Two-Dimensional Hydrogen-Bonded Nanoarchitecture Composed of Rectangular 3,4,9,10-Perylenetetracarboxylic Diimide and Boomerang-Shaped Molecules Resulting from the Dissociation of 1,3,5-Tris(4-aminophenyl)benzene

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ABSTRACT: The self-assembly of 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) with the star-shaped 1,3,5-tris(4-aminophenyl)benzene (TAPB) on Au(111) is investigated using scanning tunneling microscopy. PTCDI forms a compact canted arrangement on the gold surface. When TAPB is sublimated at a high temperature, the molecule dissociates into a 4-aminophenyl group and a boomerang-shaped compound. The boomerang molecule self-assembles with PTCDI to create a two-dimensional (2D) nanoarchitecture stabilized by N−H⋯O−C hydrogen bonds between the dissociated TAPB and PTCDI. The molecular ratio of this multicomponent structure is 1:1.

INTRODUCTION

Intense research efforts have been focused on engineering novel nanomaterials and organic nanoarchitectures.1–9 Inter-molecular as well as organometallic interactions can stabilize molecular assemblies.1,10–15 Perylene diimide derivatives are renowned compounds for their chemical and thermal stability as well as their long-lasting photostability.14 They are thus promising molecules for engineering organic devices. The perylene diimide structure can be customized to tune its electronic properties or to modify its self-assembly.6,14–22 Numerous functionalized perylene derivatives have thus been synthesized to create self-assembled two-dimensional (2D) hydrogen-bonded nanoarchitectures on flat surfaces.23–28 Multicomponent organic structures have also been achieved when mixing these rectangular compounds with complementary molecules.29–32 Other molecular shapes have also been used for engineering original nanostructures. For example, two-dimensional fractal nanoarchitectures have been fabricated by taking advantage of the self-assembly of boomerang-shaped molecules. These arrangements were stabilized by halogen bonds or metal-coordinated interactions depending on the substituents placed at each extremity of the molecules.33–35 Boomerang-shaped molecules have also been mixed with star-shaped 1,3,5-tris(4-aminophenyl)benzene (TAPB; Figure 1, right) molecules to form covalently bonded Sierpinski triangles up to the second generation, taking advantage of the Schiff-base reaction.36 Imineboroxine covalent porous hexagonal structures have also been fabricated by mixing TAPB molecules with other organic building blocks.37 Although PTCDI and TAPB can form different arrangements on metal surfaces, it is unclear if these two molecules are complementary building blocks to create new multicomponent nanoarchitectures through self-assembly.

RESULTS

The scheme of the 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) molecule is presented in Figure 1, left. This rectangular molecule is composed of a perylene center and one imide group at each side. The scheme of the 1,3,5-tris(4-aminophenyl)benzene (TAPB) molecule is presented in Figure 1, right. Here, we investigate the self-assembly of 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) and TAPB molecules on Au(111). Scanning tunneling microscopy (STM) in ultrahigh vacuum reveals that PTCDI self-assembles with dissociated TAPB molecules to form a two-dimensional two-component nanoarchitecture stabilized by hydrogen bonds.

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This star-shaped molecule is composed of a benzene central ring surrounded by three 4-aminophenyl groups.

STM images of the PTCDI self-assembled arrangement on the Au(111) surface after the deposition of molecules at room temperature are presented in Figure 2a,b. STM reveals that the molecules form chains running parallel to each other. Molecules from neighboring chains are rotated in the opposite direction by the same angle of ±12° (see the molecular scheme superimposed on the STM image in Figure 2b). The PTCDI arrangement is stabilized by double-hydrogen bonds (N–H···O) between imide groups of adjacent molecules, as it is demonstrated by density functional theory calculations.26 The network unit cell of this “canted” structure is a parallelogram with ~1.7 and ~1.5 nm unit-cell constants and an angle of ~95° between the axes.

STM images of the step edge of PTCDI domains after the deposition of TAPB molecules are presented in Figure 3a–c. STM shows that intact star-shaped TAPB molecules can be locally observed. As a guide for the eyes, these molecules have been colored in blue in the images. STM also reveals that additional organic species coexist in the organic layer. These species have either a boomerang shape or an egg shape. These species have been colored in red and green in Figure 3a–c. It thus appears that some TAPB molecules have been dissociated during the sublimation process, as described in the scheme shown in Figure 3d. The egg-shaped species observed on the surface correspond to TAPB 4-aminophenyl groups (green species in Figure 3d), whereas the boomerang-shaped species correspond to two 4-aminophenyl groups connected to a benzene ring (red species in Figure 3d). The STM images do not provide evidence of whether the broken bond is homolytic or heterolytic or whether the two compounds are two radicals or one cation and one anion.

A two-dimensional PTCDI–TAPB nanoarchitecture is locally observed on the surface. An STM image of this multicomponent structure is presented in Figure 4a. In this arrangement, the PTCDI molecules form parallel chains. In contrast to the PTCDI self-assembly (Figure 2), the PTCDI molecules are parallel and are aligned along the main axis of the page.

**Figure 2.** (a) Large-scale STM image of the PTCDI self-assembly on Au(111) 15 × 13 nm² (Vₛ = 0.6 V; Iₜ = 200 pA). (b) High-resolution STM image of the PTCDI self-assembly, 6 × 6 nm² (Vₛ = 0.6 V; Iₜ = 200 pA). As a guide for the eyes, the network unit cell (dashed white lines) and molecular schemes are superimposed onto the STM image.

**Figure 3.** STM images of PTCDI domain edges after the deposition of TAPB molecules: (a) 12 × 7 nm²; (b) 5 × 5 nm²; (c) 10 × 5 nm² (Vₛ = 0.6 V; Iₜ = 200 pA). (d) Scheme of the TAPB dissociation into two compounds.
PTCDI molecules can form various hydrogen-bonded nanoarchitectures on flat surfaces. The canted arrangement is the most observed network at room temperature on Au(111). This structure is stabilized by double N−H⋯O bonds between imide groups of adjacent molecules and C−H⋯O between molecules of neighboring chains, as revealed by theoretical calculations. Star-shaped molecules with a central benzene ring and three functionalized benzene arms can also self-assemble into numerous structures, either porous or compact, depending on the nature of the substituents.

When PTCDI and star-shaped TAPB are deposited simultaneously, a 2D multicomponent nanoarchitecture is locally observed on the Au(111) surface (Figure 4). The typical domain size is ∼500 nm². STM reveals that the TAPB molecules are partially dissociated in this structure, that is, one 4-aminophenyl group is missing from the TAPB skeleton. It appears that the high temperature selected for the sublimation of the molecules from the Knudsen cell leads to the dissociation of the TAPB molecules. The boomerang TAPB molecules are expected to be highly reactive radicals. It would thus be expected that two molecules react together and form dimers (see Figure 5b). There is however no evidence of the formation of covalent bonds between TAPB molecules in the STM images of the PTCDI−TAPB network. The separation between two neighboring TAPB molecules appears first dark in the STM images, and the measured distance between nitrogen atoms of neighboring TAPB molecules is 1.4 nm in the network (Figure 5a). This has to be compared with the theoretical 1.1 nm separation if a dimer was formed (Figure 5b). This 26% increase in size rules out the formation of covalent dimers. Dissociated molecules are expected to be highly reactive, but previous scanning probe microscopy (SPM) observations revealed that dehalogenated and dehydrogenated molecules can be stable on insulating thin films as well as metal surfaces. The canted arrangement is the most observed network at room temperature on Au(111). This structure is stabilized by double N−H⋯O bonds between imide groups of adjacent molecules and C−H⋯O between molecules of neighboring chains, as revealed by theoretical calculations. Star-shaped molecules with a central benzene ring and three functionalized benzene arms can also self-assemble into numerous structures, either porous or compact, depending on the nature of the substituents.

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![Figure 4](image_url)

**Figure 4.** High-resolution STM images of the self-assembled nanoarchitecture on Au(111): (a) 20 × 18 nm²; (b) 6 × 5 nm² (V₀ = −0.4 V, I₀ = 400 pA). (c) Model of the PTCDI−TAPB molecular arrangement observed in (a, b).

The STM image reveals that PTCDI molecules can be locally observed in the 2D architecture cavities. The fuzzy pattern often observed in the other cavities probably results from organic species diffusing inside the cavities.
structures. These observations should motivate experimental investigations with low-temperature nc-AFM with a function-alized tip to locally characterize the charge and the stability of dissociated molecules.

**Experimental Section**

Experiments were performed in an ultrahigh-vacuum (UHV) chamber at a pressure of $10^{-8}$ Pa. The Au(111) surfaces were sputtered with Ar$^+$ ions and then annealed in UHV at 600 °C for 1 h. PTCDI molecules (Figure 1, left) and TAPB molecules (Figure 1, right) were evaporated from Knudsen cells at 250 and 280 °C, respectively, on a gold surface kept at room temperature. The molecular coverage was less than 0.2 monolayer. Cut Pt/Ir tips were used to obtain constant-current STM images at room temperature with a bias voltage applied to the sample. STM images were processed and analyzed using the homemade FabViewer application.

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**Figure 5.** (a) Scheme of the 1.4 nm separation between two dissociated boomerang-shaped TAPB molecules in the PTCDI–TAPB network. (b) Theoretical length of the covalent TAPB dimer (1.1 nm). (c–f) High-resolution STM images of cavities of the PTCDI–TAPB network, $3 \times 3.5 \text{ nm}^2$ ($V_s = -0.4$ V, $I_t = 400$ pA). As a guide for the eyes, schemes of PTCDI, TAPB dissociated 4-aminophenyl groups, and dissociated boomerang TAPB molecules have been superimposed onto the STM images in (c–f).
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