



# Impact of molecular tilt angle on the absorption spectra of pentacene:perfluoropentacene blends

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We investigate the relation between the optical properties and the average molecular tilt angle for blends of pentacene and perfluoropentacene, which can be considered as a prototypical donor–acceptor complex. Combining near-edge X-ray absorption fine-structure spectroscopy and optical spectroscopy we study thin films of these compounds prepared at three dif-

ferent substrate temperatures  $T_{\text{sub}}$ . For  $T_{\text{sub}} = 180$  K we observe a larger average tilt angle than for blends prepared at higher substrate temperatures. This orientational change has significant impact on the uniaxial anisotropic optical properties of the mixed films which we measure post growth as well as in real-time during growth.

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**1 Introduction** The optical properties of organic semiconductor (OSC) thin films are crucial for many device applications [1–3]. However, for complex systems such as blends consisting of donor-acceptor pairs with strong intermolecular interactions, they are not yet understood. Apart from possible charge-transfer processes, the short and long range order within the film and the molecular arrangement (including the molecular tilt angle) are known to affect the optical properties [3–10]. For a better understanding of these effects, experiments elucidating the molecular arrangement within the film are mandatory, such as near-edge X-ray absorption fine-structure spectroscopy (NEXAFS) [11–14], which is a well-established technique to investigate the ensemble averaged molecular tilt angle in thin films. Blends of the prototypical organic semiconductor pentacene (PEN,  $C_{22}H_{14}$ ) [15–18] and its perfluorinated counterpart perfluoropentacene (PFP,  $C_{22}F_{14}$ ) [18–24] are a model system for a donor-acceptor complex [25–27] and exhibit strong intermolecular interactions, including charge-transfer upon excitation [9, 10]. For an equimolar mixing ratio, these two compounds mix on a molecular level and form a crystal structure with different unit cell parameters [23, 27]. Using X-ray diffraction it was found that there are domains with two orientations observable in

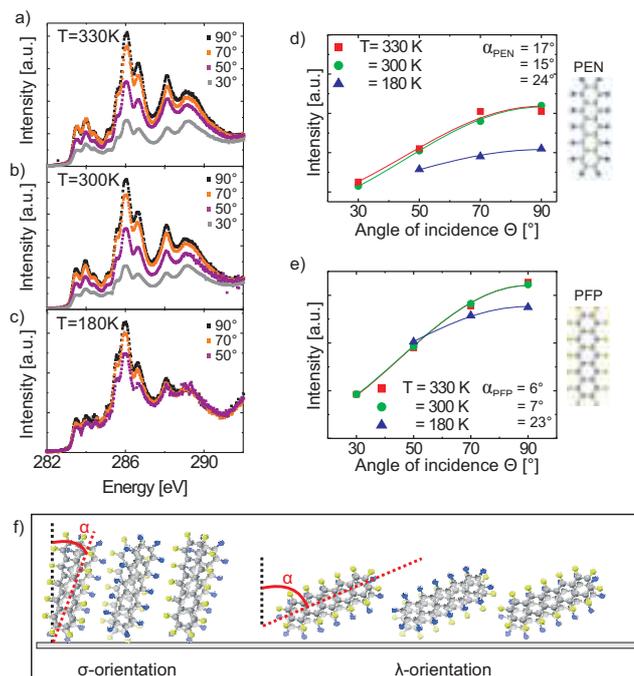
PFP: PEN blends, one with molecules standing nearly upright on the substrate surface ( $\sigma$ -orientation) and one with molecules lying nearly parallel on the substrate ( $\lambda$ -orientation). The amount of molecules in these two orientations changes with the preparation temperature [27]. So far, no quantitative value for the tilt angle of the molecules in the two different orientations was determined, which is of interest not only for a detailed understanding of the optical properties and intermolecular interactions, but may also contribute to attempts to solve the full crystal structure of this complex system, including the orientation of the molecules in the unit cell, as well as to rationalise the optical anisotropy.

In this Letter, we determine the average molecular tilt angle in equimolar blends of PFP and PEN using NEXAFS. The uniaxial anisotropic optical properties of the mixed thin films are investigated using variable angle spectroscopic ellipsometry (VASE) and differential reflectance spectroscopy (DRS) post growth and in real-time during growth. With the results of our NEXAFS experiments we are able to assign peaks in specific spectral regions of the absorption spectra in the visible range to the response of molecules in lying down ( $\lambda$ ) and standing up ( $\sigma$ ) orientation. Furthermore, following the film growth in real-

time using optical spectroscopy we observe pronounced changes in the relative intensity of specific peaks in the absorption spectra of the equimolar blends indicating thickness dependent changes in the average molecular tilt angle.

**2 Experimental** Equimolar mixtures of PEN (purchased from Sigma Aldrich, 99.9% purity) and PFP (purchased from Kanto Denka Kogyo Co., 99% purity) in thin films with thicknesses  $d = 20 - 25$  nm were prepared by organic molecular beam deposition (OMBD) similar to Refs. [10, 27] at a base pressure of  $2 \times 10^{-10}$  mbar on a silicon substrate covered with a native oxide layer (NativeSi,  $d_{\text{SiO}_2} = 2$  nm). Three different substrate temperatures  $T_{\text{sub}}$  (180 K, 300 K, and 330 K) were chosen, as the nucleation of the  $\lambda$ -orientation is expected to be most pronounced for low substrate temperatures, while with increasing preparation temperature more molecules in  $\sigma$ -orientation and fewer molecules in  $\lambda$ -orientation are found [27]. On the different samples the average molecular tilt angle was determined by measuring NEXAFS around the K-edges of carbon and fluorine, respectively, at the Optics beamline PM4 using the SurICat endstation at BESSY II (HZB, Germany). Four angles of incidence (AOI)  $\Theta$  relative to the substrate surface were chosen ( $30^\circ$ ,  $50^\circ$ ,  $70^\circ$  and  $90^\circ$ ). As reference a Au(111) single crystal was measured and the mirror current was recorded to correct for fluctuations in the beam intensity. A comparable set of samples was prepared simultaneously on two silicon substrates covered with oxide layers of different thickness  $d_{\text{SiO}_2}$  (ThermSi,  $d_{\text{SiO}_2} = 147$  nm and NativeSi) and the optical properties were investigated post growth by variable angle spectroscopic ellipsometry (VASE) in the energy range from 1.4 eV to 3 eV performing a multi-sample analysis [28]. In the visible spectral range the samples exhibit uniaxial optical anisotropy [10], i.e. their optical properties can be described by two dielectric functions  $\varepsilon_j = \varepsilon_{1,j} + i\varepsilon_{2,j}$  ( $j = xy, z$ ), where  $xy$  ( $z$ ) denotes the direction parallel (perpendicular) to the substrate surface. During the NEXAFS and VASE measurements the sample temperature was kept constant at 300 K. Finally, on a third set of samples grown on glass substrates,  $\varepsilon_{2,xy}(E)$  was studied in real-time during growth using differential reflectance spectroscopy (DRS) [29–31] in the energy range from 1.4 eV to 3 eV.

**3 Results** Figure 1a–c shows NEXAFS data of mixed films of PFP and PEN prepared at three different substrate temperatures  $T_{\text{sub}}$  measured at the K-edge of carbon with four different angles of incidence  $\Theta$ . Based on the results of NEXAFS measurements of pure PEN [17, 32] and pure PFP [22, 32] we are able to assign the peaks observed in the NEXAFS data of PFP: PEN blends measured at the carbon K-edge to the pure compounds, see Ref. [33]. For data measured at the fluorine K-edge [33], the peak assignment is more difficult, as in this case  $\pi^*$ - and  $\sigma^*$ -orbitals contribute to the signal [14]. Compared with the peak positions in pure films of PEN or PFP we observe



**Figure 1** a)–c) NEXAFS data measured at the carbon K-edge of PFP: PEN mixtures prepared at different substrate temperatures  $T_{\text{sub}}$ . The NEXAFS signals have been normalized to the intensity measured 40 eV away from the K-edge. d) and e) NEXAFS peak intensities as a function of angle of incidence  $\Theta$ , corresponding fit (solid lines) based on Eq. (1) and the average molecular tilt angle  $\alpha$  resulting from the fit. The estimated error is  $\pm 3^\circ$  for both compounds. d) Peak at 283.5 eV, which can be assigned to PEN [17] and e) peak at 286 eV which can be assigned to PFP [22] after subtracting the NEXAFS signal of pure PEN [17]. f) Schematic picture showing a cut through the two possible molecular arrangements ( $\sigma$ - and  $\lambda$ -orientation). Possible rotations of a PFP/PEN-dimer around its long axis are not considered. Note that the tilt angle  $\alpha$  measured in the experiment is generally a weighted average of the  $\sigma$ - and the  $\lambda$ -orientation if the two orientations coexist. For details see main text.

only relatively small peak shifts of  $\sim 0.4$  eV in the NEXAFS data of the blends.

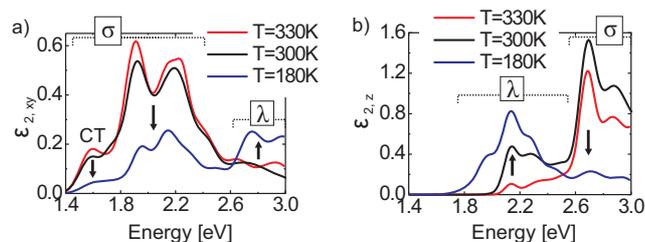
In order to determine the average molecular tilt angle relative to the surface normal [33] the intensity of the peaks at 283.5 eV and 286 eV was plotted as a function of the angle of incidence  $\Theta$  of the X-ray beam (Fig. 1d and e) and fitted according to [12, 13]

$$I = C[0.96 (\cos^2 \Theta \cos^2 \beta + \frac{1}{2} \sin^2 \Theta \sin^2 \beta) + 0.02 \sin^2 \beta]. \quad (1)$$

Here,  $I$  is the intensity of a peak in the NEXAFS data and  $\beta$  is the tilt angle of the  $\pi^*$ -orbital relative to the surface normal. From this, the tilt angle  $\alpha$  of the molecular plane relative to the surface normal can be calculated via  $\alpha = 90^\circ - \beta$ . The fit results compiled in Fig. 1d, e confirm that the  $\sigma$ -orientation dominates at high  $T_{\text{sub}}$ . Without background subtraction in the NEXAFS spectra the fits

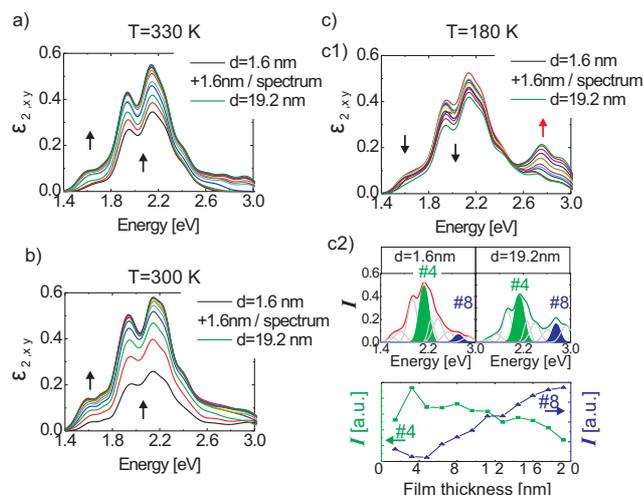
would yield for a given temperature  $T_{\text{sub}}$  similar values of the average tilt angle for both compounds. For PFP, a subtraction of the NEXAFS signal of pure PEN [17, 33] results in a quantitative change for the values of the average tilt angle in the samples prepared at 300 K and 330 K, see Fig. 1e. We note that a more elaborate analysis, taking possible effects of intermolecular interactions on the NEXAFS signal of the blend into account, would require detailed theoretical calculations and is beyond the scope of this work. For the sample prepared at 180 K we find  $\alpha \approx 24^\circ$  for both compounds, which is significantly larger than the value for higher substrate temperatures. This confirms that in films prepared at low substrate temperatures more molecules are in the  $\lambda$ -orientation, which is consistent with the trend observed in X-ray diffraction experiments [27]. In Ref. [27] the out-of-plane lattice spacing  $d_\perp$  for the  $\sigma$ - and the  $\lambda$ -orientation was determined, which allows to estimate a minimum molecular tilt angle relative to the surface normal of  $\sim 17^\circ$  for the  $\sigma$ -orientation, in good agreement with the results of our NEXAFS experiments, and  $\sim 66^\circ$  for the  $\lambda$ -orientation. Based on these values an upper limit for the fraction  $x_\lambda$  of molecules in the  $\lambda$ -orientation in the sample prepared at  $T_{\text{sub}} = 180$  K can be calculated. For simplicity, we use for the average tilt angle  $\alpha_\sigma$  the average of the results obtained for PEN and PFP, i.e.  $\alpha_\sigma \approx 12^\circ$ . Assuming further that the average tilt angle of the molecules in the  $\lambda$ -orientation is  $66^\circ$ , the fraction  $x_\lambda$  can be estimated according to  $\alpha = \alpha_\sigma(1 - x_\lambda) + \alpha_\lambda x_\lambda$ , with  $\alpha$  being the average molecular tilt angle. This rough estimate yields  $x_\lambda \approx 20\%$ . Since the actual tilt angle  $\alpha_\lambda$  in the sample may be larger than  $66^\circ$ , 20% is an upper limit for  $x_\lambda$  in the sample prepared at  $T_{\text{sub}} = 180$  K.

We investigated the influence of the molecular tilt angle on the optical properties of the mixtures by performing a multi-sample analysis [28] on a comparable set of samples. For a complete characterisation of the temperature dependent optical properties of PFP:PEN blends we determined the optical anisotropy of the samples in the visible spectral range. In agreement with the results of structural investigations [27] we found uniaxial anisotropic optical properties, which can be described by two complex dielectric functions  $\varepsilon_j(E)$  with  $j = xy$  ( $j = z$ ) describing the optical properties parallel (perpendicular) to the substrate surface. In the following we will concentrate on



**Figure 2** Imaginary part  $\varepsilon_{2,j}$  of the dielectric function in the visible spectral range for PFP:PEN mixtures prepared at different substrate temperatures. a)  $\varepsilon_{2,xy}(E)$ , b)  $\varepsilon_{2,z}(E)$ .

$\varepsilon_{2,j}(E)$  (Fig. 2), which is related to the absorption. As can be seen in Fig. 2 the increased average molecular tilt angle for the sample prepared at  $T_{\text{sub}} = 180$  K strongly influences the optical properties in comparison with the samples prepared at higher substrate temperatures. The arrows in Fig. 2a and b indicate changes in the shape of the spectra with decreasing substrate temperature. With decreasing substrate temperature we observe for  $\varepsilon_{2,xy}(E)$  a decreasing intensity of the peaks in the spectral range  $E = 1.4 - 2.4$  eV and an increase in intensity of the peaks at 2.7 eV and 2.9 eV (Fig. 2a). For  $\varepsilon_{2,z}(E)$  the behaviour is reversed (Fig. 2b). Based on the results of NEXAFS and X-ray diffraction [27] experiments, these observations allow us to assign peaks in those specific spectral regions to the spectral response of molecules in lying down ( $\lambda$ ) and standing up ( $\sigma$ ) orientation in the film. The temperature dependence of the intensity of the peaks in the range  $E = 1.4 - 2.4$  eV can be understood by the orientation of the transition dipole moments. The transition dipole moment of a charge transfer (CT) transition between PEN and PFP [9, 10] at 1.6 eV as well as that of the HOMO–LUMO transitions of PFP and PEN, respectively, is oriented perpendicular to the long molecular axis [10, 15, 18]. Therefore, the intensity of the corresponding peaks is expected to be maximal in  $\varepsilon_{2,xy}(E)$  ( $\varepsilon_{2,z}(E)$ ) for molecules in  $\sigma$ -orientation ( $\lambda$ -orientation). The peaks at 2.7 eV and 2.9 eV can be assigned to PFP and have a transition dipole moment which is oriented rather along the long axis of the molecule [18]. Accordingly, for molecules in  $\sigma$ -orientation ( $\lambda$ -orientation) the intensity of these peaks is expected to be high in  $\varepsilon_{2,z}(E)$  ( $\varepsilon_{2,xy}(E)$ ). For  $\varepsilon_{2,xy}(E)$  our results are in agreement with a recently published study [24], where the optical properties of PFP:PEN blends parallel to the substrate surface were investigated. We note also the dependence of the intensity of the CT-peak on the preparation temperature, which is due to differences in the intermolecular interactions between PFP and PEN with changing tilt angle. From the temperature dependence of the peak intensities assigned to the  $\sigma$ -orientation, the fraction of molecules in  $\lambda$ -orientation  $x_\lambda$  can be estimated based on the VASE results. This yields  $x_\lambda \approx 20\%$  in agreement with the results of the NEXAFS experiments. Finally, we studied the absorption spectra of the three different blends in real-time during growth. Already for pure films significant transient effects are reported [31], which may be even more pronounced in complex systems such as blends. Furthermore, the differences in the substrate temperature during preparation may significantly influence the growth of the film and may also lead to possible molecular re-orientations during growth. This can only be investigated using fast real-time optical spectroscopy techniques such as DRS. Due to the normal incidence geometry of the DRS-setup, only  $\varepsilon_{2,xy}(E)$  is probed. The data were analyzed as described in Ref. [31] based on a Gaussian-oscillator model of  $\varepsilon_{2,xy}(E)$ . The results of the DRS measurements for equimolar blends prepared at different substrate temperatures are shown in Fig. 3. The arrows indicate changes in the shape of  $\varepsilon_{2,xy}(E)$



**Figure 3** Real-time evolution of  $\varepsilon_{2,xy}(E)$  for equimolar blends of PFP: PEN prepared at three different substrate temperatures: a)  $T_{\text{sub}} = 330$  K, b)  $T_{\text{sub}} = 300$  K, c)  $T_{\text{sub}} = 180$  K. c1) The arrows indicate changes in the shape of  $\varepsilon_{2,xy}(E)$  with increasing film thickness  $d$ . c2) Upper graphs: Oscillators describing  $\varepsilon_{2,xy}(E)$  for two different film thicknesses  $d$ . Lower graph: Evolution of the relative intensity  $I$  of two peaks at  $E = 2.1$  eV (#4) and  $E = 2.7$  eV (#8).

with increasing film thickness  $d$ . Apart from a small increase in overall intensity, the spectra of the blends prepared at  $T_{\text{sub}} = 300$  K and 330 K are not changing for the different film thicknesses (Fig. 3a and b). In contrast, the shape of  $\varepsilon_{2,xy}(E)$  of the blend prepared at  $T_{\text{sub}} = 180$  K changes significantly during growth (Fig. 3c1). Clearly, the intensity of the peak at 2.7 eV, which is assigned to the  $\lambda$ -orientation, is increasing in intensity relative to the other peaks in the spectrum. This is a strong indication to differences in the nucleation of the domains in  $\sigma$ - and  $\lambda$ -orientation. For small film thicknesses  $d$ , the  $\sigma$ -orientation dominates and the shape of  $\varepsilon_{2,xy}(E)$  resembles that of the blends prepared at higher substrate temperatures (see upper row of Fig. 3c2). With increasing film thickness the intensity of the peak at 2.7 eV is increasing as domains with molecules in  $\lambda$ -orientation begin to grow.

**4 Conclusion** In conclusion, we determined the average molecular tilt angle  $\alpha$  in equimolar blends of PFP and PEN for different substrate temperatures. For the samples prepared at  $T_{\text{sub}} = 330$  K and 300 K,  $\alpha$  was found to be around  $15^\circ$  for PEN and  $\sim 7^\circ$  smaller for PFP. Consistent with the trend of X-ray diffraction results [27], the average tilt angle is  $\sim 10^\circ$  larger in the sample prepared at  $T_{\text{sub}} = 180$  K, indicating a higher amount of molecules in  $\lambda$ -orientation. An estimation of the upper limit for the fraction of molecules in this  $\lambda$ -orientation yielded  $\sim 20\%$ . Finally, the influence of the average tilt angle on the optical properties in the visible spectral range was investigated post growth. Combining the results of structural investigations with optical spectroscopy experiments, peaks in spe-

cific spectral regions in  $\varepsilon_{2,xy}(E)$  and  $\varepsilon_{2,z}(E)$  in the visible range could be tentatively assigned to the spectral response of molecules in lying down ( $\lambda$ ) and standing up ( $\sigma$ ) orientation in the films. By following  $\varepsilon_{2,xy}(E)$  in real-time during growth, strong changes in the spectral shape were observed, which point towards a delayed nucleation of domains consisting of molecules in the lying down orientation. The results of our *in situ* studies underline the importance of real-time experiments to observe transient effects in optical spectra during growth of OSC-blends, which are highly sensitive to changes in the molecular arrangement and the resulting intermolecular interactions.

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