Electronic Supplementary Information

Porous Metal-Organic Framework Based on a Macrocyclic Tetracarboxylate Ligand Exhibiting Selective CO_2 Uptake

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Synthesis of H_4tactmb:

The H_4tactmb ligand was prepared as the following procedures. To a solution of 1,4,7,10-tetracyclododecane (3mmol, 516mmg) and methyl 4-(bromomethyl)benzoate (14.4 mmol, 3.3g) in 200 mL of CH_3CN, potassium carbonate (4.0g, 29 mmol) was added. The suspension was refluxed for 24h. The solvent was removed, and the residue was partitioned between CH_2Cl_2 and water, extracted water phase with CH_2Cl_2 (100 mLx3). The combined organic layer was washed with brine, dried with sodium sulfate, crystallized from mixture solvent of hexane and ethyl acetate to afford product (1.62g, 73%). This solid was dissolved in methanol (100 ml), and a solution of potassium hydroxide (0.94g, 17mmol) in water (5 ml) was added. The solution was refluxed overnight. The volatile was evaporated under reduced

pressure, and the solution was neutralized with HCl (1M). Then precipitated solid was washed thoroughly with deionized water. The solid was collected and lyophilized to give product H_4tactmb(1.02g, 69%).

Synthesis of MMCF-1:

A mixture of H_4tactmb (0.003g), $Cd(NO_3)\cdot 4H_2O$ (0.010g) and 1.0 mL dimethylformamide (DMF) was sealed in a Pyrex tube under vacuum and heated to 105 ^oC for 48 hours. The resulting colorless block crystals were obtained (yielding: 65% based on the ligand).

General method:

Commercially available reagents were purchased as high purity from Fisher Scientific or Frontier Scientific and used without further purification. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res from 30^oC to 700 ^oC at the speed of 10 ^oC/min.

Gas Adsorption Experiments:

Gas adsorption isotherms of MMCF-1 were collected using the surface area analyzer ASAP-2020. Before the measurements, the freshly prepared samples were washed with methanol, and then activated with supercritical CO_2 in a Tousimis Samdri PVT-3D critical point dryer. CO_2 gas adsorption isotherm was measured at 195K using a liquid acetone-dry ice bath, while CO_2 and N_2 gas adsorption isotherms were measured at 273K using a water-ice bath. CO_2 gas adsorption was also collected at 298K with a water bath.

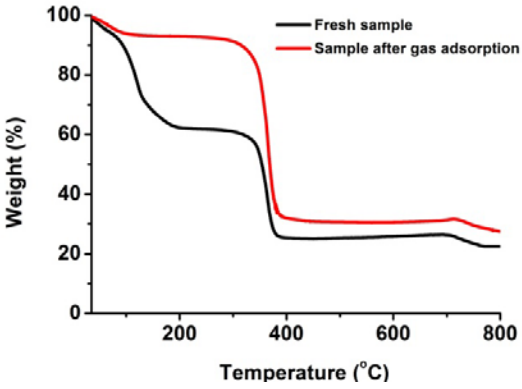


Fig. S1 TGA plots of MMCF-1.

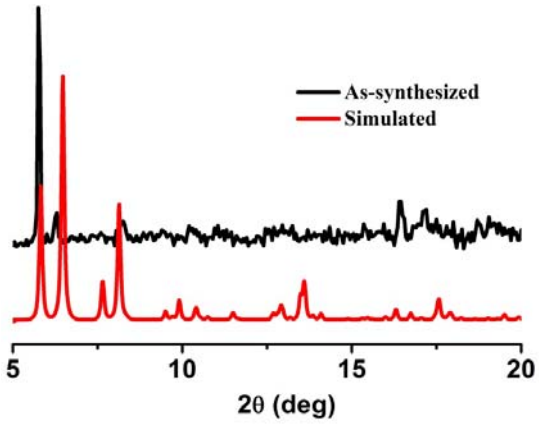


Fig. S2 PXRD patterns of MMCF-1.

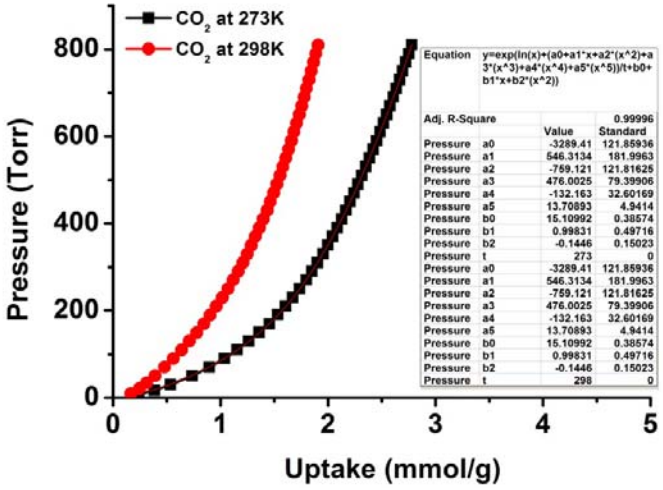
Heat of Adsorption (Q_{st}) Calculations.

The virial equation of the form given in Equation (1) was employed to calculate the enthalpies of adsorption for CO_2 on MMCF-1.

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

where P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m and n represent the number of coefficients required to adequately describe the isotherms. The equation was fitted by using the the least-squares method; m and n were gradually increased until the contribution of a and b coefficients toward the overall fitting is statistically trivial, as determined by the t-test. The values of the virial coefficients $a_0 \ldots a_m$ were then used to calculate the isosteric heat of adsorption by the following expression:

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



Equation	y=exp(ln(x)+(a0+a1*x+a2*(x^2)+a3*(x^3)+a4*(x^4)+a5*(x^5))/(1+b0+b1*x+b2*(x^2))		
Adj. R-Square			0.99996
		Value	Standard
Pressure	a0	-3289.41	121.85936
Pressure	a1	546.3134	181.9963
Pressure	a2	-759.121	121.81625
Pressure	a3	476.0025	79.39906
Pressure	a4	-132.163	32.60169
Pressure	a5	13.70893	4.9414
Pressure	b0	15.10992	0.38574
Pressure	b1	0.99831	0.49716
Pressure	b2	-0.1446	0.15023
Pressure	t	273	0
Pressure	a0	-3289.41	121.85936
Pressure	a1	546.3134	181.9963
Pressure	a2	-759.121	121.81625
Pressure	a3	476.0025	79.39906
Pressure	a4	-132.163	32.60169
Pressure	a5	13.70893	4.9414
Pressure	b0	15.10992	0.38574
Pressure	b1	0.99831	0.49716
Pressure	b2	-0.1446	0.15023
Pressure	t	298	0

Fig. S2 The plots of virial equation of MMCF-1.

The Ideal Adsorption Solution Theory (IAST) calculation

The ideal adsorption solution theory (IAST) was utilized to predict the binary mixture composed of CO_2 (15%) and N_2 (85%) from the experimental pure-gas isotherms. Herein the single-component isotherms were fit to the Langmuir equation. The selectivity $S_{A/B}$ in a binary mixture of component A and B is defined as $(x_A/y_A)/(x_B/y_B)$, where x_i and y_i are the mole fractions of component i (i=A,B) in the adsorbed and bulk phases respectively.

Single-Crystal X-ray Diffraction for MMCF-1

The X-ray diffraction data were collected using synchrotron radiation, λ = 0.49594 Å, at Advanced Photon Source, Argonne National Lab, Argonne, Il. Indexing was performed using *APEX2* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in APEX2 [1] and WinGX v1.70.01 [4,5,6,7] programs packages. All non-H atoms were found in the Fourier difference map.

SIMU restraints were used to refine the anisotropic displacement parameters of pairs of atoms: C1 and N2, C3 and C4, C17 and O4. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). The contribution of heavily disordered solvent molecules was treated as diffuse using Squeeze procedure implemented in Platon program [8, 9]. Crystal data and refinement conditions are shown in Table 1.

Table S1. Crystal data and structure refinement for MMCF-1

Identification code	MMCF-1
Empirical formula	C40 H40 Cd2 N4 O9
Formula weight	945.56
Temperature	100(2) K
Wavelength	0.49594 A
Crystal system, space group	Monoclinic, *P*21/*c*
Unit cell dimensions	*a* = 17.8372(19) A *alpha* = 90 deg. *b* = 21.164(2) A *beta* = 90.300(2) deg. *c* = 21.721(2) A *gamma* = 90 deg.
Volume	8199.7(15) A^3
Z, Calculated density	4, 0.766 Mg/m^3
Absorption coefficient	0.181 mm^-1
F(000)	1904
Crystal size	0.05 x 0.02 x 0.01 mm
Theta range for data collection	0.80 to 18.13 deg.
Limiting indices	-22<=h<=22, -21<=k<=24, -26<=l<=21
Reflections collected / unique	91148 / 16212 [R(int) = 0.0648]
Completeness to theta = 18.13	95.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9982 and 0.9910
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16212 / 18 / 497
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0725, wR2 = 0.1930
R indices (all data)	R1 = 0.1012, wR2 = 0.2019
Largest diff. peak and hole	1.397 and -1.569 e.A^-3

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