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Adsorption height alignment at heteromolecular hybrid interfaces

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The formation of metalorganic hybrid interfaces is determined by the fine balance between molecule-substrate and molecule-molecule interactions at the interface. Here, we report on a systematic investigation of interfaces between a metal surface and organic monolayer films that consist of two different molecular species, one donor and one acceptor of electronic charge. Our x-ray standing wave data show that in heteromolecular structures, the molecules tend to align themselves to an adsorption height between those observed in the respective homomolecular structures. We attribute this alignment effect to a substrate-mediated charge transfer between the molecules, which causes a mutual enhancement of their respective donor and acceptor characters. We argue that this effect is of general validity for π-conjugated molecules adsorbing on noble metal surfaces.

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The future success of organic electronic devices depends strongly on the ability to control the structural properties of active organic materials as well as the charge injection into the organic film. Both are directly related to the properties of the first organic layer adsorbing on a metal surface, since these molecules make the electronic contact with the metal, and act as a template for the further growth of the thicker organic films. This has motivated many recent experimental and theoretical studies of the adsorption of small planar molecules on crystalline noble metal surfaces [1–16].

On rather inert metal substrates such as Au, the molecule-substrate interaction is dominated by van der Waals forces. The molecules essentially float above the charge-density spill-out of the metal surface at a contact distance equal to the sum of the van der Waals radii of the involved atomic species [17–19]. To reach this equilibrium height, the molecules repel a certain portion of the metallic spill-out back into the surface (the so-called push-back effect). For more reactive surfaces, besides this physisorptive interaction, there is an additional chemical component of the molecule-substrate interaction, which leads to hybridization of the molecular and metal states, and to charge reorganization across the metalorganic interface. This has two consequences: (i) For acceptor molecules, the lowest unoccupied molecular orbital (LUMO) may become partially populated [19–23], and it also may be subject to bond stabilization [24] resulting in an increased orbital binding energy; see the discussion below. (ii) Due to this charge transfer into the molecule, the charge-density spill-out of the metal becomes smaller, which allows the molecule to approach the surface further. This contributes to the smaller adsorption heights being observed on more reactive surfaces. Hence, the observation of a lower molecular adsorption height is commonly expected to be accompanied by a larger binding energy of the (partially filled) LUMO, both indicating a stronger chemical interaction.

The scenario described above was frequently reported in the literature for various homomolecular adsorbate systems on metal surfaces [8–13,17–22]. We consider it to represent the normal relationship between the (chemical) molecule-metal interaction strength and the geometric and electronic observables. However, whether it holds for heteromolecular adsorbate systems consisting of (at least) two different molecules in mixed structures has not been investigated so far. Although technologically relevant, systematic studies of such systems are performed only recently [25–42]. Some of them deal with mixed films of pentacene, phthalocyanines, and perylene derivates [31–42] and hence are rather closely related to our work.

In this paper, we present a comprehensive investigation of the adsorption geometry (in particular, adsorption heights and molecular distortions) of several different heteromolecular structures: Normal incidence x-ray standing wave (NIXSW) results are reported for four structures that differ in (i) the concentration of donor and acceptor molecules (i.e., the mixing ratio of the molecules) or (ii) the relative strength of the charge donating/accepting character (i.e., with either the donor or the acceptor molecule replaced by a weaker or a stronger one) [43]. The NIXSW experiments were performed at the beamlines ID32 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and I09 of the Diamond Light Source (DLS, Didcot, UK) [44].

At first we focus on heteromolecular structures formed by 3,4,9,10-perylene tetracarboxylic-acid dianhydride (PTCDA)

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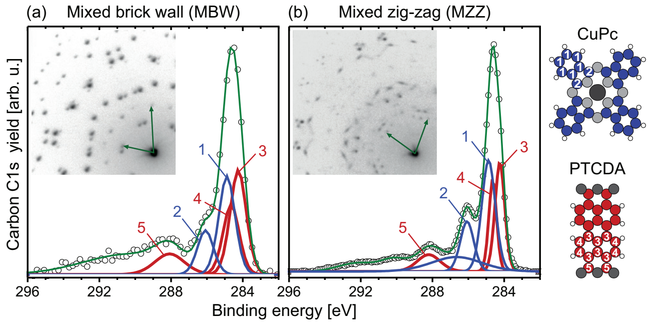
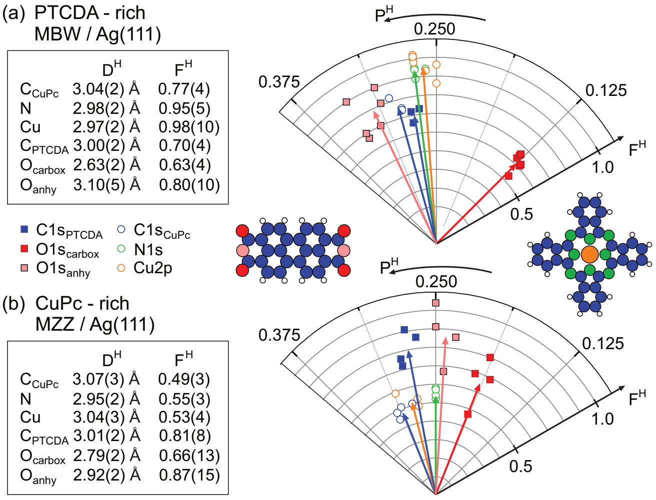


FIG. 1. (Color online) C 1*s* core-level spectra (background subtracted) for (a) the PTCDA-rich MBW and (b) the CuPc-rich MZZ structure. The fitting models contain contributions from CuPc (blue) and PTCDA (red). A Gaussian contribution representing the energy-loss tail at higher binding energies is not shown. The data are recorded at $h\nu = 2.64$ keV, i.e., at a photon energy slightly higher than that used for the XSW measurements.

and copper-II-phthalocyanine (CuPc). We compare two structures with different acceptor to donor ratios, namely the PTCDA-rich "mixed brickwall" (MBW) structure (CuPc:PTCDA = 1:2) and the CuPc-rich "mixed zig-zag" (MZZ) structure (ratio 2:1). Using the NIXSW technique, we have determined the adsorption heights of all atomic species. While O 1*s*, N 1*s*, and Cu 2*p* photoelectrons are emitted from either CuPc or PTCDA, the C 1*s* signal contains components from both molecules. These components can be disentangled by a line-shape analysis based on the C 1*s* binding-energy shifts, which unveils the XSW modulations of the individual components and thus allows us to determine the molecular backbone to silver distances for the two molecules independently. In Fig. 1, the corresponding C 1*s* core-level data are shown for the MBW and the MZZ structures together with the best fits. The insets show the corresponding low-energy electron diffraction (LEED) patterns of the heteromolecular structures. The fitting models [44] used here were derived from many high-resolution x-ray photoelectron spectroscopy studies performed on PTCDA and different metal-Pc molecules [45–49]. The spectrum for the MZZ structure was measured during the first XSW beamtime at I09 at the DLS. The smaller widths of all components in this spectrum reflect a better experimental resolution provided by this new beamline compared to ID32, where the MBW data were recorded.

In Fig. 2, the XSW parameters coherent fraction and coherent position are presented in a so-called Argand diagram [50–52]. Each individual measurement is shown as a polar vector with its length and polar angle representing the coherent fraction F^H and position P^H, respectively. The spread of the data points can be used as a measure of the experimental error. The measured adsorption heights of all atomic species are illustrated by colored spheres in the models shown in Fig. 3. Gray spheres indicate the adsorption heights of the corresponding homomolecular structures [10,21]. All results are listed in detail in Table 1 of the Supplemental Material [44].



	D^H	F^H
C_{CuPc}	3.04(2) Å	0.77(4)
N	2.98(2) Å	0.95(5)
Cu	2.97(2) Å	0.98(10)
C_{PTCDA}	3.00(2) Å	0.70(4)
O_{carbox}	2.63(2) Å	0.63(4)
O_{anhy}	3.10(5) Å	0.80(10)

	D^H	F^H
C_{CuPc}	3.07(3) Å	0.49(3)
N	2.95(2) Å	0.55(3)
Cu	3.04(3) Å	0.53(4)
C_{PTCDA}	3.01(2) Å	0.81(8)
O_{carbox}	2.79(2) Å	0.66(13)
O_{anhy}	2.92(2) Å	0.87(15)

FIG. 2. (Color online) Argand diagram with fitting results for all individual XSW scans for (a) the MBW and (b) the MZZ structure. The arrows indicate the coherent position P^H and fraction F^H averaged over all single XSW scans of one atomic species.

Figure 3(a) shows that the adsorption heights of the aromatic parts of the two molecules (i.e., the perylene backbone of PTCDA and the tetra-azaporphyrin core of CuPc) are almost identical in the MBW phase, in contrast to the homomolecular structures [53]. This alignment of adsorption heights of the molecules in the MBW structure is achieved by lifting the PTCDA molecular backbone and lowering the entire CuPc molecule. To understand this leveling of adsorbate heights, we have a look at the homomolecular phases first. Previous ultraviolet photoelectron spectroscopy (UPS) studies have revealed a more pronounced charge transfer from the surface into the LUMO for PTCDA/Ag(111) than for CuPc/Ag(111), indicating that on the Ag(111) surface, PTCDA is the stronger acceptor compared to CuPc. By uptaking this charge, PTCDA reduces the charge spill-out from the surface and is therefore able to approach the surface further. For CuPc this effect is smaller and the interaction with the silver is dominated by the push-back effect, which limits the approach of CuPc toward the silver surface, resulting in a larger adsorbate height. A detailed experimental and theoretical study of the electronic properties of the MBW phase [54] has revealed that the different electron affinities of the two molecules cause a rearrangement of the metallic charge spill-out underneath the molecules. CuPc can now push the evanescent electron density also toward the neighboring PTCDA adsorption sites. This reduces the charge spill-out underneath the CuPc molecules and in turn reduces the adsorption height of CuPc while the opposite effect occurs to the PTCDA. Note that an enhanced charge transfer into the PTCDA LUMO can only partly compensate this effect. It was found experimentally and in DFT calculations that the overall process (i.e., the formation of the MBW structure) is energetically favorable as compared to the separated homomolecular phases [54].

In contrast with the molecular backbones, the adsorption height of the carboxylic oxygen atoms (of PTCDA) is hardly affected by the interaction between CuPc and PTCDA. In both homo- and heteromolecular structures, the carboxylic oxygen atoms bend toward the silver surface, more strongly in the MBW structure than in the homomolecular film (as the carbon atoms are further away from the surface in the former case). In fact, the commensurate registry [54,55] in both cases facilitates the formation of Ag-O bonds between PTCDA and the silver surface localized at the carboxylic oxygen atoms.

We now turn to the discussion of the CuPc-rich MZZ structure having a CuPc:PTCDA ratio of 2:1 [Figs. 2(b) and 3(b)]. We find again that the aromatic parts of both molecules are located at almost identical adsorption heights as in the MBW structure [56].

This indicates that the alignment of the molecular adsorption heights in these heteromolecular layers does not depend on the relative concentration of the donor and acceptor molecules. A second finding is the obvious difference in the distortion of the PTCDA molecule in the MBW and MZZ structures. Instead of the typical saddlelike geometry found for PTCDA/Ag(111) [10] and for the MBW structure, in the MZZ structure both oxygen species lie underneath the carbon backbone plane. The resulting "M-like" distortion of the molecule was already reported earlier for PTCDA on more reactive surfaces such as Ag(100) and Ag(110) [22,57]. For these commensurate structures, the M shape was explained by an enhanced interaction between the anhydride oxygen atoms and the silver surface. But since the LEED pattern of the MZZ structure [see the inset of Fig. 1(b)] indicates only a line-on-line registry with the silver surface lattice [55,58], the molecules do not obtain uniform adsorption sites, which prevents the formation of well-defined Ag-O bonds.

The effect of such localized Ag-O bonds becomes obvious when comparing the height differences between hetero- and homomolecular structures for C and $O_{carbox.}$ species: In the incommensurate (line-on-line) MZZ structure, these two species lie above their homomolecular heights by approximately the same distance. But upon formation of the MBW structure, only the carbon backbone moves up; the carboxylic oxygens hardly change their adsorption height. Apparently, the local Ag-O_{carbox} bonds, which can only form in the latter commensurate structure, prevent the oxygen atoms from moving upward together with the carbon backbone.

Nevertheless, regarding the distortion of PTCDA (saddle- or "M" -shape) and its correlation with charge redistribution at the metalorganic interface, we can identify similar trends in heteromolecular and homomolecular phases. For the homomolecular systems, the transition from a saddlelike distortion on Ag(111) to the M-like distortion on Ag(100) and Ag(110) is accompanied by a downward shift of the LUMO (i.e., an increase of the LUMO binding energy) [22]. Similarly, in the MBW structure (saddlelike distortion), the PTCDA LUMO is found in UPS at a binding energy that is 70 meV smaller than in the MZZ structure [55] (M-like distortion). Both of the above homo- and heteromolecular cases suggest that the change to the M-like distortion of PTCDA may be related to an enhanced stabilization of the LUMO (i.e., a shift to higher binding energy). However, in contrast to the homomolecular phases, the LUMO stabilization in the MZZ structure does not arise from the molecule-substrate interaction but rather from a substrate-mediated charge reorganization between CuPc and PTCDA. We also note that due to the inverted donor/acceptor ratio, in the MZZ structure each PTCDA molecule is surrounded by four times more CuPc molecules than in the MBW structure. This difference in the stoichiometry of the heteromolecular film changes the amount of charge redirected from CuPc toward the PTCDA molecules. It is much larger for the MZZ structure than for the MBW structure, leading to a more effective PTCDA LUMO filling for the former, which in turn may be responsible for the M-like distortion of PTCDA.

So far we have tuned the ratio of donors and acceptors in the mixed film. In the following, we discuss two systems with either the donor or the acceptor replaced by molecules with different donor/acceptor strengths. This will make the interplay between charge reorganization and molecular adsorption heights at the heteromolecular hybrid interfaces even clearer.

Figure 4(a) shows the adsorption heights obtained for a structure containing 1,4,5,8-naphthalene tetracarboxylic-acid dianhydride (NTCDA) instead of PTCDA, while in Fig. 4(b) CuPc was replaced by tin-II-phthalocyanine (SnPc). Both structures are Pc-rich, so they should be compared with the CuPc-PTCDA MZZ phase [44].

Most remarkably, we find in both of the new structures that the two molecules involved adjust their molecular adsorption heights to an intermediate value, similar to the case of the mixed CuPc-PTCDA structures. This suggests that the alignment of adsorption heights in heteromolecular films is a general trend, at least for those systems exhibiting weak chemisorption [62]. Furthermore, in both modified structures the acceptor molecules show also an M-like distortion, similar to the case of the MZZ structure. However, a closer inspection reveals some quantitative differences in the adsorption geometries. While the adsorption heights of the donor molecules (CuPc and SnPc) are reduced by almost the same amount in

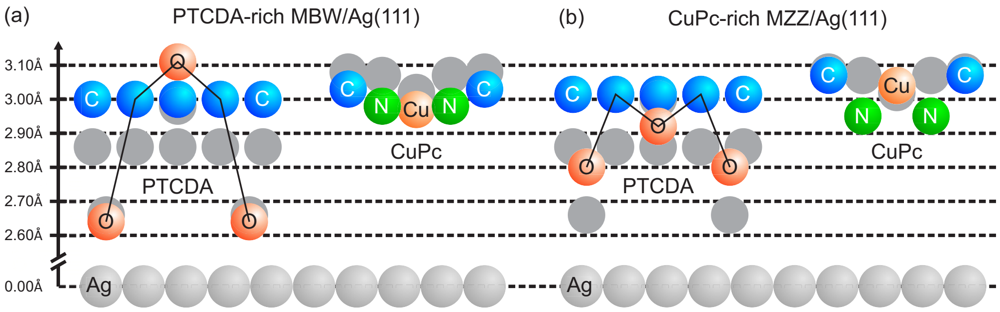


FIG. 3. (Color online) Models for the vertical adsorption geometry of CuPc and PTCDA in (a) the MBW and (b) the MZZ structure. For PTCDA we show a view on its short side, for CuPc we only indicate the adsorption heights of the individual atomic species. Colored and gray spheres correspond to the hetero- and homomolecular structures, respectively [10,21].

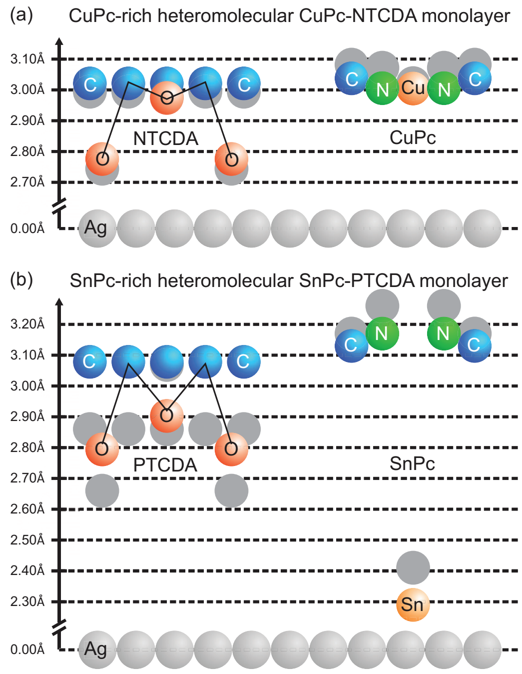


FIG. 4. (Color online) Models for the vertical adsorption geometries in Pc-rich phases consisting of (a) CuPc and NTCDA, and (b) SnPc and PTCDA on Ag(111). Colored and gray spheres correspond to the hetero- and homomolecular phases, respectively [59–61,65].

all heteromolecular structures (relative to the homomolecular phases), the displacements of the acceptor molecules (PTCDA and NTCDA) depend on the combination of donor/acceptor molecules. In the CuPc-NTCDA structure, the detected change in the adsorption height of NTCDA is within the experimental uncertainty and much smaller than in the CuPc-PTCDA MZZ case. We attribute this to already rather similar heights of NTCDA and CuPc observed for the homomolecular phases, but also to the smaller electron affinity of NTCDA compared to PTCDA [63], which does not allow NTCDA to take up as much charge from the neighboring CuPc adsorption sites as PTCDA does. This results in less charge reorganization and very small changes in the adsorption height of the acceptor molecules in the mixed CuPc-NTCDA structure.

For the structure with the donor molecule replaced [SnPc-PTCDA; see Fig. 4(b)], the carbon backbone of PTCDA is pushed even further away from the silver surface than in the MZZ structure. This may be caused by the particular adsorption configuration of the nonplanar SnPc molecule, where the Sn atom is positioned below the molecular plane. Apart from the fact that the Sn-down configuration leads to a substantially larger adsorption height (of the tetra-azaporphyrin core) in homomolecular SnPc layers, which requires a larger upward shift of PTCDA to equalize the heights in the heteromolecular layer, it also has significant consequences for the charge reorganization, since the electron density of the Sn-derived states (mainly the HOMO-1) reaches far out of the molecular plane and, due to the tin-down configuration, further into the silver substrate than any state of the planar CuPc molecule in the MZZ structure [9]. Hence, a strongly enhanced push-back effect can be expected for (Sn-down) SnPc molecules compared to CuPc, such that even more charge is displaced from the SnPc adsorption sites toward the neighboring PTCDA sites. This would in turn lead to an increased charge accumulation underneath the PTCDA backbone, which, compared to the mixed CuPc-PTCDA films, pushes the molecule further away from the silver surface, just as we have observed in our NIXSW study. The carboxylic and anhydride oxygen atoms, however, are found at almost exactly the same heights as in the MZZ structure. This indicates that the interaction strength between the functional oxygen groups and the silver surface is not significantly influenced by the enhanced charge accumulation at the PTCDA site in the SnPc-PTCDA film.

In conclusion, we have investigated the alignment of adsorption heights of different molecules in heteromolecular monolayer structures adsorbed on Ag(111) by varying both the ratio of donors and acceptors, and the strength of their charge-accepting or -donating character. We find that the original characters of the molecular species are mutually enhanced by the formation of mixed films, i.e., strong charge acceptors become stronger, weak acceptors become weaker and even turn to donors. This can be explained by substrate-mediated charge transfer from the donor to the acceptor; for details, see Ref. [54]. In mixed films, donor molecules can push back the evanescent electron density spill-out of the metal substrate not only toward its surface (as in homomolecular phases), but also toward the acceptor molecules. This reduces (increases) the charge spill-out below the donor (acceptor) molecules, which consequently decreases (increases) their adsorption heights. In the end, both molecules of the heteromolecular film are aligned to almost the same adsorption height. We propose that this effect is not limited to the molecular systems presented here, but is a general behavior of weakly interacting, π-conjugated molecules adsorbed in heteromolecular films on noble metal surfaces.

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[43] We note here that all molecules studied in the present paper are acceptor molecules when deposited on Ag(111) in homomolecular films. However, when co-adsorbed, the weaker acceptors act as donors *vis à vis* the stronger acceptor [54]. For this reason, we refer to the weaker acceptor of a pair as a (relative) donor.

[44] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.89.161407 for details of sample preparation, identification of different phases, and the NIXSW experiment.

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[56] A slightly larger adsorption height for all CuPc species in the MZZ layer is caused by a small amount of ≈ 0.15 ML of CuPc molecules adsorbed in the second organic layer. This

is a consequence of the sample preparation procedure for the MZZ phase, and it can also explain the slightly lower coherent fractions for the CuPc species compared to the PTCDA species (see also Table 1 in the Supplemental Material [44]).

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[63] The smaller electron affinity of NTCDA compared to PTCDA is also reflected by the larger adsorption height of NTCDA homomolecular films compared to PTCDA, and it indicates a weaker chemical character for the molecule-substrate bond of NTCDA with Ag(111).

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