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Chiral Kagome Network from Thiacalix[4]arene Tetrasulfonate at the Interface of Aqueous Solution/Au(111) Surface: An in Situ Electrochemical Scanning Tunneling Microscopy Study

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A Kagome lattice, also known as trihexagonal tiling in mathematics, represents a periodic arrangement of interlaced triangles such that each point where two triangles cross has four neighboring points.[1] This pattern initially attracted attention in the area of magnetism for its relevance in the field of spin-frustrated magnetic materials.[2] Recently, the Kagome network is also finding interest in the area of two-dimensional (2D) molecular self-assembly. This is because the 2D Kagome network is formed through self-assembly of organic molecules not only providing an ideal 2D model system for studying magnetic frustration physics but also containing triangular and hexagonal voids which may serve as a site-selective template for guest molecules.[3] To date, a few 2D Kagome networks stabilized by hydrogen bonding, van der Waals interaction, and metal−organic coordination have been fabricated on a solid surface through molecule self-assembly.[4] However, molecules used for the formation of a 2D Kagome network are very limited. Most of these molecules are relatively simple planar molecules, such as tetraacid analogues,[3a,4a,b] dehydrobenzo[12]annulene derivatives,[4c,d] ditopic molecular bricks,[4e,f] porphrins,[4g] and phthalocyanines.[3b] Novel complex supramolecules, which are important building blocks in supramoelcular chemistry, are rarely used to prepare 2D Kagome lattices.

Calixarene is one of the most widely investigated supramolecules. They possess a good complexing ability to guest molecules. In particular, thin films of calixarenes are found to have potential applications in microsensors, pyroelectrical devices, and nonlinear optical materials.[5] Thiacalix[4]arene tetrasulfonate (TCAS) is a novel water-soluble calixarene. As shown in Figure 1, its bridge groups are S atoms instead of methylene, and its upper and lower rims are substituted by sulfonate and hydroxyl groups, respectively. These substituents give TCAS many interesting functions. For example, it can complex a variety of guest molecules, including fullerenes, benzene derivatives, pyridinium ions, and metal ions.[6] Meanwhile, some fascinating supramolecular structures, such as bilayers and channel, can be formed by TCAS in the presence of suitable guest molecules.[7]

Herein, we report on the fabrication of a stable Kagome network of TCAS at an aqueous/Au(111) interface. High-resolution STM images reveal that two enantiomorphous structures are formed in the adlayer. It represents a hierarchical chirality composed of achiral TCAS that arranged into chiral triangular subunits, which again enclose a hexagon and form a 2D chiral Kagome network. To the best of our knowledge, this is the first example of the formation of a 2D Kagome network using a complicated stereo calixarene as a building block, which opens the possibility to construct a 2D Kagome network with various functional supramolecules.

The TCAS adlayer was prepared by immersing a clean Au(111) surface in a 1 × 10^{-4} M TCAS aqueous solution for 1 min. The obtained adlayer was then transferred to an electrochemical cell for cyclic voltammetry or scanning tunneling microscopy (STM) measurements. Cyclic voltammograms reveal that a cathodic current appears at ∼300 mV vs RHE (reversible hydrogen electrode) and reaches a maximum at 200 mV for TCAS/Au(111) surface. The cathodic current decreases gradually with continuous scanning (see Figures S1 and S2 in the Supporting Information). It is inferred that an irreversible desorption of TCAS from the Au(111) surface occurs at a potential more negative than 300 mV. Therefore, the substrate potential was first kept at 550 mV in the STM experiments. Figure 2a is a typical STM image of the resulting adlayer. A well-ordered hexagonal open network was formed. The ordered nanoporous array can be clearly observed. The diameter of the pore is ∼1.4 nm, and the pore-to-pore distance is ∼3.6 nm. A rhombic unit cell can be defined, with parameters $a = b = 3.6 \pm 0.1$ nm,

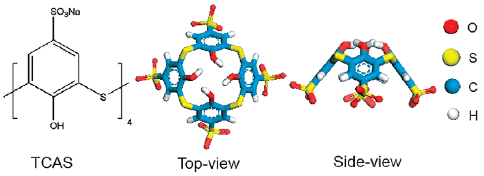

Figure 1. Molecular structure of TCAS and the space filling model.

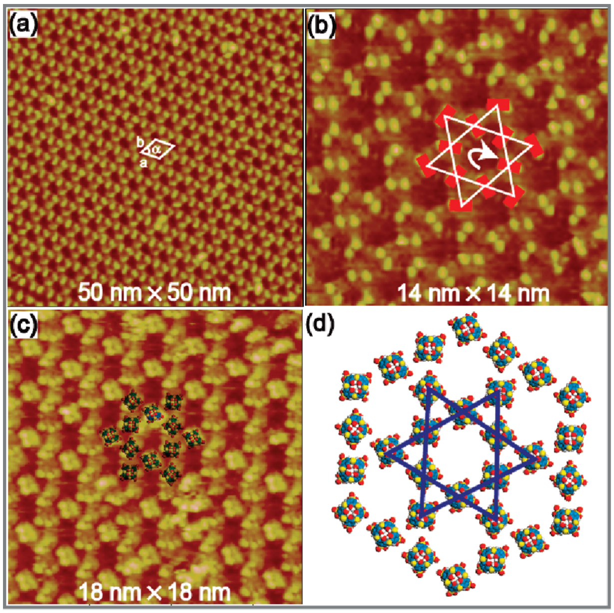

Figure 2. (a,b,c) STM images of TCAS adlayer on Au(111) surface. (d) Proposed structural model of the TCAS adlayer. Tunneling conditions: (a) $E_{sub} = 550$ mV, $E_{bias} = -493$ mV, $I = 823$ pA; (b) $E_{sub} = 550$ mV, $E_{bias} = -415$ mV, $I = 299$ pA; (c) $E_{sub} = 550$ mV, $E_{bias} = -605$ mV, $I = 580$ pA.

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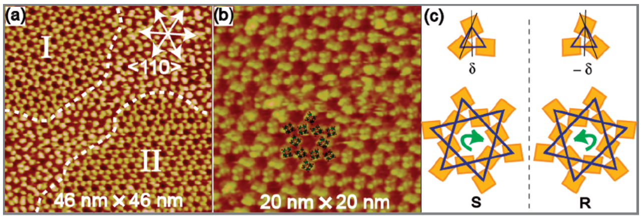

Figure 3. (a) STM image of TCAS adlayer on Au(111) surface. (b) High-resolution STM image of R domain. (c) Illustration of the origin of the 2D chirality. Tunneling conditions: (a) $E_{\text{sub}} = 550$ mV, $E_{\text{bias}} = -666$ mV, $I = 899$ pA; (b) $E_{\text{sub}} = 550$ mV, $E_{\text{bias}} = -415$ mV, $I = 299$ pA.

$\alpha = 60°$. More details about the network and the adsorbed molecules are revealed in Figure 2b. It is clear that the building block of the network is a set of two bright spots (represented by a red rod). Every three sets of spots arrange triangularly, whereas six triangles enclose a regular hexagon in a vertex-sharing manner, as illustrated by white lines in the image. This supramolecular arrangement features a 2D Kagome structure. Noticeably, the Kagome network bears chirality. According to the rotational direction of the windmill formed by six building blocks around the pore, the open nanoporous network in Figure 2 was designated as an S-type.

A higher resolution STM image with detailed internal structural information of TCAS is obtained at optimized tunneling conditions, as shown in Figure 2c. Each building block can be imaged as a set of four spots with different contrast. From the STM image, we found that the size of each spot is equal to the dimension of a phenyl. Therefore, a spot is ascribed to a phenyl group of TCAS. The result is consistent with previous literature reports.[8] For comparison, several TCAS molecules were superimposed in Figure 2c. Note that the appearance and the contrast of the phenyls in STM image are varied. It may be a result of the different orientation and registry of the phenyls of each TCAS on a Au(111) surface, considering the flexibility of calixarenes. It also accounts for the observation of two bright spots in some tunneling conditions. Based on the above analysis, a structural model can be proposed. In view of the strong interaction between sulfate and the Au(111) surface,[9] TCAS molecules are supposed to adsorb on the substrate in an upside-down manner; that is, the sulfonate groups interact with the surface whereas the hydroxyls point to the solution. This adsorption conformation is similar to the cone-shaped conformation of TCAS in the solid state.[7b] Figure 2d shows the proposed structural model. No obvious directional intermolecular interaction exists. TCAS molecules interact through a nonspecific van der Waals force and form molecular trimers that further result in the Kagome network (illustrated with blue network).

An enantiomorphous network of the S-type Kagome lattice was observed in the adlayer. As shown in Figure 3a, two domains, as marked with I and II respectively, are contained in the STM image. The structure in domain I shows an S-type Kagome lattice, as shown in Figure 2. Figure 3b is the high resolution STM image of domain II. The appearance and internal structure of domain II are similar to those of domain I, except for the rotational direction of the windmill, suggesting an opposite handedness. This means that domain II is an enantiomer of domain I. It shows an R-type Kagome lattice. Since the TCAS molecule is achiral, the chirality of the nanoporous network should originate from the molecular assembly. After careful inspection, it is found that there is a small off angle δ between the axis of TCAS and that of the triangular subunit. This suggests that the trimer unit is unsymmetrical. When the trimers self-assemble on the surface, the chirality of each trimer is further passed onto the hexagons and then to the adlayer, as illustrated in Figure 3c. The structure represents a hierarchical chirality composed of achiral TCAS that arranged into a chiral Kagome 2D nanoporous network.

After revealing the details of the adlayer at 550 mV, the substrate potential was negatively shifted step by step. At 300 mV, the ordered structure disappears and clean Au(111) terraces are present. This result is consistent with the cyclic voltammograms.

In summary, we have demonstrated the formation of a chiral Kagome network structure using TCAS as a building block at an aqueous/Au(111) interface with potential control. The interesting feature of the system is that the building block of the chiral Kagome network is a structure-complicated supramolecule calixarene rather than simple planar or near-planar organic molecules. It opens the possibility to construct a 2D nanoporous network by various functional supramolecules. Furthermore, thanks to the versatility of TCAS, which can interact with guest molecules through hydrogen bonding as well as hydrophilic/hydrophobic and $\pi-\pi$ stacking interaction, a plethora of host−guest complexes could be integrated into the Kagome network. Finally, the construction of a chiral cavity array in aqueous media would facilitate single molecular recognition with biological active chiral molecules. This study is currently under investigation in our group.

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Supporting Information Available: Cyclic voltammograms of Au(111) and TCAS/Au(111) electrodes in 0.1 M $HClO_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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