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Highly Symmetric 2D Rhombic Nanoporous Networks Arising from Low Symmetry Amphiphiles

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Molecular self-assembly at the liquid/solid interface is now established to provide well-defined two-dimensional (2D) crystals with nanostructured features in a size regime where traditional lithographic techniques fail.[1] These physisorbed molecular assemblies have been investigated with the aid of scanning tunneling microscopy (STM), offering structural and mechanistic insights.[2] Recently, an exotic class of 2D crystals has emerged with void spaces that constitute 2D porous networks.[3] Molecular inclusion of the sort long attainable in three dimensions is now being realized on surfaces due to the ability of nanoporous monolayers to act as hosts for guest molecules.[4] Thus far, most 2D porous networks have been constructed by utilizing high molecular symmetry in concert with noncovalent intermolecular interactions such as hydrogen bonding and van der Waals (vdW) interactions.[3b,5,6] For example, honeycomb networks are formed through extended hydrogen bonding of trimesic acid[5] or vdW interaction of a star-shaped stilbenoid compound.[6] The 3-fold symmetric geometries of those molecules play a critical role in forming the 3-fold rotation axes in the honeycomb network. Here, we present an unusual example of the formation of a high symmetry nanoporous network from a low symmetry molecular building block. This symmetry generation in the 2D crystal is accompanied by formation of molecular aggregates in the crystallographic asymmetric unit with three inequivalent molecules ($Z' = 3$), in itself a rare occurrence.

During the course of investigations on the self-assembly of aromatic primary amides bearing *para* substituents with long alkyl chains (Chart 1), the presence of more than one monolayer structure was observed. Although a close packed structure is the default behavior for physisorbed monolayers,[7] a 2D nanoporous network was unexpectedly observed. This structure is in the plane group *p*6 and contains rhombic voids. The presence of high symmetry and porosity in the monolayer is also a rare occurrence for a molecule with C_s symmetry.[8]

Chart 1. Structures of Amphiphilic Molecules Investigated

1 **2**

n = 11 (a), 13 (b), 15 (c), 17 (d)

The occurrence of multiple packing forms in 2D crystallization is seeing increased scrutiny.[9] The amide structures investigated here provide a particularly dramatic example (Figure 1). We hypothesized that the two packing structures of the amide amphiphiles differ most dramatically in the hydrogen bonding and vdW interactions; experiments varying the functional groups and alkyl chain lengths to examine the relative role of intermolecular interactions support this claim. The amide compounds with alkyl chains with between 12 and 18 carbons were synthesized, and their 2D crystal structures formed at the 1-phenyloctane/highly oriented pyrolytic graphite (HOPG) interface were investigated by STM. The monolayer formed by **1d**, the amide compound with the longest alkyl chain investigated, satisfies close packing (Figure 1a). The shorter alkyl chain compounds, **1a**, **1b**, and **1c**, formed a phase containing rhombic voids (Figure 1c). The coexistence of a close packing and a rhombic nanoporous structure was observed without phase transformation for **1c** and **1b**. The area covered by the rhombic structure increased as the alkyl chain length decreased. The close packing structure exists as the major phase for **1c**. For **1b**, the nanoporous structure is the major phase and the nanoporous structure is observed as the sole phase for **1a** (see Supporting Information). In other words, the close packing structure is preferred for long chains at a given concentration.[9c] The direction of alkyl chains in the rhombic nanoporous network matches the symmetry of HOPG, and this suggests that the substrate may affect the crystal structure; however, a structure-determining role for alkyl-chain substrate alignment can be ruled out because longer alkyl chains do not favor the nanoporous structure. These results are consistent

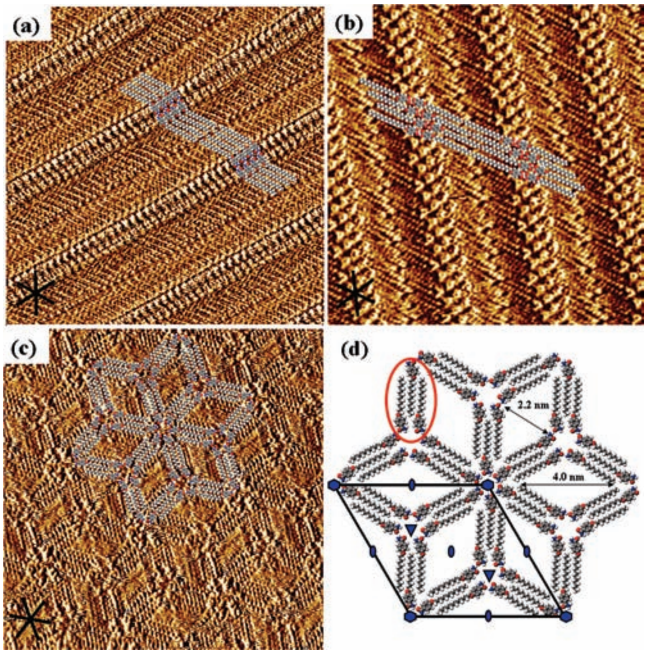

Figure 1. STM images (20 × 20 nm^2, 10.2 Hz, 800 mV, 300 pA) and the computed models of the monolayers of amphiphilic molecules formed at the 1-phenyloctane/HOPG interface. (a) **1d**, (b) **2d**, (c) **1a**, and (d) a computed model of (c) with a unit cell. The computed models are superimposed on STM images to facilitate interpretation. The black axes indicate the symmetry of HOPG under the monolayer. The red oval indicates an asymmetric unit of the rhombic nanoporous network.

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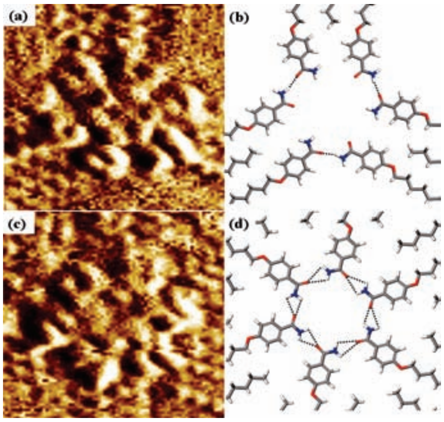

Figure 2. STM images (3×3 nm^2, 10.2 Hz, 800 mV, 300 pA) of 3- and 6-fold rotation axes in the rhombic nanoporous network and their computed models showing the corresponding hydrogen bonding networks.

with the notion that as the alkyl chain length decreases, the hydrogen bonding interactions play a relatively more important role (see Supporting Information). To examine the role of hydrogen bonding, carboxylic acid analogues were synthesized with the expectation that the same phenomenon could arise (Chart 1). However, in contrast to the amide case, only a close packed phase was observed for the carboxylic acid amphiphiles. Both **2d** and **2a** satisfy close packing, though in a manner differing from **1d** (Figure 1b). The absence of a porous phase is discussed below in the context of hydrogen bonding in the amide phase.

To our knowledge, rhombic void space has not been observed previously in 2D networks formed at the liquid/solid interface. The void widths of 2.2 and 4.0 nm (Figure 1d) are comparable to the cavity sizes observed in other systems (~1−5 nm).[9] The *p*6 symmetry of the monolayer is unexpected because the molecular symmetry of the amphiphilic molecules is C_s and therefore does not allow for 3- or 6-fold rotation axes coincident with the molecule. To put this result in context, the relationship between molecular symmetry and monolayer symmetry was scrutinized by searching the Two-Dimensional Structural Database (2DSD), a catalog of packing patterns for molecules adsorbed at the liquid/solid interface.[7] The frequency of the plane group *p*6 was only 2.2% among all unique entries in the 2DSD. Most *p*6 symmetry monolayers are generated from molecules with 3- or 6-fold rotation axes (82%). Hydrogen bonding[3d,8,10] and other geometric effects[9b] have also induced *p*6. Thus, the fact that the carboxylic acid compounds do not adopt *p*6 symmetry suggests that the structure of the hydrogen bonding network of the amide groups differs from that of the acid. High resolution images of each rotation axis in the nanoporous structure reveal six benzene rings (Figure 2).[11] The computed models of these provide molecular structures in detail. These axes are constructed from hydrogen bonding between aggregates, where an aggregate consists of three crystallographically inequivalent amide molecules ($Z' = 3$) in an asymmetric unit (indicated by a red oval in Figure 1d).[12] If there were only one molecule in the asymmetric unit, this low-symmetry amide could not reasonably form the 3- and 6-fold symmetric hydrogen-bonding patterns seen here. Through aggregate formation, this symmetry generation is possible. In the 3-fold rotation axis, a typical arrangement can be invoked (Figure 2b). However, an unusual hydrogen bonding structure involving a ring of 12 donors and 6 acceptors exists at the 6-fold axis, one which has not been reported in 2D or 3D crystal structures (Figure 2d). This model is supported by two facts: (1) it is found in several cases of three-dimensional crystal structures of amide compounds that two lone pairs on oxygen make hydrogen bonds with two hydrogen atoms in an amide,[13] and (2) the arrangement of benzene rings apparent in the high resolution STM image (Figure 2c) matches well with the computed model.[11] The absence of a porous phase for an acid might be due to a geometrical difference of hydrogen bonding; the bifurcated hydrogen bonds in an amide are not possible between acid groups.

In conclusion, this investigation shows the formation of high symmetry nanoporous molecular networks containing rhombic voids uncorrelated with molecular symmetry. Remarkably, amide amphiphilic molecules overcome this barrier to symmetry generation through forming an aggregate of three desymmetrized molecules as an asymmetric unit. The role of high Z' values in symmetric pattern generation requires additional scrutiny to determine if this is a general two-dimensional crystal engineering strategy capable of generating nanometer voids using low symmetry molecules.

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Supporting Information Available: Experimental details, modeling and computation of 2D crystals, additional STM images, the unit cell parameters and plane groups of 2D crystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) See Supporting Information (Figure S2). Computed models are superimposed on Figure 2a and 2c with symmetry elements of the monolayer to clarify the slight difference between these two axes.

(12) A search of the 2DSD reveals that $Z'=3$ is very uncommon, occurring in 0.6% of entries.

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