Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Post-metalation of porous aromatic frameworks for highly efficient carbon capture from CO_2+N_2 and CH_4+N_2 mixtures

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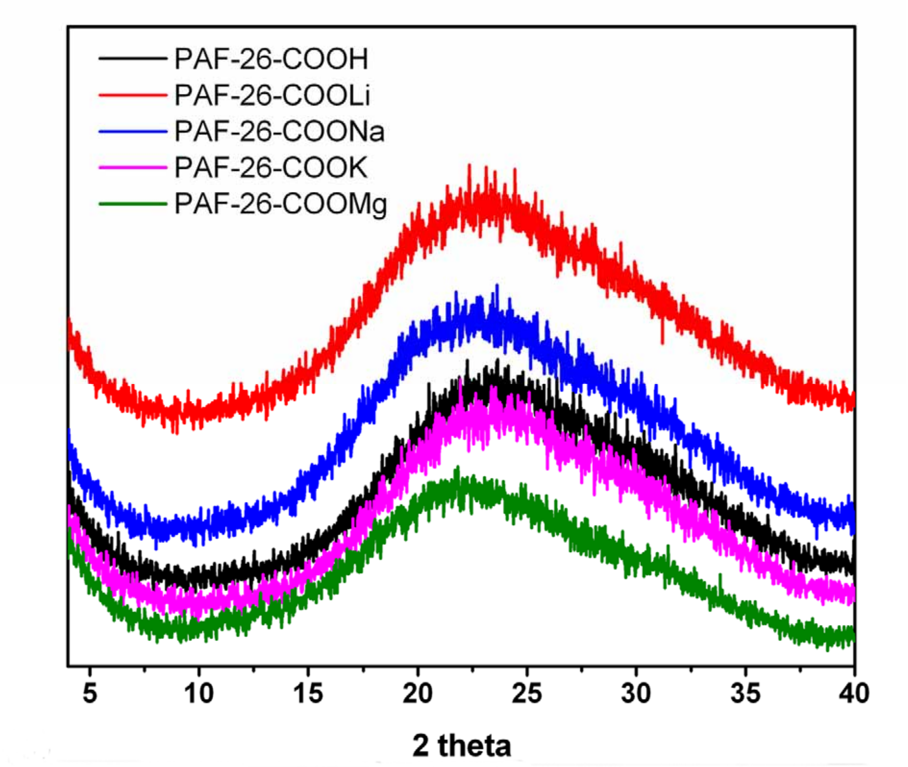

Fig. S1 XRD patterns of PAF-26-COOH, PAF-26-COOLi, PAF-26-COONa, PAF-26-COOK and PAF-26-COOMg samples.

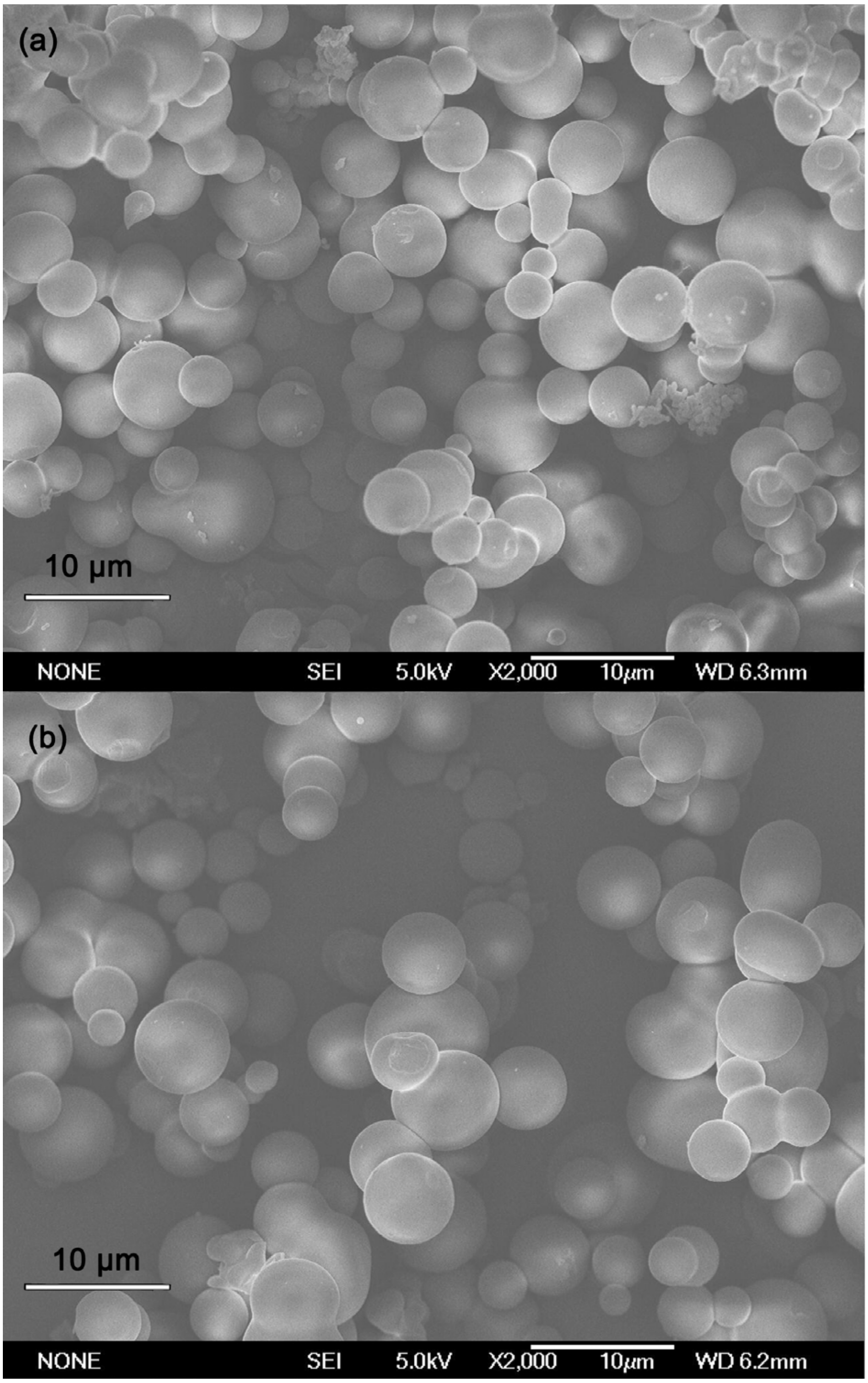

Fig. S2 SEM images of PAF-26-COOH (a) and PAF-26-COOMg (b).

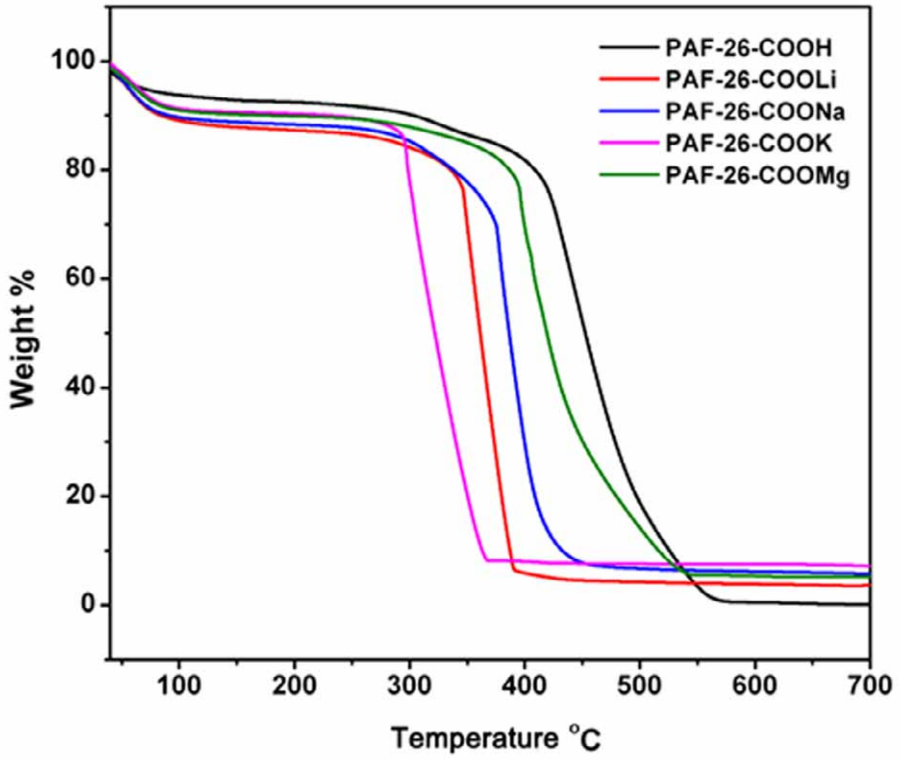

Fig. S3 TG curves of PAF-26-COOH and PAF-26-COOM samples.

Table S1. Elemental analysis of PAF-26-COOH.

	C (wt %)	H (wt %)	N (wt %)	S (wt %)
Theoretical value	86.5	3.68	0	0
Experiment value	87.2	3.54	0.02	0.028

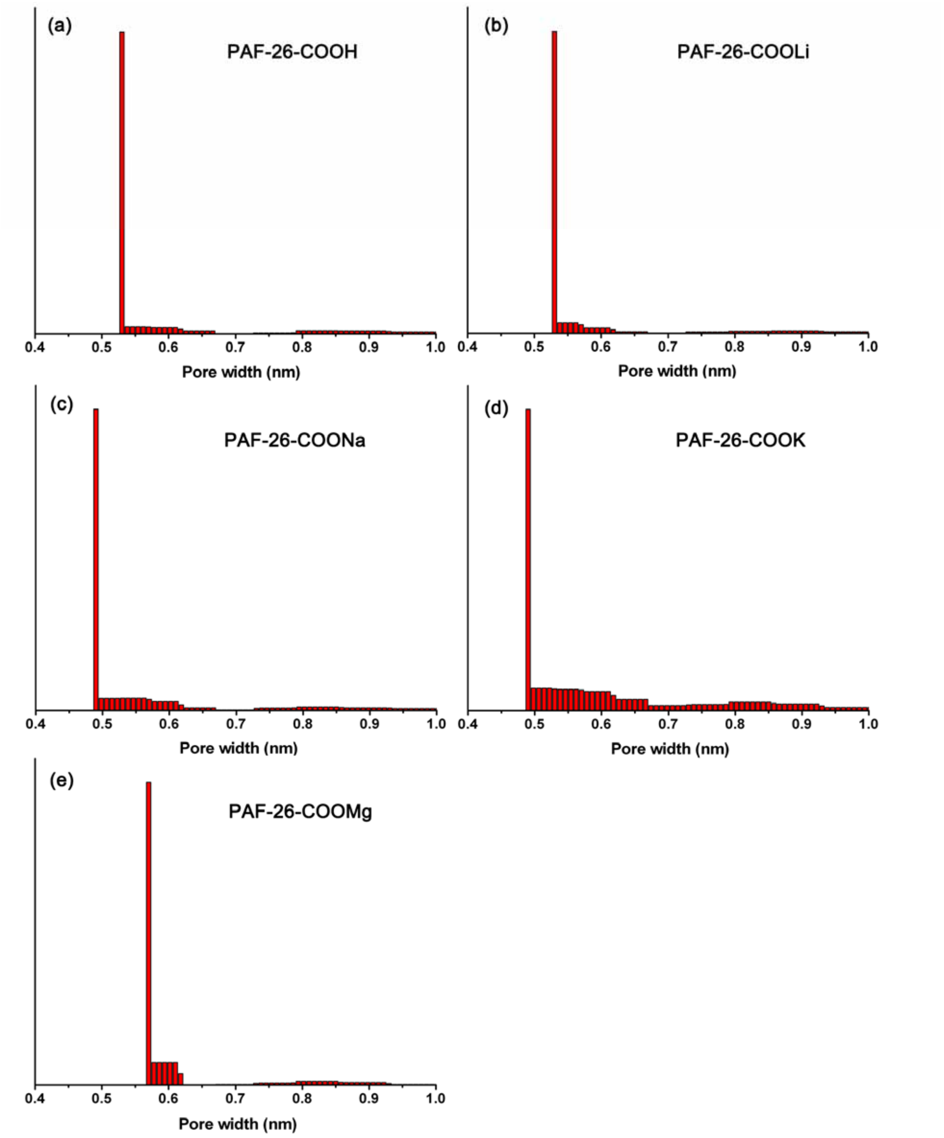

Fig. S4 Pore size distribution of PAF-26-COOH (a), PAF-26-COOLi (b), PAF-26-COONa (c), PAF-26-COOK (d), and PAF-26-COOMg (e) samples.

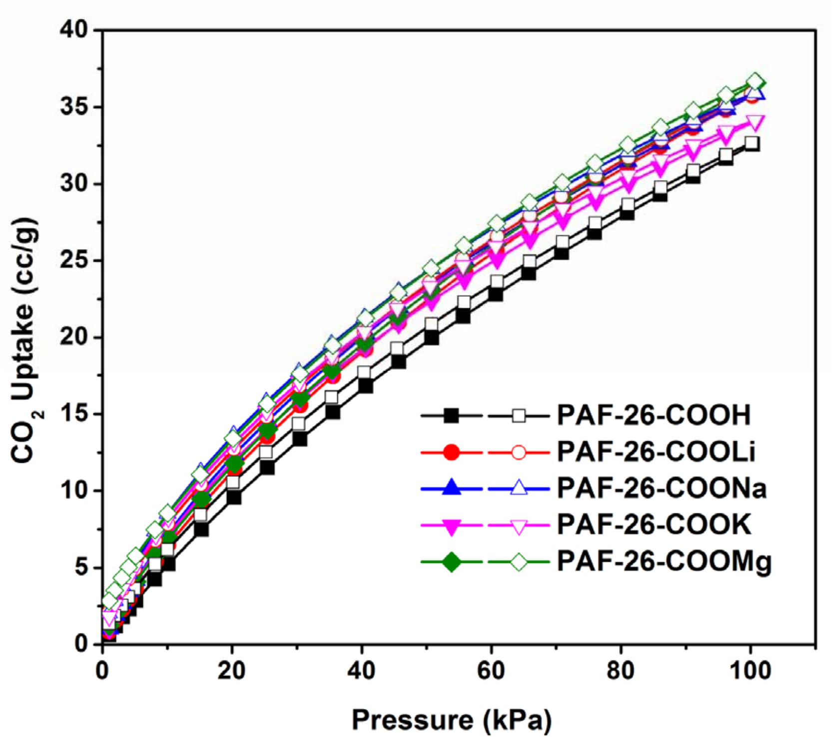

Fig. S5 CO_2 adsorption isotherms for PAF-26-COOH and PAF-26-COOM at 298 K.

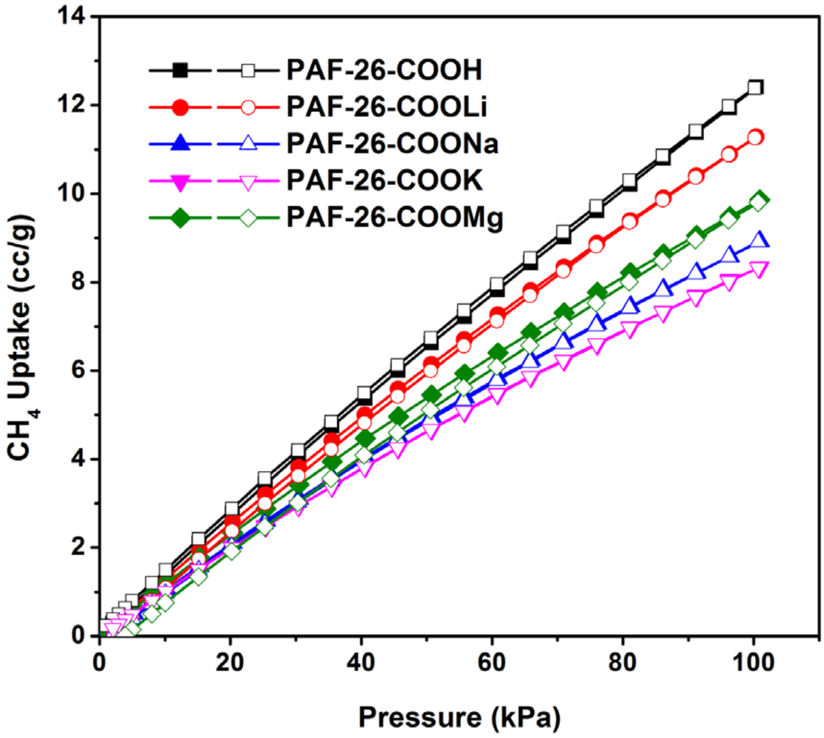

Fig. S6 CH_4 adsorption isotherms for PAF-26-COOH and PAF-26-COOM at 298 K.

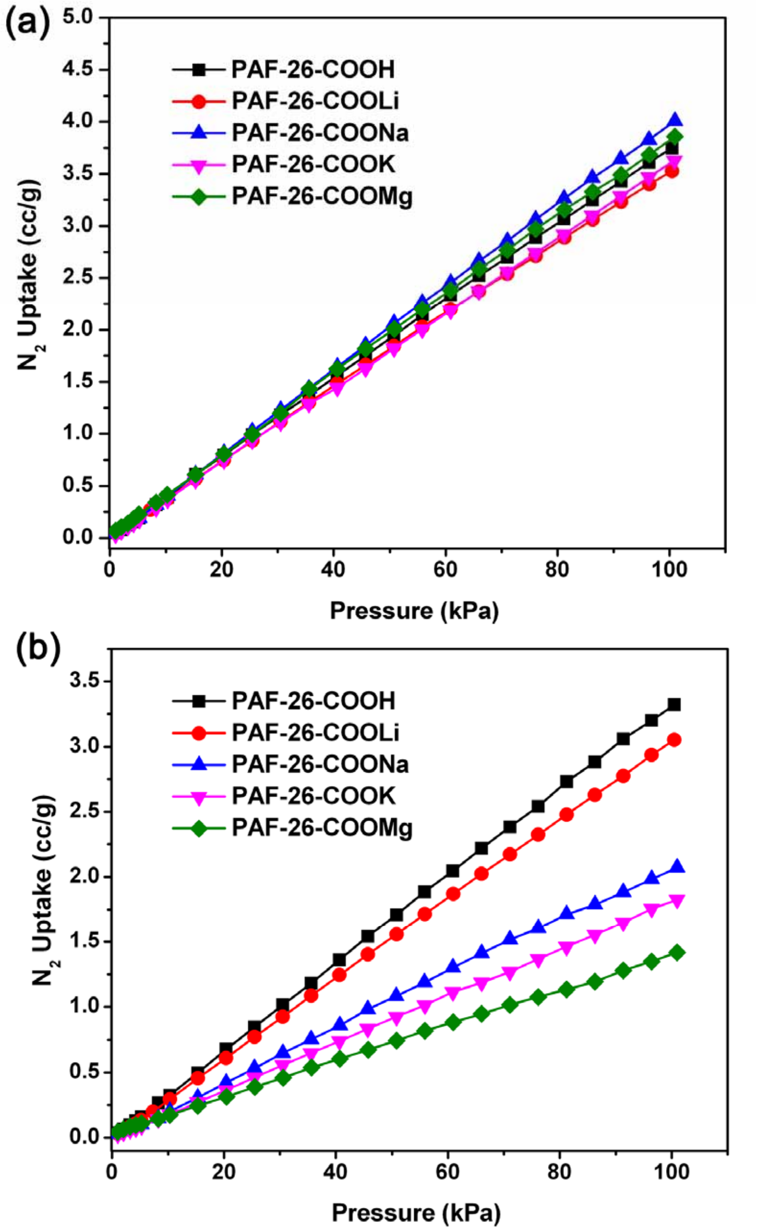

Fig. S7 N_2 adsorption isotherms for PAF-26-COOH and PAF-26-COOM at 273 K (a), and at 298 K (b).

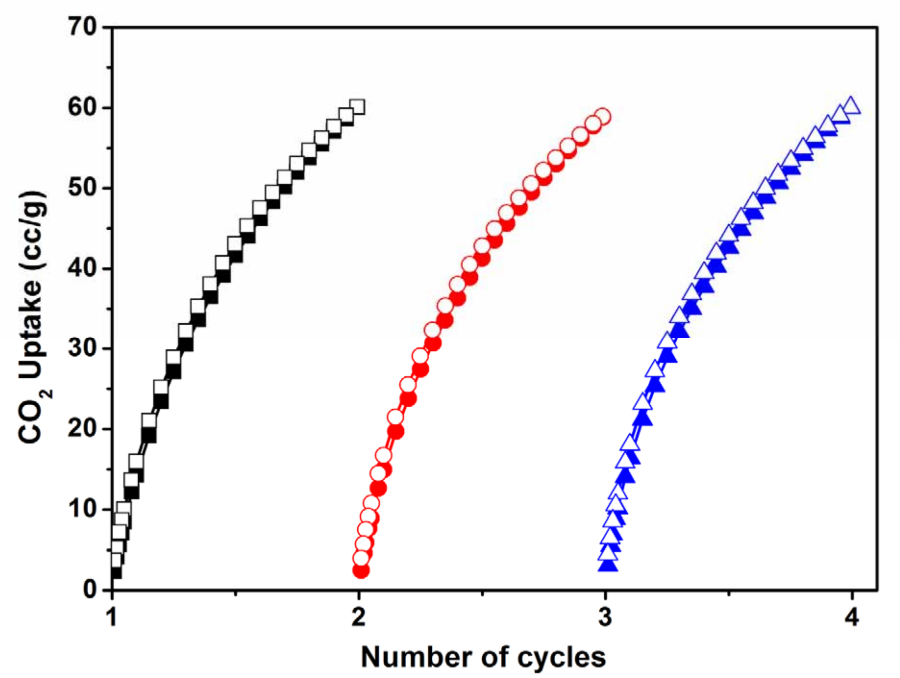

Fig. S8 Cyclic CO_2 adsorption–desorption of freshly prepared PAF-26-COOMg (black), after 2 months (red) and 4 months (bule) exposure in air. Before measurement, the sample was degassed at 80 ^{o}C for 5 h.

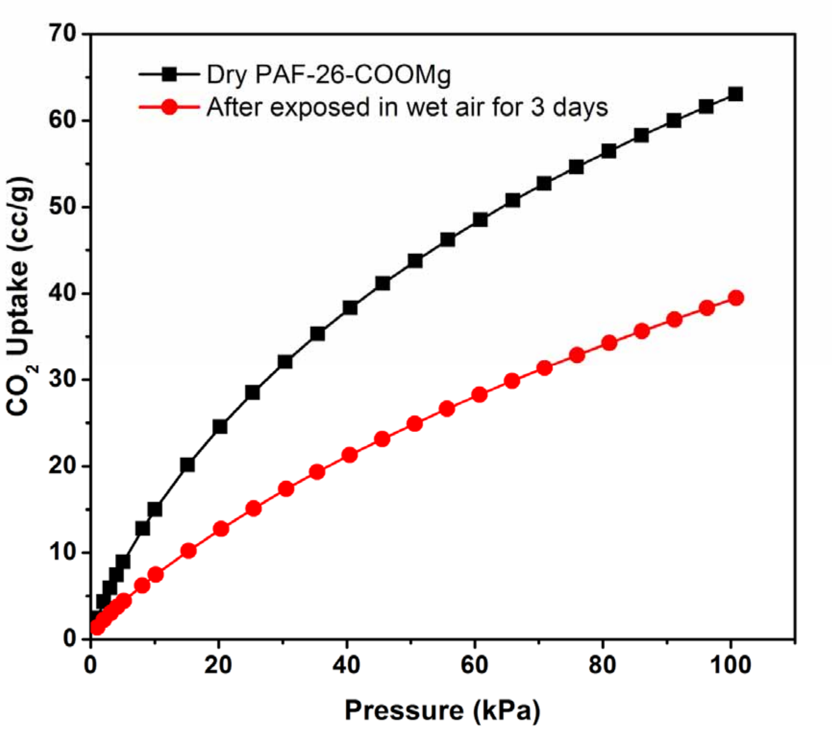

Fig S9. CO_2 adsorption isotherms of PAF-26-COOMg and CO_2 adsorption of PAF-26-COOMg obtained after 3 days exposure in wet air at 273 K.

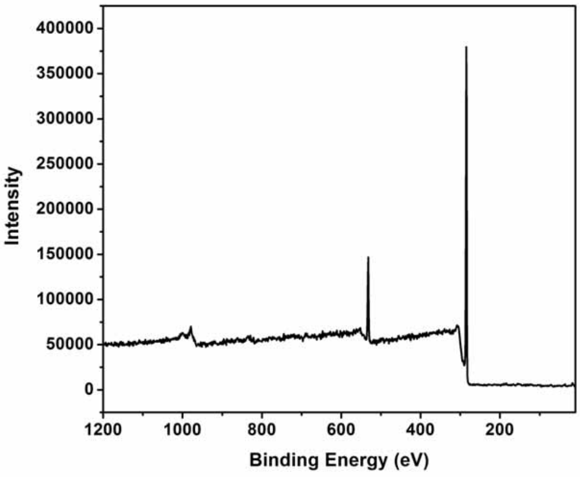

Fig S10. XPS spectra of PAF-26-COOH.

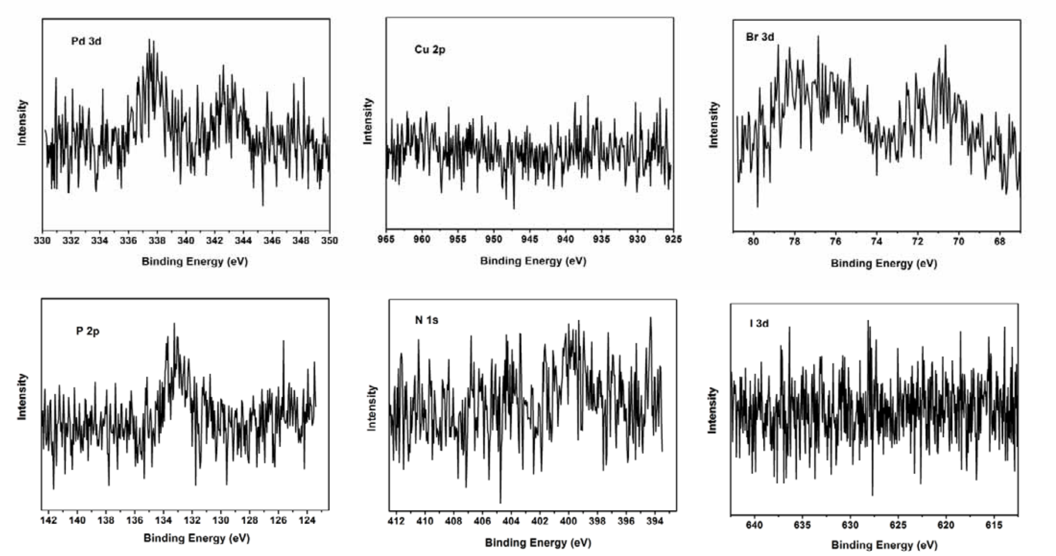

Fig. S11 Enlarged views of XPS spectra of Pd 3d, Cu 2p, Br 3d, P 2p, N 1s, and I 3d in the PAF-26-COOH sample.

Q_{st} Calculations

The Q_{st} of CO_2 and CH_4 was calculated as a function of the gas uptake based on the adsorption isotherms at 273 K and 298 K (the isotherms and fitting parameters are shown in Fig. S9-S13). The data was modelled with a virial-type expression composed of parameters a_i and b_i according to *equation* 1. The isosteric heats of adsorption were calculated by fitting the parameters according to *equation* 2. In these two equations, p is the pressure, N the amount adsorbed, T the temperature, and R the universal gas constant, m and n determine the number of terms required to adequately describe the isotherm, a_i and b_i are virial coefficients.

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

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

The basicity of metalized PAF-26 is estimated by the moles of ion contained in the material multiplied by the hydrolysis constants of the metal ion; thus, the pKb for PAF-26-COOLi: 2.46*13.8=33.948, PAF-26-COONa: 2.6*14.6=37.96, PAF-26-COOK: 2.4*15=36, PAF-26-COOMg: 1.3*11.6=15.08, respectively.[a]

[a] C. F. Baes, R. E. Mesmer, The Hydrolysis of Cations. A Wiley-Interscience publication, 1976.

Selectivity Calculations

The ideal adsorption solution theory (IAST) was used to predict the binary mixture adsorption of CO_2/N_2 and CH_4/N_2 from the experimental pure-gas isotherms. It has been reported that IAST can accurately predict gas mixture adsorption in many nanoporous materials, including porous-organic frameworks. The single-component isotherms were fitted using a dual-site Langmuir-Freundlich equation:

$$q = q_{m1} \cdot \frac{b_1 \cdot p^{1/n_1}}{1 + b_1 \cdot p^{1/n_1}} + q_{m2} \cdot \frac{b_2 \cdot p^{1/n_2}}{1 + b_2 \cdot p^{1/n_2}}$$

Here, p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol g^{-1}), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mmol g^{-1}), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (kPa^{-1}), and n_1 and n_2 represent the deviations from an ideal homogeneous surface.

The IAST adsorption selectivity, S, for binary mixtures of CO_2(1)/N_2(2) or CH_4(1)/N_2(2), is defined as

$$S = \frac{q_1 / q_2}{p_1 / p_2}$$

where q_i and p_i (i=1, 2) are the mole fractions of component 1 and 2 in the adsorbed and bulk phases, respectively.

Table S2. Comparison of Q_{st} for CO_2 and CH_4, and selectivities for CO_2 and CH_4 over N_2 at 298 K using PAF-26 materials in this work with other porous materials from open literatures.

Adsorbent	Q_{st} for CO_2 (kJ mol^{-1})	Selectivity for CO_2 over N_2	Q_{st} for CH_4 (kJ mol^{-1})	Selectivity for CH_4 over N_2	Reference
13 X zeolite				2.3–4.0	S1
Silicalite-1				1.8–3.0	S1
H-ZSM-5				3.0–3.6	S1
Activated carbon				4.0–5.5	S1
BILP-1- BILP-7	26.7-28.8	62-113	13-18.4	-	S2
CMP-1-(OH)2	28.5	-	-	-	S3
CMP-1-(CH_3)2	28.6	-	-	-	S3
CMP-1-COOH	35	-	-	-	S3
CMP-1-NH_2	27.8	-	-	-	S3
PPN-6-SO_3H	30.5	150	-	-	S4
PPN-6-SO_3Li	36	414	-	-	S4
UMCM-1	12		10	2[a]	S5,S6
ZIF-68		18.7	15.7	3.5[b]	S5,S6
ZIF-69		20	16.2	3[b]	S5,S6
IRMOF-1	17		9.98	2[c]	S5,S6

MIL-47(V)	25	10	14.7	5[c]	S5,S6
HKUST-1	35	32	18.4	3[c]	S5,S6
IR-MOF-11- 14	17-25	3-11	10-20	2-4[c]	S5,S6
Cu(Me-4py-trz-ia)	30		18.5	4.4[d]	S7
Basolite A100			19.8	4[d]	S7
PAF-26-COOH	28.1	20	14.3	4.2[e]	This work
PAF-26-COOLi	31.8	24	16.5	4.4[e]	This work
PAF-26-COONa	30.0	53	26.0	5.0[e]	This work
PAF-26-COOK	32.6	50	24.0	5.8[e]	This work
PAF-26-COOMg	35.0	73	21.5	6.0[e]	This work

Adsorption selectivities of CH_4 over N_2 [a] at 4 Mpa, [b] at 3 MPa, [c] at 2 MPa, [d] at 1 MPa, [e] at 0.1 MPa and at the temperature of 298 K.

References:

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