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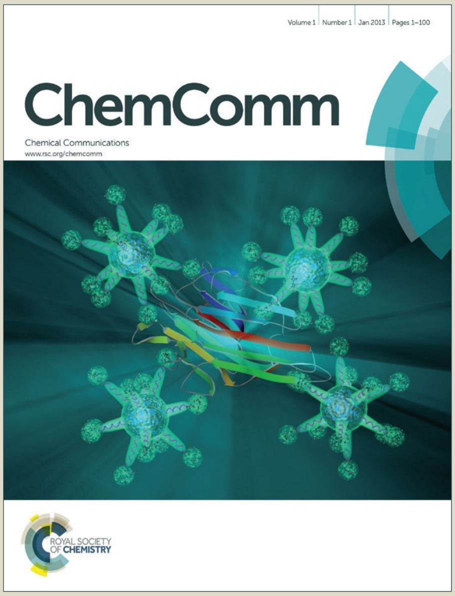

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COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

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

Ji-Na Hao, Bing Yan*

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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A highly selective and sensitive fluorescent sensor for Cd^{2+} in aqueous solution based on a lanthanide post-functionalized metal-organic framework was developed.

Among various heavy metal ions, cadmium (II) is one of the most dangerous ions due to its high toxicity and carcinogenicity.[1] It is widely used in many fields, such as industry, agriculture, military affairs, etc.[2] These sources lead to high level of cadmium exposure and contamination. Further, toxic Cd^{2+} can be easily absorbed and accumulated in plants and other organisms. This may result in serious diseases and even certain forms of cancers.[3] Bearing in mind the elevated risks related to human health, qualitative and quantitative detection of cadmium can be considered to be an aspiration of primary importance.

Various analytical techniques [4] such as atomic absorption spectrometry, inductively coupled plasma mass spectrometry, and synchrotron radiation X-ray spectrometry have been developed for determination of Cd^{2+}. However, these analytical methods are often restricted by complicated sample preparation, sophisticated instruments and high cost. Thus, it is of great significance to develop a simple and sensitive method for Cd^{2+} detection. Recently, fluorescent sensors have been considered as some of the promising and compelling devices for sensing metal ions because of their abilities to provide a simple, sensitive, selective, precise, and economical method for online monitoring without any pretreatment of the sample together with the advantages of spatial and temporal resolution.[5] Among fluorescent chemosensors, of particular interest are luminescent lanthanide-organic frameworks (Ln-MOFs) because their brilliant optical properties originating from the 4f electronic configuration of lanthanides make them especially attractive for application in luminescent probes.[6] In the past decade, studies on luminescent Ln-MOFs for sensing various chemical species, including Ag^+,[7] Cu^{2+},[8] H^+,[9] CrO_4^{2-},[10] halide ions,[11] acetone,[8b,10,11b,12] explosives, proteins and so on, have been developed significantly. Nevertheless, there are very few reports on the use of Ln-MOFs for the detection of Cd^{2+}. Besides, it is still a great challenge to rationally design and synthesize the desired Ln-MOFs because of the higher coordination numbers and more flexible coordination geometry of Ln^{3+}.[13] Many recent developments in the study of MOFs such as the postsynthetic modification (PSM) have become both an active area of research and an important tool for exploiting and expanding their unique properties.[14] PSM of MOFs, whose chemical modification was performed on the fabricated material rather than on the molecule precursors, provides an alternative to construct Ln-MOFs. In the past years, an increasing number of excellent advancements in the area of PSM of MOFs have been made.[15] Such progress inspires and guides us to construct the desired Ln-MOFs for host-guest recognition and to tune their functional properties.

In this work, the facile yet versatile postsynthetic approach was utilized to fabricate a highly efficient luminescent Ln-MOF by encapsulating Eu^{3+} cations into the pores of Uio-66(Zr)-$(COOH)_2$ (**1**).[16] Its sufficiently porous structure and available functional groups (free carboxyl) on the ligand are amenable to coordination with metal cations. What's more, the Eu^{3+} incorporated crystals of **1** (Eu^{3+}@**1**) was developed as a fluorescent probe for Cd^{2+} and the sensor has features including simple preparation procedure, high selectivity, excellent sensitivity, and fast detection time. This is the first example for detecting Cd^{2+} in aqueous solution based on a lanthanide functionalized MOF.

The reactions of $ZrCl_4$ and H_4btec in water at 100 °C for 24 h produced a white solid of Uio-66(Zr)-$(COOH)_2$ (**1**). The experimental PXRD pattern of **1** synthesized in this study (Figure 1A) agrees well with the pattern simulated from Uio-66 single crystal structure, as well as the previous work,[16] validating that compound **1** was successfully synthesized. The structure of **1** is built up from a cluster of 6 Zr atoms ($Zr_6O_4(OH)_4$) which are interconnected by H_4btec ligands to form a three dimension framework with tetrahedral and octahedral cages. It is noteworthy that only two carboxylate arms of the H_4btec play the role of linker while the two remaining are non-bonded. Infrared spectroscopy (Figure S1) confirms this since the bands observed at 1715 cm^{-1} are assigned to the free –COOH functions. Compound **1** maintains its permanent pore after guest removal, as demonstrated by N_2 adsorption-desorption isotherm (Figure 1B) showing a BET surface area of 382 m^2/g. Because of the reactive nature of the uncoordinated carbonyl group and the sufficiently permanent porosity, Uio-66(Zr)-$(COOH)_2$ can be described as a typical PSM of MOFs. We therefore loaded the Eu^{3+} ions into the pores of **1** via PSM, yielding Eu^{3+}@**1**. The representative structure of Eu^{3+}@**1** is depicted in Figure 1C. The XPS and ICP-MS analysis proved the Eu^{3+} cations were successfully

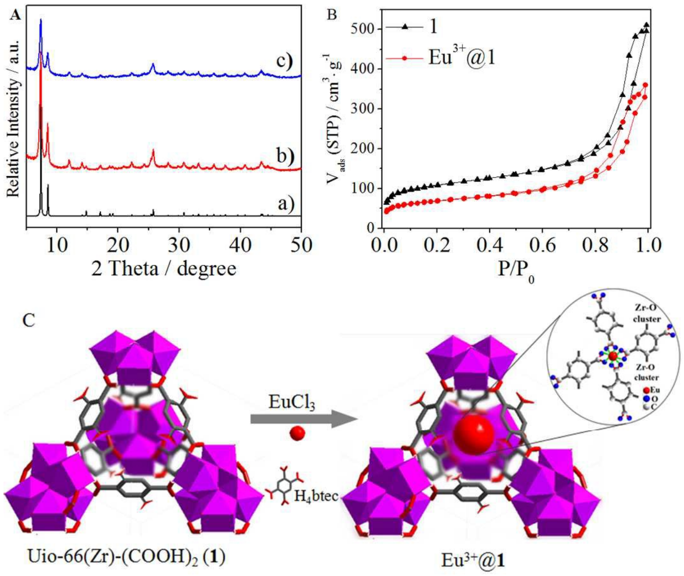

Figure 1 (A) PXRD patterns of a) simulated Uio-66, b) as-synthesized Uio-66(Zr)-$(COOH)_2$ (**1**), and c) Eu^{3+}@**1**. (B) N_2 adsorption-desorption isotherms of **1** and Eu^{3+}@**1**. (C) Synthetic scheme and representative structure of Eu^{3+}@**1**, the inset is schematic representation of Eu^{3+} tethered to the free carboxyl sites of **1.**

coordinated to the free carboxyl in the pores of **1**. As shown in Figure S2, the O 1s peak from free carboxylic oxygen atoms at 529.0 eV in **1** is shifted to 529.7 eV after functionalized by Eu^{3+} in Eu^{3+}@**1**, suggesting the existence of coordination interaction between Eu^{3+} cations and the uncoordinated carboxylic oxygen.[8b,10,17] The ICP measurement (Table S1) indicates the molar ratio of Zr^{4+}/Eu^{3+} is about 2, which suggests the formation of $0.5Eu^{3+}$@Uio-66(Zr)-$(COOH)_2$ (abbreviated as Eu^{3+}@**1**) and also demonstrates that four non-coordinating carboxyl groups are coordinated with one Eu^{3+} cation (inset of Figure 1C). The incorporation of Eu^{3+} ions does not influence the crystalline integrity and the thermostability of the framework, as confirmed by PXRD (Figure 1A) and TGA (Figure S3), respectively. The Eu^{3+}@**1** samples exhibit similar N_2 sorption behaviour with **1** (Figure 1B), but the BET surface area of Eu^{3+}@**1**, as expected, shows reduced values of 278 m^2/g, which is due to the steric hindrance of the Eu^{3+} cations within the channels.

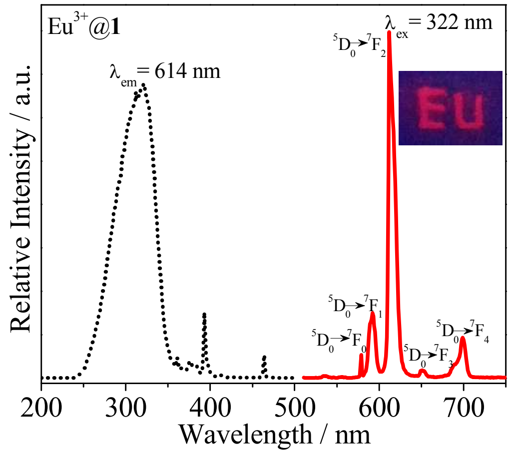

Figure 2 Excitation and emission spectra of Eu^{3+}@**1**. The inset is the corresponding luminescence picture under UV-light irradiation of 254 nm.

The successful formation of Eu^{3+}@**1** was also confirmed by spectroscopic studies. Compound **1** displays a wide emission band centered around 450 nm (Figure S4), which arise from $\pi \rightarrow \pi^*$ transitions of the ligands. After incorporating Eu^{3+} cations, the ligand-centered (LC) emission disappears, instead, the typical narrow-band emission of Eu^{3+} cations originating from the Eu(III) lowest emitting state $^5D_0$ to $^7F_0$ (578 nm), $^7F_1$ (591 nm), $^7F_2$ (614 nm), $^7F_3$ (650 nm) and $^7F_4$ (695 nm) levels emerges (Figure 2), indicating the successful encapsulation of Eu^{3+} inside the framework. The emission at 614 nm has the highest intensity, yielding an intense red color output under UV-light irradiation (inset of Figure 2). The diminished LC emission in Eu^{3+}@**1** and the strong red luminescence are the qualitative indications of lanthanide sensitization. Moreover, the long lifetimes (341.7 μs) and high quantum yields (20.5%) of Eu^{3+} in Eu^{3+}@**1** further supports the efficient energy transfer from the sensitizer embedded in the framework **1** (H_4btec) to the Eu^{3+} cations, as well as it can be an excellent candidate for luminescent sensors.

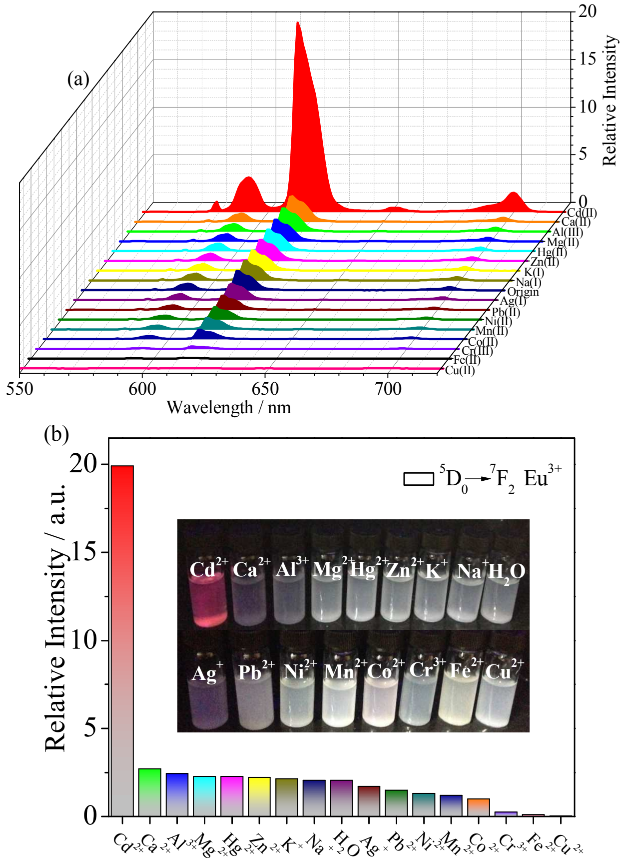

Figure 3 (a) Suspension-state PL spectra and (b) the relative intensities of $^5D_0 \rightarrow ^7F_2$ at 614 nm for Eu^{3+}@**1** dispersed in various metal ions aqueous solutions (10 mM) when excited at 322 nm. Inset in (b): the corresponding photographs under UV-light irradiation.

To examine whether the Eu^{3+}@**1** possess the potential as a fluorescent probe for metal ions in aqueous media, the structural and luminescent stability of Eu^{3+}@1 in aqueous solution have been investigated. The structure of Eu^{3+}@**1** is water-stable, as evidenced by the PXRD of the sample dispersed 24 h at 373 K in water (Figure S5). The fluorescence intensity of Eu^{3+}@**1** has no obvious change for at least 10 days' storage in water (Figure S6), implying that Eu^{3+}@**1** has excellent fluorescence stability. The good ability to be compatible with aqueous environment makes Eu^{3+}@**1** competent for fluorescence sensor in aqueous media.

In the light of the excellent luminescence and good water stability of Eu^{3+}@**1**, the Eu^{3+}@**1** has been developed as a luminescent sensor for metal ions. Different kinds of metal ions (K^+, Ca^{2+}, Na^+, Mg^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+}) have been introduced to the system of Eu^{3+}@**1**, and the Eu^{3+}@**1** is insoluble and stable in various metal ions' aqueous solutions, confirmed by the PXRD (Figure S7). The suspension-state luminescent measurements illustrated that various metal ions displayed markedly different effects on the luminescence intensity of Eu^{3+}@**1**. As shown in Figure 3, when in contact with Cr^{3+}, Fe^{2+} and Cu^{2+}, the luminescence of Eu^{3+} was almost quenched. By contrast, the interaction with Cd^{2+} drastically enhanced the luminescence intensity, with a maximum of more than 8.0 times as much as that of the original. The rest of the metal ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Hg^{2+}, Ag^+, Pb^{2+}, Ni^{2+}, Mn^{2+}, and Co^{2+}) had a negligible effect on the luminescence of Eu^{3+}. As a result, when irradiated under UV light, only Cd^{2+} could induce a red-colored luminescence which could be clearly seen by naked eye, while no visible change could be observed upon the addition of other metal ions (inset of Figure 3b). The above results indicate the high selectivity of Eu^{3+}@**1** for the sensing and specific recognition of Cd^{2+} in aqueous media. In addition, the effect of metal ions on the luminescence of Eu^{3+}@**1** was also evaluated by the fluorescence decay time of Eu^{3+}. Table S2 shows that metal ions except Cd^{2+} have a negligible or quenched effect on Eu^{3+} emission lifetimes of Eu^{3+}@**1**. However, in the presence of Cd^{2+}, the lifetime of Eu^{3+}@**1** increased from 0.18 ms to 0.76 ms. This agrees well with the luminescence responses of Eu^{3+}@**1** towards various metal ions.

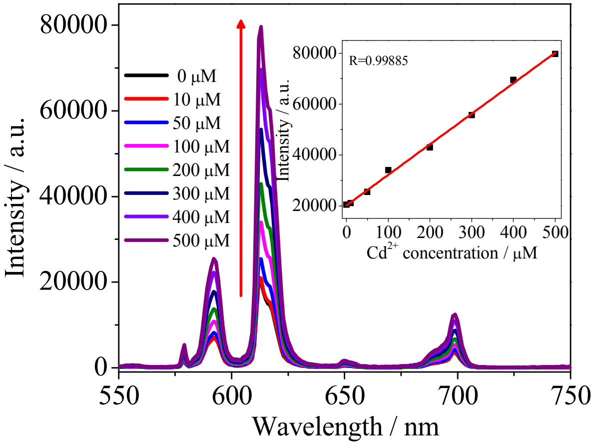

Figure 4 Fluorescence intensity of Eu^{3+}@**1** at 614 nm as a function of Cd^{2+} concentration in aqueous solution (λ_{ex} = 322 nm). Inset: linear relationship of the emission intensity of Eu^{3+}@**1** enhanced by Cd^{2+} ions.

We measured the fluorescence responses of Eu^{3+} @**1** in the presence of different concentrations of Cd^{2+}. As demonstrated in Figure 4, when Cd^{2+} concentration increased from 0 to 500 μM, the emission intensity of Eu^{3+}@**1** was gradually enhanced and a good linear relationship (correlation coefficient R = 0.99885) between the emission intensity of Eu^{3+} at 614 nm and concentration of Cd^{2+} was observed. From the slope of the fitting line (S) and the standard deviation for twenty replicating fluorescence measurements of blank solutions (S_b), the detection limit ($3S_b/S$) of Eu^{3+}@**1** towards Cd^{2+} was calculated to be 0.06 μM (Figure S8), which is comparable to that of well-designed organic compounds for Cd^{2+} ion sensing.[5a,18] Additionally, Cd^{2+}-induced fluorescence enhancement reaction is very fast. The emission intensity of Eu^{3+} ions at 614 nm has been increased to more than 7.0 times in 1 min and a constant value in 8 min (Figure S9). This response is much faster than that in the previous report (about 24 h or 72 h).[6d,6e] In order to evaluate the analytical efficiency of the sensor, the real samples, containing different concentrations of Cd^{2+} in tap water and lake water collected from Tongji University, were regularly analyzed by Eu^{3+}@**1**. As summarized in Table S3, all measured results from this PL sensor were close to the originally spiked Cd^{2+}, indicating that Eu^{3+}@**1** can be practically used to quantitatively detect Cd^{2+} in water samples.

It is well-known that the luminescent intensity of Ln^{3+} relies on the efficiency of "antenna effect" (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^{3+}).[19] If there is efficient intramolecular energy transfer, Ln^{3+} can be excited more effectively, producing an enhanced fluorescence of lanthanides. It has been reported that the addition of certain transition metal ions can lead to a more efficient intermolecular energy transfer from ligand to lanthanide ions.[20] Herein, the mechanism of luminescent enhancement induced by Cd^{2+} ions can be proposed that Cd^{2+} ions interact with the Lewis basic carboxylic oxygen sites within Eu^{3+}@**1** and facilitate the efficiency of energy transformation from ligands to Eu^{3+} ions. To confirm this hypothesis, X-ray photoelectron spectroscopy (XPS) was performed (Figure S10). The O 1s peak from Eu^{3+}@**1** at 529.7 eV is shifted to 530.1 eV with addition of Cd^{2+}, suggesting the coordination of Cd^{2+} to the carboxyl in Cd^{2+}-Eu^{3+}@1.[8b,10,17] Meanwhile, the ICP-MS analysis of Cd^{2+}-Eu^{3+}@**1** (Table S1) reveals the molar ratio of metal components Zr^{4+}, Eu^{3+} and Cd^{2+} is 8.2:3.5:1. The unchanged molar ratio of Zr^{4+}/Eu^{3+} suggests H_4btec could act as a linker to bridge Cd^{2+} and Eu^{3+} in Cd^{2+}-Eu^{3+}@**1**. The complexation of Cd^{2+} ions in Eu complexes results in a more efficient energy transition from ligand to Eu^{3+} for the following reasons: i) the coordination of Cd^{2+} can reduce various non-radiative deactivations and decrease energy loss, evidenced by the longer emission lifetime for Cd^{2+}-Eu^{3+}@**1** than Eu^{3+}@**1** (Table S2).[19b] This facilitates ligand-to-Eu energy transfer, and thereof benefits Eu emissions; ii) Cd^{2+} ion has heavy atom effect, which can promote intersystem crossing energy transfer (S1→T1) and thus lead to a more effective intramolecular energy transfer from ligands to Eu^{3+};[21] iii) Cd^{2+} has a d^{10} closed shell electronic configuration, in which d-d transitions are impossible. And the ligand-to-metal (Cd^{2+}) charge transfer (LMCT) will change the energy level of the excited state of the ligands, which makes the energy-matching between the ligands and Eu^{3+} more suitable, and thus result in a more efficient energy transfer from the ligands to Eu^{3+}.[22] The metal ions (Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.) with a unsaturated $d^{1\sim9}$ electron configuration, however, have low-lying metal-centered levels formed by their partially filled d-orbital, and the d-d transitions among these levels are non-emissive and lead to strong reabsorption, and thus usually weaken the luminescence of the Ln-MOFs.[23] The alkali and alkaline earth metal ions (such as Na^+, K^+, Ca^{2+} and Mg^{2+}) have saturated electron configuration and are not bound to free carboxyl group, they have no effect on the luminescence.[8c] Therefore, the enhanced emission intensity of Eu^{3+}@**1** upon Cd^{2+}-binding results from more effective intramolecular energy transfer from H_4btec ligand to Eu^{3+} ion.

In summary, compound **1** loaded with Eu^{3+} cations (Eu^{3+}@**1**) have been designed as a stable fluorescence sensor for detecting Cd^{2+} in aqueous solutions. This luminescent probe shows high selectivity for sensing Cd^{2+} in aqueous solution with about 8-fold enhancement in luminescence intensity of Eu^{3+}, excellent sensitivity with a detection limit of 0.06 μM, and fast response speed (~ 1 min). Moreover, it is capable of detecting Cd^{2+} in environmental water samples, indicating its high potential in practical application. The mechanism of Cd^{2+}-enhanced luminescence is ascribed to the coordination of Cd^{2+} to Eu^{3+}@**1** causing more effective energy transfer from H_4btec to Eu^{3+}. Comparing the reported examples of Ln-MOFs sensing for metal ions,[6c-d,8b-c,20a,] the present one shows several advantages, i.e. working in pure aqueous media rather than in organic solvents, possessing a lower detection limit and broader linear range, displaying higher selectivity over other cations, making it more potential for applying in daily life.

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).

Notes and references

Shanghai Key Lab of Chemical Assessment and Sustainability, Department of Chemistry, Tongji University, Shanghai 200092, China.
Fax: +86-21-65982287; Tel: +86-21-65984663;
E-mail: byan@tongji.edu.cn

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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