

A Surface Coordination Network Based on Copper Adatom Trimers**

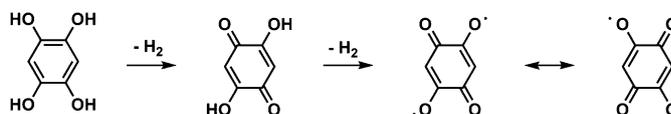
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Abstract: Surface coordination networks formed by co-adsorption of metal atoms and organic ligands have interesting properties, for example regarding catalysis and data storage. Surface coordination networks studied to date have typically been based on single metal atom centers. The formation of a novel surface coordination network is now demonstrated that is based on network nodes in the form of clusters consisting of three Cu adatoms. The network forms by deposition of tetrahydroxybenzene (THB) on Cu(111) under UHV conditions. As shown from a combination of scanning tunneling microscopy, X-ray photoelectron spectroscopy, and density functional theory calculations, all four hydroxy groups of THB dehydrogenate upon thermal activation at 440 K. This highly reactive ligand binds to Cu adatom trimers, which are resolved by high-resolution STM. The network creates an ordered array of mono-dispersed metal clusters constituting a two-dimensional analogue of metal–organic frameworks.

Metal–organic frameworks (MOFs) have emerged as an important new class of designable nanoporous materials with many potential application areas, not least within gas storage and catalysis.^[1] MOFs consist of metal cations interconnected by organic linkers in a crystalline three-dimensional matrix. Motivated by sensing and other interface-related applications, thin-film MOFs have been synthesized by growing or adsorbing MOFs on surfaces.^[2] The extreme case of truly two-dimensional, molecular monolayer-thick analogues of MOFs is approached from the complementary direction of

surface coordination networks.^[3] These structures result from advances in surface supramolecular chemistry under ultra-high vacuum (UHV) conditions and are synthesized by co-adsorbing organic ligands with metal atoms on metal single-crystal surfaces. Early work in this direction demonstrated formation of metal–organic clusters^[4] and networks^[5] from coordination between carboxylates and Cu or Fe adatoms. Subsequently, many well-ordered surface coordination networks have been synthesized,^[6] notably demonstrating systematic control of network pore size and symmetry from appropriate choice of ligand (size and chemical functionality), metal center, and metal substrate.^[7] Bulk MOFs are based on network nodes that in many cases go beyond simple cations, for example, small metal^[8] or metal-oxide clusters, such as Zn₄O clusters in the classic MOF-5.^[9] In contrast, surface coordination networks have typically been based on single metal adatom nodes or coordination nodes with two (separated) adatoms.^[6c,10] Achieving more complex network nodes^[11] in surface coordination networks is an interesting prospect, as the properties of the network nodes can be key to the functionality of the MOF/surface coordination network, for example, in terms of magnetic properties^[10,12] or catalytic activity.^[13]

Herein we use a combination of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations to demonstrate the synthesis of a novel surface coordination network with Cu adatom trimers as network nodes. The nanoporous network forms spontaneously on a Cu(111) single crystal surface by thermal activation of adsorbed tetrahydroxybenzene (THB), which undergoes dehydrogenation of its hydroxy groups to form a highly reactive ligand (Scheme 1). Our findings open prospects for synthesizing more complex two-dimensional MOF analogues on surfaces.



Scheme 1. Sequential dehydrogenation of tetrahydroxybenzene (THB), yielding first dihydroxybenzoquinone (DHBQ) and then a 2,5-dioxy-p-benzoquinone diradical.

To obtain the network, THB was deposited in situ by vacuum sublimation onto a Cu(111) surface held at room temperature, followed by annealing of the surface to 440 K. As shown in the STM image of Figure 1 a, large portions of the surface were then covered by islands of a porous honeycomb network of monomolecular height. Figure 1c shows a zoom-in on the network which can be described by

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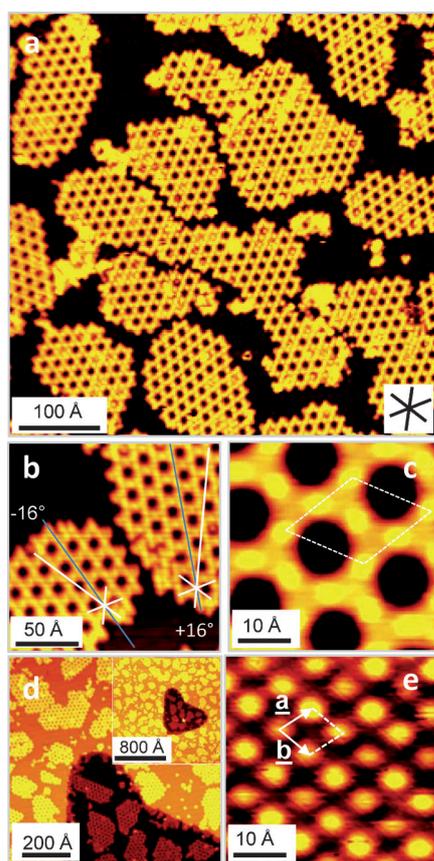


Figure 1. STM images obtained after depositing THB on Cu(111) and annealing to 440 K. a) Overview of porous network structure ($I_t = -0.33$ nA, $V_t = -1.40$ V). The star indicates substrate close-packed $\langle 10\bar{1} \rangle$ directions, which are identical for all panels. b) Rotational domains oriented at $\pm 16^\circ$ to a close-packed direction ($I_t = -0.35$ nA, $V_t = -1.40$ V). c) Zoom-in on network structure with indicated unit cell ($I_t = -0.31$ nA, $V_t = -1.25$ V). d) Vacancy island observed after network formation. ($I_t = -0.35$ nA, $V_t = -1.25$ V) Inset shows large-scale image. e) Close-packed high-coverage phase ($I_t = -0.29$ nA, $V_t = -1.40$ V).

a hexagonal unit cell with 17.4 ± 0.7 Å dimension. The network was observed in two domains oriented at $\pm (16 \pm 2)^\circ$ with respect to the close-packed directions of the Cu(111) surface (Figure 1b). The network islands are terminated by serrated edges resulting from interruption of the honeycomb structure. In some instances, network islands come in close proximity without merging (see Figure 1a). Close inspection of these adjacent network islands often reveals that their relative positions are shifted such that a translational phase shift domain boundary would result if they merged. That these defects are not annealed out indicates a strong coupling of the network to the substrate.

To elucidate the network structure, it is essential to know the chemical state of the constituting molecules. We previously investigated the adsorption of THB on Cu(111) and showed that the molecule undergoes dehydrogenation of two of its hydroxy groups to form dihydroxybenzoquinone (DHBQ) by annealing to 370 K.^[14] Figure 2 shows X-ray photoelectron spectra for the network structure obtained after annealing to 440 K. The O 1s region (Figure 2a) is

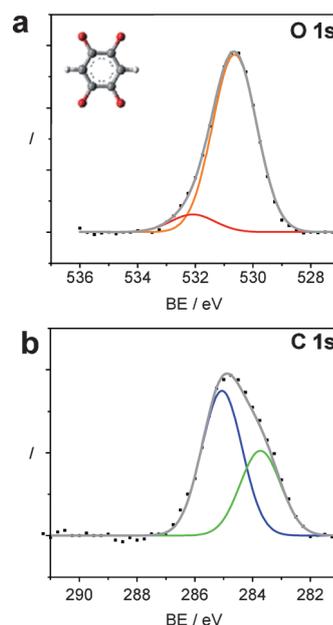


Figure 2. XP spectra obtained after depositing THB on Cu(111) and annealing to 440 K. a) O 1s region. b) C 1s region.

dominated by a feature at a binding energy (BE) of 530.7 eV with a small shoulder at lower binding energy. From our previous study, these features can be ascribed to carbonyl and hydroxy oxygen atoms, respectively.^[14] The XPS data thus show that THB undergoes essentially complete dehydrogenation of all four hydroxy groups upon annealing to 440 K. The corresponding C 1s spectrum (Figure 2b) exhibits two features with an intensity ratio of 2:1 which are ascribed to C atoms bound to oxygen (BE 285.1 eV) and hydrogen (BE 283.7 eV), in agreement with an intact ring structure.^[14] The formation of a fully dehydrogenated THB species is an example of on-surface synthesis, as this species cannot be synthesized ex situ and directly deposited. We tentatively ascribe the dehydrogenated THB species to a surface-stabilized 2,5-dioxy-*p*-benzosemiquinone diradical, which is known from liquid-phase electrochemical studies.^[15] Control experiments in which DHBQ was deposited on Cu(111) followed by annealing to 440 K reveal an identical network as expected from Scheme 1 (see also the Supporting Information).

Large-scale STM images (Figure 1d) show extended monoatomically deep vacancy islands in the Cu surface after annealing to 440 K, suggesting that the Cu surface is eroded during the network formation. It is well known that Cu adatoms can be released on the Cu(111) surface by thermal activation,^[16] and such Cu adatoms have previously been observed to participate in metal–organic coordination networks.^[6b,c,17] A precursor to the network is a close-packed hexagonal phase of DHBQ molecules formed after annealing at 370 K.^[14] The periodicity of the honeycomb network (17.4 Å) is larger than twice the lattice constant of this DHBQ close-packed hexagonal phase (7.5 Å). The network can thus not be obtained by simply removing entities from the hexagonal DHBQ structure, but also involves expansion, which is consistent with the participation of Cu adatoms in the

network structure. The THB molecule lacks the three-fold symmetry required to form a honeycomb lattice employing linear linkers. We therefore attribute the bright protrusions in Figure 1c to the dehydrogenated THB molecules and the network nodes to Cu adatoms. Contrary to the well-known bulk coordination chemistry of Cu, surface-confinement shrinks the coordination number drastically, typically leading to two-fold coordination motifs.^[17a,b,18] However, cases of three-fold coordination have been reported both in bulk^[19] and at surfaces.^[6b,c,20] The individual metal atom centers in surface coordination networks are rarely resolved by STM.^[6a,11,17a,b,18] Here, however, high-resolution STM images obtained under special tip conditions show three protrusions at the network nodes (Figure 3a). Importantly, these images strongly suggest that Cu trimers constitute the network nodes, which would readily provide the threefold symmetry necessary for the construction of a honeycomb lattice.

To investigate the coordination motif further, we employed DFT calculations. Four different unit cells on the Cu(111) surface consistent with the experimentally determined network dimensions were considered, and both single Cu adatoms and Cu adatom trimers were tried as network nodes. In each cell a systematic investigation was conducted of possible adsorption configurations for the fully dehydrogenated THB species. The optimized structure resulting from this search is the network based on Cu adatom trimers depicted in Figure 3b. The orientation of the molecules allows each molecule to coordinate to two adatoms in each trimer, in agreement with the STM image displayed in Figure 3a. Interestingly, the calculated network structure is chiral because the oxygen atoms do not coordinate symmetrically to the Cu trimers (see Figure 3c). The chiral structure in Figure 3b makes an angle of 16° with the close-packed $[10\bar{1}]$ direction, whereas a domain with an orientation of -16° would have the opposite handedness. The mirror-image domains are degenerate in energy because the constituent species are achiral, and both are indeed observed (Figure 1b).

Experiments in which THB was dosed beyond full monolayer coverage followed by annealing to 440 K did not lead to formation of the porous network. Instead, the close-packed structure shown in Figure 1e was observed. Here each entity is attributed to a fully dehydrogenated THB molecule, as confirmed by XPS measurements (Supporting Information, Figure S3). A model for this structure was also determined by DFT. The energetically preferred structure (Figure 4c) consists of aligned molecules adsorbed on bridge sites. The unit cell of $a = b = 7.6 \text{ \AA}$ and an orientation of 0° with respect to the $[10\bar{1}]$ direction is in good agreement with the experimental data. The side view demonstrates that the molecules adsorb close to the surface with a distance between the carbon ring and the surface of 2.2 \AA . In contrast, the molecules in the network structure reside at a significantly larger distance of 2.9 \AA above the surface (Figure 3d). This is consistent with the observed difference in apparent height between the two structures (Supporting Information, Figure S4).

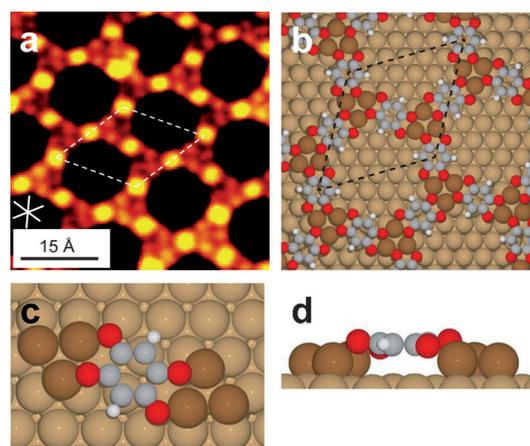


Figure 3. Surface coordination network based on Cu adatom trimers. a) High-resolution STM image, obtained under special tip conditions (see the Supporting Information), revealing structure at the network nodes ($I_t = -0.36 \text{ nA}$, $V_t = -1.25 \text{ V}$). Substrate close-packed directions are indicated. b) Calculated optimum network structure. Unit cell corresponding to (a) is indicated. The calculated unit cell has 16.0 \AA side lengths and is rotated by 16° to the substrate close-packed $[10\bar{1}]$ direction (horizontal). Light brown: atoms of Cu(111) substrate, dark brown: Cu adatoms. C gray, O red, H white. c) Detail of molecular interaction with Cu adatom trimers. d) Same in side view.

The energetics of the dehydrogenation and network formation is summarized in Figure 4. In analogy to our earlier results for partial dehydrogenation of THB,^[14] the full dehydrogenation (Figure 4b) gives rise to an increase in enthalpy (black line), but the entropic contribution of the released H_2 and zero point energy effects leads to a total free energy gain of 1.61 eV per molecule. Incorporation of the molecules into the close-packed structure (Figure 4c) decreases the energy slightly. Formation of the network structure (Figure 4d) leads to an even larger energy gain per

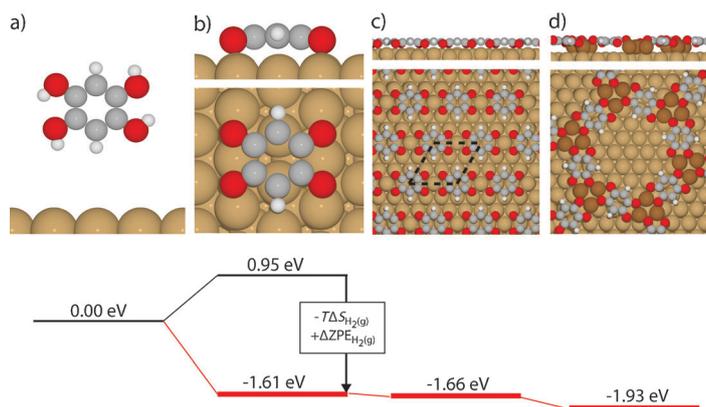


Figure 4. Calculated energies for THB dehydrogenation and subsequent structure formation. Energies are reported per molecule relative to intact THB in the gas phase as shown in (a). Black bars represent DFT calculated enthalpies and red bars represent free energies at RT including the entropic contribution of desorbed H_2 and zero point energy effects.^[14] b) Dehydrogenated molecule adsorbed on Cu(111). c) Close-packed structure corresponding to Figure 1e. d) Network structure. The reported formation energy includes the cost of forming the Cu adatom trimers.

molecule, even when the formation energy of the Cu trimers is taken into account. The network structure is less dense than the close-packed structure and although it has the highest energy gain per molecule, the energy gain per surface area is highest for the close-packed structure (3.27 eV nm^{-2} vs 2.71 eV nm^{-2} for the network). The total energy gain will thus be maximized if the porous network forms until a coverage where this structure covers the whole surface. For higher coverage, a mixture of the two phases is expected. Experimentally, co-existence of the two phases was observed for preparations involving annealing at lower temperature/short time (Supporting Information, Figure S4).

In conclusion, THB can be deprotonated on all four hydroxy groups to form a species that is highly active towards coordination with Cu adatoms. The resulting porous metal coordination network is based on Cu trimers in analogy to some bulk metal-organic frameworks.^[8] In general, the ability to create two-dimensional surface analogues of MOFs based on monodispersed and homogeneously distributed small metal clusters is interesting for example in regards to applications within catalysis and magnetic data storage.

Experimental Section

The STM and XPS experiments were carried out in a UHV system (SPECS) containing a variable-temperature Aarhus STM and an XPS system consisting of a non-monochromatic Al K_{α} source and a hemispherical electron energy analyzer.

THB was synthesized as described previously.^[14] The molecule was sublimated from a home-built Knudsen cell type evaporator at a temperature of 330 K. The Cu(111) sample was held at room temperature during deposition. STM images were obtained at room temperature. XP spectra were acquired at room temperature under an emission angle of 30° .

DFT calculations were performed with the GPAW software,^[21] which is a grid-based implementation of the projector augmented wave method.^[22] A grid-spacing of 0.16 \AA was used and the exchange and correlation energy was calculated with the *meta*-GGA functional M06L.^[23] The surface was modelled by four layers of copper. The bottom two layers were fixed in the bulk geometry, using the lattice constant of 3.59 \AA determined by M06L. Periodic boundary conditions were employed in the *x*- and *y*-direction, whereas the *z* direction was aperiodic with a minimum distance of 6 \AA between the slab and the cell boundary. The two upper layers of the slab, the molecules and the adatoms were relaxed until all atomic forces were below 0.05 eV \AA^{-1} , using 2×2 k points for the network structure and 4×2 k points for the $c(3 \times 6)$ unit cell used for the close-packed structure.

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