Supporting Information

A Heterometallic Metal-organic framework based on mulit-nuclear clusters exhibiting high stability and selective gas adsorption

Dongmei Wang[a], Zihua Liu[a], Lili Xu[a], Chunxia Li[a,*], Dian Zhao[a], Genwu Ge[b], Zhenling Wang[b,*] and Jun Lin[c,*]

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, P. R. China. E-mail: cxli@zjnu.edu.cn; dmwang@zjnu.edu.cn.

[b] Henan Key Laboratory of Rare Earth Functional Materials, Zhoukou Normal University, Zhoukou, P. R. China. E-mail: zlwang2007@hotmail.com

[c] *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China.* E-mail: jlin@ciac.ac.cn

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/Tb-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 0.64 $cm^3\ g^{-1}$ 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.

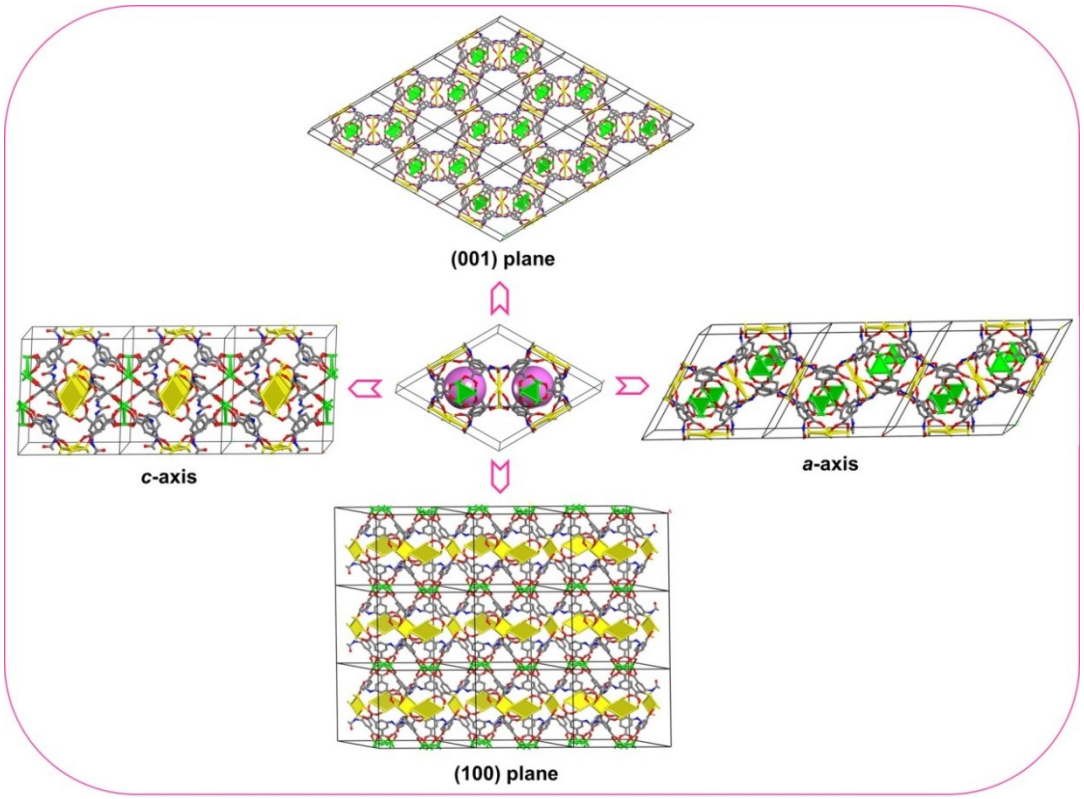

Figure S1 The cell structure of **In/Tb-CBDA** extends along *a*-axis and *c*-axis, and expands at (001) and (100) plane.

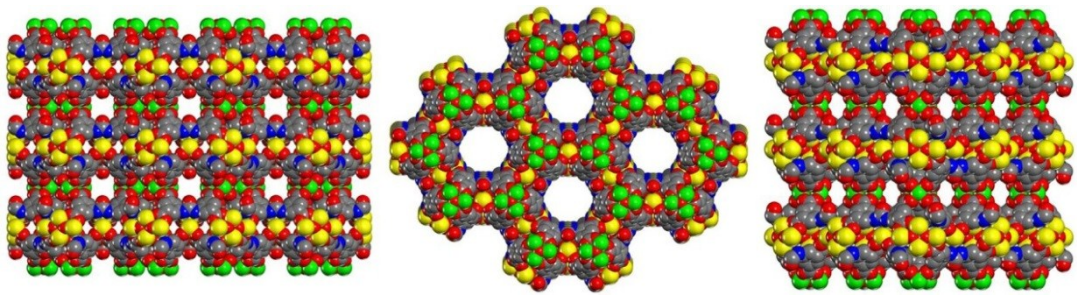

Figure S2 Space-filling view of the structure of **In/Tb-CBDA** showing multiple pores along different directions.

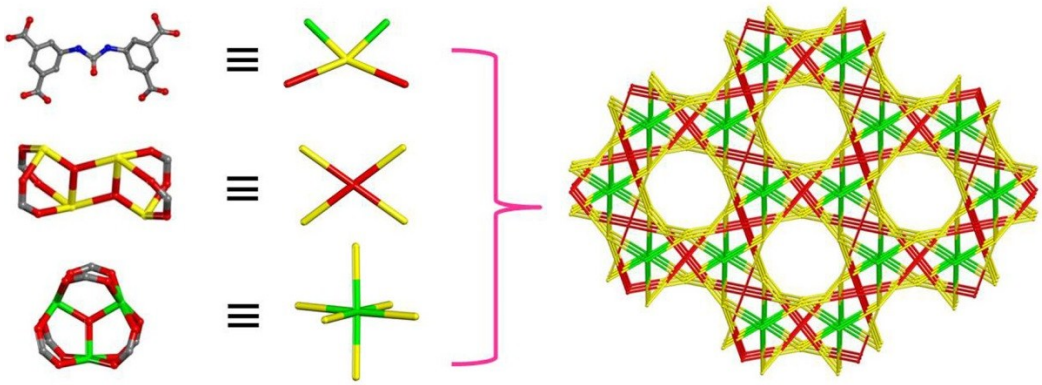

Figure S3 Illustration of topology of **In/Tb-CBDA**: simplification of the $[In_4O_2(COO)_4]$ (4-c node), $[Tb_3O(COO)_6]$ (6-c node) linked by ligand (4-c node) leads to a new (4,4,6)-c net.

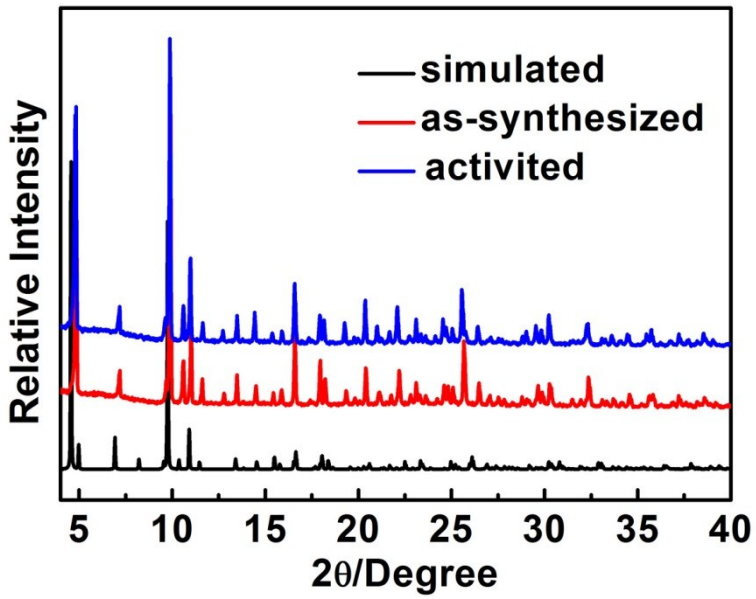

Figure S4 PXRD patterns for **In/Tb-CBDA** samples: simulated, as-synthesized, and activated.

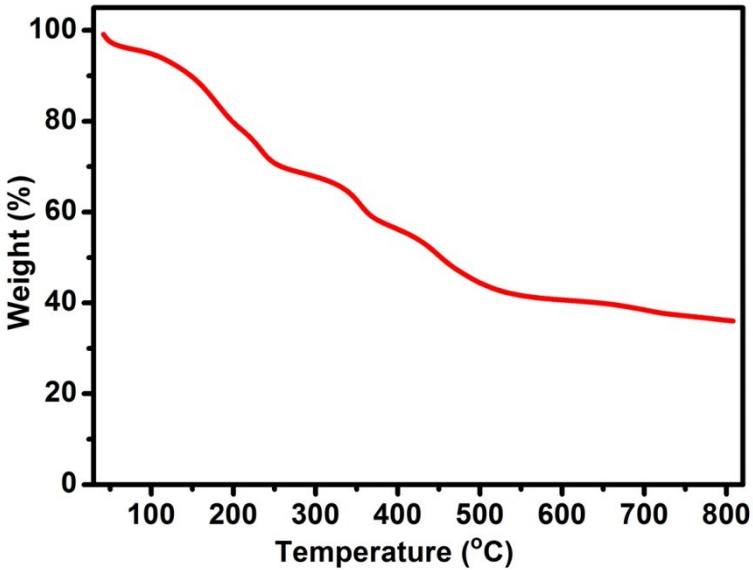

Figure S5 TGA curves of **In/Tb-CBDA**.

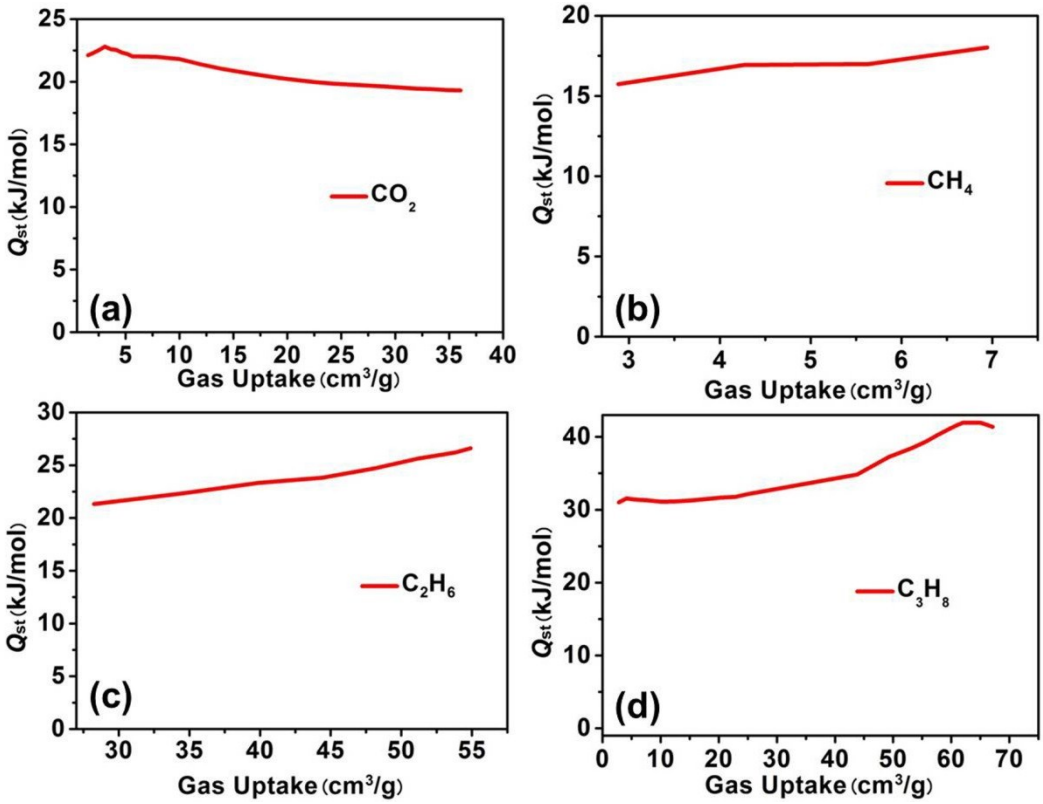

Figure S6 a) Isosteric heat of CO_2 (a), CH_4 (b), C_2H_6 (c), and C_3H_8 (d) for **In/Tb-CBDA**.

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

Compound	**In/Tb-CBDA**
Empirical formula	C_{51} H_{30} In_6 N_6 O_{52} Tb_3
Formula weight	2724.49
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Trigonal
Space group	*P -3 1 m*
a (Å)	21.0227(12)
b (Å)	21.0227(12)
c (Å)	16.8234(18)
α (deg)	90
β (deg)	90
γ (deg)	120
Volume (Å^3)	6439.0(10)
Z	2
Dcalc (Mg/m^3)	1.405
F(000)	2566
Reflections collected	40660
Unique (R_{int})	0.0866
Goodness-of-fit on F^2	1.134
R_1, wR_2 *[I>2σ(I)]*	0.1020, 0.3318
R_1, wR_2 *(all data)*	0.1289, 0.3744

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/Tb-CBDA**.

Tb(1)-O(1A)	2.0400(7)	Tb(1)-O(4)	2.147(7)
Tb(1)-O(4)#1	2.147(7)	Tb(1)-O(2)	2.162(7)
Tb(1)-O(2)#1	2.163(7)	Tb(1)-O(1)	2.171(12)
Tb(1)-Tb(1)#2	3.5334(13)	Tb(1)-Tb(1)#3	3.5334(13)
O(8)-In(2)	2.101(14)	In(2)-O(12)	2.05(2)
In(2)-O(29)	2.057(18)	In(2)-O(8)#4	2.101(14)
In(2)-O(10)#4	2.130(13)	In(2)-O(10)	2.101(14)
In(2)-O(10)#4	2.130(13)	In(2)-O(10)	2.130(13)
In(3)-O(6)#4	2.139(18)	In(3)-O(6)	2.139(18)

In(3)-O(53)#4	2.33(2)	In(3)-O(53)	2.33(2)
In(3)-O(20)	2.36(5)	In(3)-O(29)	2.395(17)
In(3)-O(29)#5	2.417(17)	O(1A)-Tb(1)#3	2.0400(7)
O(1A)-Tb(1)#2	2.0400(7)		
O(1A)-Tb(1)-O(4)	93.3(2)	O(1A)-Tb(1)-O(4)#1	93.3(2)
O(4)-Tb(1)-O(4)#1	173.4(4)	O(1A)-Tb(1)-O(2)	93.4(2)
O(4)-Tb(1)-O(2)	90.9(3)	O(4)#1-Tb(1)-O(2)	88.7(3)
O(1A)-Tb(1)-O(2)#1	93.4(2)	O(4)-Tb(1)-O(2)#1	88.7(3)
O(4)#1-Tb(1)-O(2)#1	90.9(3)	O(2)-Tb(1)-O(2)#1	173.2(4)
O(1A)-Tb(1)-O(1)	180.0(4)	O(4)-Tb(1)-O(1)	86.7(2)
O(4)#1-Tb(1)-O(1)	86.7(2)	O(2)-Tb(1)-O(1)	86.6(2)
O(2)#1-Tb(1)-O(1)	86.6(2)	O(1A)-Tb(1)-Tb(1)#2	30.0
O(4)-Tb(1)-Tb(1)#2	72.6(2)	O(4)#1-Tb(1)-Tb(1)#2	113.5(2)
O(2)-Tb(1)-Tb(1)#2	72.6(2)	O(2)#1-Tb(1)-Tb(1)#2	113.7(2)
O(1)-Tb(1)-Tb(1)#2	150.0	O(1A)-Tb(1)-Tb(1)#3	30.0
O(4)-Tb(1)-Tb(1)#3	113.5(2)	O(4)#1-Tb(1)-Tb(1)#3	72.6(2)
O(2)-Tb(1)-Tb(1)#3	113.7(2)	O(2)#1-Tb(1)-Tb(1)#3	72.6(2)
O(1)-Tb(1)-Tb(1)#3	150.000(1)	Tb(1)#2-Tb(1)-Tb(1)#3	60.0
O(12)-In(2)-O(29)	179.3(8)	O(12)-In(2)-O(8)	84.5(6)
O(29)-In(2)-O(8)	96.0(6)	O(12)-In(2)-O(8)#4	84.5(6)
O(29)-In(2)-O(8)#4	96.0(6)	O(8)-In(2)-O(8)#4	90.4(9)
O(12)-In(2)-O(10)#4	82.8(6)	O(29)-In(2)-O(10)#4	96.7(5)
O(8)-In(2)-O(10)#4	88.2(6)	O(8)#4-In(2)-O(10)#4	167.3(6)
O(12)-In(2)-O(10)	82.8(6)	O(29)-In(2)-O(10)	96.7(5)
O(8)-In(2)-O(10)	167.3(6)	O(8)#4-In(2)-O(10)	88.2(6)
O(10)#4-In(2)-O(10)	90.3(8)	O(6)#4-In(3)-O(6)	72.6(19)
O(6)#4-In(3)-O(53)#4	147.5(11)	O(6)-In(3)-O(53)#4	97.6(12)
O(6)#4-In(3)-O(53)	97.6(12)	O(6)-In(3)-O(53)	147.5(11)
O(53)#4-In(3)-O(53)	73.8(12)	O(6)#4-In(3)-O(20)	76.7(12)
O(6)-In(3)-O(20)	76.7(12)	O(53)#4-In(3)-O(20)	70.9(10)
O(53)-In(3)-O(20)	70.9(10)	O(6)#4-In(3)-O(29)	131.2(9)
O(6)-In(3)-O(29)	131.2(10)	O(53)#4-In(3)-O(29)	78.9(7)
O(53)-In(3)-O(29)	78.9(7)	O(20)-In(3)-O(29)	141.9(11)
O(6)#4-In(3)-O(29)#5	79.1(9)	O(6)-In(3)-O(29)#5	79.1(9)
O(53)#4-In(3)-O(29)#5	130.5(6)	O(53)-In(3)-O(29)#5	130.5(6)
O(20)-In(3)-O(29)#5	149.8(11)	O(29)-In(3)-O(29)#5	68.3(7)
Tb(1)#3-O(1A)-Tb(1)#2	120.0	Tb(1)#3-O(1A)-Tb(1)	120.0
Tb(1)#2-O(1A)-Tb(1)	120.0		

Table S3 The topological information for **In/Tb-CBDA**.

Vertex figure	**Coordination Sequence**										
Vertex	**CS1**	**CS2**	**CS3**	**CS4**	**CS5**	**CS6**	**CS7**	**CS8**	**CS9**	**CS10**	**Cum10**
V_1(4-c)	4	12	42	76	154	196	324	368	552	576	2305
V_2(4-c)	4	15	35	84	125	225	266	419	464	686	2324
V_3(6-c)	6	15	42	71	144	189	312	356	564	588	2288
Vertex	**Extended point symbols**										
V_1(4-c)	[6(3).6(3).8(4).8(4).8(10).8(10)]										
V_2(4-c)	[4.6.6(2).6(2).8(9).8(9)]										
V_3(6-c)	[4.4.4.6.6.6.6.6.6.6(2).6(2).6(2).8(5).8(5).8(5)]										

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/Tb-CBDA** at 298 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	14.78272	0.00153	0.92993	0.15467	0.07437	0.92526	0.9999
CH_4	2.5	1.15779E-4	1.51121	0.10842	0.01115	1.44559	0.9999
C_2H_6	0.6419	0.10133	0.88176	2.78648	0.00196	1.52964	0.9999
C_3H_8	1.91332	0.08808	1.79333	2.86669	0.0679	0.48475	0.9999