Electronic Supplementary Information (ESI)

A Zn(II) metal-organic framework constructed by a mixed-ligand strategy for CO_2 capture and gas separation

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S1. Calculation procedures of selectivity from IAST

The measured experimental data is excess loadings (q^{ex}) of the pure components CO_2, CH_4 and C_2H_6 for compound **1**, which should be converted to absolute loadings (q) firstly.

$$q = q^{ex} + \frac{pV_{pore}}{ZRT}$$

Here Z is the compressibility factor. The Peng-Robinson equation was used to estimate the value of compressibility factor to obtain the absolute loading, while the measure pore volume 0.509 cm^3 g^{-1} is also necessary.

The dual-site Langmuir-Freundlich equation is used for fitting the isotherm data at 298 K.

$$q = q_{m_1} \times \frac{b_1 \times p^{1/n_1}}{1 + b_1 \times p^{1/n_1}} + q_{m_2} \times \frac{b_2 \times p^{1/n_2}}{1 + b_2 \times p^{1/n_2}}$$

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^{-1}), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol kg-1), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), n_1 and n_2 are the deviations from an ideal homogeneous surface.

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as

$$S = \frac{q_1/q_2}{p_1/p_2}$$

q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

S2. Supporting Figures

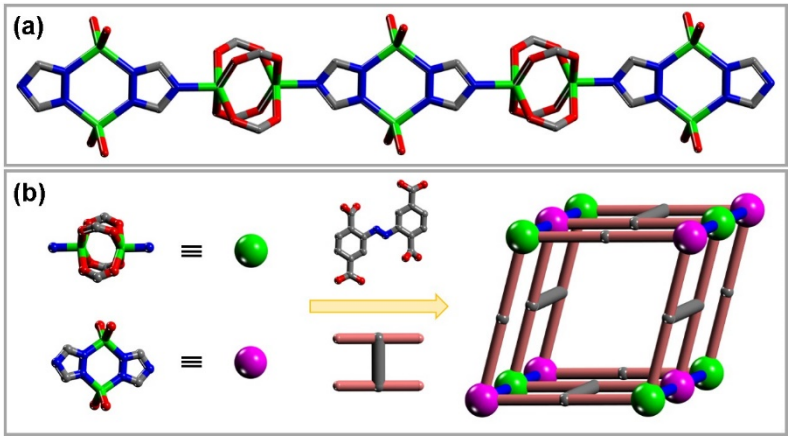


Fig. S1 (a) Two types of inorganic SBUs of compound **1** are alternatively connected to each other to form a 1D chain structure; (b) each 1D chain is further linked by $ABTC^{4-}$ ligands to generate a 3D porous structure.

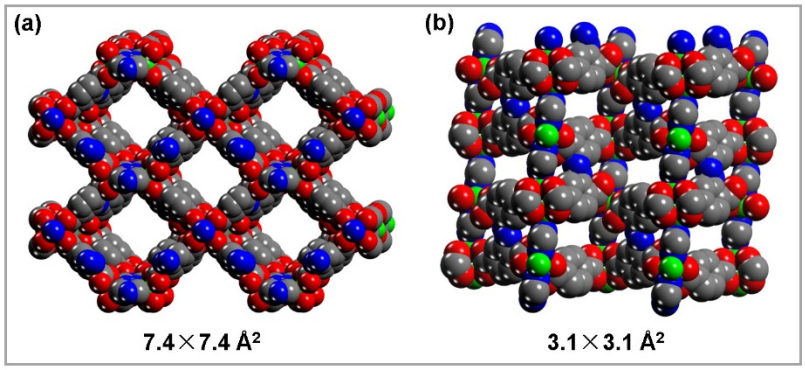


Fig. S2 Space-filling view of the structure of compound **1** showing multiple pores in [110] (a) and [101] direction (b) respectively (regardless of van der Waals radii).

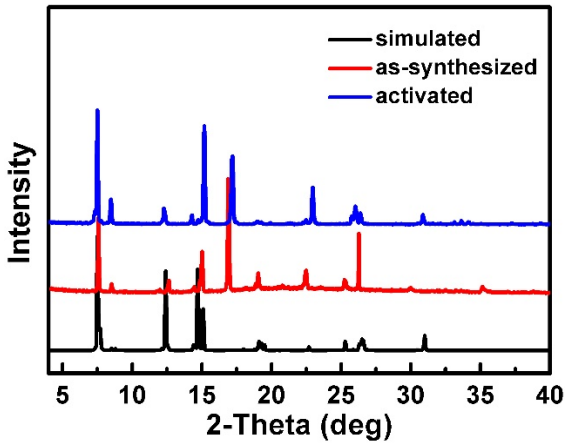


Fig. S3 PXRD patterns of compound **1** for simulated, as-synthesized and EtOH-exchanged samples.

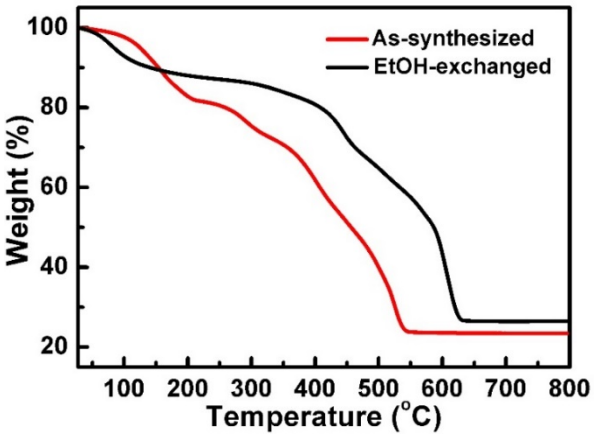


Fig. S4 Thermogravimetric analysis curves of compound **1** for the as-synthesized and EtOH exchanged sample.

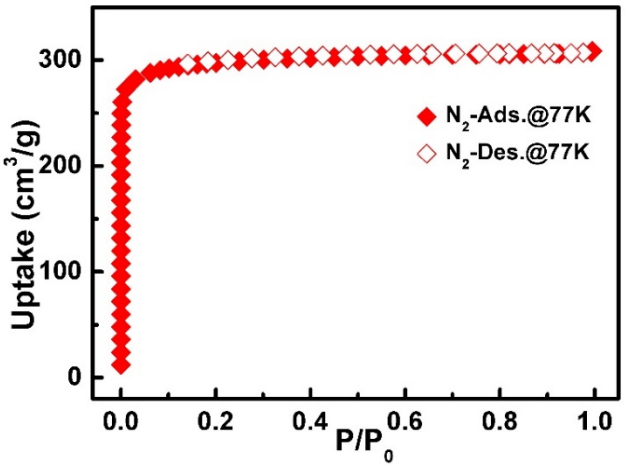


Fig. S5 N_2 isotherms for compound **1** at 77 K under 1 atm.

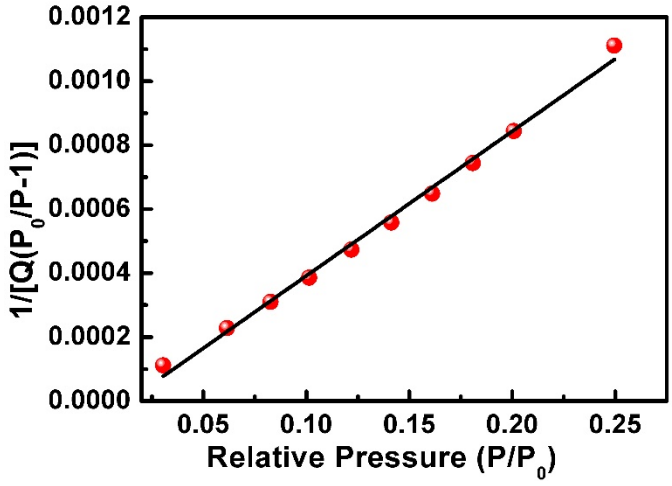


Fig. S6 The linear fitting curve for calculating BET surface area of compound **1**.

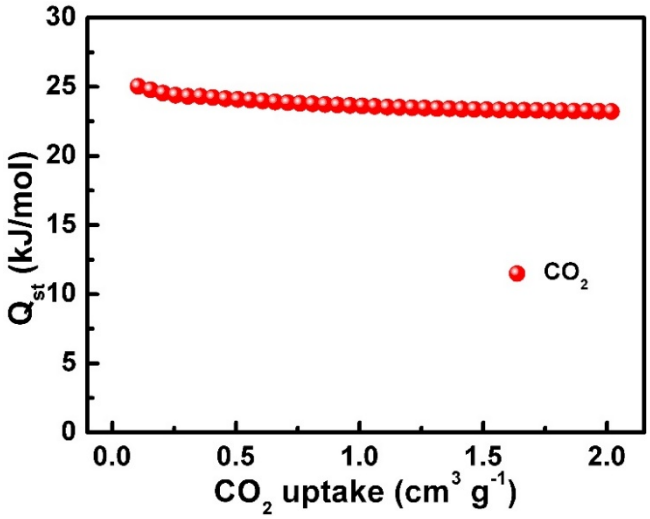


Fig. S7 Q_{st} of CO_2 for compound **1** calculated by MicroActive soft.

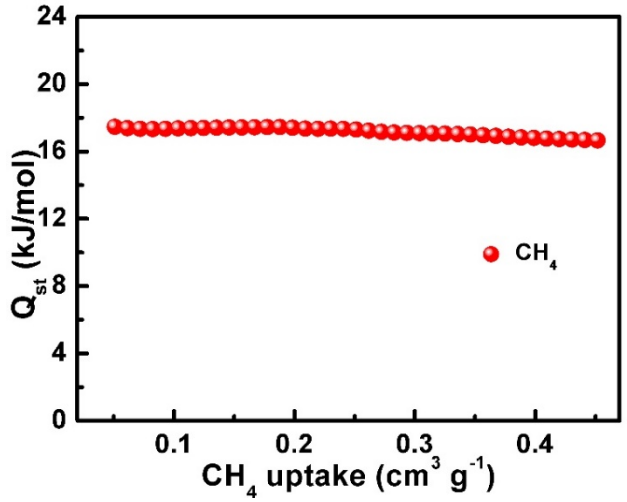


Fig. S8 Q_{st} of CH_4 for compound **1** calculated by MicroActive soft.

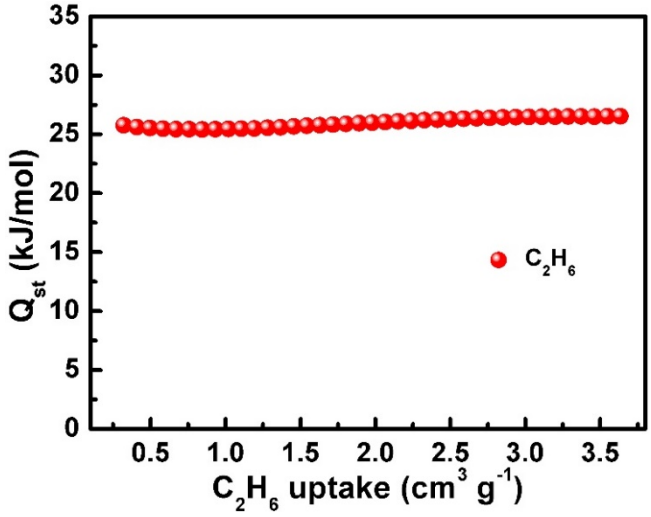


Fig. S9 Q_{st} of C_2H_6 for compound **1** calculated by MicroActive soft.

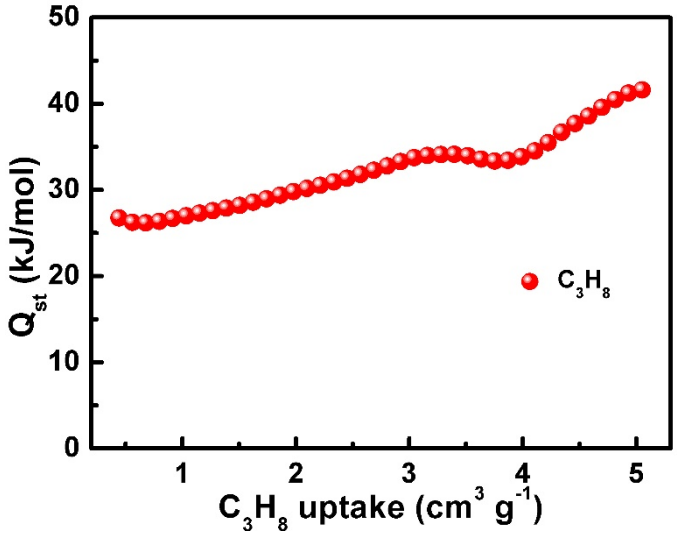


Fig. S10 Q_{st} of C_3H_8 for compound **1** calculated by MicroActive soft.

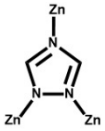
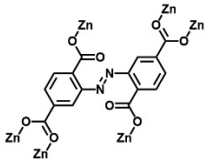
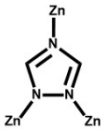
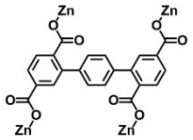
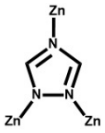
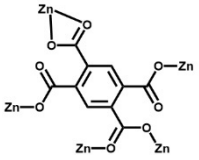
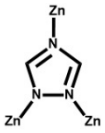
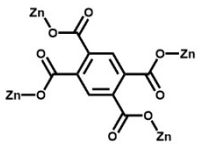
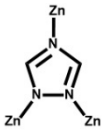
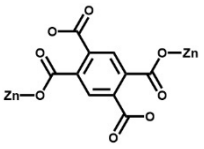
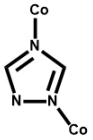
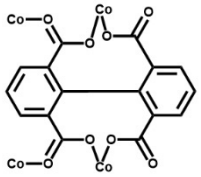
S3. Supporting Tables

Table S1. Crystal data and structure refinements for compound **1**.

Compound	**1**
Formula	$C_{29}H_{37}N_9O_{11}Zn_2$
F_w	818.42
Temp (K)	293(2) K
Wavelength(Å)	0.71073
Crystal system	Monoclinic
Space group	C2/m
a (Å)	20.076(5)
b (Å)	19.744(4)
c (Å)	14.250(3)
α (°)	90
β (°)	133.285(6)
γ (°)	90
V(Å^3)	4112.0(16)
Z	4
D_c (Mg m^{-3})	1.322
Absorption coefficient (mm^{-1})	1.196
F(000)	1100
Limiting indices	-23 <= h <= 23, -23 <= k <= 23, -16 <= l <= 16
Reflections collected/unique (R_{int})	17414 / 5221 [*R*(int) = 0.0560]
Goodness on fit	1.041
Final R indices [I > 2σ(I)]	R_1 = 0.0306, wR_2 = 0.0846
R indices (all data)	R_1 = 0.0454, wR_2 = 0.0917
Largest diff. peak and hole	0.503 and -0.422 e.A^{-3}

$R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $wR_2=[\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

Table S2. Structural properties of the mixed-ligand MOFs containing 1,2,4-triazole ligand and different tetracarboxylic acid coligands reported in publications.

Compound	The coordination mode of 1,2,4-Triazole	The coordination mode of polycarboxylate	Reference
Compound 1			This work
$[Me_2NH_2]_4[Zn_6(qptc)_3(trz)_4]\cdot 6H_2O$			1
$[Zn_7(trz)_6(1,2,4,5\text{-}BTC)_2(H_2O)_6]\cdot 8H_2O$			2
$[Zn_3(bta)(trz)_2(H_2O)_4]\cdot 2H_2O$			3
$[Zn(trz)(H_2betc)_{0.5}]\cdot DMF$			4
$[Co(bta)_{0.5}(Htz)(H_2O)]_n$			5

H_4qptc = terphenyl-2,5,2′5′-tetracarboxylic acid, 1,2,4,5-BTC = 1,2,4,5- benzenetetracarboxylate, btaH_4 = benzene-1,2,4,5-tetracarboxylic acid, H_4betc = pyromellitic acid, H_4bta = biphenyl-2,2′,6,6′-tetracarboxylic acid.

Table S3. Comparison of compound **1** with other Zn-MOFs which exhibits high capture ability for CO_2 at 273 K under 1 bar.

Compound	BET ($m^2 g^{-1}$)	CO_2 ($cm^3 g^{-1}$)	Q_{st} (kJ mol^{-1})	Reference
ZTF-1	355.3	125.2	25.4	6
$[Me_2NH_2][Zn_2(BDPP)(ATZ)]\cdot 4DMF$	1019	124.1	22	7
$[Me_2NH_2][Zn_2(BDPP)(HTZ)]\cdot 4DMF$	1157	107.1	22	7
$Zn(BPZNO_2)$	916	105.3	20.5	8
SNU-4	N.A.	104.9	N.A.	9
$Zn_2(BTetB)$	1370	100.3	N.A.	10
Zn(BPZ)	390	98.6	23.7	11
$Zn_2(C_2O_4)(C_2N_3H\text{-}NH_2)_2$	782	97.2	N.A.	12
Compound 1	976	92.1	25.0	This work
$[Zn_3(Atz)_3(PO_4)]$	470	88.1	32	13
Bio-MOF-1	1630	87.4	24.2	14
$\{[Zn_4(bpydb)_3(datz)_2(H_2O)](DMF)_4(EtOH)_5(H_2O)_8\}_n$	415	80.9	30.33	15
ZnDDQ	N.A.	73.9	N.A.	16
ZIF-20	N.A.	63.1	N.A.	17
TMU-4	517.9	61.1	25.6-27.8	18
TMU-5	502.7	59.15	43.4	18
$Zn_2(TCPB)(DPG)$	740	59.1	N.A.	19
IRMOF-3	1808	53.8	25.1-21.8	20
SNU-9	824	28	N.A.	21

N.A.: Not Available. The article does not list the data.

Table S4. The refined parameters for the Dual-site Langmuir-Freundlich equations fit for the pure isotherms of CO_2, CH_4, C_2H_6 and C_3H_8 for compound **1** at 298 K.

	q_{m1}	b_1	$1/n_1$	q_{m2}	b_2	$1/n_2$	R^2
CO_2	0.23061	0.05142	0.91846	15.71028	9.66954 E-4	1.07083	0.9999
CH_4	5.93217	5.89731E-5	1.44645	0.35949	0.01221	0.96227	0.9999
C_2H_6	6.9505	0.00878	0.96039	0.80574	4.11907 E-4	2.06608	0.9999
C_3H_8	5.20293	0.10768	1.14642	0.09069	3.3422 E-13	6.44967	0.9999

Table S5. Comparison of compound **1** with other MOFs which exhibits high selectivity for CO_2 over CH_4 at 298 K under 1 bar.

Compound	Selectivity	Reference
JLU-Liu33H	13.9	22
ZJNU-55a	13.1	23
Mg-MOF-74	11.5	24
JLU-Liu46	9.8	25
JLU-Liu22	9.4	26
Cu-PEIP	8.9	27
JLU-Liu6	7.4	28
JLU-Liu20	5.9	29
ZJNU-84	5.85	30
Compound 1	5.1	This work
JLU-Liu2	4	31
MOF-5	2.3	32
MIL-53(Al)	2.3	33
$Cu_3(BTC)_2$	2.3	33
UMCM-1	1.8	33
ZIF-8	1.32	33
MOF-177	0.9	33

Reference:

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