Supplementary Material (ESI) for CrystEngComm.

Iodine-templated assembly of an In(III) complex with a single-crystal-to-single-crystal transition

Yuan-Chun He, Wei-Qiu Kan, Jiao Guo, Yan Yang, Peng Du, Ying-Ying Liu* and Jian-Fang Ma*

Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

* Correspondence authors

E-mail: liuyy147@nenu.edu.cn (Y.-Y Liu)

E-mail: majf247@yahoo.com (J.-F. Ma)

Fax: +86-431-85098620 (J.-F. Ma)

Materials and methods

All chemicals and solvents were of analytical grade and used without further purification. X-ray powder diffractions were conducted on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu K_α radiation (λ = 0.154 nm) at 2θ ranging from 5 to 50°. The C, H and N elemental analyses were measured on a Perkin–Elmer 2400 elemental analyzer. IR-spectra were carried out on a Mattson Alpha-Centauri spectrometer at the range of 4000–400 cm^{-1}. The fluorescence data were recorded on a FLSP920 Edinburgh Fluorescence Spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 600 °C under nitrogen gas. All UV/vis spectra were measured on a TU-1900 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., China). Diffuse reflectance spectra were collected on a finely ground sample with a Cary 500 spectrophotometer equipped with a 110 mm diameter integrating sphere, which were measured from 200 to 800 nm. The gas adsorption-desorption experiments were performed on automatic volumetric adsorption equipment (V-Sorb 2800S).

X-ray crystallography

Single-crystal X-ray diffraction data for **1** were recorded on an Oxford Gemini R Ultra diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. All the structures were solved by Direct Method of SHELXS-97[1] and refined by full-matrix least-squares techniques using the SHELXL-97 program[2] within WINGX.[3] Non-hydrogen atoms were refined with anisotropic temperature parameters. All hydrogen atoms on carbon atoms were generated geometrically and refined using a riding model with d(C–H) = 0.93 Å, U_{iso} = 1.2U_{eq}(C) for aromatic. Hydrogen atoms of water molecules were not included in the model. Selected bond distances and angles are given in the Table S2.

References

1 G. M. Sheldrick, SHELXL-97, *Programs for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

2 G. M. Sheldrick, SHELXL-97, *Programs for X-ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

3 L. J. Farrugia, WINGX: *A Windows Program for Crystal Structure Analysis*; University of Glasgow: Glasgow, UK, 1988.

The experimental data for compound 1a

Compound **1a** was obtained by heating the sample of **1** at 200 °C for 15 hours in the oven. Elemental Anal. Calcd (%) for **1a**, $C_{42}H_{24}In_4N_6O_{27}$: C, 33.54; H, 1.61; N, 5.59; found: C, 33.40.; H, 1.57; N, 5.65. IR spectrum (KBr, cm^{-1}): see Fig. S9.

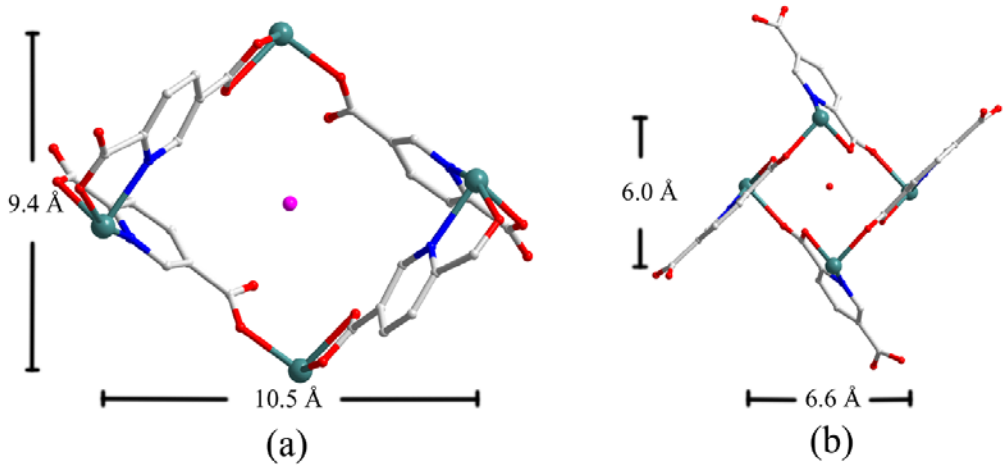


Fig. S1 Channels A and B with the corresponding sizes.

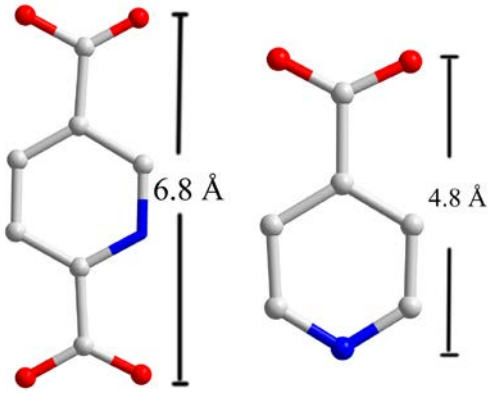


Fig. S2 The lengths of H_2pydc and HIN.

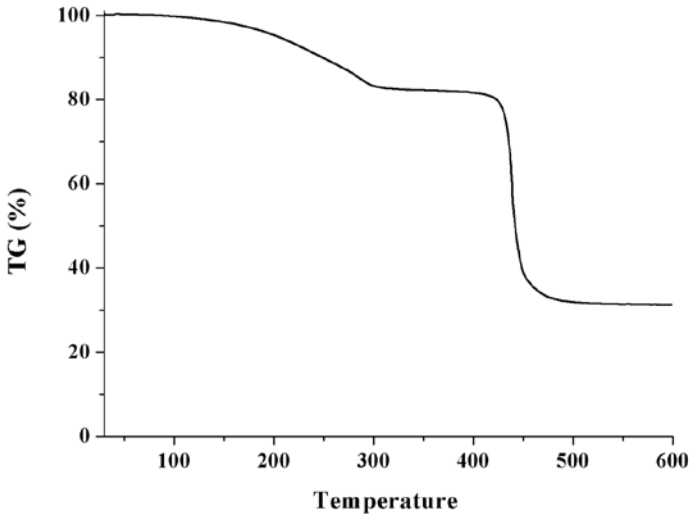


Fig. S3 The TG curve of compound **1**.

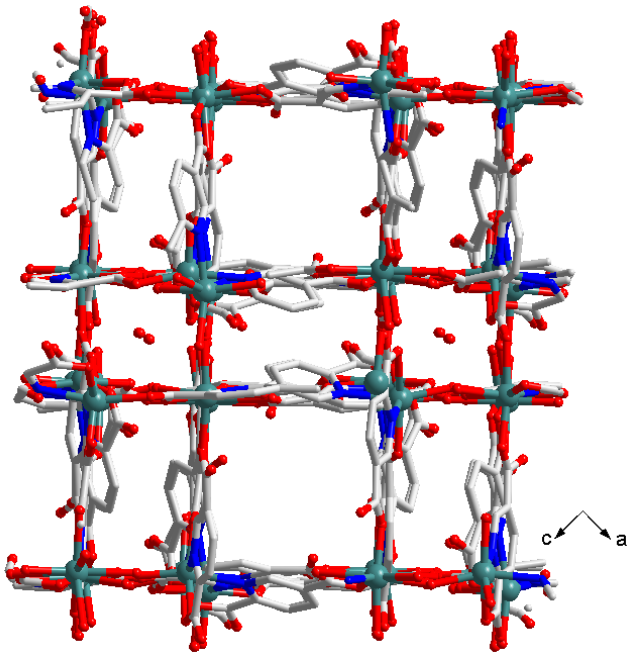


Fig. S4 Schematic representation of the 3D framework of **1a**. Compound **1a** has the same 3D framework and two same types of square channels as **1**, except that iodine molecules were removed from the network.

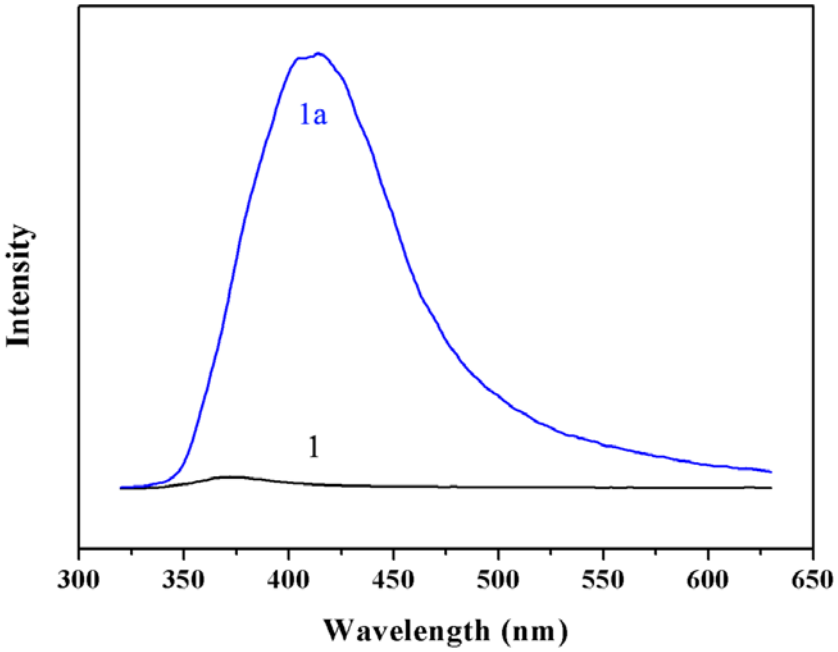
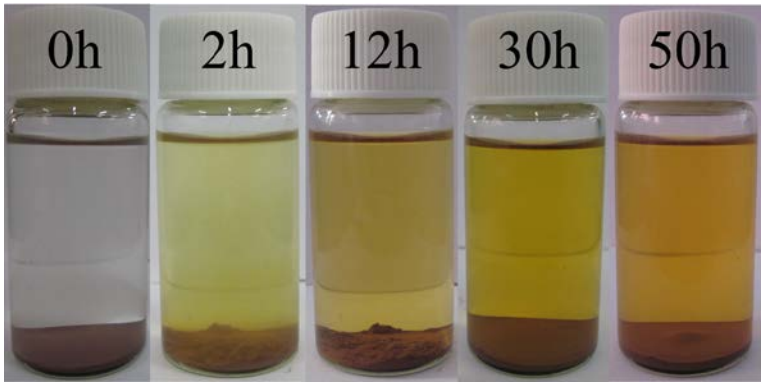
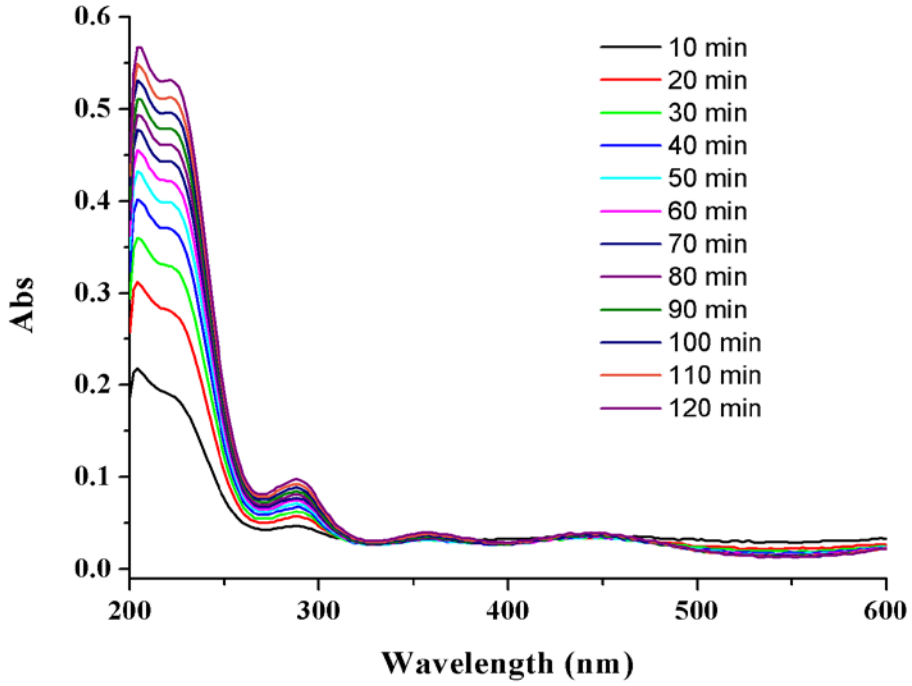


Fig. S5 Emission spectra of **1** and **1a**.

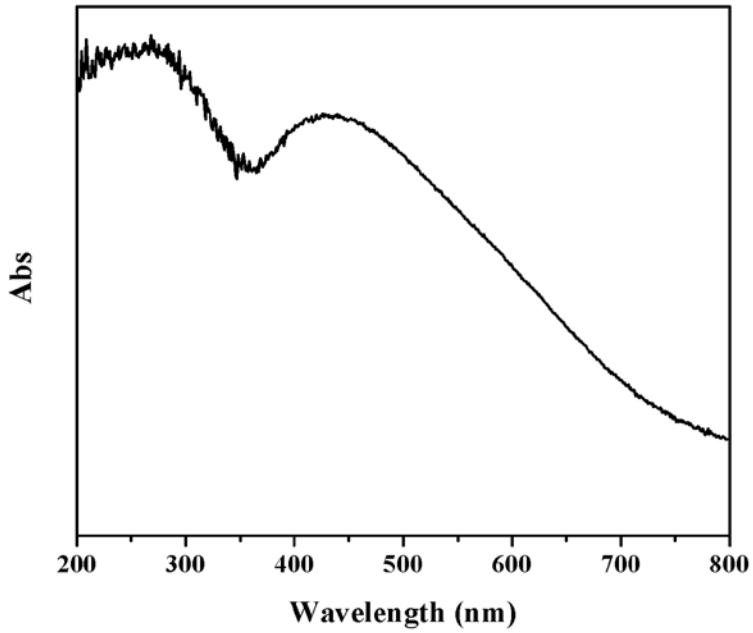


(a)

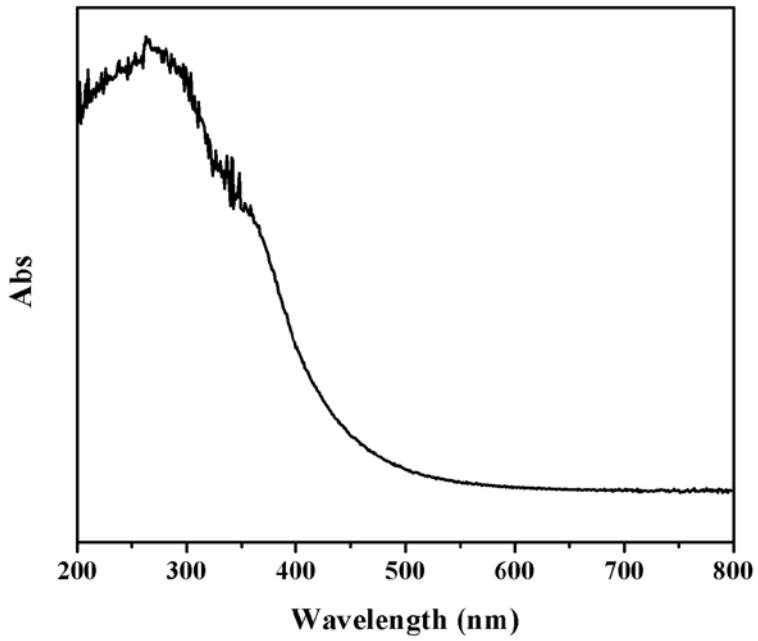


(b)

Fig. S6 (a) Iodine releasing process of 100 mg of **1** soaking in 10 mL of methanol. (b) Temporal evolution of UV/vis absorption spectra for the I_2 delivery from **1** in methanol.



(a)



(b)

Fig. S7 The diffuse reflectance spectra of compounds **1** and **1a**. After removal the lattice iodine molecules, the peak at 420 nm disappeared.

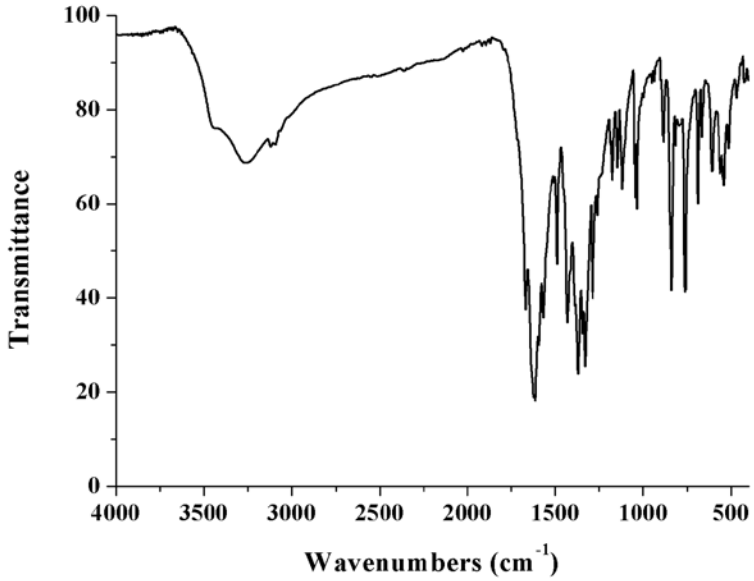


Fig. S8 IR spectrum of compound **1**.

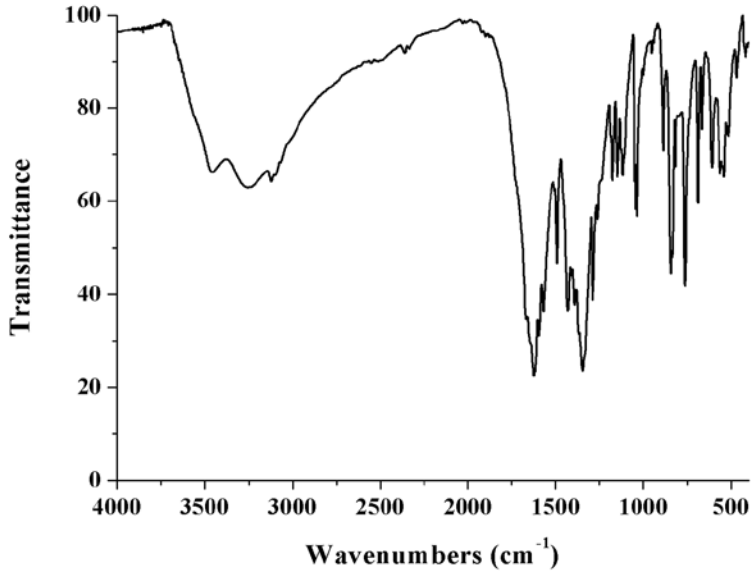


Fig. S9 IR spectrum of compound **1a**.

Table S1. The CO_2 maximum uptake of each cycle.

Cycle number	1	2	3	4	5
CO_2 uptake ($cm^3\ g^{-1}$)	33.67	33.17	30.73	30.49	31.37

Table S2. Crystal data and structure refinement for compound **1**.

	1
Formula	$C_{42}H_{24}In_4I_2N_6O_{27}$
Fw	1757.76
Crystal system	Orthorhombic
Space group	*Pccn*
a /Å	16.0630(8)
b /Å	16.4850(9)
c /Å	19.0250(8)
α / °	90
β / °	90
γ / °	90
V /Å^3	5037.8(4)
Z	4
D_c/ g cm^{-3}	2.318
F(000)	3344
R(int)	0.0628
GOF on F^2	1.079
R_1 [$I > 2\sigma(I)$]	0.0690
wR_2 (all data)	0.1868

Table S3. Selected bond distances and angles for compound **1**.

In(1)-O(4)	2.130(8)	In(1)-O(2)#1	2.191(8)
In(1)-O(12)#2	2.198(7)	In(1)-O(1W)	2.240(8)
In(1)-O(7)#3	2.269(8)	In(1)-O(8)#3	2.018(4)
In(1)-N(3)#2	2.339(9)	In(2)-O(11)#4	2.112(8)
In(2)-O(9)	2.117(8)	In(2)-O(5)	2.128(7)
In(2)-O(1)	2.204(7)	In(2)-N(1)	2.223(9)
In(2)-N(2)	2.246(10)	O(4)-In(1)-O(2)#1	162.7(3)
O(4)-In(1)-O(12)#2	90.7(3)	O(2)#1-In(1)-O(12)#2	93.5(3)
O(4)-In(1)-O(1W)	85.0(3)	O(2)#1-In(1)-O(1W)	79.8(3)
O(12)#2-In(1)-O(1W)	75.5(3)	O(4)-In(1)-O(7)#3	86.3(3)
O(2)#1-In(1)-O(7)#3	81.8(3)	O(12)#2-In(1)-O(7)#3	150.5(3)
O(1W)-In(1)-O(7)#3	74.9(3)	O(4)-In(1)-O(8)#3	93.7(3)
O(2)#1-In(1)-O(8)#3	90.2(3)	O(12)#2-In(1)-O(8)#3	153.0(3)
O(1W)-In(1)-O(8)#3	131.4(3)	O(7)#3-In(1)-O(8)#3	56.5(3)
O(4)-In(1)-N(3)#2	109.9(3)	O(2)#1-In(1)-N(3)#2	87.4(3)
O(12)#2-In(1)-N(3)#2	72.4(3)	O(1W)-In(1)-N(3)#2	144.5(3)
O(7)#3-In(1)-N(3)#2	135.9(3)	O(8)#3-In(1)-N(3)#2	81.1(3)
O(11)#4-In(2)-O(9)	94.9(3)	O(11)#4-In(2)-O(5)	86.8(3)
O(9)-In(2)-O(5)	108.6(3)	O(11)#4-In(2)-O(1)	91.5(3)
O(9)-In(2)-O(1)	160.2(3)	O(5)-In(2)-O(1)	90.4(3)
O(11)#4-In(2)-N(1)	109.0(3)	O(9)-In(2)-N(1)	85.1(3)
O(5)-In(2)-N(1)	158.5(3)	O(1)-In(2)-N(1)	75.1(3)
O(11)#4-In(2)-N(2)	160.9(3)	O(9)-In(2)-N(2)	96.0(4)
O(5)-In(2)-N(2)	74.9(3)	O(1)-In(2)-N(2)	83.5(3)
N(1)-In(2)-N(2)	87.5(3)		

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

Table S4. Crystal data and structure refinement for compound **1a**.

	1
Formula	$C_{42}H_{24}In_4N_6O_{27}$
Fw	1503.94
Crystal system	Monoclinic
Space group	$P2_1/n$
a /Å	16.0572(10)
b /Å	37.872(5)
c /Å	16.346(2)
α / ^{o}	90
β / ^{o}	90
γ / ^{o}	90
V /Å^3	9940.2(19)
Z	4

D_c/ g cm^{-3}	2.010
F(000)	5840
R(int)	0.1517
GOF on F^2	1.125
R_1 [$I > 2\sigma(I)$]	0.2399
wR_2 (all data)	0.4360