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A two-dimensional molecular network structure of trimesic acid prepared by adsorption-induced self-organization†

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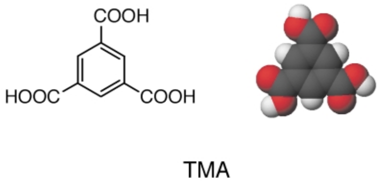
A two-dimensional molecular network of trimesic acid on Au(111) was visualized by *in situ* scanning tunneling microscopy with submolecular resolution. The supramolecular structures including an 'order to order' phase transition were constructed by precise potential-controlled adsorption based on adsorption-induced self-organization.

The construction of two-dimensional (2D) molecular patterns at the submolecular scale will be a crucial step in creating molecular devices in the near future. Recently, studies on carefully designed molecular assemblies have focused on supramolecular chemistry.[1] Molecules with several connections spontaneously form 2D or three-dimensional (3D) molecular networks *via* H-bonds[2,3] or coordination bonds.[4] The preparation and *in situ* STM observation of highly-ordered molecular adlayers with supramolecular arrangements on well-defined surfaces have been reported.[3b–e,5] A 'wet process' technique to form highly-ordered molecular adlayers was proposed, using the 'adsorption-induced self-organization' concept based on appropriately controlled adsorption from a solution and the subsequent two-dimensional self-organization on a surface.[6] By choosing a suitable substrate[6d,e] and carefully setting the electrode potentials,[6a–c] one can produce relatively weak adsorption to induce self-organization, *via* the acceleration of molecular mobility on the surface or *via* the promotion of the adsorption–desorption equilibrium. Molecular adlayers prepared by this technique have 2D-supramolecular arrangements, which strongly reflect the intermolecular interactions. Therefore, we attempted the 2D self-organization of trimesic acid (TMA, Scheme 1) based on this adsorption-induced self-organization technique.

TMA is known to form a network structure by forming intermolecular H-bonds between carboxylic acid residues in bulk crystals.[2,7] Herbstein and Zaworotko have predicted the possibility that a honeycomb framework of '2D-network' structure consisting of TMA can be formed.[2] Here, we report the successful *in situ* STM visualization of highly-ordered TMA adlayers on Au(111) surfaces prepared by adsorption-induced self-organization, which was regulated by the electrode potentials.

The *in situ* STM observation of TMA adlayers on an Au(111) surface in 0.1 M perchloric acid aqueous solution containing *ca.* 0.1 mM TMA (Nakarai Chemical Co. Ltd. Japan) was performed essentially in the same manner as previously described.[6] The structure and orientation of the TMA adlayers observed by *in situ* STM changed markedly with the electrode potential. At a near open circuit potential (approximately +0.8 V *vs.* RHE.), which means no potential control, the TMA molecule adsorbs randomly onto a bare Au(111) surface due to strong interactions between the TMA molecules and the substrate. On the other hand, the desorption of TMA from the Au surface and an intact reconstructed Au(111) surface are observed at negative potentials of less than +0.1 V. In the mid-range between the 'desorption' and 'random adsorption' potentials, TMA molecules show highly-ordered adlayers under potential control conditions (typically +0.2 V to +0.6 V), resulting in the self-organization of molecules onto the surface. The potential dependence for TMA adsorption is essentially identical to that reported for cyclodextrins.[6a,b] This proves that the electrode potential can regulate the interactions between adsorbates and substrates to induce self-organization on the surface.



Scheme 1 Chemical structure of trimesic acid.

Surprisingly, two different ordered arrays of TMA, a '2D-network' structure and a nearly 'closed packed' structure, were observed at specific potentials. When the potential moved to a more positive region (+0.2 to +0.4 V) from a more negative potential region, a '2D-network' structure of TMA started to appear. Fig. 1 shows typical STM images of the '2D-network' of the TMA adlayers. The '2D-network' array extended over the wide and atomically flat terrace of Au(111), as shown in Fig. 1A. Despite the relatively large area covered by the image, the individual features of the '2D-network' can be recognized. The uniformity of the structure is quite high, and there are very few phase boundaries. Interestingly, these '2D-network' arrays were typically observed on the reconstructed Au(111) surface. Typical double corrugation lines can be seen underneath the '2D-network' array in the image.

Submolecular high-resolution STM imaging clearly reveals the architecture of this '2D-network'. Fig. 1B and 1C show the surface plot of the '2D-network' of TMA adlayers and the corresponding arrangement model, respectively. The honeycomb framework of the '2D-network' consists of flat-oriented TMA molecules. The individual shapes of the observed features in the image clearly correspond to the known chemical structure and size of a flat-oriented TMA dimer (Fig. 1C). Furthermore, the image proves that the TMA molecules are connected to each other *via* carboxylic acid units. This might mean that the dominant driving force for the formation of this '2D-network' is intermolecular interactions between the carboxylic acids, the same as in the bulk crystal.

On the other hand, the array is entirely epitaxially controlled, and the commensuracy is (8 × 8)-Au(111). This also proves that the network structure is regulated by both the intermolecular interactions and the adsorbate–substrate interactions. Interestingly, in the 2D-array, the intermolecular distance between the carboxylic units for a dimer to dimer linkage seems to be longer than that within a dimer, although the distance between each TMA molecule is equal in a 2D-plane in the bulk crystal.[2,7] Therefore, the TMA dimer builds the framework with two different sized cavities. The structural difference between 2D-crystals observed here and 3D-crystals described in other studies suggests the contribution of epitaxial interaction from Au(111) surfaces in 2D-crystals.

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† Electronic supplementary information (ESI) available: materials and methods. See http://www.rsc.org/suppdata/cc/b2/b207556c/

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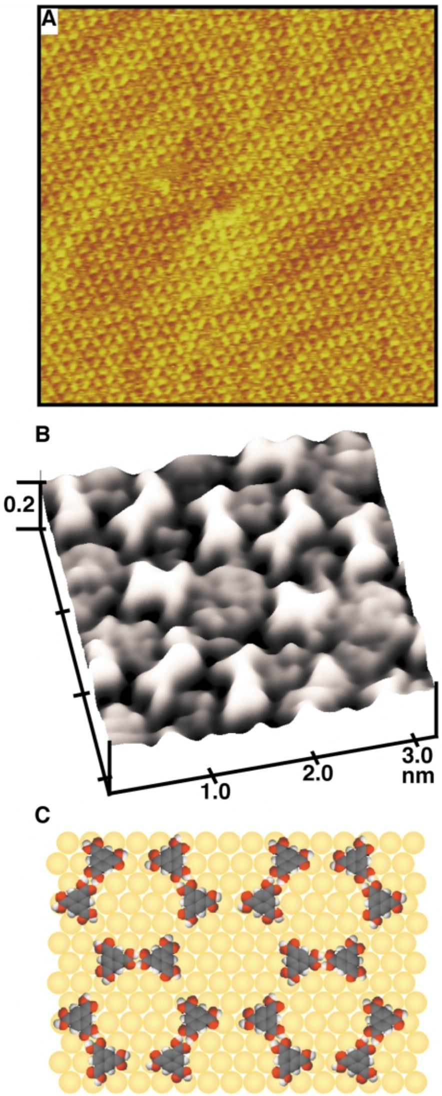

Fig. 1 Typical *in situ* STM images (A, top view 36 × 36 nm^2 and B, surface plot) and the corresponding molecular arrangement model (C) of the 2D-network of the TMA adlayers on an Au(111) surface in 0.1 M perchloric acid in the presence of 0.1 mM TMA. The conditions in image A were +0.3 V, +0.41 V and 1.08 nA for the electrode potential (E_s), tip potential (E_t) and tunneling current (I_t), respectively. For the image B, E_s, E_t and I_t were +0.2 V, +0.51 V and 10 nA, respectively.

In contrast, when the potential is made more positive (approximately +0.6 V), a completely different adlayer in which the TMA molecules are nearly closed packed, appears instead of the ‘2D-network’. Fig. 2 shows the typical ‘closed-pack’ structure of TMA observed at +0.6 V. In the image, the TMA is still in a dimer and aligns with the quasi-hexagonal lattices in the same rotational orientation. It is worth noting that the phase-transition between the ‘2D-network’ and ‘closed-pack’ structures is electrochemically reversible. The phase transition from the ‘2D-network’ to the ‘closed-pack’ structure is caused by increased adsorbate–substrate interactions. As we mentioned above, four phases of TMA adsorption onto an Au(111) surface, ‘desorption’, ‘2D-network’, ‘closed-packed structure’ and ‘disordered’, can be observed as the potential is increased from negative to an open circuit. Surface coverage also increases with an increasing potential. This indicates that the structure of the TMA adlayers can be thermodynamically managed by the surface coverage of TMA, which is controlled by the electrode potential.

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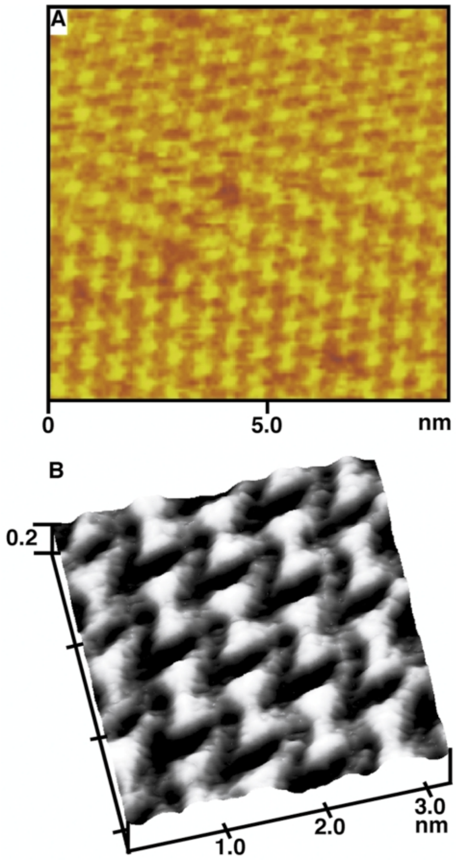

Fig. 2 High-resolution STM images (A, top view 9.2 × 9.2 nm^2 and B, surface plot) of a ‘closed-packed’ structure of the TMA adlayers on an Au(111) surface in 0.1 M perchloric acid in the presence of 0.1 mM TMA. The conditions in the STM image were +0.6 V, +0.51 V and 10 nA for E_s, E_t and I_t, respectively.

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