Two-Dimensional Self-Assembly of a Symmetry-Reduced Tricarboxylic Acid

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ABSTRACT: Investigations of the self-assembly of simple molecules at the solution/solid interface can provide useful insight into the general principles governing supramolecular chemistry in two dimensions. Here, we report on the assembly of 3,4′,5-triphenyltricarboxylic acid (H₃BHTC), a small hydrogen bonding unit related to the much-studied 1,3,5-benzenetricarboxylic acid (trimesic acid, TMA), which we investigate using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. STM images show that H₃BHTC assembles by itself into an offset zigzag chain structure that maximizes the surface molecular density in favor of maximizing the number density of strong cyclic hydrogen bonds between the carboxylic groups. The offset geometry creates “sticky” pores that promote solvent coadsorption. Adding coronene to the molecular solution produces a transformation to a high-symmetry host–guest lattice stabilized by a dimeric/trimeric hydrogen bonding motif similar to the TMA flower structure. Finally, we show that the H₃BHTC lattice firmly immobilizes the guest coronene molecules, allowing for high-resolution imaging of the coronene structure.

INTRODUCTION

Molecular self-assembly is one of the most ubiquitous driving forces in materials design in the natural world. Examples including DNA, cellular membranes, and spider silk demonstrate the potential for encoding information and for producing specific biological or mechanical function using only a small number of relatively simple molecular building blocks. To mimic these properties in engineered material systems, it is imperative to study molecular self-assembly in a systematic manner. Investigating self-assembly at the interface between a molecular solution and a solid provides a number of advantages: the experiment is simple and working at a surface introduces a symmetry reduction that simplifies the energetics of the system and allows us to use surface science techniques to characterize the system.

The thermodynamic driving force behind 2D molecular self-assembly at the solution/solid interface is the minimization of the Gibbs free energy of the system, which depends on the interplay between entropy (maximized for molecules in solution) and enthalpy (maximized for molecules assembled on the surface). An overarching motivation for studies in 2D self-assembly is to gain an understanding of how the different enthalpic interactions relate to one another, with the aim of developing more sophisticated predictive power for 2D self-assembled architectures that could ultimately lead to controlled structural design.

One of the key mechanisms for establishing this type of understanding is the molecular-level study of model systems. Extensive scanning tunneling microscopy (STM) investigations have been conducted on the self-assembly of TMA, a small, 3-fold-symmetric hydrogen-bonding unit (Figure 1) in ultrahigh vacuum (UHV), in electrochemical cells, and at the solution/highly oriented pyrolitic graphite (HOPG) interface. Solution/HOPG STM has revealed that solutions of TMA in carboxylic acid solvents give rise to a surface-supported chicken-wire structure of hexagonally arranged pores bounded by six molecules and stabilized by cyclic dimeric O···H···O associations. In general, solutions with a higher TMA concentration favor a different structure, the so-called flower structure, which incorporates trimerically associated molecules between chicken-wire pores. These polymorphs are members of a homology of structures spanning from exclusively dimeric to exclusively trimeric associations between the constituent molecules. Ultrahigh vacuum (UHV) experiments with TMA on the Au(111) surface have demonstrated the coverage dependence of these dimeric/trimeric structures. The pores in the TMA mesh, approximately 1.1 nm wide, have been used...
to host a variety of guest molecules, including fullerenes,\textsuperscript{24,28} coronene,\textsuperscript{33,34} and heterocirculenes.\textsuperscript{35}

The effects of imposing systematic structural variations on a well-studied molecule such as TMA are of considerable interest because they demonstrate the relative importance of different aspects of the molecular building block (e.g., core size and location of bonding groups) in the self-assembly process. Working at the solution/HOPG interface, a number of groups have documented the effects of some of the possible variations. Benzene bicarboxylic acids form ordered arrays of linear tapes as long as the carboxyl groups are not ortho-positioned.\textsuperscript{36} 1,2,4,5-Benzenetetracarboxylic acid forms three different concentration-dependent polymorphs that rely almost exclusively on cyclic O−H⋯O dimers, whereas 1,2,4-benzenetricarboxylic acid forms a disordered dense layer because of its low symmetry.\textsuperscript{37} 1,3,5-Benzetribenzoic acid (BTB), which has a larger core than TMA, stabilizes into both porous chicken-wire meshes bounded by cyclic O−H⋯O dimers and more densely packed phases that comprise weaker cyclic O−H⋯O trimers, trading off the stronger H bonds for increased molecular packing.\textsuperscript{38,39} Morrison et al. studied the effects of changing the bonding geometry of benzenetricarboxylic acids by varying the number and location of carboxylic acids, revealing a remarkable diversity of structures in the corresponding 2D layers.\textsuperscript{40} The even larger 1,3,5-tris[4′-carboxy(1,1′-biphenyl-4-yl)]benzene (TCBPB) forms a variation on the chicken-wire structure, where the molecular density on the surface is increased through the offset of molecules and the incorporation of weak C−H⋯O bonds instead of the stronger O−H⋯O bonds associated with the unperturbed chicken-wire structure.\textsuperscript{41} The versatility of carboxylic hydrogen bonding means that a wealth of possible structures are accessible even with relatively simple modifications to the constituent molecules.\textsuperscript{42}

In this article, we report on the self-assembly of biphenyl-3,4′,5-tricarboxylic acid (H₃BHTC), shown in Figure 1. H₃BHTC is different from TMA in two important ways: it incorporates a core of more than double the size, and it has a reduced symmetry of C₁ᵥ rather than Cᵥ. Studies of the incorporation of H₃BHTC into 3D coordination compounds have recently been published.\textsuperscript{43−45} The surface self-assembly of biphenyls has been studied previously, but only with a higher symmetry introduced by using either two\textsuperscript{46,47} or four\textsuperscript{48} symmetrically distributed carboxylic groups. Other work has focused on the surface self-assembly of tetracarboxylic acids with even longer linear cores.\textsuperscript{49−51} We find that H₃BHTC self-assembles into an offset interdigitated zigzag structure on HOPG. Introducing coronene into the molecular solution induces the formation of a higher-symmetry guest−host structure that incorporates two types of pores that firmly immobilize the coronene guests. These structures emphasize the increased importance of the principle of closest packing with increasing molecular size and demonstrate the possibility for the exact rotational positioning of guests within a room-temperature 2D supramolecular assembly on HOPG.

### Experimental Section

**Biphenyl-3,4′,5-tricarboxylic acid (Sigma-Aldrich, 96%) and coronene (Sigma-Aldrich, 97%, shown in Figure 1) were used as received. Saturated solutions were prepared in heptanoic acid (Sigma-Aldrich, 99%). HOPG (Structure Probe Inc.) was cleaved with sticky tape immediately before use. STM measurements were performed with a Digital Instruments Nanoscope III using tips cut from 80/20 Pt/Ir wire (Nanoscience Instruments Inc.) All measurements were made at room temperature using constant-current imaging. Image processing was done using free WSxM software\textsuperscript{52} and was limited to flattening and smoothing unless otherwise noted. Gas-phase DFT calculations were performed at the B3LYP/6-31G(d) level using Gaussian 09.\textsuperscript{53}

**Results**

**STM Results.** The deposition of a solution of H₃BHTC onto the HOPG surface results in the immediate formation of a dense monolayer comprising up to three rotational domains aligned 60° with respect to one another. The appearance of the individual molecules within the layer depends strongly on the tip geometry, but the structure consistently exhibits a linear motif. The individual domains often incorporate long linear stacking faults, and a linear moiré pattern, caused by the interference between the molecular superlattice and the underlying HOPG, can be seen in large-area images (Figure 3a).

An analysis of images with clear and distinct molecular resolution, as in Figure 3b, provides us with a preliminary understanding of the structure of the molecular layer. The structure in Figure 3c shows the zigzag arrangement of H₃BHTC suggested by the image. The interdigitated zigzag
The unit cell parameters of the overlayer were obtained from an image containing both the molecular structure and atomic resolution on the underlying HOPG, which was lattice corrected to the HOPG dimensions (SI). The oblique unit cell has $a = (1.67 \pm 0.05)$ nm, $b = (1.93 \pm 0.05)$ nm, and $\gamma = (97^\circ \pm 3)^\circ$. We note that the unit cell is chiral and that the linear stacking faults arise from the inclusion of a row of cells of the opposite chirality. In similar self-assembled structures observed at the solution/solid interface, solvent molecules have been observed or hypothesized to coadsorb in the voids of the primary molecular lattice, $^{41,55-57}$ a possibility that we will discuss further later.

Adding a drop of coronene solution to the existing H$_3$BHTC structure produces an immediate structural transformation. The linear zigzag pattern of H$_3$BHTC is replaced by a porous structure with hexagonally arranged pores that each contain a coronene molecule. The coronene can be imaged with striking submolecular resolution (Figure 4a) that reveals two important characteristics of this structure: (1) two distinct pore types are present in two interpenetrating superlattices and (2) the submolecularly resolved coronene molecules all have exactly the same rotational orientation with a given domain. In Figure 4a, the two pore types are manifest as pores containing either a clearly defined molecule or a molecule with a streaked overlay. The streaked contrast within the second pore type is characteristic of this particular set of image parameters and is not observed under other tunneling conditions. In other images, coronene molecules in both pore types can be resolved with submolecular resolution (Figure 4c); these images confirm that the coronene molecules in both pore types have identical orientations within a given domain. Images containing the simultaneous resolution of the molecular structure and the underlying HOPG allowed us to estimate the periodicity of the hexagonal pores at $(1.67 \pm 0.05)$ nm (SI).

An examination of images of this structure over a range of bias voltages, together with the periodicities determined above, led us to the molecular model presented in Figure 4b. In accordance with the coronene contrast observed in Figure 4a, the structure contains two distinct pore types that describe two interpenetrating superlattices. Six H$_3$BHTC molecules associated through cyclic dimers bound one pore type. The second pore type is bounded by the sides of four H$_3$BHTC molecules. Two of the vertices are located at dimer bonds of the first pore type, and the other two vertices are located at trimer bonds that associate with three neighboring pores of the second type (Figure 4b). The bonding motif defined by the dimer-bonded pores and the trimer-bonded molecules surrounding them is the same as in the TMA flower structure; we therefore refer to this structure as an H$_3$BHTC flower structure.

**DFT Results.** Further insight into the observed structures can be gained from DFT calculations and by comparison to the self-assembly of TMA.

Table 1 contains the calculated energies for the bonding geometries shown in Figure 5.

The strongest bonds identified for H$_3$BHTC are the cyclic dimer bonds between two H$_3$BHTC molecules arranged end-to-end (Figure 5c). The geometry obtained by combining this bonding motif with zigzag dimer bonds (Figure 5a) produces the fully dimeric mesh shown at the domain boundary in Figure 3c. However, we observed this polymorph only in limited quantities at domain boundaries, indicating that it is not energetically favored.
A consideration of the molecular density of the different structures helps elucidate the energetics governing the system. Table 2 shows the unit cell parameters calculated on the basis of the bond geometries given by DFT, along with the molecular density for the pure H$_3$BHTC phases and the density of coronene guests for a (hypothetical) fully dimeric guest/host structure and the observed flower guest/host structure.

**DISCUSSION**

Our STM observations clearly support the formation of a zigzag chain of H$_3$BHTC. The chains capitalize on the strength of the O−H···O cyclic dimers and maintain the symmetry of the molecule. The zigzag motif has been observed in other assemblies of carboxylic acids and also predicted theoretically. Isophthalic acid and its derivatives, which have only two carboxylic groups, form a zigzag structure stabilized by O−H···O cyclic dimer bonds (Figure 2a).$^{27,36}$ Monte Carlo simulations predicted the stability of this zigzag phase for a model system composed of triangular molecules with strongly interacting vertices.$^{58}$ By dissolving TMA in 1-phenyloctane, Ha et al. demonstrated that solvophobic effects drive the higher-symmetry molecule to assemble into a dense dimerically associated zigzag structure, where O−H···O cyclic dimerization occupies only two of the carboxylic groups on each molecule and the third is involved in a single O−H···O bond, maximizing the surface molecular density.$^{25}$

Although the experimental and calculated geometries for the strong bonding along the zigzag chain agree, the DFT-predicted geometry deviates from our observed geometry along the direction governed by the weak bonds. The observed unit cell is larger than the predicted one by ∼0.1 nm along this direction. This discrepancy could be due to a substrate-driven effect that is neglected by our gas-phase calculations. The discrepancy could also arise if solvent molecules are coadsorbing within the H$_3$BHTC structure. At the experimentally observed size, each H$_3$BHTC unit cell is able to accommodate and form strong O−H···O dimer bonds with two heptanoic acid molecules (SI).

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**Table 1. Gas-Phase Association Energies of H-Bonded Clusters Calculated by DFT at the B3LYP 6-31G(d,p) Level**

<table>
<thead>
<tr>
<th>bond</th>
<th>geometry (Figure 6)</th>
<th>energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$BHTC trimer</td>
<td>a</td>
<td>−9.90</td>
</tr>
<tr>
<td>H$_3$BHTC trimer</td>
<td>b</td>
<td>−10.01</td>
</tr>
<tr>
<td>H$_3$BHTC trimer</td>
<td>c</td>
<td>−10.17</td>
</tr>
<tr>
<td>H$_3$BHTC trimer</td>
<td>d</td>
<td>−2.10</td>
</tr>
<tr>
<td>H$_3$BHTC trimer</td>
<td>e</td>
<td>−8.74</td>
</tr>
<tr>
<td>H$_3$BHTC trimer</td>
<td>f</td>
<td>−8.79</td>
</tr>
</tbody>
</table>

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A consideration of the molecular density of the different structures helps elucidate the energetics governing the system. Table 2 shows the unit cell parameters calculated on the basis of the bond geometries given by DFT, along with the molecular density for the pure H$_3$BHTC phases and the density of coronene guests for a (hypothetical) fully dimeric guest/host structure and the observed flower guest/host structure.
Table 2. Calculated Unit Cell Parameters (a, b, γ), Number of Molecules Per Unit Cell (n), and Molecular Density (ρ) for Three Polymorphs of H₃BHTC

<table>
<thead>
<tr>
<th>Structure</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>γ (deg)</th>
<th>n</th>
<th>ρ (mol/ nm²)</th>
<th>ρ_cor (mol/ nm²)</th>
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<tr>
<td>fully dimeric</td>
<td>1.68</td>
<td>2.43</td>
<td>70</td>
<td>2</td>
<td>0.52</td>
<td>1</td>
</tr>
<tr>
<td>offset zigzag</td>
<td>1.68</td>
<td>1.81</td>
<td>99</td>
<td>2</td>
<td>0.67</td>
<td>4</td>
</tr>
<tr>
<td>flower</td>
<td>3.37</td>
<td>3.37</td>
<td>60</td>
<td>6</td>
<td>0.61</td>
<td>4</td>
</tr>
</tbody>
</table>

*Only the second two polymorphs are observed experimentally in extended domains. The final two columns show the number of coronene guests that can be accommodated per unit cell (n_cor) along with the areal density of coronene (ρ_cor) within the porous polymorphs.*

Figure 6. (a) DFT-calculated LUMO and LUMO + 1 for coronene. (b) STM image of coronene immobilized in a H₃BHTC pore (V_b = −0.279 V, I = 119 pA). The bias voltage at which the image was collected corresponds approximately to the energy of the LUMO + 1.

which contribute to both the total intermolecular bond enthalpy and the areal molecular density (surface–molecule adsorption enthalpy).

A similar offset geometry, where a strong cyclic carboxylic dimer is disfavored with respect to an increased packing density, has been observed previously for TCBPB (Figure 2b), which also hosts solvent molecules within the structure. The offset geometry may emerge as a common phenomenon for tricarboxylic molecules with elongated cores: because their fully dimeric porous structures have inherently low molecular densities, the offsetting of molecules serves both to increase the density of the molecular lattice and to invite solvent coadsorption through the formation of “sticky” cavities, especially for carboxylic solvent molecules.

The addition of coronene to H₃BHTC produces a transformation to the flower structure, as shown in Figure 4. This type of guest-induced transformation has been observed previously in self-assembled structures at the solution/solid interface and commonly occurs in densely packed structures that cannot natively accommodate guest molecules. This is the case for the offset zigzag structure, which does not offer sufficient access to the underlying HOPG for coronene to adsorb in a flat conformation. The fully dimeric structure, however, offers a pore that should just be large enough to accommodate one coronene at its center (SI). However, we have never observed the dimeric structure after the addition of coronene. The calculated density of coronene guests for the dimeric and flower structures, as shown in Table 2, suggests the reason for this. The density of H₃BHTC is higher in the flower structure than in the fully dimeric polymorph (0.61 molecules/nm² compared to 0.52 molecules/nm²), and geometry dictates that the density of coronene is higher in the flower structure (0.41 vs 0.26 molecules/nm², respectively), as is the ratio of H₃BHTC/coronene (3.2 vs 2.1, respectively.) Furthermore, the host/guest interactions are maximized in the flower structure, which has cavities that are better matched to coronene in both shape and size (models in Figure 4b and SI).

Overall, the hydrogen-bonding energetics of the H₃BHTC flower structure lattice are very similar to those of the TMA flower structure. The dimeric hydrogen bonds involved have identical energies (−10.01 kcal/mol), and the trimeric bonds are nearly identical (−8.79 kcal/mol for TMA, −8.74 kcal/mol for H₃BHTC). However, because of the large pores and the concomitant low molecular density, the H₃BHTC structure is not stable in the absence of coronene guest molecules. We note that although H₃BHTC forms this dimeric/trimeric flower structure and can hypothetically form both a fully dimeric and a fully trimeric lattice (SI), these are its only accessible polymorphs that are analogous to the TMA homology. Symmetry constraints preclude the formation of an extended lattice of any of the higher-order mixed dimeric/trimeric polymorphs.

Returning to the coronene guest molecules, a comparison of a submoloeclarly resolved image of coronene with the calculated molecular orbitals reveals a remarkable similarity, as shown in Figure 6. The calculated LUMO and LUMO + 1, shown as a composite in Figure 6a, are the only states accessible at the bias voltage of the STM image in Figure 6b. The resemblance between the calculated and experimental appearance confirms that coronene is rigidly fixed within the H₃BHTC pore. This submoloeclarly resolution also confirms that the orientation of the coronene is consistent with the lowest-energy structure calculated by Blunt et al. for a coronene guest in a circular hexaisophthalate pore.

The complete immobilization of full domains of coronene has not previously been described for a tricarboxylic mesh. The simplest explanation of the immobilization of the coronene is based on the geometry of the flower structure. Although the pores that are bounded by cyclic dimers are functionally identical to the pores of the TMA mesh (inner diameter = 1.1 nm), the second type of pore, bounded by the long axes of four H₃BHTC molecules, has a limiting inner dimension that is 0.2 nm smaller. The accommodation of coronene within these pores would require a slight distortion, which in turn should be propagated onto the neighboring pores of the first type. This lattice distortion could result in a stronger interaction between the lattice and the guest molecules, manifesting in their immobilization.

**CONCLUSIONS**

The self-assembly of H₃BHTC at the heptanoic acid/HOPG interface provides a demonstration of the subtlety of the energetics governing 2D molecular self-assembly. The native structure formed by H₃BHTC alone is an offset zigzag chain structure, which comprises strong cyclic hydrogen bonds along the length of the zigzag chains but only weak associations between neighboring chains. This arrangement produces a higher molecular packing density than would a fully dimerically bonded lattice and creates the possibility for the coadsorption of solvent molecules within the pore. The increased enthalpy of adsorption associated with the resulting higher packing density compensates for the lower bond energy of the weak hydrogen bonds between neighboring chains. Adding coronene molecules...
to the solution transforms the lattice to a higher-symmetry host–guest lattice that incorporates coronene into two distinct types of pores, one of which is bounded by dimerically bonded H₂BHTC and the other by a mixture of dimerically and trimerically associated H₂BHTC. This host lattice firmly immobilizes the coronene guests, allowing for their exceptionally distinct resolution in STM images.

**REFERENCES**


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