Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Recyclable lanthanide-functionalized MOF hybrids to determine hippuric acid in urine as a biological index of toluene exposure

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Experimental section

Materials

All chemicals were purchased from commercial sources and used without purification. Lanthanide chlorides were obtained from the corresponding oxides in HCl (37.5%).

Synthetic procedures

Synthesis of MIL-121 (1): $Al(NO_3)_3 \cdot 9H_2O$ (1.2 g, 3.2 mmol), 1,2,4,5- benzenetetracarboxylic acid (H_4btec, 0.4 g, 1.6 mmol), and 5 ml H_2O were placed in a 50 ml Teflon-lined autoclave. The mixture was heated at 210 °C for 24 h. The resulting white powder was separated from the mixed dispersion by centrifugation and washed with deionized water.[1] To remove the remaining free acid encapsulated within the pores of as-synthesized sample as much as possible, the activation was further carried out by Soxhlet extraction in methanol for 24 h and then the product was dried at 80 °C under vacuum overnight.

Preparation of Eu^{3+}@1: Eu^{3+}@**1** was prepared by stirring the mixture of 50 mg of compound **1** and $EuCl_3 \cdot 6H_2O$ (1 mmol) in 10 mL ethanol at 60 °C for 48 h. The solid was then filtered off, extensively wash with ethanol and dried under vacuum at 80 °C overnight.

Water-stability investigation of Eu^{3+}@1

The structure stability of Eu^{3+}@**1** in water was examined by immersing the as-synthesized samples (10 mg) in water (10 mL) for 48 h at room temperature. After 2 days' storage in water, the samples were centrifuged and dried before PXRD characterization.

The luminescence stability of Eu^{3+}@**1** in water was tested by immersing 3 mg of the as-synthesized samples in 3 mL H_2O. After ultrasonic for 5 minutes, the luminescent spectrum of the suspension was recorded. Afterwards, the suspension was sealed in a glass bottle (5 mL) and kept statically for 3 days, and then the sample was sonicated for 5 minutes and the suspension - state luminescent measurement was recorded. After another two days' soakage in water, the emission spectrum of Eu^{3+}@1 in water was measured again.

pH-stability investigation of Eu^{3+}@1

The structure stability investigation of Eu^{3+}@**1** in aqueous solutions with the pH value ranging from 4 to 8: 10 mg of Eu^{3+}@**1** powders was immersed in each aqueous solution (10 mL) with a pH value of 4, 5, 6, 7, 8, respectively, and then sealed in glass bottles (20 mL). The bottles were kept statically for 72 h, and then the samples were collected via centrifugation and dried at 80 °C.

Subsequently, PXRD were measured.

The pH-independent luminescent stability: 3 mg of Eu^{3+}@**1** was immersed in 3 mL of aqueous solutions with pH value ranging from 4 to 8 for 12 h, and then the suspension-state luminescence spectra were measured after sonicating for 5 min.

Experimental details for luminescent sensing [2]

For the experiments of sensing urine chemicals, 3.0 mg of Eu^{3+}@**1** powders were simply immersed into the aqueous solutions (3 mL, 10 mM) of different urine chemicals {Creatinine (Cre), Creatine, KCl, NaCl, Na_2SO_4, NH_4Cl, Urea, Uric acid (UA), Glucose (Glu), Hippuric acid (HA)}. Then the luminescence spectra of the suspensions were measured after sonicating for 30 min.

Experimental details for testing the recyclable performance of Eu^{3+}@1 sensor for HA

The Eu^{3+}@**1** (1mg/mL) was simply immersed in aqueous solutions in the absence and presence of 10^{-2} M HA, respectively. After ultrasonic for 2 min, the luminescence spectra were recorded. Then, the suspensions were centrifuged, and the collected powders were immersed in 10 mL water and sonicated for 2 min. After three times repetition of ultrasonic washing and centrifugation, the suspension-state emission spectra of the samples were recorded. Five runs performed by sequential addition of HA and ultrasonic washing.

Experimental details for preparing urine test paper based on the fluorescent sensor [3]

The filter paper was cut into strips of 1cm × 2.5 cm. The dispersion of Eu^{3+}@**1** (1 mg/mL) in ethanol was dropped on the strips, and then left to dry at room temperature. For the determination of HA in urine, the strips with Eu^{3+}@**1** were immersed into urine sample for 1 min and then exposed to air for drying.

Experiment procedures for the recyclable utilize of the test paper: the used test paper containing HA was immersed in water and ultrasonic for 2 minutes. The detached Eu^{3+}@**1** powders were collected by centrifugation, and then washed with water under ultrasonic for three times. The resulting powders were re-dispersed in ethanol. The dispersion of the recycled Eu^{3+}@**1** in ethanol was dropped on a new filter paper and dried at room temperature. The test paper could be reused by applying the detached Eu^{3+}@**1** powder and a new filter paper.

Characterization

Powder X-ray diffraction patterns (PXRD) were recorded with a Bruker D8 diffractometer using Cu Kα radiation with 40 mA and 40 kV. Fourier transform infrared spectra (FTIR) were recorded

in the range 4000 – 400 cm^{-1} on a Nexus 912 AO446 infrared spectrum radiometer using KBr pellets. Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature using a Nova 1000 analyzer. Surface areas were calculated by the Brunauer−Emmett−Teller (BET) method. Thermogravimetric analysis (TG) was measured using a Netzsch STA 449C system at a heating rate of 5 K min^{-1} under the nitrogen protection. Measurement of Ln^{3+} and Al^{3+} was performed on an X-7 series inductively coupled plasma-mass spectrometer (ICPMS) (Thermo Elemental, Cheshire, UK). X-ray photoelectron spectra experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hυ = 1253.6 eV). The SEM mapping of the samples were conducted by a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectrometer (EDS). The photoluminescent spectra and luminescent decay times were examined by an Edinburgh FLS920 phosphorimeter.

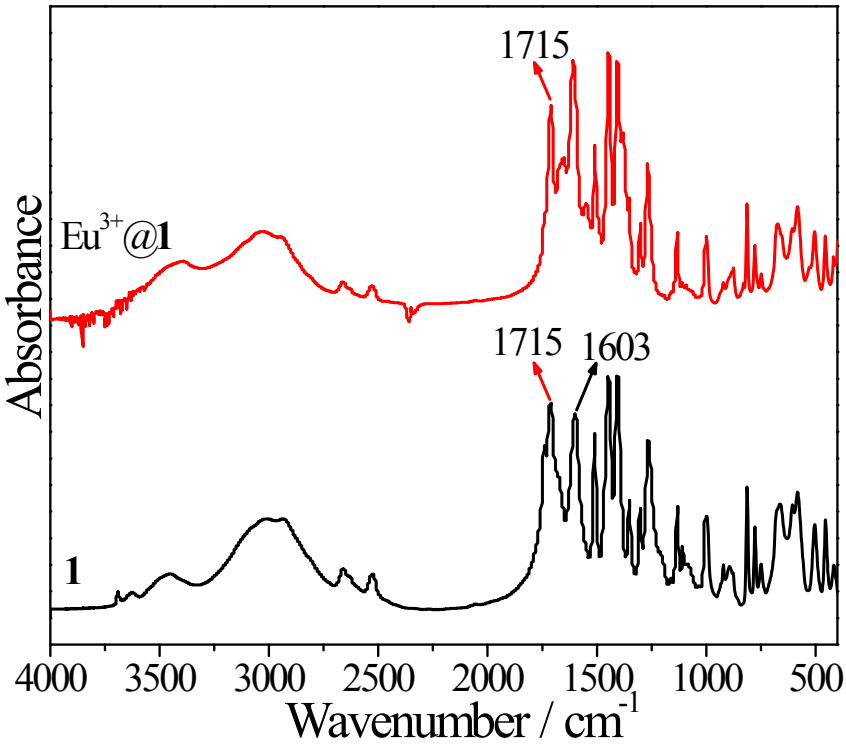

Figure S1 FTIR spectrum of **1** (black) and Eu^{3+}**@1** (red). The peak at 1601 cm^{-1} corresponds to the stretching vibration of carboxyl coordinated to the cation, whereas the vibrations at 1715 cm^{-1} are assigned to the free carboxyl.

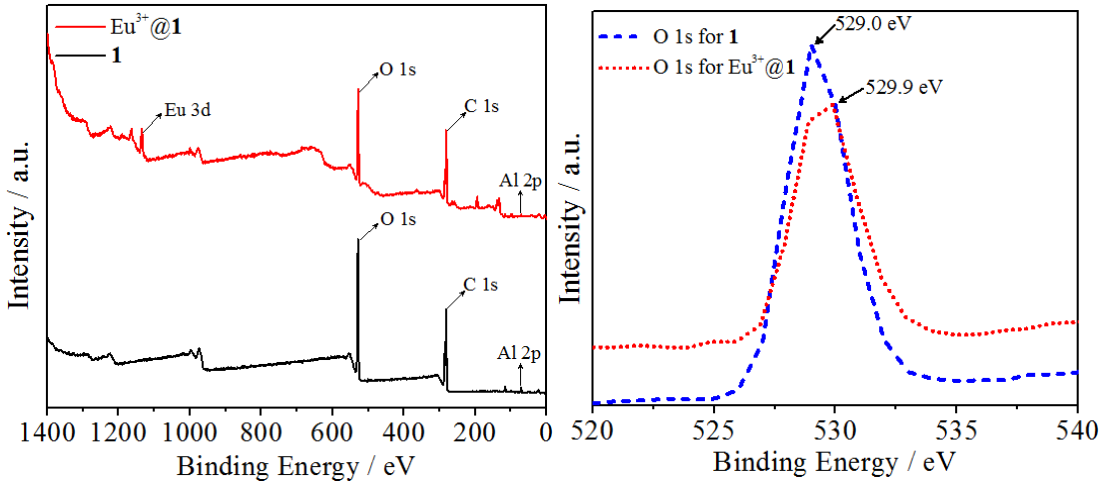

Figure S2 XPS spectra (a) and O 1s XPS (b) for **1** and Eu^{3+}**@1**.

Table S1 The ICP data for Eu^{3+} and Al^{3+} ions in Eu^{3+}**@1**

Compounds	Eu / Al mass ratio (ppm/ppm)	Eu / Al molar ratio
Eu^{3+}**@1**	72.3 / 8.03	1.6 / 1

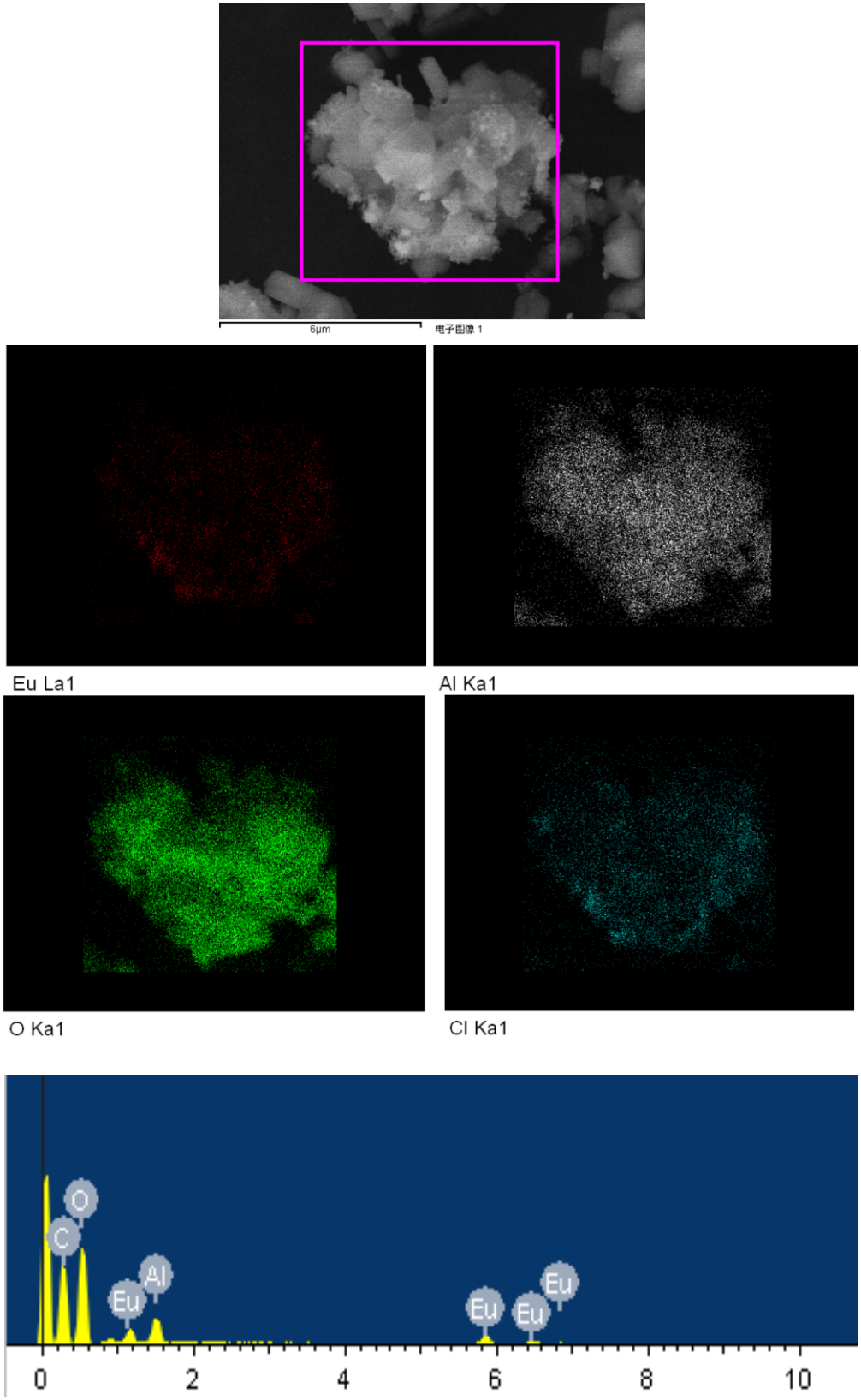

Figure S3 SEM mapping and EDS patterns of Eu^{3+}@**1** sample.

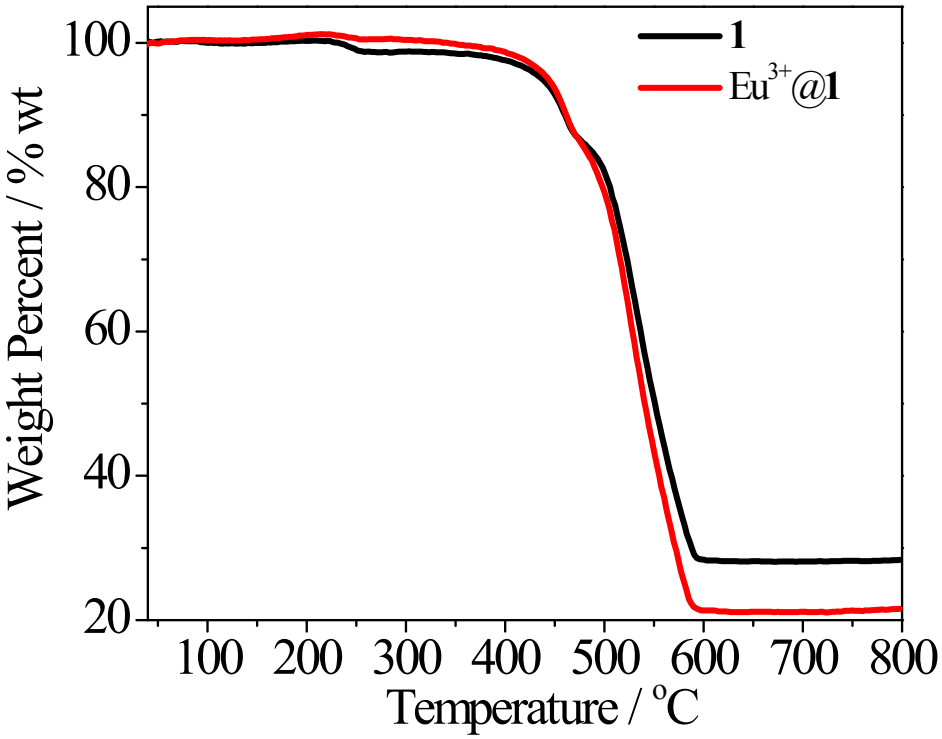

Figure S4 Thermogravimetric analysis of **1** and Eu^{3+}@**1**.

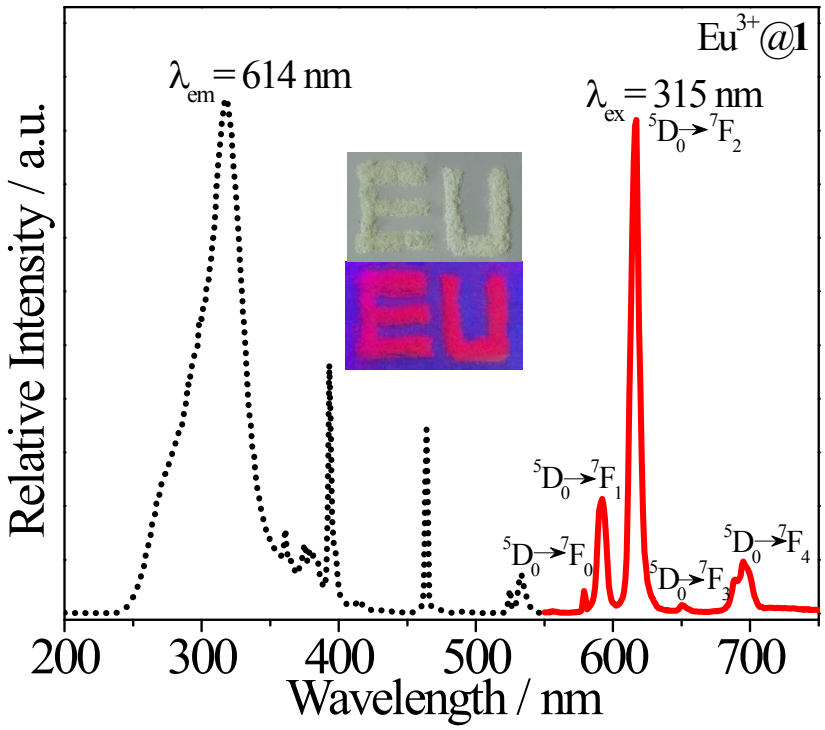

Figure S5 Excitation (black, λ_{em} = 614 nm) and emission (red, λ_{ex} = 315 nm) spectra of Eu^{3+}@**1**. The inset is the corresponding luminescence picture under UV-light irradiation of 254 nm.

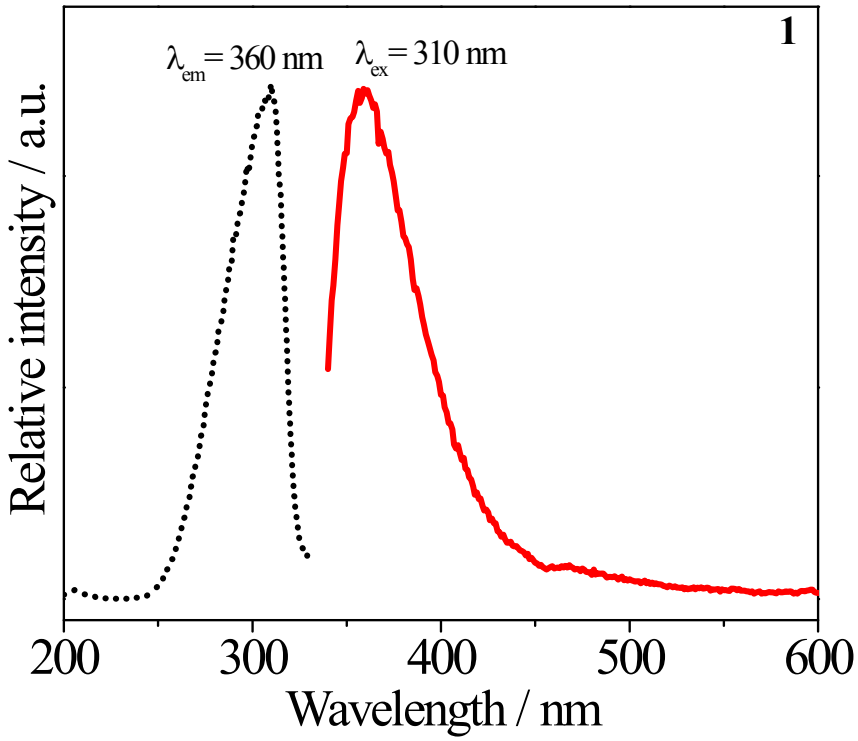

Figure S6 The excitation (black, λ_{em} = 360 nm) and emission (red, λ_{ex} = 310 nm) spectra of **1**.

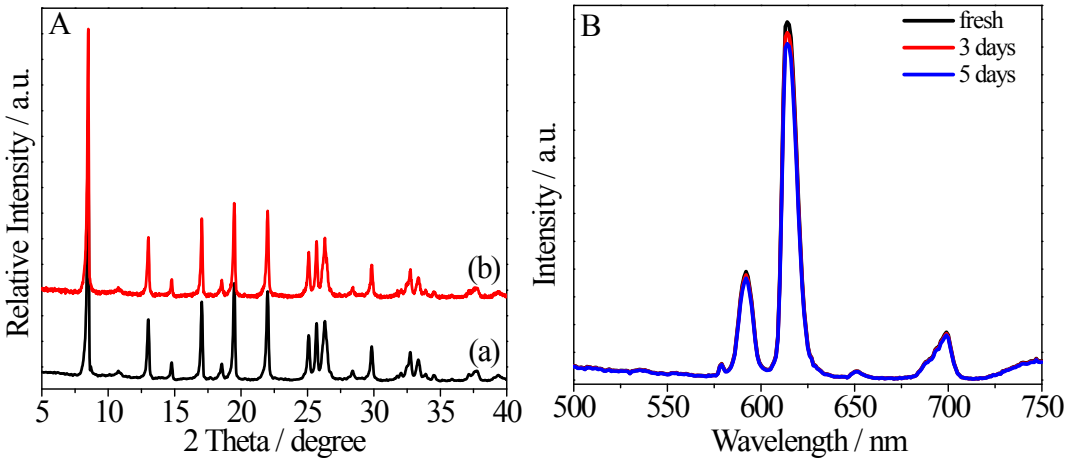

Figure S7 (A) PXRD patterns of Eu^{3+}@**1**: (a) as-synthesized; (b) after treatment in H_2O for 48 h; (B) Stability of fluorescent intensity of Eu^{3+}@**1** after 5 days' storage in H_2O.

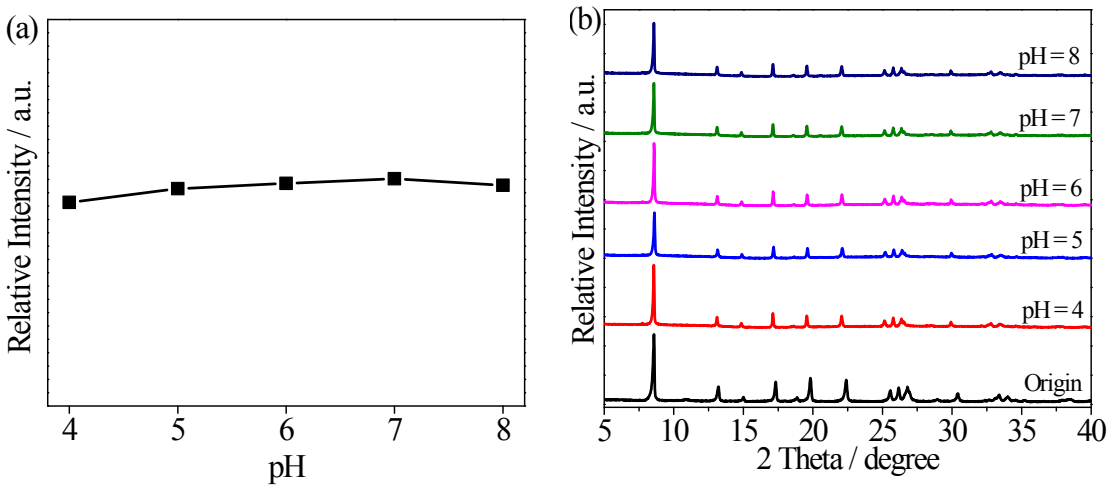

Figure S8 (a) The luminescent intensity of Eu^{3+}@**1** after immersing in different pH aqueous solutions for 12 h; (b) The PXRD patterns of Eu^{3+}@**1** after exposure to aqueous solutions with various pH values from 4.0 to 8.0 for 72 h.

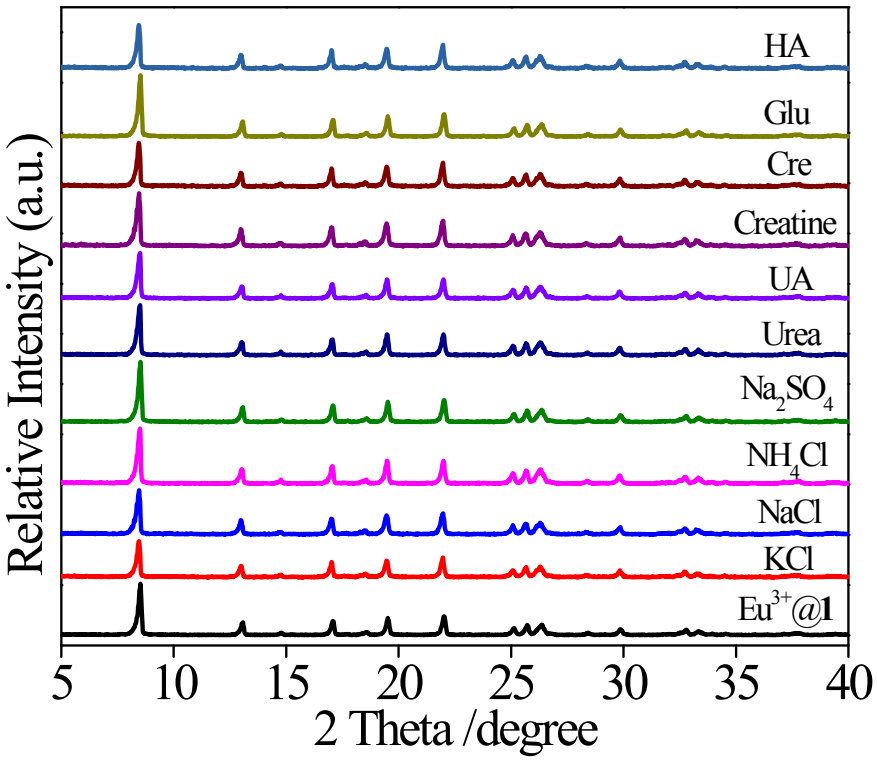

Figure S9 PXRD patterns of the Eu^{3+}@**1** after dispersing in aqueous solutions of various urine chemicals for 30 min.

Table S2 Responses of luminescence lifetimes of Eu^{3+}@**1** towards various urine chemicals in aqueous solutions (λ_{ex} = 315 nm and λ_{em} = 614 nm).

Materials	τ (μs)
Cre	190
Na_2SO_4	182
Urea	180
NH_4Cl	176
Origin	173
KCl	164
Creatine	165
NaCl	160
Glu	157
UA	162
HA	76

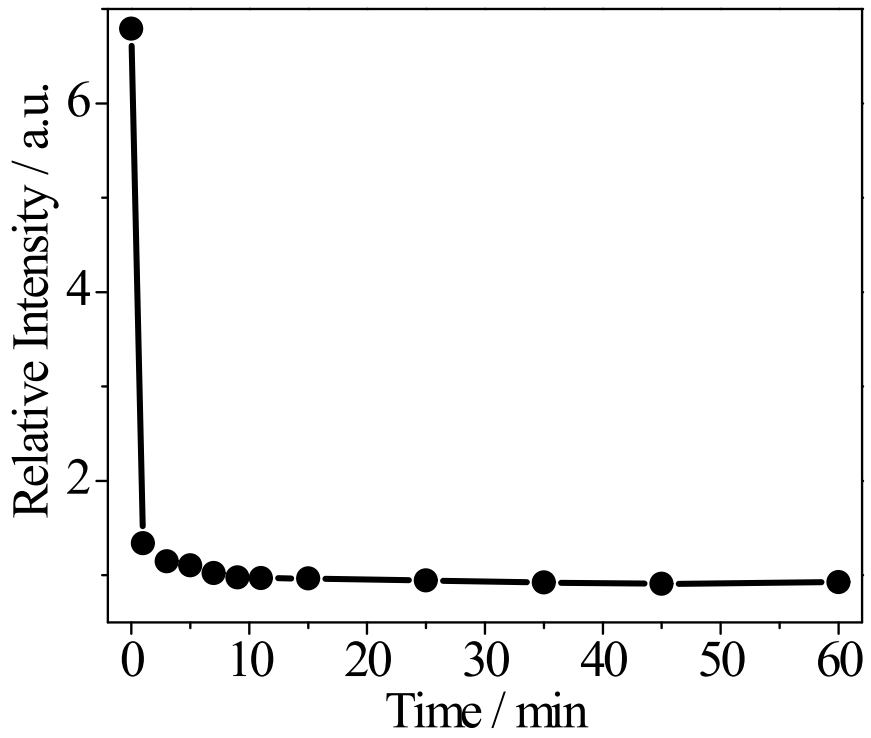

Figure S10 Variation of luminescent intensity of Eu^{3+}@**1** at 614 nm with immersion time in HA aqueous solution (10 mM), λ_{ex} = 315 nm.

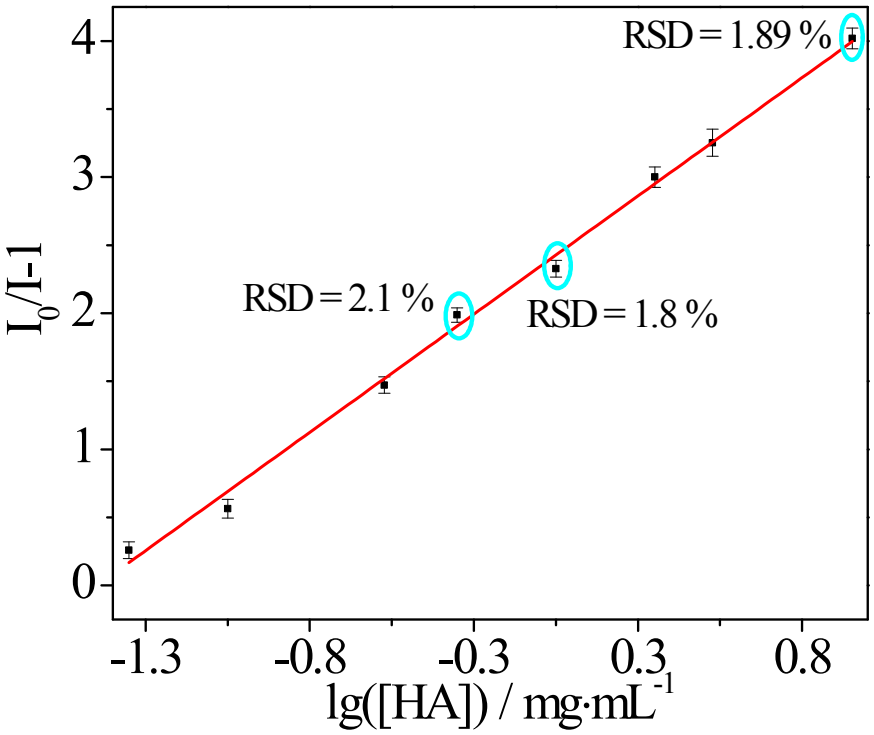

Figure S11 Plot of $I_0/I - 1$ versus the logarithm of the concentration of HA (I_0 is the fluorescence intensity of the solution of Eu^{3+}@**1** without HA; I is the fluorescence value obtained after adding a given amount of HA to Eu^{3+}@**1**). Results show mean± standard deviation in six assays.

Table S3 Determination of HA in real human urine samples [a] by standard addition method

Samples	Background HA (mg/mL)	Spiked HA (mg/mL)	Total detected HA[b] (mg/mL) by Eu^{3+}@**1** sensor	RSD[c] (%)	Recovery (%)
A	0.102	0.3	0.376 ± 0.008	2.13	93.5
		1.0	1.081 ± 0.020	1.85	98.1
		3.0	2.959 ± 0.050	1.69	95.4
B	0.314	0.3	0.585 ± 0.011	1.88	95.3
		1.0	1.326 ± 0.013	0.98	100.9
		3.0	3.198 ± 0.070	2.19	96.5
C	0.181	0.3	0.495 ± 0.004	0.81	102.9
		1.0	1.156 ± 0.018	1.56	97.9
		3.0	3.022 ± 0.052	1.72	95.0

[a] The collection experiment of human urines was performed in compliance with the ethical guidelines issued by the Ministry of Health of the People's Republic of China. The investigation was apporved by Medical and Life Sciences Ethics Committee of Tongji University. Informed consents of the experiment were obtained from participants before collection of the samples.

[b] All concentrations were expressed as mean of six measurements ±standard deviation (SD).

[c] The relative standard deviation (RSD) was defined as (SD/mean)×100%.

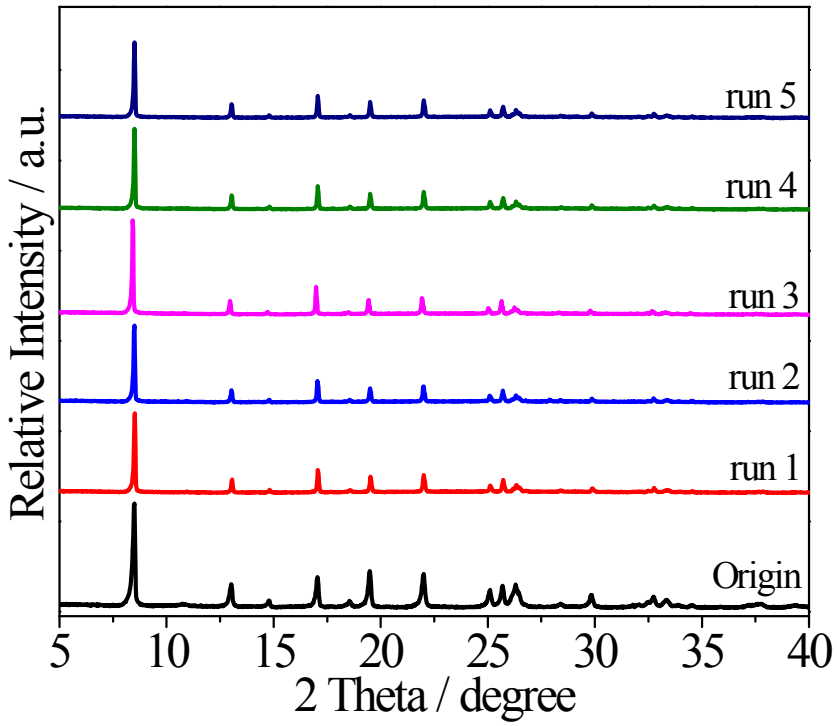

Figure S12 The PXRD patterns of Eu^{3+}@**1** after five recycles.

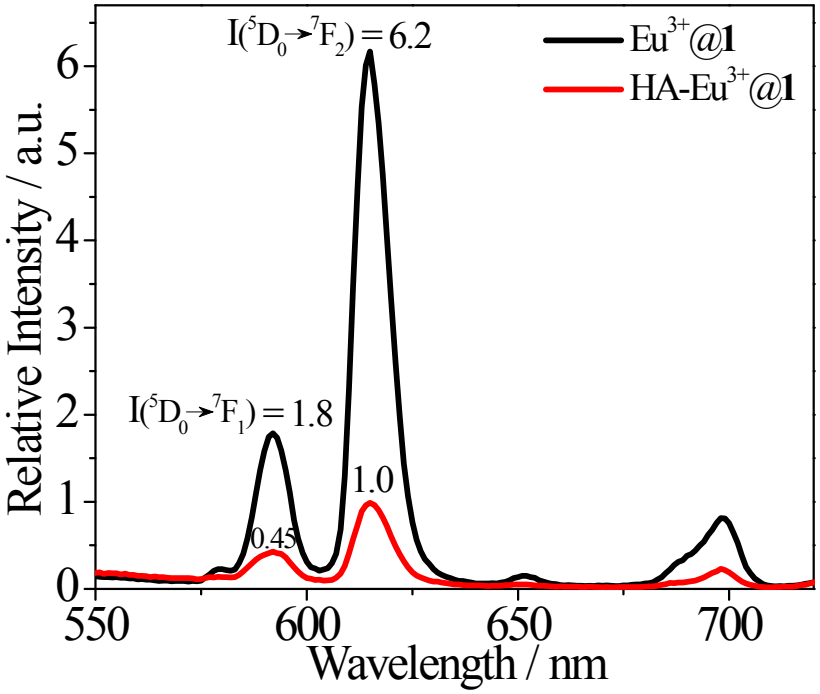

Figure S13 The emission spectra of Eu^{3+}@**1** in the absence (black line) and presence of 10^{-2} M HA (red line), λ_{ex} = 315 nm. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition at 614 nm, which is a forced electric-dipole transition, depends strongly on the chemical bonding of the Eu^{3+} ion, while the $^5D_0 \rightarrow {}^7F_1$ emission at 592 nm is due to the magnetic dipole and is independent of the surroundings of Eu^{3+}. The intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ and the $^5D_0 \rightarrow {}^7F_1$ transition is therefore a good measure for the coordination state of the Eu^{3+} ions.[4] In this case, the intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ for Eu^{3+}@**1** and HA-Eu^{3+}@**1** are equal to 3.4 and 2.2, respectively, which implies that the addition of HA induce the change of Eu^{3+} ions' coordinated environments.

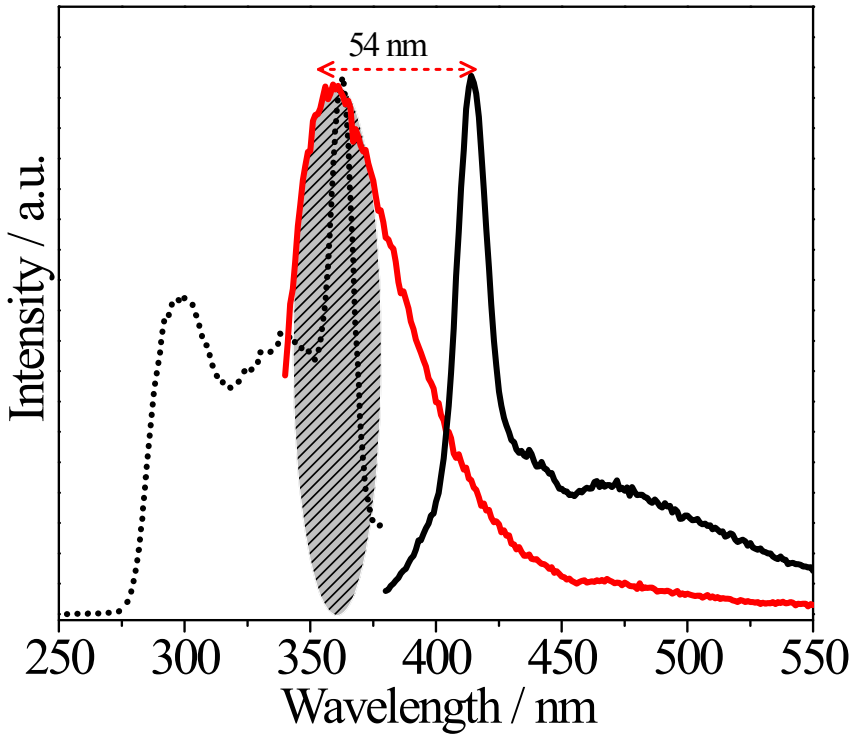

Figure S14 Excitation of HA (black dot line, λ_{em} = 414 nm), and emission spectrum of **1** (red, λ_{ex} = 310 nm) and HA (black line, λ_{ex} = 360 nm).

References

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4 a) F. S. Richardson, *Chem. Rev.*, 1982, **82**, 541; b) Q. B. Bo, H. T. Zhang, H. Y. Wang, J. L. Miao and Z. W. Zhang, *Chem. Eur. J.*, 2014, **20**, 3712; c) X. Q. Wang, L. L. Zhang, J. Yang, F. L. Liu, F. N. Dai, R. M. Wang and D. F. Sun, *J. Mater. Chem. A*, 2015, **3**, 12777.