Favorable Molecular Orientation Enhancement in Semiconducting Polymer Assisted by Conjugated Organic Small Molecules

Minji Kang, Jun-Seok Yeo, Won-Tae Park, Nam-Koo Kim, Dae-Hee Lim, Hansu Hwang, Kang-Jun Baeg, Yong-Young Noh, and Dong-Yu Kim

A bimodal texturing effect of semiconducting polymers is investigated by incorporating conjugated small molecules to significantly improve the charge transport characteristics via formation of 3D transport pathways. Solution blending of the electron-transporting polymer, poly[(N,N'-bis[2-octyldodecyl]-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)] (P(NDI2OD-T2)), with small molecular crystals of tetrathiafulvalene and tetracyanoquinodimethane is used, and the thin film microstructures are studied using a combination of atomic force microscopy, transmission electron microscopy, 2D grazing incidence X-ray diffraction, and surface-sensitive near-edge X-ray absorption fine structure. Blended thin films show edge-on and face-on bimodal texture with long-range order and microstructure packing orientation preferable for electron transport through the channel in organic field-effect transistors, which is confirmed by high electron mobility 1.91 cm² V⁻¹ s⁻¹, small contact resistance, and low energetic disorder according to temperature dependence of the field-effect mobility. Structural changes suggest a 3D network charge transport model via lamella packing and bimodal orientation of the semiconducting polymers.

1. Introduction

Polymer semiconductors have attracted much attention as potential materials for future flexible printed electronics, including organic-based solar cells,[1,2] light-emitting diodes,[3] transistors,[4,5] nonvolatile memories,[6,7] and wearable sensors.[8] These semiconducting materials offer low-cost and low-temperature processing, along with light weight and mechanical flexibility on plastic substrates. Recent advances in solution-processing techniques providing good molecular organization of organic semiconductor materials make them suitable for practical application, which can be compatible in wearable and large-area devices.[9,10] However, these solution-processable polymers still need several challenges, such as minimized defect density, well-ordered continuous films, an understanding of molecular orientation and electrical property relationship, better morphological control in the use of high resolution printing, and enhanced charge transport, before advanced device demonstration.[11]

For efficient charge transport in the semiconducting polymers, control of molecular structure and arrangement is as important as synthesis of new crystalline polymers[12–14] and interfacial engineering.[15–17] In recent years, various morphology control strategies for alignment of conjugated polymer chains have been proposed, such as shear alignment process,[4] nucleation control,[18] solubility control,[19] and addition of an antisolvent and additives.[14] These methods based on the semiconducting polymers provide a thin-film formation containing enhanced molecular ordering and crystallinity, with consequential significantly improved carrier mobility in organic field-effect transistors (OFETs).

An alternative approach using additional molecular species such as dopants has also been investigated to overcome inherent limitations in polymer semiconductors. The addition of organic dopants allows the semiconducting polymer to generate free charge carriers that lead to increased semiconductor conductivity at low molecular ratio.[20] This approach also sometimes causes unexpected structural changes in molecular structure.[21] Although high dopant ratios in the polymer semiconductor can induce structural disorder of the crystalline...
phase, low dopant concentrations have little influence on the structural quality of the semiconductor film.\textsuperscript{[24]} Some conjugated organic dopants formed particularly well-ordered polymer films and affected charge transport along the $\pi$-stacking direction of backbone.\textsuperscript{[23–25]} However, the relationship between molecular organization/morphology and charge transport in the blend system has not been investigated in detail.

In this study, we investigated the structural changes in semiconducting polymer thin-films to enhance the charge transport properties by blending with conjugated small molecules. Molecular orientation of n-type polymer semiconductor, poly($N,N'$-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl)-alt-5,5'$^\prime$-(2,2'$^\prime$-bithiophene)} (P(NDI2OD-T2)), is interestingly changed by incorporation of small amounts of tetrathiafulvalene (TTF) or tetracyanoquinodimethane (TCNQ). A combination of atomic force microscopy (AFM), transmission electron microscopy (TEM), 2D grazing incidence X-ray diffraction (GIXD), and surface-sensitive near-edge X-ray absorption fine structure (NEXAFS) was used to examine the morphology and microstructure of the blend thin films. Based on temperature-dependent behavior for charge transport, we demonstrated that the polymer semiconductor blending with TTF or TCNQ leads to low energetic disorder in OFETs. We propose a molecular packing model induced by crystals of conjugated small molecules and discuss structure–charge transport relationship.

### 2. Results and Discussion

#### 2.1. Materials

An excellent electron-transporting polymer P(NDI2OD-T2) (Figure 1), which is one of the most studied semiconducting polymers in the recent reports, was selected to study the structural and morphological changes by blending with additional organic species.\textsuperscript{[24]} P(NDI2OD-T2) thin-films typically showed an unique microstructural features of polymer lamella order and face-on rich arrangement (out-of-plane $\pi$-stacking) with respect to the substrate.\textsuperscript{[27]} Notably, spin-coated polymer thin-film normally shows inherent disorder and fluctuations along the $\pi$-stacking and lamella stacking directions.\textsuperscript{[23]} Charge transport in most polymer semiconductors, including P(NDI2OD-T2), has been shown to be sensitive to slight changes in molecular packing structure, backbone orientation, and fibrillar conformation.\textsuperscript{[27]} A molecular electron donor (TTF) and a molecular electron acceptor (TCNQ) were chosen as blend materials due to a characteristic stacking configuration in the planar crystal structure and extreme differences of their energy levels. TTF or TCNQ crystals are also formed by the strong intermolecular interactions between neighboring molecules and the strong $\pi$–$\pi$ stacking.\textsuperscript{[28,29]} Therefore, we speculated that this material property allows the molecules to form uniform size and shape in the polymer film.

#### 2.2. Charge Carrier Mobility

We preferentially measured field-effect mobilities for electrons, $\mu_{\text{FET, e}}$, from neat and blended polymer semiconductors in a top-gate/bottom-contact (TG/BC) device geometry. The transfer (drain current, $I_d$ vs gate voltage, $V_g$) and output characteristics ($I_d$ vs drain voltage, $V_d$) of the optimized OFET devices are shown in Figure 2a and Figure S1 (Supporting Information), respectively, and the corresponding device parameters are listed in Table 1. The neat P(NDI2OD-T2) film and P(NDI2OD-T2):TTF and P(NDI2OD-T2):TCNQ blend semiconductors exhibited an average $\mu_{\text{FET, e}}$ of 0.63, 1.36, and 1.61 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the saturated regime (at $V_d = 70 \text{ V}$), respectively. Maximum $\mu_{\text{FET, e}}$ of 1.91 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ was achieved with P(NDI2OD-T2):TCNQ blend semiconductor. On/off-current ratios ($I_{\text{on}}/I_{\text{off}}$) were on the order of $10^6$, and threshold voltages ($V_{\text{th}}$) of three samples were similar. Figure 2b shows the variations of $\mu_{\text{FET, e}}$ according to the change in the molar ratio of the blend materials in solution. Although gradual addition of small molecules increases the structural and energetic disorder in the film, the introduction of a small amount of molecular species (<1.0 wt%) achieves improved charge-carrier mobility in the polymer semiconductor of the OFETs.

#### 2.3. Optical and Thermal Properties

TTF and TCNQ molecules could form a charge-transfer complex with the P(NDI2OD-T2) in blended thin-films and solutions. To study these effects first, ultraviolet–visible (UV–vis) absorption spectra were measured for both thin-films and dilute solutions of neat P(NDI2OD-T2), P(NDI2OD-T2):TTF, and P(NDI2OD-T2):TCNQ, as shown in Figure 3a,b. All the samples exhibit a similar dual-band absorption spectrum in the range of 300–425 and 550–850 nm, without a distinct peak shift and no new absorption peaks in the polaron absorption region, between 800 and 1000 nm, attributed to the formation of polarons.

![Figure 1](image1.png)  
**Figure 1.** Molecular structures of P(NDI2OD-T2), TTF, and TCNQ.
of the anion (or cation).\(^{22}\) No significant peak changes are evident in the absorption spectra with increasing blend ratio, as shown in Figure S2 (Supporting Information). Thus, the TTF and TCNQ do not change the aggregation state of P(NDI2OD-T2) since these polymer chains strongly interact and aggregate. Because TTF and TCNQ have been used as conventional dopants, we also confirmed the potential for molecular doping by measuring ultraviolet photoelectron spectroscopy (UPS) and channel conductivity in OFET devices. Neat P(NDI2OD-T2), P(NDI2OD-T2):TTF, and P(NDI2OD-T2):TCNQ films also do not lead to shifts in the Fermi level, as shown in Figure 3c. Furthermore, conductivity of bilayered P(NDI2OD-T2)/TCNQ semiconductor on OFETs decreases compared to that of single-layer P(NDI2OD-T2) (Figure S3, Supporting Information). Consequently, we did not find any evidence for doping by formation of charge transfer complex. We suggest that this is due to an inefficient doping effect of the blend molecules by unfavorable energy offsets between the highest occupied molecular orbital (HOMO) of P(NDI2OD-T2) and the lowest unoccupied molecular orbital (LUMO) of TCNQ or LUMO of P(NDI2OD-T2) and HOMO of TTF, which provide an insufficient thermodynamic driving force for charge transfer. The HOMO and LUMO of P(NDI2OD-T2) are \(-5.6\) and \(-4.0\) eV, while those of TCNQ are \(-7.6\) and \(-4.2\) eV (\(-4.7\) and \(-1.2\) eV for TTF), respectively.\(^{23,30}\) Therefore, we believe that the doping effect in our blend system is negligible.

Differential scanning calorimetry (DSC) was employed to observe the nucleation efficiency of blend molecules as an additive (see Figure 3e). The lower melting point of TTF (\(\approx 119^\circ C\)) and TCNQ (\(\approx 295^\circ C\)) than P(NDI2OD-T2) (\(\approx 310^\circ C\)) is another reason to select those molecules as the plasticizer because the low melting temperature of the plasticizer can increase a mobility of the segments in polymer chains at relatively low annealing temperature. An exothermal peak of recrystallization of P(NDI2OD-T2) was observed at 283 °C, while that of P(NDI2OD-T2):TCNQ (5.0 wt%) occurred at 265 °C. The addition of TCNQ in P(NDI2OD-T2) resulted in a decrease in crystallization temperature \(T_C\) of P(NDI2OD-T2), indicating a decrease in the rate of crystallite nucleation of the polymer.\(^{18,31}\) This result implies that the blend molecule acts as a nucleation inhibitor rather than a nucleating agent, which will be discussed in detail later.

### 2.4. Morphology and Microstructure

The morphology of P(NDI2OD-T2)-based films was characterized by a combination of AFM and TEM. Figure 4a–c shows the topography and phase AFM images of the P(NDI2OD-T2) films, revealing essentially characteristic fibrillar structures. The root-mean-square roughness \((R_q)\) values of the neat P(NDI2OD-T2), P(NDI2OD-T2):TTF, and P(NDI2OD-T2):TCNQ films are \(\approx 0.57, 0.66,\) and \(0.58\) nm, respectively. In the case of the blend films, interestingly, fibrils appear to be an enhanced directional coherence in bundles of polymer chains (see phase images) without formation of aggregates on the surface of polymer films. Besides, the surface morphology of P(NDI2OD-T2):TTF and P(NDI2OD-T2):TCNQ blend films exhibit more distinct packed fibrils (see height images) and a preferential alignment, indicating elongated linear features. Therefore, those images show the polymer chains are more uniformly oriented in blend films, assisted by a few small molecules.

### Table 1. Parameters of P(NDI2OD-T2)-based OFETs.

<table>
<thead>
<tr>
<th>Semiconductors</th>
<th>Mobility [cm² V⁻¹ s⁻¹]</th>
<th>Threshold voltage [V]</th>
<th>SS [V per dec.]</th>
<th>(E_a) [meV]</th>
<th>(\gamma)</th>
<th>(T_0)</th>
</tr>
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<tbody>
<tr>
<td>P(NDI2OD-T2)</td>
<td>0.63 ± 0.20 (max. 0.95)</td>
<td>23.39 ± 2.26 (26.76)</td>
<td>−6.57 ± 0.37 (−6.00)</td>
<td>81.6</td>
<td>1.21</td>
<td>222.00</td>
</tr>
<tr>
<td>P(NDI2OD-T2):TTF (1.0 wt%)</td>
<td>1.36 ± 0.17 (max. 1.50)</td>
<td>27.63 ± 1.11 (27.03)</td>
<td>−6.09 ± 0.24 (−5.73)</td>
<td>80.6</td>
<td>1.45</td>
<td>165.24</td>
</tr>
<tr>
<td>P(NDI2OD-T2):TCNQ (0.25 wt%)</td>
<td>1.61 ± 0.27 (max. 1.91)</td>
<td>28.64 ± 1.49 (28.57)</td>
<td>−6.08 ± 0.54 (−6.10)</td>
<td>76.6</td>
<td>1.52</td>
<td>130.12</td>
</tr>
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Figure 4d–f shows more detailed fibrillar structure features obtained from TEM images. On the microscale, overlapped bundles of fibrils are present, exhibiting a layered structure. The neat polymer fibrils are locally linear but include some disorder and chain folding, related to defects and dislocation of the backbone.[32] TEM images of the blend films (Figure 4e,f) show that TTF and TCNQ molecules, isolated white dots in the images, are uniformly distributed between fibril bundles. Although the fibrillar packing structure in the blend films seems basically similar to that of the neat P(NDI2OD-T2) film, the addition of TTF or TCNQ molecules improve long-range order with decrease of chain folding, as can be observed from high magnification images. The structural organization indicates that the blended small molecules percolate uniformly into the P(NDI2OD-T2) polymer matrix without a distinct aggregation, maintaining fiber-like features with reduced 2D directional variations in the long-range organization, in agreement with the AFM results. These well-layered fibrillar structures are expected to provide good percolation pathways, and have a beneficial role by enhancing charge carrier transport properties. However, contrary to TTF and TCNQ molecules, nonplanar and relatively insoluble small molecules, such as 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C61 (PCBM) and 2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (diF-TESADT), did not present uniform distribution in the P(NDI2OD-T2), as shown in Figure S4 (Supporting Information).

2.5. Molecular Packing and Orientation in Blend Thin Films

2.5.1. Grazing-Incidence Wide-Angle X-Ray Scattering (GIWAXS)

GIWAXS was performed to gain structural information on the molecular ordering in a neat polymer and polymer:small molecules blend thin films. The GIWAXS patterns of the neat polymer film (Figure 5a) show a preferential “face-on” molecular packing with lamellar stacking (100) and chain backbone repeat (001) peaks clearly recognizable along $q_{xy}$ and a broad (010) $\pi-\pi$ stacking peak along $q_z$. The (100) peak is observed at $\approx 0.24 \text{ Å}^{-1}$ corresponding to lamellar spacing of $\approx 2.6 \text{ nm}$. The (010) peak is present at $\approx 1.6 \text{ Å}^{-1}$ in the out-of-plane direction, corresponding to face-on $\pi-\pi$ stacking distance of 0.39 nm. In blend films, the $q_{xy}$ and $q_z$ peaks remain at the same positions, but the intensity of the (010) $\pi-\pi$ stacking peak along $q_z$ slightly decreases. However, significant orientation changes on polymer lamellar spacing are evident as blend molecules intercalate between the polymer chains. There are significant $(h00)$ diffraction peaks along the $q_z$ direction, indicating the increased “edge-on” oriented crystallites in the blend films. It reveals that a bimodal orientation distribution, coexistence of face-on and edge-on crystalline domains, are present in the blend films. In particular, the $(h00)$ peaks in the P(NDI2OD-T2):TCNQ film are much stronger than the P(NDI2OD-T2):TTF film. Notably, upon incorporating of TTF or TCNQ in
polymer films, (100) peak shifts along q_z to higher values of q signify enhancement of the P(NDI2OD-T2) crystalline packing. These results show that our blend system enhanced the interpolymer packing and the degree of lamella order, which are consistent with AFM morphological features (Figure 5c). To accurately compare the peak positions of the polymer films in the 2D GIXD patterns, Figure 5b shows the out-of-plane and in-plane GIXD patterns, and Table S1 (Supporting Information) lists all diffraction peak positions and d-spacing for neat and blend P(NDI2OD-T2) films.

2.5.2. Surface-Sensitive NEXAFS Spectroscopy

NEXAFS spectroscopy was employed in order to quantitatively study the molecular orientation of the top surface of P(NDI2OD-T2) films (Figure 6).[33] The angle-dependent carbon K-edge NEXAFS is highly sensitive to the spatial orientation of the π* antibonding orbital along a π-bond, thus C-1s→π* resonances are measured at incident energies between 284 and 287 eV in the incident X-ray angle (θ) range from 15° (parallel to the conjugated plane) to 90° (perpendicular to the conjugated plane).[33,34] The largest value of the π* resonance intensity is at θ = 15° to the film surface for all samples, which indicates that the film surface is highly oriented in the face-on with respect to the substrate plane. The NEXAFS spectra of neat P(NDI2OD-T2) film vary strongly with different incidence angles compared to blend films (Figure 6a). In contrast, that of the blend films show reduced variation in π* resonance intensity with θ and increased peak intensities indicating edge-on domains, as shown in Figure 6a,b.

To determine the average tilt angle (α) of the conjugated polymer backbone, the resonance intensity was measured as a function of different incident angles. Linear fits of the resonance intensity versus cos²θ (Figure S5, Supporting Information) provide orbital orientation by using Equation (S1) (Supporting Information), which expresses the relationship between the resonance intensity and the vector orbital.[33] The average tilt angles of neat P(NDI2OD-T2), P(NDI2OD-T2):TTF, and P(NDI2OD-T2):TCNQ were 49.0°, 51.5°, and 61.2°, respectively. It reveals that the polymer backbone in blend film is preferentially composed of edge-on orientation at the top-surface compared to the neat polymer film. However, the slight nonlinearity in the curve fitting of the NEXAFS spectra from P(NDI2OD-T2):TCNQ blend film is attributed to some uncertainty of the orientation analysis.[34] This means P(NDI2OD-T2):TCNQ blend film is not likely to provide a single and uniform orientation. For simple comparisons of the orientation tendency, the dichroic ratio is defined as $R = \frac{I(90°) - I(0°)}{I(90°) + I(0°)}$. The neat P(NDI2OD-T2) has $R \approx -0.43$ for the conjugated plane, while P(NDI2OD-T2):TTF and P(NDI2OD-T2):TCNQ were 49.0°, 51.5°, and 61.2°, respectively. A more negative value of $R$ normally represents a higher degree of face-on character.[35] The dichroic ratio of neat P(NDI2OD-T2) is smaller than that of P(NDI2OD-T2):TTF and P(NDI2OD-T2):TCNQ films. This trend is similar to the polymer tilt angle, and thus it is believed that the blend films have a distinctive interfacial orientations. It should be noted
that the increase in resonance intensity at 70° and 90° incidence angle is strongly related to preferentially “edge-on” orientation, while molecular random orientation results in similar resonance intensities regardless of various θ. Therefore, the blend films are composed of mostly face-on orientation with small amounts of edge-on oriented conjugated plane at partial surfaces, adjacent to the blend molecules. This result is very consistent with the GIWAXS results, which are associated with their bimodal molecular orientation, caused by containing blend molecules in the polymer.

2.5.3. Plasticizing Effects

The initial face-on molecular orientation of the P(NDI2OD-T2) is known to be induced by kinetic trapping of the high molecular weight polymer chains during the spin-coating process.[36] Typically, a high temperature annealing or melt-annealing process is required to obtain the edge-on texture. However, Figure S6 (Supporting Information) shows mobility improvement of the blend semiconductors even at low annealing temperature, below 200 °C, and no thermal annealing for OFETs. Therefore, the plasticizing effect of the small molecules in polymer blend films should also be considered. From the DSC measurement (see Figure 3e), we found the melting and recrystallization points were significantly decreased by ≈20 °C. The melting point of P(NDI2OD-T2):TCNQ (5.0 wt%) is ≈290 °C, while pristine P(NDI2OD-T2) is ≈310 °C. The relatively slow rate of crystal growth also produces broad orientation distributions due to less interaction of P(NDI2OD-T2) with the substrate. This reveals that the addition of π-conjugated small molecules, such as TCNQ and TTF, can allow kinetically trapped polymer chains to rearrange into the more favorable edge-on texture. We speculated that the blend molecules in P(NDI2OD-T2) may function similar to an plasticizer, inducing the chain motion and providing local polymer order and elongation of polymer fibrils over neat polymer film. Because the blend molecules stay as solid in solution and do not solidify simultaneously with P(NDI2OD-T2) during film drying, they induce polymer fibril orientation upon impingement.[37] Therefore, the unique bimodal texture of our blended thin films is expected to achieve more favorable charge transport properties along the percolation pathways owing to additional interconnectivity and 3D organization within the accumulation layer of a polymer semiconductor.[38] P(NDI2OD-T2) ordered by bimodal chain packing structures possesses the π-orbitals belonging to polymer chains overlapped partially. The extended π-orbitals assist interchain charge transfer.[39] A similar trend on blend system can be observed in OFETs, fabricated by another polymer and inkjet printing (see Figures S7 and S8, Supporting Information). In addition, the contact resistance ($R_c$) of OFETs was also investigated to understand the effects of blend molecules on charge injection and transport in the semiconducting polymer. $R_c$ values were extracted from Y-function method, which measures the transfer characteristics in the linear regime with a small source–drain voltage ($V_d \ll V_g$) (see Figure S9, Supporting Information).[40] The $R_c$ for P(NDI2OD-T2):TTF and P(NDI2OD-T2):TCNQ blend devices were ≈0.85 and ≈1.05 MΩ, respectively, which is lower than that of neat P(NDI2OD-T2) device (≈2.18 MΩ). These results support the ability of blend molecules to enhance the molecular orientation of the P(NDI2OD-T2) film, leading to better charge transport pathways.

Figure 5. a) 2D GIXD patterns of neat P(NDI2OD-T2), P(NDI2OD-T2):TTF, and P(NDI2OD-T2):TCNQ films on Si substrates. b) The corresponding GIXD line cuts along the in-plane and out-of-plane directions. c) Schematic of polymeric crystallite texture.
2.6. Temperature-Dependent Charge Transport Properties

Transfer curves of the TG/BC OFETs were measured in the linear and saturation regimes at various temperatures ranged 101–298 K to investigate the effects of structural changes on the charge transport properties at the blend thin-film surfaces, as shown in Figure 7. Arrhenius-like plots were used to determine the activation energy ($E_a$) for charge transport (Figure 7a). Table 1 shows the resultant $E_a$ values, calculated from $\mu \propto \exp(-E_a/k_B T)$ where $k_B$ is the Boltzmann constant. $E_a$ on hopping transport in P(NDI2OD-T2)-based OFETs slightly decreases with addition of TTF or TCNQ in the semiconducting polymer. Lower $E_a$ values in blend semiconductors indicates that the trap-state distribution width has become narrower and shallower within the energy gap, which is consistent with the measured $\mu_{FET}$ on the three types of semiconductors. [41,42]

The temperature dependence of charge transport at saturation regime was further analyzed by the Vissenberg–Matters hopping model to determine charge carrier distribution in the 2D localized density of state (DOS) of the three-types thin films. [43] This percolation hopping model has been widely used for a carrier distribution profiles in the accumulation layer of the semiconductors. [43] As can be seen in Figure 7b–d, the transfer plots could be described by a power-law relationship, which has a form of $I_d \propto (V_g - V_t)^\gamma$ where $\gamma = (T_0/T) + 1$; and $T_0$ is the indicative parameter describing the amount of energy disorder, which is related to the DOS width of semiconductors. Although $\gamma$ for all samples increased with decreasing temperature, $\gamma$ of blend semiconductors was much closer to the temperature-independent "ideal value 2" than was the neat polymer semiconductor (Table 1). [44] We can extract the DOS width by fitting the transfer plot at the saturation region (at $V_d$ = 60 V) for the power exponent $\gamma$. Lower $T_0$ values of blend semiconductors (~165 and 130 K for P(NDI2OD-T2):TTF and P(NDI2OD-T2):TCNQ, respectively) imply more ordered 2D semiconductor than that of neat P(NDI2OD-T2) (~222 K). [45,46] Figure 7 shows the obvious differences in $T_0$ which accounts for the large difference in field-effect mobility of OFET devices. Therefore, blend semiconductors have a lower degree of energetic disorder than neat polymer semiconductor. Lower $T_0$ is also consistent with the relatively higher charge-carrier mobility of blend semiconductors. It is obvious that polymer semiconductors blended with small amounts of conjugated extra molecules can induce more ordered charge transport pathways.

Generally, the semiconducting polymer films, formed without any particular treatment, have defect sites and amorphous regions where charge transport is limited. For efficient charge carrier transport, conjugated polymer films need to improve the molecular stacking order, the connectivity between adjacent crystalline regions and alignment of charge transport pathways. [47] As discussed above, we proved that a small amount of planar small molecules in the conjugated polymer plays a key role in enhancing molecular orientation and packing with improved charge carrier mobility, despite the absence of a doping effect and increasing crystallite size. As expected from TEM and GIWAXS data, it can be seen that the conjugated small molecules, which tend to be uniformly distributed in the semiconducting polymer, can be located in the defect sites and amorphous regions, and they would lead to enhanced intra- and interchain charge transport in the polymer semiconductor of OFET devices due to continuous percolated charge transport pathways. Schematic charge transport mechanism in our blend system is suggested in Figure 8.
3. Conclusions

In summary, we demonstrated the preferential microstructure in P(NDI2OD-T2) polymer films by introducing conjugated planar small molecules (TTF and TCNQ). With the unconventional bimodal polymer texture, blend films include long-range oriented order and packed microstructure contrary to neat polymer thin-film. The blend molecules can control interpolymer orientation and packing structure in the polymer.

Figure 7. a) A plot of linear mobility versus inverse temperature for the three P(NDI2OD-T2)-based OFETs at $V_d = 5$ V. b–d) Transfer characteristics (left); replotted transfer curves on a double logarithmic scale (middle); and extracted values of $\gamma$ from replotted data versus $1/T$ (right) of (b) P(NDI2OD-T2):TCNQ, (c) P(NDI2OD-T2):TTF, and (d) neat P(NDI2OD-T2) OFETs at n-channel region.
OFETs based on TTF and TCNQ blends exhibit high electron mobilities of 1.50 and 1.91 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, which are much higher than that of neat polymer-based OFETs, regardless of the absence of a doping effect between polymer and dopant molecules. According to charge transport properties, blend semiconductors have smaller energetic disorder with lower activation energy than neat polymer semiconductor. This suggests that the new structural organization of P(NDI2OD-T2) caused by the small amount of small molecules offers 3D charge transport pathways for high charge-carrier mobility, and suggests new insights into the correlation between microstructure and charge transport in high-performance polymer semiconductors. This blend system will provide promising molecular engineering approaches, which could integrate with various solution engineering techniques to develop high performance organic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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