

Supplementary Information

to

**Orientation-dependent ionization energies and interface dipoles in
ordered molecular assemblies**

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Upper limit for the effect of surrounding molecules on photo-hole screening

In order to obtain an upper limit for the difference in photo-hole screening by differently orientated neighboring molecules, we considered the following scenario: A photo-hole created in the topmost layer of organic molecules is screened only by the lower half-space of surrounding molecules (and, possibly, the metal substrate). A photo-hole created on a molecule deeper in the organic film is screened by a lower *and* upper half-space of surrounding molecules. Clearly, the *presence* or *absence* of neighboring molecules in the upper half-space must have a more pronounced effect on the polarization energy (and thus the measured IP) than differences in the *orientation* of the neighboring molecules. Supporting the data presented in the main manuscript, we also measured the S(2p) XPS signal of a 20 Å 6T film on Ag(111) that has been buried by subsequently deposited layers of N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1-biphenyl-4,4'-diamine (α -NPD); α -NPD (Fig. S1) is an amorphous, conjugated organic material that does not contain sulfur itself^{S1}.

In Fig. S1, we see that, for the pristine 6T layer, the stronger S(2p_{3/2}) peak is centered at a binding energy of 164.58 eV. Upon subsequent deposition of 20 Å of α -NPD, the peak shifts by 0.14 eV towards lower binding energies, *i.e.*, to 164.44 eV. Upon further deposition of α -NPD, the peak energy stays constant to within ± 0.05 eV. We thus have established that the presence or absence of a half-space full of π -conjugated molecules contributes a maximum of ca. 0.15 eV to the polarization energy of the photo-hole, consistent with similar results in Refs. [S2] and [S3]. Consequently, the effect of different orientation of neighboring molecules can be expected to be less than that.

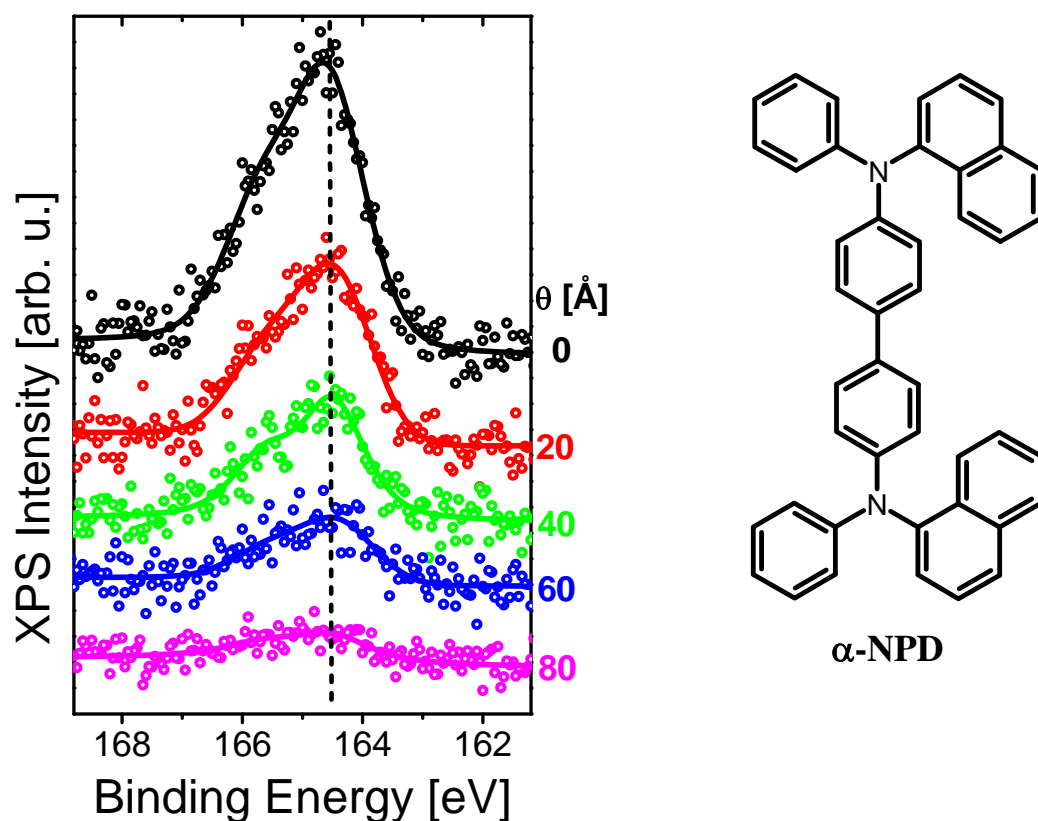


Figure S1 S2p spectra of 20 Å 6T/Ag(111) covered by α -NPD

Al $K_{\alpha/2}$ XPS spectra of the sulfur 2p region of 20 Å of 6T/Ag(111) subsequently covered with α -NPD as function of α -NPD thickness (θ) and corresponding fits. The dashed line is a guide for the eye. The inset shows the chemical structure of α -NPD.

It is harder to demonstrate the influence of capping layers on the UPS spectrum of underlying layers than on their XPS spectrum, because of the larger information depth in XPS and the simple peak assignment. However, the UPS spectra of Xe and Kr adsorbed on Pd(001) are hardly affected by the adsorption of Ar as top layer^{S4}. Because of the short lifetime of core holes^{S5}, which are filled very rapidly by electrons from the valence

region^{S6}, screening should be the same in XPS and UPS; indeed, no substantial differences could be observed for screening by the metal substrates for rare-gas multilayers in XPS and UPS^{S4}. Moreover, it has been suggested that the polarization energy for photo-holes in the valence region (probed by UPS) of conjugated organic materials is 0.3-0.4 eV smaller for the topmost molecular layer than for molecules deeper in the organic film.^{S7-S10} Consequently, one would expect the IP of molecules in the topmost layer to actually be *higher* than that of molecules deeper in the organic film. This is in stark contrast to the findings presented in the current study, where the IP in the upper (standing) layers is *lower* than in the (lying) layers below. The presence [absence] of an intrinsic surface dipole in lying [standing] layers thus *overcompensates* above-stated surface effect. Also, the fact that photo-hole screening is not included in our DFT calculations is likely to contribute to the overestimation of the calculated IP differences between lying and standing films of 6T and DH6T.

DH6T and 6T/DH6T on polycrystalline gold

The same set of experiments that are described in the main manuscript for an Ag(111) single-crystal surface were performed on a polycrystalline gold sample. The Au-substrates were at least 400 Å thick Au-films on a copper foil, evaporated *in-situ* and Ar-ion sputtered before use. In Figure S2a, the UPS spectra of the valence region of a lying monolayer of DH6T (L), and a second standing layer of DH6T (S) on polycrystalline Au are shown. Comparing the spectra of the L- and S-regime, we find a shift of several hundred meV of the HOMO peak towards lower binding energy with no further

modification of Φ (see inset); thus, the molecular IP is lower in the second standing layer (S) than it is in the first lying layer (L). Note that, as was the case on Ag(111), the HOMO:HOMO-1 intensity ratio is significantly smaller in the S-regime which is indicative of the proposed upright orientation of the molecules as opposed to the lying orientation in the L-regime.

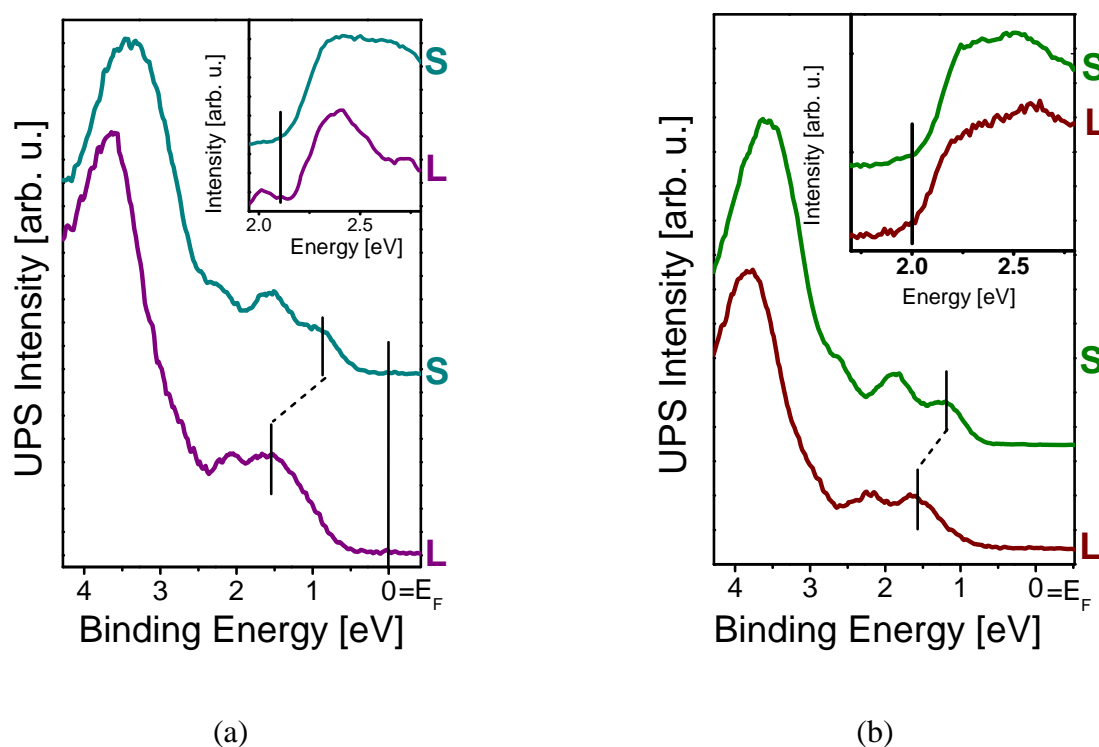


Figure S2 Experimental photoelectron spectra of DH6T and 6T/DH6T on gold

a, UPS spectra showing 8 Å of DH6T (purple), and 32 Å of DH6T (cyan) on polycrystalline Au, corresponding to a lying monolayer (L) and a second standing layer (S). **b**, UPS spectra showing the valence region of 100 Å of 6T on 4 Å of DH6T (red), and 100 Å of 6T on 40 Å of DH6T (green), corresponding to a lying (L) and standing 6T structures (S). The insets show the secondary electron cut-offs used to determine the work function of the respective sample.

Subsequently, 6T was deposited both onto the lying monolayer of DH6T and onto the standing second layer of the bilayer of DH6T. The corresponding UPS spectra are shown in Figure S2b. The difference in the HOMO:HOMO-1 intensity ratio is in line with the growth model proposed in the main manuscript. Again, we find the HOMO to be shifted towards lower binding energy in the standing 6T structure (S) compared to the lying 6T structure (L) in good agreement with the results for Ag(111). As no difference in Φ was measured (see inset), the IP of the standing 6T molecules (S) is effectively lower than that of the lying 6T molecules (L).

These results underline that the effect observed and the explanation given in the main manuscript are quite general. As long as the first DH6T layer grows lying down on the surface, which is likely to occur on a variety of metals due to the relatively strong interaction between π -system and substrate, the same situation will be encountered.

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