

Supporting information for

# Desymmetrized Vertex Design for the Synthesis of Covalent Organic Frameworks with Periodically Heterogeneous Pore Structures

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## 1. Materials and measurements

All chemical reagents and solvents were commercially available and used without further purification unless otherwise indicated. 5-bromoisophthalaldehyde,<sup>1</sup> 4-Ethynylbenzaldehyde,<sup>2</sup> 5-((4-formylphenyl)ethynyl)isophthalaldehyde,<sup>3</sup> 5-(4-formylphenyl)isophthalaldehyde<sup>3</sup> were synthesized according to the published procedure.

Flash column chromatography was performed using a 100-150 times weight excess of flash silica gel 32-63  $\mu\text{m}$  from Dynamic Absorbants Inc. Fractions were analyzed by TLC using TLC silica gel F254 250  $\mu\text{m}$  precoated-plates from Dynamic Absorbants Inc.

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. Solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on an Inova 400 NMR spectrometer.

Powder X-Ray Diffraction (PXRD) was obtained from a Bruker D-8 Discover diffractometer, using monochromated Cu  $K_{\alpha}$  ( $\lambda = 1.542 \text{ \AA}$ ) radiation.

The FT-IR spectra of starting materials and as synthesized HP-COFs were obtained from Agilent Technologies Cary 630 FT-IR.

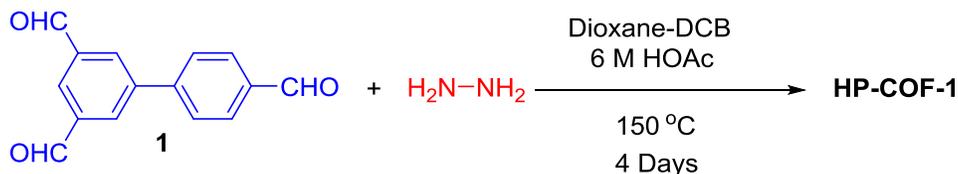
Elemental analysis (EA) was taken at an Exeter Analytical-Model CE 440 CHN Analyzer, microanalysis laboratory, University of Illinois at Urbana-Champaign.

Thermogravimetric analyses (TGA) were performed on a thermogravimetric/differential thermal analyzer by heating the samples to 800  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C min}^{-1}$  under the atmosphere of nitrogen.

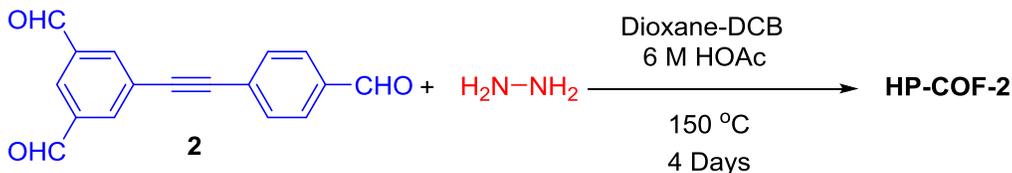
The Quantachrome Autosorb ASiQ automated gas sorption analyzer was used to measure  $\text{N}_2$  and  $\text{CO}_2$  adsorption isotherms. The samples were heated at 120  $^{\circ}\text{C}$  and kept at this temperature for at least 20 hours under the vacuum for the activation. Ultra high purity grade (99.999 % purity)  $\text{N}_2$ ,  $\text{CO}_2$  and He, oil-free valves and gas regulators were used for all free space corrections and measurements. For all of the gas adsorption measurements, the temperatures were controlled by using a refrigerated bath of liquid  $\text{N}_2$  (77 K), and ice water (273 K). The pore size distribution is calculated through NLDFT equilibrium method (slit/cylindrical pore model) based on the nitrogen sorption isotherms at 77 K using Quantachrome AsiQwin program. The materials model type is carbon.

Scanning Electron Microscopy images (SEM) were recorded using a JSM-6480LV (LVSEM) at 5.0 kV. Samples were sputter coated with gold prior to analysis.

## 2. General synthetic procedures



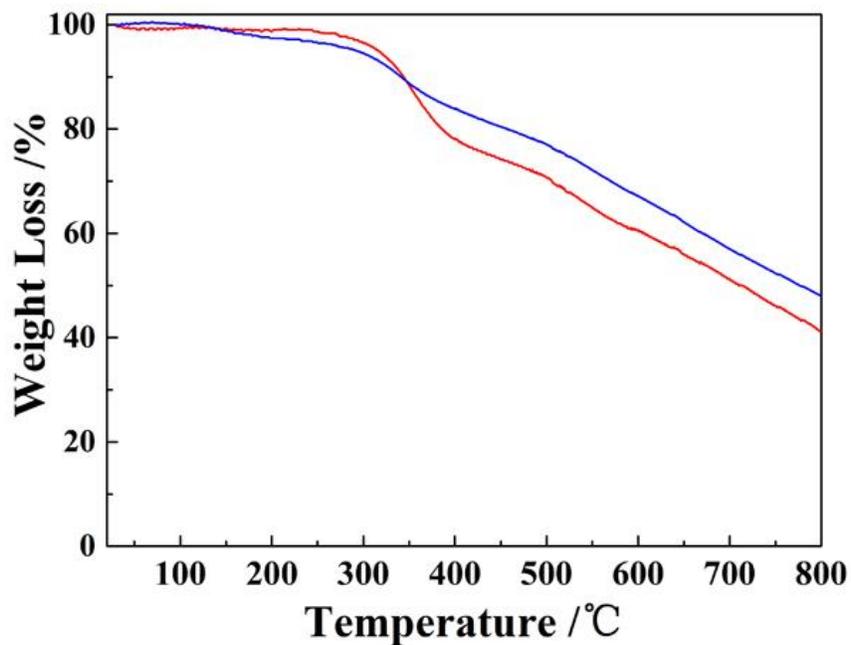
**Synthesis of HP-COF-1:** A customized glass tube (the outer diameter is 10 mm and the inner diameter is 8 mm) was charged with 5-(4-formylphenyl)isophthalaldehyde (**1**, 23.8 mg, 0.1 mmol), hydrazine monohydrate (9.4  $\mu\text{L}$ , 0.15 mmol, injected by using micropipet), 1,4-dioxane (2 mL), *o*-Dichlorobenzene (1 mL), and 6 M acetic acid (0.2 mL). The mixture was sonicated for a few minutes. The tube was then flash frozen at 77 K under liquid nitrogen bath, evacuated to the internal pressure about 100 mtorr, and sealed under the frame. The mixture was warmed to room temperature, and the reaction temperature was slowly raised to 150  $^\circ\text{C}$  over 2 hours. The reaction was kept at this temperature for 4 days and cooled to room temperature over 12 hours. The light yellow precipitate was collected by vacuum filtration, washed with large amount of dichloromethane and acetone, and dried under vacuum to yield HP-COF-1 (20 mg, 87 %): Elemental analysis calcd (%) for  $(\text{C}_{15}\text{H}_{10}\text{N}_3)_n$ : C, 77.57; H, 4.34; N, 18.09. Found: C, 72.61; H, 4.02; N, 15.09.



**Synthesis of HP-COF-2:** The above synthetic procedure for **HP-COF-1** was followed. Using 5-((4-formylphenyl)ethynyl)isophthalaldehyde (**2**, 26.2 mg, 0.1 mmol), hydrazine monohydrate (9.4  $\mu\text{L}$ , 0.15 mmol), 1,4-dioxane (2 mL), mesitylene (1 mL), and 6 M acetic acid (0.2 mL), **HP-COF-2** was obtained as a yellow precipitate. The color was a little dark compared to HP-COF-1 (22 mg, 86 %): Elemental analysis calcd (%) for  $(\text{C}_{17}\text{H}_{10}\text{N}_3)_n$ : C, 79.67; H, 3.93; N, 16.40. Found: C, 75.38; H, 3.95; N, 14.21.

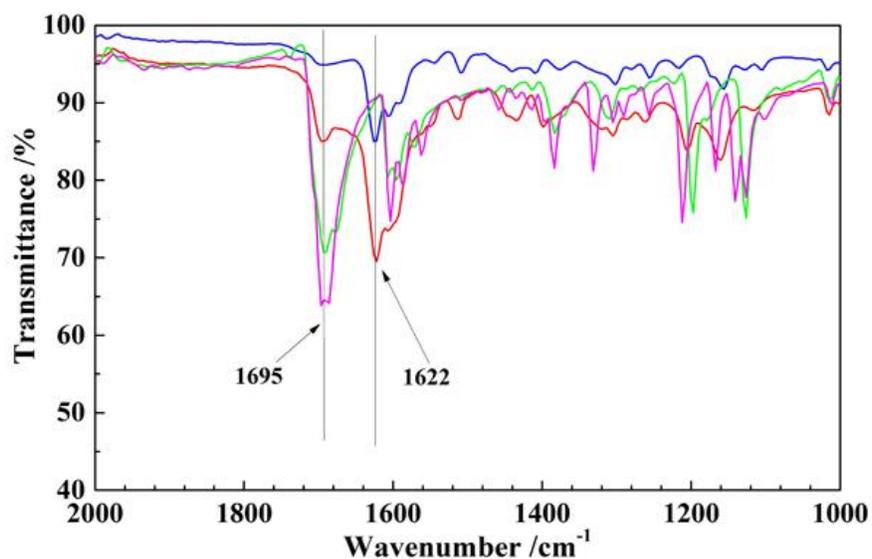
For the microwave heating method, all the chemicals and solvents are the same with the above method. Microwave temperature is 170  $^\circ\text{C}$  and radiate for 6 hours.

### 3. TGA curves of HP-COFs



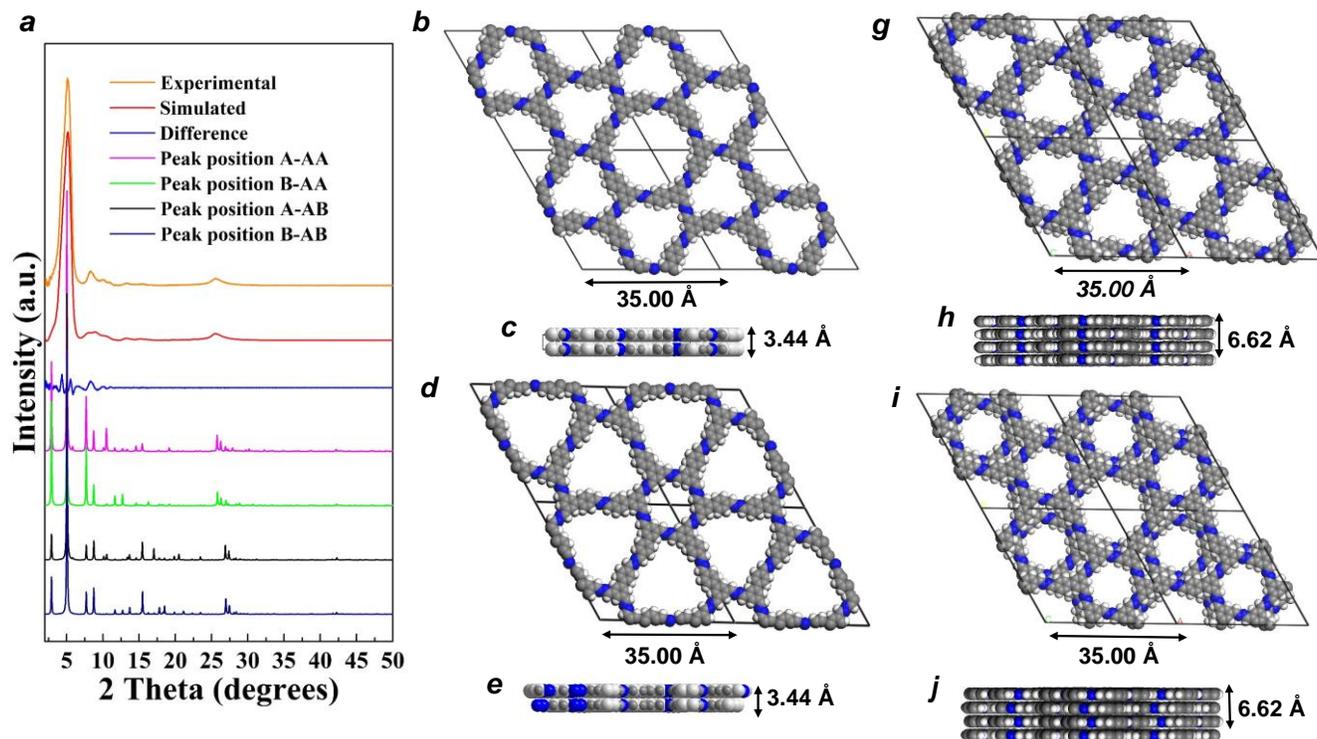
**Figure S1.** TGA curves of HP-COF-1 (red) and HP-COF-2 (Blue)

### 4. FT-IR spectra of HP-COFs and aldehydes



**Figure S2.** IR spectra of monomers and HP-COFs: HP-COF-1 (red), HP-COF-2 (blue), monomer 1 (green), monomer 2 (magenta).

## 5. Structural modeling and X-ray diffraction analyses.



**Figure S3.** (a) PXRD patterns of HP-COF-1; (b), (c) the unit cell structure of isomer A of HP-COF-1 in AA stacking (b), and the view along the Z axis (c); (d), (e) the unit cell structure of isomer B of HP-COF-1 in AA stacking (d) and the view along the Z axis (e); (g), (h) the unit cell structure of isomer A of HP-COF-1 in AB stacking (g), and the view along the Z axis (h); (i), (j) the unit cell structure of isomer B of HP-COF-1 in AB stacking (i) and the view along the Z axis (j).

All the models, including cell parameters and atomic positions were generated using the *Materials Studio* software package, employing the *Materials Visualizer* module. All the models were constructed in the hexagonal system, with the layers lying on the **ab** plane. The space groups with the maximum possible symmetry were selected. An energy minimization was performed to optimize the geometry of the building units, employing the *universal force field* implemented in the *Forcite* module of *Materials Studio*. During this process, the unit cell parameters for each model were also optimized. In **Table S1**, the values of the optimized unit cell parameters and the space group for the models constructed are summarized.

**Table S1.** Optimized unit cell parameters of the constructed models for HP-COF-1 and HP-COF-2.

	HP-COF-1		HP-COF-2	
	Isomer A	Isomer B	Isomer A	Isomer B
<b>Space group</b>	<i>P6/m</i>	<i>P6/m</i>	<i>P6/m</i>	<i>P6/m</i>
<b><i>a</i> (Å)</b>	35.00	35.00	39.89	39.89
<b><i>c</i> (Å)</b>	3.44	3.44	3.47	3.47
<b>Total Energy (kcal/mol)</b>	117.19	117.16	40.52	40.50

The corresponding powder patterns for the four models were calculated and compared with the experimental patterns, finding the best agreement for the eclipsed models. With them, full profile pattern (Pawley) refinements were performed against the experimental powder patterns obtaining the refined unit cell parameters. **Tables S2** and **S3** show the refined cell parameters and the fractional atomic coordinates of the two final models.

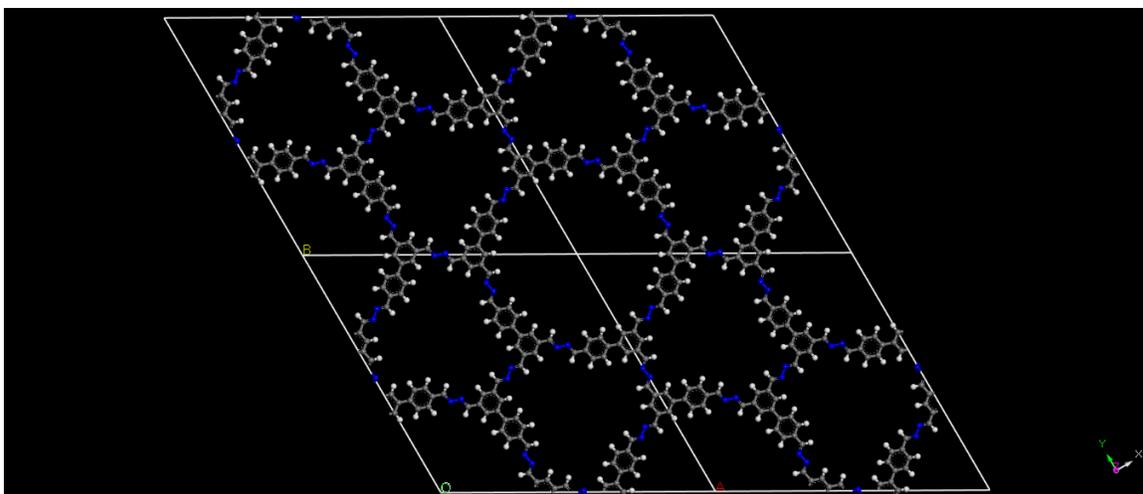
**Table S2.** Refined unit cell parameters and fractional atomic coordinates for HP-COF-1.

<b>Name</b>	HP-COF-1		
<b>Space group</b>	<i>P6/m</i>		
<b><i>a</i> (Å)</b>	35.00		
<b><i>c</i> (Å)</b>	3.44		
<b>Atom name</b>	<b><i>x</i></b>	<b><i>y</i></b>	<b><i>z</i></b>
H1	0.68877	0.82235	1.00000
C2	0.72279	0.82975	1.00000
N3	0.75428	0.87048	1.00000
N4	0.74473	0.90482	1.00000
H5	0.81017	0.95318	1.00000
C6	0.77610	0.94560	1.00000
C7	0.76630	0.98206	1.00000
C8	0.72267	0.97389	1.00000
H9	0.69691	0.93995	1.00000
C10	0.66587	0.99971	1.00000
H11	0.63285	0.92734	1.00000
C12	0.62934	0.95614	1.00000
C13	0.58599	0.94801	1.00000
H14	0.55907	0.91419	1.00000
C15	0.57729	0.98282	1.00000
C16	0.53115	0.97322	1.00000
H17	0.50458	0.93918	1.00000
N18	0.47807	0.99528	1.00000
H19	0.39296	0.94618	1.00000
C20	0.38725	0.97386	1.00000
C21	0.34382	0.96551	1.00000
H22	0.31870	0.93128	1.00000

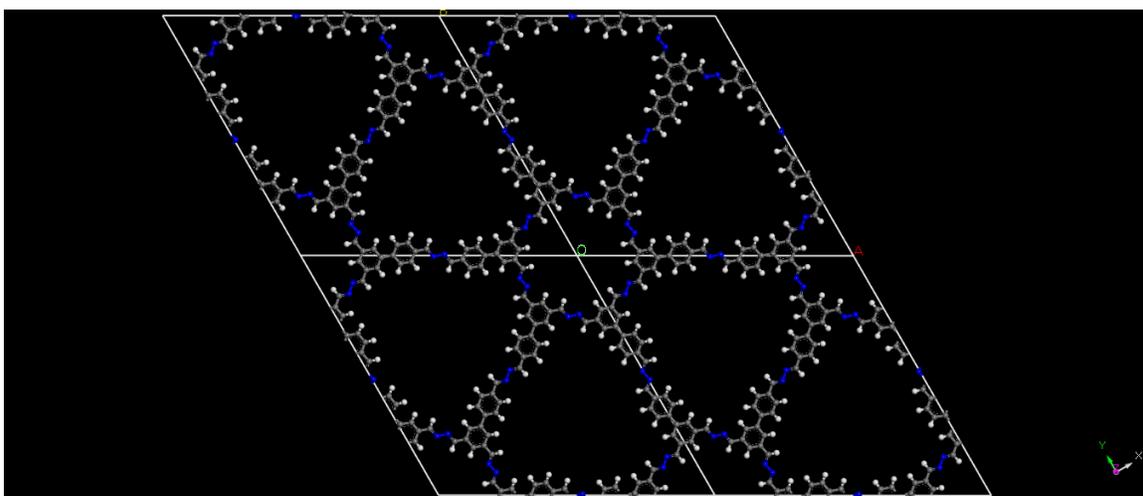
C23	0.28693	0.99130	1.00000
H24	0.25483	0.91939	1.00000
C25	0.25051	0.94772	1.00000
C26	0.20688	0.93921	1.00000
C27	0.19875	0.97379	1.00000
H28	0.16515	0.96826	1.00000

**Table S3.** Refined unit cell parameters and fractional atomic coordinates for HP-COF-2.

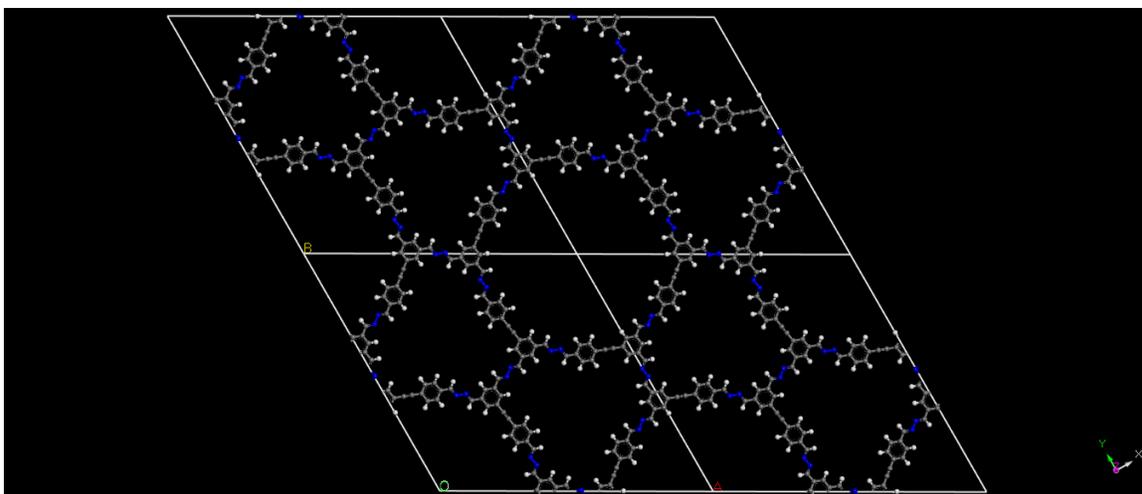
<b>Name</b>	HP-COF-2		
<b>Space group</b>	<i>P6/m</i>		
<i>a</i> (Å)	39.89		
<i>c</i> (Å)	3.47		
<b>Atom name</b>	<i>x</i>	<i>y</i>	<i>z</i>
H1	0.72600	0.84920	1.00000
C2	0.75564	0.85506	1.00000
N3	0.78383	0.89053	1.00000
N4	0.77644	0.92133	1.00000
H5	0.83428	0.96262	1.00000
C6	0.80464	0.95679	1.00000
C7	0.79719	0.98949	1.00000
C8	0.75929	0.98333	1.00000
H9	0.73468	0.95418	1.00000
C10	0.64265	0.99613	1.00000
H11	0.61594	0.93382	1.00000
C12	0.61122	0.95830	1.00000
C13	0.57340	0.95185	1.00000
H14	0.54941	0.92238	1.00000
C15	0.56663	0.98315	1.00000
C16	0.52644	0.97558	1.00000
H17	0.50272	0.94593	1.00000
N18	0.48089	0.99626	1.00000
H19	0.40595	0.95417	1.00000
C20	0.40163	0.97888	1.00000
C21	0.36383	0.97249	1.00000
H22	0.33968	0.94310	1.00000
C23	0.31847	0.99726	1.00000
C24	0.28589	0.99174	1.00000
C25	0.24703	0.98520	1.00000
H26	0.22074	0.92315	1.00000
C27	0.21560	0.94739	1.00000
C28	0.17760	0.94075	1.00000
C29	0.17142	0.97250	1.00000
H30	0.14220	0.96774	1.00000



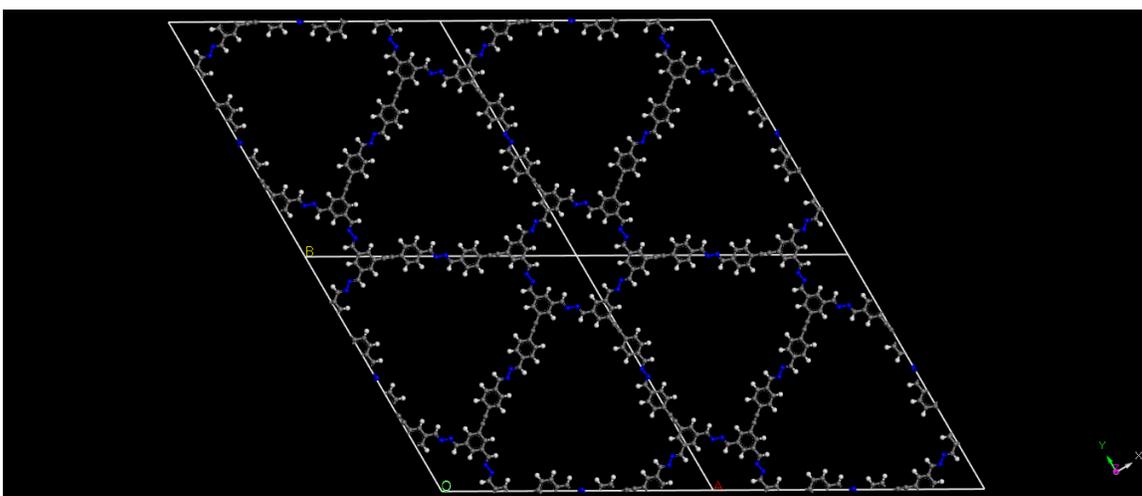
**Figure S4.** The stick model of isomer A of HP-COF-1 in AA stacking.



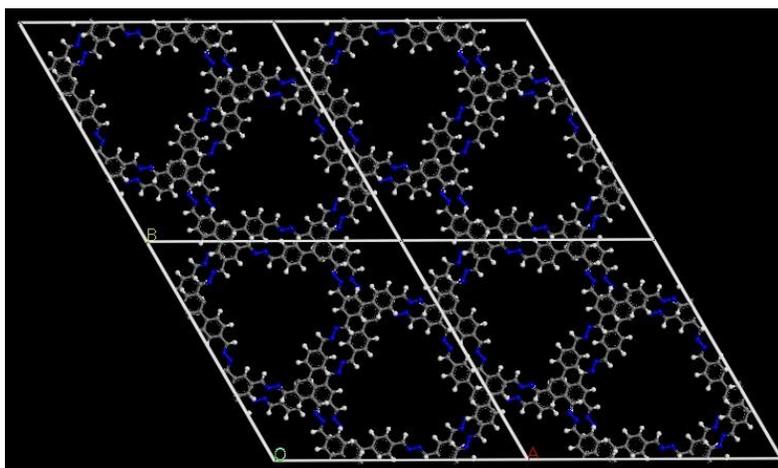
**Figure S5.** The stick model of isomer B of HP-COF-1 in AA stacking.



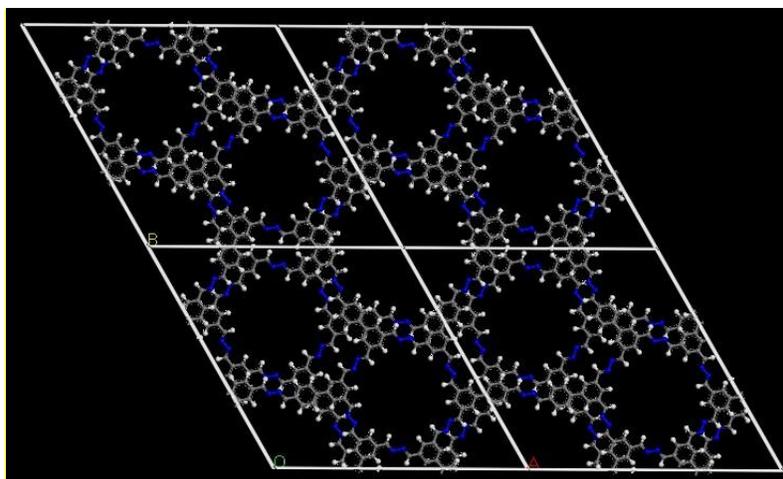
**Figure S6.** The stick model of isomer A of HP-COF-2 in AA stacking.



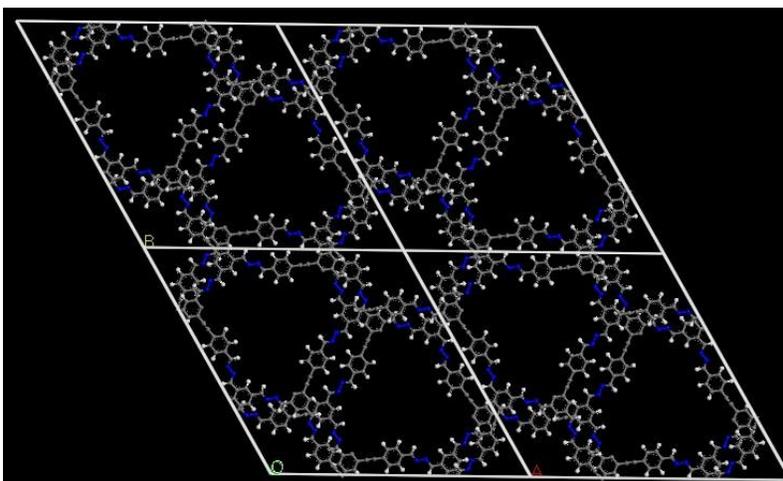
**Figure S7.** The stick model of isomer B of HP-COF-2 in AA stacking.



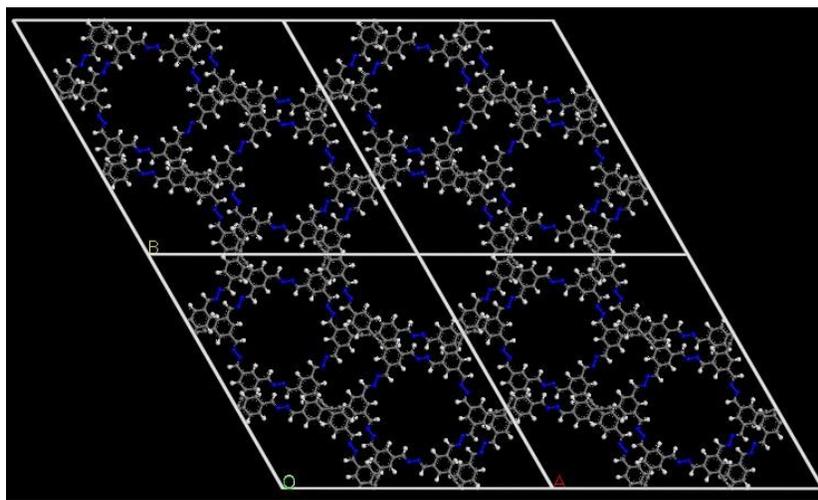
**Figure S8.** The stick model of isomer A of HP-COF-1 in AB stacking.



**Figure S9.** The stick model of isomer B of HP-COF-1 in AB stacking.



**Figure S10.** The stick model of isomer A of HP-COF-2 in AB stacking.



**Figure S11.** The stick model of isomer B of HP-COF-2 in AB stacking.

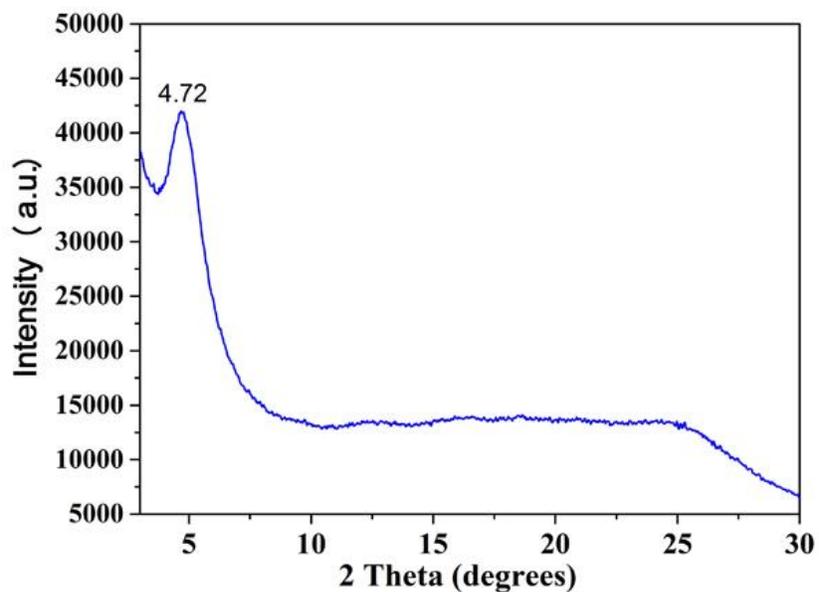


Figure S12. PXRD patterns of HP-COF-2.

### 6. CO<sub>2</sub> and N<sub>2</sub> gas adsorption data for HP-COFs

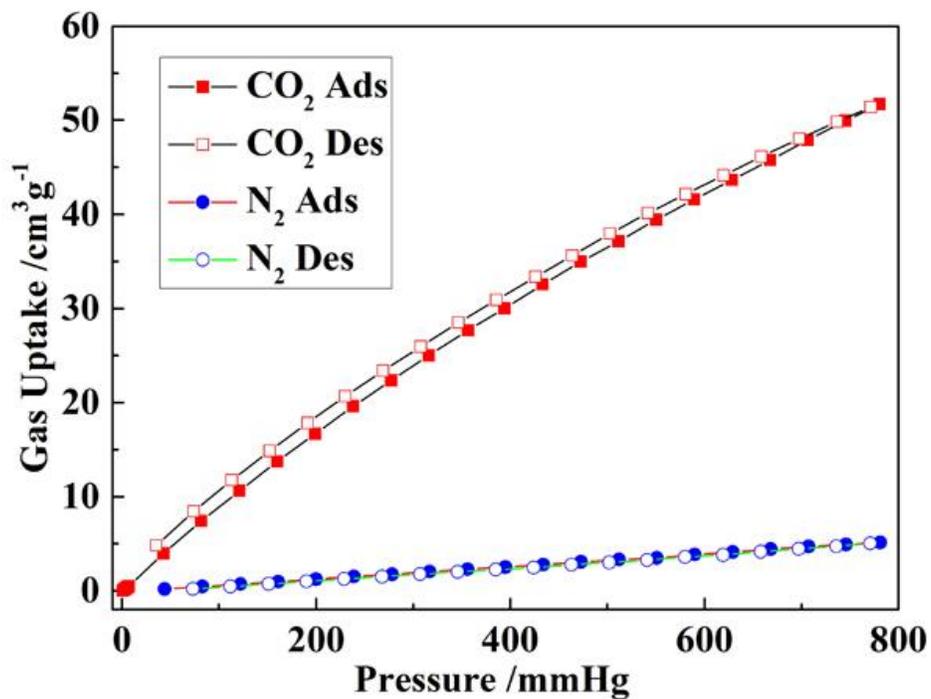
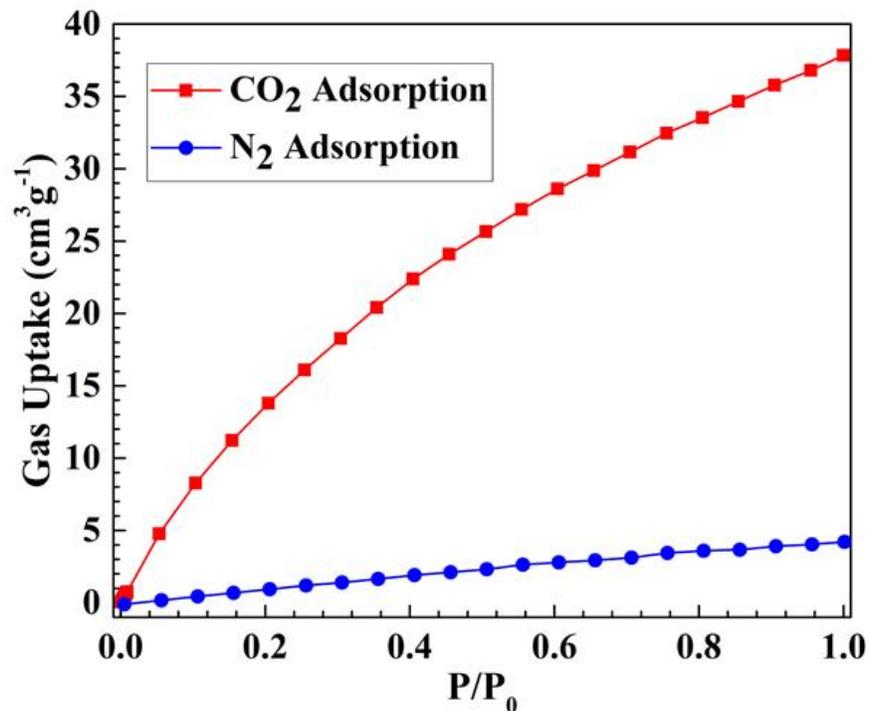


Figure S13. CO<sub>2</sub> and N<sub>2</sub> sorption isotherms of HP-COF-1 at 273 K.



**Figure S14.** CO<sub>2</sub> and N<sub>2</sub> sorption isotherms of HP-COF-2 at 273 K.

### 7. Estimation of the CO<sub>2</sub> heat of adsorption for HP-COF-1 and HP-COF-2

To determine the binding affinity of HP-COF-1 and HP-COF-2 for CO<sub>2</sub>, we estimated the  $Q_{st}$  using the virial method<sup>4</sup> based on two independent temperature gas adsorption isotherms (273 K and 295 K). In each case, the data were fitted using the following equation:

$$\ln P = \ln N + \frac{1}{T} \sum_i^m a_i N^i + \sum_i^n b_i N^i$$

Where,  $P$  is the pressure expressed in mmHg;  $N$  is the adsorption capacity expressed in mg/g;  $T$  is the absolute temperature expressed in K;  $a_i$  and  $b_i$  are virial coefficients, and  $m$  and  $n$  are the number of coefficients to describe the adsorption isotherms, usually  $m \leq 6$  and  $n \leq 3$ . The heat of adsorption is estimated through the following expression:

$$Q_{st} = -R \sum_i^m a_i N^i$$

Where  $R$  is universal gas constant.

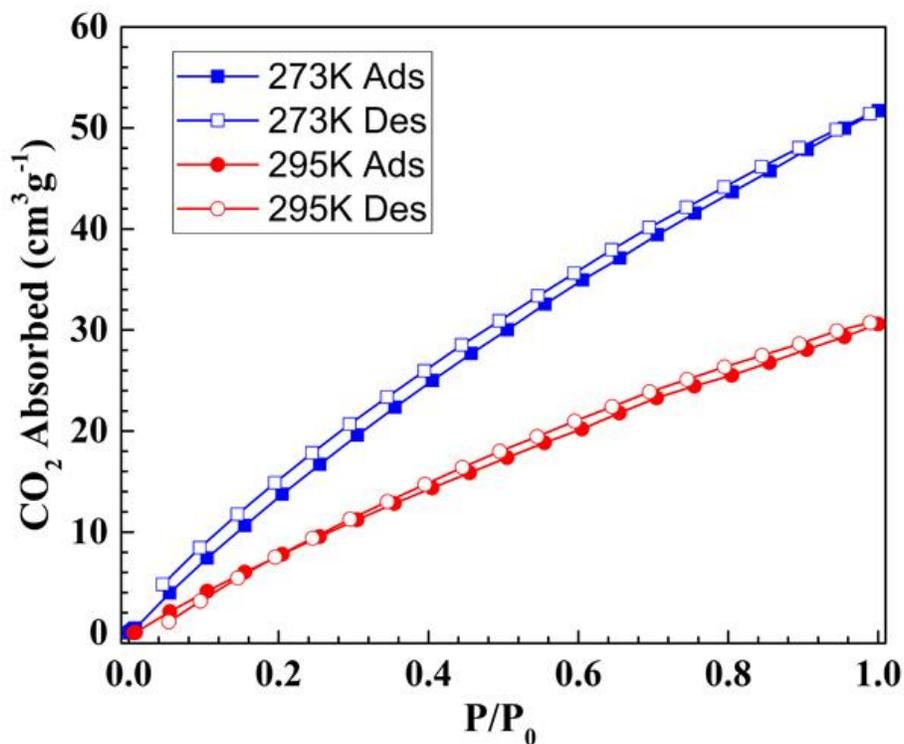


Figure S15. CO<sub>2</sub> adsorption of HP-COF-1 at different temperatures.

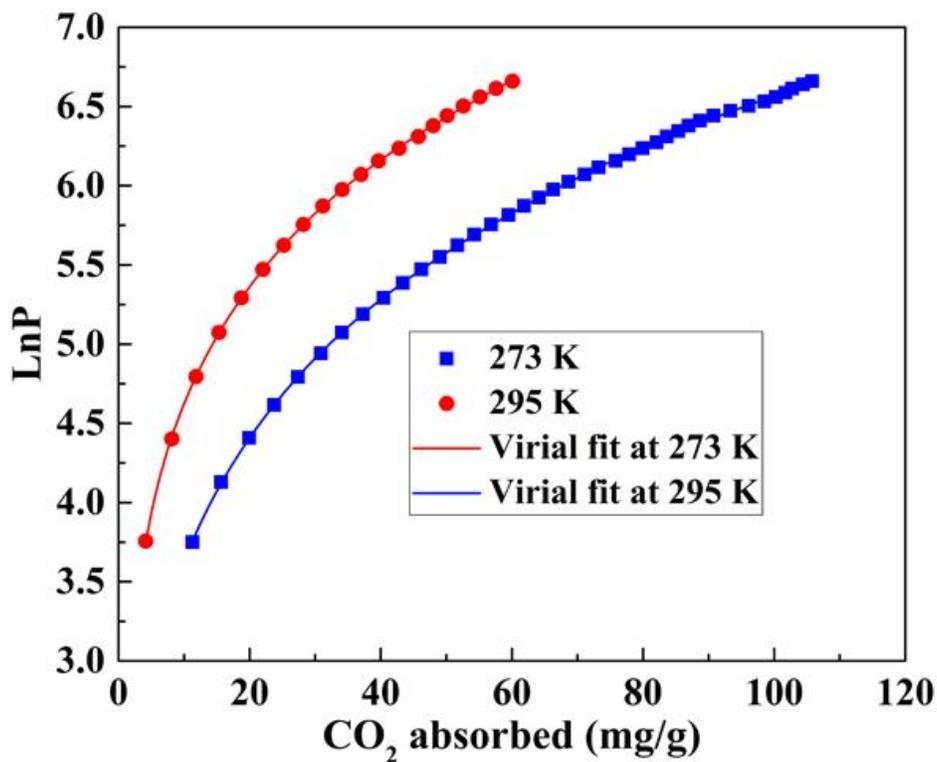
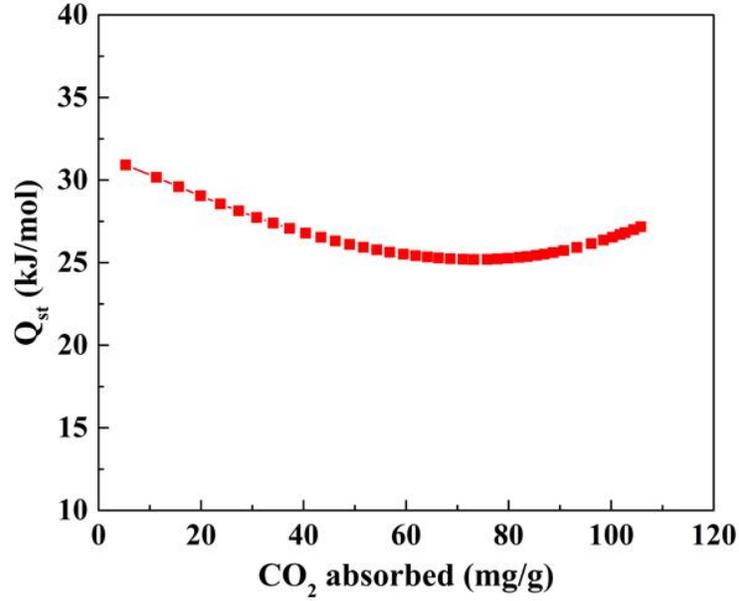


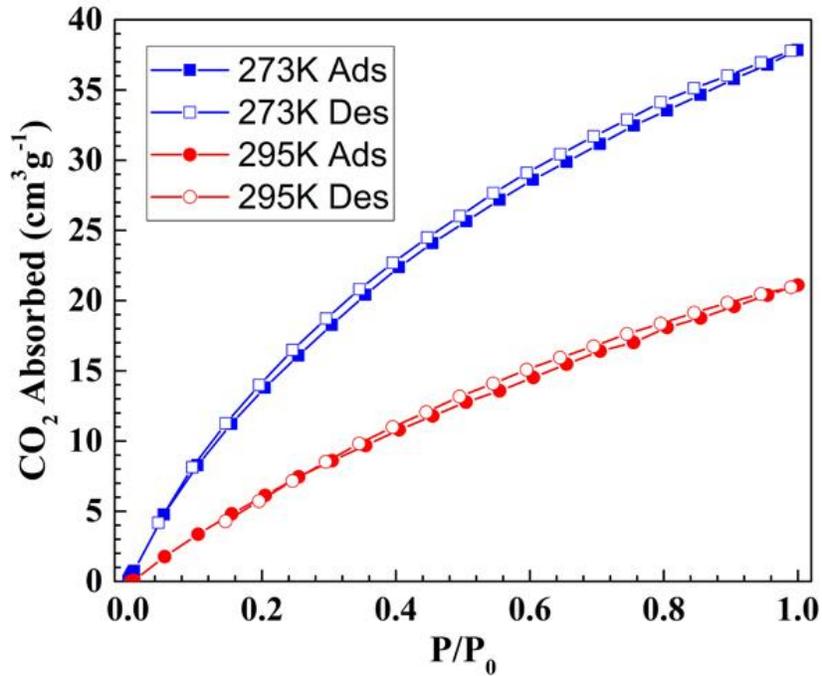
Figure S16. Virial analysis of CO<sub>2</sub> adsorption isotherms of HP-COF-1 at 273K (blue) and 295K (red).

**Table S4.** virial equation fitting results of CO<sub>2</sub> adsorption.

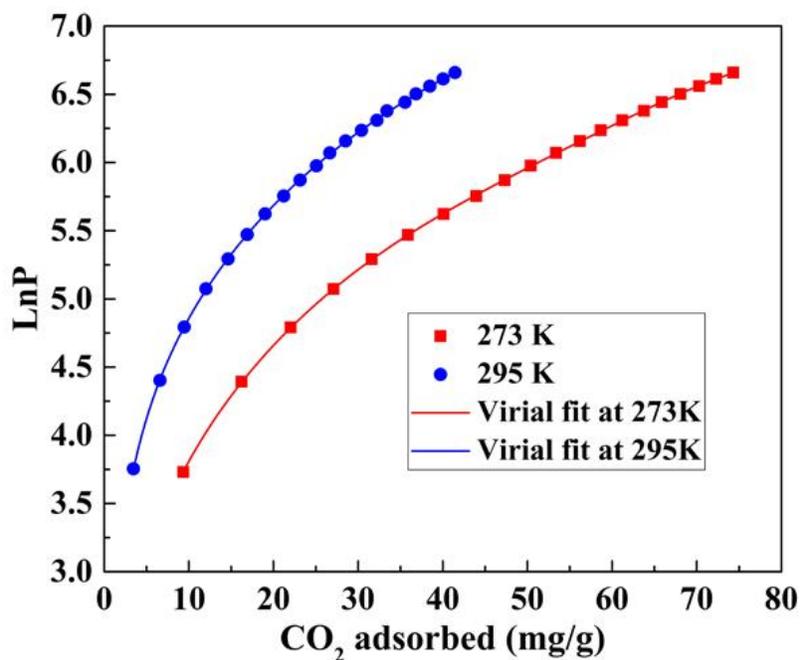
$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	$b_0$	$b_1$	$b_2$	$b_3$	$R^2$
-3790.2	12.295	0.28923	-0.01035	1.4342E-4	-1.0508E-6	2.996E-9	15.201	-0.05286	8.8762E-5	2.8238E-6	0.99991



**Figure S17.** Heat of adsorption plot of CO<sub>2</sub> adsorption for HP-COF-1.



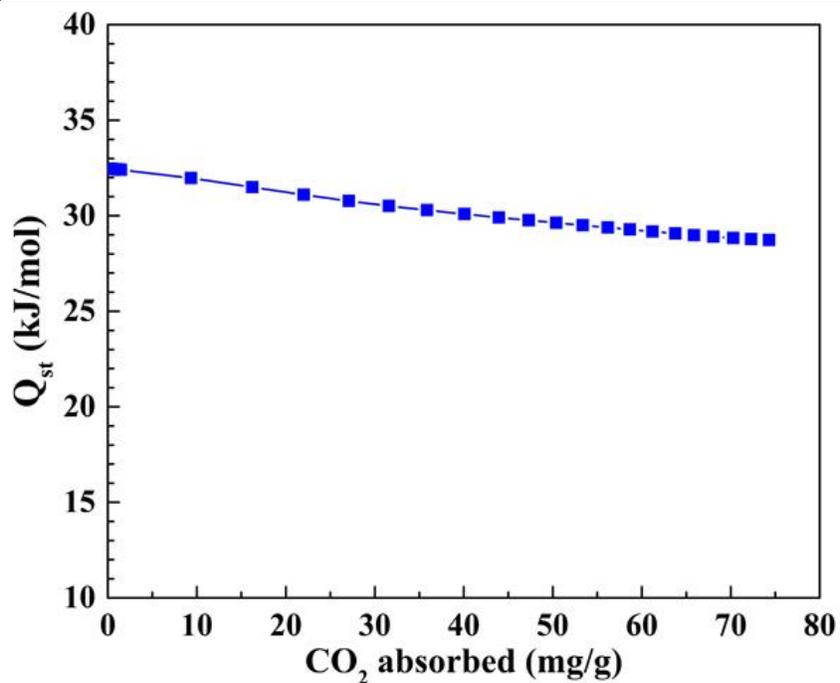
**Figure S18.** CO<sub>2</sub> adsorption of HP-COF-2 at different temperatures.



**Figure S19.** Virial analysis of CO<sub>2</sub> adsorption isotherms of HP-COF-2 at 273K (red) and 295K (blue).

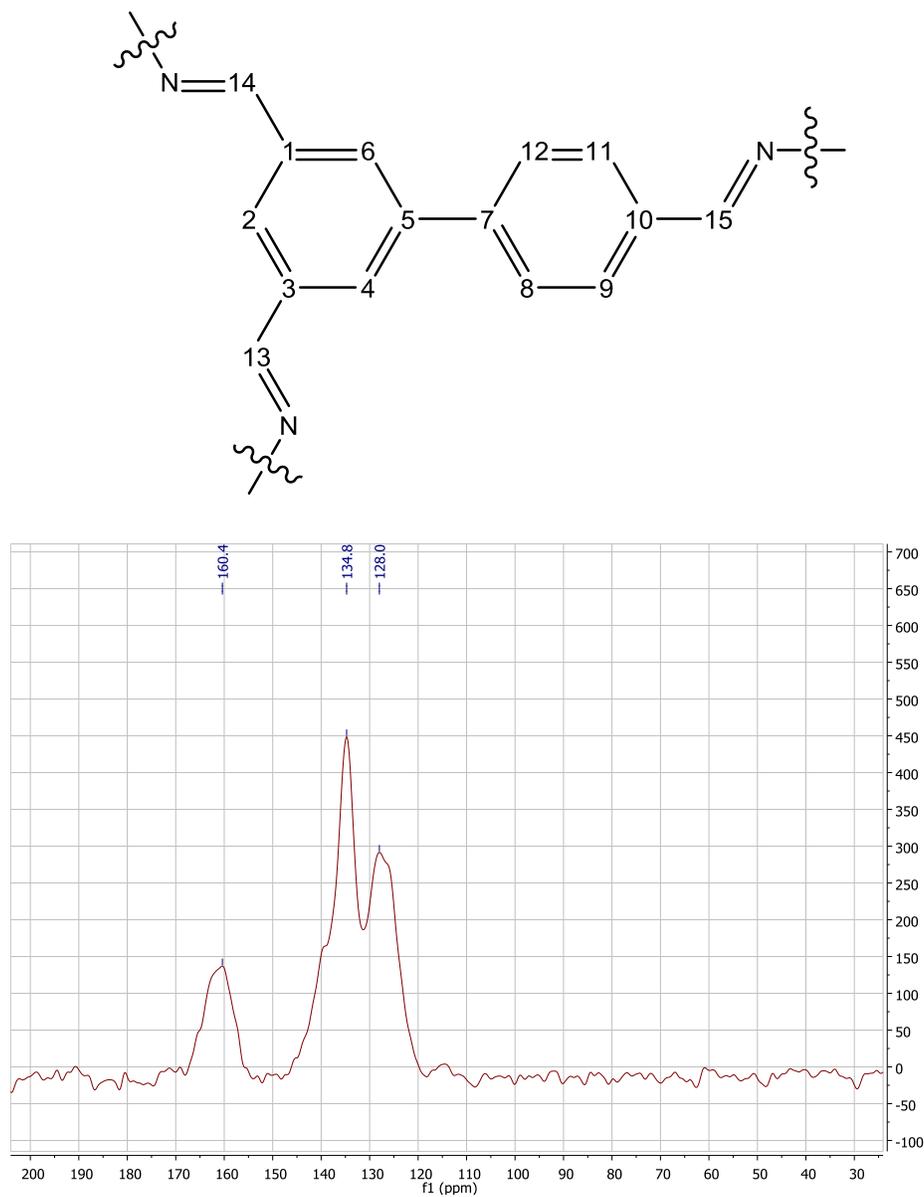
**Table S5.** Virial equation fitting results of CO<sub>2</sub> adsorption

$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$b_0$	$b_1$	$b_2$	$R^2$
-3903.7	3.5933	0.39151	-0.01344	1.8197E-4	-8.8914E-7	15.745	-0.0184	1.1332E-4	0.99996



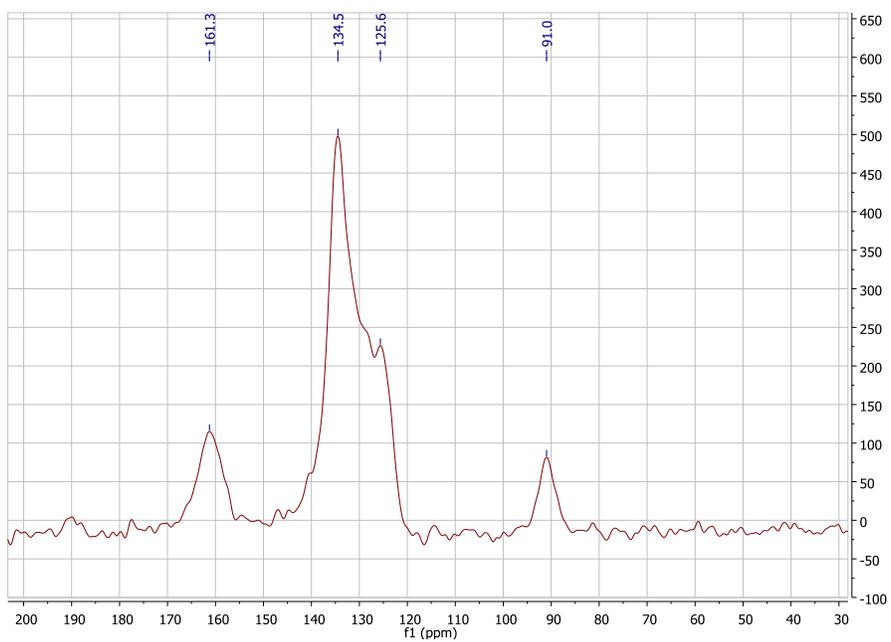
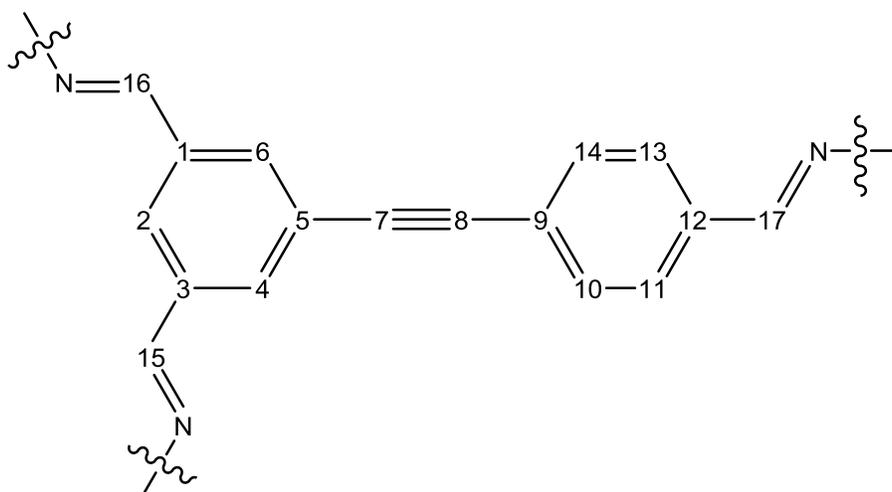
**Figure S20.** Heat of adsorption plot of CO<sub>2</sub> adsorption for HP-COF-2.

## 8. Solid-State $^{13}\text{C}$ CP-MAS spectra of HP-COFs



**Figure S21.** Solid State  $^{13}\text{C}$  CP-MAS NMR spectrum of HP-COF-1.

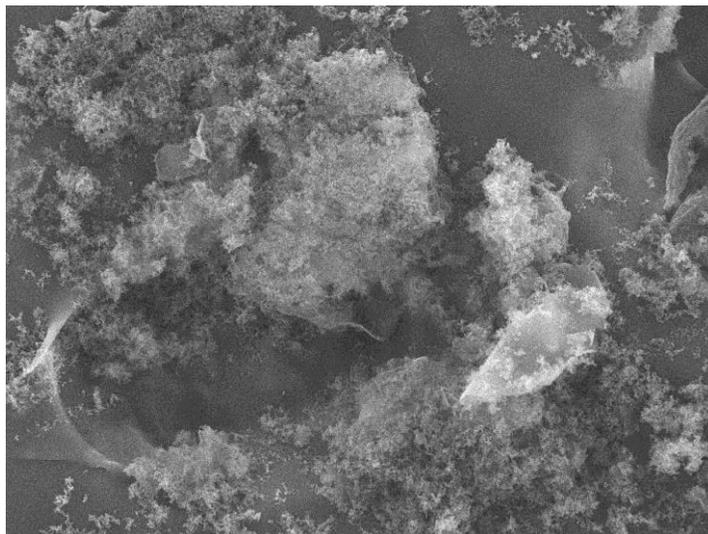
Chemical Shifts	Assignments
160.4	13, 14, 15
134.8	1, 2, 3, 4, 6, 9, 10, 11
128.0	5, 7, 8, 12



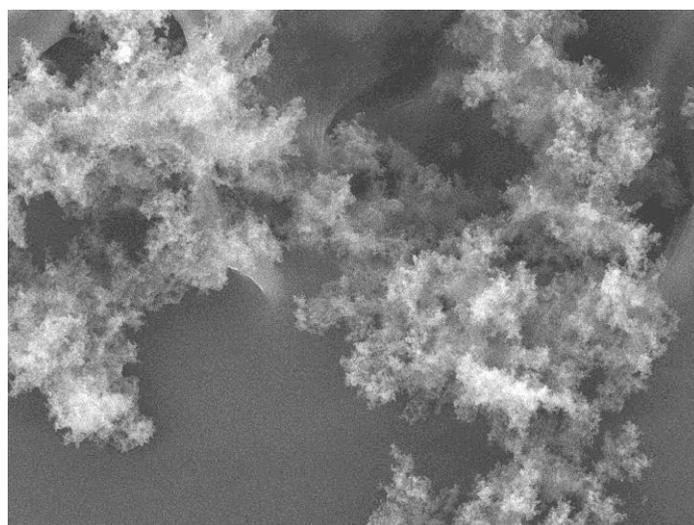
**Figure S22.** Solid State  $^{13}\text{C}$  CP-MAS NMR spectrum of HP-COF-2.

Chemical Shifts	Assignments
161.3	15, 16, 17
134.8	1, 2, 3, 4, 6, 11, 12, 13
128.0	5, 9, 10, 14
91.0	7, 8

## 9. SEM images of HP-COFs

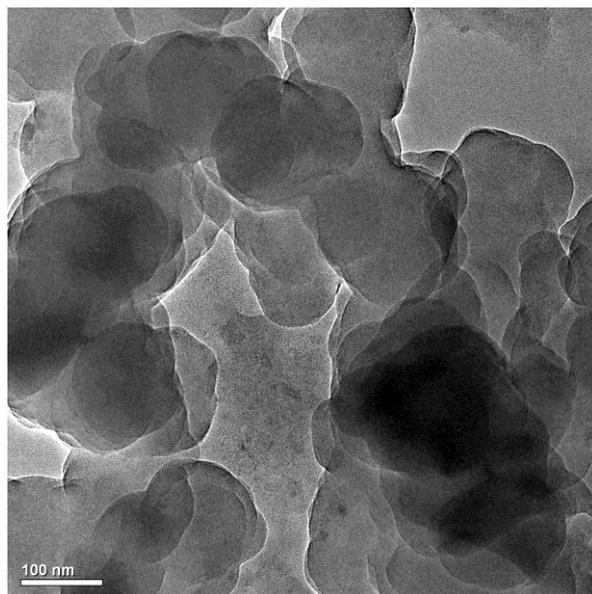


**Figure S23.** SEM image of HP-COF-1 (20 kV,  $\times 400$ ).

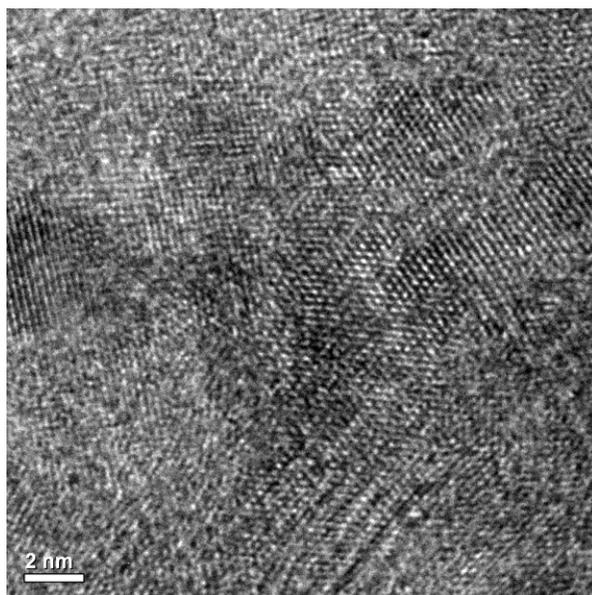


**Figure S24.** SEM image of HP-COF-2 (20 kV,  $\times 400$ ).

## 10. TEM images of HP-COFs



**Figure S25.** TEM image of HP-COF-1



**Figure S26.** TEM image of HP-COF-2 (layer by layer structure)

## 11. References

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