

Electronic Supplementary Information (ESI) for

Nitrogen-doped porous carbons derived from isomeric metal azolate frameworks

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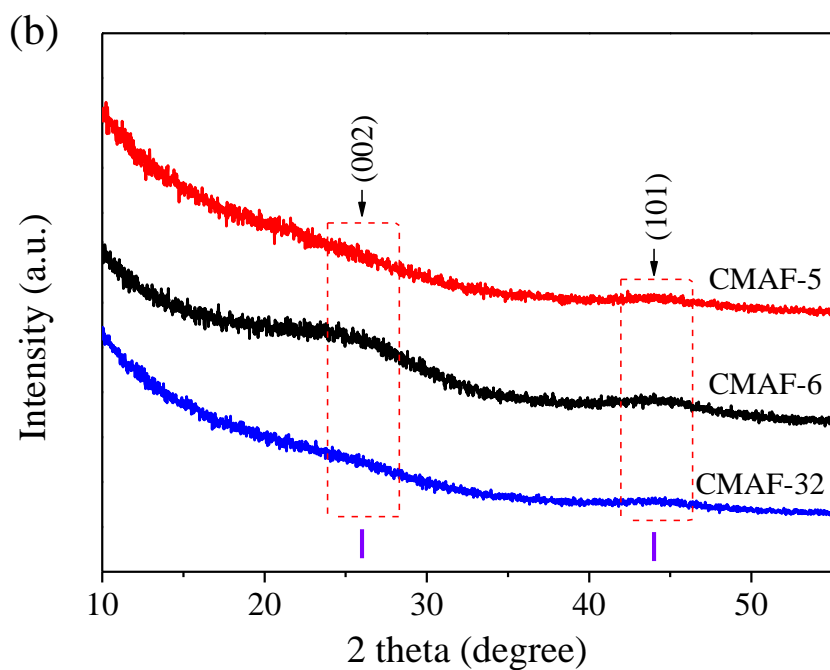
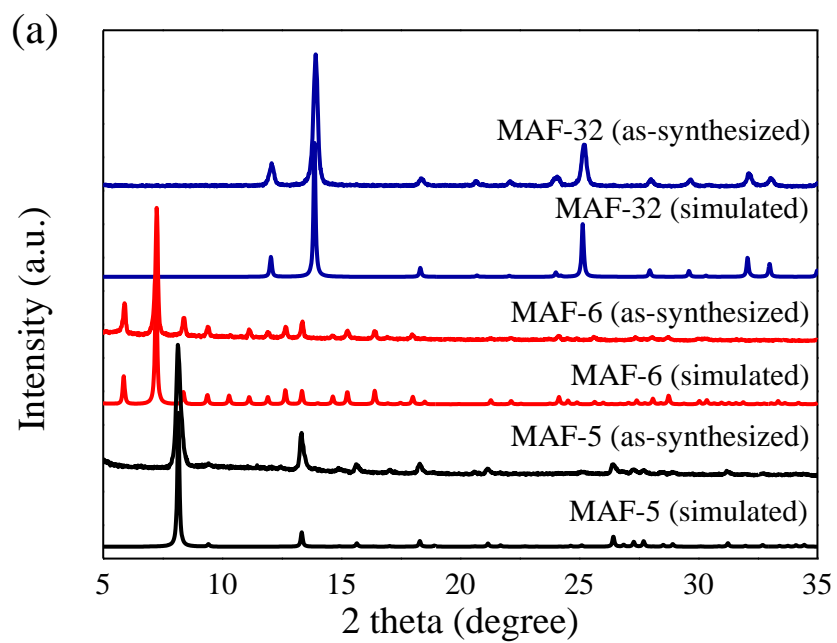


Fig. S1 (a) The experimental and simulated PXRD patterns of MAF-5, MAF-6 and MAF-32 and (b) PXRD patterns of CMAF-5, CMAF-6 and CMAF-32.

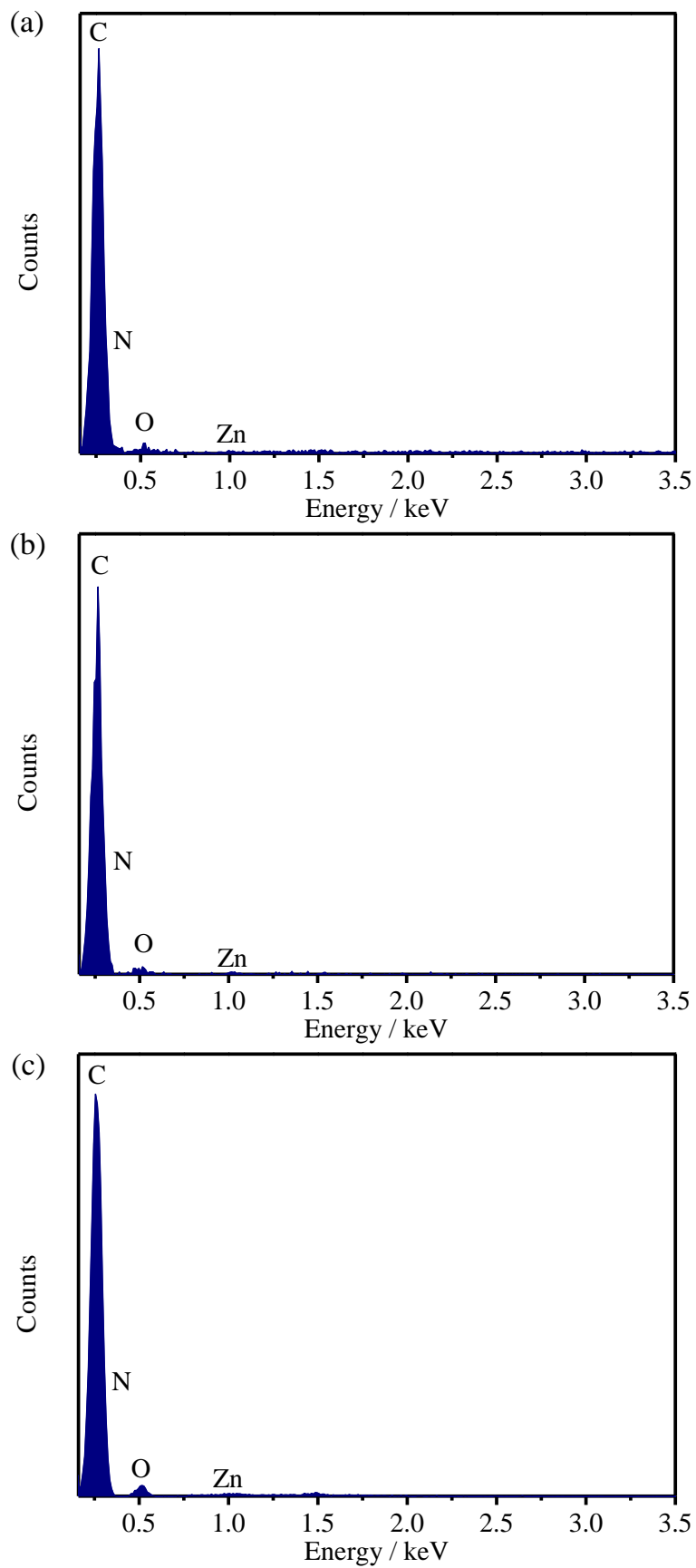


Fig. S2 EDS analyses of (a) CMAF-5, (b) CMAF-6, and (c) CMAF-32, respectively.

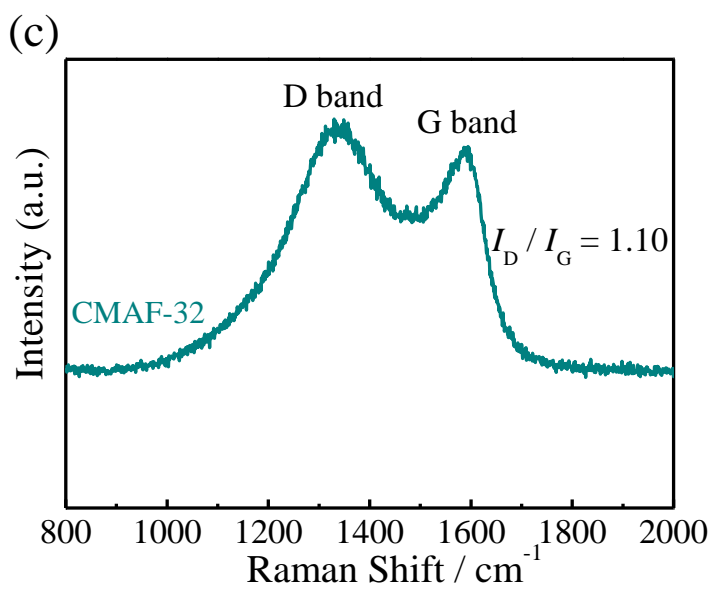
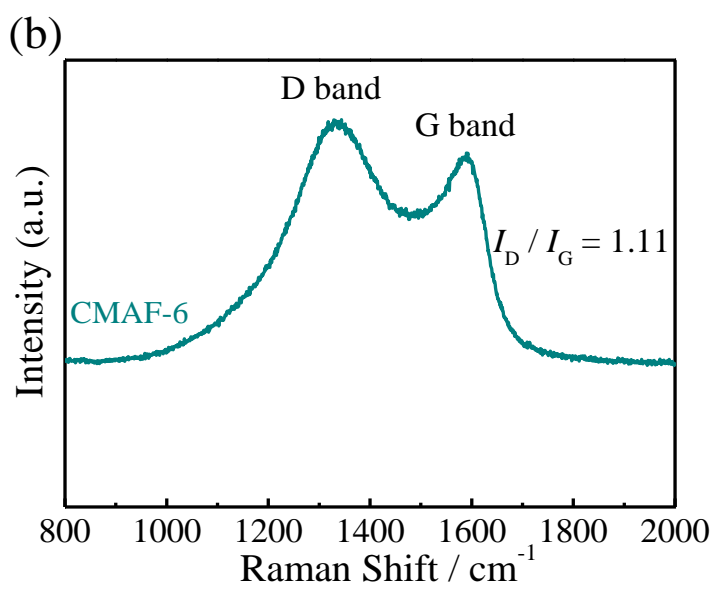
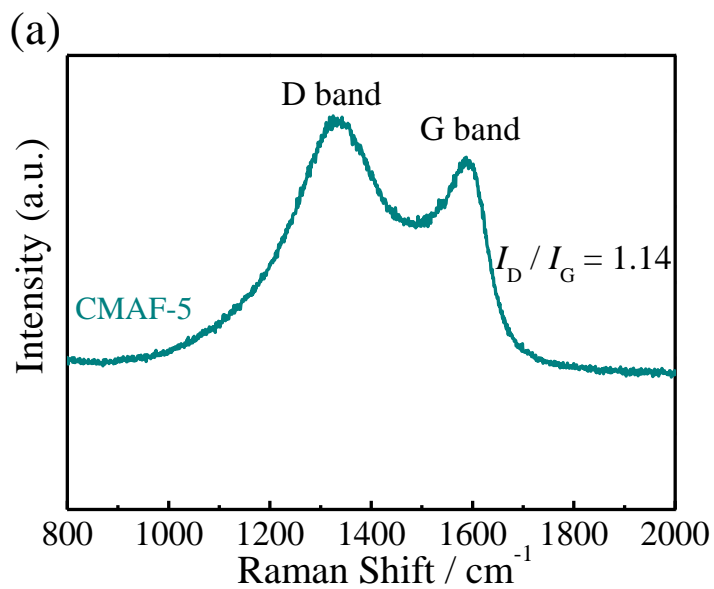


Fig. S3 Raman spectra of (a) CMAF-5, (b) CMAF-6 and (c) CMAF-32.

Table S1. Comparison of CO₂ adsorption performances of CMAF-5, CMAF-6 and CMAF-32 with other reported porous carbon materials derived from MOF or organic precursors.

	CO ₂ (mmol g ⁻¹)		N content (wt %)	ΔH (kJ mol ⁻¹)	$S_{\text{CO}_2/\text{N}_2}$ (IAST)	Ref.
	273 K, 1 bar	298 K, 1 bar				
CMAF-5 ^a	4.98	3.39	5.05	50.6	180	This work
CMAF-6 ^a	5.58	3.53	2.55	41.2	37	This work
CMAF-32 ^a	4.42	3.26	5.45	56.1	262	This work
AAC-2W	6.5	4.8	0	19.1	11	S1
NC800	5.7	3.8	14.8	26	/	S2
nZDC-700	5.12	3.51	/	~36.5	79	S3
NC900	5.1	3.9	2.7	~30	/	S4
M5-1000 ^a	5.00	3.13	0	28.1	22	S5
B100-1000 ^a	4.80	2.69	0	33.9	47	S5
M177-1000 ^a	4.75	3.30	0	27.6	20	S5
KBM-700	4.75	3.29	10.16	43	99.1	S6
IRMOF-3-800 ^a	3.99	2.78	7.76	29.6	39	S7
N-CNS	/	8.7	12.6	45.51	163	S8
SNS2-20-700	6.84	4.48	3.83	43.0	69	S9
MCN/C-600	3.05	2.35	24.9	26.2	40	S10
SU-MAC-500	6.03	4.5	5.8	46.0	39	S11
H-NMC-2.5-600	/	2.8	13.10	/	35	S12
NPC-2-600	6.35	4.02	5.25	33.5	32	S13
HCM-DAH-1-800	3.3	2.6	4.1	35.9	30	S14

^a Synthesized by direct carbonization of MOF precursors.

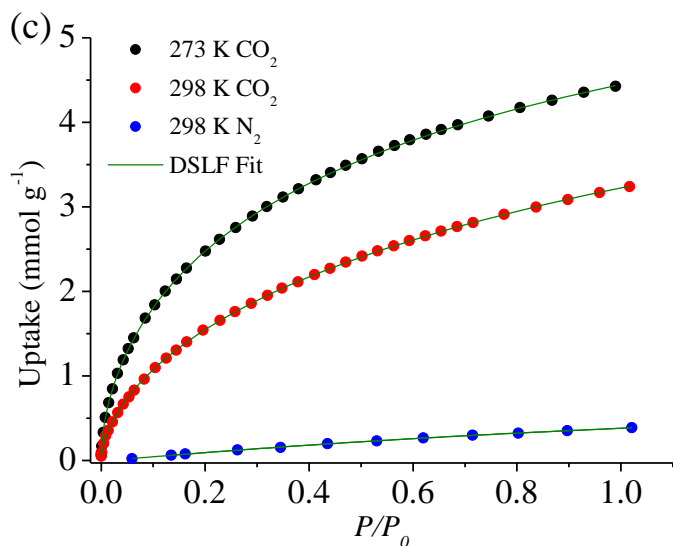
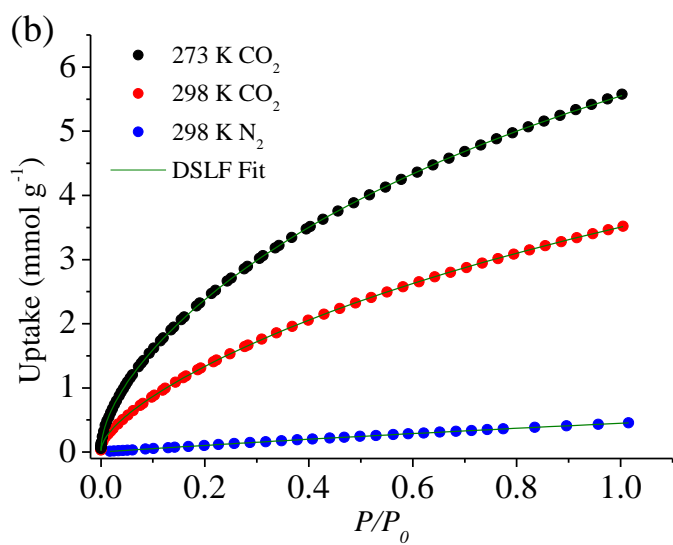
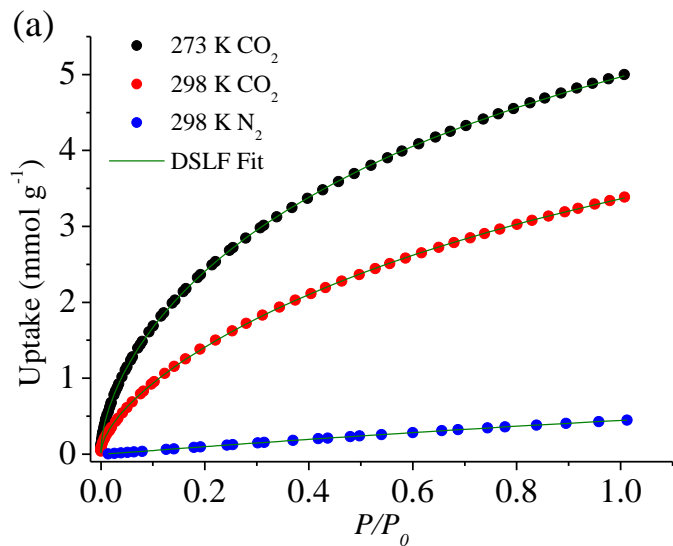


Fig. S4 CO₂ and N₂ isotherms (symbols) and DSLF fittings (lines) for (a) CMAF-5, (b) CMAF-6 and (c) CMAF-32 at 298 K.

Table S2. DSLF fitting parameters for the CO₂ adsorption isotherms.

	CMAF-5		CMAF-6		CMAF-32	
	273 K	298 K	273 K	298 K	273 K	298 K
$n_{L,A}$	8.1606	5.5301	9.9058	6.3533	7.3130	7.0891
b_A	0.8918	0.4830	0.6444	0.2594	1.1780	0.6437
t_A	1.3056	1.8828	1.1302	2.2027	1.5240	1.5530
$n_{L,b}$	3.0546	3.4638	3.7806	6.4685	1.2879	5.6859
b_B	0.5814	0.8207	0.7882	0.5138	0.6181	0.0858
t_B	2.5658	0.9681	2.2262	1.0302	3.1959	2.2513

Table S3. DSLF fitting parameters for the N₂ adsorption isotherms.

	CMAF-5	CMAF-6	CMAF-32
$n_{L,A}$	0.6272	2.5059	0.2288
b_A	1.1955	0.2007	0.0513
t_A	0.8523	1.0272	0.2373
$n_{L,b}$	0.2567	1.3024	0.7892
b_B	0.6566	0.0235	0.8794
t_B	0.3534	0.7588	0.8466

Methods for breakthrough measurement and calculation

A stainless-steel column with a length of 10 cm and an internal diameter of 0.46 cm was packed with microcrystalline sample.^{S15} The column contained 0.600 g of CMAF-32. The column was connected to the injection and sampling ports by stainless-steel pipes. The column and most parts of the pipelines between the injection and sampling ports were placed in a temperature controlling oven. The flow rates of pure gases were regulated by mass flow controllers. Before breakthrough experiments, the columns were activated by passing He and heated at 393 K for 5 hours, and then cooled to the measurement temperature of 298(2) K. Pure N₂ (0.85 mL(STP) min⁻¹) and CO₂ (0.15 mL(STP) min⁻¹) were mixed. The gas stream at the outlet of the column was analyzed on line by using a chromatographic analyzer (Agilent 7890A) with a TCD detector and a PLOT/Q column.

The amount of gas k (such as N₂ or CO₂ in N₂/CO₂ mixture, or pure He) retained by the breakthrough system can be calculated by:

$$q_k(\tau) = R_k \times \left(\tau - \int_0^\tau f_k(\tau) d\tau \right)$$

where the breakthrough curve for gas k is expressed by the function $f_k(\tau)$ and R_k is the mole fraction of gas k at the inlet.

When τ is large enough ($\tau \geq \tau_E$), we can observe $f_k(\tau) = R_k$ and $df_k(\tau)/d\tau = 0$, meaning that the breakthrough system reaches the equilibrium, and $q_k(\tau_E)$ is the equilibrium uptake of gas k in the column.

After reaching equilibrium, the amount of gas k adsorbed by the adsorbent in the column can be calculated by:

$$Q_K(\tau_E) = q_k(\tau_E) - R_k \times q_{He}(\tau_E)$$

where the $q_{He}(\tau_E)$ is the retention of He in the column and pipeline.

The selectivity is defined as $\alpha = (Q_1/y_1)/(Q_2/y_2)$, where Q_i is the adsorbed amount of compound i and y_i is the mole fraction of compound i in the gas phases.

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