A Polyhedron-Based Heterometallic MOF Constructed by HSAB Theory and SBB Strategy: Synthesis, Structure, and Adsorption Properties

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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 **In/Cu-CBDA**, which should be converted to absolute loadings (q) firstly.

$$q = q^{ex} + \frac{pV_{pore}}{ZRT} \quad (1)$$

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 1.13 cm^3 g^{-1} is also necessary.

In order to perform the IAST calculations, the single-component isotherm was fitted by the dual-site Langmuir-Freundlich (DSLF) adsorption model to correlate the pure-component equilibrium data and further predict the adsorption of mixtures. The DSLF model is described as:

$$q = q_{m_1} \times \frac{b_1 \times p^{1/n_1}}{1 + b_1 \times p^{1/n_1}} + q_{m_2} \times \frac{b_2 \times p^{1/n_2}}{1 + b_2 \times p^{1/n_2}} \quad (2)$$

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.

To investigate the separation of binary mixtures, the adsorption selectivity is defined by

$$S_{ij} = \frac{x_1/x_2}{y_1/y_2} \quad (3)$$

x_1 and x_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 x_1 and x_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

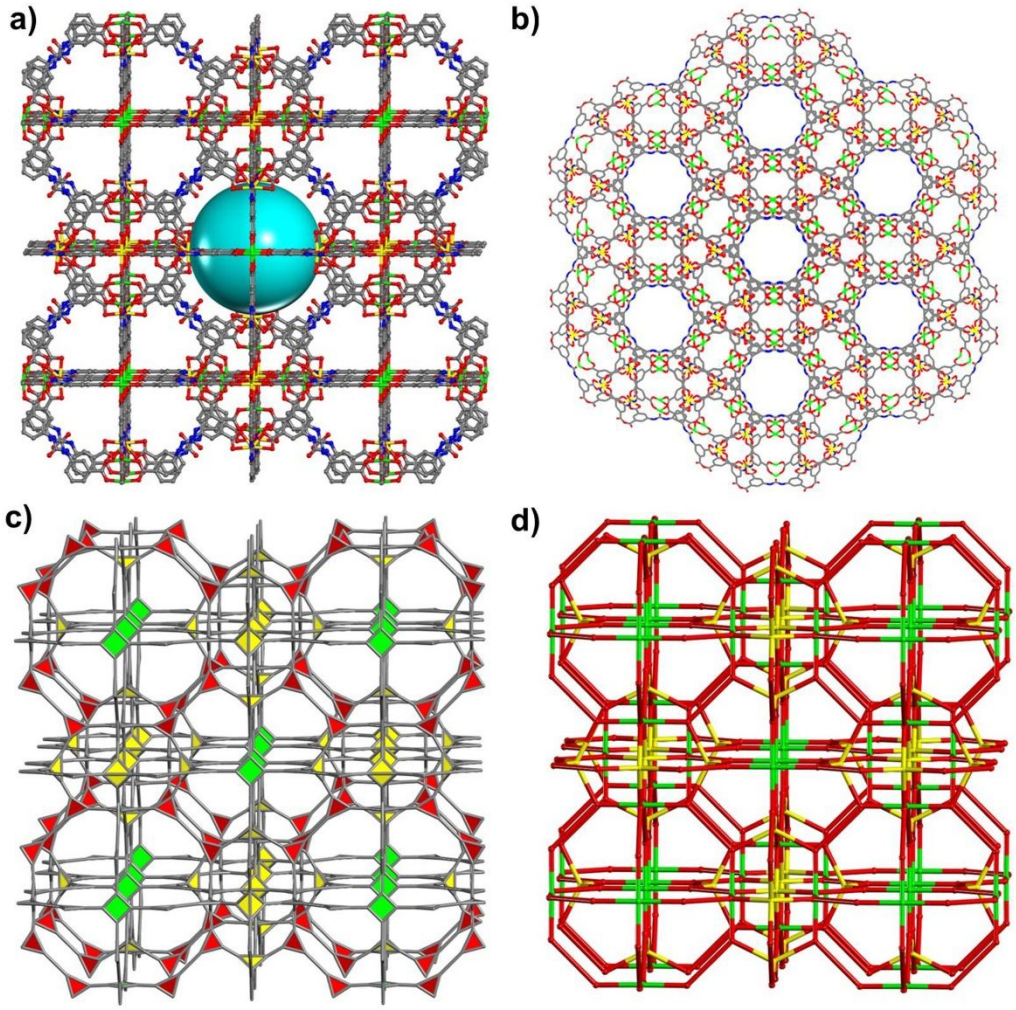

Figure S1 Single-crystal structure for **In/Cu-CBDA**: (a-b) ball-stick model of the 3D network viewed at different directions; (c-d) polyhedron and topology view of the net.

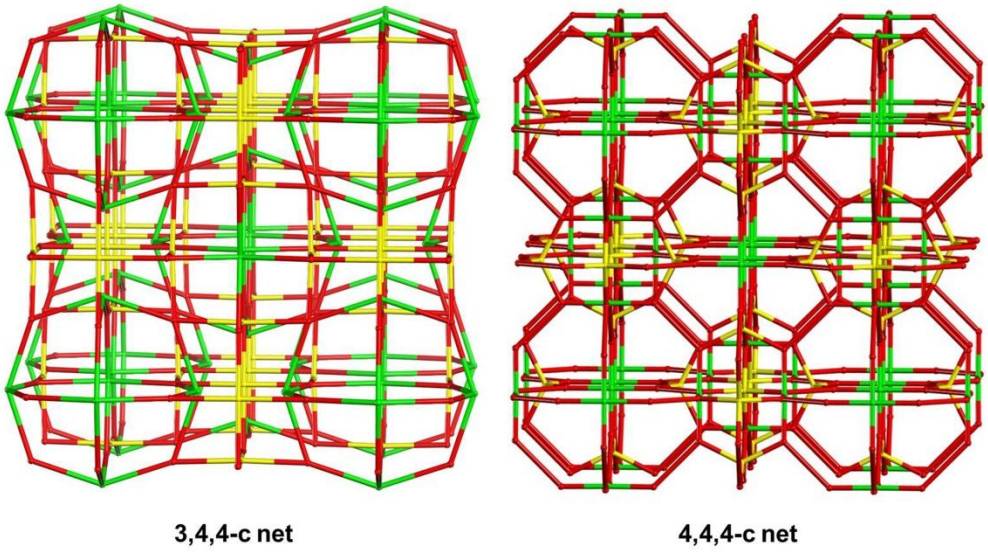

Figure S2 The topology of **In/Cu-CBDA** can be simplified as (3,4,4)-c net or 4-c net, respectively.

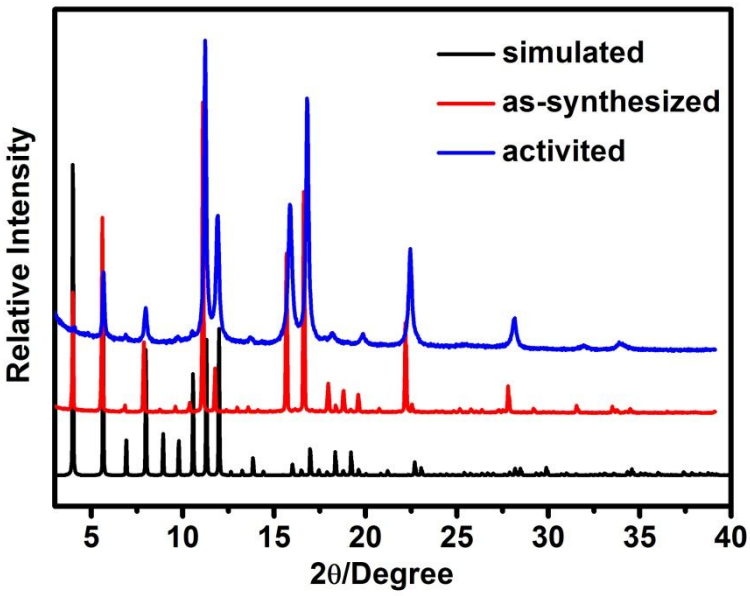

Figure S3 PXRD patterns for **In/Cu-CBDA** samples: simulated, as-synthesized, and activated.

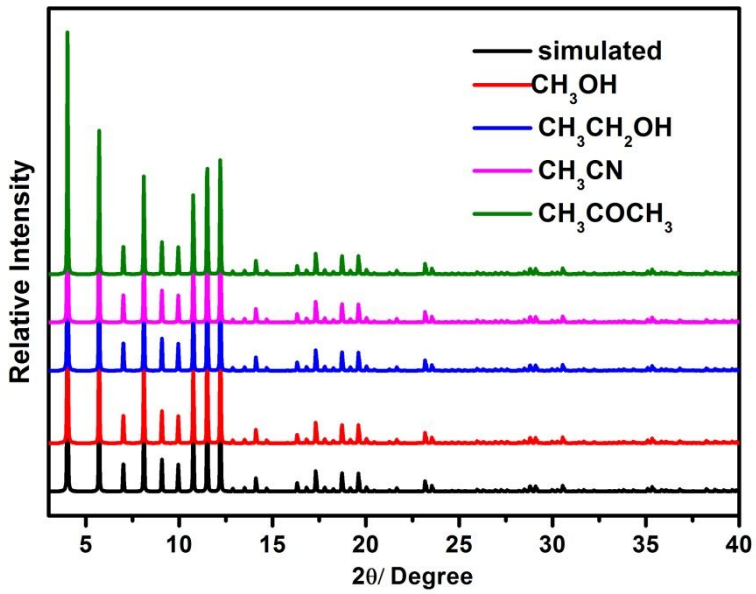

Figure S4 PXRD patterns for **In/Cu-CBDA** samples immersed in different solvents are commendable consistent with the simulated pattern, which displays that the crystal structure can remain outstanding stable in different organic solvents.

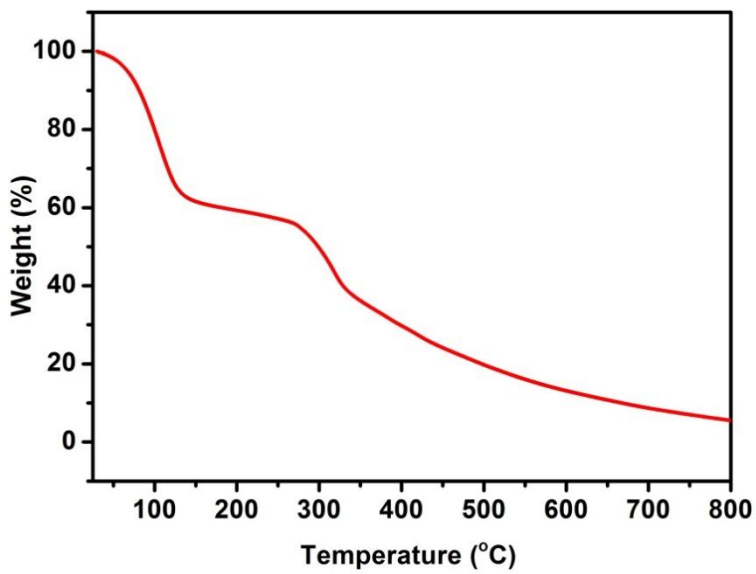

Figure S5 TGA curve of **In/Cu-CBDA**.

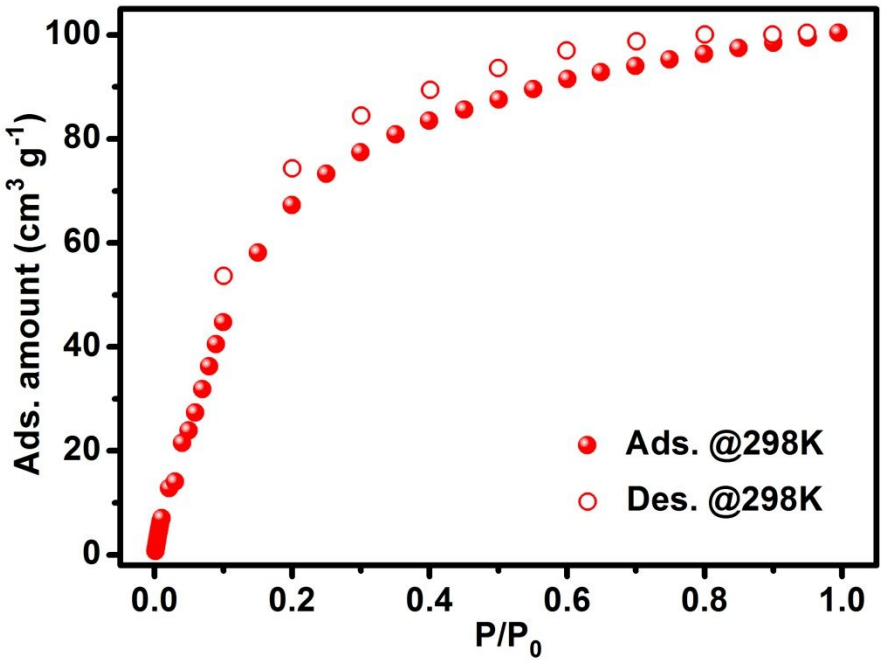

Figure S6 C_3H_8 adsorption isotherm of **In/Cu-CBDA** after exposure to air three days at 298 K.

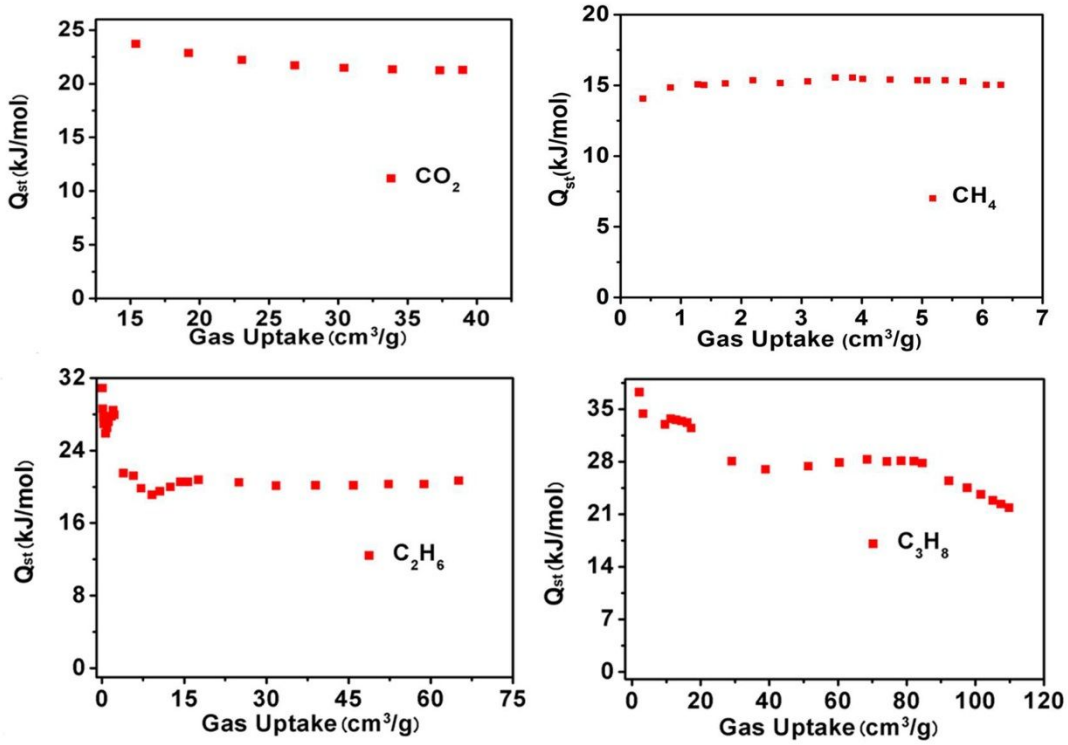

Figure S7 Isosteric heat of CO_2, CH_4, C_2H_6, and C_3H_8 for **In/Cu-CBDA**.

Table S1. Crystal data and structure refinement for **In/Cu-CBDA**.

Compound	**In/Cu-CBDA**
Empirical formula	$C_{34}H_{20}Cu_2InN_4O_{20}$
Formula weight	1046.44
Temperature (K)	296.15 K
Wavelength (Å)	0.71073
Crystal system	Cubic
Space group	Im-3m
a (Å)	31.3315(5)
b (Å)	31.3315(5)
c (Å)	31.3315(5)
α (deg)	90
β (deg)	90
γ (deg)	90
Volume (Å^3)	30757.0(15)
Z	12
Dcalc (Mg/m^3)	0.678
F(000)	6228
Reflections collected	40660
Unique (R_{int})	0.0565
Goodness-of-fit on F^2	1.057
R_1, wR_2 $[I>2\sigma(I)]$	0.0330, 0.0891
R_1, wR_2 *(all data)*	0.0496, 0.1025

The guest molecules were highly disordered and could not be modeled properly, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules. The reported refinements are of the guest-free structures using the *.hkp files produced using the SQUEEZE routine.

Table S2. Bond lengths [Å] and angles [°] for **In/Cu-CBDA**.

In(1)-O(2)#1	2.392(2)	O(1)#2-In(1)-O(2)#2	133.78(8)
In(1)-O(2)#2	2.392(2)	O(1)-In(1)-O(2)#1	86.48(4)
In(1)-O(2)#3	2.392(2)	O(1)#3-In(1)-O(2)#2	55.30(7)
In(1)-O(2)	2.392(2)	O(1)-In(1)-O(1)#2	133.78(8)
In(1)-O(1)#2	2.190(2)	O(1)#2-In(1)-O(1)#1	133.78(8)
In(1)-O(1)#3	2.190(2)	O(1)#3-In(1)-O(1)#2	126.86(7)
In(1)-O(1)#1	2.190(2)	O(1)-In(1)-O(1)#3	126.86(7)
In(1)-O(1)	2.190(2)	O(1)-In(1)-O(1)#1	78.48(11)
In(1)-C(8)#2	2.649(3)	O(1)#3-In(1)-O(1)#1	126.86(7)
In(1)-C(8)#1	2.649(3)	O(1)#3-In(1)-O(1)#2	78.48(11)
In(1)-C(8)#3	2.649(3)	O(1)-In(1)-O(1)#3	126.86(7)
Cu(2)-Cu(1)	2.6162(8)	O(1)-In(1)-O(1)#1	78.47(11)
Cu(2)-O(3)#4	1.9593(19)	O(1)#3-In(1)-O(1)#1	126.86(7)
Cu(2)-O(3)#5	1.9593(19)	O(1)-In(1)-C(8)#1	106.05(9)
Cu(2)-O(3)	1.9592(19)	O(1)#2-In(1)-C(8)#1	107.75(5)
Cu(2)-O(3)#6	1.9593(19)	O(1)#3-In(1)-C(8)#2	106.05(9)
Cu(2)-O(6)	2.141(4)	O(1)#3-In(1)-C(8)#3	27.58(8)
Cu(1)-O(5)	2.107(4)	O(1)#2-In(1)-C(8)#3	106.05(9)
Cu(1)-O(4)#5	1.9511(19)	O(1)#1-In(1)-C(8)#3	107.75(5)
Cu(1)-O(4)#6	1.9511(19)	O(1)-In(1)-C(8)#3	107.75(5)
Cu(1)-O(4)#4	1.9511(19)	O(1)#1-In(1)-C(8)#1	27.58(8)
Cu(1)-O(4)	1.9511(19)	O(1)#2-In(1)-C(8)#2	27.58(8)
O(2)-In(1)-O(2)#2	90.359(8)	O(1)#3-In(1)-C(8)#1	107.75(5)
O(2)-In(1)-O(2)#3	90.359(8)	O(1)-In(1)-C(8)#2	107.75(5)
O(2)#1-In(1)-O(2)#2	90.359(8)	O(1)#1-In(1)-C(8)#2	107.75(5)
O(2)#2-In(1)-O(2)#3	170.92(10)	C(8)#3-In(1)-C(8)#2	133.63(14)
O(2)#1-In(1)-O(2)#3	90.359(8)	C(8)#3-In(1)-C(8)#1	98.92(5)
O(2)-In(1)-O(2)#1	170.92(10)	C(8)#2-In(1)-C(8)#1	98.92(5)
O(2)-In(1)-C(8)#2	88.21(2)	O(3)#6-Cu(2)-Cu(1)	84.13(6)
O(2)#3-In(1)-C(8)#2	161.36(9)	O(3)#5-Cu(2)-Cu(1)	84.13(6)
O(2)-In(1)-C(8)#1	161.36(9)	O(3)#4-Cu(2)-Cu(1)	84.13(6)
O(2)#2-In(1)-C(8)#2	27.73(8)	O(3)-Cu(2)-Cu(1)	84.13(6)
O(2)-In(1)-C(8)#3	88.21(2)	O(3)#5-Cu(2)-O(3)#4	89.401(12)
O(2)#2-In(1)-C(8)#1	88.21(2)	O(3)#6-Cu(2)-O(3)#4	89.401(12)
O(2)#1-In(1)-C(8)#3	88.21(2)	O(3)#5-Cu(2)-O(3)#6	168.27(12)
O(2)#1-In(1)-C(8)#1	27.73(8)	O(3)-Cu(2)-O(3)#6	89.401(12)
O(2)#2-In(1)-C(8)#3	161.36(9)	O(3)-Cu(2)-O(3)#5	89.401(12)
O(2)#1-In(1)-C(8)#2	88.21(2)	O(3)-Cu(2)-O(3)#4	168.26(12)
O(2)#3-In(1)-C(8)#1	88.21(2)	O(3)-Cu(2)-O(6)	95.87(6)
O(2)#3-In(1)-C(8)#3	27.73(8)	O(3)#4-Cu(2)-O(6)	95.87(6)
O(1)#1-In(1)-O(2)#1	55.30(7)	O(3)#5-Cu(2)-O(6)	95.87(6)
O(1)-In(1)-O(2)	55.31(7)	O(3)#6-Cu(2)-O(6)	95.87(6)
O(1)#2-In(1)-O(2)#3	133.78(8)	O(6)-Cu(2)-Cu(1)	180.0

O(1)#1-In(1)-O(2)#2	86.48(4)	O(5)-Cu(1)-Cu(2)	180.0
O(1)-In(1)-O(2)#3	86.48(4)	O(4)#6-Cu(1)-Cu(2)	84.82(6)
O(1)#3-In(1)-O(2)#3	55.30(7)	O(4)#4-Cu(1)-Cu(2)	84.82(6)
O(1)#1-In(1)-O(2)#3	86.48(4)	O(4)-Cu(1)-Cu(2)	84.82(6)
O(1)#3-In(1)-O(2)#1	86.48(4)	O(4)#5-Cu(1)-Cu(2)	84.82(6)
O(1)#2-In(1)-O(2)#1	86.48(4)	O(4)#6-Cu(1)-O(5)	95.18(6)
O(1)#3-In(1)-O(2)	86.48(4)	O(4)#5-Cu(1)-O(5)	95.18(6)
O(1)-In(1)-O(2)#2	86.48(4)	O(4)#4-Cu(1)-O(5)	95.18(6)
O(1)#1-In(1)-O(2)	133.78(8)	O(4)-Cu(1)-O(5)	95.18(6)
O(1)#2-In(1)-O(2)	86.48(4)	O(4)#6-Cu(1)-O(4)	89.533(11)
O(1)#2-In(1)-O(2)#2	55.30(7)	O(4)#5-Cu(1)-O(4)	89.533(11)
O(1)-In(1)-O(2)#1	133.78(8)	O(4)#4-Cu(1)-O(4)	169.64(12)
O(1)#3-In(1)-O(2)#2	133.78(8)	O(4)#6-Cu(1)-O(4)#5	169.64(12)
O(1)-In(1)-O(1)#2	126.86(7)	O(4)#6-Cu(1)-O(4)#4	89.533(11)
O(1)#2-In(1)-O(1)#1	126.86(7)	O(4)#4-Cu(1)-O(4)#5	89.533(11)

Table S3 Summary of adsorption selectivity of many reported MOFs at 298 K and 1 bar. N.A.: Not Available. The articles do not list the data.

Compounds	CO_2/CH_4	C_2H_6/CH_4	C_3H_8/CH_4	References
MOF-5	15.5	N.A.		Environ. Sci. Technol., **2010**, 44, 1820
MOF-177	4.4			
UTSA-15	24.2			Inorg. Chem. **2011**, 50, 3442
UTSA-5	10.2			CrystEngComm. **2013**, 15, 5232
SiF6-2-Cu	33			Nature **2013**, 495, 80
SiF6-2-Cu-i	140			
SiF6-3-Zn	231			
UiO-66(Hf)	12			Inorg. Chem., **2016**, 55, 1134
ZJNU-59	7.9			ACS Appl. Mater. Interfaces **2018**, 10, 20559
ZJNU-84	7.2			Inorg. Chem. Front., **2018**, 5, 1423–1431
$\{[Ln_2Ni(OAc)_5(HL)(L)]\bullet$solvent	16.8			Dalton Trans., **2018**, 47, 15344
UTSA-120a	370			J. Mater. Chem. A, **2019**, 7, 3128
$\{[Zn_2(bdc)_2(bpNDI)]\cdot 4DMF\}_n$	3.8-598	3.3-175	N.A.	Chem. Eur. J. **2016**, 22, 6059
ZJNU-63 (278K)	4.2	13.8	N.A.	Inorg. Chem. Front., **2018**, 5, 2227
UTSA-36a	N.A.	14.7	N.A.	Chem. Eur. J. **2012**, 18, 613
ZJU-61		49.5		Microporous Mesoporous Mater.

				2014, 190, 32
FIR-7a-ht	N.A.	14.6	78.8	Chem. Commun. **2013**, 49, 11323
PAF-40		15.2	48.2	J. Mater. Chem. A **2014**, 2, 14536
PAF-40-Fe		16.2	56	
PAF-40-Mn		30.8	246	
JUC-100		8-16	65-150	Chem. Eur. J. **2014**, 20, 9073
JUC-103				
JUC-106				
FJI-C4		39.7	293.4	ACS Appl. Mater. Interfaces **2016**, 8, 9777
UPC-21(295K)		15.3	67	J. Mater. Chem. A, **2017**, 5, 1168
JLU-Liu51		7.5	220	ACS Appl. Mater. Interfaces **2018**, 10, 31233
UPC-100-In		26.6	186.4	J. Mater. Chem. A, **2018**, 6, 24486
UPC-101-Al		8.9	37.2	
UPC-102-Zr		13	42.5	
eea-MOF-4	4.3	17	136	J. Mater. Chem. A, **2015**, 3, 6276
eea-MOF-5	7.3	22	156	
JLU-Liu22	9.4	14.4	271.5	Chem. Commun., **2015**, 51, 15287
JLU-Liu20	5.9	7.0	11.1	Chem. Commun., **2016**, 52, 3223
JLU-Liu21	6.9	7.0	99.2	
LIFM-26	36	46	202	Chem. - Eur. J. **2017**, 23, 4060
JLU-Liu7	6.9	50.4	128.5	Inorg. Chem. Front., **2017**, 4, 139
JLU-Liu37	3.8	11	206	Inorg. Chem. **2017**, 56, 4141
JLU-Liu38	5.6	15	98	
JLU-Liu46	9.8	17	169	ACS Appl. Mater. Interfaces **2017**, 9, 32820
JLU-Liu47	10.4	17	168	
UPC-33(273K)	33.12	6.64	151.5	Chem. Eur. J. **2018**, 24, 2137
In/Cu-CBDA (273K)	**7.3**	**25.3**	**191.6**	**This work**

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 **In/Cu-CBDA** at 273 K.

adsorbate	q_{m1} [mmol g^{-1}]	b_1 [kPa^{-1}]	n_1	q_{m2} [mmol g^{-1}]	b_2 [kPa^{-1}]	n_2	R^2
CO_2	0.22692	0.06337	1.12513	31.85657	7.08133E-4	1.09585	0.9999
CH_4	0.01262	0.0107	2.4707	8.66083	5.36748E-4	1.03346	0.9999
C_2H_6	41.8043	0.0024	0.92504	0.27203	0.05038	0.59662	0.9999
C_3H_8	2.22427	0.03971	2.40812	5.49823	0.12193	0.56241	0.9999