Electronic Supporting Information

Self-Exfoliation of 2D Covalent Organic Frameworks: Morphology Transformation Induced by Solvent Polarity

Na Zhang\textsuperscript{a}, Taisheng Wang\textsuperscript{a}, Xing Wu\textsuperscript{a}, Chen Jiang\textsuperscript{a}, Fang Chen\textsuperscript{a}, Wei Bai\textsuperscript{b}\textsuperscript{*}, and Ruke Bai\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a} CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, P. R. China
\textsuperscript{b} Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States.
Tel 86-551-63600722; Fax 86-551-63631760
\textsuperscript{a}E-mail: bairk@ustc.edu.cn
\textsuperscript{b}E-mail: baiwei81@gmail.com

Table of Contents

1. Instruments and Methods.

Figure S1. Synthetic route of the A\textsubscript{2}, B\textsubscript{3} and C\textsubscript{2}.

Figure S2. FT-IR spectra of A\textsubscript{2}, B\textsubscript{3}, C\textsubscript{2}, iCOFs-A and COFs-B.

Table S1. Peak assignments for FT-IR spectrum of iCOFs-A

Table S2. Peak assignments for FT-IR spectrum of COFs-B

Figure S3. Solid-state \textsuperscript{13}C-CP/MAS NMR spectroscopys of A\textsubscript{2}, B\textsubscript{3}, C\textsubscript{2}, iCOFs-A and COFs-B.

Figure S4. Element analysis of iCOFs-A.

Figure S5. Thermogravimetric analysis (TGA) of iCOFs-A and ICONs-A.

Figure S6. Experimental PXRD patterns of COFs-B.

Figure S7. Pore size distribution of COFs-B and Nitrogen sorption isotherms for COFs-B at 77 K.

Figure S8. AFM images and height profiles of nanospheres (a) and nanosheets (b,c) transformed from iCOFs-A.

Figure S9. SEM (a,b,c) and TEM (d,e,f) images of COFs-B in different solvents.

Figure S10. SEM images of the uniform ICONs-A thin films on silicon substrate (a,b), which showed the re-accumulated nanosheets; I–V profile of ICONs-A (red curve: without light irradiation; blue curve: upon light irradiation) (c); PXRD patterns of ICONs-A thin films on silicon substrate (d).

Figure S11. TEM images of iCOFs-A in various organic solvents.

Figure S12-S25. NMR Data
**Figure S26.** Synthetic route of the model compound.

1. **Instruments and Methods.**

   **Transmission electron microscopy (TEM)**

   Transmission electron microscopy was performed on a Philips CM 200/FEG transmission electron microscope. The samples were prepared by carefully dropping the corresponding solution onto the carbon coated copper grid followed by removal of the solvent under vacuum.

   **Atomic force microscopy (AFM)**

   Atomic force microscopy was carried out with a Nano scope IIIa MultiMode microscope. The samples were prepared by drop-casting of the corresponding solution (diluted with distilled water) on mica or silicon wafers, dried under air for 2 h, and then submitted to AFM characterization.

   **Fourier-transform infrared spectroscopy (FT-IR)**

   Fourier transform infrared spectroscopy was carried out with a Nicolet 380 FT-IR spectrometer. The samples for IR study were prepared as KBr pellets.

   **Thermal properties**

   Thermogravimetric analysis (TGA) was performed on a TGA 851 (Mettler Toledo) from room temperature to 600 ºC at the heating rate of 10 ºC min$^{-1}$ under N$_2$.

   **Powder X-ray diffraction**

   X-ray diffraction measurements were carried out with an X’Pert PROX system using monochromated Cu/Kα (λ = 0.15418 nm). The samples were spread on the square recess of XRD sample holder as a thin layer, respectively.

   **Photoelectricity measurements**

   Electrical conductivity and photoconductivity measurements of the iCONs-A were carried out through a two-probe method using an Agilent B1500A Precision semiconductor parameter analyzer coupled a Signatone S-1160 probe station, which is equipped with a Motic microscope and a CCD camera for in situ imaging of the device. The whole system is housed in a shielding dark box to eliminate the noise and/or scattering light for low-current and/or light-sensitive measurements. The micro-gap electrodes were fabricated by photolithography silicon wafer covered with a 300 nm thick SiO$_2$ dielectric layer. The gold electrode pair is 50 µm long and 5 µm wide, onto which nanosheets were deposited by drop-casting, followed by air-drying. We investigated the photoconductivity of iCONs-A by casting a thin film of iCONs-A on gold electrode with the irradiation from visible light (>400 nm) of
a xenon lamp.

**Figure S1.** Synthetic route of the A₂, B₃ and C₂.

**Figure S2.** FT-IR spectra of A₂, B₃, C₂, iCOFs-A and COFs-B.

**Table S1.** Peak assignments for FT-IR spectrum of iCOFs-A

| Peak (cm⁻¹) | Assignment and Notes                                      |
|------------|----------------------------------------------------------|
| 3437 (m)   | H₂O                                                      |
| 2935 (w)   | C–H stretching                                           |
| 2846 (w)   |                                                          |
| 1610 (w) C=C| stretch in typical region for fused aromatics           |
| 1522 (w) C=C| stretch in typical region for fused aromatics           |
| 1464 (m)   | C–N¹ stretch                                             |
| 1375 (m)   | B–O stretch, characteristic band for borate ester        |
| 1231 (m)   | C–O stretch, characteristic band for borate ester        |
| 1132 (w)   | C–H in plane bending modes.                             |
| 1087 (m)   |                                                          |
Table S2. Peak assignments for FT-IR spectrum of COFs-B

| Peak (cm⁻¹) | Assignment and Notes |
|-------------|----------------------|
| 3232        | H₂O                  |
| 1629        | C=C stretch in typical region for fused aromatics |
| 1495        | C=C stretch in typical region for fused aromatics |
| 1375        | B−O stretch, characteristic band for borate ester |
| 1231        | C−O stretch, characteristic band for borate ester |
| 1120        | C−H in plane bending modes. |
| 1010        |                      |
| 588         | C-Br stretch         |

Figure S3. Solid-state ¹³C-CP/MAS NMR spectroscopys of A2, B3, C2, iCOFs-A and COFs-B.

Figure S4. Element analysis of iCOFs-A.
Figure S5. Thermogravimetric analysis (TGA) of iCOFs-A and iCONs-A. Both of the TGA profiles of iCONs-A and iCOFs-A showed an initial stage of thermal weight loss below 200 °C which was attributed to the evaporation of water absorbed by ionic groups on the iCONs-A.

Figure S6. Experimental PXRD patterns of COFs-B.

Figure S7. Pore size distribution of COFs-B and Nitrogen sorption isotherms for COFs-B at 77 K.
Figure S8. AFM images and height profiles of nanospheres (a) and nanosheets (b,c) transformed from iCOFs-A.

Figure S9. SEM (a,b,c) and TEM (d,e,f) images of COFs-B in different solvents. Scale bars: a) 10 μm, b) 10 μm, c) 10 μm, d) 1 μm, e) 1 μm, f) 1 μm.
Figure S10. SEM images of the uniform iCONs-A thin films on silicon substrate (a, b), which showed the re-accumulated nanosheets; I–V profile of iCONs-A (red curve: without light irradiation; blue curve: upon light irradiation) (c) (Insert: Photocurrent when the light was turned on or off.); PXRD patterns of iCONs-A thin films on silicon substrate(d).

Figure S11. TEM images of iCOFs-A in various organic solvents.
NMR Data

Figure S12. $^1$H NMR spectrum of compound 1.

Figure S13. $^{13}$C NMR spectrum of compound 1.
Figure S14. $^1$H NMR spectrum of compound 2.

Figure S15. $^{13}$C NMR spectrum of compound 2.
Figure S16. $^1$H NMR spectrum of compound C2.

Figure S17. $^{13}$C NMR spectrum of compound C2.
Figure S18. $^1$H NMR spectrum of compound A2.

Figure S19. $^{13}$C NMR spectrum of compound A2.
Figure S20. $^1$H NMR spectrum of compound 3.

Figure S21. $^{13}$C NMR spectrum of compound 3.
Figure S22. $^1$H NMR spectrum of compound B3.

Figure S23. $^{13}$C NMR spectrum of compound B3.
Figure S24. $^1$H NMR spectrum of the compound 4.

Figure S25. $^1$H NMR spectrum of the model compound.
Figure S26. Synthetic route of the model compound.