

# Novel self-assembled monolayers of disulfides with bicyclo[2.2.2]octane moieties on Au(111)

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Received (in Cambridge, UK) 30th May 2001, Accepted 26th July 2001

First published as an Advance Article on the web 16th August 2001

A series of disulfides containing bicyclo[2.2.2]octane moieties have been synthesised and their self-assembled monolayers (SAMs) on Au(111) have been characterized using scanning tunnelling microscopy (STM).

SAMs consisting of thiols and disulfides chemisorbed on Au(111) have been extensively studied owing to their stability and ease of preparation. Among organosulfurs on gold, *n*-alkanethiols and their substituted analogues are considered the simplest case due to their linear structure of saturated hydrocarbon chain and degree of freedom in the process of self-assembling.<sup>1,2</sup> The first structural study of alkanethiols having a bulky end group was reported in 1992.<sup>3</sup> STM topographs of these SAMs exhibited a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  lattice in spite of the bulky end group that sterically hinders the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure. Later study of other bulky thiols showed incommensurate lattices.<sup>4</sup> Furthermore, new classes of SAMs consisting of spiro-alkanethiols<sup>5</sup> (organic) or polyhedral borane derivatives<sup>6</sup> (inorganic) have been recently investigated. In these reports, the authors attempted to control the film properties by designing the molecular structure of adsorbates. Detailed microscopic structures, however, remain unsolved.

In the present work, we focused on the preparation of well-defined thin rigid films. As a new class of adsorbates, structurally simple and symmetric molecules (bicyclo[2.2.2]octane derivatives) were synthesized. In comparison with *n*-alkanethiols and their substituted analogues, sulfur compounds with bicyclo[2.2.2]octane moieties are expected to have unique properties. First, the overall shape of the molecule is roughly spherical and the size is *ca.* 0.60 nm, which is larger than the nearest neighbour spacing (0.50 nm) of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure. Owing to the bulkiness of the bicyclo[2.2.2]octane moieties, they are expected to be oriented perpendicularly to the surface and thus the formation of domain structure due to the tilt of adsorbates can be avoided.<sup>1,2</sup> Second, three ethylene chains are linked at both terminals of this moiety and the structure of the bulky end group itself is rigid. Third, formation of rigid thin films is expected due to the stronger van der Waals interactions between bicyclo[2.2.2]octane moieties compared to those of *n*-butane moieties of *n*-alkanethiols with the same height. The chain ordering in the films with such short *n*-alkane chains is known to be disturbed appreciably by their vigorous thermal motion at room temperature.<sup>1</sup>

Compounds **1a** and **1b** (Fig. 1) were derived from 4-methoxybicyclo[2.2.2]octane-1-carboxylic acid<sup>7</sup> in 20–30% overall yields by a 6–7 steps procedure.† As desired adsorbates, disulfides were synthesized taking their stability and ease of purification into account. Au(111) surfaces for STM studies were prepared by thermal evaporation of gold (99.99%) onto freshly cleaved mica *in vacuo* with a background pressure of  $< 5 \times 10^{-7}$  Torr. SAMs [1/Au(111) in Fig. 1] were prepared by dipping the Au substrates for 10–72 h in 0.5 mM ethanol solutions of **1a**, **1b**, or **1a** + **1b**. All STM measurements were performed using a constant-current mode with a tungsten tip in the atmosphere at room temperature and the images were unfiltered.

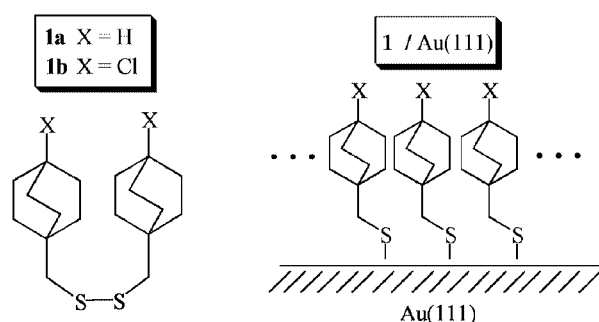


Fig. 1 Bicyclo[2.2.2]octane derivatives (**1a** and **1b**) synthesized in this study and schematic structure of their SAMs [1/Au(111)].

Fig. 2 shows a constant-current STM image of a  $20 \times 20$  nm area of a SAM of **1a**/Au(111). In the same way as with *n*-alkanethiols, single Au atom deep pit defects and a hexagonal close-packed lattice were found as shown in Fig. 2. We also investigated a SAM image of a short chain *n*-alkanethiol (pentanethiol) with a carbon number in the vertical direction equal to that of **1**. In the pentanethiol SAM, disordered structure and domains including a  $c(4 \times 2)$  superlattice of a hexagonal lattice<sup>1,2</sup> were found. Periodicities of topographic differences found in the superlattice are considered to reflect the difference in azimuthal orientation. In Fig. 2, such periodicities of topographic differences are not seen and the nearest spacing is  $0.59 \pm 0.03$  nm. This spacing is larger than the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure (Au spacing is 0.288 nm). It is also clear from Fig. 2 that rows of molecules are not always straight and that such deviations are not due to thermal drifts.

We also imaged the underlying Au(111) lattice by mechanically removing part of the SAM with the STM tip. It was found that the hexagonal lattice of the adsorbate was rotated *ca.*  $30^\circ$

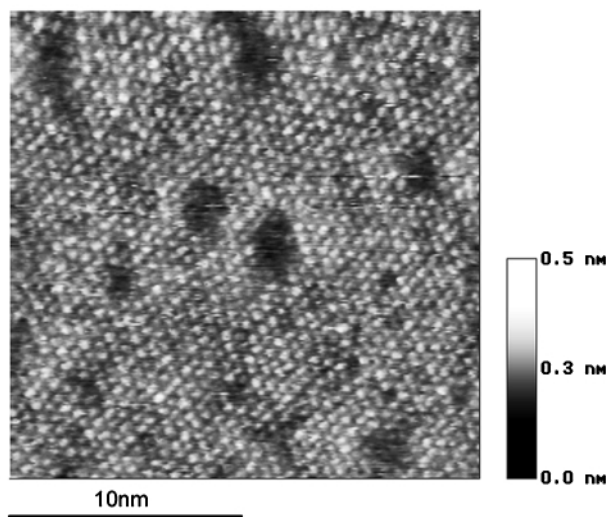
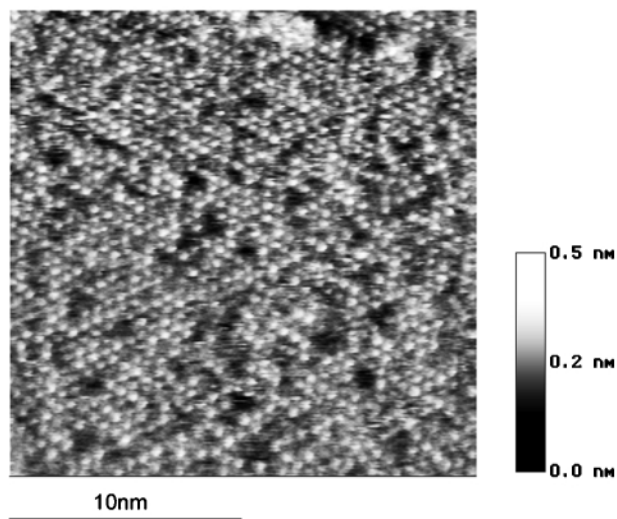


Fig. 2 Constant-current STM image of a  $20 \times 20$  nm area of a SAM of **1a** (tunnelling current = 50 pA, sample bias voltage = +1 V).



**Fig. 3** Constant-current STM image of a  $20 \times 20$  nm area of a SAM of **1b** (tunnelling current = 30 pA, sample bias voltage = +1 V).

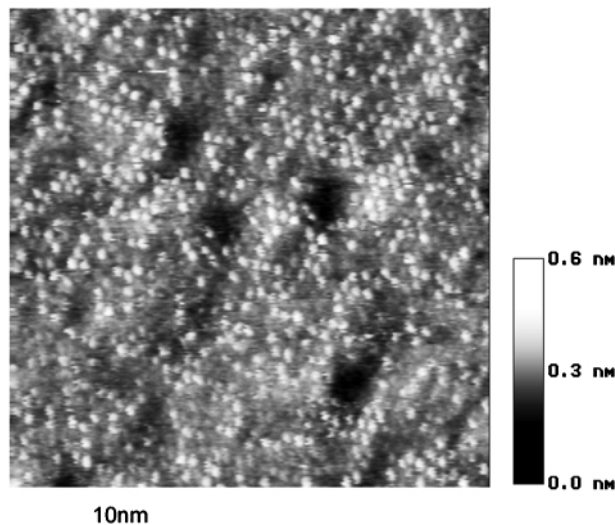
over that of Au(111). The molecular rows in the same direction went across steps and pits.

Although the shape of a bicyclo[2.2.2]octane moiety is roughly spherical as stated above, it also possesses a three-fold axis. A shorter distance of closest approach between the two bicyclo[2.2.2]octane moieties may be achieved when an ethylene chain of one moiety is located between two chains of the other moiety. We are now undertaking a study of annealing effects to obtain detailed information on the unit cell.

Fig. 3 shows a constant-current STM image of a  $20 \times 20$  nm area of a SAM of **1b**/Au(111). This film shows a slightly different feature. The depressions (pits), that are usually observed in SAMs of *n*-alkanethiols and also in a SAM of **1a**/Au(111) in Fig. 2, are not observed clearly in Fig. 3. Instead, the organic overlayer itself is more poorly ordered. Since there are tip convolution problems for imaging small size depressions, we should take care when discussing this result. This feature probably results from strong short-range interaction, *i.e.* dipole-dipole interactions among C-Cl end groups on the bicyclo[2.2.2]octane moieties, oriented perpendicularly to the Au(111) surface [**1b**/Au(111) in Fig. 1]. For this upright orientation of the terminal groups, the bridgeheads of the moieties play an important role.

Finally, we carried out adsorption of a mixture of two components (compounds **1a** and **1b**). We prepared an ethanol solution of a 1 : 1 mixture of **1a** + **1b**. Fig. 4 shows a constant-current STM image of a  $20 \times 20$  nm area of a SAM of the mixture on Au(111). The two components were molecularly dispersed. We assigned bright features (*ca.* 0.1 nm protrusions) to chloride end groups on the basis of insertion experiments of **1b** to the matrix containing **1a** carried out separately. This result clearly indicates that dots on the lattice of the STM image correspond to individual molecules and a distinction of the small difference between the H and Cl terminal atoms can be possible by STM. The observed distinction is afforded by the high structural order in the organic surface film which is, in turn, the result of interactions between the rigid sphere-shaped molecules. Most of the bright features seemed to be pairing, indicating that lateral diffusion of dissociated thiolates occurred upon chemisorption of **1a** and **1b** from the 0.5 mM mixed solution was slow.

In summary, we have investigated the structure of novel bicyclo[2.2.2]octane derivatives chemisorbed onto Au(111)



**Fig. 4** Constant-current STM image of a  $20 \times 20$  nm area of a SAM of **1a** + **1b** (tunnelling current = 50 pA, sample bias voltage = +1 V).

from 0.5 mM ethanol solutions using STM. Owing to their rigid structure, small differences between the end groups, *e.g.* between H and Cl, were distinctive. This distinction of individual molecules, to the best of our knowledge, represents one of the highest resolutions of organic monolayers on solid surfaces.<sup>8</sup> Although our knowledge of SAMs of these novel adsorbates is still limited in comparison with that of the widely used *n*-alkanethiols, the well-defined structure and the ease of detection and distinction described above will be useful for further investigation of these adsorbates and their substituted analogues. For example, their application to rigid bases for oriented dipoles, rigid spacers for molecular single electron devices, hexagonally close-packed host matrices for insertion experiments, markers for lateral diffusion dynamics, *etc.* are expected. As spacers, dimers and trimers of the bicyclo[2.2.2]octane unit will be useful.

## Notes and references

† 4-Methoxybicyclo[2.2.2]octane-1-carboxylic acid was synthesized according to a previously reported procedure.<sup>8</sup> Disulfides used for SAM formation were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra and elemental analysis giving satisfactory results. Details of the syntheses will be reported elsewhere.

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