Electronic Supporting Information for

A luminescent cadmium (II) metal-organic framework based on a triazolate-carboxylate ligand exhibiting selective gas adsorption and guest-dependent photoluminescence properties

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1- Experimental Details

Materials and Instruments.

The ligand Htba was synthesized according to the literature method. ^{S1} Other reagents and solvents were commercially available and were used without further purification. IR spectra were obtained from KBr pellets on a Bruker TENSOR27 FT-IR spectrometer in the 400-4000 cm⁻¹ region. Elemental analyses (C, H, N) were performed with a Vario EL elemental analyzer. Powder X-ray diffraction patterns (PXRD) of the bulk samples were measured on a Rigaku D-MAX 2200 VPC diffractometer (CuKα, 1.5418 Å). Thermogravimetric analyses (TGA) were performed using a Netzsch STA 449C instrument with a heating rate of 10.0 °C/min under nitrogen atmosphere. Room-temperature photoluminescence (PL) spectra were recorded using a Hitachi F-4600 fluorescence spectrophotometer equipped with a xenon lamp. The sorption isotherms for N_2 and CO_2 gas were measured with an automatic volumetric sorption apparatus (BELSORP-max, Bel Japan). The simulated powder patterns were calculated using Mercury 2.0. The purity and homogeneity of the bulk products were determined by comparison of the simulated and experimental X-ray powder diffraction patterns. Before gas sorption experiments, the as-synthesized samples of **1** were placed in the quartz tubes and dried under high vacuum at 140 °C for 5 h to remove the remnant solvent molecules prior to measurements. The samples for the study of guest-dependent luminescent properties have been treated by the flowing process. The powder samples of the activated 1 was immersed in benzene, toluene, chlorobenzene, nitrobenzene, cyclohexane, AE, MA and DMA for two days, and the solvents on the surface of the samples was removed under reduced pressure.

Synthesis of [Cd₂Cl(tba)₃] 0.5DMF 2H₂O (1).

A mixture of CdCl₂ 2.5H₂O (22.8 mg, 0.1 mmol) and Htba (18.9 mg, 0.1 mmol) in DMF-MeOH (4 mL, v/v = 3:1) was placed in a Teflon-lined stainless steel vessel (15 mL) and heated at 95 °C for 72 h

and then cooled to room temperature at a rate of 5 °C/h. Colorless, needle-like crystals of **1** were collected, washed with ether and air-dried (yield 15.0 mg, 50.6% based on Hbta ligand). Anal. Calcd (%) for C_{28.5}H_{25.5}Cd₂ClN_{9.5}O_{8.5}: C, 38.15; H, 2.86; N, 14.83. Found: C, 38.49; H, 2.79; N, 14.99. IR (cm⁻¹, KBr): 3426 (br, m), 1661(m), 1607(s), 1566(m), 1411(s) 1282(m), 1217(w), 1147(m), 1051(w), 977m), 859(m), 784(m), 725(w), 695(w), 670(m), 511(m).

2- Crystal Structure Description

Crystal structure determination.

Diffraction intensities of the compound 1 were collected on a Rigaku R-AXIS SPIDER diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by using the program ABSCOR.^{S2} The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package.^{S3} The hydrogen atoms were generated geometrically. Due to the presence of large cavities in the structure and heavily disordered solvent molecules in the cavities, the crystal of 1 scattered weakly and only low-angle data could be detected. An attempt to locate and refine the solvent molecules failed. Thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules.^{S4} The reported refinement is of the guest-free structure using the *.hkp file produced using the SQUEEZE routine guest solvent molecules) in the crystal cell was calculated using the program *PLATON*.^{S5} CCDC 1051320 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The final formula for **1** was determined by combining single-crystal structure, IR spectrum and thermal gravimetric analysis

Compounds	1
Formula	$C_{28.50}H_{25.5}Cd_2ClN_{9.50}O_{8.50}$
Formula weight	897.34
Crystal system	Orthorhombic
Space group	Pnma
a (Å)	25.786(5)
<i>b</i> (Å)	21.045(4)
<i>c</i> (Å)	7.4123(15)
α (deg)	90
β (deg)	90
γ (deg)	90
$V(\text{\AA}^3)$	4022.3(14)
Ζ	4
$D_{\rm c} ({\rm g \ cm}^{-3})$	1.482
$\mu (\mathrm{mm}^{-1})$	1.167
GOF	1.123
$R_1 \left[I > 2\sigma \left(I \right) \right]^a$	0.0523
$WR_2 \left[I > 2\sigma\left(I\right)\right]^b$	0.1243
R_1 [all data]	0.0643
wR_2 [all data]	0.1287

Table S1	Crystal dat	a and structure	e refinements	for 1	l
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 $\overline{{}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.}$

 ${}^{b}wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}.$



Fig. S1 The schematic presentation of the network of **1** formed by interlinking the $[Cd_2(\mu_2-O)_2(\mu_2-Cl)]$ chain (simplified as purple rods) through the tba ligands (blue rods).



Fig. S2 The 6-connected node in 1 and Representation of the 6-connected cap topology of 1

3-IR spectra and Powder X-Ray Diffraction



Fig. S3 IR spectra of the as-synthesis and activated sample by heating under vacuum at 150 $^{\circ}$ C. The lack of C=O stretching peak at 1661 cm⁻¹ in the IR spectrum of activated **1** also confirms the full release of DMF guests.



Fig. S4 PXRD patterns of 1 at different conditions. The PXRD patterns at different conditions maintain similar diffraction peaks to those of the as-synthesized sample, which indicates that 1 can retain its framework integrity in the absence of guest species or after gas adsorption analysis, which further highlights its framework robustness.



Fig. S5 PXRD of various guest-absorbed samples for activated 1.



Fig. S6 PXRD of activated **1** and the samples of activated **1** dispersed in ethanol. PXRD patterns for the samples activated **1** dispersed in ethanol maintain similar diffraction peaks to those of activated **1**, which indicates that activated **1** can retain its framework integrity after dispersing in ethanol

4- Thermogravimetric Analysis (TGA)



Fig. S7 TG curves of 1 and activated 1 in N_2 . The observed weight loss (7.93%) for 1 is the weight of 0.5 DMF and 2.0 water molecules (calcd: 8.09%).



Fig. S8 TG curves of various guest-absorbed samples for activated **1**. The observed weight loss for benzene (9.90%), toluene (9.50%), chlorobenzene (10.55%), nitrobenzen(11.76%), AE (11.91%), MA (5.8%), DMA (7.9%) loaded samples correspond to the weights of 1.16 benzene molecules, 0.94 toluene molecules, 0.86 chlorobenzene molecules, 0.89 nitrobenzen molecules, 1.2 AE molecules, 0.47 MA molecules, 0.59 DMA.

5- Calculation of adsorption enthalpy (Q_{st})

The adsorption enthalpy (Qst) for the CO₂ adsorption of activated **1** is calculated via the Clausius-Clapeyron equation^{S6} expatiated below. The adsorption isotherms used for the calculations are the ones measured at 273 K and 298 K given in Fig. 4 in the text.

The Clausius-Clapeyron equation^{S5} was employed to calculate the enthalpies of CO_2 adsortion:

$$Q_{st} = -R \left[\frac{\partial \ln p}{\partial \ln \left(1/T \right)} \right]_{N} \quad (E1)$$

Where p is the pressure, n is the amount adsorbed, T is the temperature, R is the universal gas constant. Integrating equation (E1) gives:

$$(\ln p)_N = -(\frac{Q_{st}}{R})(\frac{1}{T}) + C$$
 (E2)

Where *C* is a constant. Here an isotherm is first fitted to a high-order polynomial equation to obtain an expression for *N* as a function of *p*. Then the values of *p* at a given *N* for each *T* can be interpolated from the fitted equation. At each given *N*, the isostere plot of $(\ln p)N$ as a function of (1/T), which is obtained from linear regression, matches with the form of equation (*E*2), and therefore the *Q*st values can be computed from the slopes of the isostere plot. The fitting results are given in Fig. S8.



Fig. S9 The curve of CO_2 adsorption enthalpy (Q_{st}).

6- Surface Area Determination

(1) The calculation of Langmuir surface area



Fig. S10 Langmuir plot for the CO_2 adsorption isotherm of activated 1 at 195 K, the range *P* from 1.06 to 35.80 KPa satisfies for applying the Langmuir theory.

The adsorption isotherms were converted into plots of P/V vs. P for determining the appropriate range. As shown in Fig. S6, the range P from 1.06 to 35.80 KPa satisfies for applying the Langmuir theory. After having identified the appropriate low pressure Langmuir P range, the analysis proceeds according to the standard method via the linearized Langmuir equation.

$$P/V = P/V_{\rm m} + 1/BV_{\rm m}$$

from which the parameters $V_{\rm m}$ is obtained from the relation $V_{\rm m} = 1/s$, s being the slope with the ordinate of the plot P/V vs. P. The surface area is then obtained from $A_{\rm Langmuir} = V_{\rm m}\sigma_{\rm m}N_{\rm A}$ with $\sigma_{\rm m}$ being the cross-sectional area of CO₂ at liquid density (1.037x10⁻²⁶ m²), and $N_{\rm A}$ Avogadro s number.

(2) The calculation of BET surface area



Fig. S11 BET plot for the CO₂ adsorption isotherm of activated 1 at 195 K. the range P/P_0 from 0.055 to 0.204 satisfies for applying the BET theory.

The adsorption isotherms were converted into plots of $1/[V(P_0/P - 1)]$ vs. P/P_0 for determining the appropriate range. As shown in Fig. S6, the range P/P_0 from 0.0035 to 0.04 satisfies for applying the BET theory. After having identified the appropriate low pressure BET P/P_0 range, the analysis proceeds according to the standard method via the linearized BET equation.

$$\frac{1}{V(P/P_0-1)} = \frac{1}{V_m c} + (\frac{1}{V_m} - \frac{1}{V_m c})\frac{P}{P_0}$$

from which the BET parameters c is obtained from the relation c = s/i + 1, s being the slope and i being the intercept with the ordinate of the plot $1/[V(P_0/P - 1)]$ vs. P/P_0 . The parameter V_m is then given by $V_m = 1/(s + i)$. The surface area is then obtained from $A_{BET} = V_m \sigma_m N_A$ with σ_m being the cross-sectional area of CO₂ at liquid density $(1.037 \times 10^{-26} \text{ m}^2)$, and N_A Avogadro s number.

7- Photoluminescent properties



Fig. S12 Excitation and emission spectra of activated 1 in the solid state.



Fig. S13 Excitation and emission spectra of activated 1 dispersed in ethanol.



Fig. S14 Excitation spectra of activated 1 and various guest- adsorbed samples in solid state.



Fig. S15 Excitation spectra of activated 1 and various guest- adsorbed samples in solid state.



Fig. S16 The photograph of activated 1 and different guest-inclusion samples under UV irradiation.



Fig. S17 Uv-vis spectra of aromatic molecules in ethanol solution.



Fig. S18 Spectral overlap between the absorption spectra of nitrobenzene and the emission spectrum of activated 1 in ethanol (red dashed line represents the extension of emission spectrum of activated 1).



Fig. S19 Excitation (dashed line) and emission spectra (solid line) of aromatic molecules in ethanol solution.

guest	$\lambda_{\rm ex}$ / nm	λ_{\max} / nm	Stokes shifts / nm
activated 1	323	381	58
benzene	319	438	119
toluene	323	411	88
chlorobenzene	323	409	86
nitrobenzene	332	422	90
AE	386	473	87
MA	383	469	86
DMA	356	497	141

Table S2 Summary of Solid-State luminescent Data for activated 1 and various solvent adsorbed samples

8-Fluorescence Quenching Titrations in Dispersed Medium

A sample of activated 1 (2.5 mg) was dispersed in 5 mL ethanol by ultrasonication, which was subsequently placed in a quartz cell of 1 cm width for fluorescence measurements. For all measurements, the fluorescence spectra of activated 1 were recorded at 298 K with maximum emission wavelength at 355 nm (λ ex =304 nm). To check the selectivity, 200 µL solution of each anaelyte (10 mM) was added to 3 mL the dispersion of 2' in ethanol. All the titrations were carried out by gradually adding analytes (10 mM) solution in an incremental fashion. Each titration was repeated at least three times to get concordant value.

References

S1 Y.-L. Wang, J.-H. Fu, J.-J. Wei, X. Xu, X.-F. Li and Q.-Y. Liu, Cryst. Growth Des., 2012, 12, 4663.

S2 T. Higashi, ABSCOR. Rigaku Corporation, Tokyo, Japan, 1995.

S3 G. M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Germany, 1997.

S4 (a) A. L. Spek, J. Appl. Crystallogr., 2003, **36**, 7; (b) A. L. Spek, Acta Crystallogr., Sect. C: Struct. Chem., 2015. **71**, 9.

S5 A. L. Spek, *PLATON*, Utrecht University: Utrecht, The Netherlands, 2003.

S6 L. Czepirski and J. Jagiello, Chem. Eng. Sci., 1989, 44, 797.