

Supporting Information

Covalent-organic polymers for carbon dioxide capture

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Prediction of adsorption of binary mixture by IAST theory

In order to perform the IAST calculations, the single-component isotherms should be fitted by a proper model. The dual-site Langmuir-Freundlich (DSLFF) adsorption model¹ is adopted to correlate the pure-component equilibrium data and further predict the adsorption of mixtures. The DSLFF model is given by

$$N^{\circ}(f) = \frac{N_1 k_1 f^{n_1}}{1 + k_1 f^{n_1}} + \frac{N_2 k_2 f^{n_2}}{1 + k_2 f^{n_2}} \quad (\text{S1})$$

where f is the fugacity of bulk gas at equilibrium with adsorbed phase, N_i , k_i and n_i are model parameters of maximum adsorption amount at site i ($i=1$ or 2), the affinity constant, and the deviation from the simple Langmuir equation, respectively.

Based on the above model parameters of pure gas adsorption, we used the IAST model,² which was proposed by Myer and Prausnitz in 1965 to predict the multi-component adsorption. Analogous to Raoult's law for vapour-liquid equilibrium, the IAST assumes that the adsorbed solutions are ideal and all activity coefficients in the adsorbed phase are unity. Thus, the adsorption equilibrium between adsorbed and gas phases will lead to the following equation

$$P y_i \phi_i = x_i f_i^{\circ}(\pi) \quad (\text{S2})$$

where f_i° is the fugacity of the equilibrium gas phase corresponding to the spreading pressure π for the adsorption of pure gas i , ϕ_i is the gas fugacity coefficient of component i calculated by PR equation of state (EOS), and x_i and y_i are the molar fraction of component i at the adsorbed and bulk phases, respectively.

The binary gas mixing process is carried out at constant spreading pressure π and

indicated by

$$\int_0^{f_1^\circ} N_1^\circ(f_1) d \ln f_1 = \int_0^{f_2^\circ} N_2^\circ(f_2) d \ln f_2 \quad (\text{S3})$$

where the single-component adsorption amounts and selectivity are further obtained from the above equation by numerical integration and root exploration.

To investigate the separation of CO₂-CH₄, binary mixtures, the adsorption selectivity is defined by

$$S_{i/j} = \frac{x_i / x_j}{y_i / y_j} \quad (\text{S4})$$

where the selectivity refers to the first component over the second one, and the x_i , x_j and y_i , y_j denote the molar fractions of species i , j in the adsorbed and bulk phases, respectively.

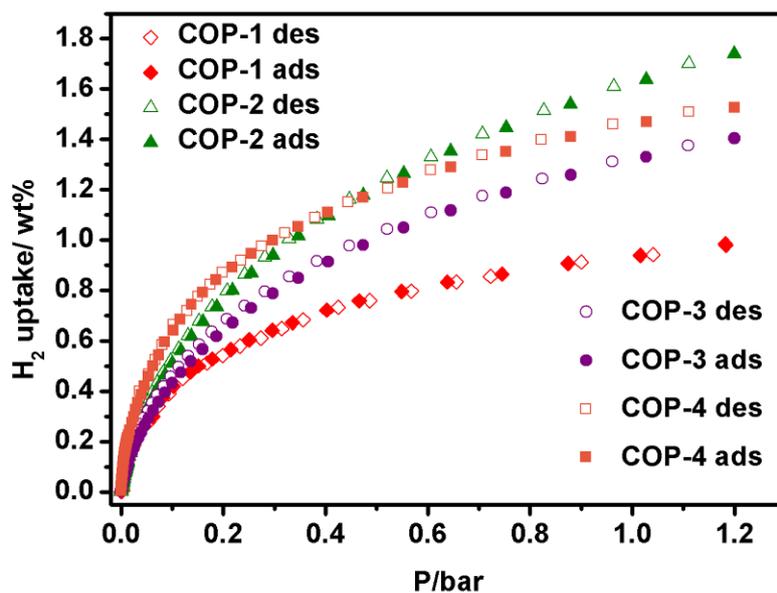


Fig. S1 H₂ uptake in COP-1 (red), COP-2 (olive), COP-3 (violet) and COP-4 (orange) at 77 K. Solid and open symbols represent adsorption and desorption amounts, respectively.

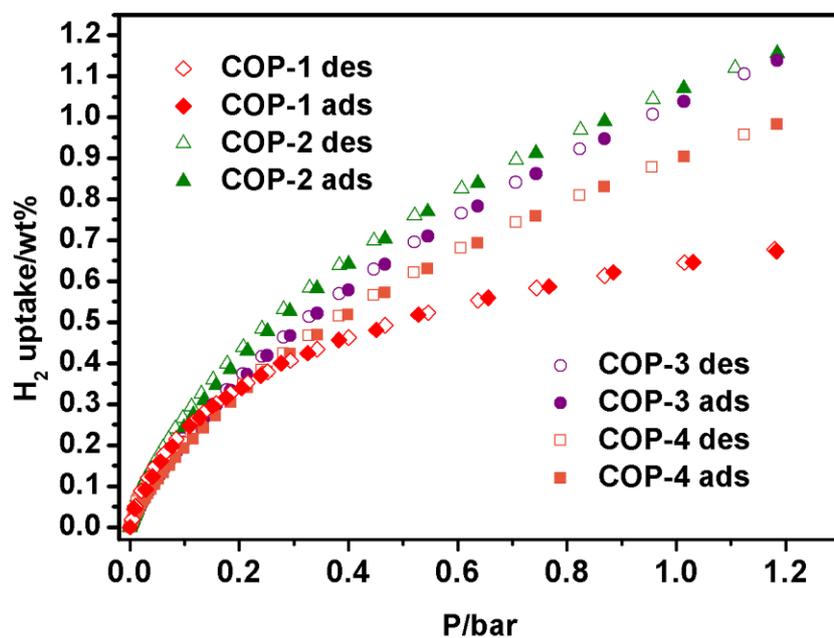


Fig. S2 H₂ uptake in COP-1 (red), COP-2 (olive), COP-3 (violet) and COP-4 (orange) at 87 K. Solid and open symbols represent adsorption and desorption amounts, respectively.

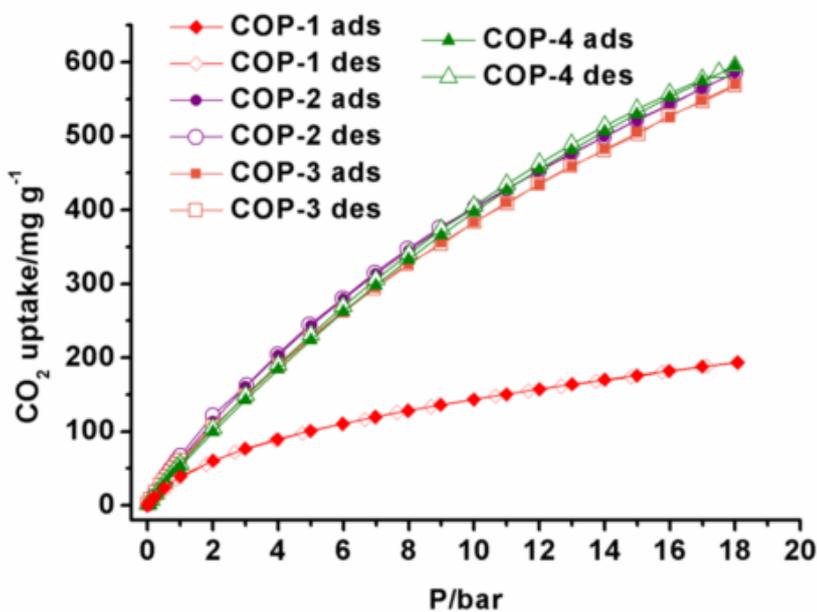


Fig. S3 CO₂ uptake in COP-1 (red), COP-2 (violet), COP-3 (orange) and COP-4 (olive) at 298 K and $P < 18$ bar. Solid and open symbols represent adsorption and desorption amounts, respectively.

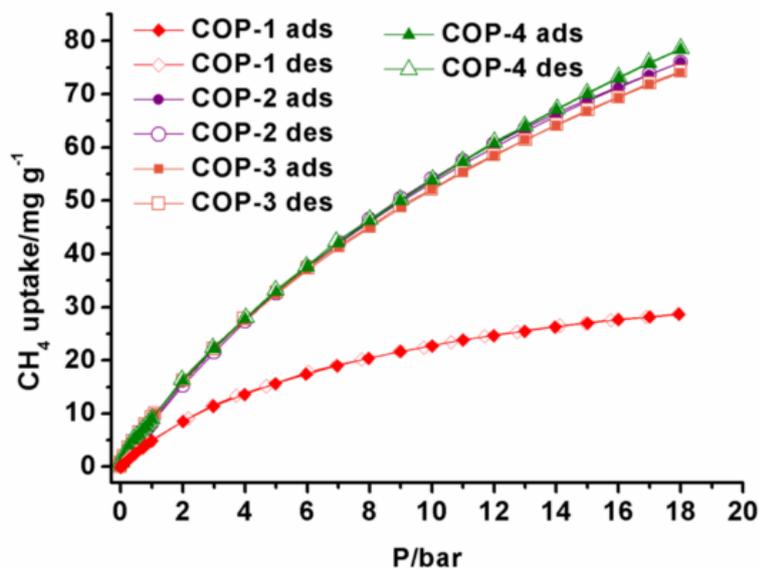


Fig. S4 CH₄ uptake in COP-1 (red), COP-2 (violet), COP-3 (orange) and COP-4 (olive) at 298 K and $P < 18$ bar. Solid and open symbols represent adsorption and desorption amounts, respectively.

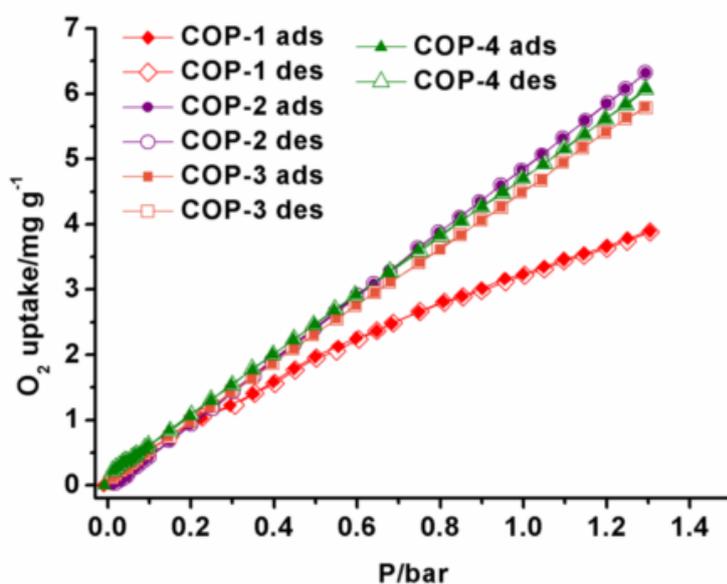


Fig. S5 O₂ uptake in COP-1 (red), COP-2 (violet), COP-3 (orange) and COP-4 (olive) at 298 K and $P < 1.3$ bar. Solid and open symbols represent adsorption and desorption amounts, respectively.

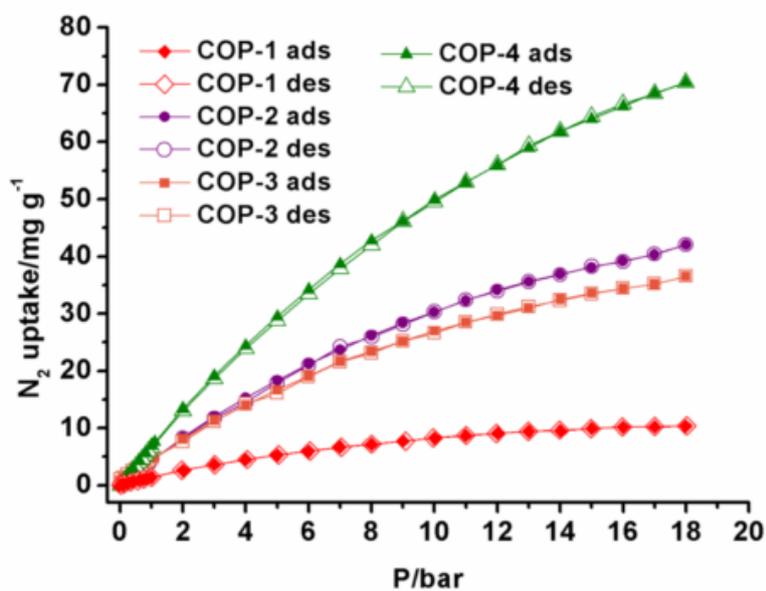


Fig. S6 N₂ uptake in COP-1 (red), COP-2 (violet), COP-3 (orange) and COP-4 (olive) at 298 K and $p < 18$ bar. Solid and open symbols represent adsorption and desorption amounts, respectively.

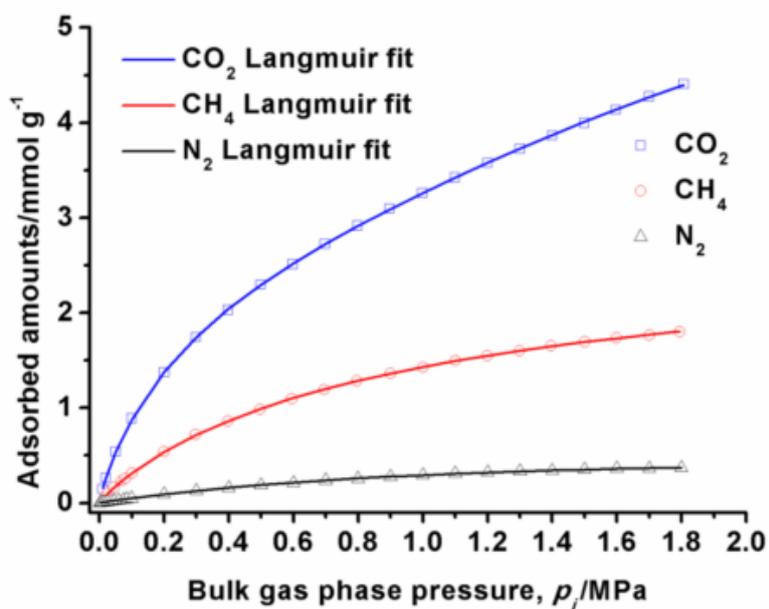


Fig.S7 CO₂, CH₄ and N₂ adsorption fit of COP-1 using dual-site Langmuir Freundlich (DSLFF) equation.

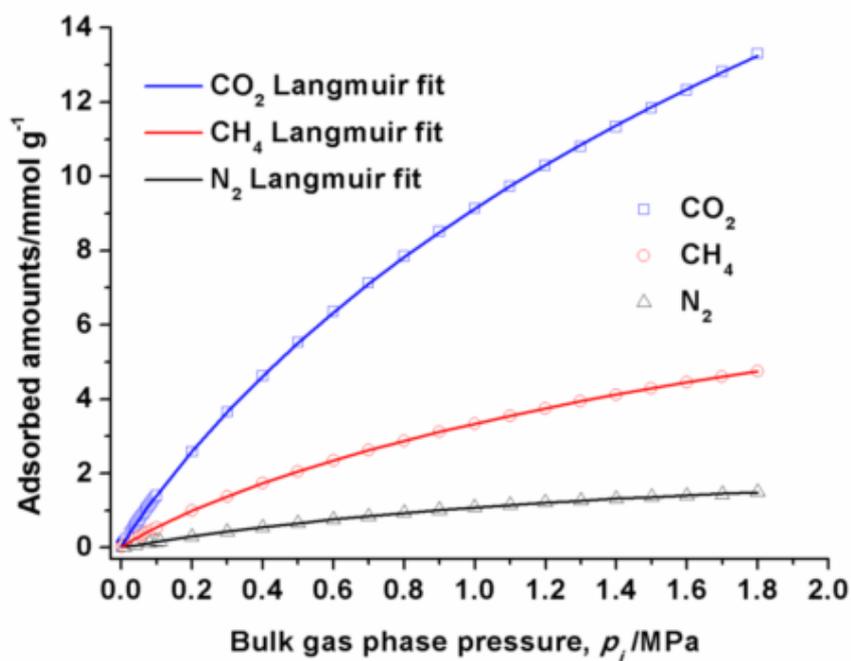


Fig.S8 CO₂, CH₄ and N₂ adsorption fit of COP-2 using dual-site Langmuir Freundlich (DSLFF) equation.

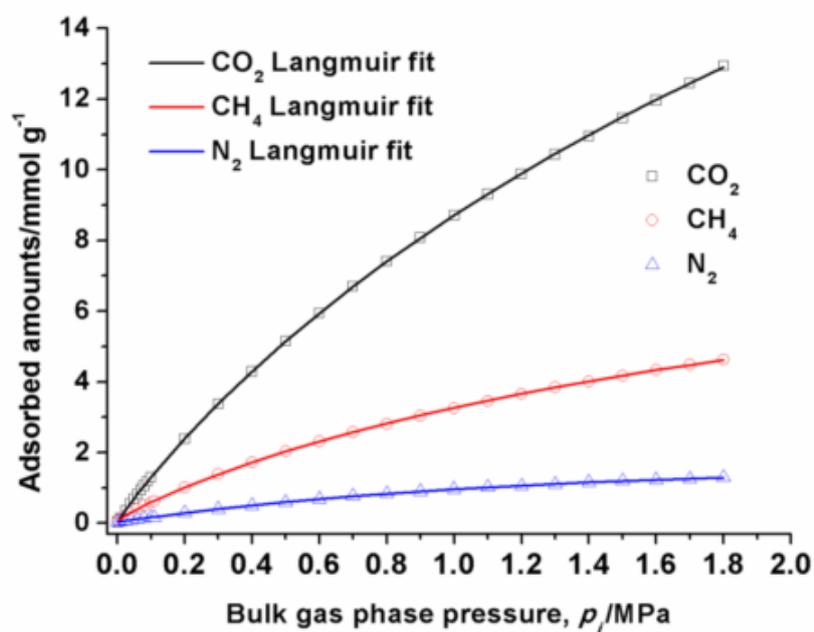


Fig.S9 CO₂, CH₄ and N₂ adsorption fit of COP-3 using dual-site Langmuir Freundlich (DSLFF) equation.

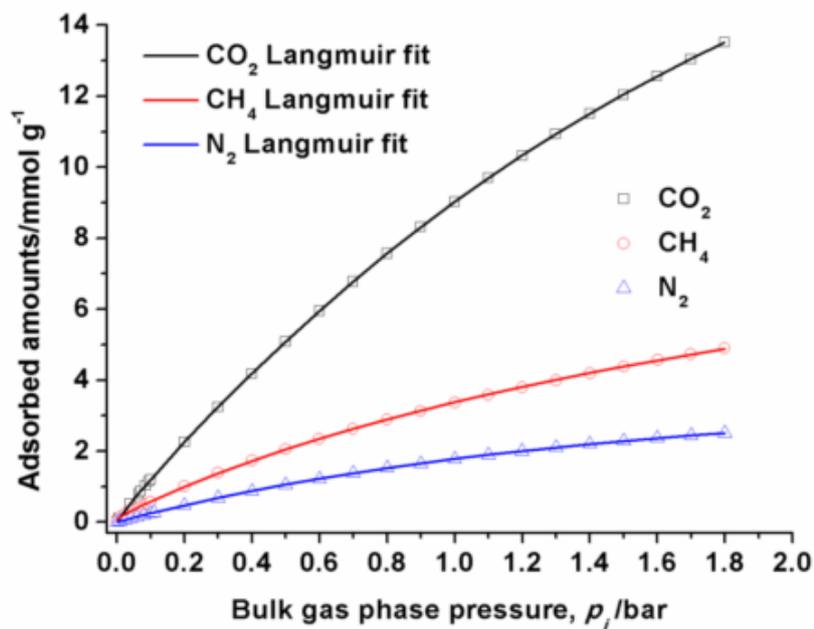


Fig.S10 CO₂, CH₄ and N₂ adsorption fit of COP-4 using dual-site Langmuir Freundlich (DSLFF) equation.

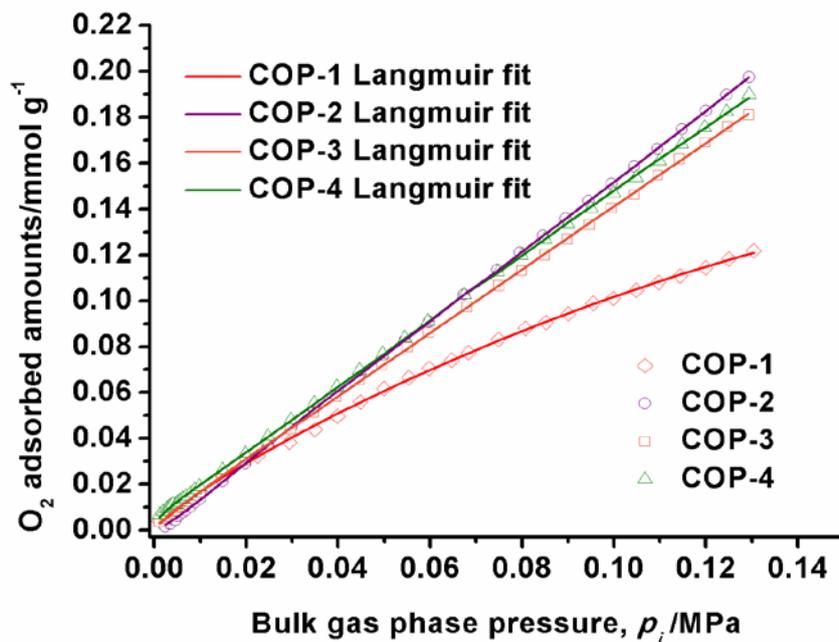


Fig.S11 O₂ adsorption fit of COP-1, 2, 3, and 4 using dual-site Langmuir Freundlich (DSLFL) equation.

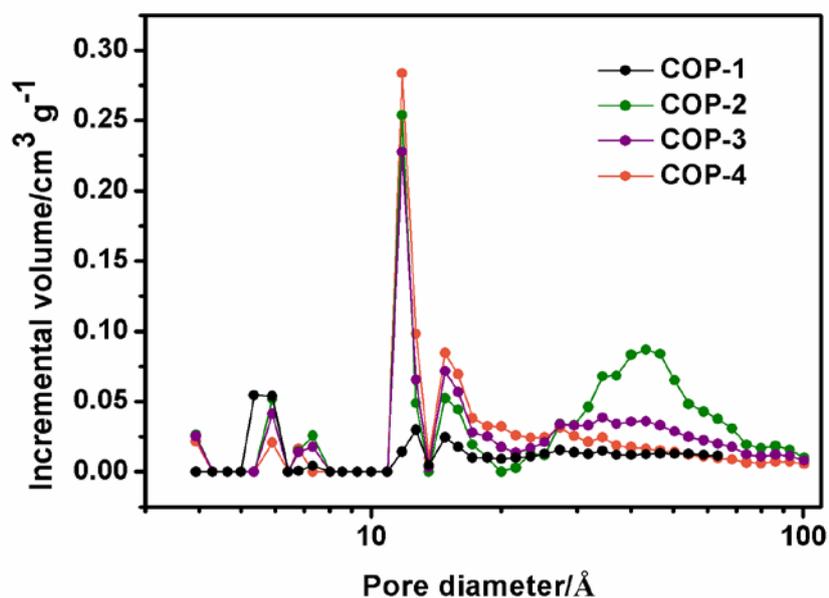


Fig. S12 Nonlocal density functional theory (NLDFT) pore size distributions of products by incremental pore volume. COP-1 (black), COP-2 (olive), COP-3 (violet) and COP-4 (orange). The data of COP-1 are taken from the Ref.³ and the data of COP-2,3 and 4 are taken from the Ref.⁴

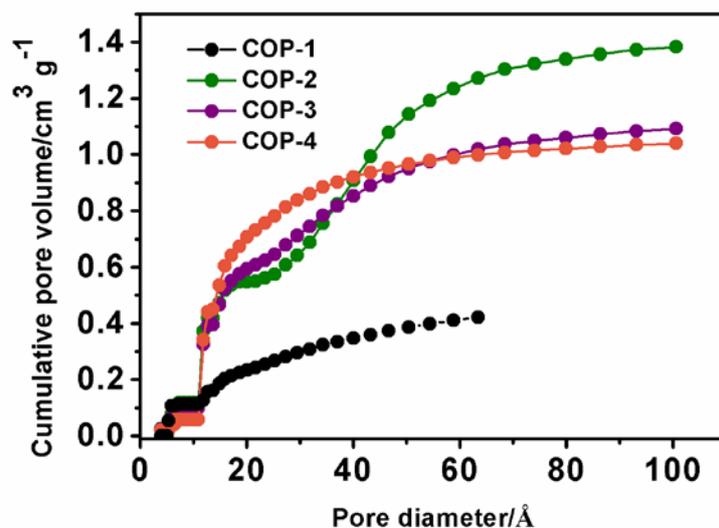


Fig. S13 Nonlocal density functional theory (NLDFT) pore size distributions of products by cumulative pore volume. COP-1 (black), COP-2 (olive), COP-3 (violet) and COP-4 (orange). The data of COP-1 are taken from the Ref.³ and the data of COP-2,3 and 4 are taken from the Ref.⁴

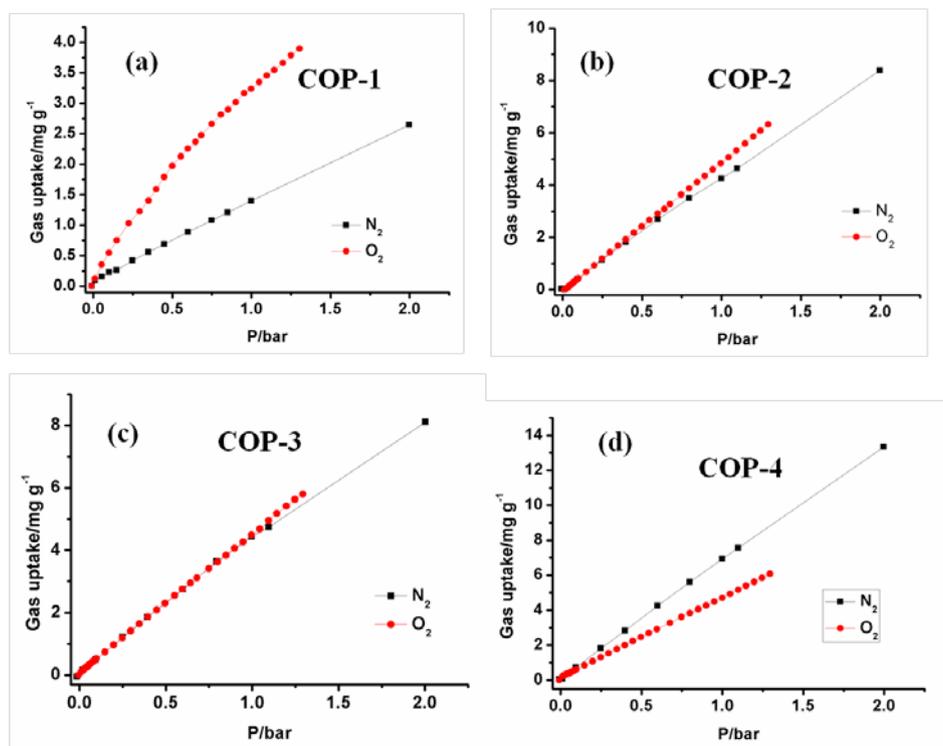


Fig. S14 The comparison of N₂ and O₂ adsorption in (a) COP-1, (b) COP-2, (c) COP-3 and (d) COP-4 at 298 K.

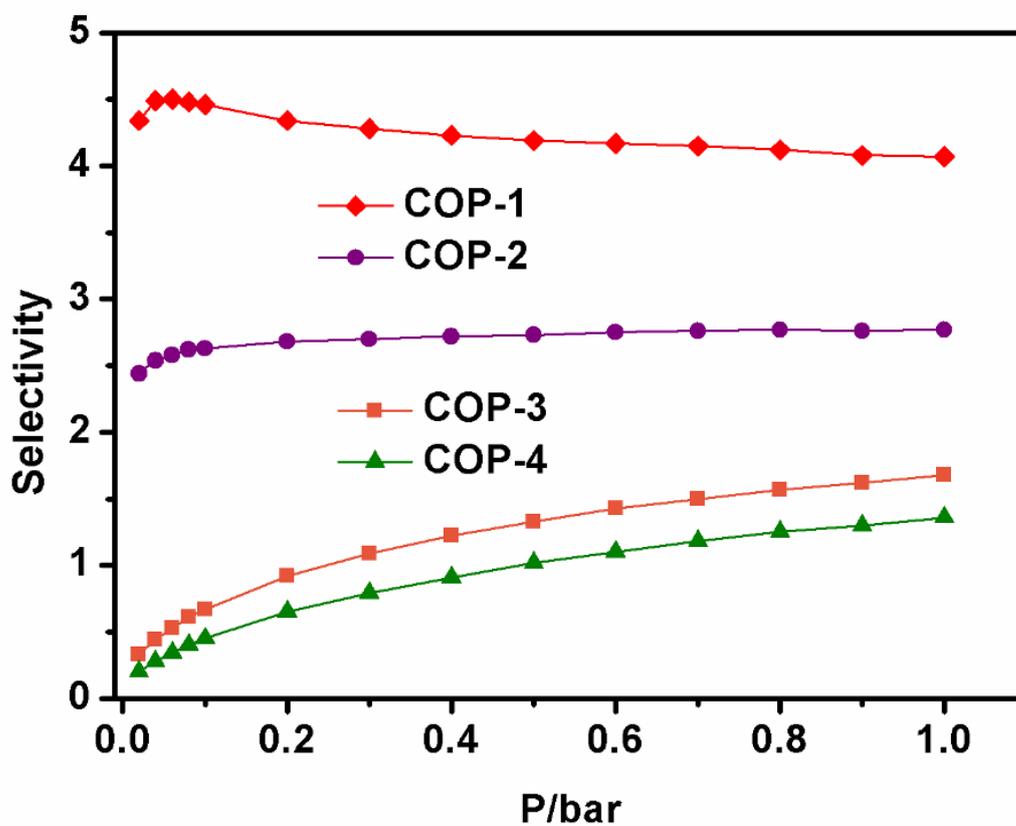


Fig. S15 IAST-predicted adsorption selectivity of CO₂/CH₄ in COP-1 (red rhombus), COP-2 (violet circle), COP-3 (orange square) and COP-4 (olive triangle) using 15/85 CO₂/CH₄ ratio at $T=298\text{K}$ and $p<1\text{bar}$.

Table S1. Parameters of Dual-site Langmuir-Freundlich equation by fitting adsorption isotherms of pure CO₂, CH₄, N₂ and O₂

adsorbent	adsorbate	N_1	k_1	n_1	N_2	k_2	n_2
COP-1	CH ₄	2.3169	1.3911	0.9463	0.2653	0.5918	2.3578
	CO ₂	27.4318	0.0606	0.8745	2.2098	3.3090	0.8858
	N ₂	0.4339	1.2567	1.2416	0.1450	0.5725	0.5480
	O ₂	0.3353	0.7334	1.8205	0.5832	1.4593	0.8571
COP-2	CH ₄	10.4182	0.4648	0.9275	0.8929	0.1052	1.9682
	CO ₂	37.3626	0.3397	0.9358	1.0307	0.0306	4.5115
	N ₂	1.7035	0.6730	1.3933	0.5744	2.3318	0.9899
	O ₂	1.1794	3.0280	1.5280	0.0738	52.2871	1.2575
COP-3	CH ₄	10.9769	0.3937	0.9569	0.4068	1.1052	0.3408
	CO ₂	47.6486	0.2348	0.9197	0.2974	0.0842	3.6664
	N ₂	1.4877	0.0472	0.1303	2.0491	0.7769	1.1197
	O ₂	1.3443	1.3514	1.2968	0.4065	0.8022	0.7048
COP-4	CH ₄	12.0175	0.3589	0.9950	0.6394	0.6692	0.2917
	CO ₂	48.2221	0.2281	0.9492	0.8139	1.4737	3.0723
	N ₂	3.0073	0.8470	0.9971	1.2578	0.4778	1.6996
	O ₂	1.0428	2.2352	1.2124	0.0534	2.0017	0.4383

References

1. Ruthven, D. M., Principles of adsorption and adsorption processes; Wiley: New York, 1984.
2. Myers, A. L.; Prausnitz, J. M., Thermodynamics of mixed-gas adsorption. *AIChE J* **1965**, *11*, 121-127.
3. Xiang, Z. H.; Cao, D. P.; Wang, W. C.; Yang, W. T.; Han, B. Y.; Lu, J. M., *J. Phys. Chem. C* **2012**, *116*, 5974.
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