Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Construction of Boronate Ester Based Single-Layered Covalent Organic Frameworks

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Materials and methods

2, 3, 6, 7, 10, 11-hexahydroxytriphenylene (HHTP, 95%) and Tetrahydrofuran (THF, 99.5%) were purchased from TCI. 4, 4'-biphenyldiboronic acid (BPDA, 90%) was purchased from Aldrich. Copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$, 98%) was purchased from Sigma. All the chemicals used in this study, unless otherwise specified, were utilized without further purification.

A Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) was used to perform the STM experiments. STM tips were prepared by mechanically cutting a Pt/Ir wire (90:10). All the STM images were recorded in constant-current mode under ambient conditions at room temperature and were shown without further processing.

Synthesis of HHTP-BPDA sCOFs

4, 4'-biphenyldiboronic acid (BPDA) and 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene (HHTP) were served as precursors. In a typical experimental procedure, 5 μL mixed THF solution containing molecule HHTP with concentration about 2.0×10^{-5} M and molecule BPDA with concentration about 8.0×10^{-5} M was deposited on freshly cleaved HOPG surface and allowed to dry. Then the HOPG loaded with precursors was put in a closed autoclave with the presence of $CuSO_4\cdot5H_2O$ powder about 1.1 g. After heating at 170 ^{o}C for 3h, the HOPG was cooled down to room temperature and taken out for STM characterization.

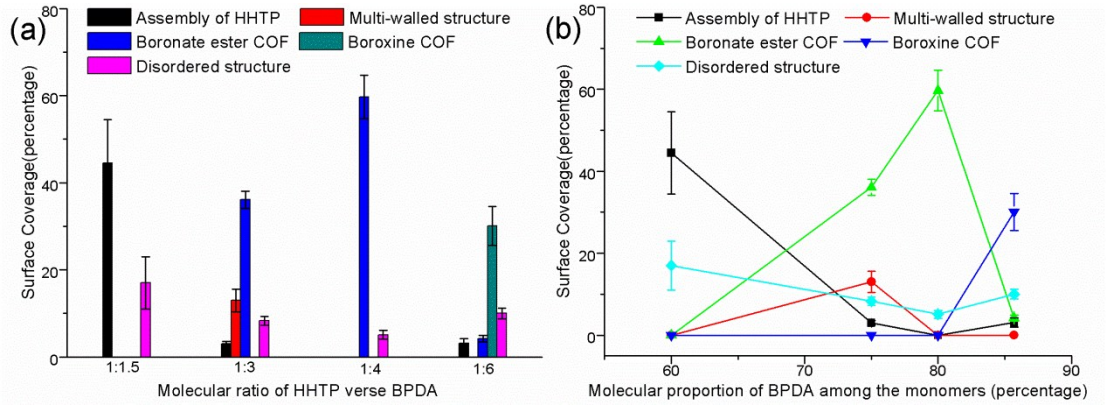

Fig. S1 The statistic on the surface coverage of different structures under different molecular ratios of HHTP verse BPDA monomer. (a) Column histogram. (b) Line chart.

1. For the surface coverage statistic under different molecular ratios, we keep the total concentration of HHTP and BPDA monomers constant (10^{-4} M). In Fig.S1 (b), the value of x-axis is calculated by: $x = \frac{the\ mole\ number\ of\ BPDA\ monomer}{the\ total\ mole\ number\ of\ HHTP\ and\ BPDA\ monomers}$.

2. More than 25 STM images were used for each molecular ratio to conduct the statistic on the surface coverage. The STM images are obtained from samples under the same experimental conditions collected at random positions on the HOPG surface. The surface coverage is calculated by the domain area of each structure in one STM image dividing the whole area of this STM image.

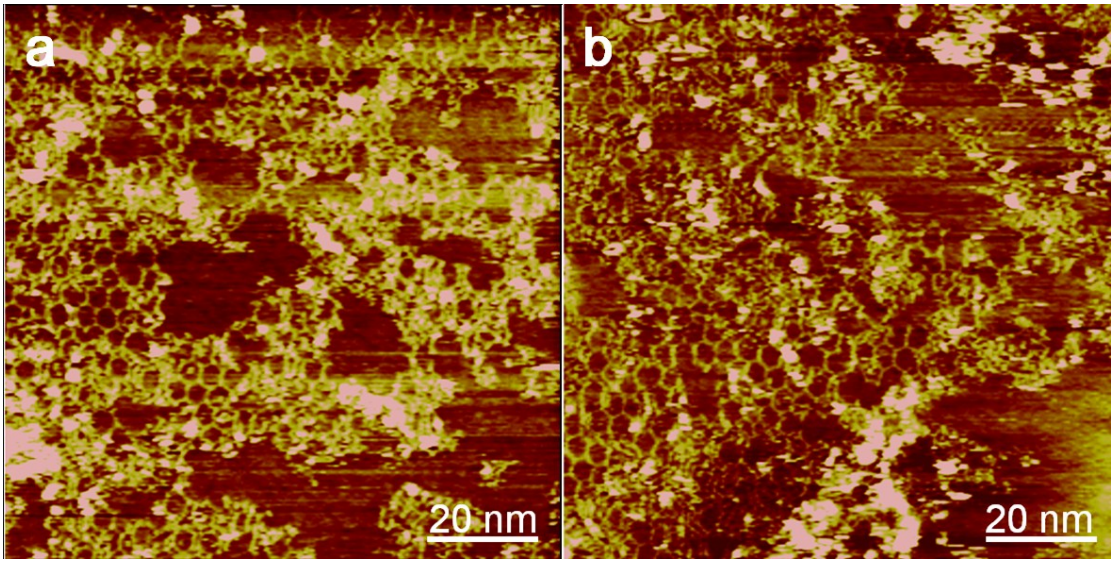

Fig. S2 STM images of structures obtained for reaction of HHTP (2.0×10^{-5} M) and BPDA (8.0×10^{-5} M) at 170 °C. (a) STM image obtained from the absence of $CuSO_4\cdot5H_2O$ powder. (b) STM image obtained from the mixed precursor solution stored for 1d. Imaging conditions: (a) V_{bias} = 700 mV, I_t = 510 pA; (b) V_{bias} = 690 mV, I_t = 520 pA.

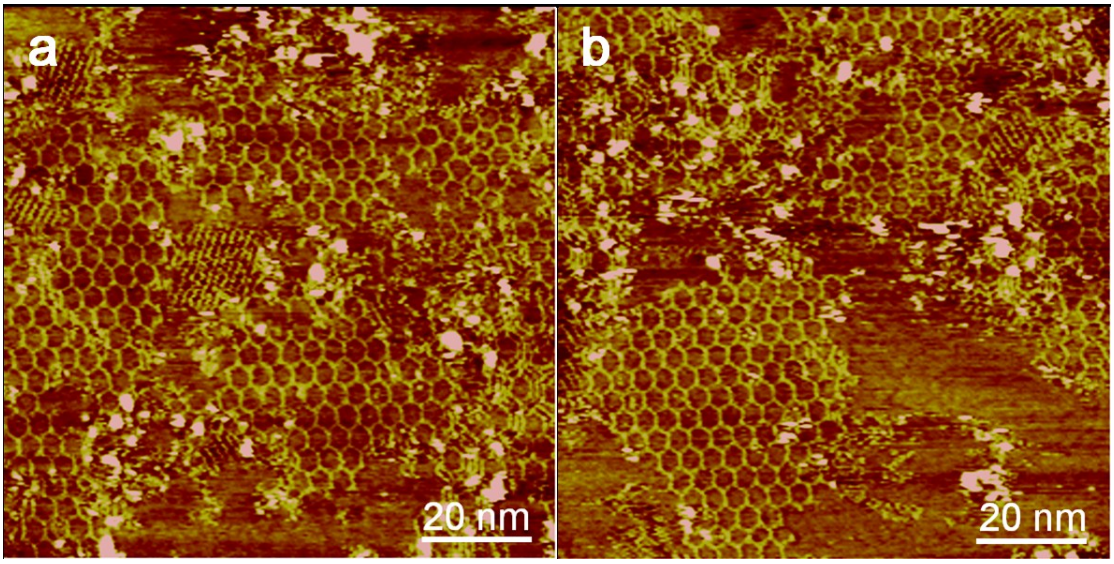

Fig. S3 The thermal stability of the HHTP-BPDA sCOFs. (a) A STM image of the as-prepared HHTP-BPDA sCOFs. (b) A STM image of the microstructure on the HOPG surface after annealing at 200 °C for 1h. Imaging conditions: (a) V_{bias} = 710 mV, I_t = 510 pA; (b) V_{bias} = 700 mV, I_t = 500 pA.

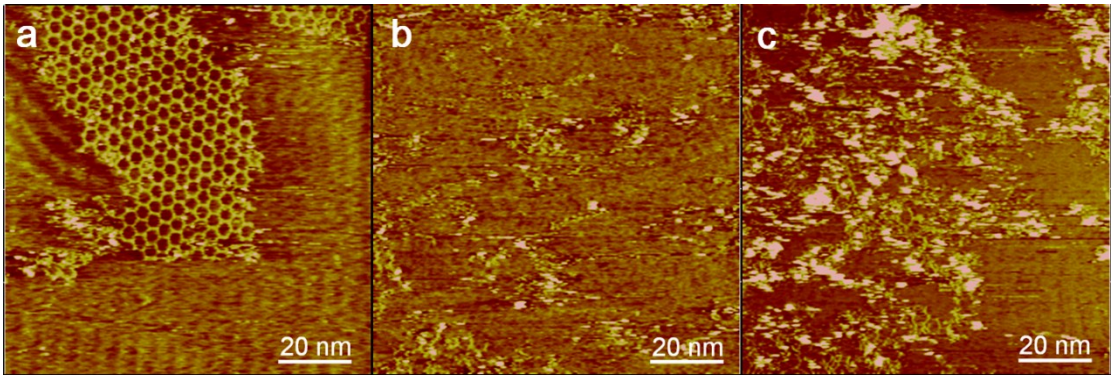

Fig. S4 The chemical stability of the HHTP-BPDA sCOFs. (a) A STM image of the as-prepared HHTP-BPDA sCOFs. (b) A STM image of the microstructure on the HOPG surface after placing at ambient atmosphere for two days. (c) A STM image of the same HOPG surface after applying the same synthetic procedure. Imaging conditions: (a) V_{bias} = 710 mV, I_t = 510 pA; (b) V_{bias} = 680 mV, I_t = 500 pA; (c) V_{bias} = 700 mV, I_t = 520 pA.