

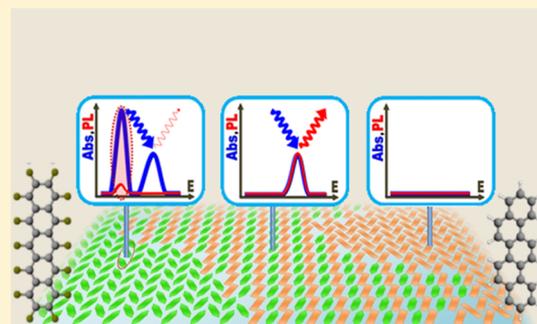
Revealing Suppressed Intermolecular Coupling Effects in Aggregated Organic Semiconductors by Diluting the Crystal: Model System Perfluoropentacene:Picene

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Supporting Information

ABSTRACT: In order to investigate the effects of intermolecular interactions on the optical properties of organic semiconductors, we employ mixing of the organic semiconductor perfluoropentacene (PFP; $C_{22}F_{14}$) with the wide band-gap organic semiconductor picene (PIC; $C_{22}H_{14}$). The binary mixed thin films are prepared by simultaneous coevaporation of PIC and PFP in vacuum. We determine the optical properties of the blends by differential reflectance spectroscopy (absorption) and photoluminescence (emission). PFP:PIC thin films are a rare case of mixed thin films with a known molecular packing. The formation of equimolar mixed domains with a crystal structure clearly different from that of the pure compounds is, in the case of nonequimolar blends, accompanied by pure domains of the excess compound. Due to the wide band gap of PIC, the effect of reduced intermolecular interactions between PFP molecules can be studied in detail without any direct contributions of PIC to the spectra. We find a strongly enhanced emission from PFP in the mixed thin films, which can be explained by decoupling. Real-time investigations of the absorption spectra during growth provide further insight into intermolecular coupling effects on optical properties.



INTRODUCTION

The electronic and optical properties of molecular solids relevant for applications^{1–4} are strongly affected by intermolecular coupling that critically depends on the precise molecular arrangement within the crystal.⁴ Blends of organic semiconductors can be a powerful tool to investigate aggregation effects by continuously varying the strength of intermolecular interactions.⁵ Instead of mixing strongly interacting donor–acceptor combinations that are used as active layers in organic solar cells, in studies of coupling effects, weakly interacting molecules are used, and the strength of intermolecular interactions between molecules of one compound is continuously reduced by incorporation of the second compound acting as a spacer material. The ideal spacer molecule has a large optical band gap, allowing us to probe essentially only the optical properties of the molecule of interest and form mixed thin films with the molecule of interest when coevaporated. A class of organic semiconductors especially suited for such studies are the phenacenes, for example, picene ($C_{22}H_{14}$, PIC), which we have used in a previous study⁵ and are also used in this work in blends with perfluoropentacene ($C_{22}F_{14}$, PFP). Importantly, PIC is transparent in the visible range; thus, features in absorption and emission spectra can be purely assigned to PFP. In conjunction with the detailed structural analysis of this mixed system presented in ref 6, this allows for a precise study of the effects

of reduced intermolecular interactions in blends of strongly interacting molecular semiconductors forming intermixed cocrystals.⁷ This mixing behavior contrasts the recent study of blends of pentacene and picene,⁵ which are weakly interacting compounds forming solid solutions. In PFP:PIC mixed films (Figure 1a), the opposite sign of the quadrupole moments of PFP and PIC results in an equimolar mixed structure accompanied by excess phases of the major compound (see Figure 1b).⁶

EXPERIMENTAL DETAILS

Mixed films of PIC (purchased from NARD Co. with 99.9% purity) and PFP (purchased from Kanto Denka Kogyo Co. with 99% purity) were grown by organic molecular beam deposition^{8,9} on Si substrates covered with a native oxide layer and on fused silica substrates. The nominal thickness of the mixed films was 20 nm, corresponding to ~ 13 molecular layers since the molecules grow standing upright.⁶ We prepared a series of samples with molar mixing ratios of 4:1, 2:1, 1:1, 1:2, and 1:4 at a substrate temperature of 297 K as well as equimolar mixtures at 370 K. Growth rates were monitored by a quartz crystal microbalance calibrated by X-ray

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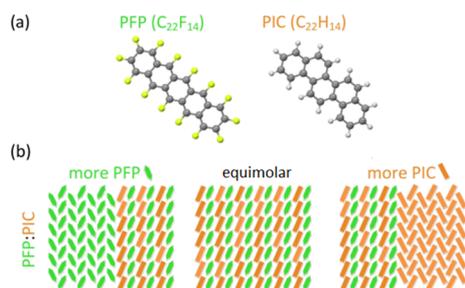


Figure 1. (a) Molecular structure of PFP and PIC. (b) Schematic mixing behavior of the PFP:PIC: equimolar structure and pure excess phases of the major compound (top view). Based on results reported in ref 6.

reflectivity. The optical properties were investigated by differential reflectance spectroscopy (DRS)¹⁰ in situ during growth probing the thickness dependence of the in-plane component of the dielectric function. The detector of the DRS setup was a fiber coupled USB2000 spectrometer and the light source a DH-2000 lamp (both Ocean Optics) with an energy range of 1.5–2.9 eV. The imaginary part of the dielectric function ϵ_2 was extracted by a Kramers–Kronig constrained variational analysis approach.^{11–13} Since PIC absorbs strongly above the measured energy range, absorption above 2.9 eV was taken into account by a parameterized extrapolation of ϵ_2 . Photoluminescence (PL) measurements were performed post growth. PL spectra were measured using a Horiba Jobin Yvon LabRAM HR spectrometer under a N₂ atmosphere (excitation at 532 nm) at temperatures between 77 and 293 K using a temperature-controlled sample stage (Linkam). For equimolar mixtures grown at 297 and 370 K, the thickness evolution of the coherently scattering grain size was extracted from GIXD data reported in ref 6.

RESULTS AND DISCUSSION

Equimolar Mixtures. Figure 2 shows the absorption (Figure 2a) and PL spectra (Figure 2b) of the blends compared to pure PFP and PIC and a comparison of the molecular arrangement in neat PFP films (Figure 2c) and in the equimolar blend (Figure 2d,e). As shown in ref 6, equimolar PFP:PIC forms two distinct equimolar polymorphs (structure I (Figure 2d) and structure II (Figure 2e)) depending on the growth temperature. At 370 K, structure II clearly dominates, whereas at 297 K, only structure I is observed. In the following, we will discuss the absorption and PL spectra of these two polymorphs by preparing equimolar PFP:PIC mixtures at 370 and 297 K, focusing on the PFP contribution.

The energetically lowest lying peak in pure PFP corresponds to the S_0 – S_1 transition assigned to the excitation of a Frenkel exciton.¹⁴ Since the Davydov splitting in PFP is only 25 meV,¹⁵ the two Davydov components cannot be resolved in our measurements. Both the emission and the absorption spectra of equimolar PFP:PIC mixtures are similar to those of monomeric PFP but clearly distinct from those of the pure PFP film. In the absorption spectra, we observe a vibronic progression due to the excitation of higher vibrational sublevels of the lowest electronically excited state with peaks at 1.92, 2.10, and ~2.3 eV corresponding to transitions from the vibrational ground state of the electronic ground state to vibronic levels 1, 2, and 3 of the excited state, respectively. The spectral shape resembles the spectrum of PFP in solution but

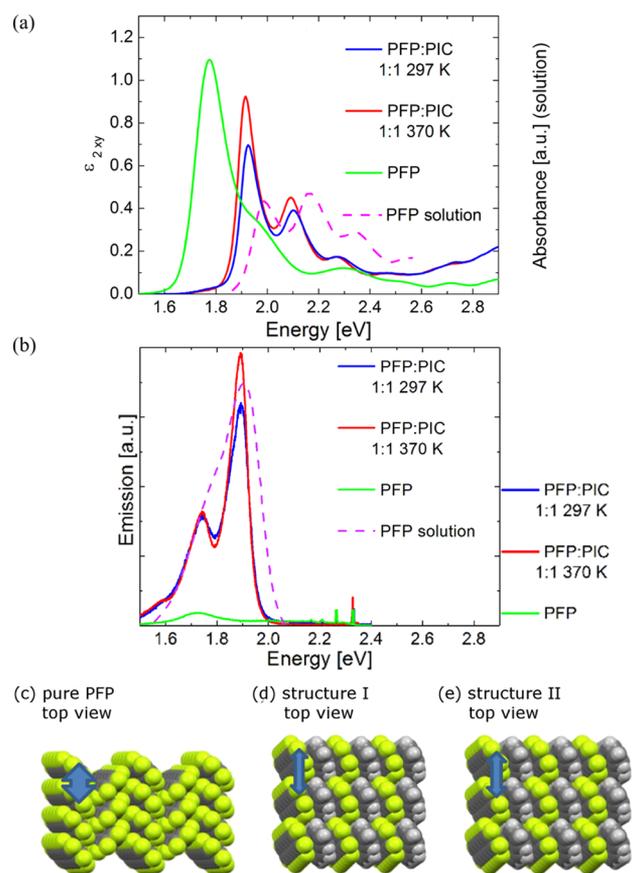


Figure 2. (a) Absorption and (b) emission of equimolar PFP:PIC mixtures deposited at substrate temperatures of 297 and 370 K measured at 293 K (arbitrarily normalized). The sharp lines at the upper end of the spectrum are caused by Raman. The reference spectra in 1,2-dichlorobenzene solution are taken from ref 29. (c) Crystal structure (top view) of PFP with slip-stacked and face-to-edge stacked PFP molecules (herringbone arrangement, atomic coordinates taken from ref 29). (d) Qualitative packing in the PFP:PIC 1:1 structure I and (e) crystal structure of PFP:PIC 1:1 structure II (dominating at 370 K) where only slip-stacked PFP molecules exist (atomic coordinates taken from ref 6). The blue arrows mark the strongest coupling direction.

with changed relative intensities (R_{abs}). The relative intensity of the peak at 1.9 eV (0–0 contribution) compared to the intensity of the peak at 2.1 eV (0–1) is lower for structure I ($R_{\text{abs}} = 1.9$) than for structure II ($R_{\text{abs}} = 2.05$) and for pure PFP ($R_{\text{abs}} = 2.8$).

The difference of the shape of the absorption spectrum of pure PFP in the thin film and in solution can be explained by J-aggregate-like coupling.^{16,17} Thus, the difference in R_{abs} in the mixed films compared to the pure PFP film indicates changes in the coupling between the transition dipole moments of the PFP molecules with weaker J-aggregate coupling corresponding to smaller R_{abs} . The changes are predominantly caused by changes in the molecular arrangement, and the fact that the crystal structure of the two polymorphs of the mixed films is known allows us to rationalize the differences in R_{abs} .

In the pure PFP phase, the molecules are arranged in a herringbone stacking configuration (Figure 2c). The resonant interactions between face-to-edge stacked PFP molecules are negligible,^{14,16} whereas the interactions between slip-stacked molecules dominate the absorption at ~1.74 eV, as indicated by the blue arrow in Figure 2c.

In the equimolar mixed structures, no PFP molecules in face-to-edge stacked configuration are found since all neighbors in face-to-edge configuration of a given PFP molecule are PIC molecules (Figure 2d,e). However, the main impact on the shape of the absorption spectrum of the blends results from changes in the arrangement of PFP molecules in slip-stacked configuration (Figure 2d,e), mainly the overlap between the π orbitals and the relative molecular tilt angle. The crystal structure shows that the overlap of two neighboring PFP molecules differs substantially. The displacement, that is, the translation of one molecule along the short molecular axis relative to its PFP nearest neighbor, is 3.1 Å for PFP but 5.8 Å for PFP:PIC (structure II; for structure I, no atomic coordinates are available). In contrast, the distance of the two cofacial molecular planes of two neighboring PFP molecules is similar (3.2 Å for PFP vs 3.3 Å for PFP:PIC structure II). Calculations investigating the effect of displacement on the coupling¹⁴ show a significant change in the coupling (corresponding to a factor of ~ 5.3 (7.9) in the LUMO (HOMO) transfer integral) for the different displacements of PFP and PFP:PIC (Figure 2c–e). Thus, we can conclude that the changes in the shape of the absorption spectrum are caused mainly by the arrangement of the PFP molecules and not solely by the reduction of the number of neighboring PFP molecules. Interestingly, in previous investigations of mixed thin films containing PFP and non-fluorinated OSCs,^{18–22,30} which form equimolar mixed phases, a significant suppression of the lowest lying PFP transition was observed as well. In those systems, the reduced coupling of PFP might also be explained by a similar mechanism.

Various Mixing Ratios. The absorption spectra for the PFP:PIC mixtures (Figure 3a) show that the intensity of the peak at 1.77 eV, which can be attributed to the pure PFP phase, decreases with increasing PIC fraction. It completely vanishes for the mixing ratios 1:1, 1:2, and 1:4 where the pure PFP phase is absent, and only the equimolar mixed phase and the pure PIC phase remain.

Surprisingly, all PL spectra of the mixed films are similar and distinct from the spectrum of a pure PFP film, which shows only one asymmetrically broadened peak (Figure 3b). Furthermore, the PL spectra of the mixtures resemble the monomeric PL spectrum except for inhomogeneous broadening, which can be attributed to solution effects.²³ Due to the PFP:PIC mixing behavior, the spectra are superpositions of the contributions from the pure PFP phase and the equimolar structure without any additional features or interference effects (Figure 3c). In pure PFP, weak PL is observed and can be related to a very efficient singlet fission (SF) process outcompeting prompt fluorescence.²⁴ Due to the fast decay of the excited S_1 state, this results in a strongly reduced direct emission at 1.9 eV, as illustrated in Figure 3c. Since the PL spectra of all mixed films look very similar, it can be concluded that the equimolar structure yields a very strong direct emission from the S_1 to the S_0 state (at 1.9 eV; see Figure 3c) compared to the pure PFP phase. Thus, the higher PL of the equimolar structure can be explained by a suppression of SF due to reduced coupling effects. Interestingly, a similar effect has been observed for pentacene mixed with PIC. In this case, this effect occurs for excitations above the optical gap of PIC²⁵ as well as for excitations within the optical gap⁵ (at 532 nm) indicating that no excited state charge transfer between PIC and pentacene is required to explain this effect. With increasing PIC fraction, the intensity of the peak at 1.89 eV

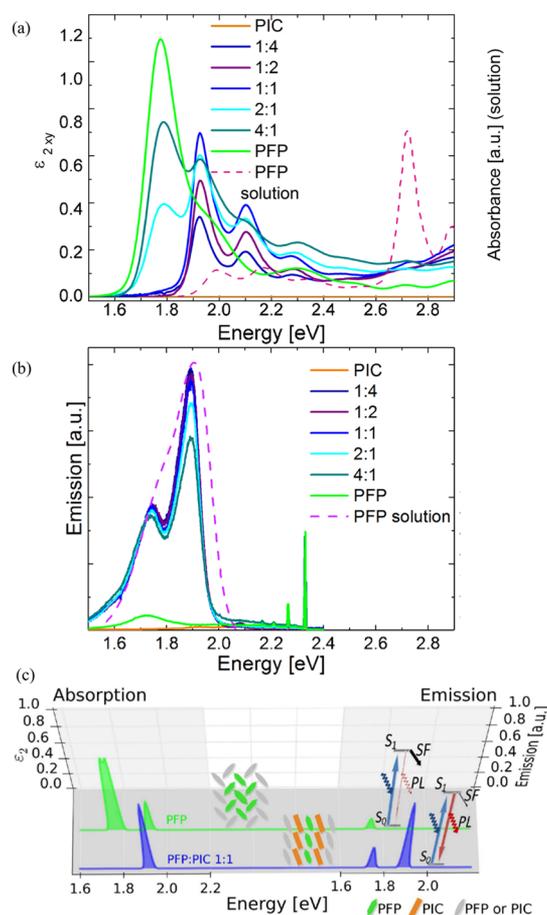


Figure 3. (a) Absorption of PFP:PIC as well as PFP thin films and PFP in liquid solution (a.u.).²⁹ (b) Emission of PFP:PIC mixed thin films measured at 293 K and of PFP in 1,2-dichlorobenzene solution²⁹ (arbitrarily normalized). (c) Schematic of the dependence of the lowest lying peaks in absorption and the emission on direct in-plane neighbors for pure PFP and the equimolar mixed structure (top view of the molecular arrangements). For emission, a competition of the decay channels of direct emission (PL) and SF is depicted.

increases slightly compared to the one at 1.74 eV. As shown in ref 6, for PIC-dominated mixtures, the appearance of another equimolar polymorph (structure II) is observed with a slightly different molecular packing. Therefore, the small differences in the PL spectra can be attributed to the slightly different coupling in the two polymorphs. Also, the PL spectra of the PFP-dominated mixtures differ slightly from the spectrum of the equimolar mixture. In these films, there are small contributions of pure PFP besides the dominant contribution of the equimolar mixed phase. We decomposed the spectra of these films into contributions from the equimolar mixed phase and the pure PFP phase and determined the fraction by which the two contributions contribute to the total integrated intensity between 1.6 and 2.0 eV. For the PFP:PIC 2:1 mixture (50% of the PFP molecules contained in the mixed phase and 50% in the pure PFP phase), pure PFP contributes 5% of the integrated intensity, whereas the mixed phase contributes 95%. For the PFP:PIC 4:1 mixture (75% of the PFP molecules contained in the mixed phase and 25% in the pure PFP phase), we find a contribution of 18% for PFP and 82% for the mixed phase. Thus, the mixed phase dominates the emission spectra, although diffusion of excitons within crystallites from the mixed phase to the pure PFP phase

cannot be excluded since the coherently scattering island size of the mixed phase crystallites is ~ 75 Å.

Real-Time. Figure 4 shows the results of differential reflection spectroscopy measurements, which probe the

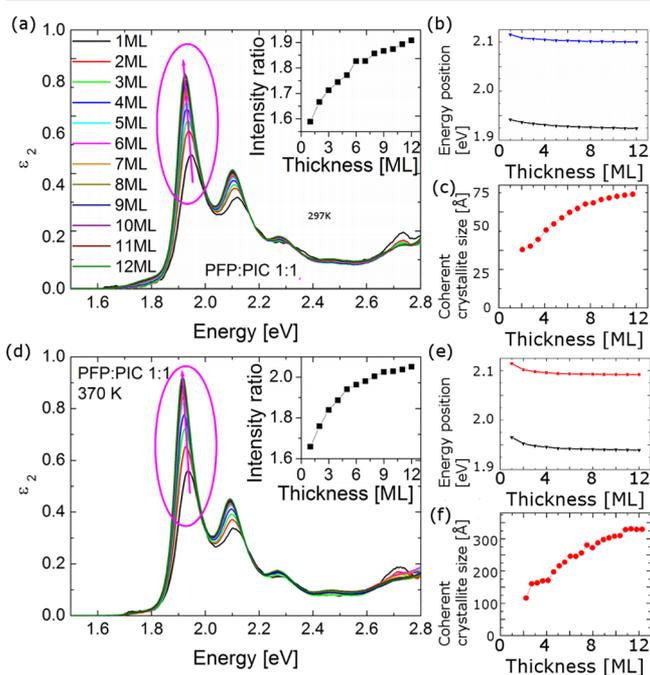


Figure 4. Thickness evolution of the absorption spectrum of an equimolar PFP:PIC mixture grown at (a) 297 and (d) 370 K. The insets show the thickness evolution of the relative intensities of the two lowest lying peaks. (b, e) Thickness evolution of the energy position of the two lowest lying peaks. (c, f) Thickness evolution of the coherent crystallite size (based on GIXD data reported in ref 6).

thickness-dependent evolution of the absorption spectra in situ and during growth. Each spectrum corresponds to the absorption of the film with a given film thickness. For the equimolar mixture grown at 297 K (Figure 4a), we observe a thickness-dependent shift in the peak position (Figure 4b). The most remarkable change in the optical properties occurs in the relative intensity and energy position of the peaks at ~ 1.9 and ~ 2.1 eV (inset of Figure 4a) caused by an increase of the coherently scattering grain size, which was observed in the real-time GIXD data (Figure 4c). At elevated temperatures (Figure 4d) where the equimolar mixed structure II dominates for thick films, a similar change can be observed (inset of Figure 4d,e). This change can be partly attributed to the increase of

the coherently scattering grain size (Figure 4f) and to a structural change as structure I dominates in the beginning and structure II after a few monolayers (ML).⁶ Figure 5 shows the absorption spectra of nonequimolar PFP:PIC mixtures grown at 297 K. For the 1:2 mixture, the optical properties are dominated by the equimolar mixed PFP:PIC structures, and, thus, exhibit a similar thickness evolution to that of the equimolar mixtures. Interestingly, the energy difference of the two lowest lying peaks significantly changes for the PFP:PIC 2:1 mixture. The lowest lying peak at ~ 1.74 eV, which increases significantly in intensity during growth, arises from PFP-PFP specific interactions. An increase in the coherently scattering crystallite size could cause a shift of this peak position to smaller photon energies, as already observed for pure PFP films.²⁶ As also observed for other mixed thin films,^{18,20,21} the absorption onset in the mixed films is shifted toward higher energies. Our data shows that this shift is related to a blueshift of the entire spectrum, and no interface effects between different phases are observed. We attribute this general mixing effect to the reduction of coupling effects such as J-aggregate-like coupling. This interpretation is also supported by recent calculations.²⁷

CONCLUSIONS

In summary, we presented a study of the impact of reduced intermolecular coupling on the optical properties of PFP in blends with PIC. Since the energy regions of intense absorption and emission of PFP are strongly distinct from those of PIC, intermolecular coupling effects in PFP can be studied by diluting PFP with PIC in detail. We found that the lowest transition observed in PFP completely vanishes in the equimolar mixed structure, which we explain with reduced intermolecular coupling. On the other hand, we revealed that the decreased coupling leads to a strongly increased PL in the mixed structure, which we attribute to a reduced SF compared to the pure PFP. Our work demonstrates that the approach of mixing molecules of interest with spacer molecules cannot only apply to chemically similar systems such as pentacene and picene or pentacene and *p*-terphenyl²⁸ but also to chemically very different systems if the molecule–spacer combination is chosen carefully to avoid charge transfer between the compounds. We believe this paves the way to obtain deeper insight into intermolecular coupling and aggregation effects.

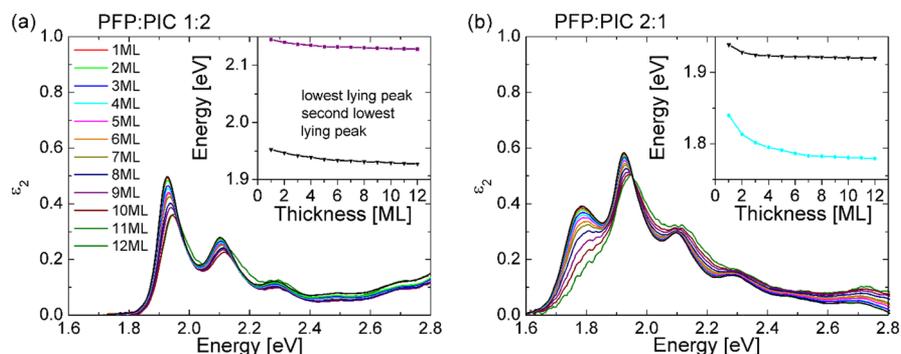


Figure 5. Differential reflection spectroscopy data for PFP:PIC (a) 1:2 and (b) 2:1 mixtures shown for various film thicknesses.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b03980.

Real-time GIXD of PFP:PIC (MP4)

PL data measured from 77 to 293 K (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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