

Supplementary Information

Isorecticular Covalent Organic Frameworks for Hydrocarbon Uptake and
Separation: The Important Role of Monomer Planarity

Jinqiao Dong[†], Yuxiang Wang[†], Guoliang Liu, Youdong Cheng and Dan Zhao*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4
Engineering Drive 4, Singapore 117585

Correspondence and requests for materials should be addressed to D.Z. (E-mail:
chezhao@nus.edu.sg).

Materials and Methods

All the reagents were obtained from commercial suppliers and used without further purification. Fourier transform infrared spectroscopy (FTIR) data were obtained with a Bio-Rad FTS-3500 ARX FTIR spectrometer. Powder X-ray diffraction (PXRD) patterns were obtained on a Bruker D8 Advance X-ray powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$) at a scan rate of 2° min^{-1} . Field-emission scanning electron microscopy (FE-SEM) was conducted on a JEOL JSM-7610F scanning electron microscope. Samples were treated via Pt sputtering for 100 s before observation. High-resolution transmission electron microscopy (HR-TEM) was conducted on a JEOL JEM-3010 transmission electron microscope. Thermogravimetric analyses (TGA) were performed using a Shimadzu DTG-60AH in the temperature range of 100 to 800 °C under flowing air (50 mL min^{-1}) and a heating rate of $10^\circ \text{ C min}^{-1}$. N_2 sorption isotherms were measured using a Micromeritics ASAP 2020 surface area and pore size analyzer. Before the measurements, the samples were degassed under high vacuum ($< 0.01 \text{ Pa}$) at 120 °C for 10 h. UV/visible spectra were collected on a Shimadzu UV-3600 spectrometer using the BaSO_4 reflectance standard at room temperature.

Synthetic Procedures

Three amine linkages tris(4-aminotriphenyl)amine (TAPA), 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 2,4,6-tris(4-aminophenyl)-s-triazine (TAPT) were synthesized as previously reported.¹⁻⁴ Briefly, a pyrex tube was charged with TAPA (29 mg, 0.1 mmol), 1,3,5-triformylbenzene (16.2 mg, 0.1 mmol), THF (0.75 mL) and mesitylene (0.25 mL). The tube was immersed in an ultrasonic bath and sonicated for 5 min. After that, aqueous acetic acid (6 M, 0.1 mL) was added and the tube was flash frozen at liquid N_2 bath, evacuated and sealed. The tube was warmed to room temperature before heating to 120 °C in a convection oven for 3 days. The resulting N-COF precipitate was isolated by vacuum filtration and then underwent solvent exchange with diethyl ether for three days, and was fully activated at 120 °C under vacuum for 8 h to afford a red powder. P-COF and T-COF were synthesized in

1,4-dioxane (1 mL) and 1,4-dioxane/mesitylene (0.5 mL and 0.5 mL), respectively, with the same synthetic procedures as that of N-COF.

Gas Sorption Measurements

N₂ sorption isotherms of the COFs were measured up to 1 bar using a Micromeritics ASAP 2020, and C₂H₆ and CH₄ sorption isotherms were measured up to 800 torr using a Quantachrome Autosorb iQ. Before the measurements, the samples were degassed under a reduced pressure (< 10⁻² Pa) at 150 °C for 10 h. UHP grade gases were used for gas sorption measurements. Pore size distribution data were calculated from the N₂ adsorption isotherms at 77 K based on non-local density functional theory (NLDFT) model in the Micromeritics ASAP 2020 software package (assuming slit pore geometry).

Calculation of Isotheric Heat of Adsorption (Q_{st})

The gas adsorption isotherms measured at 283 K and 298 K were firstly fitted to a virial equation (Equation 1). The fitting parameters were then used to calculate the isotheric heat of adsorption (Q_{st}) using Equation 2,

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (1)$$

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (2)$$

where P is pressure (mmHg), N is adsorbed quantity (mmol g⁻¹), T is temperature (K), R is gas constant (8.314 J K⁻¹ mol⁻¹), a_i and b_i are virial coefficients, m and n represent the number of coefficients required to adequately describe the isotherms (herein, $m = 5$, $n = 2$).

Calculation of Gas Selectivity Based On Ideal Adsorption Solution Theory (IAST)⁵

The gas adsorption isotherms were firstly fitted to a dual-site Langmuir-Freundlich (DSLFF) model (Equation 3),

$$q = \frac{q_{sat,A} b_A p^{\alpha_A}}{1 + b_A p^{\alpha_A}} + \frac{q_{sat,B} b_B p^{\alpha_B}}{1 + b_B p^{\alpha_B}} \quad (3)$$

where q is the amount of adsorbed gas (mmol g⁻¹), p is the bulk gas phase pressure (bar), q_{sat} is the saturation amount (mmol g⁻¹), b is the Langmuir-Freundlich parameter (bar^{- α}), α is the Langmuir-Freundlich exponent (dimensionless) for two adsorption sites A and B indicating the presence of weak and strong adsorption sites.

IAST starts from the Raoult's Law type of relationship between fluid and adsorbed phase,

$$P_i = Py_i = P_i^o x_i \quad (4)$$

$$\sum_{i=1}^n x_i = \sum_{i=1}^n \frac{P_i}{P_i^o} = 1 \quad (5)$$

where P_i is partial pressure of component i (bar), P is total pressure (bar), y_i and x_i represent mole fractions of component i in gas and adsorbed phase (dimensionless). P_i^o is equilibrium vapour pressure (bar).

In IAST, P_i^o is defined by relating to spreading pressure π ,

$$\frac{\pi S}{RT} = \int_0^{P_i^o} \frac{q_i(P_i)}{P_i} dP_i = \Pi \text{ (Constant)} \quad (6)$$

where π is spreading pressure, S is specific surface area of adsorbent ($\text{m}^2 \text{g}^{-1}$), R is gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is temperature (K), $q_i(P_i)$ is the single component equilibrium obtained from isotherm (mmol g^{-1}).

For a dual-site Langmuir-Freundlich (DSLRF) model, we have an analytical expression for the integral,

$$\int_0^{P_i^o} \frac{q_i(P_i)}{P_i} dP_i = \Pi \text{ (Constant)} = \frac{q_{sat,A}}{\alpha_A} \ln[1 + b_A (P_i^o)^{\alpha_A}] + \frac{q_{sat,B}}{\alpha_B} \ln[1 + b_B (P_i^o)^{\alpha_B}] \quad (7)$$

The isotherm parameters will be known from the previous fitting. For a binary component system the unknowns will be Π , P_1^o , and P_2^o which can be obtained by simultaneously solving Equations 4 and 6.

The adsorbed amount for each component in a mixture is

$$q_i^{mix} = x_i q_T \quad (8)$$

$$\frac{1}{q_T} = \sum_{i=1}^n \frac{x_i}{q_i(P_i^o)} \quad (9)$$

where q_i^{mix} is the adsorbed amount of component i (mmol g^{-1}), q_T is the total adsorbed amount (mmol g^{-1}).

The adsorption selectivities S_{ads} were calculated using Equation 9.

$$S_{ads} = \frac{q_1 / q_2}{p_1 / p_2} \quad (10)$$

In this study, IAST calculations were carried out assuming $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ (50/50) binary mixed gases at 298 K and pressures up to 1 bar.

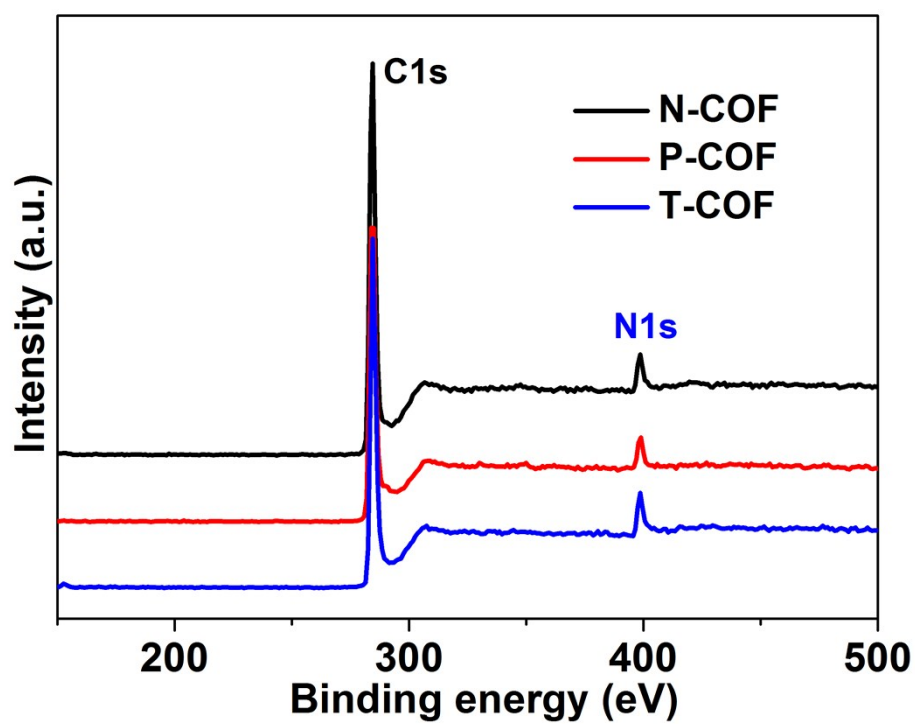


Figure S1. XPS spectra of N-COF, P-COF and T-COF.

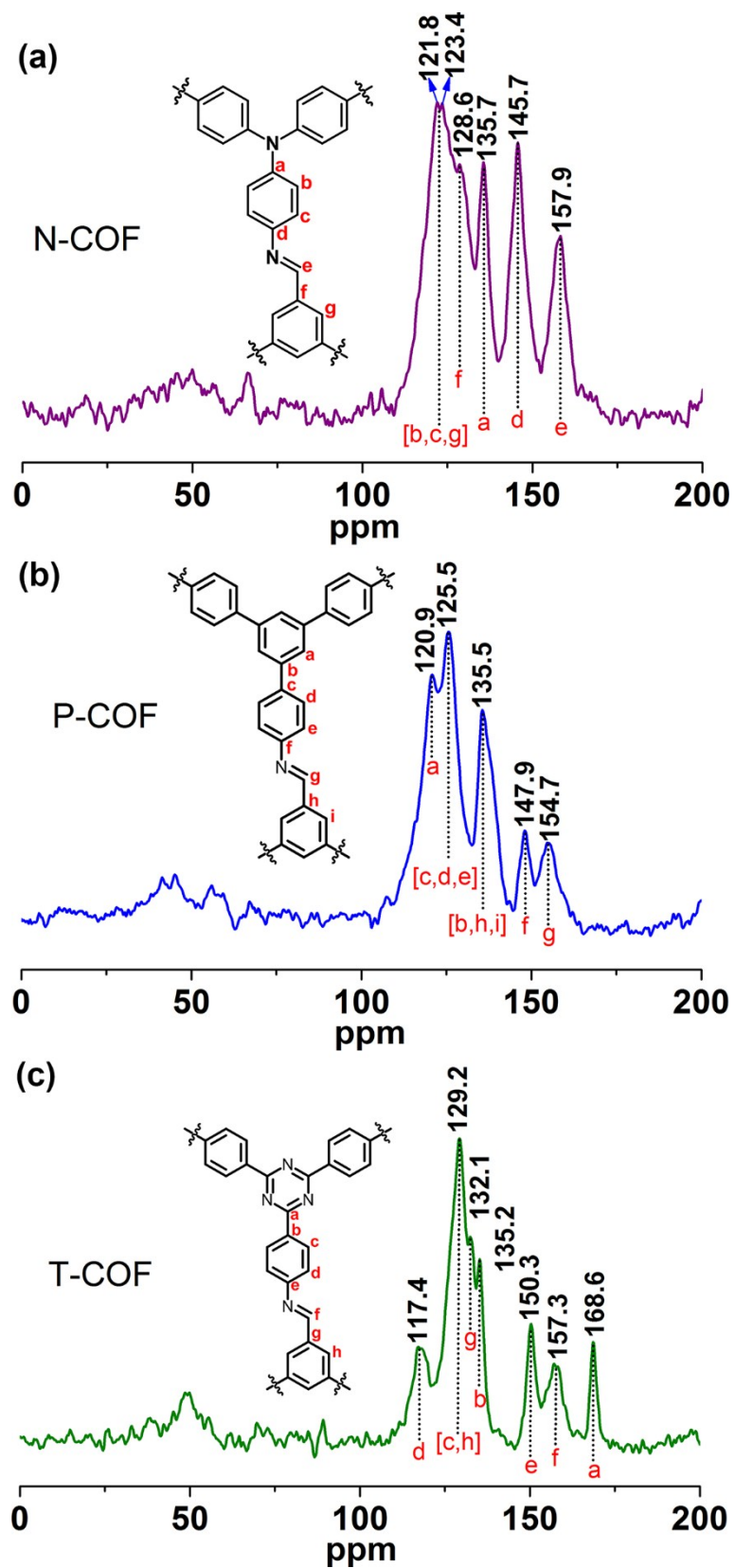


Figure S2. Solid-state ^{13}C CP/MAS NMR spectra of N-COF (a), P-COF (b) and T-COF (c).

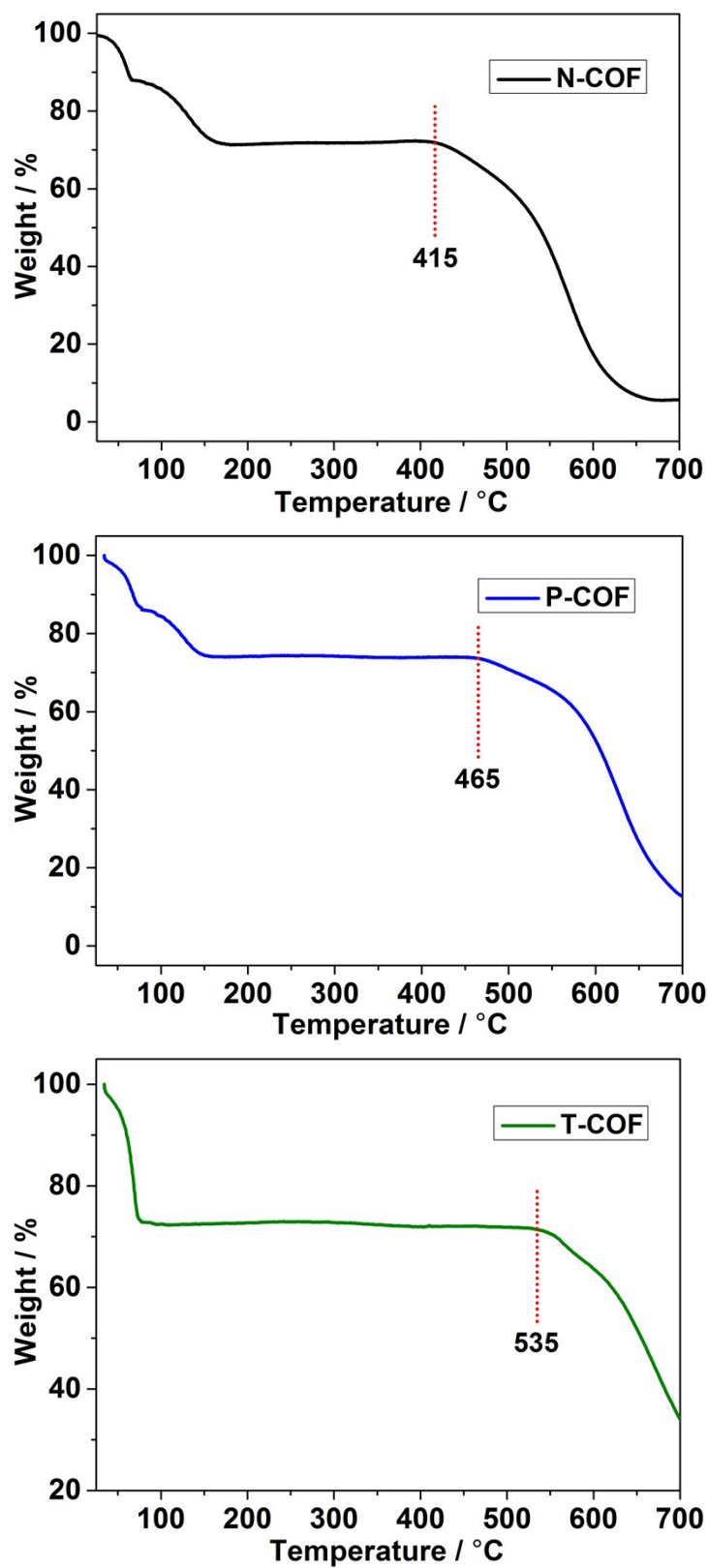


Figure S3. TGA curves of N-COF, P-COF and T-COF.

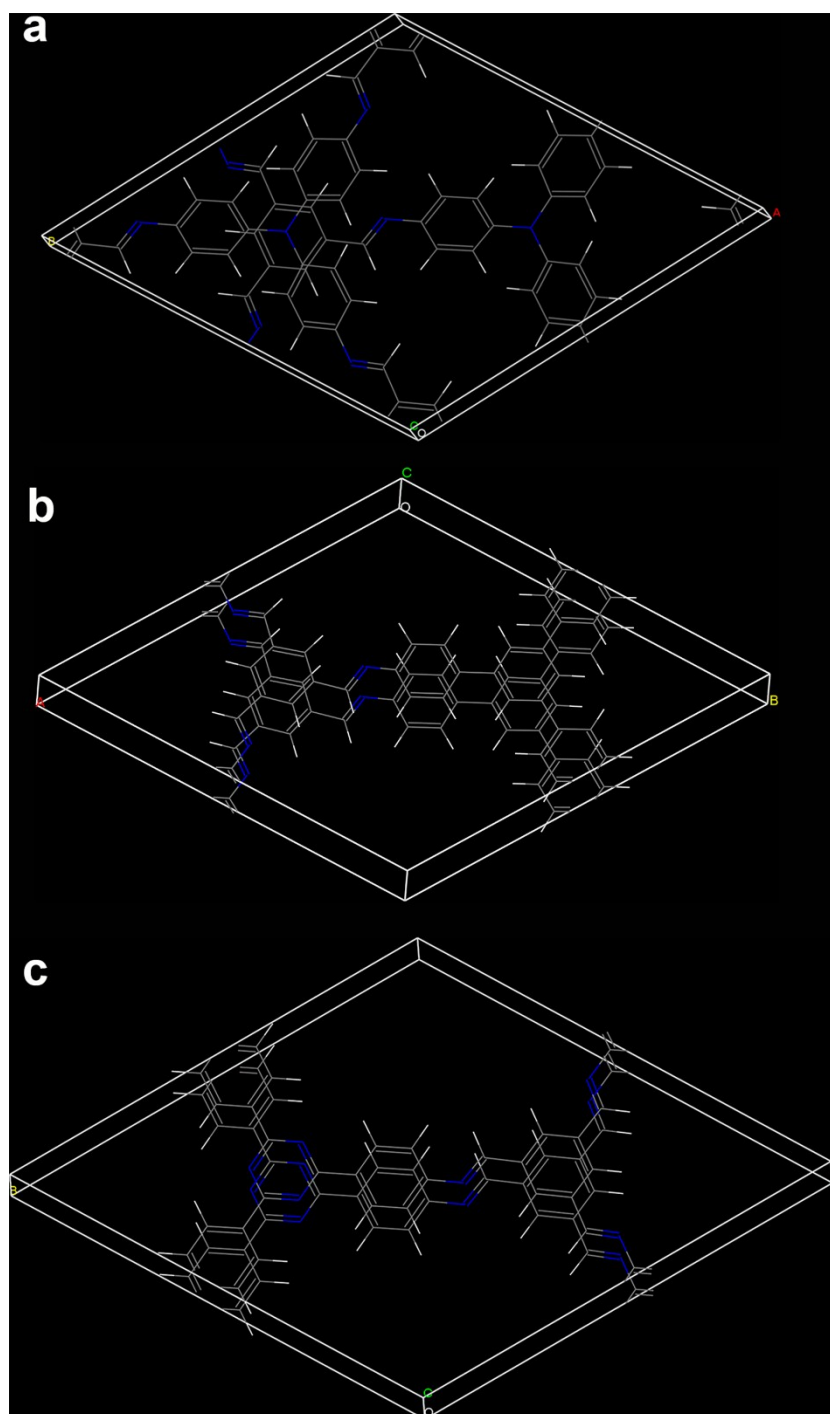


Figure S4. Cell unit images of N-COF (a), P-COF (b) and T-COF (c).

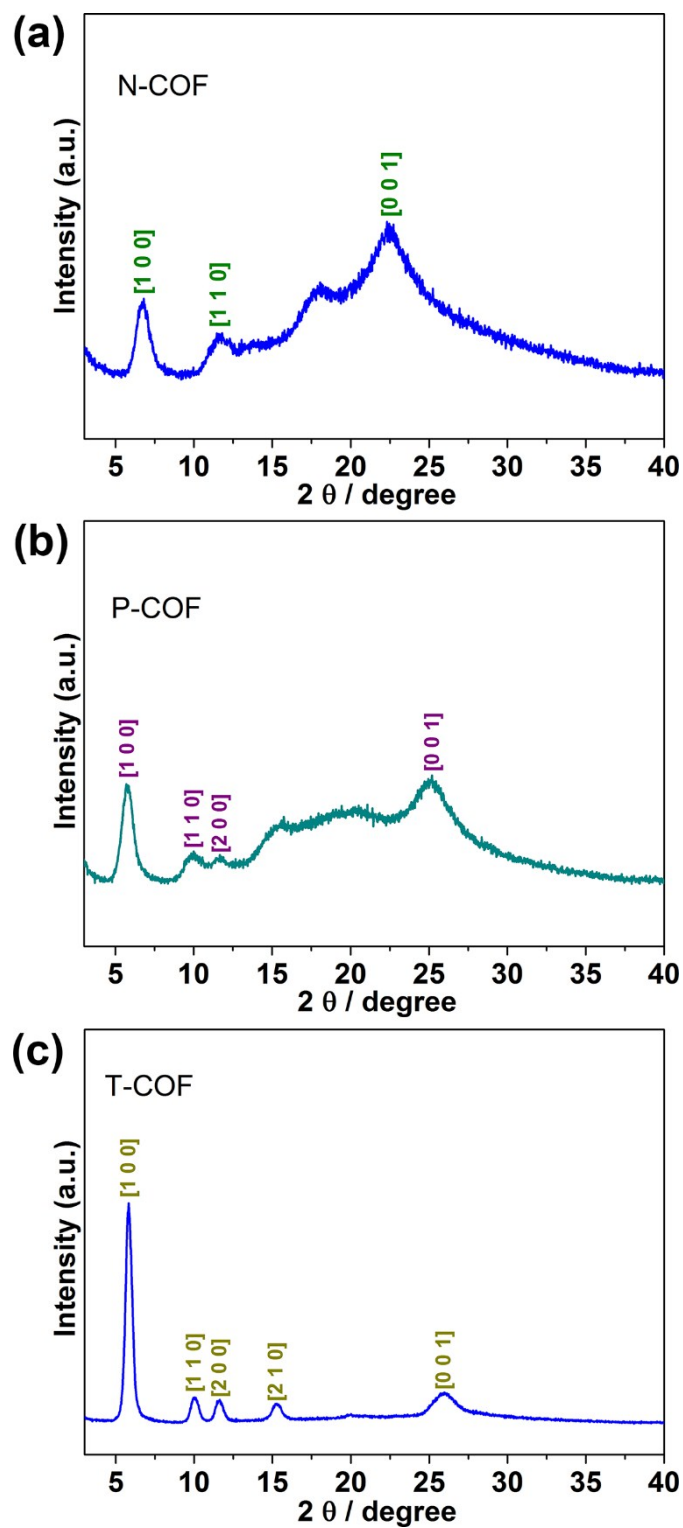


Figure S5. PXRD patterns of N-COF (a), P-COF (b), and T-COF (c) after gas sorption tests.

Table S1. Parameters for the simulated AB stacking crystal structure of N-COF.

Structure code	N-COF
Formula	$C_{54}N_8H_{36}$
M (g mol ⁻¹)	796.9
Crystal system	trigonal
Space group	<i>P</i> 3 (143)
a / Å	16.18
b / Å	16.18
c / Å	8.00
α / deg.	90
β / deg.	90
γ / deg.	120
V / Å ³	1812.6
Calculated density (g cm ⁻³)	0.73
surface area (Å ²)	604.52
Free Volume (Å ³)	982.24

Table S2. Parameters for the simulated AA stacking crystal structure of P-COF.

Structure code	P-COF
Formula	C ₃₃ N ₃ H ₂₁
M (g mol ⁻¹)	459.5
Crystal system	hexagonal
Space group	<i>P</i> -6 (174)
<i>a</i> / Å	18.67
<i>b</i> / Å	18.67
<i>c</i> / Å	3.62
α / deg.	90
β / deg.	90
γ / deg.	120
<i>V</i> / Å ³	1091.8
Calculated density (g cm ⁻³)	0.70
surface area (Å ²)	223.24
Free Volume (Å ³)	572.63

Table S3. Parameters for the simulated AA stacking crystal structure of T-COF.

Structure code	T-COF
Formula	C ₃₀ N ₆ H ₁₈
M (g mol ⁻¹)	462.5
Crystal system	hexagonal
Space group	<i>P</i> -6 (174)
a / Å	18.56
b / Å	18.56
c / Å	3.50
α / deg.	90
β / deg.	90
γ / deg.	120
V / Å ³	1043.9
Calculated density (g cm ⁻³)	0.74
surface area (Å ²)	220.29
Free Volume (Å ³)	557.84

References

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