

Supporting Information

A charge-polarized porous metal-organic framework for gas chromatographic separation of alcohols from water

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Section 1. Experimental Section

1. Materials and General Procedures

All chemicals were obtained from commercial sources and of GR/AR grade. Fourier transform (FT) IR spectra (KBr pellets) were recorded on a Bomem MB-102 FT-IR spectrometer. Elemental analyses of C, H and N were performed on a Vario EL III CHNOS elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on MiniFlex diffractometer using graphite-monochromated for Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation in the 2θ range of 5-45°. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449 C thermal analyzer in flowing air atmosphere at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from 30 to 800 °C. The samples were heated at 100°C under vacuum for 6 hours before the adsorption analysis were started. Vapor-phase (H₂O, MeOH, EtOH, CH₄) adsorption isotherms were measured with the Intelligent Gravimetric Sorption Analyser IGA100B of Hiden Corporation. The adsorption isotherm of MeCN can't be measured because this vapor may destroy some components such as valve in IGA100B. Consequently, we have adopted a method by directly immersing the evacuated sample **1'** into MeCN because the sample dose not dissolve in this solvent. Meanwhile, the same procedues have been carried out on H₂O, MeOH, EtOH, the final TGA plots demonstarte that this method is feasible since the adsorption amounts are comprable to that measured by IGA100B on their saturated vapor pressure. The ASAP 2020 surface area analyzer was used to measure the N₂ and CO₂ isotherm in which the samples were degassed at 100 °C for 10 h prior to the measurement. Gas chromatographic measurements were performed on a Agilent 6890N with a thermal-current detector (TCD).

2. Synthesis procedure

H₂BpybcCl₂ was synthesized by the procedure described previously.¹ An aqueous solution of Dy(NO₃)₃ (0.02 M, 2 mL) was carefully layered onto a mixed solution(the pH value was adjusted to 7 with 0.1 M NaOH solution) of Bpybc (0.04 mmol, 19.9 mg) and sodium oxalate (0.04 mmol, 5.4 mg) in H₂O/DMSO (8:2 v/v; 2 mL) with

H₂O/DMSO (8:1 v/v; 1 mL) placed between the two layers. Yellow plate crystals began to form after one month. Yield: 16%; Elemental analysis calcd (%) for C₂₈H₄₉DyN₂O₂₃ (944.19, [Dy(ox)(Bpybc)(H₂O)]·OH·13H₂O): C 35.62, H 5.23, N 2.97; found: C 36.64, H 4.78, N 3.15. The experimental data is more close to the calculated one (C 37.03, H 4.99, N 3.08) for C₂₈H₄₅DyN₂O₂₁ (908.16, [Dy(ox)(Bpybc)(H₂O)]·OH·11H₂O) due to the easy loss of some lattice water molecules in **1** after leaving mother liquid. IR (KBr, cm⁻¹): 3420(s), 1635(s), 1609(s), 1580(s), 1558(m), 1539(m), 1418(s), 1384(s), 1317(m), 1217(w), 1165(w), 1017(s), 953(w), 864(w), 796(m), 768(m), 712(w), 648(w), 595(w), 493(w).

3. X-ray crystallography

The X-ray diffraction data for **1** was collected on a Saturn 724+ MicroMax 007 CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 123 K. The CrystalClear program was used for the absorption correction. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares fitting on F^2 by SHELXL-97.² All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the carbon atoms were placed in a calculated position with isotropic displacement parameters set to 1.2U_{eq} of the attached atom. Lattice water molecules in the structure were highly disordered at 123 K, and therefore the contribution of solvent electron density was removed by the SQUEEZE routine in PLATON.³

4. GC separation measurements

The stainless steel packed-column (160 × 3 mm) was filled with samples of **1**. Helium (99.999 %) was used as the carrier gas (21 mL/min). Prior to the measurements, the column filled with **1** was activated at 150 °C for 5 h. The GC separation of binary mixtures of alcohols and water were performed with a temperature program: 80 °C for the first 2 min, then gradually to 140 °C with a rate of 30 °C/min and kept at this temperature for the remainder of the measurement. For a typical run, 2 μ L of the mixture was manually injected to the injection port. At the

column outlet, the response curve was measured with a thermal conductivity detector at 150 °C.

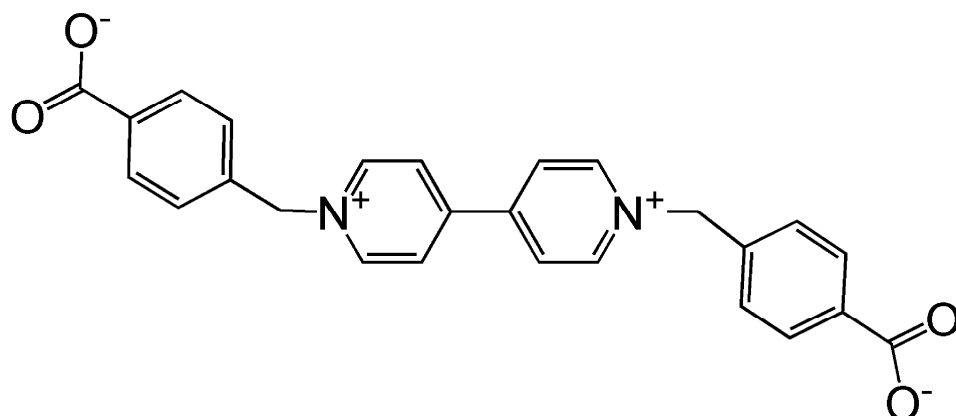
5. Computation description

The charge Mulliken population calculations were carried out by using Dmol3 program,⁴ where the GGA calculations are performed by PBE exchange correlation. In order to save the computational effort and ignore the magnetism of 4f electrons of Dy(III) during calculation, the Dy(III) were substituted by diamagnetic lanthanide Lu(III) owing to its similar ion radii and electronegativity. Mulliken charges were calculated by projecting the occupied one-electron eigenstates onto the localized atomic basis sets.⁵

Reference:

- [1] Y. Q. Sun, J. Zhang, Z. F. Ju, G. Y. Yang, *Cryst. Growth Des.*, **2005**, *5*, 1939.
- [2] (a) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7; (b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A*, **1990**, *46*, 194.
- [3] (a) G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**; (b) G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [4] (a) B. Delley, *J. Chem. Phys.*, **1990**, *92*, 508; (b) B. Delley, *J. Chem. Phys.*, **2000**, *113*, 7756.
- [5]. M. D. Segall, R. Shah, C. J. Pickard, M. C. Payne, *Phys. Rev. B*, **1996**, *54*, 16317.

Section 2. Additional characterization data and structural figures



Scheme S1. Carboxybenzyl-substituted 4,4'-bipyridinium derivative (Bpybc).

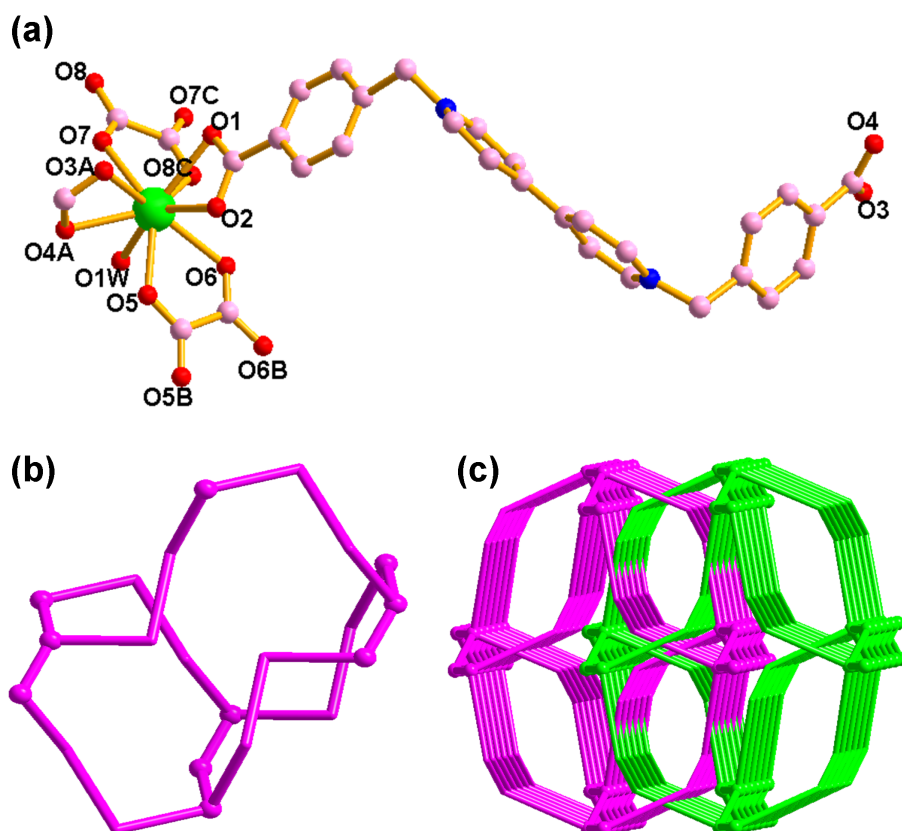


Fig S1 (a) The coordination environment of Dy(III) in compound **1**. The labeled atoms with 'A' ($1-x, -1+y, 0.5-z$), 'B' ($-x, y, 0.5-z$), 'C' ($-x, 1-y, 1-z$) are symmetrically generated; (b) a highly distorted diamond-like topology in **1**; (c) two interpenetrating network in **1**.

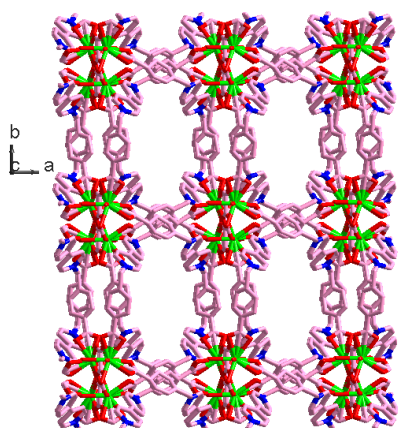


Fig S2 1D channel viewed along the c-axis direction.

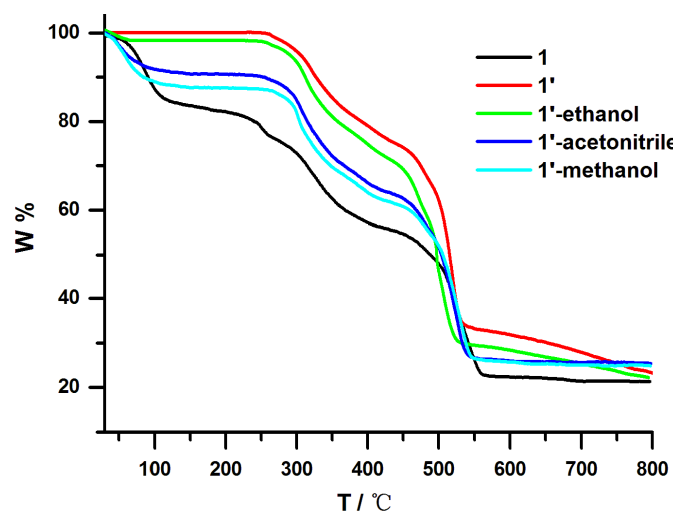


Fig S3 TG plots of **1**, evacuated **1'** as well as the sample **1'** after adsorption of various solvent molecules.

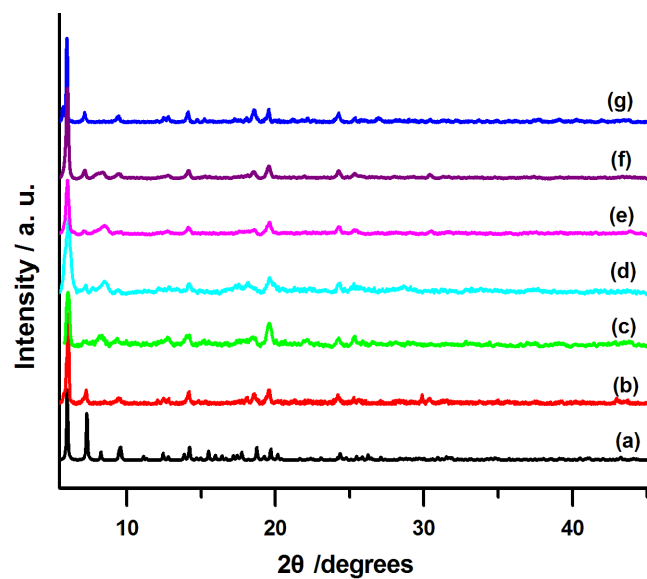


Fig S4 Powder X-ray diffraction patterns of simulated (a), as-synthesized (b), desolvated (c), after adsorption of methanol (d), after adsorption of acetonitrile (e), after a water isotherm recycle (f), exposed to water vapor for 24 h (g).

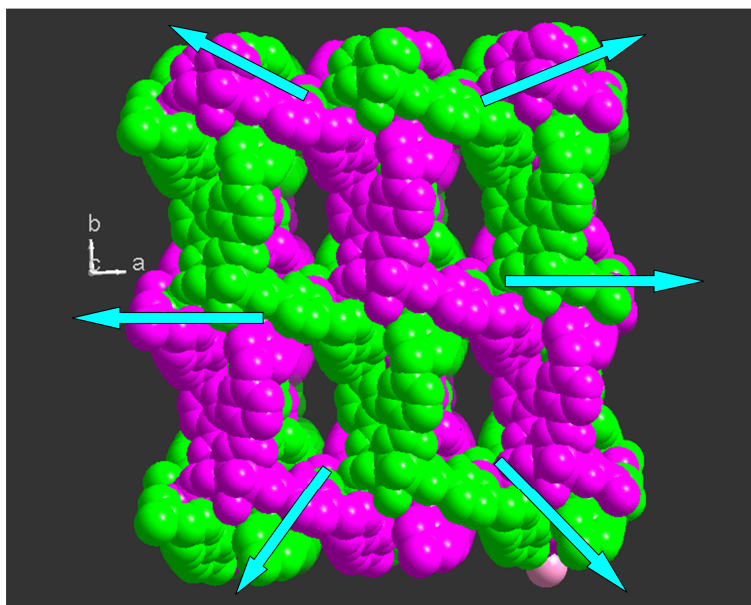


Fig S5 The intertwined entities at each corner of the pore limit the movement of two sets of interpenetrating nets.

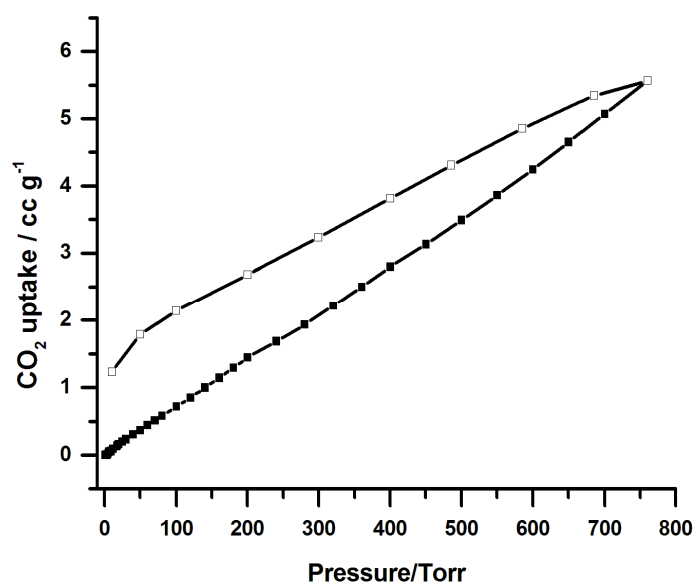


Fig S6 The adsorption isotherm of CO₂ at 273K (closed and open symbols represent adsorption and desorption branches, respectively).

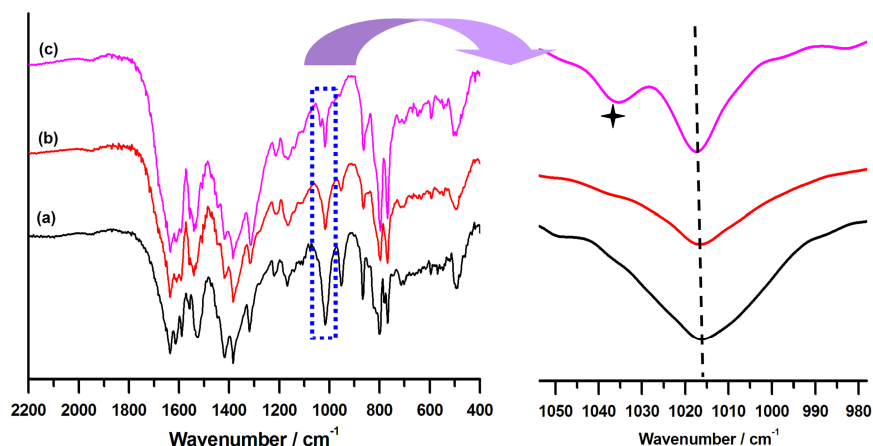


Fig S7 IR spectra of **1** (a), dried sample **1'** (b) and **1' + MeOH** (c). The asterisk symbol indicates the C-O stretch of CH₃OH molecule. The band frequency (1035.8 cm⁻¹) is higher than that observed for the methanol monomer (1029 cm⁻¹), which indicates that methanol molecules as Lewis base interact with the Lewis acid center (pyridinium units). Reference: G. Busca, P. F. Rossi, V. Lorenzelli, *J. Phys. Chem.*, **1985**, 89, 5433; J. Zawadzki, B. Azambre, O. Heintz, A. Krztoń, J. Weber, *Carbon*, **2000**, 38, 509.

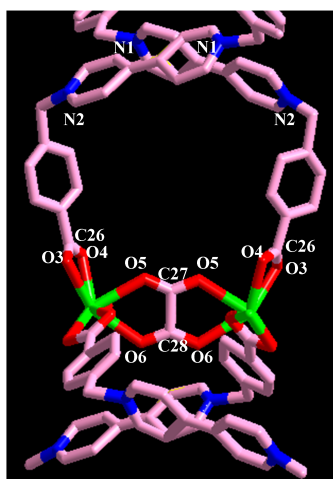


Fig S8. The labeling for charged atoms on the pore aperture. The labeling symbol related to the symmetry operation has been omitted for simplicity.

Table S1 Selected Charges from the DFT Analysis

Groups	Bipyridinium ring	Carboxylate group	Carboxylate group	oxalate group	oxalate group
Atom label	From N1 to N2	O4-C26-O3	O1-C1-O2	O5-C27- O5- O6-C28- O6	O7-C29-O7-O8- C29-O8
Total Charge	+1.175	-0.585	-0.581	-1.184	-1.266

Table S2 The crystallographic data for compound 1

complex	1
Empirical formula	C ₂₈ H ₄₉ DyN ₂ O ₂₃
Formula weight	944.19
Crystal Size (mm)	0.25*0.14*0.09
Crystal System	Monoclinic
Space group	P2/c
a (Å)	12.3743(8)
b (Å)	14.5842(7)
c (Å)	21.9435(15)
α (°)	90.00
β (°)	104.821(4)
γ (°)	90.00
Volume(Å ³)	3828.4(4)
Z	4
Density(cal.)(g/cm ³)	1.638
Absorption	2.042
F(000)	1924
Radiation(Mo Kα)	0.71073 Å
Temperature(K)	123(2)
Theta range (°) for	2.37 to 27.48
Reflections	29788 / 8716
Observed	6609
Final R indices	0.0362
[I>2sigma(I)]	0.0958
R indices (R1)	0.0429
(all data) wR2	0.0989
Goodness-of-fit	0.967

Table S3 Selected bond lengths [Å] and angles [deg] for **1**.

Dy(1)-O(5)	2.374(2)	Dy(1)-O(7)	2.375(2)
Dy(1)-O(1W)	2.392(3)	Dy(1)-O(8)#1	2.401(2)
Dy(1)-O(6)	2.414(2)	Dy(1)-O(4)#2	2.434(2)
Dy(1)-O(2)	2.467(3)	Dy(1)-O(3)#2	2.474(3)
Dy(1)-O(1)	2.475(3)		
O(5)-Dy(1)-O(7)	141.61(8)	O(5)-Dy(1)-O(1W)	78.43(9)
O(7)-Dy(1)-O(1W)	83.22(9)	O(5)-Dy(1)-O(8)#1	134.42(8)
O(7)-Dy(1)-O(8)#1	68.48(7)	O(1W)-Dy(1)-O(8)#1	72.59(9)
O(5)-Dy(1)-O(6)	67.77(8)	O(7)-Dy(1)-O(6)	139.25(8)
O(1W)-Dy(1)-O(6)	76.70(8)	O(8)#1-Dy(1)-O(6)	71.78(8)
O(5)-Dy(1)-O(4)#2	69.46(8)	O(7)-Dy(1)-O(4)#2	73.22(8)
O(1W)-Dy(1)-O(4)#2	74.27(9)	O(8)#1-Dy(1)-O(4)#2	131.41(8)
O(6)-Dy(1)-O(4)#2	131.95(8)	O(5)-Dy(1)-O(2)	75.68(9)
O(7)-Dy(1)-O(2)	131.04(9)	O(1W)-Dy(1)-O(2)	145.26(9)
O(8)#1-Dy(1)-O(2)	111.01(9)	O(6)-Dy(1)-O(2)	72.29(9)
O(4)#2-Dy(1)-O(2)	116.53(9)	O(5)-Dy(1)-O(3)#2	89.86(9)
O(7)-Dy(1)-O(3)#2	74.61(8)	O(1W)-Dy(1)-O(3)#2	126.67(9)
O(8)#1-Dy(1)-O(3)#2	135.71(8)	O(6)-Dy(1)-O(3)#2	144.87(8)
O(4)#2-Dy(1)-O(3)#2	53.14(9)	O(2)-Dy(1)-O(3)#2	76.19(9)
O(5)-Dy(1)-O(1)	128.31(8)	O(7)-Dy(1)-O(1)	84.03(8)
O(1W)-Dy(1)-O(1)	145.35(8)	O(8)#1-Dy(1)-O(1)	72.77(8)
O(6)-Dy(1)-O(1)	92.74(8)	O(4)#2-Dy(1)-O(1)	131.54(9)
O(2)-Dy(1)-O(1)	52.64(9)	O(3)#2-Dy(1)-O(1)	80.00(9)