Supporting Information

Two Stable Zn-Cluster Based Metal-Organic Frameworks with Breathing Behavior: Synthesis, Structure and Adsorption Properties

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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, C_2H_6 and C_3H_8 for compound **1**, which should be converted to absolute loadings (q) firstly.

$$q = q^{ex} + \frac{pVpore}{ZRT}$$

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 is also necessary.

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

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

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), 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 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

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

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

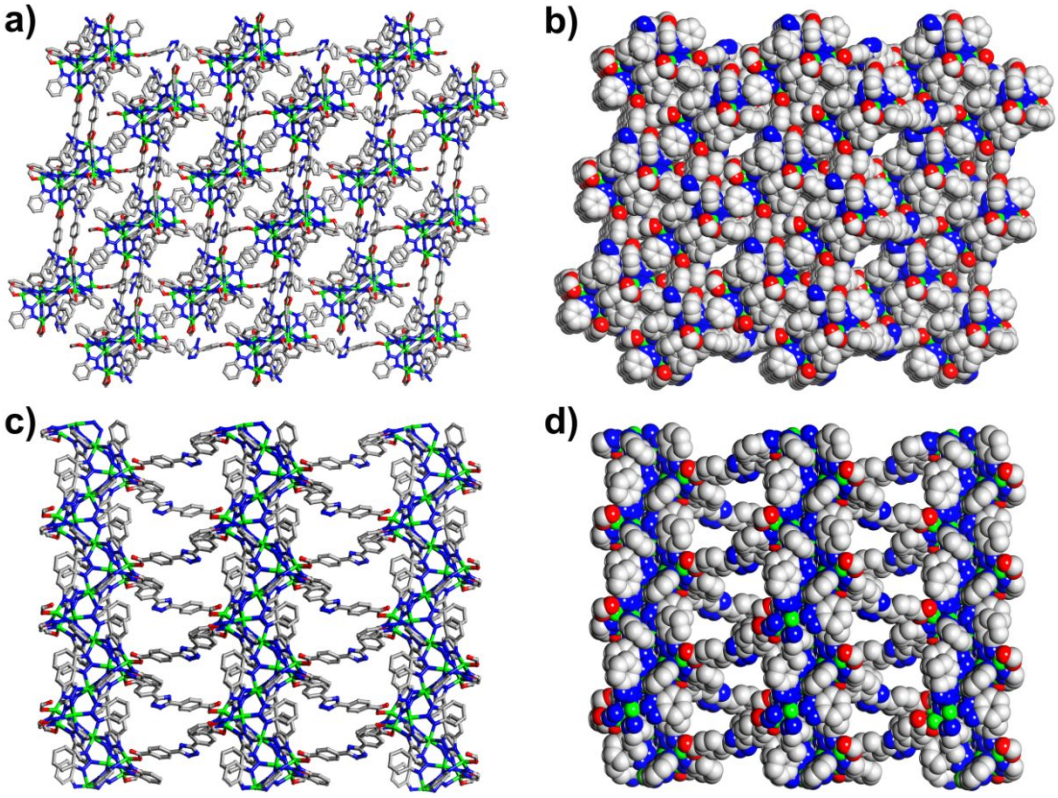

Fig. S1 (a) Ball-and-stick and (b) Space filling views of compound **1**; (c) Ball-and-stick and (d) Space filling views of compound **2**.

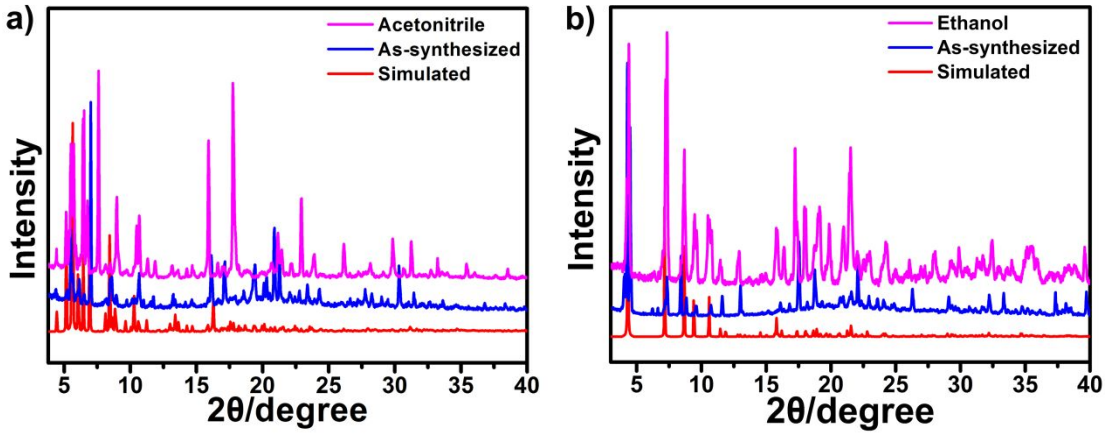

Fig. S2 (a) PXRD patterns of compound **1** for simulated, as-synthesized and acetonitrile exchanged (activated) samples; (b) PXRD patterns of compound **2** for simulated, as-synthesized and ethanol exchanged (activated) samples.

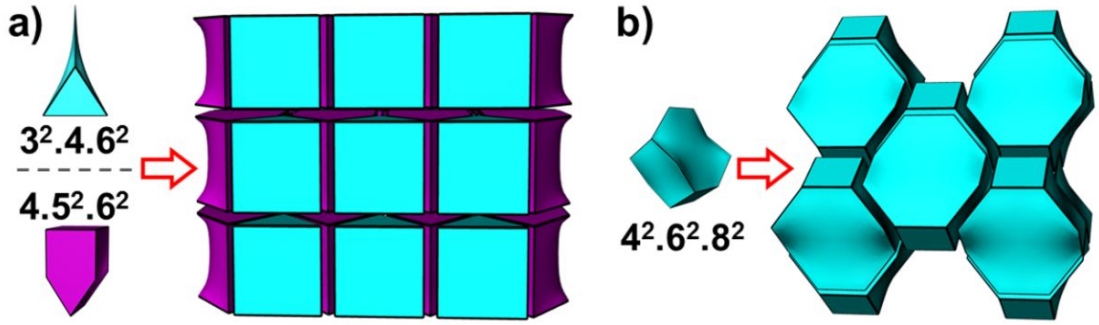

Fig. S3 (a) Topological features of compound **1** displayed by tiling; (b) Topological features of compound **2** displayed by tiling.

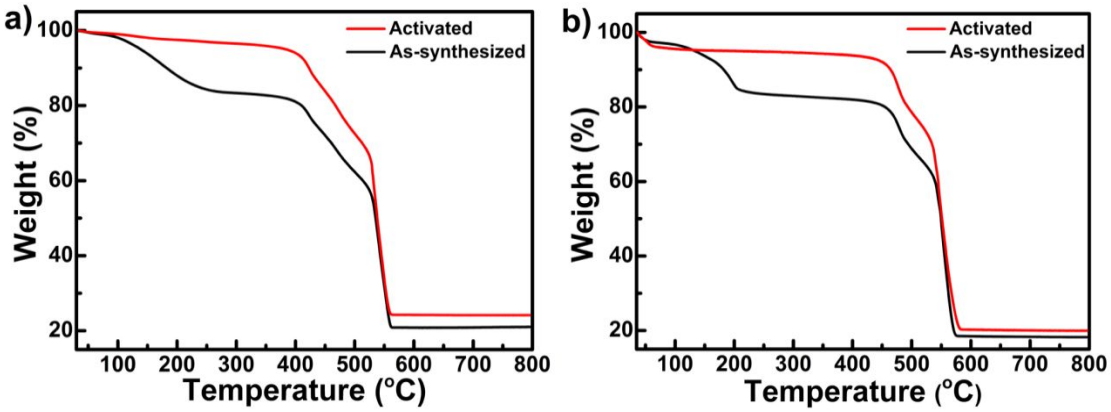

Fig. S4 (a) TGA curves of compound **1** for the as-synthesized and activated samples; (b) TGA curves of compound **2** for the as-synthesized and activated samples.

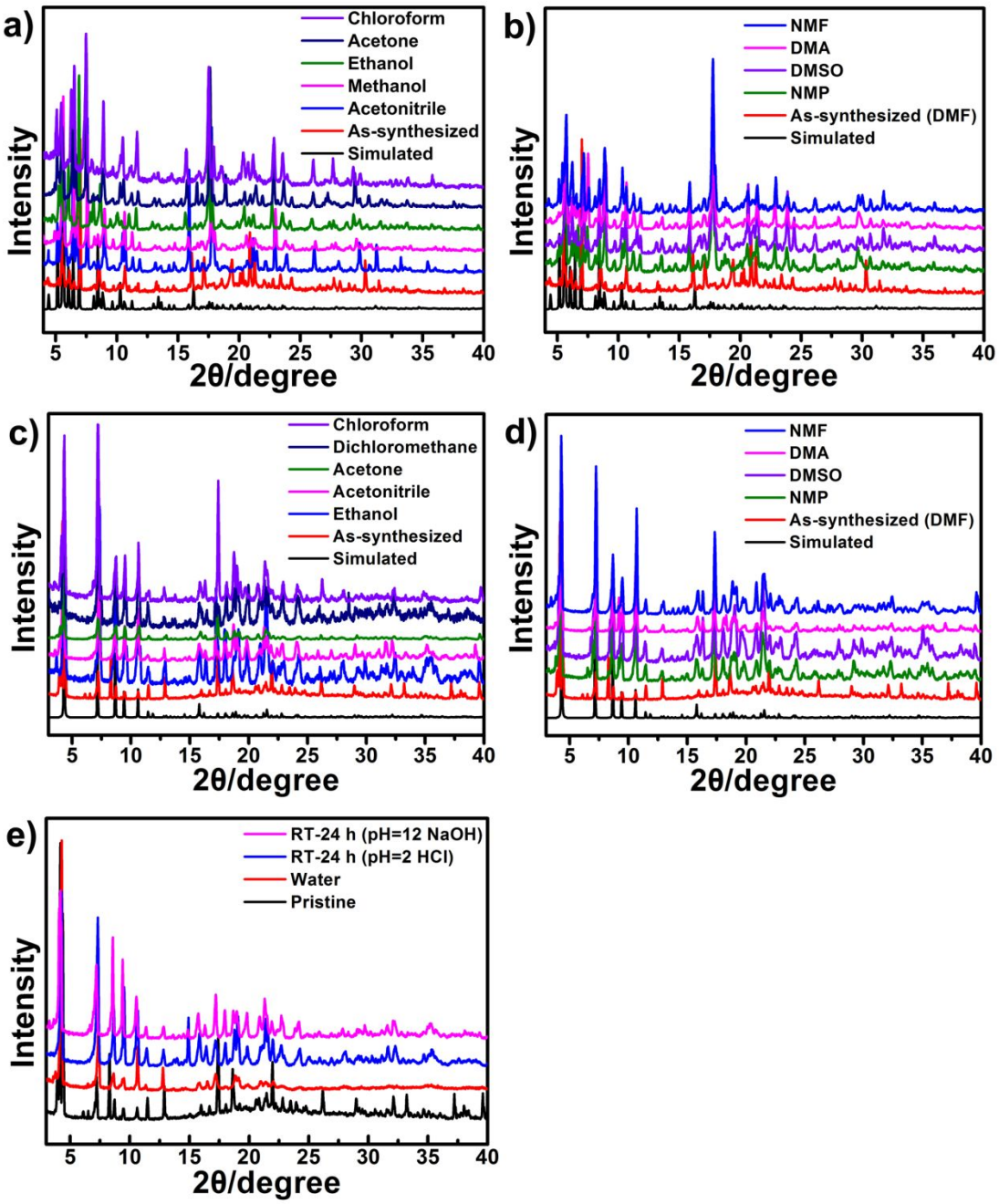

Fig. S5 (a) and (b) PXRD patterns of compound **1** after being soaked in different organic solvents (acetonitrile, methanol, ethanol, acetone, chloroform, DMF, NMP, DMSO, DMA, NMF) for 3 days; (c) and (d) PXRD patterns of compound **2** after being soaked in different organic solvents (ethanol, acetonitrile, acetone, dichlormethane, chloroform, DMF, NMP, DMSO, DMA, NMF) for 3 days; (e) PXRD patterns of compound **2** treated under water, pH = 2 and pH = 12 solutions. All PXRD patterns confirm the chemical stability of compounds **1** and **2** (DMF = N,N-Dimethylformamide, NMP = N-methyl-2-pyrrolidone, DMSO = Dimethyl sulfoxide, DMA = N,N-Dimethylacetamide, NMF = N-Methylformamide).

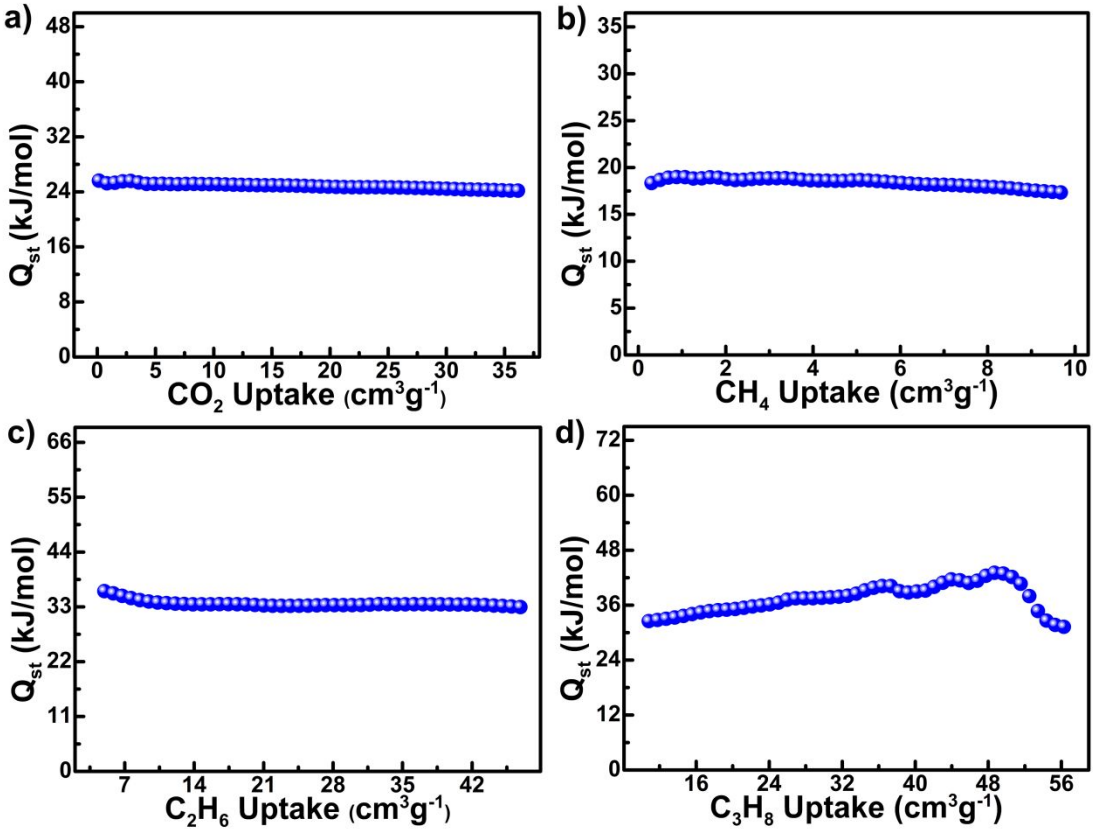

Fig. S6 (a) Q_{st} of CO_2 for compound **1**; (b) Q_{st} of CH_4 for compound **1**; (c) Q_{st} of C_2H_6 for compound **1**; (d) Q_{st} of C_3H_8 for compound **1**.

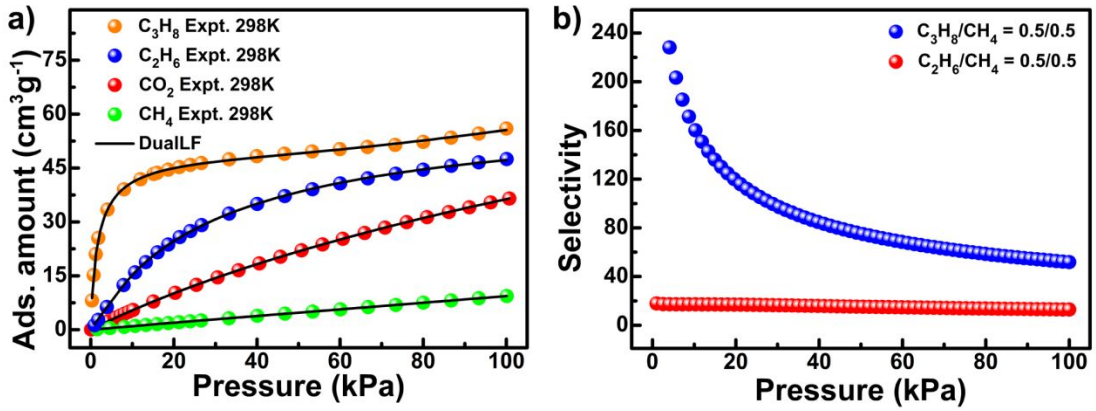

Fig. S7 (a) CO_2, CH_4, C_2H_6 and C_3H_8 adsorption isotherms of compound **1** at 298 K along with the dual-site Langmuir-Freundlich (DSLF) fits; (b) gas mixture adsorption selectivity is predicted by IAST at 298 K and 1 bar for compound **1**.

S3. Supporting Tables

Table S1. Crystal data and structure refinements for compounds **1** and **2**.

Compounds	**1**	**2**
Formula	$C_{132}H_{130}N_{52}O_{28}Zn_9$	$C_{61}H_{54}N_{24}O_7Zn_4$
Mw	3481.21	1496.76
Temp (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*Cc*
a (Å)	16.437(3)	13.686(3)
b (Å)	20.766(4)	40.876(8)
c (Å)	26.410(5)	12.433(3)
α (°)	78.16	90
β (°)	77.79	108.80
γ (°)	76.75	90
V (Å^3)	8459(3)	6585(2)
Z, D_C (Mg/m^3)	2, 1.367	4, 1.510
F(000)	3560	3056
θ range (deg)	1.02 - 25.06	1.00 - 25.09
reflns collected/unique	55418 / 29903	21391/8917
R_{int}	0.0602	0.0414
data/restraints/params	29903/163/1601	8917/142/730
GOF on F^2	1.032	1.010
R^1, wR^2 (I>2σ(I))	0.0648, 0.1684	0.0413, 0.0990
R^1, wR^2 (all data)	0.1327, 0.1838	0.0512, 0.1042

Note: The B-level errors in the checkCIF file of compound **1** due to the carbon atom of the coordinated DMF solvent molecules, which wasn't dealed with anisotropical technology. The other non-hydrogen atoms of DMF cann't be determined by direct methods using SHELXL-2014 program except for one carbon atom. The final formula of compound **1** was derived from crystallographic data combined with elemental and thermogravimetric analysis data.

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

Zn(1)-N(16)	2.139(5)	N(1)-Zn(1)-N(13)	90.9(2)
Zn(1)-N(1)	2.156(5)	N(16)-Zn(1)-N(10)	90.6(2)
Zn(1)-N(13)	2.167(6)	N(1)-Zn(1)-N(10)	89.5(2)
Zn(1)-N(10)	2.194(6)	N(13)-Zn(1)-N(10)	90.6(2)
Zn(1)-N(7)	2.194(6)	N(16)-Zn(1)-N(7)	88.1(2)
Zn(1)-N(4)	2.200(6)	N(1)-Zn(1)-N(7)	89.9(2)
Zn(2)-N(2)	2.146(5)	N(13)-Zn(1)-N(7)	178.2(2)
Zn(2)-N(5)	2.188(6)	N(10)-Zn(1)-N(7)	87.7(2)
Zn(2)-N(8)	2.199(5)	N(16)-Zn(1)-N(4)	89.1(2)
Zn(2)-N(20)	2.214(5)	N(1)-Zn(1)-N(4)	90.9(2)
Zn(2)-N(23)	2.243(6)	N(13)-Zn(1)-N(4)	90.3(2)
Zn(2)-N(26)	2.264(6)	N(10)-Zn(1)-N(4)	179.0(2)
Zn(3)-N(22)	2.030(5)	N(7)-Zn(1)-N(4)	91.4(2)
Zn(3)-N(3)	2.055(6)	N(2)-Zn(2)-N(5)	90.5(2)
Zn(3)-O(2)	2.100(6)	N(2)-Zn(2)-N(8)	89.9(2)
Zn(3)-N(19)	2.116(7)	N(5)-Zn(2)-N(8)	90.8(2)
Zn(3)-O(1)	2.279(7)	N(2)-Zn(2)-N(20)	90.6(2)
Zn(4)-O(12)#1	1.959(9)	N(5)-Zn(2)-N(20)	91.0(2)
Zn(4)-N(25)	1.995(6)	N(8)-Zn(2)-N(20)	178.1(2)
Zn(4)-N(6)	1.999(6)	N(2)-Zn(2)-N(23)	94.5(2)
Zn(4)-N(21)	2.004(6)	N(5)-Zn(2)-N(23)	174.8(2)
Zn(5)-N(24)	2.013(5)	N(8)-Zn(2)-N(23)	90.6(2)
Zn(5)-N(27)	2.024(6)	N(20)-Zn(2)-N(23)	87.5(2)
Zn(5)-O(3)#2	2.055(7)	N(2)-Zn(2)-N(26)	177.8(2)
Zn(5)-N(9)	2.069(6)	N(5)-Zn(2)-N(26)	87.3(2)
Zn(5)-O(4)#2	2.277(7)	N(8)-Zn(2)-N(26)	90.3(2)
Zn(6)-N(17)	2.134(5)	N(20)-Zn(2)-N(26)	89.3(2)
Zn(6)-N(11)	2.185(6)	N(23)-Zn(2)-N(26)	87.7(2)
Zn(6)-N(14)	2.185(5)	N(22)-Zn(3)-N(3)	103.4(2)
Zn(6)-N(35)	2.200(6)	N(22)-Zn(3)-O(2)	155.4(3)
Zn(6)-N(32)	2.256(5)	N(3)-Zn(3)-O(2)	98.4(3)
Zn(6)-N(29)	2.265(6)	N(22)-Zn(3)-N(19)	89.9(2)
Zn(7)-O(9)	1.919(6)	N(3)-Zn(3)-N(19)	94.4(2)
Zn(7)-N(28)	1.991(6)	O(2)-Zn(3)-N(19)	99.9(2)
Zn(7)-N(31)	2.001(6)	N(22)-Zn(3)-O(1)	96.9(2)
Zn(7)-N(12)	2.030(6)	N(3)-Zn(3)-O(1)	154.4(2)
Zn(8)-N(34)	2.026(5)	O(2)-Zn(3)-O(1)	59.2(2)
Zn(8)-N(30)	2.055(6)	N(19)-Zn(3)-O(1)	101.1(2)
Zn(8)-O(7)#3	2.082(5)	O(12)#1-Zn(4)-N(25)	136.3(3)
Zn(8)-N(15)	2.134(6)	O(12)#1-Zn(4)-N(6)	116.0(3)
Zn(8)-O(13)	2.388(7)	O(12)#1-Zn(4)-N(21)	102.2(3)
Zn(8)-O(8)#3	2.260(6)	N(25)-Zn(4)-N(6)	96.8(2)
Zn(9)-N(36)	2.064(5)	N(6)-Zn(4)-N(21)	102.2(3)

Zn(9)-N(18)	2.047(5)	N(25)-Zn(4)-N(21)	97.8(2)
Zn(9)-O(5)	2.079(5)	N(24)-Zn(5)-N(27)	97.6(2)
Zn(9)-N(33)	2.170(6)	N(24)-Zn(5)-O(3)#2	150.1(3)
Zn(9)-O(6)	2.240(6)	N(27)-Zn(5)-O(3)#2	93.6(3)
Zn(9)-N(38)#4	2.382(6)	N(24)-Zn(5)-N(9)	97.0(2)
O(3)-Zn(5)#3	2.055(7)	N(27)-Zn(5)-N(9)	100.4(2)
O(4)-Zn(5)#3	2.277(7)	O(3)#2-Zn(5)-N(9)	108.1(2)
O(7)-Zn(8)#2	2.082(5)	N(24)-Zn(5)-O(4)#2	101.0(2)
O(8)-Zn(8)#2	2.260(6)	N(27)-Zn(5)-O(4)#2	149.0(2)
O(12)-Zn(4)#5	1.959(9)	O(3)#2-Zn(5)-O(4)#2	58.9(3)
N(16)-Zn(1)-N(1)	177.9(2)	N(9)-Zn(5)-O(4)#2	101.7(2)
N(16)-Zn(1)-N(13)	91.2(2)	N(17)-Zn(6)-N(11)	88.3(2)
N(17)-Zn(6)-N(14)	91.1(2)	N(11)-Zn(6)-N(14)	91.6(2)
N(17)-Zn(6)-N(35)	96.3(2)	N(11)-Zn(6)-N(35)	174.6(2)
N(14)-Zn(6)-N(35)	91.2(2)	N(17)-Zn(6)-N(32)	89.2(2)
N(11)-Zn(6)-N(32)	91.8(2)	N(14)-Zn(6)-N(32)	176.5(2)
N(35)-Zn(6)-N(32)	85.4(2)	N(17)-Zn(6)-N(29)	174.8(2)
N(11)-Zn(6)-N(29)	86.7(2)	N(14)-Zn(6)-N(29)	90.3(2)
N(35)-Zn(6)-N(29)	88.7(2)	N(32)-Zn(6)-N(29)	89.7(2)
O(9)-Zn(7)-N(28)	133.7(3)	O(9)-Zn(7)-N(31)	116.3(3)
N(28)-Zn(7)-N(31)	99.2(2)	O(9)-Zn(7)-N(12)	102.4(3)
N(28)-Zn(7)-N(12)	96.6(2)	N(31)-Zn(7)-N(12)	103.7(2)
N(34)-Zn(8)-N(30)	103.0(2)	N(34)-Zn(8)-O(7)#3	157.3(3)
N(30)-Zn(8)-O(7)#3	94.0(2)	N(34)-Zn(8)-N(15)	93.0(2)
N(30)-Zn(8)-N(15)	94.1(2)	O(7)#3-Zn(8)-N(15)	100.8(2)
N(34)-Zn(8)-O(8)#3	100.6(2)	N(30)-Zn(8)-O(8)#3	152.2(2)
O(7)#3-Zn(8)-O(8)#3	59.6(2)	N(15)-Zn(8)-O(8)#3	99.0(2)
N(34)-Zn(8)-O(13)	79.9(2)	N(30)-Zn(8)-O(13)	84.2(2)
O(7)#3-Zn(8)-O(13)	87.1(2)	N(15)-Zn(8)-O(13)	172.1(2)
O(8)#3-Zn(8)-O(13)	85.9(2)	N(18)-Zn(9)-N(36)	105.2(2)
N(18)-Zn(9)-O(5)	96.4(2)	N(36)-Zn(9)-O(5)	157.9(2)
N(18)-Zn(9)-N(33)	93.5(2)	N(36)-Zn(9)-N(33)	86.4(2)
O(5)-Zn(9)-N(33)	97.2(2)	N(18)-Zn(9)-O(6)	154.8(2)
N(36)-Zn(9)-O(6)	97.8(2)	O(5)-Zn(9)-O(6)	60.1(2)
N(33)-Zn(9)-O(6)	98.1(2)	N(18)-Zn(9)-N(38)#4	85.4(2)
N(36)-Zn(9)-N(38)#4	84.3(2)	O(5)-Zn(9)-N(38)#4	92.9(2)
N(33)-Zn(9)-N(38)#4	169.92(19)	O(6)-Zn(9)-N(38)#4	86.9(2)
N(1)-N(2)-Zn(2)	125.1(4)	N(3)-N(2)-Zn(2)	122.9(4)
N(2)-N(3)-Zn(3)	123.7(4)	N(5)-N(4)-Zn(1)	123.7(5)
N(4)-N(5)-Zn(2)	125.6(5)	N(6)-N(5)-Zn(2)	122.3(4)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z+1 #2 x+1,y-1,z #3 x-1,y+1,z #4 x,y-1,z #5 x+1,y,z-1 #6 x,y+1,z

Table S3. Selected bond lengths [Å] and angles [°] for compound **2**.

Zn(1)-N(17)	2.137(5)	N(17)-Zn(1)-N(8)	88.09(18)
Zn(1)-N(8)	2.203(5)	N(17)-Zn(1)-N(14)	93.91(18)
Zn(1)-N(14)	2.217(5)	N(8)-Zn(1)-N(14)	175.2(2)
Zn(1)-N(2)	2.219(4)	N(17)-Zn(1)-N(2)	172.2(2)
Zn(1)-N(11)	2.220(5)	N(8)-Zn(1)-N(2)	85.29(18)
Zn(1)-N(5)	2.235(5)	N(14)-Zn(1)-N(2)	93.01(17)
Zn(2)-O(1)	1.897(12)	N(17)-Zn(1)-N(11)	95.75(19)
Zn(2)-O(1')	1.920(12)	N(8)-Zn(1)-N(11)	91.3(2)
Zn(2)-N(13)	2.008(5)	N(14)-Zn(1)-N(11)	84.10(18)
Zn(2)-N(4)	2.018(5)	N(2)-Zn(1)-N(11)	88.64(19)
Zn(2)-N(1)	2.044(5)	N(17)-Zn(1)-N(5)	87.57(18)
Zn(3)-O(3)#1	1.984(6)	N(8)-Zn(1)-N(5)	95.7(2)
Zn(3)-N(10)	2.003(5)	N(14)-Zn(1)-N(5)	88.79(18)
Zn(3)-N(9)	2.014(5)	N(2)-Zn(1)-N(5)	88.88(18)
Zn(3)-N(3)	2.017(5)	N(11)-Zn(1)-N(5)	172.34(18)
Zn(3)-O(4)#1	2.383(7)	O(1)-Zn(2)-O(1')	18.4(4)
Zn(4)-N(6)	2.165(4)	O(1)-Zn(2)-N(13)	118.1(4)
Zn(4)-N(16)	2.168(5)	O(1')-Zn(2)-N(13)	135.7(3)
Zn(4)-N(15)#2	2.172(4)	O(1)-Zn(2)-N(4)	137.2(4)
Zn(4)-N(18)#2	2.184(5)	O(1')-Zn(2)-N(4)	120.1(4)
Zn(4)-N(12)#2	2.187(5)	N(13)-Zn(2)-N(4)	96.1(2)
Zn(4)-N(7)	2.192(5)	O(1)-Zn(2)-N(1)	97.7(4)
O(3)-Zn(3)#3	1.984(6)	O(1')-Zn(2)-N(1)	96.0(3)
O(4)-Zn(3)#3	2.383(7)	N(13)-Zn(2)-N(1)	103.60(19)
N(12)-Zn(4)#4	2.187(4)	N(4)-Zn(2)-N(1)	98.35(19)
N(15)-Zn(4)#4	2.172(4)	O(3)#1-Zn(3)-N(10)	113.8(2)
N(18)-Zn(4)#4	2.184(5)	O(3)#1-Zn(3)-N(9)	99.8(2)
N(10)-Zn(3)-N(9)	96.7(2)	O(3)#1-Zn(3)-N(3)	138.8(2)
N(10)-Zn(3)-N(3)	100.5(2)	N(9)-Zn(3)-N(3)	98.1(2)
O(3)#1-Zn(3)-O(4)#1	58.2(2)	N(10)-Zn(3)-O(4)#1	104.2(2)
N(9)-Zn(3)-O(4)#1	154.3(2)	N(3)-Zn(3)-O(4)#1	92.7(2)
N(6)-Zn(4)-N(16)	87.66(16)	N(6)-Zn(4)-N(15)#2	90.44(17)
N(16)-Zn(4)-N(15)#2	94.17(17)	N(6)-Zn(4)-N(18)#2	85.51(17)
N(16)-Zn(4)-N(18)#2	168.72(17)	N(15)#2-Zn(4)-N(18)#2	94.84(18)
N(6)-Zn(4)-N(12)#2	176.09(18)	N(16)-Zn(4)-N(12)#2	91.34(18)
N(15)#2-Zn(4)-N(12)#2	85.87(17)	N(18)#2-Zn(4)-N(12)#2	96.06(18)
N(6)-Zn(4)-N(7)	99.16(17)	N(16)-Zn(4)-N(7)	88.85(18)
N(15)#2-Zn(4)-N(7)	170.06(18)	N(18)#2-Zn(4)-N(7)	83.40(18)
N(12)#2-Zn(4)-N(7)	84.60(18)	N(2)-N(1)-Zn(2)	119.7(3)
N(1)-N(2)-Zn(1)	122.5(4)	N(3)-N(2)-Zn(1)	125.9(4)
N(2)-N(3)-Zn(3)	118.7(4)	N(5)-N(4)-Zn(2)	118.2(4)
N(6)-N(5)-Zn(1)	125.1(3)	N(4)-N(5)-Zn(1)	123.3(4)
N(5)-N(6)-Zn(4)	122.7(3)	N(8)-N(7)-Zn(4)	123.2(4)

N(7)-N(8)-Zn(1)	124.9(4)	N(9)-N(8)-Zn(1)	123.9(4)
N(8)-N(9)-Zn(3)	118.2(4)	N(11)-N(10)-Zn(3)	121.3(4)
N(12)-N(11)-Zn(1)	124.9(3)	N(10)-N(11)-Zn(1)	123.9(4)
N(11)-N(12)-Zn(4)#4	121.6(4)	N(14)-N(13)-Zn(2)	120.1(4)
N(15)-N(14)-Zn(1)	125.6(3)	N(13)-N(14)-Zn(1)	122.9(4)
N(14)-N(15)-Zn(4)#4	121.8(3)	N(17)-N(16)-Zn(4)	124.1(3)
N(18)-N(17)-Zn(1)	123.4(4)	N(16)-N(17)-Zn(1)	125.1(4)
N(17)-N(18)-Zn(4)#4	125.6(4)		

Symmetry transformations used to generate equivalent atoms:
#1 x-3/2,-y+1/2,z-1/2 #2 x,-y,z-1/2 #3 x+3/2,-y+1/2,z+1/2 #4 x,-y,z+1/2

Table S4. Comparison of BET surface area, N_2 (77 K) and CO_2 adsorption (273 K) of compound **1** with Zn-cluster based MOFs materials.

Compound	BET ($m^2\ g^{-1}$)	N_2 ($cm^3\ g^{-1}$)	CO_2 ($cm^3\ g^{-1}$)	Ref.
$[Zn_9(btz)_{12}(atdbc)_3(DMF)]\cdot 12H_2O\cdot 3DMF$	680	213	61	This work
$[Zn_9Cl_2(bcpt)_2(Me_2bta)_{12}]\cdot 0.5DMF$	206	-	-	1
$[Zn_9(L2)_2(btz)_{12}]\cdot 14H_2O$	293	-	46	2
$[Zn_5(L1)(btz)_6(H_2O)(NO_3)]\cdot 5DMA\cdot 5H_2O$	421	-	42	2
DMOF-7	-	142	-	3
DMOF-8	-	110	-	3
$Zn_5(BTA)_6(TDA)_2$ 15DMF $8H_2O$	414	-	~55	4
$[Zn_5(btz)_6(bdc)_2(H_2O)_2]\cdot 7DMA$	850	266	-	5
$Zn_3(btz)_2(bdc)_2\cdot x(DMA)$	210	-	50	6
TPMOF-7(Fe)a	879	291	-	7
JLU-Liu33	-	319	32	8

"-"represent the data are not listed; "~"represent approximate values are obtained from the figures of publication.

Table S5. 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
compound **1**	CO_2	2.12039	0.0119	0.9698	3.00794	4.29292E-4	1.35561	1
	CH_4	6.38324	2.62085E-4	1.18102	0.06462	0.03011	1.1257	0.99998
	C_2H_6	2.63922	0.02877	1.02167	0.1	4.28975E-4	3.65977	0.99989
	C_3H_8	1.7032	1.2257E-6	2.61518	2.25676	0.58336	0.86787	0.99935

References:

(1) Li, Y.-W.; He, K.-H.; Bu, X.-H. Bottom-up Assembly of a Porous MOF Based on Nanosized Nonanuclear Zinc Precursors for Highly Selective Gas Adsorption. *J. Mater. Chem. A* **2013**, *1*, 4186-4189.

(2) Chen, Y. Q.; Qu, Y. K.; Li, G. R.; Zhuang, Z. Z.; Chang, Z.; Hu, T. L.; Xu, J.; Bu, X. H. Zn(II)-Benzotriazolate Clusters Based Amide Functionalized Porous Coordination Polymers with High CO_2 Adsorption Selectivity. *Inorg. Chem.* **2014**, *53*, 8842-8844.

(3) Lan, Y. Q.; Li, S. L.; Jiang, H. L.; Xu, Q. Tailor-Made Metal-Organic Frameworks from Functionalized Molecular Building Blocks and Length-Adjustable Organic Linkers by Stepwise Synthesis. *Chem. Eur. J.* **2012**, *18*, 8076-8083.

(4) Zhang, Z. J.; Xiang, S. C.; Chen, Y. Sheng.; Ma, S. Q.; Lee, Y.; Phely-Bobin, T.; Chen, B. L. A Robust Highly Interpenetrated Metal-Organic Framework Constructed from Pentanuclear Clusters for Selective Sorption of Gas Molecules. *Inorg. Chem.* **2010**, *49*, 8444-8448.

(5) Wang, X. L.; Qin, C.; Wu, S. X.; Shao, K. Z.; Lan, Y. Q.; Wang, S.; Zhu, D. X.; Su, Z. M.; Wang, E. B. Bottom-up Synthesis of Porous Coordination Frameworks: Apical Substitution of a Pentanuclear Tetrahedral Precursor. *Angew. Chem., Int. Ed.* **2009**, *48*, 5291-5295.

(6) Jiang, Z. Q.; Jiang, G. Y.; Wang, F.; Zhao, Z.; Zhang, J. Controlling State of Breathing of Two Isoreticular Microporous Metal-Organic Frameworks with Triazole Homologues. *Chem. Eur. J.* **2012**, *18*, 10525-10529.

(7) Qin, J. S.; Du, D. Y.; Li, M.; Lian, X. Z.; Dong, L. Z.; Bosch, M.; Su, Z. M.; Zhang, Q.; Li, S. L.; Lan, Y. Q.; Yuan, S.; Zhou, H. C. Derivation and Decoration of Nets with Trigonal-Prismatic Nodes: A Unique Route to Reticular Synthesis of Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138*, 5299-5307.

(8) Sun, X.; Yao, S.; Li, G.; Zhang, L.; Huo, Q.; Liu, Y. A Flexible Doubly Interpenetrated Metal-Organic Framework with Breathing Behavior and Tunable Gate Opening Effect by Introducing Co^{2+} into Zn_4O Clusters. *Inorg. Chem.* **2017**, *56*, 6645-6651.