Two finite binuclear $[M_2(\mu_2\text{-}OH)(COO)_2]$ (M = Co, Ni) based highly porous metal-organic frameworks with high performance of gas sorption and separation

Jiantang Li, Xiaolong Luo, Nian Zhao, Lirong Zhang, Qisheng Huo and Yunling Liu**

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China

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 **ZSA-7, ZSA-8** and **ZSA-9**, 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

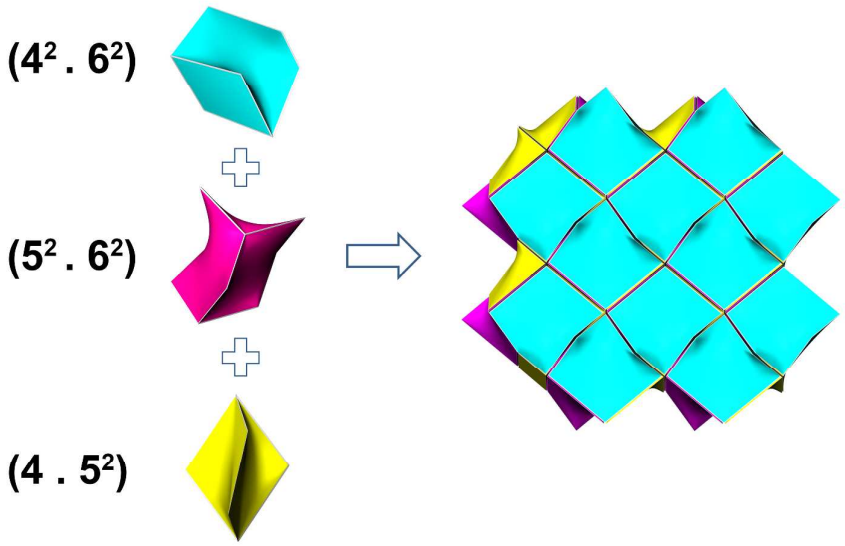

Fig. S1 Topological features of **JLU-Liu37** and **JLU-Liu38** displayed by tiles and face symbols for blue, pink and yellow tiles are (4^2•6^2), (5^2•6^2) and (4•5^2).

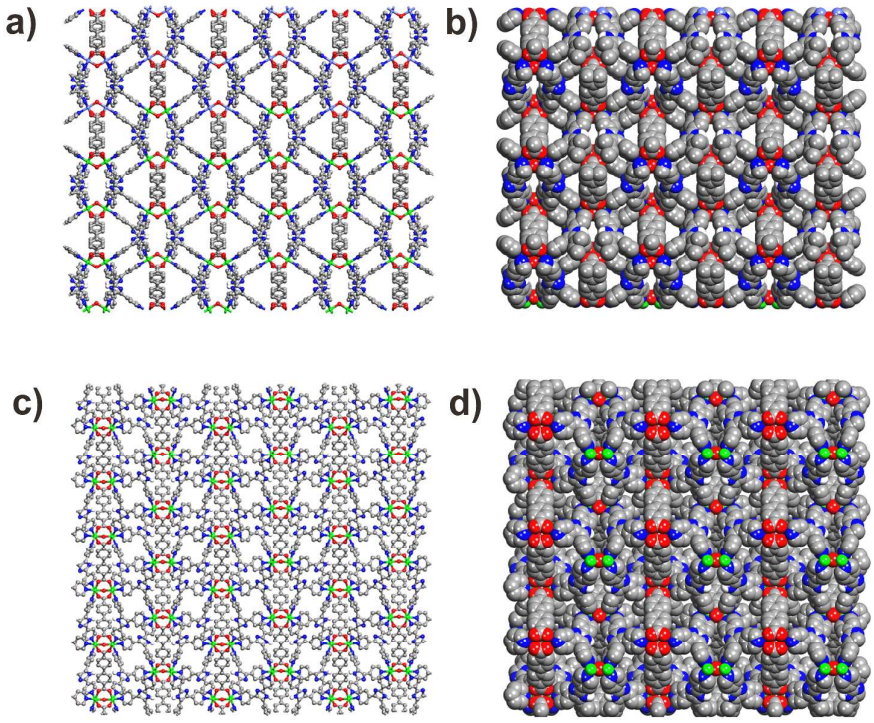

Fig. S2 Ball-and-stick models and CPK models of **JLU-Liu37** and **JLU-Liu38** via X axis (a and b) and Y axis (c and d).

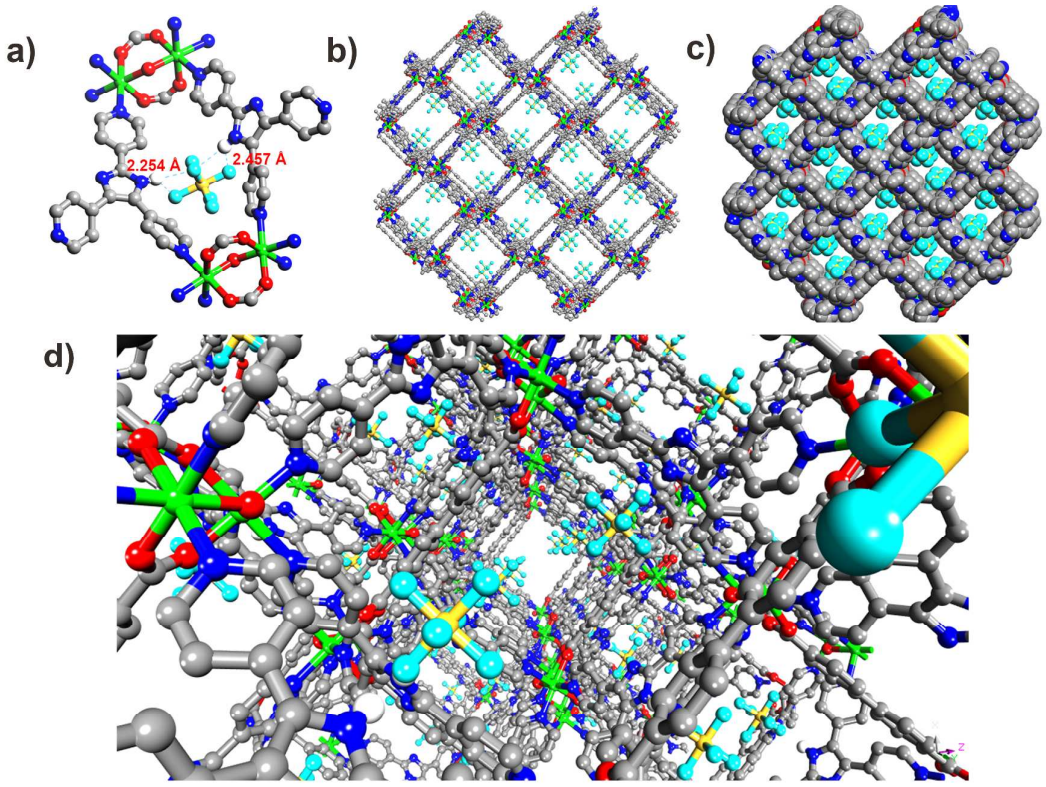

Fig. S3 (a) $[SiF_6]^-$ ion and hydrogen-bonded Htpim ligands. (b) (c) ball-and-stick models and CPK models of $[SiF_6]^-$ ion in each channels. (d) the demonstration of the arrangement of the $[SiF_6]^-$ ions in single channel.

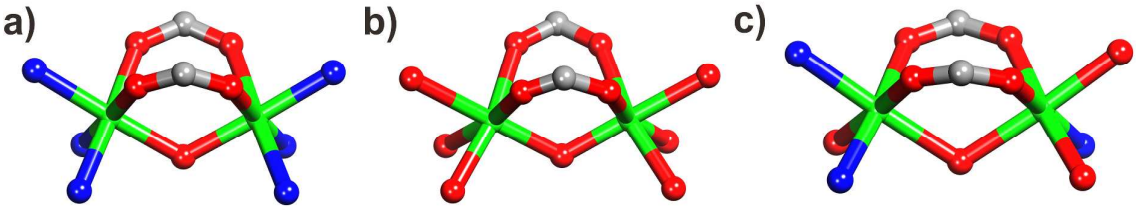

Fig.S4 A brief exhibition of similar reported SBUs. (a) This work and $[Ni_2(\mu_2\text{-}OH)(bdc)(tpt)_2][NO_3]$ •3DMA•4CH_3OH•6H_2O.[1] Connected to two carboxyl groups and six nitrogen-containing ligands to form an eight-connected SBU. (b) CPM-24.[2] Connected to two carboxyl groups and six H_2O molecules to form a two-connected SBU. (c) CPM-16.[3] Connect to five carboxyl groups and three nitrogen-containing ligands to form an eight-connected SBU.

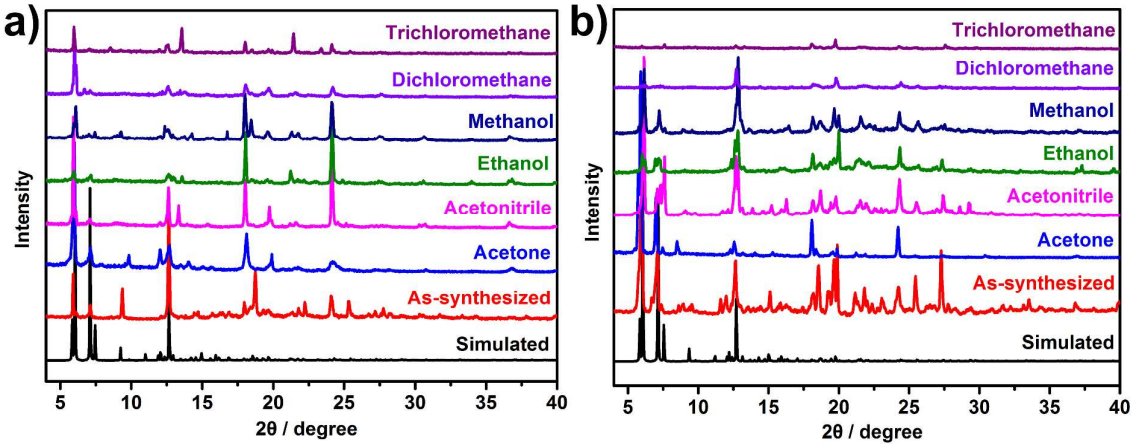

Fig. S5 PXRD patterns of **JLU-Liu37** (a) and **JLU-Liu38** (b) for simulated, as-synthesized, and solvent-exchanged samples. **JLU-Liu37** was stable in common solvents, **JLU-Liu38** was relatively unstable in dichloromethane and trichloromethane.

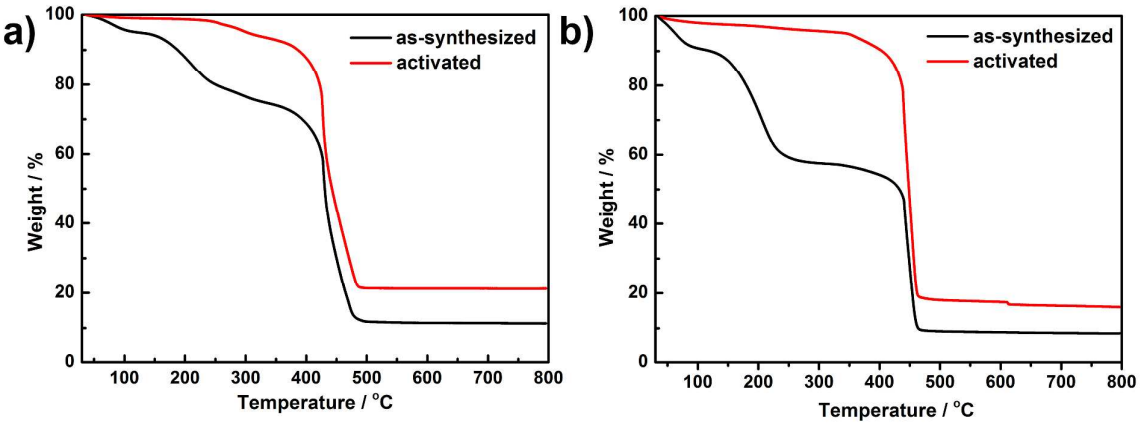

Fig. S6 TGA curves of **JLU-Liu37** (a) and **JLU-Liu38** (b) for the as-synthesized and activated samples.

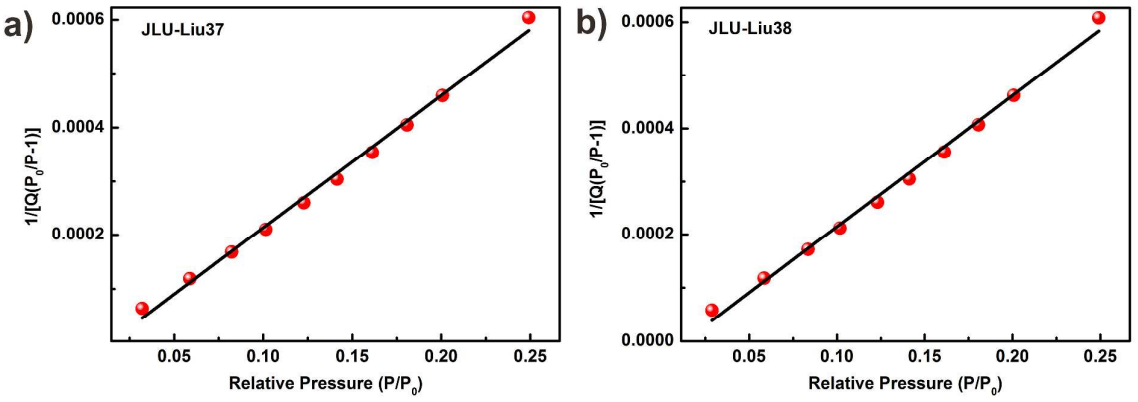

Fig. S7 The linear fitting curve for calculating BET surface areas of (a) **JLU-Liu37** and (b) **JLU-Liu38**.

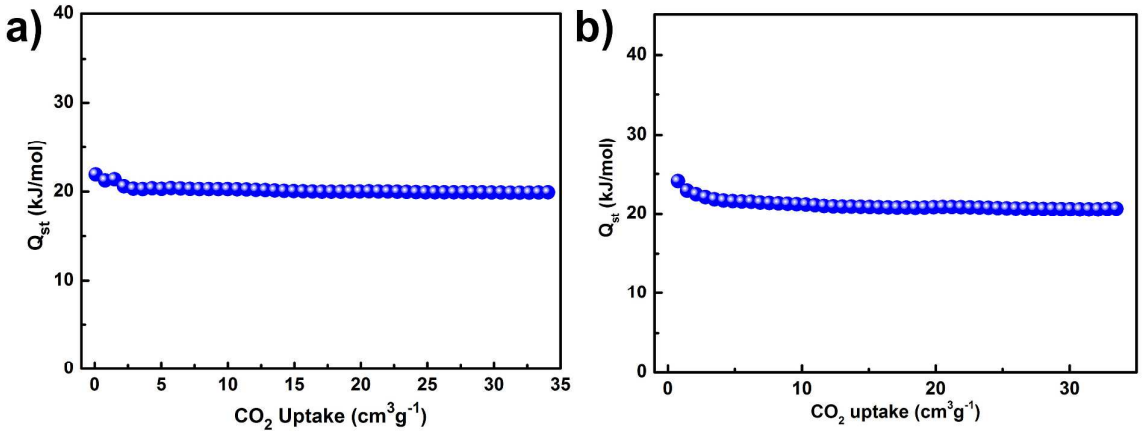

Fig. S8. Q_{st} of CO_2 for **JLU-Liu37** (a) and **JLU-Liu38** (b).

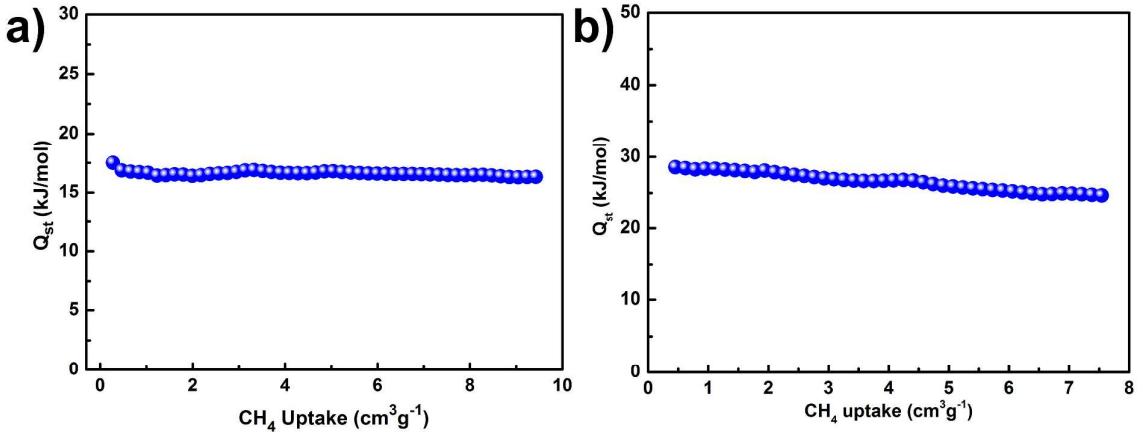

Fig. S9. Q_{st} of CH_4 for **JLU-Liu37** (a) and **JLU-Liu38** (b).

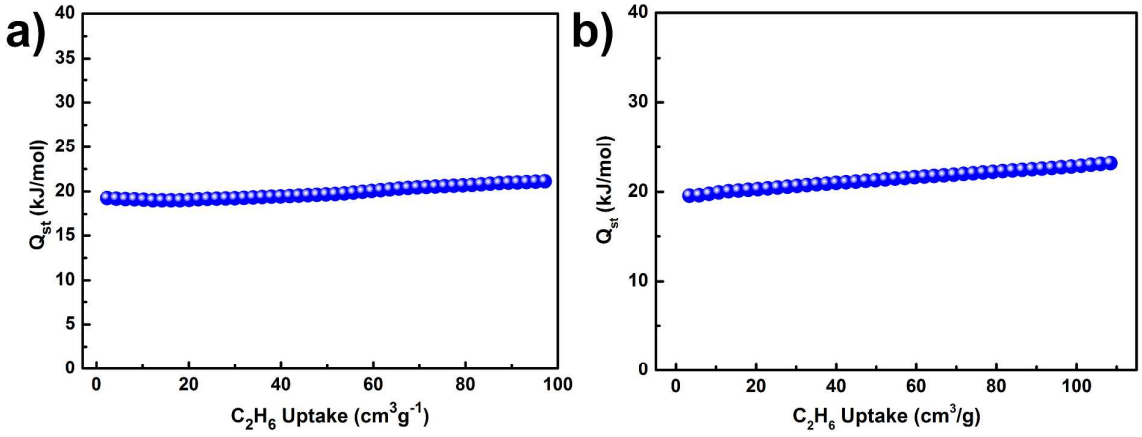

Fig. S10. Q_{st} of C_2H_6 for **JLU-Liu37** (a) and **JLU-Liu38** (b).

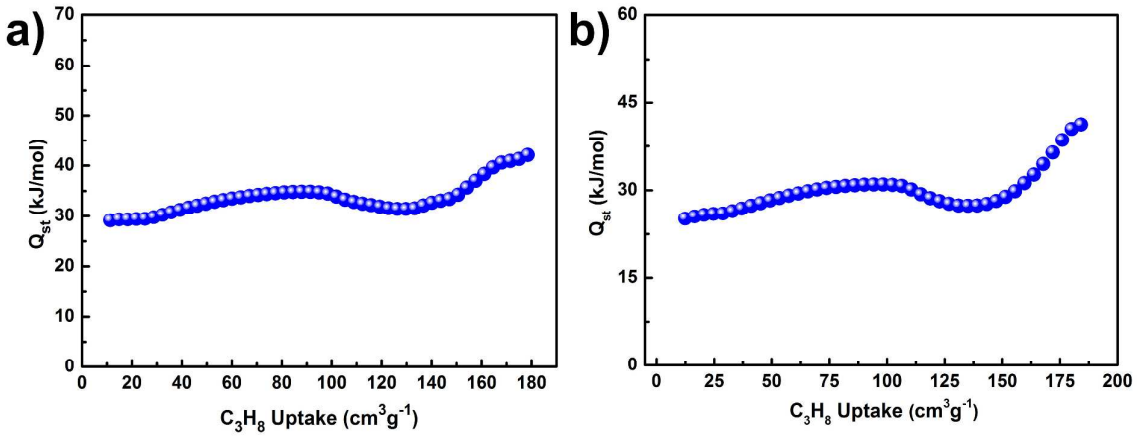

Fig. S11. Q_{st} of C_3H_8 for **JLU-Liu37** (a) and **JLU-Liu38** (b).

S3. Supporting Tables

Table S1. Crystal data and structure refinements for **JLU-Liu37** and **JLU-Liu38**.

Compound	**JLU-Liu37**	**JLU-Liu38**
Formula	$C_{66.5}H_{75.5}Co_2F_6N_{13.5}O_{11}Si$	$C_{86}H_{125.5}F_6N_{17.5}Ni_4O_{18.5}Si$
Mw	1499.85	1960.04
Temp (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma
a (Å)	21.879(2)	21.4817(9)
b (Å)	23.701(3)	23.3867(10)
c (Å)	19.687(2)	19.8758(8)
α (^{o})	90	90
β (^{o})	90	90
γ (^{o})	90	90
V (Å^3)	10208.7(19)	9985.3(7)
Z, D_C (Mg/m^3)	4, 0.976	4, 1.304
F(000)	3116	4144
θ range (deg)	1.345 - 25.073	1.345 - 25.095
reflns collected/unique	63176 / 9269	63784 / 9106
R_{int}	0.1149	0.0479
data/restraints/params	9269 / 161 / 481	9106 / 185 / 481
GOF on F^2	1.203	1.297
R^1, wR^2 (I>2σ(I))	0.0919, 0.2995	0.0788, 0.2835
R^1, wR^2 (all data)	0.1302, 0.3293	0.0879, 0.2937

Since the highly disordered guest molecules were trapped in the channels of **JLU-Liu37** and **JLU-Liu38** and could not be modeled properly, there is "Alert level A" about "Check Reported Molecular Weight" in the "checkCIF/PLATON report" files for **JLU-Liu37** and **JLU-Liu38**. The final formulas of **JLU-Liu37** and **JLU-Liu38** were derived from crystallographic data combined with elemental and thermogravimetric analysis data.

Table S2. Selected bond lengths [Å] and angles [^{o}] for **JLU-Liu37**.

JLU-Liu37			
Co(1)-O(2)	2.016(2)	O(3)-Co(1)-N(1)	177.97(17)
Co(1)-O(3)	2.058(4)	O(1)-Co(1)-N(1)	88.38(17)
Co(1)-O(1)	2.079(4)	N(5)#1-Co(1)-N(1)	92.00(17)
Co(1)-N(5)#1	2.169(5)	N(4)#2-Co(1)-N(1)	92.56(18)
Co(1)-N(4)#2	2.173(4)	C(1A)-N(1)-Co(1)	119.6(9)
Co(1)-N(1)	2.191(4)	C(1B)-N(1)-Co(1)	117.3(8)
N(4)-Co(1)#6	2.173(4)	C(2B)-N(1)-Co(1)	128.4(11)
N(5)-Co(1)#7	2.169(5)	C(2A)-N(1)-Co(1)	123.6(8)
O(2)-Co(1)#3	2.016(2)	C(12B)-N(4)-Co(1)#6	120.6(7)
O(2)-Co(1)-O(3)	94.57(16)	C(12A)-N(4)-Co(1)#6	122.6(6)
O(2)-Co(1)-O(1)	92.92(15)	C(13B)-N(4)-Co(1)#6	122.4(6)
O(3)-Co(1)-O(1)	91.98(17)	C(13A)-N(4)-Co(1)#6	119.9(5)
O(2)-Co(1)-N(5)#1	178.96(16)	C(17A)-N(5)-Co(1)#7	128.7(6)
O(3)-Co(1)-N(5)#1	86.04(17)	C(17B)-N(5)-Co(1)#7	121.8(6)
O(1)-Co(1)-N(5)#1	86.21(16)	C(18B)-N(5)-Co(1)#7	119.0(6)
O(2)-Co(1)-N(4)#2	88.79(16)	C(18A)-N(5)-Co(1)#7	117.0(6)
O(3)-Co(1)-N(4)#2	87.03(18)	C(19)-O(1)-Co(1)	132.8(4)
O(1)-Co(1)-N(4)#2	178.08(17)	Co(1)#3-O(2)-Co(1)	118.0(2)
N(5)#1-Co(1)-N(4)#2	92.08(17)	C(28)#8-O(3)-Co(1)	134.9(4)
O(2)-Co(1)-N(1)	87.40(16)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1,z-1/2 #2 x-1/2,y,-z+3/2 #3 x,-y+3/2,z #4 x+1/2,y,-z+1/2
#5 x+1/2,-y+3/2,-z+1/2 #6 x+1/2,y,-z+3/2 #7 -x+1/2,-y+1,z+1/2
#8 x-1/2,y,-z+1/2

Table S3. Selected bond lengths [Å] and angles [°] for **JLU-Liu38**.

JLU-Liu38			
Ni(1)-O(1)	1.9943(14)	O(3)-Ni(1)-N(1)	177.87(11)
Ni(1)-O(3)	2.039(2)	O(2)-Ni(1)-N(1)	88.99(11)
Ni(1)-O(2)	2.052(2)	N(4)#1-Ni(1)-N(1)	91.95(12)
Ni(1)-N(4)#1	2.105(3)	N(5)#2-Ni(1)-N(1)	92.69(11)
Ni(1)-N(5)#2	2.132(3)	C(11B)-N(1)-Ni(1)	127.4(4)
Ni(1)-N(1)	2.147(3)	C(13A)-N(1)-Ni(1)	121.3(9)
N(5)-Ni(1)#6	2.132(3)	C(13B)-N(1)-Ni(1)	116.7(4)
N(4)-Ni(1)#7	2.105(3)	C(11A)-N(1)-Ni(1)	123.6(6)
O(1)-Ni(1)#3	1.9942(14)	C(22A)-N(5)-Ni(1)#6	120.5(4)
O(1)-Ni(1)-O(3)	93.80(10)	C(22B)-N(5)-Ni(1)#6	127.1(4)
O(1)-Ni(1)-O(2)	92.52(11)	C(20A)-N(5)-Ni(1)#6	118.9(4)
O(3)-Ni(1)-O(2)	91.71(11)	C(20B)-N(5)-Ni(1)#6	117.8(4)
O(1)-Ni(1)-N(4)#1	88.61(11)	C(24B)-N(4)-Ni(1)#7	121.7(4)
O(3)-Ni(1)-N(4)#1	87.32(12)	C(26A)-N(4)-Ni(1)#7	124.3(4)
O(2)-Ni(1)-N(4)#1	178.55(12)	C(24A)-N(4)-Ni(1)#7	118.4(4)
O(1)-Ni(1)-N(5)#2	178.29(11)	C(26B)-N(4)-Ni(1)#7	120.7(3)
O(3)-Ni(1)-N(5)#2	85.35(11)	Ni(1)#3-O(1)-Ni(1)	119.71(14)
O(2)-Ni(1)-N(5)#2	86.03(11)	C(10)-O(2)-Ni(1)	133.4(3)
N(4)#1-Ni(1)-N(5)#2	92.83(11)	C(5)-O(3)-Ni(1)	134.9(3)
O(1)-Ni(1)-N(1)	88.18(11)		

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,y,-z+1/2 #2 -x+1/2,-y+1,z-1/2 #3 x,-y+1/2,z #4 x+1/2,y,-z-1/2
#5 x-1/2,y,-z-1/2 #6 -x+1/2,-y+1,z+1/2 #7 x+1/2,y,-z+1/2

Table S4. BVS calculation for **JLU-Liu37**.

Co^{2+}	r_0	r_{ij}	B	V_{ij}
Co(1) - O(2)	1.6920	2.0156	0.37	0.417
Co(1) - O(3)	1.6920	2.0589	0.37	0.371
Co(1) - O(1)	1.6920	2.0793	0.37	0.351
Co(1) - N(5)a	1.6500	2.1682	0.37	0.246
Co(1) - N(4)f	1.6500	2.1725	0.37	0.244
Co(1) - N(1)	1.6500	2.1903	0.37	0.232
$V_{Co} = \sum V_{ij} = 1.861$	$V_{O1} = 2 \times V_{Co1\text{-}O2} = 0.834$			

Co^{3+}	r_0	r_{ij}	B	V_{ij}
Co(1) - O(2)	1.6370	2.0156	0.37	0.359
Co(1) - O(3)	1.6370	2.0589	0.37	0.320
Co(1) - O(1)	1.6370	2.0793	0.37	0.303
Co(1) - N(5)a	1.7500	2.1682	0.37	0.323
Co(1) - N(4)f	1.7500	2.1725	0.37	0.319
Co(1) - N(1)	1.7500	2.1903	0.37	0.304
$V_{Co} = \sum V_{ij} = 1.928$	$V_{O1} = 2 \times V_{Co1\text{-}O2} = 0.718$			

Table S5. BVS calculation for **JLU-Liu38**.

Ni^{2+}	r_0	r_{ij}	B	V_{ij}
Ni(1) - O(1)	1.6540	1.9924	0.37	0.401
Ni(1) - O(3)	1.6540	2.0435	0.37	0.349
Ni(1) - O(2)	1.6540	2.0453	0.37	0.347
Ni(1) - N(4)c	1.7000	2.1092	0.37	0.331
Ni(1) - N(5)a	1.7000	2.1312	0.37	0.312
Ni(1) - N(1)	1.7000	2.1382	0.37	0.306
$V_{Ni} = \sum V_{ij} = 2.046$	$V_{O1} = 2 \times V_{Ni1\text{-}O1} = 0.802$			

Ni^{3+}	r_0	r_{ij}	B	V_{ij}
Ni(1) - O(1)	1.7500	1.9924	0.37	0.519
Ni(1) - O(3)	1.7500	2.0435	0.37	0.452
Ni(1) - O(2)	1.7500	2.0453	0.37	0.450
Ni(1) - N(4)c	1.7310	2.1092	0.37	0.360
Ni(1) - N(5)a	1.7310	2.1312	0.37	0.339
Ni(1) - N(1)	1.7310	2.1382	0.37	0.333
$V_{Ni} = \sum V_{ij} = 2.453$	$V_{O1} = 2 \times V_{Ni1\text{-}O1} = 1.038$			

Table S6. 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 **JLU-Liu37 and JLU-Liu38** at 298 K.

		q_{m1}	b_1	$1/n_1$	q_{m2}	b_2	$1/n_2$	R^2
JLU-Liu37	CO_2	21.00624	1.47407E-4	1.29768	0.59278	0.0205	0.93062	0.99999
	CH_4	4.30715	2.92609E-4	1.23828	0.05502	0.03168	1.17375	0.99997
	C_2H_6	10.55407	1.53143E-4	1.73697	1.49671	0.02343	1.03101	0.99999
	C_3H_8	3.46729	2.05201E-4	3.51135	5.10466	0.04579	1.08797	0.99996
JLU-Liu38	CO_2	0.19515	0.02279	1.29841	18.06472	3.47078E-4	1.2315	0.99998
	CH_4	25.26696	8.23853E-5	1.07915	0.00602	0.09287	1.19406	0.99991
	C_2H_6	31.2193	8.85383E-4	1.16141	0.05258	1.00724	0.94613	0.99993
	C_3H_8	3.86751	3.33009E-4	3.59573	5.15451	0.05477	1.04323	0.99998

REFERENCES

(1) Zhang, L.; Qian, J.; Yang, W.; Kuang, X.; Zhang, J.; Cui, Y.; Wu, W.; Wu, X.; Lu, C.; Chen, W. A (3,8)-Connected Metal-Organic Framework with a Unique Binuclear $[Ni_2(\mu_2\text{-}OH)(COO)_2]$ Node for High H_2 and CO_2 Adsorption Capacities. *J. Mater. Chem. A* **2015**, 15399–15402.

(2) Zheng, S. T.; Mao, C.; Wu, T.; Lee, S.; Feng, P.; Bu, X. Generalized Synthesis of Zeolite-Type Metal-Organic Frameworks Encapsulating Immobilized Transition-Metal Clusters. *J. Am. Chem. Soc.* **2012**, 134, 11936-11939.

(3) Zheng, S. T.; Wu, T.; Irfanoglu, B.; Zuo, F.; Feng, P.; Bu, X. Multicomponent Self-Assembly of a Nested $Co_{24}@Co_{48}$ Metal-Organic Polyhedral Framework. *Angew. Chem., Int. Ed.* **2011**, 50, 8034-8037.