Self-Assembly of a Halogenated Molecule on Oxide-Passivated Cu(110)

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Abstract: The supramolecular self-assembly of brominated molecules was investigated and compared on Cu(110) and Cu(110)−O(2×1) surfaces under ultrahigh vacuum. By using scanning tunnelling microscopy, we show that brominated molecules form a disordered structure on Cu(110), whereas a well-ordered supramolecular network is observed on the Cu(110)−O(2×1) surface. The different adsorption behaviors of these two surfaces are described in terms of weakened molecule–substrate interactions on Cu(110)−O(2×1) as opposed to bare Cu(110). The effect of oxygen-passivation is to suppress debromination and it can be a convenient approach for investigating other self-assembly processes on copper-based substrates.

Keywords: copper · dehalogenation · scanning tunneling microscopy · self-assembly · template synthesis

Introduction

On-surface noncovalent intermolecular interactions can drive supramolecular organization in two dimensions, which can lead to the stabilization of structures that may be used as active layers in organic electronic devices.[1] Known examples of 2D self-assembled molecular networks are stabilized by several interactions, such as hydrogen bonds,[2] van der Waals forces,[3] metal–organic coordination,[4] and halogen bonds.[5] Other interactions based on electrostatic forces between molecules and the support surfaces can offer additional pathways for molecular self-assembly.[6] A number of structures that are based on these intermolecular interactions have been investigated on metal surfaces under ultrahigh vacuum (UHV) and the wide range of available sub-

strates provides possibilities for enhancing or impeding the molecule–surface interactions and, by extension, affecting the structural and electronic properties of the supramolecular structures.[7] Most studies of this nature have focused on the use of bare substrates; only a handful have reported the differences between the growth modes of organic molecules on passivated surfaces.[8] Most of the results show that surface passivation decreases reactivity and favors the formation of large self-assembled and ordered structures, whereas the corresponding bare surfaces cause the molecules to chemisorb in a disordered geometry, such as terephthalic acid (TPA) on Si(111)-7×7.[8a] Some species may even be destroyed by certain surfaces, owing to dissociative adsorption, such as 3,4,9,10-perylene-tetracaboxylic-dianhydride (PTCDA) on Ni(111).[9] However, the passivation of Ni with oxygen decreases its reactivity and allows PTCDA to form an ordered network.[10] By contrast, some reports have suggested oxidation may even increase a given substrate′s reactivity, such as the self-metalation of porphyrins on Cu-(001).[11]

The {110} facet of copper is a model surface for the study of molecular adsorption and self-assembly, owing to its high anisotropy and moderate reactivity. This facet possesses a strong ability to template molecular orientation and to direct epitaxial growth, as in the case of pentacene.[12] Moreover, Cu(110) can also act as a catalyst for the Ullmann dehalogenation of organic molecules at room temperature, as has been demonstrated for diiodo- and dibromobenzene,[13] as well as for larger and more-complicated precursors.[14] However, the mitigation of this catalytic effect by passivation has not been reported so far. The Cu(110)−O(2×1) surface can be used as a template for supramolecular self-assembly,[8b,12,15] on which the adsorbed oxygen species lead to a passivation of the bare Cu(110) surface.[8b] The O(2×1) overlayer has the advantage of being well-ordered (as opposed to having only local order, as found in the oxidations

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of other low-index facets of copper),[16] and it also preserves the inherent anisotropy of the {110} facet.

Herein, we describe the effect of passivating a Cu(110) surface to facilitate the self-assembly of an ordered network of halogenated molecules. We compare the growth of 2,3,2′,3′-(tetrabromophenyl-6,6′)biquinoxalinyl (TBPBQ, Scheme 1) layers on Cu(110)−O(2×1) and Cu(110) surfaces at room temperature under UHV. X-ray photoelectron spectroscopy (XPS) and STM investigations show that TBPBQ
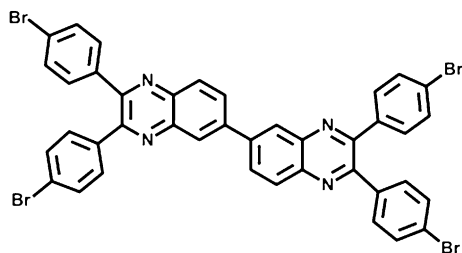
Scheme 1. Chemical structure of TBPBQ.

remains intact on Cu(110)−O(2×1) and grows into islands with a compact 2D structure, whereas the bare surface dehalogenates the molecule at room temperature.

Results and Discussion

Figure 1a shows an STM image of a bare Cu(110) surface with a submonolayer coverage of TBPBQ. Individual molecules appear as bright rectangular shapes. The TBPBQ molecules are aligned in two directions on the surface, as indicated by the blue circle and the inset image. At room temperature, we observe individual molecules, as well as a covalent dimer structures (blue and black circles, respectively). To form these structures, the Br atoms must be cleaved from the TBPBQ, which is expected for halogenated organic molecules on Cu(110) at room temperature.[13] The surface's catalytic activity is high enough that we expect every molecule to be completely dehalogenated at room temperature. Thus, we interpret the single molecules that are imaged on this surface as being bonded to the substrate at four points (which correspond to the former C−Br positions) through organometallic bonds, whereas the dimer and trimer structures represent interconnected dehalogenated TBPBQ molecules, either through direct covalent coupling or, possibly, through organometallic links that involve surface Cu atoms. Similar behavior was observed for the adsorption of 4,4″-dibromo-p-terphenyle on Cu(111),[17] thus indicating that the dehalogenative property is present, even on less-reactive facets of copper.

When the coverage of TBPBQ on Cu(110) is increased, a network of dumbbell-shaped protrusions is formed on the surface (Figure 1b) and it becomes more difficult to distinguish single molecules. These structures consist of dehalogenated molecules that are interconnected by either direct
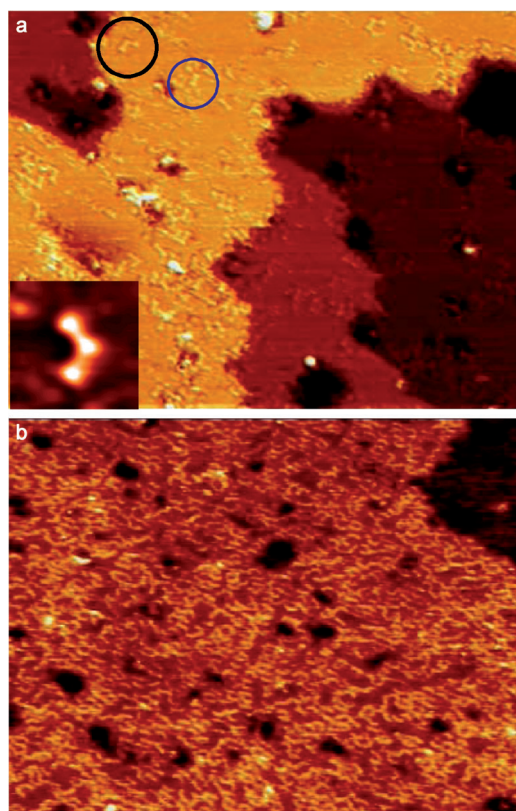

Figure 1. STM images of the Cu(110) surface after exposure to TBPBQ at RT: a) Low coverage. Single (blue circle) and dimer structures (black circle) are observed (45×45 nm^2, $U_s = -1.23$ V, $I_t = 0.59$ nA); inset shows a single TBPBQ dimer (4.1×4.1 nm^2, $U_s = -0.65$ V, $I_t = 1.0$ nA). b) Coverage close to 1 ML (50×50 nm^2, $U_s = -0.90$ V, $I_t = 1.0$ nA).

covalent linking or, possibly, by organometallic links through copper atoms.

Exposing the Cu(110) crystal to oxygen forms a (2×1) reconstruction, which dramatically decreases the surface's reactivity. Densely packed, well-ordered islands in two domain orientations are formed when TBPBQ is deposited onto Cu-(110)−O(2×1) (see the Supporting Information, Figure S1). At low coverages (0.2 ML), the perimeter of the domains is poorly resolved (Figure 2a), owing to the diffusion of TBPBQ molecules in and out of the ordered islands on much-shorter timescales than the acquisition speed of the STM data (approximately 10^{-12} s,[18] versus approximately 30 s for a typical acquisition of STM data). The high mobility of the molecules at RT is presumably responsible for the large degree of order in the islands.

We hypothesize that oxidation mitigates the catalytic activity of the surface; ex situ XPS of these surfaces at the Br 3p core level reveals a doublet with the 3p$_{3/2}$ level at a binding energy of 184.8 eV (Figure 2b). The same analysis performed on powdered TBPBQ indicates an identical binding energy. The Br 3p binding energy for copper-bound bromine should appear at significantly lower energy (3p$_{3/2}$ = 182.4 eV)[19] and, thus, we conclude that the TBPBQ molecules remain intact when deposited onto Cu(110)−O(2×1) at

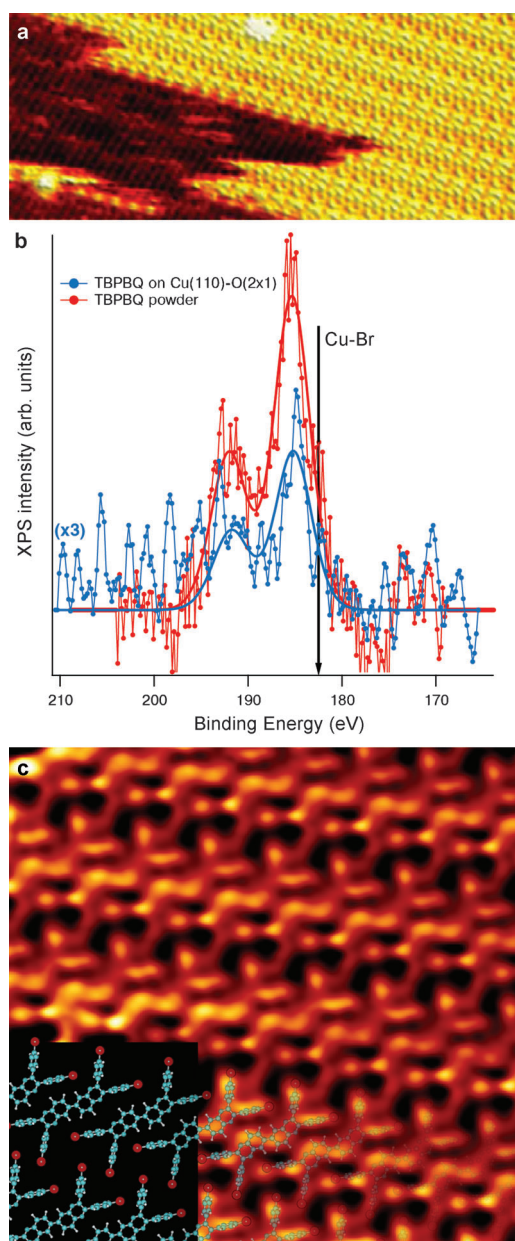Figure 2. a) STM images of TBPBQ/Cu(110)−O(2×1) with atomic resolution (30×12 nm², $U_s = -0.74$ V, $I_t = 0.77$ nA). b) XPS Br 3p core-level spectra of TBPBQ powder (red) and TBPBQ on Cu(110)−O(2×1) (blue). c) High-resolution STM image of TBPBQ on Cu(110)−O(2×1) at 150 K (7×7 nm², $U_s = -1.42$ V, $I_t = 0.74$ nA).

Figure 3. STM images that show the chirality of the TBPBQ domains: a) 5.1×5.1 nm², b) 5×5 nm² ($U_s = -1.42$ V, $I_t = 0.7$ nA). c) Determination of the adsorption site of the molecules on the surface (7.7×8 nm², $U_s = -0.74$ V, $I_t = 0.77$ nA). d) Tentative structural model of adsorbed TBPBQ molecules on the Cu(110)−O(2×1) surface.

of individual molecules. Based on these images, we may determine the experimental unit-cell parameters and the molecular orientation ($a_1 = 1.1(\pm 0.1)$, $b_1 = 3.0(\pm 0.1$ nm; $\alpha_1 = 138(\pm 1)°$), which may also be written by using the epitaxy matrix (6 −1 | 1 2), thus indicating commensurability with the surface. The matrix is written with respect to the lattice vectors $a_s = (0.361$ nm, 0) and $b_s = (0, 0.512$ nm) of the underlying Cu(110)−O(2×1) surface. From the packing geometry as observed by STM, we may determine the particular adsorption site of TBPBQ on the surface. Both the molecules and the surface are clearly identified in the same STM image (Figure 2a). A model of the molecular network can be superimposed over the image, with reference to the underlying substrate as indicated by the black grid (Figure 2c). We hypothesize that the diagonally opposite bromine atoms of TBPBQ are positioned above oxygen atoms (Figure 3) in the substrate, by using the interpretation that the bright pro-
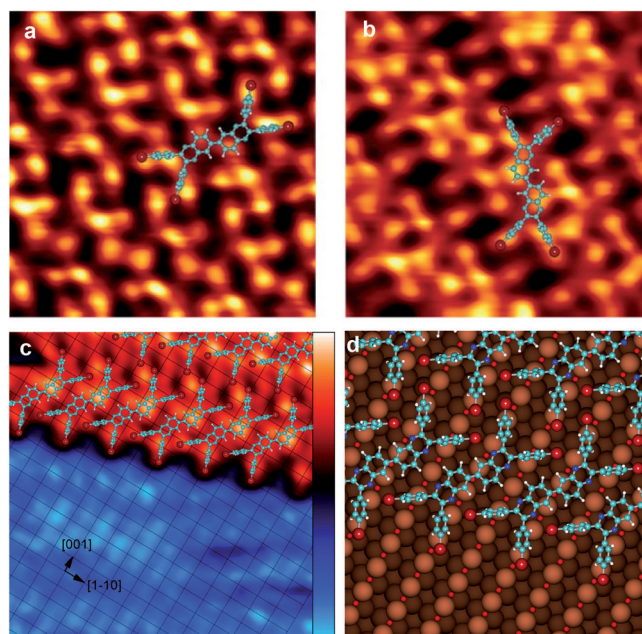
room temperature. By extension, we hypothesize that oxygen passivation of Cu(110) may be sufficient to suppress the dehalogenative adsorption of all brominated polycyclic aromatic molecules.

The driving force for self-assembly must be inherently different from the covalent coupling that is observed on the bare surface. To better understand the growth of the ordered structure, a surface with a coverage of 0.2 ML was cooled to low temperatures (150 K) and imaged (following deposition at room temperature). Figure 2c shows the TBPBQ structure at 150 K, which allows the identification

trusions of the Cu(110)−O(2×1) surface correspond to the oxygen atoms in the CuO strings.[16b] The long axis of the molecule is oriented at an angle of 35° to the [001] axis of the copper lattice.

The use of the epitaxy matrix highlights the observation that the ordered structure of TBPBQ molecules is commensurate with the lattice surface. Each domain is chirally pure because they only contain a single TBPBQ enantiomorph, as shown in Figure 3a,b. Whilst gas-phase TBPBQ is not chiral, prochiral surface adsorption has received considerable attention.[2a,b,20] The second domain orientation can be

described by the matrix (6−1| 1−2), thus indicating mirror symmetry about the [001] direction of the copper lattice.

The formation of large 2D molecular self-assembled networks of TBPBQ on a Cu(110)−O(2×1) surface is possible because of the weakened molecule–surface interactions compared to the bare substrate. The packing geometry implies the presence of several intermolecular bonds between each TBPBQ molecule and its nearest neighbours. Density functional theory (DFT) calculations were used to provide a fuller description of the forces that drive supramolecular organization. However, calculations that were performed by using periodic boundary conditions (PBCs) with the experimentally observed unit-cell parameters ($a_2 = 3.0$, $b_2 = 1.1$ nm; $\alpha_2 = 138°$) did not converge. Allowing α_2 to vary during the geometry optimization produced the model as shown in the Supporting Information, Figure S2, in which the α_2 angle increased to 142°. However, a change in the angle by 4° led to an incommensurate structure, as indicated by a schematic representation of the simulated model ($\alpha_2 = 142°$), compared to the structure observed on Cu(110)−O(2×1) ($\alpha_2 = 138°$; see the Supporting Information, Figure S3). Thus, although gas-phase modelling is an adequate method for describing self-assemblies on inert substrates,[21] it cannot reproduce the experimentally observed structure on Cu(110)−O(2×1). We conclude that the surface has a non-negligible effect on self-assembly. Because the gas-phase DFT calculations do not give a unit cell that is close the experimental one, we conclude that the surface must drive some aspects of the assembly, in particular given the commensurability of the molecular islands. This interpretation is supported by experiments at the solution/solid interface on highly oriented pyrolytic graphite (HOPG), which is a much more inert surface that can be used to investigate intermolecular forces during self-assembly with a much lower degree of influence on the adsorption site, and Au(111), which is a somewhat more-reactive surface than HOPG. Under identical conditions, no self-assembly of TBPBQ was observed on HOPG, but small domains of ordered molecules were formed on Au(111) (see the Supporting Information, Figure S4). This result is in line with our hypothesis that a non-negligible surface interaction is required to stabilize a conformation that favours the formation of intermolecular bonds. Gas-phase TBPBQ possesses a twisted conformation at room temperature (see the Supporting Information, Figure S5). A strong interaction with the surface is likely necessary to flatten the core and to provide an optimal packing geometry.

Conclusions

By pre-oxidizing a Cu(110) surface, we are able to obtain a 2D ordered pattern of TBPBQ, which is driven by a balance between molecule–molecule and molecule–surface interactions. Bare Cu(110) debrominates the molecules at RT and hinders the formation of any ordered structures. Passivation, by creating an O(2×1) reconstruction, suppresses dehalogenation and allows the self-assembly to proceed. The

need for surface interactions was demonstrated by the fact that the molecules were observed to self-assemble at the solution/Au(111) interface but not at the solution/HOPG interface, because HOPG is much less reactive than gold.

Experimental Section

Acknowledgements

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