

## Supporting Information

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**Crystal transformation synthesis of a highly stable fluorescent 3D Indium-tetranuclear  $\{\text{In}_4(\mu_2\text{-OH})_3\}$  building block based metal organic framework through a dinuclear complex**

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## 1 Section 1. Experimental Procedures

2 **Materials and Methods.** All the syntheses were performed in 15 mL Teflon-lined stainless steel  
3 autoclave under autogenous pressure. All reactants are reagent grade and used as purchased  
4 commercially without further purification. Infrared spectra were obtained from KBr pellets using a  
5 Nicolet Avatar-360 Infrared spectrometer in the 4000–400  $\text{cm}^{-1}$  region. Powder X-ray diffraction  
6 (PXRD) patterns were recorded in the  $2\theta$  range of 5–50° using Cu  $K\alpha$  radiation by Shimadzu XRD-  
7 6000 X-ray Diffractometer. Elemental analyses were performed on a Perkin-Elmer 240c element  
8 analyzer. The thermal analysis was performed on a ZRY-2P thermogravimetric analyzer from 30 °C  
9 to 700 °C with heating rate of 10 °C  $\text{min}^{-1}$  under a flow of air. Variable-temperature X-ray powder  
10 diffraction (VT-XRPD) patterns were obtained using a PANalytical X-ray diffractometer, equipped  
11 with monochromated Cu  $K\alpha$  radiation 40 mA, 40 kV. Each powder pattern was recorded in the 5–  
12 50 °C range ( $2\theta$ ) from RT to 800 °C with a step of 0.02° and a counting time of 0.4 s. The  
13 temperature ramp between two consecutive temperatures was 10 °C/min.

## 14 Section 2. Synthesis of compounds 1, 2

### 15 Synthesis of $\text{In}_3(2,6\text{-pydc})_3(1,4\text{-bda})_{1.5}(\text{H}_2\text{O})_6$ (1)

16 A mixture of  $\text{In}(\text{NO}_3)_3$  (61.0 mg, 0.2 mmol), 2, 6- $\text{H}_2\text{pydc}$  (33.4 mg, 0.2 mmol) and 1,4- $\text{H}_2\text{bda}$  (33.2  
17 mg, 0.2 mmol) was dissolved in  $\text{H}_2\text{O}$  (5 mL) and stirred at room temperature for 30 min (the pH  
18 value of the reactant was *ca.* 1.5). After that, it was transferred into a 15 mL Teflon-lined stainless  
19 steel autoclave and heated in a sealed vial at 160 °C for 96 hours. After slow cooling to room  
20 temperature, Light yellow rectangular block crystals of **1** were obtained by filtration and washed  
21 with filter liquid (yield, 59%, based on 1,4- $\text{H}_2\text{bda}$ ). High quality rectangular block were chosen  
22 for the X-ray crystallography from the as-made sample. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3368 (br, s), 2967  
23 (w), 1601 (s), 1548 (s), 1388 (vs), 1228 (w), 1053 (w), 1020 (w), 868 (w), 825 (w), 774 (m), 687  
24 (m), 535 (w). Elemental analysis (%): calc. for  $\text{C}_{66}\text{H}_{64}\text{In}_6\text{N}_6\text{O}_{53}$  (Mr: 2478.15): C, 31.95%; N,  
25 3.39%; H, 2.58%. Found: C, 32.08%; N, 3.21%; H, 2.96%.

26

### 27 Synthesis of $\{[\text{In}_{4/3}(\mu_2\text{-OH})(2,6\text{-pydc})(1,4\text{-bda})_{0.5}(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$ (2)

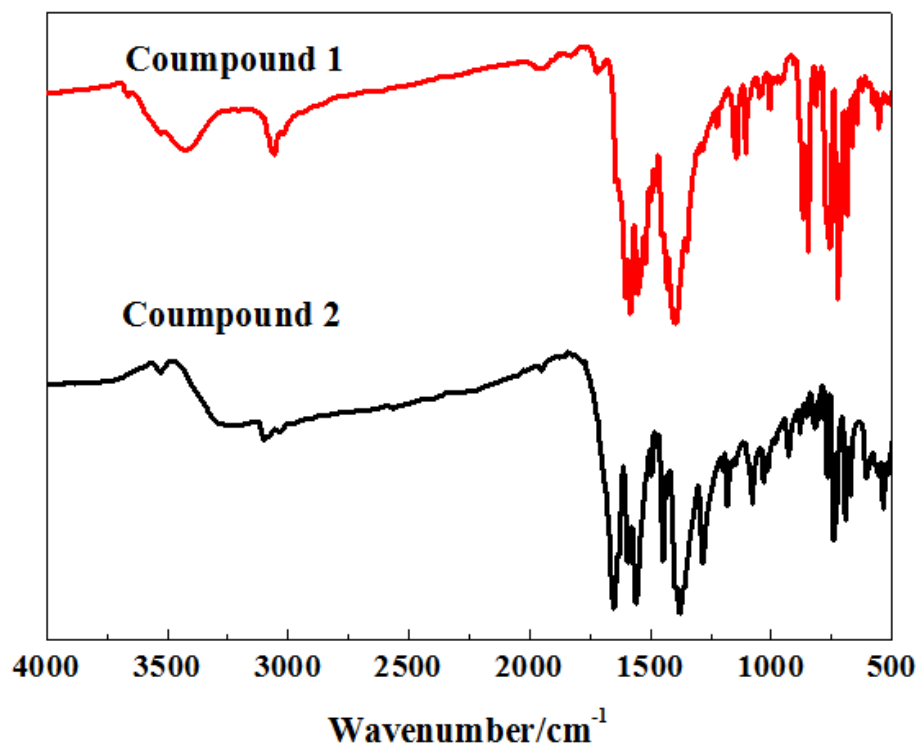
28 Freshly prepared rectangular block-type single crystals of **1** was added to the aqueous KOH (the pH  
29 value of the reactant was 8.5), and transferred into a 15 mL Teflon-lined stainless steel autoclave for  
30 hydrothermal reaction 48 hours at 160 °C. After slow cooling to room temperature, the yellow  
31 hexagon block crystalline solids were retrieved by filtration and washed with filter liquid (yield,  
32 62%, based on **1**). High quality hexagon block crystal was chosen for the X-ray crystallography  
33 from the as-made sample. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3360 (br, s), 2979 (w), 2280 (w), 1612 (s), 1551  
34 (s), 1386 (vs), 1231 (m), 1059 (m), 1021 (m), 824 (w), 773 (s), 691 (s), 530 (w). Elemental analysis  
35 (%): calc. for  $\text{C}_{66}\text{H}_{42}\text{In}_8\text{N}_6\text{O}_{45}$  (Mr: 2557.62): C, 30.97%; N, 3.28%; H, 1.64%. Found: C, 31.62%;  
36 N, 3.33%; H, 1.27%.

## 37 Section 3. Experiment of Photoluminescence (PL) investigations.

38 The fluorescence properties of compounds **1**, **2**, in the solid state, and in various solvent suspension

1 were investigated at room temperature or 77 K. The **1** and **2** suspension were prepared by  
2 introducing 1.0 mg of **1** and **2** fine powder into 50 mL of benzene, THF, CHCl<sub>3</sub>, acetone, CH<sub>3</sub>OH,  
3 CH<sub>3</sub>CN, DMF, DMSO, H<sub>2</sub>O respectively. After sonication treatment, aging for over 24 h and  
4 shaking, the fluorescence spectra were measured. To detect luminescence diminishment properties  
5 of DMSO to **2**, a small amount of DMSO were added into a certain requirement amount of **2**  
6 suspension in H<sub>2</sub>O. The photoluminescence spectra were investigated after shaking vigorously.

#### 7 Section 4. IR spectra of **1** and **2**



8

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Fig. S1 IR spectra of **1** and **2**

#### 10 Section 5. X-ray Crystallography

11 The X-ray diffraction data taken at room temperature for coordination polymers **1** and **2** were  
12 collected on a Rigaku R-Axis RAPID IP or a Siemens SMART 1000 CCD diffractometer  
13 equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal structures  
14 were resolved by direct method and refined by Semi-empirical formula from equivalents and full-  
15 matrix least squares based on  $F^2$  using the SHELXTL 5.1 software package.<sup>1</sup> All non-hydrogen  
16 atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined  
17 by using a riding mode except water molecules. The CCDC 990702 and 990703 contain the  
18 crystallographic data **1** and **2** of this paper. These data can be obtained free of charge at  
19 [www.ccdc.cam.ac.uk/deposit](http://www.ccdc.cam.ac.uk/deposit).

#### 20 Section 6. Crystal structure determination of **1** and **2**

21 **Table S1** Crystal data and structure refinement parameters of compound **1–2**.

Identification code	1	2
Empirical formula	C <sub>66</sub> H <sub>64</sub> In <sub>6</sub> N <sub>6</sub> O <sub>53</sub>	C <sub>66</sub> H <sub>42</sub> In <sub>8</sub> N <sub>6</sub> O <sub>45</sub>
Formula mass	2478.15	2557.62
Crystal system	Monoclinic	Rhombohedral

Space group	C2/c	$R\bar{3}$
<i>a</i> (Å)	33.877(7)	17.068(2)
<i>b</i> (Å)	13.224(3)	17.068(2)
<i>c</i> (Å)	21.000(4)	20.364(4)
$\alpha$ (°)	90.00	90.00
$\beta$ (°)	120.42(3)	90.00
$\gamma$ (°)	90.00	120.00
<i>V</i> (Å <sup>3</sup> )	8113(3)	5137.6(15)
<i>Z</i>	4	3
<i>D<sub>c</sub></i> /(g · cm <sup>-3</sup> )	2.029	2.480
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	1.796	2.768
<i>F</i> (000)	4879	3696
<i>2θ</i> range (°)	3.08 – 27.48	3.00 – 27.45
Limiting indices	$-43 \leq h \leq 43$	$-22 \leq h \leq 22$
	$-17 \leq k \leq 17$	$-22 \leq k \leq 18$
	$-26 \leq l \leq 27$	$-26 \leq l \leq 26$
Data/Restraints/Parameters	9098 / 0 / 591	2617 / 0 / 189
GOF on <i>F</i> <sup>2</sup>	1.110	1.023
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]		
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0495	0.0292
w <i>R</i> <sub>2</sub> <sup>b</sup>	0.1333	0.1122
<i>R</i> indices (alldata)		
<i>R</i> <sub>1</sub>	0.0617	0.0315
w <i>R</i> <sub>2</sub>	0.1396	0.1148

1 **Table S2** Selected bond lengths [Å] and angles [°] for **1**.

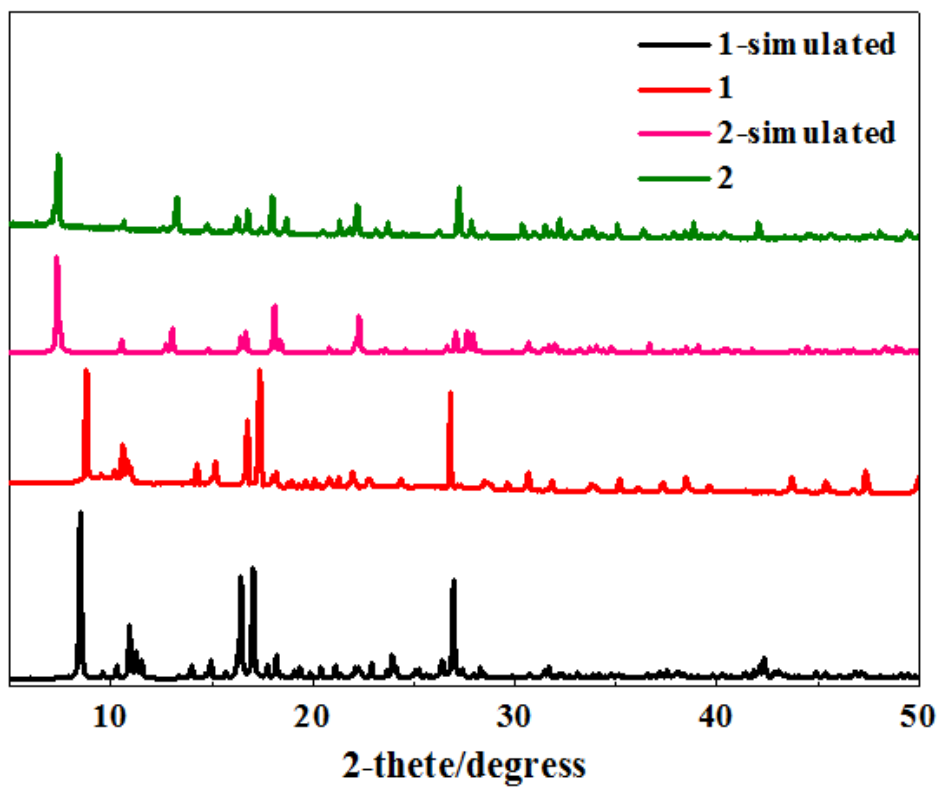
In(1)-O(7)	2.121(5)	In(2)-O(17)	2.144(5)	In(3)-O(23)	2.166(5)
In(1)-O(8)	2.155(5)	In(2)-O(18)	2.164(6)	In(3)-O(24)	2.162(6)
In(1)-O(5)	2.193(5)	In(2)-N(2)	2.218(5)	In(3)-N(3)	2.211(5)
In(1)-N(1)	2.210(5)	In(2)-O(9)	2.236(5)	In(3)-O(16)	2.224(5)
In(1)-O(1)	2.241(5)	In(2)-O(11)	2.243(4)	In(3)-O(21)	2.225(4)
In(1)-O(3)	2.286(5)	In(2)-O(14)	2.258(4)	In(3)-O(19)	2.223(4)
In(1)-O(6)	2.328(5)	In(2)-O(13)	2.257(5)	In(3)-O(15)	2.269(5)
O(7)-In(1)-O(8)	168.29(19)	O(17)-In(2)-O(18)	176.51(19)	O(23)-In(3)-O(24)	175.23(19)
O(7)-In(1)-O(5)	90.8(2)	O(17)-In(2)-N(2)	93.15(19)	O(23)-In(3)-N(3)	91.58(19)
O(8)-In(1)-O(5)	91.9(2)	O(18)-In(2)-N(2)	90.0(2)	O(24)-In(3)-N(3)	88.5(2)
O(7)-In(1)-N(1)	93.29(19)	O(17)-In(2)-O(9)	88.13(18)	O(23)-In(3)-O(16)	89.4(2)
O(8)-In(1)-N(1)	91.16(19)	O(18)-In(2)-O(9)	91.4(2)	O(24)-In(3)-O(16)	88.4(2)
O(5)-In(1)-N(1)	144.2(2)	N(2)-In(2)-O(9)	72.24(17)	N(3)-In(3)-O(16)	154.04(19)
O(7)-In(1)-O(1)	86.94(19)	O(17)-In(2)-O(11)	93.06(18)	O(23)-In(3)-O(21)	85.08(19)
O(8)-In(1)-O(1)	84.08(18)	O(18)-In(2)-O(11)	89.42(19)	O(24)-In(3)-O(21)	90.4(2)
O(5)-In(1)-O(1)	143.31(18)	N(2)-In(2)-O(11)	70.80(17)	N(3)-In(3)-O(21)	71.81(18)
N(1)-In(1)-O(1)	72.47(18)	O(9)-In(2)-O(11)	143.04(16)	O(16)-In(3)-O(21)	82.45(17)
O(7)-In(1)-O(3)	97.02(19)	O(17)-In(2)-O(14)	87.17(18)	O(23)-In(3)-O(19)	90.77(18)
O(8)-In(1)-O(3)	94.68(18)	O(18)-In(2)-O(14)	91.02(19)	O(24)-In(3)-O(19)	93.77(19)
O(5)-In(1)-O(3)	69.93(17)	N(2)-In(2)-O(14)	147.31(17)	N(3)-In(3)-O(19)	71.56(18)
N(1)-In(1)-O(3)	80.3(3)	O(9)-In(2)-O(14)	140.37(16)	O(16)-In(3)-O(19)	134.37(17)

O(1)-In(1)-O(3)	142.35(16)	O(11)-In(2)-O(14)	76.53(16)	O(21)-In(3)-O(19)	142.98(16)
O(7)-In(1)-O(6)	88.2(2)	O(17)-In(2)-O(13)	84.5(2)	O(23)-In(3)-O(15)	91.22(19)
O(8)-In(1)-O(6)	83.70(19)	O(18)-In(2)-O(13)	92.0(2)	O(24)-In(3)-O(15)	91.3(2)
O(5)-In(1)-O(6)	57.6(2)	N(2)-In(2)-O(13)	154.69(18)	N(3)-In(3)-O(15)	147.74(18)
N(1)-In(1)-O(6)	157.97(19)	O(9)-In(2)-O(13)	82.49(17)	O(16)-In(3)-O(15)	58.11(17)
O(1)-In(1)-O(6)	85.68(18)	O(11)-In(2)-O(13)	134.42(17)	O(21)-In(3)-O(15)	140.44(16)
O(3)-In(1)-O(6)	131.73(18)	O(14)-In(2)-O(13)	57.89(16)	O(19)-In(3)-O(15)	76.28(16)

1 **Table S3** Selected bond lengths [Å] and angles [°] for **2**.

In(1)-O(7)	2.047(2)	In(1)-O(1)	2.332(3)	In(2)-O(6)#3	2.208(3)
In(1)-O(3)	2.116(3)	In(1)-O(4)#2	2.482(3)	In(2)-O(6)#4	2.208(3)
In(1)-O(5)	2.196(3)	In(2)-O(7)#3	2.114(2)	In(2)-O(6)	2.208(3)
In(1)-N(1)	2.270(3)	In(2)-O(7)#4	2.114(2)	O(1)-In(1)#1	2.304(3)
In(1)-O(1)#1	2.304(3)	In(2)-O(7)	2.114(2)	O(4)-In(1)#5	2.482(3)
O(7)-In(1)-O(3)	107.31(10)	N(1)-In(1)-O(1)	70.58(10)	O(7)-In(2)-O(6)#3	90.41(11)
O(7)-In(1)-O(5)	86.94(10)	O(1)#1-In(1)-O(1)	64.96(11)	O(7)#3-In(2)-O(6)#4	90.41(11)
O(3)-In(1)-O(5)	165.45(11)	O(7)-In(1)-O(4)#2	78.27(10)	O(7)#4-In(2)-O(6)#4	95.82(10)
O(7)-In(1)-N(1)	135.83(11)	O(3)-In(1)-O(4)#2	81.38(10)	O(7)-In(2)-O(6)#4	175.57(10)
O(3)-In(1)-N(1)	94.22(11)	O(5)-In(1)-O(4)#2	105.00(11)	O(6)#3-In(2)-O(6)#4	85.46(11)
O(5)-In(1)-N(1)	76.78(11)	N(1)-In(1)-O(4)#2	67.20(10)	O(7)#3-In(2)-O(6)	175.57(11)
O(7)-In(1)-O(1)#1	85.09(10)	O(1)#1-In(1)-O(4)#2	155.19(9)	O(7)#4-In(2)-O(6)	90.41(10)
O(3)-In(1)-O(1)#1	86.24(10)	O(1)-In(1)-O(4)#2	135.63(9)	O(7)-In(2)-O(6)	95.82(10)
O(5)-In(1)-O(1)#1	92.22(11)	O(7)#3-In(2)-O(7)#4	88.42(10)	O(6)#3-In(2)-O(6)	85.46(11)
N(1)-In(1)-O(1)#1	135.52(10)	O(7)#3-In(2)-O(7)	88.42(10)	O(6)#4-In(2)-O(6)	85.46(11)
O(7)-In(1)-O(1)	145.22(10)	O(7)#4-In(2)-O(7)	88.42(10)	In(1)#1-O(1)-In(1)	115.04(11)
O(3)-In(1)-O(1)	88.80(10)	O(7)#3-In(2)-O(6)#3	95.82(10)	In(1)-O(7)-In(2)	134.48(13)
O(5)-In(1)-O(1)	77.48(10)	O(7)#4-In(2)-O(6)#3	175.57(10)		

2 **Section 7. The PXRD patterns of 1 and 2**

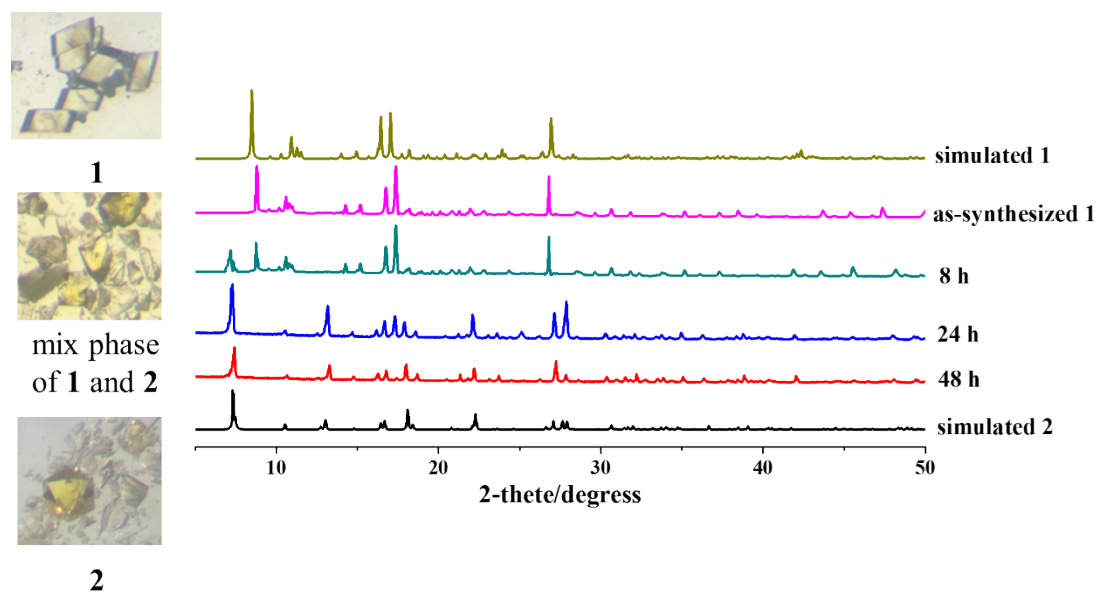


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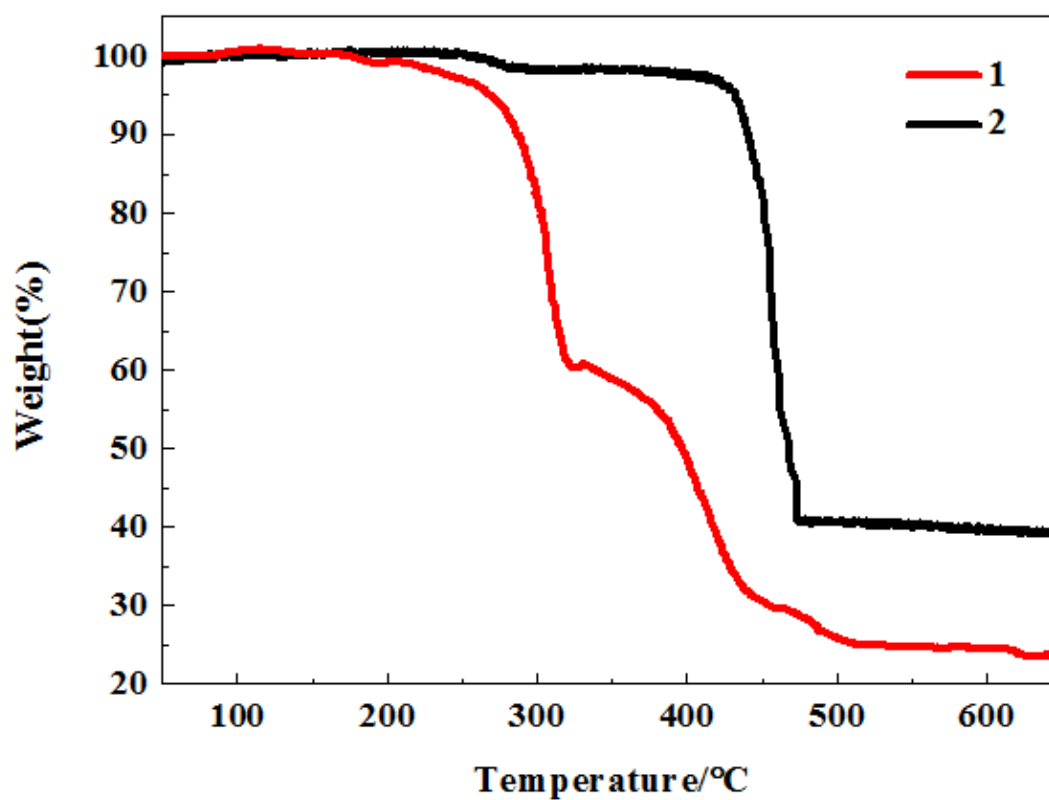
**Fig. S2** The PXRD patterns of 1 and 2 with the relevant simulated patterns.

## Section 8. The crystal transformation from 1 to 2



**Fig. S3** Photographs of the crystal transformation from **1** to **2**, and the powder X-ray diffraction patterns in the process of crystal transformation.

## Section 9. The TGA for 1 and 2.



**Fig. S4** Thermal gravimetric curves for **1** and **2**.

## Section 10. Variable-temperature X-ray powder diffraction (VT-



## XRPD)

Variable-temperature X-ray powder diffraction (VT-XRPD) patterns were obtained using a PANalytical X-ray diffractometer, equipped with monochromated Cu  $K\alpha$  radiation 40 mA, 40 kV. Each powder pattern was recorded in the 5–50 °C range ( $2\theta$ ) from RT to 800 °C with a step of 0.02° and a counting time of 0.4 s. The temperature ramp between two consecutive temperatures was 10 °C/min.

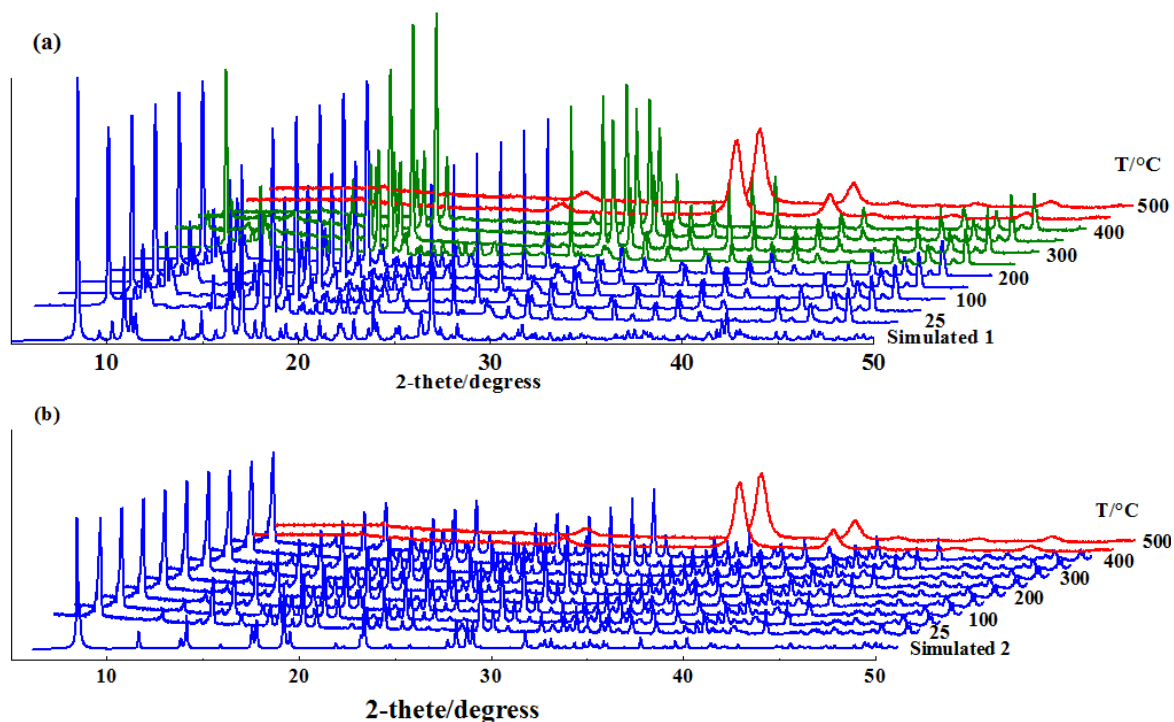
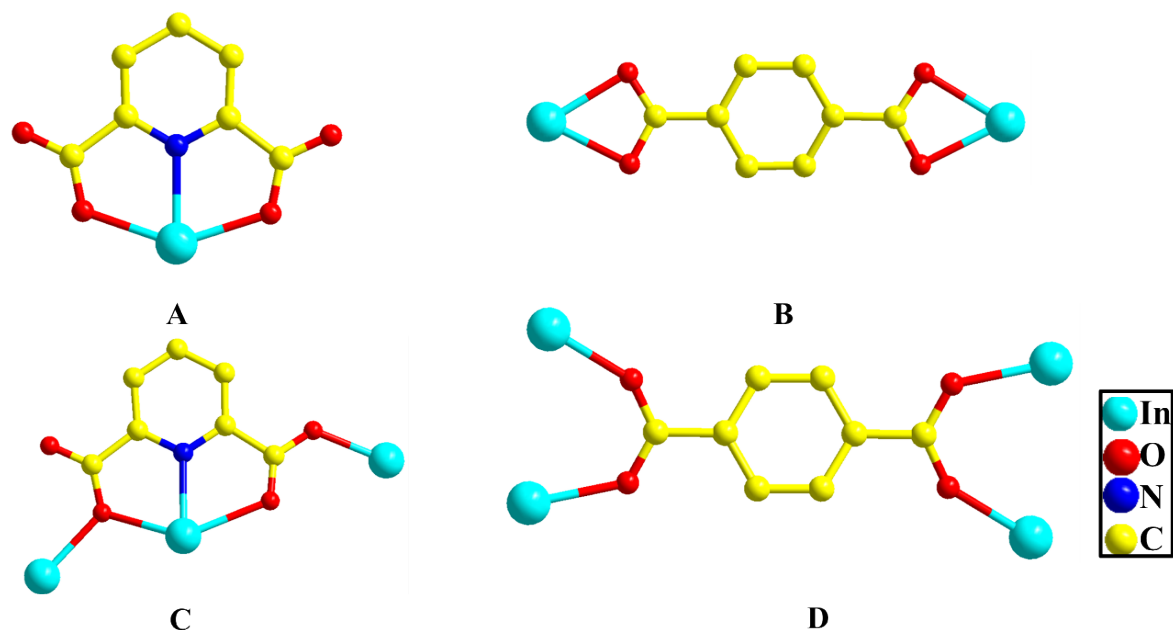


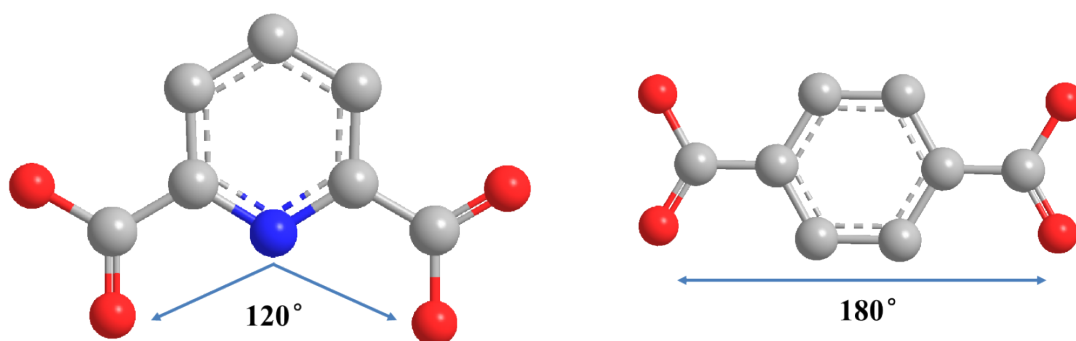
Fig. S5 X-ray thermodiffractograms of **1** (a) and **2** (b)

The thermogravimetric curves and variable-temperature X-ray powder diffraction (VT-XRPD) showed that the compounds start to undergo phase transition above *ca.* 250 °C for **1**, and 450 °C for **2**, which induces the structure collapse. The TG curves of **1** display two distinct weight losses, the first one from 200 to 250 °C corresponds to the loss of the six coordinated H<sub>2</sub>O molecules, and the structure starts to undergo a phase transition. The observed weight loss of 4.66% is in agreement with the calculated value of 4.36%. After that, an additional weight loss of 66.60% up to 450 °C can be attributed to the gradual release of the coordinated 2,6-pydc<sup>2-</sup> and 1,4-bda<sup>2-</sup> ligands (calculated 66.34%). In the 3D framework of **2**, the inter-cluster linkers are not only capable of transmitting the inherent properties of the cluster into the polymeric system but also make the usually exceptional stability of polymerized frameworks. For **2**, the TG curve displays two distinct weight losses, the first one from 270 to 438 °C corresponds to the loss of the free H<sub>2</sub>O molecules, and the structure still keeps the original framework. The observed weight loss of 8.65% is in agreement with the calculated value of 8.44%. The framework of **2** is stable up to 450 °C as showed in VT-XRPD. And then, the following weight loss may be attributed to the gradual release of the 2,6-pydc<sup>2-</sup> and 1,4-bda<sup>2-</sup> ligands ended at 500 °C with a retention of weight of 41.84% (calculated 42.69%), corresponding to In<sub>2</sub>O<sub>3</sub>.<sup>2</sup> The X-ray thermodiffractograms of **1** and **2** are consistent well with the TG analyses.

## Section 11. The coordination modes and structural information of the 2,6-H<sub>2</sub>pydc and 1,4-H<sub>2</sub>bda ligand



**Fig. S6** The coordination modes of the 2,6-H<sub>2</sub>pydc and 1,4-H<sub>2</sub>bda ligand found in compound **1** (mode A, B) and **2** (mode C, D)



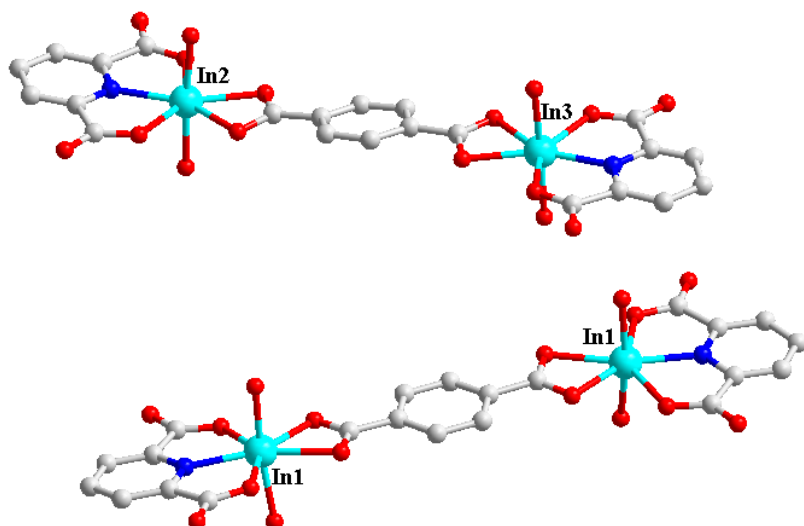
**(a) bent dicarboxylic acid**

**(b) straight dicarboxylic acid**

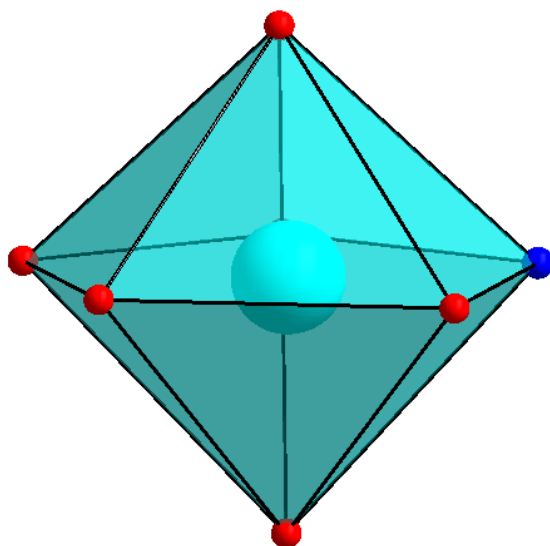
**Scheme S1** Two symmetry-complementary 2,6-H<sub>2</sub>pydc and 1,4-H<sub>2</sub>bda ligands.

The synthetic strategies contributing to our successful trapping of highly elusive tetramer is the use of mixed dicarboxylic linkers with 120° (2,6-H<sub>2</sub>pydc) and 180° (1,4-H<sub>2</sub>bda) angles as complementary. The dicarboxylic linker with 120° bend angle is chosen because of their ability to connect the sideward In(III) with various coordinated mode under the appropriate reaction conditions. While the combination of di- and tricarboxylates (or two dicarboxylates) has been exploited in the synthesis of MOFs,<sup>3</sup> mixed angle-complementary rigid dicarboxylates have been little examined.

## Section 12. Structural Information for **1** and **2**.

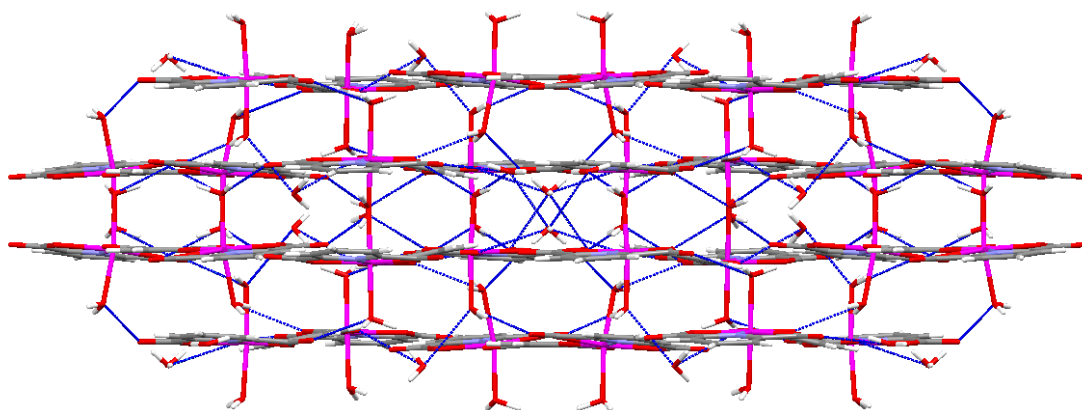


**Fig. S7** The dinuclear structure of **1**. Hydrogen atoms and free water molecules were omitted for clarity.



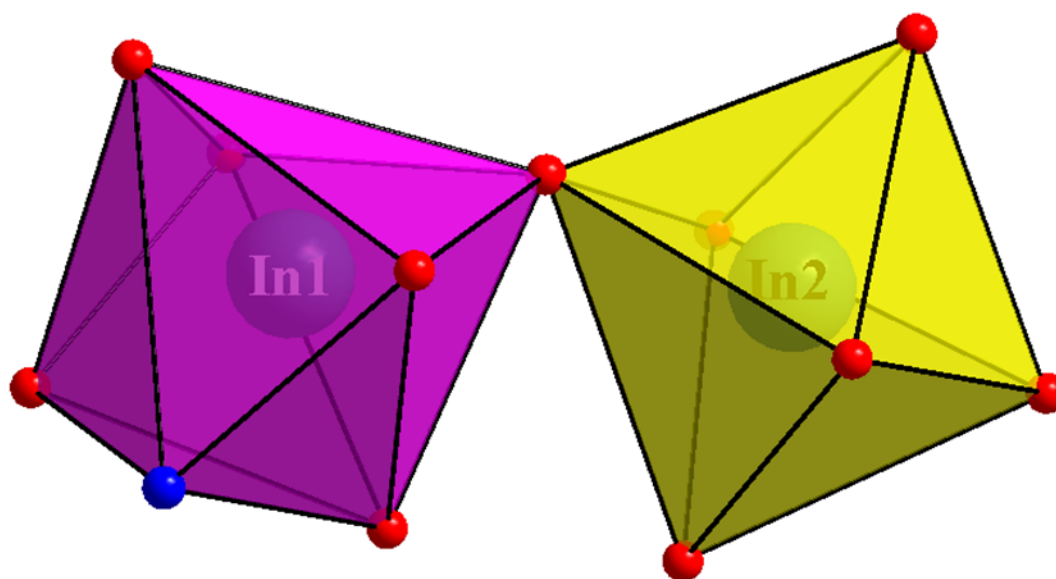
**Fig. S8** The coordinating polyhedron of **1**

The In(III) ions of **1** are seven-coordinated with standard pentagonal bipyramid geometries in which the ligands occupy the basal plane and water molecules set on the apical site. The In-O bond lengths vary from 2.121(5) to 2.328(5) Å and In-N range from 2.210(5) to 2.218(5) Å, which are in accord with those observed in most other In(III) complexes.<sup>4</sup>

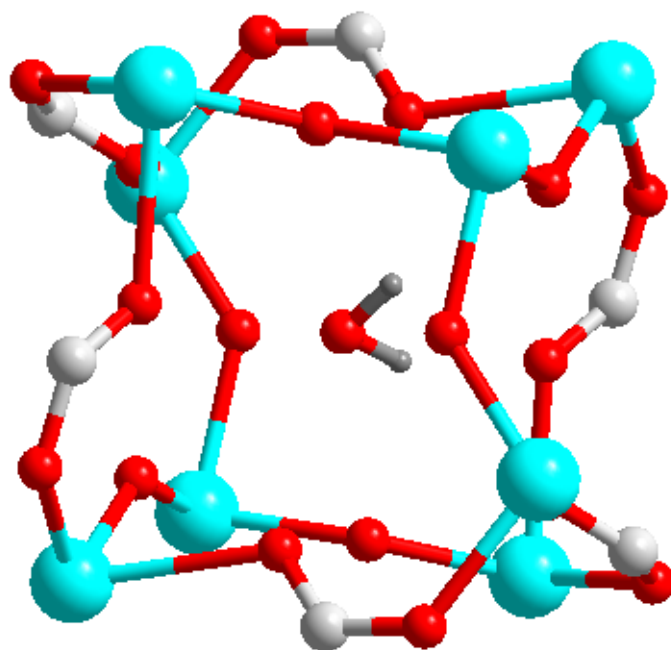


**Fig. S9** Schematic illustration of 3D supermolecular structure of **1**. The hydrogen bonds are indicated by dotted lines.

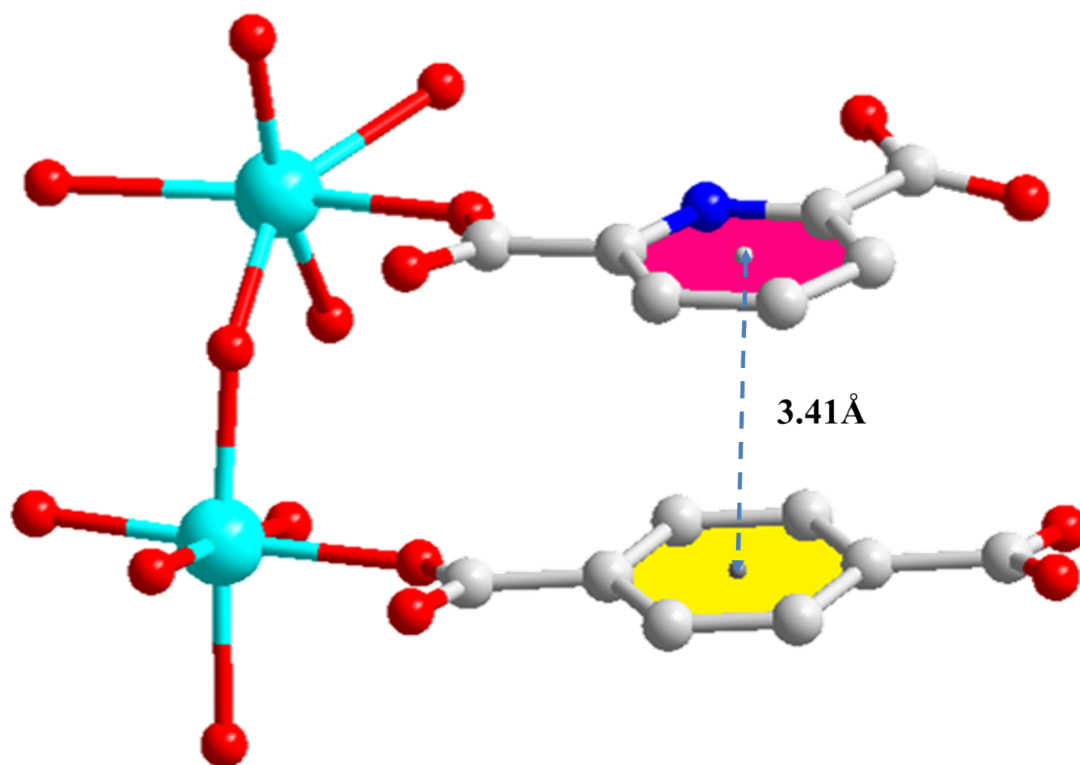
The packing of the complex **1** in the crystal lattice is worth mentioning. There are intermolecular hydrogen bonds among the  $\text{O}_{\text{COO}^-}$  from 2,6-pydc<sup>2-</sup> (O1, O2, O4, O9, O20, O21), the  $\text{O}_{\text{COO}^-}$  of 1,4-bda<sup>2-</sup> (O13, O14, O16), coordinated water oxygen atom (O7, O8, O17, O18, O23, O24), and guest water oxygen atom (Ow1, Ow2, Ow3) with distances from 2.605 Å (O7-H7A...O10) to 3.472 Å (O18-H18B...O1) and corresponding angles of 142.49° and 142.41°, respectively. These hydrogen bonds give rise to an infinite three dimensional network and keep the stability of this network.



**Fig. S10** The coordinating polyhedron of **2**



**Fig. S11** Schematic representation of the hexahedral cage in **2**



**Fig. S12** The  $\pi \cdots \pi$  stacking interaction between pydc<sup>2-</sup> and bda<sup>2-</sup> ligands with the distance is 3.41 Å.

**Table S4** Important hydrogen bond interactions in **1**

D–H···A	D–H / Å	H···A / Å	D···A / Å	∠D–H···A/°
O7–H7A···O10 [-x+1/2, -y+1/2, -z+1]	0.960	1.777	2.605	142.49
O7–H7B···O3[-x, -y+1, -z]	0.959	1.785	2.705	159.64
O7–H7B···O5 [-x, -y+1, -z]	0.959	2.576	3.198	122.73
O8–H8C···O14[x, -y+1, z-1/2]	0.850	2.435	2.891	114.41
O8–H8C···O23[x, y+1, z]	0.850	2.643	3.074	112.8
O17–H17A···O2[-x+1/2, -y+1/2, -z+1]	0.960	1.726	2.578	146.00
O17–H17B···O18[-x+1/2, y-1/2, -z+3/2]	0.960	2.434	3.118	128.03
O18–H18A···O20[-x+1/2, -y+1/2, -z+1]	0.960	2.098	2.649	114.91
O18–H18B···O1[x, -y+1, z+1/2]	0.960	2.662	3.472	142.41
O23–H23A···O8[x, y-1, z]	0.960	2.365	3.074	130.31
O23–H23C···OW3	0.960	1.663	2.616	171.29
O24–H24A···O7	0.960	2.355	3.195	145.85
O24–H24D···O4[-x, -y+1, -z]	0.960	1.881	2.638	133.85
OW1–HW1A···O21[-x, y, -z+1/2]	0.850	2.387	3.185	156.54
OW1–HW1B···O16[-x, y, -z+1/2]	0.850	2.505	3.032	120.95
OW2–HW2A···O13[-x+1/2, y+1/2, -z+3/2]	0.850	2.225	2.938	141.49
OW2–HW2A···O9[-x+1/2, y+1/2, -z+3/2]	0.850	2.614	3.312	140.28
OW3–HW3B···O12[x, -y, z-1/2]	0.850	1.987	2.819	165.86
OW3–HW3C···OW1	0.850	2.392	2.811	110.99

**Table S5** Important hydrogen bond interactions in **2**

D–H···A	D–H / Å	H···A / Å	D···A / Å	∠D–H···A/°
O7–H7B···O2 [-x-2/3, -y-1/3, -z-1/3]	0.970	1.963	2.874	155.41
OW1–HW1A···O4 [-x-4/3, -y-2/3, -z-2/3]	0.835	2.321	2.705	153.66
OW1–HW1A···O7[-x+y-1, -x-1, z]	0.835	2.413	2.905	118.43
OW1–HW1A···O4[-x+y-1, -x-1, z]	0.835	2.579	3.091	120.88
OW1–HW1C···O7[y-1/3, -x+y-2/3, -z-2/3]	0.850	2.111	2.905	155.25
OW1–HW1C···O7[-x-4/3, -y-2/3, -z-2/3]	0.850	2.396	2.905	118.97
OW1–HW1C···O7[x-y-1/3, x+1/3, -z-2/3]	0.850	2.426	2.905	116.34
OW2–HW2D···O6 [-x+y-1, -x-1, z]	0.831	2.360	2.980	131.85

**Table S6** Summary of In(III) hydroxy-bridging secondary building units (SBUs)

Empirical formula	Structural unit	Dimension	References
In <sub>2</sub> (HCOO) <sub>5</sub> (OH)	Dimer In–OH–In	3D	Inorg. Chem. 2007, 46, 8403-8409
In(HCOO) <sub>2</sub> (OH)	Dimer In–OH–In	3D	Inorg. Chem. 2007, 46, 8403-8409
[In(aip)(μ <sub>2</sub> -OH)] <sub>n</sub> ·3nH <sub>2</sub> O	Dimer In–OH–In	3D	CrystEngComm, 2009, 11, 1831–1833
[In <sub>2</sub> (Hsip) <sub>2</sub> (μ <sub>2</sub> -OH) <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub> ·2nH <sub>2</sub> O	Dimer In–OH–In	3D	CrystEngComm, 2009, 11, 1831–1833
[In <sub>2</sub> (OH)(nic) <sub>5</sub> ]·2CH <sub>3</sub> CN	Dimer In–OH–In		Angew. Chem. Int. Ed. 2011, 50, 8858-8862

$[\text{CH}_3\text{NH}_3]_2[\text{In}_2(\text{OH})(\text{btc})_{7/3}] \cdot \text{solvent}$	Dimer In–OH–In	3D	Angew. Chem. Int. Ed. 2011, 50, 8858-8862
$[(\text{C}_2\text{H}_5)_2\text{NH}_2]_2[\text{In}_2(\text{OH})(\text{btc})_{5/3}(\text{btb})_{2/3}] \cdot \text{solvent}$	Dimer In–OH–In	3D	Angew. Chem. Int. Ed. 2011, 50, 8858-8862
$[\text{In}_3(\mu_2\text{-OH})_2(\text{Hdptc})(\text{dptc})\text{H}_2\text{O}]_n$	Trinuclear $\text{In}_3(\mu_2\text{-OH})_2$	3D	Inorganica Chimica Acta, 2012, 386, 36–45
$\text{In}(\text{OH})(1,4\text{-BDC}) \cdot 0.75\text{H}_2\text{BDC}$	1D chains –In–OH–In–	3D	J. Am. Chem. Soc., 2005, 127, 15000–15001
$\text{In}(\text{OH})(1,2\text{-BDC}) \cdot \text{H}_2\text{O}$	1D chains –In–OH–In–	2D	Acta Cryst., 2006, C62, m395–m397
$\text{In}_{12}\text{O}(\text{OH})_{12}(\{\text{OH}\}_4\{\text{H}_2\text{O}\}_5)[\text{btc}]_6 \cdot \approx 31\text{H}_2\text{O}$	1D chains –In–OH–In–	3D	Materials Research Bulletin, 2006, 41, 948– 954
$[\text{In}(\text{C}_8\text{H}_4\text{O}_4)(\text{OH})(\text{H}_2\text{O})]_n$	1D chains –In–OH–In–	2D	Acta Crystallographica Section C., 2006, C62, m395±m397
$\text{In}(\text{OH})(\text{Hippb}) \cdot 0.5\text{Pyridine}$	1D chains –In–OH–In–	2D	Chem. Mater., 2008, 20, 72–76
$[\text{In}(\text{OH})(\text{Hpdc})(\text{H}_2\text{O})]_n$	1D chains –In–OH–In–	2D	J Chem Crystallogr, 2008, 38, 891–894
$(2,2'\text{-bipy})[\text{In}_2(\text{OH})_2(\text{H}_2\text{O})](\text{SO}_4)_2$	1D chains –In–OH–In–	2D	Journal of Solid State Chemistry, 2008, 181, 842–847
$[\text{H}_3\text{O}][\text{In}_2(\text{btc})(\text{bdc})(\text{OH})_2] \cdot 5.5\text{H}_2\text{O}$	1D chains –In–OH–In–	3D	Journal of Solid State Chemistry, 2009, 182, 3067–3070
$\text{In}_6(\text{OH})_6(\text{btcc})_3(\text{H}_4\text{btcc}) \cdot 8\text{--}14\text{H}_2\text{O}$	1D chains –In–OH–In–	3D	Solid State Sciences, 2011, 13, 1488–1493
$[\text{In}_2(\mu_2\text{-OH})_2(\text{obb})_2]_n \cdot 2n\text{DMF}$	1D chains –In–OH–In–	3D	Chem. Commun., 2011, 47, 770–772
$\text{In}(\text{OH})(1,4\text{-NDC}) \cdot 2\text{H}_2\text{O}$	1D chains –In–OH–In–	3D	Microporous and Mesoporous Materials, 2012, 155, 281–286
$\{[\text{EMIM}][\text{In}_3(\mu_3\text{-OH})_2(1,2,4,5\text{-BTC})_2 \cdot 2\text{H}_2\text{O}]\}_n$	1D chains $[\text{In}_3(\mu_3\text{-OH})_2]_n$	3D	Inorganic Chemistry Communications, 2013, 28, 16–19

### Section 13. The PXRD patterns of 2 in different solvent.

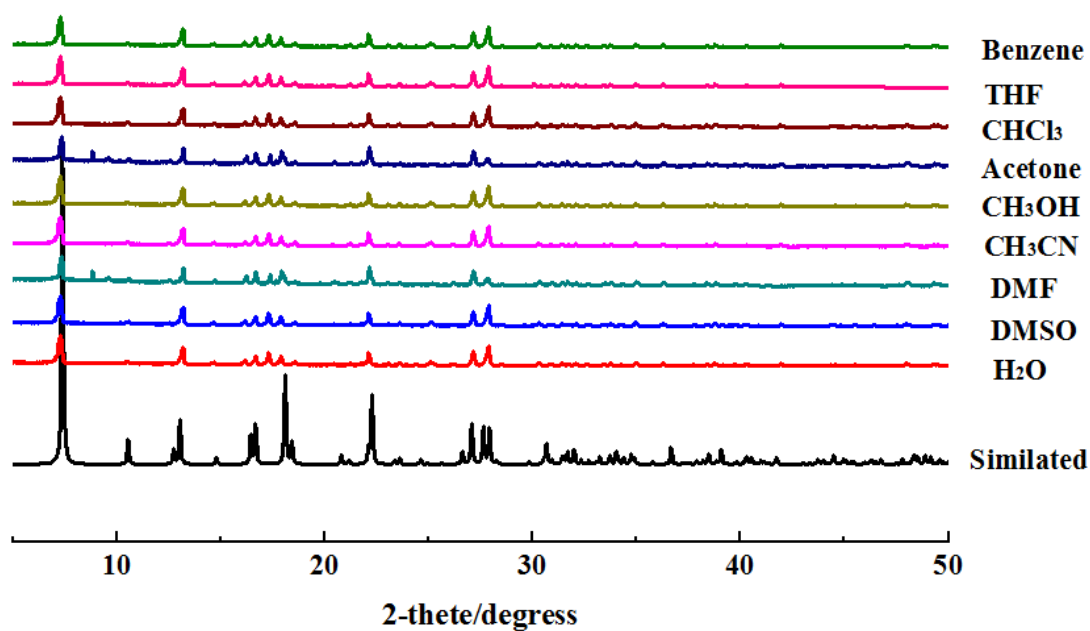


Fig. S13 The PXR D patterns of **2** in boiling water and different organic solvent

## Section 14. Photophysical studies

UV-vis spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer.

### UV-vis spectrum

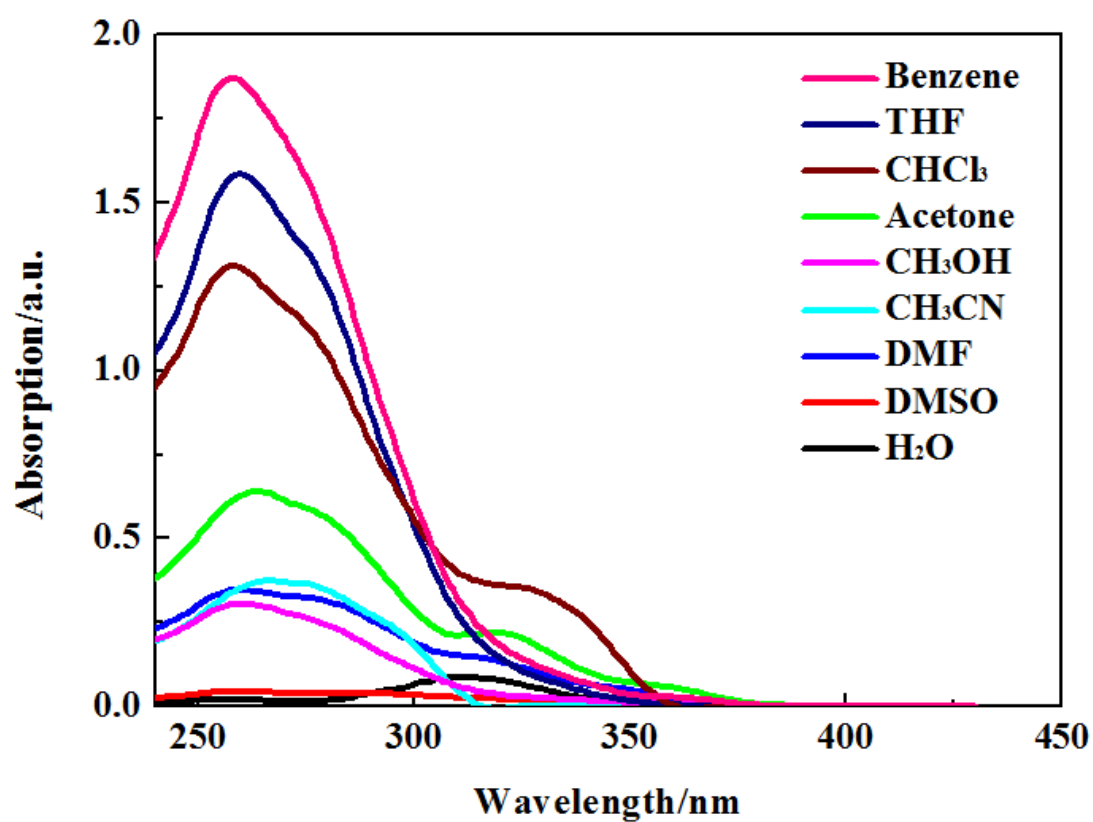


Fig. S14 UV-vis spectra of **2** introduced into various pure solvents

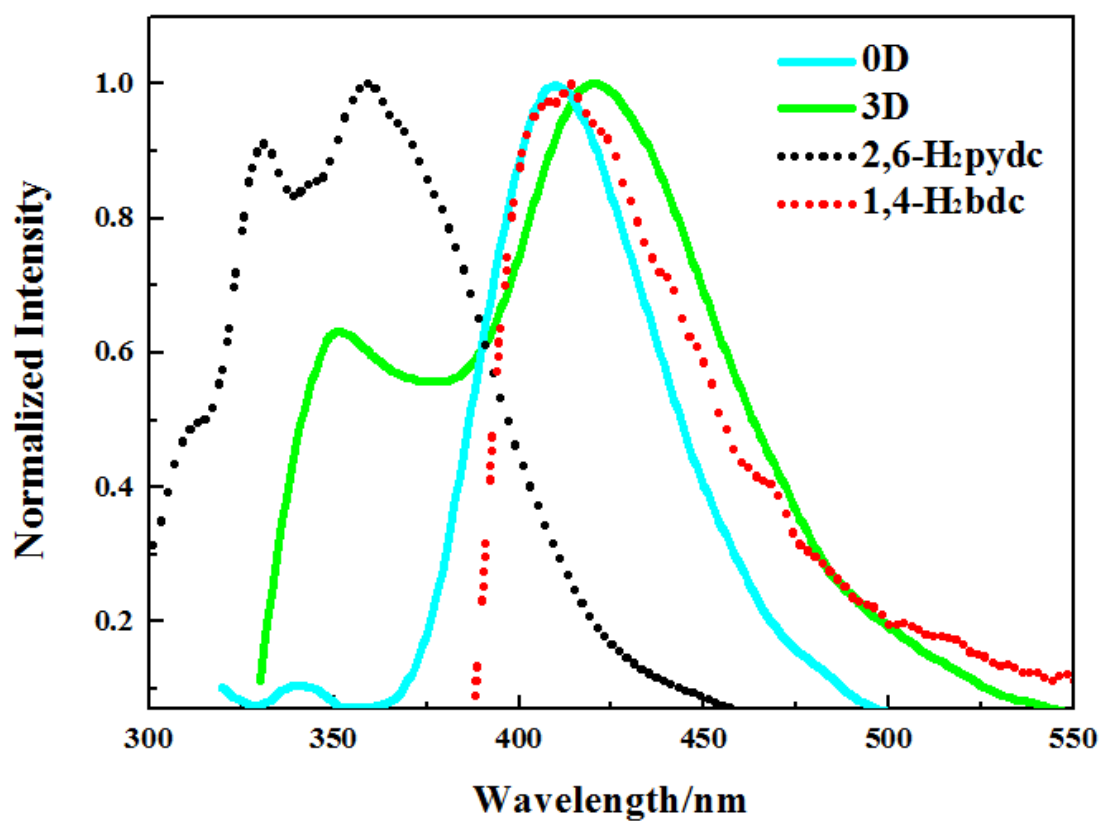


**Table S8** Photoluminescent data for **1** and **2** in the solid state at 298 K and 77K

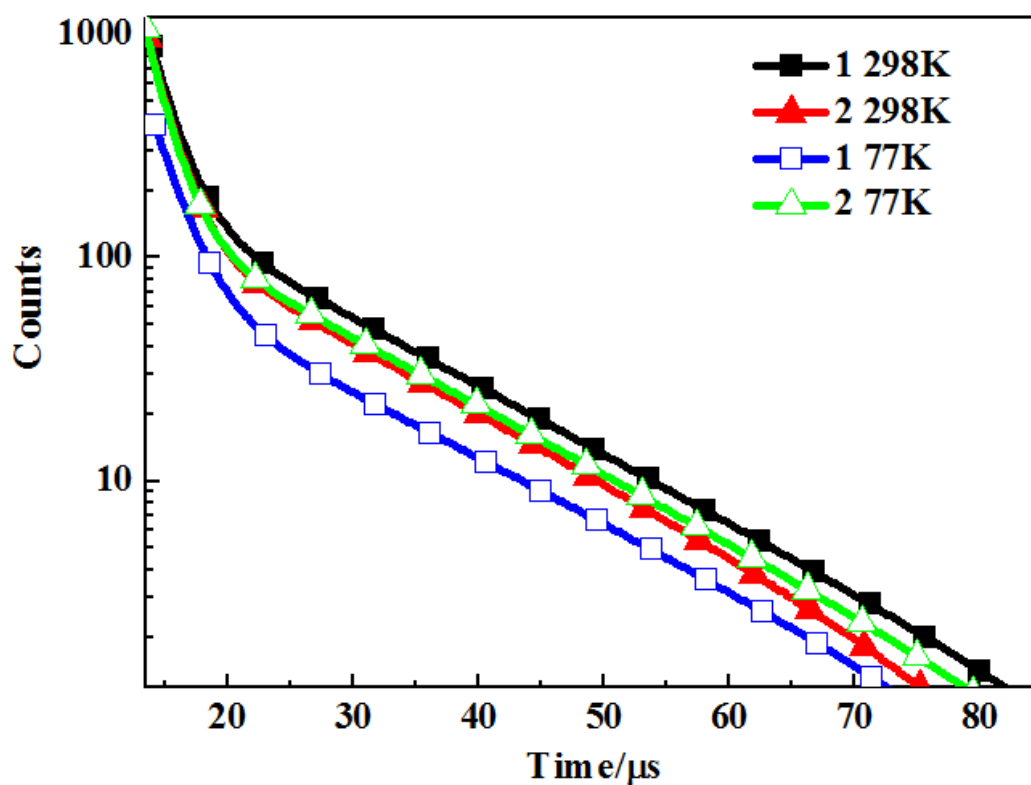
Compound	Temperature(K)	Excitation ( $\lambda_{\text{ex}}$ , nm)	Emission ( $\lambda_{\text{max}}$ , nm)	CIE (x, y)	$\tau_1$ ( $\mu\text{s}$ )	$\tau_2$ ( $\mu\text{s}$ )	$\langle\tau\rangle$ ( $\mu\text{s}$ )
<b>1</b>	298	260	412	(0.17,0.07)	1.83 (38.11%)	14.38 (61.89%)	13.47
	77	260	400	(0.17,0.10)	2.15 (41.09%)	15.23 (58.91%)	14.06
<b>2</b>	298	260	351 <sup>sh</sup> , 421 <sup>sh</sup>	(0.16,0.09)	1.77 (46.79%)	14.17 (53.21%)	12.94
	77	260	455 <sup>sh</sup> , 536	(0.30,0.39)	1.71 (46.55%)	14.41 (53.45%)	13.23
2,6-H <sub>2</sub> pydc	298	260	332 <sup>sh</sup> , 359	(0.17,0.13)	2.73 (44.86%)	16.46 (55.14%)	14.83
1,4-H <sub>2</sub> bda	298	260	414	(0.18,0.13)	0.99 (48.10%)	7.67 (51.90%)	6.95

**Table S9** Photoluminescent data for **2** introduced in different solvents at 298 K

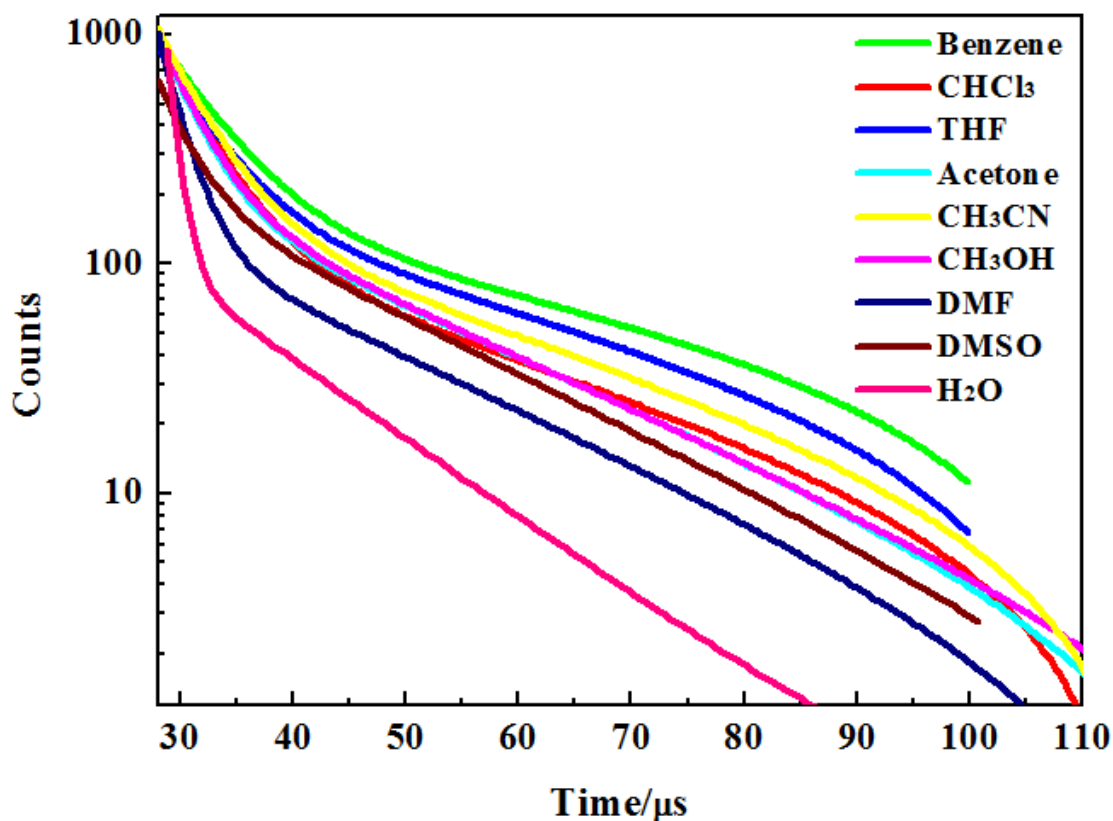
Solvent	Excitation ( $\lambda_{\text{ex}}$ nm)	Emission( $\lambda_{\text{max}}$ , nm)	$\tau_1$ ( $\mu\text{s}$ )	$\tau_2$ ( $\mu\text{s}$ )	$\langle\tau\rangle$ ( $\mu\text{s}$ )
Benzene	260	411 <sup>sh</sup> , 436, 459 <sup>sh</sup>	5.24 (30.21%)	54.30 (69.79%)	52.23
THF	260	407 <sup>sh</sup> , 433, 459 <sup>sh</sup>	4.58 (31.51%)	39.86 (68.49%)	38.09
CHCl <sub>3</sub>	260	410 <sup>sh</sup> , 434, 458 <sup>sh</sup>	4.16 (43.87%)	30.33 (56.13%)	27.80
Acetone	260	406 <sup>sh</sup> , 432, 458 <sup>sh</sup>	3.14 (36.30%)	20.45(63.70%)	19.06
CH <sub>3</sub> CN	260	404 <sup>sh</sup> , 432, 461 <sup>sh</sup>	4.01 (44.32%)	28.78 (55.68%)	26.30
CH <sub>3</sub> OH	260	410 <sup>sh</sup> , 436, 462 <sup>sh</sup>	3.19 (39.65%)	19.75 (60.35%)	18.17
DMF	260	409 <sup>sh</sup> , 433, 460 <sup>sh</sup>	2.06 (47.12%)	19.13 (52.88%)	17.64
DMSO	260	433	2.88 (30.26)	18.02 (69.74%)	16.99
H <sub>2</sub> O	260	436	0.91 (57.20%)	12.49 (42.80%)	11.47



**Fig. S15** Emission spectra of **1**, **2** and free 2,6-H<sub>2</sub>pydc, 1,4-H<sub>2</sub>bda ligands in the solid state at 298 K (excited at 260 nm).



**Fig. S16** The luminescence decay curves of **1** and **2** in the solid state at 298 K and 77K.



**Fig. S17** The luminescence decay curves of **2** in different solvents at 298 K.

#### Reference

- 1 G. M. Sheldrick, SHEIXTL NT Crystal Structure Analysis Package, Version 5.10, Bruker Axs, Analytical X-ray System, Madison, WI 1999
- 2 (a) B. Liu, R. L. Zhao, G. P. Yang, L. Hou, Y. Y. Wang and Q. Z. Shi, *CrystEngComm*, 2013, **15**, 2057; (b) C. Volkringer, M. Meddouri, T. Loiseau, N. Guillou, J. Marrot, G. Fe'rey, M. Haouas, F. Taulelle, N. Audebrand and M. Latroche, *Inorganic Chemistry*, 2008, **47**, 11892; (c) C. Volkringer, T. Loiseau, N. Guillou, G. F'erey, E. Elka and A. Vimont, *Dalton Trans.*, 2009, 2241; (d) W. Kaneko, M. Ohba and S. Kitagawa, *J. AM. CHEM. SOC.* 2007, **129**, 13706.
- 3 (a) T. Panda, T. Kundu and R. Banerjee, *Chem. Commun.*, 2013, **49**, 6197; (b) B. Yuan, D. Ma, X. Wang, Z. Li, Y. W, Li, H. M. Liuc and D. Hec, *Chem. Commun.*, 2012, **48**, 1135. (c) W. B. Ji, H. L. Hu, W. S. Zhang, H. Huang, X. D. He, X. Han, F. F. Zhao, Y. Liu and Z. H. Kang, *Dalton Trans.*, 2013, **42**, 10690.
- 4 (a) K. C. Stylianou, R. Heck, S. Y. Chong, J. Bacsá, J. T. A. Jones, Y. Z. Khimiyak, D. Bradshaw, and M. J. Rosseinsky, *J. AM. CHEM. SOC.* 2010, **132**, 4119; (b) Y. X. Tan, F. Wang, Y. Kang and J. Zhang, *Chem. Commun.*, 2011, **47**, 770.