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## Graphic abstract

### Four 2D Ln-Cd heterometal-organic coordination polymers based on tetra-nuclear Ln-Cd oxo-cluster with high selective luminescent sensing of organic molecules and metal cations

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Two series of 2D layered Ln-Cd heterometal-organic complexes based on tetranuclear  $[Ln_2Cd_2]$  oxo-clusters with selective luminescent sensing, have been synthesized.

# Four 2D Ln-Cd heterometal-organic coordination polymers based on tetra-nuclear Ln-Cd oxo-cluster with high selective luminescent sensing of organic molecules and metal Cations

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Two series of novel lanthanide-cadmium (Ln-Cd) heterometal-organic coordination polymers, [Ln<sub>2</sub>Cd<sub>2</sub>(DTPA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] (H<sub>2</sub>O)<sub>4</sub> (**I**: Ln = Eu **1a**; Gd **1b**) and [Ln<sub>2</sub>Cd<sub>3</sub>(DTPA)<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>] (**II**: Ln = Eu **2a**; Sm **2b**) (H<sub>5</sub>DTPA = Diethylenetriamine penta-acetic acid) have been synthesized under hydrothermal method. Compounds **I** and **II** both possess 2D grid layer structure based on distinct tetranuclear Ln-Cd oxo-cluster units as secondary building units (SBUs). Two enantiomeric forms,  $\alpha$  and  $\beta$  exist in [Cd(DTPA)]<sup>3-</sup> in compounds **I**. Interestingly, compound **1a** displays not only a high-sensitive sensing of small molecular organic solvents, especially methanol, triethylamine and ethanol amine but also the sensing of cations, especially Cr<sup>3+</sup> and Fe<sup>3+</sup> ions. Also, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>3+</sup>, Cu<sup>2+</sup>, Nd<sup>3+</sup> cations quenched the emissions of Eu<sup>3+</sup> ions of compound **2a**. These indicate the potential of **1a** and **2a** for sensing of metal cations.

## Introduction

Lanthanide-organic coordination polymers are attracting great interests because of their unique luminescent and magnetic properties that derive from the electronic configurations [Xe]4f<sup>n</sup> (n=0-14) of lanthanide elements<sup>[1]</sup>. Varieties of lanthanide-organic coordination polymers with fascinating structural diversities and potential applications have been synthesized and researched. In order to enrich the structures and promote properties of lanthanide-organic coordination polymers, heterometallic ions, especially *d*-block ions were introduced into these compounds<sup>[1f-h, 2]</sup>. The introduced heterometallic ions not only make the structures more plentiful but also cause the energy levels of these materials more controllable<sup>[3]</sup>. To the best of our knowledge, the vast majority of these lanthanide-transition(*f-d*) heterometal-organic coordination polymers are focused on Ln-M (M=Cu<sup>[2d, 2h, 4]</sup>, Co<sup>[2j, 5]</sup>, Ni<sup>[2j, 5b, 6]</sup>, Fe<sup>[2j, 5f, 7]</sup>, Ag<sup>[8]</sup>, Mn<sup>[2b, 9]</sup> etc) and these transition metal ions are of interesting magnetic

properties. Relatively few researches are focused on the luminescent properties of these compounds that we are interested in. Most of lanthanide ions emit line-like and strong lights under stimulus. However, we all know that the *f-f* transitions of lanthanide ions (Ln<sup>3+</sup> ions) are parity-forbidden which results in very low absorption coefficients. Organic ligands with intense absorption properties are coordinated to lanthanide ions as energy donors to induce characteristic emissions of lanthanide ions. It means that energy is absorbed by organic ligands firstly, then it will be sent to lanthanide ions by intramolecular energy transfer, and this induces emissions of lanthanide ions. This way is named as "antenna effect"<sup>[10]</sup>. There has been significant interest in development of luminescent lanthanide-organic coordination polymers for applications such as optical materials<sup>[3a]</sup>, organic light-emitting diodes (OLEDs)<sup>[11]</sup>. The application of luminescent sensors is a promising research field, too<sup>[1d, 12]</sup>. The intensities of emission lights of lanthanide ions could be enhanced or quenched by some organic molecules such as acetone, acetylacetone or cations like Co<sup>2+</sup>, Cu<sup>2+</sup>. So lanthanide-organic coordination polymers are hopeful materials for chemical sensing.

In contrast to other lanthanide-transition(*f-d*) heterometal-organic coordination polymers, the researches of lanthanide-cadmium (Ln-Cd) heterometal-organic coordination polymers are very few. Cd<sup>2+</sup> ion not only itself emits luminescence by ligands-metal interactions, but also acts as a bridge of energy

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† Electronic Supplementary Information (ESI) available: Synthesis, table, supplementary 14 plots including structures, luminescent spectra, XPRD, TG and FT-IR. See DOI: 10.1039/b000000x.

transfer between organic ligands and  $\text{Ln}^{3+}$  ions. Because of their novel luminescent properties, Ln-Cd heterometal-organic coordination polymers will be useful tools as chemical sensors. To the best of our knowledge, the reported Ln-Cd heterometal-organic coordination polymers are mainly zero-dimensional(0D)<sup>[1c, 2j, 13]</sup>, one-dimensional(1D)<sup>[14]</sup> and three-dimensional(3D)<sup>[1d, 15]</sup> coordination structures. Our group reported the first 2D Ln-Cd heterometal layered structure<sup>[12e]</sup>. According to the soft-hard acid-base theory,  $\text{Ln}^{3+}$  ions belong to hard acid and have strong affinities to coordinate to hard bases like O atom, while  $\text{Cd}^{2+}$  ion is soft acid and inclines to bond to soft bases, such as S and N atoms. The competitions between  $\text{Ln}^{3+}$  and  $\text{Cd}^{2+}$  in the reaction system make it hard to synthesize Ln-Cd heterometal-organic coordination polymers. Thus, the ligands with N- and O-donors can elaborately be selected and employed to make heterometal-organic coordination polymers. Diethylenetriamine penta-acetic acid( $\text{H}_5\text{DTPA}$ ) with N- and O-donors has been used to prepare metal-organic coordination polymers with single transition metal (TM) or Ln ions<sup>[16]</sup>, and that assembly in Ln-TM-organic coordination polymers remains unexplored. We select  $\text{H}_5\text{DTPA}$  as a candidate for assembling heterometal polymers, based on the following considerations: 1) It has five carboxylate groups as hard base and three coordinated N donors as soft base, which makes it possible to bond to both  $\text{Ln}^{3+}$  and  $\text{Cd}^{2+}$  ions simultaneously in the reaction system. 2) It is a chelating agent which has strong affinities with the  $\text{Ln}^{3+}$  and  $\text{Cd}^{2+}$  ions. 3) The carboxylate acid groups and N donors of the ligand can adjust the pH value of the reaction system.

On the basis of the aforementioned points, our aim is to prepare novel Ln-Cd heterometal-organic coordination polymers with luminescent sensing. Herein, we report the syntheses, structures and luminescent sensing of two series of 2D Ln-Cd heterometal-organic coordination polymers:  $[\text{Ln}_2\text{Cd}_2(\text{DTPA})_2(\text{H}_2\text{O})_4](\text{H}_2\text{O})_4$  (I: Ln = Eu **1a**; Gd **1b**) and  $[\text{Ln}_2\text{Cd}_3(\text{DTPA})_2\text{Cl}_2(\text{H}_2\text{O})_6]$  (II: Ln = Eu **2a**; Sm **2b**), which are 2D layers based on different tetranuclear  $[\text{Ln}_2\text{Cd}_2]$  oxo-clusters with high selective luminescent sensing.

## Experimental section

### Materials and Physical Measurements

Commercially available solvents and chemicals were used without further purification. The elemental analyses for C, H and N were performed with an Elementar Vario EL III elemental analyzer. IR spectra were measured as KBr pellets on a Perkin-Elmer Spectrum 2000 FT-IR in the range 400-4000  $\text{cm}^{-1}$ . Thermogravimetric data were collected on a Mettler Toledo TGA/SDTA 851° analyzer in flowing nitrogen at a heating rate of 10 °C/min. Luminescence measurements were made with an Edinburgh Instrument FS920 TCSPC luminescence spectrometer on powder crystal material of the compounds. The **1a** solution were prepared by introducing **1a** powder (5 mg) into methanol, acetonitrile, acetone, n-butanol, ethanol, ammonia water,  $\text{H}_2\text{O}$ , DMF, i-propanol, triethylamine, pyridine, ethanediamine, 1,2-propane diamine, and ethanol amine

(5.00 mL) at room temperature. Similarly, the powder of **1a** and **2a** was immersed in aqueous solution containing different  $\text{M}(\text{NO}_3)_x$  ( $\text{M} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Li}^+, \text{K}^+, \text{Na}^+, \text{Mg}^{2+}, \text{La}^{3+}, \text{Ho}^{3+}, \text{Ce}^{3+}, \text{Tb}^{3+}, \text{Yb}^{3+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Pb}^{2+}, \text{Al}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Nd}^{3+}, \text{Pr}^{3+}, \text{Dy}^{3+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Cr}^{3+}, \text{Fe}^{3+}, \text{Ni}^{2+}$  and  $\text{Er}^{3+}$ ) and different concentrations of  $\text{Co}(\text{NO}_3)_2$ . Samples were prepared by introducing powder (5 mg) of **1a** and **2a** into aqueous solution (5.00 mL) at room temperature. Before luminescence measurements, the suspensions were oscillated for 10 minutes using ultrasonic waves to ensure uniform dispersion.

### Synthesis of compounds

**$[\text{Ln}_2\text{Cd}_2(\text{DTPA})_2(\text{H}_2\text{O})_4](\text{H}_2\text{O})_4$  (I: Ln = Eu **1a**; Gd **1b**)** A mixture of  $\text{H}_5\text{DTPA}$  (0.3931 g, 0.999 mmol),  $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  (0.5330 g, 2.000 mmol),  $\text{Ln}_2\text{O}_3$  ( $\text{Eu}_2\text{O}_3$  0.1768 g, 0.502 mmol for **1a**,  $\text{Gd}_2\text{O}_3$  0.1846 g, 0.509 mmol for **1b**), and  $\text{H}_2\text{O}$  (10 mL) was placed in 23-mL Teflon-lined stainless steel vessels, then heated to 170 °C for 7 days, and then cooled to room temperature. Colorless block crystals were obtained. Yield: 0.6390g (88% based on Eu(III)) for **1a**, 0.5173g (69.5% based on Gd(III)) for **1b**. Anal. calc. for  $\text{C}_{28}\text{N}_6\text{O}_{28}\text{H}_5\text{Cd}_2\text{Eu}_2$  **1a**: C, 23.18%; H, 3.59%; N, 5.80%. Found: C, 23.20%; H, 3.57%; N, 5.95%; for  $\text{C}_{28}\text{N}_6\text{O}_{28}\text{H}_5\text{Cd}_2\text{Gd}_2$  **1b**: C, 23.01%; H, 3.56%; N, 5.75%. Found: C, 23.15%; H, 3.65%; N, 5.60%. Selected IR peaks ( $\text{cm}^{-1}$ ): 3190(br), 1595(s), 1442(m), 1403(m), 1321(m), 1243(m), 1100(s), 989(m), 924(s), 849(m), 745(m), 719(m), 643(m), 595(w), 520(w), 448(w) (Fig. S1).

**$[\text{Ln}_2\text{Cd}_3(\text{DTPA})_2\text{Cl}_2(\text{H}_2\text{O})_6]$  (II: Ln = Eu **2a**; Sm **2b**)** A mixture of  $\text{H}_5\text{DTPA}$  (0.3939 g, 1.001 mmol),  $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  (0.2670 g, 1.002 mmol),  $\text{Ln}_2\text{O}_3$  ( $\text{Eu}_2\text{O}_3$  0.3510 g, 0.997 mmol for **2a**,  $\text{Sm}_2\text{O}_3$  0.3475 g, 0.997 mmol for **2b**), and  $\text{H}_2\text{O}$  (10 mL) was placed in a 23-mL Teflon-lined stainless steel vessels. The pH was adjusted to 2 by 0.1M HCl, and was heated to 170 °C for 7 days, and then cooled to room temperature. Colorless block crystals were obtained. Yield: 0.1665g (10.5% based on Eu(III)) for **2a**, 0.1187g (7.5% based on Sm(III)) for **2b**. Anal. calc. for  $\text{C}_{28}\text{N}_6\text{O}_{26}\text{H}_4\text{Cd}_3\text{Eu}_2$  **2a**: C, 21.04%; H, 3.01%; N, 5.26%. Found: C, 21.20%; H, 3.17%; N, 5.15%; for  $\text{C}_{28}\text{N}_6\text{O}_{26}\text{H}_4\text{Cd}_3\text{Sm}_2$  **2b**: C, 21.09%; H, 3.01%; N, 5.27%. Found: C, 21.15%; H, 3.15%; N, 5.40%. Selected IR peaks ( $\text{cm}^{-1}$ ): 3295(s), 1580(s), 1445(m), 1406(s), 1325(m), 1270(m), 1083(s), 996(w), 937(s), 865(w), 729(m), 647(m), 582(w), 500(w), 445(w) (Fig. S1).

### X-ray Crystallography.

Suitable single crystals were selected and mounted on a glass fiber. All data of **1a**, **1b** and **2b** were collected on a Rigaku R-Axis RAPID diffractometer with graphite-monochromated  $\text{MoK}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation in the  $\omega$  scanning mode at room temperature; All data of **2a** were collected on a Rigaku Saturn 724 CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation in the  $\omega$  scanning mode at room temperature. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  using the SHELXTL-97 program package<sup>[17]</sup>. Some free water molecules were refined isotropically. Hydrogen atoms bond O and C were generated geometrically (C-H = 0.93 Å, O-H = 0.85 Å) and refined with fixed isotropic displacement parameters, hydrogen atoms of some free water molecules were not generated. X-ray Powder Diffraction (XPRD) patterns Crystallographic data for

**Table 1.** Crystal data and structural refinement parameters for **1a**, **1b**, **2a** and **2b**

	<b>1a</b>	<b>1b</b>	<b>2a</b>	<b>2b</b>
formula	C <sub>28</sub> N <sub>6</sub> O <sub>28</sub> H <sub>52</sub> Cd <sub>2</sub> Eu <sub>2</sub>	C <sub>28</sub> N <sub>6</sub> O <sub>28</sub> H <sub>52</sub> Cd <sub>2</sub> Gd <sub>2</sub>	C <sub>28</sub> N <sub>6</sub> O <sub>26</sub> H <sub>48</sub> Cl <sub>2</sub> Cd <sub>3</sub> Eu <sub>2</sub>	C <sub>28</sub> N <sub>6</sub> O <sub>26</sub> H <sub>48</sub> Cl <sub>2</sub> Cd <sub>3</sub> Sm <sub>2</sub>
fw	1449.48	1460.06	1596.74	1593.52
crystal system	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	9.804(3)	9.779(2)	8.6545(17)	8.6521(17)
<i>b</i> (Å)	10.912(4)	10.868(2)	9.0700(18)	9.0758(18)
<i>c</i> (Å)	20.446(6)	20.395(4)	15.407(3)	15.422(3)
$\alpha$ (deg)	100.683(12)	100.77(3)	98.47(3)	98.43(3)
$\beta$ (deg)	92.766(9)	92.74(3)	101.37(3)	101.51(3)
$\gamma$ (deg)	91.801(11)	91.79(3)	103.33(3)	103.40(3)
<i>V</i> (Å <sup>3</sup> )	2145.1(12)	2125.2(7)	1129.9(4)	1130.5(4)
<i>Z</i>	2	2	1	1
<i>D</i> <sub>c</sub> (g/cm <sup>3</sup> )	2.244	2.282	2.347	2.341
<i>R</i> <sub>int</sub>	0.0317	0.0630	0.0310	0.0198
$\theta$ range/deg	2.99-25.00	2.99-27.47	3.19-27.49	3.13-27.47
<i>F</i> (000)	1416	1420	770	768
GOOF on <i>F</i> <sup>2</sup>	1.01	0.95	1.11	1.22
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0269, 0.0666	0.0433, 0.1109	0.0298, 0.0661	0.0243, 0.0798
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0317, 0.0685	0.0630, 0.1237	0.0317, 0.0671	0.0277, 0.0864

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

the structures reported have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers CCDC-975527 (for **1a**), -975528 (for **1b**), -975529 (for **2a**), -975530 (for **2b**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). The selected crystal parameters, data collection, and refinements are summarized in Table 1.

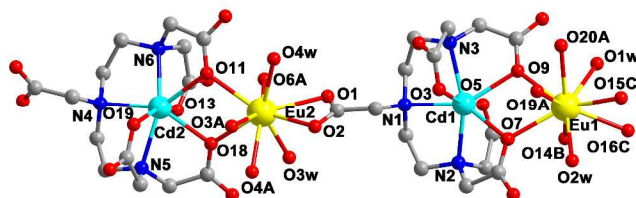
## Results and discussion

### Description of Crystal Structures

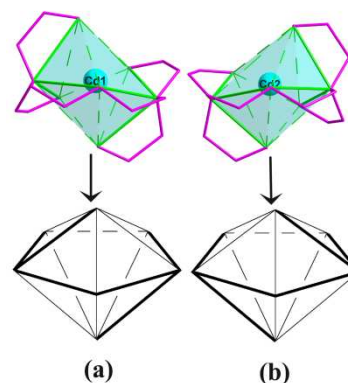
As shown in Fig. S2, the PXRD patterns of compounds **1** and **I** agree with those calculated from the structures, indicating that complexes **1a** and **1b**, **2a** and **2b** are isostructural.

[Ln<sub>2</sub>Cd<sub>2</sub>(DTPA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](H<sub>2</sub>O)<sub>4</sub> (**I**: Ln = Eu **1a**; Gd **1b**) According to single-crystal X-ray diffraction analyses and PXRD patterns, compounds **1a** and **1b** are isostructural which both crystallize in triclinic space group of *P*-1. So, only the structure of **1a** will be described in detail here. In the asymmetrical unit of **1a**, there are two unique Cd<sup>2+</sup> ions, two Eu<sup>3+</sup> ions, two DTPA<sup>5-</sup> anions and four coordinated water molecules, respectively (Fig. 1). The coordination geometries of the two seven-coordinated Cd<sup>2+</sup> ions can be viewed as slightly distorted pentagonal bipyramids: four O<sub>COO</sub><sup>-</sup> atoms and three N atoms from one DTPA<sup>5-</sup> anion (Fig. S3 and 2). Besides, the two Eu<sup>3+</sup> ions are both nine-coordinated with geometries of tricapped trigonal prisms: seven O<sub>COO</sub><sup>-</sup> atoms from four DTPA<sup>5-</sup> anions and two coordinated water molecules (Fig. S4). Cd-O and Cd-N bond lengths are in the range of 2.344(3) Å-2.417(3) Å and 2.358(3) Å-2.461(3) Å, respectively. And Eu-O bond lengths are 2.392(3) Å-2.568(3) Å, which are compared to the reported bond distances in previous paper<sup>[15]</sup>. The two DTPA<sup>5-</sup> anions in the asymmetrical unit both chelate Cd<sup>2+</sup> ions forming

pentagonal bipyramids. Interestingly, the [Cd(DTPA)]<sup>3+</sup> units, the absolute configurations around Cd<sup>2+</sup> ion, have two enantiomeric forms,  $\alpha$  and  $\beta$ . (Fig. 2 and S5). Two  $\mu_2$ -O atoms from one DTPA<sup>5-</sup> ligands bridge one Cd<sup>2+</sup> and one Eu<sup>3+</sup>, thus forming an edge-sharing heterometal binuclear [EuCd( $\mu_2$ -O)<sub>2</sub>] unit with Eu...Cd distance of 3.985(7) Å. Two binuclear [EuCd( $\mu_2$ -O)<sub>2</sub>] units are connected each other by  $\mu_2$ -O from DTPA<sup>5-</sup>



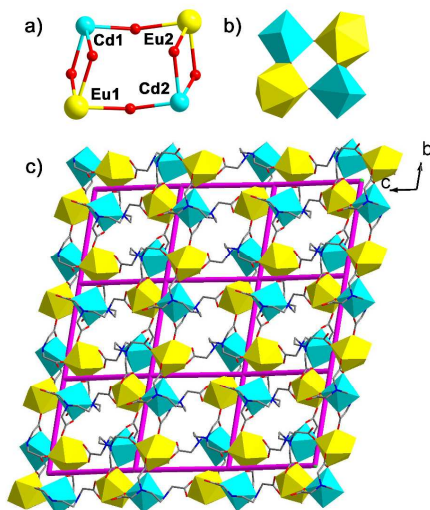
**Fig. 1** The coordination environments of Eu<sup>3+</sup> and Cd<sup>2+</sup> in **1a**. Atoms having “A”, “B” or “C” in their labels are symmetry-generated. A: 1-x, 1-y, 1-z; B: 1-x, -y, 1-z; C: -1+x, y, 1+z. Hydrogen atoms are omitted for clarity. Color code: Eu, yellow; Cd, cyan; O, red; N, blue; C, grey.



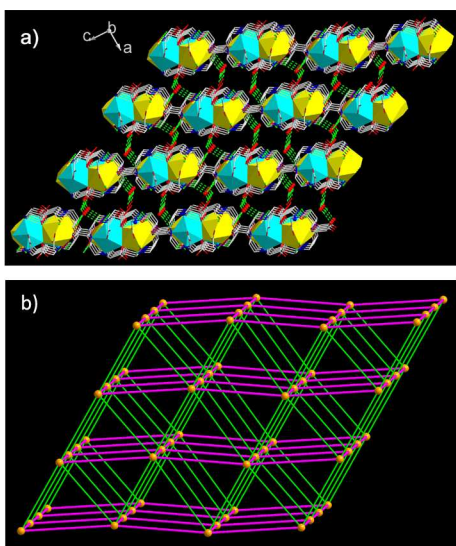
**Fig. 2** Two enantiomeric forms in [Cd(DTPA)]<sup>3+</sup> units of Type **I**. (a)  $\alpha$ , (b)  $\beta$ .



ligands between  $\text{Eu}^{3+}$  and  $\text{Cd}^{2+}$  ions to generate a cradle-like tetranuclear  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_6]$  cluster unit (Fig. 3a and 3b). Each tetranuclear  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_6]$  cluster unit acts as a four-connected node and links four other  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_6]$  cluster units by  $\text{DTPA}^{5-}$  anions forming a (4,4) grid layer in the [101] plane (Fig. 3c). The 2-D layers stack in  $-\text{AAA}-$  mode along the  $a$ -axis. Free water molecules are located between the layers. Moreover, the  $\text{O-H}\cdots\text{O}$  hydrogen bonds between free water molecules and  $\text{O}_{\text{COO}^-}$  atoms of  $\text{DTPA}^{5-}$  anions link the layers into a 3D supra-molecular structure (Fig. 5a). From the topological point of view, the 3-D supra-molecular framework of **1a** is a 8- connected net (Fig. 5b). Because only



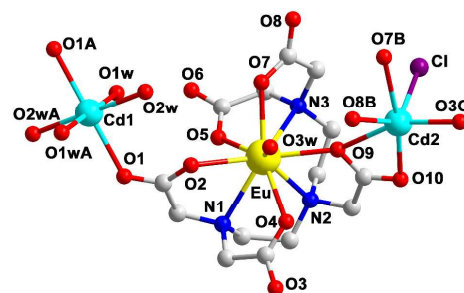
**Fig. 3** (a) Ball-stick presentation of cradle-like tetranuclear  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_6]$  cluster unit. (b) polyhedron presentation of tetranuclear  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_6]$  in **1a**. (c) The 2D grid layer of compound **1a** viewed along [201] direction.



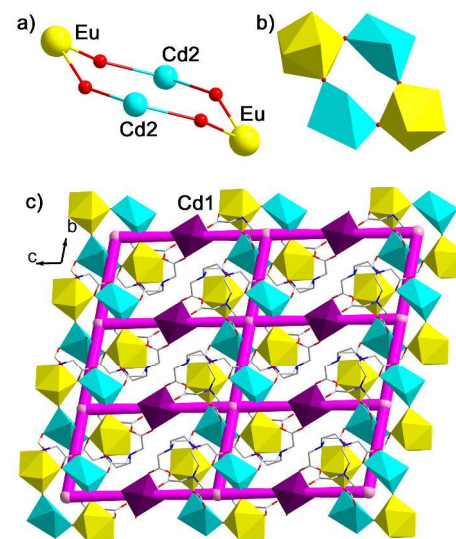
**Fig. 4** (a) The 3D supra-molecular framework *via* hydrogen bonds of  $\text{O-H}\cdots\text{O}$  for **1a** view along  $b$  axis. The green dotted lines for hydrogen bonds of  $\text{O-H}\cdots\text{O}$ ; (b) The supra-molecular net with *hex*-type topology after simplification. Key: orange,  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_6]$  units; The purple and green lines represent  $\text{DTPA}^{5-}$  anions and hydrogen bonds, respectively.

$[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_6]$  units act as eight-connected nodes, the overall framework can be represented as a *hex*-topology with the point symbol of  $(3^6.4^{18}.5^3.6)$  and the extended point symbol is  $[3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.5_2.5_2.6_6]$ .

$[\text{Ln}_2\text{Cd}_3(\text{DTPA})_2\text{Cl}_2(\text{H}_2\text{O})_6]$  (**II**:  $\text{Ln} = \text{Eu}$  **2a**;  $\text{Sm}$  **2b**) Compounds **II** were synthesized from the same raw materials as **I** but different pH value.  $\text{HCl}$  solution was added to adjust  $\text{pH} = 2$  in the syntheses of compounds **II**. Interestingly, in compounds **II**,  $\text{Cl}^-$



**Fig. 5** The coordination environments of  $\text{Eu}^{3+}$  and  $\text{Cd}^{2+}$  in **2a**. Atoms having "A", "B" or "C" in their labels are symmetry-generated. A:  $-x, -y, 1-z$ ; B:  $-x, -y, -z$ ; C:  $-x, 1-y, -z$ . Hydrogen atoms are omitted for clarity. Color code: Eu, yellow; Cd, cyan; O, red; N, blue; C, grey.



**Fig. 6** (a) Ball-stick presentation of tetranuclear  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_4]$  unit. (b) polyhedron presentation of  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_4]$  unit in **2a**. (c) The 2D grid layer of compound **2a** viewed along  $a$ -axis. Color code: Eu, yellow; Cd1, purple; Cd2, cyan; O, red; N, blue; C, grey.

anions are coordinated to  $\text{Cd}^{2+}$  ions. So the structures of **II** are different from **I**. Compounds **2a** and **2b** are isostructural and both belong to triclinic space group of  $P-1$ . In the asymmetrical unit of **2a**, there are one and a half unique  $\text{Cd}^{2+}$  ions, one  $\text{Eu}^{3+}$  ion, one  $\text{DTPA}^{5-}$  anion, three coordinated water molecules and one  $\text{Cl}^-$  anion, respectively (Fig. 6). The coordination geometries for Cd1 and Cd2 are both octahedrons (Fig. S6). Cd1 lying in a symmetry inversion coordinates to two  $\text{O}_{\text{COO}^-}$  atoms and four coordinated water molecules, while Cd2 coordinates to five  $\text{O}_{\text{COO}^-}$  atoms from three  $\text{DTPA}^{5-}$  anions and one  $\text{Cl}^-$  anion. Cd-O bond lengths are in the range of 2.212(3)

Å-2.256(3) Å, and which is shorter than that in compound **1a**. Cd-Cl bond length is 2.463(9) Å, and this is compared to reported Cd-Cl bond distances in previous paper<sup>[18]</sup>. The Eu<sup>3+</sup> ion in the structure is chelated by five O<sub>COO</sub><sup>-</sup> atoms and three N atoms from one DTPA<sup>5-</sup> anion, and one coordinated water molecule forming a tricapped trigonal prism (Fig. S7). Eu-O and Eu-N bond lengths are in the range of 2.346(3) Å- 2.450(3) Å and 2.615(3) Å- 2.752(3) Å, respectively. The DTPA<sup>5-</sup> anion effectively “cups” the Eu<sup>3+</sup> ion in a hydrophilic cleft leaving the ninth coordination site available to coordinate water. Four

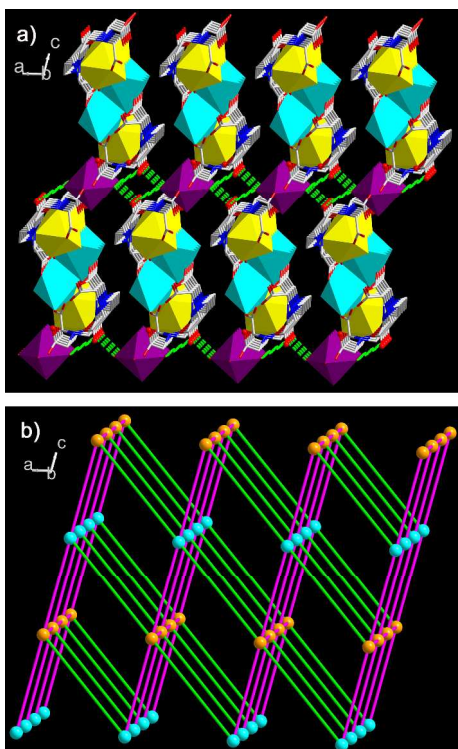
(Fig.7a). From the topological point of view, the 3-D supermolecular framework of **2a** is a (4, 6)-connected net (Fig. 7b). [Eu<sub>2</sub>Cd<sub>2</sub>(μ<sub>2</sub>-O<sub>4</sub>)] units act as six-connected nodes and [Cd(1)O<sub>6</sub>] octahedra as four-connected nodes, the overall framework can be represented as a *fsc*-topology with the point symbol of (4<sup>4</sup>.6<sup>10</sup>.8)(4<sup>4</sup>.6<sup>2</sup>) and the extended point symbol is [4.4.4.4.6<sub>2</sub>.6<sub>2</sub>.6<sub>5</sub>.6<sub>5</sub>.6<sub>5</sub>.6<sub>5</sub>.6<sub>5</sub>.6<sub>5</sub>.6<sub>5</sub>.8<sub>20</sub>] for [Eu<sub>2</sub>Cd<sub>2</sub>O<sub>4</sub>] units and [4.4.4.4.6<sub>4</sub>.6<sub>4</sub>] for [Cd(1)O<sub>6</sub>] octahedrons.

## IR Spectra

As shown in Fig. S1, the similarities between the IR spectra of **1a** and **1b**, **2a** and **2b**, respectively, suggests that **1a** and **1b**, **2a** and **2b** are iso-structural, respectively. The broad bands at 3700-2800 cm<sup>-1</sup> for **1a** and **1b** and 3700-2900 cm<sup>-1</sup> for **2a** and **2b** correspond to the stretching bands of O-H of water molecules. The bands at 1595 cm<sup>-1</sup> for **1a** and **1b** and 1580 cm<sup>-1</sup> for **2a** and **2b** correspond to the stretching bands of C=O of COO<sup>-</sup><sup>[15]</sup>. The red shifts of the bands of C=O indicate the coordination bonds between the metal cations and carboxylate groups of DTPA<sup>5-</sup>.

## Thermogravimetric Analyses

The thermal stabilities of **1a** and **1b**, **2a** and **2b** were examined by the TGA analyses in dry air atmosphere (Fig. S9). In the TGA curves of **1a** and **1b**, the weight losses of 9.30% (calcd: 9.93%) for **1a**, 9.30% (calcd: 9.86%) for **1b** were observed in the temperature range 30-310 °C, corresponding to the successive release of all coordinated and free water molecules. The decomposition of H<sub>3</sub>DTPA was observed from 310 °C to 800 °C. The residue might be Eu<sub>2</sub>O<sub>3</sub>·2CdO (calcd/found: 42.00% / 43.47%) for **1a**, Gd<sub>2</sub>O<sub>3</sub>·2CdO (calcd/found: 42.42% / 42.87%) for **1b**. Similarly, in the TGA curves of **2a** and **2b**, the weight losses of 6.73% (calcd: 6.76%) for **2a**, 6.33 (calcd: 6.78%) for **2b**, in the temperature range 50-255 °C, can be assigned to the successive release of six coordinated water molecules. The decomposition of H<sub>3</sub>DTPA and the removal of HCl were observed from 255 °C to 800 °C. The residue might be Eu<sub>2</sub>O<sub>3</sub>·3CdO (calcd/found: 46.17%/46.60%) for **2a**, Sm<sub>2</sub>O<sub>3</sub>·3CdO (calcd/found: 46.06%/48.42%) for **2b** (Fig. S9).



**Fig. 7** (a) The 3D supramolecular framework *via* hydrogen bonds of O-H...O for **2a** view along *b* axis. The green dotted lines for hydrogen bonds of O-H...O; (b) The supramolecular net with *fsc*-type topology after simplification. Key: orange, [Eu<sub>2</sub>Cd<sub>2</sub>(μ<sub>2</sub>-O<sub>4</sub>)] units; cyan, [Cd(1)O<sub>6</sub>] units. The purple and green lines represent DTPA<sup>5-</sup> anions and hydrogen bonds, respectively.

carboxylate μ<sub>2</sub>-O atoms alternately connect Eu<sup>3+</sup> ions and Cd(2) atoms to form a chair-like eight-membered tetranuclear [Eu<sub>2</sub>Cd<sub>2</sub>(μ<sub>2</sub>-O<sub>4</sub>)] cluster unit (Fig. 6a and 6b). The shortest Cd...Eu distance is 4.793(6) Å which is longer than that in compound **1a**. Each [Eu<sub>2</sub>Cd<sub>2</sub>(μ<sub>2</sub>-O<sub>4</sub>)] cluster unit is connected with two neighboring such cluster units by [Cd(1)O<sub>6</sub>] octahedrons, generating an interesting 1D necklace-like chain running along the [001] direction (Fig. 6). The interconnections of the Eu<sup>3+</sup> and Cd<sup>2+</sup> ions from two neighboring chains via carboxylate groups of DTPA<sup>5-</sup> ligands result in a 2-D grid layer in the *bc*-plane (Fig. 6c and S8). Each [Eu<sub>2</sub>Cd<sub>2</sub>(μ<sub>2</sub>-O<sub>4</sub>)] cluster unit is served as a four-node which links four other [Eu<sub>2</sub>Cd<sub>2</sub>(μ<sub>2</sub>-O<sub>4</sub>)] cluster units, so the 2D layer is a (4,4) net with *sql*-topology. The layers are connected by hydrogen bonds between coordinated water molecules and O<sub>COO</sub><sup>-</sup> atoms of DTPA<sup>5-</sup> anions to form a 3D supra-molecular framework

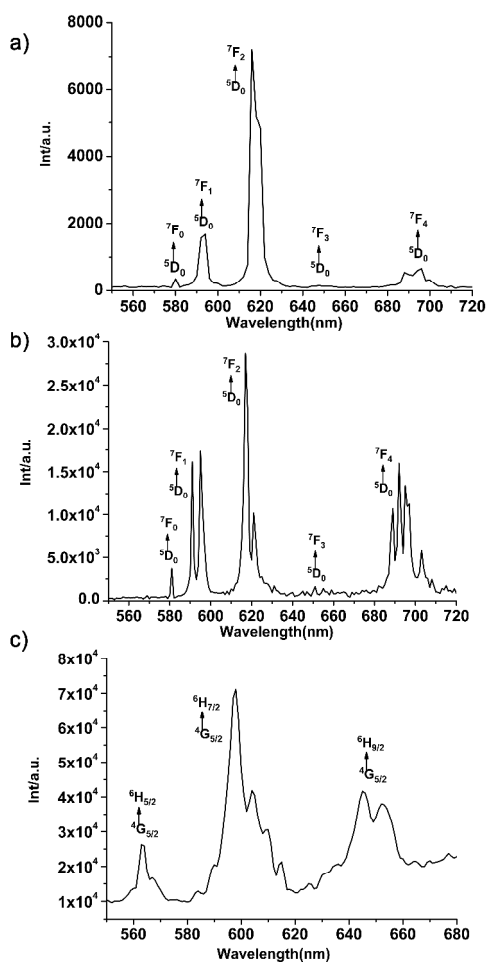
## Luminescent Properties

### Solid-state emission spectra

The room-temperature luminescent properties of the compounds **1a**, **2a** and **2b** in the solid state were measured. Compounds **1a** and **2a** show characteristic emissions of Eu<sup>3+</sup> ion in which bands at ~580, ~592, ~617, ~650, ~700 nm correspond to <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>3</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>4</sub> transitions, respectively<sup>[19a]</sup> (Fig. 8a and 8b). The intensities of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transitions (electric dipole) are stronger than that of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transitions (magnetic dipole) of compounds **1a** and **2a**, which indicate the low symmetrical coordination environment of Eu<sup>3+</sup> ions and which are agreed with the crystallographic analyses. In the emission spectra of compound **2b**, excited at 403 nm, it exhibits three bands at 563, 598 and 645 nm correspond to <sup>4</sup>G<sub>5/2</sub>→<sup>6</sup>H<sub>5/2</sub>, <sup>4</sup>G<sub>5/2</sub>→<sup>6</sup>H<sub>7/2</sub> and <sup>4</sup>G<sub>5/2</sub>→<sup>6</sup>H<sub>9/2</sub> transitions of Sm<sup>3+</sup> ions<sup>[19b]</sup> (Fig. 8c).

## Luminescent sensing

In order to investigate **1a** for the sensing of small molecules, its suspension-state luminescences were performed. The powder of **1a** were dispersed into methanol, acetonitrile, acetone, n-butanol, ethanol, ammonia water, H<sub>2</sub>O, DMF, i-propanol, triethylamine, pyridine, ethanediamine, 1,2-propane diamine and ethanol amine. As shown (Fig. 9 and S10), its luminescent spectra are largely depended on the solvent molecules. Methanol solvent can significantly improve luminescent intensity of **1a** with remarkable enhancement effect. As for acetonitrile, acetone, n-butanol, ethanol, ammonia water, H<sub>2</sub>O, DMF, i-propanol, the luminescence spectra do not show

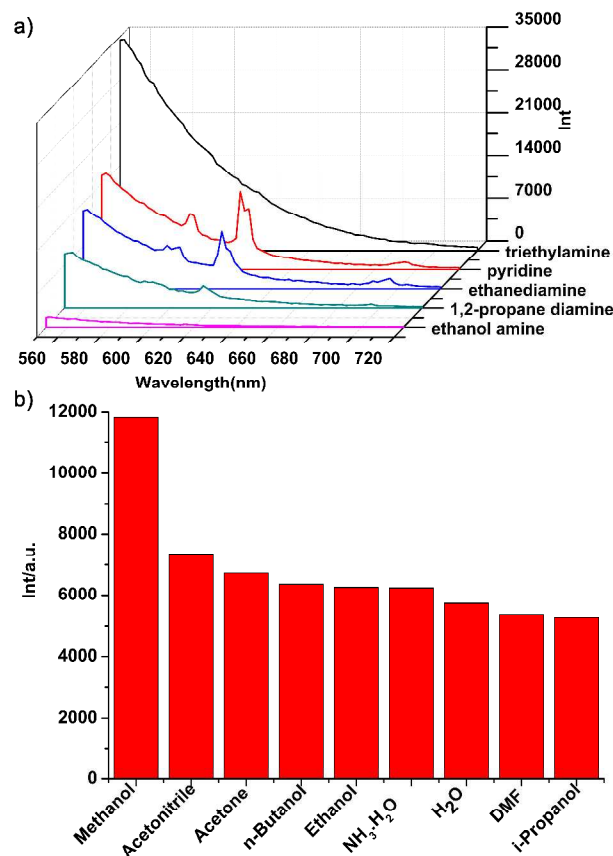


**Fig. 8** Emission spectra of **1a** ( $\lambda_{\text{ex}} = 395 \text{ nm}$ ) (a), **2a** ( $\lambda_{\text{ex}} = 395 \text{ nm}$ ) (b), **2b** ( $\lambda_{\text{ex}} = 403 \text{ nm}$ ) (c).

too much differences from each other. But for solvents like triethylamine, pyridine, ethanediamine, 1,2-propane diamine, ethanol amine, the emission spectra of **1a** were covered by emissions of these nitrogenous compounds (Fig. S10). Especially in triethylamine and ethanol amine solvents, emissions of Eu<sup>3+</sup> exhibited completely quenching of the luminescent intensity. These results suggest that **1a** could be a promising luminescent probe for methanol, triethylamine and ethanol amine. This may be due to that these nitrogenous solvents absorb the excitation light of Eu<sup>3+</sup> ions ( $\lambda_{\text{ex}} = 395 \text{ nm}$ ) (the excitation spectra of Eu<sup>3+</sup> ions fall in the UV-vis absorption spectra

of these nitrogenous solvents. As for the completely quenching of triethylamine and ethanolamine, this may be attributed to fully UV-vis absorption of the excitation light of Eu<sup>3+</sup> ions<sup>[12e]</sup>.

Similarly, the powder samples of **1a** and **2a** were dispersed into aqueous solution containing different 0.1M M(NO<sub>3</sub>)<sub>x</sub> (M = Ca<sup>2+</sup>, Sr<sup>2+</sup>, Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, La<sup>3+</sup>, Ho<sup>3+</sup>, Ce<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Al<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Nd<sup>3+</sup>, Pr<sup>3+</sup>, Dy<sup>3+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup> and Er<sup>3+</sup>) and the emissions of Eu<sup>3+</sup> ions were measured (Fig. 10 and S13). For **1a**, most cations show enhancement effect on the luminescent intensities. But for Cr<sup>3+</sup> and Fe<sup>3+</sup> ions, especially Fe<sup>3+</sup> ion, the intensity showed significant quenching effects. And Cr<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>3+</sup>, Cu<sup>2+</sup>, Nd<sup>3+</sup> ions quenched the emissions of Eu<sup>3+</sup> ion of **2a**. As illustrated in Fig. S14, the luminescent intensity of **2a** is almost completely quenched in the solution of Co(NO<sub>3</sub>)<sub>2</sub> at concentration of 10<sup>-2</sup> mol L<sup>-1</sup>. These indicate the potential of **1a** and **2a** for sensing of metal cations. We supposed that these coloured aqueous solution containing cations including Cr<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>3+</sup>, Cu<sup>2+</sup>, Nd<sup>3+</sup> had absorbed more or less the excitation light of Eu<sup>3+</sup> ions ( $\lambda_{\text{ex}} = 395 \text{ nm}$ ), and this results in the fluorescence quenching.



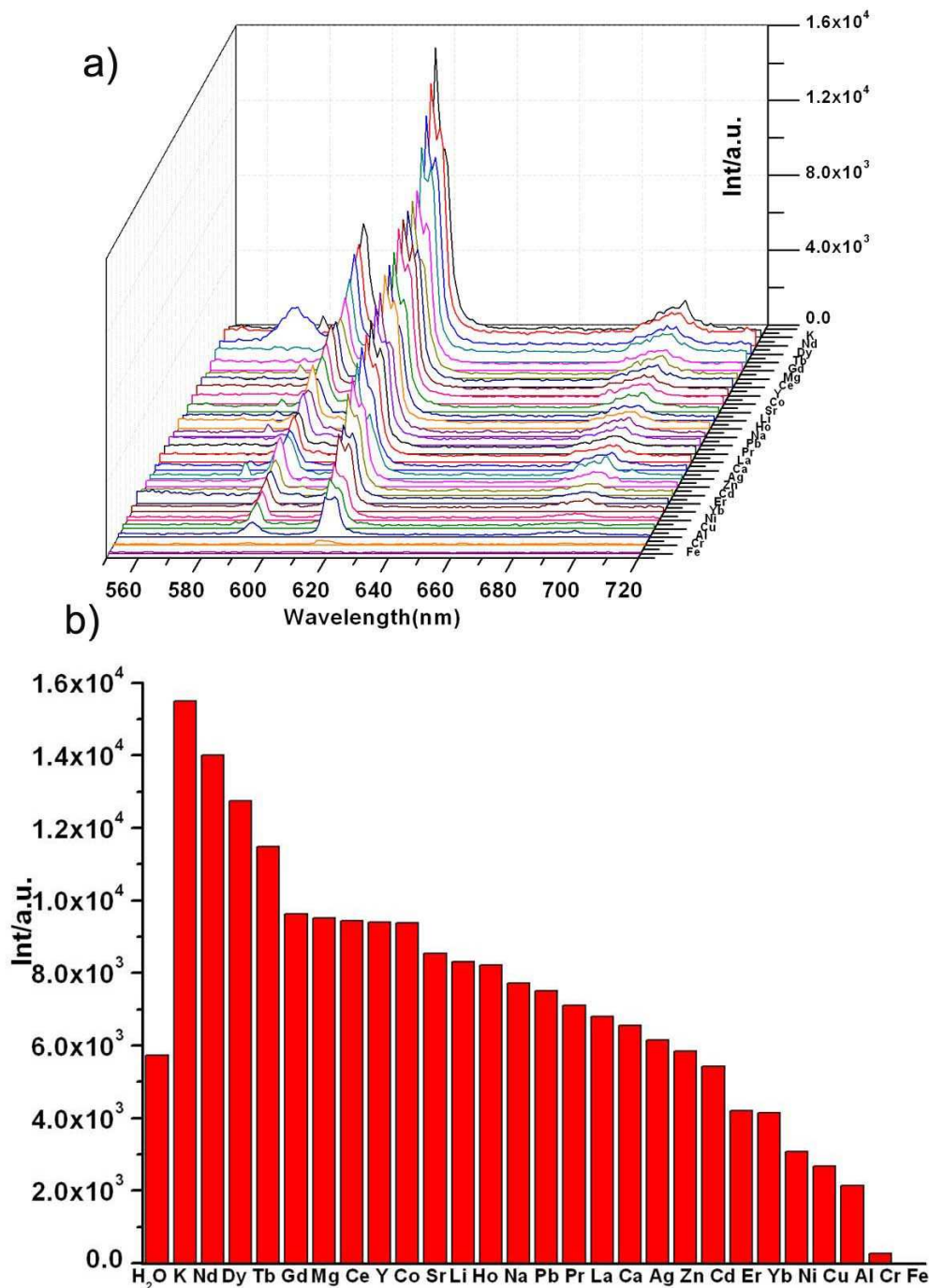
**Fig. 9** (a) Emission spectra of **1a** ( $\lambda_{\text{ex}} = 395 \text{ nm}$ ) and (b) the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition intensities of **1a** dispersed into different solvents.

## Conclusions



Two series of Ln-Cd heterometal organic coordination polymers  $\text{Ln}_2\text{Cd}_2(\text{DTPA})_2(\text{H}_2\text{O})_4$  ( $\text{Ln} = \text{Eu}$  **1a**;  $\text{Gd}$  **1b**) and  $[\text{Ln}_2\text{Cd}_3(\text{DTPA})_2\text{Cl}_2(\text{H}_2\text{O})_6]$  ( $\text{Ln} = \text{Eu}$  **2a**;  $\text{Sm}$  **2b**) have been synthesized by the hydrothermal reactions of  $\text{Ln}_2\text{O}_3$ ,  $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{H}_3\text{DTPA}$ . Although the reaction temperatures and main reactants are the same, the different ratios of reactants and the introduction of  $\text{Cl}^-$  anions changed the coordination environments of  $\text{Ln}^{3+}$  and  $\text{Cd}^{2+}$  ions, resulting in the formations of different tetranuclear  $[\text{Ln}_2\text{Cd}_2]$  oxo-cluster units. Compound **1a** possesses 2D

layered grid network based on  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_6]$  cluster units. Two enantiomeric forms,  $\alpha$  and  $\beta$  exist in  $[\text{Cd}(\text{DTPA})]^{3-}$ . These 2D layers are linked via O-H...O hydrogen bonds to generate a 3D supra-molecular architecture with a *hex*-type topology. In **2a**,  $[\text{Eu}_2\text{Cd}_2(\mu_2\text{-O})_4]$  units are connected by  $\text{DTPA}^{3-}$  and  $[\text{Cd}(\text{I})\text{O}_6]$  octahedra to form a 2D lattice layer, which are further held together by hydrogen bonds, resulting in a 3D supra-molecular framework with *fsc*-topology



**Fig. 10** (a) Emission spectra of **1a** (excitation at 395 nm) and (b) the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition intensities of **1a** dispersed into different aqueous solution containing different 0.1M  $\text{M}(\text{NO}_3)_x$

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net. Compounds **1a** and **2a** emit characteristic emissions of  $\text{Eu}^{3+}$  ion, and compound **2b** emits that of  $\text{Sm}^{3+}$  ion. More interestingly, organic molecules such as triethylamine and ethanol amine and cations like  $\text{Fe}^{3+}$  ion quenched the emission of **1a**, and  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Nd}^{3+}$  ions quenched that of **2a**. These compounds may be used as an important role in the applications of the luminescent sensing for the organic solvents and metal cations.

## Acknowledgements

This work was supported by the NNSF of China (No. 21003020), the Natural Science Fund of Fujian Province (No. 2013J01041) and the Foundation of State Key Laboratory of Structural Chemistry (project no. 20130012).

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