

Supporting Information

Controlling the free volume of type III porous liquids by tailoring solvent for enhanced CO₂ capture

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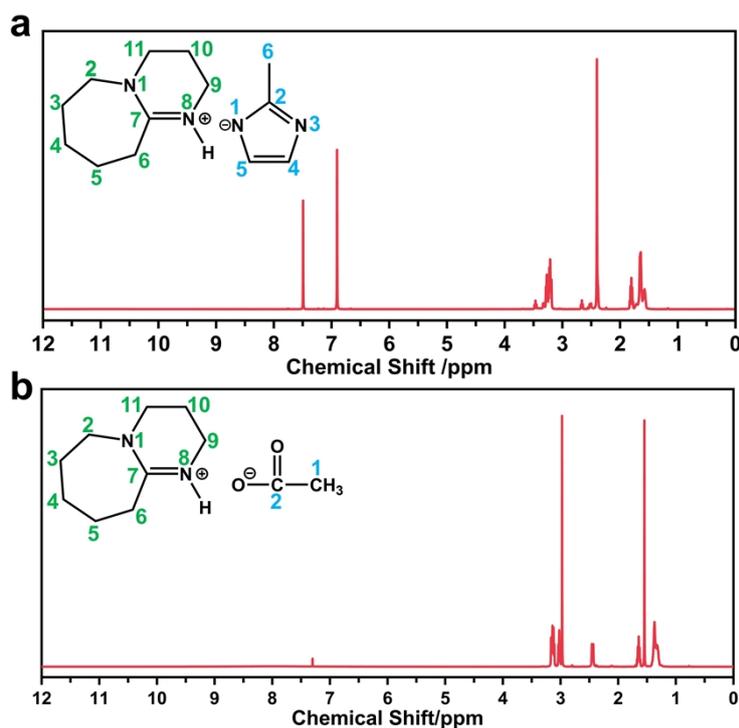
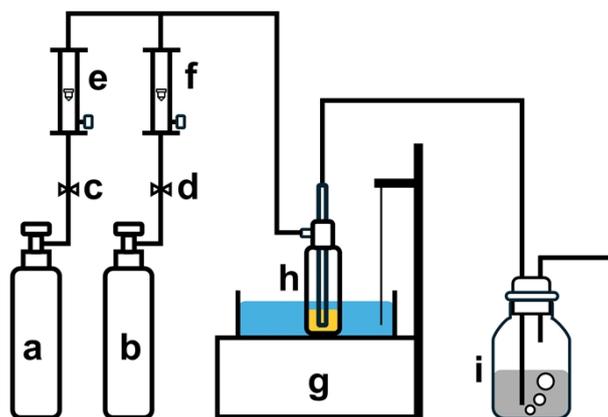


Fig. S1 ¹H NMR spectrum of (a) [DBUH][2-MeIm] and (b) [DBUH][AC].



Scheme S1 Apparatus diagram of the CO₂ absorption performance. ((a) CO₂ gas cylinder, (b) N₂ gas cylinder, (c) and (d) valve, (e) and (f) flowmeter, (g) water bath heating device, (h) absorption bottle, (i) waste gas absorber)

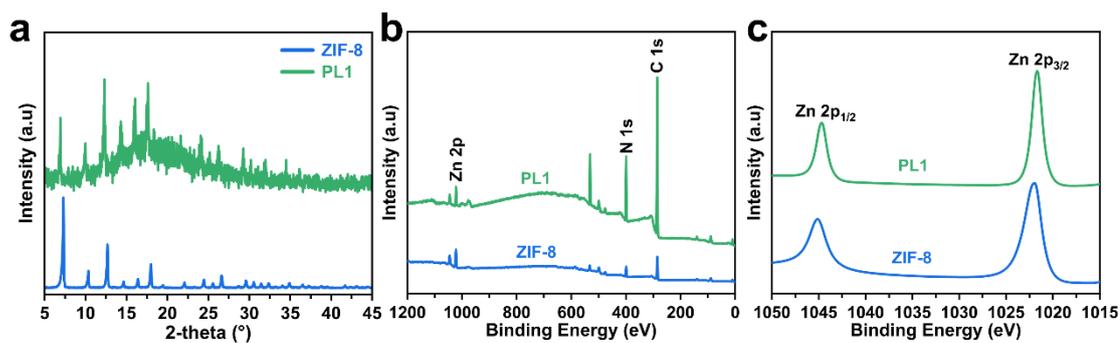


Fig. S2 (a) XRD spectrum of ZIF-8 and PL1, (b) the wide scan spectra of XPS of ZIF-8 and PL1, (c) high resolution Zn 2p spectrum of ZIF-8 and PL1.

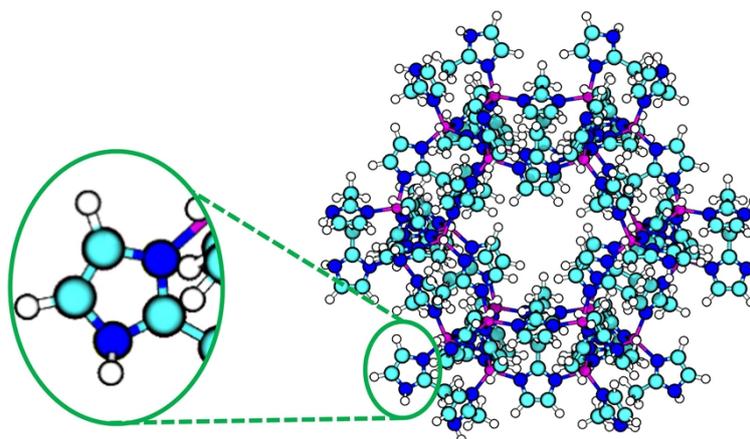
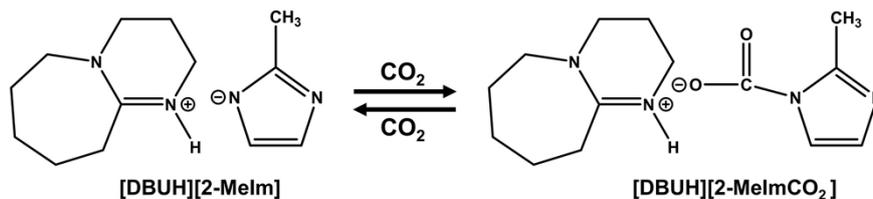


Fig. S3 Molecular Structure and local magnification diagram of ZIF-8



Scheme S2 the CO₂ absorption mechanism of [DBUH][2-MeIm]

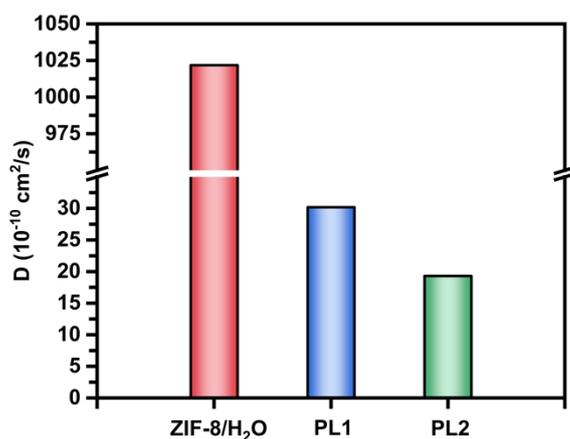


Fig. S4 The diffusion coefficient of the solvent in three systems.

Table S1 The simulation details of the free volume of PL1 and PL2.

System	Total Volume (×10 nm ³)	Free Volume (×10 nm ³)	Free Volume ratio (Free/Total ×100%)
600PL1	26.5091	10.1026	38.11
800PL1	33.9292	12.8558	37.89
1000PL1	41.6437	15.4829	37.18
600PL2	23.9865	8.7755	36.59
800PL2	30.5993	11.1391	36.40
1000PL2	37.0286	13.3138	35.96

Table S2 The simulation details of PL1 with different concentration of ZIF-8.

System	Number of ZIF-8	Number of [DBUH][2-MeIm]	Size of simulation box (nm ³)
System 1	1	1000	5.7×5.7×11.4
System 2	3	1000	5.8×5.8×11.6
System 3	5	1000	5.9×5.9×11.8
System 4	7	1000	6.2×6.2×12.3
System 5	9	1000	6.6×6.6×13.2

Table S3 The simulation details of the free volume of PL1 with different ZIF-8 concentration.

System	Total Volume ($\times 10 \text{ nm}^3$)	Free Volume ($\times 10 \text{ nm}^3$)	Free Volume ratio (Free/Total $\times 100\%$)
System 1	38.2151	13.6848	35.81
System 2	39.7245	14.5383	36.60
System 3	41.6437	15.4829	37.18
System 4	47.5257	20.3903	42.90
System 5	49.5782	21.4598	43.28

Table S4 The simulation details of the CO₂ absorption of PL1 with different ZIF-8 concentration.

System	Number of ZIF-8	Number of [DBUH][2-MeIm]	Number of CO ₂	Size of simulation box (nm ³)
System1(200)	1	1000	200	$5.7 \times 15.5 \times 11.4$
System2(200)	3	1000	200	$5.8 \times 15.5 \times 11.4$
System3(200)	5	1000	200	$5.9 \times 15.6 \times 11.6$
System4(200)	7	1000	200	$6.1 \times 15.8 \times 12.1$
System5(200)	9	1000	200	$6.2 \times 12.1 \times 12.4$

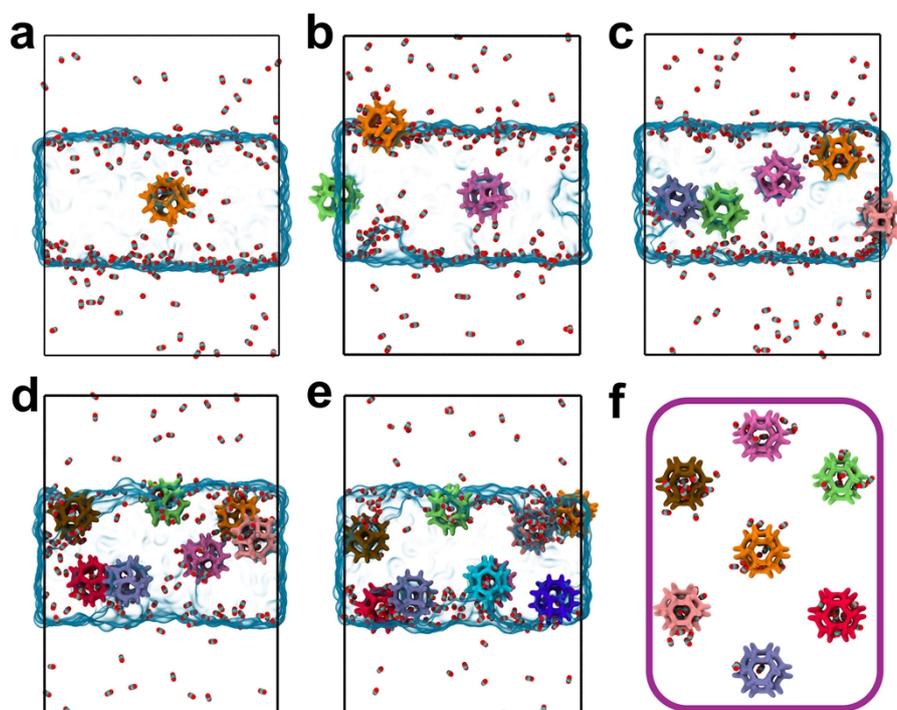


Fig. S5 (a-e) the CO₂ absorption equilibrium configuration of PL1 with five different ZIF-8 concentrations; (f) the CO₂ absorption equilibrium configuration of ZIF-8 in System 4(200).

The conversion formula for the dynamic CO₂ absorption number and the dynamic CO₂ adsorption capacity.

$$\text{Adsorption capacity (mg/g)} = \frac{N_{\text{Adsorped}}}{N_A} \times \frac{1000}{m_{PL}} \times M_{CO_2}$$

Here, N_{Adsorped} represents the amount of CO₂ absorbed by PL, N_A represents Avogadro's constant, m_{PL} represents the mass of PL in System 4, and M_{CO_2} represents the relative molecular mass of CO₂.