Fabrication of bi-Layer tetrathiafulvalene integrated surface covalent organic frameworks

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1. METHODS

STM images were recorded using the Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) with mechanically cut Pt/Ir wires (80/20) as the STM tips under ambient or solution conditions. All of the images were acquired in constant current mode and are shown without further processing. *p*-Phenylenediamine (PPDA), and tetrathiafulvalene (TTF) were purchased from J&K. Tetrahydrofuran (THF), and 1-octanol were purchased from Alfa. And all of the chemicals were used in this study without further purification. Tetrathiafulvalene tetraaldehyde (4ATTF) was synthesized according to the reported procedures.[1, 2]

Synthesis of covalent single layer and bi-layer 4ATTF-PPDA sCOFs:
To prepare the single layer sCOFs, a droplet (4 μL, 10^{-4} M) of tetrahydrofuran (THF) solution containing 4ATTF (the concentration of 4ATTF was increased to 5×10^{-4} M for the synthesis of the bi-layer sCOFs) was deposited on freshly cleaved HOPG surface. After the evaporation of THF, the treated HOPG was transferred into a 100 ml Teflon-sealed autoclave, then $CuSO_4$•$5H_2O$ powder (~ 1.1 g) and PPDA (~ 0.2 mg) were also put into the autoclave near HOPG but not contacting with each other. Teflon-sealed autoclave was filled with Ar gas, sealed, and heated at 150℃ for 3h. The sample was naturally cooled down and taken out for characterization.[3, 4]

Fabricating π-π interacted noncovalent bi-layer 4ATTF-PPDA sCOFs:
Noncovalent bi-layer 4ATTF-PPDA sCOFs was prepared by depositing a droplet (2uL) of 1-octanol solution containing TTF (or 4ATTF) (10^{-4}M) onto the HOPG surface with a single layer of 4ATTF-PPDA sCOFs pre-synthesized. Leave the

sample one night without disturbing to make the solvent evaporates completely. STM experiments were carried out after the 1-octanol solvent evaporated completely.

Fabricating covalent bi-layer 4ATTF-PPDA sCOFs via 4ATTF combined noncovalent bi-layer 4ATTF-PPDA sCOFs:
The 4ATTF combined sCOFs sample was put into a 100 ml Teflon-sealed autoclave. Then $CuSO_4 \cdot 5H_2O$ powder (~ 1.1 g) and PPDA (~ 0.2 mg) were also put into the autoclave near HOPG but not contacting with each other. Teflon-sealed autoclave was filled with Ar gas. Teflon-sealed autoclave was filled with Ar gas, sealed, and heated at 150℃ for 3h. The sample was naturally cooled down and taken out for characterization

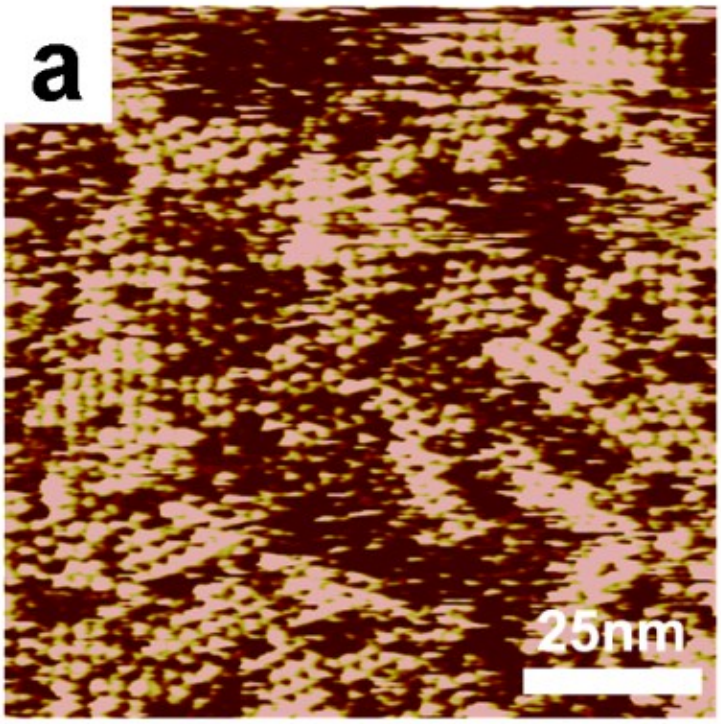

Fig. S1: Multilayer sCOFs under net 1-octanol. The upper layer sCOFs is stable under net 1-octanol and would not be dissolved. (data scale: 0.5 nm)

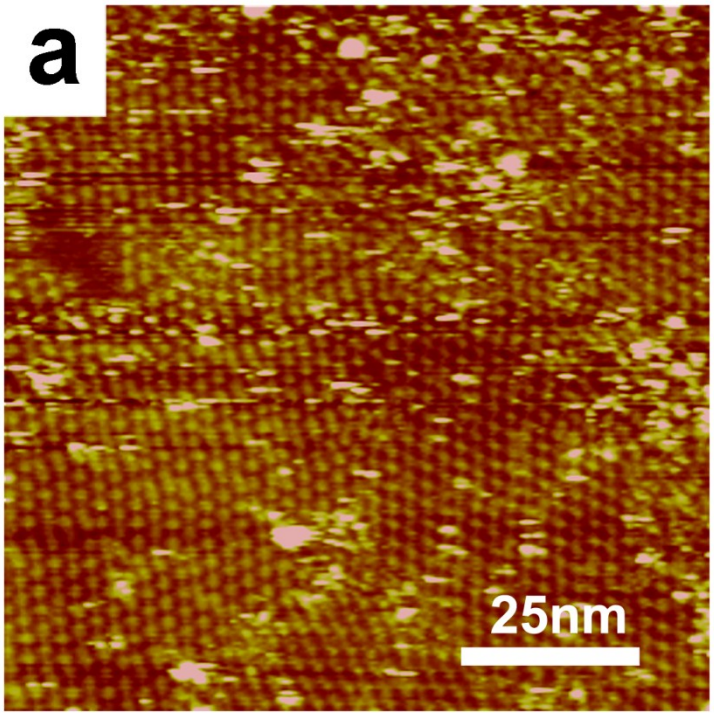

Fig. S2: STM image of sCOFs after dropping 1-octanol solution containing TTF molecules. No bilayer is observed. TTF cannot form molecular pairs with 4ATTF integrated in the sCOFs. (data scale: 0.5 nm)

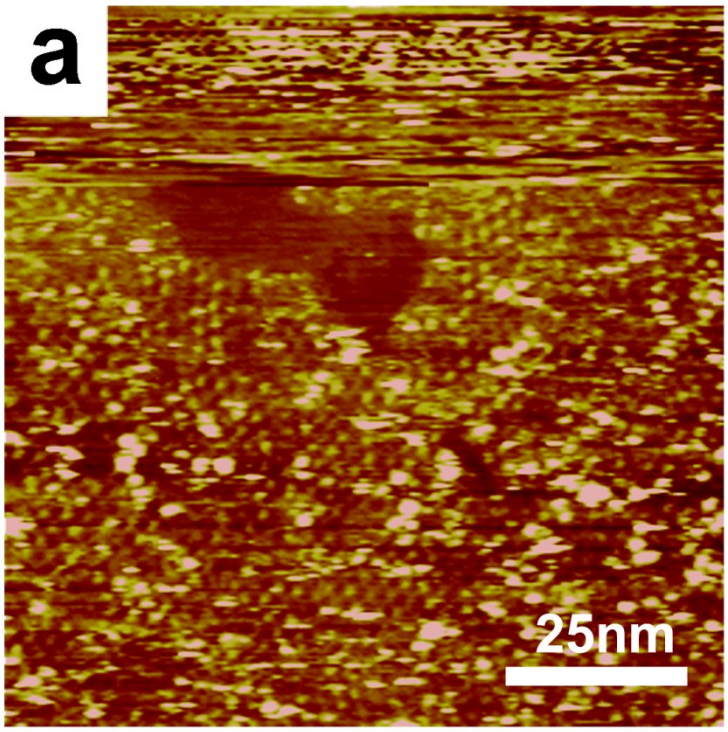

Fig. S3: STM image of the sCOFs after dripping a drop of net 1-octanol on the surface of TTF combined 4ATTF sCOFs. TTF-4ATTF molecular pairs are not stable under the solvent environment. (data scale: 0.5 nm)

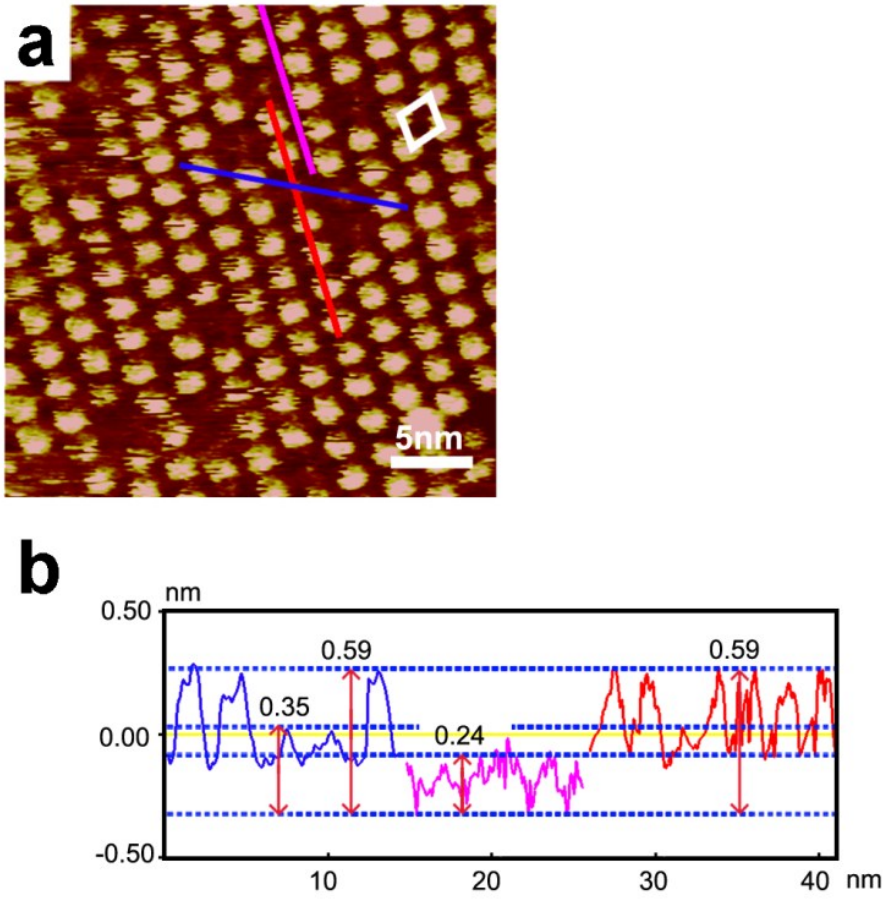

Fig. S4: Noncovalent bi-layer structure after depositing a layer of 4ATTF molecules on the top of the 4ATTF-PPDA sCOFs. (a)The STM image of the bi-layer structure. (height data scale: 0.5 nm) (b) The cross-section profiles of lines in (a) confirms the formation of nocavalent bi-layer structure. The pink line profile is along the gap of two 4ATTF molecule rows. The height of 0.24 nm is ascribed to the PPDA in the lower layer sCOFs. The blue and red lines are crossing the top of 4ATTF units in different directions, which give the height of 0.35 nm for single layer and 0.59 nm for bi-layer, confirming the formation of noncovalent bi-layer structure.

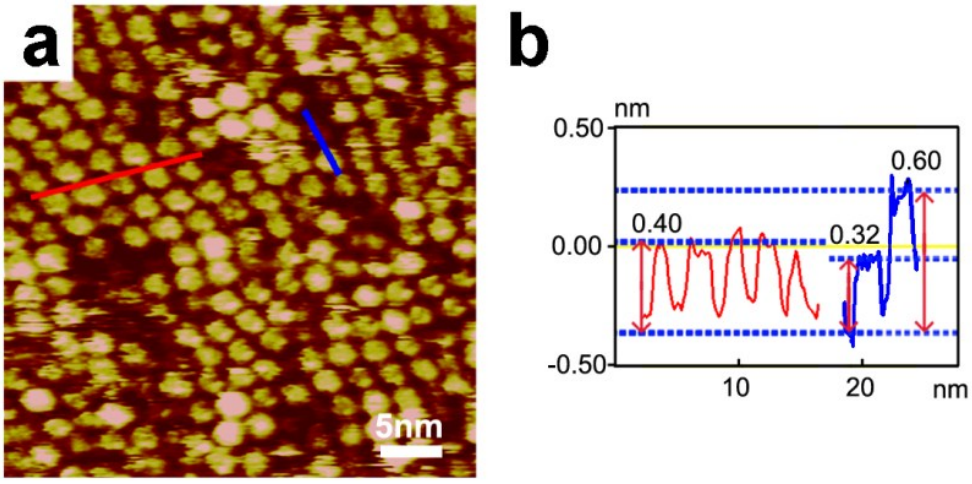

Fig. S5: Covalent double layer structure formed by using 4ATTF covered single layer sCOFs to react with PPDA molecules. (a) STM image of double layer sCOFs. (height data scale: 0.5 nm) (b) The cross-section profiles of lines in (a). The red line profile is along the gap of two 4ATTF molecule rows. The height of 0.40 nm (comparing to the result in Fig. S4) indicates the existence of PPDA (which links two 4ATTF molecules) in the upper layer sCOFs, confirming the formation of covalent bi-layer structure. The blue line is along the top of 4ATTF units, which give the height of 0.32 nm for single layer and 0.60 nm for bi-layer.

References:

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