Electronic Supplementary Material (ESI) for Chemical Communications

Construction and Repair of Highly Ordered 2D Covalent Networks by Chemical Equilibrium Regulation

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Experimental section

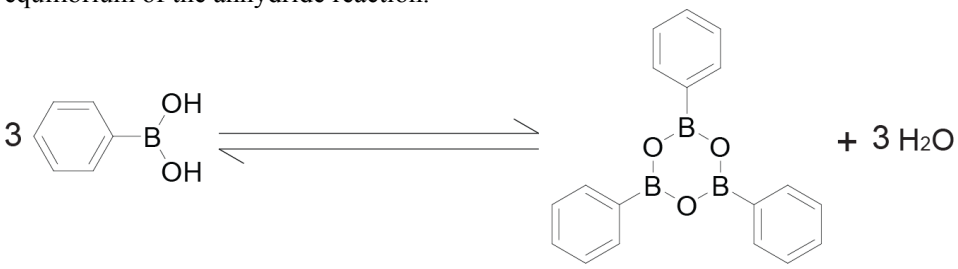
STM images were recorded using the Nanoscope IIIa SPM (Veeco) with mechanically cut Pt/Ir wires (90/10) under ambient conditions. All of the images were performed in constant-current mode and are shown without further processing. All of the chemicals used in this study were purchased from Sigma and used without further purification.

The adlayers were prepared by the deposition (~ 5 μL) of dilute solutions (dissolved in THF, ~ 10^{-4} M) on freshly cleaved HOPG surfaces. After the evaporation of THF, HOPG was transferred into a 100 mL Teflon-sealed autoclave which containing $CuSO_4 \cdot 5H_2O$ (~1.1 g). The heating temperature for BPDA, BDBA and DFBA are 150 °C, 100 °C and 150 °C respectively. The dehydration occurred in the closed autoclave at a given temperature for 1h.

Computational details

Theoretical calculations were performed within the framework of dispersion-corrected density functional theory (DFT-D) using the DMol3 code.[1-3] Standard parameter set of GGA-BLYP potential functionals was used without any parameter optimization.[4-6] The atomic orbitals were treated by a double-numeric-quality basis set with d-polarization functions (DNP). The calculations were all used with a convergence criterion of 10^{-5} au on the energy and electron density.

Herein we calculated the Gibbs free energy (ΔG^{Θ}) for the formation of a boroxine ring through dehydration reaction of borate (as shown in table 1). DFT calculation indicates that the ΔG^{Θ} for phenylboronic acid is determinate to be -11.665 kJ/mol at the reaction temperature of 100°C. It's so small that the partial pressure of water (p^{H2O}) plays a relatively key role in the equilibrium of the anhydride reaction.



(A) (B) (1)

$$\Delta G^{\Theta} = \Delta G^{\Theta}_{B} + 3\Delta G^{\Theta}_{H_2O} - 3\Delta G^{\Theta}_{A} \quad (2)$$

Table 1. ΔG^{Θ} for phenylboronic acid and phenylboronic acid at different temperature

	298.15 K	375 K	425 K
ΔG^{Θ} (p^{Θ}, T, kJ/mol)	-2.837	-11.665	-17.272

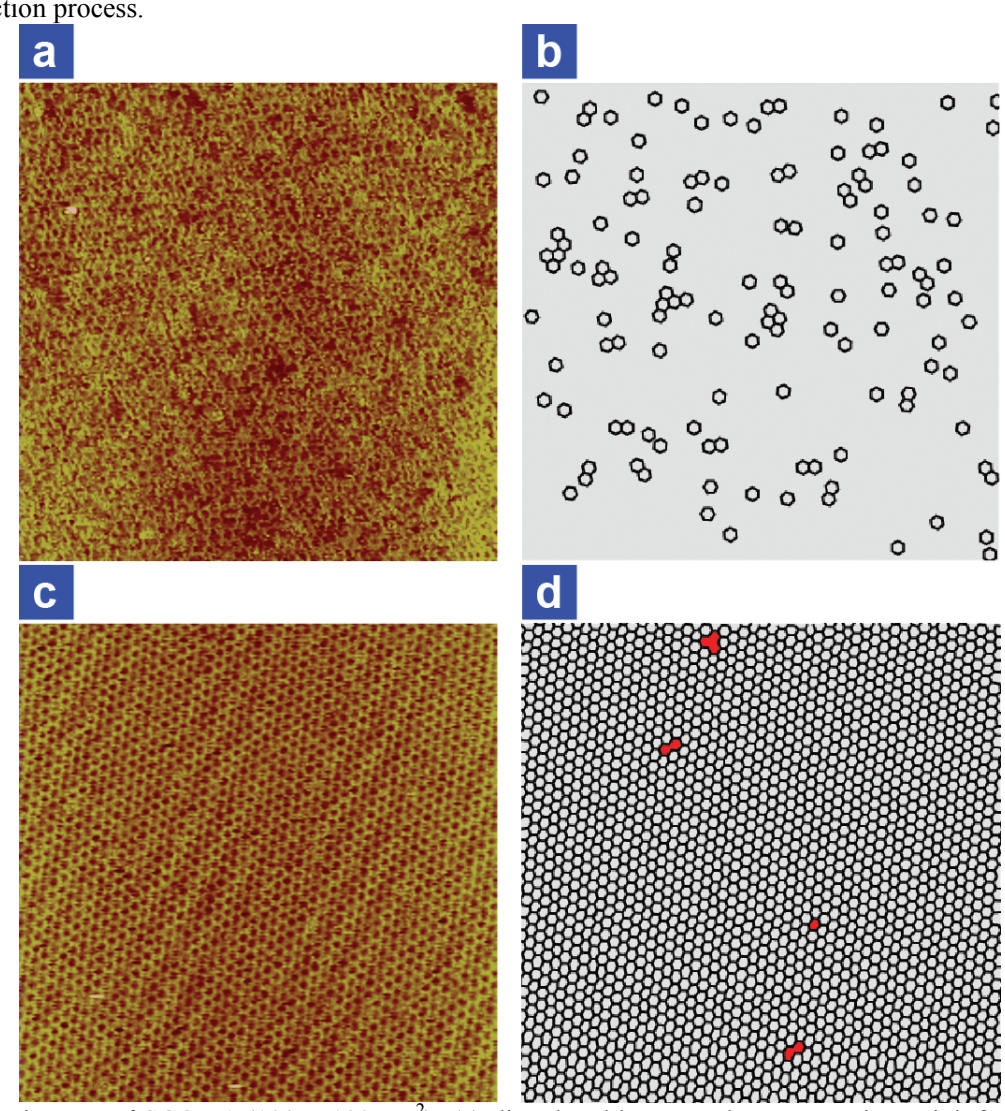
Fig. S1

The existence of water in the dehydration reaction is essential to the uniformity and orderliness of SCOF-1. Figure (a) and (c) were all formed after the dehydration of BPDA precursors at 150 °C for 1 h. The difference was that (a) is formed in open system without the presence of water while figure (c) is formed in closed system with the participation of water. The STM images showed the orderliness had obviously improvement with the participation of water. To quantify the order improvement, the STM images in (a) and (c) were delineated with hexagons as shown in (b) and (d) respectively.[7-8] On the basis of the unit cell of SCOF-1, the coverage of SCOF-1 can be calculated as:

$$\theta = \frac{N \times a^2 \times \sin 60^\circ}{A}$$

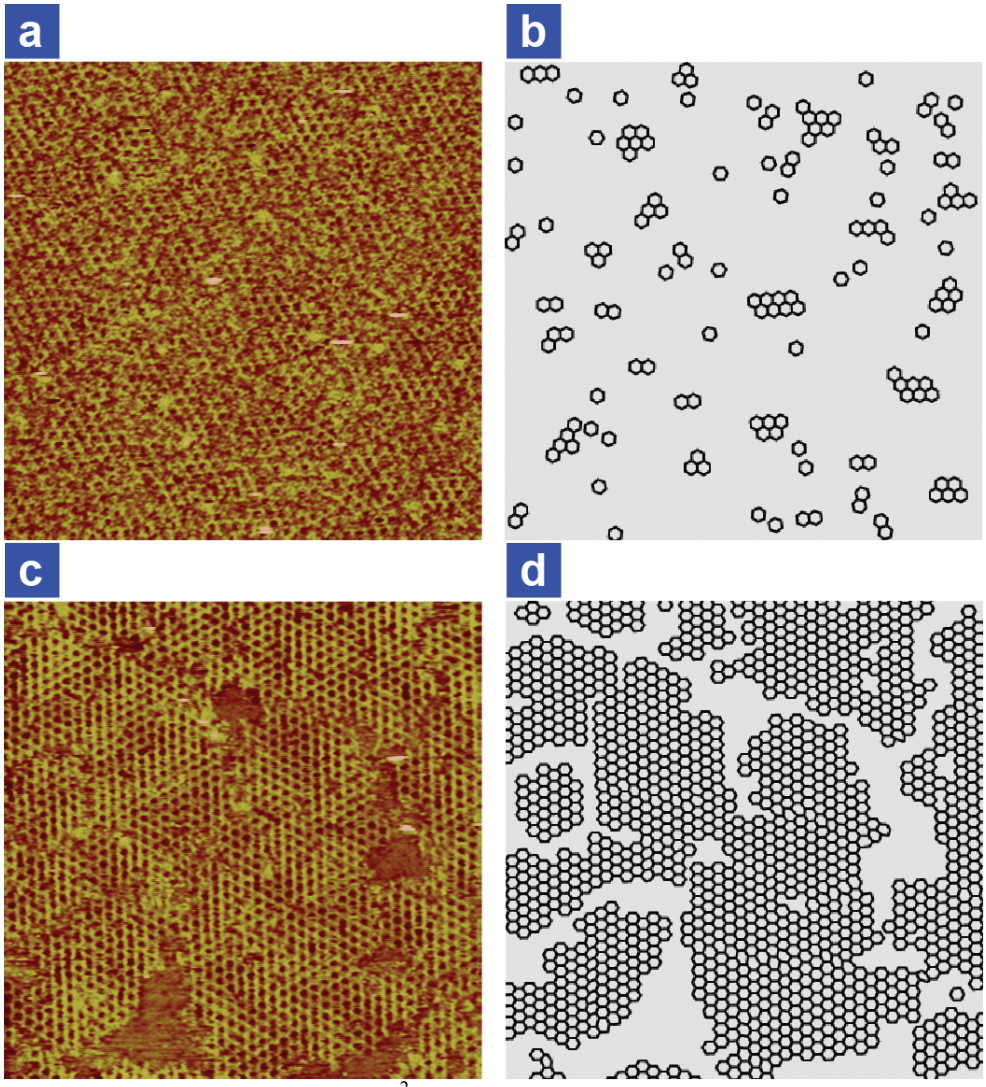
Where θ is the coverage of ordered SCOF;
N is the number of hexagons in the selected STM image.
A is area of the selected STM image.
a is the unit cell length of SCOF.

The occupancy of hexagons improves from 6% to over 98% with the introduction of water in reaction process.



STM images of SCOF-1 (100 × 100 nm^2): (a) disordered hexagonal structure via straightforward dehydration in open system without the participation of water (V_{bias} = 577 mV, I_t = 492 pA); (c) well-developed hexagonal structure via introducing small amount of water (V_{bias} = 594 mV, I_t = 322 pA); (b/d) hexagons constructed from a/c showing the orderliness of the frameworks.

Fig. S2

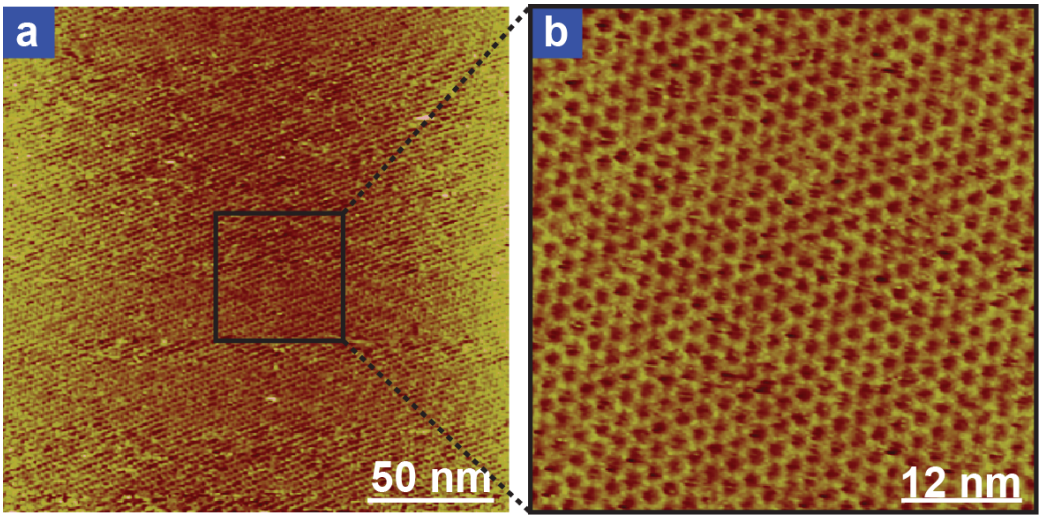


STM images of SCOF-2 (100 × 100 nm^2): (a) disordered hexagonal structure via straightforward dehydration in open system without the participation of water (V_{bias} = 552 mV, I_t = 446 pA); (c) well-developed hexagonal structure via the introducing small amount of water (V_{bias} = 677 mV, I_t = 518 pA); (b/d) hexagons constructed from a/c showing the order of the frameworks.

The occupancy of hexagons improves from 8% to 71% for SCOF-2 with the introduction of water.

Fig. S3

Large scale STM image of SCOF-1with dimension larger than 200 × 200 nm^2. Few defects can be found in the framework. (V_{bias} = 639 mV, I_t = 428 pA)



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