

Electronic Supporting Information for:

A zinc(II) metal-organic framework based on triazole and
dicarboxylate ligands for selective adsorption of hexane isomers:
synthesis, structure and adsorption property

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1. General

All reagents were purchased from commercial sources and used as received except the Hdmtrz synthesized by the method described previously.^[S1] Powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 powder diffractometer at 40 kV, 40 mA with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Thermogravimetric analyses (TGA) were carried out with a METTLER TOLEPO TGA/SDTA851 analyzer in N₂ with a heating rate of 10 K·min⁻¹. Elemental analyses were done on the Elementar Vario EL III microanalyzer. IR spectra were measured from a KBr pellets on a Nicolet Nexus 470 FT-IR spectrometer in the range 4000 – 400 cm⁻¹. Gas-chromatography (GC) measurements were performed on a SC-200 (China) with a thermal-current detector (TCD). The packed-column (300 × 2 mm) was filled with samples of **1**. Nitrogen (99.999 %) was used as the carrier gas. The temperature of carburettor and column was set to be 443 and 323 K, respectively. Before GC experiments, the column was activated at 333 K with the N₂ flow for 30 min.

(S1) Y. Ling, Z.-X. Chen, Y. M. Zhou, L. H. Weng, D. Y. Zhao, *CrystEngComm*, 2011, doi:10.1039/C0CE00546K

2. Single-crystal X-ray crystallography

Single crystal data of **1** and **1'** were collected at room temperature using a Bruker APEX diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å). Data reduction and cell refinement were performed with the SAINT program, and the absorption correction program SADABS^{S2} was employed to correct the data for absorption effects. The structures were solved by direct methods and refined using full-matrix least-squares treatment (SHELXTL-97)^{S3} with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the phenyl were theoretically added, the hydrogen atoms of the guest molecules were not added because of their disorders.

(S2). Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Goettingen: Goettingen, 1996.

(S3) Sheldrick, G. M. SHELXS 97, Program for Crystal Structure Refinement; University of Goettingen: Goettingen, 1997.

3. Adsorption Measurements

N₂ Sorption isotherm study of **1** was performed volumetrically as a function of relative pressure by using the ASAP 2020. Samples of acetone-exchanged **1** were degassed at 60 °C (increasing rate 10 °C/min from room temperature to 60°C) for 12 hours on degassing station. The temperature for N₂ adsorption experiment was controlled by a refrigerated bath of liquid nitrogen (77 K). Hexane isomer (n-HEX, 3MP, 22DMB) adsorption isotherms (298 K) were measured in a temperature-controlled water bath on IGA gravitometer adsorption apparatus. The samples were acetone-exchanged and degassed at 60 °C (increasing rate: 5 °C/min, outgas rate: 50 mbar/min) for 8 hours.

4. Synthesis

Zn(OAc)₂·2H₂O (0.32 mmol, 0.072 g) and Hdmtrz (0.21 mmol, 0.020 g) was dissolved in DMF (5.0 mL), the solution was stirred for 10 min., and then added to 5.0 mL DMF solution of H₂BDC (0.19 mmol, 0.033 g). The mixture was further stirred for another 10 min. Then the mixture was sealed in a teflonlined stainless steel autoclave (15 mL) and heated at 140 °C for 3 days, followed by cooling down to room temperature. Rod-like crystals were collected by filtration, washed with DMF (5 mL × 3) and acetone (5 mL × 3) respectively, and dried in vacuum. Yields: 51 % based on Zn(II). Elemental analysis calcd. for **1** (C₂₁H₂₅N₄O₁₀Zn₂, 624.19): C, 40.41; H, 4.04; N, 8.98 %. Found: C, 40.50; H, 3.78; N, 9.41 %. IR (KBr pellets): 3449 (br), 1656(s), 1625(s), 1562(s), 1503(m), 1406(s), 1341(m), 1100(w), 1018(w), 826(m), 747(m), 664(w), 595(w), 512(w). Keeping other conditions the same, but replacing DMF by DEF, **1'** was isolated. CCDC: 806626 & 806627 for **1** and **1'**, respectively.

Table S1. Crystal and Structure Refinement Data for **1** and **1'**

	1	1'
Formula	C ₂₁ H ₂₅ N ₄ O ₁₀ Zn ₂	C ₂₂ H ₂₅ N ₄ O ₉ Zn ₂
F.W.	624.19	620.20
Space group	C2/m	C2/m
<i>a</i> (Å)	21.222(19)	20.915(7)
<i>b</i> (Å)	17.716(16)	18.796(6)
<i>c</i> (Å)	14.376(13)	14.350(9)
β (°)	127.821(9)	130.717(4)
<i>V</i> (Å ³)	4270(7)	4276(3)
<i>Z</i>	4	4
<i>D_c</i> (g cm ⁻³)	0.957	0.949
μ (mm ⁻¹)	1.159	1.156
<i>F</i> (000)	1240	1232
<i>T</i> (K)	293	293
Total collected	8880	9422
Unique data, <i>R</i> (int)	3972, 0.084	3948, 0.069
Observed [<i>I</i> > 2σ(<i>I</i>)]	2518	2685
GOF on <i>F</i> ²	1.08	1.12
<i>R</i> , ^a <i>wR</i> ₂ ^b	0.0816, 0.2674	0.0731, 0.2447
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ⁻³)	1.27, -1.02	1.09, -0.98
CCDC.	806626	806627

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

Table S2. Selected bond lengths [Å] and angles [°] for **1** and **1'**

1			
Zn(1)–O(1)	2.013(7)	O(1)–Zn(1)–N(1)	103.9(3)
Zn(1)–N(1)	2.023(10)	O(1)–Zn(1)–O(2) ⁱ	88.6(3)
Zn(1)–O(2) ⁱ	2.045(8)	O(1)–Zn(1)–O(2) ⁱⁱⁱ	157.3(3)
Zn(2)–N(2) ⁱⁱ	2.010(6)	O(1)–Zn(1)–O(1) ^{iv}	86.3(3)
Zn(2)–O3	1.947(8)	O(2) ⁱ –Zn(1)–N(1)	98.8(3)
O(1)–C(1)	1.251(11)	O(2) ⁱ –Zn(1)–O(2) ⁱⁱⁱ	87.6(3)
O(2)–C(1)	1.249(15)	O(3)–Zn(2)–O(3) ^v	102.8(3)
O(3)–C(8)	1.16(2)	O(3)–Zn(2)–N(2) ⁱⁱ	102.6(3)
O(4)–C(8)	1.24(2)	O(3)–Zn(2)–N(2) ^{iv}	120.9(3)
		N(2) ⁱⁱ –Zn(2)–N(2) ^{iv}	108.4(2)
1'			
Zn(1)–O(1)	2.025(6)	O(1)–Zn(1)–N(1)	103.5(3)
Zn(1)–N(1)	2.037(10)	O(1)–Zn(1)–O(2) ⁱ	87.0(2)
Zn(1)–O(2) ⁱ	2.058(7)	O(1)–Zn(1)–O(2) ⁱⁱⁱ	157.3(3)
Zn(2)–O(3)	1.925(7)	O(1)–Zn(1)–O(1) ^{iv}	89.6(2)
Zn(2)–N(2) ⁱⁱ	1.999(5)	O(2) ⁱ –Zn(1)–N(1)	99.2(3)
O(1)–C(1)	1.265(9)	O(2) ⁱ –Zn(1)–O(2) ⁱⁱⁱ	87.5(3)
O(2)–C(1)	1.227(12)	O(3)–Zn(2)–O(3) ^v	100.5(3)
O(3)–C(8)	1.208(17)	O(3)–Zn(2)–N(2) ⁱⁱ	121.5(3)
O(4)–C(8)	1.253(15)	O(3) _b –Zn(2)–N(2) ^{iv}	103.2(2)
		N(2) ⁱⁱ –Zn(2)–N(2) ^{iv}	108.15(18)

Symmetry codes used for **1**: i: 1-x,y,2-z; ii: 1/2-x,1/2-y,2-z; iii: 1-x,1-y,2-z; iv: x,1-y,z; v: -x,y,1-z; vi: -1/2+x,1/2-y,-1+z;

Symmetry codes used for **1'**: i: 1-x,y,-z; ii: 1/2+x,1/2-y,1+z; iii: 1-x,1-y,-z; iv: x,1-y,z; v: 2-x,y,1-z; vi: 3/2-x,1/2-y,-z

Fig.S1 The structural coordination motif of **1** (Hydrogen atoms are omitted for clarity).

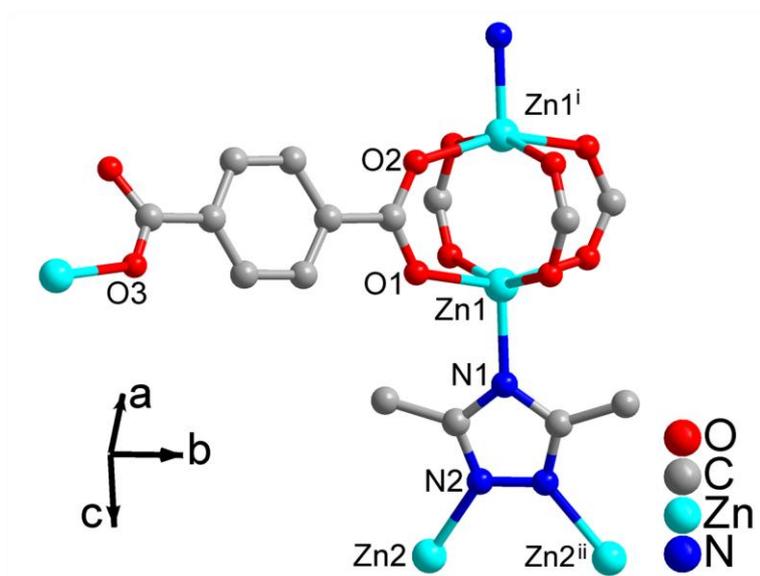


Fig. S2 (a) the PXRD data of **1** compared with simulated data (**a**: simulated data; **g**: as-made sample; **h**: after N₂ adsorption; **i**: after vapor-phase adsorption of n-HEX; **j**: after vapor-phase adsorption of 3MP; **k**: after vapor-phase adsorption of 22DMB); (b) The TG curve of **1**

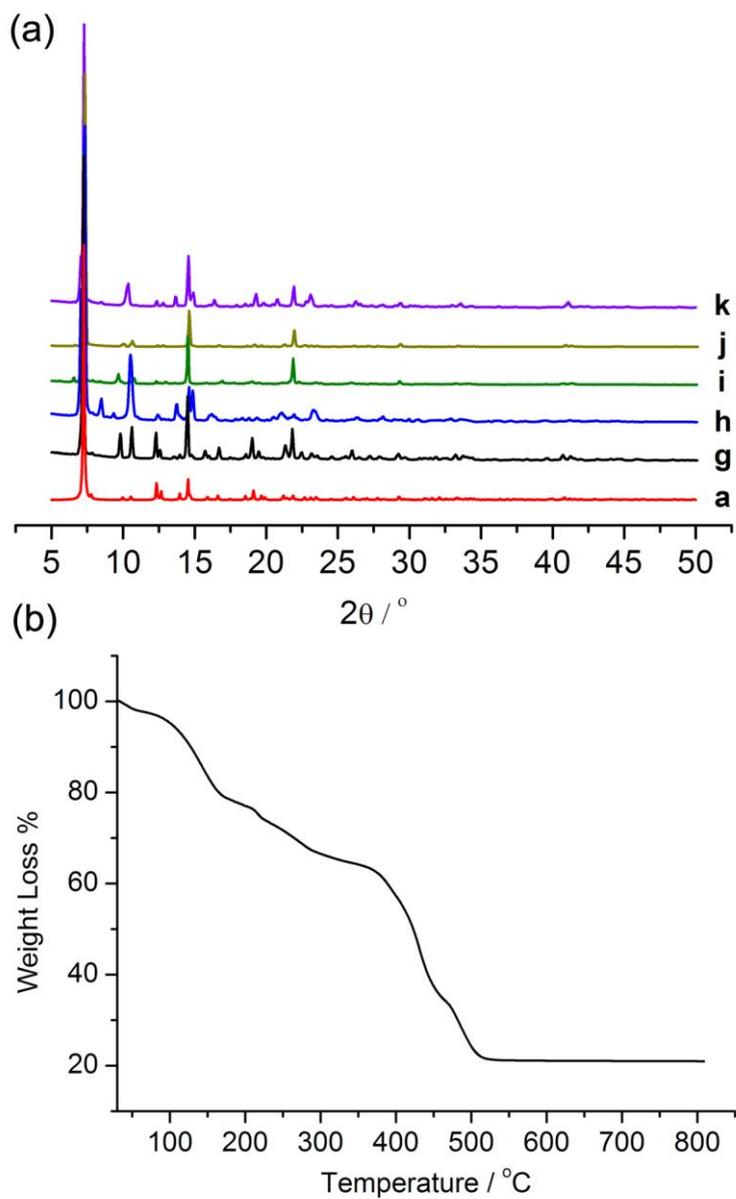


Fig. S3 (a) the N₂ sorption isotherm at 77 K. Å (Insert: the pore width distribution) and (b) the uptake of CO₂ on **1** at 298 K.

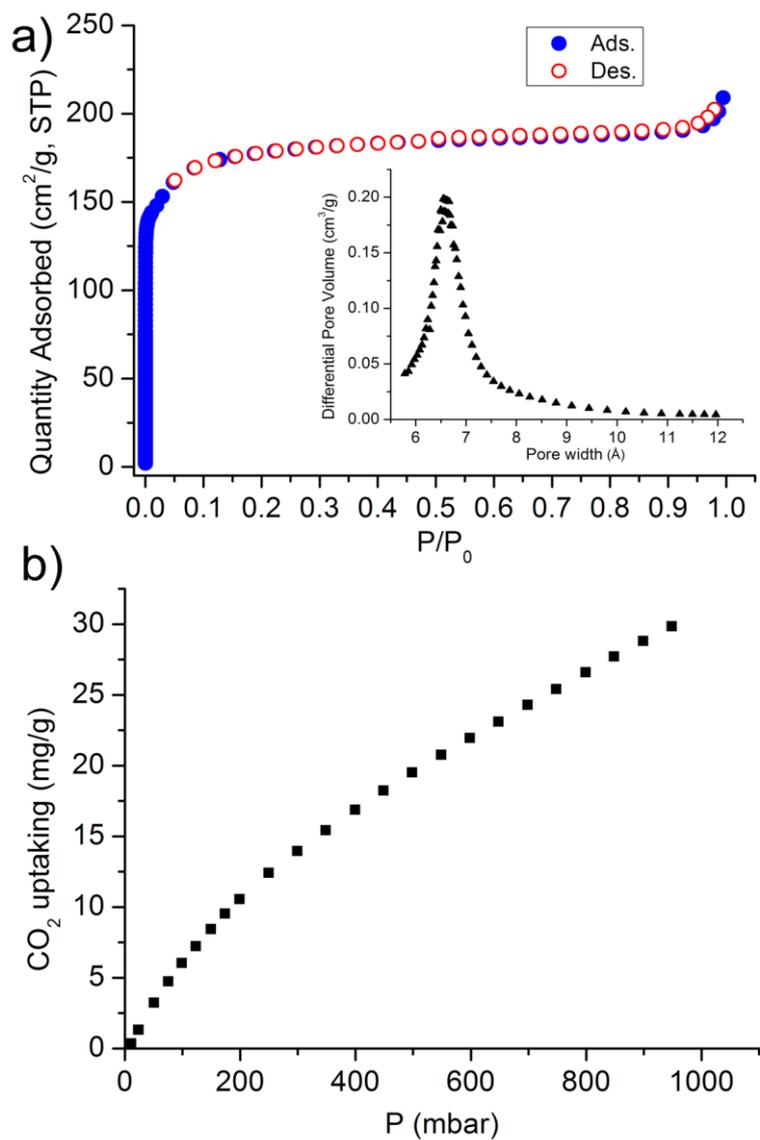


Fig. 4S The framework breathing of **1**

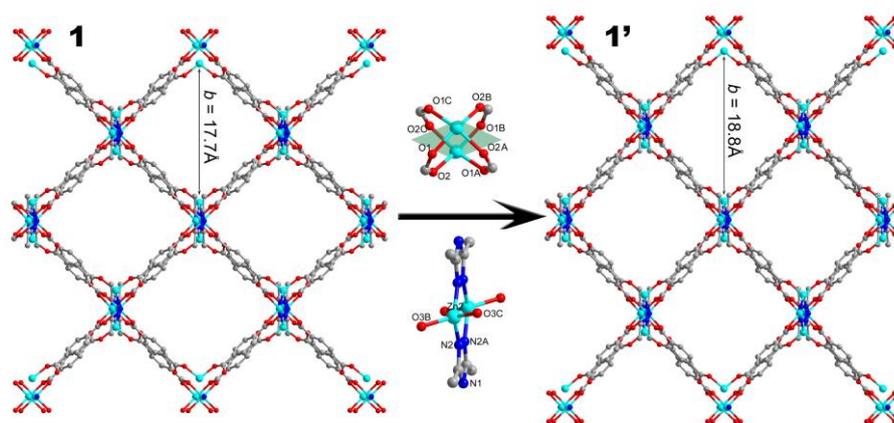


Fig. S5 The increased uptake of *n*-HEX, 3MP, and 22DMB on **1** after changing the activation condition (Activation condition: 75 °C degas for 8 h, the pressure is normalized with their saturated pressure at 298 K for *n*-HEX, 3MP, and 22DMB, respectively)

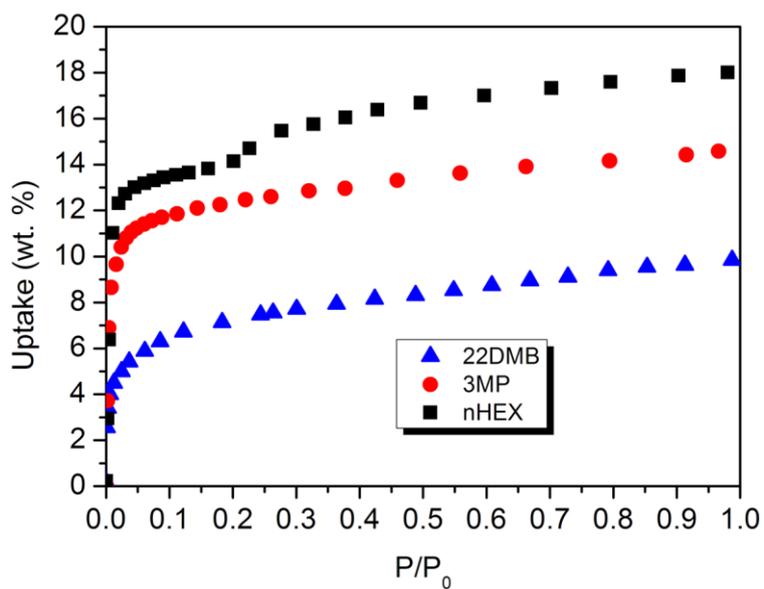
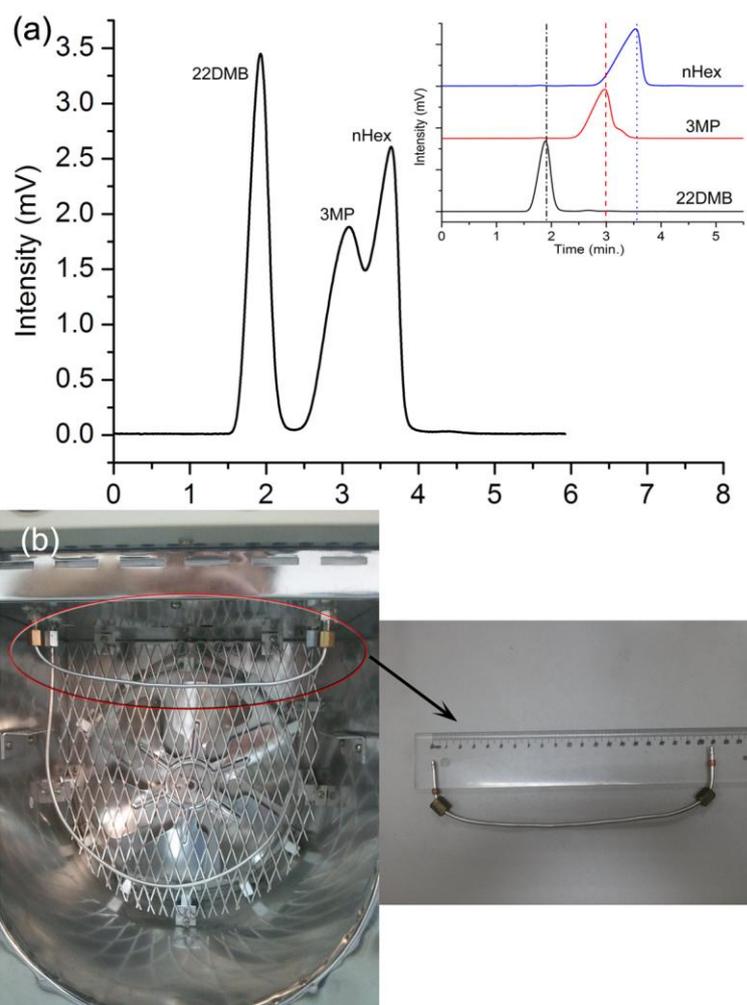


Fig. S6 (a) the GC separation data of hexane isomers on the column packed by sample **1** (300 mm long \times 2 mm i.d.) at 50 °C under the N₂ flow (*n*-HEX: 3-MP: 22-DMB = 1: 1: 1, 6 μ L; insert: single component GC data with an injection of 2 μ L for each); (b) a view of the GC apparatus equipped with a **1** packed column (300 mm long \times 2 mm i.d.) using the thermal conductivity detector.



Entry	residence time (min.)	the number of theoretical plates	efficiency of separation
22DMB	~1.9	313	0
3MP	~2.9	336	1.4
nHex	~3.5	335	0.6