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# Optical Properties of Blends: Influence of Mixing-Induced Disorder in Pentacene:Diindenoperylene versus Perfluoropentacene:Diindenoperylene

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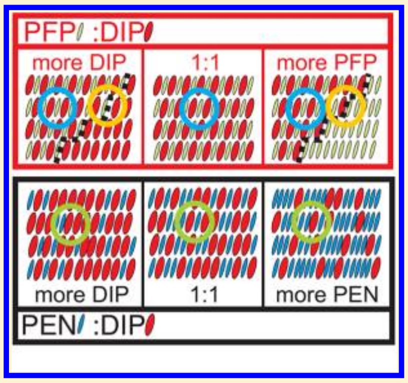
*Supporting Information*

**ABSTRACT:** The optical properties of mixed films of pentacene:diindenoperylene and perfluoropentacene:diindenoperylene in various mixing ratios are studied using spectroscopic ellipsometry and polarization dependent transmission spectroscopy. Compared to the spectra of films of the pure compounds, the absorption spectra of the blends are found to be significantly influenced by interactions of the comixed compounds and the mixing-induced disorder. On the basis of the comparison of the two mixed systems, we address the effects of mixing and ordering behavior on the specific optical transitions of the different blends by analyzing the line shape of the spectra and the energy positions and widths of the characteristic peaks. The results are important for a fundamental understanding of organic semiconductor blends and possible charge transfer effects in these systems relevant for device applications.



## INTRODUCTION

Blends of organic semiconductors have attracted increasing attention during the past years as they are functional parts in many organic optoelectronic devices such as organic solar cells.[1−4] For device optimization, the absorption and emission spectra and in particular their dependence on the structure of the mixed film are crucial. On a more fundamental level, investigations of the optical properties shed light on intermolecular interactions within the systems.[5] In particular, the degree of charge transfer (CT) in mixed films as studied in refs 6−11 is widely discussed using spectroscopic methods. Depending on the coupling strength, different scenarios are possible: (i) CT between materials A and B already in the ground state; (ii) CT in the excited state; (iii) very weak/no CT. Obviously, the structure and molecular orientation strongly influence not only CT phenomena but also the optical properties in general. Examples of this, mostly on single-compound films, are given in refs 12−16. In blends, there are different possible mixing scenarios,[5] from phase separation to cocrystals and various intermediate states.[17] This, in turn, leads to a potentially complex relationship between structure and optical properties, which is not understood on a fundamental level, despite its implications for device-relevant issues.

In this paper we investigate the optical properties of mixed films of pentacene (PEN, $C_{22}H_{14}$), perfluoropentacene (PFP, $C_{22}F_{14}$), and diindenoperylene (DIP, $C_{32}H_{16}$), three prototypical small-molecule organic semiconductors with relevance for applications.[5,18−25] We concentrate on blends of PEN:DIP and PFP:DIP. The optical properties of PFP:PEN blends, which are characterized by relatively strong coupling effects and a clear CT excitation, were already reported[10,11] and will be used for comparison.

A comparison of PEN:DIP blends with PFP:DIP blends provides the possibility to systematically address the influence of the film structure on the optical properties. While the pure compounds crystallize in a herringbone arrangement and are well-ordered in thin films, the ordering behavior observed for the mixed systems differs significantly.[17,26] Blends of PEN:DIP (Figure 1a) exhibit "frozen smectic-C" like structural order for the equimolar mixture; i.e., the films are almost perfectly ordered perpendicular to the substrate surface, but the structural order vanishes parallel to the substrate surface.[17] In the case of nonequimolar mixing ratios, a random replacement of lattice sites by minority molecules in the lattice of the majority compound is reported,[17] associated with an increase of in-plane order. This is in contrast to the mixing and ordering behavior described for PFP:DIP blends[26] (Figure 1b). PFP:DIP blends form a new crystal structure in the case of equimolar mixing ratios and exhibit phase separation between the new mixed crystal phase and the pure film phase of the excess compound for nonequimolar blends. Since for PFP:DIP blends the full crystal structure is not solved, it remains to be elucidated whether the molecules in the blend arrange in a herringbone structure. The same applies to blends of PEN:DIP, where the determination of the arrangement of the molecules is challenging due to the anomalous ordering behavior. We

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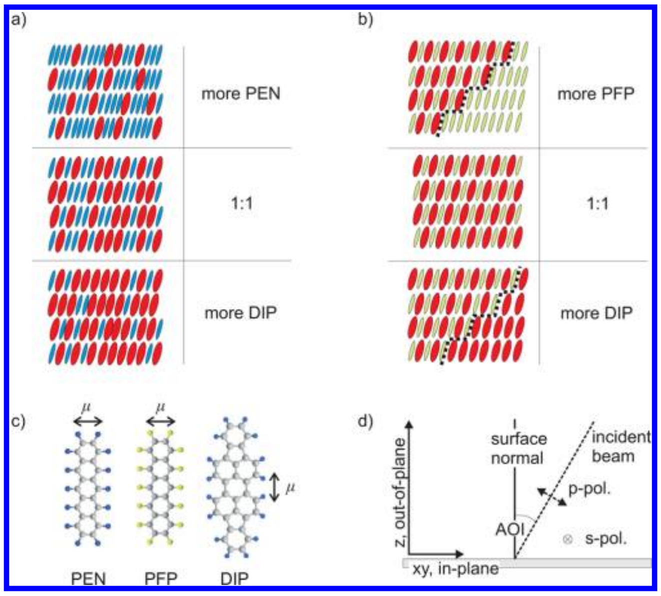

**Figure 1.** Schematic mixing scenarios for (a) PEN:DIP[17] and (b) PFP:DIP[26] depending on the mixing ratio. (c) Sketches of the molecules. The arrows indicate the orientation of the transition dipole moments of the respective HOMO−LUMO transitions. (d) Direction of the *E*-field vector for s- and p-polarization for oblique angle of incidence AOI (dotted lines) and definition of the directions *in-plane* and *out-of-plane* used in the text.

address the question which implications the observed differences in the mixing and ordering behavior have for the absorption spectra of the two systems, in particular regarding the line shape and energy positions of specific peaks.

The paper is organized as follows. After introducing the experimental methods, the absorption spectra of mixed films of PEN and DIP with various mixing ratios will be presented. By discussing our results considering the mixed film structure (for details see refs 17 and 26), we find that the spectral shape is strongly influenced by structural disorder. Finally, the optical properties of blends of PFP and DIP are shown, and the influence of mixing and ordering behavior on the absorption spectra of the two systems is discussed.

## ■ EXPERIMENTAL SECTION

We study mixed films containing PEN (purchased from Sigma-Aldrich, 99.9% purity) and DIP (purchased from Institut für PAH Forschung Greifenberg, Germany, 99.9% purity) or PFP (purchased from Kanto Denka Kogyo Co., 99% purity) and DIP. The samples were prepared by organic molecular beam deposition (OMBD)[27,28] similar to refs 11, 17, and 19 at a base pressure of $2 \times 10^{-10}$ mbar. In order to determine the optical properties with a multisample analysis,[30] the films were grown simultaneously on two silicon substrates covered with silicon oxide layers of different thickness $d_{\mathrm{SiOx}}$ (ThermSi, $d_{\mathrm{SiOx}}$ = 147 nm, and NativeSi, $d_{\mathrm{SiOx}}$ = 2 nm). We chose five different mixing ratios for both PEN:DIP and PFP:DIP blends (4:1, 2:1, 1:1, 1:2, and 1:4) with an estimated error of the stoichiometry of about 10% determined by the error of the quartz crystal microbalance. The substrate temperature was kept constant at 26 °C. Under these conditions PEN and DIP grow in the mixed films nearly upright standing relative to the substrate surface,[17] while a small amount of lying molecules may be present in PFP:DIP blends.[26] Detailed structural characterization was performed using X-ray scattering (see refs 17 and 26). The optical properties were investigated *ex situ* by variable angle spectroscopic ellipsometry (VASE) in the energy range from 1.5 to 3 eV using a Woollam M-2000 ellipsometer with rotating compensator.[30] Additionally, polarization-dependent transmission measurements were performed *ex situ* on a comparable series of samples grown on quartz glass using a PerkinElmer Lambda 900 spectrometer equipped with Glan−Taylor polarizers and a depolarizer using light polarized parallel (p) and perpendicular (s) to the plane of incidence. Three different angles of incidence (AOI) were selected for each mixed system. At oblique incidence, p-polarized light has a component of the electric field increasing with the AOI, which probes the out-of-plane direction. The data are corrected for the absorbance of the substrate, but not for the reflectance of the sample. In addition, a constant offset is subtracted for better comparison.

## ■ RESULTS AND DISCUSSION

**Blends of PEN and DIP.** *Absorbance at Different Angles of Incidence.* In order to provide an overview of the optical properties of PEN:DIP mixed films grown on glass, including possible anisotropies, the absorbance *A* of some of the samples is shown in the left column of Figure 2, including the simulated absorbance of the pure compounds based on refs 20 and 31. Together with the normal incidence spectra (AOI = 0°), also the oblique incidence (AOI = 30° and 60°) spectra are reported, as collected under p-polarization. As expected, the spectra collected under s-polarization exhibit perfect similarity with those collected at normal incidence. The absorbance of the two blends which are not shown follows a monotonic trend with changing mixing ratio.

Three main characteristic spectral ranges can be identified in the spectra in the left column of Figure 2: (i) below 2.2 eV with peaks at 1.9 and 2.0 eV; (ii) between 2.2 and 2.6 eV with the most representative and intense peak at about 2.5 eV; (iii) above 2.6 eV with peaks at 2.7 and 2.8 eV. The spectral ranges i and iii are clearly related to the spectral response of pure PEN and DIP films, respectively (see Figures 2a1 and 2e1).

In all the spectra of the PEN:DIP blends strong effects of the AOI on the measured spectral shape can be observed. The most pronounced effect is a decrease (increase) in intensity of peaks in range i (range iii) with increasing AOI, which can be found independently of the mixing ratio. This leads to the conclusion that the corresponding transition dipole moments are oriented nearly parallel (perpendicular) to the substrate surface. The transition dipole moment of the HOMO−LUMO transition of PEN (DIP) is indeed M (L) polarized[20,31,32] (see Figure 1c1). Since the molecules in the blends are arranged upright standing on the substrate surface, this result is in excellent agreement with the structural characterization of PEN:DIP blends reported in ref 17.

The mixed and the pure film spectra exhibit clear similarities but also significant differences in particular in the relative intensities. Compared to the pure film spectrum of PEN, the relative intensity of the peaks in spectral range i is significantly different and strongly changing with the mixing ratio (see Figure 2a1 and Figure 2b1−d1, left column). Also the two peaks in spectral range iii change with the mixing ratio not only in absolute but also in relative intensity. Remarkably, the intensity of the peak at 2.8 eV depends much stronger on the AOI in the blend than in the pure film (compare Figure 2d1 and Figure 2e1), which may indicate a change in the molecular arrangement. Finally, in the intermediate spectral range ii, where the spectral response of PEN and DIP are overlapping,

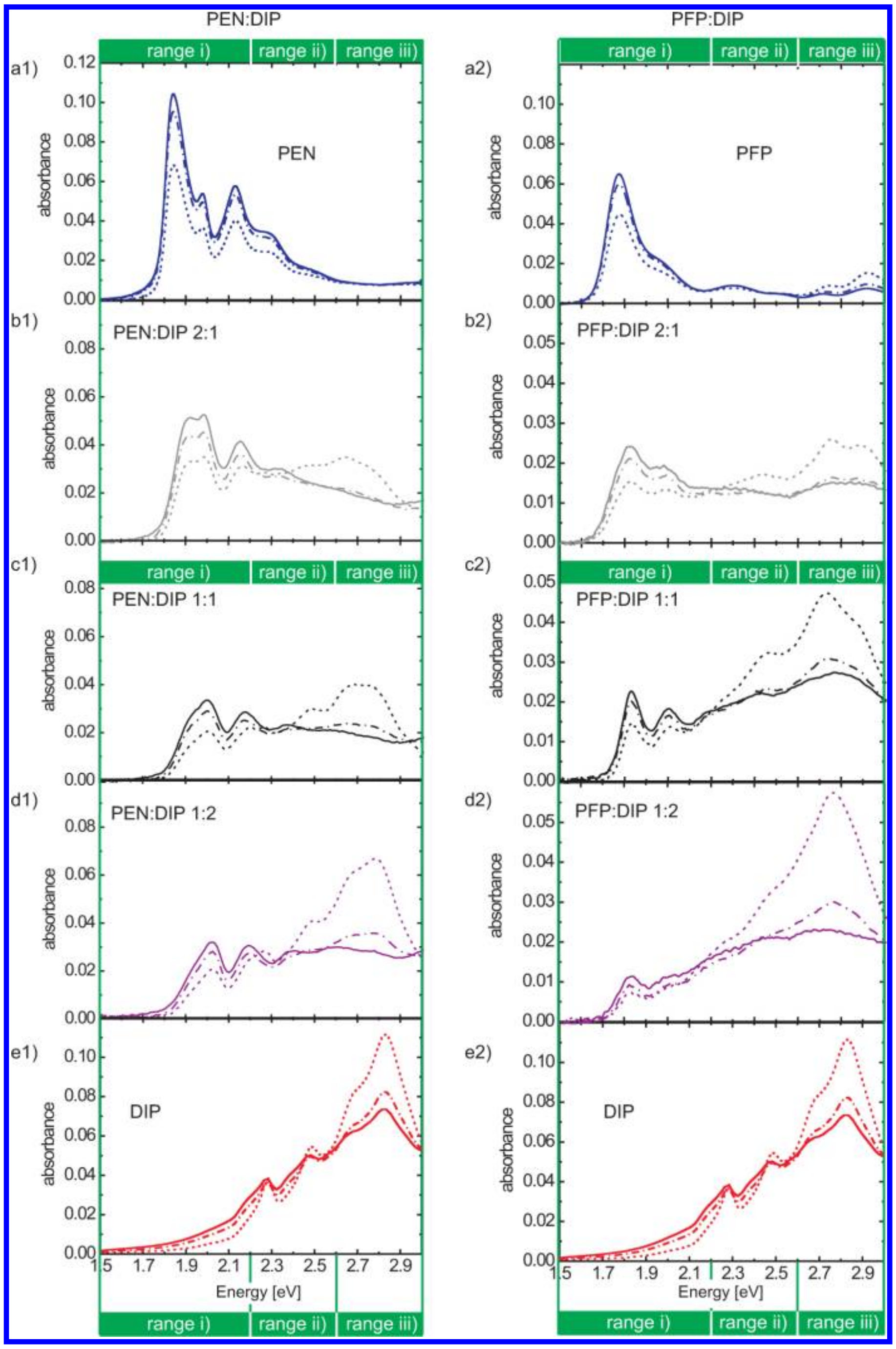

**Figure 2.** Left column: absorbance $A$ of (a1) pure PEN (simulated based on ref 20), (b1−d1) PEN:DIP blends with three different mixing ratios, and (e1) pure DIP (simulated based on ref 31). Right column: absorbance $A$ of (a2) pure PFP (simulated based on ref 20), (b2−d2) PFP:DIP blends with three different mixing ratios, and (e2) pure DIP (simulated based on ref 31). The green boxes illustrate the three spectral ranges i−iii mentioned in the text.

the peak at about 2.3 eV shifts slightly in energy position with changing AOI, indicating that it is composed of two transitions differing in the orientation of the transition dipole moments.

*Influence of the Film Structure on the Spectral Shape of $\varepsilon_{2,xy}(E)$.* The significant changes observable in the mixed film spectra with increasing AOI give evidence for anisotropic optical properties. Combining the results of oblique incidence transmission measurements and VASE measurements, we found uniaxial anisotropy (see Figure 1d) in agreement with the results of structural investigations,[17] which can be described by two dielectric functions $\varepsilon_i = \varepsilon_{i,1} + i\varepsilon_{i,2}$ $(i = xy, z)$.[33,34] We will refer to $\varepsilon_{xy}$ as the *in-plane component* (describing the optical properties in the substrate plane) and to $\varepsilon_z$ as the *out-of-plane component* (describing the optical properties perpendicular to the substrate plane) (see Figure 1d).

In order to determine $\varepsilon_{xy}$ and $\varepsilon_z$ independently, a multisample analysis using VASE data was performed as described in ref 30. The reliability of the results of this analysis was tested by simulating the absorbance at normal and oblique incidence. The simulated spectra resemble relatively well the experimental ones (see Supporting Information[41]), but the absolute intensity of $\varepsilon_z$ is strongly influenced by uncertainties in the film thickness. Since we found for the line shape of $\varepsilon_z$ only a weak dependence on the mixing ratio (see Supporting Information[41]), we will in the following restrict our discussion to $\varepsilon_{xy}(E)$ (see Figure 3).

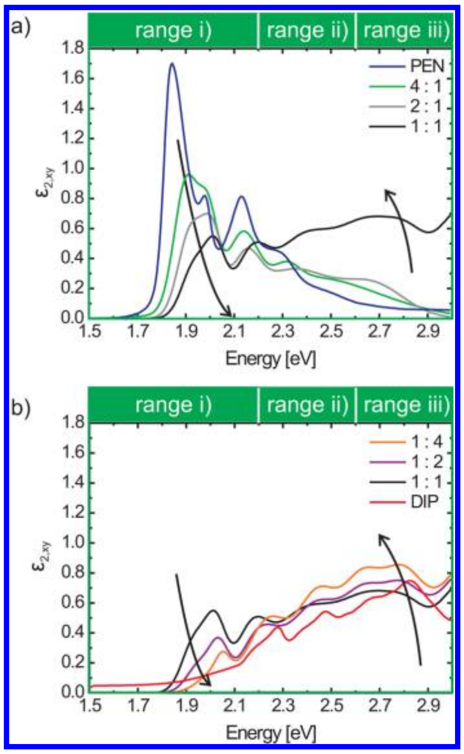

**Figure 3.** $\varepsilon_{2,xy}(E)$ of PEN:DIP thin films with different mixing ratios determined by VASE. The arrows indicate changes with increasing amount of DIP. Reference spectra of the pure films are taken from ref 20 (PEN) and ref 31 (DIP). (a) Mixing ratios PEN:DIP 4:1, 2:1, and 1:1. (b) Mixing ratios PEN:DIP 1:1, 1:2, and 1:4. The three spectral ranges i−iii correspond to the characteristic ranges identified in the absorbance spectra.

Similar to the absorbance also the shape of $\varepsilon_{2,xy}(E)$ changes continuously with the mixing ratio. The contributions of the pure film spectra of PEN and DIP can clearly be distinguished. For nonequimolar mixing ratios the spectral shape is dominated by the more abundant molecular species. However, there are significant differences observable regarding the relative intensities of the peaks (see arrows in Figure 3a,b). These differences might be caused by different intermolecular interactions due to differences in the molecular environment resulting from the presence of two compounds (PEN and DIP), different molecular orientations, and the influence of structural disorder in the blends and will be discussed in the following.

In range iii, which is dominated by the spectral response of DIP, the peak at 2.7 eV is part of the vibronic progression of the HOMO−LUMO transition of DIP, in contrast to the peak at 2.8 eV, which arises in pure films from intermolecular coupling between the DIP molecules.[31,35] In $\varepsilon_{2,xy}(E)$ of the blends, the relative intensity of these two peaks is different compared to their relative intensity in pure DIP films and changes with the mixing ratio. The differences can be rationalized by the presence of PEN in the blend and a comparably high degree of disorder present in the mixed films.[17] For blends containing more PEN, the interaction between DIP molecules is hindered by surrounding PEN molecules, so that the peak at 2.8 eV cannot be observed. On the contrary, this peak occurs for the PEN:DIP 1:4 mixture, where the interaction between DIP molecules is facilitated. The higher degree of disorder present in the blends affects the interactions between DIP molecules, resulting in a reduced intensity of the peak at 2.8 eV compared to that observed in the pure films.

The most remarkable influence of structural disorder on the spectral shape is found for the peaks at 1.9 and 2.0 eV in range i, which are related to the spectral response of PEN, although their positions are blue-shifted by 40 meV. In pure films the peak at 1.9 eV is very intense, and the peak at 2.0 eV can be observed as giving a less intense shoulder.[20] This is changed in the mixed films, where the intensities of the two peaks differ for the different mixing ratios (Figure 3). With increasing amount of DIP the overall intensity of the two peaks decreases and a change in the relative intensities is observed, as the peak at 1.9 eV becomes less intense compared to the peak at 2.0 eV and vanishes almost completely in the spectrum of the PEN:DIP 1:4 film.

The change in overall intensity of the two peaks with the mixing ratio is possibly caused by a changing amount of PEN in the mixed films, changes in the short-range order and in interactions between neighboring PEN molecules, but also by a probable change in the tilt angle of the molecules with the mixing ratio as reported in ref 17. The reason for the differences in the relative intensities is less obvious. In pure PEN films, the two peaks are related to two Davydov components originating from the HOMO−LUMO transition.[32,36] Therefore, a change of the intensities of these peaks points toward a change in the intermolecular interactions due to a change in the molecular arrangement in the mixed films compared to the pure films. From the comparison of $\varepsilon_{2,xy}(\mathrm{E})$ of PEN:DIP 4:1 and 2:1 blends with disordered PEN, reported in ref 12, one can even deduce that the crystalline order is significantly decreased in the blends. Although the present films do not exhibit the same thickness as those in ref 12, we find it worth pointing out that this interpretation of the shape of $\varepsilon_{2,xy}(E)$ is in remarkable agreement with the results of structural investigations of PEN:DIP mixed films, which were discussed in ref 17. There, independent of the mixing ratio, a lower crystallinity of the films was found with a complete vanishing of in-plane order for the equimolar mixture.

The observation of two Davydov components in the highly disordered blends can be explained by short-range order,[12] since $\varepsilon_{2,xy}(E)$ is mainly influenced by nearest-neighbor interactions.[37] Furthermore, we observe a change in the relative intensities of the low- and high-energy Davydov components with the mixing ratio. It is not obvious why the high-energy Davydov component is more intense than the low-energy component in $\varepsilon_{2,xy}(E)$ of the PEN:DIP blends with mixing ratios 2:1, 1:1, 1:2, and 1:4. Yet, this behavior can be rationalized considering the origin of the peaks visible in the PEN single crystal absorption spectrum (see ref 32). Relevant for this work are absorption spectra for light polarized parallel to the a- and $b$-axis ($E\parallel a$ and $E\parallel b$), as in thin films of PEN a superposition of these two components is observed.[20]

There are two pronounced peaks observable for $E\parallel a$ ($E\parallel b$) at 1.82 and 2.10 eV (1.9 and 2.12 eV).[32] The first two peaks in $\varepsilon_{2,xy}(E)$ of the PEN:DIP blends can be assigned to the peaks at 1.82 eV ($E\parallel a$) and 1.97 eV ($E\parallel b$) in the single crystal absorption spectrum of pure PEN, with the former peak being the low-energy and the latter peak being the high-energy Davydov component.[20,32] The origin of the peaks at higher photon energies in the PEN single crystal spectrum, which are in $\varepsilon_{2,xy}(E)$ of the PEN:DIP blends overlapping with contributions from DIP, is still under debate.[20,38−40] They are either assigned to arise from charge transfer between neighboring PEN molecules[38] or attributed to vibronic replica of the main electronic transition.[39,40] Both assignments allow to rationalize the behavior of the two Davydov components in $\varepsilon_{2,xy}(E)$ of the PEN:DIP blends with changing mixing ratio based on the reduced efficiency of charge transfer between neighboring PEN molecules in the blend compared with the pure PEN film due to the presence of DIP. For a detailed discussion see the Supporting Information.[41] This result is important in view of organic photovoltaic applications, where the dissociation of photoinduced excitons into charge transfer pairs at donor/acceptor interfaces is the first fundamental step.

Interestingly, the differences in the optical properties of the PEN:DIP blends compared to the pure films can almost completely be rationalized by the film structure, in particular the decrease in crystalline order, which results in changes in the intermolecular environment and, consequently, the intermolecular interactions. This of course does not rule out that other mechanisms may also be at work, which can only be elucidated by demanding theoretical calculations.

**Blends of PFP and DIP.** *Absorbance at Different Angles of Incidence.* Similar to PEN:DIP blends, the absorbance of PFP and DIP blends was measured (right column of Figure 2) to provide an overview of the optical properties. Three characteristic spectral ranges can be identified: (i) below 2.2 eV with peaks at about 1.8 and 2.0 eV, (ii) between 2.2 and 2.6 eV with one peak at 2.44 eV, and (iii) above 2.6 eV with the most representative and intense peaks at 2.7 and 2.8 eV. The spectral range i is clearly related to the spectral response of pure PFP, although the peak positions are blue-shifted of about 50 meV with respect to the pure PFP (see Figure 2a2). Note that PFP:DIP blends on $SiO_2$ exhibit a crystalline phase with lying PFP molecules.[26] This phase can make a contribution to the optical response mainly in spectral range iii with peaks at about 2.75 and 2.9 eV, overlapping with the optical response of DIP. Thus, the assignment of the peaks in the spectral ranges ii and iii of spectra collected at oblique AOI is less straightforward.

All mixing ratios exhibit a strong dependence of the spectral shape on the AOI, with no observable peak shifts, but changes in the relative intensities of transitions. Remarkably, the relative intensities of the two peaks in range i is notably different in the blends compared to the pure film. In addition, the peak at 2.0 eV increases in intensity relative to the peak at 1.82 eV with increasing AOI, which can be observed in the pure film spectrum only to a much lower degree. This observation will be discussed in more detail below.

The spectrum of the PFP:DIP 2:1 blend (Figure 2b2) resembles the pure PFP spectrum except for the change in relative intensities of the two peaks in spectral range i and the peak in range ii. The intensity of the peak at 2.44 eV increases notably with increasing AOI, indicating that the corresponding transition dipole moment is oriented rather perpendicular than parallel to the substrate surface. Since this peak becomes more pronounced with increasing amount of DIP (compare Figure 2b2−d2), we tentatively assign it to DIP. This is reasonable because the transition dipole moment of the HOMO−LUMO transition of DIP is L-polarized and DIP molecules are upright standing. This peak cannot be attributed to lying-down molecules because the peak intensity increases with AOI. In the spectral range iii the peaks at 2.76 and 2.88 eV can tentatively be assigned to PFP, as their relative intensities and energy positions are similar to the corresponding peaks in pure PFP, although a contribution from DIP (arising from the peak at 2.83 eV) cannot be excluded.

For the equimolar PFP:DIP mixture (Figure 2c2) we observe two broad peaks at 2.73 eV and around 2.86 eV in the spectral range iii where PFP and DIP contribute to the absorbance. As there is a very strong peak related to DIP at 2.83 eV, it is likely that the absorbance in this spectral region is composed of at least three contributions, two stemming from PFP and one from DIP.

Finally, the spectral shape of the PFP:DIP 1:2 blend (Figure 2d2) resembles pure DIP with some differences. The peaks in the spectral range i are still observed. In the spectral ranges ii and iii all peaks are significantly broadened compared to pure DIP or the other blends and their intensities exhibit a strong dependence on the AOI. There is only one peak at 2.76 eV clearly discernible in the spectral range iii, which is 30 meV blue-shifted from the corresponding peak in the equimolar mixture and may also stem from a superposition of contributions by PFP and DIP.

*Influence of the Film Structure on the Spectral Shape of $\varepsilon_{2,xy}(E)$.* Similar to the pure films and blends of PEN:DIP, also blends of PFP:DIP exhibit uniaxial anisotropic optical properties, as reported for the equimolar PFP:DIP mixture.[26] However, the mixing and ordering behavior is significantly different (Figure 1a). For the equimolar blend mixing on a molecular level with the formation of an intermixed crystal structure is observed, while there is phase separation between the intermixed crystal phase and the pure film phase of the excess compound found for nonequimolar blends. We determined the in-plane and out-of-plane component separately by a multisample analysis, but also in this case we restrict our discussion to $\varepsilon_{2,xy}(E)$, since the absolute intensity of this component can be determined most accurately. $\varepsilon_{2,z}(E)$ can be found in the Supporting Information[41] as well as a comparison of the absorbance and the VASE measurements.

Figure 4 shows $\varepsilon_{2,xy}(E)$ for PFP:DIP blends with five different mixing ratios. The data of the equimolar mixture are consistent with the results published in ref 26. In the following, we focus on the concentration dependence. The shape of $\varepsilon_{2,xy}(E)$ changes continuously with the mixing ratio, and the contributions of the pure films can still be discerned. Compared to the corresponding peaks in the pure film spectra, most of the peaks in the spectra of the blends are broadened probably due to inhomogeneities in the local molecular environment, caused by the polycrystallinity of the samples.[26]

For all mixing ratios there are two peaks observed in range i, which is related to the spectral response of PFP. In pure PFP these two peaks are either related to the two Davydov components of the HOMO−LUMO transition or to the HOMO−LUMO transition and a corresponding vibronic progression.[18,20] In the blends, their relative intensity is significantly different compared to the corresponding peaks in pure PFP, but only slightly changing with the mixing ratio. In contrast to blends of PEN:DIP, the change in the relative intensities in range i is not resulting from a decreased long-range order within the films, but possibly from the differences in the crystal structure in the blend compared to the pure film and the corresponding differences in molecular arrangement and local environment.[26] For blends with a higher PFP volume

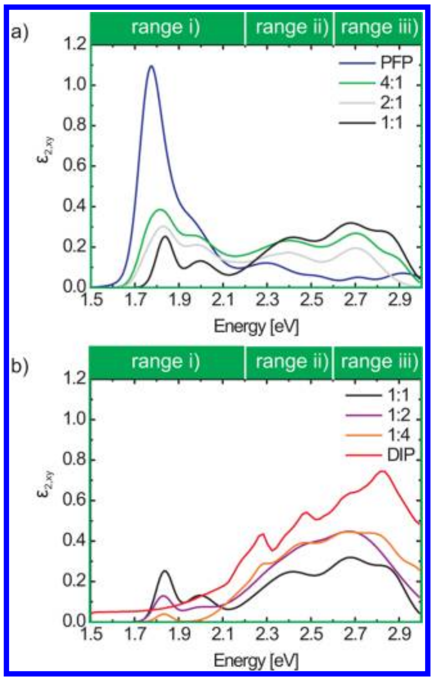

**Figure 4.** $\varepsilon_{2,xy}(E)$ of PFP:DIP mixed films. For comparison the pure film spectra from ref 20 (PFP) and ref 31 (DIP) are shown. (a) Mixing ratios PFP:DIP 4:1, 2:1, and 1:1. (b) Mixing ratios PFP:DIP 1:1, 1:2, and 1:4. The three spectral ranges i−iii correspond to the characteristic ranges identified in the absorbance spectra.

fraction, we observe a small shoulder at 1.74 eV, which influences the observed peak positions and widths and can be attributed to PFP due to its energy position.

The shapes of the spectra of blends containing more DIP show clear similarities to pure DIP, although the peaks are significantly broadened (Figure 4b). For $\varepsilon_{2,xy}(E)$ of the PFP:DIP 1:2 mixture almost no distinct peaks can be observed, but only very broad absorption features indicating a comparably high degree of disorder in the blends with a higher volume fraction of DIP, which is consistent with the results of X-ray scattering experiments.[26]

**Comparison.** In the following we further discuss our findings regarding the influence of film structure on the optical properties of blends by comparing the dependence of the spectral shape on the mixing ratio for the different systems. In order to complete and complement the study which was performed in ref 17, we shall also compare the spectra to those of PFP:PEN blends. The shape of $\varepsilon_{2,xy}(E)$ of this third possible combination of the molecules discussed here is significantly different[11] from $\varepsilon_{2,xy}(E)$ of the pure compounds, which makes it difficult to attribute specific peaks in the spectra of PFP:PEN blends to PFP or PEN. The spectra of the mixed films are strongly influenced by intermolecular interactions, including CT.[10,11] Interestingly, although PFP:DIP blends behave similarly to PFP:PEN blends regarding their mixing and ordering behavior and are expected to exhibit a comparably strong intermolecular interaction, we observe no CT between PFP and DIP using optical spectroscopy.[26] This may be due to the fact that the peak corresponding to the CT transition can be expected at higher energies and is possibly overlapping with the strong peaks assigned to pure PFP. This assumption is based on the larger energy difference between the HOMO state of DIP and the LUMO state of PFP[43] in comparison to the HOMO of PEN and the LUMO of PFP, which may potentially also increase the energy of a CT transition.

The dependence of the spectral line shape on the mixing ratio for blends of PEN:DIP and PFP:DIP exhibits several differences regarding the relative intensity of the first peaks in the spectral range i, which can be related to PEN and PFP, respectively. While the relative intensities of these peaks are strongly influenced by structural disorder or changes in the intermolecular interactions due to differences in the local molecular environment or a varying molecular tilt angle, their dependence on the mixing ratio is different. For blends of PEN and DIP the relative intensity of the first two peaks changes significantly, resulting in the observation of one peak with a weak shoulder for the mixing ratio PEN:DIP 1:4. For PFP:DIP blends, however, the change in relative intensity of these two peaks is very weak. This can be understood by differences in the mixed film structure (continuous mixing vs phase separation between a new crystal phase and the phase of the excess compound) of the two systems which influences the intermolecular interactions due to the differences in long-range order and local environment.

Finally, the dependence of the energy position of the first pronounced peak on the PEN (PFP) volume fraction for the two mixed systems (left panel of Figure 5) was investigated. Compared to pure PEN (PFP), the peak positions are significantly blue-shifted probably due to a change in the polarizability of the intermolecular environment in the mixed films. The dependence of the peak position on the mixing ratio is significanly different for the two systems. While the peak position shifts continuously for PEN:DIP blends, there is a clear maximum observable in the blue-shift for the equimolar PFP:DIP mixture. This behavior can be rationalized by the

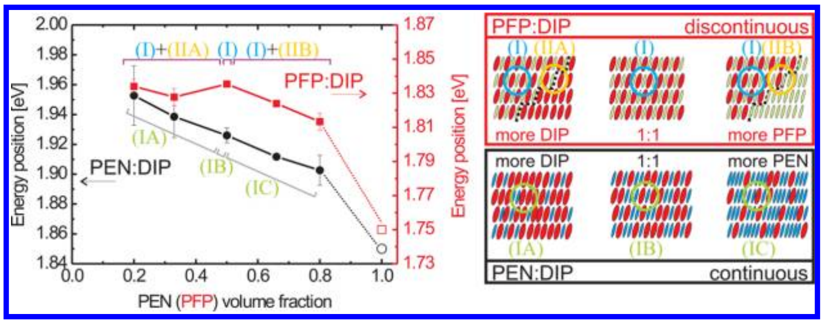

**Figure 5.** Left panel: energy position of the first pronounced peak in the mixed films of PEN:DIP (black dots) and PFP:DIP (red squares). Right panel: schematic mixing scenarios for the two systems depending on the mixing ratio as reported in refs 17 and 26 (see also Figure 1a,b). The circles highlight the presence of molecules with differing local molecular environment, which changes with the mixing ratio.

differences in the mixing and ordering behavior of the two systems as reported in refs 17 and 26.

In the following we will consider the molecular environment (blue circles (I) in Figure 5, upper row) of one specific PFP molecule (green) in a PFP:DIP blend. In the case of an equimolar mixture the molecule is surrounded equally by PFP or DIP molecules ((I) in Figure 5, upper row). The energy position of the first peak in the absorption spectrum of this molecule is blue-shifted compared to that of the same molecule in a pure film. This is due to the presence of DIP and the corresponding change in the polarizability of the intermolecular environment. For nonequimolar mixing ratios the environment of the molecule in the blue circle ((I) in Figure 5, upper row) is not changing. However, in this case there are PFP molecules at the boundary between the intermixed phase and the pure film phase of the excess compound (see orange circles, (IIA) or (IIB), in Figure 5, upper row). These molecules encounter a different local molecular environment depending on the excess compound ((IIA) or (IIB) in Figure 5, upper row), which leads to an additional blue-shift of the first peak. The superposition of both effects ((I) and (IIA) or (IIB) in Figure 5, upper row) results in a nonmonotonic shift of the first peak with the mixing ratio.

The scenario differs significantly for one specific PEN molecule (blue) in a PEN:DIP blend (green circles in the right panel of Figure 5, lower row). In the equimolar blend the PEN molecule is randomly surrounded by PEN and DIP molecules ((IB) in Figure 5, lower row). Therefore, the energy position of the first peak in the absorption spectrum of this molecule is blue-shifted compared to that of the same molecule in a pure film. For nonequimolar mixing ratios there is no phase separation between the intermixed phase and the pure phase of the excess compound,[17] which is in contrast to blends of PFP:DIP. The local environment of a given molecule in the PEN:DIP blends changes continuously with the mixing ratio from PEN dominated ((IA) in Figure 5, lower row) to DIP dominated ((IC) in Figure 5, lower row). Because of this continuous change, also the polarizability is expected to change continuously, resulting in a continuous shift of the energy position.

## CONCLUSION

To conclude, we investigated the optical properties of mixed films of PEN:DIP and PFP:DIP with various mixing ratios. We compared the line shape of the spectra and its dependence on the mixing ratio for the two systems. Although PFP and DIP are expected to exhibit strong and favorable interaction, interestingly, no strong signatures of charge transfer in the absorption spectra of the mixed films are observed. This is in contrast to blends of PFP and PEN, where the absorption spectra are dominantly influenced by intermolecular interactions[10,11] and may be due to the relative position of HOMO and LUMO for PFP and DIP, respectively. For blends of the weakly interacting compounds PEN and DIP we observed significant differences between the absorption spectra of the mixed and the pure films, in particular regarding the relative intensities of two Davydov components of the HOMO−LUMO transition related to PEN. Importantly, these differences can be explained largely by the mixing-induced structural disorder in the blends and the reduced efficiency of CT between neighboring PEN molecules.

Finally, the differences in the local molecular environment, resulting from the different mixing and ordering behavior of the two systems, were found to influence the energy position of the first observable peak in the absorption spectra and its dependence on the mixing ratio. While the local molecular environment changes continuously for PEN:DIP blends, the scenario is more complex for blends of PFP and DIP, in particular for nonequimolar mixing ratios. Accordingly, we observed for PEN:DIP blends a continuous shift of energy position, while in blends of PFP:DIP a maximum energy shift was found for the equimolar mixture. Our findings illustrate the influence of the film structure on the optical properties of blends. Furthermore, they point towards the possibility to tune the efficiency of CT between neighboring molecules of one compound (e.g., PEN) by adding another weakly interacting compound. These results are not only relevant for device applications, where the dissociation of photoinduced excitons into charge transfer pairs at donor/acceptor interfaces is the first step, but may also contribute to a deeper understanding of CT processes themselves.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

Discussion of the relative intensities of the two Davydov components in $\varepsilon_{2,xy}(E)$ of PEN:DIP blends, $\varepsilon_{2,z}(E)$ of PEN:DIP and PFP:DIP blends, and comparison of absorbance and VASE data. 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.

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## REFERENCES

(1) Brütting, W., Adachi, C., Eds. *Physics of Organic Semiconductors*; Wiley-VCH: Weinheim, 2012.

(2) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028−5048.

(3) Wagner, J.; Gruber, M.; Hinderhofer, A.; Wilke, A.; Bröker, B.; Frisch, J.; Amsalem, P.; Vollmer, A.; Opitz, A.; Koch, N.; et al. High Fill Factor and Open Circuit Voltage in Organic Photovoltaic Cells with Diindenoperylene as Donor Material. *Adv. Funct. Mater.* **2010**, *20*, 4295−4303.

(4) Kendrick, M. J.; Neunzert, A.; Payne, M. M.; Purushothaman, B.; Rose, B. D.; Anthony, J. E.; Haley, M. M.; Ostroyerkhova, O. Formation of the Donor-Acceptor Charge-Transfer Exciton and Its Contribution to Charge Photogeneration and Recombination in Small-Molecule Bulk Heterojunctions. *J. Phys. Chem. C* **2012**, *116*, 18108−18116.

(5) Hinderhofer, A.; Schreiber, F. Organic-Organic Heterostructures: Concepts and Applications. *ChemPhysChem* **2012**, *13*, 628−643.

(6) Veldman, D.; Ipek, O.; Meskers, S. C. J.; Sweelssen, J.; Koetse, M. M.; Veenstra, S. C.; Kroon, J. M.; van Bavel, S. S.; Loos, J.; Janssen, R. A. J. Compositional and Electric Field Dependence of the Dissociation of Charge Transfer Excitons in Alternating Polyfluorene Copolymer/Fullerene Blends. *J. Am. Chem. Soc.* **2008**, *130*, 7721−7735.

(7) Veldman, D.; Meskers, S. C. J.; Janssen, R. A. J. The Energy of Charge-Transfer States in Electron Donor-Acceptor Blends: Insight

into the Energy Losses in Organic Solar Cells. *Adv. Funct. Mater.* **2009**, *19*, 1939−1948.

(8) Ruani, G.; Fontanini, C.; Murgia, M.; Taliani, C. Weak Intrinsic Charge Transfer Complexes: A New Route for Developing Wide Spectrum Organic Photovoltaic Cells. *J. Chem. Phys.* **2002**, *116*, 1713−1719.

(9) Benson-Smith, J. J.; Goris, L.; Vandewal, K.; Haenen, K.; Manca, J. V.; Vanderzande, D.; Bradley, D. D. C.; Nelson, J. Formation of a Ground-State Charge-Transfer Complex in Polyfluorene/[6,6]-Phenyl-C61 Butyric Acid Methyl Ester (PCBM) Blend Films and Its Role in the Function of Polymer/PCBM Solar Cells. *Adv. Funct. Mater.* **2007**, *17*, 451−457.

(10) Anger, F.; Ossó, J. O.; Heinemeyer, U.; Broch, K.; Scholz, R.; Gerlach, A.; Schreiber, F. Photoluminescence Spectroscopy of Pure Pentacene, Perfluoropentacene, and Mixed Thin Films. *J. Chem. Phys.* **2012**, *136*, 0547011−0547018.

(11) Broch, K.; Heinemeyer, U.; Hinderhofer, A.; Anger, F.; Scholz, R.; Gerlach, A.; Schreiber, F. Optical Evidence for Intermolecular Coupling in Mixed Films of Pentacene and Perfluoropentacene. *Phys. Rev. B* **2011**, *83*, 2453071−2453075.

(12) Hesse, R.; Hofberger, W.; Bässler, H. Absorption Spectra of Disordered Solid Tetracene and Pentacene. *Chem. Phys.* **1980**, *49*, 201−211.

(13) Opitz, A.; Wagner, J.; Brütting, W.; Hinderhofer, A.; Schreiber, F. Molecular Semiconductor Blends: Microstructure, Charge Carrier Transport, and Application in Photovoltaic Cells. *Phys. Status Solidi A* **2009**, *206*, 2683−2694.

(14) Sakurai, T.; Fukasawa, R.; Saito, K.; Akimoto, K. Control of Molecular Orientation of Organic p-i-n Structures by Using Molecular Templating Effect at Heterointerfaces. *Org. Electron.* **2007**, *8*, 702−708.

(15) Yoshida, Y.; Takiguchi, H.; Hanada, T.; Tanigaki, N.; Han, E.-M.; Yase, K. Control of Growth Mechanism and Optical Properties of P-Sexiphenyl Thin Films on Ionic Crystal Substrates. *J. Cryst. Growth* **1999**, *198*, 923−928.

(16) Heutz, S.; Sullivan, P.; Sanderson, B.; Schultes, S. M.; Jones, T. S. Influence of Molecular Architecture and Intermixing on the Photovoltaic, Morphological and Spectroscopic Properties of CuPc:C60 Heterojunctions. *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 229−245.

(17) Aufderheide, A.; Broch, K.; Novák, J.; Hinderhofer, A.; Nervo, R.; Gerlach, A.; Banerjee, R.; Schreiber, F. Mixing-Induced Anisotropic Correlations in Molecular Crystalline Systems. *Phys. Rev. Lett.* **2012**, *109*, 1561021−1561025.

(18) Breuer, T.; Witte, G. Epitaxial Growth of Perfluoropentacene Films with Predefined Molecular Orientation: A Route for Single-Crystal Optical Studies. *Phys. Rev. B* **2011**, *83*, 1554281−1554288.

(19) Götzen, J.; Schwalb, C. H.; Schmidt, C.; Mette, G.; Marks, M.; Höfer, U.; Witte, G. Structural Evolution of Perfluoro-Pentacene Films on Ag(111): Transition from 2D to 3D Growth. *Langmuir* **2011**, *27*, 993−999.

(20) Hinderhofer, A.; Heinemeyer, U.; Gerlach, A.; Kowarik, S.; Jacobs, R. M. J.; Sakamoto, Y.; Suzuki, T.; Schreiber, F. Optical Properties of Pentacene and Perfluoropentacene Thin Films. *J. Chem. Phys.* **2007**, *127*, 1947051−1947056.

(21) Breuer, T.; Celik, M. A.; Jakob, P.; Tonner, R.; Witte, G. Vibrational Davydov Splittings and Collective Mode Polarizations in Oriented Organic Semiconductor Crystals. *J. Phys. Chem. C* **2012**, *116*, 14491−14503.

(22) Schmidt, C.; Breuer, T.; Wippermann, S.; Schmidt, W. G.; Witte, G. Substrate Induced Thermal Decomposition of Perfluoro-Pentacene Thin Films on the Coinage Metals. *J. Phys. Chem. C* **2012**, *116*, 24098−24106.

(23) Salzmann, I.; Duhm, S.; Heimel, G.; Rabe, J. P.; Koch, N.; Oehzelt, M.; Sakamoto, Y.; Suzuki, T. Structural Order in Perfluoropentacene Thin Films and Heterostructures with Pentacene. *Langmuir* **2008**, *24*, 7294−7298.

(24) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. Perfluoropentacene: High-Performance p-n Junctions and Complementary Circuits with Pentacene. *J. Am. Chem. Soc.* **2004**, *126*, 8138−8140.

(25) Dürr, A. C.; Schreiber, F.; Münch, M.; Karl, N.; Krause, B.; Kruppa, V.; Dosch, H. High Structural Order in Thin Films of the Organic Semiconductor Diindenoperylene. *Appl. Phys. Lett.* **2002**, *81*, 2276−2278.

(26) Reinhardt, J. P.; Hinderhofer, A.; Broch, K.; Heinemeyer, U.; Kowarik, S.; Vorobiev, A.; Gerlach, A.; Schreiber, F. Structural and Optical Properties of Mixed Diindenoperylene:Perfluoropentacene Thin Films. *J. Phys. Chem. C* **2012**, *116*, 10917−10923.

(27) Schreiber, F. Organic Molecular Beam Deposition: Growth Studies Beyond the First Monolayer. *Phys. Status Solidi A* **2004**, *201*, 1037−1054.

(28) Witte, G.; Wöll, C. Growth of Aromatic Molecules on Solid Substrates for Applications in Organic Electronics. *J. Mater. Res.* **2004**, *19*, 1889−1916.

(29) Hinderhofer, A.; Frank, C.; Hosokai, T.; Resta, A.; Gerlach, A.; Schreiber, F. Structure and Morphology of Coevaporated Pentacene-Perfluoropentacene Thin Films. *J. Chem. Phys.* **2011**, *134*, 1047021−1047028.

(30) Heinemeyer, U.; Hinderhofer, A.; Alonso, M. I.; Ossó, J. O.; Garriga, M.; Kytka, M.; Gerlach, A.; Schreiber, F. Uniaxial Anisotropy of Organic Thin Films Determined by Ellipsometry. *Phys. Status Solidi A* **2008**, *205*, 927−931.

(31) Heinemeyer, U.; Scholz, R.; Gisslén, L.; Alonso, M. I.; Ossó, J. O.; Garriga, M.; Hinderhofer, A.; Kytka, M.; Kowarik, S.; Gerlach, A.; Schreiber, F. Exciton-Phonon Coupling in Diindenoperylene Thin Films. *Phys. Rev. B* **2008**, *78*, 0852101−08521010.

(32) Dressel, M.; Gompf, B.; Faltermeier, D.; Tripathi, A.; Pflaum, J.; Schubert, M. Kramers-Kronig Consistent Optical Functions of Anisotropic Crystals: Generalized Spectroscopic Ellipsometry on Pentacene. *Opt. Express* **2008**, *16* (No. 24), 19770−19778.

(33) Ossó, J. O.; Schreiber, F.; Kruppa, V.; Dosch, H.; Garriga, M.; Alonso, M. I.; Cerdeira, F. Controlled Molecular Alignment of Phthalocyanine Thin Films on Stepped Sapphire Surfaces. *Adv. Funct. Mater.* **2002**, *12*, 455−460.

(34) Alonso, M. I.; Garriga, M.; Karl, N.; Ossó, J. O.; Schreiber, F. Anisotropic Optical Properties of Single Crystalline PTCDA Studied by Spectroscopic Ellipsometry. *Org. Electron.* **2002**, *3*, 23−31.

(35) Heinemeyer, U.; Broch, K.; Hinderhofer, A.; Kytka, M.; Scholz, R.; Gerlach, A.; Schreiber, F. Real-Time Changes in the Optical Spectrum of Organic Semiconducting Films and Their Thickness Regimes during Growth. *Phys. Rev. Lett.* **2010**, *104*, 2574011−2574014.

(36) Helzel, J.; Jankowski, S.; El Helou, M.; Witte, G.; Heimbrodt, W. Temperature Dependent Optical Properties of Pentacene Films on Zinc Oxide. *Appl. Phys. Lett.* **2011**, *99*, 2111021−2111023.

(37) Lim, S.-H.; Bjorklund, T. G.; Spano, F. C.; Bardeen, C. J. Exciton Delocalization and Superradiance in Tetracene Thin Films and Nanoaggregates. *Phys. Rev. Lett.* **2004**, *92*, 1074021−1074024.

(38) Sebastian, L.; Weiser, G.; Bässler, H. Charge Transfer Transitions in Solid Tetracene and Pentacene Studied by Electroabsorption. *Chem. Phys.* **1981**, *61*, 125−135.

(39) Haas, S.; Matsui, H.; Hasegawa, T. Field-Modulation Spectroscopy of Pentacene Thin Films Using Field-Effect Devices: Reconsideration of The Excitonic Structure. *Phys. Rev. B* **2010**, *82*, 1613011(R)−1613014(R).

(40) Yamagata, H.; Norton, J.; Hontz, J.; Olivier, Y.; Beljonne, D.; Brédas, J. L.; Silbey, R. J.; Spano, F. C. The Nature of Singlet Excitons in Oligoacene Molecular Crystals. *J. Chem. Phys.* **2011**, *134*, 2047031−20470311.

(41) See the Supporting Information for a discussion of the relative intensities of the two Davydov components in $\varepsilon_{2,xy}(E)$ of PEN:DIP blends, $\varepsilon_{2,z}(E)$ of PEN:DIP and PFP:DIP blends, and a comparison of absorbance and VASE data.

(42) Kowarik, S.; Broch, K.; Hinderhofer, A.; Schwartzberg, A.; Ossó, J. O.; Kilcoyne, D.; Schreiber, F.; Leone, S. R. Crystal Grain Orientation in Organic Homo- and Heteroepitaxy of Pentacene and

Perfluoropentacene Studied with X-ray Spectromicroscopy. *J. Phys. Chem. C* **2010**, *114*, 13061−13067.

(43) Opitz, A.; Wagner, J.; Brütting, W.; Salzmann, I.; Koch, N.; Manara, J.; Pflaum, J.; Hinderhofer, A.; Schreiber, F. Charge Separation at Molecular Donor-Acceptor Interfaces: Correlation Between Morphology and Solar Cell Performance. *IEEE J. Sel. Top. Quantum Electron.* **2010**, *16*, 1707−1717.