# Macromolecules

# Molecular Interactions and Ordering in Electrically Doped Polymers: Blends of PBTTT and F<sub>4</sub>TCNQ

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**Supporting Information** 

**ABSTRACT:** Identifying how small molecular acceptors pack with polymer donors in thin and thick (bulk) films is critical to understanding the nature of electrical doping by charge transfer. In this study, the packing structure of the molecular acceptor tetrafluorotetracyanoquinodimethane ( $F_4TCNQ$ ) with the semiconducting polymer poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno-[3,2-b]thiophene) (PBTTT-C<sub>14</sub>) is examined. A combination of solid-state NMR, synchrotron X-ray scattering, and optical spectroscopy was used to determine the packing motif for blends of PBTTT-C<sub>14</sub> and  $F_4TCNQ$  in thin and bulk films. These results indicate that  $F_4TCNQ$  and PBTTT-C<sub>14</sub> order in a cofacial arrangement where charge transfer is near 100% efficient in the solid state. These results provide crucial insights into the structures



and compositions of ordered domains in doped semiconducting polymers and suggest a model for the microstructure where the location of the molecular acceptors are correlated rather than randomly dispersed.

### INTRODUCTION

Semiconducting polymers have excellent performance in applications including organic-based light-emitting diodes (high brightness),<sup>1</sup> thin film transistors (high charge carrier mobility),<sup>2</sup> and solar cells (power conversion efficiency near 10%).<sup>3</sup> Despite this progress, it remains difficult to control the electrical conductivity of semiconducting polymers, which is a function of both the carrier concentration and the carrier mobility.<sup>4</sup> Semiconducting polymers are rendered conductive by chemical or electrochemical doping through charge transfer reactions that result in oxidation or reduction of the backbone.<sup>5</sup> In chemical doping, small organic or inorganic species must be incorporated into the polymer, causing changes in the molecular ordering. Because molecular order is intimately linked with electrical properties in semiconducting polymers,<sup>6</sup> it is essential to understand how incorporation of molecular dopants changes their physical structures. Such understanding is particularly important for the emerging study of the thermoelectric (TE) properties of semiconducting polymers where the carrier concentration and microstructure impacts both the electrical conductivity and Seebeck coefficient.<sup>8–10</sup>

We report here a study on the structural changes in thin films of the high mobility polymer poly(2,5-bis(3-tetradecylthio-phen-2-yl)thieno[3,2-b]thiophene) (PBTTT-C<sub>14</sub>) electrically doped by charge transfer in blends with tetrafluorotetracyano-quinodimethane (F<sub>4</sub>TCNQ), a molecular electron acceptor (Figure 1). PBTTT is a well-characterized semicrystalline

polymer with high charge-carrier mobility (~1 cm<sup>2</sup>/(V s)) in thin film transistors.<sup>11–18</sup> The ionization energy (IE) and electron affinity (EA) of PBTTT-C<sub>14</sub> are -5.1 eV and -3.2 eV, respectively, while those of F<sub>4</sub>TCNQ are -8.3 eV and -5.2eV.<sup>19,20</sup> The favorable energy offset between the IE of PBTTT, and the EA of the small molecule acceptor, F<sub>4</sub>TCNQ, allows charge transfer in solutions and in thin films, thereby electrically doping the polymer. By examining the microstructure of thin films of blends of PBTTT and F<sub>4</sub>TCNQ using a combination of methods including wide-angle X-ray scattering (WAXS) and solid state nuclear magnetic resonance (NMR) spectroscopy, we propose a structural model for molecular packing in the solid state and discuss the implications for charge transport.

Electrical doping of semiconducting polymers and small molecules with  $F_4TCNQ$  has been widely studied.<sup>20–28</sup> Addition of  $F_4TCNQ$  to a polymer leads to charge transfer if the offset of the IE (HOMO) of the electron-donating material and the EA (LUMO) of  $F_4TCNQ$  is sufficient to provide a thermodynamic driving force for electron transfer.<sup>4,29</sup> For example, films of poly(3-hexylthiophene), P3HT (IE ~ 4.9 eV), doped with  $F_4TCNQ$  have shown a significant increase in conductivity from  $6.8 \times 10^{-5}$  S/cm (neat polymer) to 1.8 S/cm at ~0.2 acceptors/repeat unit of polymer.<sup>26</sup> It has been

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Figure 1. Chemical structures, ionization energy, and electron affinity of  $F_4TCNQ$  and PBTTT- $C_{14}$  (based on literature values for isolated materials in solid films). Electron transfer is favorable from PBTTT- $C_{14}$  to  $F_4TCNQ$ .

observed for a series of semiconducting polymers that the electrical conductivity decreases as the IE of the polymer donor increases.<sup>21</sup> Because of the difficulty in measuring the free carrier concentration in materials with low charge carrier mobility, it is uncertain what the contributions of mobility and carrier concentration are to the overall conductivity. For example, in TFTs the charge carrier mobility can change by more than an order of magnitude by processing.<sup>2</sup> Whether charge transfer occurs, or not, in molecular donor–acceptor crystals is known to depend on electrostatic interactions, the Madelung energy, and the difference in IE and EA of the donor and acceptor.<sup>30</sup> In blends of polymeric donors and acceptors with structural disorder it is difficult to predict such effects, but they are of clear importance as well.

The molecular packing structure of blends of dopants and polymers has been studied for several systems. X-ray scattering studies of chemically doped polyaniline,<sup>31</sup> poly(p-phenylenevinylene),<sup>32</sup> polyacetylene,<sup>33</sup> and poly(3-alkylthio-phene)<sup>34-37</sup> has provided structural models for blends with dopants such as sodium and I2. Substantial changes in X-ray scattering patterns of polythiophenes are known from studies of doping with  $I_2$  from vapor leading to compression of the  $\pi$ -spacing.<sup>36,37</sup> The packing structure of polymers doped by  $F_4TCNQ$  has not been widely explored other than for P3HT.<sup>26,38</sup> In one report, no change of the  $\pi$ -spacing between cofacial chains of P3HT was found by X-ray scattering,<sup>22</sup> but whether this observation implies that the doped regions of P3HT are disordered is not clear. In another study, two distinct crystalline phases were found in doped films comprising neat P3HT crystallites and cocrystals composed of an unknown stoichiometric ratio of P3HT:F4TCNQ.26 Because of the significant question of the role of molecular packing on charge transfer leading to electrical doping, this state of knowledge limits our ability to control the electrical conductivity of semiconducting polymers.

Recent work has demonstrated that blends of fullerenes and semiconducting polymers having widely spaced solubilizing side chains along the backbone may cocrystallize in thin films.<sup>39-41</sup> In particular, phenyl-C<sub>61</sub>-butyric acid methyl ester, PCBM, can intercalate into aliphatic regions of polymers with sufficient distance between aliphatic side chains attached to the backbone, such as PBTTT.<sup>41</sup> Interestingly, the model structure proposed for I2-doped poly(alkylthiophenes) also places the anion in the aliphatic side chains of the polymer,<sup>37</sup> suggesting that similar structures might occur with charge-transfer dopants. Indeed, it has been reported that F4TCNQ may intercalate with PBTTT, but the only evidence provided was a small shift ( $\sim 1$  Å) in the alkyl stacking spacing.<sup>40</sup> However, due to its relatively planar structure,  $F_4TCNQ$  could intercalate between aromatic backbone segments<sup>26</sup> in contrast to PCBM,<sup>40</sup> which prefers the interstitial cavities in the aliphatic side chain segments. Such structures have been predicted based on infrared and Raman spectroscopy as well as models using density functional theory (DFT).

In this study, the effect of adding  $F_4TCNQ$  on the microstructure of thin films of PBTTT is investigated with the molecular packing structure of the blend determined using a combination of X-ray scattering and solid-state NMR. Our results indicate that charge transfer from PBTTT to  $F_4TCNQ$  is highly efficient in blend films and that  $F_4TCNQ$  intercalates between the  $\pi$ -stacked polymer chains. On the basis of this packing motif, we propose model structures for the microstructure, as a function of blend composition, with these packing models suggesting that while the introduction of the dopant causes structural disorder, the location of dopants in ordered semiconducting polymers may not be random as assumed in many transport models.

#### RESULTS AND DISCUSSION

Processing Solids Films of Blends of F<sub>4</sub>TCNQ and PBTTT. Casting of uniform films from stable, processable solutions of blends of F4TCNQ and PBTTT-C14 required significant care. The main difficulties were the low solubilities of the neat materials and the formation of aggregates of chargetransfer salts in solutions of their mixtures.<sup>26,28</sup> The casting solutions for blends were made via addition of a F4TCNQ solution, having a bright orange-red color, to the solution of PBTTT-C<sub>14</sub>, with a bright red color, whereupon the color changed to dark red, or black, depending on the weight percent (wt %) of acceptor added. F4TCNQ is soluble in odichlorobenzene but begins to precipitate at concentrations  $\geq$ 3 mg/mL at room temperature; to maintain the desired concentrations, the solutions were first heated to 150 °C for 30 min and then kept at 110 °C. PBTTT-C<sub>14</sub> was processed in a similar manner to F4TCNQ; solutions of 10 mg/mL were prepared in a 1:1 mixture of chlorobenzene (CB):odichlorobenzene (ODCB) at 150 °C for 30 min and then kept at 110 °C, at which point the neat solutions were filtered and the blend solutions mixed. If the polymer was allowed to cool below 80 °C, gelation was observed; the gelation process occurs to an even greater extent in the solutions of the blends due to the change in solubility caused by formation of positive charge on the polymer backbone. We therefore kept the blend solutions at 110-120 °C prior to casting in order to maintain the polymer and dopant in solution and to reach the desired thickness of the various samples. The molar ratios, MR, of F4TCNQ to monomer of PBTTT-C14 were calculated based upon the wt % of F4TCNQ added to the solutions. For



Figure 2. UV-vis spectra of neat PBTTT- $C_{14}$  (black), neat  $F_4TCNQ$  (magenta), and blends with MR of 0.025 (green), 0.075 (blue), and 0.25 (orange) in (a) solution and (b) thin films.

example, a ratio of ~13 PBTTT repeat units per  $F_4TCNQ$  is achieved at 3 wt % (MR of 0.075), while a ratio of 4 repeats per  $F_4TCNQ$  is reached at 10 wt % (MR of 0.25).

Fabrication of blended samples of  $F_4TCNQ$  and PBTTT-C<sub>14</sub> was performed in three ways. The first method was to drop-cast 100 mg of blend solution onto a clean watch glass at 80 °C set in a vacuum oven flushed with nitrogen to drive off solvent and form the bulk film. These bulk samples were then scratched off the glass and tightly packed into NMR rotors for analysis. The second method was to drop-cast small amounts of the blend solutions onto silicon substrates, which were dried in the same manner as the larger samples to form  $1-5 \mu$ m thick films. The third method was to spin-cast samples from a hot solution using warm glass pipettes followed by a low-temperature anneal at 80 °C for 10 min under a nitrogen atmosphere to remove residual solvent. We refer to films made by drop-casting methods as "bulk" or "thick films", while those made by spin-casting are referred to as "thin films".

Electrical Conductivity of PBTTT:F<sub>4</sub>TCNQ Films. Successful doping of the PBTTT-C<sub>14</sub> by F<sub>4</sub>TCNQ was verified by measuring the electrical conductivity of thin films. A fourpoint collinear measurement was made using gold contacts evaporated on top of films cast onto a sapphire substrate under a nitrogen atmosphere. The electrical conductivity values ranged from  $4 \times 10^{-5}$  S/cm for the neat polymer to as high as 2 S/cm for the blend with MR of 0.25 (Table S1). These results are comparable to literature reported results on P3HT:F<sub>4</sub>TCNQ films at similar MR.<sup>21,24,26</sup> The IE of PBTTT is ~0.2 eV larger than that of P3HT, but the electrical conductivity suggests that the formation of carriers by charge transfer is still efficient in the solid state.

**F**<sub>4</sub>**TCNQ Forms Charge Transfer Complexes with PBTTT in Solution and in the Solid State.** Because of the difficulty in processing blended films, it is important to understand whether the  $F_4$ TCNQ is well mixed into PBTTT- $C_{14}$  or if isolated domains of each of the materials form. Using ultraviolet–visible (UV–vis), infrared spectroscopy (IR), and solid-state <sup>19</sup>F magic angle spinning (MAS) NMR, we find that blends of PBTTT- $C_{14}$  and  $F_4$ TCNQ form films with no evidence of phase segregation at all compositions. These complementary methods demonstrate the existence of chargetransfer complexes in solution that are maintained in the thin and bulk film states.

Charge transfer between acceptors and donors can be observed via UV–vis spectroscopy by changes in the absorption spectra due to suppression of the optical absorption of the neutral polymer and formation of the  $F_4TCNQ$  anion.<sup>21,24,28</sup> The UV–vis absorption spectra were measured

for dilute solutions of neat PBTTT-C14, F4TCNQ, and blends of PBTTT- $C_{14}/F_4TCNQ$  in a solvent mixture of CB and ODCB (Figure 2a). Neat PBTTT-C<sub>14</sub> has a large absorption between 400 and 635 nm with a pronounced shoulder near 580 nm and no absorption between 800 and 1100 nm. Similarly, neat F<sub>4</sub>TCNQ has a strong absorption between 300 and 560 nm and no significant absorption between 600 and 1100 nm. In both solution and in thin films, the spectral band of the anion of F4TCNQ can be seen between 800 and 1100 nm at a MR of 0.025 F<sub>4</sub>TCNQ along with a decrease in the main absorption of PBTTT- $C_{14}$  (Figure 2b). The polaron (cation) of PBTTT- $C_{14}$ should present a feature near 700 and 950 nm, but the overlap with the spectral features of F4TCNQ makes the features difficult to deconvolve.<sup>42</sup> The spectral features due to charge transfer become more pronounced with an increase in  $F_4TCNQ_1$  as does the decrease in absorption of neutral PBTTT-C14. For the 0.075 and 0.25 MR blend a peak that scales with increasing acceptor concentration is observed between 350 and 450 nm. In solution at a MR of 0.50 MR, which is approximately one F<sub>4</sub>TCNQ molecule per every two polymer repeat units, there is also a peak at 390 nm that correlates to undoped F<sub>4</sub>TCNQ (Figure S1). These results indicate that below this point all of the F4TCNQ molecules can associate within the backbone units of PBTTT-C14 forming charge transfer complexes. These observations of aggregation and charge transfer in solution are similar to the behavior of P3HT and F<sub>4</sub>TCNQ.<sup>26–28</sup>

To further determine whether F<sub>4</sub>TCNQ quantitatively forms charge-transfer complexes with the repeat units of PBTTT-C14 in blended thick films, solid-state <sup>19</sup>F MAS NMR measurements were performed (Figure 3). Neat F<sub>4</sub>TCNQ yields two <sup>19</sup>F NMR signals in its crystalline form due to the presence of two distinct crystallographic sites with long longitudinal  $(T_1)$  spinlattice relaxation times of approximately 600 s.43 No 19F signal is observable in either of the blends with molar ratios of 0.075 or 0.25. This result can be explained by the presence of a delocalized free electron caused by the charge transfer from PBTTT- $C_{14}$  to  $F_4TCNQ_4$  which shortens the transverse relaxation time, such that the <sup>19</sup>F signal is too broad to be observed. The complete absence of a <sup>19</sup>F signal suggests quantitative signal transfer and that for MR values of both 0.075 and 0.25 charge transfer is most likely nearly 100% efficient. Even at higher degrees of loading and at 160 K (to extend the transverse  $(T_2)$  spin-spin relaxation time), no <sup>19</sup>F signal is detected for the 0.25 MR blend. These results support the UV-vis spectroscopic data, indicating that there is no residual neat crystalline F<sub>4</sub>TCNQ in films even for a molar ratio of acceptor-to-repeat unit of 0.25 and that charge transfer is near



Figure 3. Solid state <sup>19</sup>F MAS NMR spectra of neat  $F_4TCNQ$  (black) and a blend of PBTTT- $C_{14}$  and  $F_4TCNQ$  with MR of 0.075 (red) and 0.25 (blue). The upper two spectra were acquired at 293 K and 12.5 kHz MAS while the latter spectrum was acquired at 160 K and at 5.5 kHz MAS.

100% efficient at or below at this value of MR. These results agree with photothermal-deflection measurements reported for thin films of  $P3HT^{26}$  and support the view that ionization is efficient between semiconducting polymers and  $F_4TCNQ$ .

The UV–vis and NMR data provide evidence that each  $F_4TCNQ$  molecule is ionized in the solid state. FTIR spectra of the thin films were acquired to further verify if any unreacted  $F_4TCNQ$  remained in the blend and to potentially identify the nature of any structural changes. In spectra for both the neat polymer and blends with MR values of 0.075 and 0.25 there is an absorption peak at 2191 cm<sup>-1</sup> corresponding to the anion of  $F_4TCNQ$  and only a minor peak for neutral  $F_4TCNQ$  2212 cm<sup>-1</sup> in the sample MR of 0.25 (Figure S2).<sup>44,45</sup> In both blends, we observe a broad absorption from ~1500 to 4000 cm<sup>-1</sup> that scales with the MR and is indicative of a polaronic positive carrier in PBTTT.<sup>42</sup> Thus, the UV–vis, FT-IR, and <sup>19</sup>F MAS NMR data indicate that essentially each  $F_4TCNQ$  molecule undergoes charge transfer with PBTTT up to the highest MR (0.25) examined.

**Structural Order in PBTTT-C**<sub>14</sub>:**F**<sub>4</sub>**TCNQ Blends.** A combination of X-ray scattering and solid-state NMR measurements was used to characterize the microstructure of the blend in the thin and bulk films. The two techniques are sensitive to different domains of the blends: X-ray scattering only probes the ordered regions of the films, while NMR probes the both ordered and disordered regions; both have been used previously to examine molecular order in PBTTT:PCBM blends.<sup>41</sup> In contrast, our blends are composed of ionized

molecules, restricting the ability of NMR to easily determine precise structural features in regions with relatively free electrons, due to the differences in relaxation times of associated species. We therefore expected that the NMR measurements would provide the most information about regions in the blends where there are no charge carriers.

GIWAXS Reveals Cocrystallization. PBTTT-C<sub>14</sub> forms semicrystalline films that are highly ordered relative to most semiconducting polymers.<sup>11,15,17</sup> The presence of scattering peaks attributed to mixed index reflections in grazing incidence wide-angle X-ray scattering (GIWAXS) along with spectroscopic studies indicate good structural order. The proposed unit cell of PBTTT- $\tilde{C}_{14}$  is triclinic with the following parameters: a = 21.5 Å, b = 5.4 Å, c = 13.5 Å,  $\alpha = 137^{\circ}$ ,  $\beta = 86^{\circ}$ , and  $\gamma = 89^{\circ}$ .<sup>17,18</sup> In this cell, the backbones are planar and tilted with respect to each other by ~14°. The  $\pi - \pi$  spacing, defined as the separation of the stacked conjugated backbones, is  $\sim$ 3.58 Å. This separation is determined by the tilt of the conjugated backbones in the unit cell and the spacing of the scattering peak near  $q_{xy} = 1.71$  Å<sup>-1</sup> (*d*-spacing of 3.67 Å) assigned to (110) or (010) reflection, which was previously defined as the (010) reflection.<sup>16-18</sup> The lamellar packing is due to interdigitation of the side chains, the *a*-axis spacing, and is dependent on processing, specifically thermally annealing conditions, with experimental values typically between 21.0 and 22.0 Å. It is important to realize that even the most ordered regions are still defective relative to crystalline solids, and the correlation length of order is relatively small (i.e., ~10 nm in the  $\pi$ -stacking direction based on the peak width).

We expected that the PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ films would display a complex phase behavior. For example, the blend could exhibit one phase or instead a mixture of cocrystallized domains and separate neat polymer and F<sub>4</sub>TCNQ domains. We also expected the potential for disruption of the packing structure of neat PBTTT because, relative to neat films, bimolecular crystals of PBTTT:PCBM, where the fullerene intercalates into the side chains of the polymer, are more disordered.<sup>41</sup> The intercalation of PCBM with PBTTT leads to in an increase in the  $\pi$ - $\pi$ spacing between the polymer backbones and distortions of the side chains from an *all-trans* conformation. Blends of P3HT:F<sub>4</sub>TCNQ exhibit separate domains where the packing structure of the cocrystallized regions is disrupted relative to the neat film.<sup>26</sup>

X-ray scattering from films of PBTTT- $C_{14}$ : $F_4TCNQ$  blends shows highly textured semicrystalline domains with a similar *d*spacings and pattern to neat PBTTT- $C_{14}$ . 2D GIWAXS patterns obtained with a two-dimensional detector from thin



Figure 4. 2-D GIWAXS diffraction images for (a) as-cast thin neat PBTTT- $C_{14}$  and blends with  $F_4$ TCNQ at (b) MR = 0.075 and at (c) MR = 0.25.

films of PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ are shown in Figure 4 and for thick films in the Supporting Information (Figures S3 and S4). For the thin film, the predominant peaks near the  $q_z$  axis correlate to the intense (h00) reflections of the lamella-stacked side chains that are oriented out-of-plane with respect to the substrate. Strong scattering peaks are observed along  $q_{xy}$ corresponding to *d*-spacings that are similar to the spacing along the backbone and  $\pi$ -spacing between chains in neat PBTTT-C<sub>14</sub>. In the bulk film, the crystallites are less textured with similar peaks to those observed for the thin films and amorphous scattering near  $q_{xy}$  of 1.4 Å<sup>-1</sup> (Figure S3). Importantly no evidence is observed of scattering from F4TCNQ crystalline domains (Figure S5). In contrast, the scattering from PBTTT:PCBM shows a change in the progression due to the intercalation of PCBM in the side chains. These results suggests that the packing structure is different from the one observed in PBTTT:PCBM blends and more similar to observations for P3HT:F4TCNQ blends.

The in-plane scattering peaks of neat PBTTT-C<sub>14</sub> are known to be relatively insensitive to thermal annealing; therefore, we can attribute any changes to the addition of F<sub>4</sub>TCNQ. We collected high-resolution, in-plane GIWAXS data using a point detector that has better instrumental resolution than the 2D detector used to assess the texture of domains in the film. We find that the scattering at  $q_{xy} = 1.41 \text{ Å}^{-1}$  (assigned as (1–13) in neat PBTTT- $C_{14}$ ) is little changed by addition of  $F_4TCNQ$  or by thermal annealing (Figure 5 and Table 1). The scattering peak associated with  $\pi$ -stacking peak at  $q_{xy} = 1.71 \text{ Å}^{-1}$  does shift with both the MR of F4TCNQ and thermal processing. For ascast thin films, a clear shift in this spacing to higher q (lower dspacing) is observed with a maximum decrease of 0.06 Å for MR of 0.25. The peak for MR of 0.25 does not broaden significantly relative to the neat film for either as-cast or annealed samples. It is possible to fit the scattering profile with two separate narrower peaks, e.g., a smaller area peak with the undoped *d*-spacing. It is therefore difficult to perfectly rule out the presence of two populations; however, at this point we choose to use the model with one reflection based on our assessment of structural disorder in the doped films (vide infra). Our results suggest one population unlike the two populations in blends of P3HT:F4TCNQ with a clear separation of a larger (3.85 Å) and smaller (3.59 Å)  $\pi$ -stacking reflection for undoped and doped domains, respectively.<sup>26</sup> It is interesting to note that here the spacing in the doped films is nearly identical despite the difference in backbone structure of the two polymers. The d-spacing shows a simple decrease with MR of F4TCNQ for ascast films, but samples annealed at 150 °C show a different trend. For a very low MR value of 0.001, the *d*-spacing increases from 3.68 to 3.71 Å compared to that of the neat film (3.67 Å). This suggests that the addition of F4TCNQ allows a different packing structure to be accessed even at low MR that could arise from a change in the tilt of the backbones. If we examine the trend from this low MR, the *d*-spacing does decrease as a function of MR leading to a shift by ~0.1 Å. The change in spacing clearly shows the conjugated planes are coming closer together with doping, but the detailed molecular geometry is difficult to model with the relatively few diffraction peaks present in the samples.

To further verify that the change in the  $\pi-\pi$  *d*-spacing is caused by the formation of charge-transfer complexes rather than a polymorphic structure, we examined blends of TCNQ which is nearly isostructural with F<sub>4</sub>TCNQ with PBTTT-C<sub>14</sub>. Because the magnitude of the EA of TCNQ is smaller than the



**Figure 5.** High-resolution in-plane scattering for (a) as-cast and (b) annealed thin films of neat PBTTT-C<sub>14</sub> (black) and blends PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ of with MR of 0.00125 (purple), 0.0125 (magenta), 0.025 (green), 0.075 (blue), and 0.25 (gold). The data are scaled to provide an offset for visualization.

 Table 1. In-Plane X-ray Scattering Peaks of Thin Films from

 High-Resolution GIWAXS

processing condition and MR of F <sub>4</sub> TCNQ	peak (Å <sup>-1</sup> )	d- spacing (Å)	$\stackrel{fwhm}{({\rm \AA}^{-1})}$	peak (Å <sup>-1</sup> )	d- spacing (Å)	$\stackrel{fwhm}{({\rm \AA}^{-1})}$
as-cast 0	1.410	4.46	0.07	1.713	3.67	0.107
annealed 0	1.410	4.46	0.08	1.711	3.67	0.06
as-cast 0.01	1.410	4.46	0.00	1.707	3.68	0.09
annealed 0.01	1.411	4.45	0.07	1.711	3.71	0.08
as-cast 0.025	1.410	4.46	0.07	1.716	3.67	0.1
annealed 0.025	1.410	4.46	0.07	1.700	3.70	0.07
as-cast 0.075	1.411	4.45	0.1	1.737	3.62	0.1
annealed 0.075	1.410	4.45	0.09	1.690	3.70	0.1
as-cast 0.25	1.414	4.44	0.09	1.741	3.62	0.12
annealed 0.25	1.410	4.46	0.09	1.733	3.61	0.08

IE of PBTTT, there should be no charge transfer during the casting process. For MR values of 0.025 MR and 0.25 MR, TCNQ has no impact on the  $\pi$ -spacing (Figures S6 and S7), and the 2D scattering pattern shows the presence of pure TCNQ crystallites. These results show that either TCNQ phase separates out of the crystallites of PBTTT-C<sub>14</sub>, or it may be intercalated into the backbone region like F<sub>4</sub>TCNQ, but without affecting the *d*-spacing.

High-resolution specular scattering for PBTTT neat films and blends provides information about the ordering in the alkyl stacking direction, (h00), due to the texture of the crystallites in the films. For the as-cast thin films, a monotonic increase in the (h00) *d*-spacing is observed with an increase in MR of F<sub>4</sub>TCNQ, from 22.2 Å for neat PBTTT-C<sub>14</sub> to 23.2 Å for the 0.25 MR blend (Figure S8, Tables S2 and S3). Upon thermal annealing the *d*-spacing is nearly identical for all cases with a value of 22.4 Å for the neat film and 22.7 Å for the film with a MR of 0.25. More significant differences are observed in the widths of the peaks, which are related to the size and correlation length of the order in the *a*-direction (Figure 6).



**Figure 6.** Full width at half-maximum (fwhm) of scattering peaks as a function of diffraction order for (a) as-cast and (b) annealed films of neat PBTTT-C<sub>14</sub> (black) and blend of PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ with MR of 0.075 (blue) and 0.25 (gray).

The apparent crystallite size in the *a*-direction in as-cast films, as determined by the Williamson-Hall method, is ~100 Å for all films. Upon annealing, the size increases for all films but is largest for the neat film ~440 Å, comparable to the thickness of the film. More telling is the slope of the width as a function of diffraction order that increases with MR of F4TCNQ1 indicating that the heavily doped films are have more paracrystalline disorder. We observe similar trends in bulk films as well. An increase in the MR of F4TCNQ in the thin film appears to narrow the distribution of oriented crystallites in as-cast films when compared to the neat polymer film from comparison of the scattering intensity along the azimuthal of the (200) reflection from GIWAXS (Figure 7). The distributions are all similar after thermal annealing at 150 °C. This behavior has been observed previously in PQT-12 due to aggregation of polymer chains, <sup>46</sup> which is observed here due to charge transfer in solution. Therefore, our data indicate that incorporation of F<sub>4</sub>TCNQ does not substantially alter the packing in the alkyl stacking direction but does increase the overall disorder. The Xray diffraction analyses, thus, establish that the PBTTT-C14:F4TCNQ blends form films with long-range order,



**Figure 7.** Intensity of the (200) reflection as a function of azimuthal angle (90° is near  $q_{xy} = 0$ ) for (a) as-cast and (b) annealed thin films of neat PBTTT-C<sub>14</sub> (black) and blends PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ of with MR of 0.075 (blue) and 0.25 (gold). The data do not extend to 90° due to the portion of reciprocal space that is not accessible in GIWAXS experiments.<sup>47</sup>

although with little insight into where the  $F_4TCNQ$  molecules reside.

Solid-State NMR Reveals Molecular Distributions in PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ Blends. Solid-state NMR spectroscopy is highly sensitive to local atomic environments, including the proximities of different molecular species, as manifested by mutual nuclear spin-spin interactions. In particular, solid-state 1D <sup>1</sup>H magic-angle-spinning (MAS) NMR can be used to measure and compare the chemical shifts of aromatic protons in PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ blends, as functions of the F<sub>4</sub>TCNQ molar ratio, to obtain molecular-level information on  $\pi - \pi$ stacking in the different materials. Because NMR is generally a bulk technique,<sup>41,48-51</sup> solid-state NMR analysis could not be performed on samples prepared in an identical manner to the thin films. Our X-ray diffraction data suggest that the crystalline ordering in both thin and thick samples is similar; therefore, we believe the comparison between bulk and thin films is reasonable. For comparison, bulk PBTTT-C<sub>16</sub> yields a strong <sup>1</sup>H signal at 1.4 ppm with a weak shoulder at 2.5 ppm from the aliphatic side chains and broad asymmetric intensity from aromatic protons in the range of 5.5-8.0 ppm, the latter of which can be deconvoluted into two component signals centered at 6.1 and 6.9 ppm (Figure 8). The <sup>1</sup>H signal at 6.1 ppm is assigned to well-stacked PBTTT-C14 (semicrystalline regions), while that at 6.9 ppm is attributed to more disordered stacks of PBTTT (amorphous regions).<sup>41</sup> For thick films of PBTTT-C<sub>14</sub> blended with 0.075 and 0.25 MR F<sub>4</sub>TCNQ, the <sup>1</sup>H intensity in the aromatic region decreases significantly, and the maximum is displaced to 6.7 and 7.0 ppm, respectively, relative to the aliphatic <sup>1</sup>H signals, consistent with protons near regions



**Figure 8.** Solid-state 1D <sup>1</sup>H MAS NMR spectra recorded at a <sup>1</sup>H Larmor frequency of 850 MHz under MAS conditions of 30 kHz for neat PBTTT-C<sub>16</sub> (black) and at a <sup>1</sup>H Larmor frequency of 800 MHz and 45 kHz MAS for PBTTT-C<sub>14</sub> blended with MR of 0.075  $F_4$ TCNQ (red) or 0.25  $F_4$ TCNQ (blue).

with high densities of free electrons. This displacement indicates increasing disorder in the stacked backbone regions, especially for 0.075 MR F<sub>4</sub>TCNQ for which an inhomogeneous non-Gaussian peak is observed that manifests a distribution of different environments (as corroborated separately by the <sup>1</sup>H double-quantum-filtered (DQF) MAS spectrum and analysis in Figure S9). Thus, the <sup>1</sup>H MAS NMR spectra indicate that the backbone order decreases, consistent with larger  $\pi$ – $\pi$  stacking distances between the PBTTT-C<sub>14</sub> polymer backbones in the presence of F<sub>4</sub>TCNQ.

Solid-state NMR spectra of the bulk samples also reveal evidence for a substantial decrease in the ordering of the aliphatic side chains upon incorporation of  $F_4TCNQ$  (Figure 9). For neat bulk films of PBTTT- $C_{16}$ , a large fraction of well-



**Figure 9.** Aliphatic region characterization of solid-state 1D  $^{13}C\{^{1}H\}$  CP/MAS spectra of the bulk films neat PBTTT-C<sub>16</sub> (black) and blends of PBTTT-C<sub>14</sub> and F<sub>4</sub>TCNQ with MR of 0.075 (red) or 0.25 (blue) acquired at 12.5 kHz MAS with a CP contact time of 2 ms. Colored circles identify  $^{13}C$  moieties of the aliphatic side chains with their assigned signals in the spectra and designated "c" or "a", according to their association with crystalline or amorphous side chain domains, respectively.

ordered interdigitated side chains are observed (50%), with an even higher degree of crystallinity after annealing. The solidstate 1D <sup>13</sup>C{<sup>1</sup>H} cross-polarization (CP)/MAS spectra contain no spectral features characteristic of crystalline side chains in the neat polymer film after incorporation of  $F_4TCNQ$  for molar ratios of 0.075 or 0.25, for which there are two possible explanations. The  $F_4TCNQ$  could intercalate between the side chains, thereby disrupting their ordering as PCBM does.<sup>41</sup> Alternatively, if  $F_4TCNQ$  intercalates between the conjugated backbones, as the data herein suggest, it is expected that the dopant species would allow space for additional conformational disorder and dynamics of the side chains. This is consistent with the much narrower aliphatic <sup>1</sup>H signal at 1.4 ppm observed in Figure 10 for the PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ blends, compared to



**Figure 10.** Solid-state 2D  ${}^{1}H{}^{1}H{}$  SQ–DQ MAS NMR spectrum of a blend of PBTTT-C<sub>14</sub> with F<sub>4</sub>TCNQ at a MR of 0.075 recorded with a dipolar recoupling time of 44.4 ms under MAS conditions of 45 kHz. The corresponding 1D  ${}^{1}H{}$  double quantum filtered (DQF) MAS spectrum is shown along the top horizontal axis. Correlated signal intensity originates from dipolar coupled  ${}^{1}H{}$  pairs, as depicted by colored circles along the horizontal lines.

the neat polymer, which reflects higher mobility of the side chains and correspondingly weaker dipolar interactions in the blends. This is also consistent with the broader X-ray scattering reflections associated with the alkyl groups (Figure 5), which point to an increase in long-range disorder as well.

Here, it is important also to consider the detection biases of the NMR measurements to better interpret the spectra of the PBTTT-C14:F4TCNQ blends. The infeasibility of NMR to probe directly regions where free electrons are located, as noted in the <sup>19</sup>F MAS NMR spectrum (Figure 3) discussed above, also affects the detection of signals in regions of PBTTT where the charged acceptors are localized. The <sup>19</sup>F MAS spectra separately indicate that charge transfer is nearly 100% complete and sets limits on the number of repeat units that can be observed. The protons of charged polymer backbones are virtually undetectable in the solid-state NMR spectra because the free electron spins associated with charge transfer dramatically shorten the relaxation times of nuclear spins in their vicinities, broadening the associated signals into the spectral baseline. The NMR measurements here, therefore, are biased toward the detection of those backbone regions that are not charged. For example, if the charge is localized near a repeat unit closely associated with F4TCNQ, at 0.25 MR, at least 25% of the backbone units are expected to be invisible to NMR. Because of the decrease in side chain order upon F<sub>4</sub>TCNQ incorporation (Figure 9) and without other counteracting effects (such as a more rigid backbone) present in the undoped regimes, the result is preferential detection of disordered PBTTT-C<sub>14</sub> polymer backbones that are separated by relatively large  $\pi - \pi$  stacking distances, as manifested by displacement of the <sup>1</sup>H signals associated with the aromatic backbone protons to higher frequencies.

More directly, 2D NMR correlation experiments were used to gain further insight into stacking motifs of PBTTT-C<sub>14</sub> and to probe the proximities between certain chemical moieties of PBTTT-C<sub>14</sub> and F<sub>4</sub>TCNQ in the disordered regions. The solidstate 2D  ${}^{1}H{}^{1}H{}$  single-quantum-double-quantum (SQ-DQ) MAS NMR spectrum of 0.075 MR PBTTT-C14:F4TCNQ provides information about the relative proximities of protons associated with  $\pi - \pi$  stacking interactions. Correlated signal intensities indicate separation distances of less than 4 Å for the chemical moieties, as indicated by the pairs of colored circles in Figure 10, where blue denotes <sup>1</sup>H signals principally from the aromatic PBTTT-C<sub>14</sub> backbone, orange represents signals from the side chain protons on the methylene groups nearest to the backbone, and yellow corresponds to <sup>1</sup>H signals from the rest of the aliphatic side chains. The correlated <sup>1</sup>H signal intensities at (1.3, 2.7) ppm (yellow-yellow), (6.6, 7.9) and (1.3, 7.9) ppm (yellow-blue), and (2.5, 9.2), (6.7, 9.2) ppm (orangeblue) arise from intramolecular interactions that are expected for the PBTTT architecture. By comparison, the correlated intensities at (2.5, 5.0) ppm (orange–orange) and (6.6, 13.2) ppm (blue-blue) arise from more interesting intermolecular interactions, as the intramolecular distances that separate identical aromatic backbone or backbone-bonded methylene protons are too large to yield significant double-quantum signal intensity for the conditions under which the spectrum was acquired. In particular, the intensity correlation from the aromatic backbone protons (blue–blue) is associated with  $\pi$ – $\pi$ stacking of the PBTTT-C14 backbone, while that from the backbone-bonded methylene protons (orange-orange) indicates that the aliphatic side chains on different  $\pi - \pi$  stacked PBTTT-C<sub>14</sub> backbones are also in close molecular proximities to each other. In other words, thiophene units stack on thiophene units of neighboring PBTTT-C14 polymer backbone segments, in agreement with proposed packing structures for neat PBTTT- $C_{14}$ .<sup>17,18</sup> A similar spectrum for a higher dopant loading of 0.25 MR F4TCNQ is shown in Supporting Information Figure S10. This points to the PBTTT-C<sub>14</sub> backbone segments having a higher degree of order than the aliphatic regions. Because the F4TCNQ dopant species possess no protons, the 2D <sup>1</sup>H{<sup>1</sup>H} SQ–DQ MAS spectrum cannot reveal proximities between the polymer and dopant species. Furthermore, the ordered regions of the film with free electrons are NMR-invisible, so the conclusions from the 2D  ${}^{1}H{}^{1}H{}$ correlation NMR spectrum apply to the relatively disordered or undoped regions of the blend film.

Nevertheless, the proximities between the PBTTT-C<sub>14</sub> and F<sub>4</sub>TCNQ dopant can be established by exploiting analogous heteronuclear dipolar interactions in a 2D <sup>13</sup>C{<sup>1</sup>H} heteronuclear correlation (HETCOR) NMR spectrum, which correlates the isotropic chemical shifts of dipole-dipolecoupled species. The sample for these experiments was stored in a capped NMR rotor inside a dark container under ambient conditions prior to measurement, which are known to lead to reductions in electrical conductivity of the blend material. However, any chemical reactions or degradation of the acceptor species or scavenging of free electrons is expected to lead to the detectability of backbone moieties that were previously NMRinvisible. The <sup>13</sup>C aromatic region of a 2D  ${}^{13}C{}^{1}H{}$  HETCOR spectrum is shown in Figure 11 for the 0.25 MR PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ blend. The correlated signal intensities unambiguously establish the molecular proximities of the aromatic <sup>13</sup>C moieties of the PBTTT-C14 backbones and F4TCNQ dopants to the <sup>1</sup>H moieties of the PBTTT-C<sub>14</sub> backbone, which are



**Figure 11.** Aromatic region of the solid-state 2D <sup>13</sup>C{<sup>1</sup>H} HETCOR NMR spectrum of PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ blend at MR of 0.25 acquired at room temperature with a contact time of 2 ms at 12.5 kHz MAS, with eDUMBO decoupling in the indirect <sup>1</sup>H dimension. For comparison, 1D <sup>13</sup>C{<sup>1</sup>H} CP/MAS NMR and single-pulse <sup>1</sup>H MAS NMR spectra are shown along the horizontal and left vertical axes, respectively. Colored circles identify <sup>13</sup>C moieties of the aromatic backbone with their corresponding signals in the spectra. The correlated signal intensity at (111 ppm <sup>13</sup>C, 6.0 ppm <sup>1</sup>H), highlighted by the red ellipse, indicates the molecular proximity between the cyano groups of the F<sub>4</sub>TCNQ dopant and aromatic backbone protons of PBTTT-C<sub>14</sub> (note: spectrum recorded after 50 days, hence aromatic <sup>1</sup>H shifts at 6.8 ppm).

expected to be associated with donor-acceptor contact. While most of the <sup>13</sup>C signals between 100 and 150 ppm arise from the PBTTT- $C_{14}$  backbone, the signal at 111 ppm is unambiguously assigned to the cyano groups of F4TCNQ by contact-time-dependent <sup>13</sup>C{<sup>1</sup>H} CP/MAS spectra of a 0.25 MR blend (Figure S12). The other <sup>13</sup>C moieties of  $F_4TCNQ$ are not visible due to short <sup>13</sup>C relaxation times (a consequence of the free electrons). The correlated signal intensity at 111 ppm in the <sup>13</sup>C dimension and at 6.0 ppm in the <sup>1</sup>H dimension manifests the spatial proximities of the F<sub>4</sub>TCNQ cyano groups and aromatic <sup>1</sup>H polymer moieties. There are no such detectable intensity correlations involving the aliphatic PBTTT-C<sub>14</sub> protons, due to either their mobilities or their weak (if any) interactions with the F<sub>4</sub>TCNQ molecules. The chemical shift of the correlated <sup>1</sup>H signal at 6.0 ppm is also significantly lower than that of the predominant signal (6.8 ppm) observed for the aromatic proton species. This is another manifestation of the bias toward those backbone regions of the polymer that are not directly involved in charge transfer (i.e., without free electrons adversely affecting detection of the NMR signals). This <sup>1</sup>H moiety in proximity to F<sub>4</sub>TCNQ dopant species therefore is expected to be associated with uncharged polymer segments with a stacking distance of less than 4 Å. This gives rise to a decreased chemical shift of the <sup>1</sup>H moieties due to substantial ring current effects from neighboring PBTTT-C<sub>14</sub> backbones and a  $\pi - \pi$  stacking distance that is comparable to that observed by the X-ray measurements.

These results confirm our hypothesis that the initial NMR experiments were selectively probing the nonconducting regions of the PBTTT- $C_{14}$ : $F_4TCNQ$  materials, such as the disordered or undoped regions that are devoid of significant quantities of charge-transfer complexes. It was only after a period of time in which partial degradation of the charge-

transfer complexes occurred, e.g., reacted with ambient H<sub>2</sub>O or  $O_2$  to thereby quench their free electrons, that more ordered domains could be detected and the interactions of F<sub>4</sub>TCNQ with the polymer backbone evidenced by NMR. These results lead to the conclusion that most, if not all, F<sub>4</sub>TCNO molecules are intercalated between adjacent aromatic backbone units of PBTTT-C<sub>14</sub> and not in the interstitial regions of the aliphatic chains. Consequently, the smaller  $\pi - \pi$  spacing with increasing F<sub>4</sub>TCNQ content can be concluded to be directly associated with and promote desirable interactions for charge transfer. The observed increase in lamellae disorder with increased F<sub>4</sub>TCNQ loading is most likely due to the increased spacing between adjacent alkyl side chains, which results in greater side chain mobility and an increase in the number of gauche defects that lead to distortions in lamellae packing. The data indicate that these regions are relatively disordered, in contrast to the result for neat PBTTT-C14, and suggest that the more ordered fraction of the blend probed by GIWAXS is where F4TCNQ resides. This indicates that the large majority of F4TCNQ molecules in the film blend are incorporated within the semicrystalline domains.

Molecular Packing and Microstructure. Our solid-state NMR and GIWAXS data indicate that the dopant F<sub>4</sub>TCNQ is predominantly located in the semicrystalline domains of PBTTT-C14:F4TCNQ blends and stacks between the conjugated backbones, causing disruption of the ordering of the aliphatic side chains. Density functional theory (DFT) calculations, using a functional reported to produce reasonable geometries of charge-transfer complexes (wB97X-D/6- $31+G^*$ ),<sup>52,53</sup> give an optimized spacing of ~3.5 Å for a model dimer of PBTTT and F4TCNQ and show the potential for relatively loose packing structures (see Supporting Information). Because in these blends F4TCNQ is not in a 1:1 ratio with the repeat unit of PBTTT- $C_{14}$ , one might expect phase separation into two domains, instead of semicrystalline ordering, whereas our data suggest only one phase. For example, at a molar ratio of 0.075 F4TCNQ, there are approximately 13 PBTTT-C<sub>14</sub> repeat units for every 1 acceptor, while at 0.25 MR F<sub>4</sub>TCNQ, the ratio is approximately 1  $F_4TCNQ$  to every 4 PBTTT- $C_{14}$  repeat units. Despite this difference, the intercalation of F4TCNQ between adjacent PBTTT-C<sub>14</sub> segments, nevertheless, results in ordered structures, which prompts one to consider the packing structures that might lead to this result.

We can assess candidate structures by evaluating their molecular packing densities. If the F4TCNQ molecules are in the  $\pi$ -stacked regions at low molar ratios, "voids" would form between the adjacent backbone segments, and we would expect a disruption in the  $\pi - \pi$  d-spacing as the backbones distort to fill the empty space (Figure 12). This is not observed experimentally; therefore, we suggest that the F4TCNQ molecules decorate the conjugated backbones to form highly doped regions, e.g., one F4TCNQ molecule per PBTTT-C14 repeat unit, sandwiched between the  $\pi-\pi$  stacked segments. The physical dimensions of the repeat unit of PBTTT-C<sub>14</sub> and F<sub>4</sub>TCNQ indicate that there is significant space for the acceptor to pack in adjacent spaces and still allow for slight local adjustments in the donor-acceptor orientation without coming into close proximity. This densely packed model can also be used to rationalize the 2:1 maximum ratio observed in the solution UV-vis by taking into account that 2 adjacent F<sub>4</sub>TCNQ molecules fit between 4 PBTTT-C<sub>14</sub> repeat units. This model also suggests that the change in  $\pi$ -spacing could



Figure 12. Packing model of blends with (a) random and (b) correlated placement of molecules of  $F_4TCNQ$  relative to the backbone of PBTTT-C<sub>14</sub>.

arise from a difference in the tilt of the molecular backbone caused by charge transfer interactions.

The packing structure where  $F_4TCNQ$  inserts between the conjugated backbones leads to further inferences. It is possible that the  $F_4TCNQ$  molecules form "1D" arrays that allow the PBTTT-C<sub>14</sub> molecules to pack in a manner to fill space. Our X-ray scattering data suggest that the structure of the PBTTT-C<sub>14</sub>:F<sub>4</sub>TCNQ blend is not dramatically different than the neat polymer. In this case, we propose that the 1D channels of acceptor are spaced to allow the alkyl lamellar layers above and below to fill in the gap caused by intercalation of the acceptor into the backbone. Figure 13 shows a schematic diagram that



**Figure 13.** (a) Packing model of PBTTT- $C_{14}$  with interdigitation of the side chains (not shown at top and bottom). Intercalation of  $F_4$ TCNQ between the conjugated backbones in adjacent sheets of the backbones would lead to free volume if the molecules were (b) directly positioned vertically or (c) if they were offset.

compares the structure of neat PBTTT- $C_{14}$  to our proposed "1D channel" model. This packing model would also help to explain the change in the lamella spacing and disorder in the side chains observed by NMR. An important feature that must be considered in determining a quantitative structure of the ordered regions of  $F_4TCNQ$ :PBTTT- $C_{14}$  blends is the electrostatic energy between the ionized polymer chain and

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molecular  $F_4TCNQ$  anion. Electrostatic interactions are a critical factor in the electronic structure of molecular donor–acceptor crystals<sup>30</sup> and will be complicated here by the disorder in polymer crystallites.

Our structural model implies that the  $F_4TCNQ$  is not distributed randomly throughout the film, which has important implications for modeling charge transport in these blends.<sup>29,54</sup> Most charge transport models assume that the sites are randomly dispersed in the polymer whereas here there would be chains highly decorated with  $F_4TCNQ$  and others that are not within the same domain. Thus, correlation between the dopant sites should be investigated in models of transport in these materials to determine what the impact on the apparent mobility and free carrier density.

#### CONCLUSIONS

In conclusion, blends of PBTTT-C<sub>14</sub> and F<sub>4</sub>TCNQ form ordered thin films in which the F4TCNQ molecules intercalate between the conjugated backbones of the polymer. Charge transfer occurs between F<sub>4</sub>TCNQ and PBTTT-C<sub>14</sub> in solution despite the larger IE of PBTTT compared to P3HT. This charge transfer in solution leads to aggregation that complicates processing films from solution, but with care, ordered films can be formed by spin- or drop-casting. The molecular order in the doped films was studied by GIWAXS and solid-state NMR revealing an intercalated structure. The  $\pi$ -stacking distance between polymer backbone segments in the ordered regions decreased with increasing molar ratio of the repeat units of PBTTT-C<sub>14</sub> to F<sub>4</sub>TCNQ due to charge transfer. The proposed microstructure of the blends requires that the F4TCNQ molecules cluster within the ordered domains; consequently, there may not be a simple ordering model for blend crystallites.

The electrical conductivity of blends of F<sub>4</sub>TCNQ and semiconducting polymers should be strongly affected by microstructure. It has previously been reported that polymers with an ionization energy similar to PBTTT do not have particularly high electrical conductivities and do not show signs of charge transfer by IR spectroscopy.<sup>21</sup> Our structural model suggests that F4TCNQ closely associates with the polymer chain in solution and the solid state forming  $\pi$ -stacked aggregates and crystallites. The ability to electrically dope semiconducting polymers depends critically on the formation of such domains as suggested previously for blends of P3HT and F4TCNQ where the conductivity may be limited by undoped amorphous domains. Our work here on the highly ordered semiconductor PBTTT is in agreement with such a model and further suggests that even within ordered domains that not all chains have equal probability of being doped. Future models of charge transfer doping should explore such issues and may lead to improved structure-property relationships to improve the electrical conductivity of doped polymers.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Details about preparation of thin films from the blends, characterization by optical spectroscopy, X-ray scattering, solid-state NMR, and computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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