Rational Modulation of the Periodicity in Linear Hydrogen-Bonded Assemblies of Trimesic Acid on Surfaces

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Self-assembled structures physisorbed on surfaces are a rich source of information.[1] The nature and transformations of these structures shed new light on the fundamental interactions between complex molecules.[2-8] In many self-assembled molecular networks (SAMNs), hydrogen bonding is the primary link among adjacent molecules and governs the resulting structure. One of the most extensively studied models is trimesic acid (TMA), a tricarboxylic acid with three-fold symmetry. Because the carboxyl group (−COOH) tends to form cyclic hydrogen-bonded pairs, TMA is inherently disposed to form hydrogen-bonded sheets.[6-10] A hexagonal honeycomb structure is favored in TMA crystals and is also the most common pattern formed when TMA is adsorbed on various substrates (graphite,[6-8] Au,[9] and Si[10]), both under ultrahigh vacuum and at the solid−liquid interface.[11,12]

Two different coexisting crystallographic phases have been observed at the solid−liquid interface, named the "chickenwire" and "flower" motifs. Both patterns have networks with three-fold symmetry, where all carboxyl groups participate in hydrogen bonding either by normal dimeric pairing (chickenwire) or by a hybrid combination of dimeric and trimeric association (flower). These structures depend on the solvent and can coexist in certain solvents.[7] The trigonal symmetry of TMA and the underlying three-fold symmetry of the substrate should lead inevitably to the formation of hexagonal patterns and to exclude other periodic motifs.[13] Here we demonstrate a new, unexpected pattern of self-assembly for TMA directed by hydrogen bonding at the solution−graphite (HOPG) interface.

Figure 1 shows STM images of SAMNs formed from solutions of TMA and 1-undecanol in heptanoic acid. When both components are mixed on HOPG immediately before imaging, two different patterns are clearly discerned, in which the usual TMA hexagonal flower pattern[7] is surrounded by a new linear structure (Figure 1a). Enlarged images of the two patterns are shown separately in Figure 1b,c. The linear pattern consists of tapes of TMA dimers, separated by intervening ribbons of perpendicular undecanol chains. The 2D flower pattern of pure TMA is thermodynamically less stable than the 1D tapes, and the former is completely replaced within minutes as the system equilibrates (observed by time-lapsed STM imaging, not shown here).

Two hypotheses can explain the formation of this linear pattern from the trigonal TMA unit: (i) esterification of TMA with undecanol to form the undecyl monoester (with two-fold symmetry) and (ii) formation of a hydrogen-bonded TMA/undecanol complex, leaving two carboxyl groups free to form a tape. The esterification
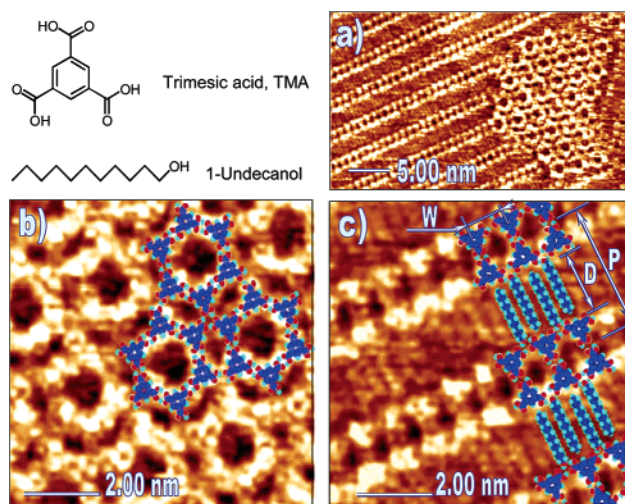
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Figure 1. (a) STM image of SAMNs formed by deposition of 1-undecanol and TMA from heptanoic acid solution on HOPG. (b) TMA flower pattern with molecular model. (c) TMA linear pattern with molecular model. Bias voltage, $U_s = -0.8$ V, tunneling current $I_t = 150$ pA.

hypothesis is plausible because a similar pattern has been observed for a structurally related compound, 5-octadecyloxyisophthalic acid.[3,14] However, it was ruled out by a control experiment with an independently prepared sample of the 1-undecyl monoester of TMA, which yields a different zigzag 1D pattern under the same conditions (see Supporting Information). We conclude that the linear nanopattern shown in Figure 1 results from coadsorption of TMA and undecanol assisted by hydrogen bonding.

Our second hypothesis is strongly supported by a recently reported crystallographic study of the hydrogen-bonded 1:1 complex formed by TMA and another alcohol, CH₃OH.[15] This complex reveals a pattern of association fully analogous to the one postulated in Figure 1c. TMA molecules are paired by standard cyclic hydrogen bonding of −COOH groups. The pairs are then linked into continuous tapes by hydrogen bonding with bridging alcohol molecules. An excellent match was achieved by fitting the STM image in Figure 1c with the atomic coordinates taken from the X-ray crystal structure, with CH₃OH replaced by 1-undecanol.[16]

In both the crystal structure and the assembly shown in Figure 1c, association in the tapes involves only TMA molecules and the −OH group of the alcohol. Changing the chain length of the alcohol should therefore not affect assembly of the tapes, but should control the spacing between them. This creates an intriguing opportunity to modulate the periodicity of these nanopatterns in a predictable way, simply by changing the alcohol. To test the idea that the observed tapes are a reliable supramolecular motif on surfaces, we

Table 1. Summary of Alcohol Coadsorption with TMA Tapes

alcohol	L (nm)[a]	D (nm)[b]	P (nm)[c]	angle (deg)[d]
$C_{11}H_{23}OH$	1.53	1.85 ± 0.05	3.50 ± 0.05	86 ± 2
$C_{16}H_{33}OH$	2.16	1.70 ± 0.05	3.40 ± 0.05	61 ± 2
$C_{17}H_{35}OH$	2.29	2.40 ± 0.10	4.10 ± 0.05	85 ± 2
$C_{22}H_{45}OH$	2.91	2.10 ± 0.05	4.10 ± 0.05	69 ± 2
$C_{27}H_{55}OH$	3.54	3.55 ± 0.10	5.25 ± 0.05	86 ± 2

[a] Calculated length of the alcohol. [b] Distance between two successive tapes. [c] Period of the pattern (see figures). [d] Angle between tape axis and alcohol chain.
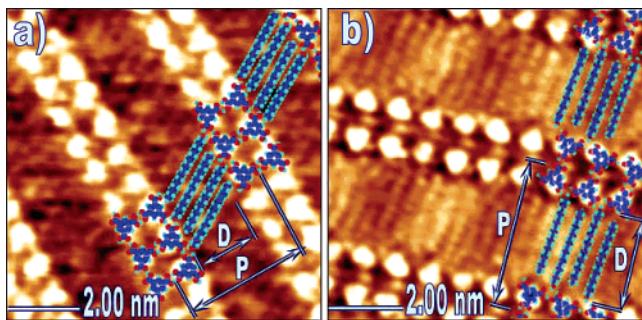

Figure 2. STM images of SAMNs obtained by mixing TMA with 1-hexadecanol (a) and 1-heptadecanol (b) in heptanoic acid solution. The insets are enlarged areas with superimposed molecular models. Tunneling parameters: $U_s = -1.4$ V, $I_t = 200$ pA (for a), and $U_s = -1.1$ V, $I_t = 200$ pA (for b).

used a longer-chain alcohol, 1-hexadecanol, to increase the inter-tape separation D, measured between the centers of the tapes. On the basis of the length of the alcohols (Table 1), we estimated that this change would increase the separation from $D = 1.83$ nm (undecanol, $L = 1.53$ nm) to $D \sim 2.4$ nm (hexadecanol, $L = 2.16$ nm). Surprisingly, the inter-tape separation actually decreased by ~ 0.14 nm. An STM image of the new assembly (Figure 2a) showed that the orientation of the long axis of the alcohol tilts from $\sim 90°$ (undecanol) to $\sim 60°$ (hexadecanol) with respect to the tape axis.

Replacing undecanol with hexadecanol changes both the number and parity of carbon atoms. The odd−even effect has long been known to affect the solid-state properties of many alkane derivatives, and its effect on SAMNs was recently observed by STM.[17] Further experiments with three other alcohols showed that the effect is persistent: all alcohols with an odd number of carbons produce a nearly orthogonal tape/alcohol orientation, whereas a tilted orientation is observed for even alcohols (Table 1).

To understand the origin of the parity effect, we examined closely the molecular structure of the postulated assemblies. The molecules strive to pack as closely as possible while avoiding excessive steric repulsion. The alkyl chains have fully extended conformations and adsorb with the zigzag plane perpendicular to the surface. Every second carbon atom lies above the surface, and the chains appear as lines with bright spots separated by 0.25 nm, which corresponds to the C−C−C distance (Figure 2b). To achieve dense packing on the surface, carbon atoms of neighboring chains should be staggered, with each "up" atom in one chain next to a "down" atom in each of the two neighbors. This condition is easily achieved in odd-numbered alcohols because the two ends of the molecule point in different directions. For even-numbered alcohols, the two ends point in the same direction, so efficient packing requires the molecules to shift by one carbon atom along the chain (see Supporting Information). This shift, exercised throughout the aliphatic domain, results in the tilt of the alcohol chains with respect to the TMA tape.

This work represents an important step toward rational molecular nanopatterning of surfaces using principles of crystal engineering.

Although a variety of patterns have already been observed with different molecules, the formation of a specific SAMN is difficult to predict and often requires a lengthy synthesis of a new molecular building block. In our case, the hydrogen-bonded motif formed by TMA and alcohols is general for a variety of normal aliphatic alcohols. This motif is distinctly different from the hexagonal patterns normally favored by TMA. Its periodicity is proportional to the length of the alcohol and thus can be modulated with high predictability by changing a readily available component. Very different properties of the tapes (hydrophilic) and inter-tape spaces (hydrophobic) create an opportunity to guide the position-specific adsorption of other atoms and molecules. We are currently exploring the use of these SAMNs as templates for the controlled deposition of metal nanowires and biomolecules.

Supporting Information Available: Experimental details, molecular model for the odd/even effect, STM image of the SAMN formed by the 1-undecyl monoester of TMA. This material is available free of charge via the Internet on http://pubs.acs.org.

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