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Controllable Distribution of Single Molecules and Peptides within Oligomer Template Investigated by STM

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Controllable distribution and dispersion of organic/bio- molecules on solid surface is a very important issue in molecular nanoscience and nanotechnology. In particular, the controllable arrangement of single molecules is the prerequisite for the development of nanodevices. For example, a uniform pattern with biomolecules will be desirable in fabricating bionanodevices.[1−4] Although STM is a powerful method to control and operate a single molecule,[5] the efficiency of this method is not high. To obtain a well-ordered distribution with nanoparticles or quantum dots, various templates such as PS beads were developed.[6] These achievements have contributed to the understanding of intermolecular and adsorbate/substrate interactions and their applications in chemistry, biology, and physics. To date it remains a challenge to control the ordering in multicomponent mixtures at the molecular level. Most binary mixtures investigated show phase separation or formation of randomly mixed monolayers.[7−9] Ordered binary 2D adlayers are only formed in a few cases.[10−16]

In this communication, we report an exciting result on the fabrication of molecular patterns in an oligomer template. The reason that the oligomer compound, end-functionalized oligo-(phenylene-ethynylene) (OPE), is used to prepare molecular template is because of its well-defined chemical structure together with its improved solubility and processibility.[17] It is found that this oligomer can form a self-assembled molecular template on a solid surface.[17] By using this template, organic molecules such as coronene (COR) and biomolecules such as tripeptide are well controlled distributed and monodispersed on a highly oriented pyrolytic graphite (HOPG) surface. Figure 1a shows the chemical structures of OPE and COR. The results described in this communication provide a significant method for distributing and dispersing molecules and demonstrate the potential application of self-assembled monolayer in molecular engineering.

The experiment was carried out using the same procedure as described previously.[17] Briefly, OPE was synthesized as described elsewhere.[18] COR was purchased from Acros. The concentration of the molecules was adjusted by mixing COR in OPE. Enkephalin 1-3 with a sequence of TGG was from Sigma. The adlayers were prepared by placing a drop of the sample solution studied on a freshly cleaved atomically flat surface of HOPG (quality ZYB). A Nanoscope IIIa STM (Digital Instruments) was used for STM observation. STM experiments were carried out under ambient air condition at room temperature. All the STM images were recorded with the standard constant current mode and represented without further processing. By controlling the molar concentration ratio of OPE to COR, various molecular patterns on HOPG surface with different distributions were prepared.

Distribution of COR within OPE Template. One-by-One Distribution. At a 1:2 molar ratio of COR to OPE, coadsorption of the two molecules results in a homogeneous molecular self-assembly. Figure 1b is a high-resolution STM image showing the molecular network with bright lines and dark parallelograms. The bright straight lines correspond to OPE conjugated backbones. The alkoxyl chains of OPE oligomer can be discerned in the image. A distinguishing feature in the image is the round bright spots distributed in the alkoxyl chains. The diameter of the round spots is measured to be ca. 0.95 nm, consistent with the molecular diameter of COR. Therefore, the bright round spots can be assigned as COR molecules dispersed in the alkoxyl chains of the OPE template. A proposed structural model is superposed in Figure 1b. A unit cell is outlined in the model with the parameters of $a = 2.3 \pm 0.1$ nm, $b = 4.9 \pm 0.1$ nm, and $\alpha = 75 \pm 2°$. The coverage of COR is 0.089 molecule/nm^2. It is observed from the image that the entrapped COR molecules are not clear because the space of OPE network by alkoxyl chains is not fully occupied by a single COR molecule. Therefore, the COR molecules cannot be totally stabilized within the space, although the molecules are well distributed within the OPE template.

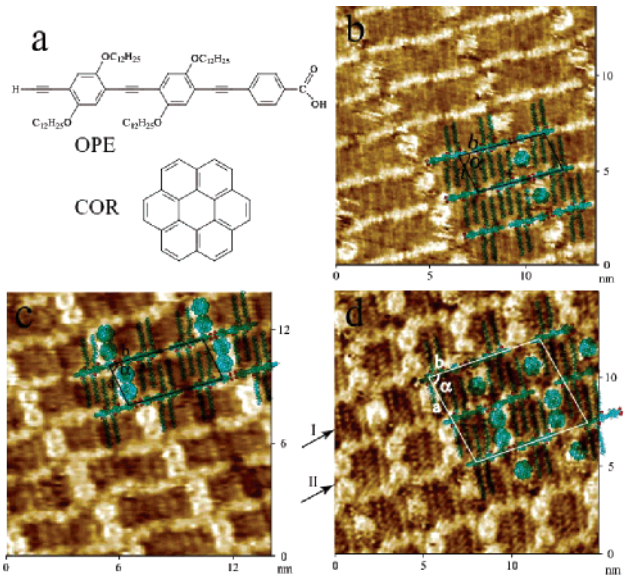

Figure 1. (a) Chemical structures of OPE and COR; (b) high-resolution STM image of one by one distribution of COR, $V = 874$ mV, $I = 498$ pA; (c) high-resolution STM image of two by two distribution of COR, $V = 759$ mV, $I = 735$ pA; (d) high-resolution STM image of one by two distribution of COR, $V = 920$ mV, $I = 652$ pA.

Two-by-Two Distribution. When the molar ratio of COR/OPE is adjusted to 1:1, the resulted adlayer of COR in OPE is shown in Figure 1c. It is clear that two COR molecules exist in every space of OPE template. With the accommodation of the COR dimer, the space provided by the molecular template is almost fully occupied. COR molecules are well stabilized. The molecules adsorb on HOPG with the molecular plane parallel to the substrate. A unit cell of the adlayer is outlined in Figure 1c. The parameters of the unit

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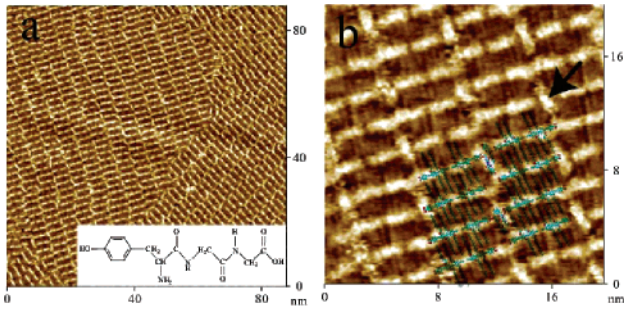

Figure 2. (a) Large-scale STM image of peptide dispersed within OPE template: $V = 880$ mV; $I = 663$ pA. The chemical structure of tripeptide is inserted at the bottom of the image. (b) High-resolution STM image of panel a: $V = 784$ mV; $I = 729$ pA.

cell are the same as that in Figure 1b ($a = 2.3 \pm 0.1$ nm, $b = 4.9 \pm 0.1$ nm, and $\alpha = 75 \pm 2°$). However, the surface coverage of COR molecules is increased to 0.177 molecule/nm^2 with the increasing amount of COR molecules in the OPE template.

One-by-Two Distribution. Controllable distribution can be continually achieved. Figure 1d is a typical STM image acquired on the molecular network when the concentration ratio of COR to OPE is 3:2. Two types of COR molecular arrays can be seen in the image marked by arrows **I** and **II**. In array **I**, a single COR molecule is filled within the space of OPE template, while a pair of molecules is in array **II**. A structural model for the molecular network of COR/OPE is presented in Figure 1d, and gives the unit cell parameters of $a = 4.6 \pm 0.1$ nm, $b = 6.1 \pm 0.1$ nm, and $\alpha = 75 \pm 2°$. A COR coverage of 0.214 molecule/nm^2 is yielded. It can be seen that with the adjustment of molecular concentration alternate single and molecular pair rows can be prepared. The above results demonstrate that COR molecules can be controllably distributed within OPE template by the concentration ratio.

Distribution of Tripeptide. Peptide TGG can also be dispersed within the OPE template. Figure 2a is a large-scale STM image showing TGG molecules in the template. The molecular network containing TGG peptide is clearly seen in several domains. The adlayer is extending in a size more than a hundred nanometers. Higher resolution STM image in Figure 2b revealed the structural details of the network. The TGG molecules are well distributed in the OPE template. From the molecular dimension in the STM image, two peptide molecules are considered to occupy in the position between the neighboring conjugated backbones indicated by an arrow. A careful observation reveals that TGG molecules appear in every other row and are interdigitated into the OPE template. A schematic illustration for the coadsorption is superimposed in Figure 2b. The TGG molecules form pairs and sit in the adjacent conjugated backbones. The hydrogen bondings between OPE backbones and TGG molecules are responsible for the dispersion. This interaction yields the structural stability of the two components forming stable and ordered molecular arrays, which have potential for development of biomolecular devices.

The chemical structure shows that the OPE molecule is composed of flexible alkyl chains and carboxyl functional groups with conjugated backbones. When the molecules were adsorbed on HOPG surface, a self-assembly structure was formed. Within the assembly structure, there exist free spaces among the alkyl chains. On the other hand, both the alkyl chains and carboxyl groups can induce hydrogen bondings. Therefore, the self-assembly structure is a good molecular template. When a foreign molecule is introduced to the template, the geometrical, spatial, and intermolecular reactions would facilitate trapping the molecule, resulting in a dispersed distribution. In the present work, COR and peptide are well dispersed in the template. We also tried to disperse modified CdS nanoparticles with the template. The same effect on distribution was observed (not shown here).

In summary, we have found an oligomer network that can function as a molecular template for controlled distribution and dispersion of organic molecules and peptides. Within this molecular template, COR molecules were controllably distributed into various regular arrays by simply adjusting molecular concentration ratio. Similarly, we also succeeded in uniformly positioning tripeptide TGG molecules at the vacancies of the OPE template. The geometrical, spatial and intermolecular reactions are expected to play important roles in the controllable distribution and dispersion. The present self-assembly method may provide a facile way to fabricate ultrasmall electronic components, sensing elements, and scaffolds for biomaterial engineering.

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Supporting Information Available: OPE template, large-scale STM image of one-by-one distribution of COR, and structural model for peptide TGG dispersed within OPE template (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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