Substrate, Molecular Structure, and Solvent Effects in 2D Self-Assembly via Hydrogen and Halogen Bonding

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Supporting Information

ABSTRACT: Recently, halogen−halogen interactions have been demonstrated to stabilize two-dimensional supramolecular assemblies at the liquid−solid interface. Here we study the effect of changing the halogen, and report on the 2D supramolecular structures obtained by the adsorption of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (TBPT) and 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT) on both highly oriented pyrolytic graphite and the (111) facet of a gold single crystal. These molecular systems were investigated by combining room-temperature scanning tunneling microscopy in ambient conditions with density functional theory, and are compared to results reported in the literature for the similar molecules 1,3,5-tri(4-bromophenyl)benzene (TBPB) and 1,3,5-tri(4-iodophenyl)benzene (TIPB). We find that the substrate exerts a much stronger effect than the nature of the halogen atoms in the molecular building blocks. Our results indicate that the triazine core, which renders TBPT and TIPT stiff and planar, leads to stronger adsorption energies and hence structures that are different from those found for TBPB and TIPB. On the reconstructed Au(111) surface we find that the TBPT network is sensitive to the fcc- and hcp-stacked regions, indicating a significant substrate effect. This makes TBPT the first molecule reported to form a continuous monolayer at room temperature in which molecular packing is altered on the differently reconstructed regions of the Au(111) surface. Solvent-dependent polymorphs with solvent coadsorption were observed for TBPT on HOPG. This is the first example of a multicomponent self-assembled molecular networks involving the rare cyclic, hydrogen-bonded hexamer of carboxylic groups, R₂(24) synthon.

INTRODUCTION

Molecular self-assembly has been widely considered for bottom-up patterning of surfaces.¹−⁵ This remarkably versatile approach can produce a virtually infinite number of nanopatterns⁶ by tuning the molecular building blocks.⁷−¹¹ In two-dimensional (2D) self-assembled molecular networks (SAMNs) the substrate serves as physical support but can also play an important role in driving formation of a specific pattern. As such, the template effect can be exploited to reinforce or work against¹² the inherent molecular symmetries.

Ordered self-assembled 2D nanostructures are typically observed when the mobility of single molecules is sufficiently high to allow them to diffuse and achieve a configuration desirable for attractive, stabilizing intermolecular interactions.¹⁰¹³ SAMNs are supramolecular systems stabilized by noncovalent bonds,¹⁴−¹⁶ which permit self-healing of defects that consequently leads to long-range order.²³,³³−³⁶ The study of self-assembly at the liquid−solid interface is interesting both for pragmatic experimental reasons, since it allows for easy and low-cost fabrication and characterization methods relative to ultrahigh vacuum (UHV) techniques,¹⁹ and fundamental considerations, considering that self-assembly phenomena observed in living systems occur in aqueous environments.¹,²,⁴,⁶,¹⁰−¹²

SAMNs can be stabilized by a number of weak forces, for example, van der Waals (vdW),²³−²⁵ π−π stacking,²⁴,²⁶ or hydrogen bonding.²⁷−²⁹ Halogen-bonded 2D structures are particularly interesting due to the peculiar double polarization of the carbon−halogen (C−X) bond, which permits the formation of geometrically stable structures with the halogen termination participating in more than one interaction.²³,³⁷,³⁸ The tip of the halogen in a C−X bond exhibits a positively charged cap (or σ-hole), while a negative ring-like charge distribution is established around the halogen atom.³⁹ The electrostatic potential at the σ-hole becomes more positive with larger halogens,⁴⁰ meaning that the strength of the interaction can be adjusted by varying the halogen substituent. Importantly, halogen-bonding interactions are independent from hydrogen bonding, which potentially allows use of both types in designing supramolecular assemblies.

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Here, we present a comparative study of two 3-fold symmetric molecules, 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (TBPT) and 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT). These are structurally related to two previously investigated molecules, 1,3,5-tri(4-bromophenyl)benzene (TBPB)\textsuperscript{12,31–45} and 1,3,5-tri(4-iodophenyl)benzene (TIPB),\textsuperscript{46–49} allowing us to elucidate the role of the triazine core in the assembly process. The triazine core of TBPT and TIPT makes these molecular building blocks planar and stiffer than TBPB or TIPB, which should translate to stronger adsorption energies and might affect the morphology of their SAMNs. The self-assembly of TBPT and TIPT was studied by scanning tunneling microscopy (STM) at the liquid–solid interface on highly oriented pyrolytic graphite (HOPG) and Au(111) surfaces. The weak molecular adsorption on HOPG allows us to comparatively explore the intermolecular interactions. Conversely, the experiments on gold, where adsorption is stronger, provide insights into the molecule–substrate interactions. The role of different solvents in the assembly of different polymorphs was also studied.\textsuperscript{13,28,50} Density functional theory (DFT) calculations corroborate experimental observations and provide insight into the nature of the weak bonds involved in the observed supramolecular structures.

**EXPERIMENTAL METHODS**

Heptanoic acid (Sigma-Aldrich, 96%), 1-phenyloctane (Sigma-Aldrich, 98%), and 1,2,4-trichlorobenzene (TCB) (Sigma-Aldrich, ≥99%) were purchased and used without further purification. These solvents have low volatility and ensured a stable imaging environment over the period of a typical experiment (i.e., a few hours). The synthesis of TIPT and TBPT is described in the Supporting Information (SI). HOPG substrates (Structure Probe, Inc.) were freshly cleaved on the (0001) basal plane with adhesive tape before each experiment. Gold films were deposited on mica\textsuperscript{51} in a vacuum evaporator with a base pressure of 10\textsuperscript{−6} mbar and a peak pressure of 10\textsuperscript{−5} mbar during film growth. Mica substrates (Electro- \n
Microscopy Sciences, V-5 quality) were degassed at 200 °C for 2 h and then held at 360 °C during gold (ESPI Metals, purity 4N) deposition, which led to (111)-oriented thin films. Once the deposition was completed, at a film thickness of approximately 20 nm, the gold samples were annealed in nitrogen (N\textsubscript{2}) at 400 °C for 1 h. This procedure led to atomically flat terraces hundreds of nanometers large. The quality of the gold films was verified using STM by the presence of the 22×\sqrt{3} herringbone reconstruction, which is typical of Au(111) surfaces.\textsuperscript{52,53} Prior to each experiment, the Au(111) samples were rinsed with deionized water, dried with N\textsubscript{2} and passed a few times over a propane flame. With this procedure it was possible to remove any molecules or macroscopic particles of dust adsorbed on the surface.\textsuperscript{51}

Solutions of known concentration were sonicated for 10 min and then deposited on the substrates using a micropipette (Eppendorf). STM experiments were performed with a Digital Instruments Nanoscope III using metallic tips mechanically cut from 80/20 Pt/Ir wire (Nanoscience Instruments, Inc.), which were immersed in a drop of solution applied onto the substrate. All images were acquired in constant-current mode at room temperature and processed with the free WSxM software.\textsuperscript{54} STM images on HOPG have been lattice-corrected using the atomic resolution of the underlying substrate, whereas it was not possible to correct the images obtained on gold (see also the SI). The reported experimental distances were averaged over several STM images.

**THEORETICAL METHODS**

Gas-phase DFT calculations were performed in Gaussian 09.\textsuperscript{55} The B3LYP functional was used for single-molecule calculations, since it can accurately describe and has been widely used for similar nonperiodic molecular systems.\textsuperscript{56–59} For calculations with periodic boundary conditions (PBCs) the performance of the B3LYP, M06-2X,\textsuperscript{60} and M06-L\textsuperscript{61} functionals was investigated (see SI). The M06 functionals are known to be more accurate for systems involving noncovalent interactions,\textsuperscript{62} and hence were chosen for the description of halogen-bonded SAMNs. Furthermore, they are more suitable for periodic systems than B3LYP because they are exact in the uniform electron-gas (UEG) limit.\textsuperscript{63} Our calculations show that the hybrid M06-2X functional is roughly 30 times more computationally expensive than M06-L (see Table S4 in the SI), but both functionals provide similar results in terms of interatomic distances and binding energy. For this reason, all computational results with PBCs reported in this work were performed with the M06-L functional. For the systems involving heavy iodine atoms, we investigated the performance of the all-electron 3-21G* Pople basis set and the effective core potential (ECP) LanL2DZ basis set as implemented in Gaussian 09. We find that LanL2DZ leads to a more accurate description of the energies of halogen-bonded systems than 3-21G*, that is, with the bonding energy (BE) of molecular complexes in the order \textit{BE}_{ECP} > \textit{BE}_{B3LYP} > \textit{BE}_{LANL2DZ} (see Figure S22 in the SI).\textsuperscript{54} For this reason, the TIPT SAMN was computed with LanL2DZ, whereas all the TBPT SAMNs were computed with 6-31G*\textsuperscript{64}. The TBPT SAMN on HOPG was also computed with LanL2DZ for comparison to the TIPT network. In the calculations we allowed the systems to relax and computed the total energy, interatomic distances, molecular orbitalts (MOs), and molecular electrostatic potential (ESP) maps. The standard convergence criteria of the Gaussian 09 program were used for optimizations. Single-molecule calculations were performed with constrained symmetries (C3). Extended 2D assembled structures were calculated using PBCs and were constrained to a plane using C\textsubscript{3} symmetry (except for the system with coadsorption of heptanoic acid molecules, where the halophenyl groups were free to rotate).

**RESULTS AND DISCUSSION**

TIPT on HOPG. Following the application of a sessile drop (approximately 5 μL) of a solution of TIPT in TCB (10\textsuperscript{−2} M) on HOPG, a 2D self-assembled network of TIPT molecules spontaneously formed at the interface between the substrate and the solution (Figure 1a). Different domains, as large as 100 nm, are rotated from one another by 120\textdegree, commensurate with the underlying 3-fold symmetric graphite lattice (green lines in Figure 1a).

High-resolution STM images allow us to elucidate the molecular packing within the adlayer, as shown in Figure 1b where the halogen atoms appear as bright protrusions and the molecular core appears dark. This qualitative behavior has already been reported for the similar molecule TIPB.\textsuperscript{48} The protrusions associated with the iodine atoms do not have the 3-fold symmetry expected for TIPT molecules. We ascribe this to an electronic effect. In the 2D lattice TIPT molecules appear to arrange in a parallel row structure, with a rectangular molecular
unit cell containing two molecules \((u = 2.04 \pm 0.09 \text{ nm}, v = 1.54 \pm 0.09 \text{ nm}, \gamma = 90 \pm 5^\circ)\). The bright rows consist of characteristic V-shaped “trimers” formed by the halogen atoms of adjacent TIP molecules (full and empty circles of Figure 1b). The angle defined by these “trimers” \((\theta)\) is equal to \(141 \pm 6^\circ\). This assembly is packed differently from that of the counterpart molecule TIPB on HOPG reported in the literature, which self-assembles with either an oblique or nearly square unit cell.\(^{46,49}\) The \(u\) vector is rotated by \(94 \pm 5^\circ\) (clockwise or counterclockwise) with respect to graphite \((10\bar{1}0)\), that is, the armchair directions, as indicated by the 2D fast Fourier transform (FFT) of STM micrographs resolving both the SAMN and the HOPG substrate (see Figure S9 and S10 in the SI). Combining this 2-fold degeneracy with the 3-fold degeneracy of the domains in Figure 1a, six different domains are in principle possible. However, they were not simultaneously observed with the STM because each domain extends over several tens of nanometers (Figure 1a).

Starting from the experimentally observed molecular structure (Figure 1b) we performed gas-phase DFT optimization of the SAMN. The geometry predicted by the DFT calculations is in reasonable agreement with the experimental STM images, namely with rows of TIP molecules along the \(u\)-vector arranged in stacks along the direction specified by the \(v\) vector (Figure 1c). This molecular configuration positions the positively charged tip of the C–I bonds toward the negatively charged belts of neighboring C–I bonds \((d_1)\); however, the calculations show that the iodines are too far apart to engage in significant halogen bonding (Table 1). Indeed, TIP molecules within the rows (rectangle in Figure 1c) and between neighboring rows (circle in Figure 1c) are mostly stabilized by I–H hydrogen-bond contacts (Table 1).\(^6\) Although the \(\sigma\)-hole of the iodine atoms points toward the nucleophilic nitrogen atom of the neighboring TIP along the \(v\)-vector (dotted line in Figure 1c), the approach to the triazine core is screened by the hydrogens of the phenyl groups (Figure 2a,b). Therefore, the nitrogen does not participate in the lateral stabilization of the assembly (Table 1). The computed net intermolecular binding energy at the M06-L/LanL2DZ level is \(-2.9\) kcal/mol per unit cell (i.e., \(-0.038\) eV/nm\(^2\)), although the total binding energy of the system should be much higher owing to attractive \(\pi\cdots\pi\) interactions with the HOPG substrate (on the order of 30 kcal/mol per TIP molecule).\(^{57,64}\) We note that DFT optimization leads to a molecular unit cell slightly different from the experimental data (see Figure 1b and Table 1). We ascribe this to the effect of the substrate, which was not taken into account in the gas-phase calculations. We have also found several other polymorphs with similar unit cell as stationary points in the optimization; the one reported here shows the best match with the observed STM contrast (see Table S1 in the SI).

The same long-range ordered self-assembly of TIP molecules at the liquid-HOPG interface is obtained using phenylcane as a solvent, whereas no long-range order was observed in heptanoic acid. The stability of the SAMN was higher in TCB than in phenylcane; imaging the latter was quite difficult due to noise and instability (see Figure S11 in the SI).

Figure 3 shows advantages of our molecular design, which increases the planarity and rigidity of the molecule compared to the triphenylbenzene systems reported elsewhere.\(^{12,41–45}\) This graph was obtained by plotting the energy of the DFT-optimized single-molecule configurations as a function of the (fixed) dihedral angle \((\delta)\) between the phenyl groups and the central ring. The planar conformation of TBPT \((\delta = 0^\circ)\) is stabilized versus the twisted one \((\delta = 90^\circ)\) by 25 kcal/mol, whereas for TBPB the planar conformation is destabilized versus the twisted one \((\delta \approx 40^\circ)\) by 7 kcal/mol, because of repulsive interactions between the hydrogen atoms. From the diagram in Figure 3 we can also conclude that TBPT is stiffer than TBPB, which can be attributed to intramolecular hydrogen bonds between the triazine nitrogens and the hydrogens of the phenyl groups (see Figure S26 in the SI).
3.53 Å, the isolated state may also lead to lower adsorption energy.

Table 1. Experimental and Computed Unit Cell Parameters and Computed Interatomic Distances (see Figure 1c and Figure 4b for Labels) of the TIPT and TBPT Molecular Network at the Solution–HOPG Interface (M06-L/LanL2DZ and 6-31G** Levels of Theory)*

<table>
<thead>
<tr>
<th></th>
<th>u (nm)</th>
<th>v (nm)</th>
<th>γ (deg)</th>
<th>θ (deg)</th>
<th>d1 (Å)</th>
<th>d2 (Å)</th>
<th>d1 (Å)</th>
<th>d2 (Å)</th>
<th>energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPT</td>
<td>2.04 ± 0.09</td>
<td>1.54 ± 0.09</td>
<td>90 ± 5</td>
<td>141 ± 6</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TBPT</td>
<td>2.05 ± 0.09</td>
<td>1.47 ± 0.09</td>
<td>89 ± 5</td>
<td>129 ± 6</td>
<td>5.43, 5.76</td>
<td>3.05, 3.25</td>
<td>4.46, 4.58</td>
<td>3.17, 3.18</td>
<td>-2.9</td>
</tr>
<tr>
<td></td>
<td>2.35</td>
<td>1.34</td>
<td>90</td>
<td>134</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td></td>
<td>2.25</td>
<td>1.32</td>
<td>90</td>
<td>146</td>
<td>5.60, 5.75</td>
<td>2.99, 3.17</td>
<td>4.43, 4.53</td>
<td>2.88, 2.93</td>
<td>5.6</td>
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<td></td>
<td>5.04</td>
<td>2.73</td>
<td>3.82</td>
<td>2.82, 2.89</td>
<td>-26.0</td>
</tr>
</tbody>
</table>

“Bold distances refer to intermolecular bonds shorter than the sum of the vdW radii of the atoms involved (2rH = 3.96 Å, rI = 3.18 Å, rBr + rH = 3.05 Å, rBr + rN = 3.40 Å).”

TBPT on HOPG. Following the application of one drop of a solution of the brominated molecule (TBPT) in TCB onto HOPG, with concentrations varying from 10−2 M to 10−3 M, no SAMN was observed. On the other hand, when TBPT was dissolved in phenyloctane (10−2 M), a stable SAMN formed over tens of nanometers (see Figure S12 in the SI). The molecular packing is similar to that in the SAMN obtained with the iodinated molecule (Figure 4a), that is, with a rectangular unit cell hosting two molecules (u = 2.05 ± 0.09 nm, v = 1.47 ±

Figure 2. Molecular ESP map (M06-L/LanL2DZ) of (a,b) TIPT and (c,d) TBPT molecules in the (a,c) gas phase (3D view) and (b,d) in the assembly (top-view). The ESPs are expressed in atomic units (a.u., Rydberg/e) on 0.004 e/Bohr3 isodensity surfaces. The black square insets in panels a and c show the details of the ESP around the halogen atoms of the isolated TIPT and TBPT, as seen parallel to (dotted square) and orthogonal to (solid square) the C–X bond direction. The color scale from blue (+ve) to red (−ve) spans the following ranges: ±2 × 10−2 a.u. for the full molecules in a, c and for the SAMNs in b, d; ±6 × 10−2 a.u. and ±1 × 10−2 a.u. in the dotted and solid black square insets, respectively.

Figure 3. Calculated relative energies (B3LYP/6-31G**) for conformations of TBPT and TBPB with increasing dihedral rotation angle (θ) of the side groups (see the TBPT molecules in the inset).

Figure 4. (a) STM image of TBPT molecules (inset) assembled at the phenyloctane–HOPG interface (6.6 × 6.6 nm2, Vc = −1.60 V, Ic = 117 pA). TBPT molecules are schematically indicated on the image; full and empty circles indicate the bromine atoms of trimeric motifs pointing down and up, respectively, which define the trimeric angle θ. The experimentally determined unit cell, with parameters u = 2.05 ± 0.09 nm, v = 1.47 ± 0.09 nm, and γ = 89 ± 5°, and the DFT-optimized cell (Table 1) are drawn in green and gray, respectively. (b) SAMN computed with gas-phase DFT calculations at the M06-L/LanL2DZ level; d1 and d2 are the bromine-to-bromine and bromine-to-hydrogen bonds, respectively. The rectangle and the circle highlight the intra-row and the inter-row interactions, respectively. The dotted line indicates the potential attractive interaction between bromine and nitrogen.
molecules in the assembled network are too far apart for Br–TBPT(phenyloctane)

oblique unit cell.

analogous molecule TBPB on HOPG, which features an

di and S14 in the SI). As was the case with TIPT, the structure of

unit cell of the SAMN 93 ± 5° either clockwise or counterclockwise with respect to the (1010) armchair
directions of the underlying HOPG surface (see Figure S13 and S14 in the SI). As was the case with TIPT, the structure of

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TBPT was dissolved in heptanoic acid (10−2 M) as expected based on

hardening of the C−Br bond (see also solid square insets in Figure 2a, c). Therefore, the computed net intramolecular

binding energy of TBPT (−5.6 kcal/mol per unit cell, −0.077 eV/nm2) is twice that of TIPT (Table 1).

TBPT-co-Heptanoic Acid on HOPG. Interestingly, when

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As in the previous case, DFT optimization gives a molecular

configuration with the halogens of each molecule participating in the stabilization of the SAMN via X···H hydrogen bonds (Table 1). The halogen atoms are again oriented toward the nucleophilic triazine core of the neighboring TBPT molecule along the v-vector (dotted line in Figure 4b), similarly to TIPT, but cannot engage in halogen bonding due to the electrostatic repulsion of the hydrogen atoms screening the nitrogen (Figure 2c,d).

The calculations indicate that the X···H contacts are closer for TBPT than for TIPT (Table 1), as expected based on

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Figure 5. (a) STM image of TBPT molecules assembled at the heptanoic acid–HOPG interface, (11.2 × 11.2 nm2, V = −1.40 V, I = 50 pA); the dotted and solid circles indicate a bright protrusion and a pore within the SAMN (1.7 nm diameter, measured from Br to Br), respectively. The two-headed arrow indicates two bromine atoms, 1.3 ± 0.1 nm apart, of a TBPT molecule; the single-headed arrow indicates the unusual internal contrast of TBPT molecules. Gray triangles highlight the chirality within the 2D lattice. The experimentally determined unit cell is u = v = 2.7 ± 0.1 nm, γ = 60 ± 5°. (b) DFT-computed bicomponent SAMN at the M06-L/6-31G** level (in the top-left part of the image the HOPG substrate is shown underneath the molecular network).

The structure of Figure 5 is topologically similar to those previously observed in monocOMPONENT halogen- and hydrogen-bonded SAMNs formed from C3-symmetric organic building blocks at the liquid–HOPG interface32,71 and in UHV.42 We ascribe the bright protrusion located at the center of the TBPT hexamers (dotted white circle in Figure 5a) to an
electronic effect in the HOPG substrate caused by adsorbed molecules.72

The alignment of the molecular pattern along the (1210) zigzag directions of the substrate further corroborates the hypothesis of coassembly of solvent molecules. In fact, this commensurability leads to a favorable adsorption geometry of the six heptanoic acid alkyl chains of each R6co(24) synthon (Figure 5b).

Figure 5a clearly shows chirality within the TBPT-co-
heptanoic acid SAMN, a phenomenon often observed in 2D molecular networks.71,73–75 In this case, the chirality manifests itself through a counterclockwise rotation of 13 ± 5° of TBPT molecules with respect to the center of the hexameric synthons (gray triangles in Figure 5a). Despite the intrinsic achirality of TBPT, enantioMorphism is introduced by the coassembled prochiral R6co(24) hexamers of heptanoic acid.

0.09 nm, γ = 89 ± 5°). As suggested by the protrusions ascribed to the halogen atoms (circles in Figure 4a), TBPT molecules are arranged in rows stacked along the v-vector. Similar to the case of the iodinated molecule, the molecular framework is rotated with respect to the substrate with the u vector of the unit cell of the SAMN 93 ± 5° either clockwise or counterclockwise with respect to the (1010) armchair
directions of the underlying HOPG surface (see Figure S13 and S14 in the SI). As was the case with TIPT, the structure of

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Gas-phase DFT calculations\(^7^6\) indicate that both carboxylic-based hydrogen bonding as well as Br···H and Br···O interactions between TBPT and heptanoic acid stabilize the structure (see Figure 5b and Table S2 in the SI). The computed net intermolecular binding energy of the bicomponent SAMN (M06-L/6-31G**), normalized per unit area, is 30% larger than that of the TBPT network of Figure 4 \((-0.51 \text{ eV/nm}^2\) vs \(-0.40 \text{ eV/nm}^2\)). This is mostly due to the presence of considerably stronger hydrogen bonds. The DFT calculations also provide additional insight into the apparent chirality of the TBPT molecules in Figure 5a. The contrast observed in Figure 5a suggests that the bromophenyl groups are rotated so that one of their sides appears higher above the surface (single-headed arrow in Figure 5a); calculations indicate a rotation off-plane by 17 ± 3°. Such rotation destabilizes TBPT single molecules by ca. 1 kcal/mol (Figure 3) and was not observed in the previously discussed SAMNs. In the TBPT-co-heptanoic acid SAMN, however, it prevents unfavorable repulsive interactions between the bromophenyl and the \(-\text{CH}_2\) groups of heptanoic acid, thus enabling the overall maximization of intermolecular interactions. The interaction with the chiral R\(^6\)(24) hexamers of heptanoic acid defines the direction (clockwise or anticlockwise) of rotation of the phenyl groups, which in turn enhances the chiral contrast due to the topographic differences discussed above. For similar systems it has been shown that simulated STM images display a distortion similar to the one in Figure 5a when the functional groups are rotated off the mirror plane with respect to the central core.\(^8^5\)

The fact that this coassembly with heptanoic acid was not witnessed for TIPT shows that the energetics involved in the stabilization of the multicomponent SAMN is extremely subtle.\(^1^1,7^7,7^8\) We ascribe this to the different size of the halogen atoms, whose vDW radii differ by 0.13 Å.\(^6^5\) This apparently minute difference can have important consequences in the delicate interplay between hydrogen bonding, maximized space filling, and commensurate (i.e., stronger) adsorption with the HOPG substrate.

**TBPT on Au(111).** Self-assembly on Au(111) was observed using solutions of much lower concentrations, which suggests stronger molecule–surface interactions compared to those using HOPG. By applying a drop \((5 \times 10^{-5} \text{ M})\) of solution of TBPT in phenylctane onto a freshly cleaned gold substrate (see Experimental Section), we observed the formation of molecular networks.

The periodicity of the herringbone reconstruction of the Au(111) surface after molecular adsorption increases by roughly 17% compared to pristine gold (see Table S5 in the SI). Similar expansions have been observed for other molecular overlayers on Au(111),\(^7^9–8^2\) and were attributed to molecule–substrate interactions that pull the gold atoms from the surface, relieving the compression along \((110)\) and consequently widening the fcc regions (i.e., larger herringbone periodicity).\(^8^4\) The widening of the herringbone periodicity can be directly related to the strength of the molecule–substrate interactions.\(^8^5–8^8\) Triphenylphosphine molecules, for instance, produce an average herringbone separation 50% larger than pristine gold.\(^8^9\) Since the gold surface reconstruction is partially lifted upon molecular adsorption it cannot be used to reliably calibrate the images, hence the experimental uncertainties are larger than the previous systems (the attempted calibration of the data on Au(111) is discussed in the SI).

The molecular network formed at the solvent-Au(111) interface exhibits two phases, labeled \(\alpha\) and \(\beta\), which both consist of rows of interdigitated TBPT molecules aligned roughly 10° off the \((112)\) herringbone direction (Figure 6a), that is, along the \(u\) vector in the \(\alpha\) phase and the \(u’\) vector in the \(\beta\) phase. The molecular packing within each row of the two phases is the same: the \(v\) vector in the \(\alpha\) phase and the \(u’\) vector in the \(\beta\) phase are equal. The difference between the two phases is the relative molecular arrangement between neighboring rows: \(\alpha\) phase has a (nearly) rectangular unit cell, whereas the \(\beta\) phase has an oblique cell. This leads to different bonding motifs between neighboring rows in the two phases (see red and yellow circles of Figure 6a). In both phases TBPT molecules within each row are oriented parallel to the \(v\) direction of the \(\alpha\)-phase unit cell (Figure 6a). A phase boundary exists along the \(v\)-vectors, where \(\alpha\) and \(\beta\) polymorphs share one molecular row between the two different regions (cyan molecules with black contour in Figure 6a). The transition occurs via a sliding of the neighboring molecular row along the \(u\) directions. The \(v\) vector in the \(\alpha\) phase and the \(v’\) vector in the \(\beta\) phase are rotated clockwise by 12 ± 6° and 26 ± 6°, respectively, from \((1\overline{1}0)\).
The similar system TBPB-Au(111) arises from the different molecular packing due to the presence of surface steps and this is not attributed to a lattice mismatch, and more likely to the surface reconstruction symmetry. In other words, the different molecular packing cannot be attributed to a lattice mismatch, and more likely arises from the difference in surface potential in the fcc and hcp regions (resulting from the different stacking structure of the topmost atomic layers). The similar system TBPB-Au(111) also exhibits different polymorphs; however, in that case no sensitivity to the reconstructed surface was observed.\(^{34}\)

(see Figure S32 in the SI). In contrast to the systems studied on HOPG, no 3-fold symmetric rotational domains were observed, presumably due to the symmetry breaking associated with the reconstruction of the Au(111) surface. Although previous works have demonstrated that dehalogenation can occur on Au(111),\(^{34,46}\) X-ray photoelectron spectroscopy (XPS) confirms that the TBPT molecules are intact when adsorbed on Au(111) (see Figure S30 in the SI).

Even though we could not rigorously lattice-correct the STM data, high-resolution micrographs provide insights into the molecular configuration. The unit cell vectors of the SAMN in both the \(\alpha\) and \(\beta\) phase were obtained as average values over several STM images. Starting from these we performed gas-phase DFT calculations with PBCs,\(^{90}\) which confirm a favorable configuration for halogen bonding in both phases. The optimized geometries were computed constraining intermolecular angles to reproduce the experimentally observed structures (see Table S6 in the SI). All the bromine atoms in both polymorphs are involved in attractive interactions through electrostatic Br--Br and/or Br--H contacts.

For the \(\alpha\) and \(\beta\) phase, net intermolecular binding energies per unit cell of \(-24.0\) kcal/mol (\(-0.35\) eV/nm\(^2\)) and \(-25.9\) kcal/mol (\(-0.38\) eV/nm\(^2\)) were found, respectively. These values are similar to the energy found for TBPT assembly on graphite (Table 1). The intermolecular bonds within each row are similar in the two phases (see rectangles in Figure 6b and intra-row contacts in Table 2), hence the difference between the binding energies in the two phases is ascribed to the larger number of intermolecular bonds between neighboring rows in the \(\alpha\) phase (see circles in Figure 6b and inter-row contacts in Table 2).

Figure 7a shows the network of assembled TBPT molecules (drawn as cyan tripods) with contrast modulated in bright and dark stripes by the reconstructed underlying gold surface. While the \(\alpha\) phase (yellow lines) seems to nucleate only on the hcp-stacked zones (i.e., on the wide, bright stripes), the \(\beta\) phase (red lines) nucleates only on the fcc-stacked zones (i.e., on the dark stripes). The implication from Figure 7a is that the two different polymorphs occur as a consequence of substrate effects, and in particular the difference between the fcc- and hcp-stacked regions. The two differently stacked areas of the reconstructed substrate have the same lattice constant and symmetry. In other words, the different molecular packing cannot be attributed to a lattice mismatch, and more likely arises from the difference in surface potential in the fcc and hcp regions (resulting from the different stacking structure of the topmost atomic layers). The similar system TBPB-Au(111) also exhibits different polymorphs; however, in that case no sensitivity to the reconstructed surface was observed.\(^{34}\)

Table 2. Experimental and Computed Unit Cell Parameters and Computed Interatomic Distances (see Figure 6b for Labels) of the \(\alpha\) and \(\beta\) Phase in the TBPT Molecular Network at the Phenyloctane–Au(111) Interface (M06-L/6-31G** Level of Theory)\(^{90}\)

<table>
<thead>
<tr>
<th>(\alpha)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha^{\text{exp}})</td>
<td>(\beta^{\text{exp}})</td>
</tr>
<tr>
<td>(\alpha^{\text{DFT}})</td>
<td>(\beta^{\text{DFT}})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(d_{1}) (Å)</th>
<th>(d_{2}) (Å)</th>
<th>(d_{1}) (Å)</th>
<th>(d_{2}) (Å)</th>
<th>energy kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.71–2.96</td>
<td>2.74–3.00</td>
<td>3.52–3.54</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Bold distances refer to intermolecular bonds shorter than the sum of the vdW radii of the atoms involved.

In addition, Figure 7a shows that the number of molecular rows in the \(\alpha\) and \(\beta\) phase of the SAMN does not follow a recursive periodicity, at least not on the scale of this image (~50 nm) (see also Figure S34 in the SI). We attribute this to the fact that the phase boundaries do not occur exactly at the faulted ridges between fcc and hcp regions (also known as

Figure 7. (a) STM image of TBPT molecules assembled at the phenyloctane–Au(111) interface (50 × 50 nm\(^2\), \(V_{x} = +0.10\) V, \(I_{t} = 200\) pA), with SAMN modulated by the reconstructed underlying substrate. TBPT molecules are superimposed (cyan tripods) to highlight the \(\alpha\) (yellow lines) and \(\beta\) phase (red lines). For clarity, only half of the TBPT molecules are shown in the model in a, b. The labels on the right indicate different stacking structures of the underlying gold substrate. Crystallographic directions are indicated by the black and white arrows. (b) \(\alpha\) (yellow) and \(\beta\) (red) domains of image a with respect to the reconstructed Au(111) surface, whose faulted soliton walls are indicated by solid black and white lines. In this diagram, half of each shared molecular row has been assigned to the \(\alpha\) phase and the other half to the \(\beta\) phase. White regions indicate defective areas of the SAMN; the regions circled in black are due to defects of the underlying gold substrate.
substrate-mediated intermolecular interactions of the two phases (see SI), which may be due to di terms of intermolecular interactions (Table 2) and because the fcc regions of the reconstructed Au(111) surface, which host the β phase, are wider than the hcp regions (assuming a similar adsorption energy on the two regions). However, Figure 7b shows instead that the area of α domains is 20% larger than that of the β domains. This can be ascribed to the fact that α-phase domains appear to be more easily able to extend over the soliton walls and occupy fcc regions of the surface. The molecular rows are misaligned with respect to the (112) direction, leading to domain boundaries along the v vectors of the unit cells (Figure 6a) as well as along the u vectors (black and white rectangles in Figure 7a and white regions in Figure 7b).

Previous studies show that the structurally similar 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) adsorbs with the triazine core and side groups (referred to as lobes) on hollow sites of the Au(111) surface (see Figure S35 in the SI). Also, for halobenzenes on Au(111) the most favorable adsorption site is with the aryl ring on a hollow site. Geometrical considerations indicate that, for molecules with the size and shape of TPTZ and TBPT, adsorption with core and lobes on hollow sites is achieved for specific rotations of the molecules with respect to the substrate (namely CW rotations of 10°, 50°, 70°, and 110° with respect to (110), see Figure S35 in the SI). In both α and β phases the two TBPT molecules per unit cell are rotated by the same angle (12 ± 6° and 72 ± 6°CW) with respect to (110). These values are in agreement with those discussed above, hence suggesting that TBPT always adsorbs with core and lobes on hollow sites of Au(111) (see Figure S36 in the SI). This hypothesis, however, does not explain the occurrence of the two phases (see SI), which may be due to different substrate-mediated intermolecular interactions involving the fcc and hcp regions of the substrate and other effects involving the soliton walls.

TBPT is the first molecule reported to form a film at room temperature that is both sensitive to the fcc and hcp regions of reconstructed Au(111) and also continuous. The existence of two different phases as a function of the surface reconstruction is ascribed to molecule–substrate interactions. Since TBPB does not show this behavior on Au(111), we hypothesize that these substrate effects are due to the triazine core, which makes TBPT molecules planar (Figure 3) and thus strengthens molecule–substrate interactions. While some molecular species show different adsorption properties on the fcc and hcp regions of the Au(111) surface (e.g., benzene, azobenzene, and iron(II) phthalocyanine), in all cases the effect is only observed at low coverage and low temperature. At room temperature, the bicomponent melanine and 3,4,9,10-perylenetetracarboxylic diimide SAMN on Au(111) shows stacking faults commensurate with the substrate reconstruction, but not the extended single-phase domains reported herein.

TIPT on Au(111). Probing the assembly of TIPT molecules on Au(111) was more challenging than for its brominated analogue. Using similar drop volumes and concentrations only small rotationally disordered domains of ordered molecules (up to ∼10 nm) were observed (Figure 8a). The tip–sample interaction was quite strong, making image acquisition difficult (see Figure S37 in the SI).

However, the experimental data still allow for a limited comparison between this system and TBPT assembly on Au(111). For instance, as opposed to the previous case, the STM micrographs do not show the presence of different phases sensitive to fcc and hcp regions nor any contrast modulation due to the underlying surface reconstruction. The latter may be a consequence of the adsorbed molecules perturbing the surface reconstruction, although we cannot exclude an influence of the tunneling parameters used for imaging. High-resolution images (Figure 8b) suggest that the assembly of TIPT on Au(111) is similar to that on HOPG (Figure 1b), and closely resembles the assembly of TIPB on Au(111), that is, with a rectangular unit cell that hosts two molecules. In some cases, however, small domains with packing similar to that of TBPT on Au(111) were also observed (see Figure S38 in the SI). Overall, the molecule–substrate interactions appear to be quite different from those in the TBPT–Au(111) system. The nature of halogen atoms not only affects the lateral stabilization of the overlay via halogen bonding, but also modulates molecule–substrate interactions with Au(111).
CONCLUSIONS AND PERSPECTIVES

We performed a systematic study of 2D supramolecular networks obtained by the adsorption of TIPT and TBPT at the solution–HOPG and solution–Au(111) interfaces. Both molecules assemble in a similar fashion on HOPG, forming SAMNs stabilized by H···X hydrogen bonding. The packing differs from that reported in the literature for similar molecules TIPB and TBPB on HOPG.41,46,49 This is attributed to stronger molecule–substrate interactions due to the presence of the triazine core, which makes TIPT and TBPT stiffer and planar precursors. Varying the solvents revealed that TBPT can form a bicomponent polymorph involving a hexameric R\textsubscript{6}\textsuperscript{2}(24) hydrogen-bonded arrangement of the solvent (heptanoic acid) molecules. This was not observed for TIPT, emphasizing the subtlety of the energetics involved in the formation of such weakly bonded SAMNs.

TIPT and TBPT exhibit different behaviors on Au(111). The former assembles with some domains similar to the structure observed on HOPG and to its counterpart TIPB on Au(111),46 as reported in the literature. TBPT self-assembles in two different phases on the two differently reconstructed regions of the surface (i.e. fcc and hcp). This is the first report of molecular networks that show different self-assembly behavior on differently reconstructed regions of the Au(111) surface at room temperature. Since this behavior is not observed for TRPB on Au(111),43,44 we ascribe it to the presence of the triazine core in the molecular structure, which planarizes the TBPT molecule and leads to stronger molecule–substrate interactions.

ASSOCIATED CONTENT

Supporting Information

Synthesis procedures for TBPT and TIPT, additional STM images, 2D-FFTs, model of the commensurability between the TBPT and TIPT network on HOPG, additional computational results, discussion on the calibration of the data on Au(111), model of the TBPT adsorption site on Au(111). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES


(90) We first computed the α phase, and starting from this geometry we computed the β phase freezing the interactions along the u’ vector, given that the difference between the two polymorphs is between neighboring rows.


