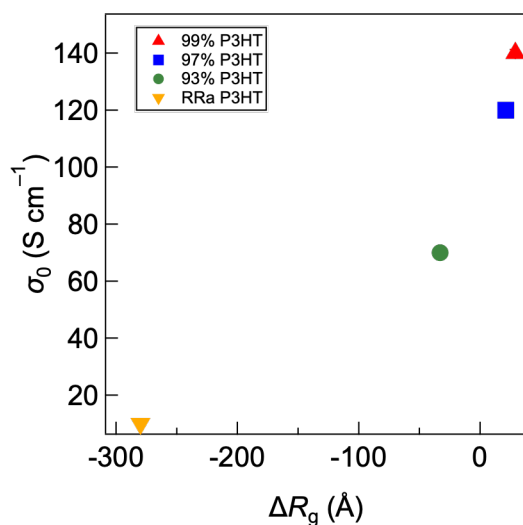


Figure D17. σ_0 plotted versus the change in R_g (ΔR_g) in the highest-doped samples for each polymer. ΔR_g was calculated by taking the difference of the doped R_g and the corresponding pristine R_g values. The monotonic trend between increased σ_0 in higher-regioregularity P3HT and increased domain correlation length R_g suggests that mesoscale ordering contributes to the enhanced TE performance in those systems.

D.10 References

- [1] I. E. Jacobs, Y. Lin, Y. Huang, X. Ren, D. Simatos, C. Chen, D. Tjhe, M. Statz, L. Lai, P. A. Finn, W. G. Neal, G. D'Avino, V. Lemaure, S. Fratini, D. Beljonne, J. Strzalka, C. B. Nielsen, S. Barlow, S. R. Marder, I. McCulloch, H. Sirringhaus, *Advanced Materials* **2022**, *34*, 2102988.
- [2] Y. Yamashita, J. Tsurumi, T. Kurosawa, K. Ueji, Y. Tsuneda, S. Kohno, H. Kempe, S. Kumagai, T. Okamoto, J. Takeya, S. Watanabe, *Commun Mater* **2021**, *2*, 45.
- [3] Y. Yamashita, J. Tsurumi, M. Ohno, R. Fujimoto, S. Kumagai, T. Kurosawa, T. Okamoto, J. Takeya, S. Watanabe, *Nature* **2019**, *572*, 634.
- [4] C. Chen, I. E. Jacobs, K. Kang, Y. Lin, C. Jellett, B. Kang, S. B. Lee, Y. Huang, M. BaloochQarai, R. Ghosh, M. Statz, W. Wood, X. Ren, D. Tjhe, Y. Sun, X. She, Y. Hu, L. Jiang, F. C. Spano, I. McCulloch, H. Sirringhaus, *Advanced Energy Materials* **2023**, *13*, 2202797.
- [5] A. Hamidi-Sakr, L. Biniek, J.-L. Bantignies, D. Maurin, L. Herrmann, N. Leclerc, P. Lévêque, V. Vijayakumar, N. Zimmermann, M. Brinkmann, *Advanced Functional Materials* **2017**, *27*, 1700173.
- [6] T. J. Aubry, K. J. Winchell, C. Z. Salamat, V. M. Basile, J. R. Lindemuth, J. M. Stauber, J. C. Axtell, R. M. Kubena, M. D. Phan, M. J. Bird, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Adv. Funct. Mater.* **2020**, *30*, 2001800.
- [7] I. E. Jacobs, G. D'Avino, V. Lemaure, Y. Lin, Y. Huang, C. Chen, T. F. Harrelson, W. Wood, L. J. Spalek, T. Mustafa, C. A. O'Keefe, X. Ren, D. Simatos, D. Tjhe, M. Statz, J. W. Strzalka, J.-K. Lee, I. McCulloch, S. Fratini, D. Beljonne, H. Sirringhaus, *J. Am. Chem. Soc.* **2022**, *144*, 3005.
- [8] G. Beaucage, *Journal of Applied Crystallography* **1995**, *28*, 717.
- [9] S. Lenz, M. Bonini, S. K. Nett, M. C. Lechmann, S. G. J. Emmerling, R. S. Kappes, M. Memesa, A. Timmann, S. V. Roth, J. S. Gutmann, *Eur. Phys. J. Appl. Phys.* **2010**, *51*, 10601.
- [10] C. Wang, D. T. Duong, K. Vandewal, J. Rivnay, A. Salleo, *Phys. Rev. B* **2015**, *91*, 085205.
- [11] E. C. Wu, C. Z. Salamat, O. L. Ruiz, T. Qu, A. Kim, S. H. Tolbert, B. J. Schwartz, *Adv Funct Materials* **2023**, *33*, 2213652.

- [12] A. J. Moulé, G. Gonel, T. L. Murrey, R. Ghosh, J. Saska, N. E. Shevchenko, I. Denti, A. S. Fergerson, R. M. Talbot, N. L. Yacoub, M. Mascal, A. Salleo, F. C. Spano, *Advanced Electronic Materials* **2022**, 8, 2100888.
- [13] M. B. Qarai, N. J. Hestand, F. C. Spano, *J. Phys. Chem. C* **2025**, 129, 812.
- [14] S. T. Hoffmann, H. Bässler, A. Köhler, *J. Phys. Chem. B* **2010**, 114, 17037.
- [15] Y. Wu, C. Z. Salamat, A. León Ruiz, A. F. Simafranca, N. Akmanşen-Kalayci, E. C. Wu, E. Doud, Z. Mehmedović, J. R. Lindemuth, M. D. Phan, A. M. Spokoyny, B. J. Schwartz, S. H. Tolbert, *Chem. Mater.* **2024**, 36, 5552.
- [16] P. Y. Yee, D. T. Scholes, B. J. Schwartz, S. H. Tolbert, *J. Phys. Chem. Lett.* **2019**, 10, 4929.
- [17] R. W. Hendler, R. I. Shrager, *Journal of Biochemical and Biophysical Methods* **1994**, 28, 1.
- [18] S. C. Doan, B. J. Schwartz, *J. Phys. Chem. B* **2013**, 117, 4216.
- [19] E. C. Wu, D. G. Vidales, C. Z. Salamat, Q. M. Duong, A. León Ruiz, A. D. Ready, Z. Mehmedović, D. A. Stanfield, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Advanced Functional Materials* **2025**, 35, e07480.
- [20] M. G. Voss, D. T. Scholes, J. R. Challa, B. J. Schwartz, *Faraday Discuss.* **2019**, 216, 339.
- [21] M. G. Voss, J. R. Challa, D. T. Scholes, P. Y. Yee, E. C. Wu, X. Liu, S. J. Park, O. León Ruiz, S. Subramaniam, M. Chen, S. A. Jenekhe, X. Wang, S. H. Tolbert, B. J. Schwartz, *Advanced Materials* **2021**, 33, 2000228.
- [22] Q. M. Duong, D. Garcia Vidales, B. J. Schwartz, *Applied Physics Letters* **2023**, 123, 202101.
- [23] W. A. Wood, I. E. Jacobs, L. J. Spalek, Y. Huang, C. Chen, X. Ren, H. Sirringhaus, *Phys. Rev. Mater.* **2023**, 7, 034603.
- [24] F. Werner, *Journal of Applied Physics* **2017**, 122, 135306.
- [25] H. T. Yi, Y. N. Gartstein, V. Podzorov, *Sci Rep* **2016**, 6, 23650.
- [26] Y. Chen, H. T. Yi, V. Podzorov, *Phys. Rev. Applied* **2016**, 5, 034008.
- [27] J. Lindemuth, S.-I. Mizuta, In *Thin Film Solar Technology III*, SPIE, **2011**, pp. 65–71.
- [28] S. A. Gregory, R. Hanus, A. Atassi, J. M. Rinehart, J. P. Wooding, A. K. Menon, M. D. Losego, G. J. Snyder, S. K. Yee, *Nat. Mater.* **2021**, 20, 1414.

- [29] S. Wang, M. Ha, M. Manno, C. Daniel Frisbie, C. Leighton, *Nat Commun* **2012**, 3, 1210.
- [30] B. J. Kim, S. Chung, S. Sim, H. Lee, J. Lee, K. Cho, *Nano Energy* **2025**, 146, 111547.
- [31] O. Khatib, B. Lee, J. Yuen, Z. Q. Li, M. Di Ventra, A. J. Heeger, V. Podzorov, D. N. Basov, *Journal of Applied Physics* **2010**, 107, 123702.
- [32] Z. Q. Li, G. M. Wang, N. Sai, D. Moses, M. C. Martin, M. Di Ventra, A. J. Heeger, D. N. Basov, *Nano Lett.* **2006**, 6, 224.
- [33] Z. Mehmedović, A. Leon Ruiz, A. N. Nguyen, K. Lo, D. Garcia Vidales, X. Liu, C. Z. Salamat, E. Doud, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. C* **2025**, 129, 15771.
- [34] D. T. Scholes, P. Y. Yee, G. R. McKeown, S. Li, H. Kang, J. R. Lindemuth, X. Xia, S. C. King, D. S. Seferos, S. H. Tolbert, B. J. Schwartz, *Chem. Mater.* **2019**, 31, 73.
- [35] A. I. Hofmann, R. Kroon, S. Zokaei, E. Järsvall, C. Malacrida, S. Ludwigs, T. Biskup, C. Müller, *Advanced Electronic Materials* **2020**, 6, 2000249.
- [36] D. Neusser, C. Malacrida, M. Kern, Y. M. Gross, J. van Slageren, S. Ludwigs, *Chem. Mater.* **2020**, 32, 6003.
- [37] V. Untilova, T. Biskup, L. Biniek, V. Vijayakumar, M. Brinkmann, *Macromolecules* **2020**, 53, 2441.
- [38] Q. M. Duong, D. G. Vidales, X. Liu, C. Z. Salamat, A. Ready, H. A. Khunaizi, M. Matsumoto, A. M. Spokoyny, S. H. Tolbert, B. J. Schwartz, *Advanced Functional Materials* **2026**, e75510.
- [39] M. Schwarze, C. Gaul, R. Scholz, F. Bussolotti, A. Hofacker, K. S. Schellhammer, B. Nell, B. D. Naab, Z. Bao, D. Spoltore, K. Vandewal, J. Widmer, S. Kera, N. Ueno, F. Ortmann, K. Leo, *Nature Mater* **2019**, 18, 242.
- [40] S. D. Kang, G. J. Snyder, *Nature Mater* **2017**, 16, 252.