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Frustrated 2D Molecular Crystallization

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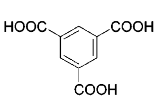
Molecules with well-defined shapes and multiple sites that engage in strong directional interactions are now widely used to build new ordered materials by design.[1] Such molecules, which have been called tectons,[2] associate spontaneously to form networks with architectures that can often be predicted in detail. Tectons are a prolific source of engineered three-dimensional (3D) and two-dimensional (2D) crystals with predefined structures and properties.[3]



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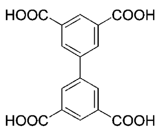

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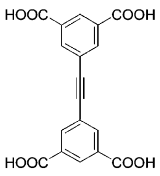

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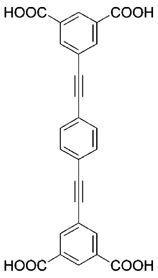

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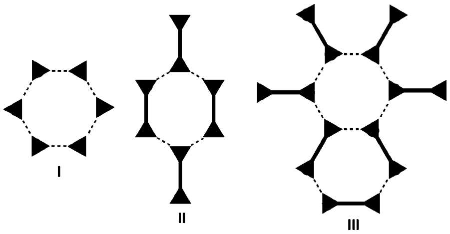

Figure 1. Portions of networks built from trimesic acid (**1**) and tetraacids **2**−**4**, with 1,3,5-trisubstituted phenyl groups represented by triangles and hydrogen bonds shown as broken lines.

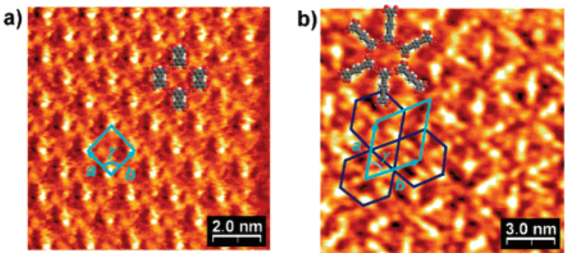

Figure 2. STM images of the 2D crystallization of tectons **2** (Figure 2a) and **4** (Figure 2b) on HOPG (deposition from heptanoic acid, with $V_{\mathrm{bias}} = -1.5$ V and $I_{\mathrm{set}} = 50$ pA). The unit cells are highlighted in light blue, the Kagomé network formed by tecton **4** is shown in dark blue, and molecular models are superimposed as an aid to visualization.

Trimesic acid (**1**) and its salts are prototypic tectons.[4] 3D and 2D crystallization of the acid is typically directed by association of the three -COOH groups as cyclic hydrogen-bonded pairs, which generates the planar hexagonal network represented by structure **I** (Figure 1).[4,5] Expanded versions of the network can be built from molecules derived from triacid **1** by inserting spacers between the -COOH groups and the 1,3,5-trisubstituted phenyl core.[6] However, the utility of tecton **1** and its extended analogues is limited by (1) the inability of normal pairwise association of the -COOH groups to program the construction of networks other than polymorph **I**[7] and (2) the small number of hydrogen bonds (6) in which each molecule can participate.

Related tetraacids **2**−**4**, as well as other derivatives with multiple isophthalic acid groups grafted to suitable cores, can provide planar networks that are both richer in variety and more robust. In particular, we have found that 2D crystallization of tectons **2**−**4** can be controlled to produce two polymorphs, parallel network **II** or Kagomé network **III**.[8] Moreover, the special connectivity of these networks allows their growth to be interrupted by a smooth transition to the alternative polymorph, without necessarily introducing defects in which tectons are missing, improperly oriented, or unable to form the optimal number of hydrogen bonds with neighbors. We show that this can frustrate crystallization, particularly when tectons **2**−**4** are mixed.

Tetraacid **2** was prepared by the reported method,[9] and elongated analogues **3** and **4** were synthesized by standard procedures.[10] Specifically, Sonogashira coupling of diethyl 5-iodo-1,3-benzenedicarboxylate with diethyl 5-ethynyl-1,3-benzenedicarboxylate,[11] followed by hydrolysis, provided tecton **3** in 71% overall yield. An analogous route converted diethyl 5-iodo-1,3-benzenedicarboxylate and 1,4-diethynylbenzene into extended tecton **4** in 68% overall yield.

In a typical 2D crystallization, a droplet of a saturated solution of tecton **2** in heptanoic acid was placed on freshly cleaved highly oriented pyrolytic graphite (HOPG) at 25 °C, and the resulting physisorbed assembly was imaged by scanning tunneling microscopy (STM) in the constant-height mode (Figure 2). Figure 2a reveals the formation of an open parallel network in which the tectons associate by hydrogen bonding according to motif **II** (Figure 1), with unit cell parameters $a = b = \sim 1.36$ nm and $\gamma = \sim 90°$. This interpretation is reinforced by the observation of homologous sheets in the 3D crystal structure of tecton **2**.[9] In the 3D structure, tecton **2** resembles other biphenyls by adopting a nonplanar conformation in which the torsional angle between the aryl rings is approximately 40°. Prominent differences of contrast within each molecule in Figure 2a may indicate that tecton **2** also adopts a twisted conformation in its 2D crystals.[12]

In contrast, adsorption of extended tecton **4** on HOPG was found to produce a Kagomé network (Figure 2b and motif **III** in Figure 1), with unit cell parameters $a = b = \sim 3.43$ nm and $\gamma = \sim 60°$. This surprising selectivity cannot be explained by differences in the density of packing or in the number of hydrogen bonds formed per tecton (8), which are identical for both motifs **II** and **III**. Instead, the preferences must arise from small variations in the strengths of the hydrogen bonds between the adsorbates or from other subtle effects related to solvation or interactions of the adsorbates with each other and with the underlying surface.

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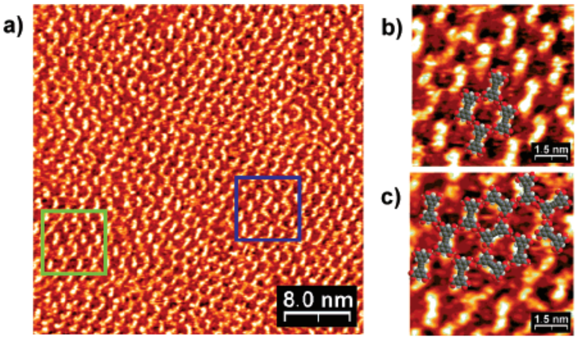

Figure 3. (a) STM image of the assembly produced by the adsorption of tecton **3** on HOPG (deposition from heptanoic acid, with $V_{\mathrm{bias}} = -1.5$ V and $I_{\mathrm{set}} = 50$ pA). (b and c) Higher-resolution images of the areas in Figure 3a highlighted in green and blue, respectively, with superimposed models. These images show regions of local order according to motifs **II** (parallel network) and **III** (Kagomé network), as well as the smooth transition between them.

According to a recent study of the 2D crystallization of tectons on HOPG, directional interactions between adsorbates can be more important than diffuse interactions with the surface in determining the ultimate structure and its orientation.[13] Extensive hydrogen bonding of tectons **2**−**4** should make interadsorbate interactions particularly important. Indeed, the tetraethyl esters of tectons **3**−**4** produced distinctly different nanopatterns on HOPG. Moreover, networks derived from tectons **2** and **4** did not show a preferred orientation with respect to the underlying surface.

DFT/B3LYP calculations have suggested that the contrasting preferences of tectons **2** and **4** for networks **II** and **III** result in part from subtle differences in hydrogen bonding.[10,14] For short tecton **2**, the cyclic tetramer that generates parallel network **II** is estimated to be 0.95 kcal/mol more stable per hydrogen bond than the Kagomé alternative **III**; in contrast, elongated analogue **4** is estimated to favor the Kagomé structure by 0.42 kcal/mol.

For intermediate compound **3**, however, the two possible networks are predicted to have virtually identical energies. Adsorption of tecton **3** on HOPG generated a nanopattern strikingly unlike those produced by analogues **2** and **4** (Figure 3a). In the new pattern, individual molecules were again well resolved, presumably in part because they are held in place by multiple hydrogen bonds. Motifs **II** and **III** (Figure 1) can be clearly discerned in small areas of local order (Figure 3b,c); however, large-scale periodicity apparently cannot be attained, possibly because the two motifs are closely matched in energy and can merge smoothly. Nevertheless, the assembly shows a high degree of order, and most molecules have specific orientations relative to their neighbors, resulting from the formation of hydrogen bonds according to motifs **II** and **III**. We suggest that Figure 3a provides an atomically resolved image of the organization of a 2D molecular glass. It is possible to imagine an alternative aperiodic arrangement in which the molecular components do not have preferred orientations with respect to their immediate neighbors. In this way, Figure 3a illustrates in 2D the possibility of polyamorphism, in which a single molecular material can exist as distinctly different amorphous phases.[15]

The frustrated crystallization of tecton **3** suggested that the 2D cocrystallization of mixtures of compounds **2**−**4** would also prove to be difficult. Deposition of a 1:1 mixture of tectons **3** and **4** on HOPG under the standard conditions failed to yield large periodic domains, as determined by STM.[10] Again, the images showed clearly resolved molecules oriented locally according to motifs **II** and **III**; however, sustained growth of single crystalline phases was not observed. We attribute the frustrated crystallization to a combination of two synergistic effects: (1) the feasibility of moving smoothly from motif **II** to motif **III** without introducing defects, and (2) the structural similarity of tectons **3** and **4**, which allows them to be interchanged without completely interrupting the growth of an extensively hydrogen-bonded network. Further experiments revealed that 2D crystallization of tecton **4** can be thwarted by the addition of less than 15% of compound **3**.

Our work demonstrates that a deep understanding of 2D and 3D molecular assembly can be attained by an integrated approach using the tools of X-ray diffraction, STM, computation, and molecular synthesis. In particular, our results provide new guidelines for designing 2D and 3D molecular glasses,[16] as well as detailed models for their structures and the phenomenon of polyamorphism. Furthermore, our work confirms that molecules with well-defined shapes and multiple sites that engage in strong directional interactions are a consistently productive source of new materials with properties not previously observed.

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Supporting Information Available: Syntheses of compounds **3-4**, detailed description of the calculations, and additional STM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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