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Charge-induced distortion and stabilization of surface transfer doped porphyrin films

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The interaction between zinc-tetraphenylporphyrin (ZnTPP) and fullerenes (C_{60} and $C_{60}F_{48}$) are studied using ultraviolet photoelectron spectroscopy (UPS) and scanning tunneling microscopy (STM). Low temperature STM reveals highly ordered ZnTPP monolayers on Au(111). In contrast to C_{60} , a submonolayer coverage of $C_{60}F_{48}$ results in long-range disorder of the underlying single ZnTPP layer and distortion of individual ZnTPP molecules. This is induced by substantial charge transfer at the organic-organic interface, revealed by the interface energetics from UPS. However, a second layer of ZnTPP prevents $C_{60}F_{48}$ guests from breaking the self-assembled porphyrin template. This finding is important for understanding the growth behaviour of “bottom-up” functional nanostructures involving strong donor-acceptor heterojunctions in molecular electronics. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4815978>]

I. INTRODUCTION

Organic semiconductor materials play a central role in new architectures for field-effect transistors,^{1,2} light-emitting diodes,^{3,4} and solar cells.^{5,6} The electronic characteristics of these nanoscale devices are governed to a large extent by the choice of molecular species and their behaviour at interfaces. Small variations in electronic properties of the interfaces can dramatically influence the performance and efficiency of the electronic devices, and the optimisation of device architectures therefore relies on a complete understanding of both the electronic and structural properties of nanoscale organic interfaces.

The energy level alignment in conjunction with interfacial charge transfer (CT) has been examined via photoelectron spectroscopies for different interface architectures: organic-metal,^{7–9} organic-organic,^{7,9,10} and organic-oxide.¹¹ The orientation and assembly of molecular layers have been probed via Near edge X-ray absorption fine structure (NEXAFS) and scanning probe methods.¹² Charge transfer not only impacts the electronic properties by modifying the energy level alignment at organic interfaces,¹³ but can also trigger structural rearrangement. Recently, for the case of organic-metal interfaces, there have been a number of reports of the CT-induced distortion both of individual molecules in the adlayer^{14,15} and of the underlying metallic surface.^{15,16} Romaner *et al.*¹⁴ have investigated the interface energy level alignment of tetrafluoro-tetracyanoquinodimethane (F_4TCNQ) on Cu(111) and shown that strong geometric distortion of the F_4TCNQ molecule depends on the electron transfer and electron back

transfer at the molecule-metal interface. Bedwani *et al.*¹⁶ have observed structural modification of the topmost Cu(100) surface layer by adsorbing tetracyanoethylene (TCNE). Tseng *et al.*¹⁵ have demonstrated a CT-induced structural rearrangement at both sides of the $TCNQ/Cu(100)$ interface.

Interactions at organic-organic interfaces are generally less disruptive than at organic-metal interfaces due to the weaker van der Waals forces governing the former. While a large number of organic heterojunctions revealed vacuum level alignment to within 0.1 eV,¹⁷ spontaneous charge transfer for organic heterojunctions where the ionisation potential (IP) of the donor molecule is in the vicinity of the electron affinity (EA) of the acceptor molecule leads to substantial interface dipoles. For example, a considerable change of 0.6 eV in the work function was measured for $TCNQ$ evaporated on top of tetrathiafulvalene (TTF), where EA_{TCNQ} and IP_{TTF} are 4.6 eV and 5.0 eV, respectively.¹⁸

This paper demonstrates for the first time the structural disorder and molecular distortion induced by charge transfer at an organic-organic interface. The system examined is zinc-tetraphenylporphyrin (ZnTPP) which is *p*-type doped by fullerene (C_{60}) and fluorofullerene ($C_{60}F_{48}$). Using a combination of ultraviolet photoelectron spectroscopy (UPS) and scanning tunneling microscopy (STM), it is shown that submonolayer coverage by the strong acceptor $C_{60}F_{48}$ gives rise to both disorder of an underlying monolayer (ML) ZnTPP film and geometric distortion of the individual porphyrin molecules despite negligible ZnTPP- $C_{60}F_{48}$ chemical interaction. As the driving force for these structural changes, we identify a substantial integer charge transfer in the system by comparing it with the ZnTPP/ C_{60} case where neither significant charge transfer nor molecular distortion or disorder of the porphyrin film is observed. Furthermore, we show that the

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growth of a double-layer ZnTPP film is sufficient to stabilize the porphyrin film against the charge-induced effects.

II. EXPERIMENTAL DETAILS

The experiments were conducted in two separate (UPS, LT-STM) ultrahigh vacuum (UHV) systems (2×10^{-10} mbar). ZnTPP, C_{60} , and $C_{60}F_{48}$ (containing D_3 and S_6 symmetries) were purchased from Porphyrin Systems (purity > 98%), Aldrich (purity > 99.9%), and Term USA (purity > 98%), respectively, and used without further modification. The molecules were evaporated *in situ* from separate home built low temperature Knudsen cells and were deposited onto the pre-cleaned Au(111) sample at room temperature. Ad-layer thicknesses were controlled with a quartz crystal microbalance during evaporation. The STM experiments were performed using a Createc LT-STM operating at 77 K. Self-assembled monolayers of ZnTPP on Au(111) were prepared by evaporation of multilayers at 300 K and subsequent thermal desorption of excess ZnTPP at 550 K.¹⁹ The cleanliness and completeness of the ML was checked by STM prior to the deposition of fullerene adsorbates. All molecular depositions were conducted on substrates at room temperature and subsequently cooled to 77 K for STM measurements. All STM scans were performed in constant current mode. For UPS

measurements, a spectrometer equipped with a SPECS Phoibos 150 MCD-9 analyzer and a helium lamp ($h\nu = 21.22$ eV) was employed. All UPS spectra were taken with the sample biased at -6 V and processed by satellite subtraction. All molecular orbital positions were determined by linear extrapolation of the onsets of the measured peaks. However, this method possesses a relatively big error due to adding a tangent to the peak. Therefore, all energy level shifts were determined by comparing the maxima of the peaks which has proven to be more accurate.

III. RESULTS AND DISCUSSION

The changes in the energy level alignment at the ZnTPP– C_{60} and ZnTPP– $C_{60}F_{48}$ interfaces were probed via photoemission. Figure 1 shows the secondary electron distribution and the corresponding near Fermi-edge spectra obtained for a ZnTPP film covered with C_{60} (a) and $C_{60}F_{48}$ (c). In both cases, the bottom spectrum is obtained for a 15 ML ZnTPP thin film deposited on a clean Au(111) substrate, with the bare Au surface providing the energy calibration for all spectra relative to its Fermi edge. From the measured position of the low-energy cut-off of the secondary electron distribution, the work function of the bare ZnTPP film was determined to be 3.8 ± 0.1 eV. Submonolayer C_{60} coverages do not cause

FIG. 1. Evolution of the secondary electron cut-off and the occupied molecular orbitals from UPS as C_{60} (a) and $C_{60}F_{48}$ (c) are deposited on ZnTPP. The vertical lines mark the secondary electron cut-off and HOMO positions. The energy level diagrams for both interfaces before contact are shown in (b) and (d).

the ZnTPP energy levels to change, as highlighted by the vertical line connecting the ZnTPP HOMO peaks. Only when C_{60} monolayer coverage is reached, does the work function increase by 0.1 eV and the ZnTPP HOMO shifts by 0.1 eV towards the Fermi level. The ZnTPP HOMO is attenuated upon C_{60} deposition as expected. It is worth noting that the ZnTPP HOMO-1 would also be attenuated, but this is not evident in Figure 1(a) because of the emergence of the C_{60} HOMO-1 peak at approximately the same binding energy. As a reference, a spectrum obtained for a 10 monolayer film of C_{60} is shown at the top of the figure. No charge transfer is possible for submonolayer C_{60} coverages, because the LUMO of molecular C_{60} (EA = 2.65 eV²⁰) is significantly above the Fermi level of ZnTPP (WF = 3.8 eV), as illustrated in the energy level diagram in Figure 1(b). Charge transfer is only expected to occur as the EA of C_{60} increases towards 3.6 eV, the value for the fullerite solid.^{21,22} Indeed, for a closed ML of C_{60} the 0.1 eV level shifts of ZnTPP are indicative of a small amount of charge transfer from ZnTPP to C_{60} of about 0.01 electron per C_{60} molecule.

In contrast, very significant shifts in both the work function and ZnTPP HOMO are induced by doping with submonolayer coverages of $C_{60}F_{48}$ (Figure 1(c)). In this case, the deposition of up to a ML of $C_{60}F_{48}$ induces an increase in the work function by 1.85 eV and a shift in the ZnTPP HOMO of 0.67 eV. These large energy level shifts originate in the substantial charge transfer at the interface between $C_{60}F_{48}$ and ZnTPP that occurs due to the fact that EA of $C_{60}F_{48}$ (molecular form 4.06 eV,²³ solid form 5.0–5.27 eV^{23,24}) exceeds the work function of the bare ZnTPP film,²⁵ as shown in the energy level diagram in Figure 1(d). Therefore, it is energetically beneficial for electrons to transfer from ZnTPP to $C_{60}F_{48}$ and the work function increases on account of the electrostatic dipole potential established across the ZnTPP– $C_{60}F_{48}$ interface by the separated charges. As has been established elsewhere, the initial energy level alignment of ZnTPP and $C_{60}F_{48}$ is such that no activation energy is necessary for charge transfer and each adsorbed $C_{60}F_{48}$ molecule accepts a unit charge from the substrate up to a coverage of about 0.5 ML, i.e., the doping efficiency is one.²⁴ That implies that the same charge transfer holds also at low temperatures where the current STM work was performed. Beyond 0.5 ML, a mounting activation energy for charge transfer reduces the doping efficiency gradually to zero with increasing coverage. We stress that the changes in energy levels of substrate and adlayer have been quantitatively modeled in terms of the Schottky-Mott model, i.e., without resource to direct chemical interaction between the two molecular species. A more detailed discussion of our organic doping model can be found elsewhere.^{13,24}

The $C_{60}F_{48}$ HOMO cannot be seen with ease, as there is no significant peak visible due to overlapping molecular orbitals of ZnTPP. As reference, a spectrum of a thick $C_{60}F_{48}$ film on Au(111) is presented on top of the other spectra (dashed line in Fig. 1(b)) with the HOMO visible at 4.41 eV below E_F . This implies that there is no interference of $C_{60}F_{48}$ states with the HOMO and HOMO-1 of ZnTPP. Furthermore, there is no evidence for any kind of new valence band structure with $C_{60}F_{48}$ coverage in this energy window that would be indicative of rehybridisation between $C_{60}F_{48}$ LUMO and

FIG. 2. STM images (1 V, 0.1 nA) of (a) 18 nm $\times$ 18 nm monolayer of ZnTPP on clean Au(111) and (b) detail 5 nm $\times$ 5 nm of ZnTPP self-assembly with unit cell indicating an almost perfectly square unit cell with $a = b = 1.4$ nm, $\theta = (88 \pm 1)^\circ$, $\delta = (34 \pm 1)^\circ$, and $\gamma = (66 \pm 1)^\circ$.

ZnTPP HOMO, as has been recently observed for the pentacene (PEN)/ F_4 -TCNQ interface, for example.²⁶ Also, the ZnTPP core levels do not exhibit any structural modifications in terms of new chemically shifted components.

To summarize the results from the photoemission experiment, $C_{60}F_{48}$ interacts strongly with ZnTPP in terms of integer charge transfer, with a single hole introduced in the underlying porphyrin film for each $C_{60}F_{48}$ acceptor up to about 0.5 ML coverage and less beyond. C_{60} , in contrast, exchanges an insignificant amount of charges with ZnTPP, as indicated by the ~ 0.1 eV energy level shift and does so only at full monolayer coverage. In both cases, there is no evidence for direct chemical interaction between donor and acceptor.

Having established the contrasting levels of doping behaviour exhibited by C_{60} and $C_{60}F_{48}$, we now turn to LT-STM to address the influence of the varying degrees of charge transfer in the C_{60} -ZnTPP and $C_{60}F_{48}$ -ZnTPP systems on the structural aspects of the interface. As a starting point, we examine the assembly of thin ZnTPP films on the Au(111) surface. Figure 2 shows typical LT-STM images of a self-assembled monolayer of ZnTPP on an underlying Au(111) substrate. ZnTPP molecules lie flat on the surface, indicating effective overlap of the organic π -orbitals and the metallic electronic states. The completely close-packed structure, detailed in Figure 2(b), is due to an edge-to-face stacking of the phenyl rings rather than a face-to-face π - π stacking.²⁷ Buchner *et al.*²⁸ have previously demonstrated on the basis of densely packed H_2 TPP, CoTPP, and FeTPP on Ag(111), that

FIG. 3. STM image (1 V, 0.2 nA) of 0.2 ML of C_{60} molecules evaporated on top of a predeposited ZnTPP monolayer on Au(111), showing both C_{60} single molecules and island formation. The underlying ZnTPP monolayer remains intact and ordered.

adjacent porphyrin phenyl rings preferably appear to be in the edge-to-face “T-shape” stacking configuration. Even though the unit cell is almost perfectly square with $a = b = 1.4$ nm and $\theta = (88 \pm 1)^\circ$, the intramolecular conformation does not exhibit a perfect “cross-like” geometry, given $\delta = (34 \pm 1)^\circ$ and $\gamma = (66 \pm 1)^\circ$ (angles of the opposite phenyl rings with respect to the unit cell), where $\delta + \gamma = 100^\circ > 90^\circ$. Furthermore, the opposing pyrrole groups in x-direction seem to be more stretched than the ones in y-direction, since the distance between the perimeters of the macrocycles is larger in y-direction ($c = 0.42$ nm) than in x-direction ($d = 0.15$ nm), as indicated by the dashed lines in Figure 2(b); this presumably arises from the preferred molecular orientations in the self-assembled ML film.

Self-assembled monolayers of metallated porphyrin and other porphyrin derivatives on top of metal substrates have been thoroughly examined in previous studies.^{28–30} Rojas *et al.*²⁹ examined a range of metallated and non-metallated porphyrin derivatives on top of metal substrates and found that a subtle balance between molecule-molecule and molecule-substrate interactions governs the occurrence of self-assembly. Whereas most porphyrin molecules self-

assemble into closely packed monolayers, H_2 TPP adsorbates are arranged randomly on top of Cu(111) indicating strong molecule-substrate interaction in terms of charge transfer. In the present study, charge transfer between ZnTPP and Au(111) can be excluded, given that ZnTPP molecules self-assemble on Au(111) indicating small surface migration barriers. This provides the ideal platform for further investigation of the fullerene-porphyrin interfaces.

Figure 3 shows a STM image of the ZnTPP monolayer with 0.2 ML coverage of C_{60} . The fullerenes are present as single molecules as well as aggregated to islands. Single molecules appear to be larger than the ones within an island which we ascribe to lateral movement of the molecules during the scan. The fact that C_{60} possesses considerable lateral mobility on top of ZnTPP is confirmed by changes in position from scan to scan which in turn indicates a low mobility barrier on account of weak C_{60} -ZnTPP interaction. We suggest that the interaction between C_{60} and ZnTPP is small on account of the weak mixing of the planar ZnTPP π -orbitals with the spherically disposed C_{60} π -orbitals. More importantly, we note that there is no apparent disorder or distortion of the underlying ZnTPP film in response to deposition of C_{60} .

The behaviour for the case of fluorinated fullerene is very different. Figure 4 shows a STM image obtained for a ZnTPP monolayer covered by the same coverage (0.2 ML) of $C_{60}F_{48}$. In contrast to the assembly seen in the case of fullerene, $C_{60}F_{48}$ molecules do not form islands. Unlike the case of C_{60} , the surface morphology of $C_{60}F_{48}$ is not solely governed by the attractive van der Waals interaction but also by Coulomb repulsion, because $C_{60}F_{48}$ doping is accompanied by the development of a significant interfacial electrostatic dipole since each fluorofullerene molecule is singly charged.^{24,31} This repulsive interaction is apparently sufficient to overcome the attractive van der Waals interaction between the adsorbed molecules so that the fluorofullerenes remain dispersed. The deposition of $C_{60}F_{48}$, even at this low coverage, leads to a dramatic change in the morphology of the underlying ZnTPP ML. The ZnTPP ML no longer exhibits the original order of the self-assembled structure and the individual molecules are randomly oriented. In addition, a considerable number of porphyrin molecules not in direct contact with $C_{60}F_{48}$

FIG. 4. STM image (0.7 V, 0.1 nA) of 0.2 ML $C_{60}F_{48}$ on a full layer of pre-deposited ZnTPP on Au(111). The insets (a)–(c) show examples of $C_{60}F_{48}$ -induced deformation of ZnTPP molecules. For comparison, an undistorted ZnTPP molecule from a self-assembled ML on Au(111) is depicted in (d).

appear distorted and asymmetrical in shape (for example, Figures 4(a)–4(c)). The apparent structure of ZnTPP molecules in Figure 4 appears to be random and in many cases the molecular structure observed cannot be derived solely from a simple reorientation of an otherwise undistorted molecular structure as observed for the bare ZnTPP film (Figure 4(d)).

The atomic *p*-states of porphyrin meso-carbons and pyrrolic β -carbons contribute significantly to the wavefunction of the ZnTPP HOMO.³² Given further that, on energetic grounds, the positive charge resulting from the charge transfer to C₆₀F₄₈ resides preferentially in the HOMO, it is evident that the charge is primarily localized spatially on the meso- and pyrrolic β -carbon atoms. Hence, the significant and localized charge redistribution will also give rise to a reoptimization of the intramolecular conformation. In particular, the reduced electron density on the β -carbons relaxes the steric hindrance, which originally forces the plane of the phenyl rings out of the porphyrin macrocycle plane allowing them to take on a more co-planar configuration after charge transfer. Yokoyama *et al.*³³ reported that the orientations of both phenyl- and pyrrole groups are interlinked, i.e., reorientation of the phenyl rings causes the pyrrolic β -carbons to move up or down. As a result of this charge transfer-induced intramolecular distortion, the maximal packing density of the self-assembled ZnTPP monolayer can no longer be maintained which is one factor bringing about the observed disorder of the ZnTPP ML. CT-induced deformation has been observed previously at a metal/organic interface. It was shown that electrons are transferred from TCNQ to the Cu(100) substrate and that structural rearrangements exist for both metal substrate and organic molecules.¹⁵

Furthermore, the unit cell of the ZnTPP self-assembly determined earlier corresponds to 5.1×10^{13} molecules/cm² for a full monolayer. Given further that 0.2 ML coverage of C₆₀F₄₈ corresponds to 1.6×10^{13} molecules/cm² (ML = 7.8×10^{13} molecules/cm²), it can be estimated that, on average, the ratio of guest to host molecules is only about 1:3. The disorder induced by 30% distorted molecules will free all molecules from the constraints of a closed packed structure and will in general give the freedom for a wider range of molecular conformations for ZnTPP. Porphyrin molecules have been demonstrated to possess a high degree of conformational freedom, as the macrocycles exhibit both planar and nonplanar (saddled and ruffled) structures in solution.³⁴ Hence, in response to the 30% fraction of distorted ZnTPP molecules the nonplanar nature of the remaining molecules is enhanced and distinctly saddled and ruffled structures are favoured. It is furthermore conceivable that part of the charge on the contact porphyrin is shared with two or three immediate neighbours that then undergo similar distortions.

The lower half of the STM image in Figure 5(a) shows C₆₀F₄₈ molecules on a double-layer of ZnTPP on Au(111). Similar to the single-layer case, the adsorbates do not adopt preferred adsorption sites and are randomly distributed over the surface. In this case, however, the underlying ZnTPP double layer is not disturbed by the guest molecules and highly ordered rows of porphyrin are clearly visible in the underlying film. This suggests that the deposition of a second porphyrin

FIG. 5. (a) STM image (2 V, 0.1 nA) containing C₆₀F₄₈ on top of single-layer and double-layer ZnTPP. (b) Line profile along the highlighted line in (a) with the zero of the abscissa corresponding to the uppermost end of the line in Fig. 4(c).

layer is sufficient to stabilize the ZnTPP film against charge-induced distortion when C₆₀F₄₈ is subsequently deposited. The dramatic contrast in behaviour of the ZnTPP film is illustrated further in the top half of Figure 5(a), where a single layer ZnTPP is visible in the same STM scan. The difference in ordered double layer and disordered single layer is evident and is quantified in the line profile in Figure 5(b). Periodic protrusions are present for the double layer but not the single layer, signalling the high structural order of the ZnTPP self-assembly in the former case and its absence in the latter. It is worth noting that Figure 5(a) may give the impression that up to 50% of the molecules appear to be paired. We have analysed a large number of similar STM images and the proportion of molecules that could be regarded as paired is less than 10%.

Based upon these observations we come up with the following interpretation. Single porphyrin layers possess a marginal 2D intermolecular attraction due to effective “T-shape” stacking of the phenyl groups, which enables the ZnTPP molecules to form highly ordered structures. However, this lateral force is not sufficient to prevent disorder upon charging by C₆₀F₄₈ adatoms. The fact that distortion of the ZnTPP film is not observed for a double layer, confirms that the observed distortion does not arise from chemisorption by C₆₀F₄₈, for example, via covalent bonding of fluorine to the underlying film as has been shown to be the case for fluorinated fullerenes on Si(111),^{35,36} or via hydrogen bond formation between C₆₀F₄₈ fluorine atoms and ZnTPP phenyl and pyrrole groups. The latter has been ruled out through a series of synchrotron based high resolution core level photoemis-

sion measurements.²⁴ In these measurements, precise analysis of ZnTPP C 1s core level line shapes showed no modification as would be expected from charge redistribution of the involved ZnTPP groups arising from hydrogen bond formation. The second ZnTPP layer enhances the intermolecular attraction within the ZnTPP film by incorporating additional π - π stacking of the porphyrin macrocycles. The combination of the lateral “T-shape” stacking and the perpendicular π - π stacking gives rise to a substantial cohesion of the double-layer porphyrin film. In addition, as the ZnTPP film thickness increases, the charge transferred from C₆₀F₄₈ would be screened in-plane and out-of-plane within the double-layer film. This improved screening effect minimizes the repulsive ZnTPP⁺-C₆₀F₄₈⁻ dipole interaction for an overall more stable ZnTPP double layer and reduces the charge on individual molecules preventing their distortion.

IV. CONCLUSION

In summary, we have demonstrated the structural disorder and molecular distortion induced by charge transfer at an organic-organic interface. UPS studies reveal the presence of strong integer charge transfer between ZnTPP and C₆₀F₄₈ adsorbates, which is proven to be the driving force for the structural disorder seen in LT-STM, because neither charge transfer nor structural disorder are seen for C₆₀ on ZnTPP. We have demonstrated that two layers of ZnTPP significantly improve the structural stability of ZnTPP in the presence of integer donor-acceptor charge transfer. Further modeling of the molecular structure of the ZnTPP films would enhance our understanding of why the charge-induced structural changes at the interface are dramatically different for the single-layer and double-layer porphyrin films. The control of molecular self-assembled layers has significant relevance for the design and construction of nanoscale molecular electronic devices.

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