Supporting information

Flow-induced-crystallization: tailoring host-guest supramolecular co-

assemblies at the liquid-solid interface

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1.1 Flow method

The HOPG direction can be identified by STM in the experiments. Fig. S1 defines the lattice axes and normal direction of HOPG.



Fig. S1 Illustration of the lattice axes and normal direction of HOPG.

By scrutinizing the linear assembly, it is found that the long axis of a TPTC molecule is along with the normal direction to the main symmetry axes of HOPG. The lamellar direction of the linear packing defined here is orthogonal to the "normal". To test, the flow was deliberately applied to the HOPG lattice direction and the normal direction, respectively. Experimentally, the former yielded mirror phases while the latter produced a large domain (e.g., millimeter level, mm²). This can be explained by the carton shown in Fig. 4 in the main manuscript where an equal possibility of the appearance of two assemblies can exist after the flow is applied along one of the 3-fold symmetric lattice directions of HOPG. By contrast, the flow applied to the normal direction can readily generate a uniform pattern due to the relatively simple packing manner.

In addition, the formation of a large domain of linear molecular packing crucially depends on the flow speed which is determined by the volume of sample solution drop-casted on the HOPG surface. The thin-film alignment took place upon applying a flow with a liquid droplet large enough (e.g., 10 μ L). The flow speed was estimated to be 0.5~0.6 mm/sec by optical microscopy.¹⁻²

1.2 Force field calculation for the binding energy

The binding energy was calculated provided by Forcite package using the Materials Studio 7.0 software. The details for the calculated binding energy for the van der Waals interaction (ΔE_V) and adsorption energy (ΔE_{ads}) are as follows.

The calculation for the adsorption energy of the five basic porous structures on HOPG

ΔE_{ads} :

For the simulation of adsorption energy, a graphene layer was used to represent the graphite. During the adsorption process, the molecule-substrate van der Waals interaction is the main driving force that stabilizes the molecules. Thus, the calculation mainly considered the van der Waals interaction factor. The TPTCs are packed with their π -conjugated groups showing commensurability with the graphite lattice.

 E_{total} is the energy of the entire system, consisting of the network of the model A/B/C/D/E/F pores and the graphite sheet.

 E_{TPTC} represents the energy for one TPTC molecule.

E_{graphite} is the energy for graphite.

N represents the number of TPTC molecules in the A/B/C/D/E pores.

Then the adsorption energy is calculated as:

 $\Delta \mathbf{E}_{ads-TPTC} = (\mathbf{E}_{total} - N\mathbf{E}_{TPTC} - \mathbf{E}_{graphite})/N(kJ mol^{-1}).$

Task: Geometry Optimization Quality: ultra-Fine Force field: Universal Forcite Non-Bond Options: van der Waals

The calculation for the adsorption energy of C_{60} in the five basic porous templates

 E_{total} is the interaction energy of the entire system, consisting of one C₆₀, the network of the model A/B/C/D/E/F pores, and the graphite sheet.

 E_{C60} represents the energy for one C_{60} molecule.

 $E_{template}$ is the total energy for the graphite and the A/B/C/D/E pores.

Then the adsorption energy is calculated as:

 $\Delta \mathbf{E}_{ads-C60} = \mathbf{E}_{total} - \mathbf{E}_{C60} - \mathbf{E}_{template} \, (kJ \, mol^{-1}).$

Task: Geometry Optimization Quality: ultra-Fine Force field: Universal Forcite Non-Bond Options: van der Waals

We used the "ultra-fine" quality and chose the correct calculation options. The binding energies are not sensitive to other parameters in the force field.

Table S1 Calculation details for the adsorption energies for the five basic TPTC porousstructures on the HOPG substrate

Pore types	Models	N	<i>E_{TPTC}</i> (kcal mol ⁻¹)	E _{graphite} (kcal mol ⁻¹)	<i>E_{total}</i> (kcal mol ⁻¹)	ΔE_{ads} (kJ $ m mol^{-1}$)
А		3	60.122909	1841.623257	1858.875805	-227.5
В		4	60.122909	2618.612134	2641.443761	-227.7
С		4	60.122909	2453.778933	2478.936173	-225.2
D		5	60.122909	3774.938727	3802.559662	-228.4
E		6	60.122909	4286.173377	4318.998748	-228.7

N represents the number of molecules in pores. E_{total} is the total energy that contains all the TPTCs and the graphite. $\Delta E_{ads} = (E_{total} - E_{graphite} - N \times E_{TPTC})/N$

 $1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$

Table S2 Calculation details for the adsorption energies of C_{60} in the five basic TPTC porous structures on the HOPG substrate

Pore	Madala	Ν	$E_{template}$	E_{C60}	E_{total}	$\Delta E_{ads-C60}$
types	Widdels		(kcal mol ⁻¹)	(kcal mol ⁻¹)	(kcal mol ⁻¹)	(kJ mol ⁻¹)
A		3	1129.181987	987.798210	2802.093512	-186.5
В		4	1210.318915	987.798210	3585.963147	-181.1
С		4	1208.295514	987.798210	3421.264313	-190.2
D		5	1273.323260	987.798210	4753.616854	-153.7
E		6	1340.276034	987.798210	5270.465717	-152.0

N represents the number of molecules in pores. $E_{template}$ is the energy of all the TPTC and graphite, which means the state before C_{60} is trapped. E_{total} is the total energy that contains all the TPTCs, the graphite, and the guest C_{60} , which means the state after C_{60} is trapped.

 $\Delta E_{ads-C60} = E_{total} - E_{template} - E_{C60}$

 $1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$

The adsorption energies for the A, B, C, D, and E types of pore on the HOPG substrate were calculated to be -227.5, -227.7, -225.2, -228.4, and -228.7 kJ mol⁻¹, respectively. These results illustrate that the adsorption strength of these five pores on HOPG displays a small difference, indicating that none of them shows priority over the others during the process of forming the TPTC self-assembly layers. These calculation results also correspond well with the

previously reported work that the five pores appear with similar probability.³⁻⁴ However, when comparing the adsorption energies of C_{60} in these five kinds of templates, which are -186.5, -181.1, -190.2, -153.7, and -152.0 kJ mol⁻¹, it is clear that the A, B, and C types of templates are stronger than the other two on accommodating the guest C_{60} molecules. This indicates that C_{60} shows priority in A, B, and C types of pores when adsorbing into the template, which can explain why C_{60} in the porous TPTC is not dense-packing.



Fig. S2 Chemical structures of the impurities: (a) TPTC, (b) QPTC, and (c) QQPTC.



Fig. S3 Large-scale STM images for TPTC at the OA-HOPG interface using saturated TPTC concentration. (a) Upon the solution being deposited onto the HOPG surface, at the beginning multiple small domains of linear phase formed. (b) About 6 hours later, the linear phase transferred into the porous one. Scanning parameters: $V_s = -0.7 \text{ V}$, $I_t = 75 \text{ pA}$.



Fig. S4 Real-time STM monitoring of the TPTC assembling behavior upon the flow treatment. (a-d) STM images for TPTC at the OA-HOPG interface. The green arrows represent the scanning direction. The flow direction is indicated by the yellow arrows. In panel (b), the blue dotted line represents the position where the flow treatment was applied. This procedure was conducted by stopping the scanning, then flowing, and then scanning again. The flow treatment can trigger the phase transition from the porous phase to the linear one. Scanning parameters: $V_s = -0.7 \text{ V}$, $I_t = 75 \text{ pA}$.



Fig. S5 STM images showing the feature of anisotropic close packing of C_{60} at surfaces after the flow. The results present that the anisotropic close packing of C_{60} is extended over a large area (mm level). The distance between each measurement point is ca. 2 mm. The close packing is around $5 \times 5 \text{ mm}^2$ (at least C_{60} coverage>75% from an STM image). The a1~a3 represents one experimental section and b1~b3 show the repeated result. From our examinations, the efficiency of the flow-induced C_{60} templating depends on the distance from the tissue-paper contact line (see up, right panel). A nearer distance shows a better efficiency (higher coverage of close packing C_{60}). The lower right panel shows an enlarged STM image of the linear template underneath. The flow was applied after drop-casting a TPTC- C_{60} mixing solution. The flow creates the anisotropic linear template followed by C_{60} adsorption spontaneously at the interface. The result also revealed that the flow impact on the TPTC phase transition from random-tiling to linear is around 5 mm in length. Scanning parameters: $V_s = -0.9 \text{ V}$, $I_t = 75 \text{ pA}$.



Fig. S6 A high-resolution STM image showing the bilayer TPTC template. In the upper circle, the second layer of TPTC can be observed. The first layer of TPTC can be revealed by increasing the tunneling current, as indicated by the circle in the bottom right corner. The dashed line indicates the switching of tunneling parameters from 75 to 300 pA. Scanning parameters: $V_s = -0.9 \text{ V}$, $I_t = 75/300 \text{ pA}$.



Fig. S7 Large-scale STM images showing the reversible manipulations of trapping C₆₀ between the linear and porous templates. (a, b) The phase transition from linear TPTC-C₆₀ to porous TPTC-C₆₀ upon depositing a neat solvent (40°C) onto the close packing TPTC-C₆₀ surface. The shadow near the C₆₀ indicates that the TPTC and C₆₀ molecules are mobile in panels a) and c), respectively. (c) the surface of equilibrium after drop-casting a solvent. (d) Switching lowdensity TPTC-C₆₀ packing to close packing TPTC-C₆₀ upon re-applying the flow again, shows the reversibility. Scanning parameters: $V_s = -0.9 V$, $I_t = 75 pA$.



Fig. S8 The positions of trapped C₆₀ in the random-tiling template. (a) Large-scale STM and (b) schematic diagram showing the positions of trapped C₆₀ in the random-tiling template. The C₆₀ molecules in the domain boundaries and inside the domains are marked by green and red circular dots, respectively. In panel a), the domain boundaries are indicated by white dotted lines. Scanning parameters: $V_s = -0.9 \text{ V}$, $I_t = 75 \text{ pA}$. For Fig. 6 in the main text, the statistics of the C₆₀ positions were counted based on three $120 \times 120 \text{ nm}^2$ STM images, as shown in detail below (Fig. S7).



Fig. S9 Representative large-scale STM images of C_{60} trapping by TPTC templates. The case of (a) liquid-solid interface (wet surface), (b) solvent evaporation, and (c) flow treatment. Scanning parameters: $V_s = -0.9 \text{ V}$, $I_t = 75 \text{ pA}$.

Table S3 Statistics of the C_{60} trapped positions in the cases of the normal liquid-solid interface (wet surface), spontaneous solvent evaporation, and flow treatment. They correspond to the STM images in Fig. S9.

Scanning	Total	At	Inside	Percentage of C ₆₀	Confining
states	C ₆₀	domain	domain	at the domain	efficiency*
		boundary		boundary	
Wet surface	628	192	436	30.6%	69.4%
Solvent	978	586	392	59.9%	40.1%
evaporation					
Flow	2161	55	2106	2.5%	97.5%
treatment					

* The confining efficiency represents the percentage of C_{60} molecules inside the domains, as indicated by the red dots in Fig. S8. We provided the 0.1% accuracy, which is calculated based on 628, 978, 2161 C_{60} in total for the cases of a wet surface, solvent evaporation, and flow treatment, respectively.

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