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Self-Assembly and Properties of Nonmetalated Tetraphenyl-Porphyrin on Metal Substrates

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Abstract

The structure–electronic structure relationship of nonmetalated *meso*-tetraphenyl porphyrin (2H-TPP) on the (111) surfaces of Ag, Cu, and Au was studied with a combination of scanning tunneling microscopy, photoelectron spectroscopy, and density functional theory. We observe that the molecules form a 2D network on Ag(111), driven by attractive intermolecular interactions, while the surface migration barriers are comparatively small and the charge transfer to the adsorbed molecules is minimal. This is in contrast to a significant charge transfer observed in 2H-TPP/Cu(111), resulting in repulsive forces between the molecules that prevent molecular adlayer network formation. It is shown that the limiting factor in formation of self-organized networks is the nature of the frontier orbital overlap and the adsorbate–interface electron transfer. Further, the electronic structure, most notably the HOMO–LUMO splitting, are found to be dependent on the substrate as well. The comparison of the results in this article with published work on similar porphyrins suggests that the molecule–substrate interaction strength is determined by the molecule's metalation, and not so much by the ligands.

Introduction

The self-assembly of porphyrins on well-defined surfaces is attracting considerable interest because it promises to create surface patterns with nanometer dimension that exhibit specific electronic, sensoric, optic, or catalytic functionality^{1–3} or even interesting magnetic properties.^{4,5} The ability of porphyrin to show self-organization and to accommodate metal atoms in their macrocycle is exploited, for instance, to form metal–organic frameworks or adsorbed layers for catalysis.^{6–9} The self-assembly is mainly driven by noncovalent metal–organic coordination interactions, which is well-known and important in solution-based 3D supramolecular chemistry.^{10–15}

Porphyrin molecules have been adsorbed onto surfaces to form supramolecular networks from solution,^{16–19} electrochemically^{20,21} or by thermal evaporation under vacuum conditions.^{22–28} While there is a rich literature on the electronic structure of these adsorbates, the surface adlayer structures have also been characterized with scanning force microscopy, scanning tunneling microscopy, or X-ray absorption near-edge structure analysis.²⁹ The rationale of such experiments on 2D structures has been to study the long-range interactions that determine the self-assembly processes. It has been demonstrated that the bottom-up fabrication of highly organized porphyrin layers, as well as of porphyrin-based multicomponent molecular entities, depends on the interplay of molecule–molecule and substrate–molecule interactions. Molecule–substrate interactions will set limits to the mobility of the adsorbed molecules and may alter the electronic structure of the adsorbed molecules, or the electronic states at the surfaces may become locally perturbed by the adsorbate.⁶⁰ A consequence is that the established concepts of solution-based coordination chemistry cannot be ap-

plied without appropriate modification. The substrate thus becomes an additional parameter to control the adsorption energy of the molecules and, hence, their diffusivity at surfaces. An intriguing demonstration of this effect is the self-assembly of porphyrins, which are decoupled from their metal substrate by insulating NaCl layers of varying thickness.²³ The interaction was shown to be dependent on the NaCl layers, and the thicker the NaCl the weaker the interaction and the more delayed the onset of network formation. The occupation of the center ring of the porphyrin may affect the molecular adsorption at surfaces. As an example, free-base or Cu-incorporated porphyrin molecules show different arrangements along step edges on Cu(100) surfaces. While 2H-TBPP bridges over the step edges, Cu-TBPP sits on either side of step edges.²⁷ In contrast, no difference in the network architecture was found for differently metalated TPP on Ag(111).⁵⁷ Such a subtle dependence of adsorption site on metal incorporation, if fully understood, may become useful to control the self-assembly or the properties of the molecules on surfaces.

The goal of the present work is to investigate the competition between noncovalent intermolecular interactions and molecule–substrate interactions for 2H-TPP on Ag(111), Cu(111), and Au(111) and to establish the structure–properties relationship and its dependence on interactions with the supporting substrate.

Experimental Section

Ag(111) and Cu(111) single crystals of purity >99.999% were prepared by repeated cycles of Ar ion sputtering and annealing at temperatures of 850 and 800 K, respectively, for multiple cycles in ultrahigh vacuum (UHV) conditions ($<1 \times 10^{-10}$ mBar). The substrate's cleanliness was checked by STM at 80 K before deposition of organic material, as well as by photoemission.

The 5,10,15,20-tetraphenyl-21H,23H-porphine (2H-TPP) was purchased from Frontier Scientific (purity >97%) and used without further modification. Molecules were deposited by evaporation using a home-built Knudsen Cell evaporator. Molecules were evaporated at a rate of approximately 0.05 ML/min at crucible temperatures of approximately 500 K. Coverages were initially limited to approximately $\Theta \approx 0.01$ ML, where a monolayer (ML) is defined as coverages of approximately 5.1×10^{13} molecules/cm², and gradually increased by successive evaporation cycles as needed. For a comparison of molecular adsorption, the 2H-TPP adlayers were studied after evaporation onto Ag(111) and Cu(111) under identical growth conditions.

Samples were immediately transferred in situ to an adjoining chamber for scanning tunneling microscopy (STM) measurements. Image data were obtained under constant current mode using an Omicron Nanotechnology low temperature STM (LT STM) with a tungsten tip at 80 K and pressures of low 10^{-11} mBar. Combined photoemission (UPS) and inverse photoemission spectra (IPES) were taken in a separate UHV system using the same single crystal substrates and evaporators. In all spectroscopy measurements, the binding energies are referenced with respect to the Fermi level of the substrates in close contact with the sample surface. The IPES were obtained by using variable energy electrons incident along the sample surface normal while measuring the emitted photons at a fixed energy (9.7 eV) using a Geiger-Müller detector. The instrumental line width is 400 meV, as described elsewhere.³⁷ The angle integrated photoemission (UPS) studies were carried out using a helium lamp at $h\nu = 21.2$ eV (He I) and a Phi hemispherical electron analyzer with an angular acceptance of $\pm 10^\circ$ or more, as also described elsewhere.³⁷

Calculations were performed using density functional theory (DFT) utilizing the generalized-gradient approximation (GGA-DFT) HCTH functional.⁴⁰⁻⁴² The double numerical polarized basis sets (DNP) with the semicore pseudo potentials were applied for all atoms, including Ag, C, N, and H atoms.^{43,44} A 2-layer 10×10 silver slab was used to simulate the Ag(111) surface substrate. In addition, a layer with 10×4 Ag(111) surface was placed on top of the slab to simulate the step-edge effects. In order to reduce the computational cost, the substrate was frozen while the 2H-TPP was fully relaxed. All calculations were performed by using the DMol³ software package.^{43,44}

Growth Studies with STM

2H-TPP on Ag(111). The 2H-TPP adlayers were studied after evaporation onto Ag(111) and Cu(111) under identical growth conditions. First, submonolayer aliquots of the 2H-TPP molecules were evaporated onto a Ag(111) substrate at 300 K. The substrate was subsequently cooled to liquid nitrogen temperatures ($T = 77$ K) for STM studies. For very low 2H-TPP coverage, ($\Theta < 0.01$ ML), molecules are exclusively observed at the substrate step edges, while nothing is seen on the terraces. Higher resolution STM images, as in Figure 1 (a), show that those 2H-TPP molecules straddle the step edges, with the phenyl ligands oriented with an angle of approximately $\phi = 21^\circ$ relative to the boundary of the step-edge. All observed step-edge phase molecules sit across the Ag(111) step-edges in apparently identical geometries. These molecules are not seen to engage in any lateral motion even over the period of several hours. Increasing the 2H-TPP coverage resulted in an increase of the step-edge occupancy, until every step edge was fully occupied.

Molecules nucleated into clusters on the terraces only after complete occupation of the step-edges, resulting in ordered two-dimensional networks as those seen in Figure 1b,c. Clearly

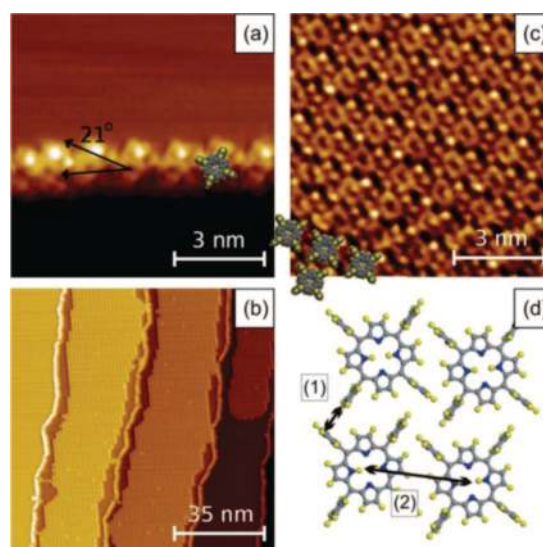


Figure 1. STM images of 2H-TPP molecules adsorbed on Ag(111). (a) $\Theta < 0.01$ ML, all observed molecules located saddling step edges. (b) $\Theta \approx 0.5$ ML, (c) Close-up of molecules on terraces from (b) showing the relative orientation of the molecules. (d) Schematic illustration of measured intermolecular distances for (1) CH- π interaction at 3.9(3) Å and (2) unit cell dimension of 13.9(9) Å. All images taken at $I = 0.8$ nA, $V_{\text{Gap}} = -0.90$ nA.

visible in this figure is the coexistence of the step-edge phase²⁷ with extended 2D networks of 2H-TPP at a coverage of ($\Theta \approx 0.5$ ML), while (c) provides a detailed view of the molecular arrangement in the network. The molecules are found to order in tetragonal unit cells of length $a = 13.8$ Å, and to be rotated by 16° relative to the axis of the network (Figure 1d). Similar 2D arrangement can be found in bulk phases of TPP molecules incorporated with various metals such as Ti, V, Cr, Fe, Co, Cu, Zn, Ru, Mg, Sn, and Ge.⁴⁵⁻⁴⁷ The tetragonal unit cell parameter a obtained from X-ray single crystal diffraction of these phases ranges from 13.3 to 13.8 Å,⁴⁵⁻⁴⁷ comparable to the same parameter from our surface pattern. Interestingly, the metal free 2H-TPP molecules in bulk phase do not form this observed tetragonal 2D pattern.⁴⁵⁻⁴⁷ The CH- π spacing of 3.9 Å, found in Figure 1d, is also comparable to the tetragonal phase of metalated TPP bulk phases.

The orientation of the adsorbed molecules shows a clear influence of the underlying substrate crystallography, as we found three characteristic domains with main directions separated by roughly 60° , following Ag(111) substrate symmetry.

We conclude from the STM studies that 2H-TPP is highly mobile on Ag(111) at 300 K except at step-edges, with a mean diffusion length significantly larger than the mean terrace width of our substrate. The substrate step-edges, however, provide efficient pinning sites for the porphyrin molecules. The 2D network formation on the terrace is mainly driven by attractive molecule-molecule interaction while the interaction between the molecules and the substrate, specifically the migration barriers, are comparatively weak.

The same arrangement of molecules has been reported for 2H-TPP on the same substrate, as well as on Au(111).^{56,57,59} The geometry of the molecules and the limitations imposed by multiple interactions with neighboring molecules, including potential CH- π interactions between phenyl ligands and C-H pairs on neighboring macrocycles, determines the arrangements of molecules at surfaces, has, for example, been suggested in Reference 57. Calculations were performed to further examine these interactions and will be discussed later.

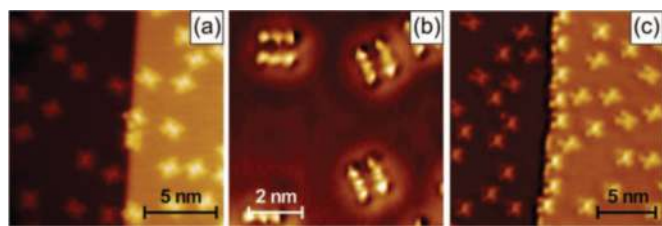


Figure 2. STM images of 2H-TPP chemisorbed on a cleaned Cu(111) substrate at $T = 300$ K and taken at $V = -0.8$ V with a tunneling current of $I = 0.90$ nA (a), a close-up image of the molecule taken at $V = +0.4$ V and $I = 0.8$ nA (b), and after annealing to $T = 350$ K taken with bias voltage of $V = -1.0$ V and $I = 1.4$ nA (c).

2H-TPP on Cu(111). 2H-TPP molecules were evaporated onto Cu(111) under conditions described in the previous section. STM images of submonolayer coverages of 2H-TPP on Cu(111), taken at 77 K, are summarized in Figure 2. The molecules were not observed to form 2D networks on Cu(111), unlike Ag(111). Rather, they tend to be randomly distributed across the terraces and remain isolated from neighboring molecules. No tendency toward step decoration was observed. The molecules appear to be oriented along the principal crystallographic directions of the underlying surface structure, as concluded from the generally observed angle of 120° between the major axes of any two closely adjacent molecules.

Observation of the molecules over significant lengths of time showed no lateral motion of the molecules over the substrate, contrary to what was seen for terrace-adsorbed molecules on Ag(111). Furthermore, the molecules on Cu(111) appear topologically distinct from the same molecular species adsorbed on the Ag(111). Under identical scanning conditions, the molecules appear with a raised center and 2-fold symmetry on Cu as seen for metalated species,⁴⁸ while on Ag they appear as ring-like structures with dark centers and clearly resolved arms. However, the appearance of the molecules is dependent on the bias voltage during the STM experiment, as a comparison of Figure 2, panels a and b, shows. At sufficiently low bias voltage, a ring becomes visible in the substrate in the vicinity of chemisorbed molecules (Figure 2b). This ring is ascribed to the formation of a surface dipole at the molecule site by drawing electrons from the substrate, leaving the molecules negatively charged. This surface induced dipole, along with greatly increased migration barrier for Cu(111)⁴⁹ seems to be related to the absence of self-assembled ordered structures of 2H-TPP on Cu(111).

In an attempt to overcome the diffusion barriers, the molecule–substrate system was annealed to higher temperatures (Figure 2c). Following moderate annealing to 350 K for 2 min, the molecules were seen to partially decorate the step edge, shown in Figure 2c. The step-edge occupancy was observed to become complete only after all further annealing to 450 K. The molecules occupying the step-edges in the 2H-TPP/Cu(111) remained seated at the top of the step-edge on the terrace and aligned with the axis of the molecule parallel with the step-edge boundary. No bridging of the step-edges, similar to 2H-TPP/Ag(111), was observed. Despite this observed motion on the terraces, the 2H-TPP molecules did not exhibit any 2D lateral organization on the Cu(111) terraces for all annealing temperatures studied up to 450 K.

Photoelectron Spectroscopy. Combined photoemission and inverse photoemission spectra have been taken for submonolayer, monolayer, and multilayer coverages of 2H-TPP on Ag, Au, and Cu substrates. The goal was to correlate the occupied and unoccupied electronic states of the molecules in contact with the

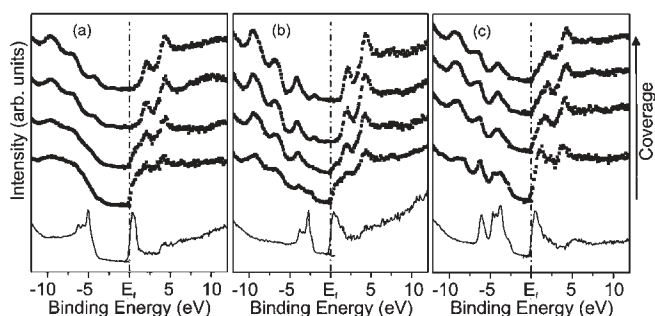


Figure 3. Coverage dependent photoemission and inverse photoemission spectra (symbols) of metal-free porphyrin (2H-TPP) adsorbed at 300 K in coverages (from bottom to top) of ≈ 0.5 , 1, 3, and 8 ML on (a) Ag(111), (b) Cu(111), and (c) Au(111). Shown at the bottom of each panel is the spectra of the pristine substrates as reference.

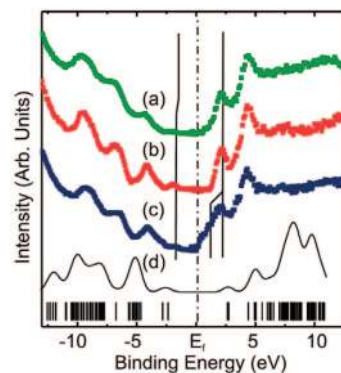


Figure 4. Comparison of photoemission and inverse photoemission spectra of multilayers of 2H-TPP (nominally 5 ML) on Ag(111) (a), Cu(111) (b), and Au(111) (c). The barcodes at the bottom are the calculated molecular orbital eigenvalues, and spectra (d) is the calculated single molecule density of states. The LUMO splitting from Au to Ag and Cu as well as the HOMO are indicated by vertical lines between spectra.

metal surfaces with the observed structures. UPS and IEPs spectra obtained as function of molecule coverage, together with spectra from the pristine substrates, are summarized in Figure 3.

Features resulting from the occupied and unoccupied molecular orbitals were clearly observed at all coverages for the Cu(111) and Au(111) systems (Figure 3b,c) in the combined photoemission and inverse photoemission. In contrast, peaks due to the molecular orbitals are difficult to distinguish in the occupied states at low 2H-TPP coverages on Ag(111) (Figure 3a). All the photoemission spectra show a rapid decrease in those peaks of the underlying substrates with increasing molecule coverage. The generally good agreement of the low coverage combined photoemission and inverse photoemission spectra of 2H-TPP on Cu(111) and Au(111) is remarkable, and consistent with the observed planar adsorption geometry. The absence of clear states at low coverages for 2H-TPP on Ag(111) is attributed to the coexistence of different adsorption geometries as observed with STM, and will be discussed later.

At greater thicknesses, features from the molecules become resolved also on Ag(111) (Figure 4). Similarities of the electronic structure in 2H-TPP films are apparent for all three substrates studied. Those features are also in good agreement with the calculated spectra, also shown at the bottom of Figure 4. The calculated spectrum is based on simplistic single molecule semiempirical method NDO-PM₃ model calculations based on Hartree–Fock formalism, neglecting differential diatomic overlap and assuming a parametric model number of 3, all performed using SPARTAN 8.0.⁵⁰ Geometry optimization of the molecule

Table 1. Orbitals and Energies of a Single 2H-TPP Molecule^a

	calculated	Cu	Ag	Au
HOMO - 1 (eV)	-2.73	-4.10	-4.30	-4.10
HOMO (eV)	-2.37	-1.90	-1.90	-1.90
LUMO (eV)	2.63	2.10	2.10	1.00
LUMO + 1 (eV)	2.82			2.10
gap (eV)	5.00	4.00	4.00	2.90
radius		1.45	1.65	1.74

a. Calculated values are from PM₃ calculations in SPARTAN; Cu, Ag, and Au are from 8 ML samples on the respective substrates.

was performed by obtaining the lowest restricted Hartree–Fock energy states. The calculated density of states (DOS) shown was obtained by applying equal Gaussian envelopes of 1 eV full width half-maximum to each molecular orbital and then summing to account for the solid state broadening in photoemission. This model density of states calculation was rigidly shifted in energy, largely to account for the influence of work functions on the orbital energies, and no corrections were made for molecular interactions and final state effects.

Photoemission and inverse photoemission are final state spectroscopies, and the HOMO–LUMO gap has been estimated from the vertical energies, with corrections included for the measured instrumental line widths. The combined photoemission and inverse photoemission provides an estimate of the HOMO–LUMO gap of 4.00 to 2.90 eV, depending on substrate, as summarized in Table 1. This means the HOMO–LUMO gap of a thin film is strongly dependent on the underlying substrate, showing a difference as large as 25%. We further note that the HOMO–LUMO gap predicted by the ground state theory is larger than that measured, which is unusual. The observed HOMO–LUMO gaps for the 2H-TPP/Ag(111) and 2H-TPP/Cu(111) systems differ from those reported for bulk samples⁵¹ in that they are significantly larger. A splitting of the LUMO state is seen for the 2H-TPP/Au(111) system, and weakly also for the 2H-TPP/Ag(111) system. Such splitting indicate either strong intermolecular or substrate interactions, and is in fact consistent with the close packed 2H-TPP on Ag(111), as discussed later. No such splitting is seen for the Cu(111).

Density Functional Theory. Calculations of molecules and dimers of 2H-TPP on Ag(111) were performed in order to gauge the effect of molecule–molecule and molecule–substrate interactions, and their influence on the aggregation of molecules at the surface. It is known that traditional DFT methods often cannot reproduce the weak interactions qualitatively and quantitatively due to the lack of dispersion.⁵² In order to test the applicability of the HCTH functional in this system, we examined the binding energy of a benzene dimer. Binding energies for the T-shaped and sandwich benzene dimer of 0.04 and 0.02 eV were obtained, respectively. Although these values are much smaller than the results based on high level CCSD(T) calculations,⁵³ it gives a correct qualitative description of van der Waals interactions, which means the HCTH functional could be used to evaluate the σ - π and π - π interactions.

With our calculations we optimized a 2H-TPP monomer on a Ag terrace and on a step edge, as well as free 2H-TPP dimers. On the Ag(111) surface, the molecules were found to exhibit little distortion of the overall shape, with the porphyrin molecules centered above a Ag(111) lattice site. The dihedral angle of the phenyl arms of 2H-TPP on a Ag(111) terrace was found to be 70.5°, which is reasonably close to previously reported 60° for an isolated 2H-TPP molecule.^{56,60,61} On the step edge, the phenyl arms

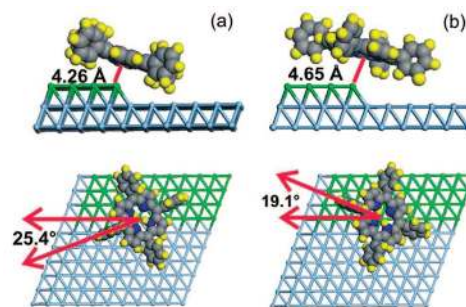


Figure 5. GGA-HCTH calculated adsorption geometry of 2H-TPP at a step-edge initially oriented with ligand directions at (a) 45° and (b) parallel to the direction of the step-edge.

are rotated between 69° and 74° depending on adsorption geometry. Considering the very slight energy change (0.03 eV) with the dihedral rotation from 60° to 90°,⁶⁴ the small dihedral angle change of 2H-TPP reflects the interaction between Ag surface and the 2H-TPP molecule.

The molecule–molecule total binding energy for a free porphyrin dimer was found to be 0.15 eV, due to a combination of van der Waals, electrostatic, CH- π , and π - π interactions. In contrast, the resulting binding energy of a 2H-TPP monomer to the Ag(111) terrace was found to be 0.44 eV. The diffusion barrier for a single molecule on the Ag(111) surface was found to be 0.032 eV, on the same order as that seen for other organic adsorbates on Ag(111) surfaces.⁵⁴ For comparison, the kinetic energy at 300 and 77 K would be 0.026 and 0.007 eV respectively. Such a small surface diffusion barrier would allow for the molecules to move along the surface, making single lattice jumps before interacting with another at a reduced rate. The resulting distance of a CH- π interaction in 2H-TPP dimers on a Ag(111) terrace was found to be 3.03 Å, which is only slightly shorter than what was observed with the STM.

Further DFT calculations show the binding between 2H-TPP and the Ag(111) terrace comes from modest electron transfer between the Ag surface and the adsorbed 2H-TPP molecule, where the molecule takes up 0.191 e according to a Hirshfeld analysis. Meanwhile, the electrostatic potential surface (ESP) indicates that the negative electrostatic potential of the inner porphyrin ring of 2H-TPP has an interaction with the positive electrostatic potential of the Ag(111) surface, which could explain the nature of the 2H-TPP adsorption on Ag(111) surface.

Calculations were undertaken for individual molecules bridging the step-edge in multiple orientations. First, a single 2H-TPP molecule was tested with the molecule initially bridging a Ag(111) step-edge with all phenyl ligands 45° to the boundary of the step-edge. It was found by structural optimization that in this orientation the molecule bound to the substrate at an angle of 28° between the molecule plane and the substrate surface, and at a distance of 4.26 Å (Figure 5). The phenyl arms and the step edge enclose an in-plane angle of 25.4°, and the net binding energy was calculated as 0.39 eV. When calculations were run with the molecule initially oriented with two phenyl arms parallel to the boundary of the step-edge and two normal, this molecule rotated upon optimization to an orientation similar to that observed by the STM (exp: in-plane angle of 21°, calculated: in-plane angle of 19°; Figures 1a and 5b, respectively). The resulting molecule–substrate distance was found to be 4.65 Å and the binding energy was found to be 0.55 eV and the Hirshfeld analysis found the Ag gives 0.193 e to 2H-TPP molecules. In both examples, the binding energy for the molecules at the step edge is larger than on flat terraces, explaining the found preferential step decoration.

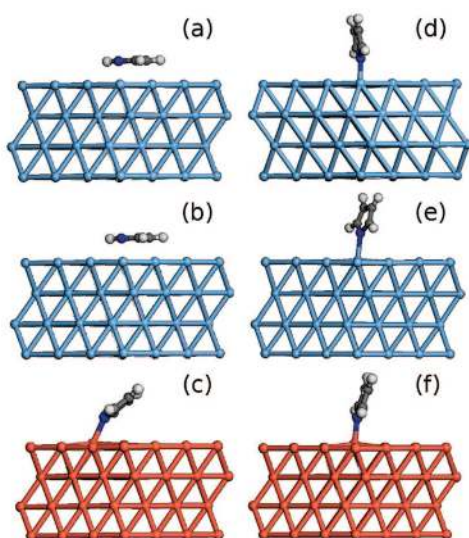


Figure 6. Calculated adsorption geometry of pyrroline molecules at Cu(111) and Ag(111) surfaces. The orientations of the molecules (a) initially parallel to the substrate and after convergence for (b) pyrroline parallel to Ag(111) and (c) pyrroline parallel to Cu(111). The orientations of the molecules (d) initially normal to the substrate and after convergence for (e) pyrroline normal to Ag(111) and (f) pyrroline normal to Cu(111).

Computation of the interactions of the 2H-TPP molecule or dimer on the Cu(111) substrate were infeasible for us. However, given the highly preferential binding of the 2H-TPP molecules over step edges on Ag(111), the limiting interaction of the 2H-TPP/Cu(111) system were thought to be due to the nitrogens of the porphyrin macrocycle interacting strongly with the underlying Cu(111) atoms as per similar interactions claimed for 2HT-PyP/Cu(111).⁵⁵ In making a computational comparison between the Ag(111) and Cu(111) systems, calculations were thus performed for lone pyrroline molecules as representing components of the porphyrin macrocycle which have the strongest potential interaction with the substrate. Two types of calculations were performed, one with the pyrroline initially parallel to the substrate, representing 2H-TPP in the terrace phase (Figure 6a) and one with the pyrroline initially normal to the substrate, representing 2H-TPP in the step-edge phase (Figure 6d).

It was found that for those pyrroline molecules which began initially parallel to the underlying substrates, the simulations of the pyrroline on Ag(111) did not converge (Figure 6b), despite being attempted in several different initial orientations. For the pyrroline/Cu(111) system the molecule bound to the underlying substrate with an energy of 1.49 eV (Figure 6c). For those pyrroline molecules initially normal, both the pyrroline/Ag(111) (Figure 6e) and the pyrroline/Cu(111) (Figure 6f) converged to a strong chemical bond with the substrate. However, the energy of the pyrroline/Cu(111) bond (1.50 eV) was more than twice that of the pyrroline/Ag(111) bond (0.73 eV). In both cases for the Cu(111) substrate, the molecule-substrate system converged to a strong bond due to overlap of the π -orbitals of the pyrroline with the d orbitals of the underlying Cu as per the LDOS.

Taken from these results it is concluded that for the 2H-TPP/Cu(111) system, there was no energetic preference for the molecules binding to the step edge over binding to the underlying terrace. The overlap in the orbitals calculated would be strong enough to create a significant bond of the porphyrin macrocycle with the underlying substrate regardless of initial orientation. In contrast, a clear preference for step decoration

was seen both experimentally and from the 2H-TPP/Ag(111) and pyrroline/Ag(111) calculations.

Discussion

Our observations can be summarized as follows: (i) 2H-TPP are highly mobile on Ag(111) and prefer to occupy substrate step edges in a bridging position, with an angle between phenyl arms and the step edge of approximately 20° . Upon achieving 100% step-edge occupancy, extended 2D networks are formed on the terraces. (ii) 2H-TPP on Cu(111) does not show any tendency of surface diffusion or self-assembly. The mobility was increased at elevated temperatures, but still no network formation or step edge bridging was observed. The formation of a surface dipole at the molecule sites is observed with STM. (iii) Photoelectron spectroscopy of the occupied and unoccupied states show distinct and easily discernible peaks generally matching published UPS data and theoretical expectations.^{63,82-84} For low and moderate 2H-TPP coverages on Ag, distinctive molecular orbital features of the occupied states are absent and peak splitting of the LUMO is observed for 2H-TPP/Au(111) by inverse photoemission. (iv) DFT calculations show that the binding energy for 2H-TPP on Ag in various positions and geometries is largest for a bridging position at step edges, with rotated "X" geometry, whereas the binding energy of the nitrile components of the macrocycle is larger by more than a factor of 2 on Cu(111) and independent of the adsorption site.

The observed ordering of the molecules on the terraces of Ag(111) has also been reported for the same molecules on Ag(111)^{58,59} and for metalated TPP molecules on Cu(111)⁵⁷ and is consistent with what has previously been reported for similar systems of porphyrin molecules on noble metal substrates.^{21,56,66-70} However, the very strong preferential and ordered bonding the molecules show toward the surface step-edges has not been reported thus far. Also, the observed absence of self-assembly for 2H-TPP on Cu(111) is in striking difference to the networks reported for Co-TPP or Cu-TPP on Cu(111).⁵⁷

To explain the preferred step edge adsorption, we have presented energy calculations by DFT-GGA for various absorption geometries on step-edges, by varying the angle between the phenyl arms and the step edge as well as the inclination of the molecule against the step-edge. As a result, the experimentally observed orientation of the 2H-TPP was found to have the highest binding energy, about 125% higher than what was calculated for the molecules occupying terrace sites. The preferential step edge decoration is not related to the 2H-TPP macrocycle metalation, as comparative measurements with Ag-TPP on the same Ag(111) substrate showed, which is also in agreement with arguments made in Reference 57. We thus suggest that the observed geometry is largely due to a simple energetic favorability of geometrical orientations. The achieved geometrical closeness of the nitrogen atoms in the porphyrin macrocycle to the Ag atoms of the step-edge cannot be achieved on terraces where the rotated phenyl arms determine the macrocycle-substrate distance, explaining the higher binding energy at the step edges.

Our calculation showed further that the energy of the T-type interaction between neighboring phenyl ligands is 1 order of magnitude smaller than the total binding energy of a 2H-TPP dimer. It is thus concluded that the self-assembly of 2H-TPP into the 2D networks observed on Ag(111) is the result of the interplay between several factors. It is driven by the attractive interaction between the molecules, but only possible if the 2H-TPP interacts weakly with the substrate underneath so that diffusion barriers are sufficiently low. The attractive CH- π bonds, regarded as the

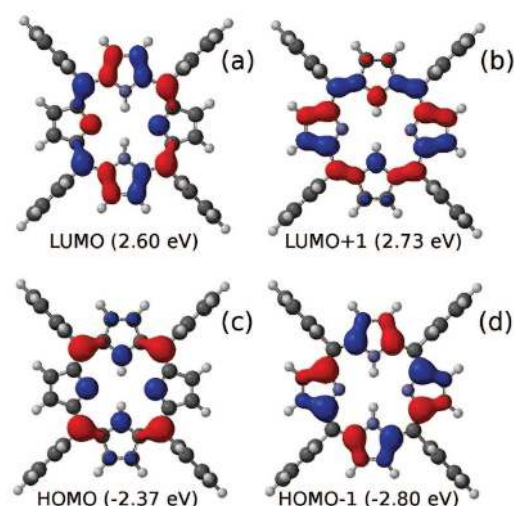


Figure 7. Orbitals corresponding to semiempirical NDO-PM3 model calculations. (a) LUMO, (b) LUMO + 1, (c) HOMO, and (d) HOMO - 1.

driving force for network formation in Reference 57, are alone insufficient to overcome the diffusion barriers on Ag(111), but do determine the alignment of neighboring molecules with respect to each other, or in other words, the network's geometry.

In contrast to what has been found for 2H-TPP on Ag(111) and for metalated TPP on Cu(111),⁵⁷ no self-assembly of 2H-TPP is observed on Cu(111). Networks are also not formed at increased temperatures, when the molecule's diffusion rates are already substantial. It is thus concluded that on Cu(111) the interaction between 2H-TPP is repulsive, which can only be the result of the interaction with the Cu substrate. The pickup of charges by the molecules from the substrate can result in the formation of an electric dipole and hence electrostatic repulsion between molecules, thereby inhibiting network formation. Such a charge pickup by the 2H-TPP is observed with STM on Cu(111), where the modification of the substrate around isolated 2H-TPP molecules is clearly visible as a ring, which is in analogy to the observed sombrero-like shape of charged metal atoms on insulating films⁷⁵ or TCNE molecules on Ag(100).⁸¹ This modified electronic structure surrounding the molecule corresponds well with those predicted and observed for simple two body molecules on Cu(001).⁷⁸ This electron exchange then leads to long-range, electrostatic repulsive molecule-molecule interactions as seen also for other species.^{79,81}

A comparison of our findings on 2H-TPP on Cu(111) with published STM data on metalated TPP or TPyP on the same substrate^{48,57,62} seems further to suggest that not the ligands but rather the macrocycle metalation is controlling the self-assembly: nonmetalated molecules with different ligands (2H-TPP, TPyP) remain isolated on the Cu(111), while only metalated TPP are observed to form networks. This conclusion is backed by related studies of molecule-substrate interactions that conclude that the metal ion in the porphyrin macrocycle plays the central role in the electronic interaction between the complexes and the metal surface, which was even found to result in additional electronic states.⁶³

Qualitatively, the Cu system possesses a d_z^2 orbital extending into the vacuum while the outermost orbitals for the Ag and the Au system are more dominated by the frontier s orbitals. The calculated molecular orbitals from our semiempirical calculations of the free molecule, and matching those found with GGA-DFT calculations, are shown in Figure 7. It is apparent that the HOMO orbital possesses a_{1u} symmetry and the LUMO and

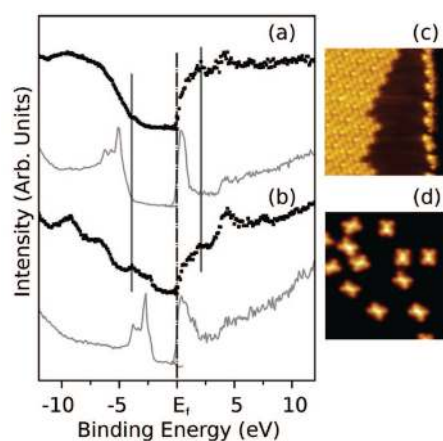


Figure 8. Comparison of photoemission and inverse photoemission spectra of thin film 2H-TPP (0.5 ML) on (a) Ag(111) and (b) Cu(111), along with the spectra of the corresponding clean substrate at room temperature. STM images of 1/3 ML thick 2H-TPP on (c) Ag(111) and (d) Cu(111) are shown on the right side of the Figure (10 × 10 nm). $U_{\text{bias}} = -0.8$ V.

LUMO + 1 orbitals possess b_{1g} symmetry. Given this, the former will be dominated by d_z^2 levels while the later will be dominated by p_x and p_y levels. This results in a greater cross-sectional overlap of the 2H-TPP HOMO levels with both the d_z^2 and $4s$ frontier orbitals of the Cu(111) system versus only the $5s$ and $6s$ orbitals of the Au(111) and Ag(111) systems. Given that the former will have a much larger cross-sectional overlap with the orbitals of the adsorbed porphyrin than will the later, enhanced electron transfer and therefore, tunneling, directly from the tip to the metal substrate via the adsorbed molecules is achieved. This interaction can create enough charge in the molecule-substrate system to hinder 2D network growth through Coulomb repulsion. This is similar in concept to Co-TPP^{76,77} and Fe-TPyP^{56,65} deposited on metal substrates, as the d_z^2 orbital of the metal in the molecule provides the same general overlap with the underlying metal that the Cu has with the adsorbed molecules here.

Given that the substrates are, by themselves, similarly electronegative, it is this greater frontier orbital overlap which transfers a greater amount of charge between the substrate and the adsorbate. The charge transfer is then responsible for the significant electronegativity seen in the HOMO state of the surface 2H-TPP on Cu(111) of Figure 2b as well as the apparent modified electronic structure surrounding the molecule.

From the location of the LUMO of the 2H-TPP on the macrocycle, as seen in Figure 7, a perturbation of the LUMO by the formation of weak CH- π bonds with the phenyl arms of neighboring molecules can be expected. This perturbation may lead to the splitting of the LUMO states by 1.1 eV observed in the inverse photoemission data, see Figure 4d. This level splitting is observed on Au(111) and, to lesser extend on Ag(111) where the 2H-TPP molecules are observed to form a network structure.^{57,71,72} This splitting is not observable on Cu(111), where the molecules remain isolated.

In Figure 8 we compare UPS/IPES spectra for submonolayer coverages of 2H-TPP on Ag and Cu with STM images taken at such coverages. Striking here is the absence of discernible peaks in the UPS spectra of 2H-TPP/Ag(111). We suggest that the coexistence of different structural phases with fundamentally different orientation relative to the substrate in multiple energetic orientations smear out peaks in the UPS spectra as seen for other adsorbate-surface systems.⁸⁰ DFT calculations support this observation by showing that step-edge sites held significantly higher binding energies than terrace sites for the 2H-TPP/Ag(111)

system. Electronic features similar to those of free 2H-TPP molecules appear only at coverages above 3 ML where the layer stacking is the dominating structural arrangement.

Conclusion

It has been demonstrated that the tendency of porphyrins to self-organize is limited by interactions with the substrate. While a rather significant molecule–substrate bond exists for 2H-TPP on all substrates studied, the limiting factor in formation of self-organized islands is apparently the nature of the frontier orbital overlap and resulting electron transfer, which is mainly involving the macrocycles of the molecules.

The self-assembly of near charge neutral 2H-TPP molecules into extended 2D networks on Ag(111) is due to a combination of van der Waals, electrostatic and CH– π interactions between the molecules. The relative orientation of neighboring molecules is mainly given by the CH– π interactions, due to which there is a perturbation of the electronic states of the adsorbed molecules. Charge pickup and dipole formation of 2H-TPP on Cu(111) results in repulsive Coulomb interactions which seem to dominate over attractive intermolecular interactions, thus preventing network formation. A zone of modified electronic structure is observed around the molecules on Cu(111), which is indicative of such strong molecule–substrate interactions and charge uptake by the molecules. This mechanism seems to be absent for 2H-TPP/Ag(111) and 2H-TPP/Au(111), where the orbital overlap differs significantly from that of the 2H-TPP/Cu(111) system. The comparison of our results with published work on Co-TPP, Cu-TPP, and TPyP suggests that the molecule–substrate interaction strength is governed by the molecule's metalation, and not so much by the ligands.

The morphology of the substrate surface is also important as the molecules are observed to preferentially bridge the substrate step-edges before island nucleation starts on the terraces. The discussed examples showed that the properties of 2D layers of organic materials can be controlled by interactions with the supporting substrate. Specifically, it was shown that the structural arrangement, HOMO–LUMO gap, and details of the electronic structure are determined by the substrate, thereby improving our understanding of planar organic molecular adsorption and self-assembly on surfaces.

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