Supporting Information

A photoluminescent indium-organic framework with discrete cages and 1-dimensional channels for gas adsorption

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S1. Materials and Methods

1.1. Materials and Instruments

All the reactions were carried out in 25 ml Teflon-lined autoclave at 393 K under the autogenous pressure. All relevant materials were commercially purchased from reagent provider without further purification.

Laboratory powder X-ray diffraction (PXRD) patterns of the obtained samples were recorded on Bruker D8 advance X-ray diffractometer with graphite monochromatized Cu K α radiation (λ = 1.5405 Å) with a step of 0.02° at a scanning speed of 4°/min in 2-theta ranging from 5° to 40°.

Single component gas adsorption measurements were performed in the Accelerated Surface Area and Porosimetry 2020 System (ASAP2020). All gas were used in the adsorption experiment of 99.9999% purity or higher.

Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FLS920 with 450W xenon light.

Thermogravimetric analyses (TGA) were recorded on a NETZSCH STA 449C unit at a heating rate of 10 K• min⁻¹ under the flowing nitrogen atmosphere.

Elemental analyses (EA) for C, H and N were carried out on a G a EA1112 elemental analyses in the Zhejiang Key Laboratory of Carbon Materials of Wenzhou University, Wenzhou.

1.2. Synthesis of [InEu(BTC)₂(H₂O)₄]•6H₂O•3DMF (InOF-14)

The colorless single crystal **InOF-14** can be solvothermally synthesized in high yield by heating the mixture of InCl₃ (0.14 mmol, 30.0 mg) (when we used the indium nitrate instead of indium chloride, the product can also be obtained but not pure with some precipitation), Eu(NO₃)₃ (0.08 mmol, 30.0 mg), H₃BTC (0.29 mmol, 60.0 mg, H₃BTC = benzene-1,3,5-tricarboxylic acid) in 5 ml DMF (DMF = N,N'-dimethyl formamide) solvent with an additional 0.1 ml HNO₃ was sealed in a 25 ml Teflon-lined bomb holding at 358 K for 5 days, which then cooled down to room temperature. After washed by fresh MeCN, the colorless sample was obtained in *ca*. ~40% yield based on the organic ligand H₃BTC. Meanwhile, the phase purity of the microcrystal sample has been confirmed by the powder X-ray diffraction (PXRD) analysis (Fig. S5). In the end, we propose the whole crystal formula as a neutral [InEu(BTC)₂(H₂O)₄]•6H₂O•3DMF network which is calculated from the combination of thermogravimetric analysis and elemental analysis (Fig. S6). Elemental analyses were calculated for **InOF-14**: C, 29.85%; H, 4.92%; N, 3.87%. Found: C, 29.88%; H, 4.73%; N, 3.94%.

1.3. Single-Crystal X-ray Crystallography

The structure data of **InOF-14** was collected on a SuperNova, Dual, Cu at zero, Atlas diffractometer at the State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou. The crystal was kept at 100 K during collection process.

By using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package. Crystallographic data and structure refinement parameters for this crystal is summarized in Table S1 as follows. The final chemical formula was calculated from the SQUEEZE results combining together with elemental analysis data and TGA data. More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Information as CIF files. Crystallographic data for the structure reported in this paper has been deposited. The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number (CCDC No.) 1400146 for InOF-14. These data can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data request/cif.</u>

Items	InOF-14		
formula	C ₁₈ H ₆ EuInO ₁₆		
mass	745.01		
crystal system	Tetragonal		
space group	P42/mcm (#. 132)		
<i>a</i> (Å)	12.6261(5)		
b (Å)	12.6261(5)		
<i>c</i> (Å)	29.234(3)		
α (°)	90.00		
в (°)	90.00		
γ (°)	90.00		
V (ų)	4660.4(5)		
<i>Т</i> (К)	173 (2)		
Ζ	4		
F(000)	1416		
R _{int}	0.0684		
R ₁	0.0803		
wR ₂	0.2057		
Theta_full	0.999		

Table S1. Summary of Crystal Data and Refinement Results for InOF-14

1.4. Bifunctional Method

Thinking outside the box, our group previously has been innovatively embedded functional Cu-based units into the indium-organic system by taking the bifunctional ligand-directed method, called Bifunctional Method, it is interesting to synthesize InOF materials in which carboxylate-affinitive In(III) ions only bind to carboxylate groups while N-affinitive Cu-based units only bind to pyridyl N-centers. The success of our synthetic strategy derives from essentially different affinity with donor centers between two kinds of metal ions.

On the other hand, herein, we are trying to extend our Bifunctional Method a little bit, namely, by utilizing one multi-carboxylate ligand to simultaneously capture mutually competitive carboxylate-affinitive centres/clusters, which is illuminated in Fig. S1 as follow.



Bifunctional Method

for the Construction of functional heterometallic indium-organic frameworks

M1 = ln(III)

(strong carboxylate-affinitive centre)

M2 = Eu(III) Dy(III) Sm(III) Er(III)

Cu(II) Zn(II) Ni(II) etc.

(including lanthanide metals: strong carboxylate-affinitive centres; OR transitional metals: weak carboxylate-affinitive centres)

M3 = Cu(I) Cu4l4 clusters (strongpyridyl N-affinitive components)

Fig. S1 Schematic illustration of our Bifunctional Method.

S2. Additional Crystal Structural Figures



Fig. S2 Illustrations of the structure of CPM-4. (a) View of the 3D indium-BTC framework with 1D hexagonal channels along the c axis. (b) Top and (c) side views of one hexagonal channel containing captured paddlewheel cobalt dimers.



Fig. S3 (a) The 3-dimensional structure of **InOF-14.** (b) The 3-dimensional structure of **InOF-14** with the removal of terminally coordinated water molecules. (c1) and (c2) The 2-dimensional structure of **In-BTC** framework when eliminating the $[Eu_2(CO_2)_4(H_2O)_4]$ paddle wheels in the *a*-axis and *b*-axis, respectively.

S3. Topological Analyses

For InOF-14,

Structure consists of 3D framework with TiSc Structure consists of molecules (ZD1). The composition of molecule is C6H3 Structure consists of molecules (ZE1). The composition of molecule is C4O8In Structure consists of molecules (ZF1). The composition of molecule is C4O20Eu2

Topology for ZD1

Atom	ZD1 links by	bridge ligan	ds and has			
Comm	non vertex w	vith			R(A-A)	f Total SA
ZF 1	0.5000	0.5000	0.5000	(000)	5.394A	1 34.07
ZE 1	0.5000	1.0000	0.2500	(010)	5.510A	1 32.97
ZE 1	0.0000	0.5000	0.2500	(000)	5.510A	1 32.97
Topol	ogy for ZE1					
Atom	ZE1 links by	bridge ligan	ds and has			
Comn	non vertex w	vith			R(A-A)	f Total SA
ZD 1	0.6803	0.3197	0.3520	(110)	5.510A	1 25.00
ZD 1	0.3197	0.3197	0.1480	(010)	5.510A	1 25.00
ZD 1	0.6803	-0.3197	0.1480	(1-10)	5.510A	1 25.00
ZD 1	0.3197	-0.3197	0.3520	(0-10)	5.510A	1 25.00
Topol	ogy for ZF1					
Atom	ZF1 links by	bridge ligan	ds and has			
Comm	non vertex w	vith			R(A-A)	f Total SA
ZD 1	0.6803	0.3197	0.6480	(001)	5.394	1 25.00
ZD 1	0.3197	0.6803	0.6480	(111)	5.394A	1 25.00
ZD 1	0.6803	0.3197	0.3520	(110)	5.394A	1 25.00
ZD 1	0.3197	0.6803	0.3520	(000)	5.394A	1 25.00
Coord	lination sequ	- iences				
ZD1:	1 2 3	4 5 6	78	9 10		
Num	3 9 1 5 3	3 45 82	90 153 15	50 239		
Cum	4 13 28 61	L 106 188 27	8 431 581 8	320		
 ZE1:	1 2 3	456	78	9 10		
Num	4 8 20 3	60 68	120 126 20	0 180		
Cum	5 13 33 63	3 123 191 31	1 437 637 8	817		

S5

 ZF1:
 1
 2
 3
 4
 5
 6
 7
 8
 9
 10

 Num
 4
 8
 20
 30
 60
 68
 120
 126
 200
 180

 Cum
 5
 13
 33
 63
 123
 191
 311
 437
 637
 817

TD10=818

Vertex symbols for selected sublattice

ZD1 Point (Schlafli) symbol:{6^3} Extended point symbol:[6.6.6]

ZE1 Point (Schlafli) symbol:{6^2.8^4} Extended point symbol:[6(2).6(2).8.8.8.8]

ZF1 Point (Schlafli) symbol:{6^2.8^2.10^2} Extended point symbol:[6(2).6(2).8(2).8(2).10(4).10(4)]

Point (Schlafli) symbol for net: {6^2.8^2.10^2}{6^2.8^4}2{6^3}4 3,4,4-c net with stoichiometry (3-c)4(4-c)2(4-c); 3-nodal net



Topological representation for InOF-14 EU4In4BTC4

Fig. S4 The 3-dimensional 3,4,4-connected structure of **InOF-14** (Left); the topological representation for a small micro-sized octahedral cage between two neighboring $[Eu_2(CO_2)_4(H_2O)_4]$ SBUs along the *c* axis, which is assembled from 4 $[In(CO_2)_4]$ SBUs, 2 $[Eu_2(CO_2)_4(H_2O)_4]$ SBUs and 4 BTC³⁻ ligands.

S4. Powder X-ray Diffraction Pattern



Fig. S5 PXRD patterns of **InOF-14**: simulated from the crystallographic information file (black); from the as-prepared sample (red); from the acetone-exchanged sample (blue); from the desolvated sample (green).

S5. TGA data



Fig. S6 TGA curves for InOF-14 samples before and after activation process.

S6. Photographical and SEM Images



InOF-14

Fig. S7 Photographical pics and SEM images for **InOF-14** samples; bottom-lined pics are taken by an iPhone in the UV-Vis lamp.

S7. Sorption Analyses.

 N_2 , H_2 , CH_4 and CO_2 Isotherms. All the N₂, H₂ and CO₂ isotherms for InOF-14 were determined using an IGA gravimetric adsorption apparatus in a clean ultra high vacuum system. Before measurements, about 100 mg solvent-exchanged samples were loaded into the sample basket within the adsorption instrument (ASAP 2020) and then degassed under dynamic vacuum at 100 °C for 10 h to obtain the fully desolvated samples. The N₂ sorption measurement was performed at 77 K and 273 K; the H₂ sorption measurement was performed at 77 K and 87 K; CO₂ and CH₄ sorption measurement was performed at 273 K and 295 K.

 H_2 isotherms measured at 77 K and 87 K for **InOF-14** were fit to the following Equation 1.^{S1} The adsorption isostere is represented by

 $\ln (P/P_0) = q_i/RT + C$ (1)

where:

 q_i = isosteric heat of adsorption C = unknown constant

The isosteric heat of adsorption, q_i is determined by finding the slope of ln (P/P₀) as a function of 1/RT for a set of isotherms measured at different temperatures.



Fig. S8 (a) CO_2 , CH_4 and N_2 adsorption isotherm curves in the range of 0 ~ 110 kPa at 273 K. (b) CO_2 and CH_4 adsorption isotherm curves in the range of 0 ~ 110 kPa at 295 K, meanwhile, the very few of N_2 adsorption capacity at 295 K is not represented here.

S8. References.

[S1] ASAP 2020 Accelerated Surface Area and Porosimetry System Operator's Manual V4.00, Appendix C, C-43.