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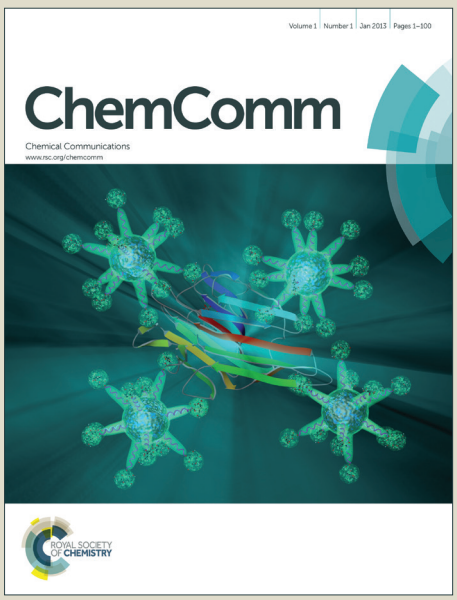

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COMMUNICATION

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A lanthanide-functionalized MOF with extremely high water toleration was developed as a fluorescent probe for hippuric acid (HA) in urine which is considered as the biological indicators of toluene exposure. For the first time, the urinary HA was detected by fluorescence spectrometry based on a recyclable Ln-MOF sensor.

Urine can reflect physiological and biochemical parameters, urine constituents' measurements as evaluation of Biological Exposure Indices (BEIs) are used in several fields of occupations. Among them, urine hippuric acid (HA) that is the ultimate and major metabolites of toluene is considered as the biological indicators of toluene exposure. This is because approximately 80 % of the inhaled toluene is excreted in urine as HA and the urinary concentration of HA is proportional to the level of toluene exposure.[1] Toluene is a broadly applied solvent for chemical synthesis, paints, detergents, adhesives, thinners, rubbers, silicone sealants and many chemicals, however, it is toxic. Those who are chronically exposed to toluene have been found to suffer from anatomical changes in the brain and neurobehavioral impairments.[2] Therefore, simple monitoring of exposure to toluene is very important in occupational health care. However, because of the heterogeneous factors of individuals, monitoring the environmental toluene could not accurately estimate people's real intoxication level. Therefore, it is more significant to determine the concentration of toluene's metabolites (HA) in human body, which could better reflect the real toluene exposure and intoxication of human beings.

Urinary HA concentration is usually measured by enzyme linked immunosorbent assay (ELISA), gas chromatography (GC), or high performance liquid chromatography (HPLC).[3] Drawbacks associated with these methods include expensive equipment and chemicals, complicated procedures, trained technicians, and considerable time. To overcome these limitations, a simple, precise, low-cost and eco-friendly method for real-time monitoring of HA in human urine was put forward in this paper. A fluorescent sensor based on a lanthanide mental-organic framework (Ln-MOF) was developed for qualitative and quantitative detection of urinary HA. To date, luminescent probes based on Ln-MOFs were mainly used to recognize the following types of targets: (1) cations, such as Fe^{3+},[4] Al^{3+},[4a,5] Cu^{2+},[6] Zn^{2+},[7] Cd^{2+},[8] Hg^{2+},[9] and Ag^{+};[10] (2) anions, like F^{-},[11] CrO_4^{2-},[11b,12] and PO_4^{3-};[13] (3) small molecules, including DMF,[14] acetone,[14b,c] cyclohexane,[15] and nitroaromatic explosives;[16] (4) others, including humidity,[17] temperature,[18] and pH.[19] Nevertheless, to our best knowledge, Ln-MOFs as sensors for urinary HA have never been explored.

In this contribution, a new method based on a fluorescent sensor for determination of urinary HA was reported. A Eu-functionalized MOF with extremely high water toleration was presented as a highly selective and sensitive luminescent probe for HA. The sensor for detection of HA simultaneously realized easy preparation, short response time, broad linear range and quick regeneration. The above excellent performances of the sensor make it capable of determining HA in human urines with recoveries in the range of 93.5 % – 102.9 %. For the first time, the urinary HA was detected by fluorescence spectrometry based on a recyclable Ln-MOF sensor.

MIL-121 (**1**) was generated from a carboxyl-rich ligand of 1,2,4,5-benzenetetracarboxylic acid (H_4btec) and $Al(NO_3)_3{\cdot}9H_2O$ under hydrothermal conditions. The resulting white solid shows an identical PXRD pattern to that simulated from the single crystal structure (Figure 1A), as well as the previously reported work,[20] validating compound **1** was successfully synthesized. The three dimensional framework with one-dimensional channels of **1** is constructed by bridging H_4btec linkers with infinite trans-connected aluminium-centered octahedral $AlO_4(OH)_2$. It is noteworthy that compound **1** not only possesses permanent porosity (BET surface area: 181 m^2/g, Figure 1B) but also contains two uncoordinated carboxyl groups on a ligand (IR, Figure S1, $\upsilon_{free\ C=O}$: 1715 cm^{-1}). The two features of **1** encourage us to employ it as a host to encapsulate Ln^{3+} ions. Through soaking of the freshly prepared samples in ethanol solutions of europium chloride, Eu^{3+} ions were

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† Electronic Supplementary Information (ESI) available: Experimental section; IR spectra; XPS spectra; ICP data; PXRD patterns; TGA curves and other luminescence

introduced into the channels of **1**, yielding Eu^{3+}**@1** (Figure 1C). The XPS and ICP-MS analysis of Eu^{3+}**@1** proved the successful loading of

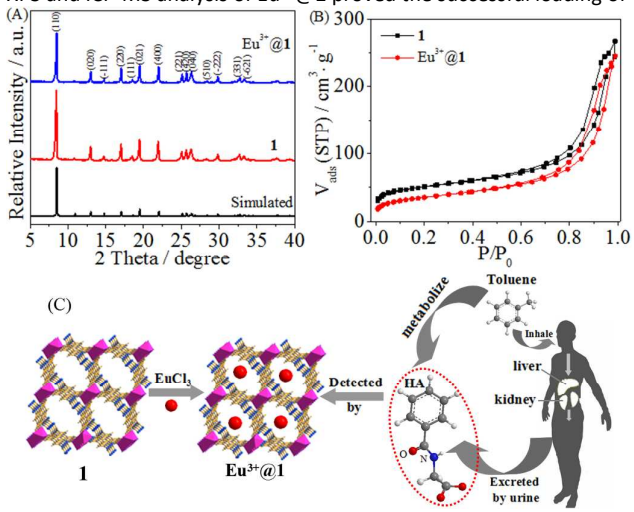

Figure 1 (A) PXRD patterns of simulated **1**, as-synthesized **1**, and Eu^{3+}**@1**; (B) N_2 adsorption-desorption isotherms of **1** and Eu^{3+}**@1**; (C) Schematic representation of the fabricated Eu^{3+}**@1** as a fluorescent sensor for urinary HA.

Eu^{3+}. As shown in Figure S2, the O 1s peak from free carboxylic oxygen atoms at 529.0 eV in **1** is shifted to 529.9 eV in Eu^{3+}**@1**, indicating the Eu^{3+} cations coordinate with the free carboxyl on the ligands of **1**.[12,21] The coordination of Eu^{3+} to the free carboxyl only weakens the absorption band of free C=O at 1715 cm^{-1}, and the remaining absorption band of free C=O implies the existence of uncoordinated carboxyl in Eu^{3+}**@1** (Figure S1). The Eu^{3+} loading level in **1** was quantified by ICP-MS measurement (Table S1), which shows the molar ratio of Eu^{3+}/Al^{3+} is 1.6. The SEM mapping (Figure S3) demonstrate Eu are homogenously distributed in Eu^{3+}**@1**. The reduced BET surface area of Eu^{3+}**@1** (125 m^2/g, Figure 1B) causing by the steric hindrance of the Eu^{3+} cations within the channels also suggests the successful encapsulation of Eu^{3+}. The successful Eu^{3+} loading does not influence the crystalline integrity and thermostability of **1**, as demonstrated by PXRD (Figure 1A) and TGA (Figure S4).

The successful formation of Eu^{3+}**@1** was also confirmed by spectroscopic studies. Upon excitation at 315 nm, Eu^{3+}**@1** exhibited characteristic sharp emissions of Eu^{3+} at 579, 592, 614, 650, and 695 nm (Figure S5). Under irradiation of a UV lamp, Eu^{3+}**@1** emitted a distinctive red color, which could be regarded as a qualitative indication of Eu sensitization. In addition, the intraligand emission of the framework (330 – 450 nm, Figure S6) in Eu^{3+}**@1** is suppressed by the energy transfer from ligand to Eu^{3+} ions. These results demonstrate that the framework, which possesses electron-conjugated systems that bind with the Eu^{3+} cations, is good chromophores for the efficient luminescent sensitization of Eu^{3+} cations. In this case, the Eu^{3+}**@1** can be utilized as an excellent candidate for luminescent sensors.

Urine can reflect physiological and biochemical parameters, and thus urine constituents' measurements are especially important to human. To be a qualified fluorescent sensor for specific urine component, water toleration is essential to Eu^{3+}**@1**. Therefore, its stability in water was investigated. As shown in Figure S7, after several days' storage in water, the PXRD and the fluorescence intensity of Eu^{3+}**@1** have no obvious changes,

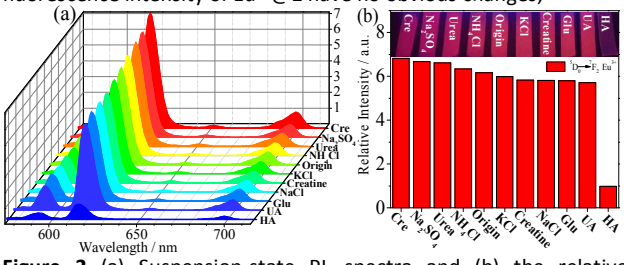

Figure 2 (a) Suspension-state PL spectra and (b) the relative intensities of $^5D_0 \rightarrow {}^7F_2$ at 614 nm for Eu^{3+}**@1** dispersed in various metal ions aqueous solutions (10 mM) (λ_{ex} = 315 nm). Inset in (b): the corresponding photographs under 254 nm UV-light irradiation

indicating its water toleration is extremely high. The Eu^{3+}**@1** also exhibit good pH-independent luminescence and structure stability in the range of urine pH value (4 – 8), as proved in Figure S8. The good ability to be compatible with aqueous environment makes Eu^{3+}**@1** competent for a fluorescence sensor of specific urine component.

The ingredients of human urine mainly include H_2O, creatinine (Cre), creatine, urea, uric acid (UA), hippuric acid (HA), SO_4^{2-}, Na^+, K^+, NH_4^+, Cl^- or glucose (Glu). Hence, in chemistry, urine could be defined as water solutions containing various chemicals. Urinalysis, essentially, is the detection of such chemical substances. Therefore, to obtain insight into the sensing properties of Eu^{3+}**@1** toward urine, these various chemicals mainly included in urine have been introduced to the system of Eu^{3+}**@1**, respectively. The Eu^{3+}**@1** is insoluble and stable in these various chemicals' aqueous solutions, confirmed by the PXRD (Figure S9). The suspension-state luminescent measurements were recorded and compared in Figure 2. The results clearly show that only HA induced a remarkable reduction (84 %) of luminescence intensity of Eu^{3+}**@1** at 614 nm. However, under identical conditions, nearly no fluorescence intensity changes were observed in emission spectra of Eu^{3+}**@1** with other urine chemicals. In accordance with the changes in fluorescence spectra, under the irradiation of a UV lamp, only HA incorporated Eu^{3+}**@1** shows a significantly darker luminescence than that from the original one, which could be distinguished easily by naked eyes (inset of Figure 2b). The results indicated the high selectivity of Eu^{3+}**@1** towards HA in aqueous media. The quenching effect of HA on the luminescence intensity of Eu^{3+}**@1** has been further examined by emission lifetime studies of Eu^{3+}. As shown in Table S2, the lifetime of Eu^{3+}**@1** is greatly reduced from 176 μs to 76 μs in the presence of HA, while other urine chemicals have no significant effects on the emission lifetimes of Eu^{3+}. This agrees well with the luminescence responses of Eu^{3+}**@1** towards various urine components.

Since the chemicals (Cre, creatine, urea, Glu, UA, HA, SO_4^{2-}, Na^+, K^+, NH_4^+ and Cl^-) are coexisting in urine, achieving high selectivity toward HA over the other competitive species is a very important feature to evaluate the performance of the sensor. Therefore, competition experiments were conducted. Figure 3A shows that when HA was added into the solution of Eu^{3+}**@1** with excess amount of other urine chemicals, the intensity change at 614 nm displayed a similar pattern to that with HA only. This suggests the

quenching effect of HA on the emission of Eu^{3+} is not influenced by the coexisting components, further confirming that Eu^{3+}**@1** could act as a highly promising sensor for HA.

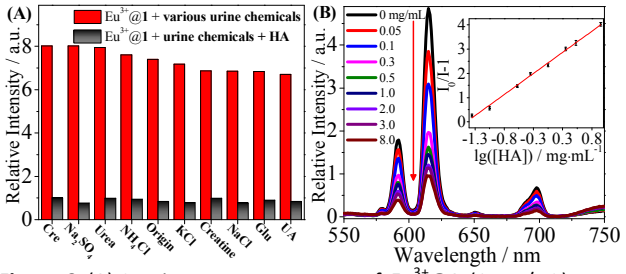

Figure 3 (A) Luminescence responses of Eu^{3+}**@1** (1 mg/mL) upon the addition of HA (0.01 M) in the presence of background of various urine chemicals (0.02 M) in aqueous solution (λ_{ex} = 315 nm); (B) The luminescence spectra of Eu^{3+}**@1** in the presence of different concentrations of HA aqueous solutions (λ_{ex} = 315 nm), and the Plot of $I_0/I - 1$ versus the logarithm of the concentration of HA.

A temporal scan of the fluorescence intensity of Eu^{3+}**@1** at 614 nm after adding HA was carried out to examine the response time of Eu^{3+}**@1**. As shown in Figure S10, the fluorescent emission gave a sharp reduction immediately after HA addition and levelled off in 10 minute, showing the fast response rate of the method.

Referring to American Conference of Governmental Industrial Hygienists (ACGIH), the cutoff concentration of HA in urine was determined to be 2 mg/mL, which means that people whose urinary HA level was more than 2.0 mg/mL would be a toluene sniffer.[1b,22] To evaluate the sensitivity of Eu^{3+}**@1** toward HA, fluorescence titration experiments were carried out (Figure 3B). It is observed that the emission intensity of in Eu^{3+}**@1** at 614 nm gradually decreased with increasing HA concentration. A good linear relationship (R = 0.997) is found between the emission intensity ratios ($I_0/I - 1$) and the logarithm of HA concentration over the range from 0.05 to 8 mg/mL ($I_0/I - 1 = 2.427 + 1.736$ lg[HA]). The limit of detection (LOD) determined following the 3σ IUPAC criteria,[23] is 9 ug/mL, which is sufficient for detection of millimolar concentrations of HA in urine. The relative standard deviation for six repetitive measurements of Eu^{3+}**@1** suspensions containing 0.5, 1.0, and 8.0 mg/mL HA is 2.1 %, 1.9 %, and 1.89 %, respectively, indicating the good reproducibility of the fluorescence response and the proposed method is stable and reliable (Figure S11).

Considering that it is necessary for a newly designed sensor to evaluate its analytical efficiency and accuracy in practical applications, the real urine samples were determined before and after being spiked HA. As summarized in Table S3, all HA quantity measured by the sensor was close to the total amount of background and spiked HA. All the recoveries are more than 90 %, indicating that the proposed method can be used to quantitatively and accurately detect HA in human urine. Therefore, we further applied the developed method to determine the urinary HA concentration in thirty human urines offered by the volunteers from the undergraduate students in Tongji University. Of the 30 individuals invited to participate in the study, half are organic chemistry researchers who are frequently exposed to toluene, and the rest are non-exposure individuals. The distribution diagrams of HA levels in the non-exposed and exposed individuals were depicted in Figure 4. The average level of HA in non-exposed urine specimens determined by the sensor was 0.366 ± 0.243 mg/mL, which is consistent with the previously reported work.[22b] The HA

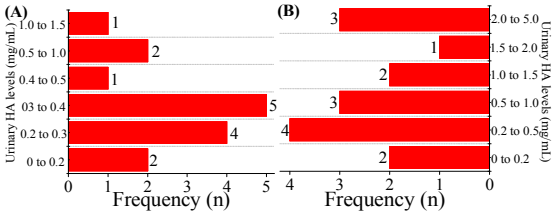

Figure 4 Distributions of HA concentration in the urines of non-exposed (A) and exposed (B) individuals.

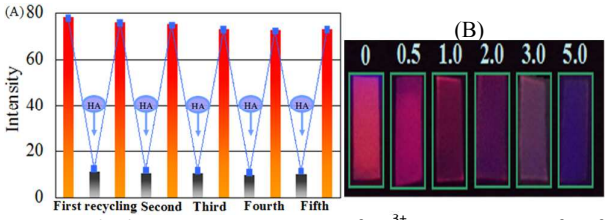

Figure 5 The luminescence intensity of Eu^{3+}**@1** at 614 nm after five recycles. (λ_{ex} = 315 nm); Optical images under 254 nm UV-light irradiation of the test paper after immersing into urines with different concentrations (mg/mL) of spiked HA for 1 min.

level in the 15 studied organic chemistry researchers varied from 0.19 to 4.3 mg/mL (Figure 4B). Among the analysis results of specimens, three of them turned out to be positive (HA level > 2.0 mg/mL), indicating these three students have high probability of being toluene sniffers.

The regenerable performance for a sensor plays an important role in its applications. Herein, to investigate the recyclable performance of Eu^{3+}**@1**, we attempted to disperse Eu^{3+}**@1** in an aqueous solution of 10^{-2} M HA for 2 minutes, and then the sample was centrifuged, ultrasonically washed with water for three times. As shown in Figure 5A, after the fluorescence reduction induced by HA, the following ultrasonic washing would make the fluorescence intensity recovers to the level before HA addition. Five runs performed by sequential addition of HA and ultrasonic washing, the luminescent intensity (Figure 5A) and PXRD (Figure S12) of the recycled Eu^{3+}@1 are well consistent with that of the original one, suggesting that Eu^{3+}**@1** could be reused to detect HA. Additionally, the fast and simple regeneration method also implies that the interaction between Eu^{3+}**@1** and HA should be weak and the luminescence of Eu^{3+}**@1** recovered by ultrasonic washing is due to the removal of HA.

All the above results demonstrate that the newly designed method is suitable for analysis of HA in human urine. In order to make the detection more simple and portable, a fluorescent test paper for rapid detection of urinary HA was developed. The test paper was prepared by dropping the dispersion of Eu^{3+}**@1** in ethanol on a filter paper (1 × 2.5 cm^2) and drying it at room temperature. For the detection of HA in urine, the test paper was immersed in urine samples with different concentrations of HA for 1 min and then exposed to air for drying. As shown in Figure 5B, under the irradiation of UV light of 254 nm, the fluorescent colors of the test paper changed from bright red to dark red, faint red and finally black as soaked in 0.5, 1.0, 2.0, 3.0 and 5.0 mg/mL of HA

spiked urines. To the naked eyes, one can distinguish the colors of different intensities, thus judging the degree of toluene intoxication.

The mechanism for such quenching effects of HA on Eu^{3+}@**1** could be ascribed to the following reasons: i) Both the shortened emission lifetime (Table S2) and the variation of intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ of HA-Eu^{3+}@**1** (Figure S13) indicate that HA weakly coordinated to Eu^{3+} sites.[14b,24] This increases the non-radiative deactivations through the vibrations of HA (such as N-H) and leads to the reduction of luminescence, as evidenced by the decreased lifetime of HA-Eu^{3+}@**1**.[24] ii) Due to the intermolecular interactions between ligands and HA (such as hydrogen bond and π–π stacking),[15,16] the energy absorbed by the ligand could be transferred to the HA molecules, which will decrease in the efficiency of intersystem crossing $^1\pi\pi^* \rightarrow {}^3\pi\pi^*$ and thus reduce the efficiency of ligand to Eu energy transfer, resulting in the quenching effect on the luminescent intensity of Eu^{3+}. As proved by Figure S14, the emission band of H_4btec within Eu^{3+}@**1** is located from 330 to 450 nm, which is largely overlapped with the excitation band of HA (350−376 nm), suggesting that energy transfer is happened between the ligands and HA.[25] What's more, the emission of HA is red shifted relatively to that of compound **1**, which also benefits the non-radiative process and reduce the fluorescent intensity.

In summary, the Eu-loaded MOF with extremely high water toleration have been developed as a stable fluorescent sensor for the detection of HA. The fabricated sensor for HA has several appealing features, including high sensitivity, excellent selectivity, fast response time (~ 1 min), broad linear range (0.05 ~ 8.0 mg/mL), and good reversibility and regeneration. More significantly, this sensor has been successfully applied to determination of HA in human urines with recoveries in the range of 93.5 % − 102.9 %. Compared with the reported method for detecting urinary HA, this approach offers unique advantages of low cost, easy preparation and operation, eco-friendly, time saving and high accuracy. Therefore, the excellent performances of the proposed method based on the fluorescent sensor make it promising for point-of-care (POC) diagnosis of urinary HA in people occupationally exposed to toluene.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (91122003), Developing Science Funds of Tongji University and Science & Technology Commission of Shanghai Municipality (14DZ2261100).

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