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Microstructure and optoelectronics of small-molecule charge transport networks in polymer solar cells

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MICROSTRUCTURE AND OPTOELECTRONICS OF SMALL MOLECULE CHARGE TRANSPORT NETWORKS IN POLYMER SOLAR CELLS

A dissertation submitted in partial satisfaction
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry

by

Michael Roders

June 2019

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Abstract

MICROSTRUCTURE AND OPTOELECTRONICS OF SMALL MOLECULE CHARGE TRANSPORT NETWORKS IN POLYMER SOLAR CELLS

Michael Roders

Organic photovoltaic (OPV) devices utilize thin films of organic semiconductors that can be used for low-cost solution processed solar cells for harvesting solar energy as a source of renewable energy. The active layer of OPV devices is a bulk heterojunction (BHJ) thin film blend of two or more organic semiconductors (OSCs) including conjugated polymers and small molecules that have chemical structures characterized by alternating single and double bonds that absorb photons in the visible-spectrum. Fullerene derivatives have been relied on as a quasi-spherical small molecule acceptor that facilitates isotropic intermolecular charge transport, however, fullerene derivatives have relatively low optical absorption crosssections and therefore contribute negligibly to device photocurrent. Recent progress and record power conversion efficiencies in BHJ based organic photovoltaic devices have utilized anisotropic non-fullerene small molecules in conjugated polymer blends. Despite the dramatic progress in device performance, there is a fundamental gap of knowledge in relating the small-molecule chemical structure and intermolecular interactions to the hierarchical device morphology and corresponding optoelectronic processes. The focus of this dissertation develops a deeper understanding of how the Ångstrom scale chemical structure of small molecule organic semiconductors...
influences the bulk heterojunction microstructure on the ~100 nm scale. With experiments designed around several systematically designed chemical series, this thesis interrogates the influence of multiple avenues of chemical structure dimensionality and the resulting evolution in BHJ microstructure. Using a combination of synchrotron X-ray scattering and electron microscopy techniques. Optical spectroscopy and device measurements are used to probe the device-relevant charge separation and transport processes. The correlation of the optoelectronic and microstructural characterization supports the claim that Angstrom scale details of the small molecule chemical structure and intermolecular interactions can lead to a prescribed BHJ morphology for controlling the device relevant photophysical properties. The results of this dissertation demonstrate that both coarse changes in molecular geometry, subtle modifications of the number and connectivity of peripheral functional groups, and the geometry of the linking core between interacting sidechains can have an enormous influence intermolecular packing leading to dramatic changes on the nanometer scales of phase separation and self-assembly as well as optical and charge transport properties of both small-molecule and polymer networks. The conclusions of this thesis provide insight for the future design of next-generation organic semiconductors for light harvesting applications in polymer-based solar cells.
Dedication

To my Mother Pamela – when we first met I knew no words and now I know many.

My partner Lina Maria Ramirez-Camacho - for your day-to-day support and companionship throughout my graduate research at UCSC.

My brother Brian – for your inspirational charisma, perseverance, and spirit.

My sister Katie – for your thoughtful and compassionate encouragement.
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1. Introduction

1.1 Background

Beginning with the discovery of a conductive form of doped polyacetylene that was awarded in the Nobel Prize in Chemistry in 2000\(^1\), conjugated organic semiconducting (OSCs) molecules and polymers have been investigated as “synthetic metals” for a broad range of applications in commercial electronics ranging from field-effect transistors to light emitting diodes and photovoltaic devices. Synthetic organic chemistry is used as a tool for manipulating the dimensionality of the OSC conjugated framework resulting in the control of fundamental optoelectronic processes: light absorption and emission as well as charge transfer and delocalization. The chemical structure of several OSC molecules are characterized by alternating single and double covalent bonds and are illustrated by several representative classes in Figure 1.1.

The spatial overlap of adjacent p\(_z\) orbitals allow for delocalization of \(\pi\) - electrons promoted to the lowest unoccupied molecular orbital (LUMO or valence band) via photoexcitation from the highest molecular orbital (HOMO, conduction band) or injection from a metal-OSC interface. Typical OSC HOMO-LUMO transitions are approximately 1.5 - 3 eV and therefore resonant with photon frequencies spanning the visible and near-infrared (NIR) light spectrum which is the driving motivation for their utility in light harvesting materials used in organic photovoltaic devices (OPVs).
1.1.2 Organic Photovoltaic Devices

The utility of OSCs as light harvesting material is primarily rooted in the high absorption and extinction coefficients of OSC dye molecules (~$10^5$ cm$^{-1}$) in the visible regions of the optical spectrum that is several orders of magnitude higher compared to silicon. The high absorption allows for a very thin layer of OSC (~100 nm) to absorb an equivalent number of photons using rigid Si slabs that are orders of magnitude thicker and require expensive high temperature processing and exceedingly high purities. The low required thickness of OPV is economically attractively due to the low material costs for a wide range of consumer applications that can exploit the tunability of the OSC absorption cross-section enables NIR-active OSCs for integration into photovoltaic windows that are optically transparent. Further, the mechanical flexibility of polymeric materials due to the high density of interchain entanglement, the thin OPV dimension allows for OPV fabrication onto flexible substrates for exotic emerging technologies such as wearable consumer electronics.

The challenges of OPV begins with their relatively low power-conversion efficiencies (PCE) relative to their inorganic counterparts. Although OPV are attractive to application in niche low-cost form factors, the low PCE has limited the broadened application into large-scale photovoltaic systems. Until very recently, a slow climb to an apparent 10% PCE threshold had seemingly been encountered for OPV compared to +20% for commercial polycrystalline silicon-based devices. The intrinsic
photophysical properties of OPVs that will be summarized in the context of device morphology sections.

Figure 1.1 Chemical structures of OSC polymers (a) P3HT and (b) PTB7; and molecules (c) PC60BM, (d) CuPc and (e) ITIC.
1.1.2 Bilayer and Bulk-heterojunction Device Architectures

The generation of photocurrent requires harvesting of free charge electron and holes generated from photoinduced excited states. Upon electronic excitation to the LUMO, a positively charged electron vacancy referred to as a hole remains in the HOMO. The resulting neutral excited state is a localized electron-hole pair that is a Coulombically bound Frenkel exciton. Compared to the highly mobile Wannier-mott excitons formed within inorganic crystalline materials, the low dielectric strength of conjugated hydrocarbons ($\epsilon \sim 2 - 4$) lead to that Frenkel excitons are localized on the organic lattice with a relatively high binding energy the ($\sim 0.1 - 1.0$ eV). The high binding energy coupled with the low dielectric strength lead to an energetic barrier for separated free charge carriers often leading to exciton recombination via radiative emission. This energetic barrier can be overcome by a donor-acceptor heterojunction of two OSCs with a favorable energy level offset. In this manner, an n-type OSC acts as an electron donor and hole transporter while a p-type OSC acts as an electron acceptor, illustrated in Figure 1.2.

Photoexcited electron transfer between organic semiconductors was experimentally observed early as the photoluminescence of a thin film of the conjugated polymer MEH-PPV was largely quenched at the interface with a thin film of unsubstituted C60. This bilayer type architecture illustrated in Figure 1.2 (bottom left) was discovered to be a fundamental architecture for interrogating fundamental interfacial processes, and when sandwiched between transparent electrodes with
appropriate work functions, could be utilized to harvest the free charge carriers from separated excitons. The relatively small photocurrents measured in bilayer devices are largely due to the short OSC exciton diffusion length, $L_d$ (~10 nm) leads to a low probability of exciton migration from the bulk material to a donor-acceptor interface. A large magnitude of photogenerated excitons thus recombine leading to few separated free charge carriers that can be harvested as electricity. Upon casting a solution of co-dissolved donor and acceptor molecules from a common solution, a complex landscape of increased donor-acceptor interfaces known as a bulk heterojunction (bottom right, Figure 1.2) is formed which leads to a large magnitude of free charge carriers.\textsuperscript{3-5}

Regarding exciton separation, an idealized BHJ microstructure has phase separated donor-acceptor domains on the order of $L_d$ that facilitates a low mean free path for exciton migration to donor-acceptor interfaces. Similar to the bilayer device architecture, a highly segregated network yields few charges due to the relatively low donor/acceptor interfacial area, but the charge mobility rises substantially owing to a less tortuous morphology and decreased bimolecular recombination rates. The fine balancing act of finding the “sweet spot” in a highly multidimensional processing variable space corresponding to the optimal blend morphology is a very laborious task that must be painstakingly performed for every new donor/acceptor combination

In addition to intramolecular delocalization, charge transport in OSC thin films occurs by intermolecular hopping via π - electron wavefunction overlap of adjacent molecules or polymer chains. The probability of intermolecular wavefunction overlap and charge transfer is at a maximum when neighboring chromophores are co-facially
aligned and decreases rapidly with intermolecular separation. Thus, the rate of charge transport in OSC solids is highly coupled to intermolecular packing and solid-state microstructure. As will be described in the following sections, the OSC and OPV

Figure 1.2 A cartoon illustration of absorption of radiation and excitation of a HOMO electron to the LUMO (top left) leading to the formation of an exciton separation at donor-acceptor interfaces (top right); bilayer (bottom left) and bulk heterojunction (bottom right) photovoltaic device architectures illustrating spatial charge transport pathways.
microstructure is characterized by a high degree of disorder which does not lend well to efficient charge carrier transport. Thus, the free charge carriers are still sensitive to non-geminate recombination (trap states existing on lattice sites spatially distant from the original molecule or lattice site of initial excitation) as it traverses a geometrically and energetically disordered landscape prior to being harvested at an electrode interface.

Following deposition from solution, the resulting non-equilibrium thin film microstructure is sensitive to the combined effects of intermolecular interactions, solvent evaporation rate and processing parameters. In the case of conjugated polymers, relaxation to a thermodynamically minimum free energy microstructure of semi-crystalline domains with periodic inter-chain $\pi - \pi$ stacking and sidechain-sidechain distances. The resulting solid-state microstructure is composed of polycrystalline, amorphous and mixed phases. In conjugated polymers, a relaxed morphology typically is characterized by an increase in effective polymer conjugation lengths and decreased $\pi - \pi$ stacking distances leading an increased effective charge mobility along the conjugated polymer backbone and $\pi - \pi$ stacking axes. In contrast, the alignment of alkyl sidechains between adjacent polymer chains leads to the formation of electronically insulating lamellae composed of fully saturated carbons. The combination of high charge mobility through extended and pi – pi stacked polymer chains with the energetic barrier of charge transport through sidechain lamellae is a resulting polymer microstructure that has inherently anisotropic charge mobility.
The polymer glass phase transition can lead to the aggregation of polymers as polymer crystallization occurs on thermal relaxation into a higher ordered and ordered microstructure that will drive phase separation. Fullerene derivatives are especially mobile within the polymer glass phase and their spherical geometry facilitates effective intermolecular packing into fullerene-pure domains with dimensions commensurate with $L_d$. 7-8

The relaxed microstructure can be accessed by thermal annealing above the glass transition temperature ($T_g \sim 100 - 200 ^\circ C$) that provides a driving force for the polymer
microstructure to overcome local free energy minima, followed by slow cooling to room temperature that allows the microstructure to relax to an absolute free energy minimum. Alternatively, the presence of high solvent vapor pressure can partially solvate the solid-state thin film allowing sufficient degree of freedom to access a relaxed microstructure. The increase of molecular ordering often leads to increased charge mobilities due to increased crystalline coherence and effective conjugation lengths that facilitates both inter- and intra-molecular charge transport. Solution processed OSCs with carrier mobilities have been exceeding $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ have been reported, rivaling the performance of polycrystalline silicon transistors albeit with dramatically lower fabrication costs.\(^6\)

1.1.3 The Fullerene Bulk Heterojunction and Beyond

The climb to OPV PCE of 10% and higher was primarily achieved via conjugated polymer bandgap engineering to increase the spectral overlap of the polymer absorption cross section of the solar emission spectrum, with the added requirement that appropriate energetic offset for charge separation with the fullerene LUMO ($\sim 4.0 \text{ eV}$). The quasi-spherical electronic wavefunctions of fullerenes are have high electron affinities largely due to a triply degenerate LUMO. Isotropic inter-fullerene electron transfer rates is paramount to the formation of effective electron transport network in fullerene BHJ films. However, fullerene derivatives have notably low absorption cross-sections and thus contribute relatively little to the photocurrent, particularly in the near-
IR region of the spectrum. Additionally, the frontier wavefunction energy levels of fullerene derivatives are largely insensitive to derivatization leading, therefore only a limited the breadth of polymer hosts with appropriately offset HOMO/LUMOS can be explored for fullerene BHJ devices. Several high mobility n-type semiconductors, such as poly(naphthalene diimide), have been explored, however, cannot be interfaced with fullerene derivatives in BHJ devices due to the fixed energy levels of the fullerene wavefunction that due not favorably align for efficient charge separation.\textsuperscript{10}

Though the frontier energy levels of non-fullerene OSCs can be tuned in a straightforward manner, replicating or improving upon the highly desirable mesoscale charge mobility of the fullerene network. Owing again to their spherical geometry, fullerene derivatives can effectively pack into compact and relatively fullerene-pure domains, while also are capable of percolating into interstitial regions between polymer backbones and side-chains, thus giving rise to a “mixed-phase” has been investigated as a crucial driving force for charge separation due to the small shifts in polymer HOMO and fullerene LUMO that occur due to the formation of induced dipoles and electrostatic gradient at polymer:fullerene interfaces.\textsuperscript{11}

In addition to charge transfer isotropy, an immensely important consideration in any novel combination of polymer and small molecule is the average domain length scale of phase separation which is largely dependent on the kinetics and thermodynamics of solvent evaporation processes during film deposition. The extent of phase separation and intermixing between donor and acceptor domains within the BHJ film has a limiting effect on the relative rates of electron-hole separation and the
formation of percolated donor-rich and acceptor-rich paths that allow charges to reach the electrodes.

The driving motivation of this thesis is that OPV device PCEs have reached an effective ceiling due to a lack of fundamental understanding of how the Å-scale small molecule chemical structure influences the hierarchical nanometer-scale microstructure and resulting BHJ device optical and charge transport properties. Many prominent classes of non-fullerene OSC molecules have been investigated in bulk heterojunctions, and often within each class systematic chemical series have been interrogated to optimize bandgap and polymer-energetic alignment while minimizing recombination energy losses. An exhaustive review of all non-fullerene small molecules is outside the scope of this Introduction. However, the relationship between chemical structure and the resulting BHJ microstructure is perhaps least understood and of prominent importance toward advancing OPV device performance. In this regard, several important classes of non-fullerene OSCS will be highlighted in the context of how they modulate the BHJ morphology.

Perylene diimide molecules are planar compounds composed of a fused aromatic-core that are strongly prone to cofacial pi-pi stacking leading to crystallization in polymer blends leading to large phase separated domains well in excess of excitation diffusion. This description is consistent with reports of overly phase separated domains in PDI based BHJ devices that demonstrate high charge recombination rates and poor device performance.12-14 In order to disrupt this aggregation and mimic the isotropic charge transport of fullerene derivatives, multiple planar PDI units are covalently
bonded through a variety of linking cores that lead to planar molecules less prone to aggregation while retaining high intermolecular charge transfer rates.

In contrast to the quasi-spherical fullerene cage, most organic small molecules are anisotropic, which leads to intermolecular electron transfer rates that depend strongly on the relative molecular orientation, often leading to certain charge transport directions characterized by very poor charge mobilities. Though the three-dimensional nature of fullerene derivatives and its resulting isotropic charge transports is often explored in non-fullerene small molecules, molecules characterized by a high degree of anisotropy can in principle be leveraged to manipulate the hierarchical morphology of the polymer/molecule blend film in a predictive manner. The self-assembly liquid of crystalline OSCs into charge-transporting channels with increased mobilities have been realized in BHJ OPV devices where either one or both the donor and acceptor are small molecules capable of forming semi-ordered discotic liquid-crystalline mesophases. Due to the preferred axis of columnar growth perpendicular to the pi-pi stacking direction, there is evidence that this gives rise to an enhanced charge mobility along a preferred axis of columnar growth due their large polycyclic aromatic cores. In thermally annealed conjugated polymer blends liquid-crystal-forming small molecules have been shown to crystallize into motifs that reflect their anisotropic intermolecular interactions. 15-17

Derivatives of the indacenodithiophene (ITIC, shown in Figure 1e) family are sometimes referred to as ladder molecules due to their fused planar fused core of
repeating aromatic subunits. Due to the rigid backbone, ITIC molecules are capable of extended exciton transport and intermolecular transfer as well as absorption extending to longer wavelengths with increasing conjugation length. The synthetically appended alkyl and aromatic sidechains appended onto the sp$^3$ carbons of the ladder backbone are effective in reducing crystallization and over phase segregation while maintaining effective intermolecular packing. BHJ active layers incorporating ITIC derivatives have been reported with record PCEs that out-perform fullerene blends and have been utilized in recently reported OPV PCEs. ITIC is now considered a champion non-fullerene small molecule for BHJ blends, however, there is a fundamental lack of understanding of how extending the ladder backbone influences the optoelectronic properties within the BHJ system.

### 1.2 Experimental and Analytical Methods

#### 1.2.1 Charge Transport

The performance of photovoltaic devices are typically evaluated by the measured short-circuit current, $J_{sc}$, or the amount of current density that can be extracted from a solar cell operating without any external bias, as well as the PCE. Both of these parameters rely upon a bulk photocurrent measurement that includes the sum of contributions from both electron and hole transport through small-molecule and polymer networks, respectively. However, to systematically investigate the isolated
charge transport through a small-molecule network within an interpenetrating binary BHJ requires an isolated measurement of transport through charge carrier of interest. The transport of charges within a OSC or BHJ diode architecture device is commonly parameterized by the observable current density (J) and effective charge mobility (µ) using the space-charge-limited (SCLC) defined in Equation 1.1:

$$J = \frac{\mu \epsilon V^2}{4 \pi d^3}$$  \hspace{1cm} (1.1)

where J and µ have units of A/cm² and cm²V⁻¹s⁻¹, respectively. J is the absolute magnitude of measured current (I) normalized by the cross-sectional device area, charge mobility is proportional to bulk conductivity (when scaled by the material charge carrier density), ϵ is the unitless relative permittivity of the conducting medium (~ 2 – 4 for OSCs), V is the applied bias and d is the device active layer thickness (thickness between electrodes).

The SCLC current density is typically measured at high bias in order to neglect the contribution of low ohmic current present at low bias to thermal drift mobilities. However, the experimentally observed Child’s square-voltage law is often not obeyed in OSC thin films which implies that either (a) the charge mobility is a function of the electric field, or (b) there exists an energy-dependent electronic trap distribution, P(E), described by Equation 1.2 within the SCLC formalism:\textsuperscript{10}:

$$P(E) \propto e^{-|E_{VB} - E|/k_B T_c}$$  \hspace{1cm} (1.2)
$E_{VB}$ in Equation 2 is the valence-band (HOMO) level, while $k_B$ is the Boltzmann constant, and $T_c$ is the characteristic temperature that is inversely proportional to the width of the exponential distribution of trap states with energies above the HOMO. Within this model, the magnitude of $T_c$ is extracted from the voltage power-law scaling exponent ($>2$) of the experimentally observed $J$-$V$ curve via **Equation 1.3**.

$$J \propto V^{T_c/T+1} \quad \text{(1.3)}$$

### 1.2.2 Structural Characterization with Synchrotron X-ray Scattering

Synchrotron X-ray scattering is the ideal tool to probe the microstructure of BHJ films due to the small X-ray wavelength and highly brilliant photon flux that is able to resolve the low electron density contrast of partially disordered OSC thin films on the Ångstrom and nanometer scale length scales that relevant to crystallinity and phase separation. Information from scattering experiments is extracted from the intensity of elastically scattered photons as a function of the reciprocal space scattering vector (or wavevector transfer), $Q$, defined in **Equation 1.4**:

$$hQ = h k_{in} - h k_{out} \quad \text{(1.4)}$$

where $h$ is Planck’s constant, $k_{in}$ is the wavevector incident onto a sample and $k_{out}$ is the scattered X-ray wavevectors, respectively, (defined as $k = \frac{2\pi}{\lambda}$). The magnitude
of the incident and scattered wavevector are equal in magnitude, however the absolute magnitude of \( Q \) is defined in **Equation 1.5**: 

\[
|Q| = \frac{4\pi}{\lambda} \sin \theta \tag{1.5}
\]

where \( \theta \) is half of the scattering angle defined within the Bragg equation. Both \( k \) and \( Q \) are expressed typically with the reciprocal space unit A\(^{-1}\) and utilized in order to allow comparison of X-ray scattering experiments across X-ray sources with different photon wavelength. Within the kinematical diffraction model, the observed scattering intensity, \( I(Q) \), results from the constructive interference of X-rays elastically scattered from assemblies of electrons within a sample material.\(^{22}\)

Polymer and polymer blend films are generally composed of a collection of crystallites with a random distribution of sizes and orientations and are therefore more similar to a 3-dimensional powder. Due to the distribution of orientations of crystallographic planes, polymer film diffraction patterns and scattering intensity will be dependent on the population of crystallites with a given orientation. This angle corresponding to crystallite orientation is relative to the azimuthal angle relative to the incoming X-ray beam and is often referred to as the polar angle, or \( \chi \). The use of an area detector allows for rapid acquisition of \( I(Q) \) for full \( \chi = \pm 90^\circ \) pole-figures that quantify the entire crystallite orientation distribution function.

The following paragraphs describe specific X-ray scattering experiments with experimental geometries (or X-ray energies) that broadly fall into two classes and
capture distinct small-angle or wide-angles that fall into distinct Q-ranges. It is noted that both wide-angle and small-angle X-ray scattering experiments can be performed in-transmission with $k_{in}$ propagation and penetration normal to the film surface, or in grazing-incidence where the incoming beam is oriented at an adjustable angle near the film surface for roughness sensitivity. Alternatively the incidence angle can be changed to angles just above the critical angle of total external reflection for full penetration into the bulk thin film, providing an X-ray beam that is spread out over a large scattering volume for bulk thin film characterization while also providing information regarding both in-plane and out-of-plane film texture. The critical angle for full external reflection can be calculated from the scattering X-ray wavelength and the material electron density via Equation 1.6:

$$\alpha_c = \sqrt{2\delta} = \frac{\sqrt{4\pi \rho r_o}}{k} \quad (1.6)$$

where $\delta$ is the scattering component of a material’s complex index of refraction, calculated from the respective electron density ($\rho$), the scattering length of an individual electron ($r_o$) and is dependent on the magnitude of the X-ray wavevector ($k$). In wide-angle X-ray scattering (WAXS), $Q > 0.1 \text{Å}^{-1}$ is probed corresponding to the Angstrom scale distances between crystalline lattice planes ($\pi - \pi$ stacking and inter-sidechain distances) as well as crystallite orientation distributions.25

In small-angle X-ray scattering (SAXS) where scattering vector between $10^{-3}$ $\text{Å}^{-1} < Q < 10^{-1}$ $\text{Å}^{-1}$ is measured corresponding to long-range differences in electron
density contrast, allowing for determination of the average length scale of phase separation, or domain size, within a given material.

The observed scattering intensity, \( I(Q) \), in the small-angle regime is the Fourier Transformed pair-distance distribution function (PDDF), or \( p(r) \), defined in Equation 1.7:

\[
I(Q) = 4\pi \int_0^\infty p(r) \frac{\sin qr}{qr} dr \quad (1.7)
\]

where \( p(r) \) describes the real-space electron density fluctuations of well-separated particles relative to the probed bulk average electron density, and \( r \) is an intraparticle distance between any two points described by some electron density difference relative to its average. Thus, the average length scales of electron density contrast, or phase separation, is probed in the small-angle regime allowing for the determination of domain sizes within a binary phase material such as a BHJ thin film.

A similar Q-range is probed by X-rays tuned near X-ray absorption edges in the resonant X-ray elastic scattering (REXS) technique (sometimes referred to as resonant soft X-ray scattering, or RSOXS), thus both SAXS and REXS experiments probe similar length scales of electron density modulations albeit with different experimental geometries and X-ray wavelengths. The REXS experiment relies on the implications Equation 1.8:

\[
\Delta \rho(r) \propto \Delta n = 1 - \delta(E) + i\beta(E) \quad (1.8)
\]
where δ is the scattering component of the complex index of refraction, \( n \), defined in Equation 1.6 and \( \beta \) is the complex absorption coefficient of a given material. In practice, REXS experiments are performed with X-ray energies near the atomic absorption edges in order to extract spatial contrast in the local bonding environment. Both terms of the complex index of refraction have an energy dependence that is strongly modulated near atomic absorption edges corresponding to core shell (1s) electronic excitations to unbound \( \pi^* \) or \( \sigma^* \) final states, endowing sensitivity to the local bonding environments and thus contrast to domains enriched in carbon-oxygen double bonds (carbonyl) or carbon-carbon double bonds, respectively.\(^{22}\)

The equality described in Equation 1.7 is only rigorously correct when the entire \( Q = [0, \infty] \) spectrum is integrated, however, the range of Q-space is not accessible in the SAXS/WAXS/REXS regimes to experimental geometry limitations. In order to extract real-space information from reciprocal space scattering data, the generalized indirect Fourier transform (GIFT) algorithm makes the explicit assumption that the scattering intensity can be factored via Equation 1.9:

\[
I(Q) \propto P(Q)S(Q) \tag{1.9}
\]

where \( P(Q) \) is the form factor that describes scattering from internal particle structure in reciprocal space, \( S(Q) \) is the reciprocal space structure factor that describes the spatial distribution of particles within a densely packed assembly such as in a bulk heterojunction thin film of polymer and small molecule phases with similar electron densities. The factorization of the scattering intensity implies a composed of
representative (generalized) particles described by \( P(Q) \) with some spatial distribution that can be analytically modeled by \( S(Q) \).

The assumptions of GIFT and its application for modeling X-ray scattering \( I(Q) \) are discussed further in Appendices A3.2-A3.3 in the context of describing and evaluating several analytical \( S(Q) \) models. GIFT modeling and structure factor selection can be aided \textit{a priori} by real-space information. The aid of real-space information offers a strong compliment to the reciprocal space information provided by X-ray scattering methods. While X-rays are weakly interacting probes the large X-

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{example_diagram.png}
\caption{The X-ray scattering experimental geometry, adapted from Reference 25.}
\end{figure}
ray beam cross section is capable of probing a large scattering volume thus providing a large statistical domain for characterizing bulk structure.

### 1.2.3 Transmission Electron Microscopy

Transmission electron microscopy is a real-space local probe of the BHJ microstructure and a powerful complement to reciprocal space X-ray scattering methods. High-angle Annular Dark Field Scanning Transmission Electron Microscopy (STEM-HAADF) measures inelastic scattered electrons at angles away from the primary electron beam and detected by an annular detector sensitive. The scattering angle is sensitive to the Z-contrast within a sample which includes atomic number, thickness and density contrast.\(^{26}\)

In BHJ films STEM-HAADF images can be interpreted as electron density contrast maps, providing local morphological details in real-space. The noted disadvantage is the projection of the entire thickness onto an image, rendering any out-of-plane (vertical) phase differentiation. This technique is especially suited to sub-100 nm samples and has been utilized for BHJ microstructure characterization, often relying on techniques such as EELS/EFTEM have been the most noted examples, however in Chapter have used Energy dispersive spectroscopy imaging that maps the spatial distribution of X-rays emitted from characteristic atoms within a sample. A high energy electron (200 kV) accelerating voltage is used in order to decrease the volume of a sample that interacts with the electron beam in order to provide a more localized
source of X-rays for higher spatial resolution, requiring lower exposure times for minimizing radiation-induced sample damage.

The sulfur atoms present in many thiophene-based conjugated polymers (P3HT, PTB7, etc.) can be used as atomic beacons for characterizing in-plane phase segregation contrasted with sub-domains of molecules without sulfur. The added phase or density contrast can be inferred from high HAADF-STEM intensity corresponding to densely packed crystalline regions compared to amorphous lower-density regions. This correlation of reciprocal space synchrotron X-ray scattering and real space electron microscopy is a unique and robust combination of methodology for the application of probing bulk heterojunction morphology.

1.3 Concluding Remarks

This work seeks to broadly understand how local considerations based on intermolecular packing and molecular self-assembly lead to designed long-range network formation in a nonequilibrium, crowded polymer matrix. Further, it aims to correlate how the evolving BHJ microstructure influences device-relevant photophysical properties. Instead of taking an exhaustive combinatorial approach to optimize the power conversion efficiency, we systematically investigate chemical series designed to interrogate how modifications to critical dimensions of chemical
structure influence intermolecular packing, long range BHJ phase separation and network formation, and the resulting optoelectronic device processes.

The results highlighted in Chapter 2 lay the foundation for the conclusion that BHJ morphology is combinatorial with respect to chemical structure geometry and packing motif – more specifically, that the orientation of charge transport pathways in polymer chains as well as the length scales of phase separation are intimately coupled to the chemical structure of the phase segregated small-molecule, and conversely that the microstructural nature of the conjugated polymer host, ranging from amorphous to polycrystalline, will modulate the packing mode of the blended small-molecule.

In Chapter 3, a combination of STEM-EDS microscopy and resoannat X-ray scattering analyzed with GIFT is developed as robust set of methods for probing BHJ phase separation within a series of Spiro-bifluorene molecules ranging in the number and connectivity of peripheral subunits in P3HT and PTB7 polymer blends. With the developed methodology, an improved understanding of the influence of subtle modifications to the connectivity and number of peripheral side-groups connected to a common core on the long range BHJ phase separation and resulting polymer carrier mobility is obtained.

Chapter 4 investigates the influence of the core-linking group on the molecular geometry of OSCs with multiple linked chromophores and the resulting self-assembly into nanostructured small-molecule networks that form percolated charge transport networks in polymer blends. The results illustrate the utility of using molecular self-
assembly to control both formation of percolated charge-transporting channels over the hierarchy of relevant device length scales, as well as the ability to impede phase separation over large distances.

In Chapter 5, the extended fused-aromatic core that is present in the champion ITIC non-fullerene family is investigated in the context conjugation length extension with increasing number of aromatic rings. The optical properties of a ladder oligomer series is investigated in order to interrogate the length dependence of the electronic structure within environments of increasing dielectric strength. This work is aimed at developing an improved understanding of how the chemical structure of derivatives such as ITIC and other organic semiconductors leads to record high device power-conversion efficiencies.
1.4 References


2. Towards a Better Understanding of Conjugated Polymer Blends with Non-Spherical Small Molecules: Coupling of Molecular Structure to Polymer Chain Microstructure

ABSTRACT

This chapter is our attempt to move towards forming a link between small molecule chemical structure and the morphological hierarchy of the blend. We focus on geometric motifs of small molecule organic semiconductors which have 2D, non-spherical 3D and quasi-spherical 3D molecular orbital extent. We find that phase separation in these blends is a function of the molecular structure, and that the small molecule chemical structure is coupled to the crystallite orientation distribution of the polymer matrix. We further find that the ability of a molecule to form a network with a well-defined length scale of phase separation depends on the polymer persistence length.
2.1. INTRODUCTION

The organic photovoltaic (OPV) field has matured substantially since the initial discovery of ultrafast photoinduced electron transfer from a conjugated polymer to a fullerene derivative in a thin blend film.\(^1\) After the quick realization that efficient OPV devices must incorporate a large density of electron donor/acceptor interfaces, the bulk heterojunction architecture (BHJ) was born.\(^2\) Though various combinations of conjugated polymer and small molecule devices have been explored to date, conjugated polymer/fullerene derivative blends have by far received the most attention, primarily due to their facile thin film processing.\(^3\)-\(^5\) In OPV devices, photogenerated electronic excited states (excitons) spatially diffuse until they relax to the ground state or encounter a donor/acceptor interface, where electron-hole pair disassociation occurs, leading to holes localized on the donor(s) and electrons on the acceptor(s). If the spatially separated electron and hole can overcome their binding energy, both charges migrate away from the heterointerface, driven by a combination of electric and chemical potential gradients.\(^5\)-\(^8\)

It is a remarkable fact that a straightforward means of creating a relatively efficient OPV device is by simply letting the solvent evaporate from a thin liquid layer of solution comprised of the donor/acceptor blend. The nonequilibrium thermodynamics of solvent evaporation along with the hydrodynamic forces acting on the solution during thin film formation determine the initial state of the blend film. The resulting solid film contains an interpenetrating donor/acceptor network, whose mean
length scale of phase separation is known to be a function of various processing variables, such as choice of solvent, thermal and solvent annealing, solvent additives, etc.\textsuperscript{4,9-13} As the extent of donor/acceptor phase separation varies, the volume spanned by charge-transporting paths changes for both charges, thus changing the tortuosity of charge flow.

The extent of phase separation and intermixing between donor and acceptor molecules within the BHJ film has a limiting effect on the relative rates of electron-hole separation and the formation of percolated donor-rich and acceptor-rich paths that allow charges to reach the electrodes. A fundamental requirement is that the mean length scale of donor/acceptor segregation be commensurate with the exciton diffusion length – the distance that excitons traverse during their lifetime. The exciton diffusion length of typical organic semiconductors is of order 10 nm.\textsuperscript{14-19} Thus, the relevant morphological length scales lie in the 10s of nanometers range. Too fine a mixing between donor and acceptor molecules results in large charge generation yields but low photocurrents due to poor charge mobilities and large recombination rates. A highly segregated network yields few charges due to the relatively low donor/acceptor interfacial area, but the charge mobility rises substantially owing to a less tortuous morphology and decreased bimolecular recombination rates. The fine balancing act of finding the “sweet spot” in a highly multidimensional processing variable space corresponding to the optimal blend morphology is a very laborious task that must be painstakingly performed for every new donor/acceptor combination.
The latest progress in the polymer-based OPV field has primarily been achieved via conjugated polymer bandgap engineering to increase the spectral overlap of the polymer absorption coefficient with the solar emission spectrum.\textsuperscript{20-22} At the same time, the most commonly utilized electron acceptors, the mono-functionalized C\textsubscript{60} and C\textsubscript{70} derivatives PC\textsubscript{60}BM and PC\textsubscript{70}BM, respectively – employed with overwhelming frequency – have changed very little. Due to their quasi-spherical electronic wavefunctions, fullerenes are remarkable electron acceptors that boast nearly isotropic inter-fullerene electron transfer rates – qualities that are paramount to an effective electron transport network.\textsuperscript{23-24} However, fullerene derivatives have notably low absorption cross-sections and thus contribute relatively little to the photocurrent, particularly in the near-IR region of the spectrum.\textsuperscript{25} Additionally, the reliance on fullerene derivatives as a standard molecular acceptor has potentially limited the breadth of polymer hosts that have been explored, as polymer energy levels must match those of the fullerene.

Improving upon fullerene-based OPV devices with a non-fullerene electron acceptor is an extremely tall order. Though the frontier energy levels can be matched in a straight-forward manner,\textsuperscript{26} replicating the highly desirable mesoscale charge mobility of the fullerene network is very challenging. This is primarily because most organic small molecules are anisotropic, which leads to intermolecular electron transfer rates that depend strongly on the relative molecular orientation,\textsuperscript{27-29} expectedly leading to certain charge transport directions characterized by very poor charge mobilities. Progress is substantially hampered by a lack of fundamental understanding that
connects the chemical structure of the small molecule to the hierarchical, Å- to nanometer-scale microstructure of the BHJ film. The purpose of this manuscript is to begin to systematically make this connection. To do so, we have used a combination of X-ray scattering techniques to interrogate polymer/small molecule blends as a function of small molecule structure and polymer chain microstructure. The small molecule set contains three distinct geometric motifs, which can be roughly characterized as representing 2D, quasi-spherical 3D and non-spherical 3D frontier molecular orbital extent. Our results show that, not only is the morphology a sensitive function of the small molecule chemical structure and the polymer chain microstructure, but that the polymer crystallite orientation distribution similarly depends on the small molecule structure. Our results underscore that when designing new electron acceptors, the polymer/small molecule blend must effectively be viewed as a coupled super-molecule, and that the polymer microstructure may dictate the preferred geometric motif of the small molecule.

2.2 RESULTS

To begin elucidating the influence of both small molecule chemical structure and polymer host chain microstructure on the morphology of thin blend films, we have used synchrotron X-ray scattering to simultaneously characterize the Å- and the nanometer (meso)-scale morphology of the molecular series shown in Figure 2.1. Recent work has shown that high crystallinity of the polymer matrix is not a necessary
condition for efficient device function, and that largely amorphous polymer can yield substantial power conversion efficiencies.\textsuperscript{30} Thus, it is important to understand the behavior of the small molecule in blends that encompass both amorphous and semicrystalline polymer matrices. As such, below we have focused on both the amorphous regiorandom poly(3-hexylthiophene) (raP3HT) and the polycrystalline regioregular P3HT (reP3HT), with the two polymers having very similar molecular weights.

![Chemical structures](image)

**Figure 2.1.** Chemical structures of the small molecules (a-c) and conjugated polymers used in this investigation. (a) perylene diimide derivative (PDI) with 2D spatial frontier orbital extent; (b) spirobifluorene derivative (Spiro-MeOTAD) with frontier electron density delocalized in 3D due to its equilibrium geometry; (c) mono-functionalized fullerene derivative (PCBM), whose molecular orbitals are delocalized over the quasi-spherical cage. (d) regiorandom P3HT; (e) regioregular P3HT. Regiorandom P3HT contains a distribution of relative monomer orientations, of which only one is captured by the shown structure.
This work is concerned with the influence of molecular shape and molecular orbital dimensionality of the small molecule on the film microstructure; therefore, the small molecule set shown in Figure 2.1 comprises several representative dimensionality classes. The methoxyphenyl perylene diimide (PDI) derivative has a planar conjugated core, which contains the bulk of the frontier orbital electron density, and thus represents a quasi-2D molecule with highly anisotropic intermolecular interactions due to π-stacking of the core. The Spiro-MeOTAD derivative, though usually not an acceptor itself based on the relative position of energy levels, is a small molecule with molecular orbitals that do not lie in the same plane due to the bridging sp3 carbon atom and the peripheral tertiary amines. As such, this is an example of a molecule with a quasi-3D molecular orbital extent. Such a geometry represents a case of a small molecule, whose inter-molecular interactions may lead to more isotropic charge transfer rates. Indeed, this general geometry has recently been used as the basis for a new non-fullerene electron acceptor. Finally, as the representative of the quintessential 3D quasi-spherical molecule, phenyl-61-butyric acid methyl ester (PCBM) will be used as the reference point due to its previously explored morphology.

To characterize local order on the Å scale, which strongly influences intermolecular electron transfer rates, we begin by discussing 2D grazing-incidence X-ray diffraction (GIXD) patterns,31–35 followed by analysis of the polymer crystallite orientation distribution functions. We then move to grazing-incidence (diffuse) small-angle X-ray scattering (GISAXS) to probe the mesoscale morphology of the blend, which ultimately dictates both the efficiency of exciton dissociation and percolated
long-distance charge transport through the interpenetrating polymer/molecule network. To further aid interpretation of the mesoscale morphology, GISAXS measurements are complimented by resonant elastic X-ray scattering (REXS) measurements performed in the vicinity of the carbon K-edge absorption onset.

We start by exploring reP3HT and its blends. As expected, pristine reP3HT forms ordered semicrystalline films illustrated by three orders of \((h00)\) Bragg peaks in the out-of-plane direction, indicative of end-to-end lamellar packing with a spacing of

![Figure 2.2](image)

**Figure 2.2.** 2D GIXD patterns of thermally annealed thin film blends of reP3HT with (a) PCBM, (b) PDI, and (c) Spiro-MeOTAD, as well as raP3HT with (d) PCBM, (e) PDI, and (f) Spiro-MeOTAD. reP3HT blends show characteristic \((h00)\) lamellar diffraction peaks of the semicrystalline polymer and no obvious Bragg peaks due to any of the small molecules. In contrast, raP3HT is completely amorphous, while only the raP3HT:PDI blend shows obvious diffraction peaks of PDI. The largely vertical Bragg rods of PDI indicate that its crystallites are highly oriented relative to the substrate.
\( d = 16.5 \, \text{Å} \), consistent with previous reports.\( ^{11,13,36-38} \) This is shown in Figure 2.8 of the Supporting Information (SI). Bragg reflections in reP3HT films are angularly dependent, with highest intensity occurring along the \( Q_z \) axis, indicating that lamellae are packed predominantly edge-on with respect to the substrate. Consistent with this orientation, the inter-chain backbone \( \pi \)-stacking is primarily in-plane, as evident by a high-intensity \((010)\) reflection near \( Q_{xy} \approx 1.67 \, \text{Å}^{-1} \) with a \( d \)-spacing of 3.76 Å.

Figure 2.3 shows GIXD images for both reP3HT and raP3HT blended with the three small molecules at a fixed monomer/molecule mole ratio corresponding to a 1:1 w/w P3HT:Spiro-MeOTAD blend. All shown films were thermally annealed. Blending reP3HT with PCBM results in the addition of a broad halo centered at \( Q \approx 1.35 \, \text{Å}^{-1} \) due to scattering by amorphous PCBM aggregates. The polycrystalline features of reP3HT are retained with a bimodal lamellar crystallite orientation distribution indicated by the \( Q = 0.38 \, \text{Å}^{-1} \) \((100)\) reflection with intensity peaking near the \( Q_z \) and \( Q_{xy} \) axes. Such a distribution is consistent with the presence of a bimodal \((010)\) Bragg reflection. GIXD images of reP3HT blends with PDI (Figure 2.2b) follow a qualitatively similar trend compared to PCBM blends, with \((h00)\) reflections with highest intensity along the \( Q_z \) and \( Q_{xy} \) axes, indicating preferred crystallite orientations in both edge-on and face-on fashions. Blends of reP3HT with Spiro-MeOTAD show a P3HT crystallite orientation distribution that differs qualitatively from both PCBM and PDI. Specifically, the orientation changes to primarily edge-on, similar to neat reP3HT films.
In contrast to reP3HT, raPHT is amorphous in both neat films and blends, even after thermal annealing. This is due to the fact that, on average, raPHT has a shorter delocalization length of its electronic wavefunction compared to reP3HT, leading to weak inter-chain interactions and thus little propensity to crystallize. This is evident in the lower panels of Figure 2.2, which show a complete absence of P3HT Bragg peaks. PDI was the only small molecule that showed crystallite formation in raP3HT, which is consistent with its relatively planar core, leading to relatively strong π-stacking interactions. Interestingly, this suggests that in reP3HT blends, partial crystallization of the polymer may limit crystallization by the PDI. We found that changing the solvent from the rapidly evaporating chloroform to the lower vapor pressure chlorobenzene leads to the appearance of (isotropic) diffraction rings due to PDI as illustrated in Figure A2.2. Thus, kinetic trapping of the initial film state may evidently lead to stunted PDI crystallization even after thermal annealing. The GIXD images above clearly show that the distribution of reP3HT crystallite

Figure 2.3 Orientation distribution functions of the reP3HT lamellar (100) Bragg reflection as a function of the polar angle in neat reP3HT films as well as in blends with small molecules at the same monomer/small molecule mole ratio. The polar angle = 0° for the surface normal. PDI and PCBM blends show dual texture with a large face-on-oriented crystallite fraction, whereas Spiro-MeOTAD blends show primarily edge-on-oriented reP3HT crystallites.
orientations relative to the substrate is a function of the small molecule chemical structure. To put this observation on a more quantitative footing, we have reduced 2D (100) reP3HT Bragg reflections to 1D crystallite orientation distribution functions (ODFs) by (i) first radially integrating the Bragg peak in polar coordinates over a small Q region centered about the peak, (ii) scaling the resulting intensity with a sin(polar angle) factor to account for the angular dependence of the number of crystallites contributing to diffraction at a given Q-space point,\textsuperscript{13,39} and (iii) by normalizing the corrected intensity by its integral over the accessible polar angle range.

The ODF for pristine reP3HT films indicates lamellar crystallites with a preferred edge-on orientation between approximately 10-45° of the surface normal with a peak centered about 25°. As mentioned previously, both PCBM and PDI blends with reP3HT show bimodal texture; closer inspection of the ODFs for both molecules shows that the predominant P3HT crystallite orientation is face-on (π-stacking out-of-plane), with a minor fraction displaying an edge-on orientation. Interestingly, the ODF for the

![Figure 2.4](image_url)  
**Figure 2.4** Horizontal 1D line cuts of GISAXS patterns taken near the image horizon for (a) reP3HT and (b) raP3HT blends with different small molecules. Only reP3HT:PCBM and raP3HT:Spire-MeOTAD blends show the appearance of shoulder-like features in this Q range, which are associated with formation of a characteristic length scale of polymer/small molecule phase separation on the nanometer scale. This feature is substantially more pronounced in the reP3HT:PCBM blend.
reP3HT:Spiro-MeOTAD blend indicates that P3HT crystallites in this blend are not only primarily edge-on-oriented, in contrast to the other small molecules, but that they are *more highly* edge-on-oriented than neat, thermally annealed reP3HT films. We can operationally define the ratio of face-on- to edge-on-oriented crystallite populations as the ratio of ODF integrals from ~ 0° to 45° and 45° to ~ 90°. This calculation yields ratios of 0.52, 0.65, 1.04 and 1.23 for reP3HT:Spiro-MeOTAD, neat reP3HT, reP3HT:PDI and reP3HT:PCBM, respectively.

We have used GISAXS link the Å-scale microstructure of our blend films with its nanometer-scale morphology responsible for long-distance charge transport through the interpenetrating polymer/molecule network.\(^40\-43\) Figure 2.4 shows in-plane line cuts obtained from 2D GISAXS images near the image horizon. The monotonically decreasing GISAXS curve for the reP3HT:PCBM blend (Figure 2.4a) shows two shoulders (plateau-like regions) at \(Q_{xy} \sim 0.03\ \text{Å}^{-1}\) and \(Q_{xy} \sim 0.08\ \text{Å}^{-1}\), corresponding to two distinct characteristic length scales of roughly 20 nm and 8 nm, respectively. These data are consistent with previous reports on this system. We interpret these features as arising due to the presence of a hierarchical blend network mesostructure, as no such features exist for pure reP3HT films. The 20 nm feature is likely related to phase-separated P3HT crystallites – a size scale that has previously been observed for reP3HT blends using AFM.\(^44\-46\) The second length scale of ~ 8 nm is consistent with small, largely disordered PCBM clusters, which give rise to the broad scattering ring at wide angles at ~ 1.4 Å\(^{-1}\) (Figure 2.2a). We note in passing that, though tempting, using the Guinier approximation\(^47\) to calculate effective radii of gyration from shoulder-like
features in SAXS curves is problematic for thin blend films due to the expected importance of inter-particle scattered wave interference.

In stark contrast, reP3HT:PDI films give rise to a featureless GISAXS curve in the accessible Q range, suggesting two possible explanations: The PDI is fully miscible in the polymer matrix and forms no phase-separated aggregates on these length scales, or PDI aggregates are large enough so as to fall outside the limits of detection. For reP3HT:Spiro-MeOTAD blends, the GISAXS profile is similarly featureless with no obvious characteristics of phase separation over this length scale range.

Figure 2.4b shows GISAXS curves for raP3HT blend films. raP3HT:PCBM and raP3HT:PDI display featureless monotonic curves with no well-defined length scales of phase separation. Though similar to reP3HT:PDI blends, for PCBM this represents a drastic change in the microstructure relative to its morphology in the reP3HT matrix. This is not altogether surprising. Early work on organic solar cell performance based on conjugated polymer:PCBM blends showed that for semicrystalline reP3HT, the polymer:fullerene weight ratio that led to the maximum power conversion efficiency was close to 1:1.49 However, for PCBM blends with amorphous MEH-PPV polymer, the optimal polymer:fullerene weight ratio was in the vicinity of 1:4, corresponding to an increased fullerene mole fraction relative to reP3HT blends.50-51 Thus, if the electron current is largely limited by the microstructural state of the fullerene network, it may be hypothesized that the PCBM mole fraction leading to a near-optimal charge transport network within a conjugated polymer matrix depends on the polymer crystallite concentration. A detailed study of the microstructure
evolution as a function of small molecule mole fraction is beyond the scope of this work.

Interestingly, the GISAXS curve for raP3HT:Spiro-MeOTAD blends shows a shoulder-like feature at \( Q_{xy} \approx 0.09 \, \text{Å}^{-1} \), corresponding to an approximate length scale of 7 nm. This is similar to PCBM in rP3HT films. Thus, it appears that Spiro-

![Graph showing GISAXS curves for as-cast and thermally annealed blends of poly(isobutylmethacrylate) (PIB) with different small molecules. The chemical structure of PIB is shown as an inset. Upon annealing, only the PIB:Spiro-MeOTAD shows the appearance of a well-defined shoulder. A similar feature is evident in as-cast PIB:PCBM blends but largely disappears upon annealing. The lower panels show GIXD patterns for annealed blends of PIB with (b) PCBM, (c) PDI, (d) Spiro-MeOTAD. The images show that, similar to raP3HT blends, PDI forms highly oriented crystallites within the polymer matrix.](image)

Figure 2.5. (a) GISAXS curves for as-cast and thermally annealed blends of poly(isobutylmethacrylate) (PIB) with different small molecules. The chemical structure of PIB is shown as an inset. Upon annealing, only the PIB:Spiro-MeOTAD shows the appearance of a well-defined shoulder. A similar feature is evident in as-cast PIB:PCBM blends but largely disappears upon annealing. The lower panels show GIXD patterns for annealed blends of PIB with (b) PCBM, (c) PDI, (d) Spiro-MeOTAD. The images show that, similar to raP3HT blends, PDI forms highly oriented crystallites within the polymer matrix.
MeOTAD – a non-spherical small molecule with 3D frontier molecular orbital extent – preferentially results in relatively well-defined length scale of polymer/molecule phase separation in the (thermally annealed) amorphous polymer host. This behavior is diametrically opposed to what we observed in P3HT blends with PCBM – the quintessential quasi-spherical small molecule. However, in both cases the small molecule gave rise to no obvious Bragg reflections in either polymer host; this differs qualitatively in raP3HT blends for PDI with its 2D molecular orbital extent. To gain a better understanding of the difference in small molecule behavior as a function of polymer chain microstructure, we have used GIXD and GISAXS to interrogate blends of the three small molecules with a different amorphous polymer host. For this purpose, we have used poly(isobutylmethacrylate) (PIB), which has a molecular weight that is comparable to P3HT but a chemical structure that differs qualitatively from P3HT. The chemical structure of PIB is shown as an inset in Figure 2.5, which displays GISAXS curves for both as-cast and thermally annealed PIB:molecule blends.

Figure 2.5a and 2.5c show that, similar to its behavior in raP3HT blends, PDI forms oriented crystallites and gives rise to a largely featureless scattering curves in both its as-cast and annealed states over the Q range accessible with GISAXS. The situation is entirely different for both PCBM and Spiro-MeOTAD. In PIB:PCBM films, the GISAXS curve for the as-cast film shows a shoulder-like feature at Q ~ 0.02 Å⁻¹, corresponding to a characteristic phase segregation length scale of roughly 30 nm. This feature partially disappears upon thermal annealing. In PIB:Spiro-MeOTAD blends, we observe precisely the oppositely behavior. Namely, the as-cast film gives rise to a
featureless GISAXS profile, but upon thermal annealing a shoulder at $Q \sim 0.01 \, \text{Å}^{-1}$ ($d \sim 60 \, \text{nm}$) becomes prominent. Thus, both molecules with little propensity for crystallization within the polymer matrix lead to phase separation on a length scale of the same order as common exciton diffusion lengths. However, for one molecule this corresponds to a kinetically frozen state (PCBM), whereas for the other (Spiro-MeOTAD), this state is located substantially closer in free energy to thermodynamic equilibrium.

The differences primarily between the morphology of polymer blends with PCBM and Spiro-OMeTAD – the two small molecules with a 3D molecular orbital extent – are intriguing yet puzzling. In particular, although Spiro-MeOTAD has demonstrated the ability to phase-segregate on the 10s of nanometers length scale upon thermal annealing, GISAXS data implies that it does so only in amorphous polymer matrices. In an attempt to better understand these observations and to improve the comparison across the small molecule series, we have performed resonant elastic X-ray scattering (REXS) measurements in the vicinity of the carbon K-edge.\textsuperscript{52-54} At these energies, this technique is sometimes referred to as resonant soft X-ray scattering.\textsuperscript{55-58} Because atomic scattering factors become complex in the vicinity of an absorption edge, the scattering contrast can be tuned (and enhanced) by tuning the X-ray energy across the transition threshold. This technique not only allows us to extend our scattering measurements to lower Q and thus larger length scales, but we can also compare scattering off- and on-resonance (in the near-edge $1s \rightarrow \pi^*$ transition region)
to potentially gain additional insight into the nature of the scattering inhomogeneities due to energy-dependent scattering contrast differences.

**Figure 2.6** shows REXS curves of reP3HT (a, c) and raP3HT (b, d) blend films. reP3HT:PCBM films both off- and on-resonance look qualitatively similar: The scattered intensity appears to plateau at $Q \sim 0.01 \, \text{Å}^{-1}$, which is very consistent with the

![Graphs showing REXS curves](image)

**Figure 2.6.** REXS curves collected in the vicinity of the carbon K-edge for reP3HT (a, c) and raP3HT (b, d) blends with the three small molecules. The top panels (a, b) correspond to scattering of 250 eV photons, which is well below the carbon K-edge absorption onset. The bottom panels (c, d) correspond to 284.4 eV photons, which is just above the absorption onset. Higher energies did not give rise to curves that differed qualitatively from those collected at 284.4 eV. reP3HT: Spiro-MeOTAD and reP3HT: PDI show signatures of clustering on the 100 nm scale, which is too large for efficient charge generation. All raP3HT blends give rise to relatively featureless curves, though with power law exponents (over certain $Q$ windows) that differ significantly among the three small molecules.
position of the well-defined shoulder observed with GISAXS in the same blends. Further support for this is shown in Figure A2.5 of the supporting information, which shows that the on-resonance REXS curve for this blend is qualitatively similar to GISAXS data. For reP3HT:PDI blends, the off-resonant scattering intensity $I$ is well represented by power law scaling over the measured Q range, that is, $I \propto Q^p$, where $p$ is negative. On resonance, however, the reP3HT:PDI curve displays a relatively well-defined shoulder roughly corresponding to a 90 nm length scale. This implies that the contribution of the so-called pure resonant scattering function to the total intensity becomes substantial, thus modifying the effective contrast responsible for low-Q scattering. This must be due to reasonably strong contrast between the $\pi$-electron density (when probing near the absorption edge) and the surrounding matrix. We may expect this to be the case for highly segregated PDI clusters.

Interestingly, off-resonant REXS curves of reP3HT:Spiro-MeOTAD films contain a shoulder at a fairly low Q of ~ 0.003 Å⁻¹, which corresponds to approximately 210 nm. The location of this feature moves slightly to lower Q when the X-ray energy is tuned on resonance while at the same time becoming more pronounced. Thus, together with GISAXS data, our results show that reP3HT:Spiro-MeOTAD blends are devoid of well-defined morphological features on the 10 nm scale but contain large scattering inhomogeneities well in excess of expected exciton diffusion lengths. We note that at larger Q, the intensity is well represented by a power law; in the Figure we have indicated the values of $p$ obtained from fitting the intensity to such a model.
REXS curves for raP3HT blends with all three small molecules display significant differences in slope among the different molecules but no obvious shoulder-like features commonly associated with relatively well-defined length scales of phase separation. Such behavior may result from fractal-like morphologies, though we are unable to verify this at the moment. However, as mentioned above, raP3HT:Spiro-MeOTAD does show evidence for clustering on the 10 nm scale, which stands in contrast to both PCBM and PDI in raP3HT.

2.3. DISCUSSION

We begin by discussing the implications of Å-scale structural measurements. The GIXD images show that the polymer crystallite ODF differs qualitatively for different small molecules. Compared to the neat reP3HT film, the small molecule chemical structure effectively dictates whether polymer crystallites are oriented edge-on, corresponding to poor vertical charge transport through the crystalline regions, vs. face-on, which is nominally desired for optimal vertical hole mobilities. Thus, it can generally be expected that the thickness-averaged intermolecular hole transfer rate through the P3HT network is generally a sensitive function of the small molecule chemical structure. However, the data do not make clear why PDI and PCBM tend to result in a predominantly face-on oriented crystallite distribution and why Spiro-MeOTAD in fact improves the propensity for P3HT crystallites to orient edge-on. The possibility of modifying the small molecule chemical structure to tune the polymer
ODF is intriguing, though it may be important to appreciate that the nanometer-scale morphology may in principle depend on the ODF. Nevertheless, though both PDI and PCBM resulted in a primarily face-on reP3HT ODF, their mesoscale blend morphology differed drastically.

The morphology of PCBM blends stood out among the small molecule series as the only one that in reP3HT – a semicrystalline polymer matrix – showed a well-defined feature of phase segregation on a length scale that is compatible with expected polymer exciton diffusion lengths. The propensity to phase segregate on comparable length scales for PCBM was lost in the amorphous raP3HT. The latest understanding of semicrystalline reP3HT films paints a picture of nanocrystallites connected to one another via tie chains.\textsuperscript{36,60-62} Space between crystallites is considered largely amorphous; PCBM boasts a relatively large solid state solubility in these regions.\textsuperscript{36,60} We hypothesize that P3HT crystallites confine fullerene molecules to the intercrystallite space, where their spherical shape and fairly small size (van der Waals volume $\sim 734 \text{Å}^3$) lead to highly efficient packing and well-defined interpenetrating network formation. In entirely amorphous raP3HT, there is little confinement due to relatively dense polymer regions, and PCBM disperses evenly throughout. Such a situation would give rise to a fairly featureless scattering curve at low $Q$, which is what we observed.
In contrast to PCBM, due its planar conjugated core, PDI has a propensity to form large aggregates and crystallites upon thermal annealing. This leads to little evidence for phase separation on a length scale relevant for exciton diffusion, independent of the polymer chain microstructure. This is consistent with the substantially decreased photovoltaic power conversion efficiencies for PDI blends relative to PCBM. In addition to the fact that for such a highly anisotropic molecule, inter-PDI electron transfer is a sensitive function of the relative molecular orientation, the strong anisotropic π-stacking interactions lead to large-scale aggregate or crystallite growth that is incompatible with efficient exciton harvesting.

Figure 2.7 A cartoon illustration of the relative aggregation and crystallite orientation distributions of reP3HT blends with (a) PCBM, (b) PDI and (c) Spiro-MeOTAD.
The behavior of Spiro-MeOTAD appears to be more complex and at the moment quite puzzling. First, it is curious that this is the one small molecule, whose reP3HT blends resulted in a population of face-on-oriented polymer crystallites that was smaller than the neat polymer film itself. Second, Spiro-MeOTAD showed no evidence for phase-segregated mesoscale network formation in reP3HT. It is possible that Spiro-MeOTAD is simply too large to form a molecular network the penetrates through the amorphous P3HT regions connecting polymer crystallites, or that its molecular packing is poor relative to the quasi-spherical PCBM. REXS measurements showed that the film does show a characteristic length scale that is of order 100 nm, too large to form an interpenetrating network with a significant internal quantum efficiency. This does not appear to hold for raP3HT and PIB blends with Spiro-MeOTAD, which show signatures of phase segregation on the 10 nm scale, though neither was as pronounced as reP3HT:PCBM. We hypothesize that perhaps removal of the physical constraints imposed by polymer crystallites lead to a somewhat enhanced ability to form relatively nanoscale small clusters, though additional experiments are necessary to fully understand this behavior. This suggests that for relatively large non-spherical small molecules, a largely amorphous polymer matrix may be desired. Figure 2.7 shows cartoons of local networks in semicrystalline reP3HT as a function of small molecule that emerges from our results. Future work will focus on elucidating the influence of peripheral functional groups of a Spiro derivative series on the polymer crystallite ODF and the mesoscale morphology.
The data presented above make it unambiguously clear that, for a given set of processing parameters, the chemical structure of the small molecule along with the polymer chain microstructure can drastically alter the interpenetrating polymer/molecule network that underpins charge transport in such blend films. Our results make clear that the polymer chain microstructure couples to the small molecule structure in directing the end-state morphology. Thus, it makes little sense to take a nominally high-performance conjugated polymer optimized for, say, PCBM and to expect that the same polymer will form a comparable charge transport network when a different electron acceptor is used. Conversely, this suggests that polymers discarded due to nominally poor performance in PCBM blends may well reach their full potential when combined with a small-molecule electron acceptor with an entirely different molecular geometry.

One conclusion is that the current inability to appreciate the morphological implications of component chemical structures at the outset may lead to substantial synthetic and processing efforts that ultimately fail to explore the relevant chemical structure-dependent parameter space. For the OPV field to successfully move beyond the fullerene electron acceptor in a systematic fashion, elucidating such a link will likely prove pivotal. This manuscript was an attempt to move in such a direction, though we have barely scratched the surface of this extremely complex many-body problem. However, our work shows that we can make progress through careful examination of microstructure as a function of chemical structure simultaneously across multiple length scales.
2.4. CONCLUSIONS

The motivation for this work was to begin to systematically understand how the chemical structure of the small molecule influences the local and meso-scale microstructure in the blend polymer/molecule film. Though there is a near-infinite synthetic space to explore, we focused on a few small molecules, whose geometry and molecular orbital extent different qualitatively. We found that the different small molecules resulted in different long-range order of the semicrystalline polymer matrix. Further, we showed that the nanometer-scale morphology is a sensitive function of the small molecule chemical structure, and that the ability of a molecule to form clusters associated with desirable phase-separated networks is coupled to the polymer chain microstructure. These results highlight the need for a continued in-depth exploration of the microstructural hierarchy in polymer/small molecules blends for different geometric and electronic molecular motifs.

Acknowledgements

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GISAXS and REXS data were acquired at the Advanced Light source at Lawrence Berkeley National Laboratory also operated by the U.S. Department of Energy, Basic Sciences Division; the authors acknowledge Cheng Wang and Mike Brady for their beamline training and support. GISAXS data were reduced using a MATLAB program written by Victoria Savikhin (Stanford University). REXS data was reduced using the Nika analysis package written in Igor by Jan Ilavsky (Advanced Photon Source, Argonne Lab). Solvent excluded volume and surface area calculations were performed by Cameron Pye (University of California Santa Cruz) using Biovia’s Discovery Studio.

2.5. EXPERIMENTAL METHODS

Doped silicon wafers (Silicon Quest International, 0.005 Ω·cm resistivity) were cleaned by ultrasonication in acetone followed by isopropyl alcohol and subsequently blown dry under a nitrogen stream. Substrates were then exposed to UV-ozone treatment (Novascan, PSD-UV4) for 30 minutes in order to remove organic contaminants as well as to increase substrate wettability. An aqueous suspension of PEDOT:PSS (Heraeus, Clevious PH 1000) was spin-coated at 5000 rpm for 60 seconds to mimic a common surface found in organic photovoltaic devices. PEDOT:PSS-coated Si slides were then annealed for 30 minutes at 150° C in air to drive off residual moisture. Chloroform solutions of PCBM (Solenne b.v), PDI (Solarmer), Spiro-MeOTAD (Sigma-Aldrich), regioregular P3HT (Reike Metals, MW = 57,000 g/mol, polydispersity = 2.9, 92% regioregularity), regiorandom P3HT (Reike Metals, MW =
57,000 g/mol, polydispersity = 2.9) and poly(isobutylmethacrylate) (Sigma Aldrich, MW = 70,000 g/mol) were prepared by dissolving the solid and stirring overnight at 45°C. All materials were purchased and used as is. All polymer/small molecule solutions were prepared at a total polymer concentration of 10 mg/mL. The P3HT:Spiro-MeOTAD solution was fixed at 1:1 w/w, while P3HT:PCBM and P3HT:PDI ratios were matched by mole to that of the Spiro-MeOTAD blend solution, resulting in weight ratios of 1:0.74 and 1:0.84, respectively. Blend solutions were filtered with a 0.45 μm PTFE filter (Fisher Brand) prior to thin film deposition. Thin films were spin-coated from chloroform at 1500 RPM for 1 min. Samples were annealed on a hot plate at 150°C for 30 min in a N₂ atmosphere and then transferred to a room-temperature metal surface in the same atmosphere.

For REXS measurements, PEDOT:PSS and polymer/small molecule blend films were deposited in a nearly identical fashion as described above. However, PEDOT:PSS was not annealed to allow for its sacrificial dissolution upon exposure to water. This results in a free-standing film, which can be picked up with a soft X-ray-transparent substrate. A 0.5 cm² section of film was cut with a diamond scribe and dipped into a petri dish filled with deionized water at an approximate angle of 45° with respect to the water surface. The thin film was then floated off of the silicon wafer and picked up by a 100 nm-thick silicon nitride membrane supported by a silicon frame (Norcada, 5100XC). Excess water was wicked off with a Kimwipe, and the membranes were then dried under vacuum. Samples were annealed in a N₂ atmosphere at 150°C for thirty minutes followed by cooling on a room-temperature metal surface.
Grazing incidence x-ray diffraction (GIXD) was performed at the Stanford Synchrotron Light Source beamline 11-3 using a 26-pole, 2.0-Tesla ID source operating at 12.7 keV (0.974 Å). The sample-to-detector distance and scattering vector were calibrated using a polycrystalline lanthanum hexaborate sample. Samples were exposed to the incident beam for 180 s. 2D scattering data collected using an area detector and processed in the WxDiff software package. Grazing-incidence small-angle X-ray scattering (GISAXS) was performed at the Advanced Light Source beamline 7.3.3 using a 10 keV (1.24 Å) beam from a bend magnet source. The sample-to-detector distance (approximately 4 m) was calibrated with a crystalline silver behenate standard. Measurements were performed at multiple positions along the surface of a sample in order to collect statistically representative data. Scattering data was collected by a Pilatus 2M detector and normalized by the incident photon flux. One-dimensional line cuts of intensity versus scattering vector Q were taken at $Q_z = 0.18 \text{ Å}^{-1}$ using MATLAB. Grazing incidence angles greater than the calculated critical angle for materials comprising the thin films are used for GIXD (0.12°) and GISAXS (0.15°) in order to probe the bulk of the films. We performed incident angle-dependent GISAXS measurements to ensure that the bulk of the film was probed (not shown).

Transmission resonant elastic X-ray scattering (REXS) measurements were performed at the Advanced Light Source beamline 11.0.1.2 using a 5.0 cm period elliptical polarization undulator (EPU5) source in a high vacuum scattering chamber ($10^{-7}$ Torr) with a 150 mm sample-to-detector distance calibrated with 300 nm polystyrene spheres. Prior to scattering measurements, near-edge X-ray absorption
spectra were collected using a photodiode detector to determine the X-ray energy set used for REXS measurements. 2D REXS images were collected using an in-vacuum CCD for nine positions per sample and reduced to one-dimensional curves by angular averaging in the Nika analysis package written in IGOR by Jan Ilavsky (Advanced Photon Source, Argonne National Lab). Scattering due to the silicon nitride substrate was subtracted from the total scattering.

2.6. References


30. Wang, S.; Fabiano, S.; Himmelberger, S.; Puzinas, S.; Crispin, X.; Salleo A.; Berggren, M. Experimental evidence that short-range intermolecular aggregation is


A2. Supporting Information

Figure A2.1 shows GIXD images of as-cast neat polymer films spin-coated from chloroform solutions. The regioregular P3HT (reP3HT) film (Fig. S1a) shows expected diffraction peaks due to lamellae (h00) and backbone π-stacking (0k0). reP3HT crystallites are oriented predominantly edge-on, though the distribution is quite broad. The absence of Bragg peaks in regiorandom P3HT (raP3HT) and
poly(isobutylmethacrylate) (Figs S1b and S1c, respectively) show that both polymers are amorphous.

**Figure A2.2** shows GIXD images of as-cast (a) and thermally annealed (b) reP3HT:PDI blends spin-cast from chlorobenzene, which has a slower evaporation rate than chloroform, allowing more time for the components to lower their free energies before the film morphology becomes locked in. The annealed blend image shows that PDI forms unoriented crystallites in reP3HT when cast from chlorobenzene, which is in contrast to the same blend cast from chloroform. The latter showed no evidence for PDI crystallization.

![GIXD patterns](image)

**Figure A2.2** GIXD patterns for (a) as-cast and (b) annealed blends of rrP3HT and PDI spin-coated from chlorobenzene (B.P. 131 °C). Contrasting films spin-coated from chloroform (61 °C), the amorphous PDI phase evolves into isotropic crystallites upon thermally annealing indicated by the presence of several concentric rings.
**Figure A2.3** shows the as-cast rrP3HT crystallite orientation distribution functions in neat films and in blends as a function of small molecule. Though quantitatively this data differs from thermally annealed ODFs, qualitatively the trends are still preserved. The only qualitative difference is in Spiro-MeOTAD blends, which appear to contain rrP3HT crystallites that are less oriented edge-on relative to neat rrP3HT.

**Figure A2.3** Orientational distribution functions of the rrP3HT lamellar (100) Bragg reflections as a function of the polar angle in *as-cast* thin films of neat rrP3HT films as well as in blends with small molecules at the same monomer/small molecule mole ratio. The polar angle = 0° for the surface normal.
**Figure A2.5** shows 1D GISAXS curves for as-cast blends in both reP3HT and raP3HT matrices. All curves appear relatively featureless, indicating that the small molecules are well-dispersed in polymer matrices. This is consistent with the rapid evaporation kinetics of chloroform, which suppress small molecule clustering on the 10s of nanometers length scale.

![GISAXS curves](image)

**Figure A2.4** GISAXS curves for (a) rrP3HT and (b) raP3HT blends of small molecules. All curves are monotonic corresponding to films with no phase segregation on the order of 1-100 nm.

The REXS curve of a thermally annealed reP3HT:PCBM blend collected above the absorption threshold at 284.4 eV is shown in **Figure A2.6** over a Q range that has been extended to higher values relative to Figure 6c of the main text. The extended REXS curve makes the similarity with the corresponding (off-resonant) GISAXS curve (Figure 5a of the main text) clear, as both curves exhibit a well-defined plateau region.
We interpret this as a signature of a relatively well-defined length scale of blend phase separation.

**Figure A2.5** REXS curve collected at 284.4 eV for a blend film of reP3HT and PCBM showing a distinct shoulder at approximately $Q \sim 0.01 \, \text{Å}^{-1}$. This is in good agreement with results from GISAXS measurements. An extended $Q$-range is collected by stitching together measurements from the same sample and two sample-to-detector distances (50 and 150 mm).

**TABLE A2.1** Molecule parameters calculated using Biovia’s Discovery Studio

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Solvent Excluded Volume (Å$^3$)</th>
<th>Surface Area (Å$^2$)</th>
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<td>734.42</td>
<td>541.37</td>
</tr>
<tr>
<td>PDI</td>
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<td>1306.1</td>
</tr>
<tr>
<td>Spiro-MeOTAD</td>
<td>1463.4</td>
<td>1216.7</td>
</tr>
</tbody>
</table>
Abstract

This chapter uses a combination of resonant elastic X-ray scattering and elemental mapping, we investigate the influence of relatively small chemical changes to a non-planar conjugated small molecule on the nanoscale morphology of the resulting polymer/molecule blend. We find that subtle modifications of the number and placement of peripheral functional groups can have an enormous influence on the length scale of phase separation. We then quantify the extent of phase separation by using the generalized indirect Fourier transform to convert resonant scattering intensities to pair-distance distribution functions. Our results point towards the large influence of the molecular excluded volume as a major morphology determinant. This work has implications for synthetic efforts to create non-fullerene electron acceptors that can substantially outcompete fullerenes in OPV devices.
3.1 Introduction

The discovery of the organic bulk heterojunction (BHJ) photovoltaic architecture more than two decades ago started a massive effort aimed at extracting the full potential of a molecular photovoltaic device.\(^1\)-\(^3\) The main advantages of organic photovoltaics (OPV) include their inexpensive roll-to-roll fabrication, facile bandgap engineering and amenability to flexible and stretchable platforms.\(^4\) Although various combinations of polymer/polymer and small-molecule/small-molecule BHJs have been studied extensively, the polymer/small-molecule device active layer has received an overwhelming share of attention. Though a myriad of novel conjugated polymers have been utilized as photoinduced electron donors, the electron acceptor small molecule was almost always a fullerene derivative.\(^3\), \(^6\)-\(^14\) Fullerenes are remarkably efficient electron acceptors;\(^15\) coupled with their quasi-isotropic intermolecular charge transfer rates, these molecules were deemed to be the ideal acceptor type.\(^16\) However, fullerenes suffer from relatively low molar extinction coefficients, particularly in the red and near-IR parts of the spectrum.\(^17\) Further, derivatization of the fullerene cage leads to progressive departures from charge transfer isotropy, as well as a change in electronic structure.\(^17\)-\(^19\)

Despite substantial polymer bandgap engineering, single-junction polymer/fullerene device conversion efficiencies appear to have plateaued in the vicinity of 10%. A clear path towards higher efficiencies is to use electron donor/acceptor combinations with increased complementary absorption, while pushing
both bandgaps ever further to the red. However, the departure from the fullerene small-molecule motif generally leads to an associated loss of the quasi-isotropic charge transport.\(^{16, 20-21}\) To date, a great variety of non-fullerene small molecules have been used together with conjugated polymers in OPV devices. Nevertheless, the majority of these candidates have lagged behind the fullerene motif in OPV performance.

In addition to charge transfer isotropy, an immensely important consideration in any novel combination of polymer and small molecule is the spatial extent of component phase separation.\(^{8, 22-24}\) The latter invariably takes place to varying degrees when the casting solution densifies and eventually becomes solid.\(^{23, 25-26}\) If the mean length scale of phase separation exceeds the relevant exciton diffusion length – a quantity that often falls in the 10 – 20 nm range – device performance suffers drastically.\(^{3, 27}\) We and others have shown that fullerenes often lead to phase separation on a length scale that is commensurate with the exciton diffusion length. However, there is no general understanding of how the chemical structure of a given small molecule dictates the nanoscale, nonequilibrium microstructure in the blend film. Recently, major advances in efficiencies using the ITIC (indacenodithieno[3,2-b]-thiophene)-based family of electron acceptors have underscored the fact that we still do not understand why this chemical structure motif results in performance improvements, even relative to the fullerene family.\(^{28}\)

Our overarching goal is to understand how different classes of small-molecule chemical structure – and specific derivatization patterns therein – influence the
nonequilibrium hierarchical microstructure in polymer/molecule blends. We began to systematically examine this question in our previous work, where we studied the coarse effect of small molecule geometry and π-electron density extent on the morphology of polymer/molecule blends.\textsuperscript{29-30} In this work, we extend our investigation to the amorphous spiro-bifluorene series of small-molecule derivatives in two chemically distinct, semi-crystalline polymers. The chemical structures between the derivatives differ only in the connectivity and number of identical functional groups on the molecular periphery. Neither derivative has particularly strong intermolecular interactions, leading to amorphous aggregates in all cases. This allows us to make a comparison of the hierarchical microstructure without the complication of large differences in intermolecular interactions and thus molecular packing. To characterize the microstructure on the nanometer scale, we have used a combination of elemental mapping and resonant elastic X-ray scattering. Furthermore, we have used the generalized indirect Fourier transform method to generate pair-distance distribution functions, allowing us to systematically and quantitatively interrogate the morphology of polymer blends with different small molecules. Our results point towards the importance of the molecular excluded volume as a major factor in determining the nanoscale length scale of phase separation. Further, we find that the connectivity of peripheral functional groups on the small-molecule plays a role in the nanoscale morphology. This work has implications for the current efforts to design small molecules that can outcompete fullerene derivatives, thereby systematically moving the non-fullerene research effort towards greater efficiencies.
3.2 Results

In this work, we explore how subtle modifications to the chemical structure of a molecular semiconductor in a BHJ thin film influences the hierarchical morphology for a given conjugated polymer and processing condition set. For this study, we focus on a chemical series of three spiro-bifluorene (Sp) derivatives (Figure 2.1) with varied number and configurations of peripheral phenylamino branches. The Sp series is comprised of $2,2',7,7'$-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Sp-M); commonly known as Spiro-MeOTAD), $2,7$-bis[N,N-bis(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Sp-Z), and $2,2'$-bis[N,N-bis(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Sp-E). The three Spiro derivatives, shown in Figure 3.1, share a common bridging sp$^3$ carbon that twists the adjacent fluorene groups nearly perpendicular to one another based on molecular geometry optimizations, preventing crystallization similar to fullerene derivatives that form amorphous small-molecule domains. The choice to investigate the Sp chemical series is rooted in the fact that these molecules do not exhibit long-range order in thin films; thus, our measurements are not affected by differences in small-molecule degrees of crystallinity. Future work building on this report will systematically move beyond such considerations. We focus on equimolar blends of each Sp derivative with the archetypical semi-crystalline conjugated polymers P3HT and PTB7, and use a combination of electron microscopy and synchrotron X-ray scattering techniques to probe multiple length scales of the thin film morphology.
We characterized the nanoscale structure of polymer:Sp blends in real space using scanning transmission electron microscopy energy-dispersive spectroscopy (STEM-EDS) performed at 40 kX magnification with a 200 kV accelerating voltage. This technique is suitable for mapping phase segregation in P3HT and PTB7 blends due to S atoms in the conjugated backbones of both polymers, which are absent in Sp derivatives.

To probe the hierarchical morphology in our blend films in reciprocal space, we have used grazing-incidence X-ray diffraction (GIXD)\textsuperscript{31-32} and resonant elastic X-ray scattering (REXS).\textsuperscript{33-40} GIXD carries information about polymer crystallinity alone, as the small-molecules form amorphous aggregates. The combination of STEMEDS and REXS provides a comprehensive real- and reciprocal-space nanoscale

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{chemical_structures.png}
\caption{Chemical structures of the Sp series (a) Sp-Z, (b) Sp-M and (c) Sp-E; chemical structures of host conjugated polymers (d) P3HT and (e) PTB7.}
\end{figure}
characterization on the order of 10 – 100 nm. The simultaneous use of both nanoscale probes allows us to reach robust conclusions about the dependence between Sp chemical structure and film morphology.

GIXD is well-suited to studying crystallinity of thin films composed of low-Z materials. 2D-GIXD images for neat thin films of regioregular P3HT and PTB7 are shown in Figures 3.2a and 3.2b, respectively, as a function of the in-plane and out-of-plane scattering vector components (Q_{xy} and Q_z, respectively). Thin films of P3HT are semi-crystalline, as expected, which is evident from three orders of (h00) Bragg reflections along the Q_z axis and the (010) Bragg reflection peaked near the Q_{xy} axis. The (100) Bragg reflection is located at Q = 0.38 Å^{-1} which corresponds to lamellar packing of d = 16.5 Å, while the (010) Bragg reflection is located at Q ~ 1.67 Å^{-1} and corresponds to a π-stacking distance of 3.76 Å. The (100) Bragg reflection in neat P3HT thin films has peak intensity on the Q_z axis, which indicates that the polymer is primarily oriented edge-on with respect to the substrate. That is, the inter-chain π-stacking occurs largely in the substrate plane.

Thin films of PTB7 are also semi-crystalline but less so than P3HT, which is evident from the broad (100) with no higher-order harmonics. The (100) Bragg reflection is located at Q = 0.315 Å^{-1} and corresponds to lamellar packing with a spacing of d = 19.9 Å, while the (010) Bragg reflection is located at Q = 1.58 Å^{-1} and corresponds to π-stacking with a spacing of d = 3.98 Å. The (100) Bragg reflection in neat PTB7 has peak intensity on the Q_{xy} axis, which indicates that the polymer
crystallites are oriented face-on (sidechains parallel to substrate plane) with respect to the substrate.

We find that in blends of either polymer with Sp derivatives, GIXD polymer peak positions are not affected. Perhaps a more interesting question is whether the polymer crystallite orientation distribution depends on the presence and chemical structures of Sp molecules. Our previous work has shown that broad classes of small-molecules blended with regioregular P3HT in certain cases led to drastic modifications of the P3HT crystallite orientation distribution function (ODF, or pole figure) relative to the neat film.41-43 To investigate whether relatively subtle modifications of a given small-molecule class similarly alter the polymer ODF, the intensity of the lamellar (100) Bragg reflection was converted from Cartesian to plane polar coordinates to generate one-dimensional ODF vs. polar angle plots, shown in Figures 3.2c and 3d for P3HT and PTB7, respectively. The pole (0°) is normal to the film surface; the (h00) intensity near this region corresponds to the edge-on crystallite population. A polar angle close to 90° corresponds to the face-on fraction population.
Figure 3.2c shows that the ODF of neat P3HT is peaked near 0°, expectedly consistent with the scattering image. Interestingly, ODFs of neat P3HT and P3HT: Sp thin films have similar peak positions and similar peak widths. P3HT:Sp-M and P3HT:Sp-E have slightly narrower ODF widths, but the broad take-away is that the P3HT ODF in blends is only minorly affected in both position and shape relative to neat films. More specifically, the ratio of face-on to edge-on crystallites as calculated

![Figure 3.2](image.png)

**Figure 3.2.** Pure polymer GIXD images films and polymer:Spiro crystallite orientation distribution functions (ODFs) for P3HT (a & c) and PTB7 (b & d) thin films. The grey bars near zero angle correspond to the forbidden region in a grazing geometry, while the bars near 90° block the Vineyard-Yoneda wings. Both are consequences of the grazing incidence geometry.
from ODF integration is slightly higher for all three P3HT:Sp blends compared to pristine P3HT, as detailed in Table S1. The ODFs of PTB7:Sp blends are shown in Figure 3.2d. Compared to P3HT blends, the neat PTB7 ODF in Figure 3.2d indicates the presence of primarily face-on-oriented crystallites with a small population of edge-on-oriented ordered crystallites. When blended with Sp derivatives, the crystallographic texture remains primarily face-on. On the other hand, PTB7 blends have lower face-on to edge-on ratios compared to pristine PTB7, also detailed in Table S1. Thus, the polymer ODF remains qualitatively unchanged for either polymer with this small-molecule series. However, in each case the presence of small molecules moves the polymer ODF closer to isotropy, albeit from different ends of the distribution.

Having understood the influence of each small molecule on the polymer ODF, we next ask whether there are concomitant changes to the charge transport characteristics through the polymer alone that accompany the differences in the polymer ODFs. To do this, we have used steady-state dark current injection measurements on polymer : Sp blend films in diodic architecture devices. Specifically, we have taken advantage of the fact that with the electrode configuration used herein, the current injected directly through Sp derivatives is negligible compared to the current supported by either P3HT or PTB7. We have found this to be the case with a PEDOT:PSS anode and an Al cathode. We believe this is primarily due to the mismatch between the small-molecule ionization potential with the Fermi levels of the electrodes, which could lead to formation of injection/collection barriers at the metal/organic interface. In fact, we
were unable to measure meaningful currents in either pure Sp devices or in Sp blends with an insulating polymer. Thus, our changes in current as a function of small-molecule chemical structure are evidently overwhelmingly due to changes in the effective hole mobility of the polymer network alone.

**Figure 3.3** shows dark current density/voltage plots for as-cast polymer : Sp blends on linear and double-logarithmic scales, respectively. We note that annealing the films led to a substantial drop in current for all films, in some cases disabling the

![Figure 3.3](image)

**Figure 3.3** Dark Current Density-Voltage measurements of P3HT (a & b) and PTB7 (c & d) blend devices. Dashed lines in (b) and (d) correspond to power-law fits in the high-voltage region, and symbols correspond to the average measured curve.
device completely. Thus, Figure 3.3 displays only as-cast device performance. Relative to pure P3HT films, Figure 3.3a shows a current decrease for P3HT:Sp-M devices by approximately a factor of 2 at 10 V, and even more so for the P3HT:Sp-Z and P3HT:Sp-E films. We observed a similar decrease in current for PTB7:Sp devices compared to pristine PTB7. Transport characteristics for both Sp-Z and Sp-E blends appear to cluster together for both P3HT and PTB7 blends. In P3HT, the Sp-M blend current slightly exceeds that of the other two derivative blends. In PTB7, this trend is reversed, as Sp-M blends lead to the smallest injected current. Upon further inspection, it is evident that the curves for the other two derivatives are no longer clustered together to the same extent as P3HT. Although the injected current as a function of bias appears comparable for the two, there is a clear slope difference, which shows that, if pushed to higher voltages, the two curves diverge. We have verified that this is in fact the case up to device breakdown, which occurs in the vicinity of 15 V. The trends illustrated in Figure 3.3 cannot be explained on the basis of the GIXD data alone, highlighting the importance of characterizing the blend film morphology over the entirety of its microstructural hierarchy relevant to device operation, i.e. from Å’s to 100s of nanometers.

We used a combination of REXS and STEM-EDS to characterize morphology over 10-100s of nm – length scales relevant for exciton diffusion and long-range charge transport. STEM-EDS elemental maps provide a semi-quantitative characterization of the nanoscale phase separation. However, EDS images are two-dimensional projections; as such, it is challenging to extract accurate quantitative
information from the images alone. To this end, we have performed REXS experiments, which contain information about the nanoscale morphology averaged over the film thickness, with X-ray energies near the C 1s $\rightarrow \pi^*$ absorption edge (285 eV). This provides increased scattering contrast compared to conventional hard x-ray scattering techniques. The P3HT:Sp-M EDS map (Figure 3.4a) displays 200-300 nm globular regions of high nitrogen (green) content embedded within regions of varying concentrations of sulfur (red), indicating the formation of large, mostly pure phase-separated Sp-M aggregates. We find that the superimposed S and N maps are clearly anti-correlated with very good agreement between the two measurements (see Supporting Information for further details). The P3HT:Sp-Z EDS map (Figure 3.4b) shows globular sulfur-rich polymer domains that form an interconnected network, as well as nitrogen-rich regions with sub-100 nm dimensions. P3HT:Sp-E blends show a qualitatively similar extent of polymer/molecule phase separation as Sp-Z blends, albeit with less defined small-molecule regions.
Figure 4d shows REXS intensities as a function of the scattering vector length, Q. We note that in the organic solar cell literature, REXS is frequently referred to as RSoXS. The three curves for the different Sp derivatives differ qualitatively, indicating substantial differences in the morphology. The curves have not been scaled by a monotonically increasing function of Q; thus, peaks and shoulders in the scattering intensity represent physically significant correlations in real space. Unfortunately, extracting quantitative information from low-Q scattering experiments within a necessarily limited Q window is challenging. This is because structural correlations as a function of position are related to the scattering intensity in reciprocal space through

![Image of Figure 3.4](image_url)

**Figure 3.4** (a)-(c) STEM-EDS Elemental Maps for (a) P3HT:Sp-M, (b) P3HT:Sp-Z, and (c) P3HT:Sp-E blends; Sulfur signal is represented by red while nitrogen signal is represented by green; (d) REXS $I(Q)$ curves modeled in GIFT including $S(Q)$; (e) pair distance distribution functions, $p(r)$, from GIFT calculations.
the Fourier transform, which requires data sampled at all $Q$. This is a long-standing problem particularly in small-angle X-ray scattering.

One solution to this problem appropriate to a diverse set of systems is the generalized indirect Fourier transform (GIFT) technique pioneered by Glatter.\textsuperscript{45-49} We are aware of one prior instance of the application of GIFT to polymer/molecule blends.\textsuperscript{50} However, few details about the fitting models were provided; therefore, prior results are of limited utility for understanding the range of validity and applicability of GIFT to thin blend films. We have thus undertaken the task of systematically applying GIFT to the systems described in this manuscript. To the best of our knowledge, this represents the first comprehensive attempt at using GIFT to understand the nanoscale organic semiconductor film morphology as a function of small-molecule structure. This analysis technique may be relatively unfamiliar to the organic optoelectronics community; therefore, we have summarized the main principles below prior to describing our results.

Insofar as the scattering intensity can be written as

$$I(Q) \propto P(Q)S(Q)$$ \hspace{1cm} (3.1)

where $P(Q)$ is the form factor of the scattering particle and $S(Q)$ is the structure factor, the GIFT algorithm allows for a model-free determination of the pair-distance distribution function (PDDF), $p(r)$, via
Here, \( r \) is an intraparticle distance that connects two points described by some electron density difference relative to its average. Such a factorization of the scattering intensity implies a model, where the sample is composed of representative (generalized) particles with an internal structure described in reciprocal space by \( P(Q) \), and whose spatial distribution in a densely packed assembly is governed by \( S(Q) \). Unlike \( p(r) \) and, by extension, \( P(Q) \), GIFT does not provide a model-free determination of \( S(Q) \). Thus, selecting a physically appropriate model is of some significance. The structure factor is related to the radial distribution function, \( g(r) \), through the orientationally averaged Fourier transform as

\[
P(Q) = 4\pi \int_0^\infty p(r) \frac{\sin Qr}{Qr} dr \quad (3.2)
\]

\[
S(Q) = 4\pi \int_0^\infty [g(r) - 1] r^2 \frac{\sin Qr}{Qr} dr \quad (3.3)
\]

In GIFT, a specific multi-parameter model for \( g(r) \) is chosen and Fourier-transformed to yield the structure factor.

In a particle, whose electron density fluctuations relative to the medium (or the scattering contrast) are independent of position over nanometer length scales, the PDDF simply describes the distribution of distances encountered within the particle. As such, the PDDF contains information about the size and shape of the particle, or the statistically representative scattering inhomogeneity. In such a case, \( p(r) > 0 \) for all \( r \). When the factorization in Equation 1 is rigorously correct, the distance at which the
PDDF approaches zero may be associated with the (orientationally averaged) size of the scattering particles. When the representative scattering inhomogeneity includes regions where the scattering contrast is a function of $r$, $p(r)$ may change sign. The distance over which this occurs contains information about the average length scale that characterizes the change in intraparticle scattering contrast. In a polymer/molecule blend, this metric is related to the mean spatial phase separation extent in the interpenetrating network.

The explicit assumption made in GIFT is that the scattering is isotropic, leading to a PDDF that depends only on the particle distance as opposed to vector orientation. Our results clearly show that the polymer phase contains crystalline domains with some orientational preference with respect to the substrate. This can give rise to anisotropic scattering, as others have observed. Our averaging of the scattered intensity over the polar angle, as described in the Supporting Information, thus averages away the polymer anisotropy. Though this results in some loss of information, (i) the polymer crystallite volume fraction has been previously estimated to be the minority fraction, which is further lowered in blend films, and (ii) the blend polymer crystallite ODF is not sharply peaked. Thus, we believe this kind of orientational averaging corresponds to a reasonable compromise in polymer/small molecule blends. We note that in this sample set, we did not observe anisotropic scattering.

In this work, we focus on two physically plausible models for the structure factor: that of polydisperse hard spheres and mass fractal aggregates. The presence of
peaks in the scattering intensity in some samples over the 0.1 to 1 nm\(^{-1}\) range suggests that it is reasonable to approximate the system as a dense collection of quasi-spherical particles of some average spatial extent. At the same time, on general grounds it may be expected that over some range of length scales, the largely disordered, highly branched and interpenetrating microstructure of a polymer/molecule blend could be associated with a fractal dimension along with its corresponding structure factor.\(^{51-53}\) These two structure factor models are by no means exhaustive. Substantially more intricate structure could be envisioned; however, this would be at the cost of an increase in the number of fitting parameters. Furthermore, as we show in Figures 3.4 and 3.5, we find that in practice both the polydisperse hard spheres and fractal structure factor models give rise to qualitatively – and sometimes quantitatively – similar PDDFs. However, the generality of this observation is as-yet unclear. Further details about the above structure factor models can be found in the Supporting Information.

Figure 3.4d shows the REXS scattering intensity collected near the C 1s $\rightarrow$ $\pi^*$ absorption edge for P3HT:Sp derivative blends corresponding to the TEM images above along with corresponding GIFT fits, which are shown as solid lines in Figure 3.3d. The resulting normalized PDDF plots are shown in Figure 4e. We find that for the P3HT:Sp-M blend, only the mass fractal aggregate (MFA) model for the structure factor was able to capture the details of the scattering intensity. The resulting $p(r)$ is nonzero for all $r$, and it is substantial even for relatively large $r$, well in excess of the expected exciton diffusion length of P3HT. Evidently, the positivity of $p(r)$ implies the existence of large particles with an electron density that is approximately constant on
nm length scales. The distance at which the PDDF goes to zero is of order 200 nm, consistent with the STEM-EDS image in Figure 3.4a.

Figure 3.4e shows that the PDDFs for P3HT blends with Sp-Z and Sp-E have a substantially different functional form compared to the Sp-M blend. The PDDF for these two derivatives undergoes a sign change – an indication that the representative “particle” or scattering inhomogeneity consistent with Equation 1 is composed of regions of varying scattering contrast. That is, the scattering inhomogeneity contains phase-separated regions that are enriched in P3HT or in Sp. We associate the length scale of the zero crossing with a metric related to the mean length scale of polymer/molecule phase separation. The P3HT:Sp-E blend is characterized by a $p(r)$ with the first positive maximum at 29 nm, a negative minimum at 91 nm, and zero crossing at 59 nm. We found that, similar to P3HT:Sp-M blends, only the MFA structure factor model was able to describe the data for Sp-E.
In contrast to the previous two blends, we were able to describe the P3HT:Sp-Z scattering profile satisfactorily with both the MFA and PHS models. For consistency, we have included both resultant PDDFs in Figure 3.4e. The MFA P3HT:Sp-Z blend PDDF exhibits the first positive maximum at 52, a negative minimum at 157 nm, and a zero crossing at 102 nm. Figure 3.4e shows that, although the shape of the PDDF for \( r < 200 \) nm is similar between the two structure factor models, the zero crossing differs by 20 nm between the two results. Furthermore, the PHS model gives rise to an additional positive maximum at \( r > 200 \) nm, a physical dimension that appears to be inconsistent with our TEM results.

**Figure 3.5** (a)-(c) STEM-EDS Elemental Maps of (a) PTB7:Sp-M, (b) PTB7:Sp-Z, (c) PTB7:Sp-E; Sulfur signal is represented by red while nitrogen signal is represented by green; (d) REXS \( I(Q) \) curves modeled in GIFT including \( S(Q) \); (e) pair distance distribution functions, \( p(r) \), from GIFT calculations.
TEM and REXS data for PTB7 are shown in Figure 3.5. Somewhat similar to P3HT blends, the PTB7:Sp-M sample displays 100-200 nm N-rich regions segregated from somewhat globular S-rich regions. Nevertheless, the Sp-M regions in P3HT blends appear larger and of substantially higher contrast relative to P3HT. The calculated \( p(r) \) functions using both MFA and PHS structure factor models are in agreement with the EDS map; the zero crossing is \( \sim 100 \) nm. Though both polymers share some similarities when blended with Sp-M, the shape of the PDDF for PTB7 differs from that of P3HT, which had \( p(r) > 0 \) for all \( r \). This again suggests less pure representative scattering inhomogeneities in PTB7 than in P3HT, consistent with the sulfur/nitrogen contrast in TEM images. We note that for this sample, PHS and MFA structure factor models gave effectively identical PDDFs.

The TEM images for PTB7 blends with both Sp-E and Sp-Z show substantial intermixing as judged by the overlap of S- and N-containing regions. The qualitative trend across the derivatives is similar to P3HT; however, P3HT blends consistently gave rise to significantly more pronounced phase separation. The PDDF for Sp-Z contains a zero crossing at 48 nm, which is substantially smaller than that of Sp-M blends. For Sp-E blends, obtaining a reliable PDDF was complicated due to the shape of the scattering curve; the flattening of the intensity at \( Q > 0.2 \) nm\(^{-1}\) is likely related to the presence of an intensity plateau similar to the Sp-Z sample but occurring at higher \( Q \) outside the experimental window. As such, the PTB7:Sp-E PDDF likely has the largest uncertainty associated with it, even though the intensity fit appears to be quite satisfactory.
3.3 Discussion

Our results immediately allow us to make several qualitative statements about the microstructure of conjugated polymer/small-molecule blends. First, we have previously shown that among three diverse small-molecule classes that included planar (perylene diimide derivative), quasi-spherical (PCBM) and non-spherical/nonplanar geometries (Sp-M), some members drastically altered the conjugated polymer ODF (PCBM, perylene diimide), while Sp-M left it largely unchanged. The question remained whether it was the coarse small-molecule geometry that determined the polymer crystallite ODF, or whether fine changes to the molecule structure were sufficient to result in substantial modification of the ODF relative to the neat polymer film. The polymer ODF curves shown herein indicate that small changes to the overarching molecular motif of an amorphous small molecule, as exemplified by the spiro-bifluorene core, do not appear to qualitatively alter the polymer ODF. This result is supported by both P3HT and PTB7 measurements.

The two polymers in this work differed not only in their ODF but also in their relative degree of crystallinity: The PTB7 film showed only a first-order lamellar Bragg reflection, whereas P3HT showed several. On the nanometer scale, EDS maps imply that the relative contrast between the P3HT and all three small molecules is larger than the corresponding blends in PTB7. A possible conclusion that emerges is that with increasing polymer crystallinity, the phase-separated features become more enriched in polymer and small-molecule components, respectively. That is, polymer
crystallization partially drives phase separation – an idea that has been articulated previously.\textsuperscript{22, 54} However, we cannot currently rule out the contribution that the difference in polymer molecular weights or small differences in polymer film thickness could make to this consideration.

Interestingly, in P3HT:Sp-M blends with large scattering contrast and large Sp-M features, the polymer dark current density was higher than in blends with the other two derivatives. In PTB7:Sp-M blends, which showed less defined phase separation and somewhat smaller Sp-M particles relative to P3HT blends, the device current was smaller than the other derivatives. We hypothesize that with large, well-separated Sp-M particles, more P3HT chains and crystallites are on average clustered together, leading to relatively rapid charge transport between the Sp-M grains. In contrast, the still relatively large but less defined Sp-M particles in PTB7 blends present more frequent energetic impediments to transport of charges through the polymer. In other words, we speculate that when the size of the phase-separated small-molecule features becomes quite large, more well-defined phase segregation of the two components is net beneficial for the charge mobility along the polymer network. In the latter scenario, though the presence of large particles leads to effectively less volume for polymer charge transport, the conducting channels themselves are characterized by a larger effective mobility than in the case of frequent geometric impediments in a loosely segregated network. We note that this qualitative analysis of the differences in the current/voltage response of the blends relies on the implicit assumption that the different blends have at least comparable degrees of vertical phase segregation (if any).
Unfortunately, we are currently unable to make a direct evaluation of this effect. Thus, this possibility must be born in mind.

Second, the stark morphological result that was similarly robust across the two polymer hosts was that Sp-M blends consistently showed feature sizes that were well in excess of expected exciton diffusion lengths for conjugated polymers. This was not the case for Sp-E and Sp-Z blends, where the characteristic length scale of phase separation between polymer-rich and small-molecule-rich domains was more commensurate with the exciton diffusion length. Thus, although relatively small chemical changes on the Å-scale may not substantially alter the ODF, *they are sufficient to induce nanoscale morphological differences*. This has direct implications for the synthesis of small-molecule guests for polymer/molecule blends.

Though it is evident that a much more sophisticated understanding of the link between chemical structure and morphology is required, we believe our work points to an important consideration. Within the Sp derivative series that we examined, Sp-M stood out in its large morphological features in both polymer blends. Sp derivatives here differ only in their connectivity and number of branching peripheral groups. They have nearly identical calculated angles between the sp$^3$-linked fluorene units, so that we may reasonably expect that the molecular packing would not differ drastically among the three molecules. With these similarities in mind, combined with the common amorphous packing of all three Sp derivatives, we believe it is unlikely that the intermolecular interactions in the thin film differ substantially across this chemical
series. Furthermore, at normal device blend ratios, all three Sp derivatives display comparable solubilities.

These considerations suggest that the excluded molecular volume may play a role. Indeed, the solvent-excluded volume of Sp-M is 1.46 nm$^3$ compared to 0.959 nm$^3$ for both Sp-Z and Sp-E isomers. The change in this volume is not drastic, but evidently it is sufficient to change the mean length scale of phase segregation from $\leq 50$ nm to $> 100$ nm in PTB7 blends and from $\leq 50$ nm to $> 200$ nm in P3HT blends. To date, a great variety of non-fullerene small-molecule electron acceptors blended into donor polymers (or donor molecules into acceptor polymers) have been explored. In both cases, the range of small molecules spans a large range of molecular excluded volumes.

A reasonable argument rooted in charge transport considerations is that a small molecule characterized by an intermolecular electronic coupling that is quasi-independent of relative orientation is desired. Though promising in principle, several classes of such molecules have been unable to overtake PC$_{60}$BM and PC$_{70}$BM fullerene derivatives in photovoltaic efficiency.$^{55-70}$ To the best of our knowledge, these facts have not been reconciled rigorously in any systematic manner. Our work suggests that relatively small synthetic modifications to the volume and/or connectivity of a given small molecule motif are important considerations when evaluating the bulk heterojunction morphology and resulting device photocurrent – a framework that could potentially be applied to more recent high-performance non-fullerene acceptors such as ITIC and fused PDI derivatives. We do not aim to suggest that all molecules of a particular size are expected to perform poorly when blended with some conjugated
polymer. Rather, within a given small-molecule motif, our data suggests that systematically increasing the excluded volume is expected to ultimately detrimentally affect the morphology. It is likely that a systematic application of GIFT across blends with a broad small-molecule chemical series would improve our morphological understanding of non-fullerene polymer/molecule blends.

Finally, we find that the molecular connectivity difference between Sp-E and Sp-Z does in fact lead to some nanoscale morphological differences. EDS maps of P3HT blends indicate that Sp-Z shows more defined phase separation, whereas Sp-E is somewhat more intermixed, in good agreement with the zero-crossing of the respective p(r) results. The data show that precise connectivity between certain functional groups may in some cases cause differences in polymer/small molecule intermixing. This has implications for the three-phase hypothesis, which states that the blend morphology may be described as a coexistence between pure polymer crystallite, intermixed amorphous polymer and small-molecule regions, as well as regions enriched or containing pure small-molecule domains. The thee-phase morphology has previously been associated with beneficial photovoltaic effects.\cite{14,44} Our results suggest that changes in functional group placement may tune the molecular miscibility in the polymer phase.

In PTB7 blends, the differences between the two smaller derivatives are more challenging to discern, though it is clear from the shape of the scattering curves that differences persist. Interestingly, comparing either derivative in PTB7 to its corresponding blend in P3HT shows that P3HT leads to more defined phase separation.
Previously, we showed that semicrystalline (regioregular) and amorphous (regiorandom) P3HT consistently gave rise to large morphological differences. Our results indicate that, even with two semicrystalline conjugated polymers, the precise influence of the small-molecule chemical structure on the blend film morphology appears to be a function of the conjugated polymer structure.

3.4 Conclusions

In summary, we have interrogated blends of two chemically distinct, semicrystalline conjugated polymers blended with a spiro-bifluorene small-molecule chemical series over multiple decades of length scale. In the molecular series, the connectivity and number of peripheral functional groups was varied while the Sp molar concentration and bifluorene-core motif was fixed. We found that the number of peripheral phenylamine arms, and thus the molecular excluded volume, was the dominant factor in determining the nanoscale microstructure of the thin film for both polymers. Further, we found more subtle morphological differences as a function of small-molecule connectivity, the extent of which differed between the two polymers. To the best of our knowledge, this work represents the first systematic application of the indirect Fourier transform to analysis of low-Q scattering curves of organic semiconductor thin films. It appears that in the course of a single scattering measurement, this technique can yield quantitative information about the nanoscale morphology that is in good qualitative agreement with real-space STEM-EDS
elemental mapping. Further systematic application of GIFT on a broad small-molecule series may allow the organic photovoltaics field to begin to rationally move beyond the fullerene derivative towards power conversion efficiencies approaching (and possibly exceeding) 15%.

3.5 Experimental Methods

All chemicals were obtained commercially and used as received. Blend solutions of P3HT (10 mg/mL, Reike Metals, \( M_w = 57 \text{ kDa}, \text{PDI} = 2.9, 92\% \) regioregularity) and PTB7 (10 mg/mL, 1-Material, \( M_w = 97.5 \text{ kDa}, \text{PDI} = 2.1 \)) were prepared in HPLC grade chloroform (Sigma Aldrich). P3HT blends with Sp-M (Sigma-Aldrich) were prepared at a 1:1 w/w ratio while the P3HT:Sp-Z and P3HT:Sp-E ratios were matched by mole to that of Sp-M, resulting in weight ratios of 1:0.63 for Sp-Z and Sp-E (Lumtec). The same mole-matching regime is followed for 1:1.5 w/w blends of PTB7:Sp-M resulting in weight ratios of 1:0.94. All solutions were stirred in the dark under air (12 hours, 45° C) and subsequently filtered with a 0.45 μm PTFE filter (Fisher Brand). A layer of p(ethylenedioxythiophene):p(styrenesulfonic acid) (PEDOT:PSS; Heraeus, Clevios PH 1000) was spin-coated at 5,000 rpm for 60 s onto pre-cleaned (acetone, isopropyl alcohol, dried with \( \text{N}_2 \) gas, UV-Ozone treatment using a Novascan, PSD-UV4) doped silicon wafers (Silicon Quest International, 0.005 Ω·cm resistivity) and annealed at 150° C for 30 min prior to spin-coating of the polymer/Sp solutions at 1,500 rpm for 60 s.
REXS and STEM-EDS thin films were prepared in a nearly identical fashion using as-cast PEDOT:PSS as a sacrificial water-soluble layer. A diamond scribe was used to cut a small portion of the film, which was dipped into deionized water in order to float-transfer the BHJ layer onto X-ray transparent SiN\textsubscript{x} membranes (Norcada, 5100XC) or ultrathin/lacey carbon support film copper TEM grids (Ted Pella, 400 mesh). Finally, films were thermally annealed at 150° C on a hot plate in an inert N\textsubscript{2} atmosphere for 30 minutes, followed by cooling on a room-temperature metal surface.

Films for charge injection measurements were prepared on pre-patterned ITO wafers (140 nm), which were cleaned using a detergent/DI-H\textsubscript{2}O/acetone/isopropyl alcohol solvent series, blown dry with N\textsubscript{2} gas and treated with UV/Ozone prior to spin-coating. Al (99.99%, Kurt Lesker) top-contacts were thermally evaporated at 2 x 10\textsuperscript{-6} Torr using a shadow mask with a 6.5 mm\textsuperscript{2} device area.

GIXD (incidence angle = 0.12°) was performed at the at the Stanford Synchrotron Radiation Lightsource (SSRL), beamline 11-3 (12.7 keV, 2 x 10\textsuperscript{12} photons/s flux) generated by a 24-pole, 2-Tesla wiggler insertion device. The samples were exposed for 180 s at a sample-to-detector distance of 315 mm. The sample-to-detector distance and the scattering vector were calibrated with a polycrystalline lanthanum hexaborate sample. Variable upstream slit widths shape the profile of the X-ray beam, which has a standard beam footprint of 3.0 x 0.15 mm. TIFF files were generated at the beamline from the 2D area detector, which were reduced and processed in WxDiff. ODF curves were generated by integrating the scattering intensity of the
first order lamellar reflection over a small Q range centered about the peak. The curves were then corrected by a factor of sin(θ), where θ is the polar angle, to account for differences in crystallite population density probed at a θ.72

REXS measurements were performed at the Advanced Light Source beamline 11.0.1.2, Lawrence Berkely National Lab, with beam flux = 10^{13} photons/s generated by a 5.0 cm-period elliptical polarization undulator (EPU5) source in a high vacuum scattering chamber (10^{-7} Torr). Scattering experiments were performed in the transmission geometry with the sample-to-detector distance calibrated using a drop-cast dispersion of 300 nm polystyrene beads. Two-dimensional scattering images were collected using an X-ray photon energy of 284 eV with an in-vacuum CCD. Scattering images are reduced to 1-D I(Q) curves by circular averaging using the Nika package in Igor.73

Pair distance distribution functions (PDDF) are generated via the generalized indirect Fourier transformation of experimentally collected REXS I(q) curves in the PCG software package. The Boltzmann Simplex Simulated Annealing (BSSA) algorithm (Temperature = 20°C, 20 steps) is used to find the global minimum of the nonlinear function that contains the product of transformed spline coefficients of the form factor multiplied with the structure factor parameter vector. A set of ten BSSA solutions are generated by Lagrange multipliers of increasing stabilization. The correct result is selected that produces a minimum mean deviation between the experimental
and calculated scattering curve, as well as a minimum in the first derivative in $N_c$ term that eliminates artificial oscillations in the PDDF.\textsuperscript{74}

STEM-EDS elemental mapping was performed with a FEI Titan microscope operated at 200kV at the National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Lab. The STEM probe had a convergence angle of 10 milliradians and a beam current of $\sim$300-400 pA. The EDS detector was a SDD quadrature windowless detector with a solid angle of 0.7 steradians. Image processing was performed with the Bruker Esprit software using a moving average filter. The S K$_\alpha$ X-ray EDS signal (2.3 keV) was used as an atomic marker to map the distribution of polymer throughout the bulk of the thin film blend due to its high signal-to-noise ratio and good spectral separation from the EDS signal arising from other elements present within the film (C, O, N) and TEM substrate (C and Cu), as shown in Figure A3.1. Though mapping the N distribution arising from the small-molecules is possible, the N K$_\alpha$ signal (0.39 keV) is not as resolved from the C K$_\alpha$ (0.28 keV) signal as the S signal is for the polymers. The high-angle annular dark-field (HAADF) images shown in Figures A3.2 and A3.3 show cloudy white networks ascribed to atomic and phase contrast between sulfur present within the semi-crystalline polymer phase contrasted against the lower-Z elements present within the amorphous small-molecule-rich domains.

Molecular geometry optimization calculations were performed in the Discovery Studio suite using the adopted basis Newton-Raphson minimization algorithm using
the Merck molecular force field.\textsuperscript{3} Solvent-excluded volumes were calculated using a solvent probe radius of 1.4 angstroms using a 2D approximation based on the Shrake-Rupley algorithm.\textsuperscript{75}

Dark current/voltage measurements were collected in an inert nitrogen glovebox ($< 0.1$ ppm H\textsubscript{2}, $< 0.1$ ppm O\textsubscript{2}) using a Keithley 2450 sourcemeter interfaced with an 8-channel relay module (Advantech, USB-4761) and a LabVIEW virtual instrument developed in-house.

Acknowledgements

Work at the Molecular Foundry and Advanced Light Source was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is used by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. Molecular geometry optimization and solvent-excluded volume calculations were performed by Mr. Chad Townsend at UCSC.
3.6 References


A3. Supporting Information

A3.1 GIXD Crystallite Orientation Distribution Function (ODF) Details.

A sin (θ) correction factor is included in the ODF to account for the crystallite density contributing to a given solid angle as a function of the polar angle:

\[ \text{ODF} \propto I(\theta) \times \sin(\theta) \quad (A3.1) \]

Relative face-on and edge-on crystallite populations were estimated by integrating the ODF from 45-85° (omitting scattering intensity arising from the Vineyard-Yoneda peak) and 5-45° for the edge-on population, respectively.

\[ R = \frac{\int_{45}^{85} \text{ODF} \, d\theta}{\int_{5}^{45} \text{ODF} \, d\theta} \quad (A3.2) \]

<table>
<thead>
<tr>
<th></th>
<th>P3HT face-on : edge-on ratio</th>
<th>PTB7 face-on : edge-on ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0.13</td>
<td>1.22</td>
</tr>
<tr>
<td>Sp-M blend</td>
<td>0.13</td>
<td>0.84</td>
</tr>
<tr>
<td>Sp-Z blend</td>
<td>0.16</td>
<td>0.92</td>
</tr>
<tr>
<td>Sp-E blend</td>
<td>0.15</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Table S3.1. Calculated face-on : edge-on ratios of pristine polymer and polymer/Sp blends from integrated ODFs.

A3.2 Interpretation and Justification of GIFT Assumptions
The most general means of describing the scattering observed from a sample is to provide its autocorrelation function as a function of position everywhere within the scattering volume. If the entirety of Q range were experimentally accessible, a straightforward inverse Fourier transformation would yield the desired correlation function. This would then correspond to the most complete description in an elastic scattering measurement. In practice, a finite Q range precludes such a calculation. A common approach is to simply use positions in scattering intensity peaks or shoulders, if available, to infer approximate length scales that may be of relevance in the sample. Such a description is far from satisfactory and can at best serve as a very coarse structural metric.

To arrive at a middle ground that allows for a reasonably accurate microstructural description given a limited accessible Q range, we make the approximation that is inherent in GIFT. That is, we assume that the scattering intensity can be viewed as being due to an ensemble of representative particles described by some intraparticle scattering contrast $p(r)$ and assembled in space in a manner reflected by the particles’ $g(r)$. Given that the blend film is a partially disordered network of polymer chains and interpenetrating small-molecule domains, it is not entirely clear what is meant by “particle” in this circumstance. In this context, we have interpreted “particle”, or scattering electron density inhomogeneity, as referring to regions of space that, along with the appropriate effective $g(r)$, can on average be used to roughly fill the volume of the film. Thus, such generalized “particles” simply carry information about statistically representative regions of space, condensed into an assembly from
infinity, in a way that describes the sample scattering. Within this interpretation, we are able to understand changes in the sign of the scattering contrast, which is in generally good agreement with real-space STEM-EDS maps shown in the main text.

Given the above simplifying assumption, we necessarily expect GIFT to provide an imperfect description of the polymer/molecule network morphology in the thin blend film. Nevertheless, once the underlying assumption is understood, we believe that such an approach is superior to simply estimating peak positions from the scattering curve. Thus, we argue that the GIFT algorithm allows us to obtain physically significant structural metrics in polymer/molecule films that can be used to make quantitative comparisons across a molecular series. However, due to the above considerations, we caution against overinterpretation of the structure factor fitting parameters that we extract.

A3.3 Details of Structure Factor Models

Polydisperse Hard Spheres (PHS): Using a collective-coordinate description, Percus and Yevick derived an integral equation for the radial distribution function, $g(r)$. They then used this description to calculate $g(r)$ for a dense gas of hard spheres within a virial expansion. Fourier-transforming yields a structure factor for a dense gas of hard spheres. We have further incorporated polydispersity with a Gaussian distribution. This was done by averaging the partial structure factors for spheres of different diameters. The results of the GIFT calculations with this model include $S(Q)$ itself, the polydispersity, and the volume fraction of hard sphere.
Mass Fractal Aggregates (MFA): Many disordered systems, including those composed of multi-component blends, often display fractal-like cluster/aggregate scaling over a (necessarily) limited length scale range, bounded from below by the molecular size. Such a description may be particularly appropriate for a network of clustered particles with a branched or cross-linked spatial distribution. The fractal dimension of such an assembly, $D$, describes how the number of particles within a cluster scales with the cluster radius $r$, as described in Equation A3.3, where $r_o$ is a characteristic length scale associated with the size of an individual scatterer. By relating the particle number density found within a given radial distance to the $g(r)$, a structure factor can be derived for such a fractal spatial distribution.

An analytic expression for the structure factor for a mass fractal aggregate model was developed by Teixeira. Its functional form is given by

\[
S(Q) = 1 + \left( \frac{1}{Qr_o} \right)^D \frac{\Gamma(D-1)}{(1+\frac{1}{Q^2\xi^2})^{D-1}} \left( \frac{D-1}{\tan(Q\xi)} \right) \tag{A3.4}
\]

where $\xi$ is a characteristic size of the mass fractal, above which the scaling described in Equation 4 is not observed, and $\Gamma$ is the Gamma function. It is important to note that fractal scaling can reasonably only be expected over a limited range of length scales. In the $Q \to 0$ limit, the structure factor approaches
\[ S(Q) = \Gamma(D + 1) \left( \frac{\xi}{\Gamma_0} \right)^D \left( 1 - \frac{D(D + 1)Q^2 \xi^2}{6} \right) \]  \hspace{1cm} (A3.5)

The nonlinear Boltzmann Simplex Simulated Annealing method was used to generate the pair distance distribution function (PDDF) using the generalized indirect Fourier Transform. A stabilized result of the fitted structure and form factors was chosen from Lagrange multipliers that produced a minimum mean deviation between the experimental and calculated result.

### A3.5 Summary of GIFT Structure Factor Parameters

**Table A3.2** shows best structure factor fitting parameters obtained using GIFT. Though we again caution against overinterpretation, a couple of samples gave rise best-fit parameters that deserve a comment. First, MFA fit for P3HT:Sp-Z blend, though satisfactory, yielded parameters that make little sense. The fractal dimension was 3, which suggests that a fractal description may not be appropriate. Second, the radius of

<table>
<thead>
<tr>
<th>Sample</th>
<th>R_{spheres} MFA (nm)</th>
<th>R_{spheres} PHS (nm)</th>
<th>Fractal Dim. (D)</th>
<th>Cut-off Length (nm)</th>
<th>Volume Fraction</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT blends</td>
<td>Sp-M 23.8</td>
<td>-</td>
<td>2.2</td>
<td>77.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Sp-Z 37.9</td>
<td>88.5</td>
<td>3.0</td>
<td>28.6</td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>Sp-E 36.6</td>
<td>-</td>
<td>2.9</td>
<td>295.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Sp-M 19.6</td>
<td>282</td>
<td>1.0</td>
<td>281</td>
<td>0.05</td>
<td>0.0004</td>
</tr>
<tr>
<td>PTB7 blends</td>
<td>Sp-Z 25.2</td>
<td>-</td>
<td>2.5</td>
<td>281</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Sp-E 46.8</td>
<td>-</td>
<td>3.0</td>
<td>275</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table A3.2.** Structure factor parameter results from GIFT calculations described in the main text.
spheres that expectedly follow fractal scaling was larger than the (upper) cut-off length – a nonsensical result that again highlights that the morphology does not show self-similarity over the measured length scales.

The second sample that deserves particular caution is the PTB7:Sp-E blend. As mentioned in the main text, we believe that the available Q range was insufficient to capture the details at the curve that seems likely to emerge at higher Q. Thus, this particular fit is not a good representation of the sample morphology, which is again underscored by a fractal dimension of 3. Indeed, the resulting p(r) contains features that are unexpected (see Figure 5 in the main text) and are likely not relatable to any real structural information.
A3.6 Energy Dispersive X-ray Spectroscopy (EDX/EDS) Imaging

![EDS spectra for P3HT:Sp-M and PTB7:Sp-M](image)

**Figure A3.1** Representative EDS spectra for P3HT:Sp-M and PTB7:Sp-M demonstrating the well-resolved and high signal-to-noise sulfur signal.

**P3HT:Spiro blends**  
![Elemental contributions](image)

**Figure A3.2** Elemental (left, sulfur/red, middle nitrogen/green) contributions to STEM-EDS Elemental maps and high-angle annular dark field (HAADF) (right) images for Sp-M (top), Sp-Z (middle) and Sp-E (bottom).
4. Charge-Transport Networks via Small-Molecule Self-Assembly in Conjugated Polymer Bulk Heterojunctions

Abstract

This chapter aims to answer the question, how do the inter-small-molecule interactions that lead to local self-assembly influence the formation of molecular networks on the nano and meso length scales? We interrogated two derivatives with the same peripheral chromophores but differing in their linking to the central core. We find that a triphenylamine core leads to robust self-assembly into nanowires that percolate through a polymer matrix but do not overly phase-separate, retaining efficient exciton harvesting. In contrast, a flourene core results in fractal, tortuous networks in the same polymer blend, which have substantially lower effective charge mobilities compared to nanowires. Our results have significant implications for non-fullerene organic photovoltaic devices.
4.1 Introduction

Organic photovoltaic (OPV) devices based on bulk heterojunctions of conjugated polymers and small molecules have recently displayed record performance, leading to 17.3% power-conversion efficiency in a tandem device.\textsuperscript{1} Such advances have primarily relied on careful engineering of absorption coefficients of the two components. This in turn required that the formerly champion electron acceptor – the fullerene derivative – was replaced with a non-fullerene small molecule. Due to the generally anisotropic shape of non-fullerene small molecules, the strength of intermolecular interactions and thus their propensity to crystallize and percolate through the polymer matrix can differ drastically relative to the quasi-isotropic fullerenes. The structure of the heterojunction across the set of device-relevant length scales in the bulk-heterojunction thin film thus depends critically on the chemical structure of the small molecule. A recent record-setting example of the balancing act between intermolecular interactions and desirable device morphology is the indaceno-dithiophene-type (ITIC) class of derivatives. They contain a highly planar core with substantial bulky sidechains that protrude out of plane with respect to the rigid fused-ring core.\textsuperscript{2-3} Though this lowers the propensity for π-stacking, the molecule is prevented from forming overly phase-segregated crystallites with dimensions well in excess of expected exciton diffusion lengths. Unfortunately, the reduced intermolecular interaction lowers the charge mobility along the π-stacking direction, which has negative ramifications for OPV device performance, particularly precluding the use of thicker films with larger light absorption.
Though the anisotropy of non-fullerene small molecules can be a complication, it can in principle be leveraged to manipulate the hierarchical morphology of the polymer/molecule blend film in a predictive manner. An intriguing strategy is to use molecular self-assembly to build in the propensity for forming percolating charge-transporting channels characterized by substantial local mobilities. Self-assembly has been realized in OPV devices where either one or both the donor and acceptor are small molecules capable of forming semi-ordered nematic and/or discotic liquid-crystalline mesophases.\textsuperscript{4-6} There is evidence that this gives rise to an enhanced charge mobility along a preferred axis of columnar growth due their large polycyclic aromatic cores. In conjugated polymer blends, upon thermal annealing, liquid-crystal-forming small molecules have been shown to crystallize into motifs that reflect their anisotropic intermolecular interactions.\textsuperscript{7-8}

However, the relationship between chemical structure and self-assembly of small molecule networks within an intrinsically crowded polymer matrix remains poorly understood and hinders the ability to use self-assembly to rationally control the hierarchical device morphology. Broadly, what is desired is progress towards a direct link between small-molecule chemical structure and the mesoscale structure of the phase-separated network that underpins long-range charge transport. In this work, instead of taking an exhaustive combinatorial approach to optimize the power conversion efficiency, we ask a fundamental question of broad relevance to non-fullerene small-molecule organic semiconductors: Can local considerations based on molecular self-assembly lead to designed long-range network formation that reflects
the local self-assembly interactions in a nonequilibrium, crowded polymer matrix? To begin to answer this complex question, we focus on two small-molecule derivatives that contain identical peripherical chromophores but differ in their central linking cores. For this set of derivatives, we perform a comprehensive structural and electrical characterization that allows us to extract insight that connects local self-assembly with the mesoscale structure of the blend and its charge transport.

We demonstrate that by varying the conjugated core of the small molecule for a given set of interacting “arms”, the network mesostructure can be manipulated qualitatively. Specifically, a triphenylamine core with three peripheral indigo-thiophene subunits leads to the formation of a self-assembled nanowires that (i) percolate through the polymer matrix, (ii) do not lead to formation of large crystallites, and (iii) efficiently harvest excitons. We find that the percolating nanowire motif is qualitatively insensitive to the nature of the polymer matrix. We further show that linking only two indigo-thiophene subunits with an alkylfluorene core changes the small-molecule network qualitatively, resulting in a highly fractal, tortuous morphology. Using a matrix within which only the small-molecule network can transport charge, we find that the current percolation threshold is lower and the current magnitude is significantly higher for the nanowire morphology relative to a more branched spatial distribution. Our results show that the interaction potential of the small molecule can be rationally manipulated so as to tune the percolated, self-assembled molecular network that underpins the device-scale charge mobility within a conjugated polymer matrix. This has important implications for the next generation of conjugated
small molecules that target a specific mesoscale charge-transport network at the chemical-structure level.

4.2 Results & Discussion

We focus on two bay-annulated indigo-thiophene (BAI) derivatives with two different core motifs, shown in Figure 4.1. The synthetic protocol and steady-state optical properties of the BAI derivatives have been previously reported. In both derivatives there is reinforced planarity of the indigo moiety via ring-fusion by the formation of an imide with thiophene groups appended internally towards the core-linkage, while the exterior bay position has an alkoxyalted benzene. The (NBAI) trimer

![Chemical structures of (a) PPDI2T, (b) NBAI, and (c) FBAI. 2D GIXD images for (d) neat PPDI2T, (e) PPDI2T:NBAI blend, and (f) PPDI2T:FBAI blend.](image)

Figure 4.1. Chemical structures of (a) PPDI2T, (b) NBAI, and (c) FBAI. 2D GIXD images for (d) neat PPDI2T, (e) PPDI2T:NBAI blend, and (f) PPDI2T:FBAI blend.
is covalently linked by a triphenylamine core that connects three BAI groups distorted out-of-plane in a propeller-like fashion due to the nitrogen lone-pair electrons, while the (FBAI) dimer consists of two BAI groups linked through thiophene rings to a dihexylfluorene core, giving rise to a chemical structure with a rod-like core with bent BAI arms. The alkyl sidechains for both molecules was chosen so as to yield similar solubilities in common organic solution-casting solvents. Incorporation of thiophene rings into the BAI donor-acceptor motif results in a relatively high-lying HOMO (~ 5.0 eV) and a LUMO level that is ~ 3.5 eV. Therefore, a derivative of poly(perylenedicarboxyimide-alt-thiophene) (PPDI2T) (Figure 4.1a) was used as an electron-accepting polymer with a favorable energy level offset for exciton dissociation.11

We first used grazing-incidence X-ray diffraction (GIXD) to investigate whether changing the BAI linking motif led to a change in intermolecular packing and crystallinity on the Å scale within the PPDI2T matrix. 2D GIXD images for PPDI2T:BAI blends and neat PPDI2T are shown in Figure 1d-f as a function of in-
plane and out-of-plane scattering vector components, $q_{xy}$ and $q_z$, respectively. The presence of a single, prominent (100) Bragg reflection centered about $q \sim 0.3$ Å$^{-1}$ across all samples indicates that there is a minor propensity for alkyl sidechain alignment of the polymer in both neat and blend films. The broad halo centered near $q \sim 1.3$ Å$^{-1}$ is due to inter-monomer correlations of the largely amorphous polymer. The reduced 1D GIXD intensity $I(q)$ (Figure A4.1) shows the most prominent low-q feature for the PPDI2T:NBAI blend, which may be indicative of short range periodicity between neighboring NBAI trimers. The $I(q)$ curve also shows a shoulder near $q \sim 1.7$ Å$^{-1}$, suggesting that there is short-range π-stacking between the small molecules within the blends, which is qualitatively similar to GIXD patterns of neat BAI films (Figure A4.1).

Figure 4.2. (a) UV/Vis absorption spectra for neat PPDI2T, NBAI and FBAI. PL intensity for (b) PPDI2T:NBAI and (c) PPDI2T:FBAI blends as a function of PPDI2T:BAI mole ratio.
The UV-Vis absorption spectra for the BAI derivatives and PPDI2T are shown in Figure 4.2a. Both derivatives have broad absorption peaks due to low-lying excitonic transitions with $\lambda_{\text{max}}$ near 625 nm, while the NBAI spectrum extends to slightly longer wavelengths. The low-lying exciton of PPDI2T spectrally overlaps the main BAI absorption peaks. Photoluminescence (PL) spectra for neat films of the BAI derivatives and PPDI2T normalized by their respective absorbance at the excitation wavelength (650 nm) are shown in Figure A4.2. The pure PPDI2T emission spectrum ($\lambda_{\text{max}} \sim 790$ nm) is broad with a relatively large quantum yield due to its mostly amorphous morphology and thus relatively few nonemissive inter-chain exciton traps. In contrast, the propensity for either BAI derivative to $\pi$-$\pi$ stack results in PL quantum yields that are two orders of magnitude lower than that of the polymer due to self-quenching. Despite being unable to selectively excite either component of a blend PPDI2T:BAI film due to their overlapping absorption spectra, PL from blend films is dominated by emission from radiative relaxation due to PPDI2T.

PL quenching measurements shown in Figure 4.2b-c provide evidence of polymer exciton dissociation at the polymer/molecule interface for both PPDI2T:NBAI and PPDI2T:FBAI blends. The PPDI2T PL does not spectrally overlap the small-molecule absorption spectrum, therefore we can rule out the influence of electronic energy transfer on PL quenching. This indicates that polymer PL is quenched due to charge transfer. Moreover, since both the polymer HOMO and LUMO levels lie below that of the small molecule, polymer excitons are converted to charges via hole transfer between the corresponding polymer and molecule valence-band states.
Beyond relating the small-molecule chemical structure to its assembly and network formation, we aim to elucidate how the small-molecule network evolves and coarsens as a function of molecular mole fraction for a fixed polymer amount. We examined a series of blends with PPDI2T monomer-to-BAI molecule mole ratios spanning an order of magnitude, from 1:0.05 up to 1:0.46, corresponding to the 1:1 w/w % PPDI2T:NBAI blend. The magnitude of PL quenching in the NBAI blend increases monotonically with small-molecule concentration. At the lowest 1:0.05 mole ratio, 67% of polymer excitons are quenched, increasing to 83% at the intermediate mole ratio (1:0.23) and 87% at the highest mole ratio. Interestingly, the PL quenching trend for the PPDI2T:FBAI mole-ratio series is non-monotonic, beginning with 71% at the lower mole fraction, a maximum of 90% at 1:0.23 and dropping to 75% at the highest mole ratio. Given the relatively large PL quantum yield of neat PPDI2T, the PL quenching fractions are expected to be faithful representations of the relative exciton-harvesting efficiencies of the blends.
To better understand differences in exciton harvesting efficiency between the different PPDI2T:BAI blends and relate them to the network structure, we investigated the mesoscale morphology in both real and reciprocal space. To do this, we used a combination of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging and resonant elastic X-ray scattering (REXS or RSXS) at the carbon K-edge. HAADF-STEM imaging measures incoherently scattered (Rutherford) electrons arising from mass, thickness or density phase contrast (Z-contrast). We note that the HAADF-STEM images of pure amorphous PPDI2T are featureless, which is to be expected from an amorphous material with a homogenous structure.

**Figure 4.3.** HAADF-STEM images at 40 kX magnification of (a-c) PPDI2T:NBAI as a function of increasing mole ratio; (d) REXS $I(q)$ profiles (open symbols) and GIFT fitting results (lines) and (e) resulting peak-normalized PDDF.
bulk density and no significant ordering on the nanoscale. HAADF-STEM images are 2D projections of the structure, whereas X-ray scattering measurements average over the film volume.

HAADF-STEM images of the PPD12T:NBAI mole ratio series are shown in Figure 4.3a-c. At the lowest 1:0.05 PPD12T:NBAI mole ratio, NBAI networks (white regions) form long-range branched (fractal) networks with average cross sections of ~20 nm. The interstitial regions separating the NBAI networks are greater than 200 nm and are assumed to be enriched in PPD12T. As the NBAI ratio is raised to 1:0.23, dense, interwoven nanowires form with a cross section approximately between 50 and 100 nm, which further grow to ~140 nm at the 1:0.46 mole ratio. The molecular nanowires are seen to percolate through the polymer film. Along with increasing cross-sectional thickness, the nanowires become closer packed with narrower interstitial regions. We found that solvent annealing with the spin-coating solvent, chloroform, gave rise to negligible morphological differences. A more extensive investigation of the impact of post-processing conditions will be the subject of future work.

Information regarding the statistically representative length scale of phase separation of the bulk morphology averaged across the film volume can be extracted from 1D REXS $I(q)$ profiles. X-ray energies near the C 1s $\rightarrow \pi^*$ absorption edge (284 eV) give rise to increased electron-density contrast relative to off-resonant scattering.\textsuperscript{12-13} We converted $I(q)$ to the orientationally averaged pair-distance distribution function, $p(r)$ or PDDF, via the generalized indirect Fourier transform (GIFT) using a fractal
model for the structure factor. The PDDF allows for a quantitative comparison of the nanoscale morphology across samples in a consistent manner. The zero-crossing of $p(r)$ can be associated with a change in sign of the electron density contrast within the scattering inhomogeneity. We previously showed this metric to be in good agreement with the average length scale of phase segregation when compared to TEM images.\textsuperscript{14} Details and results of modeling REXS $I(q)$ profiles are described in the Supporting Information and our prior work.

Figure 4.3d and 4.3e show $I(q)$ and $p(r)$ curves, respectively, for PPDI2T:NBAI blends as a function of NBAI mole fraction. The film with the lowest PPDI2T:NBAI mole fraction has the lowest scattering intensity and a subtle slope change at 0.007 Å\textsuperscript{-1}. The corresponding $p(r)$ shows a zero-crossing at r $\sim$ 16 nm. For the intermediate ratio, the magnitude of $I(q)$ increases, while the $p(r)$ zero-crossing moves to $\sim$38 nm. At the highest mole-ratio, the scattering curve has maximal intensity, suggesting the largest electron density contrast likely due to densely packed nanowire bundles. A prominent shoulder is evident at q $\sim$ 0.004 Å\textsuperscript{-1}, as well as a small feature near q $\sim$ 0.01 Å\textsuperscript{-1} that together suggest a hierarchical morphology. To help visualize the latter, in the Supporting Information we have plotted the derivative of the scattering curves, which show the change in slope at q $\sim$ 0.016 Å\textsuperscript{-1}. The presence of multiple length scales of electron-density contrast is captured in the PDDF (Figure 4.3e) as a local minimum near r $\sim$ 36 nm and a zero-crossing at 74 nm.
HAADF-STEM images for PPDI2T:FBAI are shown in Figure 4.4a-c with identical small-molecule mole fractions and processing conditions as with NBAI. At the lowest FBAI ratio, a fractal, dendritic network extends over long distances in a manner that is qualitatively similar to blends with NBAI at the same mole fraction. As the FBAI mole fraction is increased, the PPDI2T:FBAI morphology becomes starkly different compared to that of corresponding NBAI blends. The network mesostructure remains highly fractal, while the average branch length and cross-section grow, giving rise to shorter distances between adjacent clusters. At the 1:0.46 PPDI2T:FBAI mole ratio, the clusters coalesce, forming a highly interconnected and highly branched morphological structure.

Figure 4.4. HAADF-STEM images at 40 kX magnification of (a-c) PPDI2T:FBAI as a function of increasing mole ratio; (d) REXS $I(q)$ profiles (open symbols) and GIFT fitting results (lines) and (e) resulting peak-normalized PDDF.
network. Overall, we conclude that FBAI forms a mesoscale percolated network that is devoid of a predominant self-assembly motif. The fractal nature of the network at all mole fractions is reminiscent of structures formed via diffusion-limited aggregation (DLA) in a diverse set of systems. Just as DLA is a nonequilibrium phenomenon, so is the formation of kinetically trapped small-molecule networks inside the polymer matrix upon solvent evaporation and solid film formation.

The REXS $I(q)$ curve for the lowest mole-fraction FBAI blend (Figure 4.4d) shows a clear change in slope around $q = 0.01 \text{ Å}^{-1}$, indicative of a morphological hierarchy. The $p(r)$ (Figure 4.4e) of this blend at low $r$ is monotonically decreasing but albeit with a shoulder just below 20 nm; the curve then changes sign at 25 nm. In the intermediate FBAI mole-fraction sample, the zero-crossing of $p(r)$ decreases to 18 nm, and there is no longer evidence of a shoulder at low $r$. Along with the decrease in scattering intensity relative to the 1:0.05 sample, we interpret this as a formation of a slightly more homogeneous distribution of small molecules through the polymer matrix, decreasing the nanoscale scattering contrast and lowering the mean length scale of phase separation. $I(q)$ for the 1:0.46 blend shows the highest intensity at $q \sim 0.03 \text{ Å}^{-1}$ compared to the two smaller mole ratios, as well as a significant slope change at $q \sim 0.004 \text{ Å}^{-1}$, again indicative of a hierarchical multi-length scale morphology. This results in a further downward shift of the $p(r)$ zero-crossing to ~10 nm, consistent with formation of a large density of branching points with relatively small branches.
The trends in polymer exciton harvesting for different PPDI2T:BAI blends can be interpreted in light of the morphological characterization shown in Figure 4.3 and 4.4. As the mole ratio of PPDI2T:NBAI increases, progressively larger NBAI nanowires segregate emissive PPDI2T into smaller interstitial domains. Thus, shorter distances are required for excitons formed within PPDI2T to diffuse to PPDI2T:NBAI interfaces, resulting in a higher population of generated charge carriers. However, increases in nanowire cross section must also mean that small molecules that would have broadly distributed through the polymer become sequestered away, somewhat decreasing the effective interfacial area available for exciton quenching. Thus, the PL quenching efficiency undergoes a negligible increase as the small-molecule concentration is doubled from the intermediate to the largest value.

In the case of PPDI2T:FBAI, maximum PL quenching occurs at the intermediate 1:0.23 mole ratio that corresponds to a branched network morphology with an average length scale of phase segregation of ~20 nm. This length scale is reasonably commensurate with the expected polymer exciton diffusion length. It is worth highlighting the fact that the intermediate-ratio FBAI blend also showed the smallest X-ray scattering intensity among the three mole fractions. This is consistent with a somewhat more homogeneous morphology, which would be expected to lead to the largest exciton harvesting efficiency, consistent with our PL quenching results. At the largest mole fraction, the coalesced fractal network of the FBAI blend possibly results in a decrease in PPDI2T:FBAI interfacial area. This would lead to a decrease in exciton harvesting and a corresponding increase in polymer PL intensity. However, we believe
another possibility must be considered. The local $\pi$-stacking within the NBAI nanowire leads to formation of H-aggregate-type excitons, which have vanishing PL quantum yields. As FBAI is evidently unable to form well-defined, relatively ordered structures in polymer blends, significant PL yields may originate from FBAI domains. Since the polymer and FBAI PL spectra overlap very strongly (Figure A4.1), we believe that the increase in small-molecule PL at the largest FBAI fraction may contribute to the increase in total PL signal observed at the largest ratio. This would in turn lead to an error in estimating the exciton quenching efficiency.

Though we have shown that the two small-molecule chemical structures lead to drastically different nanoscale morphologies within a conjugated polymer matrix, the question remains as to which qualitative network motif would be characterized by more facile charge transport. We first sought to directly relate the PPDI2T:BAI blend photocurrent to the real-space mesostructure observed in TEM measurements; as such, the photocurrent measurements were performed on relatively thin blend films (~50 nm). This film thickness (and thus light absorption) was significantly lower than what is expected for optimized solar cells. Nevertheless, we constructed single-junction photovoltaic devices based on these blends and observed an order-of-magnitude higher short-circuit current for PPDI2T:NBAI blends relative to PPDI2T:FBAI. This result is consistent with an enhancement in charge transport efficiency along the small-molecule-rich phase along the nanowire vs. fractal morphology. However, the total photocurrent consists of the sum of both hole and electron contributions along the
small-molecule and polymer networks, respectively, which complicates the ability to relate charge transport to the small-molecule network alone.

Our overarching goal was to elucidate the electronic connectivity of the two different BAI networks by focusing on the transport of charge exclusively through the small-molecule network. We first attempted to do so by measuring the injected current density in PPD2T:BAI blends with carrier-selective electrodes. We found that at all reasonable electrode combinations, the current due to PPDI2T was large enough so as to make evaluation of the small-molecule network transport quite difficult. We thus chose to perform current injection measurements with an insulating (non-conjugated) polymer matrix, which guaranteed that transport occurred via charge transfer between small molecules only. The prior utility of such an approach has been demonstrated previously.\textsuperscript{19-21} Naturally, conjugated and non-conjugated polymer matrices can be qualitatively different due to the presence of polarizable \(\pi\)-electrons in the former. Hence, we must first verify that qualitatively, the small-molecule networks that form in non-conjugated polymer matrices are sufficiently similar so as to serve as a meaningful relative comparison between the two BAI derivatives.

We chose to use poly(hexylmethacrylate) (PHM) as the insulating polymer matrix due to its hexyl sidechain that mimic solubilizing sidechains typically appended onto conjugated polymer backbones. Figure 4.5a-b show STEM-HAADF images of PHM:NBAI and PHM:FBAI, respectively, at the same polymer : molecule ratio. Similar to PPDI2T, PHM thin films are largely amorphous. We see that NBAI forms a
qualitatively similar nanowire network within PHM as in PPDI2T, though there are quantitative differences in the average cross-sectional thickness of the nanowires. The nanowires are nevertheless seen to percolate through the polymer film. On the other hand, the PHM:FBAI blend appears to have a network with branched FBAI domains imbedded within the polymer phase. The small-molecule network is again rugged and lacking a discernable self-assembly motif. Interestingly, blends of FBAI with another archetypal insulating polymer, poly(styrene), similarly display a fractal, highly branched morphology, while NBAI also forms nanowires (Figure A4.3). Thus, qualitatively, the propensity for a specific network self-assembly motif, or lack thereof, appears to transcend the precise molecular details of the polymer matrix. This indicates that the mesoscale network can, at least partially, be reduced to the small-molecule chemical structure and its resultant (many-body) intermolecular interactions. In future work, the generality of this observation should be tested as a function of the relative polymer crystallinity.
Having characterized the network structure, we prepared devices with PHM:BAI blend active layers with a similar range of BAI concentrations for a fixed PHM concentration. Injected current was measured in the diode configuration. Figure 4.5c shows the injected current density at a fixed voltage of 14 V as a function of small-molecule/monomer mole fraction for NBAI and FBAI. The fixed-voltage choice was
made to ensure that the current was well within the space-charge-limited regime, with the current showing power-law scaling. At the lowest ratio of 0.05, both blends show a relatively small current, which is consistent with a relatively similar diffuse fractal morphology for both derivatives at the lowest mole ratio, shown in Figure 4.3 and 4.4. This ratio likely lies close to the current percolation threshold of the network. With increasing small-molecule concentration, the current in NBAI blends increases significantly more rapidly than for FBAI. At the highest PHM:BAI ratio, there is a three-fold increase in current density through the NBAI network, indicating a significantly higher effective charge mobility compared to the more rugged FBAI network. We note that the same qualitative trend in the magnitude of current-density as a function of mole fraction was observed independent of the chosen fixed voltage, including at relatively low voltages. This is shown in Figure A4.5 of the Supporting Information.

To better understand the transport differences between the two small-molecule networks, Figure 4.5d shows the current density as a function of applied bias with double-logarithmic scaling for the largest mole fractions only. At higher positive bias, the current density for both PHM:BAI blends follow voltage power laws with exponents greater than two. Thus, Child’s square-voltage law is not obeyed, which, within the space-charge-limited current formalism, implies that either (i) the charge mobility is a function of the electric field, or (ii) there exists an energy-dependent electronic trap distribution.22-26 Both models have previously been applied with reasonable success. We have chosen to model the device current-voltage behavior
using the latter, since the physical network structure shown in our STEM-HAADF images can be reasonably expected to give rise to the formation of electronic traps due to site-energy disorder.\(^{27}\)

We assume that the distribution of hole trap states with energies above the HOMO level can be described by an exponential distribution peaked at the HOMO, which we believe is reasonable in the absence of additional information. Within this model, the magnitude of the power-law scaling exponent of the current-voltage curve is inversely proportional to the characteristic temperature of the trap distribution, \(T_c\), such that

\[
J \propto V^{T_c/T+1} \quad (4.1)
\]

where \(T\) is the thermodynamic temperature. \(T_c\) is related to the energetic \(1/e\) width of the trap distribution via

\[
P(E) \propto e^{-|E_{VB}-E|/k_BT_c} \quad (4.2)
\]

\(E_{VB}\) is the valence-band (HOMO) level, and \(k_B\) is the Boltzmann constant.\(^{23}\) We find a slightly larger scaling exponent of the PHM:FBAI blend (4.55) blends relative to PHM:NBAI (4.39). Within the exponential-trap model, this implies a broader distribution with a larger density of relatively deep traps, changing \(T_c\) from 1058 K for FBAI to 1010 K for NBAI. Though the difference is small, we believe it is consistent with the physical network structure. Furthermore, the fact that the difference in trap distribution is relatively small strengthens the validity of our comparison of current
density as a function of mole fraction between the two derivatives, as differences in the electric-field dependence of the transport (whether due to a field-dependent mobility or a trap distribution) are seen to be minor.

Thus, we have shown that NBAI self-assembles into mesoscopic nanowires that percolate through the polymer matrix, leading to charge-transport networks characterized by a larger effective charge mobility and somewhat fewer deep electronic traps compared to fractal FBAI networks. The lack of significant long-range crystallographic (d-spacing) order within the nanowires is characteristic of the formation of liquid crystals, suggesting that there is nevertheless significant orientational order. Coupled with a propensity for π-π stacking of three BAI chromophores, the broken reflection symmetry of the propeller-shaped NBAI gives rise

**Figure 4.6.** A cartoon illustrating the connection between small-molecule packing in the polymer blend and the complex energetic landscape (as a function of a collective configuration coordinate), which determines the practically accessible
to columnar growth similar to bowlic liquid-crystal mesophases.\textsuperscript{28-29} The alignment of alkyl sidechains protruding orthogonal to the axis of columnar growth gives rise to close packing of individual NBAI columns into fibers as the network coarsens.

The multidimensional free energy landscape that underpins the structure of the percolated small-molecule network is highly complex, reflecting the totality of many-body molecule-molecule, molecule-polymer and polymer-polymer interactions, as well as the entropy of mixing. We find that the self-assembly of NBAI nanowires is highly robust, forming within both conjugated and non-conjugated polymer hosts at a wide range of NBAI concentration. Our observations suggest that there exists a relatively deep minimum in the NBAI network landscape that corresponds to collective formation of percolated nanowires. This is schematically shown in Figure 4.6 as a function of some collective configuration coordinate. We speculate that this is due to the presence of three BAI-thiophene arms and the asymmetric propeller-like shape. The formation of nanowires provides quasi-discrete pathways for long-range charge transport throughout the conjugated polymer matrix. The relatively low network tortuosity appears to be quite beneficial for transport.

There is a critical small-molecule mole fraction, beyond which the self-assembled nanowire motif becomes dominant. Above the critical mole fraction, further increases in small-molecule concentration lead to substantial network coarsening but no qualitative change in self-assembly. As an interesting comparison, we have also formed networks with Cu phthalocyanine bearing an alkyl sidechain periphery – a molecule
that has a large propensity to form highly anisotropic co-facial π-stacks due to the planar π-electron-rich macrocycle (Figure A4.6). We find that this small molecule also forms needle-like structures, but they become highly crystalline in the polymer blend immediately upon solvent evaporation. This leads to an overly phase separated morphology, shown in the Supporting Information. This underscores the critical importance of using the molecular structure to control self-assembly on the nanoscale while minimizing crystallite-induced large-scale segregation that is detrimental to exciton harvesting.

In contrast to NBAI, FBAI contains only two BAI-thiophene arms and a somewhat bent-core geometry. In this sense, FBAI is reminiscent bent-core and flexible alkyl sidechains that can form smectic liquid-crystalline phases with long-range orientational order but lacking positional order.30-32 However, the presence of alkyl sidechains appended to the fluorene core likely limits the ability to form percolated liquid-crystalline phases. As such, we propose that the many-body energetic landscape of thin-film FBAI contains a number of relatively shallow minima, leading to a broad distribution in relative intermolecular orientation between proximal FBAI molecules (bottom of Figure 4.6). FBAI ultimately forms a mesoscale network in a DLA-type fashion, where molecules are added to a growing cluster with a sticking probability that likely depends relatively weakly on orientation between cluster molecules at an edge and the next approaching molecule. We believe that the bent geometry also likely means that FBAI can act as a molecular “tie-chain”, connecting adjacent molecules via peripheral BAI tails. We expect that this would give rise to a large cluster branching
ratio and eventually a high-tortuosity network for charge transport, leading to lower effective charge mobilities.

Our results illustrate the utility of using built-in molecular assembly to control both formation of percolated charge-transporting channels over the hierarchy of relevant device length scales, as well as the ability to impede phase separation over large distances detrimental to performance. Though we focused on donor-type small-molecules in (acceptor-type) conjugated and insulating polymer matrices, we believe our work has important implications for non-fullerene small-molecule acceptors blended with donor conjugated polymers. This is because the basic considerations that determine network formation and charge transport therein largely transcend the precise electronic structure of the small molecule. Thus, we anticipate that the insight provided herein on assembly in such confined, highly crowded matrices under nonequilibrium conditions will be of relevance for all manner of polymer blends with highly anisotropic small molecules.

4.3 Conclusion

In conclusion, we have reported the self-assembly of long-range small-molecule networks within conjugated and non-conjugated polymer matrices with morphologies that are sensitive to the strength and orientation dependence of intermolecular interactions. We have shown that the nanowire motif can lead to larger effective charge
mobilities compared to a more fractal network, and that the chemical structure can be
tuned so as to maintain assembly while minimizing large-scale crystallization. One of
the significant implications of our work is the demonstration that molecular assembly
appears to be highly promising for controlling the mesoscale morphology of the
conjugated polymer-based blend device. It is thus important to not only vary the
chemical structure to maximize light absorption and the open-circuit voltage, but to
also build-in noncovalent interactions that will direct formation of specific charge-
transport channels on nano-and meso-length scales. We believe that further progress in
this direction will ultimately yield sensitive control over the transport and
recombination rates, allowing for the use of thick devices with non-fullerene small
molecules.33

4.4 Experimental Methods

NBAI and FBAI were prepared and purified following previously detailed
protocols.10,34 PPDI2T (1-Material, MW = 80,000 Da, PDI = 2.5) and PHM (Polymer
Source, Inc., MW = 47,500 Da, PDI = 1.7) were used as is. Stock solutions of PPDI2T
(5 mg/mL) and PHM (20 mg/mL) were prepared in HPLC grade chloroform (Sigma
Aldrich) and filtered through a 0.450 µm PTFE syringe filter. PPDI2T:BAI blends were
prepared by dissolving solid BAI in PPDI2T chloroform solution, resulting in 1:1,
1:0.5, and 1:0.1 wt/wt ratios, which corresponds to PPDI2T monomer to NBAI molar
ratios of 1:0.46, 1:0.23 and 1:0.05, respectively. PPDI2T:FBAI blend solutions were prepared identically with matched molar ratios of PPDI2T:FBAI. PHM:BAI solutions were prepared with BAI concentrations identical to the respective PPDI2T:BAI blend. All solutions were stirred in the dark overnight at 45 °C.

Glass substrates (Corning 2948) and doped silicon wafers (Silicon Quest International, 0.005Ω·cm resistivity) were used for optical spectroscopy and GIXD measurements, respectively. Substrates were precleaned via sonication for 5 min in acetone, followed by isopropyl alcohol, dried with a stream of N₂ gas, and subsequently treated with UV/ozone using a Novascan instrument (PSD-UV4). A ~25 nm layer of poly(ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS; Heraeus, Clevios PH 1000) was spin-coated at 5,000 rpm for 60 s and thermally annealed at 150°C for 30 min in air prior to spin-coating the organic layer at 1,500 rpm for 60 s. All spin coating was performed with a Laurell Technologies instrument (WS-650MZ-23NPPB) at ambient conditions under a stream of nitrogen gas.

Thin films for HAADF-STEM and REXS measurements were prepared in a similar fashion with as-cast PEDOT:PSS as a sacrificial water-soluble layer for thin film transfer. An approximately 0.5 cm² portion of film was scored with a diamond scribe and dipped into deionized water to float-transfer the BHJ layer onto X-ray-transparent silicon nitride membranes (Norcada, 5100XC) for transmission X-ray scattering and TEM grids (Copper coated with ultrathin lacey carbon support film; Ted Pella, 400 mesh). Excess water was wicked from the float-transferred film, after which the film-
coated substrate was stored under vacuum to remove residual moisture. All PPD12T:BAI films were solvent-annealed in the dark for one hour by placing the sample in a sealed jar with an open vial containing 1 mL of chloroform.

PHM:BAI derivative films (120 +/- 20 nm) for charge injection measurements were prepared on pre-patterned ITO wafers (140 +/- 10 nm) coated with PEDOT:PSS, which were cleaned using a detergent/DI-H2O/acetone/isopropyl alcohol solvent series, blown dry with N₂ gas and treated with UV/ozone prior to spin-coating. Silver cathodes (50 nm, 99.99%, Kurt Lesker) were thermally evaporated at a rate of 1 Å/s at 2 x 10⁻⁶ Torr using a shadow mask with a 6.5 mm² device area.

GIXD (incidence angle = 0.12°) was performed at the at the Stanford Synchrotron Radiation Lightsource (SSRL), beamline 11-3 (12.7 keV) generated by a 24-pole, 2-Tesla wiggler insertion device. Exposure times of 180 s were used at a detector distance of 315 mm, and sample-detector distance calibration was performed with polycrystalline lanthanum hexaboride. Diffraction data was collected using an area detector and reduced in WxDiff.

Absorption spectra were measured on thin films coated onto glass in 1.0 nm increments with a Shimadzu UV-2700 spectrophotometer using an integration time of 0.1 s and a 2 nm slit width. Photoluminescence spectra were collected with 10 s integration times in front-face geometry on a home-built apparatus using a pulsed (picosecond) supercontinuum laser (NKT) and detected with a back-illuminated CCD.
camera (Princeton Instruments PIXIS 100BR; deep depletion) coupled to an Acton SP-2300 monochromator (2 nm bandpass). The home-built apparatus has been described previously.\textsuperscript{35} Emission was measured at approximately 45\textdegree \ relative to the excitation source, and a 665 nm long-pass filter was used to minimize reflections of the excitation beam.

STEM-HAADF imaging was performed with a FEI Titan microscope operating at an acceleration voltage of 200 kV at the National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory. The STEM probe had a convergence angle of 10 milliradians and beam current of \(~500\text{ pA} \).

REXS measurements were performed at the Advanced Light Source beamline 11.0.1.2, Lawrence Berkeley National Lab, with a beam flux = \(10^{13}\) photons/s generated by a 5.0 cm-period elliptical polarization undulator (EPU5) source in a high vacuum scattering chamber (10\textsuperscript{-7} Torr). 2D scattering images were collected using an in-vacuum CCD using with an X-ray photon energy of 284 eV with an approximate 200 \(\mu\text{m}\) beam cross-section. Scattering was performed at 50 mm and 150 mm sample-to-detector distances. Scattering images were collected from four positions per film, which were reduced to 1D \(I(q)\) curves by circular averaging using the Nika package in Igor.\textsuperscript{36}

Pair-distance distribution functions (PDDF) were generated using the generalized indirect Fourier Transform (GIFT) of REXS \(I(q)\) curves.\textsuperscript{37,14} Scattering functions are factored into a form factor and a mass-fractal-aggregate structure factor. A detailed description of the structure factor modeling has been described previously.\textsuperscript{38} Structure
factor parameter results are summarized in Table A4.1. In some cases, $I(q)$ curves were smoothed with a moving-average filter in MATLAB prior to modeling with GIFT in order to reduce the influence of low-intensity background scattering at high $q$.

Dark current/voltage measurements were collected in an inert nitrogen glovebox in an inert glovebox (< 0.1 ppm H$_2$O & O$_2$) using a Keithley 2450 source meter interfaced with an 8-channel relay module (Advantech, USB-4761) and a LabVIEW virtual instrument developed in house. Data from twenty devices per sample condition were averaged to produce the error bars shown in the main text.

**Acknowledgements**

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4.6 References


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A4. Supporting Information

A4.1 Grazing Incidence X-ray Diffraction

GIXD images were converted to reduced 1D $I(q)$ profiles, shown in Figure A4.1. The weak peak centered near $q \sim 0.3$ Å$^{-1}$ corresponds to the (100) reflection of PPDI2T shown in the main text and attributed to alkyl sidechain ordering. Neat films of both BAI derivatives have reflections centered at $q \sim 0.35$ Å$^{-1}$ corresponding to short-range ordering of their slightly shorter solubilizing alkyl sidechains. Both PPDI2T:BAI blends have a low-q peak centered about 0.32 Å$^{-1}$, which is likely a linear combination of the low-q features from PPDI2T and the respective BAI derivative. This is indicative

![Figure A4.1](image)

**Figure A4.1.** Reduced 1D $I(q)$ from GIXD images of PPDI2T:BAI derivative blends and neat PPDI2T.
of short-range order of alkyl sidechains for each component being preserved within the blend films. Similarly, the 1D $I(q)$ curves for both neat and blend films show a broad feature at $q \sim 1.3$ Å$^{-1}$, representative of a largely amorphous morphology. The shoulder at approximately $q = 1.7$ Å$^{-1}$, however, suggests some propensity for $\pi-\pi$ stacking over short length scales.

**A4.2. Photoluminescence Spectroscopy**

Photoluminescence spectra shown in Figure A4.2 were normalized by the respective optical densities at the excitation wavelength (650 nm) and are

![Diagram](image)

**Figure A4.2** PL spectra of neat PPDI2T, NBAI and FBAI thin films normalized by their respective optical density at the excitation wavelength (650 nm).
representative of the relative quantum yields of each the polymer : small molecule blends discussed in the main text. The neat BAI films (inset) are nearly two orders of magnitude less emissive per unit absorption compared to neat PPDI2T, thus, the emission spectra shown in Figure 1h-i in the main text are dominated by emission from unquenched excitons localized on PPDI2T.

**A4.3. STEM-HAADF Microscopy**

STEM-HAADF images of polystyrene blends with NBAI and FBAI (Figure A4.3a & b, respectively) showing qualitatively similar self-assembled networks relative to those observed in PPDI2T and PHM blends with BAI derivatives.

![Figure A4.3](image) HAADF-STEM images of (a) polystyrene:NBAI (28.5 kX magnification) and b) polystyrene:FBAI (80 kX magnification).
A4.3 Derivatives of REXS $I(q)$ Curves

Subtle features and changes in slope of REXS $I(q)$ vs. $q$ curves contain information about the length scales of electron density contrast and average domain sizes in polymer : small molecule blends. To help visualize such relatively subtle features, $d \log I(q)/d \log q$ are plotted in Figure A4.3.

**Figure A4.4** Plots of the derivatives of REXS $I(q)$ curves converted for (a) PPDI2T:NBAI and (b) PPDI2T:FBAI mole ratio series. Solid lines are used to illustrate the $d(\log I)/d(\log q)$ vs. $\log q$ curves while the log Intensity vs. $\log q$ are shown with dotted lines.
A4.4. Generalized Indirect Fourier Transform (GIFT) Modeling Results

In this work, a mass-fractal-aggregate structure factor model was utilized.\textsuperscript{14, 38} Within the model, the fractal dimension, $D$, describes the scaling of the number of particles within a cluster as a function of radius, $r$. The characteristic length scale of individual particles within the cluster is described by $R_{\text{sphere}}$, and the cut-off length is the characteristic size of the mass fractal aggregate, above which fractal scaling is not observed. Structure factor parameter results from the best fitting non-linear GIFT modeling are summarized in Table A4.1.

<table>
<thead>
<tr>
<th></th>
<th>Fractal Dimension</th>
<th>$R_{\text{sphere}}$ (Å)</th>
<th>Cut-off Length (Å)</th>
</tr>
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<tbody>
<tr>
<td>PPDI2T:NBAI:0.46</td>
<td>2.85</td>
<td>64.4</td>
<td>741.5</td>
</tr>
<tr>
<td>PPDI2T:NBAI:0.23</td>
<td>2.44 - 2.59</td>
<td>64.8 - 67.9</td>
<td>761.1 - 841.2</td>
</tr>
<tr>
<td>PPDI2T:NBAI:0.05</td>
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<td>69.2 - 97.3</td>
<td>307.3 - 321.6</td>
</tr>
<tr>
<td>PPDI2T:FBAI:0.46</td>
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<td>17.3 - 18.3</td>
<td>918.5 - 1107.5</td>
</tr>
<tr>
<td>PPDI2T:FBAI:0.23</td>
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<td>95.4 - 105.1</td>
<td>309.9 - 410.9</td>
</tr>
<tr>
<td>PPDI2T:FBAI:0.05</td>
<td>2.86 – 2.99</td>
<td>85.4 – 86.1</td>
<td>396.1 – 522.0</td>
</tr>
</tbody>
</table>

Table A4.1 Structure factor parameter results from GIFT modeling of REXS $I(q)$ curves reported in the main text.
A4.5. Current Density at Lower Bias of PHM:BAI Devices

The trend in the magnitude of current density at relatively low applied bias (3 V) as a function of mole fractions is qualitatively similar to the higher voltage (14 V) J-V data shown in the main text.

![Graph showing current density at 3 V as a function of PHM:BAI mole ratio]

**Figure A4.5** Injected current density at 3 V as a function of PHM:BAI mole ratio

A4.6 Structure of PPDI2T:CuPc-8H Blends

The alkyl-substituted copper (II) phthalocyanine (CuPc-8H) derivative shown in **Figure S6a** has a chemical structure with a large, planar aromatic core and is thus is
capable of forming large anisotropic columnar assemblies. The GIXD image of the PPDI2T:CuPc-8H blend (Figure S6b) shows a high-intensity, relatively narrow Bragg reflection at $q \sim 0.3 \ \text{Å}^{-1}$, suggesting formation of large crystalline regions. This is further supported by the STEM-HAADF image in Figure S6c, where highly phase-segregated needle-like structures can be readily seen. We observed these features with dimensions of several hundreds of nm to be present independent of the PPDI2T:CuPc-8H mole ratio, which is contrast to the PPDI2T:NBAI blend that formed non-crystalline nanowire structures with dimensions that were sensitive to the NBAI concentration.

**Figure S6** a) Chemical structure of copper (II) phthalocyanine derivatized with hexyl sidechains on the periphery of each benzene ring (CuPc-8H). b) 2D GIXD image of a PPDI2T:CuPc-8H blend. c) HAADF-STEM (7.1 kX magnification) of a PPDI2T:CuPc-8H blend.
5. Optical Progression of Solution-Processable Benzene Ladder

Oligomer Length Series

Abstract

Extended conjugated ladder systems have shown promise in organic electronic materials due to their rigid structure that is capable of electronic delocalization and effective intermolecular packing and charge transport along the fused aromatic backbone. There is however a fundamental lack of knowledge of how the electronic structure is influenced by increasing the effective conjugation length by synthetic addition of aromatic rings. In this work, we investigate a series fused aromatic ring ladder oligomers and their optical absorption and emission properties in increasing dielectric strength environments. Our results show that there is a length dependence for the sensitivity of the vibronically coupled electronic states to the surrounding dielectric environment that leads to thermally activated intersystem crossing to non-emissive states. This evidence provides insight into the nature of the excited state wavefunction relative to the extent of conjugation length.
5.1 Introduction

Recent progress and record power-conversion efficiencies (PCE) of organic photovoltaic (OPV) bulk heterojunction devices have been observed with non-fullerene acceptors based on indacenodithiophene derivatives with highly rigid, fused conjugated backbones. These ladder-type small molecules display substantial electronic wavefunction delocalization due to the backbone planarity, as well as decreased reorganization energies, which is beneficial for light harvesting and intermolecular charge transport. The highly anisotropic shape of the ladder motif molecules counters the conventional wisdom of how the chemical structure of small molecules contributes to a hierarchical polymer blend-film. Previously, fullerene derivatives such as PC$_{60}$BM have been relied on as the archetypical small-molecule due to the sphere-like fullerene cage that facilitates quasi-isotropic intermolecular charge transfer rates and intermediate domain sizes commensurate with the average organic semiconductor exciton diffusion length ($L_d \sim 10 – 20$ nm). In contrast, the functionalization of $sp^3$-hybridized carbons along the planar ITIC backbone with solubilizing sidechains hinders the propensity for pi-pi stacking and aggregation leading to over phase segregation in excess of $L_d$. Appropriate selection of phenyl or thiophene sidechains can also promote intermolecular packing, however, less is understood of how the ITIC electronic structure is modulated by the extension of the ladder core from the five-membered fused aromatic backbone of IDTIC to seven (ITIC) or nine (INIC) fused aromatic rings.$^{1-3}$ The decrease in optical bandgap with increasing conjugation length
is often invoked to account for an increased absorption extinction coefficient and device PCE, however, the influence of intermolecular interactions and the environment dielectric environment on recombination rates has not been systematically interrogated.

5.2 Results

This report investigates the optical properties of the benzotetraphene (BTP) oligomer series ranging in length from five to eleven fused benzene rings is shown in Figure 5.1; the synthesis and basic optical properties have been reported previously.\textsuperscript{4} The non-linear BTP ladder motif is composed of four fused benzene rings and thus highly planar, while solubility is afforded by synthetically appended branched alkoxy chains at the BTP termini.

In order to investigate the electronic spectra of isolated molecules, absorption and emission spectra are collected in dilute solution (~2e-7 M, OD <0.05) in order to negate effects of aggregation and intermolecular coupling. The rigid chemical structure of the fused-benzenes ring BTP5 – BTP11 conjugated backbone gives rise to low conformational disorder and fine-structured absorption and emission spectra with resolved energetic vibronic progression (Figure 5.1 b,c respectively). The rigid planarity of the fused BTP core is maintained with increased number of benzene rings as shown by the associated red-shift and increase in vibronic structure of the absorption and emission spectra. This is consistent with excitonic delocalization across the increasing length of the BTP backbone and associated decrease in the optical energetic bandgap. The absorption spectra (Figure 1b) are shown normalized to the first
prominent low energy transition in order to highlight the relative increase of extinction coefficient of the lower energy absorption features with conjugation length. In addition to the prominent absorption, all BTP oligomers have a set of low extinction coefficient peaks at the red-edge of the respective absorption spectra (Figure 1e, inset) that likely correspond to the lowest $S_1$ vibrational levels.

The emission spectra of dilute/degassed BTP oligomers normalized by the excitation OD in chlorobenzene is shown in Figure 1c and representative of the relative photoluminescence quantum yield (PLQY). The PLQY and emission features are

![Chemical structures and spectra](image)

**Figure 5.1** (a) The chemical structures of the BTP ladder oligomer length series; (b) absorption spectra with low energy vibronic progression inset and (c) emission spectra normalized by the excitation OD with inset of the PL normalized by the 0-0 emission intensity highlighting the increase of intensity of the higher energy emission peak.
largely independent of excitation wavelength and solution concentration. The prominent highest energy emission peak for BTP5 is centered at 3.05 eV and likely corresponds to the 0-0 transition that corresponds to emission from the lowest vibrational level of the first excited electronic state ($S_1$) to the lowest vibrational ground electronic state ($S_0$). The energetic separation of the vibronic progression of BTP5 is approximately 0.17 eV which is consistent with the vinyl stretching mode in other oligoacene and ladder systems.

An increase in vibronic structure correlating to an overlapping of vibronic progressions is present in BTP7 and longer ladder oligomers, including a distinctly low PLQY feature. While the relative PLQY of the main vibronic structure decreases with increasing conjugation length the PLQY of the highest energy feature in BTP7-BTP11 increases relative to the 0-0 emission intensity with conjugation and effective exciton delocalization length, as shown inset in Figure 5.1c.

In order to understand how the electronic structure is perturbed by intermolecular solvent environmental interactions, absorption and emission spectra are collected for BTP5 compared to BTP9 in a solvent-series with increasing dielectric strength. ODCB), shown in Figure 5.2. BTP9 is used as a comparison as its increased vibronic structure relative to BTP5 is representative of the longer oligomers. An increasing dielectric environment is expected to screen the change in excited state and ground state dipole moments leading to a redistributed excited state
wavefunction density and bond length distribution due to solvent dipole reorganization effects.

Increasing the dielectric solvent environment in ethanol (EtOH, \(\epsilon = 24.5\)) and acetonitrile (MeCN, \(\epsilon = 36.5\)) BTP solutions leads to a reverse blue shift of the emission spectra and the emergence of low PLQY emission from a higher energetic state in the BTP5 oligomer (Figure 2c) that is similar to the higher energy feature in the low-polarity BTP7-BTP9 oligomers. Notably, the PLQY of the higher energy emission increases with dielectric strength from EtOH to MeCN.

![Figure 5.2](image)

**Figure 5.2** Solvent dependent (a, b) absorbance and emission (c, d) spectra of (a, c) BTP and (b, d).
The photoluminescence excitation spectra (PLE) shown in (Figure 5.3a) demonstrates that excitation at the 0-0 emission peak (E = 3.05 largely overlaps the BTP5 OD spectrum while, as expected, no emission is observed at higher energy excitation (E = 3.29 eV). In BTP5 ethanol, the 0-0 PLE emission similarly overlaps the respective OD while the higher energy PLE does not track the prominent OD but shows evidence of population of a higher energy (>4.0 eV) state.

BTP9 chlorobenzene PLE at excitations corresponding to both the 0-0 and higher energy emission features overlaps the OD, in contrast, the PLE of the higher

![Figure 5.3 Photoluminescence excitation spectra of (a, b) BTP 5 and (c, d) BTP9 in (a, c) chlorobenzene and (b, d) ethanol solutions.](image)
energy BTP9 emission feature is increased, perhaps suggesting that the higher vibrational levels of S1 overlap with a higher electronic state.

The increase in dielectric solvent is consistent with a stabilization of the excited state energy levels. The emergence of a higher energy BTP5 emission feature suggests the population a second electronic state (S2) as illustrated in the Jablonski diagram in Figure 5.4.

In order to understand higher energy state deactivation pathways, temperature-dependent PL (Figure 5.5) is measured for BTP5 and BTP9 in CB and EtOH are collected. The BTP5 PL intensity is observed to decrease monotonically by a factor of 2/3 from room temperature to 70 °C (below the respective solvent boiling points) for all emission features. The temperature dependence suggests a thermal activation to intersystem crossing to the non-emissive triplet state that is higher energy relative So. The BTP9 CB PL decreases similarly with temperature, however, the higher energy

Figure 5.4 A Jablonski diagram illustrating the lowering of energy and population/emission of So and S1 in high dielectric strength solvents.
feature remains constant, suggesting that there is no activation barrier for intersystem crossing from this higher energy electronic state.

While the main vibronic progressions in ethanol follow a similar temperature dependence as observed in chlorobenzene, both higher BTP5 and BTP9 high energy emission features gain temperature equal in magnitude. This evidence supports the claim that the increased solvent dielectric strength leads to a stabilization and lowering of the higher energetic state leading to thermally activated intersystem crossing to the non-emissive triplet state.

**Figure 5.4** Temperature dependent PL emission spectra for (a, c) BTP5 and (b, d) BTP9 in (a, b) chlorobenzene, (c and d) ethanol. All spectra are normalized by the respective PL intensity at 5 °C.
The unique temperature dependence in increased dielectric environment is consistent with previous studies of the emissive states of fused-ring anthracene investigated in ethanol.\textsuperscript{5} The PL-temperature dependence measured in a non-polar solvent followed a monotonic decrease in magnitude with increasing temperature, similar to the observed BTP temperature dependence in non-polar solvents, while the ethanol temperature dependence showed a unique non-linear PL trend at lower temperatures that was attributed to a thermally activated triplet population with an additional relaxation pathway via the formation of an exciplex between ethanol and the anthracene excited state. Similar evidence of an exciplex deactivation pathways have been reported in acetylanthracene derivatives in methanol.\textsuperscript{6} Similar vibronic structure has also been reported for a sulfur containing oligothioacene ladder length series.\textsuperscript{7} Interestingly, the PLQY of these systems is shown to increase with the extension of the thiophene ladder core. Future work may investigate the effects of the heavy sulfur atoms presence along the conjugated backbone. Theoretical density-functional theory (DFT) calculations revealed that the excited state wavefunction is largely localized on the inner thiophene rings which is consistent with earlier time DFT studies on the BTP series.\textsuperscript{4}

\textbf{5.3 Conclusions}

This work has shown that there is a length dependence to the electronic structure of the BTP ladder series. The shortest BTP\textsubscript{5} oligomer is unique in that only one
emissive state is observed in low-dielectric environments, however, higher electronic
states are populated upon solvation and stabilization in higher dielectric solvents which
is consistent with a redistribution of the excitonic wavefunction. In future work, the
activation energy for singlet-triplet intersystem crossing will be extracted by fitting the
PL-temperature dependence to an Arrenhius model. In addition, evidence of triplet
states will be investigated using time-dependent density functional theory (TDDFT)
and transient absorption spectroscopy.

5.4 Experimental Methods

Solutions of 2 x 10^{-7} M BTPX in spectrographic grade solvents were degassed
by bubbling N_{2} gas through a submerged syringe for 5 minutes in order to displace
dissolved O_{2} in 1x1 cm quartz cuvettes. Absorption spectra of degassed solutions of
were collected in 0.5 nm wavelength increments at room temperature (~20 °C) using a
Shimadzu UV-2700. Emission spectra were collected with a Horiba Fluoromax
photoluminescence spectrophotometer using symmetric 2 nm bandpass
monochromator excitation/emission filters with 0.1 s integration time using excitation
wavelengths at the red edge of the respective BTP OD spectra. Temperature dependent
PL spectra were collected while stirring at 1,200 rpm while N_{2} gas purged the cuvette
holder in order to prevent water vapor condensation during low-temperature
measurements.
Absorption and emission spectra were converted to energy scaling using a Jacobian transformation for proper calibration. Photoluminescence excitation spectra (PLE) were prepared by taking representative column slices of three-dimensional excitation-emission spectra.
5.5 References


5. Greiner, G. The unusual temperature dependence of the fluorescence intensity and lifetime of anthracene in ethanol. *J. Photochem Photobio. A. Chem.*, 2000, 137, 1-
