Electronic Supplementary Information (ESI) for:

Novel Iso-Reticular Zn(II) Metal-Organic Frameworks constructed by Trinuclear-Triangular and Paddle-Wheel Units: Synthesis, Structure and Gas Adsorption

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Table S1. Crystal and Structure Refinement Data for **MAC-4** and **MAC-4-OH**

	MAC-4	**MAC-4-OH**
Formula	$C_{39}H_{40}N_{10}O_{15}Zn_5$	$C_{39}H_{48}N_{10}O_{22}Zn_5$
F.W.	1215.66	1335.72
Space group	Pnma	Pnma
a(Å)	15.508(11)	15.585(4)
b(Å)	19.220(13)	19.237(5)
c(Å)	25.211(17)	25.305(7)
V(Å^3)	7515(9)	7587(3)
Z	4	4
Dc (g cm^{-3})	1.075	1.169
μ(mm^{-1})	1.621	1.618
F(000)	2456	2712
T(K)	293(2)	293(2)
Total collected	36894	34119,
Unique data, R(int)	6992, 0.138	7018, 0.202
Observed [I > 2σ(I)]	3438	3487
GOF on F^2	0.89	1.04
R_1,[a] wR_2[b]	0.0551, 0.1700	0.1067, 0.3441
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	-0.55, 0.84	-1.04, 1.49

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

Table S2. Selected bond lengths [Å] and angles [°] for **MAC-4 and MAC-4-OH**

MAC-4			
Zn1–O7	2.024(3)	Zn1–N1	2.013(5)
Zn1–N4	2.037(5)	Zn1–O5 ^{i}	2.263(9)
Zn1–O6^{i}	2.034(9)	Zn2–O1	2.063(5)
Zn2–O3	2.046(5)	Zn2–N3	2.028(6)
Zn2–O2^{ii}	2.055(6)	Zn2–O4 ^{ii}	2.047(5)
Zn3–O7	1.990(5)	Zn3–N2	1.989(6)
Zn3–N5^{iii}	1.949(6)		
O7–Zn1–N1	97.0(2)	O7–Zn1–N4	93.80(19)
O5^{i}–Zn1–O7	88.4(2)	O6 ^{i}–Zn1–O7	135.0(3)
N1–Zn1–N4	110.1(2)	O5 ^{i}–Zn1–N1	102.6(2)
O6 ^{i}–Zn1–N1	117.0(3)	O5 ^{i}–Zn1–N4	146.7(2)
O6 ^{i}–Zn1–N4	100.5(3)	O1–Zn2–O3	87.4(2)
O1–Zn2–N3	99.4(2)	O1–Zn2–O2^{ii}	158.4(2)
O1–Zn2–O4 ^{ii}	87.6(2)	O3–Zn2–N3	99.9(2)
O2 ^{ii}–Zn2–O3	87.5(2)	O3–Zn2–O4 ^{ii}	159.1(2)
O2 ^{ii}–Zn2–N3	102.2(2)	O4 ^{ii}–Zn2–N3	101.0(2)
O2 ^{ii}–Zn2–O4 ^{ii}	89.7(2)	O7–Zn3–N2	98.10(16)
O7–Zn3–N5^{iii}	112.2(3)	N2–Zn3–N5 ^{iii}	117.80(17)
N2–Zn3–N2^{iv}	109.3(2)		
2			
Zn1–O7	2.021(6)	Zn1–N2	2.021(8)
Zn1–O5^{i}	2.367(14)	Zn1–O6 ^{i}	2.002(13)
Zn1–N5^{v}	2.036(10)	Zn2–O1	2.051(10)
Zn2–O3	2.036(9)	Zn2–N3	2.032(10)
Zn2–O2^{vi}	2.036(10)	Zn2–O4 ^{vi}	2.038(10)
Zn3–O7	1.978(10)	Zn3–N1	1.998(9)
Zn3–N4	1.955(14)		
O7–Zn1–N2	96.6(4)	O5 ^{i}–Zn1–O7	88.8(5)
O6^{i}–Zn1–O7	133.0(4)	O7–Zn1–N5^{v}	93.9(4)
O5 ^{i}–Zn1–N2	97.0(4)	O6 ^{i}–Zn1–N2	117.7(5)
N2–Zn1–N5 ^{v}	110.4(4)	O5 ^{i}–Zn1–N5 ^{v}	151.9(4)
O6 ^{i}–Zn1–N5 ^{v}	102.2(4)	O1–Zn2–O3	88.6(4)
O1–Zn2–N3	98.5(4)	O1–Zn2–O2^{vii}	158.5(4)
O1-Zn2-O4 ^{vii}	86.3(4)	O3–Zn2–N3	99.6(4)
O2 ^{vii}–Zn2–O3	87.1(4)	O3–Zn2–O4 ^{vii}	157.9(4)
O2 ^{vii}–Zn2–N3	103.0(4)	O4 ^{vii}–Zn2–N3	102.4(4)
O2 ^{vii}–Zn2–O4 ^{vii}	89.9(4)	O7–Zn3–N1	97.9(3)
O7–Zn3–N4	112.2(5)	N1–Zn3–N4	118.0(3)
N1–Zn3–N1^{viii}	109.1(4)		

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

Figure S1. the structure motif of MAC-4-OH showing as 30% ellipsoid probability (A: x, 1.5-y, z; B: -x, 2-y, 2-z; C: -0.5+x, y, 1.5-z; D: 0.5+x, 1.5-y, 1.5-z; E: 0.5+x, y, 1.5-z. Hydrogen atoms and guest molecules are omitted for clarity)

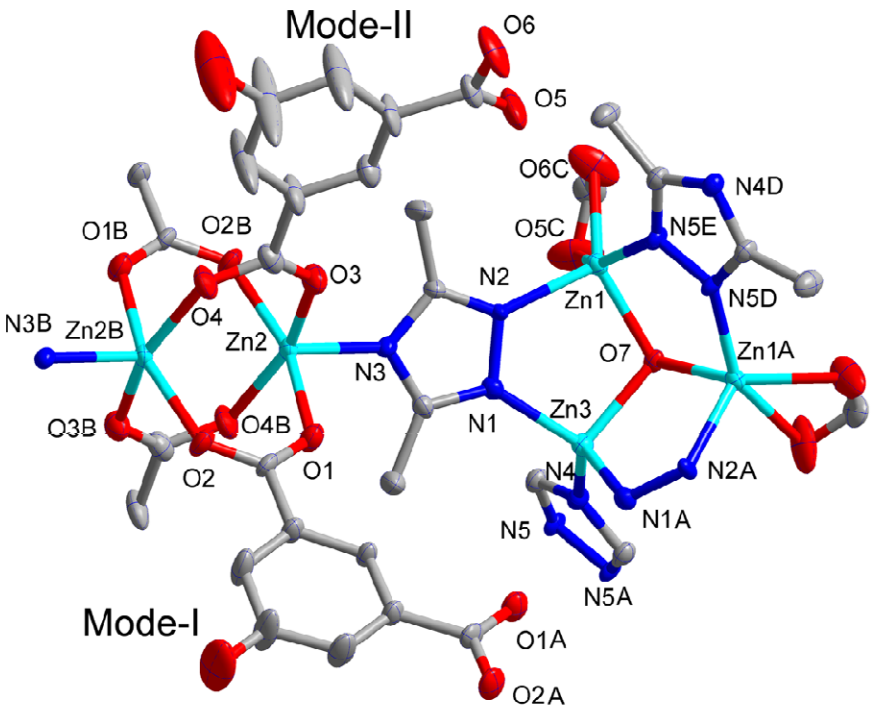


Figure S2. The PXRD patterns of as-make crystals of MAC-4 and MAC-4-OH compared with simulated one obtained from CIF data.

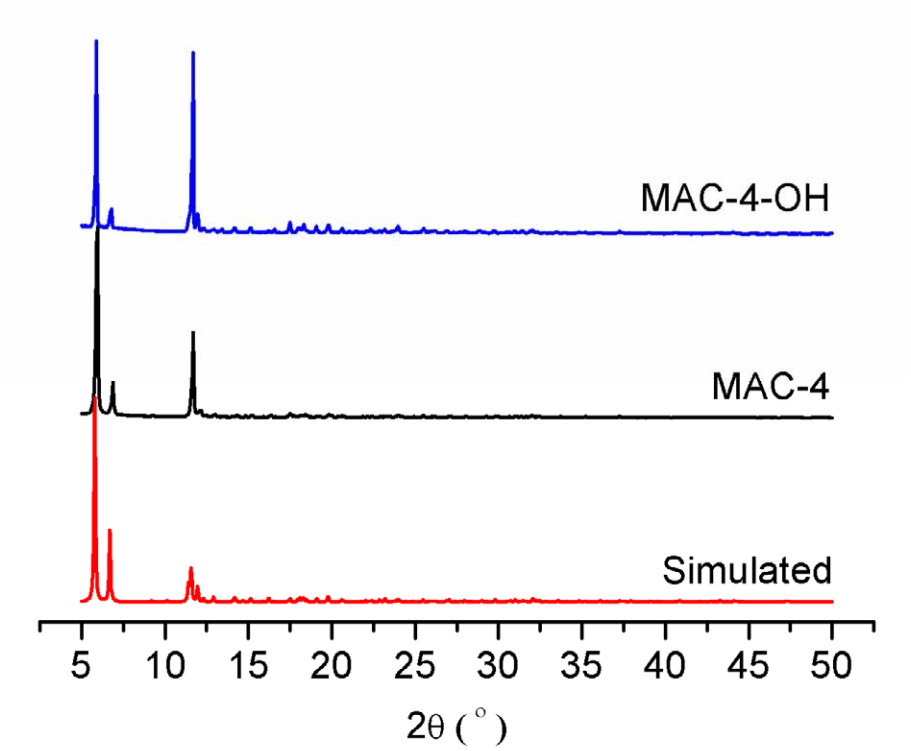


Figure S3 the TGA data of as-made MAC-4 and MAC-4-OH (a) and the variable temperature PXRD data of as-made sample of MAC-4 (b)

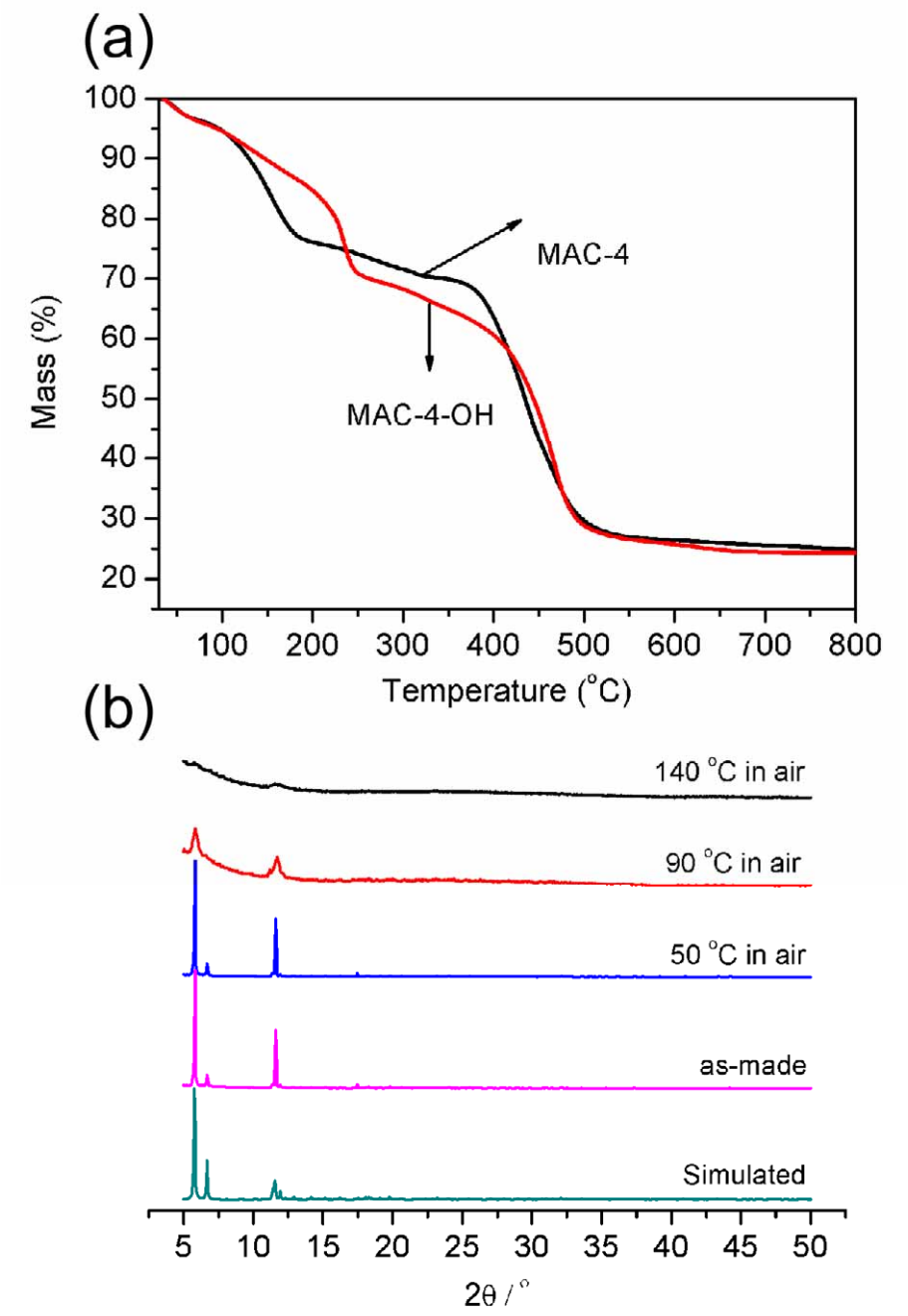


Figure S4 The high pressure CO_2 uptake on activated MAC-4-OH at 298 K.

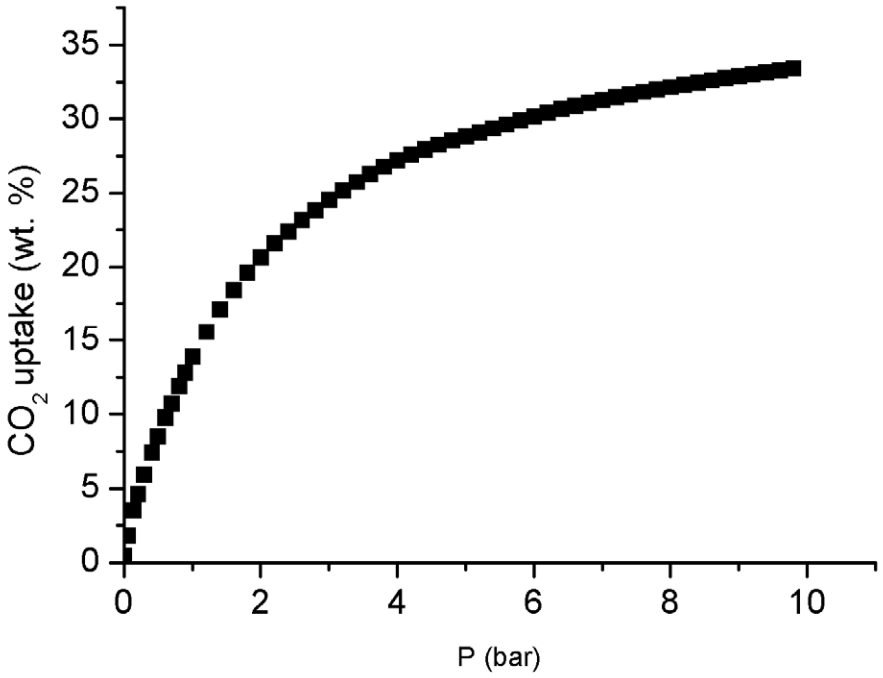
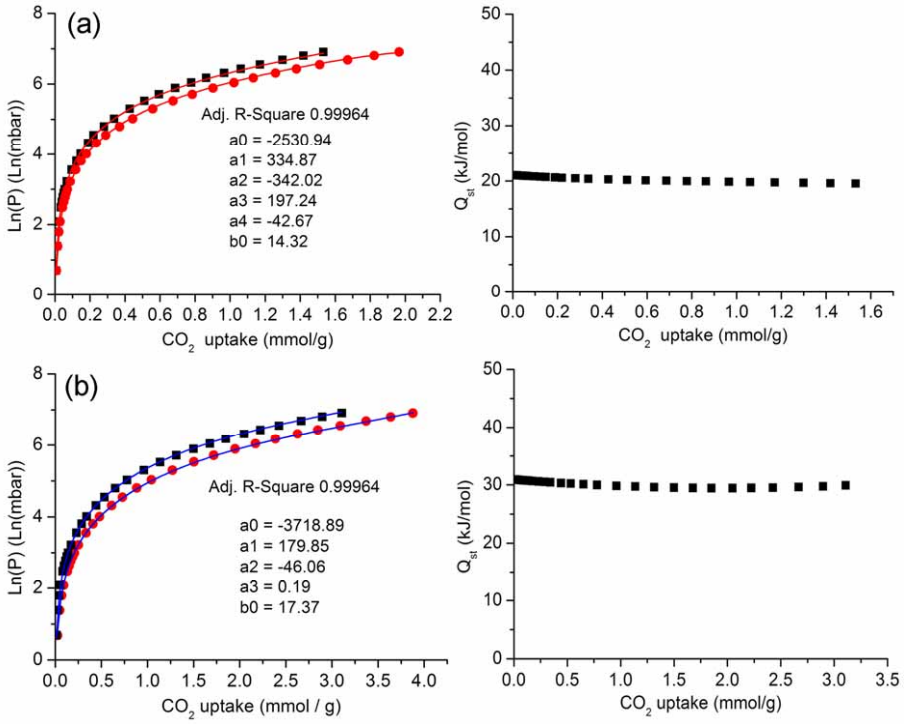


Figure S5 The CO_2 isotherms of MAC-4 (a, left) and MAC-4-OH (b, left) at 288 and 298 K fitted by Virial analyses and the isosteric heat.



Virial analyses

$$Ln(P) = Ln(x) + \frac{1}{T}\sum_{i=0}^{m} a_i x^i + \sum_{i=0}^{n} b_i x^i \qquad (1)$$

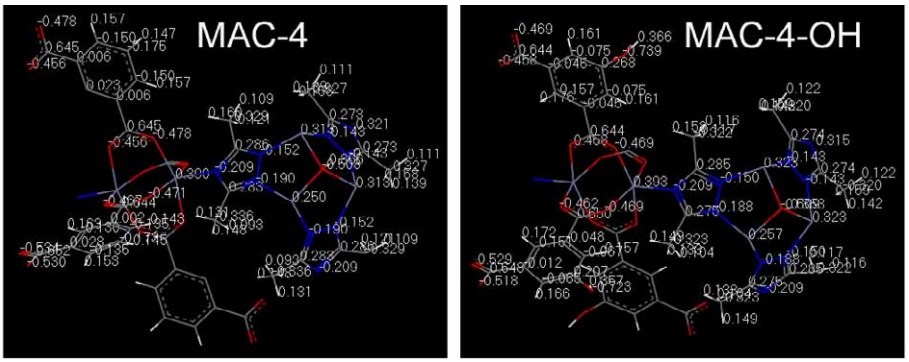
where：P is pressure，x means sorption amounts in mmol/g，T means the temperature，a 和 b 代

Isosteric heat:

$$Q_{st} = -R\sum_{i=0}^{m} a_i x^i \qquad (2)$$

where：R = 8.314 J/K·mol, a the parameter obtained by the fitting Equ. 1.

Figure S6 The QEq method calculated charges (e) on atoms of MAC-4 (left) and MAC-4-OH (right).



The GCMC simulations were performed by the Sorption program, Locate task and Metropolis method in the MS modeling 5.0 package.[1] The CO_2 was optimized by Dmol3 program. The charges for atoms of MAC-4 and MAC-4-OH and CO_2 were calculated by QEq method and QEq_neutral1.0 parameter as shown in Figure S7. The frameworks of ideally desolvated MAC-4 and MAC-4-OH and CO_2 were considered to be rigid during the simulation process. All parameters for CO_2 molecule and atoms of ideally desolvated MAC-4 and MAC-4-OH were modeled with the universal forcefield (UFF) embedded in the MS modeling 5.0 package. The cutoff radius was chosen as 12.5 Å for the L-J potential, and the cubic spline method was applied to make the potential function smoothly converge to zero at the cutoff radius. The 5×10^6 maximum loading steps, 5×10^7 production steps, automated temperature control in the annealing cycles and 40 temperature cycles were employed.

S1. Accelrys, Materials Studio Getting Started, release 5.0; Accelrys Software, Inc.: San Diego, CA, 2009.

Figure S7 Preferential CO_2 location in MAC-4-OH (a) and MAC-4 (b) obtained from GCMC calculations. (The framework shows as space filling mode, while CO_2 shows as ball-stick mode. The green circle on picture *a* and *b* shows the existence of hydrogen bonding between μ_3-OH and O atom of CO_2. As showing in picture *a*, the distance of the C atom of CO_2 labeled as yellow to O atom of the hydroxyl group of OH-IPA ligand (C···O) is *ca.* 3.35 Å, slightly larger than the sum of van der Waals radii of carbon (1.70 Å) and oxygen (1.52 Å), suggesting electrostatic attractive interaction between them)