Supporting Information

Electrostatic Interactions Shape Molecular Organization and Electronic Structure of Organic Semiconductor Blends

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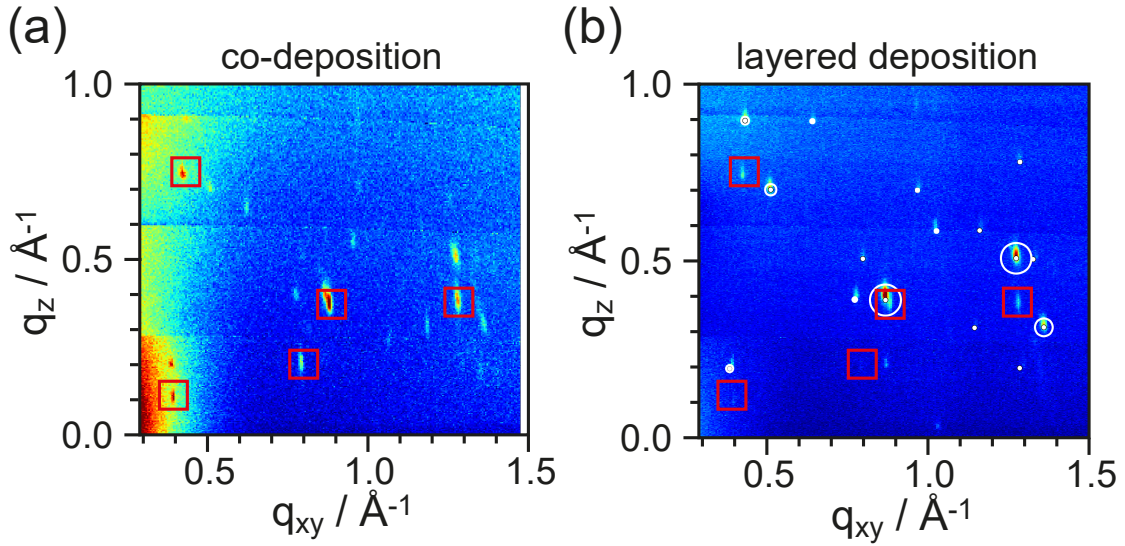
Supporting GIXRD data

Figure S1: (a) GIXRD reciprocal space map of a nominally 30 nm thick, 1:1 co-deposited PEN:PFP film on HOPG. (b) Same region as in (a), taken from Fig. 2 in the main text showing the GIXRD data for a film of same total thickness but established by layered deposition. White circles areas in (b) correspond to calculated intensities on the basis of our structure solution for the phase denoted as L in the main text (*cf.* Fig. 2). Red squares indicate five strong reflections assigned to phase L′, which are present in both films but become strongly attenuated in (b). The relative changes in peak intensity by changing the preparation protocol allowed assigning the peaks to the respective phase.
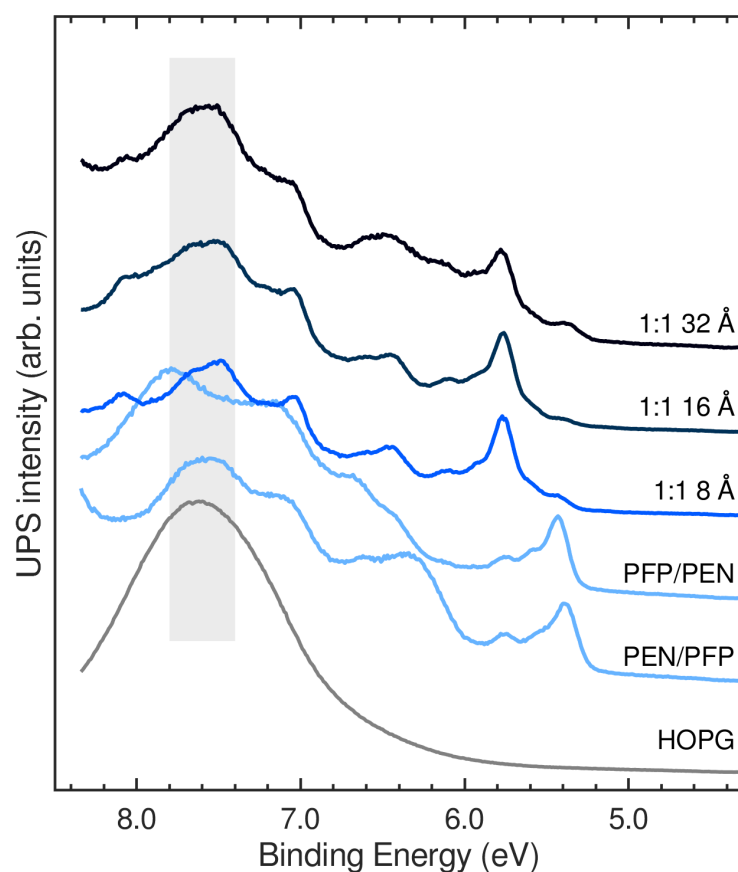
Supporting UPS data

Figure S2: Full experimental UPS of PEN:PFP mixed films on HOPG, including the spectrum of the bare HOPG substrate. The main UPS substrate feature (gray box) is present in all the spectra, irrespective of the organic adlayer thickness. This is an indication of the inhomogeneous (*Stranski-Krastanov*) growth of the film, characterized by regions of the substrate are either bare or covered by a single molecular layer.

Commensurism between HOPG and PEN:PFP lattices

The 2D cell parameters of the mixed PEN:PFP structure on the (-1 -2 1) lattice plane are $a = 14.824$ Å, $b = 16.640$ Å, $\gamma = 77.17°$, while the lattice constant of HOPG is $a = 2.461$ Å on its (0 0 1) plane. The superposition of the two lattices, shown in Figure S3, suggests a possible epitaxial relationship according to the transformation matrix:[1]

$$\begin{pmatrix} \mathbf{b_1} \\ \mathbf{b_2} \end{pmatrix} = \begin{pmatrix} 6 & 0 \\ -7/3 & 23/3 \end{pmatrix} \begin{pmatrix} \mathbf{a_1} \\ \mathbf{a_2} \end{pmatrix}$$

where $\mathbf{a_1}$ and $\mathbf{a_2}$ ($\mathbf{b_1}$ and $\mathbf{b_2}$) are the in-plane lattice vectors of PEN:PFP. The relationship above is valid in very good approximation with a lattice mismatch of <0.7%. We expect this remarkable commensurability between the two lattices to promote growth of the mixed film in this very texture.
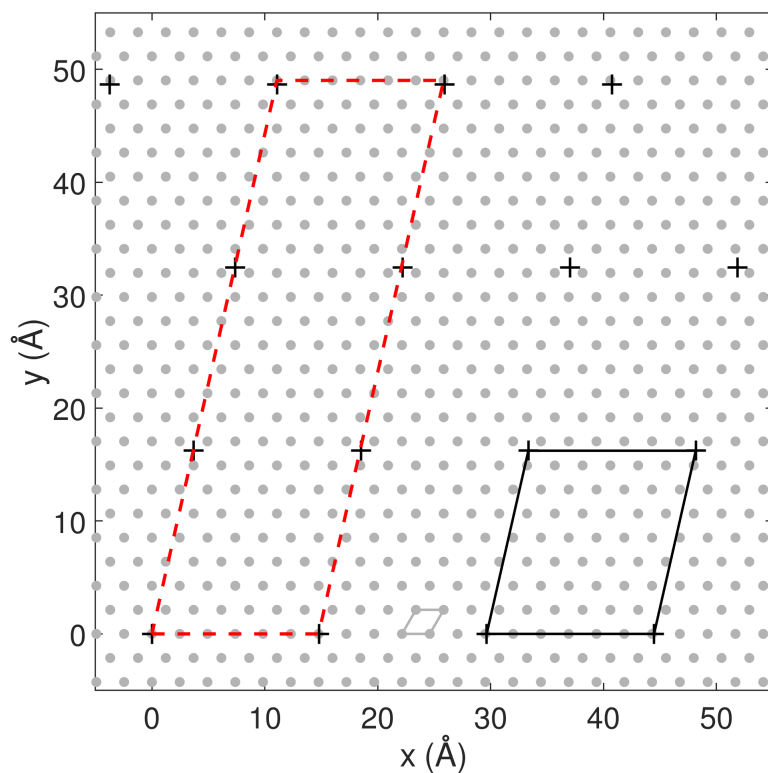
Figure S3: Illustration of the commensurism between the 2D lattice of the HOPG (0 0 1) plane (gray dots and frame) and that of the (-1 -2 1) plane of the PEN:PFP mixed crystal structure (black pluses and frame). The supercell (dashed red frame) corresponds to the transformation matrix given in the text.

Charge response (CR) model calculations

In order to gain further insight into the origin of the thickness and layer dependence of the molecular IP in PEN:PFP mixed films, we have partitioned the calculated energies into its electrostatic (Δ_E), induction (Δ_I) and substrate (Δ_S) contributions:

$$\begin{aligned} \mathrm{IP} &= \mathrm{IP_{gas}} + \Delta \\ &= \mathrm{IP_{gas}} + \Delta_E + \Delta_I + \Delta_S. \end{aligned}$$

These interaction terms were calculated from self consistent CR calculations for an infinite 2D slab as follows:

$$\begin{aligned} \Delta_E &= \sum_i \delta_i \phi_i^n \\ \Delta_I &= \frac{1}{2} \sum_i \delta_i \phi_i^\delta \end{aligned}$$

where the sum extends over the atoms of the probed molecule, $\delta_i = q_i^+ - q_i^0$ is the difference between the atomic charges of the cation and the neutral molecules and ϕ_i^n is the potential at atomic sites obtained from a self-consistent calculations in the neutral systems; ϕ_i^δ is the potential induced by the differential charge δ_i.

The substrate term is computed as the difference between $(\Delta_E + \Delta_I)$ obtained from calculations including and not including the interaction with the substrate. The interaction with the conducting HOPG substrate has been described with an image charge model[2] in which permanent charges as well as induced charges and dipoles were mirrored by a plane placed at $3.0\,\text{Å}$ distance from the first molecular layer. Varying this distance by $\pm 0.2\,\text{Å}$ affects the IP of a PEN or PFP MLs by up to $0.1\,\text{eV}$ in magnitude. Films on SiO_x have been modeled as free-standing bilayers ($\Delta_S = 0$).

The results of the IP partitioning prcedure are shown in Figure S4. In the following, we will adopt the notation n/m to identify the energy level of a given molecule in the
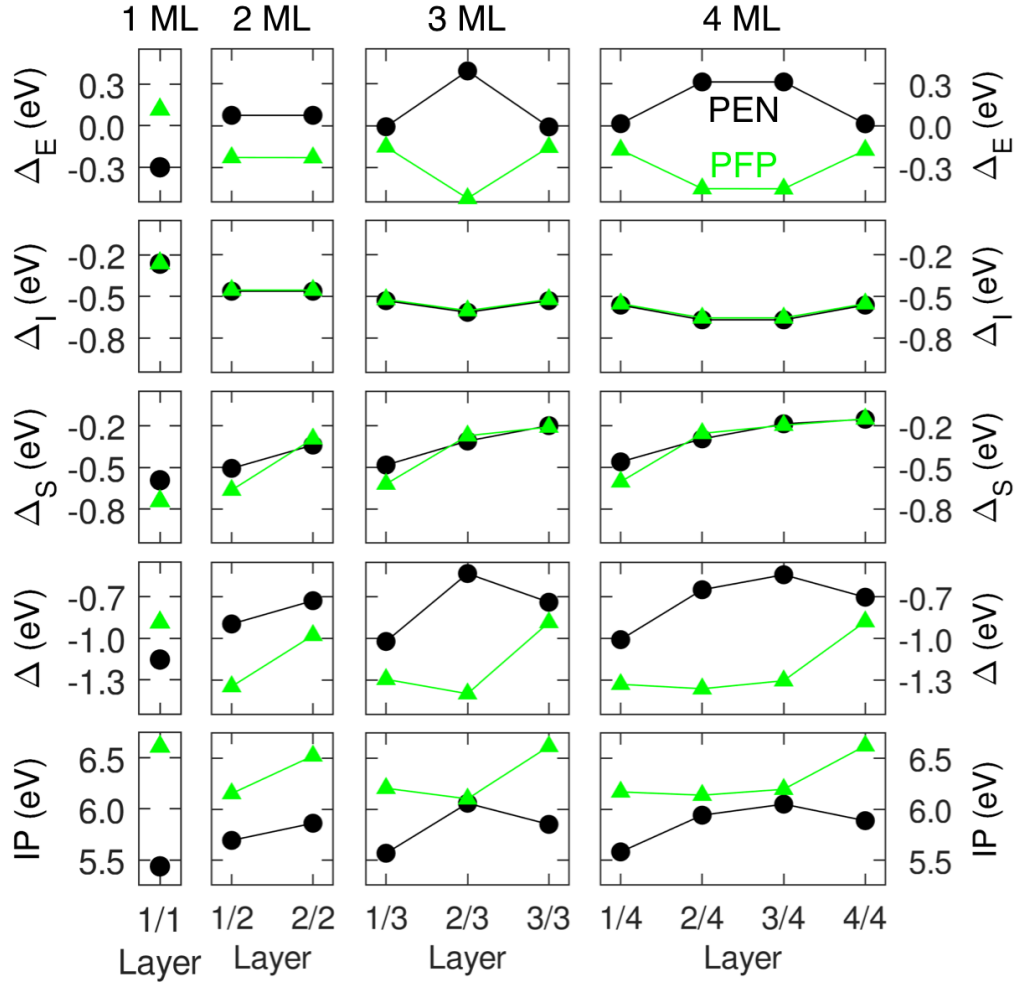
Figure S4: CR calculations results for PEN:PFP films on HOPG. Partitioning of the contributions from intermolecular (Δ_E and Δ_I) and substrate (Δ_S) interactions to the IP, as calculated for PEN and PFP in the different layers (see text).

layer n of a films of m MLs thickness. For instance, PEN 1/2 labels the PEN molecule at the interface to HOPG in two-ML film, while PFP 3/3 identifies the PFP molecule in the surface layer of a three-ML film.

We first remark that the position (layer) dependence of the electrostatic (Δ_E) and of the induction (Δ_I) terms is symmetric with respect to the midpoint of the films, as expected for free-standing films. The electrostatic term Δ_E is responsible for much of the layer and thickness dependence of molecular IPs in films of lying molecules. In 1 ML films, molecules are arranged side-by-side (see Fig. 3 in the main text), so that a PEN (PFP)

molecule is surrounded by the fluorine (hydrogen) atoms of the neighboring PFP (PEN), bearing a negative (positive) partial charge. The relevant components of the molecular quadrupoles (see Fig. 1 in the main text) are therefore the in-plane ones, which stabilize and destabilize a hole in PEN ($\Delta_E = -0.30$ eV) and PFP ($\Delta_E = 0.12$ eV), respectively.

In multilayer films, molecules stack along the plane normal with an alternating PEN-PFP pattern (see Fig. 3 in the main text). The interaction between π-stacked molecules is governed by the out-of-plane components of the molecular quadrupoles, which have opposite sign with respect to the in-plane ones. Once again, the interaction has opposite effects on PEN, where the hole gets destabilized ($\Delta_E > 0$), and on PFP ($\Delta_E < 0$). In films thicker than bilayers the electrostatic interaction is stronger for molecules in the inner layers, where molecules have neighbors along the off-plane direction on both sides, with respect to outer layers. We emphasize that the electrostatic energies of inner and outer layers are approximately converged for films of thickness above 3 ML and that the difference in Δ_E between the surface and the sub-surface layer is quite remarkable and amounts to 0.3 eV in PEN and to -0.3 eV in PFP.

The induction term is, instead, almost independent on the type and position of the ionized molecule, and is sensitive only to the thickness of the film, reflecting the increase in the volume of the polarizable medium that screens the hole. A close inspection of films thicker than 2 MLs reveals that Δ_I is slightly smaller in magnitude at surface layers, where molecules are not entirely embedded in the film, hence receiving a less effective screening by induced dipoles of the other molecules.

The symmetry in the position dependence of the energy levels with respect to the film midpoint is lifted by substrate interactions, since the IP of a molecule in a given layer is affected by the interaction between the ionized molecule and its image charge. The substrate term Δ_S in Figure S4 approximately follows a screened Coulomb potential, with holes that are more bound at the HOPG interface. Substrate interactions largely contribute to the position dependence of the IP of molecules close to the substrate, expe-

riencing the steepest part of the Coulomb potential, while in the outer layers of films of thickness above 3 ML the variations of Δ_S are less important.

Structures employed in the calculations

Films of standing pure PEN and PFP on SiO_x were modeled as $(0\,0\,1)$ and $(1\,0\,0)$ bilayers built from the respective bulk crystal structures.[3,4]

To model a lying PFP ML on HOPG we relied on the specific substrate-induced structure resolved by Salzmann *et al.* (Ref. 5). For PEN ML on HOPG we have considered both the cell proposed by Götzen *et al.* (Ref. 6) with lattice parameters $a = 17.22$ Å, $b = 6.51$ Å, $\gamma = 79.1°$ and the $(0\,2\,2)$ face of the polymorph reported by Siegrist *et al.* (Ref. 3) which were both observed for ultra-thin PEN films on HOPG. For the former structure, atomic positions were determined assuming molecules parallel to the substrate with the long axis parallel to a. The calculated IP for the two PEN ML structures give consistent estimates values: 5.83 eV for the Siegrist (0 2 2) ML (values plot in Figure 1 of the manuscript) and 6.02 eV for the Götzen ML.[6]

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