

# **Supporting Information**

## **Fabricating Organic Nanotubes through Selective Disassembly of Two-Dimensional Covalent Organic Frameworks**

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## Table of Contents

<b>Section 1.</b> Instruments and methods.....	S3-S4
<b>Section 2.</b> Synthetic procedures.....	S5-S7
<b>Section 3.</b> Characterizations of the COFs and nanotubes.....	S8-S19
<b>Figure S1.</b> Photographs of the gelation phenomenon after the condensation reactions.....	S8
<b>Figure S2.</b> FT-IR spectra of the monomers and <b>COF-OEt</b> .....	S8
<b>Figure S3.</b> Solid-state $^{13}\text{C}$ CP/MAS NMR spectrum of <b>COF-OEt</b> .....	S9
<b>Figure S4.</b> TGA profiles of the COFs.....	S9
<b>Figure S5.</b> SEM images of the COFs.....	S9
<b>Figure S6.</b> BET surface area plots for the COFs.....	S10
<b>Figure S7.</b> FT-IR spectra of <b>COF-OEt</b> before and after hydrolysis.....	S10
<b>Figure S8.</b> TEM images of <b>NT-OEt</b> .....	S10
<b>Figure S9.</b> Theoretical diameters of <b>NT-OEt</b> and <b>NT-OAl-CR</b> .....	S11
<b>Figure S10.</b> TEM images of <b>NT-OEt</b> after ultrasonic treatment.....	S11
<b>Figure S11.</b> TEM images of <b>NT-OEt</b> after ultrasonic treatment and being stood at room temperature for 12 h.....	S11
<b>Figure S12.</b> FT-IR spectra of the monomers, <b>COF-OAl</b> and <b>COF-OAl-CR</b> .....	S12
<b>Figure S13.</b> Solid-state $^{13}\text{C}$ CP/MAS NMR spectrum of <b>COF-OAl</b> .....	S12
<b>Figure S14.</b> PXRD patterns of <b>COF-OAl</b> .....	S13
<b>Figure S15.</b> $\text{N}_2$ sorption isotherm and pore size distribution profile of <b>COF-OAl</b> .....	S13
<b>Figure S16.</b> Experimental PXRD profiles of <b>COF-OAl</b> and <b>COF-OAl-CR</b> .....	S14
<b>Figure S17.</b> Solid-state $^{13}\text{C}$ CP/MAS NMR spectrum of <b>COF-OAl-CR</b> .....	S14
<b>Figure S18.</b> FT-IR spectra of <b>COF-OAl</b> and <b>COF-OAl-CR</b> .....	S14
<b>Figure S19.</b> FT-IR spectra of <b>COF-OAl-CR</b> before and after hydrolysis.....	S15
<b>Figure S20.</b> TEM images of <b>COF-OAl</b> and <b>COF-OAl-CR</b> .....	S15
<b>Figure S21.</b> TEM images of <b>NT-OAl-CR</b> .....	S15
<b>Figure S22.</b> Mechanism of alkene metathesis reaction and partial simulated crystal structure of <b>COF-OAl</b> .....	S16
<b>Tables S1-S2.</b> Fractional atomic coordinates of the COFs.....	S16-S18
<b>Figures S23-S24.</b> $^1\text{H}$ NMR (400 MHz, $\text{D}_2\text{O}$ ) spectra of the samples after soaking the COFs in $\text{D}_2\text{O}$ .....	S18-S19

## **Section 1. Instruments and methods**

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

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

### **Solid-state nuclear magnetic resonance (NMR) spectroscopy**

The  $^{13}\text{C}$  CP/MAS NMR spectra of the COFs were recorded on an Agilent DD2 600 Solid NMR System with 3.2 mm zirconia rotors. The spinning rate is 8 kHz and the contact time is 3 ms.

### **Thermal gravimetric analysis (TGA)**

Thermal gravimetric analysis was conducted on a Waters TGA Q500 instrument by heating the samples from room temperature to 1000 °C under nitrogen atmosphere with a heating rate of 10 °C/min.

### **Scanning electron microscopy (SEM)**

Scanning electron microscopy was carried out using a FEI NOVA NANOSEM 450 scanning electron microscope. The samples were dispersed over the slices of silicon wafer adhered to flat copper platform sample holders and then coated with gold using a sputter coater (ambient temperature, 85 torr pressure in an nitrogen atmosphere, puttered for 30s from a solid gold target at a current at 30 mA) before being submitted to SEM characterization.

### **Powder X-ray diffraction**

Powder X-ray diffraction measurements were carried out with an PANalytical X'Pert Powder system using monochromated  $\text{Cu}/\text{K}\alpha$  ( $\lambda = 0.1542$  nm). The samples were spread on the square recess of XRD sample holder as thin layers.

### **Structural simulations and powder X-ray diffraction analyses**

Structural simulations were carried out in Materials Studio 7.0. The predicted

structures with eclipsed (AA) or staggered (AB) stacking models were firstly optimized in geometry optimizations by the Forcite molecular dynamics module method, after which the simulated PXRD patterns were determined by the Reflex module. The Pawley refinement of the experimental PXRD was conducted by the Reflex module.

### **Nitrogen adsorption-desorption isotherm measurement**

The measurements were carried out using a Quantachrome autosorb iq system. Before the N<sub>2</sub> adsorption measurements, the as-synthesized COFs were washed by supercritical CO<sub>2</sub>. The samples were activated by degassing at 100 °C for 10 h and used for gas adsorption measurements from 0 to 1 atm at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate their specific surface areas. By using the quenched solid density functional theory (QSDFT), the pore size distributions were derived from the sorption data.

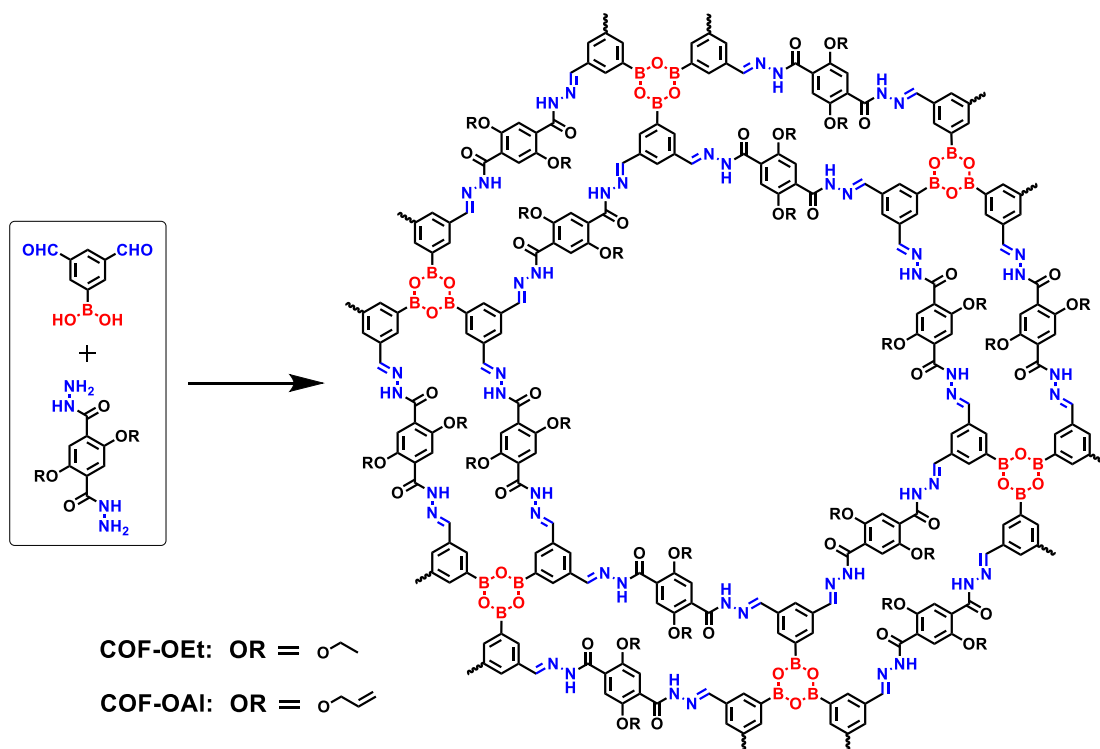
### **Transmission electron microscopy (TEM)**

Transmission electron microscopy was performed on a JEOL JEM-2100, JEOL USA JEM-F200 or Tecnai G2 F20 S-TWIN instrument. The samples were dispersed over the carbon coated copper grids with ethanol as solvent.

### **Measurement method of diameters of nanotubes**

The diameters of nanotubes were measured with the “Line with length label” tool in the Gatan DigitalMicrograph software. For each type of nanotubes, statistical analysis was applied by measuring diameters of the nanotubes at no less than 20 different regions to give the corresponding statistical diameter distribution.

## Section 2. Synthetic procedures



**Scheme S1.** Synthesis and structures of **COF-OEt** and **COF-OAl**.

### Synthesis of COF-OEt

The synthesis of **COF-OEt** was carried out with 3,5-diformylphenylboronic acid (**DFPBA**, 10.0 mg, 0.056 mmol) and 2,5-diethoxyterephthalohydrazide (**DETH**, 16.2 mg, 0.056 mmol, synthesized according to the reported procedure<sup>1</sup>) as monomers in a mixture of n-butyl alcohol and o-dichlorobenzene (1/1, 1.5 mL) in a glass ampoule. After three freeze-pump-thaw cycles, the glass ampoule was sealed under vacuum. The mixture was then heated at 150 °C for 3 days to afford a yellow colloid. After cooling to room temperature, the colloid was dried under dynamic vacuum at 120 °C for 4 h to afford crude product. Then the as-synthesized COF was further washed by ethyl alcohol and methyl alcohol and then dried to afford yellow crystallites (19.7 mg, 87%), which was insoluble in common organic solvents such as dichloromethane, ethanol, and N, N-dimethylformamide. Note: Due to the strong interactions between the framework and solvent molecules, we took into account the amount of solvents

that are encapsulated in the COF when calculating theoretical elemental constitution. By soaking **COF-OEt** in D<sub>2</sub>O for 6 days, we found that the sample consists of the COF (90.8 wt%), n-butyl alcohol (6.2 wt%) and methanol (3.0 wt%) (Figure S23). Anal. Calcd. For C<sub>20</sub>H<sub>19</sub>BN<sub>4</sub>O<sub>5</sub>·(C<sub>4</sub>H<sub>10</sub>O)<sub>0.37</sub>·(CH<sub>4</sub>O)<sub>0.42</sub>: C, 58.84; H, 5.50; N, 12.52. Found: C, 53.64; H, 5.09; N, 12.17.

### Synthesis of COF-OAI

The synthesis of **COF-OAI** was carried out with 3,5-diformylphenylboronic acid (**DFPBA**, 10.0 mg, 0.056 mmol) and 2,5-bis(allyloxy)terephthalohydrazide (**BATH**, 17.2 mg, 0.056 mmol, synthesized according to the reported procedure<sup>2</sup>) as monomers in a mixture of n-butyl alcohol and mesitylene (1/1, 1.5 mL) in a glass ampoule. After three freeze-pump-thaw cycles, the glass ampoule was sealed under vacuum. The mixture was then heated at 120 °C for 3 days to afford a yellow colloid. After cooling to room temperature, the colloid was dried under dynamic vacuum at 120 °C for 4 h to afford crude product. Then the as-synthesized COF was further washed by ethyl alcohol and methyl alcohol and then dried to afford yellow solid product (18.0 mg, 75%), which was insoluble in common organic solvents such as dichloromethane, ethanol, and N, N-dimethylformamide. Note: Due to the strong interactions between the framework and solvent molecules, we took into account the amount of solvents that are encapsulated in the COF when calculating theoretical elemental constitution. By soaking **COF-OEt** in D<sub>2</sub>O for 6 days, we found that the sample consists of the COF (95.0 wt%), n-butyl alcohol (3.3 wt%) and ethyl alcohol (1.7 wt%) (Figure S24). Anal. Calcd. For C<sub>22</sub>H<sub>19</sub>BN<sub>4</sub>O<sub>5</sub>·(C<sub>4</sub>H<sub>10</sub>O)<sub>0.20</sub>·(C<sub>2</sub>H<sub>6</sub>O)<sub>0.16</sub>: C, 61.38; H, 4.90; N, 12.37. Found: C, 60.52; H, 5.46; N, 11.57.

### Hydrolysis of COF-OEt

**COF-OEt** (8.0 mg) was added to an aqueous hydrochloric acid solution (6 M, 6 mL), and the system was set aside for 6 days at room temperature. The solid was then filtered, washed with ethanol, and then dried for characterizations.

### **Synthesis of COF-OAI-CR by cross-linking**

**COF-OAI** (26.0 mg, 0.060 mmol) and Grubbs catalyst 1<sup>st</sup> generation (Benzylidenebis(tricyclohexylphosphine)dichlororuthenium, 6.0 mg, 0.007 mmol) were added to dichloromethane (5 mL) and the system was refluxed at 45 °C for 36h. After cooling to room temperature, the mixture was filtered and the solid was washed with dichloromethane to give a yellow solid.

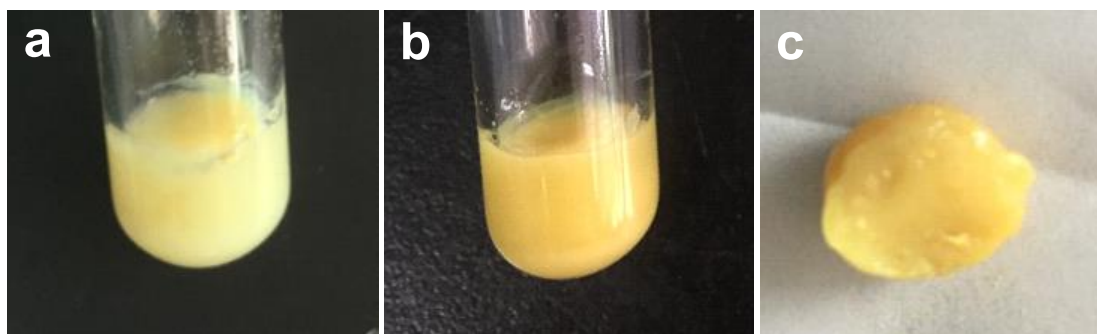
### **Hydrolysis of COF-OAI-CR**

**COF-OAI-CR** (16.0 mg) was added to a mixture of H<sub>2</sub>O (5 mL) and THF (5 mL), and the system was set aside for 6 days at room temperature. The solid was then filtered, washed with ethanol, and then dried for characterizations.

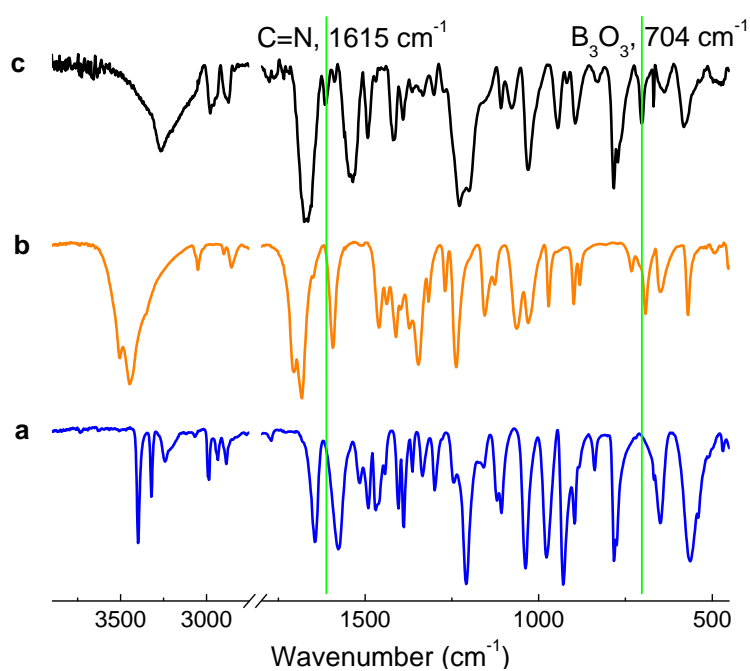
### **Reference:**

- (1) D. N. Bunck, W. R. Dichtel, *J. Am. Chem. Soc.* **2013**, *135*, 14952-14955.
- (2) B.-J. Yao, J.-T. Li, N. Huang, J.-L. Kan, L. Qiao, L.-G. Ding, F. Li, Y.-B. Dong, *ACS Appl. Mater. Interfaces* **2018**, *10*, 20448-20457.

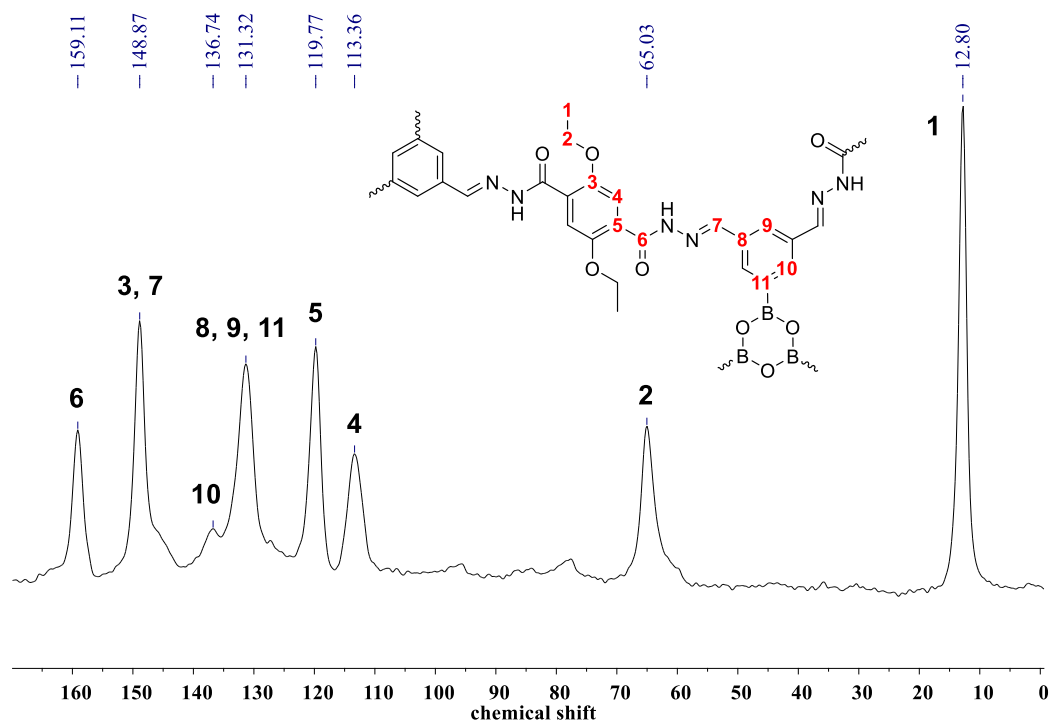
### Section 3. Characterizations of the COFs and nanotubes



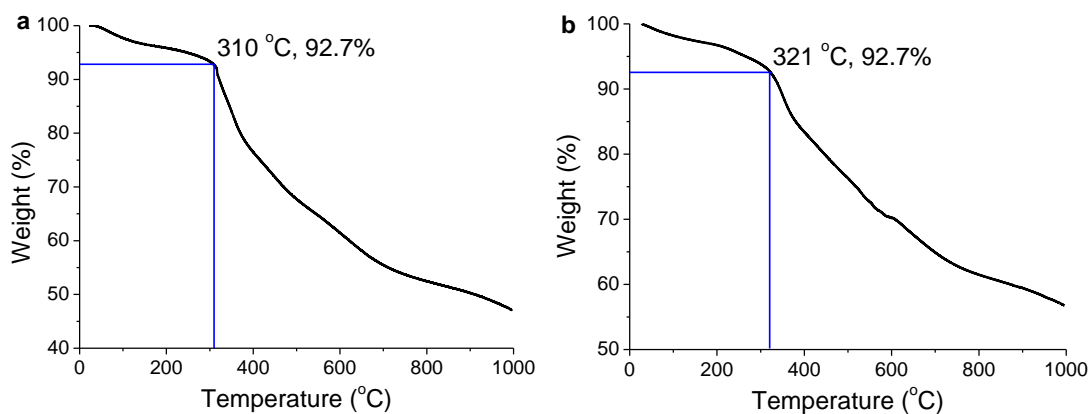
**Figure S1.** Photographs of the gelation phenomenon after the condensation reactions for the preparation of (a) **COF-OEt**, and (b) and (c) **COF-OAl**.



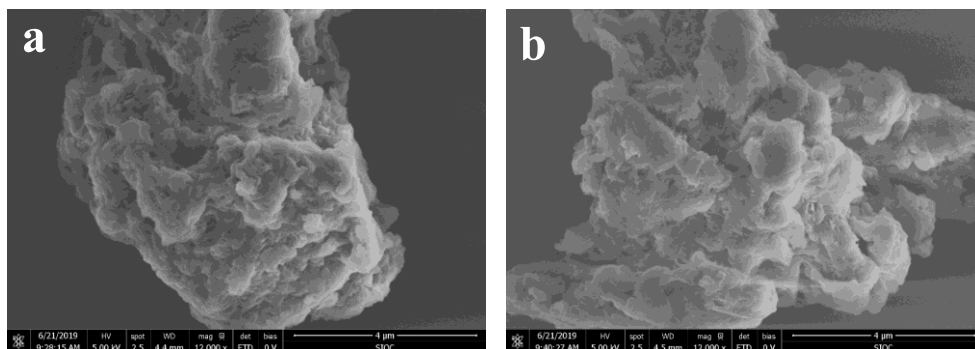
**Figure S2.** FT-IR spectra of (a) **DETH**, (b) **DFPBA**, and (c) **COF-OEt**.



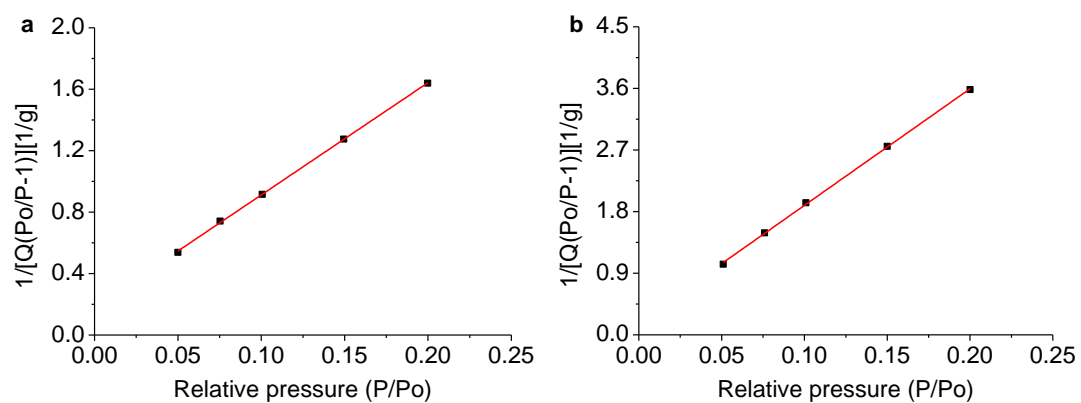
**Figure S3.** Solid-state  $^{13}\text{C}$  CP/MAS NMR spectrum of COF-OEt.



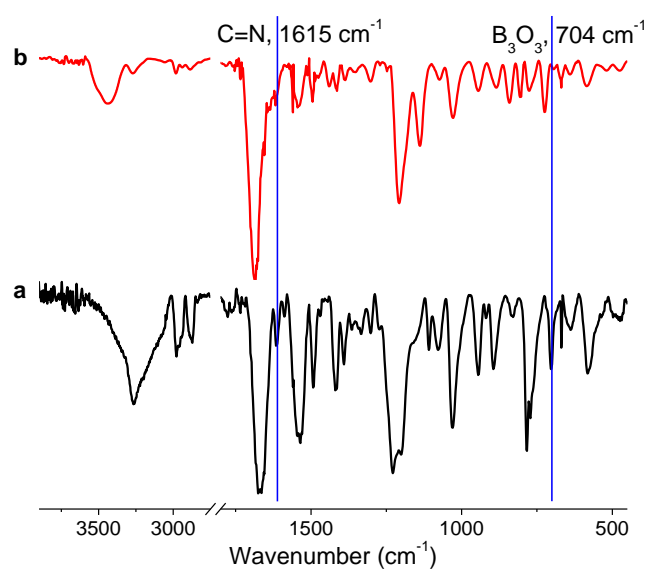
**Figure S4.** TGA profiles of (a) COF-OEt and (b) COF-OAl.



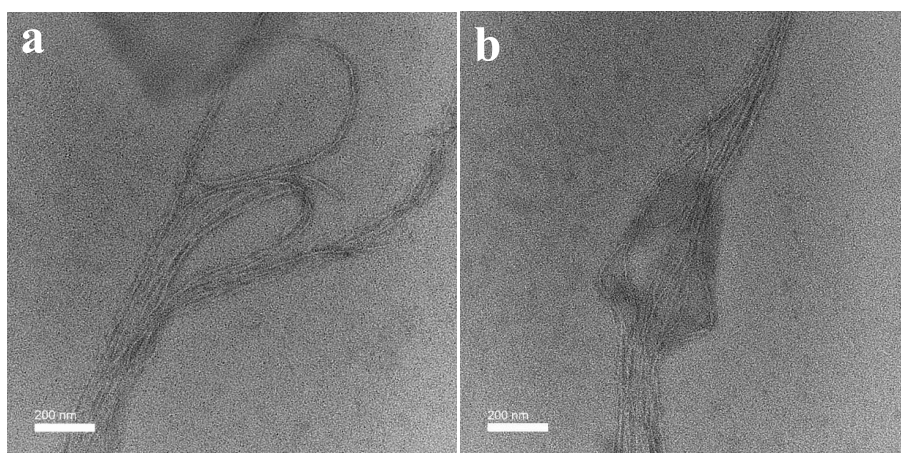
**Figure S5.** SEM images of (a) COF-OEt and (b) COF-OAl.



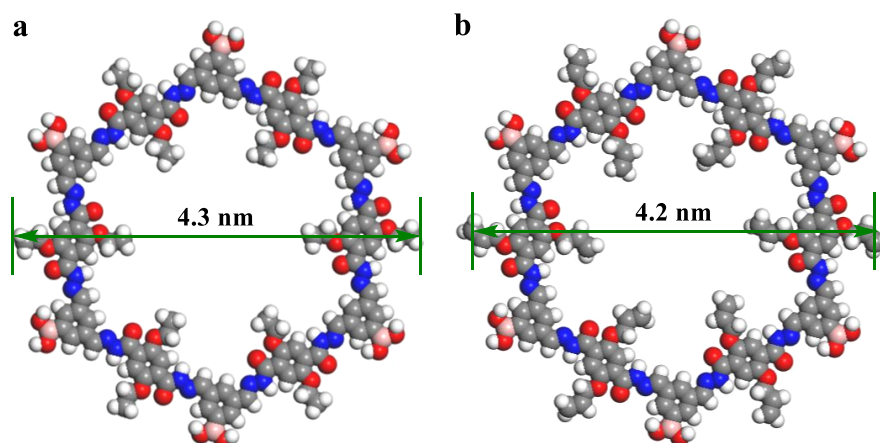
**Figure S6.** BET surface area plots for (a) **COF-OEt** and (b) **COF-OAl**.



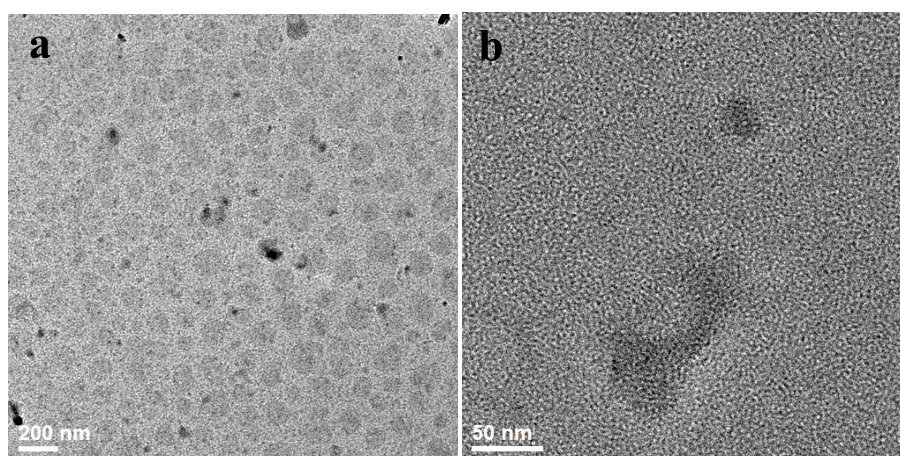
**Figure S7.** FT-IR spectra of **COF-OEt** before (a) and after (b) hydrolysis.



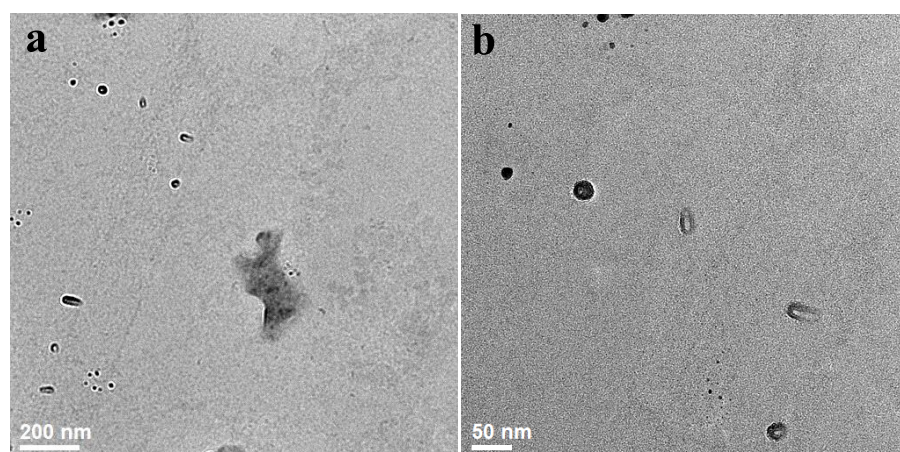
**Figure S8.** TEM images of **NT-OEt**.



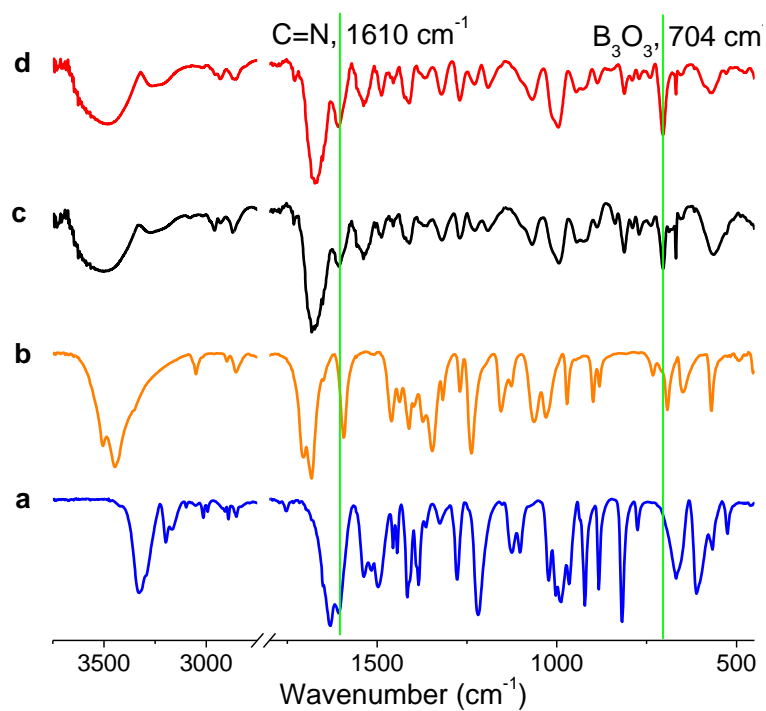
**Figure S9.** Theoretical diameters of (a) **NT-OEt**, and (b) **NT-OAl-CR**.



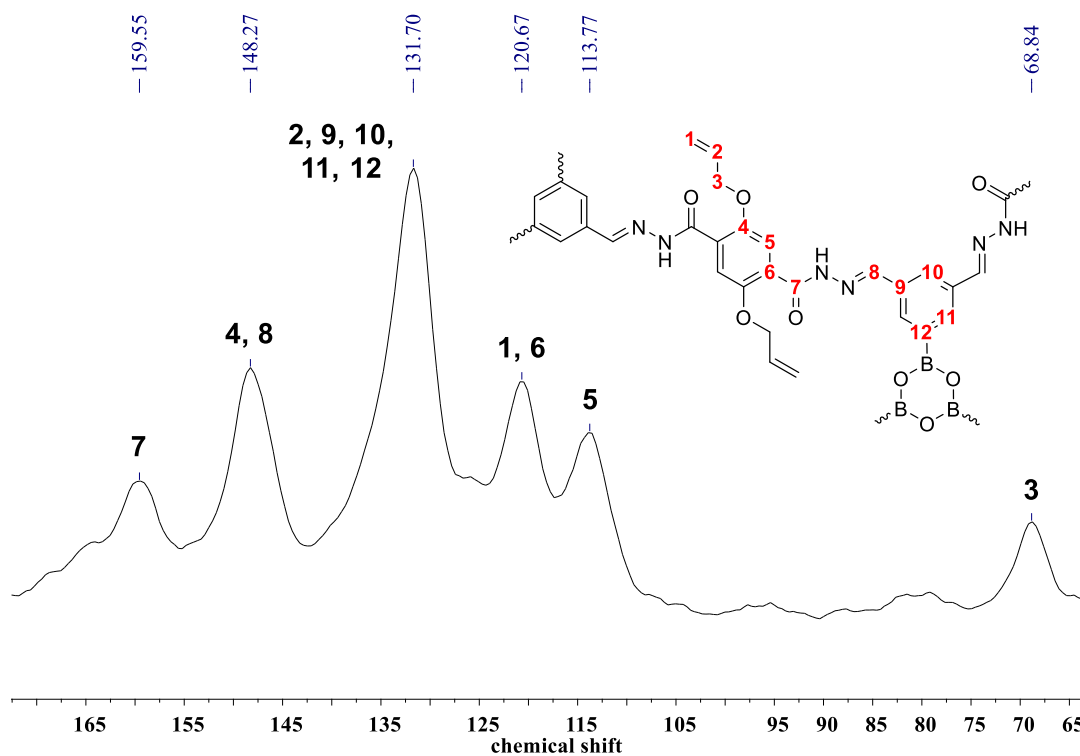
**Figure S10.** TEM images with different scales of **NT-OEt** after ultrasonic treatment.



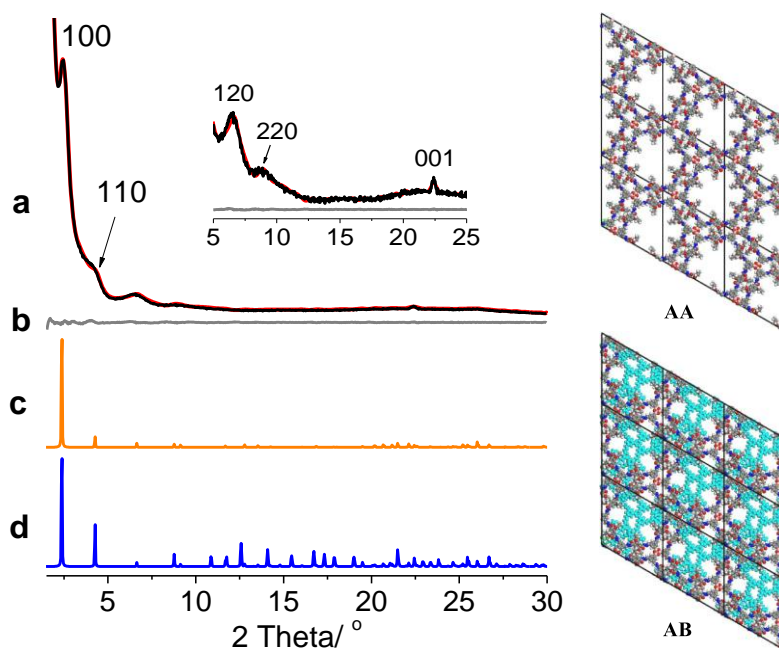
**Figure S11.** TEM images with different scales of **NT-OEt** after ultrasonic treatment and then being stood at room temperature for 12 h.



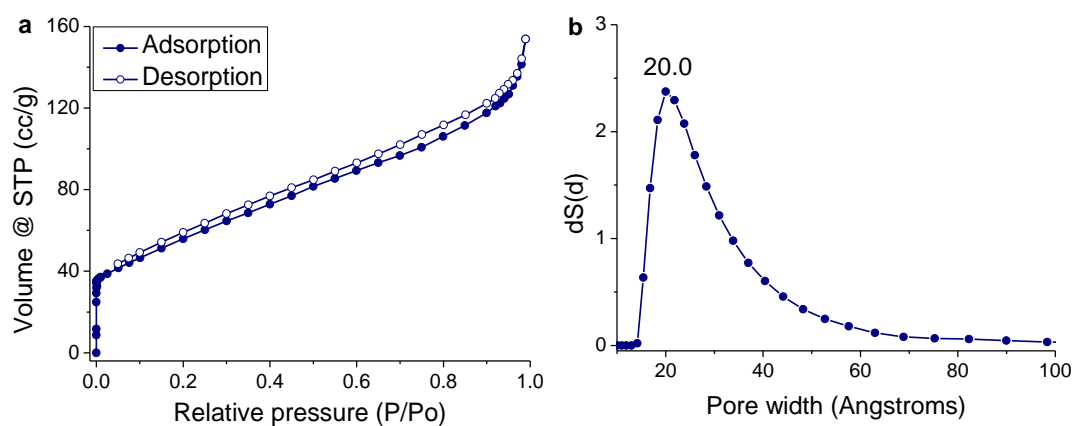
**Figure S12.** FT-IR spectra of (a) **BATH**, (b) **DFPBA**, (c) **COF-OAl** and (d) **COF-OAl-CR**.



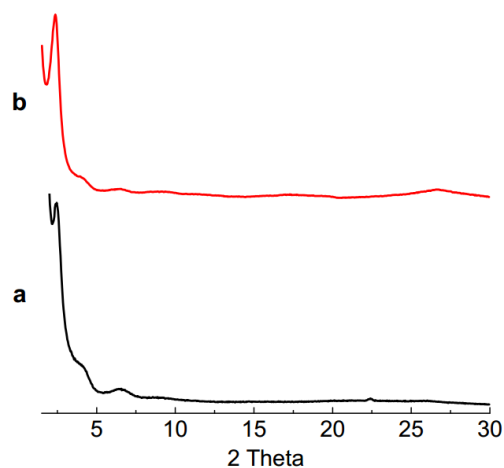
**Figure S13.** Solid-state  $^{13}\text{C}$  CP/MAS NMR spectrum of **COF-OAl**.



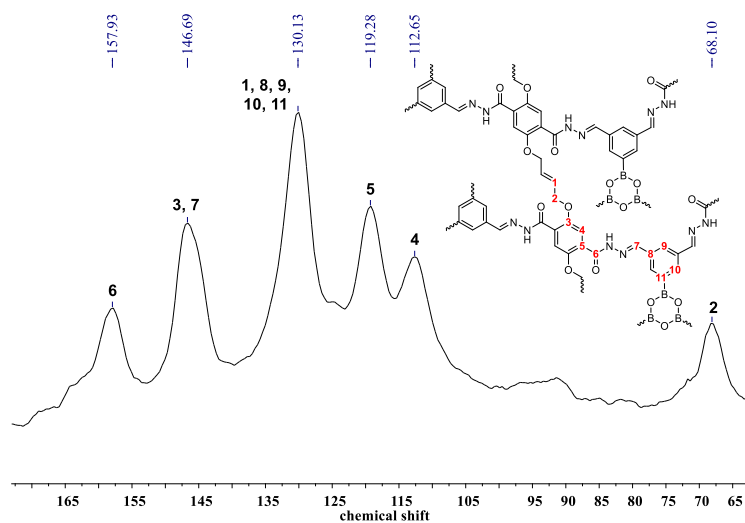
**Figure S14.** Left: (a) Experimental (black) and refined (red) PXRD patterns of **COF-OAl**. (b) Difference plot between the experimental and refined PXRD patterns. And simulated PXRD patterns of (c) AA and (d) AB stacking models. Right: Illustrations of AA and AB stacking models.



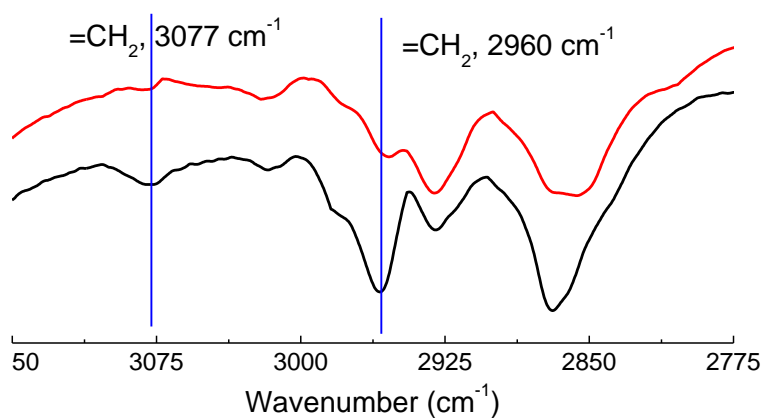
**Figure S15.** (a) N<sub>2</sub> adsorption-desorption isotherm at 77 K, and (b) pore size distribution profile of **COF-OAl**.



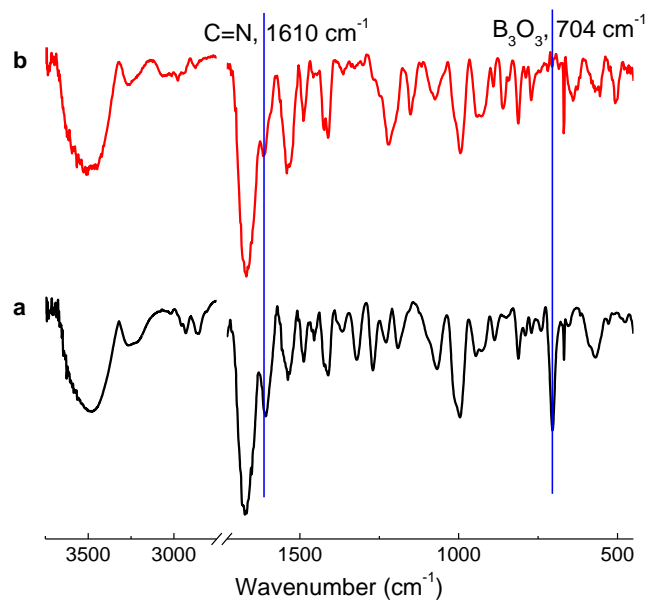
**Figure S16.** Experimental PXRD profiles of (a) **COF-OAl** and (b) **COF-OAl-CR**.



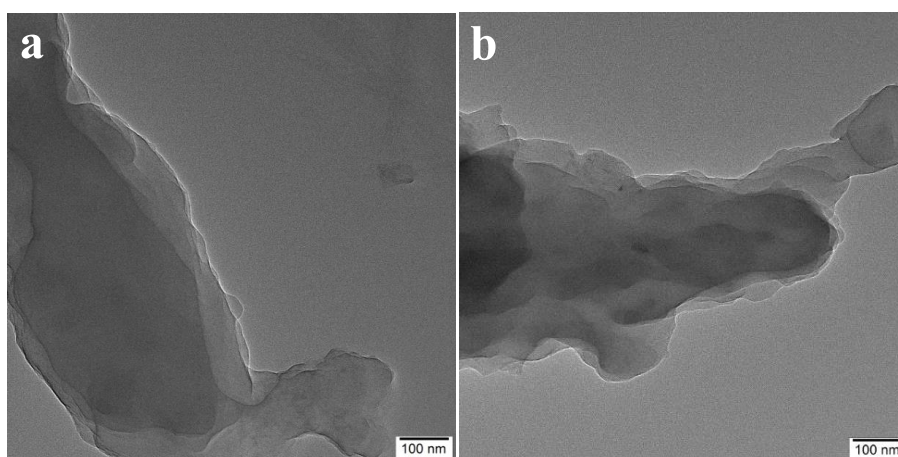
**Figure 17.** Solid-state  $^{13}\text{C}$  CP/MAS NMR spectrum of **COF-OAl-CR**.



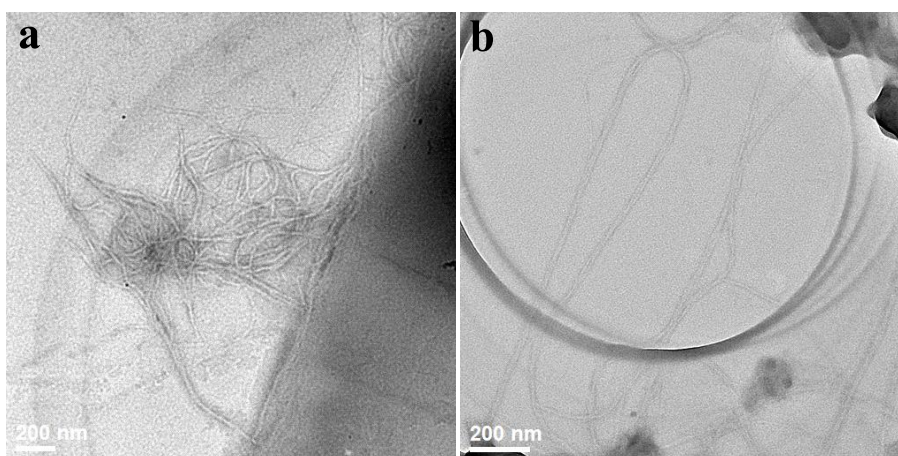
**Figure S18.** FT-IR spectra of **COF-OAl** (black) and **COF-OAl-CR** (red).



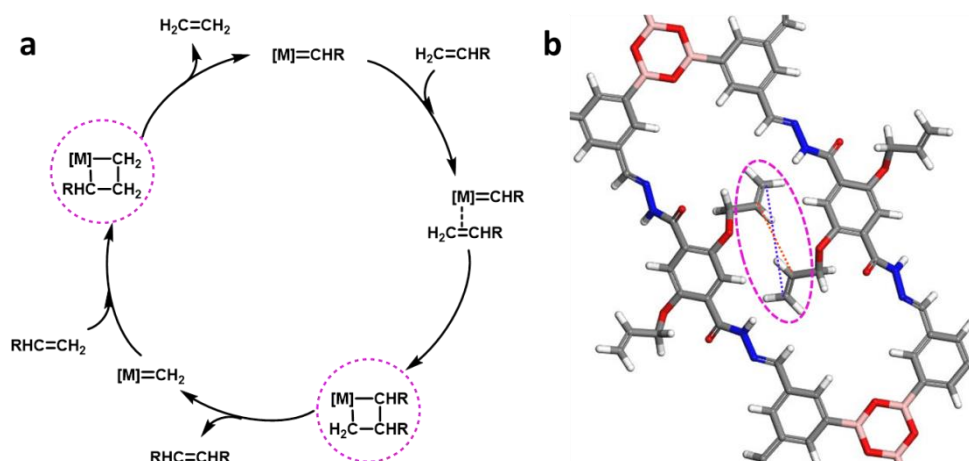
**Figure S19.** FT-IR spectra of **COF-OAI-CR** before (a) and after (b) hydrolysis.



**Figure S20.** TEM images of (a) **COF-OAI**, and (b) **COF-OAI-CR**.



**Figure S21.** TEM images of **NT-OAI-CR** before (a) and after (b) ultrasonic treatment.



**Figure S22.** (a) Mechanism of alkene metathesis reaction. (b) Partial simulated crystal structure of **COF-OAl**, indicating that inter-channel cross-linking is unfavored.

**Table S1.** Fractional atomic coordinates for the unit cell of **COF-OEt** with AA stacking.

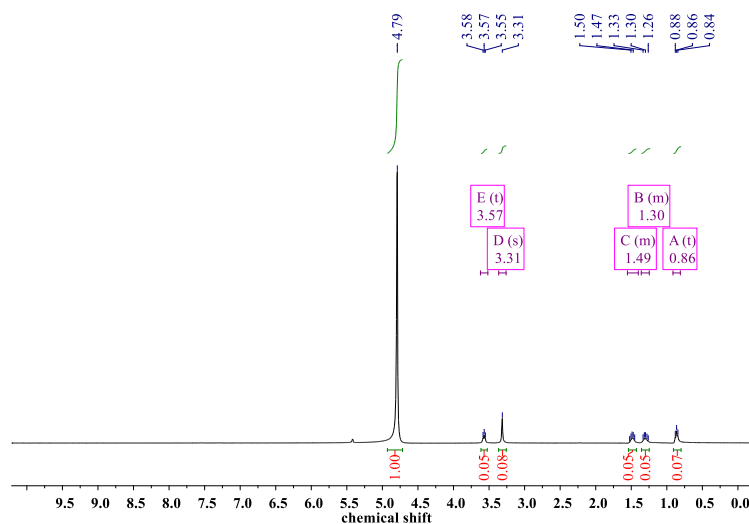
<i>P</i> 6							
$a = b = 38.55 \text{ \AA}, c = 4.07 \text{ \AA}, \alpha = \beta = 90^\circ, \gamma = 120^\circ$							
B1	0.69765	0.3761	1.18671	O26	1.05939	0.57096	1.08333
O2	0.65455	0.36499	1.1832	C27	0.97152	0.67897	1.17561
C3	0.74773	0.49178	1.36806	C28	0.99214	0.72274	1.05298
C4	0.71877	0.45075	1.31217	C29	1.08752	0.57075	1.32066
C5	0.73103	0.42257	1.22642	C30	1.07069	0.52858	1.46685
C6	0.77289	0.43646	1.18141	H31	0.68674	0.44088	1.34092
C7	0.80203	0.47785	1.23147	H32	0.7828	0.4154	1.10481
C8	0.789	0.5048	1.33575	H33	0.81086	0.53675	1.37359
C9	0.84571	0.49393	1.15746	H34	0.85525	0.47523	1.02467
N10	0.87226	0.53095	1.24335	H35	0.92313	0.53785	0.96776
N11	0.91375	0.5499	1.16013	H36	0.98446	0.54941	1.12715
C12	0.94104	0.58529	1.31783	H37	1.07346	0.6972	1.30279
C13	0.98567	0.60553	1.25092	H38	1.13397	0.70544	1.49831
O14	0.92854	0.60003	1.52443	H39	1.20606	0.7552	1.58119

C15	1.00306	0.58168	1.16424	H40	0.94318	0.67211	1.30998
C16	1.04509	0.59809	1.14591	H41	0.96285	0.6582	0.95785
C17	1.07126	0.64046	1.18867	H42	0.9715	0.72675	0.88024
C18	1.05417	0.66469	1.26993	H43	1.02069	0.73031	0.91877
C19	1.01201	0.6479	1.30166	H44	0.99952	0.7438	1.26795
C20	1.11579	0.65935	1.13553	H45	1.09381	0.59227	1.52728
N21	1.14335	0.69156	1.32144	H46	1.1167	0.57922	1.19319
O22	1.1283	0.64513	0.92496	H47	1.06896	0.50807	1.26598
N23	1.18471	0.70371	1.28936	H48	1.03992	0.51761	1.57376
C24	1.21329	0.73548	1.43644	H49	1.09142	0.52887	1.66372
O25	0.99801	0.6742	1.40201				

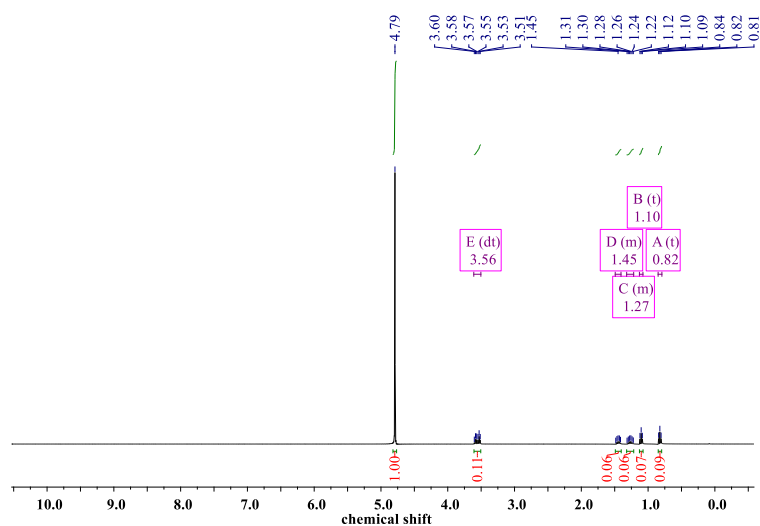
**Table S2.** Fractional atomic coordinates for the unit cell of **COF-OAI** with AA stacking.

<i>P6</i>							
$a = b = 39.00 \text{ \AA}, c = 4.07 \text{ \AA}, \alpha = \beta = 90^\circ, \gamma = 120^\circ$							
B1	0.69405	0.37642	1.01393	C27	1.0749	0.5673	1.01579
O2	0.65078	0.36107	1.01432	C28	1.05949	0.52659	0.88455
C3	0.73695	0.49204	0.92852	C29	1.08216	0.51732	0.70454
C4	0.71022	0.45085	0.96151	C30	0.96902	0.67922	1.0152
C5	0.72428	0.42381	1.00083	C31	0.99293	0.72159	1.1221
C6	0.7658	0.43938	1.02304	C32	0.97687	0.73841	1.30419
C7	0.79289	0.48057	0.99455	H33	0.67869	0.43991	0.94557
C8	0.7779	0.50614	0.93913	H34	0.77722	0.41944	1.06191
C9	0.83655	0.49679	1.03921	H35	0.79827	0.53765	0.91446
N10	0.863	0.53324	0.96132	H36	0.84622	0.4776	1.14639
N11	0.90389	0.54943	1.02923	H37	0.91209	0.53443	1.19335
C12	0.93246	0.58484	0.89373	H38	0.97303	0.54954	1.1454
C13	0.97642	0.60343	0.97158	H39	1.06458	0.69109	0.91392
O14	0.92195	0.60147	0.69845	H40	1.12621	0.69796	0.78645

C15	0.99221	0.58029	1.09045	H41	1.19587	0.74218	0.70604
C16	1.03319	0.59542	1.12674	H42	1.10169	0.57523	1.16495
C17	1.06031	0.63624	1.07098	H43	1.08333	0.58774	0.80352
C18	1.04489	0.65982	0.9573	H44	1.02933	0.50417	0.93277
C19	1.00387	0.64418	0.90896	H45	1.06973	0.48741	0.6146
C20	1.10371	0.65394	1.15113	H46	1.11274	0.53901	0.64959
N21	1.13337	0.68406	0.97186	H47	0.95935	0.65975	1.23527
O22	1.11299	0.64016	1.37998	H48	0.94201	0.67479	0.886
N23	1.17341	0.69441	1.02062	H49	1.02406	0.73872	1.0566
C24	1.2024	0.72392	0.86598	H50	0.94596	0.72189	1.37686
O25	0.99178	0.67027	0.79148	H51	0.99478	0.76896	1.38294
O26	1.04561	0.56861	1.22068				



**Figure S23.**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ) spectrum of the sample after soaking COF-OEt in  $\text{D}_2\text{O}$  for 6 days.



**Figure S24.**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ) spectrum of the sample after soaking **COF-OAl** in  $\text{D}_2\text{O}$  for 6 days.