

Supporting information for:
Optical Properties of Blends: Influence of
Mixing-Induced Disorder in
Pentacene:Diindenoperylene vs.
Perfluoropentacene:Diindenoperylene

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Discussion of the behavior of the two Davydov-components in
 $\epsilon_{2,xy}(E)$ of PEN:DIP blends

As mentioned in the main text, the origin of the peaks #2 and #4 (see Table S1), which are in $\epsilon_{2,xy}(E)$ of the PEN:DIP blends overlapping with contributions from DIP, is still under debate.^{S2–S4,S6} They are either assigned to arise from charge transfer (CT) between neighbouring

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Table S1: Energy position of peaks observable in the PEN single crystal spectrum for light polarized parallel to the a- or b-axis. Values taken from Ref. S1.

Number	Component	Energy position
#1	E a	1.82 eV
#2	E a	2.10 eV
#3	E b	1.97 eV
#4	E b	2.12 eV

PEN molecules^{S2} or are attributed to vibronic replica of the main electronic transition.^{S3,S4} Both assignments allow to rationalize the behavior of the two Davydov-components in $\epsilon_{2,xy}(E)$ of the PEN:DIP blends with changing mixing ratio based on the reduced efficiency of CT between neighbouring PEN molecules in the blend compared with the pure PEN film.

First, we consider the peaks #2 and #4 to arise from CT between neighbouring PEN molecules. As pure CT transitions usually have an oscillator strength f_{CT} , which is close to zero, they are only observed, if there is transfer of oscillator strength from the neutral transition (corresponding to peak #1 or #3) to the CT transition.^{S5} As a result of this transfer of oscillator strength, the oscillator strength of the neutral transition $f_{Frenkel}$ will decrease in the presence of CT between neighbouring PEN molecules compared to $f_{Frenkel}$ of an isolated PEN molecule. In pure PEN the transfer of oscillator strength is larger from #3 to #4 than from #1 to #2, see Ref. S1. Considering the situation in the blends, the CT between neighbouring PEN molecules will be less efficient with increasing amount of DIP because the probability decreases that a PEN molecule is surrounded by other PEN molecules. This results in a decreasing intensity of the CT transitions #2 and #4 and accordingly, in reduced transfer of oscillator strength from the neutral transition to the CT transition, leading to a higher intensity of the neutral transition (#1 and #3). As transition #3 (which is the high-energy Davydov-component) transfers more oscillator strength to the CT transition #4 than transition #1 (the low-energy Davydov-component) to #2, #3 profits more from the decreased intensity of the CT transition, resulting in a higher intensity of #3 compared to #1 with increasing volume fraction of DIP.

Second, we consider the peaks #2 and #4 to be the vibronic replica of the two main elec-

tronic transitions #1 and #3. In this case the Davydov-splitting and the relative vibronic peak intensities are mainly due to Frenkel-CT coupling, as discussed in Ref. S4. This gives two possible explanations for the lower intensity of #3 compared to #1: i) With increasing amount of DIP the polarizability of the molecular environment changes, affecting the relative intensities of the Davydov-components and their vibronic replica.^{S4} ii) As discussed in Ref. S4, the low-energy Davydov-component (#1) possesses a more enhanced CT character. With increasing amount of DIP the CT between neighbouring PEN molecules is less efficient, resulting in a lower intensity of the low-energy Davydov-component #1 compared to the high-energy Davydov-component (#3) with increasing volume fraction of DIP.

$\epsilon_{2,z}(E)$ for PEN:DIP and PFP:DIP

$\epsilon_{2,z}(E)$ of blends of PEN:DIP and PFP:DIP for different mixing ratios determined by a multi-sample analysis of VASE-data are shown in Fig. S1. For comparison $\epsilon_{2,z}(E)$ of the pure films^{S6,S7} are also shown. We note that the absolute intensity is strongly affected by uncertainties in the film thickness, resulting in an error of 50%, while the relative intensities are determined with an error of 10%. Therefore, we will restrict our discussion in the following to line shape and relative intensities.

For mixed films of PEN:DIP the spectra of $\epsilon_{2,z}(E)$ (Fig. S1a, b) change continuously with the mixing ratio and are dominated by peaks arising from DIP. This observation can be rationalized by the orientation of the transition dipole moments of PEN and DIP. The dipole moment for the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of PEN is oriented along the short molecular axes leading to a very weak out-of-plane component in the case of nearly upright standing molecules. Thus, the main contribution to absorption in the out-of-plane direction is caused by DIP molecules, for which the transition dipole moment of the HOMO-LUMO transition is oriented along the long molecular axis.

In the case of PFP:DIP blends both compounds contribute to $\epsilon_{2,z}(E)$. The shape of $\epsilon_{2,z}(E)$

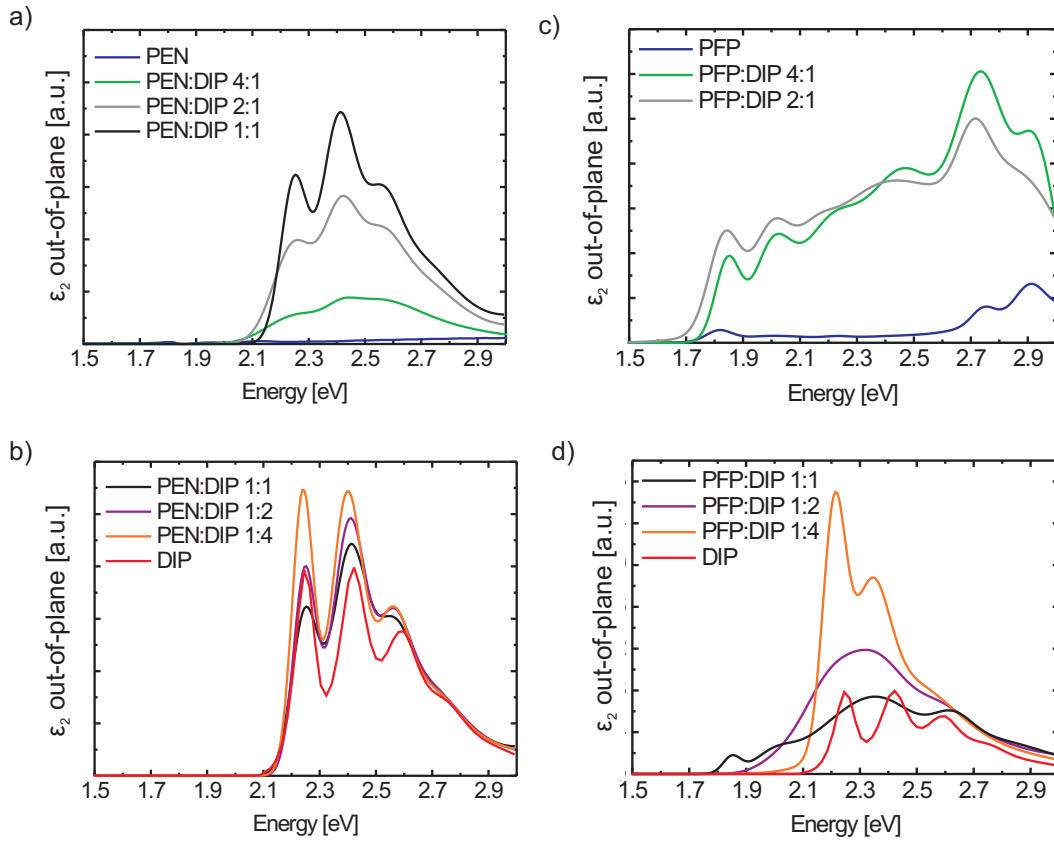


Figure S1: $\epsilon_{2,z}(E)$ of PEN:DIP (a,b) and PFP:DIP (c,d) thin films with different mixing ratios determined by VASE. Reference spectra of the pure films are taken from Refs. S6 (PEN, PFP) and S7 (DIP). Note that the absolute intensity is strongly affected by uncertainties in the film thickness, resulting in an error of 50%. a) Mixing ratios PEN:DIP 4:1, 2:1, 1:1, with a peak value of 9 resulting from the fit. b) Mixing ratios PEN:DIP 1:1, 1:2, 1:4, with a peak value of 11 resulting from the fit. c) Mixing ratios PFP:DIP 4:1, 2:1, with a peak value of 1.2 resulting from the fit. d) Mixing ratios PFP:DIP 1:1, 1:2, 1:4, with a peak value of 27 resulting from the fit.

does not change continuously with the mixing ratio, but rather "abruptly", compare Fig. S1c and d. For mixing ratios deviating from the equimolar mixture, peaks arising from the excess compound dominate $\epsilon_{2,z}(E)$. Similar to $\epsilon_{2,xy}(E)$ also the peaks in $\epsilon_{2,z}(E)$ are significantly broadened, in particular for the PFP:DIP 1:2 mixture, where almost no distinct peaks can be observed. We note that the absolute intensities of $\epsilon_{2,z}(E)$ for the PFP:DIP blends with mixing ratios PFP:DIP 1:1, 1:2 and 1:4 appear to be unrealistically high, but we do not have an explanation for this observation.

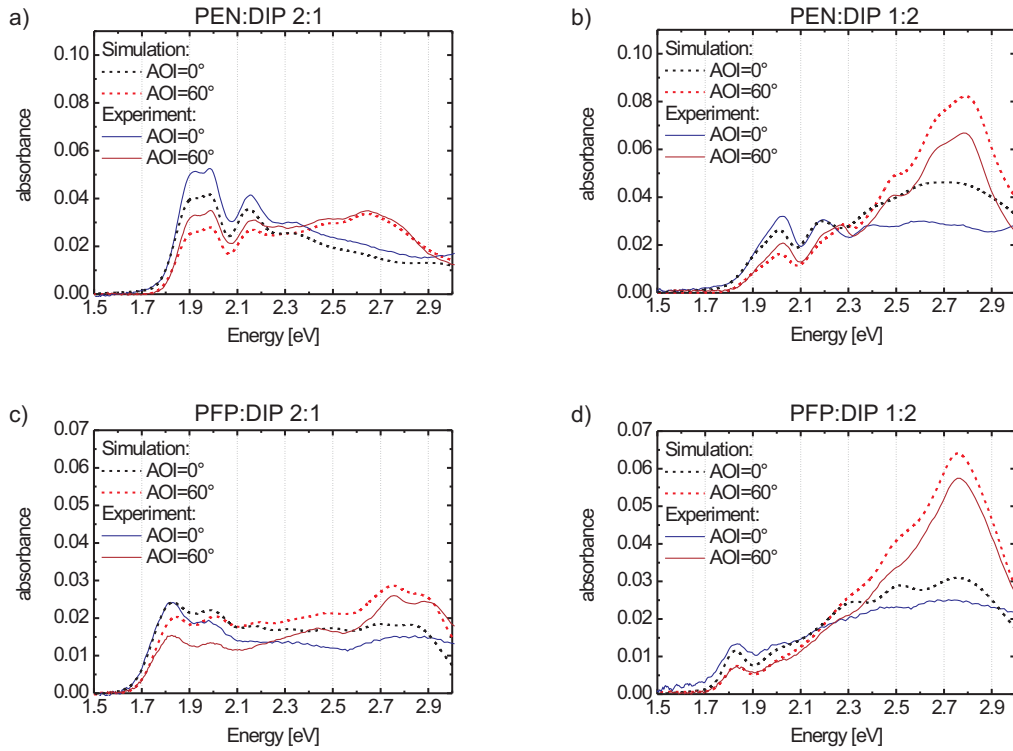


Figure S2: Comparison of simulated (thick lines) and experimentally determined (thin lines) absorbance A at two different AOI for: a) PEN:DIP 2:1, b) PEN:DIP 1:2, c) PFP:DIP 2:1 and d) PFP:DIP 1:2.

Comparison of absorbance and VASE-data

Based on $\epsilon_{2,xy}(E)$ determined on glass and on $\epsilon_{2,z}(E)$ determined by VASE the absorbance at two different AOI (0° and 60°) was simulated and compared with the experimentally determined ab-

sorbance for each of the two mixed systems. The comparison is shown exemplarily for two mixing ratios in Figs. S2. For both mixed systems the agreement between simulation and experiment is excellent. The small deviations are due to differences in film thickness and mixing ratio of the sample series measured with transmission spectroscopy and VASE.

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