Supporting Information

Pore tuning in multivariate Zr/Ce-MOFs utilizing C4 natural linkers through room-temperature synthesis for customized

adsorptive separation of gases and vapours

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S1. General Information

(1) Materials: ZrCl₄ (Thermo scientific, 98%), (NH₄)₂Ce(NO₃)₆ (Energy Chemical, 98%), Fumaric acid (Energy Chemical, 98%), L-Aspartic acid (Energy Chemical, 98%), Formic acid (Sinopharm, AR), NaOH (Sinopharm, AR), EtOH (Keshi, 99.7%), were purchased from commercial suppliers and used as received without further purification.

(2) Instruments: The powder X-ray diffraction (PXRD) data for general characterization and comparison were collected on a Rigaku Miniflex Diffractometer with Cu Ka radiation ($\lambda = 1.54059$ Å). Thermogravimetric measurements were carried out with a Mettler Toledo thermal analyzer under oxidation atmosphere, with a heating rate of 5 °C/min. SEM images were recorded with GeminiSEM 450 Field Emission scanning electron microscope. Carbon dioxide and Nitrogen sorption data from 273 K to 298 K were collected on a Micromeritics 3Flex analyzer. Nitrogen sorption data at 77 K was collected on a Micromeritics 3Star analyzer. Single-component adsorption isotherms of C6 isomers from 303 K to 363 K were collected on a Belsorp Max X analyzer. The solvents were degassed through five freeze pump-thaw cycles before analysis. MTV-MOF-801 samples was activated under dynamic vacuum at different temperature for 6 hours prior to data collection. Specifically, Ce-100%-Fum, Ce-48%-Fum, Ce-37%-Fum and Ce-26%-Fum were activated at 363 K; Ce-78%-Fum was activated at 393 K; Ce-11%-Fum and Ce-0%-Fum were activated at 373 K; Zr-100%-Fum was activated at 363 K; other Zr-X-Fum samples were activated at 323 K. ¹H-NMR spectra were recorded on AVAVCE III HD400.

S2 Synthesis Procedures

(1) Synthesis of Zr-X-Fum: 4.5 mmol of ZrCl₄ was weighted in a 50 mL roundbottom flask, 6 mL of formic acid and 24 mL of distilled water was stepwisely introduced in the reactor, following by 1 minute of stirring at 600 rpm. 4.5 mmol of fumaric acid and L-Aspartic acid (The proportion of fumaric acid was 100%, 80%, 60%, 50%, 40%, 20%), was subsequently added in the solution at room temperature. The solution became very cloudy within 24 h, indicating the formation of Zr-X-Fum. The samples were washed with water and ethanol in turn and dried in air. It should be noted that when the Asp input is greater than 50%, the solid product cannot be obtained at room temperature, so the reaction needs to be carried out at 353 K.

(2) Synthesis of Ce-X-Fum: 4.5 mmol of (NH₄)₂Ce(NO₃)₆ was weighted in a 50 mL round-bottom flask, 6 mL of formic acid and 24 mL of distilled water was stepwisely introduced in the reactor, following by 1 minute of stirring at 600 rpm. 4.5 mmol of fumaric acid and L-Aspartic acid (The proportion of fumaric acid was 100%, 80%, 60%, 50%, 40%, 20%, 0%) was subsequently added in the solution at room temperature. The solution became very cloudy within 24 h, indicating the formation of Ce-X-Fum. The samples were washed with water and ethanol in turn and dried in air.

(3) Digestion process: Take 30 mg of the washed sample, add 30 mg of NaOH and 0.6 mL of D_2O , mix for 24 hours, then take the supernatant for ¹H-NMR analysis.

S3 Methods

(1) **IAST selectivity calculation:** The dual site Langmuir-Freundlich model was adopted to fit the adsorption isotherms of MOFs, which was described as follows:

$$q = q_{A,sat} \frac{b_A P^{\nu A}}{1 + b_A P^{\nu A}} + q_{B,sat} \frac{b_B P^{\nu B}}{1 + b_B P^{\nu B}}$$

With T-dependent parameters b_A , and b_B

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right); \ b_B = b_{B0} \exp\left(\frac{E_B}{RT}\right)$$

Where *q* represents the adsorption amount of adsorbents with units of mol·kg⁻¹, $q_{A,sat}$ and $q_{B,sat}$ represent the saturated adsorption amount for adsorption site A and B, respectively. b_A and b_B are constants for species i at adsorption sites A and B, respectively. P is the total pressures of the bulk gas at the adsorption equilibrium, and v_A and v_B are the Freundlich exponent for site A and B, respectively.

Taking the CO₂/N₂ selectivity as example, the IAST selectivity is defined by:

$$S = \frac{q_1/q_2}{y_1/y_2}$$

where q_1 , and q_2 represents the adsorption amounts of CO₂, and N₂ under equilibrium condition, which are usually expressed with units of mmol g⁻¹. y_1 and y_2 are the corresponding mole fractions in the gas phase for the mixtures. The calculated IAST adsorption selectivity for the CO₂/N₂ (CO₂/N₂ = 15/85; v/v) mixtures taking the mole fractions y_1 =0.15 and y_2 = 0.85 for a total pressure of 101 kPa at 298 K.

(2) Isosteric heat of adsorption: The adsorption heat of each component was determined precisely according to the virial fitting parameters of single-component adsorption isotherms measured at 273 K, 283 K and 298 K up to 100 kPa.

 Q_{st} = -slope × R by drawing the Ln(P) versus gas uptakes, which was defined as follows:

$$Ln(P) = Ln(N) + \frac{1}{T} \sum_{i=0}^{m} a_i N_i + \sum_{i=0}^{n} b_i N_i$$
$$Q_{st} = -R \sum_{i=0}^{m} a_i N_i$$

where N is the adsorption amount, and m and n determine the number of items required to precisely fit the adsorption isotherms.

(3) Multicomponent column breakthrough tests: CO_2/N_2 Breakthrough tests were carried out in the auto mixed-gas breakthrough apparatus (3P MIXSORB) equipped with vapor generator. The mass of sample that was fed into the column (I.D. 6 mm, volume 1 mL) was 0.423 g (Zr-91%-Fum) and 0.356 g (Ce-11%-Fum). The packed adsorbent was activated by heated to 373 K for 5 h under helium purging (10 mL min⁻¹). When the helium flow was stopped, the raw mixed gases (CO_2/N_2 , 15/85 v/v) at a flow rate of 2 mL min⁻¹ were switched to pass through the adsorption bed. The outlet gas was analyzed by using a mass spectrometer (MKS).

Column breakthrough measurement was performed with a lab-scale fix-bed reactor at 303 K. In a typical experiment, 0.5 g of Ce-78%-Fum or 0.55 g of Ce-

11%-Fum material was packed into a quartz column (4.0 mm I.D. ×300 mm)

with silane treated glass wool filling the void space. A helium flow (1 mL min⁻¹) was used to purge the adsorbent. The packed adsorbent was activated by heating it to 303 K for 6 hours under helium purging at a flow rate of 20 mL min⁻¹. The fixed bed was then cooled to the analysis temperature (303 K). The flow of helium was then turned off, while another dry helium flow at a rate of 1 mL min⁻¹ was bubbled through a mixture of hexane isomers according to the following volumes (the volumes were determined through trial and error and calculated by GC: the experiment was run without any sample and the vapor phase ratios were optimized to an equimolar mixture): 2.92 mL of *n*HEX, 2.06 mL of 3MP, and 1.285 mL of 22DMB for nHEX/3MP/22DMB ternary mixture. The components of gas emitted from the column was monitored using an online GC equipped with HP-PONA column and FID.

S4 Supplementary figures



Figure S1. PXRD patterns of Zr-X-Fum and MOF-801-simulated.



Figure S2. ¹H-NMR spectrum of the Zr-X-Fum series. a) Zr-91%-Fum b) Zr-85%-Fum c) Zr-61%-Fum d) Zr-56%-Fum.



Figure S3. Scanning electron microscopy (SEM) images of Zr-X-Fum. a) Zr-100%-Fum b) Zr-91%-Fum c) Zr-85%-Fum d) Zr-68%-Fum e) Zr-61%-Fum f) Zr-56%-Fum



Figure S4. TGA curve of Zr-X-Fum series.



Figure S5. Nitrogen adsorption isotherms of the Zr-X-Fum series collected at 77 K.



Figure S6. N₂ adsorption isotherms of Zr-X-Fum series collected at 77 K showing molar ratio uptake.



Figure S7. Linear fitting of S_{BET} and V_P to percentage of fumaric acid in Zr-X-Fum. The S_{EBT} and V_{pore} values of the Zr-100%-Fum sample were taken as 100% on the ordinate.



Figure S8. CO_2 and N_2 adsorption isotherms of Zr-X-Fum collected at 273 K.



Figure S9. CO_2 and N_2 adsorption isotherms of Zr-X-Fum collected at 283 K.



Figure S10. CO_2 and N_2 adsorption isotherms of Zr-X-Fum collected at 298 K.



Figure S11. CO₂ adsorption isotherms of Zr-X-Fum series collected at 298 K showing molar ratio uptakes.



Figure S12. Comparison of PXRD before and after activation for Zr-X-Fum series. a) Zr-100%-Fum b) Zr-91%-Fum c) Zr-85%-Fum d) Zr-68%-Fum e) Zr-61%-Fum f) Zr-56%-Fum



Figure S13. Single-component sorption isotherms of hexane isomers on Zr-100%-Fum collected at 303 K.



Figure S14. Single-component sorption isotherms of hexane isomers on Zr-85%-Fum collected at 303 K.



Figure S15. Single-component sorption isotherms of hexane isomers on Zr-68%-Fum collected at 303 K.



Figure S16. Single-component sorption isotherms of hexane isomers on Zr-61%-Fum collected at 303 K.



Figure S17. Single-component sorption isotherms of hexane isomers on Zr-56%-Fum collected at 303 K.



Figure S18. PXRD patterns of Ce-X-Fum and MOF-801-simulated.



Figure S19. ¹H-NMR spectrum of the Ce-X-Fum series. a) Ce-78%-Fum b) Ce-48%-Fum c) Ce-37%-Fum d) Ce-26%-Fum e) Ce-11%-Fum.



Figure S20. Scanning electron microscopy (SEM) images of Ce-X-Fum series. a) Ce-100%-Fum b) Ce-78%-Fum c) Ce-48%-Fum d) Ce-37%-Fum e) Ce-26%-Fum f) Ce-11%-Fum g) Ce-0%-Fum.



Figure S21. TGA curve of Ce-X-Fum series.



Figure S22. Nitrogen adsorption isotherms of the Ce-X-Fum series collected at 77 K.



Figure S23. N_2 adsorption isotherms of Ce-X-Fum series collected at 77 K showing molar ratio uptake.



Figure S24. CO₂ and N₂ adsorption isotherms of Ce-X-Fum collected at 273 K.



Figure S25. CO_2 and N_2 adsorption isotherms of Ce-X-Fum collected at 283 K.



Figure S26. CO₂ adsorption isotherms of Ce-X-Fum series collected at 298 K showing molar ratio uptakes.



Figure S27. Single-component sorption isotherms of hexane isomers on Ce-78%-Fum collected at 303 K.



Figure S28. Single-component sorption isotherms of hexane isomers on Ce-48%-Fum collected at 303 K.



Figure S29. Single-component sorption isotherms of hexane isomers on Ce-37%-Fum collected at 303 K.



Figure S30. Single-component sorption isotherms of hexane isomers on Ce-11%-Fum collected at 303 K.



Figure S31. Single-component sorption isotherms of hexane isomers on Ce-100%-Fum collected at 333 K.



Figure S32. Single-component sorption isotherms of hexane isomers on Ce-100%-Fum collected at 363 K.



Figure S33. Single-component sorption isotherms of hexane isomers on Ce-26%-Fum collected at 333 K.



Figure S34. Single-component sorption isotherms of hexane isomers on Ce-26%-Fum collected at 363 K.



Figure S35. Single-component sorption isotherms of hexane isomers on Ce-11%-Fum collected at 333 K.



Figure S36. Single-component sorption isotherms of hexane isomers on Ce-11%-Fum collected at 363 K.



Figure S37. Single-component sorption isotherms of hexane isomers on Ce-0%-Fum collected at 363 K.



Figure S38. Column breakthrough curve of Ce-78%-Fum at 303 K for mixture of hexane isomers.



Figure S39. Column breakthrough curve of Ce-11%-Fum at 303 K for mixture of hexane isomers.

S5 Supplementary Table

Sample	SBET	Pore	V _{pore}	CO ₂ Uptake	IAST	Q _{st} (KJ mol ⁻¹)	
	(m² g⁻¹)	diameter (مُ)	(cm³ g ⁻¹)	1 bar/298 K	Selectivity	CO ₂	N ₂
	070	(A)	0.44		1 Dal/290 K	04.00	47.00
Zr-100%-Fum	976	6.50	0.44	2.20	50	31.68	17.63
Zr-91%-Fum	943	6.56	0.40	2.49	118	33.14	17.71
Zr-85%-Fum	851	6.48	0.37	2.46	49	28.05	22.57
Zr-68%-Fum	687	6.37	0.28	2.48	97	32.74	10.58
Zr-61%-Fum	604	6.23	0.24	2.46	151	32.07	10.52
Zr-56%-Fum	417	5.96	0.17	1.60	51	32.65	14.52
Ce-100%-Fum	756	6.18	0.35	3.21	38	28.65	18.19
Ce-78%-Fum	699	6.06	0.33	3.05	83	30.60	26.70
Ce-48%-Fum	544	6.17	0.28	2.59	52	32.19	23.02
Ce-37%-Fum	494	5.93	0.26	2.27	72	33.09	18.85
Ce-26%-Fum	476	6.04	0.26	1.91	72	33.96	22.50
Ce-11%-Fum	387	5.90	0.21	1.59	89	35.70	24.20
Ce-0%-Fum	269	5.66	0.13	0.49	100	38.82	21.80

Table S1. Summary of gas sorption results for the Zr-X-Fum and Ce-X-Fum series