

Supporting Information for

A Highly Stable Multifunctional Three-Dimensional Microporous Framework: Excellent Selective Sorption and Visible Photoluminescence

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Table S1. Crystal Data and Refinement Information for Complex **1**

1	
Formula	C ₁₆ H ₁₄ CdN ₂ O ₅
Formula weight	426.70
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.2211(5)
<i>b</i> /Å	18.1848(10)
<i>c</i> /Å	9.7227(6)
α /°	90
β /°	104.9940(10)
γ /°	90
<i>V</i> /Å ³	1574.83(16)
<i>Z</i>	4
ρ_{calcd} /g cm ⁻³	1.800
μ /mm ⁻¹	1.416
collected Reflections	13891
Unique reflections	3779
<i>R</i> ₁ [<i>I</i> > 2σ (<i>I</i>)]	0.0237
<i>wR</i> ₂ (all data)	0.0801

Table S2. Selected Bond Distances (Å) and Angles(deg) for Complex **1**^a

Cd1–O5	2.369(3)	Cd1–N1	2.290(2)
Cd1–O3#1	2.2961(19)	Cd1–O4#1	2.523(2)
Cd1–O1#2	2.3768(19)	Cd1–O2#2	2.4881(17)
Cd1–O2#3	2.3888(19)		
O1#2–Cd1–O3#1	137.01(7)	O2#2–Cd1–O4#1	141.38(7)
O3#1–Cd1–O4#1	54.04(7)	O1#2–Cd1–O2#2	54.08(6)
O2#3–Cd1–O5	170.51(8)		

^a Symmetry codes for **1**: #1 1+*x*, *y*, 1+*z*; #2 1-*x*, 1/2+*y*, 3/2-*z*; #3 1+*x*, 3/2-*y*, 1/2+*z*.

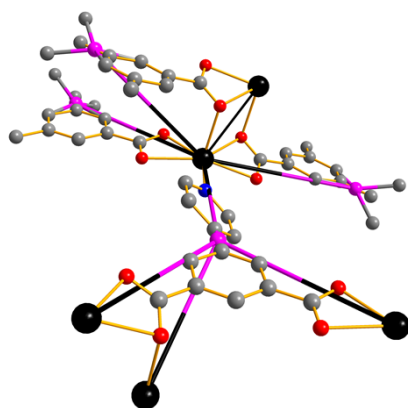


Fig. S1. Purple spheres represent the centers of L²- ligand, black spheres represent Cd atoms.

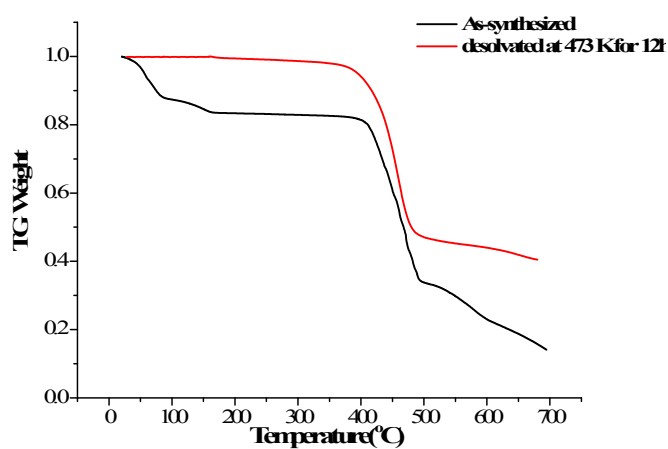


Fig. S2. TG curves of complex **1** and desolvated **1**.

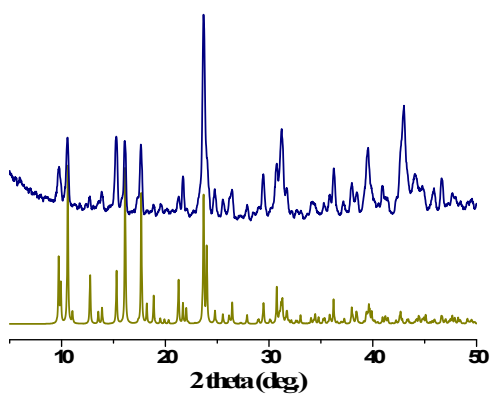


Fig. S3. The PXRD patterns of the simulated spectra from single crystal data of **1** (lower), compound **1** (upper).

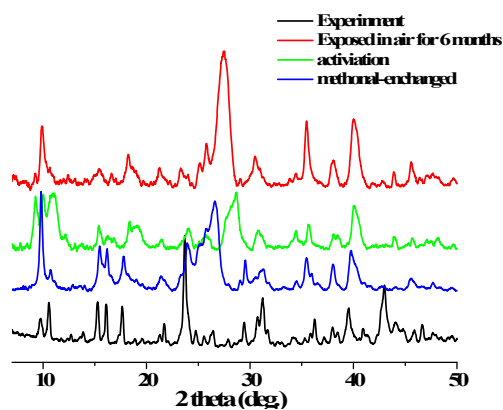


Fig. S4. The PXR D patterns of **1** under varied conditions.

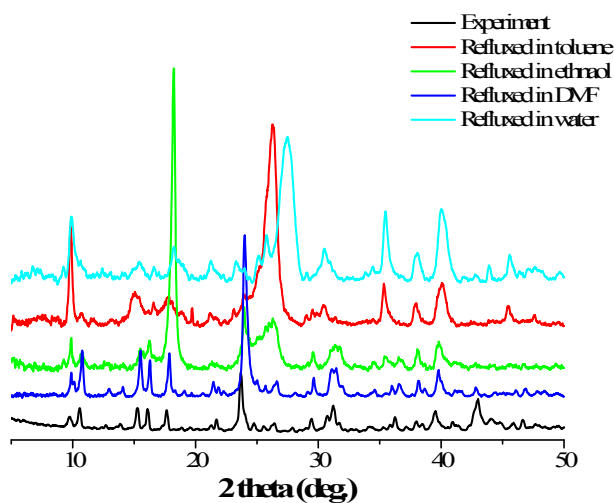


Fig. S5. PXR D patterns of **1** treated with different solvents at their boiling points for 24 h.

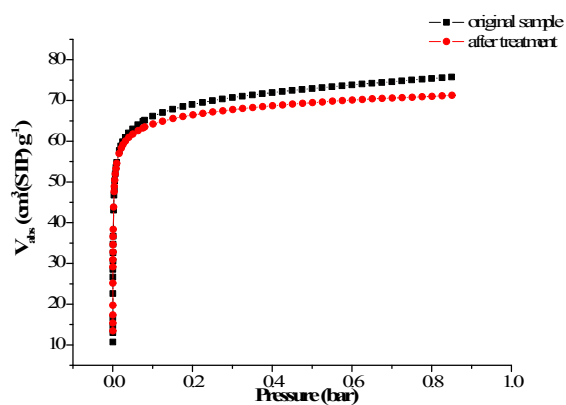


Fig. S6. The CO_2 adsorption isotherms at 195 K/1 bar before and after boiling solvent treatment.

Estimation of the isosteric heats of gas adsorption

A virial-type expression comprising the temperature-independent parameters a_i and b_i was

employed to calculate the enthalpies of adsorption for CO₂ and CH₄ (at 273 and 298 K), as well as H₂ (at 77 and 87 K) on **1**. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{j=0}^n b_j N^j$$

Here, P is the pressure expressed in Pa, N is the amount adsorbed in mmol g⁻¹, T is the temperature in K, a_i and b_j are virial coefficients, and m , n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

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

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

CO₂ Selectivity Calculations

The adsorption capacities of component n (q_n) are defined to be molar absolute adsorption capacities determined experimentally, and p_n is defined to be the pressure of component n as experimentally measured. Selectivity (S) is defined according to equation.

$$S = \frac{q_{CO_2} / q_{N_2}}{p_{CO_2} / p_{N_2}} \quad (\text{Equation S1})$$

Selectivity Prediction for Binary Mixture Adsorption: Ideal adsorbed solution theory (IAST)

Ideal adsorbed solution theory (IAST)^[1] was used to predict binary mixture adsorption from the experimental pure-gas isotherms. To perform the integrations required by IAST, the single-component isotherms should be fitted by a proper model. There is no restriction on the choice of the model to fit the adsorption isotherm, however, data over the pressure range under study should be fitted very precisely. ^[2] Several isotherm models were tested to fit the experimental pure isotherms

for CH₄, N₂ and CO₂ of **1** at 298K, and the dual-site Langmuir-Freundlich equation were found to be the best fit to the experimental data:

$$q = q_{m1} \frac{b_1 p^{1/n_1}}{1 + b_1 p^{1/n_1}} + q_{m2} \frac{b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}}$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol/kg), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol/kg), b_1 and b_2 are the affinity coefficients of the sites (1/kPa), and n_1 and n_2 are measures of the deviations from an ideal homogeneous surface. Figure S8 shows that the dual-site Langmuir-Freundlich equation fits the single-component isotherms extremely well. The R^2 values for all of the fitted isotherms were over 0.9998. Hence, the fitted isotherm parameters were applied to perform the necessary integrations in IAST.

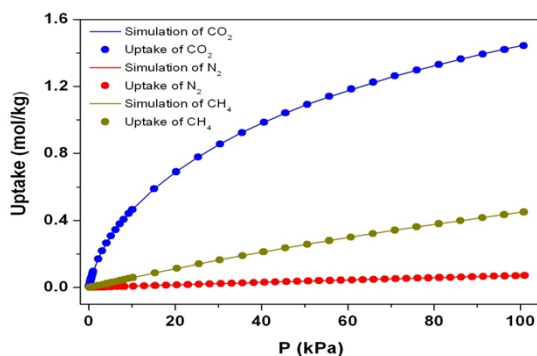
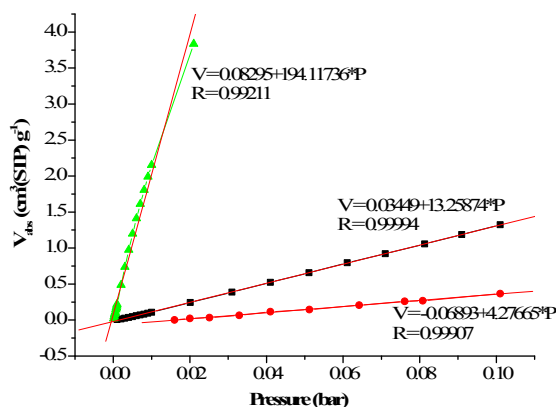
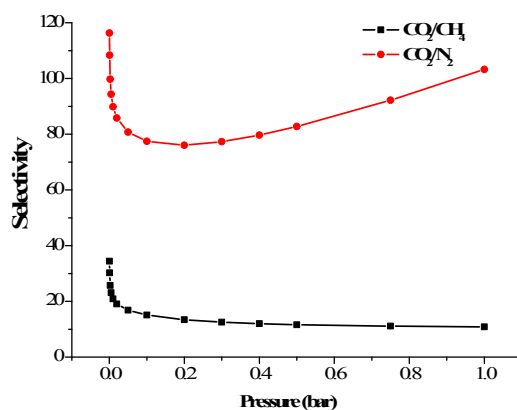


Fig. S7. Gas adsorption isotherms (circle points) and the dual-site Langmuir–Freundlich fit curves (lines) for N₂, CH₄ and CO₂.



(a)



(b)

Fig. S8. (a) Evaluation of the initial slope in the Henry region of the sorption isotherms of CO₂ (triangle), N₂ (circle), and CH₄ (square) at 298 K. The ratios of the initial slopes allowed an estimation of the sorption selectivity. (b) IAST predicted selectivity for CO₂/N₂ and CO₂/CH₄ in **1** at 298 K.

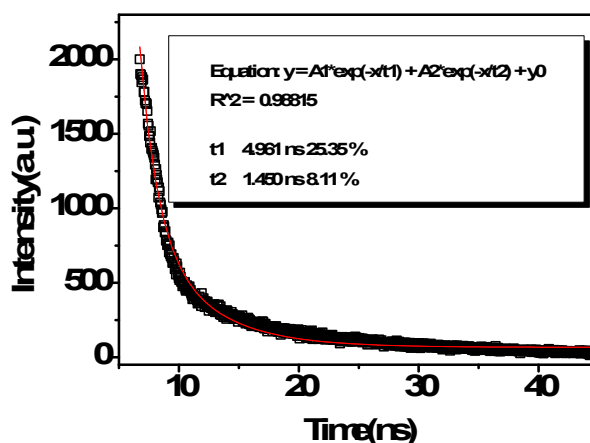


Fig. S9. The fitted decay curve monitored at 500 nm for complex **1** in the solid state at room temperature. The sample was excited at 360 nm. Blank squares: experimental data; Solid line: fitted by $\text{Fit} = A + B_1 \times \exp(-t/\tau_1) + B_2 \times \exp(-t/\tau_2)$.

Reference

- (1) A. L. Myers and J. M. Prausnitz, *Aiche J.*, 1965, **11**, 121.
- (2) a) R. Babarao, Z. Q. Hu, J. W. Jiang, S. Chempath, S. I. Sandler, *Langmuir*, **2007**, *23*, 659; b) V. Goetz, O. Pupier, A. Guillot, *Adsorption*, **2006**, *12*, 55.