Control of Fullerene Crystallization from 2D to 3D through Combined Solvent and Template Effects

Daling Cui, Maryam Ebrahimi, Federico Rosei and Jennifer M. Macleod

Abstract

Achieving precise control of molecular self-assembly to form designed three-dimensional (3D) structures is a major goal in nanoscale science and technology. Using scanning tunnelling microscopy and density functional theory calculations, we show that a 2D covalent organic framework (COF-1) can template solution-processed C60 guest molecules to form several solvent-dependent structural arrangements and morphologies via a 2D to 3D growth process. When 1,2,4-trichlorobenzene is used as solvent, C60 molecules form a template-defined close-packed structure. When heptanoic acid is used as solvent, a range of lower density architectures that deviate from the template-defined close packing are observed. We attribute this difference to the co-adsorption of the heptanoic acid solvent molecules, which is only achieved in the presence of the template. This work demonstrates the possibility to precisely control 3D molecular self-assembly through the synergistic combination of template and solvent effects.

Introduction

Understanding structure–property relationships of materials is a central objective of nanoscience. This understanding is particularly critical when a molecule or compound can aggregate in different crystalline phases, i.e., polymorphs, which exhibit altered physical or chemical properties. Predicting the occurrence of polymorphs and producing materials with unusual structures are two important challenges in materials science and engineering. Polymorphism is routinely observed in both three-dimensional (3D) and two-dimensional (2D) crystals. Several parameters can control the formation of polymorphs in molecular crystals, such as the solvent employed, temperature, and the presence or absence of a substrate that may facilitate epitaxial growth.

In 2D, the use of scanning tunnelling microscopy (STM) permits the direct visualization of molecular architectures with submolecular resolution, providing detailed insights into polymorphism. Surface-confined 2D self-assembly can be used as a means to the controlled, atomically precise nanofabrication of 3D objects and is regarded as a promising strategy to increase overall device density in the third dimension. This approach is well-suited for the realization of tailored polymorphs with out-of-plane anisotropy by bottom-up methods, effectively bridging the gap between 2D and 3D investigations.

The growth of template networks, able to form host/guest (H/G) structures, has proven to be an important approach for controlling crystallization into the third dimension using molecular building blocks. H/G structures rely on hierarchical interactions, in which the template is stabilized by relatively robust and directional interactions (such as hydrogen bonding and metal coordination), and guest molecules are templated through weaker interactions (typically van der Waals, vdW). In a monolayer 2D film, the architecture is governed by both the adsorptive interactions between the substrate and the deposited molecules (H and G) and the intermolecular H/G interactions. Beyond the first layer, the structure is stabilized by intermolecular interactions alone. The formation of a bilayer H-bonded kagomé structure and self-aggregation of π-stacked heterocirculenes have been observed as examples of growth into the third dimension, perpendicular to the surface, starting from a 2D H/G layer. The use of
nonplanar guests, e.g., fullerenes and their derivatives, when stabilized by weak interaction with 2D templates, can promote configurations that deviate from standard close-packing due to the structure defined by the template.\textsuperscript{(9, 25, 29-31)} The codependent relation between trapped fullerenes and the growth of a second layer of a supramolecular framework represents a cooperative interaction of H and G species.\textsuperscript{(32)} Although these examples demonstrate the possibility of arranging molecules from 2D to 3D, defining the 3D spatial organization of films containing small molecules still remains an important challenge,\textsuperscript{(33)} especially for small compounds without functional groups, which tend to lack directional interactions.\textsuperscript{(34, 35)}

The solvent effect is also a well-known factor that may lead to different polymorphs, through co-adsorption effects (known as pseudopolymorphism)\textsuperscript{(36-38)} and solvent-induced polymorphism\textsuperscript{(4, 5, 39, 40)} driven by thermodynamics or kinetics.\textsuperscript{(41, 42)} For example, different polymorphs of trimesic acid (TMA) and benzenetribenzoic acid (BTB)\textsuperscript{(39, 40)} have been observed when using different solvents. The solvent dependence of the formation of the molecular adlayers has been examined in terms of the properties of the solvents (polarity, solvophobicity, solubility, etc.),\textsuperscript{(4)} solvent–solvent interactions, molecular shape, and packing constraints.\textsuperscript{(36)} Co-adsorption involving different solvent molecules allows for a fine-tuning of self-assembled architectures.\textsuperscript{(43)} However, although many reports focus on either the solvent or the template, less is known about how the two effects work jointly in molecular crystal growth.

Here, we show that two distinct approaches to controlling crystallization, template and solvent, work together to define the observed out-of-plane fullerene packing in solution-processed fullerene films. Using a planar aromatic solvent molecule (1,2,4-trichlorobenzene, TCB), the monolayer porous covalent organic frameworks (COF-1) guide fullerene guest molecules to a template-defined close packing. Varying the solvent to an aliphatic (heptanoic acid), the fullerenes crystallize in a number of different less-dense polymorphs. Our STM images and density functional theory (DFT) calculations collectively suggest the observed quasi-close-packed geometries are stabilized through co-adsorption of heptanoic acid.

This work demonstrates the possibility to create new polymorphs and tune molecular packing through the synergistic effect of template and solvent co-adsorption simultaneously. The combination of these two effects can effectively control molecular packing beyond the first layer, even for highly symmetric building blocks like fullerene. The ability to arrange fullerenes into distinct packing could provide a useful approach toward improving device performance in thin-film-based architectures,\textsuperscript{(44)} such as field-effect transistors\textsuperscript{(45)} or photovoltaics.\textsuperscript{(46)}

**Results and Discussion**

COFs are a recently discovered class of porous crystalline materials with high architectural and chemical robustness and customized topologies.\textsuperscript{(47)} A high-quality extended hexagonal porous COF-1 template can be obtained through cyclocondensation of three 1,4-benzenediboronic acid (BDBA) monomers by using excess water as the chemical-equilibrium-manipulating agent (Figure 1a,b).\textsuperscript{(48, 49)} In previous work, we demonstrated that the monolayer COF-1 mesh preferentially grows in a 6 × 6 epitaxial unit cell on highly oriented pyrolytic graphite (HOPG), corresponding to a lattice parameter of 1.476 nm, and showed that C\textsubscript{60} adsorbs in the COF-1 template in two different sites, the top-site (T) and the pore-site (P).\textsuperscript{(50)} T-site and P-site geometries correspond to the adsorption of the C\textsubscript{60} guest molecule on the boroxine ring and in the hexagonal pore, respectively. Corresponding DFT simulation results are presented in Figures 1c,d and S11. We have previously reported an off-centered adsorption for P-site C\textsubscript{60} at the heptanoic acid/HOPG interface.\textsuperscript{(50)} Our present DFT calculations suggest that C\textsubscript{60} adsorbs most stably at the center of the pore (Figure S12). The off-centered adsorption observed experimentally could support the hypothesis of solvent co-adsorption (discussed later), since moving the C\textsubscript{60} off center allows solvent access to the HOPG substrate beneath the pore.
**C₆₀ Self-Assembly at Heptanoic Acid/HOPG Interface**

**Multiple-Layer Structures with P-Site as Bottom Layer**

Multilayer C₆₀ thin films were prepared by drop-deposition of fullerene guest molecules in heptanoic acid onto preprepared COF-1-covered HOPG and imaged at room temperature with STM. In previous work, the adsorbed C₆₀ molecules were observed to order into domains comprising a single adsorption site.(50) Presently, we show that combination of T and P adsorption sites can also occur in the same region through the formation of a bilayer. For instance, we have observed a bilayer structure consisting of P-site C₆₀ in combination with a T-site C₆₀, which we denote as a P-T bilayer (Figure 2a), which is consistent with the small domains reported by Plas et al.(51) In Figure 2a, a hexagonal mesh representing the COF-1 lattice is superimposed on the STM image. Bright spots are interpreted as C₆₀ molecules.
Figure 2. (a) STM image with P-T bilayer structure collected at the heptanoic acid/HOPG interface. Tunnelling conditions: \( V = -776 \) mV, \( I = 42.25 \) pA. Image dimensions: \( 19 \times 19 \) nm\(^2\). (b) STM image collected at the heptanoic acid/HOPG interface showing quasi-HCP triple-layer structure and R1\(^{1}\) layer shifts in A and B patterns. Tunnelling conditions: \( V = -800 \) mV, \( I = 33 \) pA. Image dimensions: \( 15.4 \times 15.4 \) nm\(^2\). (c) The schematic image corresponding to (b). Different architectures are marked by indicators. (d) Model of the P-T bilayer. (e) Model of the quasi-HCP triple-layer structure. The two fullerene molecules marked with “1” are adsorbed in the quasi-same position. (f) Models of the shift of a single R1\(^{1}\) layer molecule with respect to the T layer in A and B patterns. (g) The DFT calculated structure of A-pattern shift, as shown in top and side views. The relative positions of T-site and R1 C\(_{60}\) are specified in the side view. For a better visualization, the radius of C\(_{60}\) carbon atoms is enhanced.

Two T-site C\(_{60}\) molecular lattices, located over boroxine rings, can be identified and represented by open circles (T\(^{1}\)) and spots (T\(^{2}\)). These lattices coexist with P-site C\(_{60}\), defining the P-T bilayer structure (Figure 2d). The cohesive energy of P-T bilayer is \(-2.36\) eV, higher than the sum (\(-2.12\) eV) of the P-site and T-site energies (Table S1, DFT-D3). When both the P-site and the T-site are occupied, additional stability is gained from the interaction between the adjacent fullerene molecules. However, the existence of P-T structure relies on the adsorption of P-site C\(_{60}\), which can be influenced by the solvent in use.(24)

The COF-1 template can host a variety of multilayer structures. A third layer, named as the first raised layer (R1\(^{1}\)), can adsorb above the P-T bilayer to form a triple-layer structure (STM image in Figure 2b and schematic in Figure 2e). As shown in the schematic view, this triple layer presents a quasi-hexagonal close-packed (quasi-HCP) structure. We define this as a “quasi”-HCP structure because of the shift between the first and third layers (see Figure S3), which differs from the HCP in which the first and third-layer molecules are positioned in registry with one another.

**Bilayer Structures with T-Site as Bottom Layer**

A monolayer of T-layer, with no corresponding molecules in the P-site, can also form the foundation for further adsorption. In this case, the R1\(^{1}\) layer can shift in two distinct geometries with respect to the T-layer. We denote them as A-pattern shift and B-pattern shift, each of which exists in three-fold symmetry with respect to a given T-site fullerene, as shown in Figure 2f. Our calculations support this observation and show that A- and B-shifts are stable structures with the
binding energy of the R1 fullerene calculated as $E_A = -0.21 \text{ eV}$ and $E_B = -0.25 \text{ eV}$ respectively (Figure S13 and Table S1). The DFT optimized structure of the A-pattern shift is presented in Figure 2g. When full domains of R1 fullerene linearly shift in the same direction (A- or B-pattern), we denote this collective assembly as a parallel-shift (see Figure S2). The R1 pattern layer also has the same geometry (Figure 2b,c). Through a combination of distances measured from STM images and geometrical considerations, we find that the shift distance of the R1 layer relative to the given T-layer fullerene is 0.43 nm, which is the half-length of the hexagonal edge, as shown in Figure S1. This is consistent with our calculation result (0.42 nm). However, the observation of shift structures runs counter to Kitaigorodskii’s close-packing principles,(52) since the R1 layer adsorption site is not the three-fold center described by the T-layer C60, which is the enthalpically favored template-defined close-packed structure, with a binding energy of $-0.73 \text{ eV}$ (A-close packing, see Figure S13 and Table S1). We attribute the observed shift trapped R1 C60 motif to the effect of co-adsorption of solvent molecules associated with the growth process, which we explain in detail in Section 2.2.

Figure 3a shows a film where the R1 layer exhibits predominantly a parallel shift. However, another collective adsorption geometry is also possible: The R1 layer can be rotated relative to the T-layer, forming a domain with a flower-like appearance (moire pattern, Figure 3b), referred to as a rotated-shift alignment (see Figure S2). The R1 lattice and T-layer lattice are rotated by $27 \pm 1^\circ$ with respect to one another, and the schematic is given in Figure 3c. The rotation can be interpreted according to the three-fold symmetry of the shift behavior of an R1 fullerene (Figure 2f). Surrounding the rotation center, three R1 fullerenes move clockwise by a distance of half-length of a hexagonal edge, leading to a $30^\circ$ rotation of the R1 lattice with respect to the T layer (Figure 3d). The effect of stacking the rotated-shift R1 layer and T-site layer gives rise to a flower-like appearance in STM images, which can be attributed to the influence of the moiré pattern superlattice on the electronic properties probed by STM.(53)
constrained by the rotated R1 lattice. The rotated shift lattice does not perfectly match the parallel shift lattice. The local trade-off between the preference for binding sites on the T layer and the constraint of the rotated R1 lattice results in a positioning offset of the C60 molecules from one another along the R1 high-symmetry directions, creating a zigzag appearance (see blue dashed line in Figure 3b). Compared with the parallel-shift, the strain introduced by rotated-alignment seems to make this architecture energetically less favorable, consistent with Figure 3a where parallel-shift is dominant. Typically, the area of a rotated-shift domain is less than one unit cell of the superlattice of the moiré pattern (Figure S5).

**Trilayer Structures with T-Site as Bottom Layer**

For the case where the R1 shift is parallel, we observed another layer superimposed on top of the R1 layer, denoted as the raised second layer R2, which together with the R1 and T layers forms a triple-layer structure, as shown in Figure 4a. In this architecture, the R2 fullerenes adsorb in the three-fold hollow site formed by R1 fullerenes, creating the close-packed structure (Figure 4c).

Figure 4. (a) STM image collected at heptanoic acid/HOPG interface showing multiple crystallization geometries for three layer structures. Tunnelling conditions: $V = -800$ mV, $I = 200$ pA. Image dimensions: $17.3 \times 17.3$ nm$^2$. (b) The schematic of (a). (c) The schematic showing position of the R2 layer relative to the R1 layer. (d) The DFT optimized geometries of A-FCC and A-HCP. Schematic showing the positions of C60 in the T layer (bottom), R1 layer (middle), and R2 layer (top) relative to each other for an R1 layer with A-pattern shift (e) and B-pattern shift (f).

C60 molecules of R1 and R2 do not occupy the exact positions defined in a template-defined close-packed model due to the shift in the R1 layer. Using the COF-1 host template and T-layer as a reference, the parallel-shift of R1 will give two possible positions for molecules in the R2 layer. In Figure 4e, a parallel-shift in A pattern positions an R2 layer C60 nearly above a T-layer C60, defining a structure that we denote as A-HCP, and another occupied position nearly above an empty site in the T-layer, defining the A-FCC structure. A similar nomenclature can be assigned for the B pattern shift, shown in Figure 4f. R2 molecules in A-FCC and B-FCC occupy the same position with respect to the reference (T-site/COF-1) layer, although the structures themselves are non-identical due to the geometry of the R1 layer. In Figure 4b, the A pattern shift and B pattern shift are separated by a white dashed line, and the black dashed box shows the alignment of A-FCC and B-FCC. Our calculations suggest that each fullerene in R2 has an adsorption energy of $\sim -0.6$ eV (see Table S1), and the corresponding optimized geometries are given in Figures 4d and S14.

**Identification of the Solvent Co-Adsorption Effect**

The structural analysis above suggests that R1 C60 molecules, which adsorb in the less-dense shift motifs instead of template-defined close-packing, lead to the formation of this diverse array of
polymorphic structures. Using heptanoic acid as solvent, we never observed the R1 template-defined close-packed structure (the three-fold hollow site described by T layer), despite the thermodynamic advantage it offers.

There are two primary effects that could help to favor shifting, rather than close-packing, in R1 layer C_{60}: electrostatics(54) or a solvent effect.(4) To explore the electrostatic effects, we performed Bader charge analysis of the DFT simulated structures. These calculations show that the charge transferred between the T-site and the shift R1 C_{60} is negligible and that the charge distribution of the R1 shift C_{60} is essentially the same as that of a free C_{60} (see Table S2). This is consistent with our calculated energies for the binding between the shift R1 C_{60} and the corresponding T-site fullerene, which are essentially identical whether the fullerene dimer is calculated in the presence or absence of the COF-1/graphene bilayer substrate (~ $-0.2$ eV, see Table S1). These results indicate that the shift R1 C_{60} molecules are stabilized through vdw interactions with the underlying T-site fullerene, ruling out the anisotropic electrostatic effects potentially caused by the presence of the substrate.(25, 55, 56)

In Figure 5a, some smaller bright spots are visible within the T layer. The size of these features (~0.39 nm) is consistent with previous observations of upright heptanoic acid (~0.35 nm),(57) suggesting the possibility of co-adsorption of solvent molecules in the interstitial spaces. The position of a small bright feature within one pore is also influenced by the scanning direction of the STM (Figure S4). Hence, we propose that the formation of shifted R1 C_{60} can be attributed to the co-adsorption of heptanoic acid in the void spaces between C_{60} molecules in the T layer (Table S4 and Figure 5b).(4) Heptanoic acid molecules are known to orient with their carboxyl groups pointed toward the surface and their alkyl chains pointing out of the surface (Table S3 and Figure S15; the chains are likely to be disordered.(57) Heptanoic acid molecules can also orient with their carboxyl groups upward, forming a dimer with another solvent molecule.(58) Since the length of heptanoic acid (~1.0 nm for monomer and 2.1 nm for dimer) is comparable with (bigger than) the diameter of C_{60}, the protruding alkyl chains would prevent the R1 C_{60} from adsorbing in a template-defined close-packed motif (Figure S16). In STM images, the arrangement of co-adsorbed alkylated solvent molecules typically cannot be clearly resolved in 2D,(36, 37, 59) much less in our case of co-adsorption in 3D space. Thus, no conclusion can be drawn about the precise adsorption arrangement or conformation of the solvent molecules in the gaps between C_{60} molecules. However, even in the absence of a detailed understanding of the adsorption geometry, DFT calculations in which heptanoic acid molecules have been added to the unit cells of shift-structure architectures suggest that the presence of the incorporated solvent molecules stabilizes the shift structures (see Table S4).

Figure 5. (a) STM image showing the co-adsorption of heptanoic acid and T-layer C_{60} collected at the heptanoic acid/HOPG interface. Tunnelling conditions: $V = -1000$ mV, $I = 50$ pA. Image dimensions: 12 x 12 nm$^2$. The hexagonal lattice represents the COF-1 template. A single missing C_{60} is marked by a large black open circle. The features at the bottom of missing C_{60} site are assigned as COF-1 template. Three small bright spots assigned as solvent molecules are marked by small black open circles; similar adsorption occurs throughout the lattice, but has not been indicated to allow clearer visualization of the contrast modulation associated with these features.
One site without this small bright feature is marked by a black arrow. (b) Optimized structure of T-layer C_{60} with co-adsorption of heptanoic acid at both P-site and T-site (see section 5-v, SI). The T-site heptanoic acid molecules appear at each of the three boroxine rings in the COF-1 template. Only one P-site adsorbed heptanoic acid appears per pore, consistent with the slightly off-center adsorption of the T-site C_{60} molecule. For a better illustration of the model matching with the experimental data, scheme (b) has been modified from the actual DFT data by taking off the features missing from the STM image (a). (c) STM image collected at the supernatant (TCB)/HOPG interface. Image dimensions: 9.6 × 5.4 nm². Tunnelling conditions: \( V = -1000 \, \text{mV}, I = 50 \, \text{pA} \). Here, R1 C_{60} adsorbs in a template-defined close-packed geometry. (d) Schematic of (c) with TCB molecules in the pores of the COF-1 template.

**Control Experiment: C_{60} Self-Assembly at TCB/HOPG Interface**

To test the solvent co-adsorption hypothesis, we performed the same experiment using a different solvent. Instead of heptanoic acid, we applied the supernatant of C_{60} in TCB, a planar aromatic solvent without alkyl chains, to a prefabricated COF-1 monolayer. Based on our previous work, we expect the TCB to adsorb flat in the COF-1 pores.(24) Using TCB as solvent, we obtained the enthalpically favored template-defined close-packed motif of R1 C_{60}, as shown in Figure 5c. The moiré pattern formed by rotated-shift was not observed, indicating the absence of the R1 shift structure. Moreover, the C_{60} film in TCB is less stable under STM scanning than C_{60} films in heptanoic acid, as shown in Figure S8. Based on the energetics of the fullerenes alone, this observation is counterintuitive, since the template-defined close-packed R1 C_{60} is more stable than shift R1 C_{60} (Figure S13). However, taking into account the co-adsorption of solvent molecules, this observation is consistent with the increased stability of the fullerene layer due to interactions with standing heptanoic acid molecules (Table S4 and Figure S16). The planar, pore-confined TCB cannot interact with raised layers and therefore offers no stabilization.

**Solvent Co-Adsorption Leading to Polymorphism**

We suggest that the co-adsorption of solvent molecules is responsible for the observed polymorphism: Co-adsorbed heptanoic acid sterically inhibits the formation of the close-packed fullerene structure, which is instead allowed by the smaller planar TCB solvent molecules. Without the COF-1 template, C_{60} molecules crystallize into a standard-FCC C_{60} close-packed crystal on HOPG, rather than forming pseudopolymorphic phases incorporating heptanoic acid (see Figure S3).(60-62) This suggests that the co-adsorption of solvent molecules in the C_{60} film is driven by the template. Solvent co-adsorption can occur because the template-induced packing creates solvent-sized void spaces between C_{60} molecules. This is different from previous investigations, where polymorphism was driven by solvent co-adsorption through stronger solute–solvent interactions, such as hydrogen bonds, or through solvent-surface interactions.(4, 6, 36, 38, 63)

**Additional Solvent Effects on Film Packing and Morphology**

**Thermodynamics**

Besides the co-adsorption effect, the properties of solvents, such as polarity and solvophobic effect, can also influence the self-assembled structures through an environmental change for the C_{60} molecules. Although the dielectric constants of heptanoic acid (3.04) and TCB (2.24) are different, we do not expect this to affect fullerene assembly, since solvent polarity mainly influences molecular self-assembly stabilized through hydrogen bonding or dipole–dipole interaction by changing the microenvironment of adsorbates.(4, 36, 39, 40) Solvophobic effects may also play a role in this case since we have polar solvent and nonpolar solute. A nonpolar solute has a stronger propensity to form a close-packed structure in more polar solvents, to reduce the interface between them.(4) However, here the close-packed structure is obtained in a
less polar solvent, which does not follow this trend, and precludes solvophobicity as a contributing effect.

**Kinetic Effects on the Packing Motif**

Kinetic effects are also known to lead to polymorphism.\(^{(12, 41)}\) It is reasonable to assume that the R1 shift structure is kinetically favored with respect to the template-defined close-packed structure. According to Ostwald’s law of stages,\(^{(64)}\) if several states exist, the state initially adopted will not be the most stable, but will instead be the state nearest to the original state in free energy. A rapid adsorption rate (i.e., the number of molecules adsorbing from the liquid onto the surface per unit of area and time) of C\(_{60}\) may lead to the shift adsorption R1 C\(_{60}\), because the system is trapped in a higher-energy state.\(^{(41)}\) However, the TCB supernatant, which contains a higher concentration of C\(_{60}\) than heptanoic acid,\(^{(65)}\) should produce a faster adsorption rate than a heptanoic acid solution and could therefore be expected to give rise to shifted adsorption, which runs counter to our experimental observation of the R1 template-defined close-packed structure. Therefore, the adsorption-rate related kinetic trapping of the polymorph can also be ruled out.

**Kinetic Effects on the Morphologies of C\(_{60}\) Films**

Although kinetic effects do not account for the observed polymorphism, they have a discernible effect on the morphology of the film. From the heptanoic acid supernatant, C\(_{60}\) molecules have a tendency to form large domains on the COF-1 template, with domain boundaries occurring as a consequence of the domain structure of the COF-1 monolayer (Figure 6a).\(^{(51)}\) However, C\(_{60}\) molecules adsorbed from the TCB supernatant are confined in small clusters (see Figures 6b and S8). A simple size distribution analysis of C\(_{60}\) domains in Figure 6b indicates an exponential decay relationship between the number of domains and their sizes, as shown in Figure 6c, suggesting that the growth from TCB supernatant is consistent with a percolation growth model.\(^{(66)}\) Anecdotally, STM images with low coverage of C\(_{60}\) on COF-1 were much more frequently obtained in TCB than that in heptanoic acid (Figure S9). This may suggest a lower growth rate, \(R_G\), in the TCB system. We can treat the attachment of one C\(_{60}\) to a pre-existing nucleate as a monomolecular process. Following first-order chemical kinetics, \(R_G\) is proportional to \([\exp(\Delta \mu/k_B T) - 1]\),\(^{(67)}\) where \(\Delta \mu = \mu_{\text{solution}} - \mu_{\text{crystal}}\) is the difference in chemical potential of the crystallizing species, \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature. Since we used supernatant C\(_{60}\) in both heptanoic acid and TCB, the solution is equilibrated with the precipitation of C\(_{60}\), and \(\mu_{\text{heptanoic acid-solution}}\) can be assumed to be roughly equal to \(\mu_{\text{TCB-solution}}\) during the growth process. Under this assumption, the higher rate of growth, \(R_G(\text{heptanoic acid})\), can be ascribed to the lower \(\mu_{\text{heptanoic acid-crystal}}\). This is consistent with our expectation and observation stated above, i.e., the co-adsorption of heptanoic acid stabilizes C\(_{60}\) crystallization.

Figure 6. STM images collected from supernatant solutions of C\(_{60}\). (a) STM image at the heptanoic acid supernatant/HOPG interface. Tunnelling conditions: \(V = -1200\) mV, \(I = 50\) pA. Image dimensions: 60 × 60 nm\(^2\). (b) STM image at the TCB supernatant/HOPG interface. Tunnelling conditions: \(I = 100\) pA, \(V = -800\) mV. Image dimensions: 60 × 60 nm\(^2\). (c) Domain size distribution
of (b). The coverage \((P)\) of \(C_{60}\) in STM image is 55.4%. The full range distribution is available in Figure S9.

This morphological observation is similar to the competitive adsorption of two different analytes from binary mixture solutions,(68) and the same argument can be applied here. The different sizes of the domains suggest significant differences in the nucleation rate and growth rate of each morphology. The analytical model can be defined as a ratio \(r = R_G/R_N\) with the growth rate, \(R_G\), and nucleation rate, \(R_N\). A large ratio \(r\) gives rise to the formation of well-ordered domains extending over large areas, as observed for heptanoic acid. On the contrary, a small ratio \(r\) means that domains nucleate quickly yet grow slowly, yielding numerous small domains; this is consistent with the morphology of COF-templated \(C_{60}\) in TCB. As we described above, the higher solubility of \(C_{60}\) in TCB suggests the relation: \(R_N(TCB) > R_N(\text{heptanoic acid})\). In addition, the co-adsorption with different solvent molecules gives the relation: \(R_G(\text{heptanoic acid}) > R_G(TCB)\). Together these indicate that \(r(\text{heptanoic acid}) > r(TCB)\), which is consistent with our morphological observations.

Conclusions and Perspectives
Monolayer COF-1 films can induce the self-assembly of fullerene into multiple layer structures at the solution/solid interface. The template-defined packing, which deviates from standard close packing, depends on the solvent for the fullerene molecules: A template-defined close-packing motif is achieved using TCB as solvent, whereas lower-density quasi-close-packed polymorphs are observed when using heptanoic acid as solvent. The solvent-dependent polymorphism and morphologies can be described in terms of a template-driven solvent co-adsorption effect. The results presented here highlight the important role of the solvent not only in influencing 2D self-assembly but also in defining 3D architectures. Through a judicious combination of solvent and template, (pseudo)polymorphic films can be formed with packing geometries that have not been observed under other conditions. This suggests a pathway toward using the combination of 2D template and solvent effects to control molecular self-assembly precisely into the third dimension, even in the absence of directional solute–solute or solute–solvent interactions. The combination of two independent tuning parameters suggests an improved control over phase behaviors, which could give rise to previously unobserved phases in a range of related advanced materials.(69)

Experimental Section

Sample Preparation and STM Characterization
Monolayer COF-1 on HOPG was formed following procedures described previously.(48, 49) 1.0 mg and 1.4 mg of 1,4-benzenediboronic acid (BDBA, Tokyo Chemical Industry Co. Ltd.) was added to 1.5 mL heptanoic acid (99%, Sigma-Aldrich)(50) and 1.2 mL 1,2,4-trichlorobenzene (TCB, 99%, Sigma-Aldrich),(24) respectively. This step was followed by sonication for \(\sim 30\) min which produced whitish suspensions. Ten \(\mu\)L of BDBA suspension was dropped onto freshly cleaved HOPG (Structure Probe International, grade SPI-1 or SPI-2) and placed into a reactor with a volume of \(\sim 16\) mL. 130 \(\mu\)L of deionized water was added to the bottom of the reactor, and a valve to atmosphere was left slightly open to maintain an open system. The entire reactor was placed in an oven preheated to 125 °C and left for 60 min. After thermal treatment, the reactor was taken out of the oven and allowed to cool down for at least 20 min before the samples were removed.

Following the confirmation of monolayer COF-1 on the HOPG surface, 10 \(\mu\)L of a known concentration solution of fullerene (99.5%, Sigma-Aldrich) in heptanoic acid or TCB was applied onto the substrates prepared with precursors in heptanoic acid or TCB. Subsequently, the samples were characterized by STM at the solution/solid interface.

STM was performed at room temperature at the liquid/solid interface, using a Digital Instruments STM equipped with a Nanoscope IIIa controller. Tips were cut from a Pt0.8Ir0.2 wire (Nanoscience Instruments). Bias voltages are reported with respect to the STM tip. STM images were calibrated
with COF-1 lattice parameter (1.476 nm) using the free WSxM software. Images were smoothed using Gwyddion software.

**Computational Details**

Density functional theory (DFT) calculations based on a slab model were performed with the Vienna ab Initio Simulation Package (VASP) installed at the SciNet supercomputer clusters of Compute Canada. DFT calculations were made using the Perdew–Burke–Ernzerhof (PBE) approximation of the exchange–correlation potential, the projector augmented wave (PAW) method, and a plane-wave basis set. Final calculations were performed using zero-damping DFT-D2 and DFT-D3 methods of Grimme, a correction which takes into account vdw for potential energies and dispersion effects via a semiempirical approach, yielding more accurate geometries of the adsorption structures compared to those obtained from uncorrected DFT calculations. Unless stated otherwise, all the calculations were first performed at the gamma point with an energy cut off of 450 eV, followed by a higher accuracy level using 5 irreducible k-points (3 × 3 × 1 k-points) with the cut off energy of 750 eV, until the net force on each atom was <0.02 eV/Å and the energy change between the two steps was smaller than 0.00001 eV. Except for the bottom layer of graphene, all of the atoms, including top layer of graphene, COF-1, and C60 molecular layers, were relaxed during the simulation.

Bader analysis on different optimized structures was performed, and the charge distribution of C60 at different growth layers was compared with a free C60. More details are given in the SI.

**Notes**

The authors declare no competing financial interest.

**Acknowledgment**

D.C. thanks Gianluca Galeotti and Fabrizio De Marchi for sharing experience in image analysis using WSxM software and Catalin Harnagea for maintenance of the STM instrument. M.E. thanks Professor Graeme Henkelman for sharing his expertise in performing the Bader Charge Analysis calculation and providing the code. Computations were performed on the tcs supercomputer at the SciNet HPC Consortium, funded by the Canada Foundation for Innovation under Compute Canada, the Government of Ontario, Ontario Research Fund – Research Excellence, and the University of Toronto. J.M.M. acknowledges funding support from the Australian Research Council (DE170101170). F.R. is grateful to the Canada Research Chair for funding and partial salary support and also acknowledges NSERC for a Discovery Grant, Sichuan province for a 1000 talent short term award and the Government of China for a short term Chang Jiang scholar award.

**References**

1. Li, H.; Giri, G.; Tok, J. B.-H.; Bao, Z. MRS Bull. **2013**, 38, 34−42 DOI: 10.1557/mrs.2012.309

2. Kwon, O.-P.; Jazbinsek, M.; Yun, H.; Seo, J.-I.; Kim, E.-M.; Lee, Y.-S.; Günter, P. Cryst. Growth Des. **2008**, 8, 4021−4025 DOI: 10.1021/cg800218u

3. Rodríguez-Spong, B.; Price, C. P.; Jayasankar, A.; Matzger, A. J.; Rodríguez-Hornedo, N. r. Adv. Drug Delivery Rev. **2004**, 56, 241−274 DOI: 10.1016/j.addr.2003.10.005

4. Yang, Y.; Wang, C. Curr. Opin. Colloid Interface Sci. **2009**, 14, 135−147 DOI: 10.1016/j.cocis.2008.10.002
5. Bernardes, C. E.; Lopes, M. L. M.; Ascenso, J. R.; da Piedade, M. E. M. Cryst. Growth Des. 2014, 14, 5436–5441 DOI: 10.1021/cg500609g

6. Chen, J.; Trout, B. L. J. Phys. Chem. B 2008, 112, 7794–7802 DOI: 10.1021/jp7106582

7. Blunt, M. O.; Adisoejoso, J.; Tahara, K.; Katayama, K.; Van der Auweraer, M.; Tobe, Y.; De Feyter, S. J. Am. Chem. Soc. 2013, 135, 12068–12075 DOI: 10.1021/ja405585s

8. Hiremath, R.; Basile, J. A.; Varney, S. W.; Swift, J. A. J. Am. Chem. Soc. 2005, 127, 18321–18327 DOI: 10.1021/ja0565119

9. Rochford, L. A.; Jones, T. S.; Nielsen, C. B. J. Phys. Chem. Lett. 2016, 7, 3487–3490 DOI: 10.1021/acs.jpclett.6b01656

10. Cicoira, F.; Rosei, F. Surf. Sci. 2006, 600, 1–5 DOI: 10.1016/j.susc.2005.10.063

11. Ahn, S.; Matzger, A. J. J. Am. Chem. Soc. 2012, 134, 3208–3214 DOI: 10.1021/ja210933h

12. Ahn, S.; Matzger, A. J. J. Am. Chem. Soc. 2010, 132, 11364–11371 DOI: 10.1021/ja105039s

13. Lu, B.; Iimori, T.; Sakamoto, K.; Nakatsuji, K.; Rosei, F.; Komori, F. J. Phys. Chem. C 2008, 112, 10187–10192 DOI: 10.1021/jp800351z

14. Koepf, M.; Chérioux, F.; Wytko, J. A.; Weiss, J. Coord. Chem. Rev. 2012, 256, 2872–2892 DOI: 10.1016/j.ccr.2012.05.039

15. Barth, J. V.; Costantini, G.; Kern, K. Nature 2005, 437, 671–679 DOI: 10.1038/nature04166

16. Yang, J.; Yan, D.; Jones, T. S. Chem. Rev. 2015, 115, 5570–5603 DOI: 10.1021/acs.chemrev.5b00142

17. Aizenberg, J.; Black, A. J.; Whitesides, G. M. Nature 1999, 398, 495–498 DOI: 10.1038/19047

18. Fu, C.; Lin, H.-p.; Macleod, J. M.; Krayev, A.; Rosei, F.; Perepichka, D. F. Chem. Mater. 2016, 28, 951–961 DOI: 10.1021/acs.chemmater.5b04706

19. Korolkov, V.; Baldoni, M.; Watanabe, K.; Taniguchi, T.; Besley, E.; Beton, P. Nat. Chem. 2017, DOI: 10.1038/nchem.2824

20. Teyssandier, J.; De Feyter, S.; Mali, K. S. Chem. Commun. 2016, 52, 11465–11487 DOI: 10.1039/C6CC05256H

21. Cicoira, F.; Santato, C.; Rosei, F. Top. Curr. Chem. 2008, 285, 203–267 DOI: 10.1007/128_2008_2

22. Stepanow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X.; Cai, C.; Barth, J. V.; Kern, K. Nat. Mater. 2004, 3, 229–233 DOI: 10.1038/nmat1088

23. MacLeod, J.; Ivasenko, O.; Perepichka, D.; Rosei, F. Nanotechnology 2007, 18, 424031 DOI: 10.1088/0957-4484/18/42/424031
24. Cui, D.; MacLeod, J.; Ebrahimi, M.; Rosei, F. CrystEngComm 2017, 19, 4927–4932 DOI: 10.1039/C7CE00263G

25. Yoshimoto, S.; Tsutsumi, E.; Narita, R.; Murata, Y.; Murata, M.; Fujiwara, K.; Komatsu, K.; Ito, O.; Itaya, K. J. Am. Chem. Soc. 2007, 129, 4366–4376 DOI: 10.1021/ja0684848

26. Li, J.; Wieghold, S.; Öner, M. A.; Simon, P.; Hauf, M. V.; Margapoti, E.; Garrido, J. A.; Esch, F.; Palma, C.-A.; Barth, J. V. Nano Lett. 2014, 14, 4486–4492 DOI: 10.1021/nl501452s

27. Ivasenko, O.; MacLeod, J. M.; Chernichenko, K. Y.; Balenkova, E. S.; Shpanchenko, R. V.; Nenajdenko, V. G.; Rosei, F.; Perepichka, D. F. Chem. Commun. 2009, 1192–1194 DOI: 10.1039/b819532c

28. Ciesielski, A.; Cadeddu, A.; Palma, C.-A.; Gorczyński, A.; Patrońak, V.; Cecchini, M.; Samorì, P. Nanoscale 2011, 3, 4125–4129 DOI: 10.1039/c1nr10485c

29. Theobald, J. A.; Oxtoby, N. S.; Phillips, M. A.; Champness, N. R.; Beton, P. H. Nature 2003, 424, 1029–1031 DOI: 10.1038/nature01915

30. Wei, Y.; Reutt-Robey, J. E. J. Am. Chem. Soc. 2011, 133, 15232–15235 DOI: 10.1021/ja206175c

31. González, J. D. C.; Iyoda, M.; Rabe, J. P. Nat. Commun. 2017, 8, 14717 DOI: 10.1038/ncomms14717

32. Blunt, M. O.; Russell, J. C.; del Carmen Gimenez-Lopez, M.; Taleb, N.; Lin, X.; Schröder, M.; Champness, N. R.; Beton, P. H. Nat. Chem. 2011, 3, 74–78 DOI: 10.1038/nchem.901

33. De Feyter, S. Nat. Chem. 2011, 3, 14–15 DOI: 10.1038/nchem.938

34. Mezour, M. A.; Choueiri, R. M.; Lukoyanova, O.; Lennox, R. B.; Perepichka, D. F. Nanoscale 2016, 8, 16955–16962 DOI: 10.1039/C6NR04115A

35. Samorí, P.; Severin, N.; Simpson, C. D.; Müller, K.; Rabe, J. P. J. Am. Chem. Soc. 2002, 124, 9454–9457 DOI: 10.1021/ja020323q

36. Mamdouh, W.; Uji-i, H.; Ladislaw, J. S.; Dulcey, A. E.; Percec, V.; De Schryver, F. C.; De Feyter, S. J. Am. Chem. Soc. 2006, 128, 317–325 DOI: 10.1021/ja056175w

37. Sirtl, T.; Song, W.; Eder, G.; Neogi, S.; Schmittel, M.; Heckl, W. M.; Lackinger, M. ACS Nano 2013, 7, 6711–6718 DOI: 10.1021/nn4014577

38. Nangia, A.; Desiraju, G. R. Chem. Commun. 1999, 605–606 DOI: 10.1039/a809755k

39. Lackinger, M.; Griessl, S.; Heckl, W. M.; Hietschold, M.; Flynn, G. W. Langmuir 2005, 21, 4984–4988 DOI: 10.1021/la0467640

40. Kampschulte, L.; Lackinger, M.; Maier, A.-K.; Kishore, R. S.; Griessl, S.; Schmittel, M.; Heckl, W. M. J. Phys. Chem. B 2006, 110, 10829–10836 DOI: 10.1021/jp057553m
59. Tahara, K.; Furukawa, S.; Uji-i, H.; Uchino, T.; Ichikawa, T.; Zhang, J.; Mamdouh, W.; Sonoda, M.; De Schryver, F. C.; De Feyter, S. J. Am. Chem. Soc. 2006, 128, 16613–16625 DOI: 10.1021/ja0655441

60. Shin, H. S.; Yoon, S. M.; Tang, Q.; Chon, B.; Joo, T.; Choi, H. C. Angew. Chem., Int. Ed. 2008, 47, 693–696 DOI: 10.1002/anie.200704182

61. Suto, S.; Kasuya, A.; Hu, C.-W.; Wawro, A.; Sakamoto, K.; Goto, T.; Nishina, Y. Thin Solid Films 1996, 281, 602–605 DOI: 10.1016/0040-6090(96)08596-3

62. Rey, C.; Garcia-Rodeja, J.; Gallego, L.; Alonso, J. Phys. Rev. B: Condens. Matter Mater. Phys. 1997, 55, 7190 DOI: 10.1103/PhysRevB.55.7190

63. Gatti, R.; MacLeod, J. M.; Lipton-Duffin, J. A.; Moiseev, A. G.; Perepichka, D. F.; Rosei, F. J. Phys. Chem. C 2014, 118, 25505–25516 DOI: 10.1021/jp507729w

64. Davey, R.; Blagden, N.; Potts, G.; Docherty, R. J. Am. Chem. Soc. 1997, 119, 1767–1772 DOI: 10.1021/ja9626345

65. Semenov, K. N.; Charykov, N. A.; Keskinov, V. A.; Piartman, A. K.; Blokhin, A. A.; Kopyrin, A. A. J. Chem. Eng. Data 2010, 55, 13–36 DOI: 10.1021/je900296s

66. Evans, J.; Thiel, P.; Bartelt, M. C. Surf. Sci. Rep. 2006, 61, 1–128 DOI: 10.1016/j.surfrep.2005.08.004

67. Vekilov, P. G. Cryst. Growth Des. 2007, 7, 2796–2810 DOI: 10.1021/cg070427i

68. Baker, R. T.; Mougous, J. D.; Brackley, A.; Patrick, D. L. Langmuir 1999, 15, 4884–4891 DOI: 10.1021/la981658h

69. Yethiraj, A.; van Blaaderen, A. Nature 2003, 421, 513 DOI: 10.1038/nature01328

70. Horcas, I.; Fernández, R.; Gomez-Rodriguez, J.; Colchero, J.; Gómez-Herrero, J.; Baro, A. Rev. Sci. Instrum. 2007, 78, 013705 DOI: 10.1063/1.2432410

71. Nečas, D.; Klapetek, P. Open Physics 2012, 10, 181–188 DOI: 10.2478/s11534-011-0096-2

72. Kresse, G.; Hafner, J. Phys. Rev. B: Condens. Matter Mater. Phys. 1993, 47, 558 DOI: 10.1103/PhysRevB.47.558

73. Kresse, G.; Furthmüller, J. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169 DOI: 10.1103/PhysRevB.54.11169

74. Loken, C.; Gruner, D.; Groer, L.; Peltier, R.; Bunn, N.; Craig, M.; Henriques, T.; Dempsey, J.; Yu, C.-H.; ChenJ. Phys. Conf. Ser. 2010, 256, 012026 DOI: 10.1088/1742-6596/256/1/012026

75. Perdew, J. P.; Ernzerhof, M.; Burke, K. J. Chem. Phys. 1996, 105, 9982–9985 DOI: 10.1063/1.472933

76. Blöchl, P. E. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953 DOI: 10.1103/PhysRevB.50.17953
77. Kresse, G.; Joubert, D. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 1758 DOI: 10.1103/PhysRevB.59.1758

78. Grimme, S. J. Comput. Chem. 2006, 27, 1787–1799 DOI: 10.1002/jcc.20495

79. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. J. Chem. Phys. 2010, 132, 154104 DOI: 10.1063/1.3382344

80. Henkelman, G.; Arnaldsson, A.; Jónsson, H. Comput. Mater. Sci. 2006, 36, 354–360 DOI: 10.1016/j.commatsci.2005.04.010

81. Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G. J. Comput. Chem. 2007, 28, 899–908 DOI: 10.1002/jcc.20575

82. Tang, W.; Sanville, E.; Henkelman, G. J. Phys.: Condens. Matter 2009, 21, 084204 DOI: 10.1088/0953-8984/21/8/084204

83. Yu, M.; Trinkle, D. R. J. Chem. Phys. 2011, 134, 064111 DOI: 10.1063/1.3553716