Ferroelectric Polymer Matrix for Probing Molecular Organization in Perylene Diimides

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Ⓢ *Supporting Information*

ABSTRACT: Ferroelectric films of poly(vinylidene fluoride-*co*-trifluoroethylene) (PVDF-TrFE) provide a controlled environment to study the aggregation tendency of functional molecules such as perylene diimides (PDIs). The local electric field and free volume confinement parameters offered by the matrix are tailored to study the organizational and assembly characteritics of molecular acceptors. The optical properties of planar and nonplanar PDIs in the ferroelectric polymer matrix were studied systematically over a wide range that encompassed the ferroelectric transition temperature. This approach provides valuable insight into the properties of molecular materials used in applications ranging from bulk heterostructure-based photovoltaics to nonlinear optical materials.
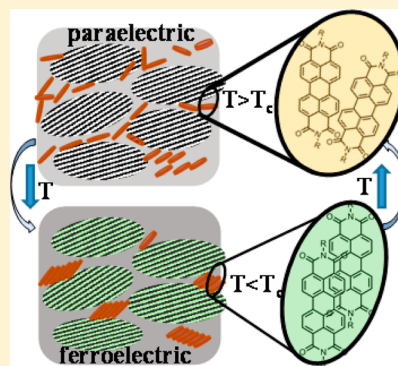
Thin films of semicrystalline ferroelectric (FE) polymers are a unique class of materials where the ordered FE phase coexists with the disordered amorphous phase. The FE ordering of the crystalline domain provides a strong local electric field that can be thermally tuned. Dispersal of a small fraction of chromophores in this polymer matrix opens up a platform to address important problems involving their molecular organization in confined volumes. Additionally, the effect of strong local fields on their aggregation can also be studied. Poly(vinylidene fluoride-*co*-trifluoroethylene) (PVDF-TrFE) in thin film form is a mixed-phase FE material ($T_c \approx 390$ K, $T_g \approx 253$ K) with crystalline domains predominating.[1,2] The FE phase generates high local electric fields that cannot be replicated by the application of an external field to an amorphous nonferroelectric matrix. When a blend of a small molecule and PVDF-TrFE is cast into a thin film from a uniform solution phase, the small molecules are likely to be confined in the amorphous phase. The simultaneous combination of confined space and temperature-dependent local electric field provides a valuable control over the aggregation behavior of the small molecule. Moreover, PVDF-TrFE does not absorb in the visible region. This enables the use of absorption spectroscopy to study the aggregation behavior of the embedded small molecule. As a case study, we investigated the aggregation behavior of perylene diimides (PDIs) embedded in this matrix.

Recent studies from our laboratories and other groups have been directed toward the design, synthesis, and study of PDIs as an alternative to fullerenes for bulk heterojunction (BHJ) organic photovoltaics (OPVs).[3−8] In the course of these studies, we identified a twisted perylene (TP, Chart 1) as a

viable electron transporter. The origin of bulk properties such as short-circuit current-density and fill-factor were attributed to the nonstacking propensity of TP.[3,5] TP is expected to have a disrupted stacking, while planar PDIs have a tendency to aggregate. However, the aggregation of these molecules in a donor assembly has not been resolved. This structural aspect is needed to understand the enhanced performance of nonplanar PDIs in BHJ solar cells.[9,10] Typically, dimer or higher-order aggregate formation modifies the relevant energy levels, and the effects can be clearly followed via absorption spectroscopy.[11] Aggregation of small molecules in a polymer matrix is influenced by the polymer's physical properties such as glass transition, free volume distribution, dielectric constant, and crystallinity.[12] The chain motion associated with the structural rearrangements of the host can strongly influence the aggregation and photophysics of the small molecules dispersed in the matrix.[13] It can also depend on innate properties of the small molecule like van der Waals interactions, molecular structure, hydrogen bonding, magnitude of dipole moments, and electrostatic interactions.[14,15] The PDIs chosen for the present studies (Chart 1) have negligible dipole moments (<1 D, estimated by DFT calculations, Table S1 and Figure S5 in the Supporting Information) but have large quadrupole moments. Absence of dipole moment reduces the tendency of these molecules to align in antiparallel pairs. Under an electric field, a random bulk of quadrupolar dyes can give rise to

Chart 1. Structures of Perylenes Used in This Study

Planar Perylene (PP)
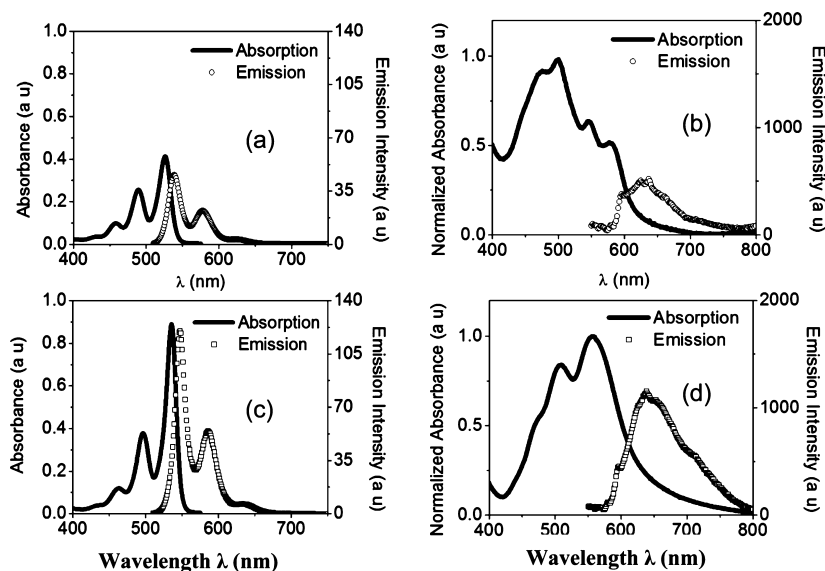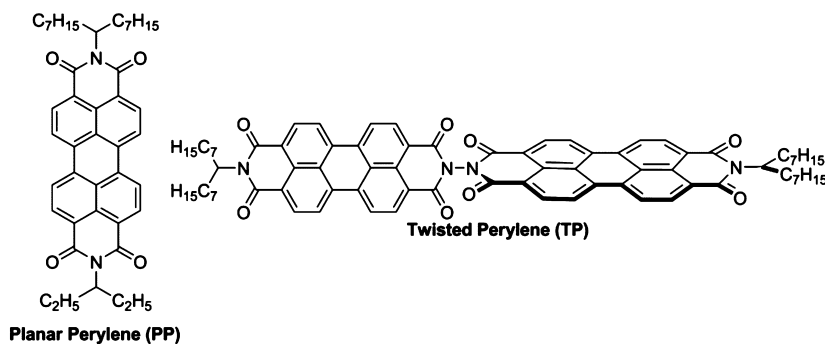
Twisted Perylene (TP)

Figure 1. Absorption and fluorescence spectra of (a) PP in toluene, (b) PP:PDVF-TRFE film, (c) TP in toluene, and (d) TP:PDVF-TRFE film, with $\lambda_{excitation}$= 470 nm for all emission spectra and at 300 K. Concentration of PP and TP in solution was 5 μg/mL corresponding to molar concentration of 7.4×10^{-6} M and 4.2×10^{-6} M for PP and TP, respectively, whereas the concentration in film was 0.62 wt %. (See the Supporting Information.)

broad and red-shifted emission from a broken symmetry state.[16] Therefore, the aggregation of these small molecules in a polymer matrix is dependent on the structural features of the matrix as well as the small molecule. PVDF-TrFE provides a unique platform for delineating the features responsible for aggregation due its temperature-dependent FE properties. It is to be noted that application of an external field to an amorphous nonferroelectric matrix does not appear to provide an equivalent magnitude of local electric field density and confinement. By studying the temperature-dependent ($T < T_c$ as well as $T > T_c$) absorption and emission spectra in this matrix and comparing to similar spectra in a non-FE matrix, we have gleaned insights into the microstructure of polymer/PDI blends. Interesting counterintuitive features, such as the dramatic rise in PDI emission intensity as the film is heated and crosses T_c, provide insight into the microstructural organization and its energetics. Density functional theory (DFT) studies of these model systems also assist in arriving at a microscopic model for the organization of these model PDI systems in confined-polar environment along with the implications.

UV−vis absorption and fluorescence spectra of the PDIs in dilute toluene solutions were initially studied. Under these conditions, the molecules are expected to be disaggregated. The solution-phase absorption spectra (Figure 1) at low concen-

tration showed an excited state vibronic progression of 1400 cm^{-1} as evaluated from the peak positions of the S(0,0) and S(0,1) bands.[17] In the case of fluorescence, the vibronic spacing was 1300 cm^{-1}, indicating a difference in the ground-state level spacing. These vibronic features can be utilized to track the appearance of intermolecular interactions at higher concentration and when dispersed in the polymer matrices. We then evaluated the crystallinity of pristine PDI films using X-ray diffraction (XRD). For pristine PP, a clear 2θ of ~19° corresponding to an interplanar spacing of 0.45 nm was observed, indicating organization of molecules with a crystalline order (Figure S1 in the Supporting Information). An annealed film of pristine TP did not show any pronounced peak.

The organization of PP and TP was then studied in PVDF-TrFE. The dielectric constant of this polymer increases with temperature until T_c. As temperature is raised above T_c, the polymer chains undergo a structural rearrangement from polar all-trans (β-phase) form to the less polar alternating trans−gauche (tg+tg−) form (α-phase) along with a reduction in the bulk dielectric constant.[1,2] The dielectric constant $\varepsilon_r(T)$ was measured over a wide temperature range ($70 < T < 400$ K). In the paraelectric (PE) phase where the polarization is absent, the polymer retains its semicrystalline nature with a 10% increase in lattice spacing.[18] Both PDI molecules reveal aggregation in the PVDF-TrFE matrix as evidenced by the considerable

modification of the absorption spectrum and red shifting of emission, as shown in Figure 1. The concentration dependence of the PP absorption spectra in a polar solvent such as butanone also indicates a modification in the absorption spectrum, as shown in Figure S2 in the Supporting Information. Additionally, this resembles the absorption spectrum of a thin film of pristine PP, which shows crystalline order (vide supra). In the molecular excitonic framework, the molecular ground-state photophysics is strongly correlated with the relative orientation of the molecules.[19] The red shift of the onset of absorption spectra is attributed to the aggregation of the molecules, which delocalizes the ground-state wave function over a cluster of molecules.[20] In emission spectra, clustering results in modification of spectral features such as the peak position and area under the bands. The emission spectrum of TP:PVDF-TrFE is significantly different from that of TP in toluene and is indicative of TP cluster formation. The modifications of the absorption spectrum for TP in the solid matrix indicate that a significant fraction of TP molecules are in close physical proximity in the ground state, despite the disrupted stacking.

To better understand the role of the FE matrix in the above experiments, we resorted to control experiments with poly-(methyl methacrylate) (PMMA) as a nonferroelectric matrix. In the case of PMMA, ε_r ($\approx$ 3) is temperature-independent over a wide T range.[1,21,22] Figure S3 in the Supporting Information shows the absorption and fluorescence spectra (excitation at 473 nm) of PP and TP in this matrix at room temperature (300 K). The absorption spectrum of PP:PMMA films retains the rich vibronic features observed for molecules in dilute solution (Figure 1). For PP molecules in PMMA matrix, the ratio of the intensities of (0,0) and (0,1) emission bands ($I(0,0)/I(0,1)$) is less than unity, indicating a low degree of clustering. In the case of TP:PMMA film, a broader red-shifted spectrum superimposed with vibrational features is obtained. This is in sharp contrast with the spectrum obtained in dilute solution (Figure 1). The emission spectra of TP:PVDF-TrFE and TP:PMMA are significantly different from that of TP monomers and are indicative of TP cluster formation.

As previously mentioned from X-ray studies, pristine PP films exhibit crystallinity. These trends suggest that dispersion of PP in PVDF-TrFE results in the formation of crystalline domains of PP. It is interesting to note that PP shows features of aggregate absorption only in the PVDF-TrFE matrix, unlike TP, which shows aggregated absorption in both PMMA and PVDF-TrFE. The absorption spectrum does not vary on changing the matrix for TP. This behavior of TP can be attributed to its molecular geometry and dimensions that prevent it from getting uniformly dispersed in the matrix. Alternatively, this could also be due to solvent exclusion factors in the early stages of film drying. However, this clustering does not result in large-scale aggregation through π-stacking interactions. This can be gleaned from the fluorescence spectra of the perylenes when they are dispersed in PVDF-TrFE. For an equal number of perylene units in both the samples, it was found that the PL intensity of TP:PVDF-TrFE was ~2.5 times that of PP:PVDF-TrFE. This feature is possibly due to the nonplanar geometry of TP, which prevents large-scale aggregation. It should be noted that the PDI molecules are distributed and confined in the amorphous regions of the semicrystalline polymer PVDF-TRFE. This picture for associating the guest molecules with the amorphous regions in PVDF:TRFE can be justified by the following reasons: (i)

dilute quantity of PP in PMMA exhibits features of isolated molecules, whereas aggregate features are observed in PVDF:TRFE; (ii) FE property persists in PVDF:TRFE after inclusion of the guest molecules (Figure 2); (iii) XRD data
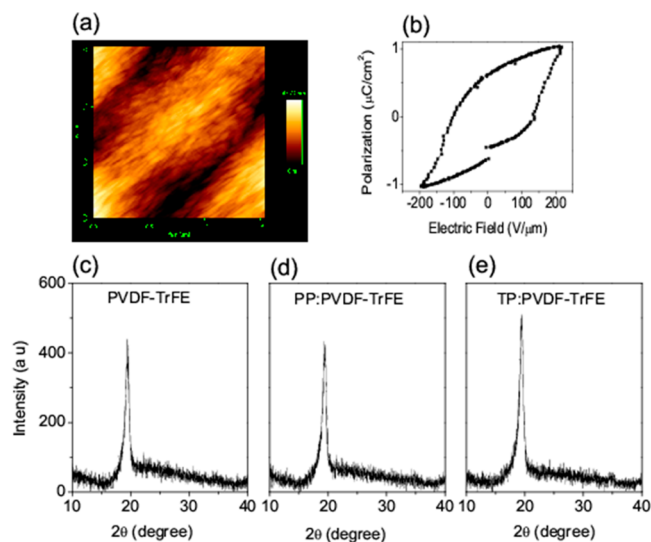

Figure 2. (a) Atomic force microscopy (AFM) image (1.5 × 1.5 μm^2) showing the ellipsoid-shaped crystallites of PVDF-TrFE in the FE phase. (b) Polarization−electric field curve showing the retention of polarization at zero applied electric field and XRD data obtained from annealed PVDF-TrFE (c) and PVDFTrFE dispersed with PP (d) and TP (e).

collected from annealed samples of PP:PVDF-TrFE and TP:PVDF-TrFE (Figure 2) show a diffraction peak at 2θ of ~20° corresponding to the crystalline FE phase;[18] and (iv) EFM, AFM, and confocal images depict profiles that are consistent with this interpretation.

To understand the effect of local electric field on the aggregation of PDI, we dispersed the perylenes in PVDF:TrFE, and their fluorescence spectra were recorded. PVDF-TrFE in the FE regime can hold a typical surface charge density of 10 μC/cm^2 and has been demonstrated as an effective source of polarization fields in the field-effect transistor geometry.[1] The internal electric field within the amorphous regions of PVDF:TrFE can have contributions from the remnant polarization ($P(r)$) from the collective bulk as well as from localized fields due to the polarized β-phase crystallites. In essence, the average field experienced by the PDI molecules in the amorphous regions is very high. For PVDF-TrFE (70:30), this internal field has been reported to be on the order of 10^8 V/m.[23] The high field can polarize the embedded molecules, and field-induced electrostatic interaction between the molecules plays an important role in their aggregation. The internal electric field dramatically reduces upon crossover to the PE region. It should be noted that such an electric-field magnitude and distribution cannot be achieved in pristine amorphous matrix like PMMA under external bias without a breakdown. The contributions from the electric field and confinement effects in PVDF:TRFE can be sorted out by carrying out temperature-dependent studies above and below T_c.

Fluorescence spectra of PP and TP in the FE polymer at 90 K are shown in Figure 3, while Figure 4 depicts the emission characteristics in the high-T range ($<T_c$ and $> T_c$ range). At $T =$
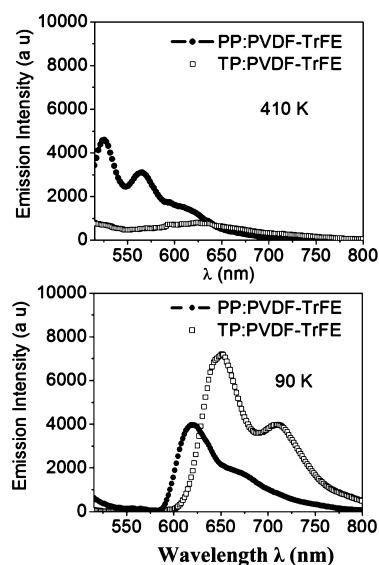
Figure 3. Emission spectra of PP:PVDF-TrFE and TP:PVDF-TrFE at 410 and 90 K.
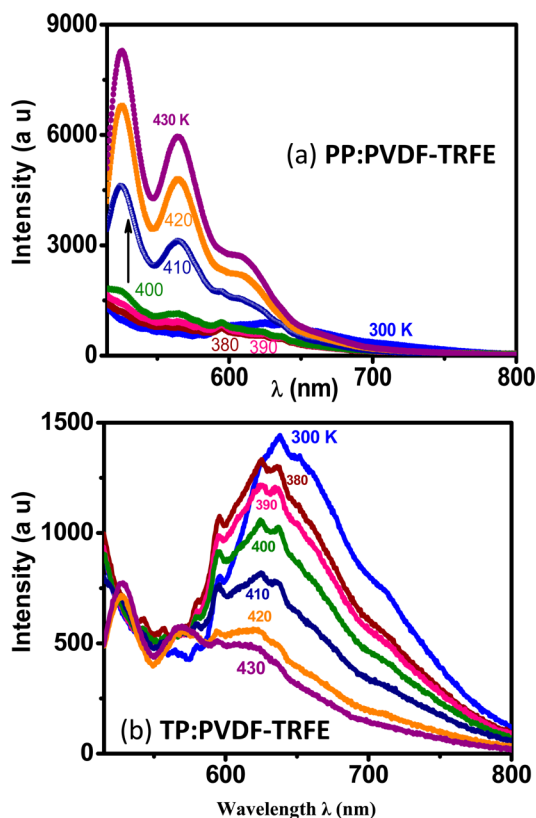

Figure 4. Temperature dependence of fluorescence emission of (a) PP:PVDF-TRFE and (b) TP:PVDFTRFE. Note the different Y-scale values.

90 K, monomer features were not observed in the emission spectra of both the systems. In this low T regime, the embedded molecules in the small amorphous volume exhibit significant intermolecular interaction, leading to a broad red-shifted emission for both TP and PP. This interaction via a strong exciton coupling between adjacent molecules can arise from the formation of excimers or aggregates. It has been reported that in this regime ($T < 100$ K) PDIs crystallites

indeed exhibit excimer type fluorescence at 630 nm.[24,25] However, in the present case, the existence of vibronic features in the emission and the observation of sizable red shift in comparison with monomer absorption point to the role of aggregates rather than excimers.[26] The formation of excimers requires a finite duration upon primary photoexcitation, and thus the absorption spectrum is not expected to change. Therefore, we attribute the intense emission to slip-stacked perylene molecules forming a highly emissive molecular chain during the shrinkage of the host polymer at low temperature. This is similar to the highly emissive supramolecular J aggregates reported by Würthner et al.[14] The formation of these emissive molecular chains upon matrix shrinkage clearly shows the initial confinement of the PDIs in the amorphous region of the matrix region. It is interesting to note the higher propensity of TP to stack linearly. A qualitative description of this organization is depicted in Figures 5 and 6.
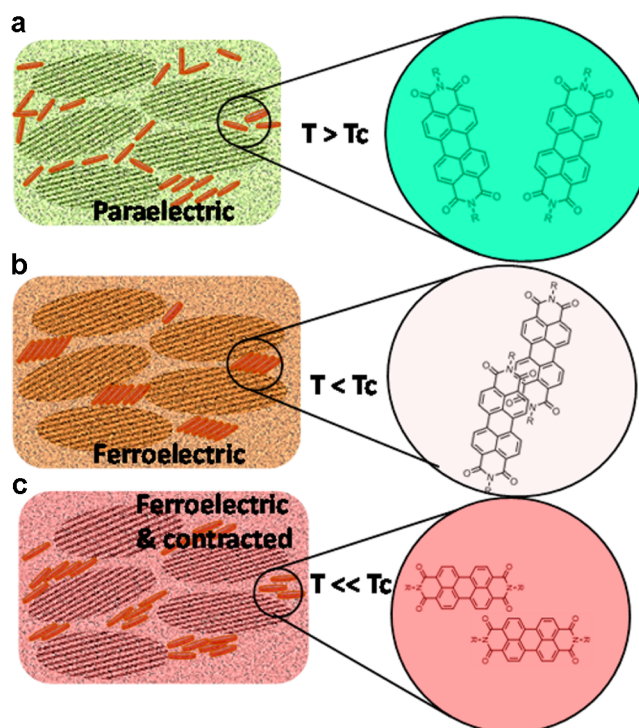

Figure 5. Depiction of PP molecular arrangement in the ferroelectric polymer matrix in the different temperature regimes: (a) High-temperature paraelectric phase of matrix depicting independent-dispersed PP. (b) Nonemissive aggregate state of PP molecules in the ferroelectric environment. (c) PP aggregate states in a contracted and ferroelectric matrix depicting red-shifted emissive stacking.

The high-temperature regime of the emission of PP in PVDF-TFE reveals a dramatic and interesting trend with the schematic describing the physical state depicted in Figure 5. In the temperature range of 385−400 K, a transition from FE to the high-temperature PE phase of the polymer is observed. This is accompanied by a sharp shift in the emission spectra and increase in the emission intensity. The PP emission switches to that of monomer states with a vibrational separation of ~1300 cm^{-1}, accompanied by a sharp increase in intensity as the matrix crosses over to the PE phase. In effect, the nonexistence of long-range FE order in the matrix results in the disaggregation of PP, as reflected in the emission spectra. The heating and cooling cycle in vacuum do not affect the
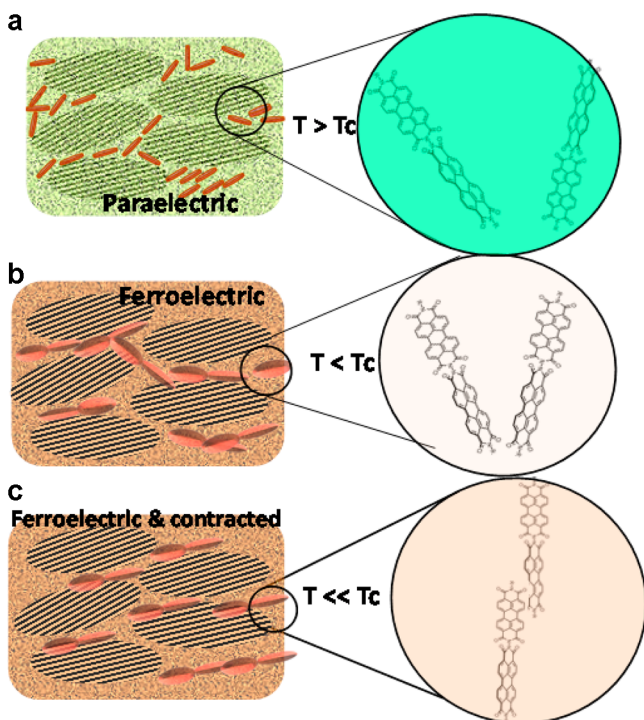
Figure 6. Depiction of TP molecular arrangement in the ferroelectric polymer matrix in the different temperature regimes: (a) High-temperature paralectric phase of matrix depicting loosely clustered TP. (b) Nonemissive aggregate state of TP clusters in the ferroelectric environment. (c) TP aggregate states in a contracted and ferroelectric matrix depicting red-shifted emissive linear stacking.

photophysical properties of the material, as evidenced by the completely reversible intensity change in the fluorescence shown in Figure S4 in the Supporting Information. This effect clearly shows that the aggregation of PP is dependent on the dielectric constant of the medium. Upon raising the temperature beyond T_c, the emission intensity increases, which indicates the increasing fraction of the monomer content. The increase in monomer fraction comes at the expense of the decrease in the crystallinity of the matrix in this temperature range. Figure 5 depicts the schematic of PP organization in PVDF-TFE in the different temperature regime.

In the case of TP in PVDF-TRFE, phase transition of the matrix is not accompanied by significant emission intensity increase or features indicative of abrupt onset of monomer emission (Figure 4). Instead, only a continuous decrease in the emission intensity with increasing temperature is observed in the (FE-PE) crossover regime. This behavior is equivalent to the PP behavior in PVDF-TrFE in the lower temperature regime of 80 to 300 K, as shown in Figure S6 in the Supporting Information. Apparently, the TP cluster does not get seriously affected by the changes in the electrostatic environment. It is to be noted that TP has a sizable quadrupole moment, and this factor may need to be taken into account to explain the spectral changes. (See Table S1 in the Supporting Information.) In T range beyond T_c, a blue shift in the spectra is observed. This is indicative of an increase in the monomer fraction. However, a situation where monomer emission dominates as compared with PP is not observed in TP. The cluster formation in TP primarily does indeed appear to be a stable configuration (schematic Figure 6). Temperature-dependent emission spectra were also carried out in PMMA matrix (Figure S3 in the

Supporting Information). We found that the PP molecules are well-dispersed, as expected in a low dielectric medium. However, the TP is present in a clustered state, and these clusters show an increase in emission intensity at the low-temperature regime.

One of the implications of the results is related to ongoing efforts in PDI-based BHJ solar cells.[27] A clearer picture about the phase separation and organization of TP in BHJ solar cell emerges. For example, an optimized interpenetrating network of donor and acceptor is essential for all efficient OPV cells relying on the BHJ concept. However, large-scale phase separation of perylenes due to crystallite formation is detrimental to device performance. As seen from the above results, TP appears to provide an optimal balance between phase separation and crystallite formation. The absorption studies in the two matrices show that formation of TP clusters is independent of the crystallinity and the dielectric constant of the polymer matrix. This should help in the phase separation of TP from the polymer matrix. At the same time, it appears that clustering does not lead to long-range ordering. The lack of crystallite formation probably prevents the formation inter-molecular states, which can lead to the decay of excitons generated in TP.

Comparative studies of two model PDI molecular systems dispersed in two different types of polymer matrix reveal a method to gauge intermolecular interactions and the role of local environment. The effects of symmetry and geometry of the molecule are highlighted by the tendency of TP to form clusters even at low levels of concentration along with the inability to form larger size domain. The symmetric planar PDI on the other hand forms a uniform molecular dispersion at dilute levels. The PP molecules embedded in the FE matrix exhibit intermolecular interaction effects that are promoted by the electric field, leading to characteristic stacking. The electrostatic contribution to the PP aggregate directly manifests as a dramatic emission spectral shift with a corresponding increase in intensity as T exceeds T_c. Beyond $T > T_c$, linear changes in the spectral profiles signify the volume expansion of the amorphous regions and the corresponding increase in intermolecular separation. We hope to utilize the understanding from these studies in controlling the morphology of a bulk heterostructure film and achieve efficient devices.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Details of spectroscopic studies, spectra, and theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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