Supporting Information

Solution and air stable host/guest architectures from a single layer covalent organic framework

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S1. Experimental Methods

***Synthesis of BDBA COFs*:** BDBA COFs were formed following procedures described previously.[1, 2] 1 mg of 1,4-benzenediboronic acid (Tokyo Chemical Industry Co. Ltd) was added to 1.5 ml heptanoic acid (99%, Sigma- Aldrich), and then sonicated for approximately 30 min. This produced a whitish suspension 7.5 μl of this BDBA suspension was dropped onto freshly cleaved HOPG (Structure Probe International, grade SPI-2) and put into a reactor with a volume of ~16 ml. 130 μl 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 ℃ and left for 60 min. After the thermal treatment, the reactor was taken out of oven and allowed to cool for at least 20 min before the samples were removed. Subsequently, the samples were characterized by scanning tunnelling microscopy at the solid/air interface.

***H/G synthesis by drop-casting*:** Following the experiment of drop-wise test, 10 μl of a solution of fullerene (99.5%, Sigma- Aldrich) in heptanoic acid (99%, Sigma- Aldrich) with a concentration of 2 $\times 10^{-5}$ M, close to saturation,[3] was applied onto a substrate with a previously-grown COF. Dried films were formed by leaving these same samples in ambient for 12-16 hours.

H/G synthesis by dipstick: Following the experiment of dipstick test, the HOPG substrate with preparation of BDBA COFs was dipped into a suspension of fullerene (10^{-3} M) in heptanoic acid. The HOPG was held in the solution for less than five seconds and was subsequently left to dry under ambient conditions for 12 hours.

STM measurements: STM was performed at room temperature under ambient conditions, using a Digital Instruments STM equipped with a Nanoscope IIIa controller. Tips were cut form $Pt_{0.8}Ir_{0.2}$ wire (Nanoscience Instruments). Bias voltages are reported with respect to the STM tip. STM images were processed using the free WSxM software.[4] The images were rendered using the standard grayscale color mapping, after which false colour (brown) was overlaid on the COF-1 in Figure 2.

S2. The scheme of chemical reaction of template

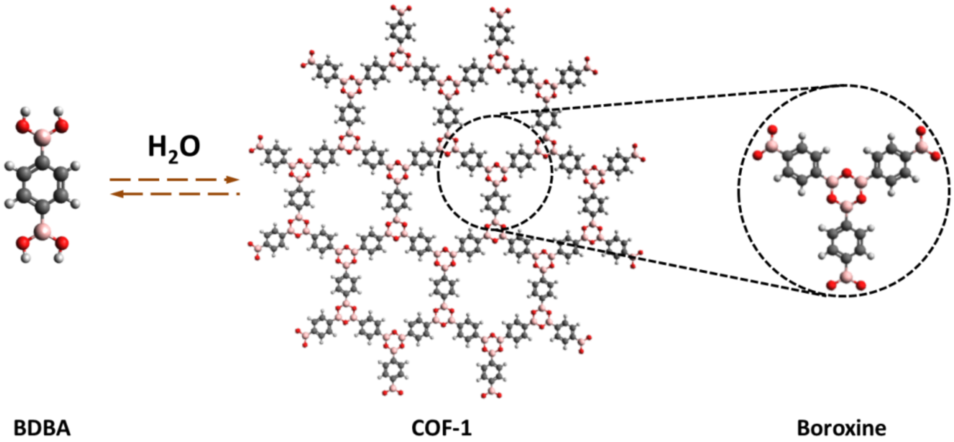

Figure S.1 the scheme of chemical reaction for synthesizing template: self-condensation of BDBA monomers gives rise to 2D COF-1 template wherein defects are recovered through reversible reaction by offering excess water. Boroxine ring is shown specifically.

S3. Calculations of fullerene adsorption

Adsorption geometries for fullerene adsorption were investigated using molecular mechanics calculations using MM+ as implemented in HyperChem.[5] A cluster representing COF-1 was placed on top of larger hexagonal graphene cluster (Figure S.2) all coordinates of which were frozen. The optimization was run until the energy change was <0.000001 kcal/mol over 100 cycles. The achieved gradient was <0.02 kcal/mol/Å (in most cases <0.01 kcal/mol/Å).

The COF-1 was found to be the most stable with its unit cell vector coaligned with the graphene zigzag direction. Alignment along the armchair direction was disfavoured by 0.2 kcal/mol. Although the structure for the COF-1 pore does not reflect the exact epitaxial relationship identified in our experiments, we expect that the geometry used in these calculations correctly captures the relative energetics between the different adsorption sites.

Fullerene adsorption was examined for the pore site, and for two possible top site adosorptions: over a boroxine ring and over a phenyl ring in the COF-1. In all cases, C_{60} is most stable when adsorbed with a hexagonal ring facing down.

The most stable adsorption was found to be in the pore site, at E_b = -32.1 kcal/mol. This was followed by adsorption in a boroxine top site (E_b = -11.2 kcal/mol) and finally a benzene top site (E_b = -10.2 kcal/mol). The calculated geometries are shown in Figure S.2.

Using gas-phase density functional theory (DFT), as implemented in the Gaussian09 software,[6] we considered the adsorption geometries of the fullerene molecules above the COF-1 pore. Since the graphene layer was not included in these calculations, several dihedral angles were frozen in the COF-1 pore in the vicinity of the fullerene. Calculations were performed at the B3LYP/6-31G level, which we do not expect to capture all relevant dispersive interactions. Calculations of the fullerene/COF-1 geometries show in Figure S.2b and S.2c converged with respect to forces (both force and RMS force) and revealed the same relative energetics indicated by the molecular mechanics calculations: adsorption above the boroxine was favoured as compared to adsorption above the benzene (calculated E_b values were -1.31 kcal/mol for adsorption above boroxine and -0.48 kcal/mol for adsorption above benzene).

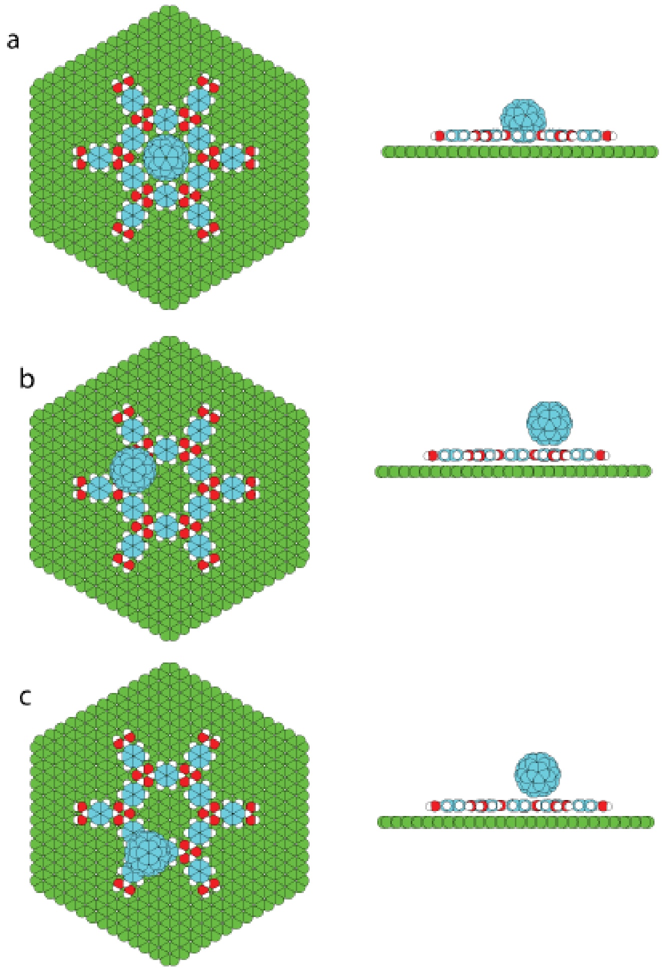

Figure S.2: molecular mechanics calculated geometries for pore site adsorption (a), top site adsorption over a phenyl ring (b) and top site adsorption over a boroxine ring (c).

S4. Adsorption of C_{60} in COF-1 at air/solid interface

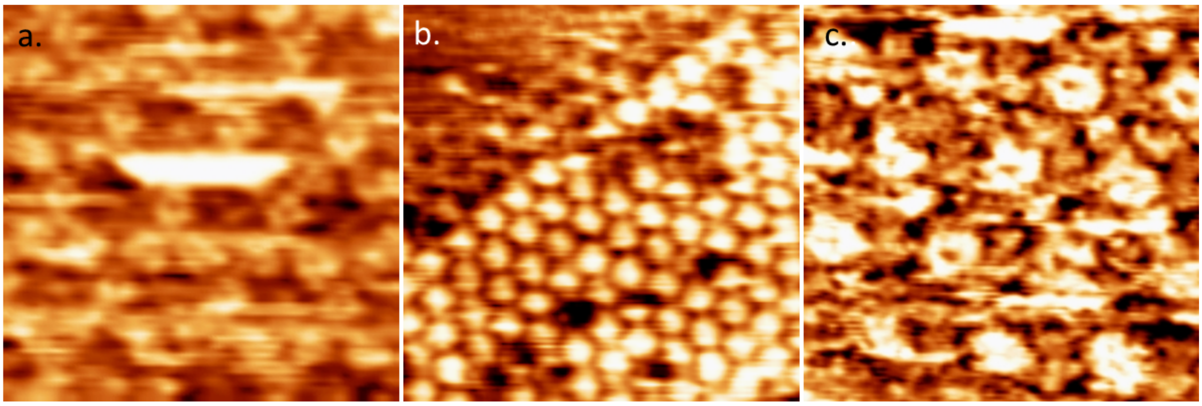

Figure S.3 H/G structures at the air/solid interface. The images in (a) and (b) show top site adsorption and image in (c) shows pore site adsorption, respectively. (a) shows an isolated fullerene molecule and (b) is a stable domain of top site adsorption of C60 molecules at air/solid interface. Imaging parameters: voltage U=-800 mV, tunneling current I=100 pA. Image width: (a) 5.6 nm (b) 17.2 nm (c) 5.4 nm.

Figure S.3a demonstrates a difference between adsorption at the solution/solid interface and the air/solid interface: at the air/solid interface, and with sparse guest population, top-site C_{60} can be moved laterally along the rim of the COF by the STM tip. We could not similarly manipulate the top-site fullerenes at the solution/solid interface, suggesting that the solution may play a role in stabilizing the fullerenes in this site, or that the C_{60} can be easily removed to solution by the tip. We also found that the top-site fullerene guests in dried films could not be moved with the tip when the relative concentration of guest molecules was high, see S.3b, suggesting that isolated guest molecules are destabilized with respect to those contained in a regular lattice of guests.

S5. Additional STM images

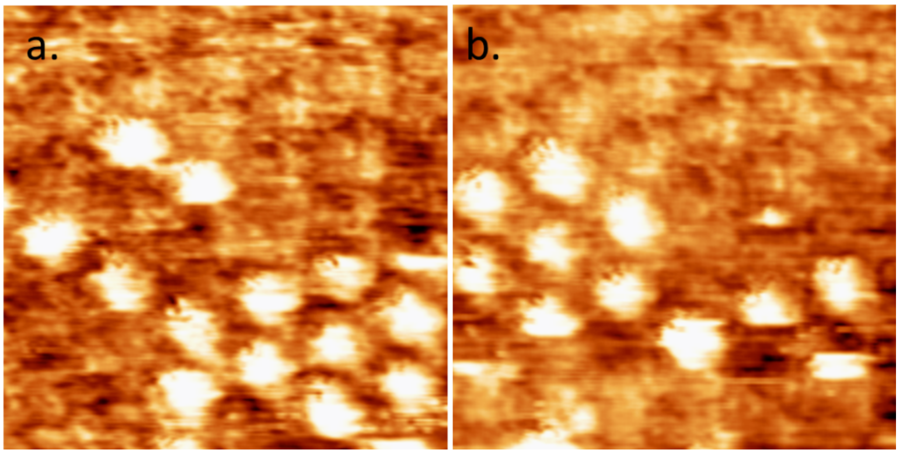

Figure S.4 Consecutive STM images of H/G architecture: (a) the starting geometry with a small domain of C_{60} guest molecules inside the host template; (b) final geometry in the same area with C_{60} molecules in a new distribution which demonstrates a transfer of guest molecules induced by STM tip. Image width: 8.5 nm.

References

1. J. r. F. Dienstmaier, A. M. Gigler, A. J. Goetz, P. Knochel, T. Bein, A. Lyapin, S. Reichlmaier, W. M. Heckl and M. Lackinger, ACS Nano, 2011, 5, 9737-9745.
2. J. r. F. Dienstmaier, D. D. Medina, M. Dogru, P. Knochel, T. Bein, W. M. Heckl and M. Lackinger, ACS Nano, 2012, 6, 7234-7242.
3. K. Semenov, N. Charykov, A. Pyartman, V. Keskinov, V. Lishchuk, O. Arapov and N. Alekseev, Russian Journal of Applied Chemistry, 2007, 80, 456-460.
4. I. Horcas, R. Fernández, J. Gomez-Rodriguez, J. Colchero, J. Gómez-Herrero and A. Baro, Review of Scientific Instruments, 2007, 78, 013705.
5. HyperChem(TM) Professional 7.51, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA.
6. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.