Planar Anchoring of C$_{70}$ Liquid Crystals Using a Covalent Organic Framework Template

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Abstract

The surface-induced anchoring effect is a well-developed technique to control the growth of liquid crystals (LCs). Nevertheless, a defined nanometer-scale template has never been used to induce the anchored growth of LCs with molecular building units. Scanning tunneling microscopy results at the solid/liquid interface reveal that a 2D covalent organic framework (COF-1) can offer an anchoring effect to template C$_{70}$ molecules into forming several LC mesophases, which cannot be obtained under other conditions. Through comparison with the C$_{60}$ system, a stepwise breakdown in ordering of C$_{70}$ LC is observed. The process is described in terms of the effects of molecular anisotropy on the epitaxial growth of molecular crystals. The results suggest that using a surface-confined template to anchor the initial layer of LC molecules can be a modular and potentially broadly applicable approach for organizing molecular mesogens into LCs.

Introduction

The control of liquid crystal (LC) phases is a topic of considerable interest for fundamental studies as well as for practical applications.[1] By designating boundary conditions, such as the LC/surface interaction, the growth of LC molecules can be easily controlled. For example, through surface treatment and topographic confinement, known as surface anchoring effects, the ordering and orientation of various types of LC phases can be directed over a range of scales.[2] The use of epitaxial interaction with a substrate can provide an anchoring effect to direct the growth of LCs out of plane. Various substrates with different properties have been
used to modify the surface anchoring conditions at the micrometer scale.[3, 4] Similar effects have also been observed at the nanometer scale. Some organic molecules can be confined on the intrinsic lattice of 2D single-crystalline substrates, such as MoS$_2$ and highly ordered pyrolytic graphite (HOPG), forming LC monolayers that are distinct from their bulk counterparts.[5, 6] Tailoring the surface is an obvious and straightforward approach to defining the anchoring effects through interactions and surface topography.[7-12] For example, the orientation of LC materials can be constrained by using topographical templates of aligned double-stranded DNA molecules.[13] However, modifying the surface with a defined nanometer-scale template to induce the anchored growth of LC molecules is still an unexplored approach.

Here, we report the use of a host template to induce the growth of an ellipsoid molecule, C$_{70}$, into several mesophases that have not been observed under other conditions. Using a template to control guest molecular deposition and layer structure is a well-established approach in surface science.[14-19] However, this kind of template-guided growth is rare in 2D or 3D crystalline engineering.[14, 15, 20-24] In particular, the introduction of anchoring conditions by a monolayer host template has not yet been explored in LC growth. C$_{70}$ molecules exhibit an elliptical shape and anisotropic polarizability.[25, 26] Although this anisotropy can result in the disruption of ordering and the formation of LC at the micrometer scale,[27-30] C$_{70}$ molecules can only form crystals under certain conditions of pressure and temperature.[31] This is because, apart from the shape of mesogens, the formation of an LC is also related to the volume fraction.[32, 33] Compared to colloidal particles, the large surface-to-volume ratio gives rise to a much stronger interaction between nanometer-sized molecular particles, resulting in denser packing and reduced control of the volume fraction.

We used scanning tunneling microscopy (STM) at the solid/liquid interface to image the adsorption of C$_{70}$ molecules on the template defined by a benzenediboronic acid-based covalent organic framework (COF) known as COF-1, dispersed on HOPG. In contrast to traditional spectroscopic techniques that collect spatially averaged information from bulk molecular crystals, STM imaging can offer considerable insights into local effects with sub-molecular resolution.[34-36] We find that the primary structural parameter, the in-plane density of the C$_{70}$ layer, can be effectively modulated by the templated anchoring.[37] Since the ordering between layers is associated with the in-plane density,[33] the modulation of the latter by the COF-1 template can generate a number of distinct multiple-layer structures. Comparison between C$_{60}$ and C$_{70}$ systems enables insight into the effect of nanometer-scale anisotropy on the formation of these architectures.
Results

COF-1 was preprepared on freshly cleaved HOPG following the method of direct on-surface polycondensation.[38] The COF-1 network grows as a $6 \times 6$ epitaxial unit cell on HOPG, giving a lattice parameter of 1.476 nm as shown in Figure 1a.[21] After introducing the C$_{70}$ solution, molecules can be observed in a number of adsorption sites: the top-site (T), defined as adsorbed over boroxine ring; the pore-site (P), defined as adsorbed in pore, and the pore-top bilayer (P-T), defined as co-adsorption of P-site and T-site. The observed architectures are similar to those of C$_{60}$ in COF-1, but with additional distinction of polymorphs based on the molecular anisotropy.[21, 23] The formation of different architectures of C$_{70}$ can be rationalized as arising from kinetic effect. In schematic images, we use different colors of ellipsoids or spheres to represent the geometries of C$_{70}$ molecules in different layers. A legend defining the different adsorption sites and layers for C$_{70}$ molecules is provided in Figure S1 (Supporting Information).

Due to the reduction of symmetry (Figure 1b), the adsorption of C$_{70}$ in COF-1 gives rise to adsorption geometries that are not accessible to the higher symmetry C$_{60}$ molecule. The primary
axis of lying-down C\textsubscript{70} is used to define molecular orientation. The COF-1 lattice is used as crystallographic reference, i.e., the basis vectors in the C\textsubscript{70} crystallographic unit cell are defined by the COF-1 unit cell. Two phases (\(\alpha\) and \(\beta\)) can be identified. We denote a C\textsubscript{70} molecule with its orientation along the zigzag direction of the COF-1 lattice as \(\alpha\) phase (dashed white ellipsoids) and one with its orientation along the armchair direction of the COF-1 lattice as \(\beta\) phase (dashed black ellipsoids). Due to the symmetry of the honeycomb lattice, each phase has three degenerate sub-phases. The \(\alpha\) phase C\textsubscript{70} molecules with orientation along [001\(\overline{0}\)][001\(\overline{0}\)], [1000], and [0100] are assigned as \(\alpha^{-1}\), \(\alpha^{-2}\), and \(\alpha^{-3}\) phases. The \(\beta\) phase C\textsubscript{70} molecules oriented along [11\(\overline{0}\)0], [11\(\overline{0}\)0], [101\(\overline{0}\)0], [101\(\overline{0}\)0], and [011\(\overline{0}\)0] are assigned as \(\beta^{-1}\), \(\beta^{-2}\), and \(\beta^{-3}\) phases, as shown in Figure 1d.

Using the above definitions, we can analyze STM images of C\textsubscript{70} in COF-1. In Figure 2a, T-site C\textsubscript{70} is observed on the left and a P-T bilayer of C\textsubscript{70} is observed on the right. Most of the C\textsubscript{70} molecules adsorbed in T-sites are lying down, with their primary axes parallel to each other, similar to the energetically favored aligned phase for a C\textsubscript{70} monolayer confined on a surface, but with the in-plane density specified by the template lattice.[39, 40] C\textsubscript{70} molecules adsorbed in a standing-up orientation are less common, as was also observed in a previous study of C\textsubscript{70} adsorbed on Cu(111).[41] The preference for lying-down adsorption has also been observed for C\textsubscript{70} adsorbed on other organic molecules.[42] This geometry maximizes the contact interface between the C\textsubscript{70} molecules and the COF-1 template, giving a stronger interaction with the side π surfaces of C\textsubscript{70}. Besides interpreting the bright circles as the standing-up C\textsubscript{70} molecules, we propose that they can also plausibly be interpreted as C\textsubscript{60} impurities (Figure S12, Supporting Information). T-site C\textsubscript{70} molecules adhere to the \(\beta\) phase when adsorbed without a corresponding P-site C\textsubscript{70}, but follow an \(\alpha\) orientation when adsorbed in a P-T bilayer. This difference could be due to the presence of P-site C\textsubscript{70}, which can contribute additional interactions and steric strain on the T-site C\textsubscript{70}.[28] Although the orientation of P-site C\textsubscript{70} cannot be clearly distinguished in Figure 2a, we tentatively assign it as \(\beta^{-1}\) phase for the purposes of the model shown in Figure 2b.
Figure 2  a) STM image of C\textsubscript{70} in COF-1. Image dimensions: 14.0 × 8.5 nm\textsuperscript{2}. Scanning tunneling conditions: \( V = -1200 \text{ mV}, I = 100 \text{ pA} \). b) Schematic representation of (a). The inset COF-1 unit cell in (b) is used to identify molecular orientation. \( \alpha \) and \( \beta \) lying-down C\textsubscript{70} molecules are marked by blue and black dashed ellipsoids, respectively. Standing-up orientation C\textsubscript{70} molecules are marked by a red dashed circle. The corresponding nomenclature for each motif is indicated.

Building up from a T-layer foundation, we term the subsequent adsorbed layer as the raised layer (R). The addition of R-layer C\textsubscript{70} can lead to a hexagonal porous structure (Figure 3a, left). The magnified image (Figure 3f) enables us to observe the orientations of T and R C\textsubscript{70} molecules: the T-layer C\textsubscript{70} adsorbs as \( \beta^{-1} \) phase, and the R-layer as \( \beta^{-2} \) phase. In addition, at domain edges, a T-layer domain with a different orientation (\( \beta^{-2} \) phase) is visible, as shown in the magnified image (Figure 3d,e). This observation is enabled by the removal of two T-site C\textsubscript{70} molecules (black ellipsoids in Figure 3a) by the STM tip, which suggests that the stability of the adsorbed molecules is compromised where the lattice is incomplete.[23] A proposed T-layer model is shown in Figure 3b. The dashed blue line was used to represent the border of two \( \beta \) phases. The phase of the T-layer changes from \( \beta^{-1} \) (left) to \( \beta^{-2} \) (right). A full model of Figure 3a is shown in Figure 3c.

Figure 3  a) STM image showing a COF-1 template with T-layer and R-layer C\textsubscript{70}. Image dimensions: 14 × 14 nm\textsuperscript{2}. Scanning tunneling conditions: \( V = -1000 \text{ mV}, I = 100 \text{ pA} \). The addition of the R-layer C\textsubscript{70} onto a layer comprising T-layer C\textsubscript{70} gives a unique hexagonal porous structure. The regions (d* and f*) marked by squares are magnified in (d) and (f), respectively. b) Partial schematic image prepared according to (a) showing the bottom T-layer. The inset unit cell is used to identify the orientation of the adsorbed molecules. The dashed line is used to distinguish different phases, labeled by corresponding nomenclature. c) The full schematic image corresponding to (a) showing both R-layer and T-layer simultaneously. d) Magnified STM image corresponding to the d* square in (a), taken at a later time. Image dimensions: 6.4 × 6.4 nm\textsuperscript{2}. e) Schematic model of (d). f) Magnified STM image corresponding to the f* square in (a). Image dimensions: 4.1 × 4.1 nm\textsuperscript{2}. g) Proposed model of (f), superimposed by suggested dipoles. The green dashed lines represent attraction and the red dashed lines represent repulsion.

The C\textsubscript{70}/COF-1 system can also exhibit a structural shift between the T and R-layers. Figure 4a shows an image where a small defect region was identified in a lattice of C\textsubscript{70}/COF-1. This allows us to use geometric considerations to identify this lattice as a parallel-shifted R-layer.
A similar shift geometry was observed for C₆₀ and explained by a template-induced solvent co-adsorption effect within the T-layer. The same argument can also be applied for C₇₀ (Figure S5, Supporting Information). We suggest that the T-layer C₇₀ molecules are adsorbed in the β−1 phase and that the R-layer C₇₀ should be assigned an adjusted orientation, which we label as the β−1′ phase. The T-layer β−1 phase can be identified since other T-site orientations (β−2 or β−3) will give a hexagonal porous appearance (Figure 3a). In Figure 3d, the orientation of R-layer C₇₀ is adjusted by an angle of 11 ± 1° with respect to the defined direction of the β−1 phase. Thus, we indicate this rotated orientation as the β−1′ phase.

A P-T bilayer of C₇₀ is also able to form the foundation for crystallization. In the P-T bilayer structure, we labeled the T-site C₇₀ as α-phase and P-site tentatively as β-phase. The growth of an R-layer on the P-T bilayer produces the α-phase orientation, which together with the P-T bilayer forms a trimer, as shown in Figure 5. An image showing the coexistence of hexagonal porous structures and trimeric phase is provided in Figure S4 (Supporting Information). In addition, we also observed that C₇₀ molecules can form two quasi side-by-side contacts (consistent with a Gay–Berne potential; see below) with underlying C₇₀ molecules at the bridge site (Figure 5c). This structure diverges from the shift model (Figure 6). This bridge adsorption can be a new site for R C₇₀, or adsorption site for C₇₀ above the R-layer since we cannot unequivocally identify the bottom layer as T-layer (Figure S11, Supporting Information). Compared with the shift packings,
this arrangement maximizes the coordination number of the upper-layer C\textsubscript{70}, offering favorable intermolecular interactions between the π surfaces of upper and underlying C\textsubscript{70} molecules.[24]

**Figure 5** a) STM image showing the growth of R-layer C\textsubscript{70} fullerenes onto a P-T bilayer. Image dimensions: 7.7 × 7.7 nm\textsuperscript{2}. Tunneling conditions: \(V = -800\) mV, \(I = 150\) pA. A schematic image was superimposed over the region at the bottom right. A trimer is marked by the black open triangle. b) Schematic image of (a). The inset unit cell is used to assign the orientation of the C\textsubscript{70} molecules. c) STM image showing the bridge site adsorption of C\textsubscript{70} molecules. Scanning tunneling parameters: \(V = -1000\) mV, \(I = 30\) pA. Image dimensions: 14.2 × 14.2 nm\textsuperscript{2}.

**Figure 6** a) Geometry of the ideal shifts of C\textsubscript{70} based on the model of C\textsubscript{60}. The red dashed line represents the reflection plane of mirror symmetry. b) Formation of the β−1′ phase with orientational adjustment in the A-shift direction. The red dashed line represents the high symmetry axis along the A-shift direction. c) The proposed schematic potential energy well for C\textsubscript{70} in the A-shift direction. d) Schematic image showing the B-shift with the proposed dipole–dipole interaction. e) The formation of hexagonal porous features with positional and orientational adjustments in the B-shift direction. The red dashed line represents the high symmetry axis along the B-shift direction. f) Schematic of the proposed “Mexican hat” potential for C\textsubscript{70} in the B-shift direction. The red dashed line represents the high symmetry axis as in (e).
Summarizing the phase orientation in different cases, we find that: (i) when solely β-phase T-layer forms the base for crystallization, both porous hexagonal features and parallel shifts maintain the β-phase R-layer; and (ii) when a P-T bilayer forms the base for subsequent crystallization, where the T-layer is α-phase, the R-layer also maintains the α-phase.

Considering the general structures of condensed phases formed by ellipsoid-like molecules, except the nematic phase, the categories of the smectic and soft crystal phases can be evaluated in terms of the degree of order.[33, 37] In our cases, the lying-down orientation of C₇₀ can be categorized as a tilted phase. The packing structures exhibit in-plane periodic order and the periodicity is defined by the COF-1 template. The range of ordering is correlated to the domain size of the template; 2D in-plane ordering can be assigned as long range if the template is large enough. In the out-of-plane direction, since several possibilities for positional order exist, we cannot identify a correlation between layers. Therefore, the crystals formed by template C₇₀ molecules have 2D in-plane long-range ordering accompanied by 1D out-of-plane short-range order. These multiple-layer structures can be regarded as the mesophases of an LC from hexatic phases to soft crystals.[33]

Discussion

In previous work, we have shown that the R1 layer C₆₀ molecule can shift with respect to the given T-layer C₆₀, which exists in threefold symmetry, forming a less-dense molecular packing. The shifted positions were found to be stable states explained by a template-induced solvent coadsorption effect.[23] The same argument can also be applied for C₇₀, where the co-adsorbed solvent molecules are correspondingly observed (Figure S5, Supporting Information). However, C₇₀ molecules create new structural crystallizations that are absent in the C₆₀ molecular crystal. This suggests that, besides the solvent co-adsorption effect, the anisotropy of the molecular building blocks also plays a role in this type of epitaxial growth.

In the C₇₀ case, for flat-lying molecules, the ideal threefold symmetric shift model reduces to a mirror symmetric shift, as shown in Figure 6a. We define the two mirror-reflected shift directions as A-shift and the shift along the mirror plane as B-shift. Although this model partially predicts the adsorbed positions of C₇₀ molecules, it cannot explain the orientational ordering in R-layer C₇₀. Small geometric adjustments were observed in STM observations compared with the ideal shifted model. In the A-shift direction, an orientational change of 11° leads to the formation of the β−1′ phase (Figures 4 and 6b); in the B-shift direction, both positional and orientational change were observed, giving rise to the hexagonal porous structure (Figures 3 and 6e).
These structural adjustments are consistent with the anisotropic shape of C_{70}. Unlike isotropic C_{60}, the anisotropy creates different energetic potential surfaces in A and B-shift directions. The interactions between C_{70} molecules can involve both van der Waals (vdW) and electrostatic dipole–dipole interactions. For the vdW interactions, the potential energy between ellipsoids can be represented by a Gay–Berne potential in different relative orientations.[43] In this potential, side-by-side and end-to-end orientations have different potential functions with respect to intercentre distance.[28] In the ideal shift model, the R-layer C_{70} forms a quasi-side-by-side orientation in the A-shift direction and end-to-end orientation in the B-shift direction with respect to the given T-layer C_{70}. The interactions from neighboring T-layer C_{70} molecules will impact the R-layer C_{70}, resulting in different structural adjustments for A and B-shift directions. In the A-shift direction, the formation of the β−1’ phase instead of the β−1 will better balance the forces (Figure 6b) and accesses a higher binding energy in a potential well (Figure 6c). However, for the B-shift direction, the formation of a hexagonal porous structure, as the result of a break in mirror symmetry (Figure 6e), suggests that spontaneous symmetry breaking of the energetic potential surface occurs, presenting as a “Mexican hat” potential (Figure 6f).[44] The latter can be understood on the basis that the R-layer C_{70} can form two end-to-end interactions with the underlying T-layer C_{70} molecules through the positional and orientational adjustments. The local potential can also be affected by solvent effects (see below).

The different potential energy surfaces can also relate to electrostatic interactions. C_{60} is a highly symmetric molecule with isotropic polarizability (\(\alpha^2 = 0\)), whereas C_{70} has lower symmetry and therefore has anisotropic polarizability (\(\alpha^2 = 132.89\)). Along the principal axis of C_{70} (\(\alpha_{zz}\)), the polarizability increases more (34\%) than in the other two directions (19\%) compared with C_{60} (see Table 1). In Figure 6d, the B-shift along the principal axis of C_{70} will induce stronger polarization between the R-layer C_{70} and T-layer C_{70} (1), especially in the presence of possible charge transfer between C_{70} and the COF-1 template.[23, 45, 46] To simplify, we select only three dipoles in the T-layer C_{70} molecules (1, 2, and 3 in Figure 6d) to form the background electric potential and treat the negative charge in the R-layer C_{70} as a point charge. The electric potential energy mapping is schematically shown in Figure S2 (Supporting Information); we find that the “Mexican hat” potential is also formed. In such a potential surface, the arrangement of the R-layer C_{70} to form the hexagonal porous structure can optimize electrostatic interactions (Figures 3g and 6d). For the A-shift directions, since the polarizability of C_{70} in the \(xy\)-plane is comparable with that of C_{60}, the shifted position of C_{60} is maintained in the C_{70} case and only a small orientational adjustment is adopted due to the interactions from neighboring T-layer C_{70} molecules.
Table 1. Eigenvalues of polarizability tensor, average polarizability, and anisotropy of polarizability of C₆₀ and C₇₀

| Molecule | Eigenvalues of polarizability tensor (Å³) | α (Å³) | α² (Å³) |
|----------|------------------------------------------|--------|---------|
|          | αₓ  | αᵧ  | αₗ     |        |        |
| C₆₀      | 82.7 | 82.7 | 82.7   | 82.7  | 0.00   |
| C₇₀      | 98.8 | 98.8 | 110.5  | 102.5 | 132.89 |
| C₇₀/C₆₀  | 1.19 | 1.19 | 1.34   | 1.24  |        |

These structural adjustments can be regarded as the result of vdW interactions, electrostatic interactions, or some combination thereof. However, we cannot exclude the possibility that co-adsorbed solvent molecules alone could lead to these observed architectures. The solvent may contribute to structural adjustments through two mechanisms. First, the lying-down T-layer C₇₀ molecules could lead to asymmetric co-adsorption of heptanoic acid. As shown in Figure S5b (Supporting Information), the bright spot assigned as vertical co-adsorbed heptanoic acid is located asymmetrically in the interstitial void formed by three neighboring T-layer C₇₀ molecules. This can generate different steric hindrance (energetic potential surfaces) in the A and B-shift directions. Second, the polar functional group, the carboxyl group in heptanoic acid, can orient toward the R-layer C₇₀, which could induce a dipole and influence the packing geometries. Finally, the adsorbed solvent molecule could modify the local dielectric properties in a way that would affect the electrostatics.

Role of the Template

The presence of the COF-1 template offers several advantages for identifying the anisotropic effects of C₇₀ in molecular growth.

The template-directed fullerene films pack with a defined in-plane molecular density (volume fraction), which is the primary structural parameter determining the LC phase. It has been previously proven that the volume fraction is a critical factor for phase transitions; for example, ellipsoids tend to organize in a disordered manner at small volume fraction and to crystallize at large volume fractions.[48, 49] With colloidal particles, it is easy to control the volume fraction.
because the range of the relevant interactions, e.g., vdW interactions, is much smaller than the size of the colloidal particles but comparable with the size of molecular building blocks.[50] Therefore, colloids with weak interactions are typically regarded as hard particles and their phase behavior can be easily determined by the volume fraction.[32] At the molecular scale, however, the volume fraction is difficult to control since aggregation occurs automatically when building blocks are soft particles. The anchoring effect imposed by the template can effectively address this challenge and induces LC growth of anisotropic molecules with a well-defined volume fraction, resulting in the formation of several novel mesophases of C$_{70}$ that cannot be obtained by other methods.

Moreover, the COF-1 template can direct the growth of both C$_{60}$ and C$_{70}$ into periodic structures with specific symmetry. Unlike other statistical investigations,[48] through the comparison of symmetries and changes in packing motifs, we can easily distinguish the effect of anisotropic building blocks in crystallization; for instance, the threefold shift for C$_{60}$ reduces to mirror symmetric shift for C$_{70}$. A deep understanding about the role of anisotropic properties in the phase transition from solid to liquid can be gained through such stepwise symmetric breakdown.

**Conclusions and Perspectives**

We have used a monolayer COF-1 template to impose anchoring effects on the LC growth of elliptical C$_{70}$ molecules. A number of mesophases with distinctive packing geometries were imaged by STM, and layer-by-layer structural models were developed. The observed structures and packing motifs of C$_{70}$/COF-1 architectures are different from the C$_{60}$/COF-1 system due to the symmetry breaking of the ellipsoid molecule, which can be interpreted through a qualitative analysis of the anisotropic interactions of elliptical C$_{70}$. These results reveal the stepwise breakdown in ordering caused by the anisotropy and suggest that using a surface-confined template to anchor the initial layer of LC molecules could be a modular and potentially broadly applicable approach to organizing molecular mesogens to form new LCs. Moreover, our previous work has shown that solvents can be used to select the adsorption sites of guest molecules in similar systems.[23, 51] Even though several C$_{70}$ mesophases were observed in heptanoic acid, exploiting a different solvent molecule, such as 1,2,4-trichlorobenzene, may selectively form a single phase. The combination of template, solvent, and anisotropy of building blocks implies an effective approach to controlling molecular packing from 2D to 3D, which has the potential to provide structural control over properties in device-relevant films.[52-55]
Experimental Section

Monolayer COF-1 on HOPG was formed following procedures described previously.[38, 56] 1 mg of 1,4-benzenediboronic acid (1,4-BDBA, Tokyo Chemical Industry Co. Ltd) was added to 1.5 mL heptanoic acid (99%, Sigma- Aldrich), and then sonicated for ≈30 min. This produced a whitish suspension. 10 µL of BDBA suspension was dropped onto freshly cleaved HOPG (Structure Probe International, grade SPI-2) and placed into a reactor with a volume of ≈16 mL. 130 µL of deionized water was added to the bottom of the reactor, and a valve to ambient 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 for at least 20 min before the samples were removed.

Following the confirmation of monolayer COF-1 on the HOPG surface using STM, 10 µL of different concentration ($10^{-5}$ M, $2 \times 10^{-5}$ M, $4 \times 10^{-5}$ M, $2 \times 10^{-4}$ M) solution of C$_{70}$ (97%, Alfa Aesar) in heptanoic acid (99%, Sigma-Aldrich) was applied onto the substrate. Unless specified, the STM image was collected in the $2 \times 10^{-4}$ M solution. The saturated fullerite (C$_{60}$/C$_{70}$ mixture, Sigma-Aldrich) solution was also adopted to attest the difference in the appearances between C$_{60}$ and C$_{70}$ molecules. Subsequently, the samples were imaged by STM at the solution/solid interface at room temperature using a Digital Instruments microscope equipped with a Nanoscope IIIa controller. Tips were cut from Pt$_{0.8}$Ir$_{0.2}$ wire (Nanoscience Instruments). Bias voltages are reported with respect to the STM tip. STM images were calibrated to the COF-1 lattice parameter (1.476 nm) using the free WSxM software.[57]

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