

Electronic Supplementary Information for:

**Simultaneous construction of two linkages for the on-surface
synthesis of imine-boroxine hybrid covalent organic frameworks**

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S1. Experimental section

STM experiment: All the STM experiments were performed by a Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA). STM tips were obtained by mechanically cutting a Pt/Ir wire (90:10). All the STM data were recorded in constant-current mode in ambient conditions at room temperature and were displayed without further handling.

Materials: Molecule 1, 3, 5-tris (4-aminophenyl) benzene (TAPB) was purchased from TCI. Molecule 4-formylphenylboronic acid (4FPBA) and molecule 3-formylphenylboronic acid (3FPBA) were purchased from J&K. All the chemicals used in this study were utilized without further purification.

The synthesis of hybrid sCOFs by gas-solid interface reaction method¹: TAPB and 4FPBA (or 3FPBA) were applied as precursors. 4 μ L THF solution containing molecule TAPB with concentration about 10^{-5} mol/L was preloaded on freshly cleaved HOPG and 0.2 mg 4FPBA (3FPBA) powder was placed beside the HOPG in a reactor. Then the reactor was sealed in an autoclave with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ powders about 1.1 g as chemical equilibrium control agent. After heated at 120 °C for 3h, the HOPG was cooled down to room temperature and taken out for STM characterization.

The control experiment: The control experiment was done by depositing 4 μ L THF solution including molecule TAPB and 4FPBA with

concentration about 10^{-5} mol/L on fresh cleaved HOPG surface. Then the treated HOPG was placed in a reactor with the presence of about 1.1 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ powders at the bottom of an autoclave. Then the reactor was transferred into the autoclave and sealed. The autoclave was put into a heating oven at 120°C for 3h. The HOPG was cooled down to room temperature and taken out for STM characterization.

Experiments on exploring the stability of the sCOFs: Firstly, the hybrid sCOF was synthesized by the method mentioned above.

Thermal stability: The HOPG covered with sCOFA was put into a heating oven and heated at 180°C for 1h. The HOPG was cooled down to room temperature and characterized by STM.

pH stability: $4\mu\text{L}$ 10^{-3} M HCl/ H_2O solution and 10^{-3} M KOH/ H_2O solution were dropped on the substrate covered with sCOFA, respectively. After 5 min, the residual acid or base was removed by absorbent paper. Then the treated HOPG was characterized by STM.

The stability in the ambient environment: The HOPG covered with sCOFB was stored in the ambient environment. After 20 days, the treated HOPG was characterized by STM.

XPS experiment: X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromatic Al $K\alpha$ radiation. The $500\mu\text{m}$ X-ray spot was used for SAXPS analysis. The base pressure in the analysis chamber was about

3×10^{-10} mbar. The hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing. The TAPB sample was prepared by drop-casting the molecule TAPB on fresh cleaved HOPG surface with the concentration about 10^{-5} mol/L. The sCOFB sample was quickly washed by THF for 3 times before the XPS test, in order to remove the residual unreacted molecule TAPB as much as possible.

S2. The epitaxial orientation of sCOFA domains to the underlying substrate

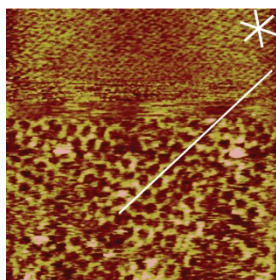


Fig. S1 A composite STM image of HOPG substrate ($10 \text{ nm} \times 5 \text{ nm}$, the upper part) and sCOFA ($50 \text{ nm} \times 30 \text{ nm}$, the lower part). Imaging conditions: $V_{\text{bias}} = 700 \text{ mV}$, $I_t = 500 \text{ pA}$ (the lower part); $V_{\text{bias}} = 35 \text{ mV}$, $I_t = 1.96 \text{ nA}$ (the upper part).

The growth orientation of sCOFA domains to the underlying substrate was obtained by comparing the STM image of adlayer and the atomic image of HOPG of the same area obtained at proper tunnelling condition. As shown by the white line in Fig. S1, the network forms at fixed direction to the substrate. The angle between the growth orientation of sCOFA and the lattice of the underlying substrate is nearly 0° .

S3. The trans-conformation and cis-conformation of the imine linkages

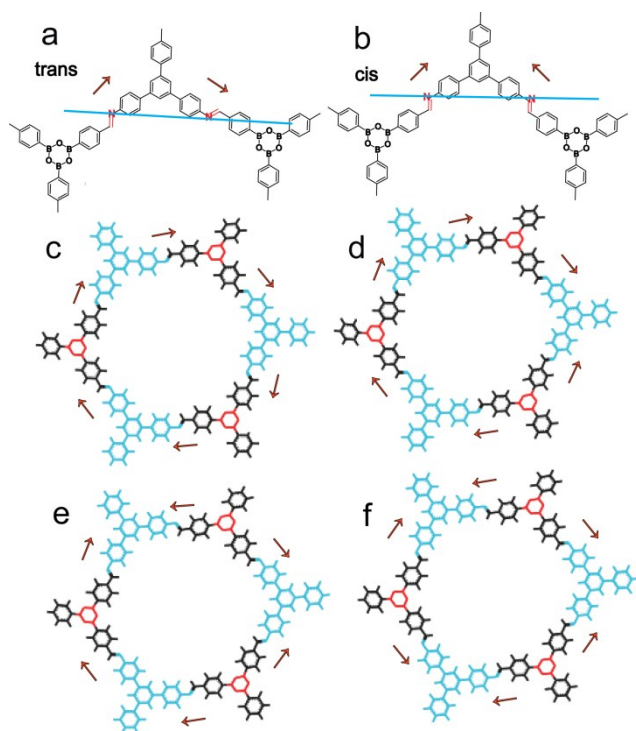


Fig. S2. The trans-conformation (a) and cis-conformation (b) of the imine linkages.(c, d, e, f) The representative chemical structures of the distorted hexagons resulting from the rotation of the formed imine bonds.

When the imine bonds distribute in opposite side of the blue line (Fig. S2a), trans-conformation is got. When the imine bonds distribute in the same side of the blue line, cis-conformation is obtained (Fig. S2b). Due to the rotated direction of the imine bond, diverse conformation contained hexagons may be formed on the surface. Four hexagons with different conformations are displayed in Fig. S2c-f, as representatives. However, the rotated direction of the formed imine linkage cannot be recognized by STM image.

S4. The comparison between the trimer condensed by 4FPBA and molecule TFPB

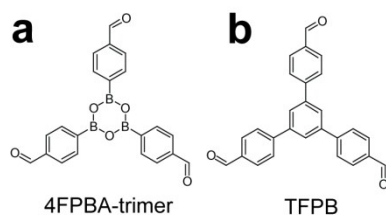


Fig. S3. The chemical structure of (a) trimer condensed by 4FPBA; (b) TFPB.

Since the boroxine ring and benzene ring have close size, therefore, the trimer condensed by 4FPBA and molecule TFPB have similar size. Thus, sCOFA has similar lattice parameters to the sCOF fabricated by molecule TAPB and TFPB.²

S5. The epitaxial orientation of sCOFA domains to the underlying substrate

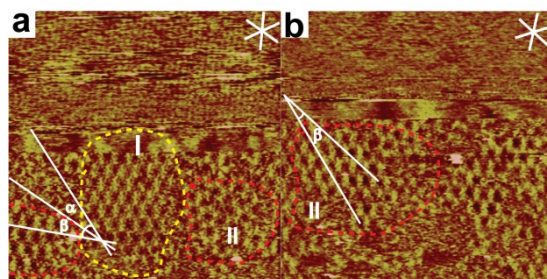


Fig. S4 (a) A composite STM image of HOPG substrate (10 nm × 4 nm, the upper part) and sCOFB (50 nm × 25 nm, the lower part). (b) A composite STM image of HOPG substrate (10 nm × 3 nm, the upper part) and sCOFB (50 nm × 30 nm, the lower part). Imaging conditions: $V_{\text{bias}} = 700$ mV, $I_t = 500$ pA (the lower part); $V_{\text{bias}} = 40$ mV, $I_t = 1.76$ nA (the upper part). The red dotted line areas represent the CCW-sCOFB and the yellow dotted line areas are on behalf of the CW-sCOFB.

The epitaxial orientation of sCOFB domains to the underlying substrate was obtained by comparing the STM image of adlayer and the atomic

image of HOPG of the same area obtained at proper tunnelling condition. As shown by the white line in Fig. S4, the angle between the CW-sCOFB and the underlying HOPG substrate is about $\alpha = 20 \pm 2^\circ$ and the angle between the CCW-sCOFB and the underlying HOPG substrate is about $\beta = -20 \pm 2^\circ$.

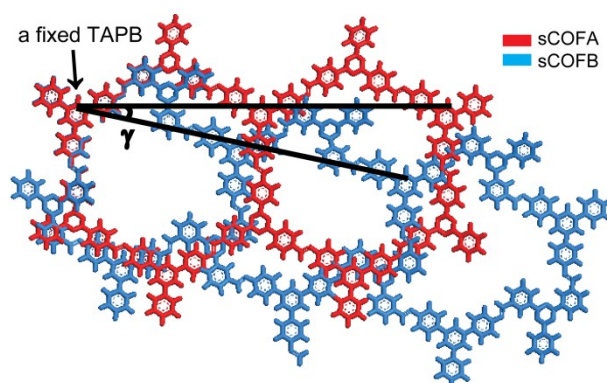


Fig. S5 The comparison of the growth orientation between sCOFA and sCOFB. We attempt to explore the theoretical growth orientation of the two hybrid sCOFs. Based on a fixed molecule TAPB, displayed by the black arrow in Fig. S5, the structure models of the two hybrid sCOFs were built up. The red module represents sCOFA while the blue component stands for sCOFB. The angle between the unite cell of the two hybrid sCOFs is measure to be $\gamma = 18.4^\circ$, in accord with the experiment result $20 \pm 2^\circ$.

S6. The XPS results of the unreacted TAPB sample and sCOFB

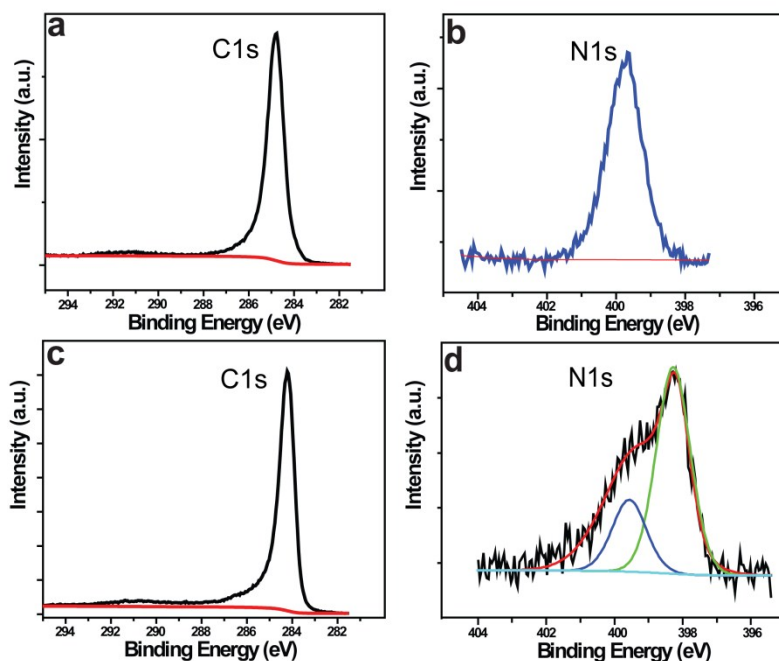


Fig. S6 (a) The C1s spectrum of the unreacted TAPB; (b) The N1s spectrum of the unreacted TAPB; (c) The C1s spectrum of sCOFB; (d) The N1s spectra of sCOFB.

For the unreacted TAPB sample, the peak of C1s spectrum is at 284.8 eV, which can be attributed to the C in molecule TAPB and HOPG. In the sCOFB, the spectrum of C1s is similar to that in TAPB sample. Since the carbon in the imine bonds account only for $\sim 5\%$ of all carbons in the COF, and this ratio is getting even lower when the HOPG substrate is also taken into account, the carbon in the imine bond cannot be detected at all given the huge background of other carbons.³ For the TAPB sample, the peak of N1s spectrum is 399.8 eV and attributed to the N in the amine group. In sCOFB, the N1s spectra can be deconvoluted two bands at 399.8 eV and 398.5 eV. The new band at 398.5 eV, in the N1s spectra, results from the N in the imine bond. The areas ratio of the two bands in

N1s spectra in sCOFB is about 1:3, which indicates that the imine is the major N species. The unreacted amine group may come from domain boundaries, defects, and unreacted TAPB molecules.

S7. STM images of the control experiment by depositing the precursors on HOPG together

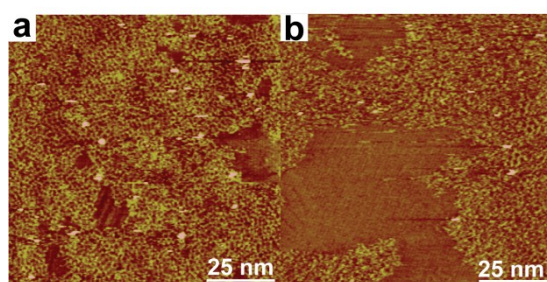


Fig. S7. STM images ($100 \times 100 \text{ nm}^2$) of sCOFs obtained by mixed deposition method. (a) The reaction between TAPB and 4FPBA; (b) The reaction between TAPB and 3FPBA. Imaging conditions: $V_{\text{bias}} = 700 \text{ mV}$, $I_t = 500 \text{ pA}$

By depositing the precursors TAPB and 4FPBA/3FPBA on HOPG together while keeping the other experimental condition the same, only disordered structures with incomplete reaction intermediates and oligomers can be obtained in Fig. S6.

S8. The effect of the thermodynamic regulation agent

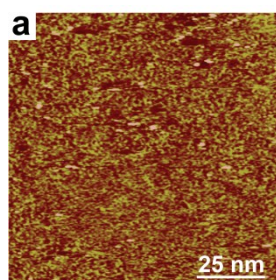


Fig. S8. STM image shows the reaction result between TAPB and 4FPBA on HOPG

by gas-solid interface reaction route at 120 °C without $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ powders.

Without the thermodynamic regulation agent, the defects produced in the reaction process cannot be repaired efficiently and the disordered structures cover the substrate.

S9. The stability of the hybrid sCOFs

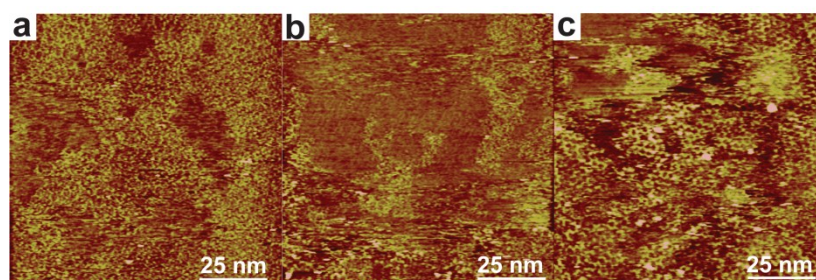


Fig. S9 The thermal and pH stability of sCOFA. (a) The STM image of sCOFA after heated at 180 °C for 1h. (b) The STM image of sCOFA after kept in pH = 3 conditions for 5 min. (c) The STM image of sCOFA after kept in pH = 11 conditions for 5 min.

After a heating process at high temperature, such as 180 °C, order sCOFA can still be observed. This indicates that the hybrid sCOF can tolerate a thermal process. When sCOFA is put in a pH = 3 or 11 environment, the areas of the ordered networks decrease and chaotic structures come out, which may be ascribed to the breakage of the linkages.

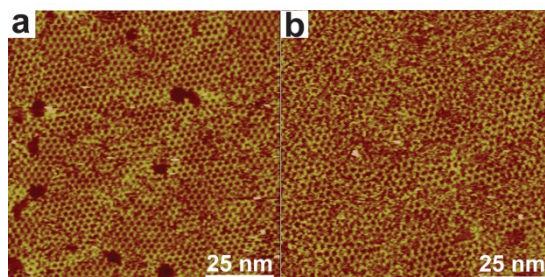


Fig. S10 The stability of the hybrid sCOF in the ambient environment. (a) The STM

image ($100 \times 100 \text{ nm}^2$) of the newly fabricated sCOFB. (b) The STM image ($100 \times 100 \text{ nm}^2$) of sCOFB after exposed in the air for 20 days. Imaging conditions: $V_{\text{bias}} = 700 \text{ mV}$, $I_t = 500 \text{ pA}$.

After being stored in the air for 20 days, highly ordered sCOFB can also be inspected, which demonstrate that the hybrid sCOF is more stable to the single boroxine ring linked sCOFs.

S10. References

- 1 X.-H. Liu, C.-Z. Guan, S.-Y. Ding, W. Wang, H.-J. Yan, D. Wang and L.-J. Wan, *J. Am. Chem. Soc.*, 2013, **135**, 10470-10474.
- 2 X.-H. Liu, C.-Z. Guan, Q.-N. Zheng, D. Wang and L.-J. Wan, *J. Chem. Phys.*, 2015, **142**, 101905-101910.
- 3 Y. Hu, N. Goodeal, Y. Chen, A. M. Ganose, R. G. Palgrave, H. Bronstein and M. O. Blunt, *Chem. Commun.*, 2016, **52**, 9941-9944.