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COMMUNICATIONS

Rectangular Nanostructuring of Au(111) Surfaces by Self-Assembly of Size-Selected Thiacrown Ether Macrocycles

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Surface modification by self-assembled monolayers (SAMs) has continuously attracted considerable attention because of several potential applications in domains such as nanopatterning, biosensors and chemical sensors, and microelectronics.[1,2] Organo-sulfur derivatives such as *n*-alkanethiols R−SH and dialkyl disulfides R−S−S−R′ are the most extensively studied SAMs adsorbed on various metal surfaces such as gold, silver, or copper.[3,4] In comparison, very few studies have been reported on SAMs based on thioethers R−S−R′. However, in an early report Troughton et al. studied the spontaneous self-assembly of symmetrical and unsymmetrical dialkyl sulfides onto gold substrates.[5] More recently, Noh et al. investigated the adsorption of dioctadecyl sulfide SAMs on Au(111) by scanning tunneling microscopy (STM) and high-resolution electron energy loss spectroscopy.[6] It has been observed in particular that the C−S−C motif of dioctadecyl sulfide remains intact after adsorption on gold, that is, without cleavage of the C−S bonds.

Among thioethers, thiacrown ethers (TCEs) are cyclic thioethers consisting of an alternance of sulfur atoms and $(CH_2)_n$ methylene bridges.[7,8] Saturated TCEs can be viewed as the sulfur counterparts of the well-known crown ethers and contain a variable number of sulfur atoms, each separated by a variable number of CH_2 groups. TCEs can behave as soft Lewis bases to interact selectively with metal ions such as Ag^+, Hg^{2+}, Cu^+, and Pd^{2+} and form inclusion complexes.[9,10] If the basic process involved in coordination of TCEs with metal ions is well-understood,[11−13] interaction of TCEs with metal substrates has not been explored yet. Because of the cyclic geometry of the TCE molecules, it can be expected that their adsorption on metal surfaces would take place via sulfur-metal interactions and result in self-organized domains of cavities with various sizes and shapes. Such a size-selected nanostructuring of metallic surfaces could then be used to form highly ordered 2D inclusion networks and investigate electron-transfer processes between a metal substrate on one hand and various systems such as (bio)macromolecules on the other hand.

Recently, Stang et al. reported ordered cavity structures relating to the self-organization of supermolecular metallacyclic rectangles on Au(111).[14,15] Besides, Yoshimoto et al. studied the formation of crown ether substituted phthalocyanine arrays on Au substrate.[16] Although ordered cavities can be realized by self-organization, the interaction with the substrate may be too weak to allow further application.

In this Communication, we investigate the formation of ordered SAMs of two families of TCEs (Figure 1), namely tetrathiacrown ethers **1** (12S4) and **2** (14S4) and hexathiacrown ether **3** (18S6), by means of STM at the liquid/solid interface.[17−19]

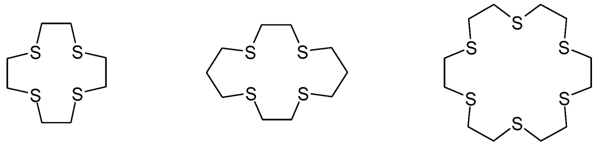

Figure 1. Molecular structures of the three thiacrown ethers (TCE) used in this study.

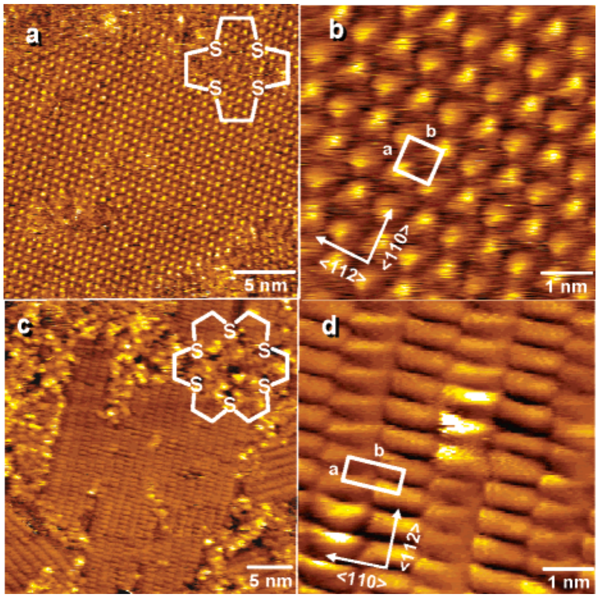

Figure 2. STM images of highly organized domains of tetrathiacyclododecane **1** (a,b) and hexathiacyclooctadecane **3** (c,d) at the *n*-tetradecane/Au(111) interface: (a) 25 × 25 nm^2, $V = 0.520$ V, $I = 18$ pA; (b) 6 × 6 nm^2, $V = 0.520$ V, $I = 18$ pA; (c) 34.4 × 34.4 nm^2, $V = 0.500$ V, $I = 20$ pA; (d) 6.1 × 6.1 nm^2, $V = 0.500$ V, $I = 70$ pA.

Figure 2 shows typical STM images obtained by depositing solutions of TCE **1** and **3** in *n*-tetradecane (∼0.05 mg/mL) on an annealed Au(111) substrate. For the two molecules, large-scale STM images reveal ordered domains rotated at 120°, reflecting the threefold symmetry of Au(111). These domains have an average lateral size of several tens of nanometers. In both cases, the ordered domains are separated by apparently disordered regions. Randomly distributed depressions are observed at the domain boundaries as well as in the ordered phases. These pits exhibit an average depth of ∼2.4 Å, which corresponds to the thickness of a monatomic layer of the Au(111) substrate, showing that individual Au atoms have been removed from the surface (see Supporting Information). The occurrence of etched pits implies that strong Au−S chemical

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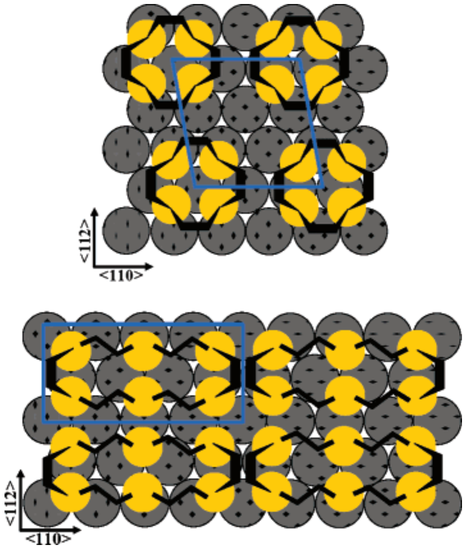

Figure 3. Proposed structural models for the self-assembled monolayers of thiacrown ethers **1** and **3** on Au(111).

bonds are formed between the thiacrown ethers and the Au substrate.

For **1**, the highly ordered domains are composed of bright spots with sizes ~4 Å arranged in a close-packed quasi-square structure (Figure 1a,b), each dot being assigned to an individual molecule. Analysis of cross-section profiles (see Supporting Information) leads to a unit cell with $a = 0.78 \pm 0.02$ nm, $b = 0.73 \pm 0.02$ nm, and $\alpha = 80 \pm 2°$, containing one molecule with an average area of 57 Å^2/molecule.

In sharp contrast, **3** self-organizes on gold into lamellae aligned uniaxially along the ⟨112⟩ direction. Again, various domains oriented at 120° are observed. Surprisingly, molecular resolution reveals that each lamella consists of individual rectangular protrusions with 10 × 4 Å^2 dimensions, each of them having a rather uniform tunnel contrast (Figure 1d). All rectangular protrusions are arranged parallel to each other and correspond to individual molecules. The slight intramolecular modulation of the STM contrast which is sometimes observed at high resolution (see Figure 1d) may have different origins. It can either be induced by mechanical interactions between the tip and the monolayer or arise from slightly different conformations of molecule **3** on the substrate. The unit cell has the following parameters: $a = 0.6 \pm 0.05$ nm, $b = 1.2 \pm 0.1$ nm, and $\alpha = 90 \pm 2°$ and contains one molecule with an average area of 72 Å^2/molecule.

Figure 3 represents the best possible surface models of **1** and **3** SAMs on gold as deduced from the STM images. Molecule **1** arranges in an all-cis conformation, while **3** clearly adopts a trans conformation along its long axis and a cis conformation along its short one. In analogy to thiol-based SAMs,[20] the sulfur atoms of both TCE molecules are assumed to be positioned on three hollow sites of the gold lattice. Such a model indicates that, in spite of its size and flexibility, no cavity is formed inside macrocycle **3** once adsorbed on gold. This is in agreement with the unresolved STM images inside individual molecules where the backbone of the macrocycle is not apparent.

Interestingly, we never observed any adsorption of **2** on Au(111). This molecule is a tetrathiacyclotetradecane with alternating two- and three-carbon bridges between sulfur atoms. The additional CH_2 group into two of the four intersulfur bridges of molecule **2** as compared to molecules **1** and **3** may induce an unfavorable conformation for its adsorption on Au(111).

In summary, thiacrown ethers **1** and **3** form SAMs on Au(111). The presence of etch-pits implies a strong chemical interaction between gold and the sulfur atoms of TCE molecules. SAMs of **3** consist of a rectangular nanostructuring of the gold surface at the molecular level. Each individual molecule is then observed as a uniform featureless rectangle without a central cavity. The use of thiacrown ethers as molecular bricks for size-controlled rectangular nanostructuring of Au surfaces has been demonstrated. We now extend our study to larger and unsymmetrical TCE macrocycles adsorbed on various metals.

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Supporting Information Available: Experimental procedures, STM images of Au(111) substrates, and complementary STM images with cross-section lines. This material is available free of charge via the Internet at http://pubs.acs.org.

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