

# Ln-Cd heterometal organic-inorganic hybrid materials based on diverse Ln-Cd oxo-cluster Chains: syntheses, structures and visible Luminescence

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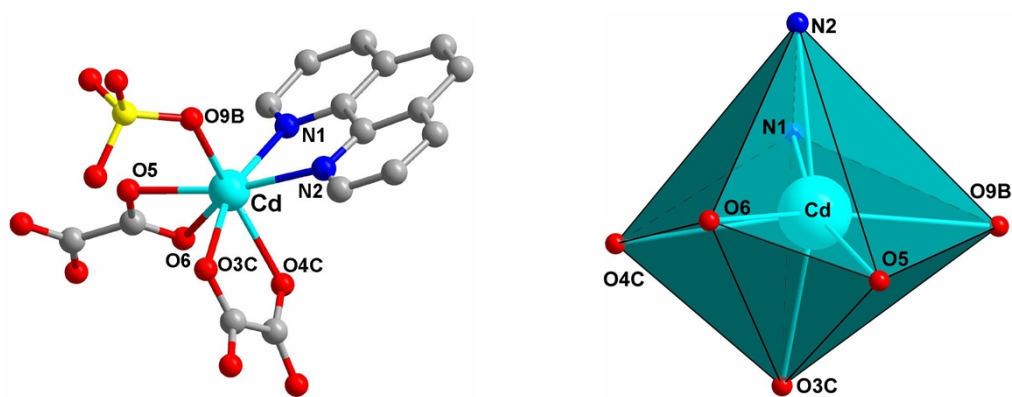
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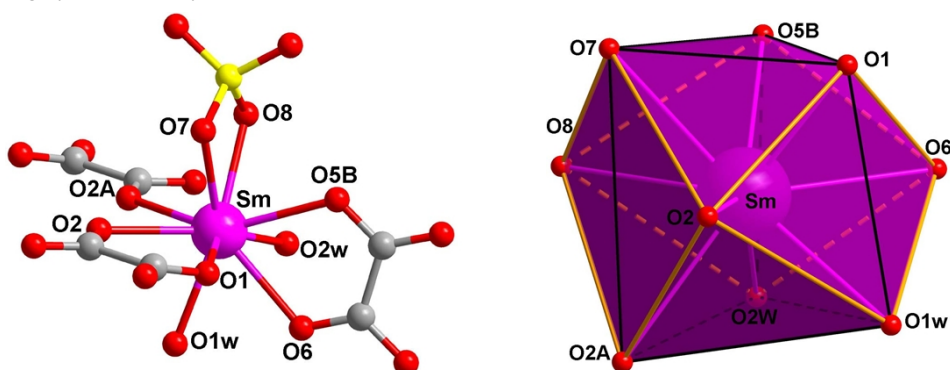
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**Table S1 Selected Bond Distances (Å) for 1a, 1b and 2.**

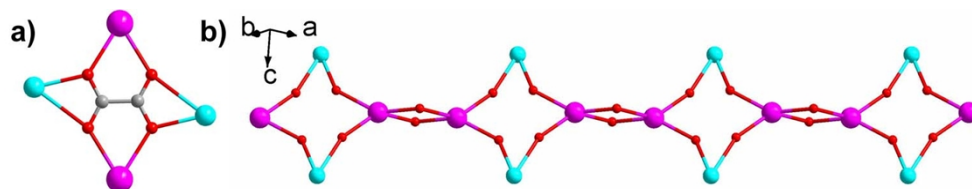
<b>1a</b>					
Sm-O(1)	2.415(6)	Sm-O(2)	2.530(6)	Sm-O(2W)	2.414(6)
Sm-O(1W)	2.479(8)	Sm-O(2)#1	2.565(5)	Sm-O(5)#2	2.569(6)
Sm-O(6)	2.546(6)	Sm-O(7)	2.478(7)	Sm-O(8)	2.473(6)
Cd-O(3)#3	2.262(6)	Cd-O(6)	2.873(6)	Cd-N(1)	2.355(8)
Cd-O(4)#3	2.431(6)	Cd-O(9)#2	2.339(6)	Cd-N(2)	2.310(7)
Cd-O(5)	2.342(6)				
#1: -x, 2-y, 1-z; #2: 1-x, 1-y, 1-z; #3: -x, 1-y, 1-z.					
<b>1b</b>					
Eu-O(1W)	2.452(6)	Eu-O(4)#1	2.507(5)	Eu-O(6)	2.499(5)
Eu-O(2W)	2.375(5)	Eu-O(5)	2.376(6)	Eu-O(7)	2.444(6)
Eu-O(3)	2.522(5)	Eu-O(6)#2	2.521(5)	Eu-O(8)	2.427(5)
Cd-O(1)	2.400(5)	Cd-O(4)	2.830(5)	Cd-N(1)	2.328(7)
Cd-O(2)	2.239(5)	Cd-O(9)	2.326(5)	Cd-N(2)	2.289(7)
Cd-O(3)	2.314(5)				
#1: -x, 2-y, 2-z; #2: 1-x, 1-y, 2-z					
<b>2</b>					
Eu-O(2)#2	2.253(3)	Eu-O(3)#2	2.456(3)	Eu-O(7)#4	2.444(3)
Eu-O(2W)	2.406(4)	Eu-O(4)#3	2.470(3)	Eu-O(10)	2.378(3)
Eu-O(3)#3	2.534(3)	Eu-O(6)#4	2.292(3)	Cd(1)-O(1W)	2.288(4)
Cd(1)-N(1)	2.245(4)	Cd(1)-O(7)#4	2.434(3)	Cd(1)-O(9)	2.371(4)
Cd(1)-O(4)	2.382(3)	Cd(1)-O(8)#4	2.400(3)	Cd(1)-O(10)	2.484(4)
Cd(2)-O(5)	2.491(4)	Cd(2)-O(8)#5	2.396(3)	Cd(2)-N(4)#5	2.281(4)
Cd(2)-O(1)	2.377(4)	Cd(2)-N(2)	2.242(4)	Cd(2)-N(3)	2.226(4)
#1: 1-x, -y, -z; #2: x, -1+y, z; #3: 1-x, 1-y, -z; #4: 1+x, -1+y, z					



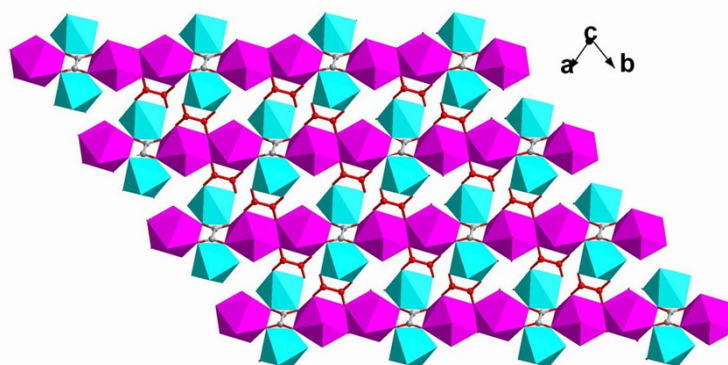
**Fig. S1** The coordination environments of Cd atom in **1a**. (left) The ball-stick representation. (right) The polyhedral representation. Symmetry code A:  $-x, -y+2, -z+1$ ; B:  $1-x, 1-y, -z+1$ ; c:  $-x, 1-y, 1-z$ . Color code: Cd, cyan; O, red; C, grey; N, blue; S, yellow.



**Fig. S2** The coordination environments of Sm atom in **1a**. (left) The ball-stick representation. (right) The polyhedral representation. Symmetry code: A:  $-x, -y+2, -z+1$ ; B:  $1-x, 1-y, -z+1$ . Color code: Sm, purple; O, red; C, grey; S, yellow.

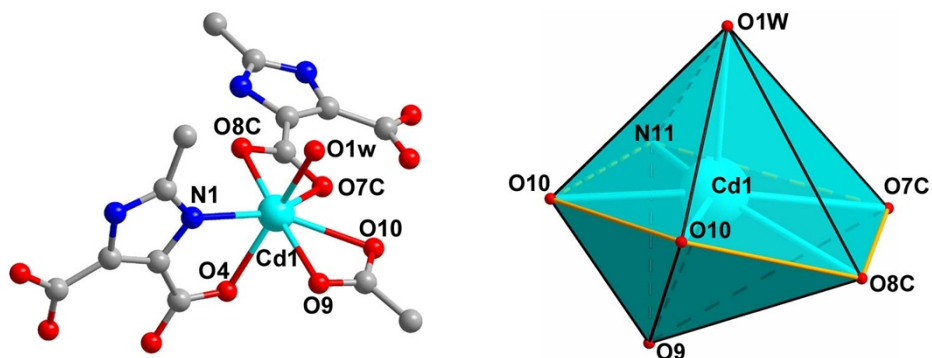


**Fig. S3** (a) Ball-stick view of the star-like  $\text{Ln}_2\text{Cd}_2\text{O}_4$  tetranuclear cluster with the  $\text{ox}^{2-}$  anion in the center. (b) View of the inorganic centipede-like heterometallic cluster chain running along the  $[1-10]$  direction. Color code: Sm, purple; Cd, cyan; O, red; N, blue; C, grey; S, yellow.

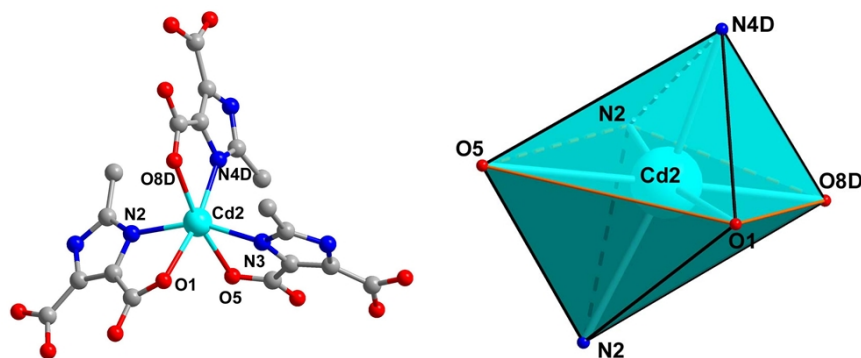


**Fig. S4** View of 2-D bilayer in the  $ab$ -plane constructed from heterometallic cluster chains bridged by  $\text{ox}^{2-}$  anions

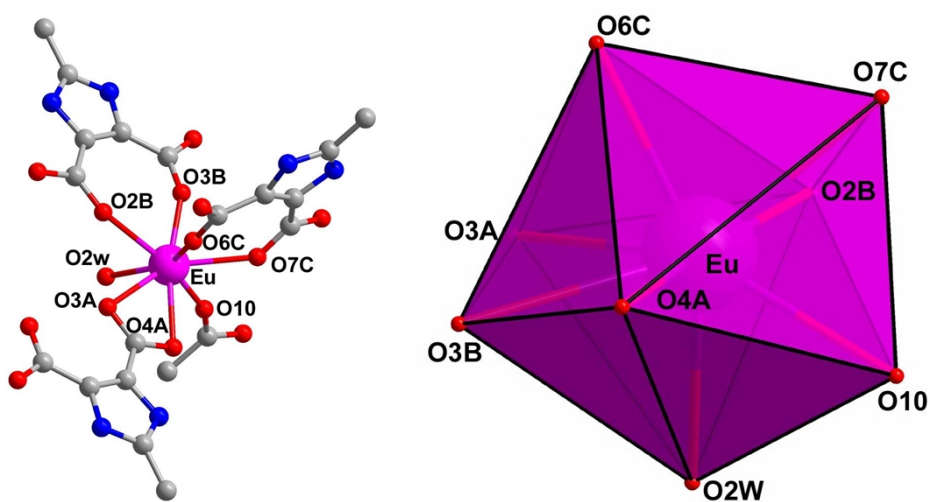
(red). The  $\text{SO}_4^{2-}$  anions and phen ligands were omitted for clarity. Color code: Sm, purple; Cd, cyan; O, red; N, blue; C, grey; S, yellow.



**Fig. S5** The coordination environments of Cd1 atom in **2**. (left) The ball-stick representation. (right) The polyhedral representation. Color code: Sm, purple; Cd, cyan; O, red; N, blue; C, grey; S, yellow. Atoms having “C” in their labels are symmetry-generated. C:  $1+x, -1+y, z$ .



**Fig. S6** The coordination environments of Cd2 atom in **2**. (left) The ball-stick representation. (right) The polyhedral representation. Color code: Sm, purple; Cd, cyan; O, red; N, blue; C, grey; S, yellow. Atoms having “D” in their labels are symmetry-generated. D:  $-0.5-x, -0.5+y, 0.5-z$ .



**Fig. S7** The coordination environments of Eu atom in **2**. (left) The ball-stick representation. (right) The polyhedral representation. Atoms having “A”, “B”, “C” or “D” in their labels are symmetry-generated. A:  $1-x, 1-y, -z$ ; B:  $x, -1+y, z$ ; C:  $1+x, -1+y, z$ ; D:  $-0.5-x, -0.5+y, 0.5-z$ .

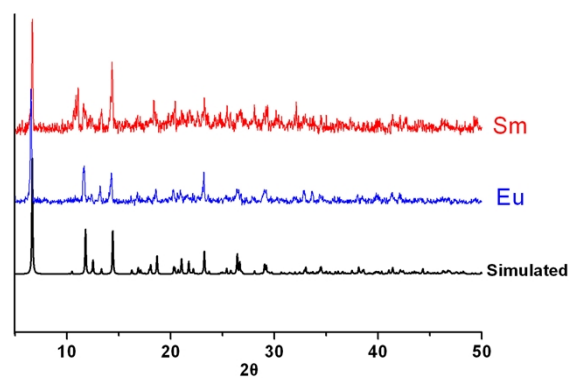


Fig. S8 PXRD pattern of **1a**(Sm), **1b**(Eu) and simulated, respectively.

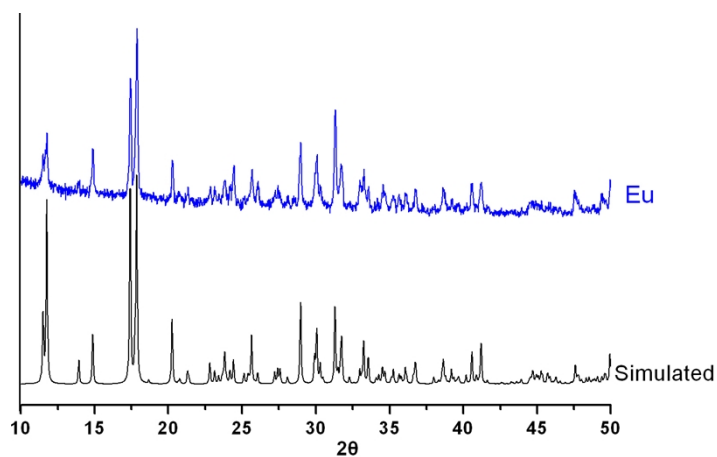


Fig. S9 PXRD pattern of **2** and simulated, respectively.

The PXRD patterns of **1a**, **1b** and **2** are very close to each other, which coincide with simulated, indicating the purity of the crystals.

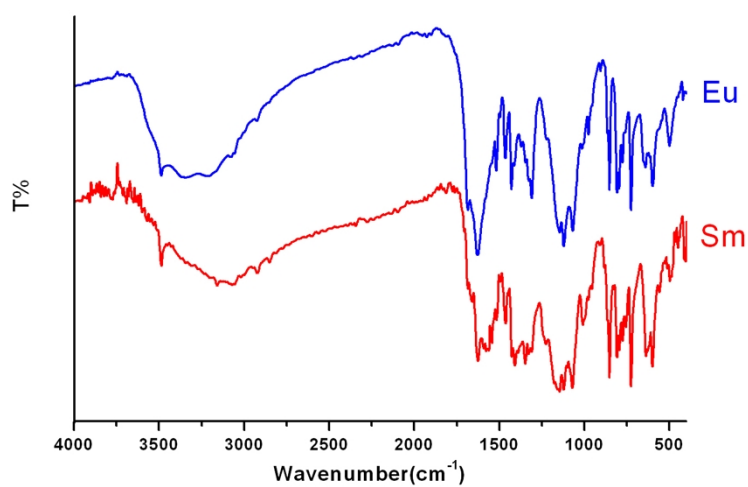
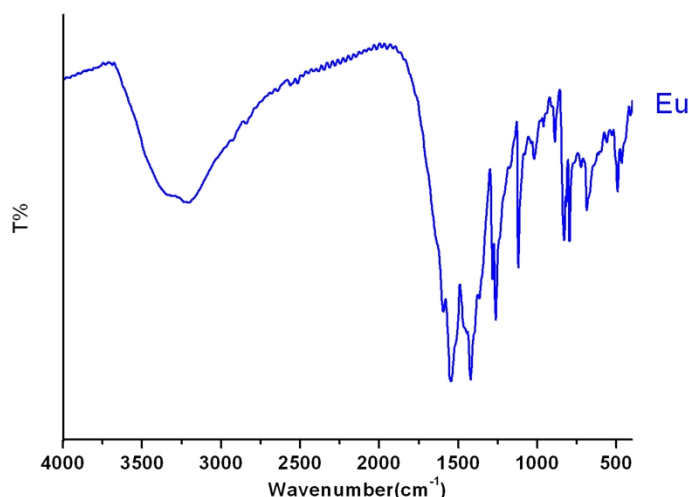
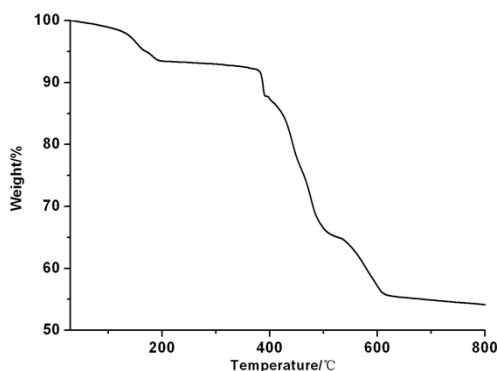


Fig. S10 IR spectra of **1a**(Sm), **1b**(Eu) respectively.



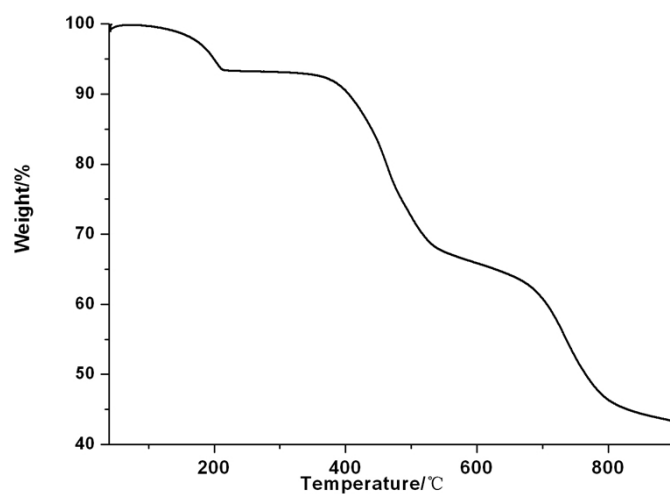
**Fig. S11** IR spectra of **3(Eu)**.

IR spectra of **1a** and **2** exhibit strong bands at 1620, 1433  $\text{cm}^{-1}$  for **1a** and 1543, 1431,  $\text{cm}^{-1}$  for **2** associated with  $\nu_{\text{asym}}(\text{C}=\text{O})$  and  $\nu_{\text{sym}}(\text{C}=\text{O})$ , respectively (Fig. S10, S11). Compared with the corresponding ligands they are both shifted to lower wave numbers corresponding to the  $\nu(\text{C}=\text{O})$  of the coordinated carboxylate moieties. According to G. Deacon rules, Compound **1a** and **2** with low ( $\Delta(\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)) < 200 \text{ cm}^{-1}$ ) value has chelating and bridging carboxylate moieties, which are good agreement with the crystal structure. Bands characteristic of the S=O stretching modes of the  $\text{SO}_4^{2-}$  in **1a** are observed at approximately at 1117 and 1073  $\text{cm}^{-1}$ .



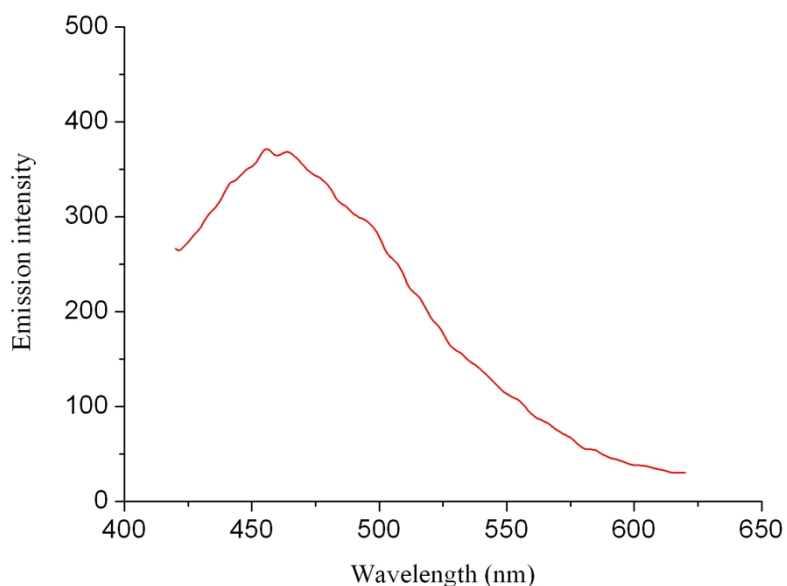
**Fig. S12** TGA of **1b**.

Thermal gravimetric analyses (TGA) of **1b** were performed in a dry nitrogen atmosphere from 30  $^{\circ}\text{C}$  to 800  $^{\circ}\text{C}$  (Fig. S11). The TG curve of **1b** displays the weight loss of 7.47% (calcd: 7.43%) in the temperature range 30-350  $^{\circ}\text{C}$ , corresponding to the successive release of one free water molecules and two coordinated water molecules per formula unit. The decomposition of  $\text{H}_2\text{Ox}$  and 1,10-phen is observed from 350  $^{\circ}\text{C}$  to 800  $^{\circ}\text{C}$ . The residue might be  $\text{Eu}_2\text{O}_3 \cdot 2\text{CdSO}_4$  (calcd/found: 52.90%/54.20%) for **1b**.



**Fig. S13** TGA of **2**.

In the TGA curve of **2**, the weight loss of 6.76% (calcd: 6.55%) in the temperature range 40-250 °C, can be assigned to the successive release of one free water molecules and two coordinated water molecules. The second weight loss of 47.91% is observed from 250 to 841 °C due to the loss of the H<sub>2</sub>Meimdc and HAc organic species (calc. 18.56%) and the slow evaporation of *ca* 0.5 CdO per formula above 558 °C (calc. 47.84%).<sup>23</sup> The residue might be 1/2Sm<sub>2</sub>O<sub>3</sub>·3/2CdO (calcd/found: 44.73%/43.30%).



**Figure S14.** Solid-state luminescent emission spectrum of the free ligand H<sub>3</sub>Meimdc at room temperature.