Electronic Supplementary Information (ESI)

Covalent organic frameworks from a monomer with reduced symmetry: polymorphism and Sierpinski triangles

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Experimental details

Solution base bulk COF synthesis using solvothermal method: A high-pressure glass vessel was charged with 1,3-benzene diboronic acid (1,3-BDBA) (50 mg, 0.3 mmol) and 2 mL of a 1:1 v:v solution of mesitylene:dioxane. After being replenished with N_2 for 15 minutes, the reaction mixture was heated at 100 ºC for 3 days yielding a white solid at bottom of the vessel which was isolated by filtration and washed with dioxane (30 mL). The powder was dried under vacuum overnight to yield 41 mg. Dozens of other reaction conditions were tested aiming to increase the crystalline (increasing/decreasing the concentration, adding water/methanol/ethanol, using pure dioxane/mesitylene or reacting at a higher or lower temperature), however none of them resulted in better crystalline COF powder than the method described above.

PXRD data was collected on a Bruker D8 Phaser LYNXEYETM instrument using nickel-filtered CuKα (λ = 0.154056 Å) radiation. Fourier-transform infrared attenuated total reflectance (FTIR-ATR) studies were done on a Bruker VERTEX 70 spectrometer equipped with a PLATINUM diamond crystal ATR unit. Solid-state ^{11}B and ^{13}C NMR spectrum were recorded on a Bruker Avance III HD (Milton, ON) operating at frequencies of 150.86 MHz. A 4 mm double resonance magic-angle spinning probe was used at a spinning frequency of 15 kHz and 13 kHz for ^{11}B and ^{13}C NMR spectrum, respectively. The N_2 gas adsorption experiments were performed on a Quantachrome Quadrasorb automatic volumetric instrument.

The synthesis on HOPG substrate: The COFs on HOPG were formed following a procedure described previously.[1, 2] Different amounts of 1,3-benzenediboronic acid (1,3-BDBA purchased from Alfa Aesar 97% and then purified by recrystallization from water to remove benzeneboronic acid impurity) were added to 1.5 ml heptanoic acid (99%, Sigma- Aldrich) to reach the desired concentration. This step was followed by sonication for ~30 min.[3] 10 μl of solution was dropped onto freshly cleaved HOPG (Structure Probe International, grade SPI-1) 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 the atmosphere was left slightly open to maintain an open system. The entire reactor was placed in an oven preheated to 125 ºC and left for 60 min. The thermal treatment evaporates all the heptanoic acid. After the 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.

STM was performed at room temperature at the heptanoic acid/HOPG interface, using a Digital Instruments STM equipped with a Nanoscope IIIa controller. Tips were cut from a $Pt_{0.8}Ir_{0.2}$ wire (Nanoscience Instruments). Bias voltages are reported with respect to the STM tip. STM images were processed with the free WSxM software.[4]

1. J. 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. F. Dienstmaier, D. D. Medina, M. Dogru, P. Knochel, T. Bein, W. M. Heckl and M. Lackinger, *ACS Nano*, 2012, **6**, 7234-7242.
3. D. Cui, J. M. MacLeod, M. Ebrahimi, D. F. Perepichka and F. Rosei, *Chemical Communications*, 2015, **51**, 16510-16513.
4. I. Horcas, R. Fernández, J. Gomez-Rodriguez, J. Colchero, J. Gómez-Herrero and A. Baro, *Review of Scientific Instruments*, 2007, **78**, 013705.

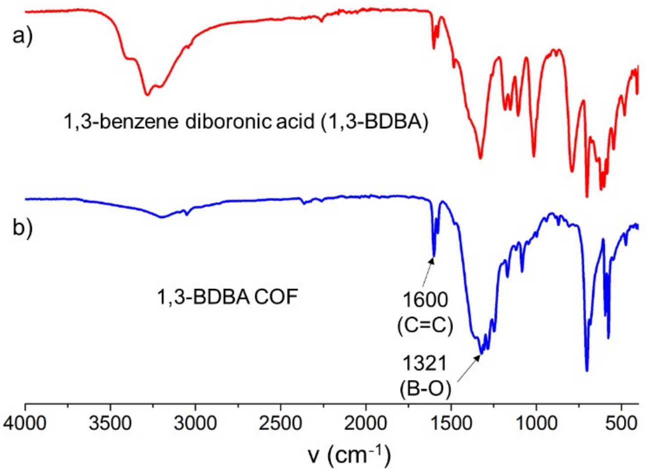

Figure S1. Comparison of FTIRART spectrum for starting material 1,3-benzene diboronic acid (1,3-BDBA, red line) and 1,3-BDBA COF (blue line). **b)** The characteristic boron functional group bands of the 1,3-BDBA COF are highlighted.

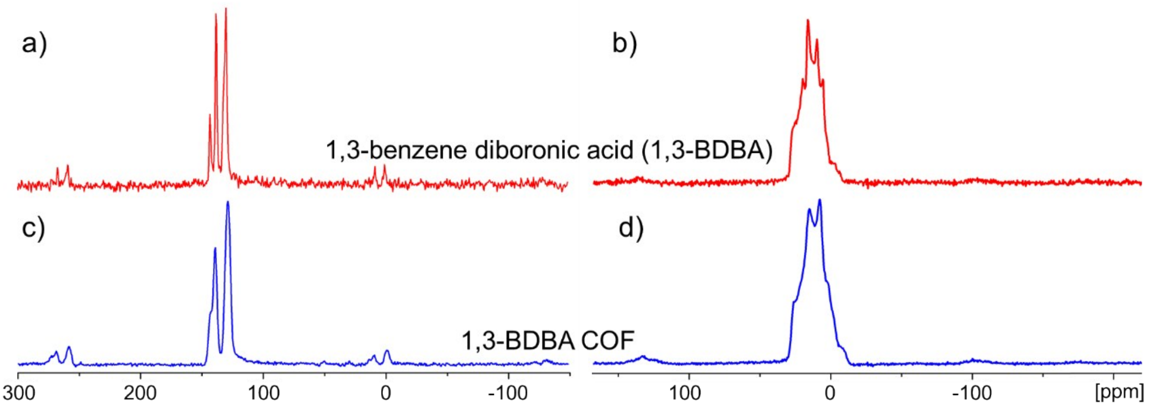

Figure S2. *Solid-state NMR* spectrum of 1,3-BDBA (red), 1,3-BDBA COF (blue). **a,c)** ^{11}B multiple quantum magic-angle spinning (MQMAS) NMR spectrum. **b,d)** ^{13}C cross polarization magic-angle spinning (CP/MAS) NMR spectrum.

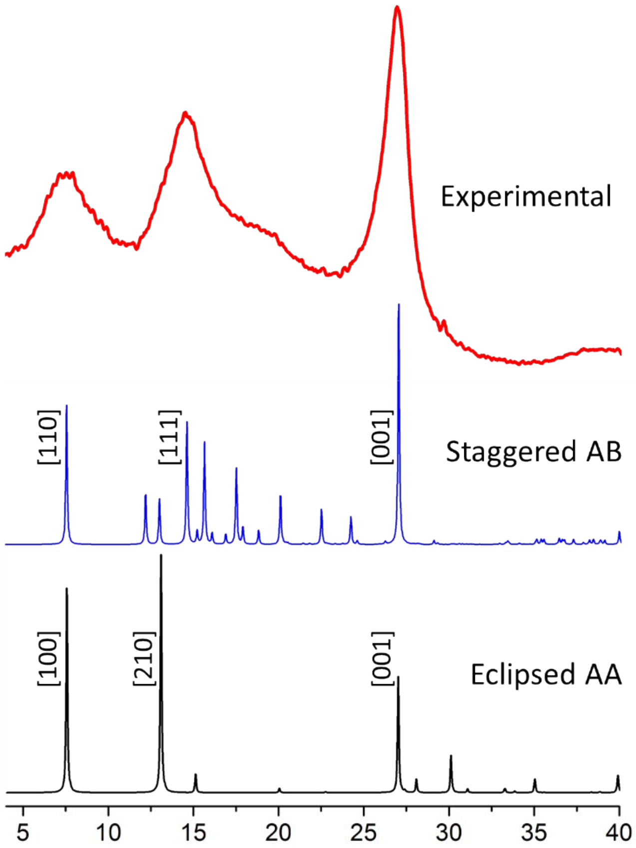

Figure S3. Experimental and simulated PXRD patterns of 1,3-BDBA COF. Experimental PXRD of as-synthesized COF (red lines), simulated XRD pattern of staggered AB stacking (blue lines) and eclipsed AA stacking (black).

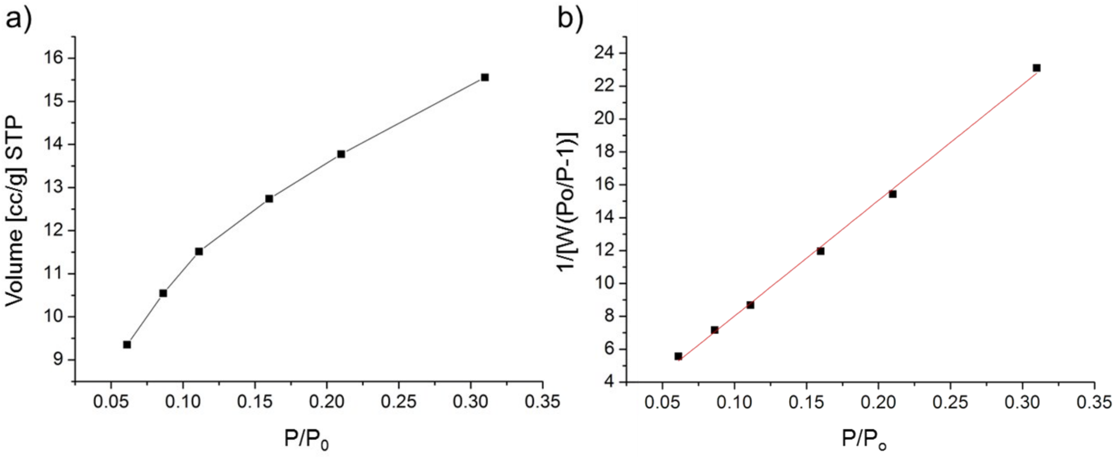

Figure S4. a) N_2 adsorption-desorption isotherm for 1,3-BDBA COF at 77.3K**.**
b) BET surface area plot calculated from the isotherm. $S_{BET} = 48.82\ m^2 / g$.

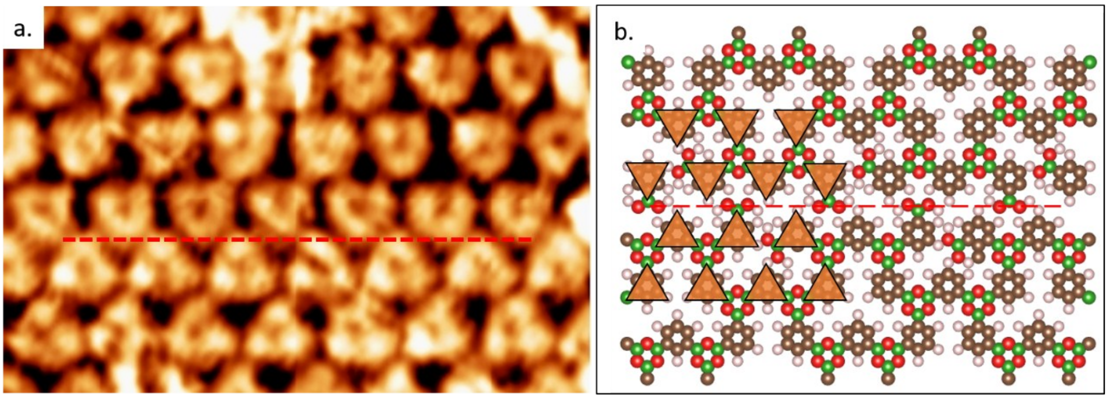

Figure S5. a) STM image elucidating the boundary between two rotationally equivalent honeycomb domains. The boundary is marked by a dashed red line. Image dimension: 6.0×4.0 nm^2. Tunnelling conditions: $V_{bias} = -1500$ mV, $I_{set} = 50$ pA.
b) Schematic image showing the boundary. The orange triangles schematically represents the orientations of benzene rings in the two domains as observed experimentally.

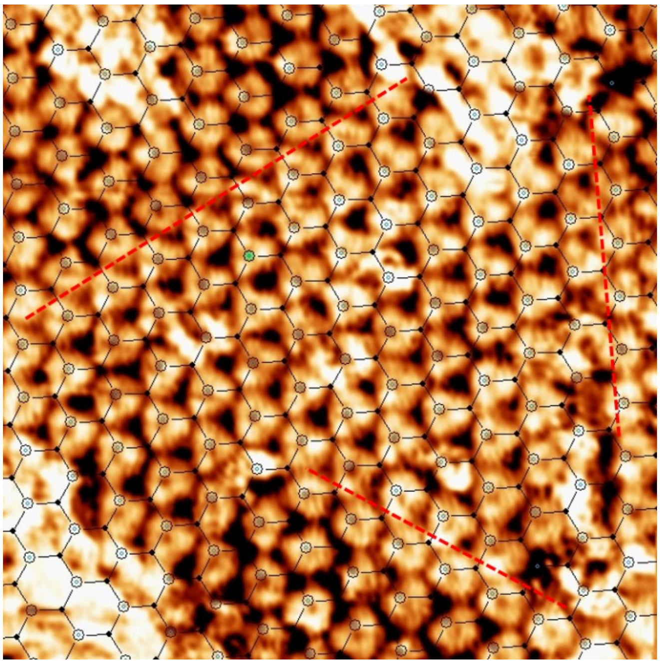

Figure S6. STM image illustrating the preservation of the apparent periodicity of the benzene rings across the domain boundaries. Image dimension: 9.5×9.5 nm^2. Tunnelling conditions: $V_{\text{bias}} = -1500$ mV, $I_{\text{set}} = 50$ pA. The boundaries are marked by red dashed lines.

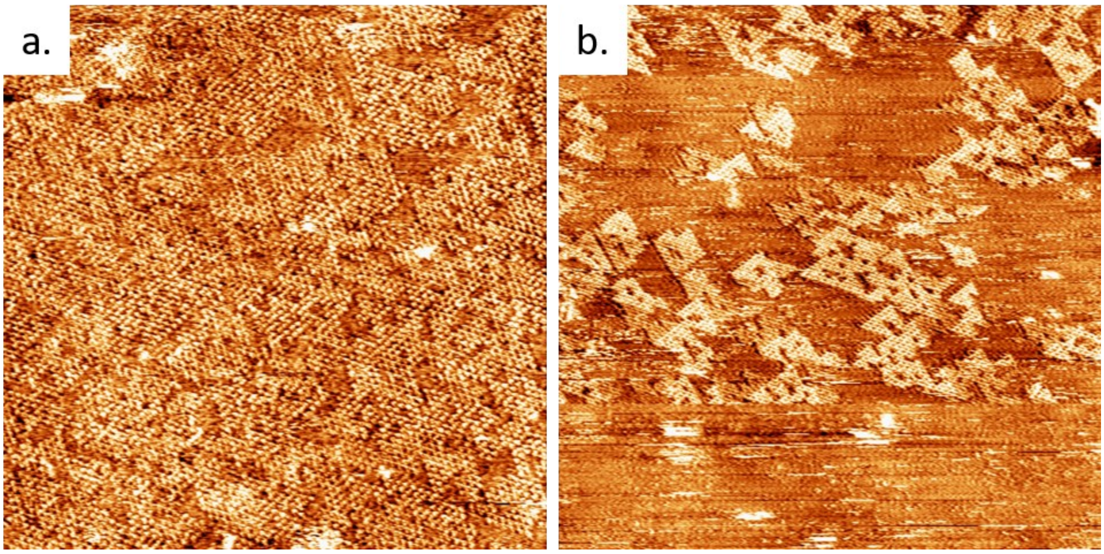

Figure S7. Large-scale overview STM images for extended COF (a) and ST structures (b) respectively. Image dimensions: (a) 60×60 nm^2; (b) 80×80 nm^2. Tunneling conditions: (a) $V_{\text{bias}} = -1500$ mV, $I_{\text{set}} = 50$ pA; (b) $V_{\text{bias}} = -1500$ mV, $I_{\text{set}} = 50$ pA.