Mixing-Induced Anisotropic Correlations in Molecular Crystalline Systems

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We investigate the structure of mixed thin films composed of pentacene and diindenoperylene using x-ray reflectivity and grazing incidence x-ray diffraction. For equimolar mixtures we observe vanishing in-plane order coexisting with an excellent out-of-plane order, a yet unreported disordering behavior in binary mixtures of organic semiconductors, which are crystalline in their pure form. One approach to rationalize our findings is to introduce an anisotropic interaction parameter in the framework of a mean field model. By comparing the structural properties with those of other mixed systems, we discuss the effects of sterical compatibility and chemical composition on the mixing behavior, which adds to the general understanding of interactions in molecular mixtures.

PACS numbers: 68.55.am, 61.05.C−, 61.66.Hq

Many modern materials and devices consist of rather complex mixtures. Recently, also organic semiconductor mixtures attracted increasing interest [1–3] and found multiple applications in optoelectronic devices (e.g., organic photovoltaic). In binary systems, not only the nominal concentration of two components A and B is relevant, but also the degree of intermixing, the crystalline order, and the morphology, as well as the characteristic length scales involved. While these structural and morphological features have a significant impact on the device performance [4], the underlying driving forces for structure formation in molecular materials are not well understood from a fundamental perspective. Compared to mixtures of elemental systems such as many binary alloys, for mixed organic systems additional issues arise, such as the influence of steric properties [5,6].

A simple theoretical description of mixtures is provided by the "regular solution model," which can also be applied to crystalline systems [7]. Here, a binary mixture is described by a mean-field approach with the free energy of mixing

$$\Delta F_{\mathrm{mix}} = k_B T[(x_A \ln x_A + x_B \ln x_B) + \chi x_A x_B], \quad (1)$$

where x_A and x_B are the respective relative concentrations. The ln terms are due to entropy, which always favors mixing and the last term is determined from the balance of the interaction energies with

$$\chi = \frac{Z}{k_B T}(W_{AA} + W_{BB} - 2W_{AB}), \quad (2)$$

where Z is the coordination number and W_{AB} and W_{AA} (W_{BB}) are the interaction energies between dissimilar compounds A and B or between like compounds A (B), respectively. Generally, this leads to different mixing scenarios [7], depending on the value of χ (Fig. 1): (a) $\chi < 0$: Intermixing; preference for A-B pairing, (b) $\chi > 2$: Phase separation, and (c) $\chi \approx 0$: Random mixing determined by entropy.

These scenarios have also been found for mixtures of organic semiconductors (OSCs), such as pentacene (PEN, $C_{22}H_{14}$), perfluoropentacene (PFP, $C_{22}F_{14}$) and diindenoperylene (DIP, $C_{32}H_{16}$) [see Fig. 2(a)], although they have usually not been discussed in terms of χ [8–14]. Importantly, in addition to other known shortcomings of mean-field approaches, this model in its original form does not take into account steric issues, anisotropies, and predications regarding crystallinity, although they may be incorporated. It is thus *a priori* not clear, if the scenario for mixtures of molecular crystals is potentially richer than the three cases described above.

In this Letter, we report on *anisotropic* structure formation in thin films of molecular mixtures of PEN and DIP [see Fig. 2(a)], which as pure systems exhibit excellent three-dimensional (3D) crystalline order. This behavior changes dramatically upon mixing. Whereas along the surface normal the mixed films exhibit nearly perfect order, for 1:1 blends the *in-plane* crystalline order essentially disappears, with some analogy to (frozen) smectic order in liquid crystals. We discuss these results in the context of other recently studied binary mixtures of OSCs [8,9,15] and rationalize their ordering behavior by proposing a model which includes steric properties and anisotropies
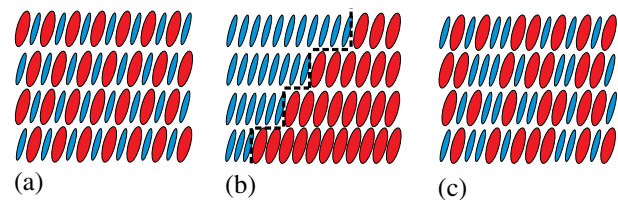

FIG. 1 (color online). (a–c) Examples of possible growth scenarios for binary equimolar mixtures of molecules with a similar length but different width.

(a)

DIP (C$_{32}$H$_{16}$)   PEN (C$_{22}$H$_{14}$)   PFP (C$_{22}$F$_{14}$)
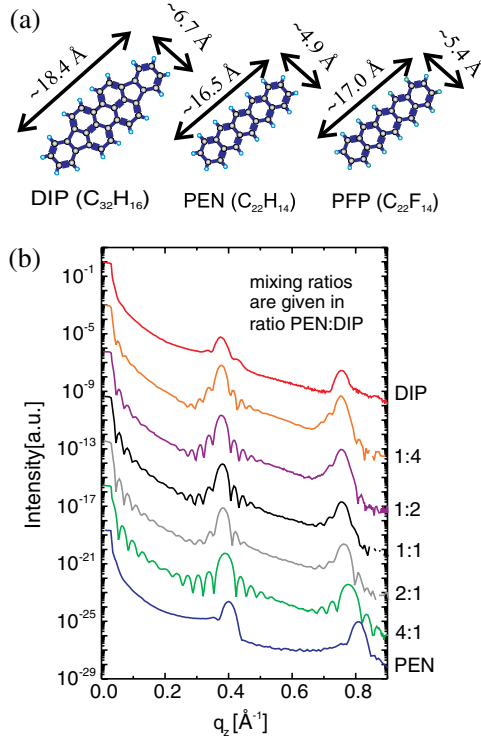
(b)

FIG. 2 (color online).   (a) Chemical structure of DIP, PEN, and PFP molecules. (b) XRR data for PEN:DIP films (offset for clarity).

and is able to motivate not only *mixing* but also *ordering* behavior in a mixed system of organic semiconducting molecules.

Thin films containing PEN (purchased from Sigma Aldrich, 99.9% purity) and DIP (purchased from Institut für PAH Forschung Greifenberg, Germany, 99.9% purity) were prepared by organic molecular beam deposition (OMBD) on Si wafers covered with a native oxide layer similar to Refs. [8,15] at a base pressure of 2×10^{-10} mbar. The substrate temperature was kept constant at 26 °C. The films studied were grown with five different mixing ratios of PEN:DIP (4:1, 2:1, 1:1, 1:2, 1:4), corrected for the differences in the volumes of the unit cells and thus referring to molar ratios. The estimated error of the stochiometry of the mixtures is about 10% determined by the error of the quartz-crystal microbalance.

After growth, the samples were investigated by x-ray reflectivity (XRR) and grazing incidence x-ray diffraction (GIXD) (for details see Ref. [8]) at the ID10B beam line of the European Synchrotron Radiation Facility using a wavelength of 1.08 Å and a point detector with slits determining the resolution. All measurements were performed under He atmosphere to reduce air scattering. Effects of air exposure and waiting time between film growth and measurements on our results were excluded by additional real-time *in situ* measurements in a vacuum chamber.

Figure 2(b) shows XRR data for pristine PEN, DIP, and their various mixing ratios. All mixed films exhibit pronounced Laue and Kiessig oscillations. The Laue oscillations result from a high out-of-plane crystallinity of the sample with a coherence length similar to the total film thickness of approximately 200 Å. The Kiessig fringes indicate that the mixed films grow even more smoothly than the pure ones. Interestingly, when varying the mixing ratio (PEN:DIP) from 1:4 to 4:1 we observed that the roughness decreases with increasing PEN ratio. A similar behavior was observed for PEN:PFP mixtures [8]. The out-of-plane lattice spacing shows a continuous shift to smaller values with increasing PEN ratio, but with a nonlinear dependence on the concentration (see Supplemental Material [16]). Overall, the order is well defined in the *out-of-plane* direction, in particular for the mixed films.

This is dramatically different for the *in-plane* order. The in-plane structure investigated by GIXD shows no order for the 1:1 mixing ratio (see Fig. 3). In particular, no peaks occur at q_{xy} different from the peak positions of the pure films. This is in contrast to PEN:PFP [8] and PFP:DIP [9] mixtures, for which new peaks appear, which were assigned to a mixed crystal phase [Fig. 1(a)] with unit cells containing both compounds. The small and broad features in the GIXD data of the equimolar mixture of PEN:DIP, which occur in the region of the DIP peaks, are attributed to a small excess of DIP molecules within the error bar of the rate determination. GIXD data from a different sample series (not shown here) do not even reveal traces of such
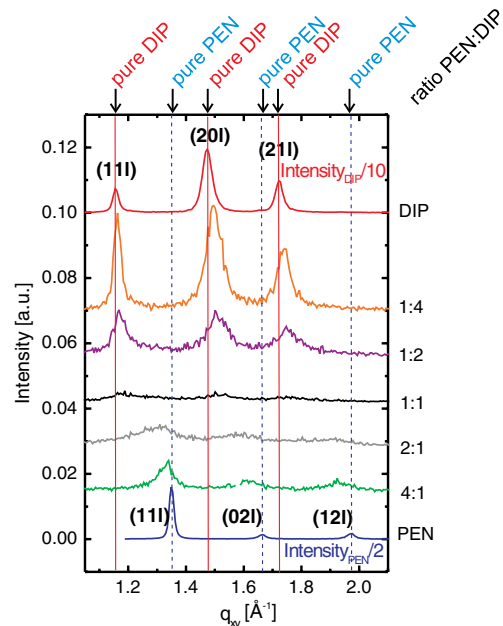

FIG. 3 (color online).   GIXD data obtained from PEN-DIP coevaporations with different mixing ratios. Data are offset for clarity. Note that the intensity of the DIP peaks has been divided by a factor of 10 and the PEN-peak intensity by a factor of 2.

features, i.e., show a complete disappearance of the *in-plane* order for the 1:1 mixture.

For the nonequimolar mixtures, peaks appear at q_{xy} positions in the vicinity of those of the component dominating the mixture. The presence of these peaks can be explained by minority molecules occupying sites in a lattice formed by the more abundant molecular species. The resulting strain in the lattice leads to the observed shift of the peak positions. The role of the strain will be discussed in more detail below.

Figure 4 shows the in-plane coherent size of crystallites, estimated from the GIXD peak widths using the Scherrer formula [17]. The experimental resolution was $\Delta q_{xy} \approx 0.01$ Å^{-1}. Thus, except for the first peak in the PEN:DIP 1:4 mixture and those of the pure films none of the GIXD peaks observed for the mixtures are significantly broadened by the resolution. Compared to the pure films the lower limit for the in-plane island size is reduced by a factor of 2–10 and highly dependent on the mixing ratio. Importantly, the reduced peak height for mixtures close to the equimolar mixture is not simply due to peak broadening, but can be assigned to vanishing in-plane order, while the out-of-plane order is preserved.

It is tempting to compare the ordering behavior of equimolar PEN:DIP mixtures to that of liquid crystalline systems. Seen in this context, it would correspond to a smectic *C* phase, characterized by crystalline order in one direction (here the out-of-plane direction) and orientational order of tilted molecules within the planes [18], but no crystalline in-plane order. Indeed, changes in the ordering behavior upon mixing have also been observed for liquid crystal systems [19–21] but we emphasize that our system
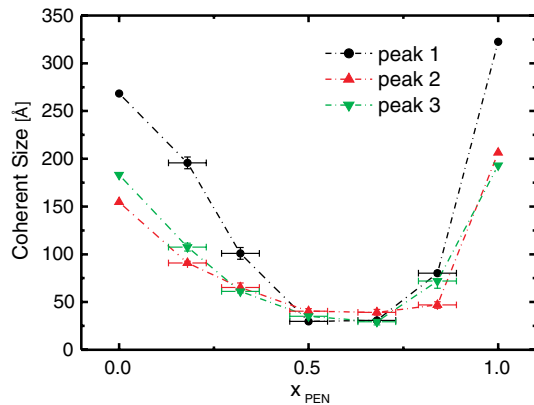

FIG. 4 (color online).   Lower limit for the coherent *in-plane* size of crystallites versus relative molar concentration of PEN (x_{PEN}), derived from the FWHM of the *in-plane* peaks in Fig. 3. Values of pure films and PEN:DIP 1:4 are resolution limited. The error bars of the coherent *in-plane* crystallite size are in the order of a few percent and thus in the range of the symbol size, whereas the error bar of the mixing ratio is 10% resulting from the inaccuracy of the quartz-crystal microbalance. The peaks are numbered in the order of ascending q_{xy} position.

is conceptually different from liquid crystalline systems, since the pure compounds show well-defined 3D order over a large temperature range. To the best of our knowledge the anisotropic change in the ordering behavior observed for equimolar mixtures of PEN:DIP is a previously unreported effect for mixed systems of this class of molecular compounds.

We attempt to rationalize this anomalous ordering behavior by extending the mean field model [Eq. (1)], within the limitations discussed in Ref. [6], to mixtures of rodlike molecules organized in layers. To do so we introduce an anisotropic interaction parameter χ to take into account anisotropies in the intermolecular interactions. χ splits into two components χ_{xy} and χ_z, which are defined according to Eq. (2), for the in-plane and the out-of-plane direction, respectively. Interactions arising from the chemical composition, sterical properties (i.e., size, shape) and the average molecular tilt angles θ_μ ($\mu = [A, B]$) with respect to the surface normal of the two compounds enter the nearest neighbour interactions energies W_{ij} ($i, j = [A, B]$). In addition, strain and lattice deformation resulting from differences in the sterical properties of two compounds, enter the free energy ΔF of the system as a strain energy term E^s. For a layered system E^s has two components E^s_{xy} and E^s_z, both depending on the elastic constant tensor $\hat{C}$, the tilt angles θ_A and θ_B, and the length ratio of the molecules $\beta_\alpha = l_{A\alpha}/l_{B\alpha}$ in the directions $\alpha = [xy, z]$. Here, $\beta_\alpha \approx 1$ and $\beta_\alpha \gtrsim 1$ indicate high and low steric compatibility, respectively. Furthermore, due to the layerwise growth using OMBD, and the associated possibility of differences in the molar concentration in the different layers, we consider our films a system of alternating layers. Within these assumptions, the free energy per molecule ΔF describing mixing and ordering of a mixed system can be written as:

$$\Delta F = \frac{1}{2} k_{\text{B}} T \left\{ x_A \ln x_A + x_A^\star \ln x_A^\star + x_B \ln x_B + x_B^\star \ln x_B^\star \right.$$
$$+ \frac{1}{2} \left[\chi_{xy}(x_A x_B + x_A^\star x_B^\star) + \chi_z(x_A x_B^\star + x_A^\star x_B) \right] \Big\}$$
$$+ E^s_{xy}(\hat{C}, \beta_{xy}, \theta_A, \theta_B) + E^s_z(\hat{C}, \beta_z, \theta_A, \theta_B), \quad (3)$$

where x_μ and $x_\mu^\star$ stand for molar concentrations in alternate layers along the vertical direction. They are related to the global molar concentrations by $x_\mu^g = (x_\mu + x_\mu^\star)/2$, with $x_A^g + x_B^g = 1$. The interplay between three contributions to ΔF predicts the ordering behavior of the system under mixing. The ln terms stem from the entropy, which favors statistical mixing. The interaction terms contain the $\chi_{xy,z}$ and the strain terms, E^s_{xy} and E^s_z, are minimized by phase separation or the formation of a new crystal structure.

We account for the anisotropic ordering behavior observed for PEN:DIP mixtures in the broader context of results on equimolar mixtures of PEN:PFP [8,15] and PFP:DIP [9] (see Fig. 5), considering all systems as
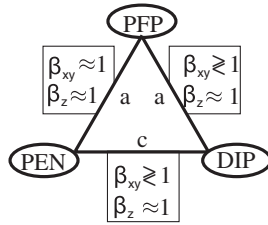
FIG. 5. Length ratios β of the molecules in the different mixed systems and the mixing behavior observed (a or c, see Fig. 1).

mixtures of rodlike molecules and discussing the interplay of the three contributions to ΔF, which is influenced by sterical properties and intermolecular interactions, defined by the chemical composition of the two compounds.

PFP and PEN are sterically highly compatible, i.e., $\beta_{xy} \approx \beta_z \approx 1$, leading to a low strain energy E_α^s in both directions $\alpha = [xy, z]$. The different charge distribution on PEN and PFP, induced by the perfluorination, is expected to give rise to an attractive interaction, i.e., $\chi_{xy} < 0$, and results in the formation of a strongly coupled molecular complex phase (with PEN:PFP 1:1) upon mixing [8,15].

In blends of PFP:DIP, the sterical compatibility is lower compared to PEN:PFP, since PFP and DIP have a slightly different shape [Fig. 2(a)], which leads to $\beta_{xy} \gtrsim 1$ while $\beta_z \approx 1$. The intermolecular interaction between PFP and DIP, though, is expected to be comparable to that between PFP and PEN, i.e., $\chi_{xy} < 0$. The resulting preference for A-B pairing, seems to outweigh the increase in entropy by statistical mixing and the in-plane sterical incompatibility, as for PFP:DIP blends the formation of a molecular complex phase was found recently [9].

Importantly, even though PEN:DIP blends exhibit similar sterical characteristics compared to PFP:DIP, i.e., $\beta_{xy} \gtrsim 1$ and $\beta_z \approx 1$, the ordering behavior is completely different. In both systems a good out-of-plane order is maintained due to $\beta_z \approx 1$. However, while a mixed crystal phase was found for equimolar mixed PFP:DIP films, equimolar PEN:DIP mixtures exhibit vanishing in-plane order and statistical mixing of PEN and DIP. This experimental observation is consistent with $\chi_{xy} \approx 0$, which can be rationalized by the chemical differences of the PFP:DIP and PEN:DIP blends. In particular, the presence of fluorine in PFP and the associated strong quadrupole moment are of importance, as the quadrupole-quadrupole interaction is expected to be a key ingredient in mixtures forming new crystal structures [22,23]. Due to the ''chemical similarity'' of PEN and DIP and the corresponding lack of significant and specific A-B interactions, which results in $\chi_{xy} \approx 0$, only the entropy and strain terms contribute to the free energy ΔF. Consequently, the preference for entropy dominated statistical mixing competes with the increase of E_{xy}^s upon mixing due to $\beta_{xy} \gtrsim 1$. As the entropy term seems to outweigh the strain term, statistical mixing in the in-plane direction takes place. This random

occupation of nearest neighbor sites in combination with the *in-plane* sterical incompatibility ($\beta_{xy} \gtrsim 1$), prevents the formation of a periodic structure in the in-plane direction and results in the observed vanishing of in-plane order.

We note that our model also covers the case of phase separation in mixed systems, as it is observed for mixtures of PEN:C_{60} [14] and DIP:C_{60} [24]. Here, the strain energies E_{xy}^s and E_z^s resulting from the huge differences in molecular shape dominate over the entropy terms and lead to phase separation. With similar arguments this behavior can also be expected for mixed films of PFP:C_{60}.

To conclude, we investigated the ordering behavior of PEN and DIP mixed films. In the framework of sterical compatibility and the interaction parameter χ, we compared our results to data reported for blended films of PEN: PFP [8] and PFP:DIP [9]. When mixing PEN and DIP, two compounds, which are crystalline as pure materials as well as in binary blends with PFP, we observed a breakdown of *in-plane* order upon mixing. Equimolar PEN:DIP mixtures exhibit an anisotropical ordering behavior, which is liquid-crystal-like and comparable to a ''frozen'' smectic C phase, with a well ordered out-of-plane structure but no detectable *in-plane* order.

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