Supporting Information

On-Surface Synthesis of One-type Pore Single-Crystal Porous

Covalent Organic Framework

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Materials and Experimental details

Experiment

All experiments were performed with LT-STM (Scienta Omicron) under ultra-high vacuum (UHV) conditions with a base pressure below 1.0×10^{-10} mbar. Ag(111) single crystals were cleaned by repeated Ar^+ sputtering (0.7 keV) and annealing (470 ℃) cycles. The cleanness is verified by STM. The TBB precursor (Sigma-Aldrich, 97 %) were thermally evaporated on the clean Ag(111) surface from quartz crucibles heated at 100 ℃. To reduce the influence of impurities, the TBB precursor is purified firstly. A standard Knudsen cell with TBB molecules were kept slightly below 100 ℃ for a few days and kept at 100 ℃ for 24 hours before thermal evaporation. All STM images were operated below 77 K in constant-current mode using a tungsten etched tip. For dI/dV spectra the tunneling current was measured at 4.3 K by a lock-in amplifier, while the sample bias was modulated by a 600 Hz, 20-30 mV (rms) sinusoidal voltage under open-feedback conditions. All STM images were processed by WSxM[1].

Calculation

We performed the Vienna ab initio simulation package (VASP) to carry all density functional theory calculations[2]. The projector-augmented plane wave (PAW) approach was used to represent the ion–electron interaction[3]. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation was adopted[4]. The energy cutoff of the plane wave was set to 600 eV with a precision energy of 10^{-4} eV/atom and a precision force of 0.02 eV/Å, and the vacuum space along the z direction was set to 15 Å to prevent the interaction between two neighboring layers. The 2D Brillouin zone integration was performed with a $6\times6\times1$ Γ-centered κ-point mesh for the unit cell.

It is assumed that the TBB molecules are unabridged and pCOFs are composed of hexagonal structures. For simplicity, but also to restrict the number of fit parameters, we approximate that total area (Stotal) consists of two parts, including the occupied area (Socc) and unoccupied area (Sunocc) of a single TBB molecule or a hexagonal structure unit. The total area Stotal is given by

$$S_{total} = S_{occ} + S_{unocc} \approx \frac{ab}{n} \tag{1}$$

where a and b are the lattice parameters of the TBB molecule or hexagonal structure, n is the number of TBB units or hexagon units. Considering the number of self-assembled TBB molecules (N) contrasts of essential number of TBB of forming one hexagon unit on same area is given by

$$N = \frac{S_{total-Hexa}}{S_{total-TBB}} \tag{2}$$

1,3,5-tris(4-bromophenyl)benzene
(TBB)

-Br
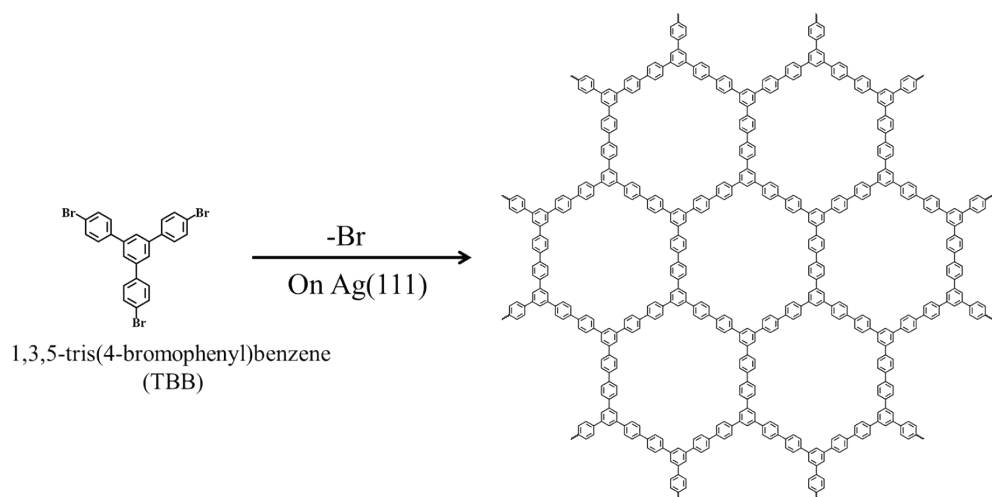
On Ag(111)

Scheme 1. Reaction scheme toward porous covalent organic framework from precursor TBB via the dehalogenated on Ag(111).

Figure S1a shows a high-resolution STM image with structural models of pCOFs superimposed in the lower-left corner, confirming that the reaction products are a precise hexagonal structure with fully phenyl-segment linking. Furthermore, a unit cell of pCOFs structure is determined to be 24.12 Å by 24.12 Å, with an angle of 60° as shown in Fig.S1b.
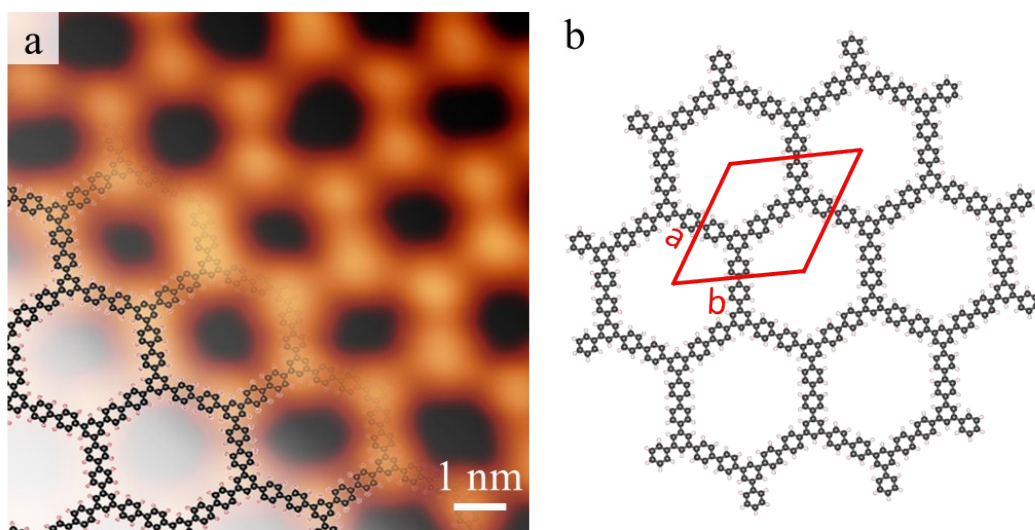

Figure S1. STM images taken after annealed at 200 ℃ with 1.0 ℃/min heater rate for deposition of TBB onto Ag(111) held at RT. (a). A model of the covalent organic frameworks is overlaid onto STM image (V = -1.5 V, I= 500 pA). (b). DFT calculated structure of the porous covalent organic frameworks. The computed unit cell is depicted in red.
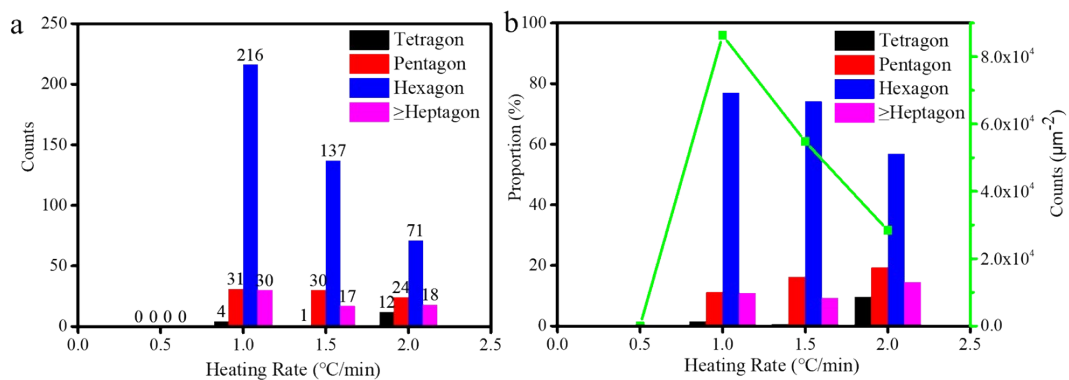
Figure S2. (a) Statistics the distribution of the different ring structure at different heating rate using STM images(Figure 2) with 50×50 nm^2 , the shape of ring cannot be recognized in figure 2a in the main text, so all polygons are counted 0. (b) Report proportion of the different ring structure and the hexagon distribution at different heating rate, confirming that the sample preparations discussed at 1.0 °C/min for the samples reported in Figure 2 are better than other heating rate.

Figure S3. STM images taken after annealed at 200 ℃ with 1.0 ℃/min rate for deposition of TBB onto Ag(111) held at RT (V = 1.0 V, I= 500 pA) .
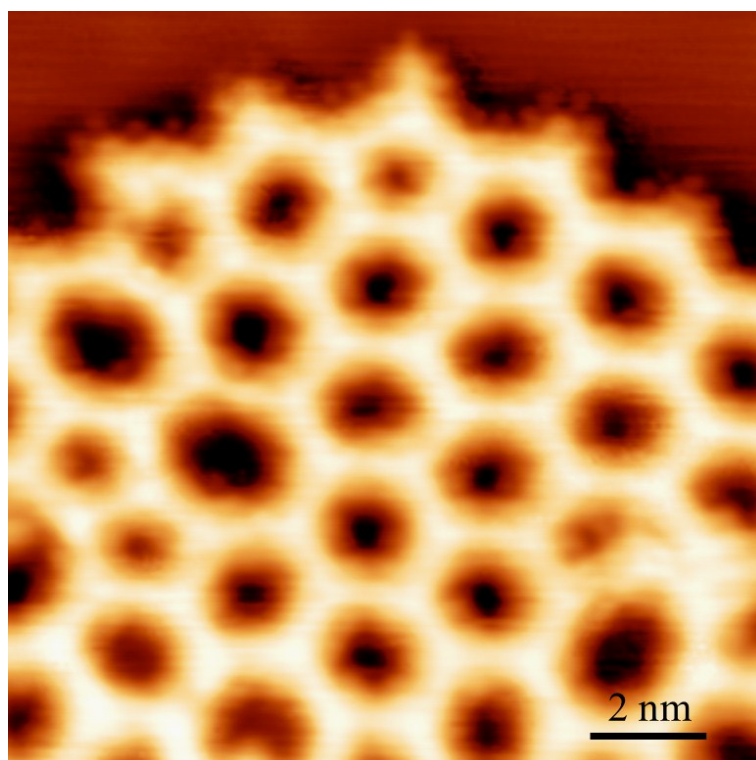
Figure S4. STM image of annealing at 200 °C after deposition of TBB onto Ag(111) held at 120 °C (V = 1.0 V, I= 800 pA).

Figure S5 shown a XPS spectrum recorded from 1ML COFs on Ag(111). The Br 3d peak with binding energy of 68.3 eV are assigned to chemisorbed bromine on Ag(111) substrate[5]. No peak is found around 70 eV, which is a typical binding energy for Br in C-Br bond[6]. That indicates the Ullman coupling reaction in our samples was fully done.
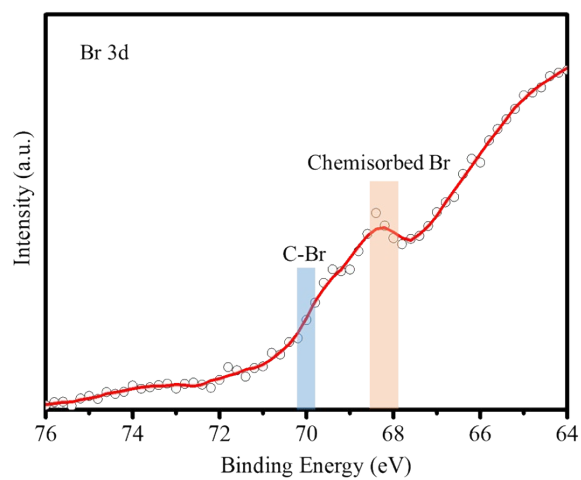

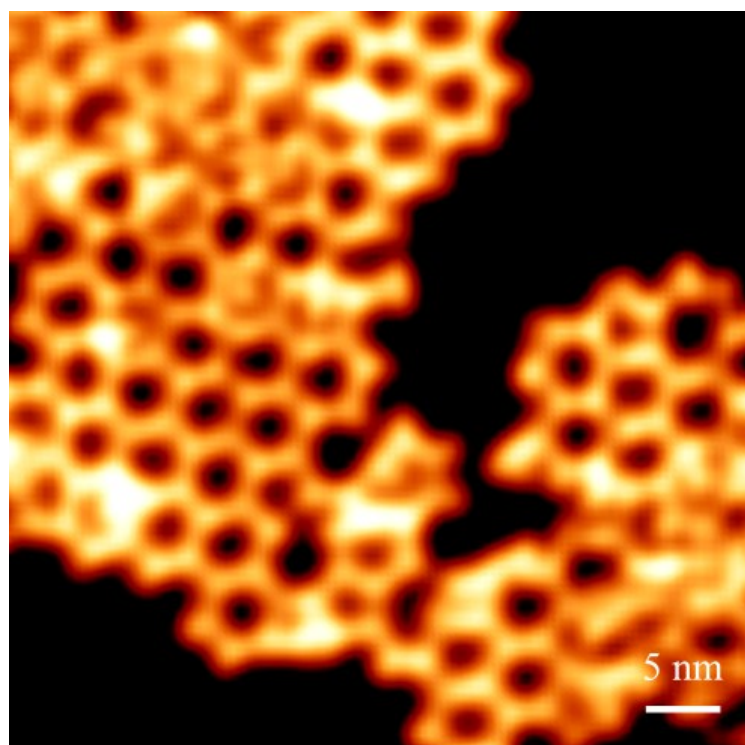Figure S5. Br 3d XPS spectrum of pCOFs on Ag(111) substrate.

Figure S6. STM image of annealing at 408 ℃ after deposition of TBB onto Ag(111) held at 200 ℃ (V = -1.0 V, I= 30 pA)**.**

We calculated the band structure and the density of states (DOS) of the pCOFs, as shown in Fig. S7, ESI,† for details. The result shows that the valence band maximum (VBM) of pCOFs is _1.00 eV and the conduction band minimum (CBM) is 1.38 eV. So the pCOFs have a DFT gap of about 2.38 eV. The result is smaller than that measured in experiment. We attribute it to the fact that pCOFs with a hexagonal structure are formed in a vacuum and not on the Ag(111) substrate.
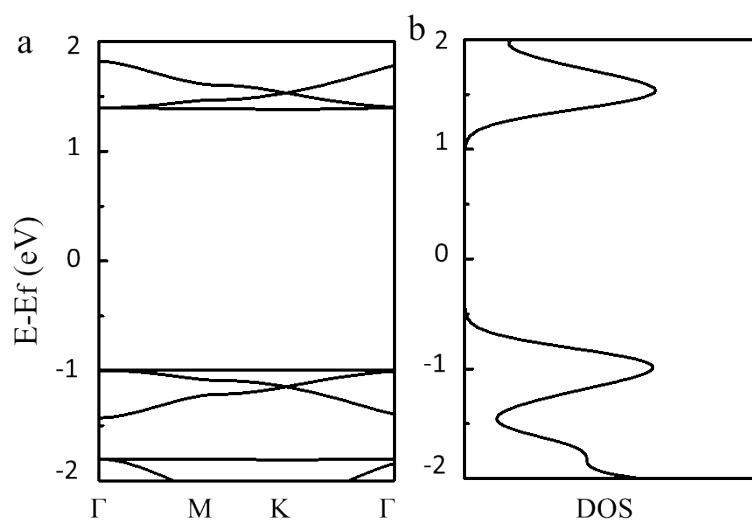

Figure S7. Calculated band electronic structure of porous covalent organic frameworks density of states (DOS) of pCOFs in vacuum (a and b).

References

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