Electronic Supplementary Information (ESI)

Three stable dinuclear $[M_2(OH)_{0.5}(NO_3)_{0.5}(RCOO)_2(RN)_4]$ (M = Cu, Ni) based metal-organic frameworks with high CO_2 adsorption and selective separation for O_2/N_2 and C_3H_8/CH_4

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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 compounds **Cu-L$_1$**, **Ni-L$_1$** and **Ni-L$_2$**, 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.

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

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), 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

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

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

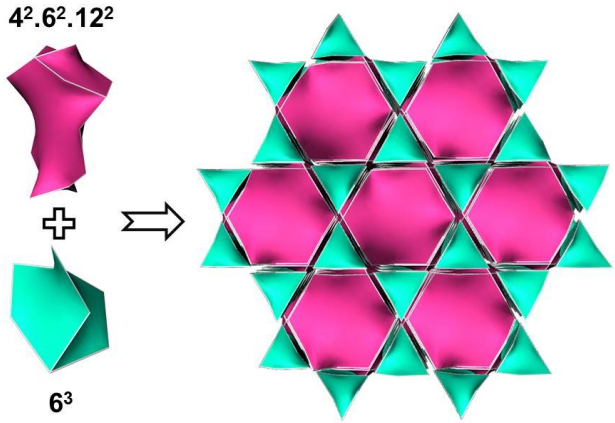

Fig. S1 Topological features of compound **Cu-L$_1$** displayed by tiles and face symbols for green (6^3) and pink (4^2▪6^2▪12^2) tiles.

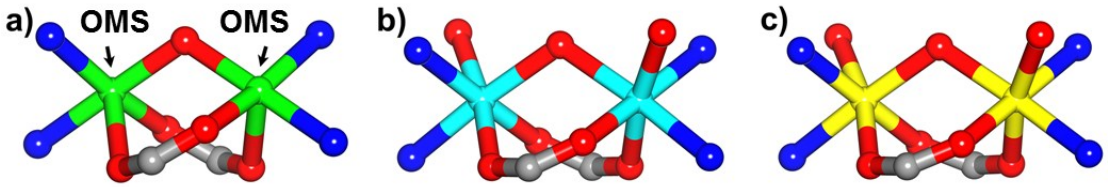

Fig. S2 Comparison of metal atom coordination modes for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c).

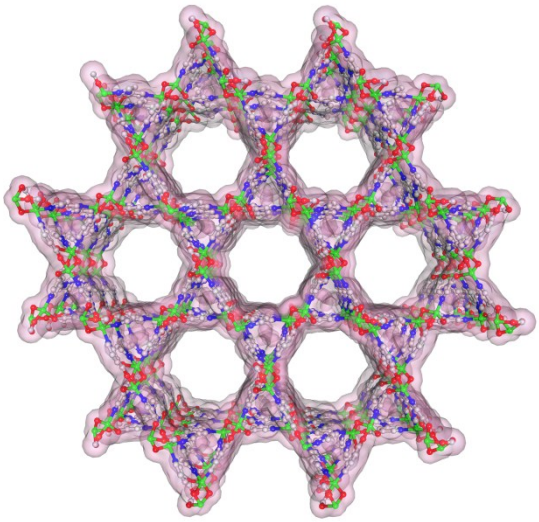

Fig. S3 The illustration of structure displayed by connolly surface areas.

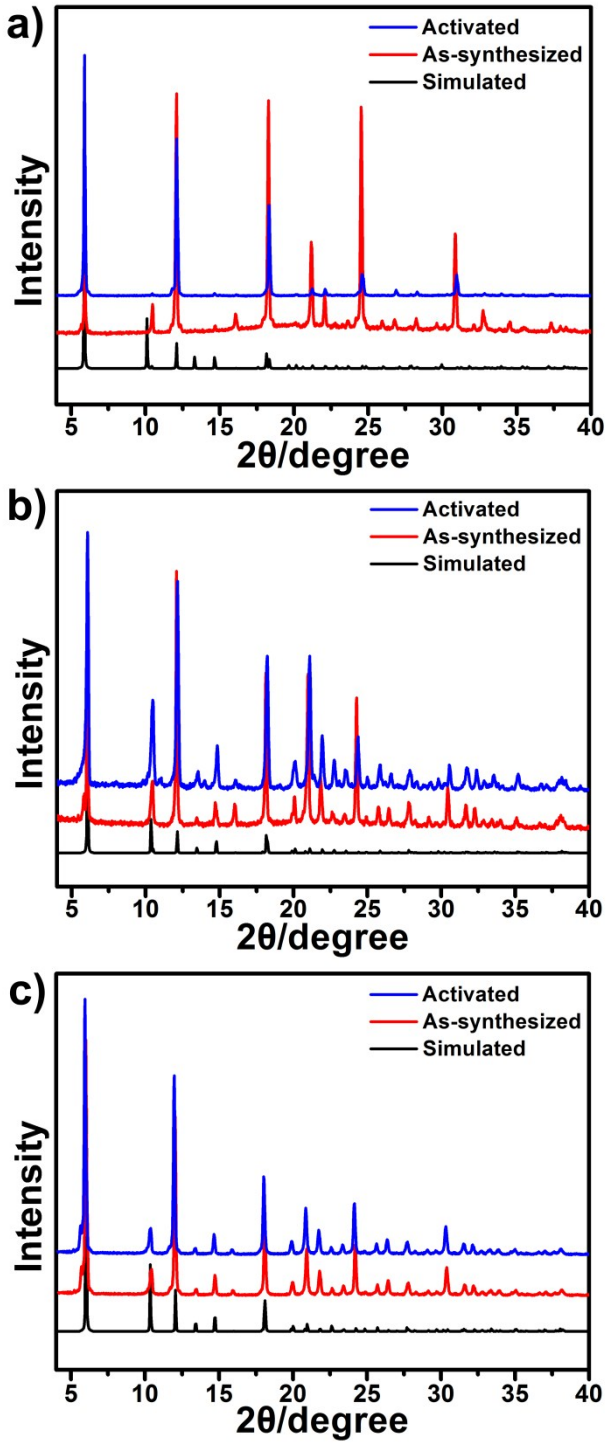

Fig. S4 PXRD patterns of compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c) for simulated, as-synthesized and activated samples.

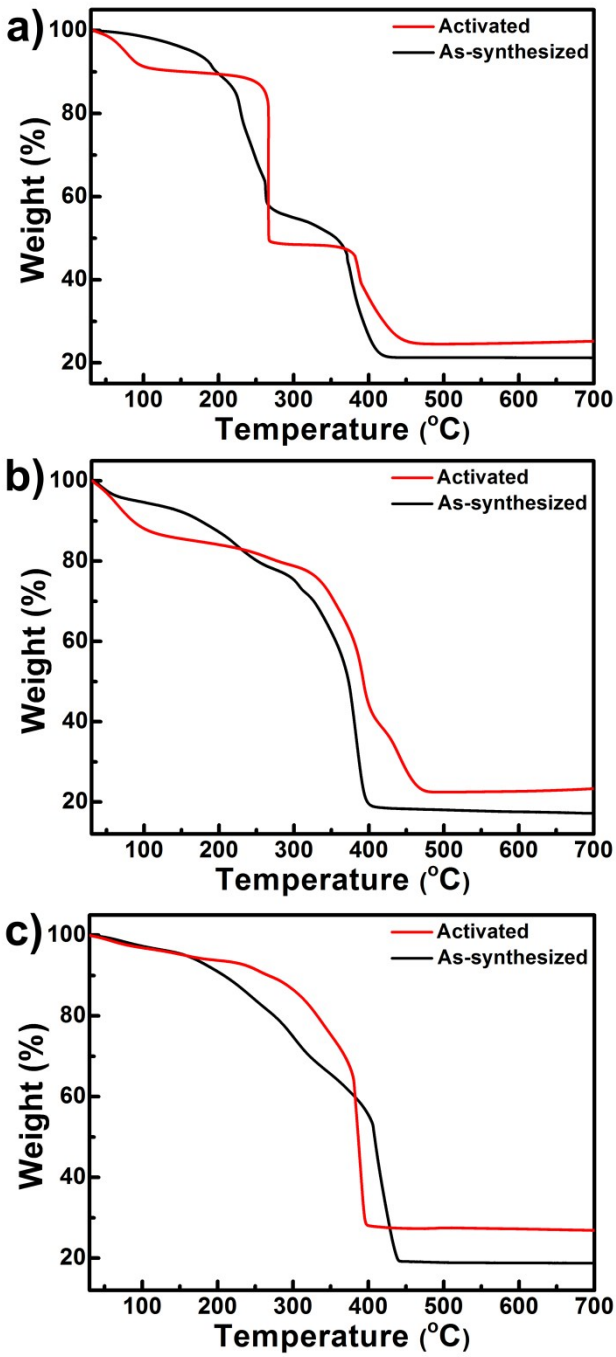

Fig. S5 Thermogravimetric analysis curves of compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c) for as-synthesized and solvent-exchanged samples.

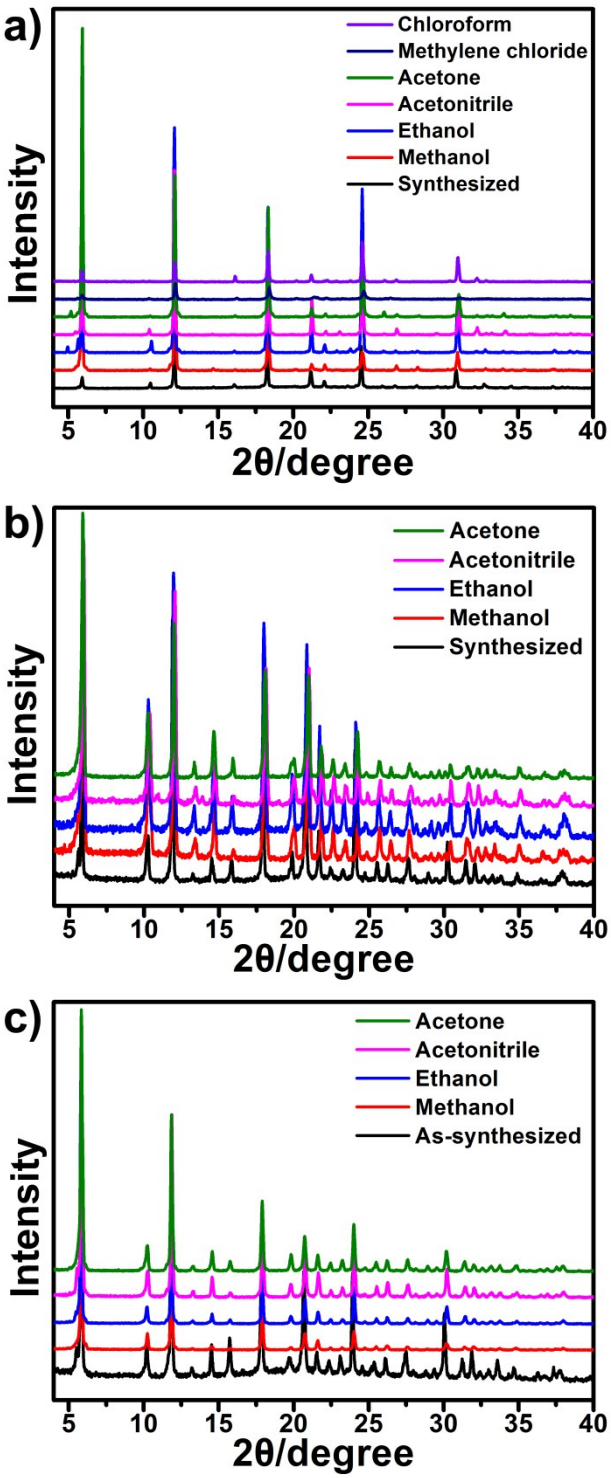

Fig. S6 PXRD patterns of compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c) for solvent-exchanged samples.

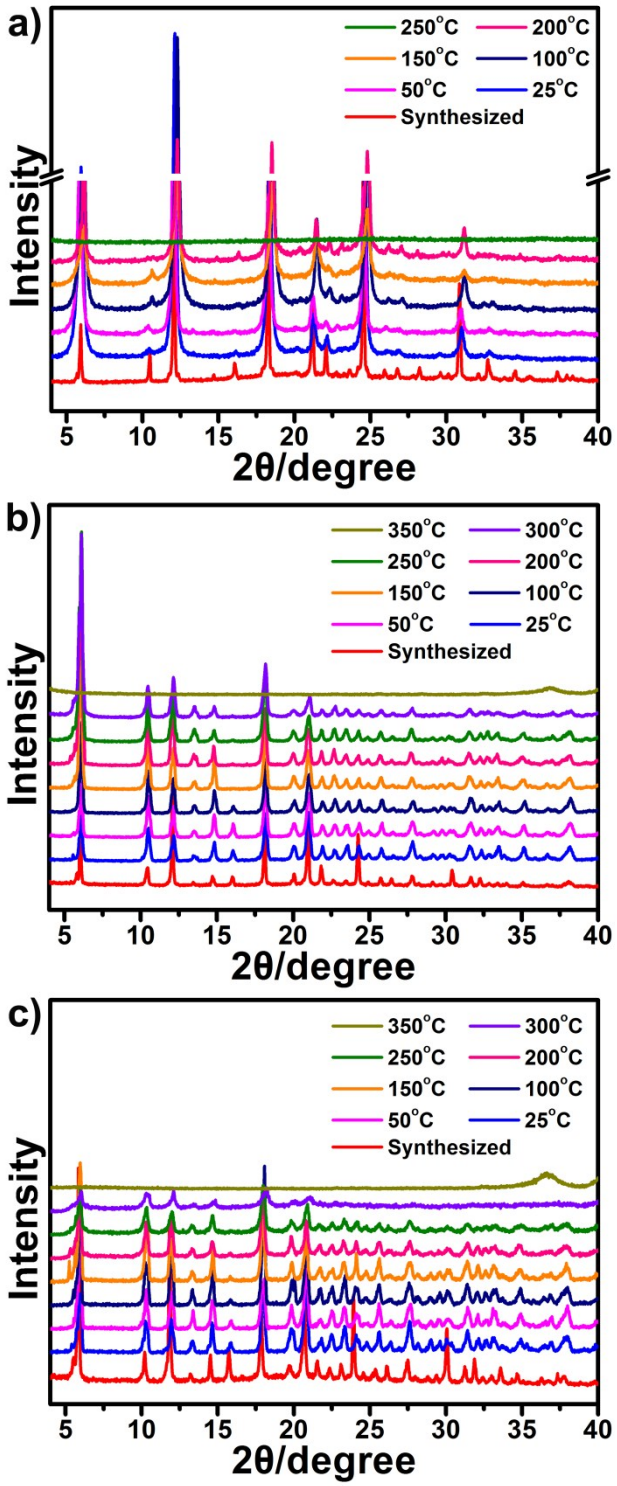

Fig. S7 Varied temperature PXRD patterns of compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c).

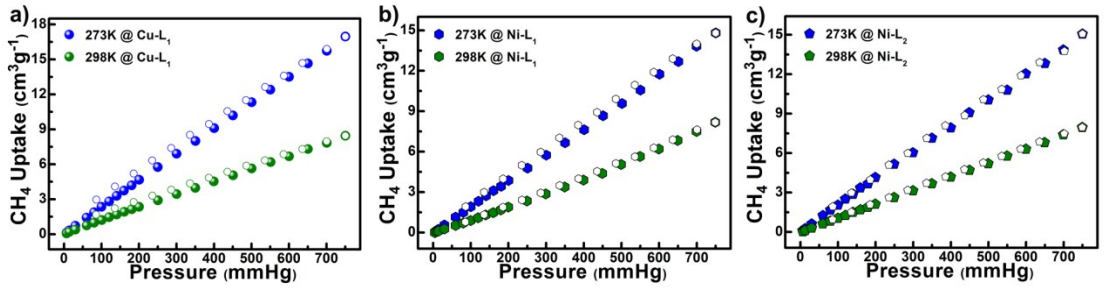

Fig. S8 CH_4 sorption isotherms for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c) at 273 and 298 K.

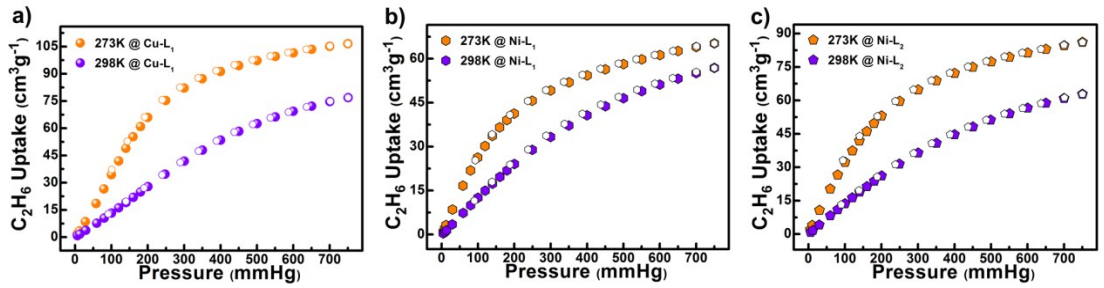

Fig. S9 C_2H_6 sorption isotherms for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c) at 273 and 298 K.

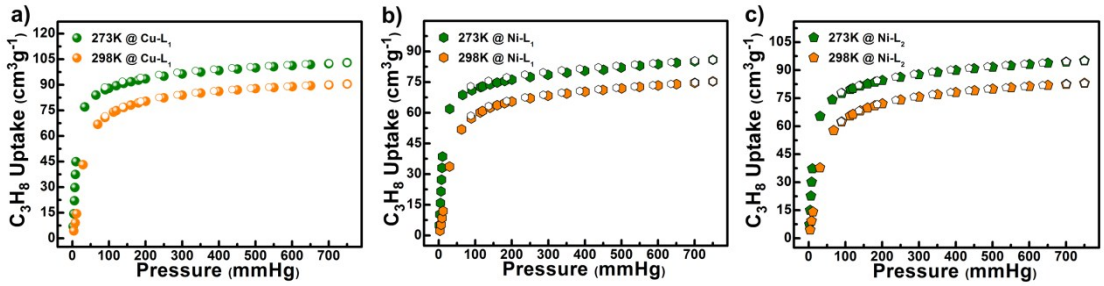

Fig. S10 C_3H_8 sorption isotherms for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c) at 273 and 298 K.

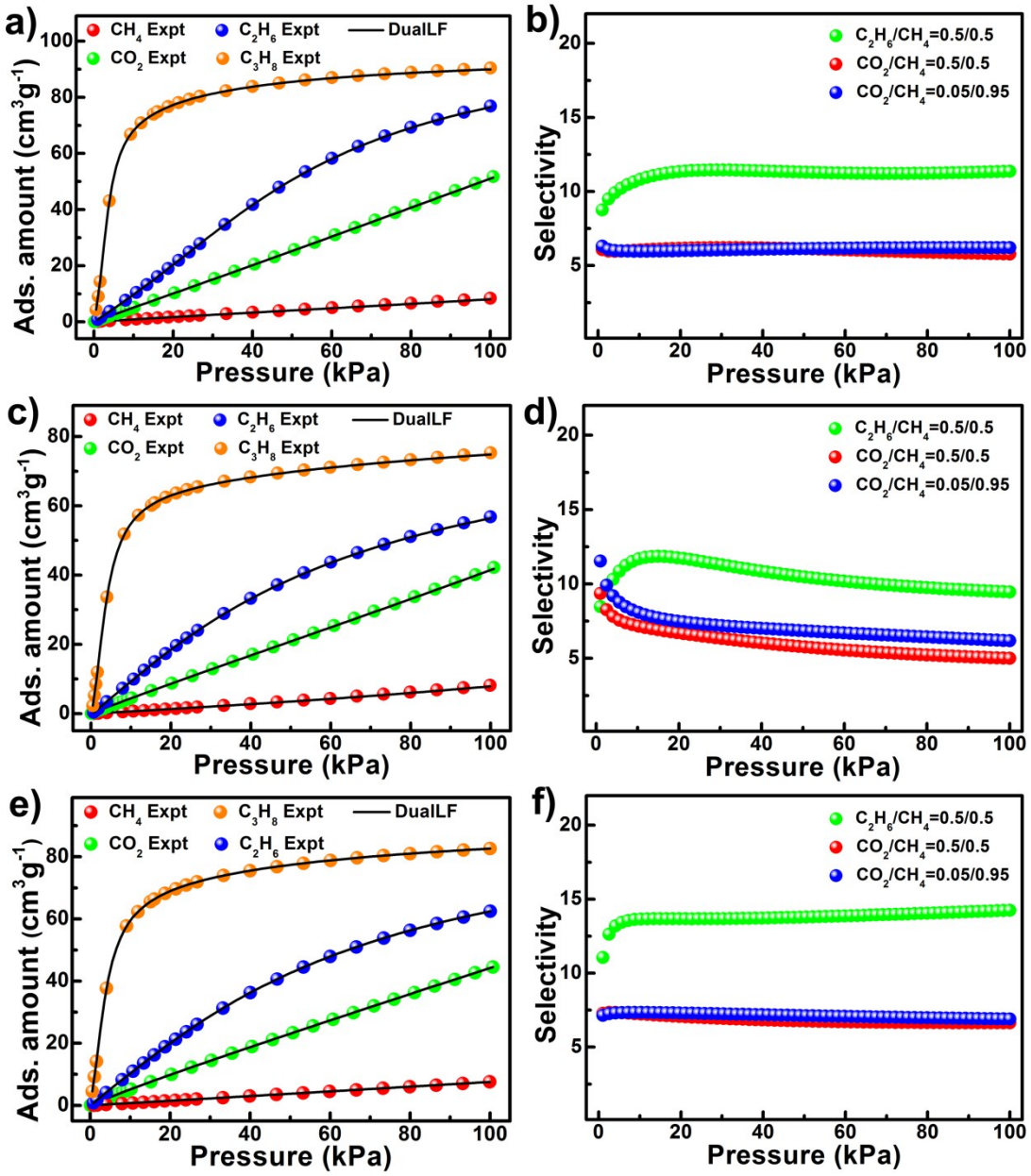

Fig. S11 CO_2, CH_4, C_2H_6 and C_3H_8 adsorption isotherms for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (c) and **Ni-L$_2$** (e) at 298 K along with the dual-site Langmuir Freundlich (DSLF) fits. The selectivity of CO_2/CH_4 and C_2H_6/CH_4 is predicted by IAST at 298 K for compounds **Cu-L$_1$** (b), **Ni-L$_1$** (d) and **Ni-L$_2$** (f).

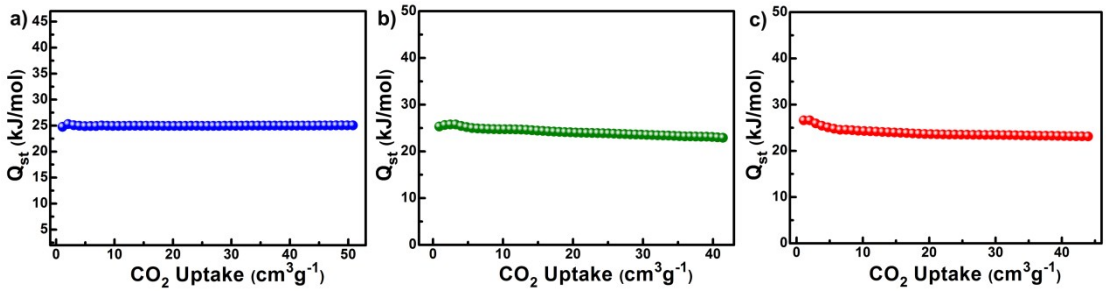

Fig. S12 Q_{st} of CO_2 for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c).

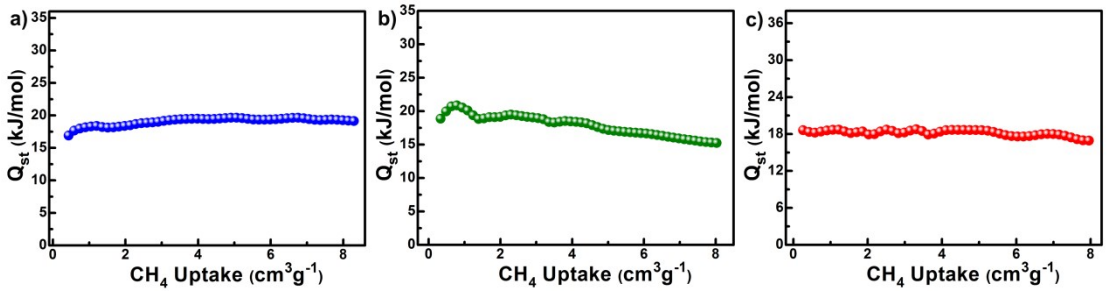

Fig. S13 Q_{st} of CH_4 for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c).

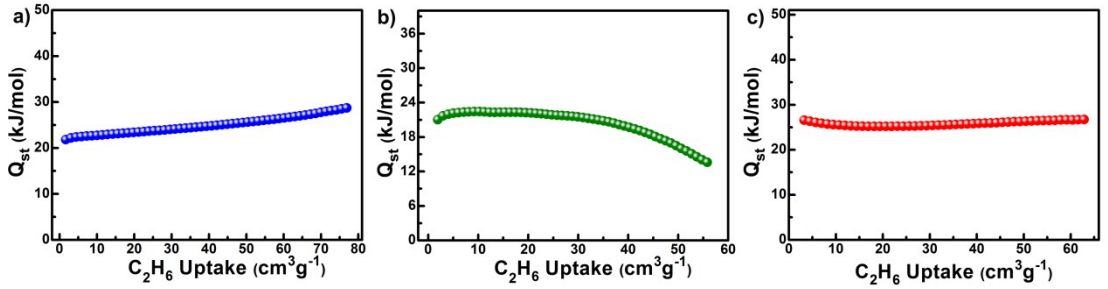

Fig. S14 Q_{st} of C_2H_6 for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c).

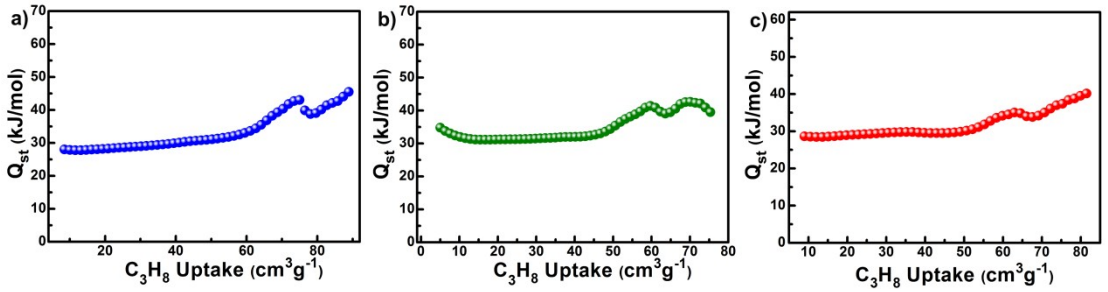

Fig. S15 Q_{st} of C_3H_8 for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c).

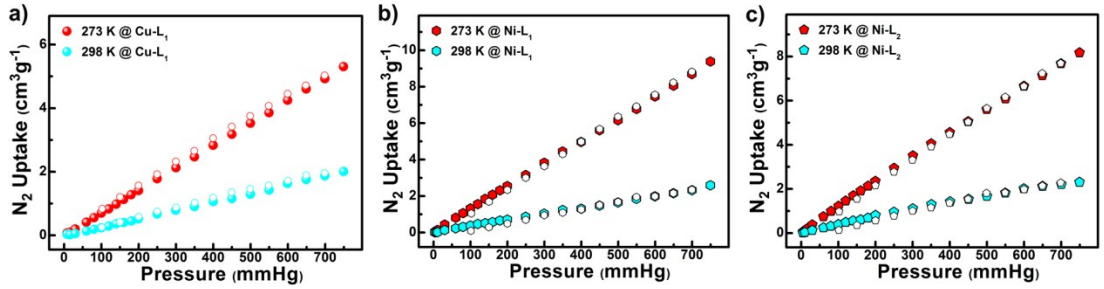

Fig. S16 N_2 sorption isotherms for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c) at 273 and 298 K.

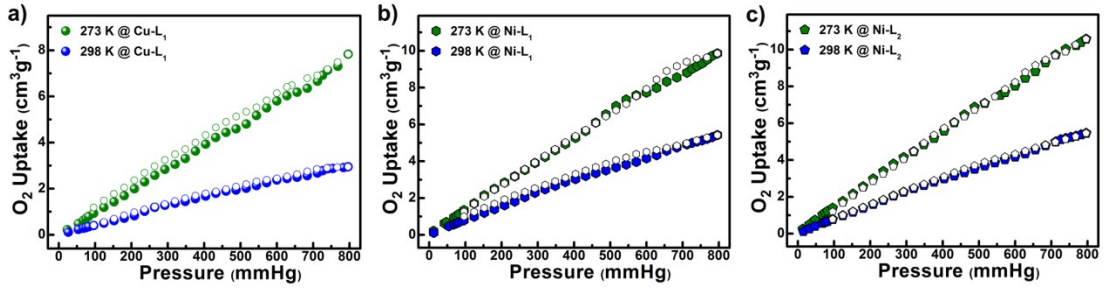

Fig. S17 O_2 sorption isotherms for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c) at 273 and 298 K.

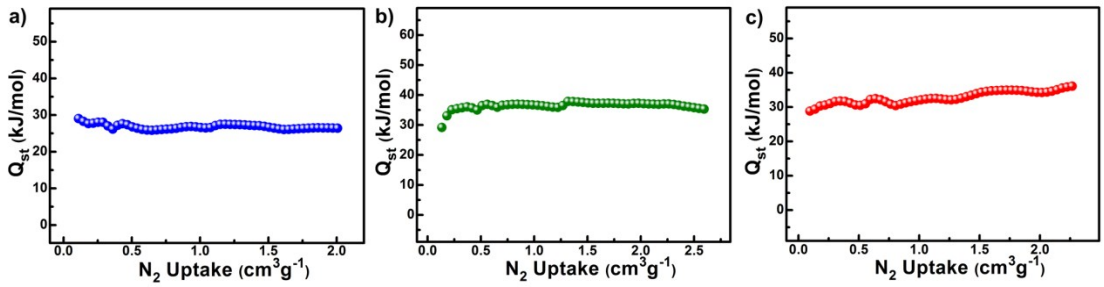

Fig. S18 Q_{st} of N_2 for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c).

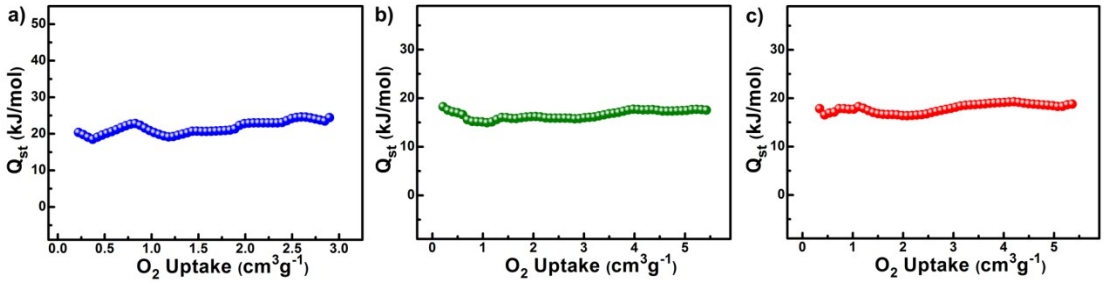

Fig. S19 Q_{st} of O_2 for compounds **Cu-L$_1$** (a), **Ni-L$_1$** (b) and **Ni-L$_2$** (c).

S3. Supporting Tables

Table S1. Crystal data and structure refinements for compounds **Cu-L$_1$**, **Ni-L$_1$** and **Ni-L$_2$**.

Compound	**Cu-L$_1$**	**Ni-L$_1$**	**Ni-L$_2$**
Formula	$C_{48}H_{53}Cu_4N_{19}O_{22}$	$C_{51}H_{68}N_{20}Ni_4O_{27}$	$C_{47}H_{56}N_{24}Ni_4O_{23}$
F_w	1502.25	1628.09	1559.99
Temp (K)	293(2) K	293(2) K	293(2) K
Crystal system	Trigonal	Trigonal	Trigonal
Space group	$P3_221$	$P3_221$	$P3_221$
a (Å)	16.547	16.851	16.943
b (Å)	16.547	16.851	16.943
c (Å)	10.580	10.518	10.504
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	120
V(Å^3)	2508.8(9)	2586.6(9)	2611.3(9)
Z, D_c (Mg/m^3)	1.50, 1.491	1.50, 1.568	1.50, 1.488
Absorption coefficient (mm^{-1})	1.339	1.170	1.153
F(000)	1149	1263	1203
Reflections collected/unique	16441/3056	17113/3240	17094/3168
R_{int}	0.0368	0.0711	0.0527
Data/restraints/ parameters	3056/24/148	3240/0/155	3168/110/203
Goodness-of-fit on F^2	1.107	1.010	1.054
R_1, wR_2 [I > 2σ(I)]	0.0698, 0.1831	0.0440, 0.1115	0.0462, 0.1201
R_1, wR_2 (all data)	0.0706, 0.1839	0.0517, 0.1157	0.0509, 0.1224

Table S2. Selected bond lengths [Å] and angles [°] for compound **Cu-L$_1$**.

Compound **Cu-L$_1$**			
Cu(1)-O(3)	1.956(5)	Cu(1)-N(3)	2.061(6)
Cu(1)-O(1)#1	1.967(5)	Cu(1)-O(2)#3	2.280(5)
Cu(1)-N(2)#2	2.019(6)	O(3)-Cu(1)-O(1)#1	91.94(19)
O(3)-Cu(1)-N(2)#2	178.24(18)	O(1)#1-Cu(1)-N(2)#2	86.4(2)
O(3)-Cu(1)-N(3)	88.7(2)	O(1)#1-Cu(1)-N(3)	167.6(2)
N(2)#2-Cu(1)-N(3)	92.9(2)	O(3)-Cu(1)-O(2)#3	92.5(2)
O(1)#1-Cu(1)-O(2)#3	101.6(2)	N(2)#2-Cu(1)-O(2)#3	88.4(2)
N(3)-Cu(1)-O(2)#3	90.8(2)	C(9)-O(1)-Cu(1)#4	127.3(4)
C(9)-O(2)-Cu(1)#5	124.5(5)	N(4)-O(3)-Cu(1)	121.7(2)
N(4)-O(3)-Cu(1)#6	121.7(2)	Cu(1)-O(3)-Cu(1)#6	116.6(5)
C(1)-N(2)-Cu(1)#7	123.2(5)	C(3)-N(2)-Cu(1)#7	132.0(5)
C(7)-N(3)-Cu(1)	121.2(4)	C(8)-N(3)-Cu(1)	119.8(4)

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

Table S3. Selected bond lengths [Å] and angles [°] for compound **Ni-L$_1$**.

Compound **Ni-L$_1$**			
Ni(1)-O(1)#1	2.012(4)	Ni(1)-N(2)#2	2.063(5)
Ni(1)-O(2)#3	2.079(4)	Ni(1)-O(4)	2.085(5)
Ni(1)-O(3)	2.097(4)	Ni(1)-N(3)	2.100(5)
O(1)#1-Ni(1)-N(2)#2	84.75(19)	O(1)#1-Ni(1)-O(2)#3	98.50(17)
N(2)#2-Ni(1)-O(2)#3	87.53(18)	O(1)#1-Ni(1)-O(4)	87.46(18)
N(2)#2-Ni(1)-O(4)	87.6(2)	O(2)#3-Ni(1)-O(4)	171.91(19)
O(1)#1-Ni(1)-O(3)	88.54(16)	N(2)#2-Ni(1)-O(3)	173.23(16)
O(2)#3-Ni(1)-O(3)	94.35(16)	O(4)-Ni(1)-O(3)	91.2(2)
O(1)#1-Ni(1)-N(3)	173.64(18)	N(2)#2-Ni(1)-N(3)	93.5(2)
O(2)#3-Ni(1)-N(3)	87.50(19)	O(4)-Ni(1)-N(3)	86.4(2)
O(3)-Ni(1)-N(3)	93.12(17)	C(9)-O(1)-Ni(1)#4	132.3(3)
C(9)-O(2)-Ni(1)#5	129.9(4)	N(4)-O(3)-Ni(1)	123.12(15)
N(4)-O(3)-Ni(1)#6	123.12(15)	Ni(1)-O(3)-Ni(1)#6	113.8(3)
C(7)-N(3)-Ni(1)	121.1(4)	C(8)-N(3)-Ni(1)	119.3(4)
C(1)-N(2)-Ni(1)#7	123.3(5)	C(3)-N(2)-Ni(1)#7	129.2(4)

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

Table S4. Selected bond lengths [Å] and angles [°] for compound **Ni-L$_2$**.

Compound **Ni-L$_2$**			
Ni(1)-O(1)#1	2.012(5)	Ni(1)-O(2)#2	2.066(4)
Ni(1)-O(3)	2.066(4)	Ni(1)-N(3)#3	2.095(6)
Ni(1)-N(4)	2.096(5)	Ni(1)-O(4)	2.122(5)
O(1)#1-Ni(1)-O(2)#2	98.2(2)	O(1)#1-Ni(1)-O(3)	89.73(17)
O(2)#2-Ni(1)-O(3)	95.33(18)	O(1)#1-Ni(1)-N(3)#3	85.1(2)
O(2)#2-Ni(1)-N(3)#3	86.8(2)	O(3)-Ni(1)-N(3)#3	174.62(18)
O(1)#1-Ni(1)-N(4)	174.0(2)	O(2)#2-Ni(1)-N(4)	87.1(2)
O(3)-Ni(1)-N(4)	92.51(19)	N(3)#3-Ni(1)-N(4)	92.5(2)
O(1)#1-Ni(1)-O(4)	87.7(2)	O(2)#2-Ni(1)-O(4)	168.9(2)
O(3)-Ni(1)-O(4)	94.1(2)	N(3)#3-Ni(1)-O(4)	84.3(2)
N(4)-Ni(1)-O(4)	86.6(2)	C(8)-O(1)-Ni(1)#6	133.0(4)
C(8)-O(2)-Ni(1)#7	129.0(4)	N(7)-O(3)-Ni(1)	122.89(15)
N(7)-O(3)-Ni(1)#4	122.89(15)	Ni(1)-O(3)-Ni(1)#4	114.2(3)
C(9)-O(4)-Ni(1)	133.0(9)	N(6)-O(4)-Ni(1)	114.9(9)
C(2)-N(3)-Ni(1)#8	121.0(5)	C(1)-N(3)-Ni(1)#8	133.2(7)
C(1')-N(3)-Ni(1)#8	126.4(7)	C(4)-N(4)-Ni(1)	119.4(5)
C(5)-N(4)-Ni(1)	122.4(4)		

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

#6 y+1,x,-z #7 -y+1,x-y,z-1/3 #8 -y+1,x-y,z+2/3

Table S5. Comparison of CO_2 adsorption data at 273 K.

Compound	BET ($m^2\ g^{-1}$)	CO_2 ($cm^3\ g^{-1}$)	Qst ($kJ\ mol^{-1}$)	Ref.
Cu-L_1	**716**	**115**	**24.8**	**This work**
JLU-Liu47	1800	192	35	1
Cu-TDPAT	1938	227	42.2	2
CPM-200-Fe/Mg	1459	207.6	34.3	3
IFMC-1	780	91.4	30.7	4
JLU-Liu38	1784	92.6	24	5
CPM-20	1009	91.2		6
FJI-C1	1726.3	64	20.7	7
$(Et_2NH_2)[In(2,6\text{-}NDC)_2]\cdot 2H_2O\cdot DEF$	891	72.2	19.6	8
$[H_2N(CH_3)_2][In(4,4'BPDC)_2]\ \bullet 4DMF\bullet 2H_2O$	638	34	25.8	9
$[Cu(F\text{-}pymo)_2]_n$		38.7	49-55	10
NOTT-202a	2220	~56	20-25	11
InOF-15	935.6	78	31.1	12

"~"represent approximate values are obtained from the figures of reported acticles.

Table S6. Comparison of C_3H_8/CH_4 selectivity (0.5/0.5) at 101 kPa and 298 K of compounds **Cu-L_1** and **Ni-L_2** with the reported MOFs.

Compound	C_3H_8/CH_4 (0.5/0.5)	Ref.
Cu-L_1	**175**	**This work**
Ni-L_2	**167**	**This work**
UPC-33	41.8	13
BSF-1	353	14
$[Cu_4(PMTD)_2(H_2O)_3]\cdot 20\ H_2O$	~105	15
JLU-Liu23	273	16
JLU-MOF51	220	17
$[Zn_{24}(BDPO)_{12}(DMF)_{12}]\cdot 6DMF\cdot 52H_2O$	125	18
FJI-C4	293	19
UTSA-35a	~80	20
eea-MOF-4	136	21

"~"represent approximate values are obtained from the figures of reported acticles.

Table S7. 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 compounds **Cu-L$_1$**, **Ni-L$_1$** and **Ni-L$_2$** at 298 K.

Cu-L$_1$	**q_{m1}**	**b_1**	**$1/n_1$**	**q_{m2}**	**b_2**	**$1/n_2$**	**R^2**
CO_2	0.38684	0.04058	0.88895	29.56189	2.91706E-4	1.1983	1
CH_4	1	0.00415	0.99341	1.9418	4.33339E-7	2.47973	0.99995
C_2H_6	3.58732	5.40009E-4	1.88337	0.7894	0.05024	1.06683	1
C_3H_8	2.25703	0.05579	2.40374	2.13085	0.1294	0.78189	0.99999

Ni-L$_1$	**q_{m1}**	**b_1**	**$1/n_1$**	**q_{m2}**	**b_2**	**$1/n_2$**	**R^2**
CO_2	7	0.00299	0.98054	16.49958	1.02113E-6	2.16191	0.99999
CH_4	2.76023	9.25777E-6	1.98086	0.2	0.01038	1.15305	0.9999
C_2H_6	0.02944	0.11866	2.24535	3.80853	0.00678	1.22221	0.99999
C_3H_8	2.51574	0.08526	1.86066	3.04433	0.02843	0.56059	0.99998

Ni-L$_2$	**q_{m1}**	**b_1**	**$1/n_1$**	**q_{m2}**	**b_2**	**$1/n_2$**	**R^2**
CO_2	0.75267	0.02757	0.92348	17.66724	2.77914E-4	1.25814	1
CH_4	1.06409	0.00329	0.9113	2.22501	1.02406E-4	1.4184	0.99985
C_2H_6	4.01293	0.00478	1.30441	0.14241	0.23661	1.09311	1
C_3H_8	2.17334	0.10758	0.61134	2.29706	0.08328	1.88911	1

Table S8. Comparison of O_2/N_2 selectivity at 20 kPa and 77 K.

Compound	**O_2/N_2**	**Q_{st} of O_2 (kJ/mol)**	**Ref.**
Cu-L$_1$	**1.44**	**24.4**	**This work**
Ni-L$_1$	**1.34**	**17.6**	**This work**
Ni-L$_2$	**1.45**	**18.8**	**This work**
Mn/Cu-BTC	1.32	~14	22
Fe/Cu-BTC	1.27	~14	22
Co/Cu-BTC	1.27	15.7	22
Cu-BTC	1.13	10.7	22
JLU-Liu31	1.34	-	23
JLU-Liu18	1.24	16	24

"~"represent approximate values are obtained from the figures of reported acticles.

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