

Supporting Information

One-Step Construction of Two Different Kinds of Pores in A 2D

Covalent Organic Framework

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Procedure for the preparation of the dual-pore COF: 4, 4', 4'', 4'''-(ethene-1, 1, 2, 2-tetra-yl)tetraaniline (**ETTA**, 60 mg, 0.15 mmol) and terephthalaldehyde (41 mg, 0.3 mmol) were dissolved in a mixture of dioxane (2 mL) and acetic acid (6 M (aq.), 0.2 mL) in a sealed glass tube. After being degassed in a liquid nitrogen bath for 20 min, the tube was purged with argon and then sealed. The tube was kept at 120 °C without disturbance for 4 days to yield a yellow solid at the bottom of the tube. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dioxane for 3 times and then dried under dynamic vacuum at 150 °C for 4 h to afford a yellow powder (81.2 mg, 90.2%), which was insoluble in common organic solvents such as acetone, ethanol, and N, N-dimethylformamide. Anal. Calcd. For C₄₂H₂₈N₄: C, 85.69; H, 4.79; N, 9.52. Found: C, 82.89; H, 5.00; N, 9.08.

Instruments and Methods.

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.

Solid-state nuclear magnetic resonance (NMR) spectroscopy

The ¹³C CP-MAS spectrum of the dual-pore COF was recorded on Agilent DD2 600

Solid NMR System with 4 mm zirconia rotors. The spinning rate is 9 kHz and the contact time is 3 ms.

Scanning electron microscopy (SEM)

Scanning electron microscopy was carried out using a JSM-6390LV scanning electron microscope. The sample was dispersed over a slice of conductive adhesive adhered to a flat copper platform sample holder and then coated with gold using a sputter coater (ambient temperature, 85 torr pressure in an nitrogen atmosphere, sputtered for 30 s from a solid gold target at a current at 30 mA) before being submitted to SEM characterization.

Thermal gravimetric analyses (TGA)

TGA were carried out on Waters TGA Q500 by heating samples from 35 to 900 °C under Nitrogen atmosphere at a heating rate of 10 °C/min.

Powder X-ray diffraction

Powder X-ray diffraction measurement was carried out with an X'Pert PROX system using monochromated Cu/K α ($\lambda = 0.1542$ nm). The sample was spread on the square recess of XRD sample holder as a thin layer.

Small angle X-ray scattering (SAXS)

SAXS experiments were conducted on SAXSess mc² system (Anton Paar, Austria) with Ni filtered Cu K α radiation source. The power of X-ray source was operated at 30 mA and 50 kV.

Structural simulation and Powder X-Ray Diffraction Analysis

The Pawley refinement of the experimental PXRD was conducted by the Reflux module in the Material Studio 7.0, resulting in the cell parameters $a = b = 37.6753$ Å and $c = 4.7576$ Å with $R_p = 3.35\%$ and $R_{wp} = 4.33\%$. Before the simulation, the structure was firstly optimized in Gaussian 09 package by semiempirical calculations

at PM3 level. The simulation of the four possible structures was carried out in Accelrys Material Studio 7.0 software package. The stimulated PXRD patterns were determined by the Reflex module. And the unit cell was optimized by Forcite module under molecular mechanics calculation using COMPASS II as the forcefield to give the relative total energy. The initial lattice parameters and fractional atomic coordinates of **AA-H** are listed in Table S1.

Table S1. Fractional atomic coordinates for the unit cell of **AA-H** calculated from the Materials Studio 7.0 modeling program.

P 6/m (175) - hexagonal			
a = b = 38.0000 Å c = 4.6000 Å			
alpha = beta = 90° gamma = 120°			
Atom	x/a	y/b	z/c
C1	0.47228	0.0281	-0.50556
C2	0.45042	0.03285	-0.73005
C3	0.44362	0.0657	-0.72769
C4	0.4582	0.09371	-0.5
C5	0.48067	0.0891	-0.27849
C6	0.48753	0.05629	-0.28008
N7	0.45181	0.12693	-0.5
C8	0.48288	0.16325	-0.5
C9	0.48157	0.20144	-0.5
C10	0.51837	0.23814	-0.5
C11	0.51839	0.27493	-0.5
C12	0.48169	0.27493	-0.5
C13	0.4449	0.23823	-0.5
C14	0.44488	0.20144	-0.5
C15	0.48038	0.31313	-0.5
N16	0.51146	0.34944	-0.5
C17	0.50506	0.38267	-0.5
C18	0.48419	0.38827	-0.27167
C19	0.47731	0.42108	-0.27308
C20	0.49095	0.44825	-0.50508
C21	0.5112	0.44248	-0.73617
C22	0.51802	0.40964	-0.73397
H23	0.47965	-0.00627	-0.50846
H24	0.43889	0.01119	-0.90777
H25	0.42699	0.06966	-0.90428

H26	0.49295	0.11132	-0.10458
H27	0.50497	0.05293	-0.10655
H28	0.51355	0.166	-0.5
H29	0.5471	0.23852	-0.5
H30	0.54706	0.30334	-0.5
H31	0.41617	0.23786	-0.5
H32	0.41621	0.17304	-0.5
H33	0.44972	0.30955	-0.5
H34	0.47315	0.36684	-0.09253
H35	0.46112	0.42522	-0.09425
H37	0.52146	0.46334	-0.91883
H38	0.53338	0.40489	-0.91556

Table S2. The Space Groups and Cell Parameters of the four possible structures of COFs constructed from **ETTA** and terephthalaldehyde.

Structure	Crystal System	Space Group	Cell Parameters
AA-H	hexagonal	P6/m	$a=b=39.2 \text{ \AA}$, $c=4.8 \text{ \AA}$, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$
AB-H	hexagonal	P63/m	$a=b=39.2 \text{ \AA}$, $c=9.6 \text{ \AA}$, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$
AA-O	orthorhombic	PMMM	$a=29.2 \text{ \AA}$, $b=25.4 \text{ \AA}$, $c=4.8 \text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$
AB-O	orthorhombic	PCMM	$a=29.2 \text{ \AA}$, $b=25.4 \text{ \AA}$, $c=9.6 \text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$

Nitrogen adsorption-desorption isotherm measurement

The measurement was carried out using a Quadrasorb SI MP. Before gas adsorption measurements, the as-prepared sample (50 mg) was activated by being immersed in anhydrous dioxane for 12 h. The solvent was decanted and the sample was dried under dynamic vacuum at 200 °C for 10 h. The resulting sample was then used for gas adsorption measurements from 0 to 1 atm at 77 K.

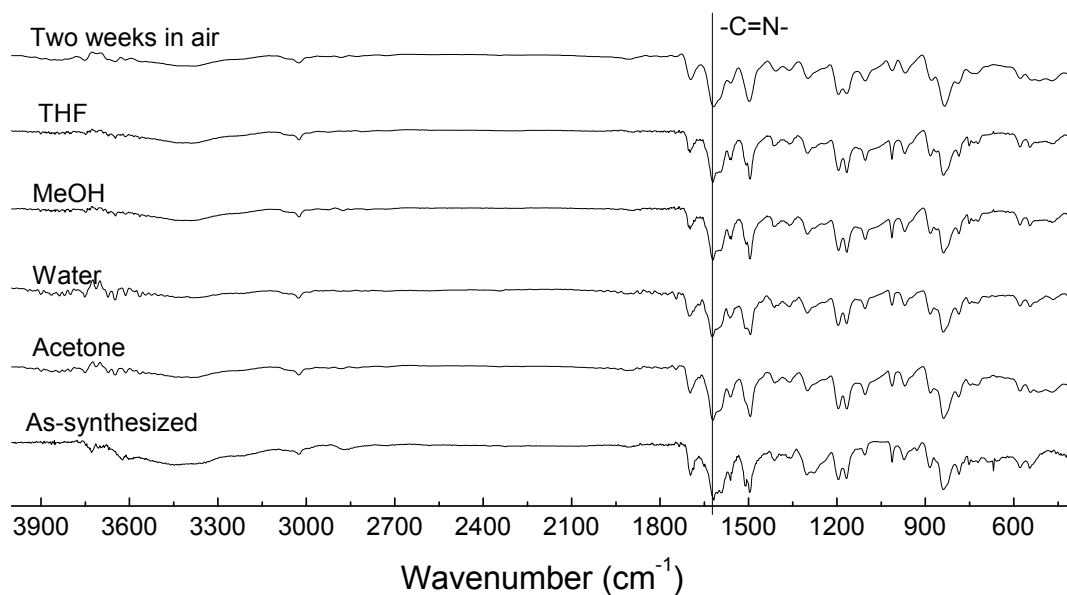


Figure S1. FT-IR spectra of the dual-pore COF samples before and after treatment with different solvents for 24 h, indicating the high stability of the COF.

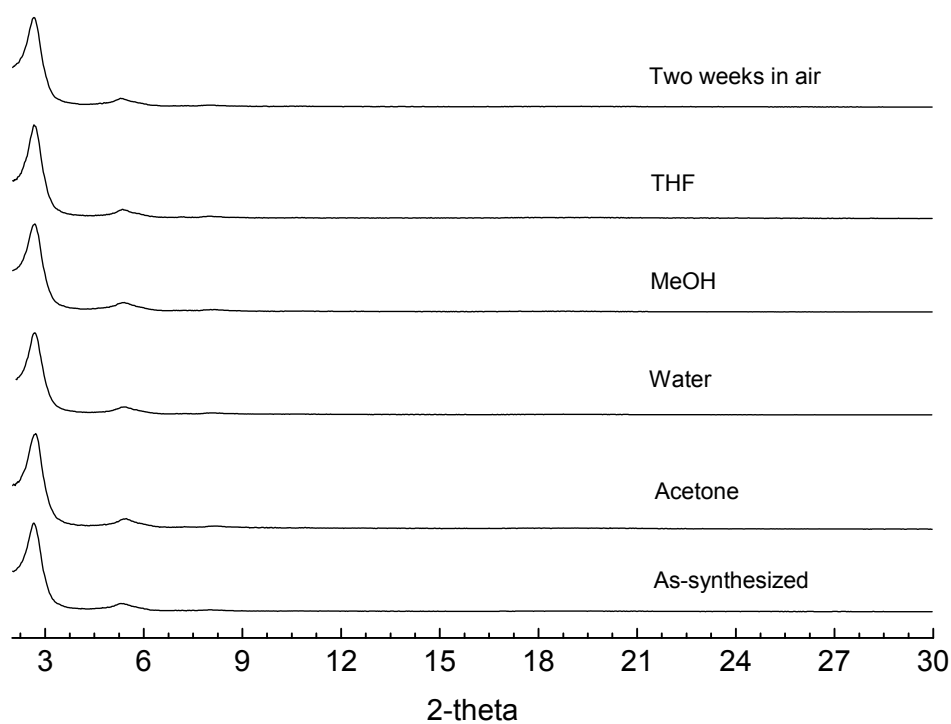


Figure S2. XRD patterns of the dual-pore COF samples before and after treatment with different solvents for 24 h, indicating the high stability of the COF.

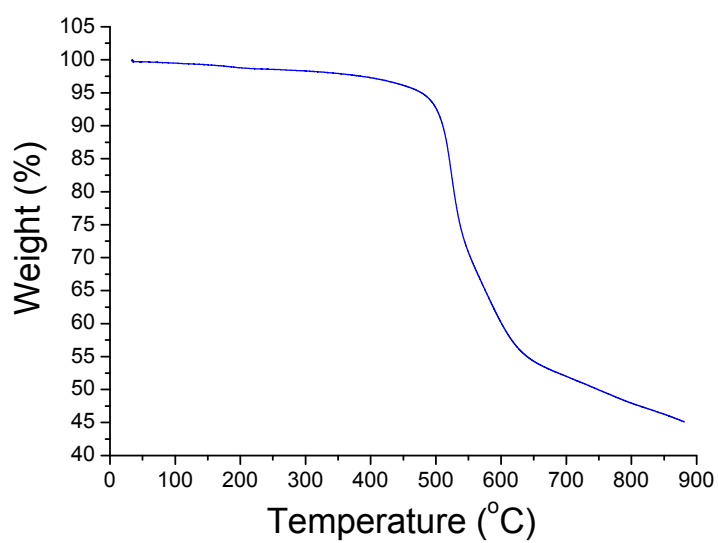


Figure S3. TGA trace of the COF.

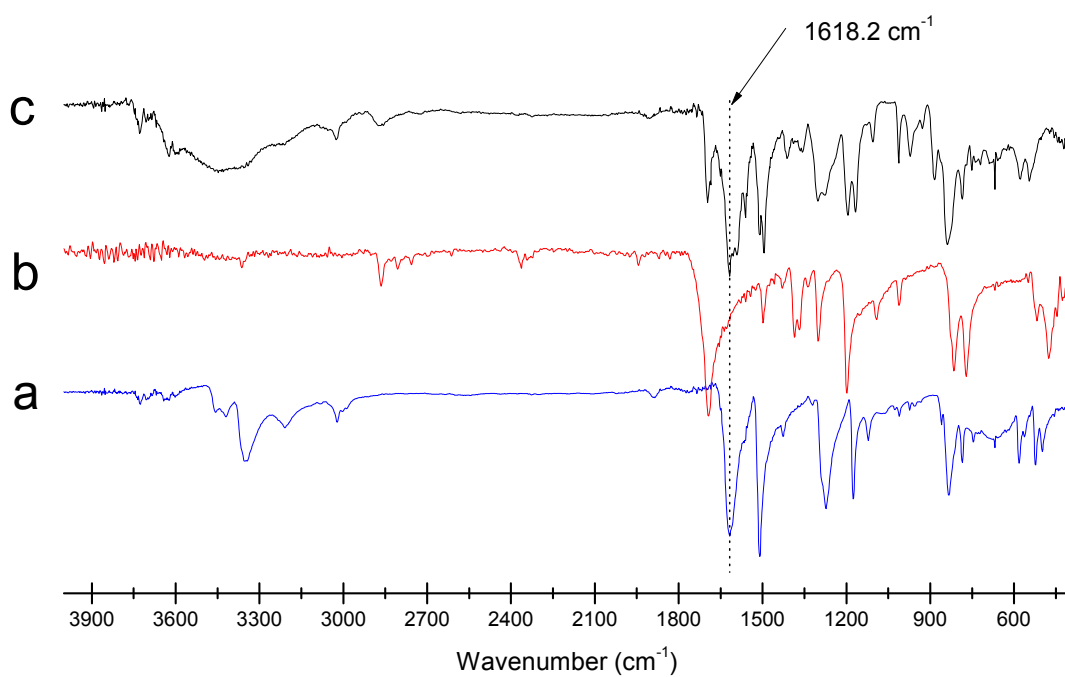


Figure S4. FT-IR spectra of (a) ETTA, (b) terephthalaldehyde, and (c) the dual-pore COF.

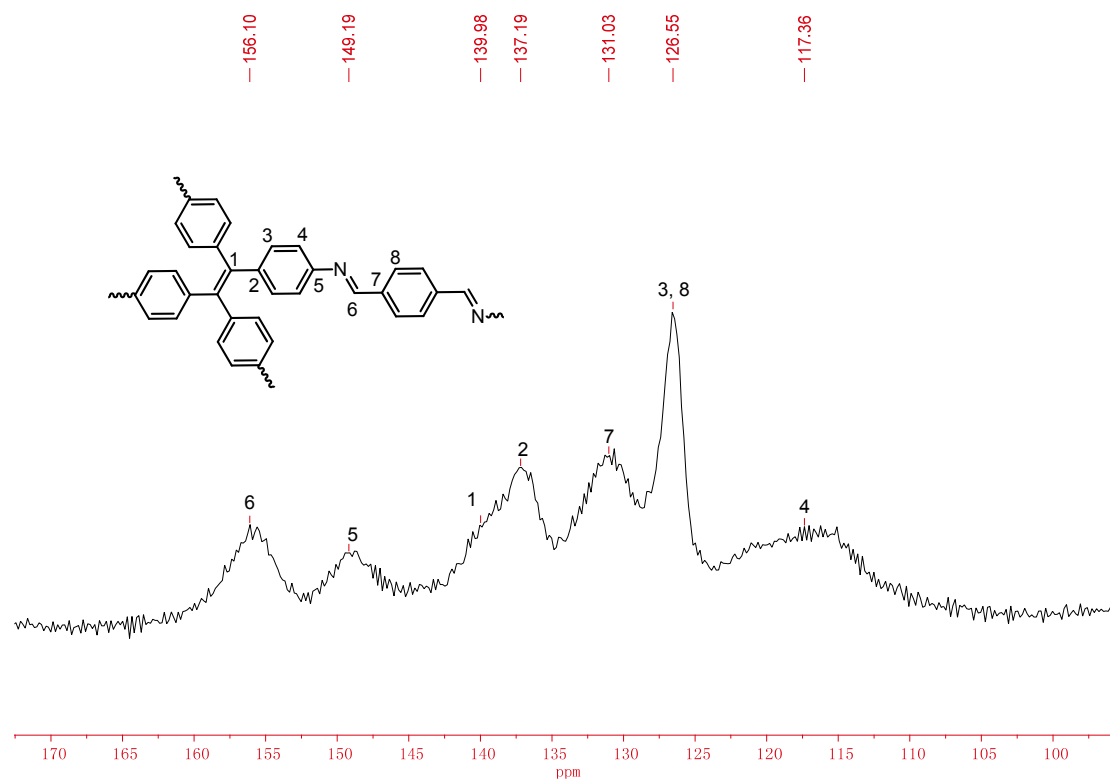


Figure S5. Solid-state ^{13}C CP-MAS NMR spectrum of the dual-pore COF.

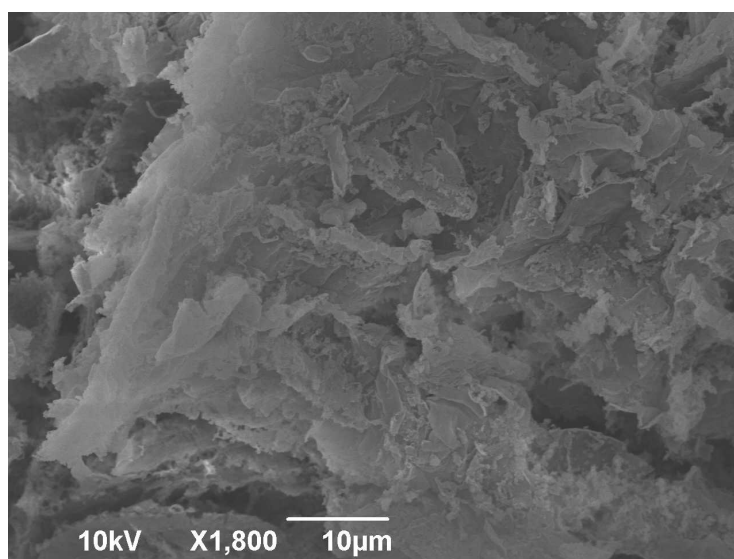


Figure S6. SEM image of the dual-pore COF.

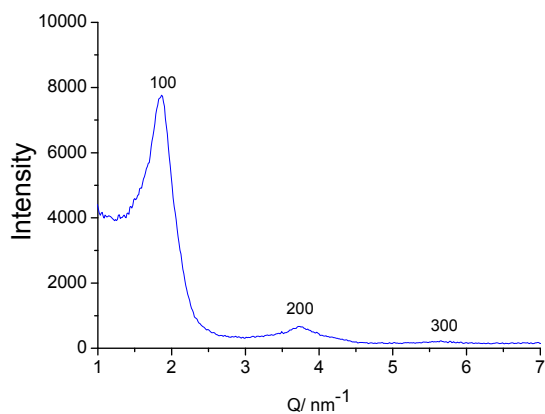


Figure S7. SAXS pattern of the dual-pore COF.

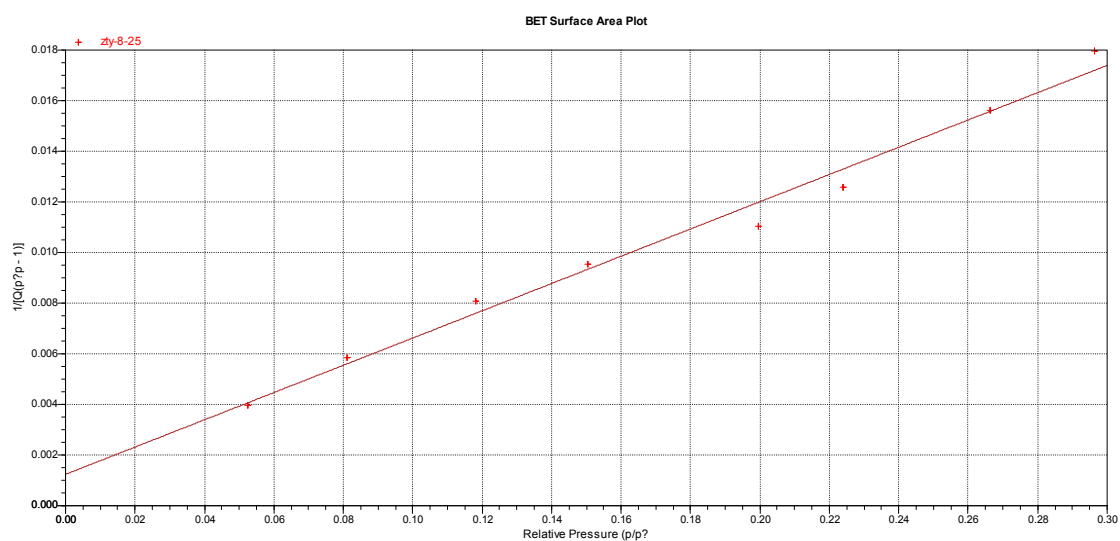


Figure S8. BET surface area plot for the dual-pore COF calculated from the isotherm.

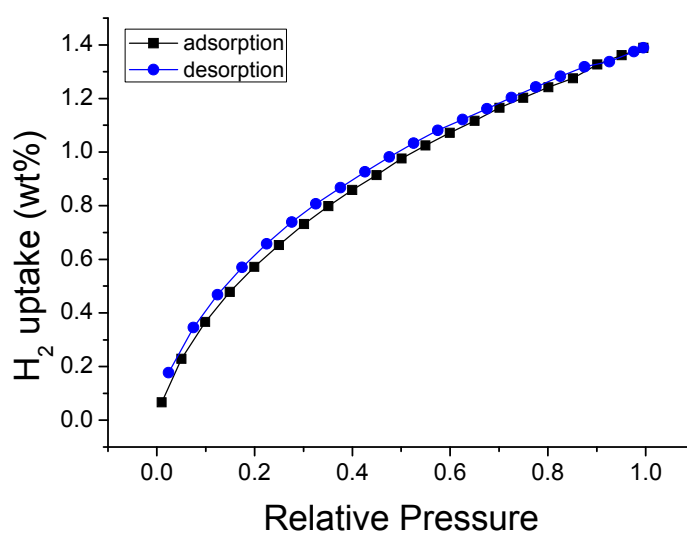


Figure S9. Hydrogen adsorption-desorption isotherm of the dual-pore-COF at 77 K.

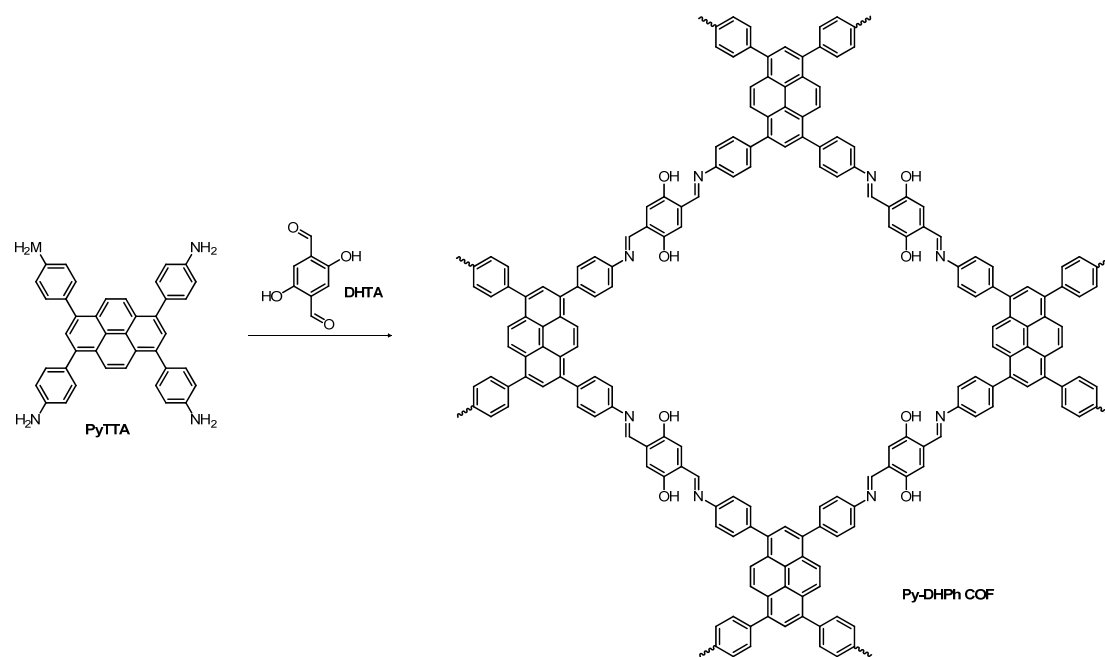


Figure S10. Chemical structure of COF **Py-DHPH** reported in literature.¹

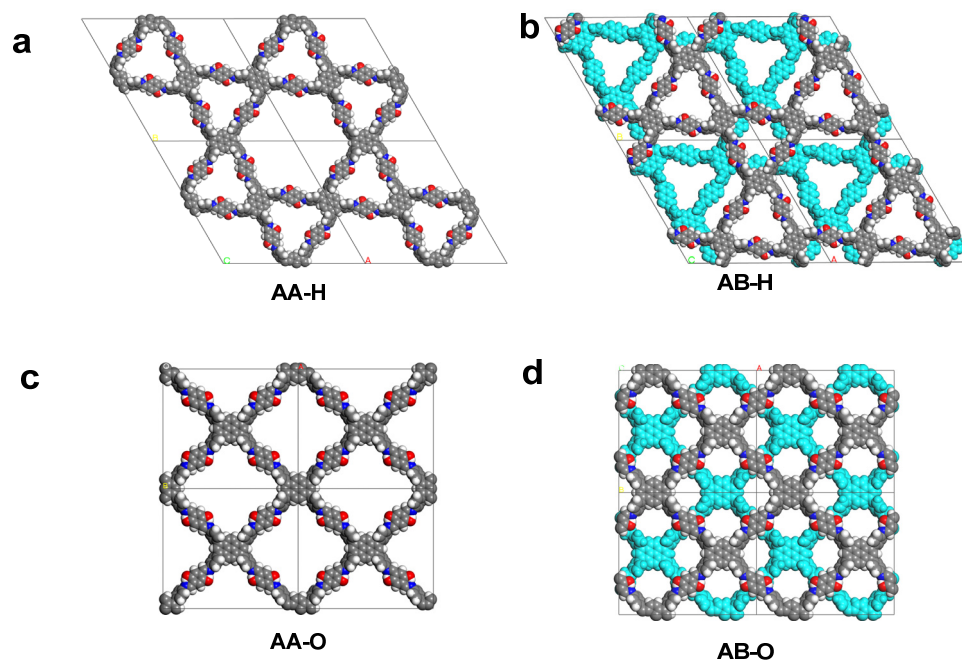


Figure S11. The four possible COF structures which might be generated by condensation of **PyTTA** and **DHTA**: (a) AA-H, (b) AB-H, (c) AA-O, and (d) AB-O.

We took COF **Py-DHPH**¹ as one representative to calculate the relative total energy of the possible structures whose monomers had similar symmetries as **ETTA** and terephthalaldehyde. Same as the condensation of **ETTA** and terephthalaldehyde, the COFs constructed from **PyTTA** and **DHTA** would also have four possible structures

(Figure S6): **AA-H**, **AB-H**, **AA-O** and **AB-O**. **AA-H** and **AB-H** belong to hexagonal system which could give dual-pore structure. **AA-O** and **AB-O** belong to orthorhombic system which only bears single-pore structure. The cell units of **AA-O** and **AB-O** were constructed according to the Jiang's article. The relative total energies were calculated by molecular mechanics calculation using COMPASS II as the forcefield. The cell parameters and relative total energies are listed in Table S3.

Table S3. The crystal system, cell parameters, and relative total energies of the four possible structures of COFs constructed from **PyTTA** and **DHTA**.

Structure	Crystal System	Cell Parameters	Relative Energy (kcal/mol)	Total
AA-H	hexagonal	a=b=46.65 Å, c=4.68 Å, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$	599.9	
AB-H	hexagonal	a=b=46.65 Å, c=9.36 Å, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$	1485.5	
AA-O	orthorhombic	a=35.82 Å, b=31.90 Å, c=4.69 Å, $\alpha=\beta=\gamma=90^\circ$	0	
AB-O	orthorhombic	a=35.82 Å, b=31.90 Å, c=9.38 Å, $\alpha=\beta=\gamma=90^\circ$	607.4	

Reference

- (1) Chen, X.; Huang, N.; Gao, J.; Xu, H.; Xu, F.; Jiang, D. *Chem. Commun.* **2014**, *50*, 6161.