Supporting information

A water-stable lanthanide-functionalized MOF as a highly selective and sensitive fluorescent probe for Cd^{2+}

Ji-Na Hao and Bing Yan*

Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China

Experimental section

Chemicals. Europium chlorides were prepared by dissolving the corresponding oxides in excess hydrochloric acid (37%) followed by evaporation and crystallization. All other staring materials were commercially available reagents of analytical grade and were used without further purification.

Synthetic procedures

Synthesis of Uio-66(Zr)-$(COOH)_2$ (1). The Uio-66(Zr)-$(COOH)_2$ solid was synthesized according to the previously described procedure.[1] In a round bottom flask equipped with reflux condenser and magnetic stirrer, 0.43 g (0.0017 mol) of 1,2,4,5-benzenetetracarboxylic acid (H_4btec) (Adamas, 98%) and 0.23 g (0.001 mol) of Zirconium tetrachloride ($ZrCl_4$) (Ourchem, 98%) were dispersed in 5 mL of distilled water at room temperature under stirring and then heated at 100 °C for 24 h. It resulted in a white gel, which was filtered off and washed with distilled water three times. To remove the remaining free acid encapsulated within the pores as much as possible, the activation was further carried out by dispersing the sample in the distilled water (~ 10 mL per 1 g of product) and heated at 100 °C for 16 h. The solid was then recovered by filtration, washed with acetone and dried at 30 °C under vacuum, yielding ~ 0.4 g of white powder.

Eu^{3+}@1 preparation. Eu^{3+}@**1** was prepared by stirring the mixture of 0.1 g of compound **1** and 0.0366 g $EuCl_3\cdot6H_2O$ in 10 mL distilled water at 60 °C for 24 h. The solid was then filtered off, extensively washed with distilled water and dried under vacuum at 60 °C overnight.

Luminescent sensing experiments. For the experiments of sensing metal ions, each sample of Eu^{3+}@1 (3 mg) was introduced into aqueous solutions (3 mL, 10^{-2} M) of $M(NO_3)_z$ (M^{z+} = Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+ , Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}).[2] The mixtures were then sonicated for 30 min to form the metal ion-incorporated suspensions for luminescent measurements.

Characterization

The crystalline phases of the products were determined by X-ray powder diffraction patterns (XRD) using a Rigaku D/max-Rb diffractometer equipped with Cu anode. Fourier transform infrared spectra (FTIR) were recorded with a Nexus 912 AO446 infrared spectrum radiometer within the wavenumber range 4000 – 400 cm^{-1} using the KBr pressed technique. Thermogravimetric analysis (TGA) data was obtained on a Netzsch STA 449C system with a heating rate of 5 K min^{-1} in air. Nitrogen adsorption/desorption isotherms were performed at liquid nitrogen temperature using a Nova 1000 analyzer. Each sample was activated under vacuum overnight at 70 °C prior to measurment. ICP-MS data were obtained on an X-7 series inductively coupled plasma-mass spectrometer (Thermo Elemental, Cheshire, UK). Photoluminescent spectra and luminescence lifetimes (τ) were examined by a Edinburgh FLS920 spectrophotometer. The outer absolute luminescent quantum efficiency was determined using an integrating sphere (150 mm diameter, $BaSO_4$ coating) from an Edinburgh FLS920 phosphorimeter. The quantum yield can be defined as the integrated intensity of the luminescence signal divided by the integrated intensity of the absorption signal. The absorption intensity was calculated by subtracting the integrated intensity of the light source with the sample in the integrating sphere from the integrated intensity of the light source with a blank sample in the integrating sphere.

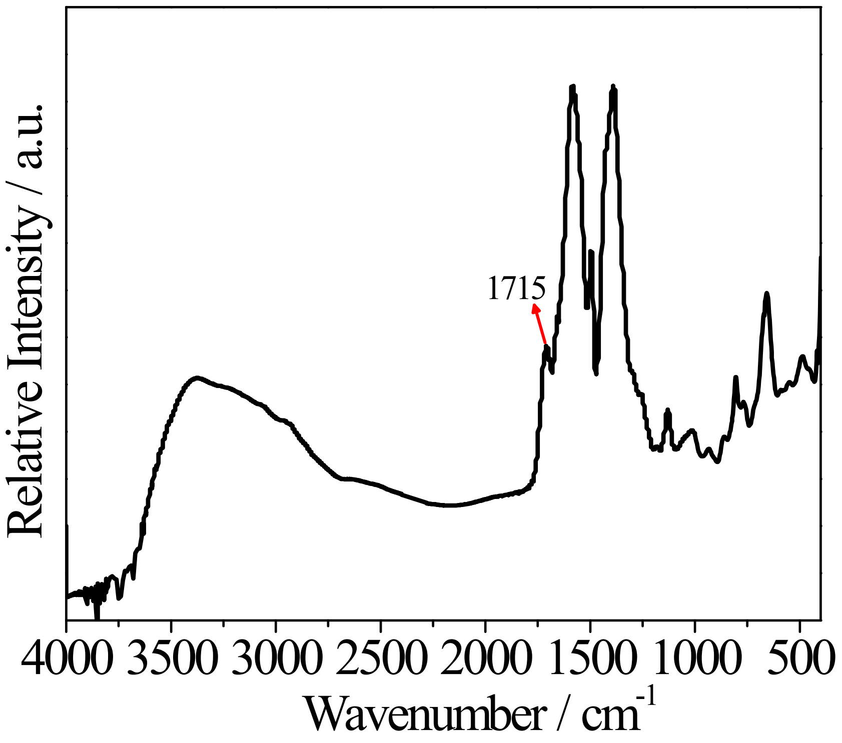

Figure S1 FT-IR spectrum of compound **1**.

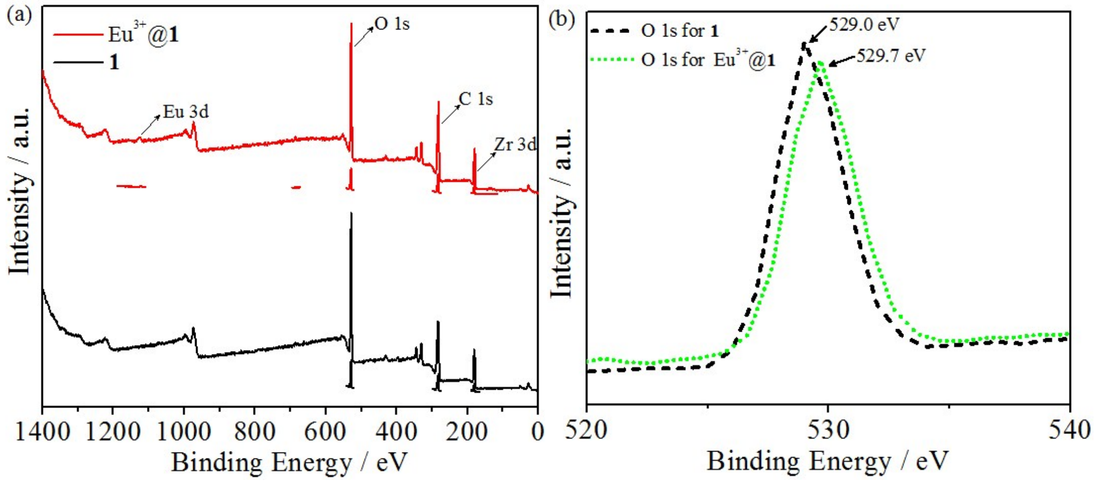

Figure S2 XPS spectra (a) and O 1s XPS (b) for **1** and Eu^{3+}@**1**.

Table S1 The ICP-MS results of Eu^{3+}@**1** and Cd^{2+}-Eu^{3+}@**1** .

Materials	Zr^{4+} (ppm)	Eu^{3+} (ppm)	Cd^{2+} (ppm)	Zr^{4+} (mM)	Eu^{3+} (mM)	Cd^{2+} (mM)	Zr : Eu : Cd
Eu^{3+}@**1**	16.97	12.43	--	0.186	0.082	--	2.3:1
Cd^{2+}-Eu^{3+}@**1**	16.46	11.90	2.50	0.180	0.078	0.022	8.2: 3.5:1

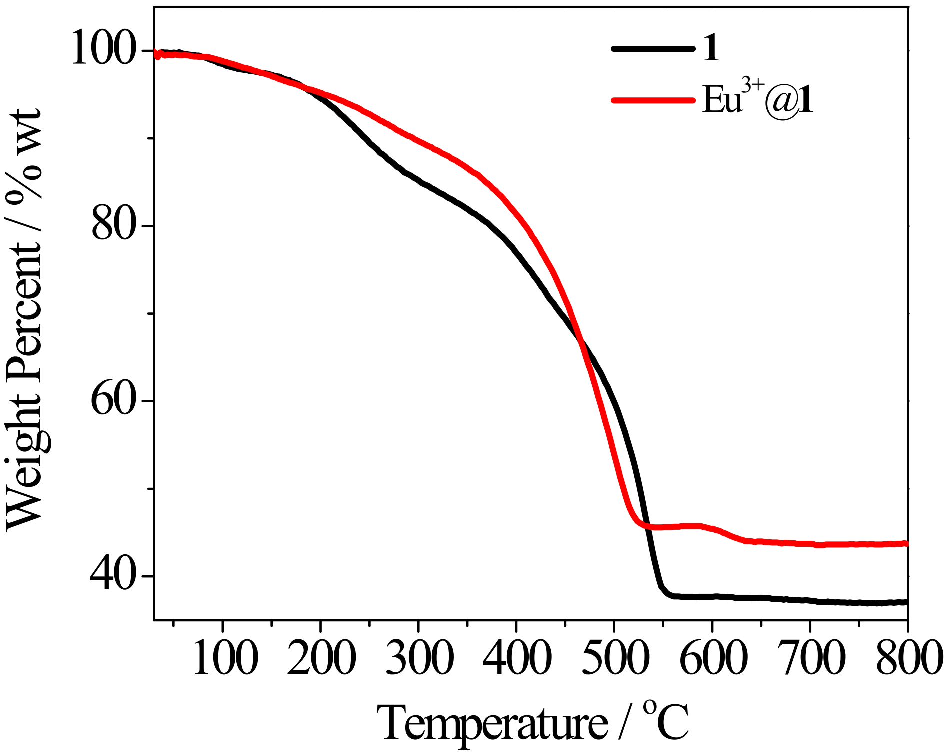

Figure S3 Thermogravimetric analysis of **1** and Eu^{3+}@**1**.

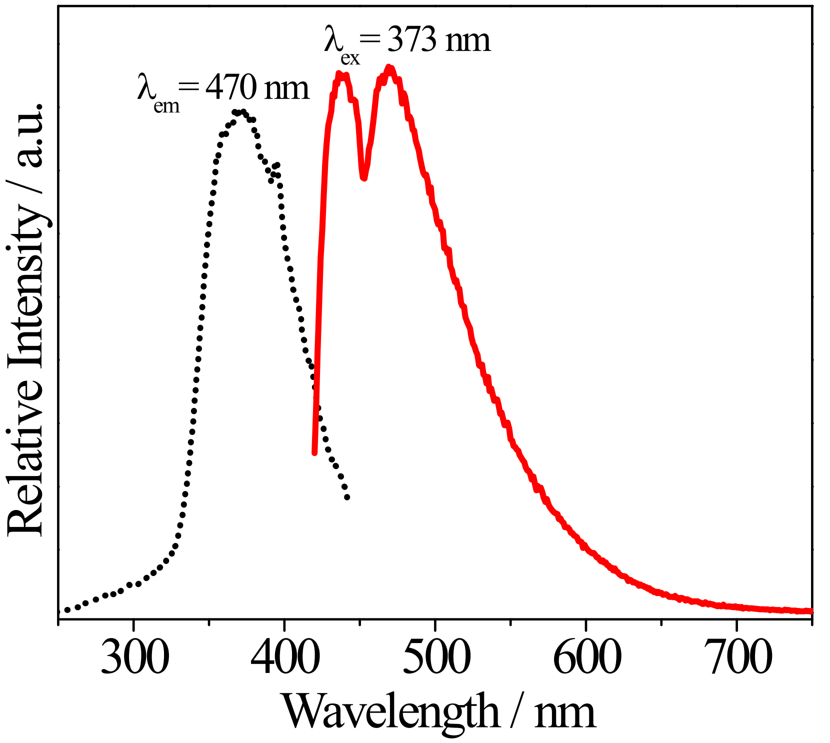

Figure S4 Excitation and emission spectra of **1**

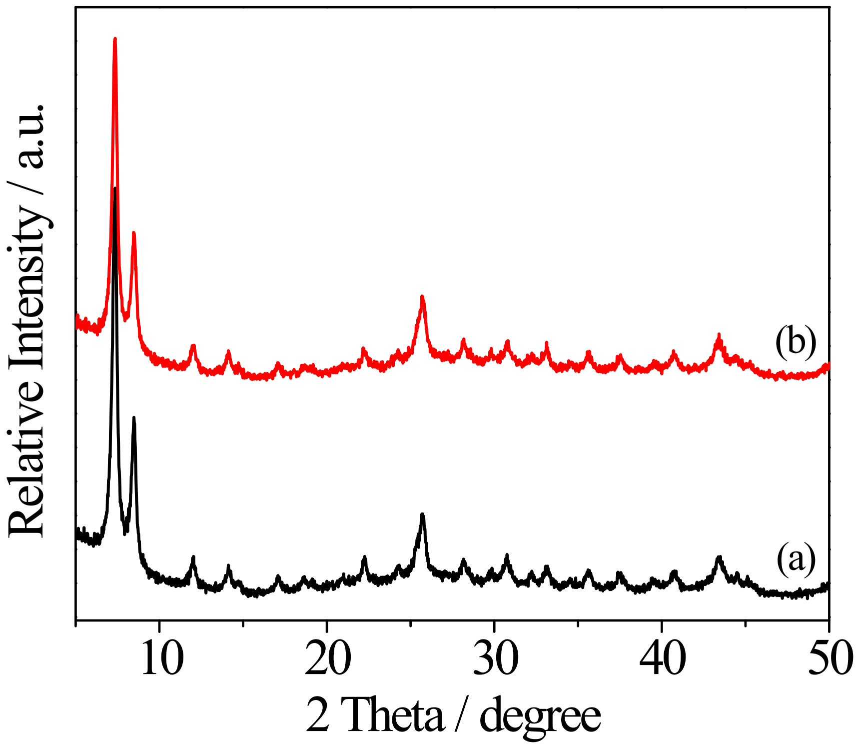

Figure S5 PXRD patterns of Eu^{3+}@**1**: (a) as-synthesized; (b) after treatment in H_2O at 373 K for 24 h.

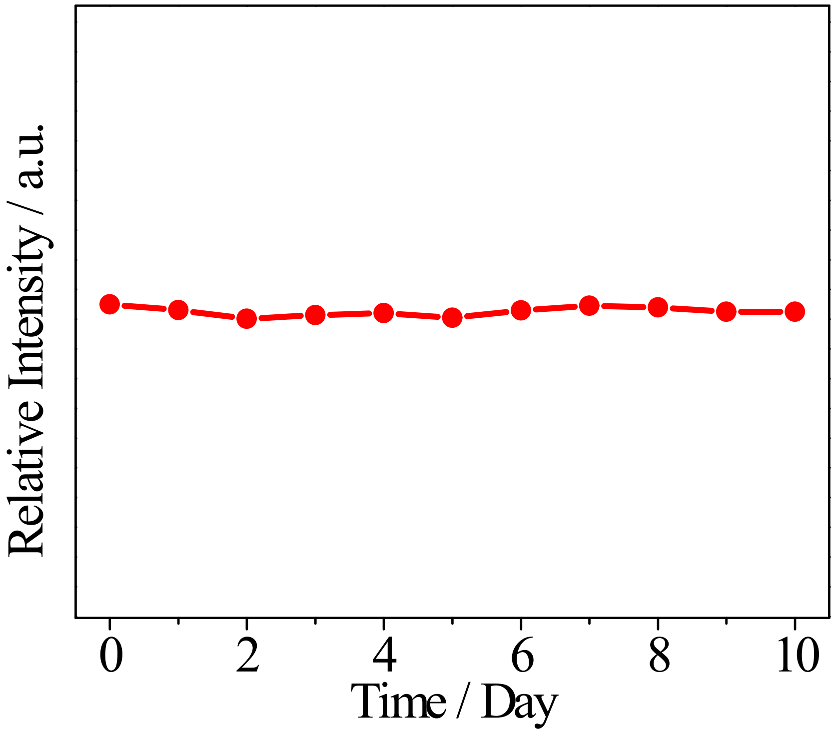

Figure S6 Stability of fluorescent intensity (at 614 nm) of Eu^{3+}@**1** in H_2O.

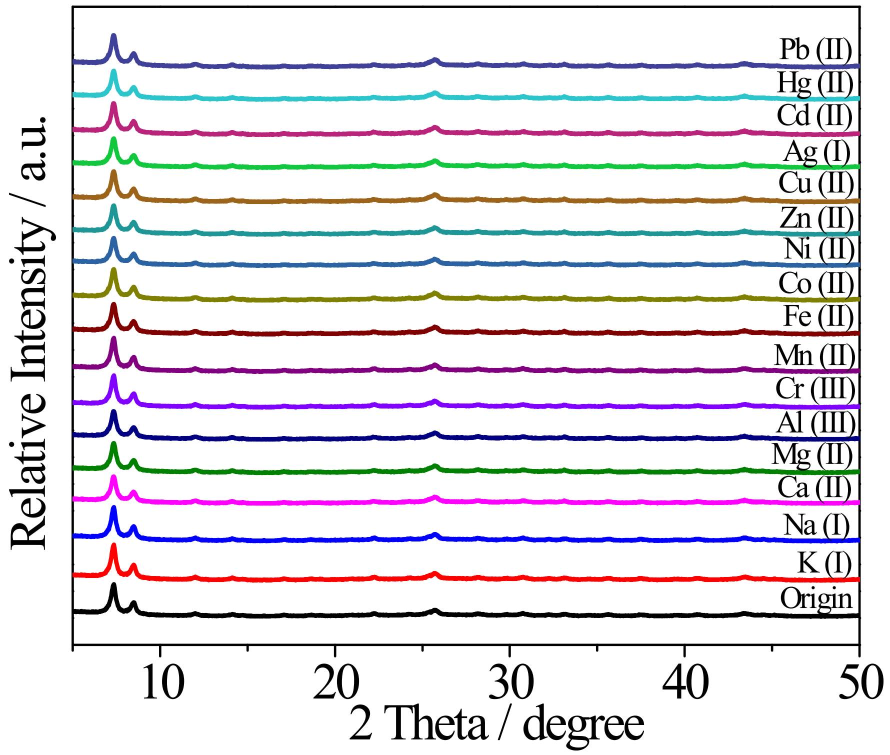

Figure S7 PXRD patterns of the Eu^{3+}@**1** treated by various metal ions aqueous solutions.

Table S2 Responses of luminescence lifetimes of Eu^{3+}@**1** towards various metal cations in aqueous solution.

Metal ions	τ (μs)
Cd^{2+}	763
Ca^{2+}	195
Al^{3+}	198
Mg^{2+}	187
Hg^{2+}	185
Zn^{2+}	190
K^{+}	189
Na^{+}	191
H_2O	181
Ag^{+}	179
Pb^{2+}	174
Ni^{2+}	169
Mn^{2+}	161
Co^{2+}	149
Cr^{3+}	117
Fe^{2+}	101
Cu^{2+}	74

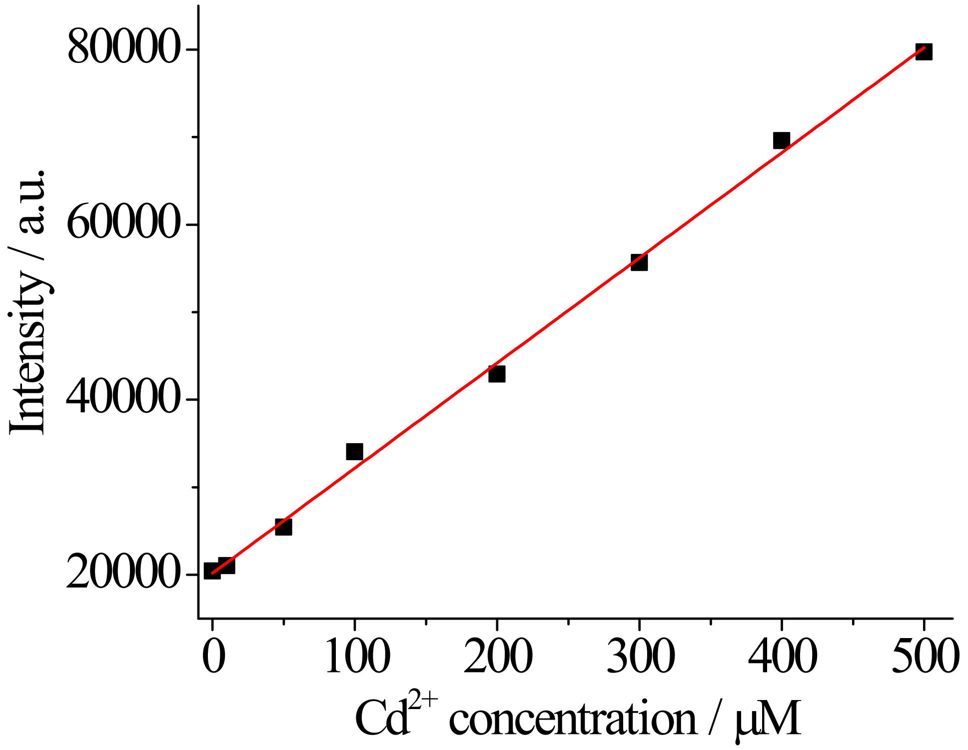

Figure S8 The fitting curve of the emission intensity (614 nm) of Eu^{3+}@**1** vs. Cd^{2+} concentration.

Linear Equation: Y = 120 X + 20188 R = 0.99885

$S = 1.2 \times 10^8\ M^{-1}$; $S_b = \sqrt{\frac{\sum (F_0 - F_1)^2}{N-1}} = 2.353\ (N = 20)$

$LOD = 3S_b/S = 0.06\ \mu M$.

S is the slope of the calibration curve; S_b is the standard deviation for replicating detections of blank solutions; F_0 is the fluorescence intensity of Eu^{3+}@**1** in water; F_1 is the average of the F_0.[3]

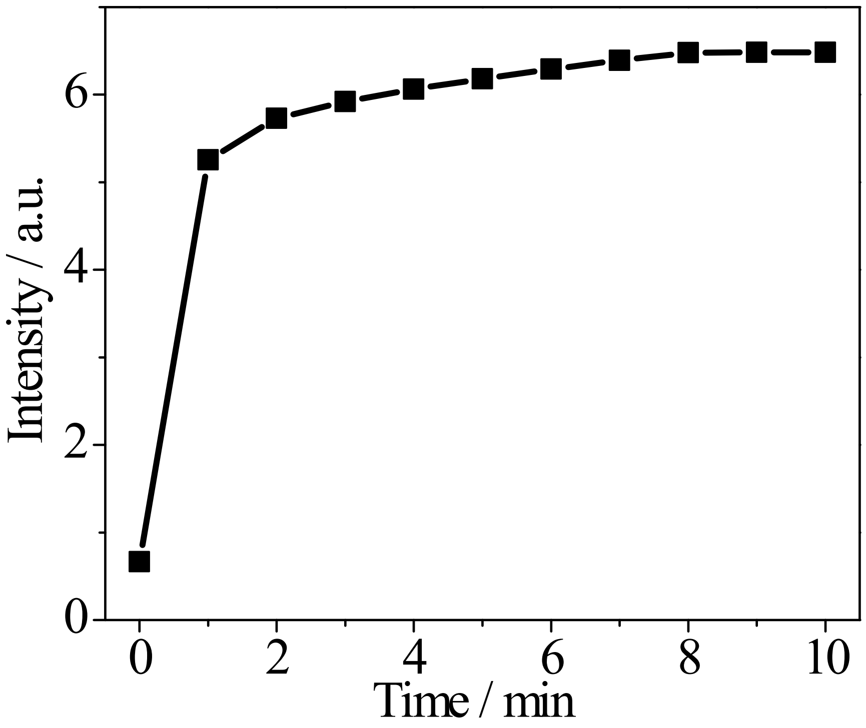

Figure S9 Variation of luminescent intensity of Eu^{3+}@**1** at 614 nm with immersion time in Cd^{2+} aqueous solution (10 mM), $\lambda_{ex} = 322$ nm.

Table S3 Determination of Cd^{2+} in real water samples by the standard addition method.

Sample	Added Cd^{2+} (μM)	Detected Cd^{2+} (μM) by Eu^{3+}@**1** sensor	Recovery (%)
Tap water 1	0	undetected	N/A
Tap water 2	5	4.85	97%
Tap water 3	50	51.26	102.52%
Tap water 4	100	99.30	99.3%
Lake water 1	0	undetected	N/A
Lake water 2	5	4.94	98.8%
Lake water 3	50	48.90	97.8%
Lake water 4	100	101.70	101.7%

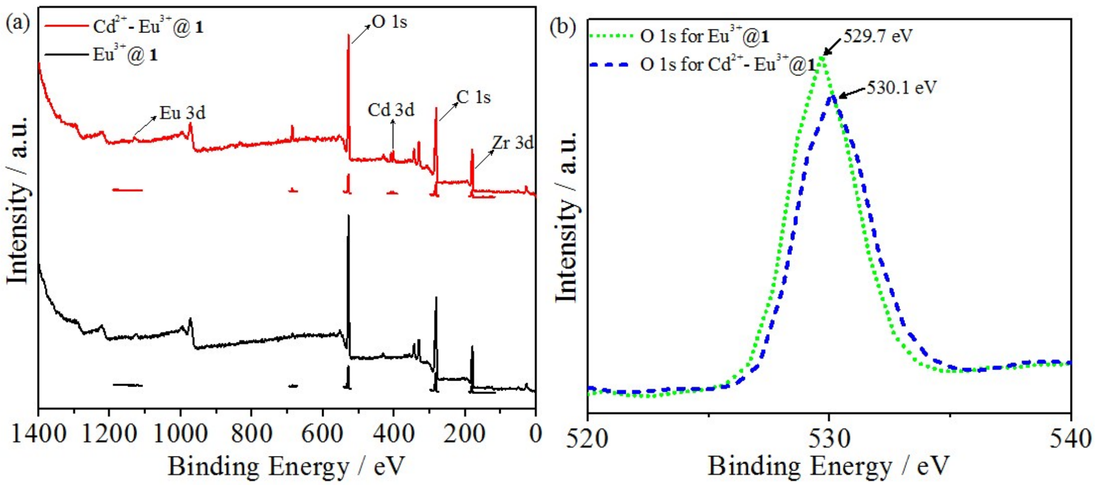

Figure S10 XPS spectra (a) and O 1s XPS (b) for Eu^{3+}@**1** and Cd^{2+}-Eu^{3+}@**1**.

References

1 Q. Y. Yang, S. Vaesen, F. Ragon, A. D. Wiersum, D. Wu, A. Lago, T. Devic, C. Martineau, F. Taulelle, P. L. Llewellyn, H. Jobic, C. L. Zhong, C. Serre, G. D. Weireld and G. Maurin, *Angew. Chem. Int. Ed.*, 2013, **52**, 10316.

2 a) Z. M. Hao, X. Z. Song, M. Zhu, X. Meng, S. N. Zhao, S. Q. Su, W. T. Yang, S. Y. Song and H. J. Zhang, J. Mater. Chem. A, 2013, 1, 11043; b) J. M. Zhou, W. Shi, H. M. Li, H. Li and P. Cheng, J. Phys. Chem. C, 2014, 118, 416.

3 G. Y. Gao, W. J. Qu, B. B. Shi, Q. Lin, H. Yao. Y. M. Zhang, J. Chang, Y. Cai and T. B. Wei, *Sensor Actuat. B-Chem.*, 2015, **DOI**: 10.1016/j.snb.2015.02.077