STM fingerprint of molecule-adatom interactions in a self-assembled metal-organic surface coordination network on Cu(111)

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A novel approach of identifying metal atoms within a metal-organic surface coordination network using scanning tunnelling microscopy (STM) is presented. The Cu adatoms coordinated in the [10] porous surface network of 1,3,8,10-tetraazaperopyrene (TAPP) molecules on a Cu(111) surface give rise to a characteristic electronic resonance in STM experiments. Using density functional theory calculations, we provide strong evidence that this resonance is a fingerprint of the interaction between the molecules and the Cu adatoms. We also show that the bonding of the Cu adatoms to the organic exodentate ligands is characterised by both the mixing of the nitrogen lone-[15] pair orbitals of TAPP with states on the Cu adatoms and the partial filling of the lowest unoccupied molecular orbital (LUMO) of the TAPP molecule. Furthermore, the key interactions determining the surface unit cell of the network are discussed.

Introduction

[20] In the aim of constructing nanoporous surface networks which serve as hosts for small molecules, the bottom up self-assembly of organic molecules as building blocks on metal surfaces has received considerable attention during the last decade. The self-assembly is known to be affected by the fine tuning of different parameters, the most general being the [25] molecule-surface and molecule-molecule interactions. Other essential parameters to control self-assembly processes are the distribution of defect sites (steps, kinks, adatoms) which affect nucleation, the dynamic behaviour at elevated temperatures, the temperature during the molecular [30] deposition, the temperature and duration of a post deposition annealing process, the cooling rate, as well as the surface concentration of molecules.[1,2]

The involvement of metal adatoms in the self-assembly of organic molecules on metal substrates has been shown to play [35] a key role in a considerable number of systems.[3-13] In the case of "non-native" metal adatoms, their role in the molecular self-assembly on surfaces can be studied directly upon varying their surface concentration by depositing them on the surface at a fixed substrate temperature.[3-5] It is a greater [40] challenge to investigate the role of "native" metal adatoms on the self-assembly since they are thermally generated from the substrate and their surface concentration depends on the substrate temperature. For example, the herringbone reconstruction of the Au(111) surface can serve as a source of [45] reactive Au adatoms.[6,7] On Cu surfaces, the adatoms result from the detachment of Cu atoms from atomic step edges at elevated temperatures.[10-13]

A direct approach to establish the presence of adatoms embedded in self-assembled porous surface network structures [50] is to image them individually by scanning tunnelling microscopy (STM). For example, single Cu adatoms have been observed in networks of trimesic acid molecules on a Cu(100) surface as protrusions in topographic STM images.[11] However, such adatoms within the coordination networks are [55] not always visible in STM. For example, Cu adatoms were shown to be coordinated to the N atoms in a porous network of 1,3,8,10-tetraazaperopyrene (TAPP) molecules[14] on a Cu(111) surface by a theoretical analysis of measured core hole level shifts by X-ray photoelectron spectroscopy (XPS).[15] [60] However, no adatoms were directly detectable by STM.[16] Another interesting possibility that has not yet been explored is to identify adatoms from characteristic electronic states in scanning tunneling spectroscopy (STS). Isolated Cu adatoms on Cu(111) have been shown to exhibit a characteristic [65] unoccupied resonance state in the band gap of Cu(111).[17,18] In fact, the appearance of this kind of resonance states was first observed for Au adatoms on the NiAl(110) surface[19] and later also for other non-magnetic as well as magnetic adatoms.[20] Therefore, it is of interest to investigate whether the adatoms [70] give rise to any characteristic resonance state in bias dependent STM images[21] when coordinated to organic molecules. This would provide a spectroscopic fingerprint even in cases in which their direct detection by STM is precluded.

[75] Here we present a combined density functional theory (DFT) and a bias dependent STM study that shows that the Cu adatoms in a porous network of TAPP molecules on the Cu(111) surface exhibit a characteristic signature in the scanning tunneling spectra. This finding confirms our [80] previous conclusion from an analysis of structural data along with the measured core-level shifts by XPS that the Cu adatoms participate in the formation of the porous network. We will also provide an analysis of the bonding of the Cu adatoms to the TAPP molecule. The nitrogen lone-pair [85] orbitals of the TAPP molecules are mixed with the Cu adatom-induced states and shifted to lower energy whilst the Cu adatoms donate electrons into the LUMO of the TAPP molecules. Finally, the role of the Cu substrate in the

formation of the commensurate surface porous network will be discussed.

Computational details

The DFT calculations of periodic systems were carried out using the Vienna Ab-initio Simulation Package (VASP).[22] The ion-core interaction was described by the projector augmented waves method.[23] Generalised gradient approximation (GGA) through the Perdew Wang 91 (PW91) functional[24] was used to describe exchange-correlation effects. The plane wave basis has been expanded up to a cut-off energy of 400 eV and a 2×2 surface k-point sampling was used.

Structural optimization was performed until the force acting on each atom was below 0.01 eV/Å. The copper substrate was modeled by a four layer slab separated by 15 Å of vacuum region, and with the two outermost layers fully relaxed. The simulated STM images were based on the Tersoff-Hamann approximation[25] where dI/dV is proportional to the local density of states (LDOS). The projected density of states (PDOS) onto molecular orbitals was calculated following the method described by Lorente and Persson.[26]

Experimental details

All experiments were performed in an ultrahigh vacuum system (UHV), consisting of different chambers for sample preparation and characterisation, at a base pressure of 10^{-10} mbar. The Cu(111) single crystal was prepared by subsequent cycles of sputtering with Ar^+ ions and annealing at approximately 500 °C. The TAPP molecules were deposited onto the metal surface from a glass crucible that was heated inside a commercial evaporator (Kentax UHV equipment) while the rate was controlled by a quartz crystal microbalance (QMB). Depending on the annealing temperature, the TAPP molecules also form two other main assemblies at submonolayer coverage: (1) a close-packed assembly where the molecules interact via van der Waals forces and hydrogen bonding; (2) chains of covalently linked molecules.[15,16] After reaching the annealing temperature the sample was cooled down and studied with STM. The STM images have been acquired using a commercial Omicron low temperature scanning tunnelling microscope (LT-STM) (Omicron NanoTechnology GmbH) operated at 5 K and equipped with wire cut PtIr tips. The STM was operated by the Nanonis SPM control system (SPECS GmbH). The bias voltages given in the manuscript refer to a grounded tip. The free software WSxM[27] was used for data processing.

Results and discussion

The commensurate porous network of TAPP molecules that forms after annealing on the Cu(111) surface was described in our recent combined experimental and theoretical study.[15] Each Cu adatom was found to be coordinated to the nitrogen atoms of two adjacent TAPP molecules, resulting in four adatoms per crossing of four adjacent molecules. First, we show that these adatoms give rise to a characteristic resonance state in bias dependent STM and discuss its origin followed by an analysis of the bonding of the adatoms to the TAPP molecules. We conclude by a discussion of the key interactions determining the surface unit cell of the network.

Fingerprint of the adatom coordination

The individual adatoms in the porous Cu-TAPP network could not be resolved in the STM images at any tunnelling parameters. However, a characteristic electronic feature was observed at high sample biases which is displayed in Figure 1 (a-c). At a sample bias of -1 V the TAPP molecules were imaged as protrusions. When increasing the sample bias to around +3 V a characteristic high tunnel current feature was observed at the location of the four adatoms. Whether this feature, which appeared as a bright protrusion, originated from the TAPP molecules or from the Cu adatoms could only be established by an analysis of calculated STM images as detailed below.

The experimental images are well reproduced by the simulated constant current STM images. At an energy of 1.0 eV below the Fermi level, the LUMO of TAPP[14] provides the dominant contribution to the simulated image, Figure 1 (d). A bright protrusion, representing a high tunnel current feature, appeared at the same location as in experiments when increasing the energy to 3.2 eV above the Fermi level, Figure 1 (e). Therefore, this observed feature can be identified with the calculated LDOS, obtained by integration from the Fermi level up to 3.2 eV.

The theoretical study has shown that the presence of the Cu adatoms is a key ingredient for the appearance of this characteristic feature in the LDOS. When removing the adatoms from the porous network while keeping the structure of the adsorbed TAPP molecules intact in the calculations, the bright protrusion at the centre of the four adatoms was found to be absent at any energy. This supports our previous postulate concerning the involvement of the Cu adatoms in the formation of the porous Cu-TAPP network.[15,16]

Additional insight into the role of the molecular states on the origin of the characteristic bias dependent STM feature associated with Cu-TAPP bonding in the porous surface network is obtained from an analysis of the calculated LDOS as a function of energy at a distance of 6 Å above the centre of the four adatoms (Figure 2). The LDOS indicates that the bright protrusion observed in the STM images of the porous surface network at large positive sample bias results from electronic states at an energy of about 3.3 eV above the Fermi energy (0.8 eV below the vacuum level). From calculations of the bands of the isolated flat Cu-TAPP coordination network formed by removing the Cu substrate while optimising the structure of the TAPP molecules and the Cu atoms, we identified a single band with a maximum energy of around 0.8 eV below the vacuum level that gives rise to a bright protrusion in the simulated STM image at the same distance from the Cu-TAPP overlayer as for the porous surface network. This band is nearly flat resulting from the combination of laterally localized orbitals. The density of this band at a distance of 5 Å above the overlayer is shown in Figure 3a. The band gap of Cu(111) ensures that this flat band

survives as a well-defined resonance with a negligible energy shift and a small increase in its dispersion and broadening. The character of this flat band is revealed by an iso-surface plot of the density at a much higher value represented in Figure 3b. The density is primarily localised around the Cu atoms and has p_z character on the Cu atoms but also prominent p_z character on the carbon atoms of the organic ligand. Furthermore, whenever iso-surfaces are plotted with decreasing values of the density, the latter seems to decay more slowly into the vacuum around the Cu adatoms than on the molecule, giving rise to the bright protrusion in the STM image.

Characteristics of the coordination bond in the Cu-TAPP network

So far we have discussed the origin of the bright protrusion, observed in the STM images recorded at high positive sample bias, demonstrating that it derives from an electronic state consisting of Cu atom states mixed with TAPP molecular states. However, this is an electronically unoccupied state which therefore does not directly contribute to the bonding between the Cu adatoms and the TAPP molecules.

A first direct indication of the involvement of the Cu adatoms in the bonding of TAPP in the porous surface network is provided by an analysis of the electron transfer between the network components. Table 1 shows the net electronic charge according to the topological analysis of electronic density distribution according to the Atoms in Molecules (AIM) approach by Bader[28] summed over the TAPP molecules and the Cu adatoms. The charge transfer of -1.14 e into each TAPP molecule for the relaxed isolated Cu-TAPP coordination network is slightly larger in magnitude than -0.86 e for the porous surface network. If the adatoms are removed from this network the net charge on each TAPP molecule is reduced substantially in magnitude to -0.18 e. Notably, the Cu-TAPP coordination network is essentially neutral (+0.08 e/molecule) when adsorbed on Cu(111). In a study by Pawin and coworkers[13] it was shown that the Cu substrate donates charge into a Cu adatom coordinated structure of 9,10-anthracenedicarbonitrile (DCA) molecules on Cu(111). This may be due to the presence of the electron withdrawing nitrile substituents in this system.

Table 1 Net electronic charge from the Bader analysis of TAPP and the Cu adatoms for the isolated Cu-TAPP overlayer and the overlayers on Cu(111) with either the adatoms or the TAPP molecules removed. The electronic charge of the Cu slab is given as negative value of the total charge over the TAPP molecules and Cu adatoms. Note that each unit cell holds two molecules and four adatoms, and each of the systems is neutrally charged.

	TAPP (e/molecule)	Cu adatoms (e/adatom)	Cu slab (e/unit cell)
Isolated overlayer	-1.14	+0.57	—
Overlayer on Cu(111)	-0.86	+0.47	-0.16
-Adatoms removed	-0.18	—	+0.18
-TAPP removed	—	+0.03	-0.12

The trend found in the Bader analysis is in agreeement with the PDOS onto the molecular orbitals of an isolated layer of TAPP molecules displayed in Figure 4 (see computational details). Upon formation of the isolated Cu-TAPP coordination network, the TAPP LUMO becomes fully occupied (Figure 4a) whereas its occupancy is reduced upon adsorption of the coordination network on the Cu substrate as shown in Figure 4b. When in turn the adatoms are removed from the porous surface network (Figure 4c), while retaining its structure, this orbital is shifted to higher energy resulting in a decreased population. The behaviour of the LUMO for these different systems correlates well with the notion of electron transfer reflected in the Bader analysis. The donation of electrons into the LUMO and its stabilization induced by the coordinated Cu atoms contributes to the chemical bonding of the molecule to the surface (vide infra).

In addition to the Cu donating electrons into the TAPP LUMO, a contribution to the bonding comes also from the energetic stabilisation of the four occupied, lone-pair orbitals of a TAPP molecule. These orbitals are localised on the nitrogen atoms of the isolated molecule. For the isolated Cu-TAPP layer, the N-centered lone-pair orbital energies are decreased on average by 2.4 eV compared to the metal free reference structure (Figure 4a), whereas there is still a substantial stabilization of about 1.6 eV in the porous surface network (Figure 4b).[29] This smaller shift is in part attributed to the fact that the bonding interaction of the Cu atoms with the Cu surface draws the Cu atoms out of the molecular plane thus reducing the in-plane bonding with the nitrogen lone pairs. In the absence of the Cu adatoms coordinating to the TAPP, there is essentially no stabilization of the nitrogen lone pairs of the adsorbed TAPP molecules (Figure 4c) and therefore no significant bonding involving these orbitals with the Cu atoms in the surface.

In summary, the coordinative bonding in the Cu—TAPP overlayer is characterised by the stabilization of the four lone-pair orbitals of the TAPP molecule by in plane σ-bonding as well as the charge transfer from the Cu adatoms to the LUMO of TAPP which may be interpreted as π-backbonding.[30] There is essentially no charge transfer from the Cu substrate to the coordination network, hence the isolated Cu—TAPP overlayer may be viewed as electroneutral.

Relationship between isolated and surface-commensurate coordination networks.

The bright protrusion observed in STM experiments performed at high positive sample bias and also the chemical bonding could be understood in principle by regarding only the electronic states of the isolated Cu-TAPP layer. However, the structural details of the porous surface network, cannot be understood alone from a consideration of the isolated Cu-TAPP overlayer. In fact, the structure is determined by a competition between lateral intermolecular bonding and molecule-surface interactions.

The role of the intermolecular bonding in the coordination network is obtained by studying the isolated Cu-TAPP layer. Based on the argument that the Cu-bond lengths should be all equal due to the symmetry of the molecular building blocks, as should also be the N—Cu—N bond angles, one finds that the energetically most favourable unit cell of the isolated coordination network has D_{4h} symmetry. The main symmetry

axes of the two molecules per unit cell are then aligned perpendicular with respect to each other and the two surface unit cell vectors are of equal length. By relaxing the internal structure of the overlayer for different sizes of the unit cells, constrained to having D_{4h} symmetry, the dependence of minimum energy structure of the isolated coordination network on the area of the unit cell could be established as depicted in Figure 5. The optimized unit cell with D_{4h} symmetry was found to have the dimensions 17.62×17.62 Å^2 and was found to be more stable than the experimentally determined unit cell by 307 meV, the dimensions of which were found to be 17.99×16.85 Å^2. This is unsurprising in view of the preference of the adatoms to chemisorb to hollow sites of the substrate, which constrains the allowed unit cells to be commensurate with the Cu(111) substrate.

By sampling all possible unit cells, which are commensurate with the Cu(111) substrate within reasonable deviations,[31] only two unit cells were found to be close in energy to the optimised unit cell. One cell corresponds to the experimentally determined unit cell defined by the matrix (1),

$$\begin{pmatrix} 8 & 5 \\ -1 & 6 \end{pmatrix}$$

whilst the second possible cell is defined by the matrix (2),

$$\begin{pmatrix} 7 & 0 \\ 4 & 8 \end{pmatrix}$$

We note that the geometries of these cells deviate from the D_{4h} symmetry. The isolated overlayer with the second alternative unit cell is 34 meV more stable than the modeled structure employing the observed data but computed for the isolated overlayer. However, upon adsorption of these Cu-TAPP coordination networks on the surface, the network corresponding to the experimental unit cell is found to be more stable by 452 meV[32] than the network with the alternative unit cell. Thus, the molecule-substrate interaction is decisive in determining the unit cell for the porous network on Cu(111).

Table 2 Structural deformation energy costs for the TAPP molecules and the Cu adatoms in the overlayers on the Cu(111) surface with the observed and the alternative unit cells defined in matrices (1) and (2), respectively.

	TAPP (eV/molecule)	Cu adatoms (eV/adatom)
Observed unit cell	0.299	0.277
Alternative unit cell	0.361	0.278

The large energy difference between the two alternative overlayers can only partly be understood in terms of the molecular and adatom structural deformation energies,[33] shown in Table 2. For the Cu adatoms, the difference in the energy cost between the two overlayers of displacing the adatoms from their equilibrium positions to the equilibrium positions they would occupy in the isolated overlayer is negligible (less than 1 meV per adatom). This result is not surprising since the adatoms in the two unit cells are positioned at equivalent adsorption sites. The structural deformation energy difference for the TAPP molecule is

larger than for the adatoms and can account partly for the stabilisation of the observed unit cell. The difference in energy cost to deform the isolated relaxed molecule upon formation of the surface coordination network is 62 meV larger per molecule in the case of the alternative unit cell than in the case of the observed unit cell. Thus this energy difference of 124 meV per unit cell accounts only for about 30% of the total energy difference.

However, the overall energy difference between the two unit cells is better understood by considering the N—Cu bond lengths shown in Table 3. For the optimised unit cell of the isolated Cu-TAPP overlayer this interatomic distance is 1.87 Å. The overlayer with the observed unit cell gives a slightly smaller distance while the overlayer with competing unit cell gives a slightly larger distance. This difference reflects the fact that the observed unit cell is smaller than the alternative one.

Table 3 N—Cu bond lengths of the Cu-TAPP overlayer for the observed and the alternative unit cells, with and without the Cu surface. Note that in the isolated Cu-TAPP overlayer the optimum N—Cu distance is 1.87 Å.

	N—Cu bond length (Å)	
	On Cu(111)	Isolated
Observed unit cell	2.03—2.11	1.85
Alternative unit cell	2.12—2.18	1.93

In contrast to the isolated Cu-TAPP network the Cu adatoms in the overlayer on the surface with the observed unit cell are located out of the molecular plane resulting in an increase of the N—Cu distances. This increase renders the average N—Cu distance of the overlayer closer to the optimum N—Cu bond length of the isolated overlayer than would be the case for the alternative unit cell. We note that the less than tetragonal symmetry of the experimentally observed Cu-TAPP layer in registry with the substrate gives rise to inequivalent Cu-N distances resulting in the ranges for the bond lengths represented in Table 3.

Conclusions

The interaction of the frontier molecular orbitals of the organic exodentate ligands with the adatom states lowers the energies of the occupied nitrogen lone-pairs orbitals and also decreases the energy of the LUMO below the Fermi level rendering it partially occupied. This can be understood in terms of the well established σ-donor, π-backbonding interaction in coordination chemistry. The molecule-surface interaction was found to be important in determining the surface unit cell of the network of TAPP molecules on the Cu(111) surface. The strong Cu adatom−surface interaction makes the overlayer nonplanar and thus a smaller surface unit cell with Cu—N bond distances closer to their optimum value is favoured.

We have also shown from scanning tunneling microscopy and density functional calculations that the Cu adatoms in the porous surface network of TAPP molecules on Cu(111) exhibit a characteristic electronic resonance that appears in scanning tunneling microscopy as a bright protrusion in the crossing between the four molecules at a sample voltage of +3

V in STM. The similarity of this resonance to the observed resonance of a single Cu adatom indicates that it should be a more general phenomenon. Further studies would establish to which extent such a fingerprint of metal adatoms in surface coordination networks may be associated with the type of resonance state identified in this work. By voltage dependent imaging at appropriately chosen parameters, coordinated single metal atoms may prove to be more reliably detected than by direct observation as a topographical feature in STM images.

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Notes and references

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31   For all unit cells considered, the angle between the two lattice vectors is in the range of 85-90°. Furthermore, only unit cells with an area deviating from the optimised cell by less than 15 Å^2 were considered.

32 This value was obtained by comparing the adsorption energy of TAPP on the surface which was calculated using the isolated relaxed TAPP molecule and the relaxed Cu slab with four adatoms as reference.

33 The structural deformation energy was defined as the energy difference of a Cu/Cu(111) system with the adatoms positioned at the equilibrium position they have in the Cu—TAPP overlayer, and a Cu/Cu(111) system where the adatoms are positioned in their equilibrium positions on the surface in the absence of TAPP molecules. For the TAPP molecules the structural deformation energy was defined as the difference in energy of an isolated TAPP molecule in the overlayer geometry and a relaxed isolated TAPP molecule.