Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

On-surface synthesis of imine-based covalent organic frameworks with non-aromatic linkage

Jie-Yu Yue,[ab] Xuan-He Liu,[ab] Bing Sun,[ab] Dong Wang*[a]

a. Key Laboratory of Molecular Nanostructure and Nanotechnology and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, P.R. China. Email: wangd@iccas.ac.cn

b. University of CAS, Beijing100049, P. R. China..

Materials and methods

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.

1, 3, 5-tris(4-formylphenyl)benzene was synthesized according to the reported procedures. Its ^{1}H NMR and ^{13}C NMR spectra are in accordance well with the reported literatures. 1, 3, 5-tris(4-aminophenyl)benzene，glyoxal, and hydrazine monohydrochloride were purchased from J&K. All the chemicals used in this study, unless otherwise specified, were utilized without further purification.

Synthesis of $sCOF_{A+B}$.

1, 3, 5-tris (4-formylphenyl) benzene (A) and hydrazine monohydrochloride (B) were served as precursors. 4 μL THF solution of molecule A with concentration about 10^{-5} mol/L was preloaded on freshly cleaved HOPG and then 4 μL water/THF solution of molecule B with concentration about 10^{-4} mol/L was deposited on the same surface. If molecular A and molecular B were mixed in the solution, pale yellow precipitation formed immediately, which indicates a drastic reaction between building blocks A and B. The HOPG loaded with precursors A and B was put in a sealed reactor with the presence of several

CuSO4·5H2O powders about 1.1 g as chemical equilibrium control agent. After heating at 140 ℃ for 3h, the HOPG was cooled down to room temperature and taken out for STM characterization.

Synthesis of $sCOF_{C+D}$

We utilized 1, 3, 5-tris (4-aminophenyl) benzene (C) and glyoxal (D) as building blocks. 4μL THF solution of molecule C with concentration about 10^{-5} mol/L and molecule D with concentration about 10^{-4} mol/L were deposited on freshly cleaved HOPG surface, respectively. Then the treated HOPG was moved into a closed autoclave with several $CuSO_4·5H_2O$ powder at the bottom of autoclave. The autoclave was heated at 80 ℃ for 3h. After cooling down, the HOPG was taken out for STM characterization.

Supplementary figures

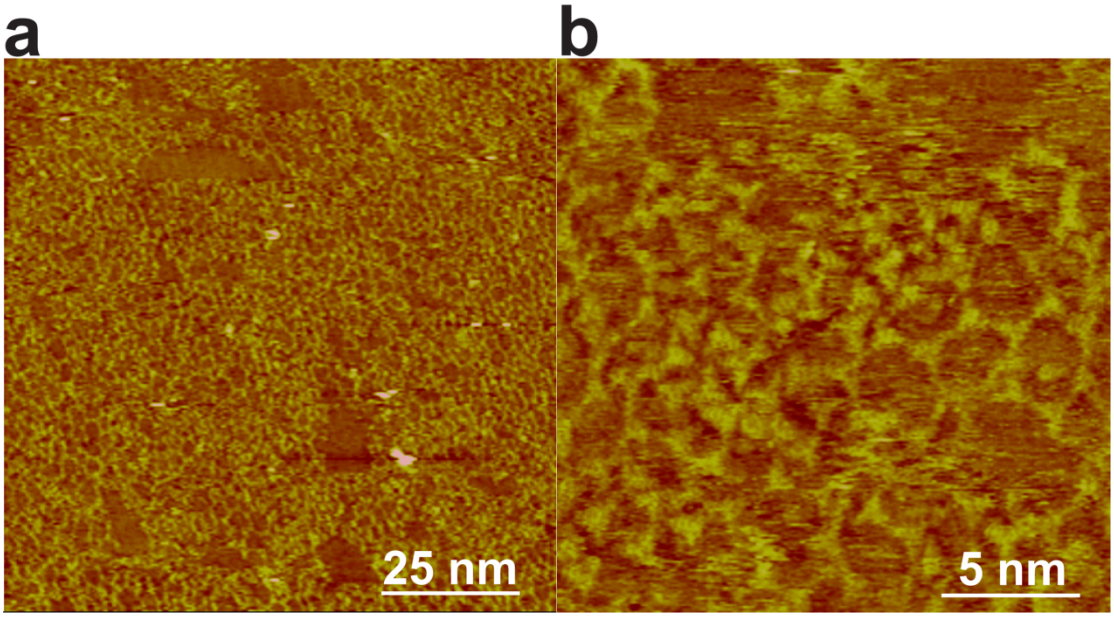

Fig. S1. STM images of $sCOF_{C+D}$ fabricated at 60 ℃. (a) Large-scale STM image (100 × 100 nm^2) of $sCOF_{C+D}$. (b) High resolution STM image (20 × 20 nm^2) of $sCOF_{C+D}$. Imaging conditions: (a) V_{bias} = 700 mV, I_t = 500 pA; (b) V_{bias} = 700 mV, I_t = 650 pA.

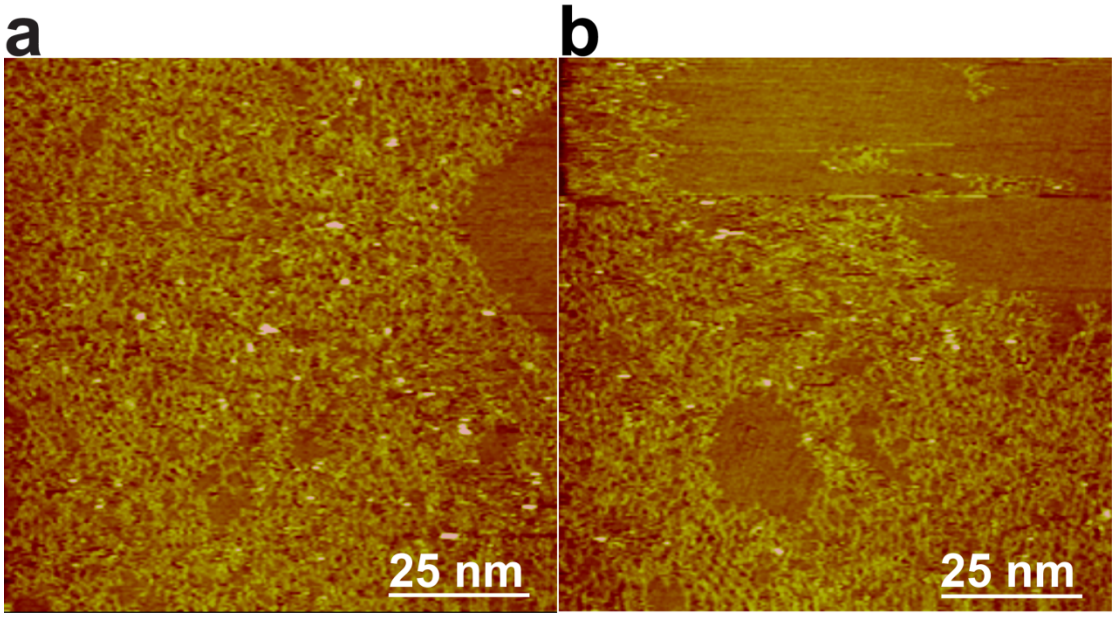

Fig. S2. Large-scale STM image (100 × 100 nm^2) of molecular C and D at 120 ℃.