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Pairs and heptamers of C_{70} molecules ordered via PTCDI-melamine supramolecular networks

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In this paper, we report on the use of two PTCDI-melamine supramolecular networks on Au(111) to trap C_{70} molecules. The different supramolecular networks were formed by changing the postannealing temperature after molecular deposition. We observed, using scanning tunneling microscopy, that the deposition of C_{70} onto a PTCDI melamine network with parallelogram cavities results in the long-range ordering of paired C_{70}, whereas the deposition of C_{70} molecules onto a PTCDI-melamine honeycomb network results in the trapping of C_{70} heptamers. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2819682]

Intense research effort is focusing on self-assembly techniques to order fullerenes on surfaces for potential applications in organic and molecular electronics. This is especially motivated by recent progress in molecular synthesis of endohedral fullerenes,[1] where one atom or a molecule is encapsulated inside a fullerene cage and can give rise to a myriad of functionalized molecules and materials. Long-range molecular ordering can be obtained by taking advantage of substrate mediated self-organization.[2–7] A more adaptable method involves exploiting intermolecular interactions by mixing different molecular species to form extended networks.[8–12] This route has been employed to control the long-range ordering of fullerene molecules,[11–14] thus offering a wider variety of structures than the basic closed-packed hexagonal ordering observed on most metal surfaces. The supramolecular architecture may be tailored by carefully selecting molecules, which bond with each other, and tuning the ratio of molecules deposited on the surface and controlling precisely the temperature during the network formation.

In this paper, we report on two 3,4,9,10-Perylene-tetracarboxylic Diimide (PTCDI) and melamine (1,3,5-triazine-2,4,6-triamine) supramolecular networks on Au(111) used to trapped C_{70} molecules. We observed, using scanning tunneling microscopy (STM), that a variation of the postannealing temperature after deposition of PTCDI and melamine lead to the formation of a supramolecular network with parallelogram cavities or hexagonal cavities. Subsequent deposition of C_{70} molecules on these networks results in the long-range ordering of paired C_{70} in one case, or in the the long-range ordering of C_{70} heptamers in the other case.

The substrates were Au(111) films grown on mica. The samples were introduced into the ultrahigh vacuum (UHV) chamber of a STM (JEOL JSTM4500S) operating at a pressure of 10^{-8} Pa. The Au(111) surfaces were sputtered with argon ions and annealed in UHV at temperatures between 600 and 800 °C typically for 30 min. PTCDI and C_{70} molecules were sublimated at 335 °C and melamine at 100 °C. Etched tungsten tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample.

Figure 1(a) shows the molecular superstructure formed after deposition of PTCDI and melamine on Au(111) followed by postannealing at 150 °C for 10 h. PTCDI molecules appear bright and melamine molecules appear dark in the image. A high resolution STM image of this network is presented in Fig. 1(b). The network is composed of succession of *Z*-shaped molecular patterns composed of a PTCDI-melamine-PTCDI-melamine-PTCDI sequential arrangement. A model of this *Z* arrangement is superposed on the molecules in the STM image [Fig. 1(b)]. PTCDI and melamine are connected through three hydrogen bonds, two $O\cdots H-N$ bonds and one $N-H\cdots N$ [Fig. 1(c), bottom left], whereas PTCDI molecules are connected to each other through two $O\cdots H-N$ hydrogen bonds, as represented in Fig. 1(c) (top right). The *Z*-shaped molecular patterns are connected to each other side by side through a single PTCDI-melamine hydrogen bond ($O\cdots H-N$ bond), as represented in Fig. 1(d). They are also connected to other *Z*-shaped patterns to their ends through PTCDI-PTCDI bonding. A model of the ordering is presented in Fig. 1(e). The unit cell of the PTCDI-melamine network is shown in Fig. 1(e); it is not rectangular but has a parallelogram shape with 2.66 and 1.98 nm lattice constants and an angle of ~81° between the axes. The PTCDI:melamine ratio is 3:2.

Figure 2(a) shows the surface after deposition of C_{70} molecules on the PTCDI-melamine supramolecular network. The C_{70} molecules are not close packed but are preferentially located between the rows of single PTCDI molecules, where the Au(111) substrate is apparent (empty pores of the supramolecular network). Further deposition of C_{70} molecules lead to the complete filling of the supramolecular pores of the network and the long-range ordering of C_{70} molecules [Fig. 2(b)]. Two C_{70} molecules are preferentially packed in the empty pores [Figs. 2(b) and 2(d)]. A model of the trapping of C_{70} molecules by the PTCDI-melamine supramolecular network is presented in Fig. 2(c). Only a few pores contain a single C_{70} molecule [Fig. 2(d)] and defects in the

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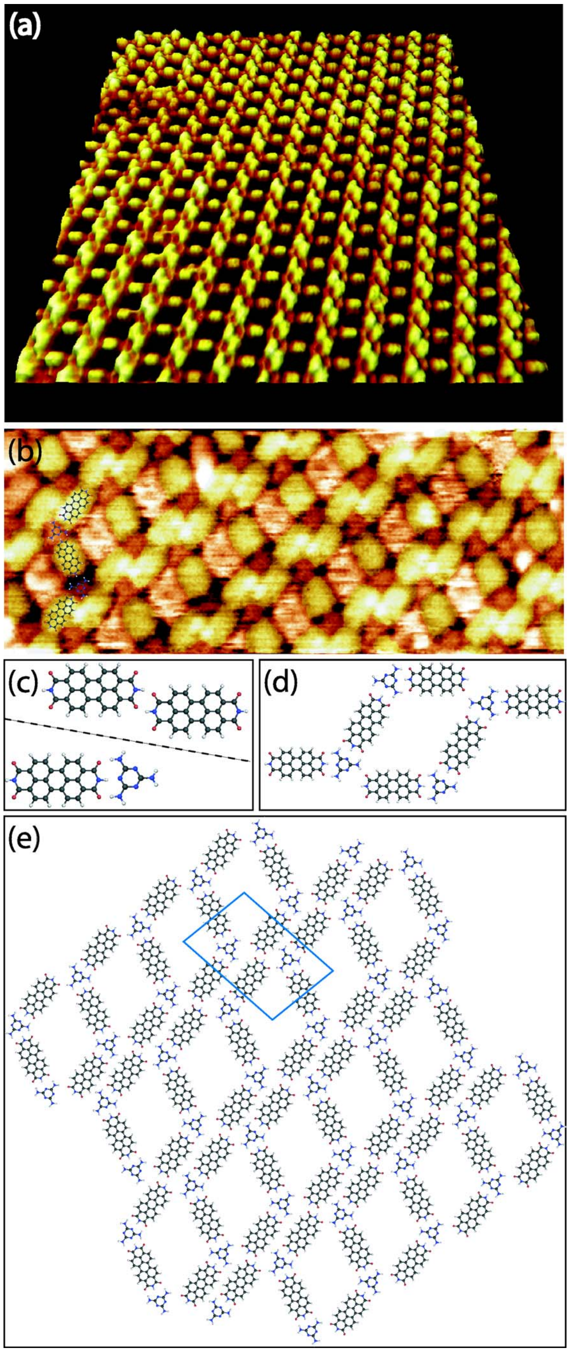

FIG. 1. (Color online) (a) Three-dimensional 3D STM image of a mixed PTCDI and melamine parallelogram domain on a Au(111) surface, 35 $\times 28$ nm^2. (b) High resolution STM image of the supramolecular network, 16×6 nm^2, $V_s=-1.8$ V, $I_t=0.1$ nA. The *Z*-shaped molecular pattern (PTCDI-melamine-PTCDI-melamine-PTCDI) is superposed on the image. (c) Top-right: PTCDI-PTCDI bonding. Bottom-left: PTCDI-melamine bonding. Gray balls represent carbon atoms, red balls are oxygen atoms, white balls are hydrogen atoms, and blue balls are nitrogen atoms. (d) A model of two *Z* patterns composed by PTCDI-melamine-PTCDI-melamine-PTCDI sequential arrangement connected to each other through two single PTCDI-melamine hydrogen bonds. (e) Model of the supramolecular PTCDI-melamine parallelogram unit cell.

PTCDI-melamine network can allow the trapping of more C_{70} molecules [Fig. 2(b)].

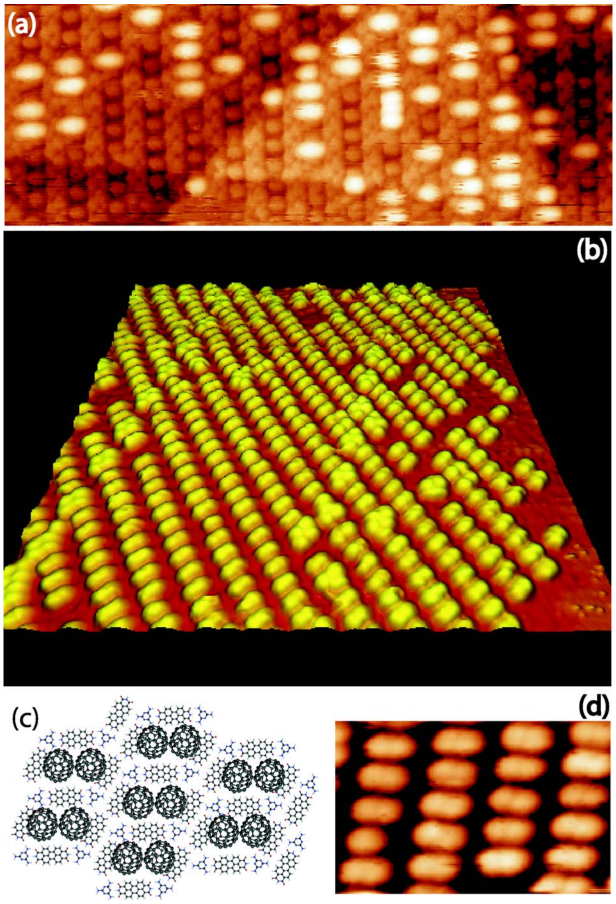

FIG. 2. (Color online) (a) STM image of a PTCDI-melamine-C_{70} domain on a Au(111) surface (48×15 nm^2; $V_s=-1.8$ V, $I_t=0.1$ nA). A 3D image of a similar domain is shown in (b) (33×26 nm^2; $V_s=-1.8$ V, $I_t=0.1$ nA) and (c) its model. (d) C_{70} pairing close up 13×08 nm^2.

Figure 3(a) shows the molecular superstructure formed by deposition of PTCDI and melamine on Au(111) followed by postannealing at 100 °C for 10 h. This domain has a honeycomb structure. The unit cell is hexagonal with a 3.45 nm parameter. The molecules assemble into a hydrogen bonded honeycomb network in which PTCDI molecules are located at the edges of the hexagonal unit and melamine molecules form the vertices. Figure 3(b) shows a high definition STM image of the honeycomb network, where melamine appears darker than PTCDI molecules. The model of the honeycomb structure is presented Fig. 3(c). The PTCDI:melamine ratio in the honeycomb structure is 3:2, the same ratio as the structure presented Fig. 1. In Fig. 3(a), the honeycomb center appears higher than the gold substrate but we have also recorded images where the honeycomb center appears lower than the substrate. These features in the STM images can result from trapped molecules or electron confinement inside the pores.

The honeycomb and parallelogram supramolecular networks are formed at postannealing temperatures of around 100 and 150 °C, respectively. At intermediate temperatures, the two networks coexist. The broad temperature window for the mixed phase indicates that the two network structures are close in energy and that the relative stabilities of the networks are intrinsically temperature dependent and most likely arises due to vibrational and configurational entropy contributions to the overall interaction energy between the network and the substrate.

Figure 4 shows the surface after deposition of C_{70} molecules on the honeycomb PTCDI-melamine network. C_{70} molecules are located inside the honeycomb pores [Fig.

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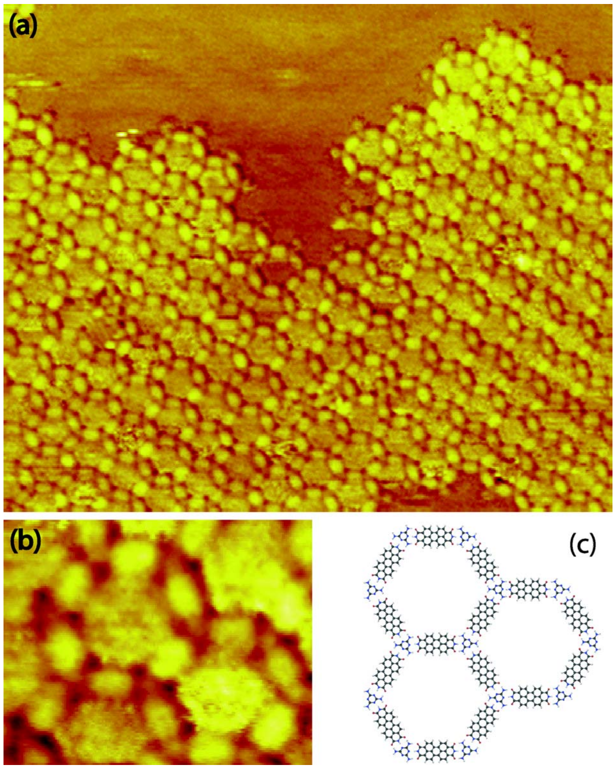

FIG. 3. (Color online) (a) STM image of PTCDI-melamine honeycomb network on a Au(111) surface (50×50 nm^2; $V_s = -1.8$ V, $I_t = 0.1$ nA). (b) Detailed image, (8×8 nm^2; $V_s = -1.8$ V, $I_t = 0.1$ nA) and (c) its model.

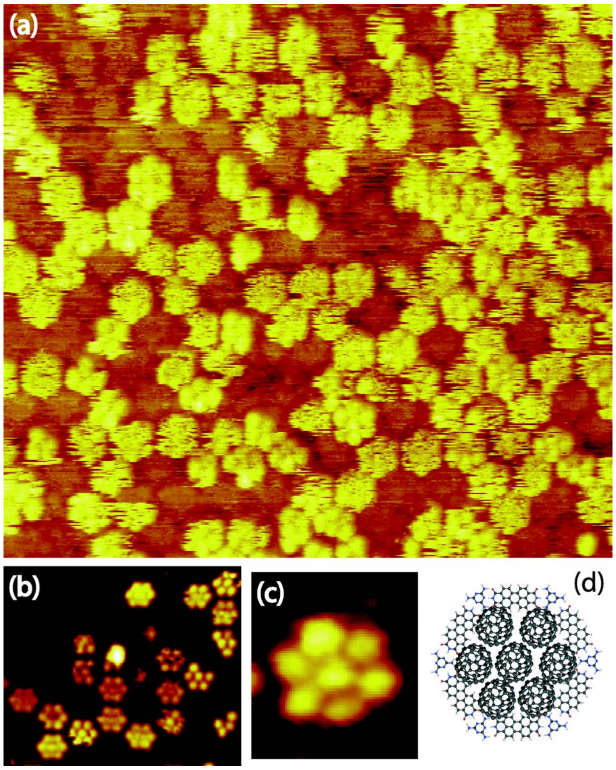

FIG. 4. (Color online) (a) STM-image of PTCDI-melamine-C_{70} domain on a Au(111) surface (50×30 nm^2; $V_s = -1.8$ V, $I_t = 0.1$ nA). (b) Molecular heptamers, (50×50 nm^2; $V_s = -1.8$ V, $I_t = 0.1$ nA) and (c) 5×5 nm^2. (d) Model of the C_{70} packing.

4(a)]. Figure 4(b) shows a STM image where the C_{70} molecules are resolved in the pores. Between one to seven, C_{70} molecules can be seen inside the pores [Fig. 4(b)]. Seven was the highest number of molecules experimentally observed from C_{70} molecules inside a single pore, as shown in Fig. 4(c). The C_{70} molecules on the PTCDI-melamine honeycomb network on gold have a similar behavior to the differently sized C_{60} and C_{84} molecules on the same supramolecular network on silver terminated silicon.[12,15]

In this paper, we have used two PTCDI-melamine supramolecular networks on the Au(111) surface used to trap C_{70} molecules. By changing the annealing conditions after PTCDI and melamine depositions, we were able to selectively form a parallelogram supramolecular network or a honeycomb network. Postdeposition of C_{70} molecules onto these networks leads to the pair ordering of C_{70} onto the parallelogram supramolecular network, whereas it leads to the formation of heptamer C_{70} islands onto the honeycomb supramolecular network. Our findings demonstrate that the self-assembly of fullerene architectures on metal surfaces can be tuned by using supramolecular structures.

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