

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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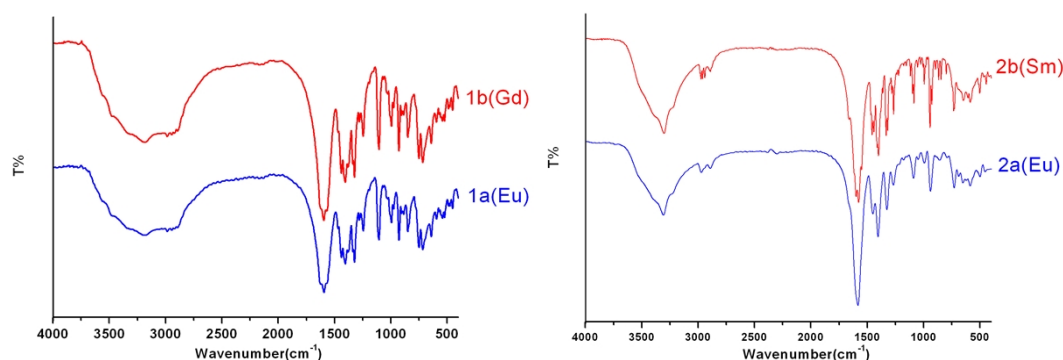


Fig. S1 IR spectra of **1a**, **1b**, **2a** and **2b**.

The similar IR spectral shapes of **1a** and **1b**, **2a** and **2b** suggest that **1a** and **1b**, **2a** and **2b** are isostructural, respectively. The broad bands at 3700-2800 cm⁻¹ for **1a** and **1b** and 3700-2900 cm⁻¹ for **2a** and **2b** correspond to the stretching bands of O-H of water molecules. The band at 1595 cm⁻¹ for **1a** and **1b** and 1580 cm⁻¹ for **2a** and **2b** corresponds to the stretching bands of C=O of COO⁻. The red shift of the bands indicates the coordination between the cations and carboxylate radicals of DTPA⁵⁻.

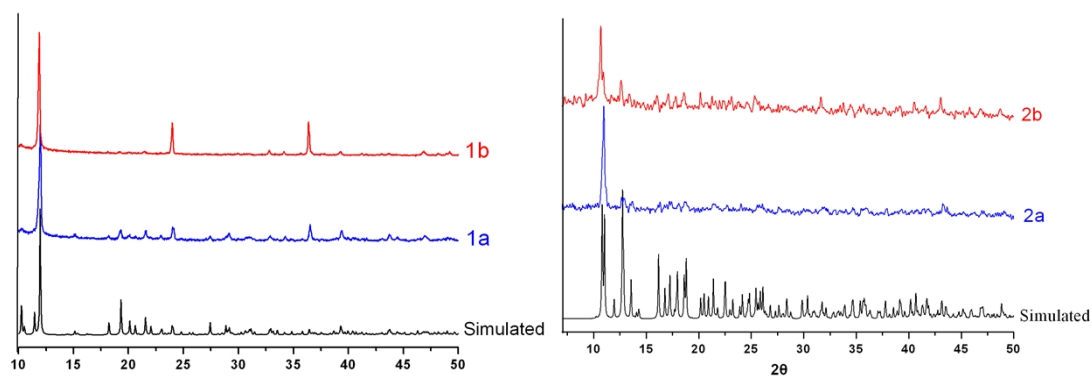


Fig. S2 The PXRD pattern of **1a**, **1b**, **2a**, **2b** and simulated respectively.

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

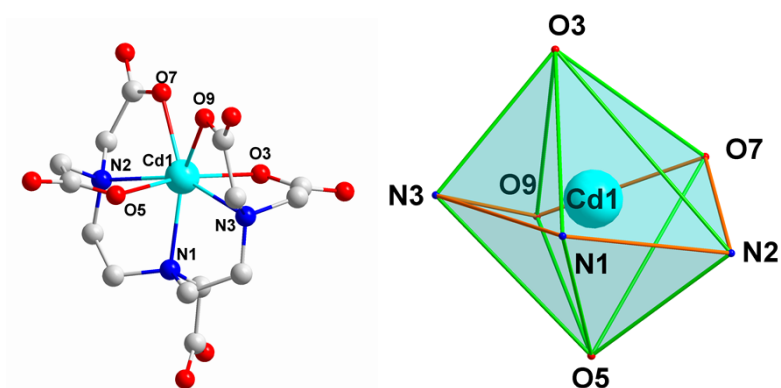


Fig. S3 The coordination environments of Cd atom in **1a**. (left) The ball-stick representation. (right) The polyhedral representation.

The coordination geometry for the two seven-coordinate Cd^{2+} ions in **1a** is close to a monocapped trigonal prism: three N atoms and four O atoms are from one DTPA^{5-} anion.

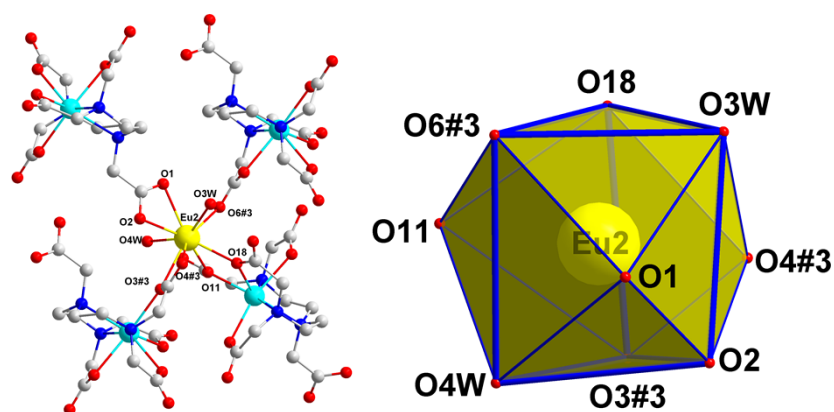


Fig. S4 The coordination environments of Eu atom in **1a**. (left) The ball-stick representation. (right) The polyhedral representation. Symmetry codes: #3, 1-x, 1-y, 1-z.

The Eu^{3+} ions in **1a** is nine-coordinated and described as a tricapped trigonal prism with seven O atoms from four DTPA^{5-} anions and two other coordinated water molecules.

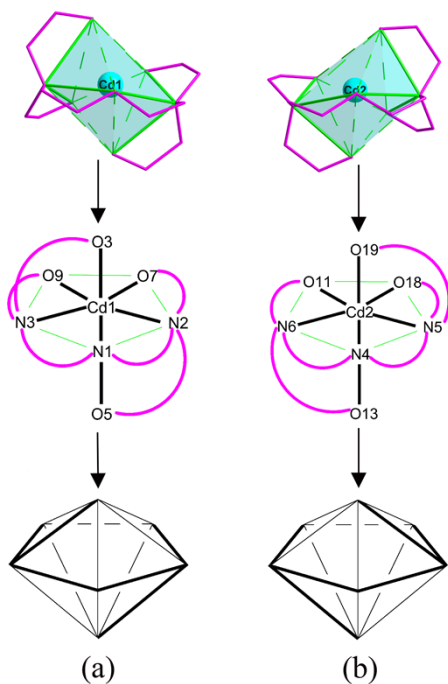


Fig. S5. Two forms of coordination modes of two DTPA^{5-} anions in the asymmetrical unit of **Type I**. (a) Mode α , (b) Mode β .

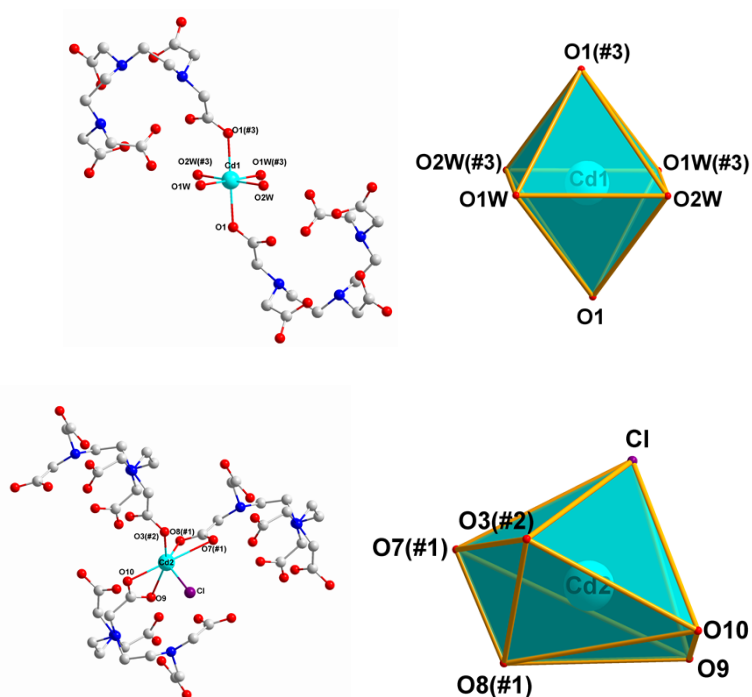


Fig. S6 The coordination environments of Cd atoms in **2a**. (left) The ball-stick representations. (right) The polyhedral representations. Symmetry codes: #1, -x, -y, -z. #2, -x, 1-y, -z. #3, -x, -y, 1-z

The coordination geometries for Cd1 and Cd2 of **2a** are both octahedron (Figure S3). Cd1 locates at a symcenter coordinates to two O_{COO^-} atoms and four coordinated water molecules. While Cd2 coordinates to five O_{COO^-} atoms from three DTPA^{5-} anions and one Cl^- anion.

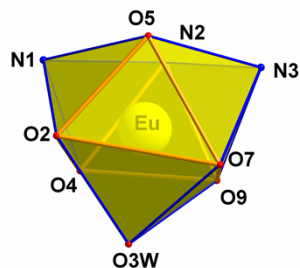
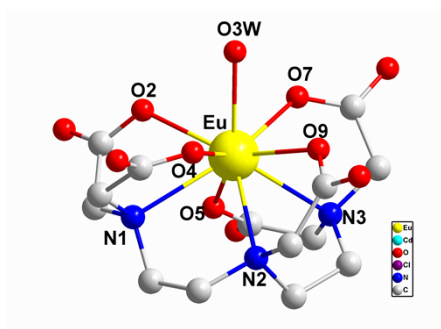


Fig. S7 The coordination environments of Eu atom in **2a**. (left) The ball-stick representation. (right) The polyhedral representation.

The Eu^{3+} ions in the structure of **2a** are chelated by one DTPA^{5-} anion, and the last coordinated point is occupied by one coordinated water molecule forming a tricapped trigonal prism.

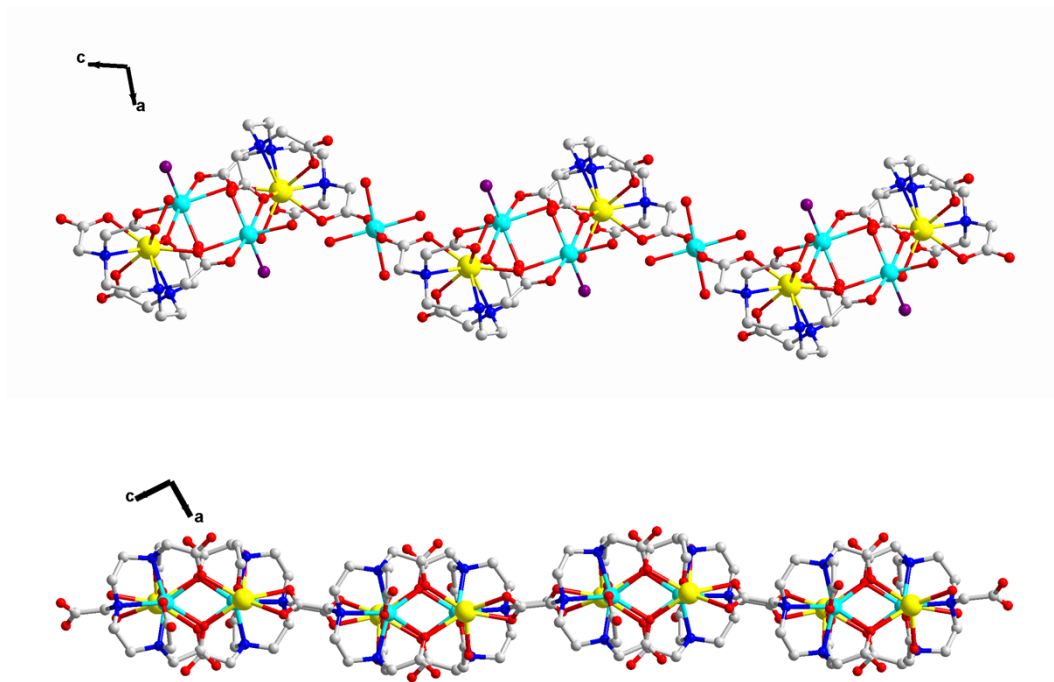


Fig. S8 The 2D layer in the structures of **1a** (up) and **2a** (down).

The 2D layer in compound **2a** is like wave while it is mostly a plane of 2D layer in compound **1a**.

Table S1 Selected hydrogen bonds for **1a**

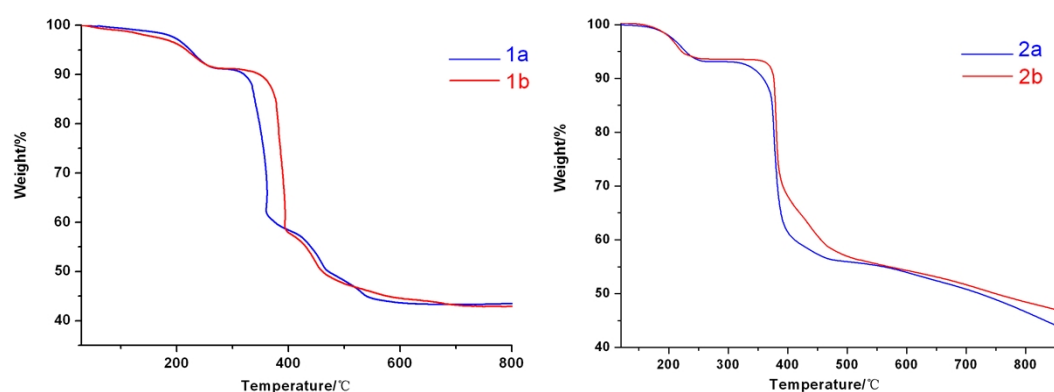
D–A···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A)(Å)	<DHA(°)
O2W–H2WB···O7W#3	0.903	2.134	2.787	128.47
O4W–H4WB···O6W#3	0.851	1.901	2.751	177.71
O6W–H6WA···O12#4	0.850	1.994	2.843	176.50
O6W–H6WB···O2	0.850	1.925	2.773	175.65
O7W–H7WA···O10#3	0.850	2.615	3.206	127.67
O7W–H7WB···O15#4	0.850	1.990	2.821	165.47

Symmetry codes: #3, -x+1, -y+1, -z+1; #4, x-1, y, z+1

Table S2 Selected hydrogen bonds for **2a**

D–A···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A)(Å)	<DHA(°)
O1W–H1WA···O6#3	0.875	2.205	2.748	119.92
O1W–H1WA···O6	0.875	2.015	2.741	139.74

Symmetry codes: #3, -x, -y, -z+1

**Fig. S9** TGA of **1a**, **1b**, **2a** and **2b**.

The thermal stability of **1a** and **1b**, **2a** and **2b** were examined by the TGA analysis in dry air atmosphere. In the TGA curve of **1a** and **1b**, the weight loss of 9.30% (calcd: 9.93%) for **1a**, 9.30% (calcd: 9.86%) for **1b** in the temperature range 30-310 °C, corresponding to the successive release of all coordinated and free water molecules. The decomposition of H₅DTPA is observed from 310 °C to 800 °C. The residue might be Eu₂O₃·2CdO (calcd/found: 42.00%/43.47%) for **1a**,

$\text{Gd}_2\text{O}_3 \cdot 2\text{CdO}$ (calcd/found: 42.42%/42.87%) for **1b**. Similarly, in the TGA curve of **2a** and **2b**, the weight loss of 6.73% (calcd: 6.76%) for **2a**, 6.33 (calcd: 6.78%) for **2b**, in the temperature range 50-255 °C, corresponding to the successive release of 6 coordinated water molecules. The decomposition of H_3DTPA , HCl is observed from 255 °C to 800 °C. The residue might be $\text{Eu}_2\text{O}_3 \cdot 3\text{CdO}$ (calcd/found: 46.17%/46.60%) for **2a**, $\text{Sm}_2\text{O}_3 \cdot 3\text{CdO}$ (calcd/found: 46.06%/48.42%) for **2b**.

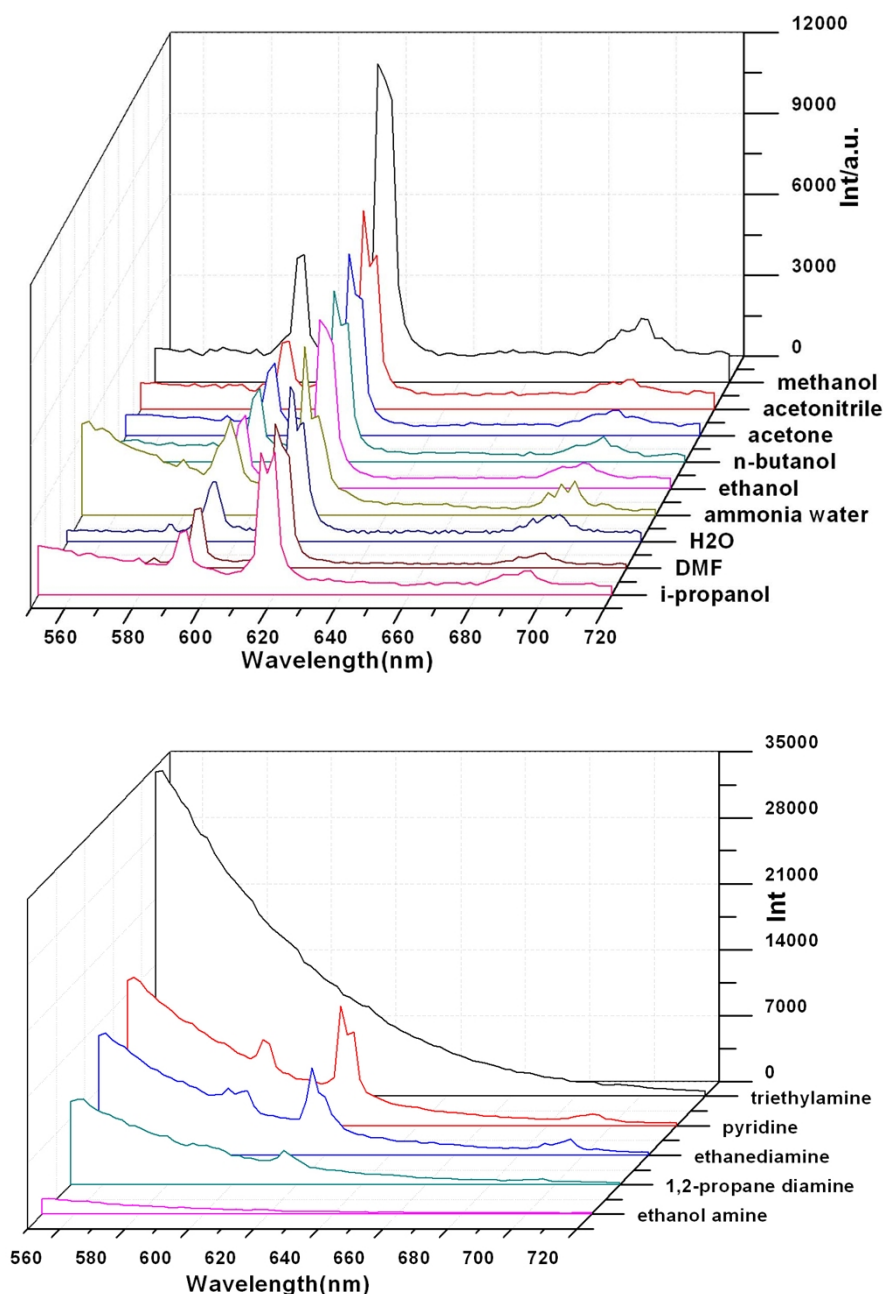


Fig. S10. Emission spectra of **1a** in different solvents.

As for acetonitrile, acetone, n-butanol, ethanol, ammonia water, H_2O , DMF, i-propanol, the luminescence spectra do not show too much difference from each other. But for solvents like triethylamine, pyridine, ethanediamine, 1,2-propane diamine, ethanol amine, the emission of **1a** were covered by emissions of these nitrogenous compounds. Especially in triethylamine and ethanol amine, emission of Eu^{3+} were completely quenching of the luminescence intensity. These

results suggest that **1a** could be a promising luminescent probe for methanol, triethylamine and ethanol amine.

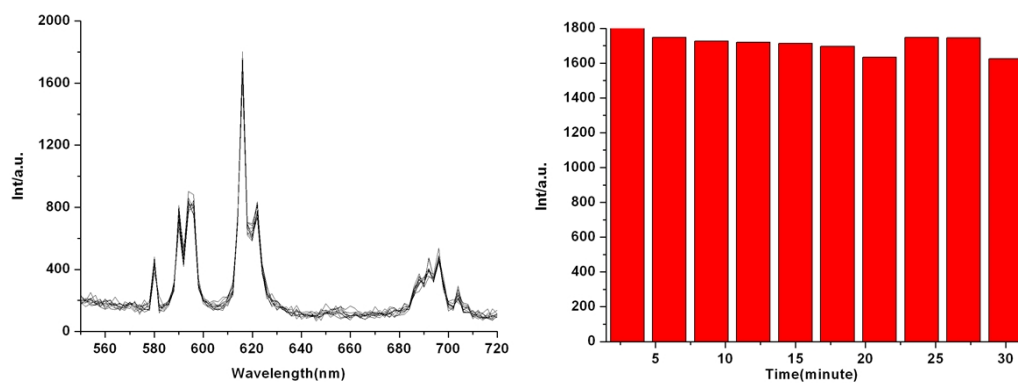


Fig. S11 (left) The luminescence spectra of **1a** in aqueous solution throughout the measure ($\lambda_{\text{ex}} = 395$ nm) in 30min. (right) The emission intensity of $^5D_0-^7F_2$ (616nm) transition versus time.

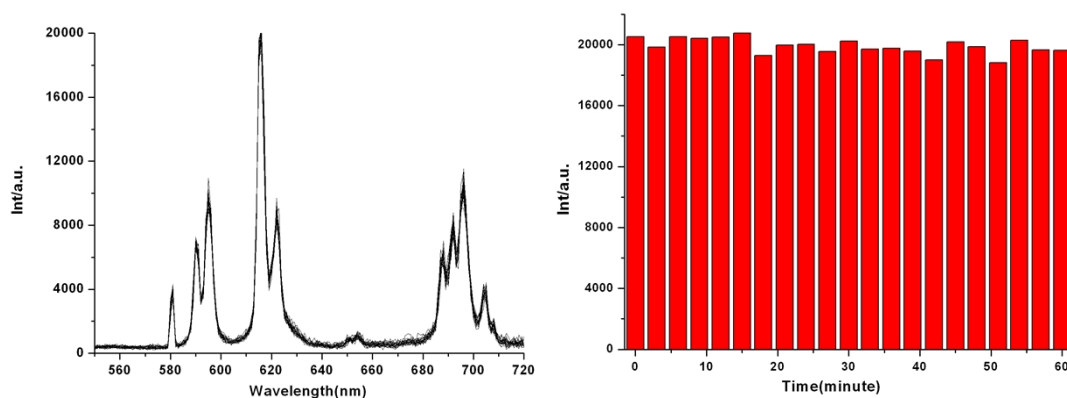
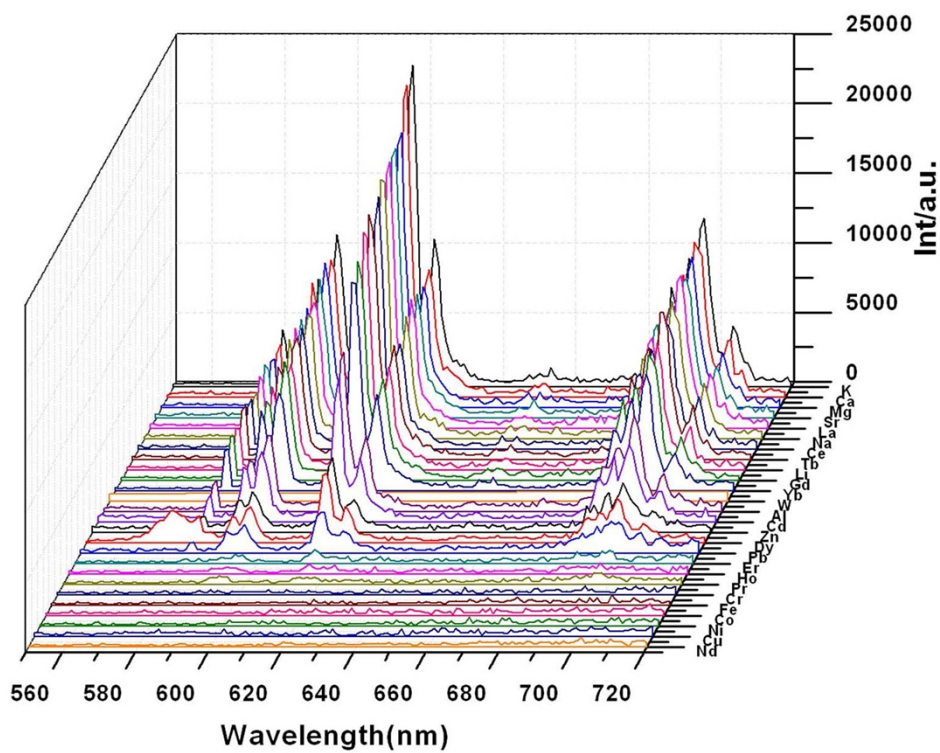
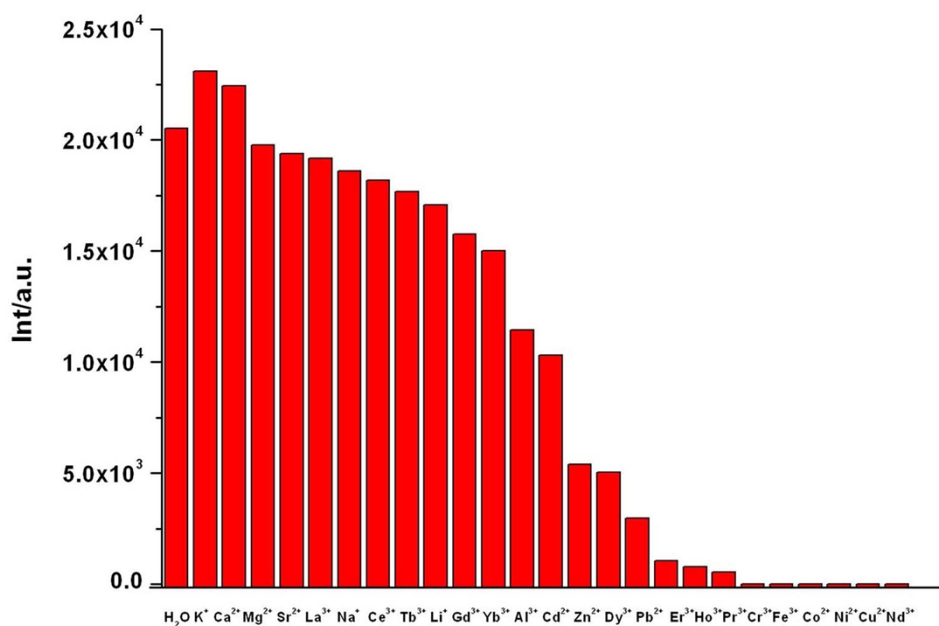


Fig. S12 (left) The luminescence spectra of **2a** in aqueous solution throughout the measure ($\lambda_{\text{ex}} = 395$ nm) in 30min. (right) The emission intensity of $^5D_0-^7F_2$ (616nm) transition versus time.



(a)



(b)

Fig. S13. (a) Emission spectra of **2a** (excitation at 395 nm) and (b) the $^5D_0 \rightarrow ^7F_2$ transition intensities of **2a** dispersed into different aqueous solution containing different 0.1M $M(NO_3)_x$.

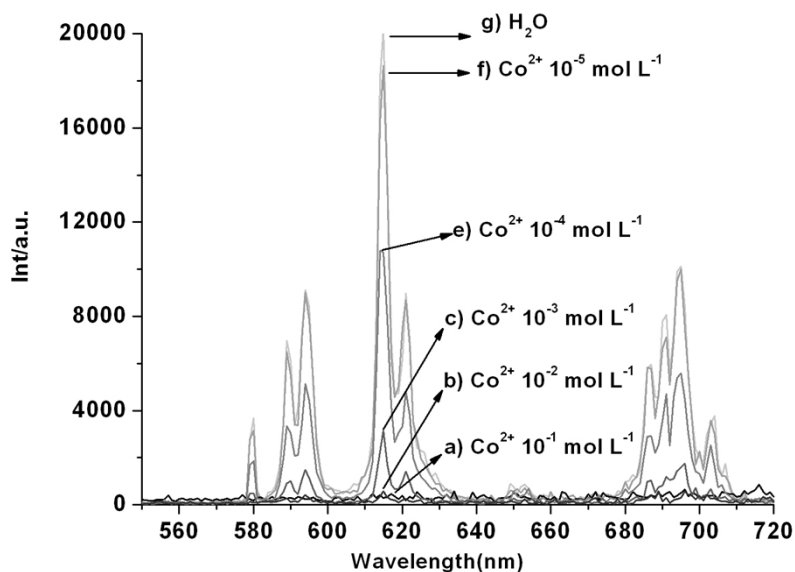


Fig. S14. The emission spectra of **2a** in DMA solutions with $\text{Co}(\text{NO}_3)_2$ at different concentrations (excited at 395 nm).

The luminescence intensity of **2a** is almost completely quenched at a $\text{Co}(\text{NO}_3)_2$ concentration of $10^{-2} \text{ mol L}^{-1}$.

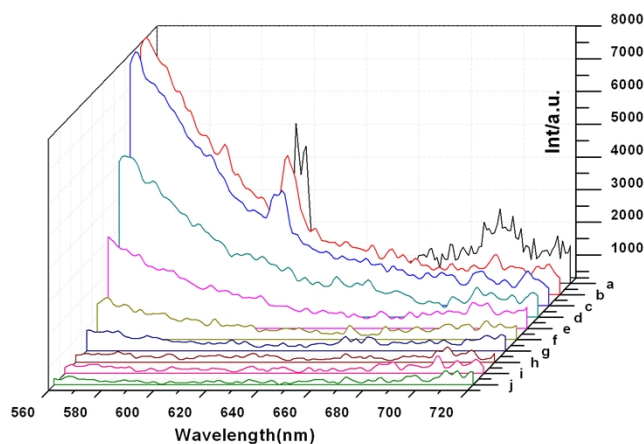


Fig. S15 Emission spectra of 5mg **1a** ($\lambda_{\text{ex}} = 395 \text{ nm}$) in 5 ML mixed solvents with different concentrations ($V_{\text{H}_2\text{O}}:V_{\text{ethanol amine}} = 5.0:0.0$ (a), 4.5:0.5(b), 4.0:1.0(c), 3.5:1.5(d), 3.0:2.0(e), 2.5:2.5(f), 2.0:3.0(g), 1.5:3.5(h), 1.0:4.0(i), 0.5:4.5(j)).

Mixed solvent system of water and ethanol amine was investigated. As shown in the Fig. 1 below. Luminescent spectra of 5 ML mixed solvents with different concentrations ($V_{\text{H}_2\text{O}}:V_{\text{ethanol amine}} = 5.0:0.0, 4.5:0.5, 4.0:1.0, 3.5:1.5, 3.0:2.0, 2.5:2.5, 2.0:3.0, 1.5:3.5, 1.0:4.0, 0.5:4.5$) contain 5mg compound **1a** were measured. When $V_{\text{H}_2\text{O}}:V_{\text{ethanol amine}} = 3.5:1.5, 3.0:2.0, 2.5:2.5, 2.0:3.0, 1.5:3.5, 1.0:4.0, 0.5:4.5$, the luminescence of compound **1a** were quenched.