

**Supporting Information**

**Simultaneous determination of indoor ammonia pollution and its  
biological metabolite in human body by use of a recyclable  
nanocrystalline lanthanide functionalized MOF**

Ji-Na Hao and Bing Yan\*

*Shanghai Key Lab of Chemical Assessment and Sustainability, Department of  
Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China*

## Experimental section

### Materials

All starting materials were commercially available reagents of analytical grade and were used without further purification.  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  and 2,2'-bipyridine-5,5'-dicarboxylic acid ( $\text{H}_2\text{bpydc}$ ) were purchased from Aldrich.  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  was prepared by dissolving  $\text{Eu}_2\text{O}_3$  in concentrated hydrochloride acid.

### Synthetic procedures

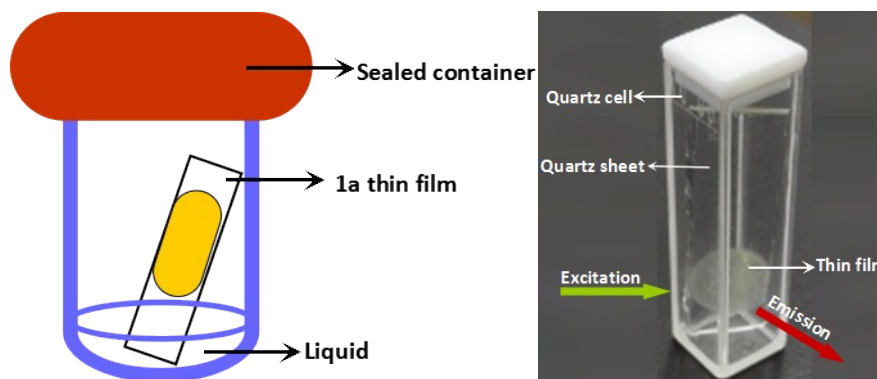
**Synthesis of  $\text{Ga}(\text{OH})(\text{bpydc})$  (COMOC-4, **1**)<sup>S1</sup>** A mixture of  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (0.1688 g, 0.66 mmol),  $\text{H}_2\text{bpydc}$  (0.1832 g, 0.75 mmol) and 15 mL DMF was placed into a Teflon cell (50 mL). After applying ultrasound for 20 minutes, the Teflon cell was sealed in the autoclave and heated in oven at 150 °C for 2 days, and then cooling to room temperature naturally. The resulting orange gel was centrifuged and washed with DMF, methanol and acetone. To remove the organic species encapsulated within the pores of the open framework, the product was washed with methanol via Soxhlet extraction for 24 h at 120 °C, followed by drying at 120 °C under vacuum overnight.

**Synthesis of  $\text{Eu}^{3+}@\mathbf{1}$  (**1a**)** As-prepared **1** (0.1 g) was soaked in 10 mL of 0.01 mol·L<sup>-1</sup>  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  ethanol solutions at 60 °C for 24h. The yellowish powder was collected, extensively washed with ethanol for several times, and dried under vacuum.

**Fabrication of luminescent **1a** film** The **1a** suspensions were prepared by dispersing the nanoparticles in ethanol. The substrates were rinsed with ethanol in an ultrasonic bath for several times before film deposition. The nano-sized **1a** film was prepared by spin-coating method through dropping the alcoholic suspensions of **1a** onto the pre-cleaned substrate which was fixed on a Laurell spin-coater. The spin-coating speed and time was kept at 1500 rpm for 30 s. The spin-coating process was repeated several times, and then the film was dried at room temperature.

**Exposure to various solvent vapors** The fabricated **1a** films were used for vapor sensing experiments. For each experiment, the film was placed into a small glass bottle (20 mL) which contains 5 mL of solvent for 1 h, thus making the films exposed to various vapors. And then the luminescence spectra of the films, before and after being exposed to the solvent vapors, were measured. The experimental setup is depicted below (a)

In order to test the response rate of **1a** for NH<sub>3</sub> vapor, an *in situ* solid-state luminescent sensor setup was designed (b).



a) Diagram of gas-sensing measurements for solvent vapors; b) designed sensor setup used for the solid-state photoluminescence measurements as a function of time in ammonia vapors.

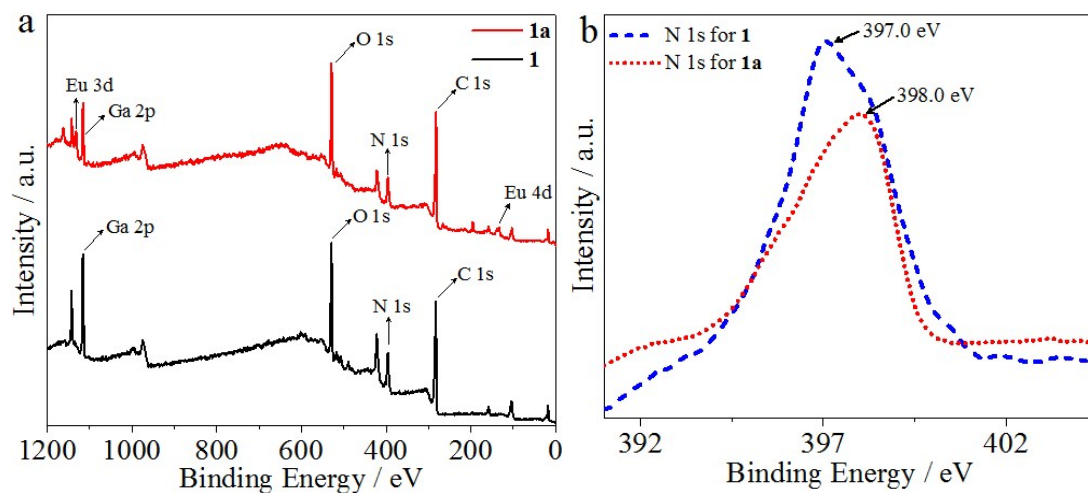
**Experimental details of luminescent sensing for urine chemicals** 3.0 mg of **1a** powders were simply immersed into 3 mL of aqueous solutions (10 mM) containing various urine chemicals {Creatinine (Cre), Creatine, KCl, NaCl, Na<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>Cl, Urea, Uric acid (UA), Glucose (Glu), Hippuric acid (HA)}. Then the luminescence spectra of the suspensions were measured after sonicating for 15 min.

### Characterization

X-ray powder diffraction patterns (XRD) were recorded with a Bruker Focus D8 at 40 kV, 40 mA for Cu-K $\alpha$  with a scan speed of 0.10 s per step and a step size of 0.02°; the data were collected within the 2 $\theta$  range of 5 – 50°. The particle shape and size was determined using a JEOL JEM-2100F transmission electron microscope (TEM) with an accelerating voltage at 200 kV. Surface morphology of thin film was investigated by using a Hitachi S-4800 Scanning Electron Microscopy (SEM). 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. Ga and Eu were determined by an X-7 series inductively coupled plasma-mass spectrometer (ICPMS) (Thermo Elemental, Cheshire, UK). X-ray photoelectron spectra (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K $\alpha$  radiation ( $h\nu = 1253.6$  eV). The photoluminescent spectra and luminescent decay times were examined by an Edinburgh FLS920 phosphorimeter.

### References

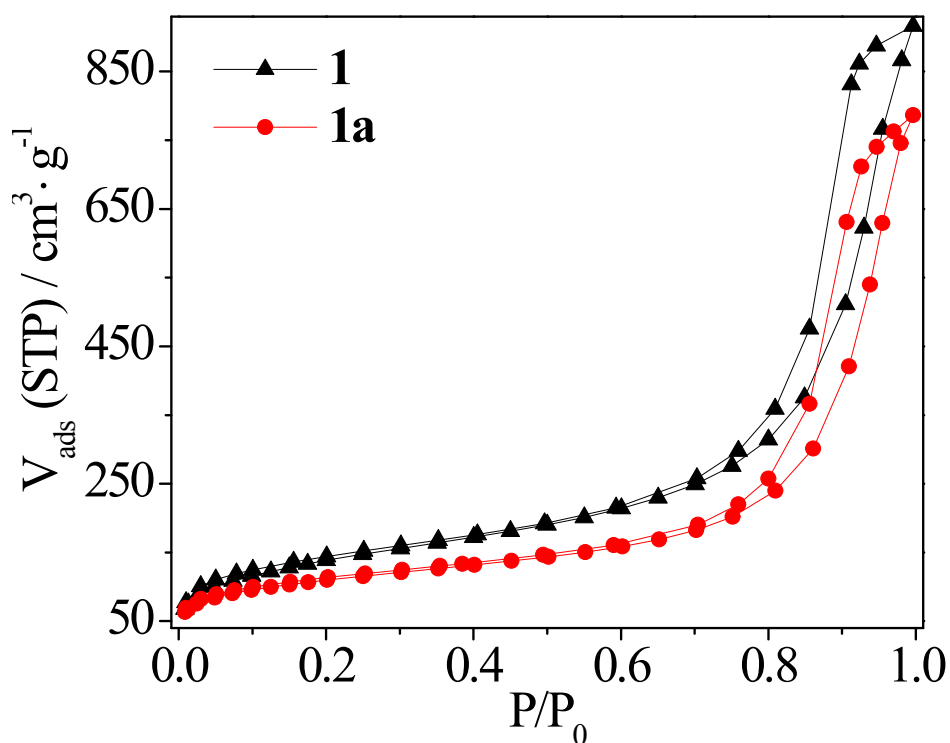
S1 Y. Y. Liu, K. Leus, T. Bogaerts, K. Hemelsoet, E. Bruneel, V. Van Speybroeck and P. Van Der Voort, *ChemCatChem*, 2013, **5**, 3657-3664.



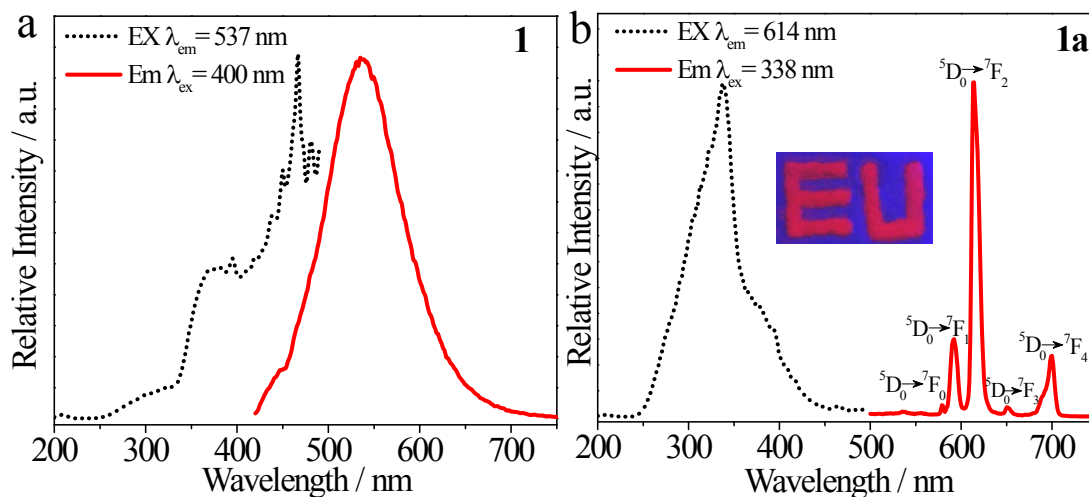
**Figure S1** XPS spectra (a) and N 1s XPS (b) for **1** and **1a**.

**Table S1** The ICP data for  $\text{Eu}^{3+}$  and  $\text{Ga}^{3+}$  ions in **1a**

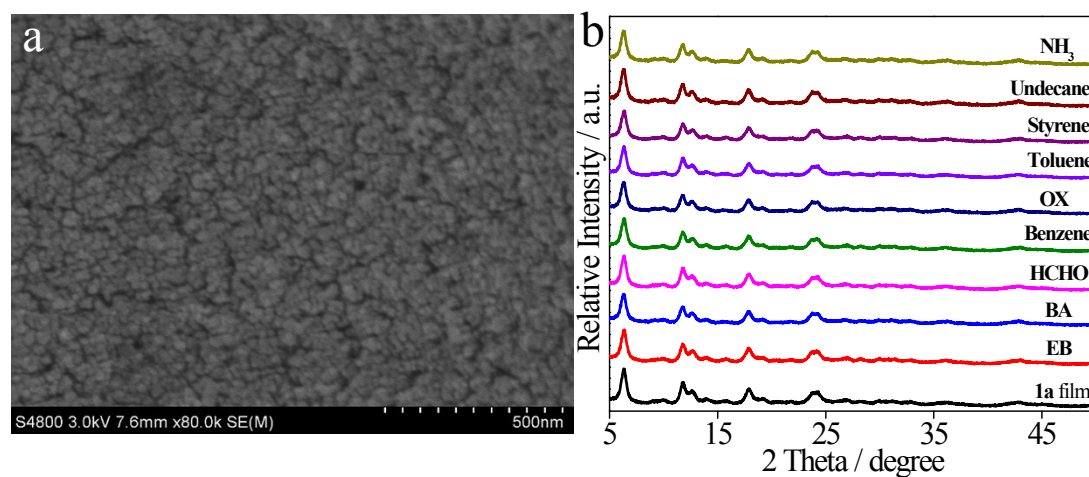
Compounds	Eu / Ga mass ratio (ppm/ppm)	Eu / Ga molar ratio
<b>1a</b>	12.37 / 70.98	0.08 / 1



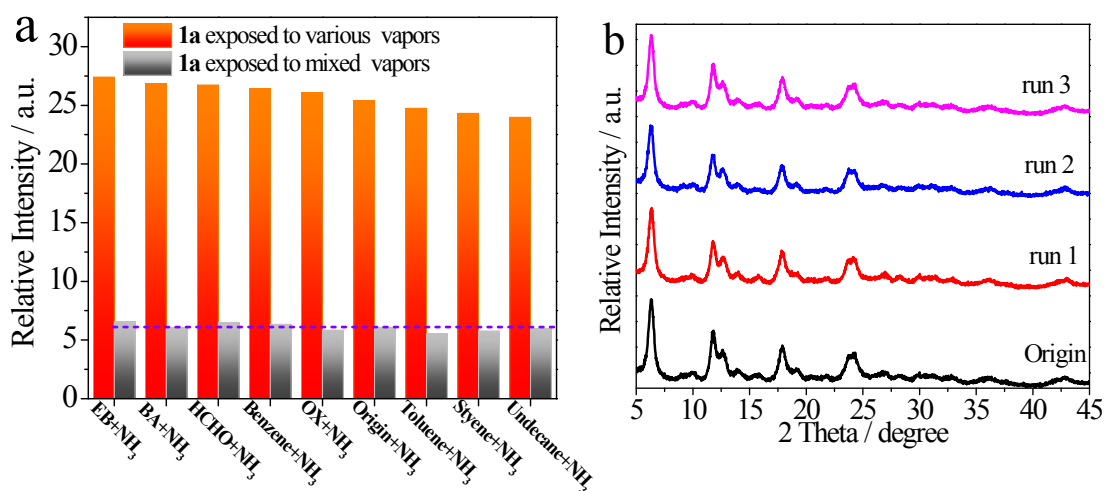
**Figure S2**  $\text{N}_2$  adsorption-desorption isotherms for **1** and **1a**.

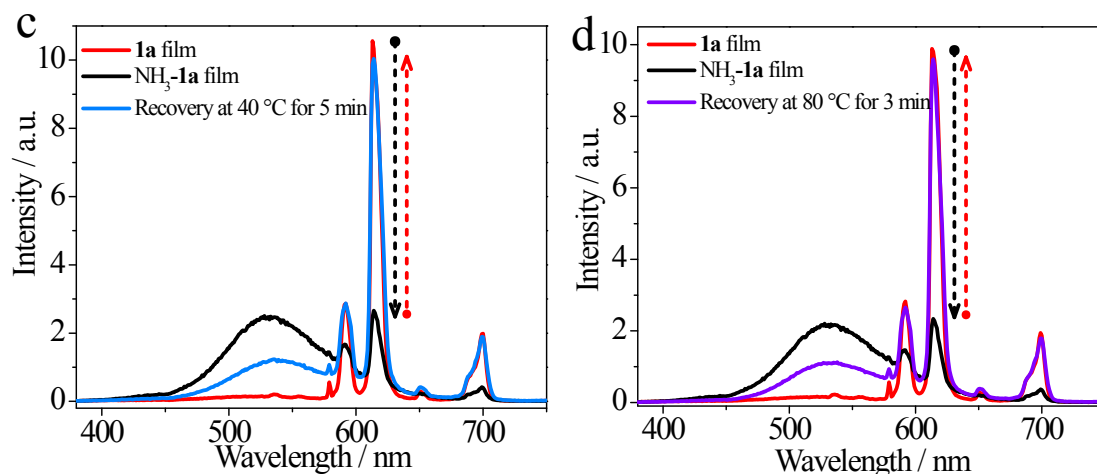


**Figure S3** The excitation and emission spectra of **1** (a) and **1a** (b).

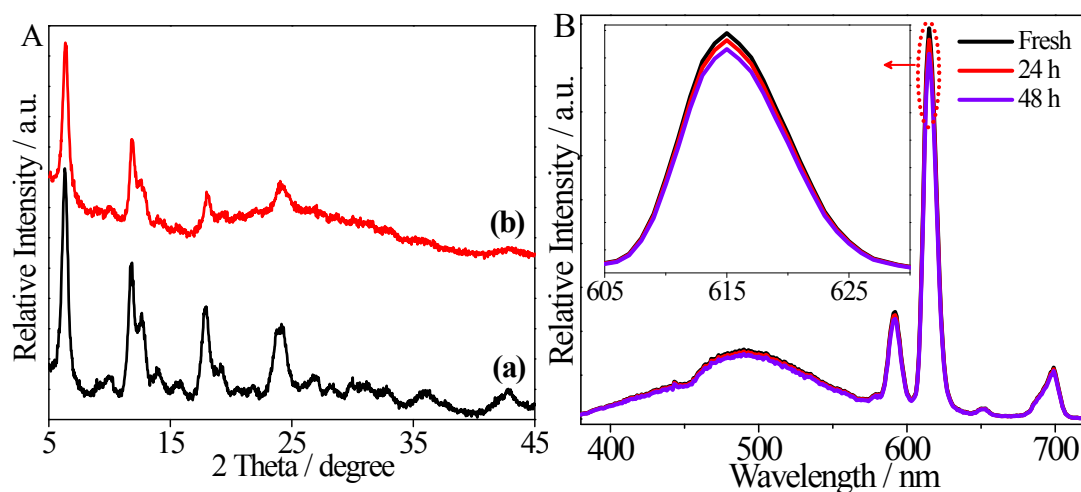


**Figure S4** (a) SEM image of the **1a** film; (b) PXRD patterns of **1a** film after exposure to various vapors for 1h.

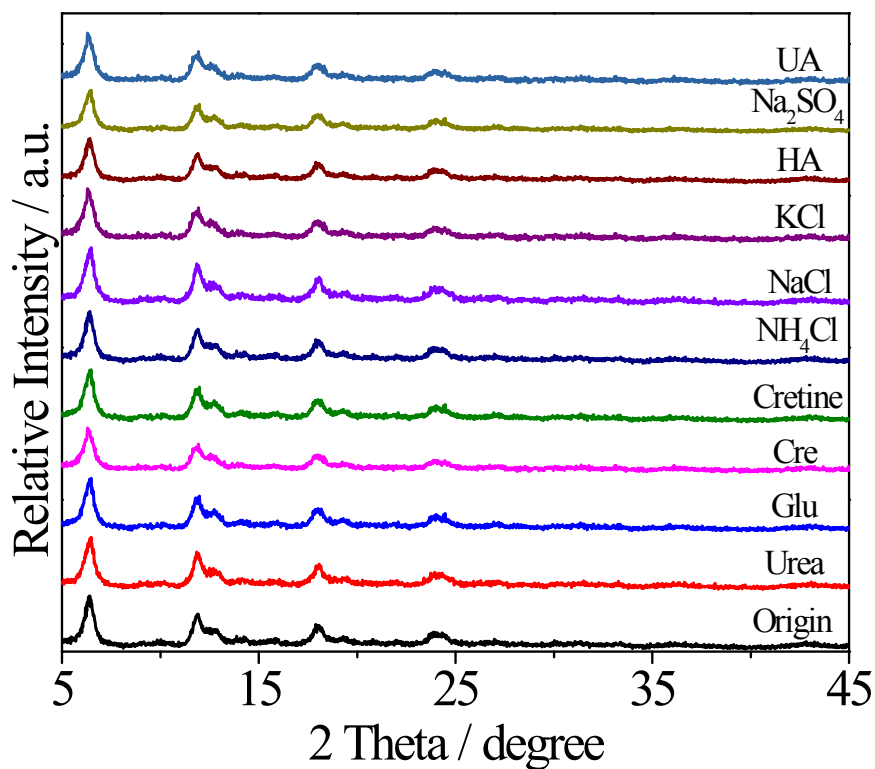




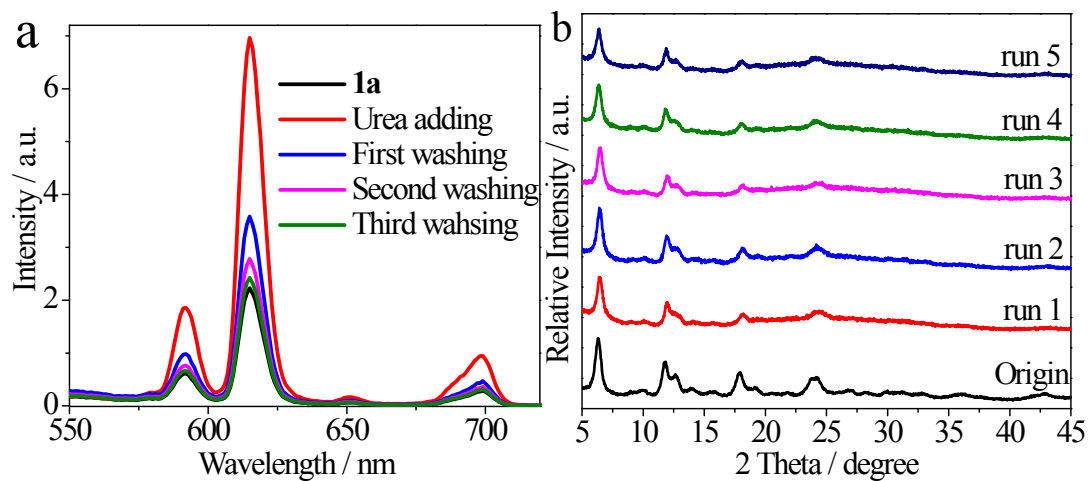
**Figure S5** (a) Luminescence responses of **1a** film toward NH<sub>3</sub> gas in the presence of background of other various indoor air pollutants ( $\lambda_{\text{ex}} = 338$  nm); (b) PXRD patterns of **1a** film after three recycles of detecting ammonia; (c,d) The luminescence responses of **1a** film sensor absorbed ammonia after heating at 40 °C (c) and 80 °C (d) for several minutes.



**Figure S6** (A) PXRD patterns of **1a** powder: (a) as-synthesized; (b) after treatment in H<sub>2</sub>O for 16 h; (B) Photostability investigation of **1a** after storage in H<sub>2</sub>O for 48 h ( $\lambda_{\text{ex}} = 338$  nm).



**Figure S7** PXRD patterns of the **1a** powder after dispersing in aqueous solutions of various urine chemicals.



**Figure S8** (a) the recovery of the emission intensity of **1a** after adding urea by washing with water for three times ( $\lambda_{\text{ex}} = 338 \text{ nm}$ ); (b) PXRD patterns of **1a** after five recycles of detecting urea in aqueous solutions.

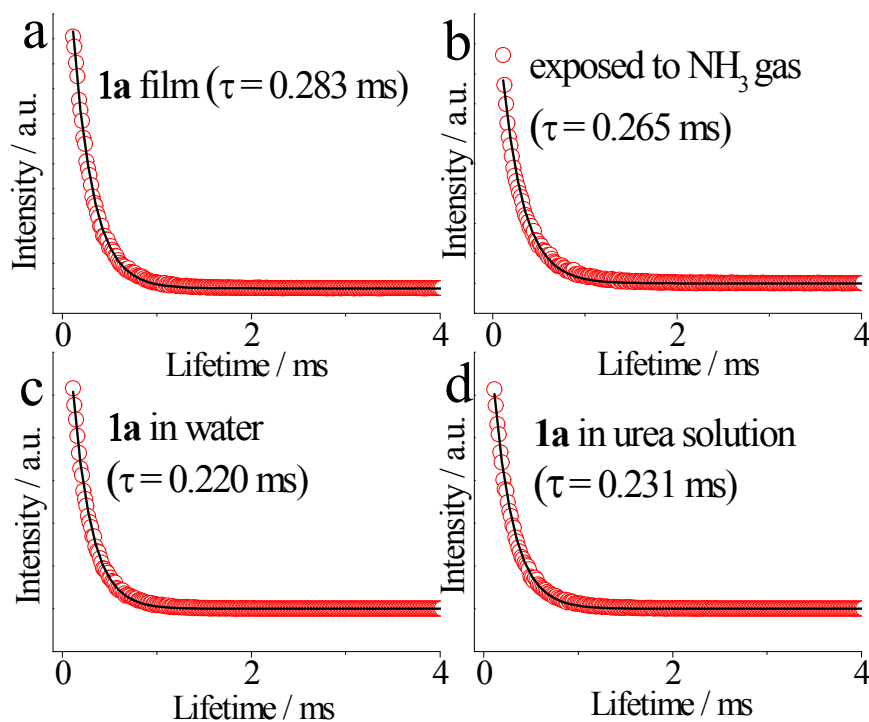
**Table S2** Determination of urea in real human urine samples <sup>a</sup> by standard addition method

Samples	Background Urea (mg/mL)	Spiked Urea (mg/mL)	Total detected Urea <sup>b</sup> (mg/mL) by <b>1a</b> sensor	RSD <sup>c</sup> (%)	Recovery (%)
A	6.4	5	11.8 ± 0.306	2.59	103.5
		10	15.7 ± 0.303	1.93	95.7
		20	27.1 ± 0.545	2.01	102.7
B	5.8	5	10.1 ± 0.335	3.32	93.5
		10	15.2 ± 0.258	1.70	96.2
		20	24.4 ± 0.412	1.69	94.6
C	9.1	5	13.9 ± 0.136	0.98	98.6
		10	19.5 ± 0.400	2.05	102.1
		20	28.5 ± 0.632	2.22	97.9

<sup>a</sup> Informed consent of the experiment was obtained from people offered the urine specimens. 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, and the Medical and Life Sciences Ethics Committee of Tongji University have approved the experiments.

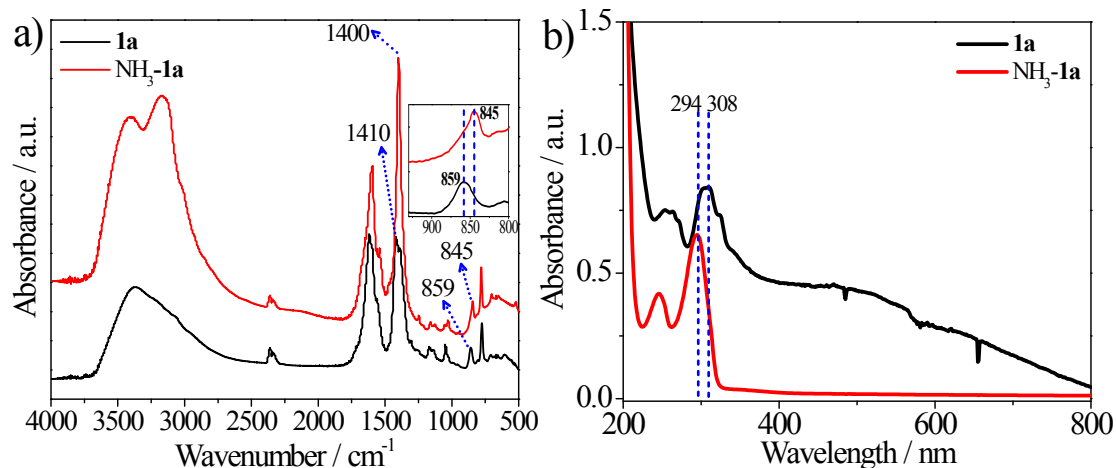
<sup>b</sup> All concentrations were expressed as mean of six measurements ± standard deviation (SD).

<sup>c</sup> The relative standard deviation (RSD) was defined as (SD/mean)×100%.

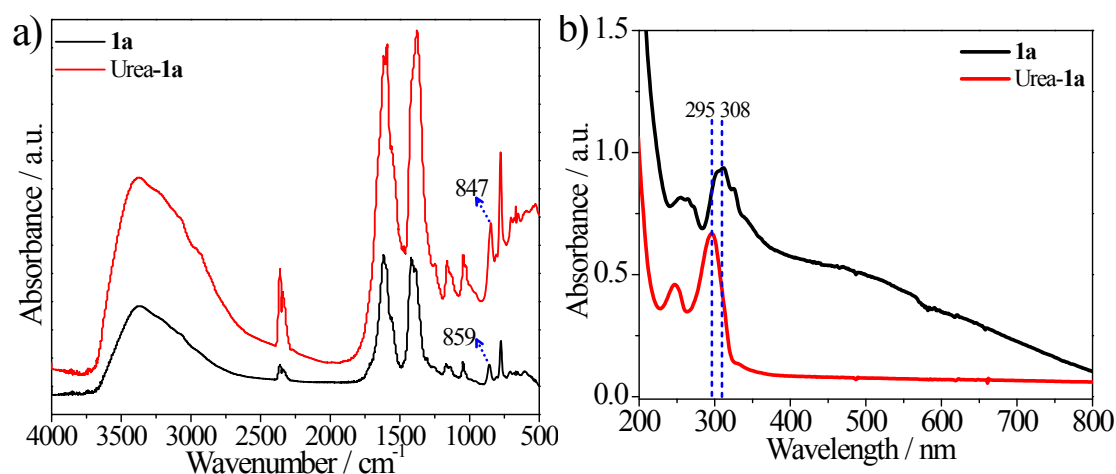


**Figure S9** Decay curve of a) **1a** film, b) **1a** film after exposure to ammonia gas; c) **1a** in water, and d) **1a** in aqueous solution of urea ( $\lambda_{\text{ex}} = 338 \text{ nm}$ ;  $\lambda_{\text{em}} = 614 \text{ nm}$ ).

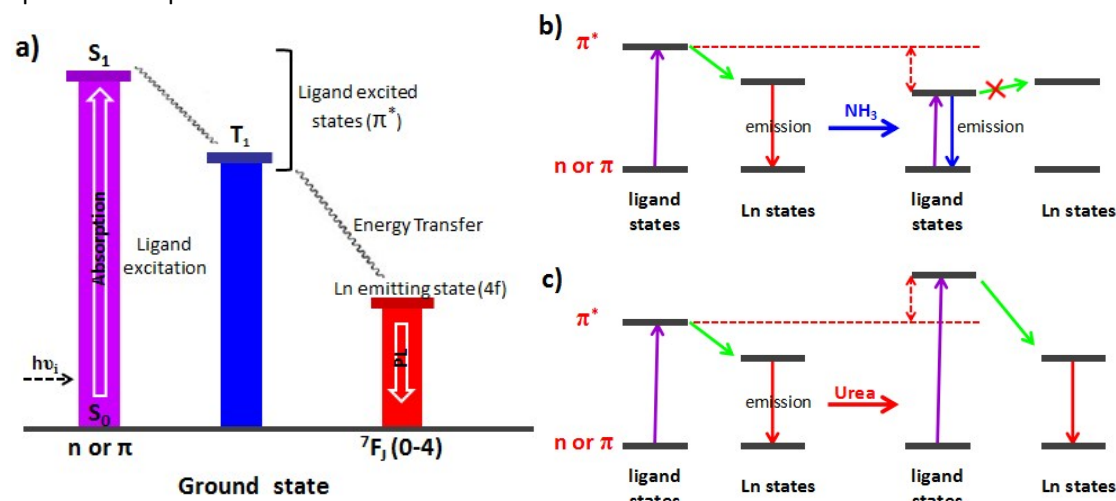




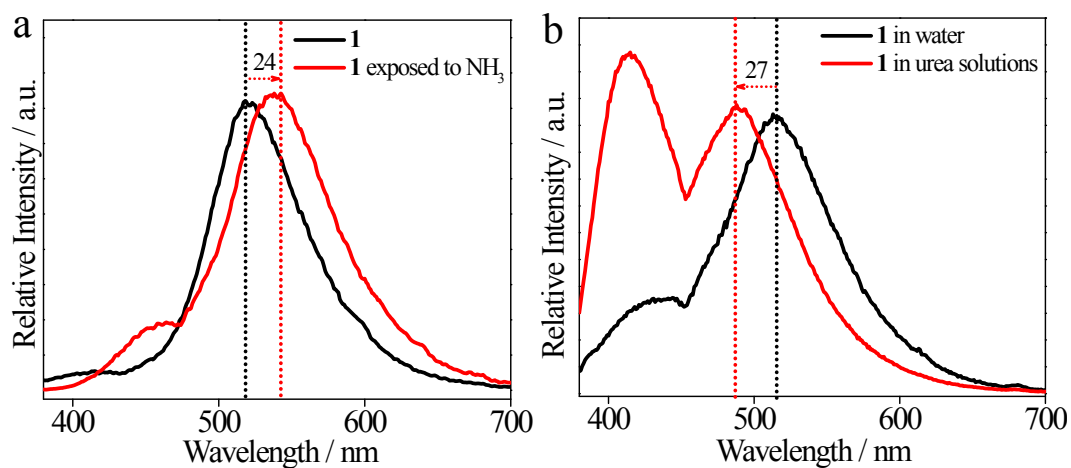
**Figure S10** (a) FT-IR spectra of **1a** before and after treatment with ammonia gas; (b) UV-Vis absorption spectra of suspended **1a** and  $\text{NH}_3\text{-1a}$  in water.



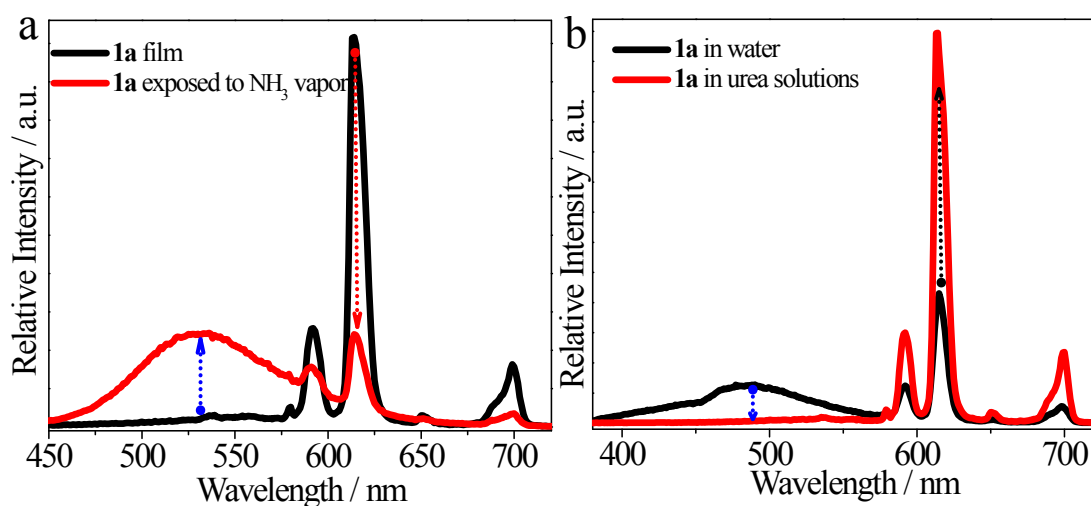
**Figure S11** (a) FT-IR spectra of **1a** before and after treatment with urea; (b) UV-Vis absorption spectra of suspended **1a** in water and urea solutions.



**Scheme S1** (a) Simplified schematic diagrams of ligand-to-Ln energy transfer in **1a**, the energy migration takes place upon ligand absorption, followed by intersystem crossing  $S_1 \rightarrow T_1$  and antenna  $T_1 \rightarrow f$  transfer, and then generating f-f emissions of Ln; (b, c) the influence of ammonia and urea on the ligand-to-Ln energy transfer.



**Figure S12** (a) The emission spectra of **1** before and after exposed to ammonia gas; (b) The emission spectra of **1** suspended in water and urea solutions ( $\lambda_{\text{ex}} = 338$  nm).



**Figure S13** (a) Emission spectra of **1a** film before and after exposure to ammonia gas ( $\lambda_{\text{ex}} = 338$  nm); (b) Emission spectra of **1a** suspension in the absence and presence of urea ( $\lambda_{\text{ex}} = 338$  nm).