A chiral pinwheel supramolecular network driven by the assembly of PTCDI and melamine

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The mixing of perylene-3,4,9,10-tetracarboxylic diimide (PTCDI) and 1,3,5-triazine-2,4,6-triamine (melamine) at room temperature in a ratio of 3 : 4 on Au(111) leads to the formation of a new chiral "pinwheel" structure.

Chiral architectures can form from molecules that are themselves chiral, and can also occur through the chiral ordering of non-chiral molecules.[1,2] To control molecular ordering, and to be able to switch between different molecular structures, is a major challenge for nanotechnology and nanoengineering. One candidate route is the autonomous ordering and assembly of different nanoblocks on atomically well-defined surfaces. Long-range molecular ordering can be achieved by taking advantage of nanostructured substrate-mediated self-organization.[3–7] A more adaptable method involves exploiting intermolecular interactions by mixing different molecular species to form extended networks.[7–12] The properties of the resulting supramolecular architectures can be tailored by modifying the functionality and structure of the molecular building blocks. The supramolecular design can be tuned by carefully selecting the appropriate molecule ratio and sample temperature during preparation. This is particularly efficient when various molecular bonds are possible. The epitaxial relationship between the molecule and the substrate can also play an important role. All these parameters can drastically affect supramolecular orderings. The prediction of the supramolecular structure is therefore complicated.

In this paper we report on the ordering of PTCDI (perylene-3,4,9,10-tetracarboxylic diimide) and melamine (1,3,5-triazine-2,4,6-triamine). We show, using scanning tunneling microscopy (STM), that mixing of PTCDI and melamine in a ratio of 3 : 4 leads to the formation of a chiral "pinwheel" structure. This result is in contrast to previous studies where non-chiral honeycomb networks with a ratio of 3 : 2 were observed[12] at high temperature. The variation of the epitaxial relationship between the molecules and the substrate is investigated for single molecular networks and the supramolecular network.

As substrate, we used 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 molecules were sublimed at 335 °C and melamine at 100 °C, and the molecules deposited on a gold surface at room temperature. The sample was not post-annealed after molecular deposition. Etched tungsten tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample.

Fig. 1a shows the Au(111) surface after deposition of PTCDI. The bare Au surface reconstructs into a complex structure composed of paired rows.[13] The resulting Au(111) reconstruction has a $22 \times \sqrt{3}$ unit cell.

Fig. 1 shows that PTCDI molecules form compact domains, which exhibit a uniform structure of molecular rows at room temperature on Au(111). The apparent height of the molecular domain coincides with the gold substrate. Although the contrast can change with tip termination,[14] we have no evidence of such changes occurring in our images. The Au(111)-($22 \times \sqrt{3}$) reconstruction is visible underneath the PTCDI domain. The PTCDI rows are aligned in the [1$\bar{2}$1] direction of Au(111)-($22 \times \sqrt{3}$). The molecules are tilted within the rows ($\pm 12^{\circ}$) to promote hydrogen bonding between imide groups. This PTCDI arrangement is stabilized by hydrogen bonds between the ends of adjacent molecules. The unit cell of the PTCDI row ordering is shown Fig. 1b, with 14.5 ± 0.5 Å and 19.8 ± 0.5 Å unit cell constants and an angle of $\sim 75^{\circ}$ between the axes. The model representing the observed PTCDI arrangement is shown in Fig. 1d. This PTCDI arrangement is similar to those observed on highly ordered pyrolytic graphite (HOPG) and MoS_2.[15]

Fig. 2 shows the surface after deposition of melamine onto Au(111). The Au(111) $22 \times \sqrt{3}$ herringbone reconstruction is visible underneath the melamine layer in Fig. 2a. Fig. 2b shows that melamine forms domains of hexagons composed of six melamine molecules. Close inspection of the high resolution image in Fig. 2b reveals the chirality of the melamine domain. The model representing the observed melamine arrangement is shown in Fig. 2d. In this model the melamine arrangement is stabilized by a double hydrogen bond, as our images indicate. Conflicting results have been published about the melamine domain orientation on Au(111). In Fig. 2c of ref. 16, it was proposed that melamine hexagon centers are aligned in the [11$\bar{2}$] direction, which does not correspond to the orientation seen in Fig. 3b of ref. 17. The Au(111) reconstruction underneath the melamine layer in Fig. 2a shows that the melamine hexagon centers are aligned in the [3$\bar{2}\bar{1}$] direction. The Fourier transform of the image (Fig. 2a, inset) shows that the melamine structure is close to a 2D hexagonal lattice structure. The melamine hexagon center–center separation is measured in

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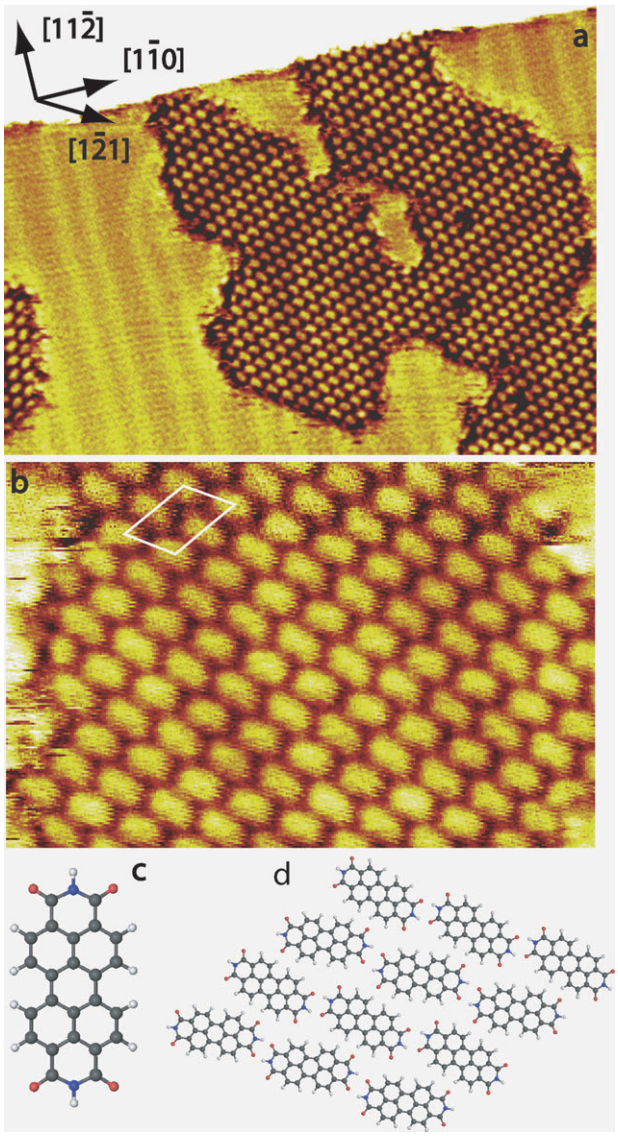

Fig. 1 STM image of a PTCDI domain on a Au(111) surface: (a) 50×45 nm^2; (b) 15×10 nm^2 (showing the PTCDI unit cell). $V_s = -1.5$ V, $I_t = 40$ pA. (c) Model of a PTCDI molecule (gray balls are carbon atoms, red balls are oxygen atoms, white balls are hydrogen atoms and blue balls are nitrogen atoms). (d) Model of PTCDI ordering.

real space at 9.6 ± 0.5 Å in the [3$\bar{2}\bar{1}$] direction, at 9.8 ± 0.5 Å in the [1$\bar{3}$2] direction and at 10.0 ± 0.5 Å in the [21$\bar{3}$] direction.

As the gold reconstruction is not lifted by PTCDA or melamine molecules in Fig. 1 and 2, the molecules are probably physisorbed and the observed orderings are attributed to the intermolecular interactions.

Fig. 3 shows the surface of a new molecular superstructure formed after co-deposition of PTCDI and melamine on Au(111). The molecules form a chiral structure having a pattern that we call a ''pinwheel'' structure. The network is hexagonal with a 37.8 ± 0.5 Å lattice parameter. The model of this supramolecular network is presented in Fig. 3b. In this configuration the center of the pinwheel is composed of a melamine arrangement, where six melamine molecules form a chiral hexagon similar to the pure melamine network on

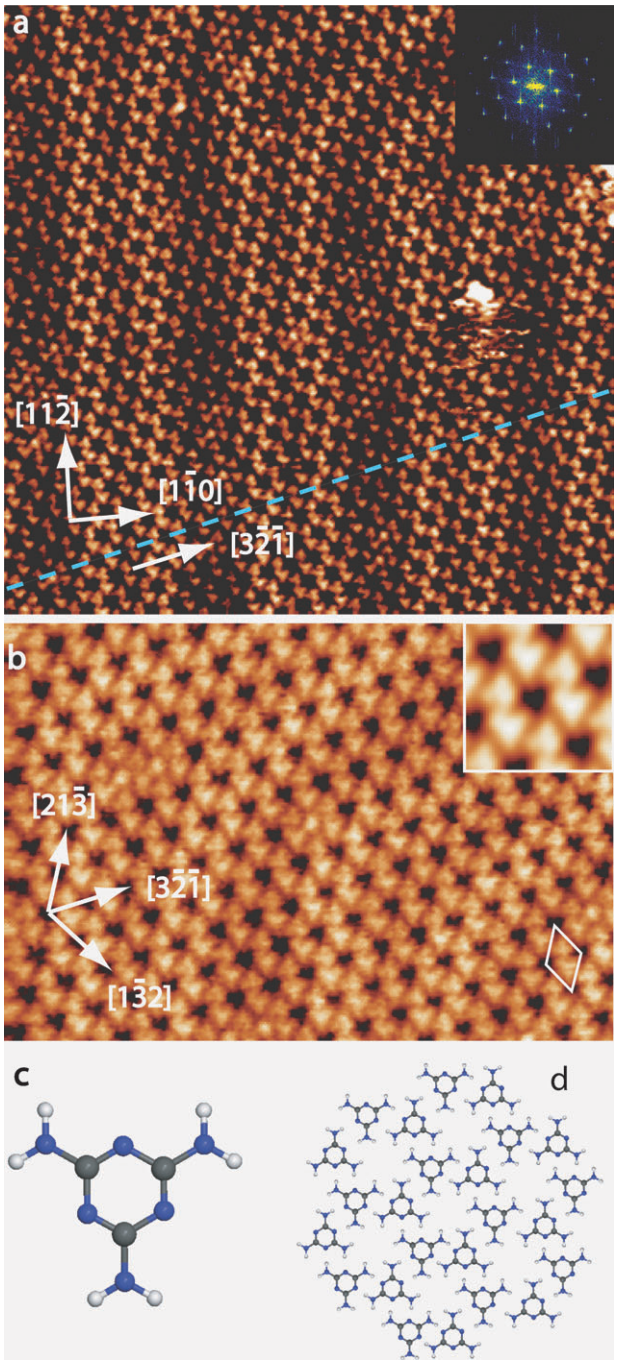

Fig. 2 STM image of a melamine domain on a Au(111) surface: (a) 24×32 nm^2, with the dotted line highlighting the melamine hexagon center alignment (inset: fast Fourier transform (FFT) of the image); (b) 15×10 nm^2, with the network unit cell indicated (inset: high resolution STM image (3×3 nm^2)). $V_s = -1.0$ V, $I_t = 0.5$ nA. (c) Model of a melamine molecule (gray balls are carbon atoms, red balls are oxygen atoms, white balls are hydrogen atoms and blue balls are nitrogen atoms). (d) Model of melamine ordering.

Au(111) (as shown in Fig. 2b). The melamine molecules appear darker than the PTCDI molecules, as also observed in another PTCDI–melamine arrangement.[12] The melamine chiral orientation is opposite in the two images but domains of both chiralities have been experimentally observed. This hexagon is surrounded by PTCDI pairs (side by side), one single

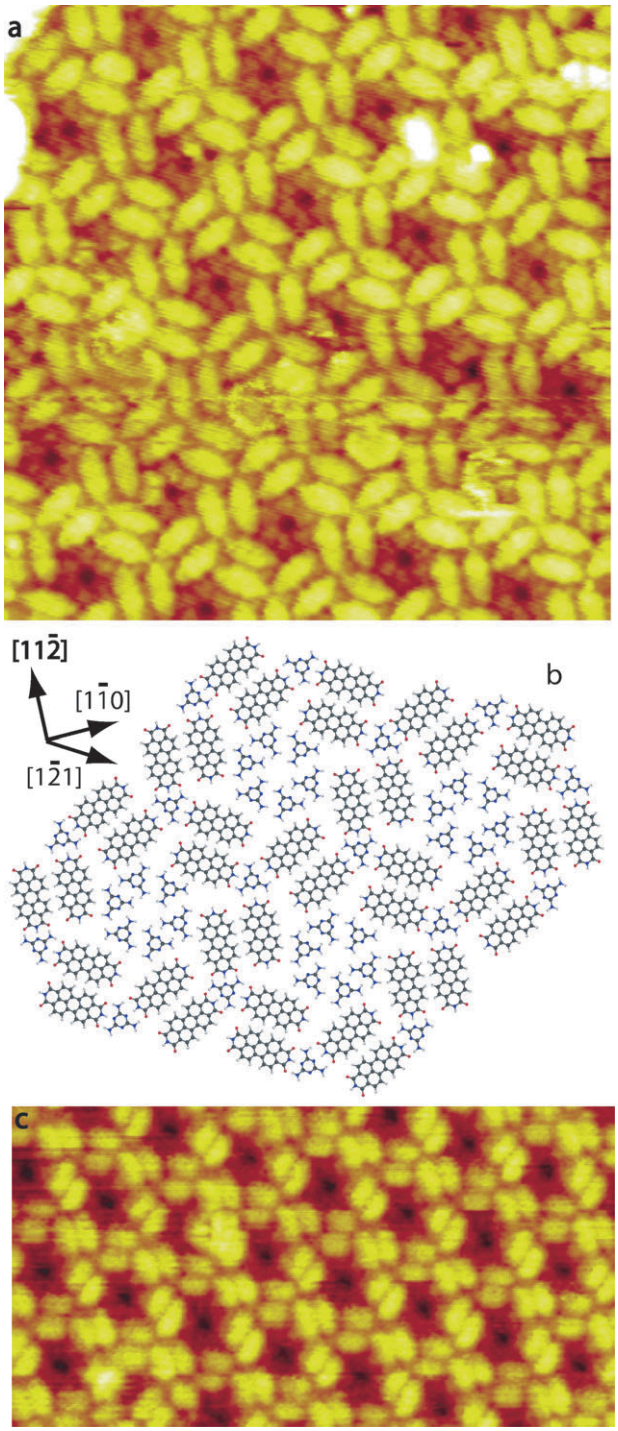

Fig. 3 (a) STM image of mixed PTCDI and melamine "pinwheel" domain on a Au(111) surface (19 × 19 nm^2; V_s = −1.4 V, I_t = 0.5 nA). (b) The proposed supramolecular structure model. (c) STM image of the pinwheel structure with opposite chiral orientation (23 × 23 nm^2; V_s = −2.6 V, I_t = 0.1 nA).

hydrogen bond connecting each inner PTCDI molecule of the pair to the melamine hexagon. In addition, a single melamine molecule is connected through three hydrogen bonds to the outer PTCDI molecule of one pair and to the inner PTCDI molecule of a neighboring pair. The PTCDI:melamine ratio for this pinwheel structure is 3 : 4.

There are defects in the pinwheel center; melamine molecules are sometimes missing and sometimes fewer than six melamine molecules are observed in the pinwheel center. In addition, a few pinwheel centers have a "fuzzy" appearance (Fig. 3a), where some melamine molecules might be trapped in the pinwheel center but be mobile, which would prevent stable STM imaging in this region.

The center of the pinwheels are aligned in the [11$\bar{2}$] direction of the Au(111)-(22 × $\sqrt{3}$). PTCDI molecules on the pinwheel structure are aligned in the [11$\bar{2}$] direction, which is close to the epitaxial relationship of pure PTCDI domains and the gold surface, as shown in Fig. 1. The orientation of the melamine hexagon on gold is rotated by ∼15° compared to pure melamine, as shown in Fig. 2. The mixed pinwheel domain coexists with melamine domains and PTCDI domains at room temperature.

In this paper we have described a chiral superstructure formed by PTCDI and melamine (ratio 3 : 4) on the Au(111) surface at room temperature. We have shown that the preferential epitaxial relationship between the molecule and the substrate is conserved in the supramolecular network. This result opens the door for further investigation of new supramolecular ordering by tuning the ratio of the two molecular components.

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