Spatially Resolving Ordered and Disordered Conformers and Photocurrent Generation in Intercalated Conjugated Polymer/Fullerene Blend Solar Cells

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Supporting Information

ABSTRACT: Resonance Raman spectroscopy was used to identify ordered and disordered conformers of poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) blended with the electron acceptor [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) in bulk heterojunction (BHJ) solar cells where PCBM intercalates into PBTTT side groups. We show that the PBTTT thiophene ring symmetric C=C stretching mode consists of contributions from ordered (ω_{C=C} = 1489 cm\(^{-1}\), fwhm \sim 15 cm\(^{-1}\)) and disordered (ω_{C=C} = 1500 cm\(^{-1}\), fwhm \sim 25 cm\(^{-1}\)) components and their relative amounts are sensitive to PCBM loading, annealing and excitation energy. The 1500 cm\(^{-1}\) PBTTT component originates from twisted thiophene rings and disordered side groups due to PCBM intercalation in a mixed kinetic phase and thermal annealing promotes ordering of PBTTT chains from the formation of bimolecular PBTTT/PCBM crystals. Density functional theory (DFT) Raman simulations of PBTTT monomers support these assignments. Resonance Raman images of annealed PBTTT/PCBM model solar cells confirm that ordered PBTTT chains are most concentrated in PCBM-rich bimolecular crystals and corresponding intensity modulated photocurrent spectroscopy (IMPS) and imaging measurements show increased nongeminate charge recombination at the boundaries of ordered/disordered regions.

1. INTRODUCTION

The degree of mixing of fullerene acceptors with conjugated polymer donors used for thin film BHJ solar cells has significant implications for determining morphologies and overall device performance.\(^{1,2}\) Blends of PBTTT and PCBM are an ideal BHJ system for understanding how molecular mixing influences the outcomes of photovoltaic processes.\(^{3-5}\) PBTTT chains readily assemble into well-ordered \(\pi\)-stacked lamellar crystalline structures,\(^{6}\) essential for establishing multidimensional charge and energy transfer pathways. Extensive X-ray scattering and diffraction,\(^{5-9}\) solid-state NMR spectroscopy,\(^{5}\) differential scanning calorimetry (DSC),\(^{5}\) and IR spectroscopy studies on PBTTT/PCBM blends have demonstrated the preponderance of fullerene intercalation into the polymer alkyl side groups resulting in bimolecular cocrystals following annealing treatments.\(^{7,10}\) PBTTT lattice spacing and paracrystalline disorder in the \(\pi\)-stacking direction increase with fullerene intercalation that is marked by broadening in X-ray diffraction peaks and increased amounts of the gauche alkyl side group conformation.\(^{5}\)

The PBTTT/PCBM system has proven a useful model for predicting optimal blend stoichiometries and morphologies, however, solar cell power conversion efficiencies are <3\%,\(^{11,12}\) well below current benchmarks.\(^{13-15}\) This result is surprising considering the relatively high charge mobilities of pristine PBTTT (>0.001 cm\(^2\)/V/s at low charge densities),\(^{16-20}\) yet it underscores the need to better understand how ground state structure and interactions influence excited state photophysical processes.\(^{21}\) Ultrafast pump–probe transient absorption spectroscopy (TAS) of PBTTT/PCBM blends show evidence of charge separation on time scales <1 ps followed by efficient geminate recombination of separated charge carriers occurring on time scales of \(\sim\)200 ps.\(^{22}\) These results are consistent with a well-mixed phase favoring efficient charge generation but separated carriers lack sufficient transport pathways and cannot escape Coulomb attractions thus recombining on fast time scales.\(^{22,23}\) Importantly, X-ray spectromicroscopy studies of PBTTT/PCBM blends produced estimates of acceptor miscibility of 42 wt %\(^9\) implying that TAS dynamics are dominated by a well-mixed phase but it is difficult to determine if this corresponds solely to bimolecular crystals. Furthermore, spectroscopic and charge transport studies have shown evidence of structurally similar PBTTT conformational
polymorphs (conformers) with energy differences of ~0.1 eV.24,25 PCBM intercalation is expected to disrupt PBT1T conformation and packing in blends but connecting specific ground state structures and interactions to the outcomes of excited state photovoltaic processes remains more elusive.

Here, we use resonance Raman spectroscopy to identify signatures of structurally distinct PBT1T conformers in PCBM blends and track their evolution by varying processing conditions, composition and excitation energies. Resonance Raman and photocurrent imaging are then used to spatially map and correlate their contributions to local material performance in model PBT1T/PCBM solar cells. We show that the PBT1T alkyl-thiophene symmetric C=C stretching vibration (~1490–1500 cm−1) can be decomposed into contributions from ordered (lower energy, hωC=C = 1489 cm−1) and disordered (higher energy, hωC=C = 1500 cm−1) PBT1T conformers which are not evident in optical spectra. We propose that both ordered and disordered PBT1T species are well-mixed with PCBM but only the former exist only in the bimolecular crystal phase. Density functional theory (DFT) Raman simulations and excitation energy dependent Raman spectra indicate that ordering of alkyl-thiophene rings defines the two observed PBT1T forms and the relative amounts of each are determined by the PCBM loading and film processing conditions. Raman excitation profiles further demonstrate that annealing converts the disordered form to bimolecular crystals suggesting that it is in fact a precursor kinetic phase. Well-resolved overtone and combination transition intensities (up to 4 quanta) – chiefly involving the dominant PBT1T CC symmetric skeletal vibrations (~1400–1600 cm−1) – are also apparent and intensities show much smaller sensitivity to PCBM loading indicating PBT1T excitations are electronically localized for both species.

Raman images demonstrate that a significant fraction of ordered PBT1T chains reside in PCBM-rich regions confirming these are indeed bimolecular crystals. However, corresponding photocurrent images show substantial losses in these regions, likely due to efficient geminate charge recombination. Intensity modulated photocurrent spectroscopy (IMPS) measurements of annealed PBT1T/PCBM devices also display positive phase shifts at low modulation frequencies (i.e., photocurrent leads the modulation frequency), which is a signature of nongeminate charge recombination becoming operative.26,27 IMPS images of these model PBT1T/PCBM solar cells reveal that this process is most prevalent at boundaries of ordered/disordered PBT1T and PCBM aggregates.

2. METHODS

2a. Materials and Spectroscopic Characterization. The C14 variant of PBT1T (Aldrich, Mw=49 kDa, PDI = 2.3) and PCBM (Aldrich) were dissolved separately in anhydrous o-dichlorobenzene (5 and 20 mg/mL, respectively) inside a nitrogen circulating glovebox (Aldrich) were dissolved separately in anhydrous o-dichlorobenzene (5 and 20 mg/mL, respectively) inside a nitrogen circulating glovebox. Blend solutions were prepared and used immediately after heating to 100 °C and stirred for over 8 h to facilitate dissolution and filtered prior to deposition. Blend thin films were produced by adding PCBM and PBT1T solutions in varying weight/weight fractions, i.e., 1:1 up to 1:8 (PBT1T/PCBM) and spin-casting at speeds of 600 rpm for 120s onto rigorously cleaned glass coverslips. Blend solutions were prepared and used immediately after heating to avoid precipitate formation or gelling. Optical absorption spectra of solutions and thin films were recorded on a UV/vis/NIR instrument (Hitachi U4100) and Raman spectra were measured on a home-built scanning microscope spectrometer system described in detail previously.26,29 Argon- and krypton-ion laser sources (λexc = 458–647 nm; 2.71–1.92 eV) as well as a NIR laser diode (λexc = 785 nm, 1.58 eV) were used to selectively excite PBT1T in PCBM blends. Single molecule images and spectra of PBT1T diluted into a polystyrene host matrix were also measured using the above confocal microscope with single photon counting techniques. Scattered excitation light was removed by Rayleigh rejection filters (Semrock) prior to entering the polychromator/CCD detector system (Andor). Relative Raman intensity profiles were constructed from comparing excitation energy-dependent Raman spectra and comparing to an in situ externalAgKα radiation standard. All spectra were corrected for instrument responses using established methods.30

2b. Solar Cell Model Device Fabrication and Imaging. Model PBT1T/PCBM solar cells were fabricated using the optimal loading ratio reported in the literature (~1:4 w/w)31 and were spun on top of PEDOT:PSS (Baytron) coated indium–tin oxide (ITO) substrates (Mevac) that had previously been heated to 150 °C for 30 min to evaporate residual water. Aluminum was next deposited on top of the PBT1T/PCBM blend under high vacuum to complete the device and current–voltage (I–V) characterization was carried out in the glovebox in the dark and under AM1.5 illumination (Newport). Typical device power conversion efficiencies were <1% due to nonoptimized morphologies. Resonance Raman spectroscopic- and photocurrent imaging was performed on as-cast and annealed PBT1T/PCBM devices using the above-mentioned Raman imaging spectrometer. PBT1T/PCBM films were annealed for ~30 min at 110 °C prior to aluminum deposition in order to generate sufficient phase separation affording better contrast in Raman and photocurrent images. Devices were studied within a home-built inert gas flow cell and no evidence of material or device degradation was observed in the course of spectral image acquisition or in subsequent images collected over the same scan area. Quasi-DC photocurrent imaging was initially performed by modulating the laser excitation (~100–200 Hz) using a mechanical chopper and current was detected using a lock-in amplifier. Photocurrent images were generated using substantially lower excitation intensities than Raman images (i.e., ~10W/cm2 vs. ~1 kW/cm2, respectively) to avoid nonlinear effects, such as exciton–exciton annihilation or other photon-induced bimolecular processes and Raman images were constructed using a procedure described previously.28 IMPS spectra and images were next recorded using a laser diode source (λexc = 488 nm, Omicron Phoxx) modulated by the reference output of the phase-sensitive detector and the frequency was swept in the range of ~1 Hz up to 20 kHz. Modulation depths were ~10% or slightly less to ensure linear response over the entire frequency range. Ensemble IMPS spectra were measured in a widefield configuration, whereas IMPS images were acquired in a confocal geometry and the modulation frequency was held constant over the entire imaging scan. A silicon photodiode with a known frequency response was used as a reference for all IMPS experiments. All photocurrent spectra or images were generated under short-circuit conditions.

2. c. Theoretical Simulations. Raman spectra of a model PBT1T monomer were calculated at the B3LYP/Def-2SVP(d) level of theory using the ORCA computational suite. The C14 side groups were replaced with ethyl (C2) groups and a fully planar BTT1T-C2 monomer and a twisted local minima variant in which the center fused ring is rotated with respect to the two thiophene rings by 29 degrees were simulated.31 Resolution of identity (RIJ) and chain of spheres (COSX)32 approximations were utilized with the equivalent quality auxiliary basis set. Atom pairwise dispersion corrections with Becke–Johnson dampening34 were employed.

3. RESULTS AND DISCUSSION

3a. Optical and Raman Spectroscopy. In general, conjugated polymers become more disordered as fullerene loading increases due to disruption of packing arrangements and reduced planarity between monomers.28,35 In crystalline polymers, such as the archetype poly(3-hexylthiophene) (P3HT) system, addition of PCBM breaks up π-stacked lamellar chains in aggregates leading to increases in a solution-

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like amorphous component with higher energy and featureless absorption lineshapes. The ability of PCBM to intercalate into PBTTT chains presents an intriguing case challenging traditional views of order/disorder transitions. Spectroscopic and electrical imaging approaches are used here to (i) identify spectroscopic markers of intercalated PBTTT chains in PCBM blends, (ii) assess how ground state structures and interactions affect excited state processes, and (iii) spatially correlate local composition and order/disorder characteristics to material performance in functioning solar cells.

We begin by re-examining the effect of variable PCBM content in PBTTT blend thin film absorption spectra which will be useful later for selection of resonance Raman excitation schemes (vide infra). Figure 1 displays as-cast (solid traces) and annealed at 140 °C for 20 min (dotted traces) PBTTT/PCBM blend thin films at several PCBM loadings. Inset: comparison of pristine PBTTT and a 1:2 w/w PCBM blend (offset for clarity).

Figure 1. Optical absorption spectra of as-cast (solid traces) and annealed (dotted traces) PBTTT/PCBM blend thin films at several PCBM loadings. Inset: comparison of pristine PBTTT and a 1:2 w/w PCBM blend (offset for clarity).

Figure 2. Resonance Raman spectra of PBTTT/PCBM blend thin films excited with 514.5 nm (2.41 eV) light corresponding to the maximum of the PBTTT absorption line shape. Resonance excitation usually leads to macroscopic transitions with electronic origin transitions separated by ~0.1 eV. Likewise, a Franck–Condon analysis of pristine PBTTT absorption lineshapes showed evidence of two distinct transitions with electronic origin transitions separated by ~0.1 eV. The relatively small difference in energy between apparent intrinsic PBTTT structures potentially complicates the use of absorptive spectroscopies for quantifying amounts and properties of these species since lineshapes strongly overlap and become even more congested in PCBM blends. Resonance Raman spectroscopy can help overcome these issues using selective resonant excitation schemes to target specific electronic excited states corresponding to distinct PCBM intercalation-dependent PBTTT conformers.

PBTTT/PCBM blend absorption spectra in Figure 1 generally resemble previously published spectra in the singlet exciton onset region but differ from other reports that show better resolution of vibronic structure near the PBTTT absorption onset. Improved resolution of vibronic structure near the PBTTT absorption onset is observed in addition to a slight red-shift (~0.04 eV) relative to the pristine PBTTT line shape (see Figure 1 inset). As PCBM loading increases, the PBTTT contribution decreases concomitantly with an increase of broad and overlapping higher energy component consistent with the PCBM absorption line shape. Spectra from annealed blends show relatively small changes compared to as-cast films suggesting that conversion from a kinetic mixed (as-cast) phase to the bimolecular crystal phase is not as efficient as reported previously for higher annealing temperatures (i.e., approaching the liquid crystalline transition of PBTTT).

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used are absent demonstrating that PBTTT Raman cross-section enhancements overwhelm those of PCBM despite that it is usually present in larger concentrations (e.g., >1:1 w/w). Well-resolved progressions of overtone and combination bands, mainly involving vibrations of PBTTT C−C and C=C stretching character (see Table 1), are visible. Comparison to

Table 1. Assignments of Main Backbone Raman Bands from PBTTT/PCBM Blends in the Fundamental (0-1) and First Overtone (0-2) Regions

<table>
<thead>
<tr>
<th>peak</th>
<th>frequency (cm$^{-1}$)</th>
<th>assignment</th>
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</tr>
<tr>
<td>3013</td>
<td>$\nu_6 + \nu_9$</td>
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“Determined from DFT simulations (see below) and ref.$^{40}$

IR absorption spectra of PBTTT/PCBM blends in the first overtone/combination band region (0−2) as well as the appearance of higher order progressions confirm these are not fundamentals of high frequency modes (i.e., C−H stretches).$^{5}$ Table 1 lists mode assignments of both fundamental and overtone/combination bands (for only the 0−2 region).

From Figure 2, we note that only the C−C and C=C symmetric stretches of the thiophene and thienothiophene backbone rings display pure overtone transitions. Higher-order (0−2) overtone/combination band clusters show greater broadening, probably because of dispersion effects (i.e., wavepacket broadening) due to coupling between nuclear motions. Weak clusters of combination bands from multiple low frequency vibrations, likely from thiophene-thienothiophene ring bends and librations, are also apparent before the 0−2 region (∼1700−2500 cm$^{-1}$). The appearance of multiple apparent progression-forming modes suggests that vibrational displacements are large (i.e., large Huang−Rhys factors, $S \approx \Sigma^{(1)}_l/2\Delta_l$ where $\Delta_l$ is the displacement for mode $l$). However, PBTTT absorption band line widths (fwhm) are not significantly different than P3HT or other crystalline polymers ($S \approx 1.0$)$^{44,45}$ meaning that the total vibrational displacements are probably similar. Raman lineshapes in Figure 2 also offer useful insights into PBTTT absorption features. Namely, the weakly resolved vibronic interval can be explained by the Franck–Condon displacement of multiple low frequency modes causing the “valleys” by dominant mode progressions (i.e., the PBTTT CC backbone symmetric stretches, $\nu_{1−3}$) to become filled in. Conversely, increased inhomogeneous broadening might also explain larger absorption vibronic line widths in pristine PBTTT, however, narrowing of line widths in PCBM blends suggests increased order or longer excited state lifetimes.

The latter effect is not expected due to the presence of intimately mixed PCBM electron acceptors. It is also useful to point out that overtone/combination band intensities show less sensitivity with increased PCBM loading (constant excitation energy) implying that either disorder effects are not important until longer times (several vibrational periods, >100 fs) or chromophores are spatially localized making them less sensitive to disorder. Typically, in large molecules with many displaced modes, overtone/combination intensities are usually extinguished before the first overtone (0−2) region because of destructive interference caused by rapid coupling to the bath or among chromophores of different energies (inhomogeneous broadening).$^{42}$ This effect appears suppressed in PBTTT systems and we speculate the persistence of the multimode overtone/combination band transitions in PBTTT/PCBM blend Raman spectra arises from weak coupling to the phonon bath and small contributions from inhomogeneous broadening effects.

3.b. Identifying Ordered and Disordered PBTTT Conformers. The qualitative picture emerging from Raman trends reported in Figure 2 is that the multidimensional excited state wavepacket survives for longer times allowing sufficient buildup of overlap and overtone/combination intensities. This scenario is most consistent with localized excitations despite the relatively high order of PBTTT (even in PCBM blends) that intuitively suggest delocalized electronic structures. The implications of localization/delocalization in polymeric solar cells are significant and have been the subject of recent investigations of ultrafast charge separation.$^{43−46}$ For example, Jamieson et al. highlighted the importance of fullerene crystallites in promoting charge separation while simultaneously suppressing geminate recombination in several polymer/fullerene systems that show varying degrees of mixing.$^{46}$ We consider these aspects for interpreting Raman/photocurrent images in the following.

Further insights into the nature of PBTTT chromophores PBTTT/PCBM blends can be obtained from resonance Raman spectra as a function of excitation energy spanning the PBTTT optical absorption line shape (∼1.9−2.7 eV). Figure 3 displays variable excitation energy Raman spectra and are normalized to the thienothiophene ring C=C symmetric stretch (1415 cm$^{-1}$ mode, $\nu_4$) for comparison. Raman patterns show significant changes with excitation energy consistent with resonant excitation of distinct PBTTT chromophores. In the 0−1 region, the relative intensity of the 1391 cm$^{-1}$ mode (thiophene symmetric C=C stretching character) decreases and the ∼1489−1500 cm$^{-1}$ band region of the symmetric C=C thiophene ring stretch gains in intensity in addition to apparent blue-shifting and broadening with increased excitation energies. Comparison of the two PCBM loadings also demonstrates specific interactions with PBTTT backbones. For example, a large increase in relative intensity is observed for the ∼1489−1500 cm$^{-1}$ mode in the 1:4 blend for excitation near the PBTTT resolved absorption onset (1.92 eV), suggestive of bimolecular crystals.

Chromophore-specific resonance enhancement is more obvious in the first overtone (0−2) region where increasing excitation energy causes intensity redistributions toward higher frequencies. Residual fluorescence masks overtone/combination bands in the background noise at the lowest excitation energy (647 nm, 1.92 eV) and these spectra were not included. For comparison, we measured Raman spectra of pristine PBTTT and as-cast 1:1 w/w PBTTT/PCBM thin films under
nonresonant conditions ($\lambda_{\text{exc}} = 785 \text{ nm}, 1.58 \text{ eV}$), that show pronounced red-shifts of the main PBTTT skeletal stretching vibrations for the blend (see the Supporting Information). It is likely that nascent bimolecular crystals in the blend become preresonant at this excitation energy, which also gives rise to very weak overtone transitions.

We propose that line shape (intensity) changes with excitation energy reflect the presence of both ordered and disordered PBTTT conformations whose populations are modulated by PCBM loading and annealing. Raman excitation profiles (REPs) are now constructed to test this hypothesis that reveal vibrational mode-specific views of the excited state potential energy landscape. Figure 4 shows REPs from as-cast PBTTT/PCBM films (solid traces) for all backbone skeletal vibrations showing appreciable intensity in resonance Raman spectra in Figures 2 and 3 ($\nu_{1-7}$) and intensities are reported relative to a nonabsorbing external standard (i.e., sapphire). Generally, REPs bear similarity to absorption lineshapes provided that Raman and absorption transitions involve only a single excited state (i.e., single absorber). REP lineshapes in Figure 4 show noticeable deviations from one-photon absorption spectra (Figure 1) confirming contributions from closely overlapping states.

We next measured REPs of an annealed 1:4 w/w PBTTT/PCBM blend (dotted traces, Figure 4) and compare these to as-cast REP lineshapes. A pronounced decrease of the higher energy REP component is apparent indicating conversion to PBTTT chains with improved backbone and side group order consistent with intercalated bimolecular crystals. This result highlights the greater sensitivity of Raman techniques to chromophore environments compared to one-photon absorption spectroscopy (Figure 1), which can obscure contributions from closely overlapping states.

We now focus on the $\sim 1489-1500 \text{ cm}^{-1}$ region assigned to the C–C symmetric stretch of the thiophene rings ($\nu_6,7$, Table 1) that are particularly sensitive to PCBM loading and excitation energy (Figure 3). Figure 5a presents resonance Raman spectra generated from a PBTTT/PCBM blend thin film of a 1:2 w/w ratio in the thiophene C–C symmetric stretching fundamental region. Excitation at the PBTTT red absorption onset (i.e., 1.92 eV) selects the $1489 \text{ cm}^{-1}$ ($\nu_6$) component that subsequently blue-shifts and coalesces into the $\sim 1500 \text{ cm}^{-1}$ mode ($\nu_7$) at higher excitation energies (i.e., 2.71 eV). These trends have been explained previously from theoretical studies of oligothiophenes where lower energy chromophores (viz. longer conjugation lengths) show red-shifted Raman-active backbone vibrations. The 1500 cm$^{-1}$ mode is proposed to originate from disordered PBTTT C–C thiophene rings, probably because of fullerene intercalation-induced disorder among the alkyl side groups causing twisting of the backbone thiophene rings and greater paracrystalline disorder. Likewise, the $1489 \text{ cm}^{-1}$ component of the symmetric thiophene C–C stretch derives intensity from ordered PBTTT.
chains in bimolecular crystals, where side group and backbone order is improved. Line widths of both PBTTT C–C thiophene forms are also consistent with their proposed structural origins, namely, ordered conformers are ∼15 cm⁻¹ compared to ∼25 cm⁻¹ for disordered chains because of heterogeneity. This feature is also consistent with improved vibronic resolution in absorption spectra of PBTTT/PCBM blends, which indicates the presence of ordered PBTTT chains in bimolecular crystals. The relative amounts of ordered and disordered PBTTT conformers are estimated by deconvoluting the C–C thiophene band using two line shape functions corresponding to the ν₆ and ν₇ bands (Table 1). We do not attempt to obtain absolute cross sections for each species but it is expected that these values are similar because of the structural similarity of ordered and disordered forms (i.e., energy difference of ∼0.1 eV or less), which is much subtler than in other crystalline polymers displaying polymorphic behavior, such as P3HT. In this description, the total C–C thiophene Raman band intensity is a linear combination of both components and we use this simple model to assess how the thiophene Raman band intensity is a linear combination of both behavior, such as P3HT. In this description, the total C–C thiophene Raman band intensity is a linear combination of both components and we use this simple model to assess how the thiophene Raman band intensity is a linear combination of both behavior, such as P3HT.

Thus far we have shown that the ability of the two species model to decompose key Raman bands into separate contributions from morphology-dependent PBTTT conformers offers a much simpler means to assess order/disorder transitions in this system. Although DFT simulations predict observed experimental behavior, they do not allow us to incorporate side group disorder and paracrystallinity. It is also important to note that ordered PBTTT chains in bimolecular crystals are twisted but side group disorder should be diminished relative to the kinetic disordered intercalated form.

3.c. Theoretical Raman Simulations. DFT Raman simulations of a planar and twisted PBTTT model monomer system (BTTT-C₂) are next performed to validate our proposed model and are shown in Figure 6 with their respective structures. Calculated DFT Raman line shape trends agree very well with experiment although nonresonant conditions are used in simulations and a scaling factor of 0.95 must be applied to calculated frequencies in order to compare with experiment. The nominal C–C symmetric stretch appearing at 1461 cm⁻¹ for the planar conformation undergoes a blue shift of ∼7 cm⁻¹ in the twisted variant. Most notably, intensity redistributions occur between the inter-ring C–C symmetric stretch (1541 cm⁻¹) and the thiophene C–C stretch (1594 cm⁻¹) depending on backbone planarity. For example, the latter increase in intensity for the twisted BTTT-C₂ variant whereas the former dominate in the planar monomer. Previous DFT simulations of planar and twisted PBTTT trimer structures show similar trends as presented in Figure 6 confirming that at least two PBTTT types are present in PCBM blends revealed from PCBM loading- and excitation energy dependent Raman spectra. Moreover, calculated frequencies and intensities of trimers were very similar to experimental Raman spectra, suggesting that excitations are probably localized to a few monomer units.

Figure 5. (a) Resonance Raman spectra of as-cast PBTTT/PCBM blend thin films (1:2 w/w) showing lineshapes of the two distinct PBTTT forms; ordered (ν₆) and disordered (ν₇) PBTTT chains. (b) Percent of disordered species present in all blend ratios as a function of excitation energy. The dashed line represents the resonance maximum excitation energy of the disordered form (2.71 eV).

Figure 6. Simulated Raman spectra of the BTTT-C₂ monomer and structures.
3.d. Spatially Mapping Order–Disorder and Photocurrent Generation in Solar Cells. Despite the relatively poor performance of PBTTT/PCBM, we have thus far demonstrated its value as a model for understanding donor/acceptor interactions and supramolecular organization and their impact material performance. Resonance Raman spectroscopic and photocurrent imaging techniques are now employed to spatially resolve how ordered and disordered PBTTT chains impact local device performance in model solar cell devices. For these experiments, as-cast and annealed PBTTT/PCBM blends in 1:4 w/w ratios (the optimal blend ratio reported for solar cells) were prepared to compare morphology-dependent order/disorder spatial distributions. Because these studies emphasize model PBTTT/PCBM morphologies, power conversion efficiencies were <1% but nonetheless show good stability and expected diode-like behavior (see the Supporting Information). We emphasize annealed devices because of better material performance in addition to better contrast in Raman and photocurrent images.

Figure 7 shows representative resonance Raman and photocurrent images of a 1:4 w/w annealed device and the active layer. Raman images represent the ∼1489–1500 cm⁻¹ spectral region of the thiophene C=C stretches and are generated using 458 nm (2.71 eV) excitation light. This excitation energy was specifically chosen to selectively interrogate disordered PBTTT chains and their spatial locations relative to ordered chains in bimolecular crystals. Because charge transfer and recombination processes are strongly dependent on local polymer ordering and composition we expect significantly different responses for each PBTTT form.50,51 Figure 7a presents the total integrated intensity of the ν₆,7 modes and corresponding photocurrent over the same area is shown in Figure 6b. Lower PBTTT intensity represents PCBM-rich areas, but an appreciable amount of PBTTT still exists in these regions indicating these are most likely bimolecular crystals. Because the PCBM loading of these devices is high (1:4 w/w), it is unlikely that PBTTT completely phase separates meaning the entire film corresponds to ordered and disordered mixed phases. Photocurrent images (Figure 7b) show much lower output in putative bimolecular crystal regions probably originating from unbalanced charge transport as expected from increased charge recombination.52,53

The PBTTT thiophene C=C stretch is now decomposed into its constituent components and Figures 7c,d shows fractional compositions of ordered (Iₖ)/I₆) and disordered ((I₅)/(I₆+I₅)) forms, respectively, using the same procedure described above. Comparison of these images with morphology-dependent frequency dispersion characteristics (Figure 7e, f, respectively) confirm that bimolecular crystals are indeed most concentrated in PCBM-rich regions (i.e., lower PBTTT intensities, Figure 7a). Although Raman signatures for PCBM are absent, direct excitation may lead to photocurrent from hole transfer to PBTTT from photoexcited PCBM. We measured photocurrent images on the same devices using 488 nm (2.54 eV) light, which is near the PBTTT absorption maximum, but identical behavior is observed (see the Supporting Information). The effects of excitation intensity and PCBM crystal size (annealing time) on local photocurrent production were also investigated and no significant differences were found (see Supporting Information). Interestingly, maximum photocurrent generation originates from regions with more disordered PBTTT content. We speculate that increased geminate charge recombination dominates in bimolecular crystals, which is consistent with previous TAS studies of PBTTT/PCBM thin films predominantly in the bimolecular crystal phase.

Raman and photocurrent images of as-cast PBTTT/PCBM (1:4 w/w) devices were also measured under the same conditions as annealed devices (see the Supporting Information). These devices generally show relatively uniform morphological features and photocurrent is at least an order of magnitude smaller than annealed devices when illuminating with a diffraction-limited laser spot.

Resonance Raman and photocurrent images have so far demonstrated that morphology-dependent variations in material performance are determined not only from the type and amounts of PBTTT species but also their spatial distributions in the device active layer. Intensity modulated photocurrent spectroscopy (IMPS) and imaging is next used to expose how specific conformers and morphologies impact loss mechanisms in PBTTT/PCBM devices, namely, charge recombination.

IMPS uses a small (~10%) sinusoidal modulation of the excitation source and the frequency is swept over several decades (typically, ~0.1 Hz up to ~1 MHz). Figure 8 shows IMPS ensemble spectra from annealed (Figure 8a, c) and as-cast (Figure 8b, d) PBTTT/PCBM (1:4 w/w) solar cells recorded by using a widefield configuration that illuminates the entire device active area (~20 mm²). Ensemble IMPS sweeps show similar behavior as reported previously in related polymer/fullerene solar cells and a characteristic maximum is observed in photocurrent sweeps and the phase decreases significantly in this region toward its maximum (~180°). photocurrents in the low frequency regime (~1 kHz) are almost entirely real and phase shifts are positive (~10°) for.
annealed devices indicating that charge carriers lead the modulation frequency. On the other hand, as-cast films typically show lower photocurrents and phase shifts start at \( \sim 0^\circ \). At larger modulation frequencies, both devices show increasingly negative phase shifts due to charge carriers lagging behind the modulation frequency.

Seminikhin and co-workers first reported positive phase shifts at low modulation frequencies or, a component in the first quadrant of the complex (Nyquist) IMPS plot from P3HT/PCBM devices.\(^{26}\) This feature has been attributed to nongeminate charge recombination that becomes more pronounced as the device ages. Luther and co-workers recently advanced this understanding by systematically studying device aging and preparation conditions and tracking IMPS responses.\(^{27}\) These authors showed that first quadrant photocurrent contributions in Nyquist plots, result from the formation of deep traps and introduced a drift-diffusion model to account for this behavior.\(^{27}\) The observation of positive phase shifts in the low-frequency modulation regime demonstrates that nongeminate recombination processes become operative in annealed PBTTT/PCBM devices indicating suppression of prevailing geminate recombination. The lack of this signature in as-cast devices (either fresh or aged) supports this view because geminate processes occur on faster time scales beyond what is currently accessible by IMPS techniques. Nonetheless, our ability to spatially correlate the formation of deep traps and introduced a drift-di logical boundaries using a hybrid IMPS imaging approach.

IMPS images were generated using the same high NA objective used for Raman and quasi-DC photocurrent images and are shown in Figure 9. Scan ranges were expanded to \( 20 \times 20 \mu m \) and laser modulation frequencies were held fixed throughout the scans using similar power densities as the quasi-DC photocurrent images shown in Figure 7. Several modulation frequencies were selected representing different charge transport and recombination regimes observed in ensemble IMPS spectra, namely, low frequency (e.g., 1 and 3 kHz), near the maximum frequency photocurrent (\( \sim 7 \) kHz) and at the high-frequency regime (\( \sim 9 \) kHz). PBTTT/PCBM blends were annealed for longer times in order to achieve greater phase separation that allows us to better resolve distinct phase boundaries. Similar to quasi-DC Raman and photocurrent images shown in Figure 7, bimolecular crystals in Figure 9 produce lower photocurrent output than the surrounding mixed phase. From the IMPS phase shift (\( \varphi \)) images, positive phase shift accumulates on the periphery of these regions. As the modulation frequency increases past the maximum, IMPS images lose contrast owing to carriers lagging behind the modulation. We infer that boundaries surrounding regions of positive phase shift (or, relative positive phase shift at higher modulation frequencies) represent recombination zones for nongeminate processes since separated electron–hole carriers can diffuse away from the interface before becoming trapped. In this case, trap sites are probably located at phase boundaries between ordered and disordered PBTTT regions, which is consistent with the current and phase maps (Figure 9). Despite loss of resolution at higher modulation frequencies, these results in general show that lateral diffusion effects are probably not significant since features of size scales comparable to the diffraction limit are resolvable.

On the basis of optical and Raman spectra of pristine PBTTT and PCBM blends, small energetic differences between ordered and disordered PBTTT species imply that charge traps are mostly shallow in nature. Troisi and co-workers reported “self-healing” phenomena occur in pristine PBTTT where facile detrapping of charges occurs due to small structural changes (\( \sim k_B T \)).\(^{28}\) However, greater disorder in blends probably results in deeper traps, which is evident from IMPS results. Although it is unclear if a similar self-healing mechanism is conceivable in PBTTT/PCBM solar cells, effective management of order–disorder boundaries through new molecular-level organization strategies may help overcome detrimental trapping effects.

![Figure 8. IMPS spectra (photocurrent and phase shift, \( \varphi \)) and Nyquist (complex) plots of (a, c) annealed and (b, d) as-cast PBTTT/PCBM (1:4 w/w) solar cells, respectively.](image)

![Figure 9. IMPS photocurrent (left) and phase shift (\( \varphi \), right) images of same area at 1 kHz, 3 kHz, 7 kHz, 9 kHz laser modulation frequency of annealed PBTTT/PCBM (1:4 w/w) device (excitation energy = 2.54 eV). Image scan area = 400 \( \mu m^2 \).](image)
Scheme 2. Proposed Morphology-Dependent Compositions in PBTTT/PCBM Films Shown in Figure 9 (see corresponding symbols in 1 kHz current image, top left)

4. CONCLUSIONS
We have shown that resonance Raman spectroscopy of PBTTT/PCBM blends can be used in a straightforward manner to extract the relative amounts of ordered and disordered PBTTT conformers. Both ordered and disordered components exist in a mixed phase but, the former are found in bimolecular crystals whereas the latter correspond to precursors of the ordered forms. The larger frequency and line width of disordered PBTTT chains in the bimolecular crystals also tend to twist although we point out that previous studies have shown that PBTTT chains in the bimolecular crystals also tend to twist around the intercalated fullerene but side group and para-crystalline disorder is reduced. This common structural trait shared between ordered and disordered PBTTT chains localizes excitations, hence, the invariance of Raman overtone-combination intensities with PCBM loading. Resonance Raman and photocurrent images next expose the morphology dependence of intercalation-induced order/disorder and its influence on local current generation. IMPS spectra and images showed evidence for increased nongeminate recombination at the boundaries between bimolecular crystals and disordered mixed zones. Overall, these experiments help bridge the gap in understanding of how ground-state structure and acceptor interactions influence the outcomes of excited state photovoltaic processes.

■ ASSOCIATED CONTENT
* Supporting Information
Absorption spectra and optical images of PBTTT/PCBM films under different annealing conditions, examples of resonance Raman spectral fits, photocurrent images of different size PCBM regions and schematics, excitation intensity dependent photocurrent images, single molecule fluorescence images of PBTTT. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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