

## 2D-supramolecular arrangements of dibenzo-18-crown-6-ether and its inclusion complex with potassium ion by potential controlled adsorption

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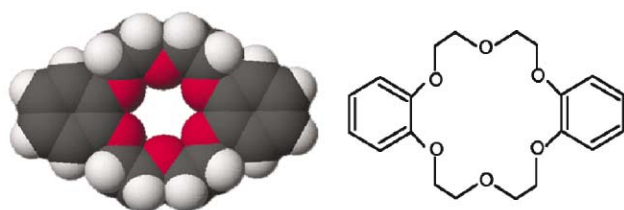
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The construction of self-organized adlayers of dibenzo-18-crown-6 and its inclusion complex with potassium ion on a Au(111) surface was independently achieved by potential-controlled adsorption. Highly-ordered adlayers both for the metal-free state and the complex were visualized by *in-situ* STM with sub-molecular visualization. The potassium ions in the complex were also clearly visualized.

Two-dimensional (2D) self-organization of organic molecules has been attracting considerable attention because of its high potential for applications in nanoscience and nanotechnology.<sup>1</sup> As a concept for the construction of 2D self-organized structures, “adsorption-induced self-organization” has been proposed.<sup>2</sup> It is based on the appropriately-controlled adsorption from a solution and the subsequent 2D self-organization on a surface. Highly-ordered molecular adlayers on well-defined surfaces for various molecules have been prepared by this technique, and were observed by *in-situ* STM.<sup>2</sup> Recently, using this technique we focused on the formation of 2D arrays with supramolecular arrangements for host molecules, such as cyclodextrins and calixarenes.<sup>2a-c</sup> These host molecules have attracted attention not only in the field of host-guest chemistry, but also in supramolecular chemistry as a part of a topological supramolecule.<sup>3†</sup>

Herein, we would like to report on highly-ordered molecular adlayers of dibenzo-18-crown-6 (DB18C6, Scheme 1)<sup>4</sup> and its



Scheme 1 Chemical structure and space filling model of DB18C6.

inclusion complex with potassium ion by potential controlled adsorption and *in-situ* STM.

One limited report on the STM observation of a crown ether derivative, an epitaxial adlayer of diaza-15-crown-5 molecules adsorbed on Cu(111) with a (4 × 4)-Cu(111) lattice, was reported by Wang and co-workers.<sup>5</sup> In addition, Rabe and coworkers reported the 2D supramolecular assembly of phthalocyanine, which has four crown ether moieties with chiral alkyl chains, on a graphite surface.<sup>6</sup>

The adlayers for DB18C6 were prepared on Au(111) surfaces by simple transfer *via* a Langmuir film at an air–water interface owing of the poor solubility. The occupied surface area was then set at 0.8 nm<sup>2</sup> molecule<sup>-1</sup>. This methodology has been already introduced as a “wet process” preparation of fullerene epitaxial adlayers.<sup>7</sup> Note that the LB-like method was applied in

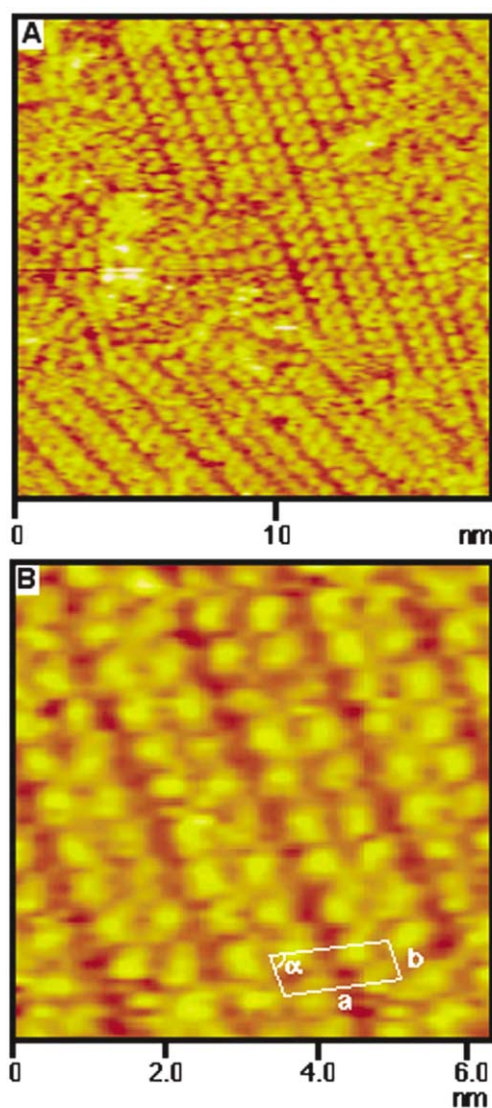


Fig. 1 *In-situ* STM images (A): 18.5 × 18.5 nm<sup>2</sup> and (B): 6.3 × 6.3 nm<sup>2</sup> of DB18C6 adlayers on Au(111) surfaces in 0.1 M HClO<sub>4</sub> solution obtained in the constant current mode at +0.66 V vs. SCE.  $I_t = 2.6$  nA,  $E_t = +0.17$  V vs. SCE.

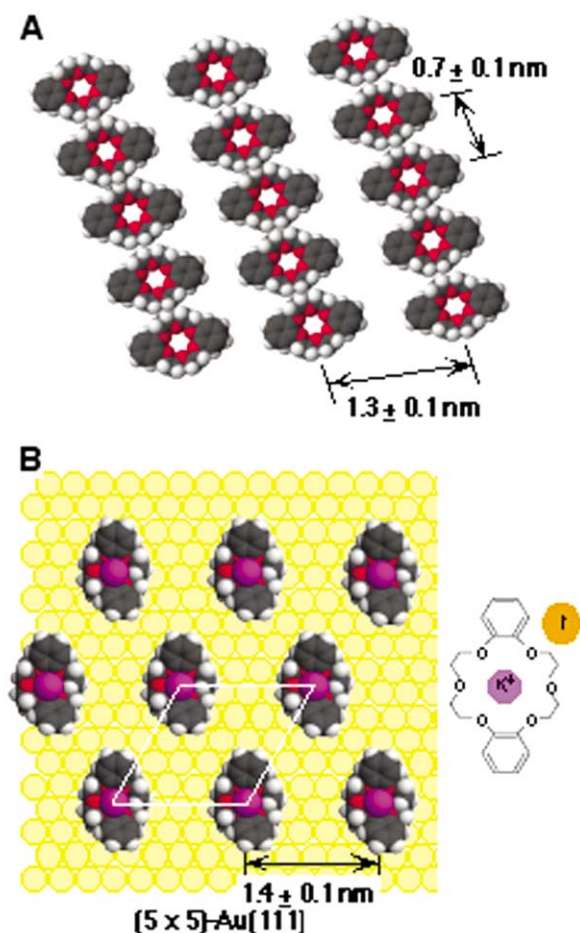
order to introduce water-insoluble molecules with near monolayer coverage. DB18C6 does not form a typical monolayer at an air–water interface because of its lack of amphiphilic properties.

The transfer of DB18C6 from an air–water interface onto Au(111) led to an atomically rough surface thoroughly covered by molecular-sized protrusions, which corresponded to

randomly-adsorbed DB18C6 molecules. This indicates that under conditions without potential control (open circuit potential approximately +0.46 V vs. SCE in perchloric acid), strong adsorbate–substrate interactions prevent the self-organization of DB18C6 on the surface.

However, when a positive potential was gradually applied on the surface, ordered arrays of DB18C6 were found to appear at +0.66 V, and the average size of the ordered domains reached several tens of nm in scale 30 min later, as shown in Fig. 1A. It is well-known that the surface coverage and adsorption strength of adsorbates are a function of the electrode potential.<sup>1a,8</sup> The weakened adsorption at the polarized surfaces allowed surface diffusion of the adsorbed molecules for adsorption-induced self-organization.<sup>2a-c</sup> It is important to emphasize that even for insoluble compounds, potential controlled adsorption would enable 2D self-organization.

Fig. 1B shows a typical high-resolution STM image of highly-ordered DB18C6 adlayers on Au(111) observed at +0.66 V. The molecules in the 2D-array aligned with a flat orientation to make a line. Each bright circular spot ordered one dimensionally in the array corresponds to a flat-oriented benzene ring of DB18C6 on both sides. The observed oblique unit cell is outlined in the image, with the lattice parameters  $a = 1.3 \pm 0.1$  nm,  $b = 0.7 \pm 0.1$  nm and with an angle of *ca.* 70°. The corners of the unit cell marked would be located at the empty center of the crown ether. The corresponding arrangement model of the array is shown in Fig. 2A. The size of DB18C6 in the ordered



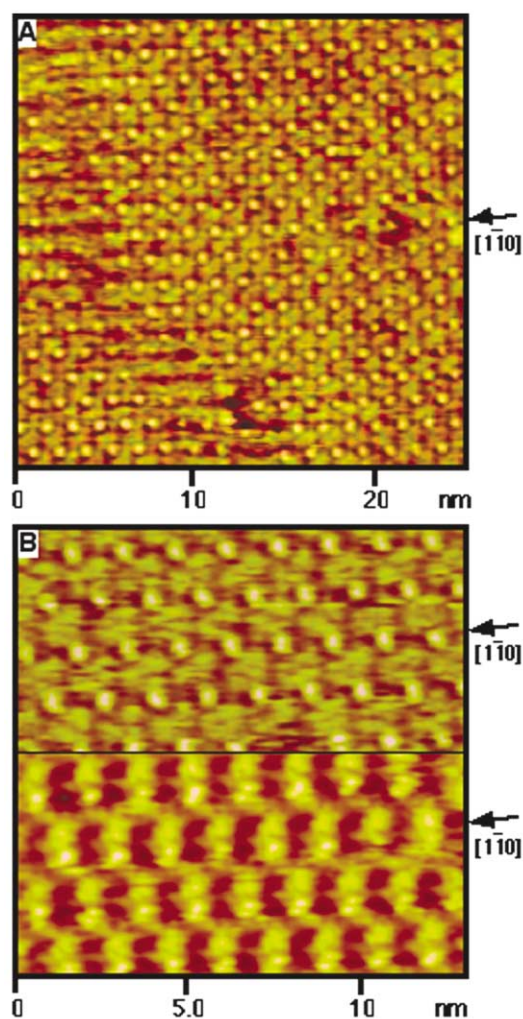
**Fig. 2** Molecular arrangement models for (A) DB18C6 and (B) DB18C6–KI complexes on Au(111) surfaces.

array is roughly consistent with that expected based on the chemical model, although the flexible crown ether moiety of DB18C6 has many possible conformations.<sup>4d</sup>

The adlayers prepared from the inclusion complex of DB18C6 with potassium iodide (DB18C6–KI) were also

investigated. The formation of these ordered arrays of the complex was also achieved by potential controlled adsorption. However, the appropriate ordered potential region for the inclusion complex was entirely different from that for the metal-free DB18C6. The adlayers of the inclusion complex were prepared by adsorption from a very dilute electrolyte solution (less than 1  $\mu$ M), because of relatively better water solubility of the inclusion complex.

At a potential region from +0.20 V to +0.76 V, a typical iodine adlayer which possessed a  $c(p \times \sqrt{3}R - 30^\circ)$  phase<sup>2d-f</sup> but no organic adlayer was observed due to the adsorption of iodide as a counter ion to the complex. When the potential moved to the negative beyond +0.01 V, the iodine lattice disappeared and an entirely new adlayer started to appear as shown in Fig. 3A. Ball-like spots aligned with a hexagonal



**Fig. 3** *In-situ* STM images of an ordered array for the inclusion complex (DB18C6–KI) on Au(111) surfaces in 0.05 M HClO<sub>4</sub> solution obtained in constant current mode at +0.01 V vs. SCE. (A): 25 × 25 nm<sup>2</sup>,  $I_t = 1.0$  nA,  $E_t = +0.29$  V (B): two superimposed images (13.1 × 13.1 nm<sup>2</sup>,  $E_t = +0.29$  V) acquired at different tunnelling currents. The upper and lower halves of the image were obtained at 1.0 and 0.67 nA, respectively. One of the molecular rows is parallel to the [110] direction (marked by arrow).

lattice at  $1.4 \pm 0.1$  nm intervals as shown in Fig. 3A. The adlayer for the complex would possess a commensurate (5 × 5)-Au(111) superlattice, and the underlying row direction of the Au lattice was marked into the image.

Interestingly, the high-resolution STM images were changed by a slight difference in tunnelling conditions. Fig. 3B shows a superimposed image consisting of two images acquired consecutively at different tunnelling currents. The upper and

lower parts of the image were obtained at tunnelling currents of 1.0 and 0.67 nA, respectively. In the upper part of image, the same features as Fig. 3A can be seen. When the tunnelling current was decreased slightly, a typical elliptical shape which consisted of two bright spots appeared in the same array. The shape can be imagined as a chemical structure of a flat-oriented DB18C6 molecule, and the two spots would correspond to the bilateral benzene rings. The molecular arrangement for the complex as a (5 × 5) superlattice expected from Fig. 3B is completely consistent with the model shown in Fig. 2B.

Both types of images were reversibly observed, and the images changed immediately upon the abrupt change of the tunnelling currents. Surprisingly, the ball-like spots observed in the image (Fig. 3B upper) obtained at relatively higher tunnelling currents were located exactly at the center of the elliptical shape in the image (Fig. 3B lower). This suggests that the ball-like spots could be attributed to a coordinated potassium ion. As another possibility, a counterion coordinated with potassium ion in the DB18C6 molecule could be seen as the spot. In addition, no changes were observed in the molecular features in the case of metal-free DB18C6.

In conclusion, sub-molecular high-resolution STM images clearly revealed the real shapes of metal-free DB18C6 and its inclusion complex. The *in-situ* visualization of the inclusion complex at high-resolution, which allowed us to distinguish the host part from a guest part, will lead to an enhanced understanding of host–guest chemistry at the submolecular scale.

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## Notes and References

† Electronic supplementary information (ESI) available: the materials and the procedure for *in-situ* STM observation. See <http://www.rsc.org/suppdata/ob/b2/b208717k/>

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