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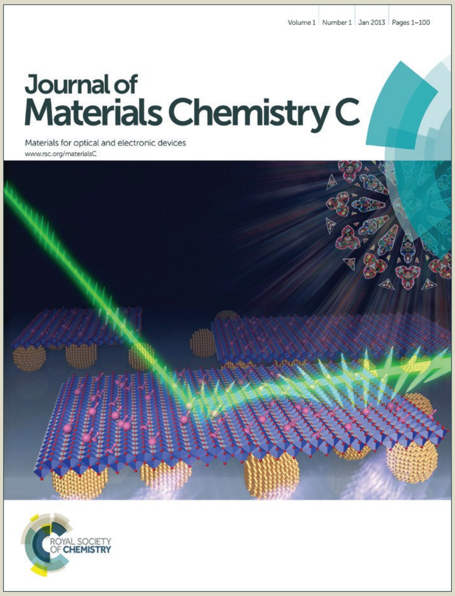

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ARTICLE

Fabrication and application of ratiometric and colorimetric fluorescent probe for Hg^{2+} based on dual-emissive metal-organic framework hybrids with carbon dots and Eu^{3+}

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A novel highly fluorescent hybrid (Eu^{3+}/CDs@MOF-253) has been synthesized based on metal-organic frameworks (MOFs) by encapsulating optical active carbon dots (CDs) and Eu^{3+}. The as-prepared fluorescent-functionalized MOFs not only maintain excellent optical properties of CDs and Eu^{3+} to give dual-emission but also have good stability in aqueous solution. It has been further used as a novel fluorescent probe for detecting of Hg^{2+}. The relative fluorescencen intensity ratio (I_{Eu}/I_{CD}) increases linearly with the increasing concentration of Hg^{2+} in the range of 0.065-150 μM with a detection limit of 13 ppb. The possible mechanism is discussed. This work represents a new approach for the fabrication of ratiometric and colorimetric Hg^{2+} fluorescent sensor, as it highlights the opportunity of exsting MOFs encapsulating CDs and sensitizing Eu^{3+}, simultaneously. In addition, removal of Hg^{2+} from its solution can also be achieved by the fluorescent MOF hybrids.

Introduction

The development of fluorescent sensors with high sensitivity and selectivity for some transition (Fe^{3+}, Cu^{2+}, Fe^{2+}) and heavy (Hg^{2+}, Cd^{2+}, Ag^{+}) metal ions has been of particular interest all the time.[1] Among them, mercury ions (Hg^{2+}) is attraction particular attention due to its significant threat to the environment and public health, such as Minamata disease.[2] The United Sates Environmental Protection Agency (EPA) standard for the maximum allowable level of Hg^{2+} in drinking water is only 2 ppb.[3] So the detection of Hg^{2+} concentration in the environmental monitoring system is very important and for household use, visual detection is a paramount goal. Until now, some Hg^{2+} sensors based on fluorescence detection method owing to its high sensitivity, portability, short response time and low cost[4] have been explored, mainly including three types: fluorescence enhancement ("turn-on")[5], fluorescence quenching ("turn-off")[6] and ratiometric fluorescence measurement[7]. Among all the detection method to Hg^{2+}, ratiometric sensing is preferable to turn-on and turn-off because it is several additional advantages.[8] A ratiometric fluorescence measurement can increase the selectivity and sensitivity of a measurement and eliminate most or all of the possible variability because the ratio of the fluorescence intensities at two wavelengths is independent of the concentration of the sensor, the fluctuation of the source light intensity, and the sensitivity of the instrument.[7] Although there are a few examples of ratiometric Hg^{2+} detectors have been documented,[7] colorimetric response to Hg^{2+} existing simultaneously is still relative backward. Therefore, the development of ratiometric and colorimetric fluorescent sensors for Hg^{2+} is of great current interest thing.

Metal-organic frameworks (MOFs), a class of crystalline hybrid materials formed from metal ions or clusters and organic linkers,[9] have received enormous attention in the last two decades due to numerous application.[10] Recently, significant progress has been made in the application of luminescent MOFs for chemical sensing, especially lanthanide luminescent MOFs (Ln-MOFs). And Ln-MOFs have been developed to detect metal ions,[1a,d] organic molecules,[1b] and explosives,[11] significantly. However, the sensing mode led by Ln-MOFs always shows "turn-on" or "turn-off" measurement and the detection limit to analytes is high due to the single emission band maybe. The efficient ligand-metal energy transfer (so-called "antenna effects") makes the Ln-MOFs long luminescence and high quantum yields[1a] by sensitizing sharp emission of lanthanide but also affects the intrinsic luminescence activities of MOFs then led to single emission band frequently.[1] And detecting Hg^{2+} using Ln-MOF is rather rare because of no obvious affect to its fluorescence could produce by Hg^{2+}. Therefore, introducing another luminescent materials whose optical property can be affected by Hg^{2+} into MOFs while basically maintaining the original structures and properties of host MOFs is an important alterative way to design desired Hg^{2+} sensor.

Most recently, an encapsulation strategy that allows several types of nanoparticles to be incorporated with crystals of MOFs has been developed.[12] It can combine the advantages of MOFs and nanoparticles. And recently emerging fluorescent carbon dots (CDs)

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have drawn the most extensive notice owning to their fascinating optical properties, chemical stability, biocompatibility and low toxicity.[13] Most importantly, Hg^{2+} can quench the fluorescence of CDs. Inspired by the previous work, we reported for the first time encapsulating CDs with strong fluorescence activity into MOF-253. The as-prepared CDs@MOF-253 not only remains the excellent optical properties of CDs but also can take on lanthanide ions (Eu^{3+}) to form dual-emissive Eu^{3+}/CDs@MOF-253. And to detect Hg^{2+}, Eu^{3+}/CDs@MOF-253 has been developed to a ratiometric and colorimetric fluorescent sensor, as expected, which shows its high sensitivity and selectivity. Our results also suggest that Eu^{3+}/CDs@MOF-253 shows its good adsorbent for Hg^{2+} removal.

Experimental Section

Materials and Reagents

All chemicals employed were of reagent grade and used without further purification. $AlCl_3·6H_2O$ (241.43 g·mol^{-1}) and 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2bpydc, 244.20 g·mol^{-1}) were purchased from Aldrich and used to synthesize Al(OH)(bpydc) (MOF-253). Citric acid and ethylenediamine were used to synthesize CDs. Europium chlorides were prepared by dissolving the Eu_2O_3 in excess hydrochloric acid (37.5%) followed by evaporation and crystallization. Aqueous solutions of Zn^{2+}, Ni^{2+}, Na^{+}, Mn^{2+}, Mg^{2+}, K^{+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, Ca^{2+}, Al^{3+}, Cr^{3+}, Co^{2+} were prepared from nitrate salts and solutions of Cd^{2+} and Hg^{2+} were prepared from chlorate salts, while Fe^{2+} solution was prepared from ferrous sulfate and used immediately.

Measurements

Powder X-ray diffraction patterns (PXRD) patterns were recorded with a Bruker D8 diffractometer under CuKa radiation and the data were collected within the 2θ in range of 5-50°. Transmission electron microscopy (TEM) and energy dispersive analysis by X-rays (EDX) were carried out on a JEOL JEM-2010F electron microscope equipped with an energy-dispersive X-ray spectrum (EDS, JEOL JXA-840) and operated at 200 kV. Fourier transform infrared spectra (FTIR) were recorded within KBr slices in the range of 4000–400 cm^{-1} using a Nexus 912 AO446 infrared spectrum radiometer. Nitrogen adsorption–desorption isotherms were measured at the liquid nitrogen temperature, using a Nova 1000 analyzer. The samples were outgassed for 3 h at 150 °C before the measurements. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. Luminescence excitation and emission spectra were examined by an Edinburgh FLS920 phosphorimeter. Luminescence lifetime measurements are carried out on an Edinburgh FLS920 phosphorimeter using a microsecond pulse lamp as excitation source. The data of life time is achieved from fitting the experiment luminescent decay. 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. The measurement of metal ion was performed on Agilent 7700X inductively coupled plasma-mass spectrometer (ICP-MS).

The detail and description of experiment

Preparation of carbon dots (CDs). CDs were prepared directly by a simple hydrothermal method according to the report.[14] In brief, citric acid (1.0507 g) and ethylenediamine (335 μL) were dissolved in 10 mL deionized water (DI-water) by stirring 30 mins. Then the reaction precursors were transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave (23 mL) and heated at 200 °C for 5 h. After the reaction, the reactors were cooled to room temperature by water or naturally to obtain the well-dispersed CDs aqueous solutions. Then the aqueous solutions were purified through a dialysis membrane (1000 MWCO) for 24 h. Dialysis here is used mainly to remove the small molecules in the as-prepared CDs solutions. Dry CDs were obtained by lyophilization of the remaining aqueous solution. It should be pointed out that the starting materials of CDs synthesis are non-toxic and environmentally friendly.

Preparation of Al(OH)(bpydc) (MOF-253).[15] The synthesis of MOF-253 nanoparticles were accomplished in the direct analogy with the microcrystalline MOF-253 products. A solution of $AlCl_3·6H_2O$ (151 mg, 0.625 mmol) and sodium acetate (123 mg, 1.5 mmol) in 10 mL N,N'-dimethylformamide (DMF) was placed in a 15 mL Pyrex tube containing H_2bpydc (153 mg, 0.625 mmol). After stirring for 30 mins, the precursor mixture was heated at 120 °C for 24 h. It's worth noting that the aim to introduce sodium acetate is to reduce the size of the product since sodium acetate can facilitate the deprotonation process of H_2bpydc ligands and enhance the nucleation rate of MOF-253. The resulting white powder was separated from the mixed dispersion by centrifugation and washed with DMF. To remove the organic species encapsulated within the pores of the open framework, the product was under vacuum for 6 h. EDX elements analysis: C, 51.2 wt%; N, 9.38 wt%; O, 30.44 wt%; Al, 8.98 wt% washed with methanol via soxhlet extraction for 24 h, followed by drying at 60 °C.

Preparation of CDs doped MOF-253 (CDs@MOF-253). For our method, CQDs wrapped inside ZIF-8 structures synthesized with $Zn(NO_3)_2·6H_2O$ and 2-methylimidazole were employed as an example to demonstrate our idea.[12a] CDs@MOF-253 composites were synthesized by the following synthetic route. The MOF precursors were prepared by mixing $AlCl_3·6H_2O$, sodium acetate and H_2bpydc in 10 mL DMF. The quantities of all materials can be found in the preparation process of MOF-253. Subsequently, 100 mg of as-synthesized CDs were added in and the solution was heated at 120 °C for 24 h after stirring for 30 mins. The obtained brown power was washed several times with DMF and DI-water. Then CDs@MOF-253 could be prepared after drying at 60 °C under vacuum for 6 h.

Preparation of Eu^{3+}/ CDs@MOF-253. The CDs@MOF-253 (50 mg) were added to a 75 mL Pyrex tube containing 50 mL ethanol solution of $EuCl_3·6H_2O$ (0.01 mol/L) and then the mixture was heated at 25 °C for 24 h. The resulting Eu^{3+}/ CDs@MOF-253 were washed with DMF and ethanol for several times to guarantee that all excess $EuCl_3·6H_2O$ is removed. Finally, the product was collected by centrifugation and dried at 60 °C under vacuum.

Detection and removal of Hg^{2+} in aqueous solution. The fluorescent detection of Hg^{2+} was performed at room temperature in DI-water. 3 mg of as-prepared Eu^{3+}/ CDs@MOF-253 and 3 mL of 100 μM aqueous solution of Hg^{2+} were added into a 4.0-mL centrifuge tube and then the mixture was shaken thoroughly and equilibrated for 5 min by ultrasound processing. For the experiments of sensing other metal ions (Zn^{2+}, Ni^{2+}, Na^{+}, Mn^{2+}, Mg^{2+}, K^{+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, Ca^{2+}, Cd^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+}, Co^{2+}), the same steps can be taken as Hg^{2+} detection.

5 mg of Eu^{3+}/ CDs@MOF-253 were added into 30 mL Hg^{2+} solutions with different concentrations (0-200 μM). After adsorption for pre-determined time, the supernatants were separated by centrifugation (12000 rpm, 3 min) and analyzed for the concentration of Hg^{2+} according to a the detection procedure. The adsorption capacity, q_e, for Hg^{2+} was calculated using the following equation: $q_e = (C_0 - C_e)/C_0$. C_0 (μM) and C_e (μM) is the initial and final concentrations of Hg^{2+}, respectively.

Preparation of the test plate based on the fluorescent sensor.[16] The test plate was prepared according to previous reports. Adding an appropriate amount of power of Eu^{3+}/CDs@MOF-253 (20 mg) to a 0.5 mL 0.5 % aqueous of carboxymethylcellulose sodium (CMC) and stirred into suspension. The resulting suspension containing Eu^{3+}/CDs@MOF-253 was added dropwise and tiled on a clean glass plate (1.5 x 3.0 cm^2).

Results and discussion

To demonstrate our strategy, we have prepared the CDs by a hydrothermal method (Fig. S1). The morphology and structure of CDs were confirmed by analysis. Fig. 1a exhibits the TEM image of the synthetic CDs, which can be seen to have a uniform dispersion without apparent aggregation and particle diameters of 1-5 nm. From the TEM image, most CDs particles are observed to be amorphous carbon particles. The amorphous state can also be testified by the XRD patterns of CDs which displayed a broad peak centered at 25° (0.34 nm) as shown in Fig. 1b.[17] EDX elements analysis revealed the composition of the CDs to C 58.64 wt%, N 10.22 wt%, and O 31.14 wt%, thus indicating these dots are carbon-rich nanodots. The surface functional groups (–OH, C=O, C-N(C=N), NH and CH) of the CDs are detected by FTIR (Fig. S2a).

The CDs are introduced into MOF-253 by one-pot procedure which mixes CDs and MOFs precursors. The resulting products are denoted as CDs@MOF-253. After CDs doped, the MOFs frameworks and nanoplate-morphology have been remained integrity according to PXRD and TEM measurements (Fig. 1c and Fig. 1d). FTIR spectroscopy (Fig. S2b) could be an anther evidence to prove this. In comparison to the strong peaks in PXRD (Fig. 1c) of the MOFs crystals, the peaks of CDs are not obviously found, presumably by virtue of their low concentrations and/or small sizes hosted by the MOFs matrix.[18] TEM image (Fig. 1d) clearly shows no obvious aggregated CDs embedded within the external surfaces of the MOFs, indicating that the entered CDs may penetrate the framework fully. Furthermore, a reduced BET surface area (S_{BET}) (386 m^2/g) can be find showing in Fig S3 when CDs were introduced into MOF-253 and the S_{BET} decreases with the increasing of CDs content added in. The results further confirm that the CDs are successfully embedded within MOF-253 to form CDs@MOF-253. Eu(III) post-functionalization of CDs@MOF-253 was soaking the solid in ethanol solution of chlorine salts of Eu^{3+}. The ICP-MS analysis of the resulting products (Al^{3+} : Eu^{3+} = 1 : 0.65) indicated successful Eu^{3+} incorporation into CDs@MOF-253 framework to obtain Eu^{3+}/CDs@MOF-253, which could be proved by the significant lower of BET surface from 386 m^2/g of CDs@MOF-253 to 207 m^2/g of Eu^{3+}/CDs@MOF-253. And the SEM mapping (Fig. S4) demonstrates Eu^{3+} are distributed homogenously in CDs@MOF-253. Moreover, Eu^{3+}/CDs@MOF-253 consistently matches its PXRD pattern and TEM image with MOF-253 shown in Fig. 1c and Fig. 1e.

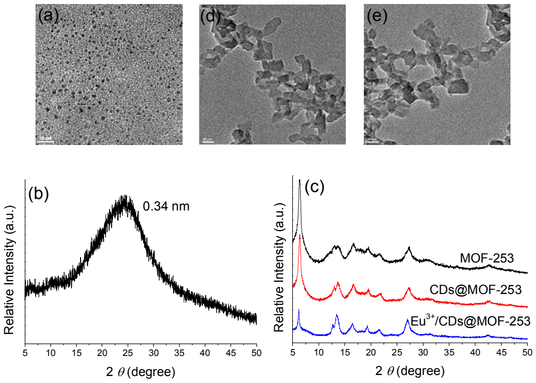

Fig. 1 (a) TEM image (scale bar: 10 nm) and (b) PXRD pattern of as-prepared CDs; (c) PXRD patterns of MOF-253, CDs@MOF-253 and Eu^{3+}/ CDs@MOF-253; TEM image (scale bar: 50 nm) of CDs@MOF-253 (d) and Eu^{3+}/ CDs@MOF-253 (e).

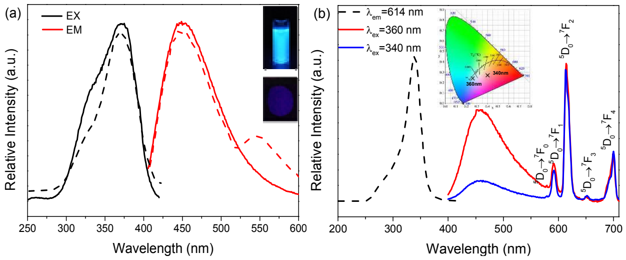

Fig. 2 (a) Room temperature excitation and emission spectra of CDs@MOF-253 in aqueous solution (solid line) and solid state (dash line) and corresponding photographs under UV light irradiation at 365 nm; (b) the excitation (λ_{em}=614 nm) and emission spectra of Eu^{3+}/CDs@MOF-253, λ_{ex}=360 nm (red) and λ_{ex}=340 nm (blue). The inset of b is CIE chromaticity diagram of Eu^{3+}/CDs@MOF-253 at different excitation wavelength.

Successful formation of CDs@MOF-253 and Eu^{3+}/CDs@MOF-253 were also confirmed by spectroscopic studies. As shown in Fig. S5a, when excited at 360 nm, the dilute aqueous solution of CDs exhibited broad emission peaks centered on 453 nm, thus leading to strong blue fluorescence (PL) emission. The bright blue PL of CDs aqueous solution can be observed by naked eyes under the illumination of a 365 nm UV light lamp (top of Fig. S5b). The as-prepared CDs@MOF-253 aqueous solution also emits strong blue PL (453 nm) under the excitation of 360 nm (Fig. 2a). Compared to that of simple MOF-253 (Fig. S6), the profile of the normalized PL emission spectrum of CDs@MOF-253 is almost the same as that of CDs, which is indicating that the optical properties of CDs in MOF-253 have not been changed. It should be noted here that the PL mechanisms of CDs are very complicated and sill argumentative. However, more and more evidence indicates the surface states of CDs could be mainly held responsible for their PL properties.[19] This result suggests that the surface states of CDs are well maintained when they are encapsulated in MOF-253. Moreover, as we all known that due to the aggregation effect of CDs, PL quenching was observed in their power samples (bottom of Fig. S5b).[14] Nonetheless, after incorporated CDs into MOF-253, blue light emission can also be founded when the samples have been dried (Fig. 2a). This obvious difference result indicates MOF-253 could be an ideal host materials to make the molecular level dispersion of CDs and prevent them aggregation, which extends its application in solid state of this material. After the post-synthetic incorporation of Eu^{3+}, as expected, the product simultaneously shows both the CDs-centered emission (I_{CD}) and characteristic sharp emissions of Eu^{3+} originating from the Eu(III) lowest emitting state $^5D_0$ to $^7F_0$, $^7F_1$, $^7F_2$ (I_{Eu}), $^7F_3$, $^7F_4$ (Fig. 2b). The excitation spectrum of Eu^{3+}/CDs@MOF-253 is obtained by monitoring the emission at 614 ($^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}), which is dominated by a broad band centered at about 340 nm. When changing excitation wavelength from 340 to 360 nm, the intensity ratio of I_{Eu} to I_{CD} makes a big difference can be observed from color variance in CIE chromaticity diagram (inset of Fig 2b): 6.5 for λ_{ex}=340 nm and 1.5 for λ_{ex}=360 nm. However, noting is changing in the characteristic emission of CDs and Eu^{3+} with the change of excitation wavelength. Then we can draw such a conclusion: MOF-253 has been an excellent choice for dispersing CDs and sensitizing Eu^{3+}, which leads to the material possessing dual-emitting characteristics for ratiometric PL sensing. In addition, the long lifetime (0.414 ms) and high quantum yield (42.3 %) of the sample support it can be utilized as excellent candidates for PL sensors.

To investigate the stability, PL intensity of Eu^{3+}/CDs@MOF-253 solution under extreme pH and water environment was measured. As shown in Fig. S7a, the PL of the Eu^{3+}/CDs@MOF-253 is stable in a wide range of pH values (4-9). Furthermore, it is found that the Eu^{3+}/CDs@MOF-253 still exhibit good photostability when stored at room temperature for about 9 days (Fig. S7b). These results reveal Eu^{3+}/CDs@MOF-253 has good structural stability (Fig. S7C) and photostability in aqueous solution, which possess great potential in the actual sensing application.

As mentioned above, the functional groups (oxygenated and nitrous) in surface of as-prepared CDs have be an important factor to produce PL and they can chelate with meal ions (especially, Hg^{2+}) to form stable chelate complexes.[20] Hg^{2+} is adsorbed onto the surface of CDs as a surface modifier and coordinated with the organic functionsl groups, which can change the surface traps or electron-hole recombination annihilation via electron or energy transfer process.[6] Therefore, the fluorescencen of CDs could be quenched efficiently. Combined with brilliant optical properties of lanthanides, we hope Eu^{3+}/CDs@MOF-253 will possess better fluorescence sensing properties for Hg^{2+} detection. Then the feasibility of Hg^{2+} detection was explored. As shown in Fig. 3a,

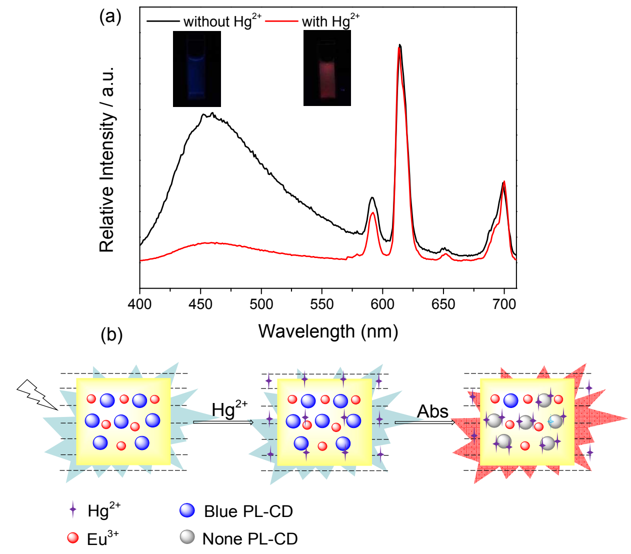

Fig. 3 (a) PL emission spectra of the Eu^{3+}/CDs@MOF-253 in the absence (blue line) and presence (red line) of 100 μM Hg^{2+} when excited by the wavelength of 360 nm and corresponding photographs under UV light irradiation at 365 nm; (b) Schematic illustration of the Hg^{2+} detection mechanism using Eu^{3+}/CDs@MOF-253.

Eu^{3+}/CDs@MOF-253 solution in the absence of Hg^{2+} exhibits both characteristic emission of CDs and Eu^{3+} (I_{Eu}/I_{CD}=1.5), which gives a faint blue light. In contrast, the composite shows a specific and visible colorimetric response to Hg^{2+} (I_{Eu}/I_{CD} =10.9), where the solution changes from blue to red under UV light, corresponding to the quenching of the CDs emission (curve red in Fig. 3a). And Fig. S8 reveals the changing process efficiency reaches a constant value within 4 min after the addition of Hg^{2+} (100 μM), which indicates that the response kinetic fairly fast. The phenomenon may be due to Hg^{2+}-induced the surface modifier of CDs through coordinated with the organic functional groups.[21] Then less affect to emission of Eu^{3+} in Eu^{3+}/CDs@MOF-253 leads to the colorimetric and ratiometric fluorescence Hg^{2+} sensor. The UV-vis absorption spectra can also demonstrate that. As shown in Fig. S9, the as-prepared CDs solution gives an UV-vis absorption with a peak at *ca*. 230 nm from the $\pi \rightarrow \pi^*$ transition of the aromatic sp^2 domains.[22] Compared with previous studies, in which the adsorption peak was generally found at 235 nm, this blue-shifted absorption peak suggests an increased number of hydroxyl and carboxylic groups on the surface of CDs.[6d] Also, one stronger adsorption peak was observed at 342 nm. The peakd might arise from the trapping of the excited state energy of the surface states, which can lead to strong fluorescence.[21,23] The characteristic absorption of CDs can also be found in the absorption spectra of Eu^{3+}/CDs@MOF-253. However, they are dramatically inhibited after treated by Hg^{2+}, which indicates the quenching effect of Hg^{2+} brought on CDs in Eu^{3+}/CDs@MOF-253 attributes to the coordination between Hg^{2+} and some functional groups in CDs. The approach is depicted in Fig. 3b. We have evaluated the analytical performance of the detection system for quantitative sensing of Hg^{2+}. As exhibited in Fig. S10, the PL intensity of CDs at 453 nm decreases gradually with increasing concentration of Hg^{2+} from 0 to 200 μM while that of Eu^{3+} maintains nearly constant. The relative PL intensities (I_{Eu}/I_{CD}) was nearly completely came to maximum value in the presence of 150 μM Hg^{2+}.

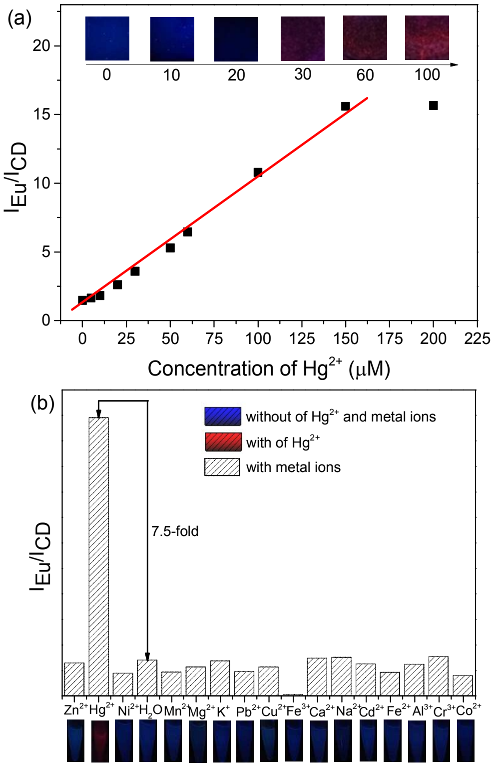

Fig. 4 (a) Line relationship between I_{Eu}/I_{CD} and $C_{Hg}{}^{2+}$ (λ_{ex}=360 nm). Inset shows photographs of the test plates treated by different concentration of Hg^{2+}; (b) Comparison of the PL intensity of I_{Eu}/I_{CD} for Eu^{3+}/CDs@MOF-253 (3 mg) dispersed in aqueous solutions containing different metal ions (100 μM) when excited at 360 nm and corresponding photographs under UV light irradiation at 360 nm.

Fig. 4a presents the relative PL intensities (I_{Eu}/I_{CD}) versus the concentration of Hg^{2+}. A good linear correlation (R^2=0.99324) is observed over the concentration range of 0-150 μM and the detection limit (LOD) is estimated to be 13 nM at a signal-to-noise ratio of 3, which is nearly close to the maximum level for mercury in drinking water permitted by the US Environmental Protection Agency (2 ppb, 10 nM).[3] The LOD of Hg^{2+} detection system was evaluated by the equations,

$$S_b = \sqrt{\frac{\sum (F_0 - F_1)^2}{N - 1}} \tag{1}$$

$$LOD = 3S_b/S \tag{2}$$

Where S_b is the standard deviation for replicating detections of blank solutions (N=30); F_0 is the fluorescence intensity of Eu^{3+}/CDs@MOF-253 in water; F_1 is the average of the F_0; S is the slope of the line relationship in Fig. 4a.[24] The relative standard deviation (RSD) for nine replicate measurements of 50 and 100 μM Hg^{2+} was 2.8% and 1.8%, respectively.

To make the detection simple and portable, we prepared a test plate for rapid Hg^{2+} sensing. The as-prepared test plate containing Eu^{3+}/CDs@MOF-253 was immersed in aqueous solutions with different concentrations of Hg^{2+} for 5 min and then exposed to air for drying. As shown inset of Fig. 4a, under the irradiation of UV light of 365 nm, the fluorescent colors of test plate changing from blue to faint blue, dark red and finally red as concentrations increasing from 0 to 100 μM of Hg^{2+}. Noted that to the naked eyes, the change of different colors is easier to identify than that of single color. Therefor we expect the dual-emission detection system for Hg^{2+} sensing in our work will have great advantage in practical application than other systems (Table 1).

Table 1 Comparison of sensitivity of other reported fluorescence detection method of Hg^{2+} with our materials.

Materials	Detection				Removal
	Fluorescence method	Linear range/μM	LOD	Addition	
Vinyl ethers[25a]	Turn-on	--	1 ppb	$AgNO_3$	--
TTP FONs[7]	Ratiometric	2.5-40	22.6 ppb	--	--
PCuS[25b]	Colorimetric	3.0-40	44 ppb	--	2105 mg/g
C-Dots[6]	Turn-off	0.01-10	0.66 ppb	--	--
Eu^{3+}/CDs@MOF-253	Ratiometric and colorimetric	0.065-150	13 ppb	--	3 mg/g

Besides sensitivity, selectivity is another important parameter to evaluate the performance of the proposed fluorescent probe, especially in real sample. Hence the effects of the potential interfering ions (Zn^{2+}, Ni^{2+}, Na^+, Mn^{2+}, Mg^{2+}, K^+, Pb^{2+}, Cu^{2+}, Fe^{3+}, Ca^{2+}, Cd^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+}, Co^{2+}) on the relative fluorescence intensity of Eu^{3+}/CDs@MOF-253 towards Hg^{2+} were examined under the same conditions. Then the fluorescent responses were recorded. A significant lower PL intensity of CDs (13.3% of origin) was observed by adding Eu^{3+}/CDs@MOF-253 into Hg^{2+} solution, while no obvious decrease occurred upon the addition of any other ions (Fig. S11). Because of this, the response of I_{Eu}/I_{CD} has been changed tremendous depended on various metal ions as shown in Fig 4b. From the figure, we can find that the I_{Eu}/I_{CD} intensity is significantly increased by 100 μM Hg^{2+}. As a result, when irradiated under UV light, only Hg^{2+} could induce a red-colored fluorescence emission clearly observed by naked eyes, which implies that Eu^{3+}/CDs@MOF-253 can be used as a colorimetric probe for selectively Hg^{2+} detection in aqueous solution.

After addition of Eu^{3+}/CDs@MOF-253 particles (5 mg) into Hg^{2+} solution (100 μM), the mixed suspension solution were centrifuged and absorbed the supernatant fluid as much as possible. Then residual Hg^{2+} in supernatant fluid was also detected by Eu^{3+}/CDs@MOF-253. Interesting, the response of I_{Eu}/I_{CD} of Eu^{3+}/CDs@MOF-253 towards Hg^{2+} in supernatant fluid can be observed almost invariably as shown in Fig. S12. Table S1 has also give the available quantities of the proposed probes for various concentration Hg^{2+} removing from its aqueous solutions. Apparently, the fluorescent CDs and Eu^{3+}-functionalized MOFs exhibit strong adsorption ability toward Hg^{2+}, which provides an efficient way to deal with water pollution caused by Hg(II). The strong Hg^{2+} adsorption ability of Eu^{3+}/CDs@MOF-253 might be attributed to the chelation of Hg^{2+} with the CDs and the removal of Hg^{2+} from its solution could due to the water-fast MOFs. Therefore, excepting for dispersing PL CDs as discussion above, MOF-253 in our work can also be high-performance "sweeper" for Hg^{2+} removal.

Table 2 Detection and removal of Hg^{2+} by Eu^{3+}/CDs@MOF-253 in natural samples by standard addition method.

Water samples	Added concentration of Hg^{2+} (μM)	Detected concentration of Hg^{2+} (μM)[a]	RSD (%)[b] and recovery (%)	Removal of Hg^{2+} (%)[c]
River water	5	4.81±0.11	2.29/96.2	92.3
	50	50.66±1.41	1.42/101.3	90.5
Fountain water	5	5.13±0.18	2.78/102.6	93.4
	50	50.45±1.312	3.51/100.9	91.7
Tap water	5	5.06±0.07	1.42/101.2	95.8
	50	49.63±0.52	1.05/99.3	97.2

[a] The result was expressed as mean of five measurements ± standard deviation (SD).
[b] The relative standard deviation (RSD) was defined as (SD/mean)×100%.
[c] The result was calculated by concentration of (initial-final)/initial×100%.

To test the applicability of the developed ratiometric and colorimetric PL sensor for Hg^{2+} detection and removal, the real samples explored by nature water (river water, fountain water and tap water) have been analyzed regularly. The ICP-MS method demonstrates that real samples almost contain none of Hg^{2+}. Then the water samples were spiked with standard solutions containing different concentrations of Hg^{2+}. The results are summarized in Table 2, which indicates that the as-prepared Eu^{3+}/CDs@MOF-253 can be practically used to detect and remove Hg^{2+} in environmental samples.

Conclusions

In summary, we report for the first time encapsulating highly fluorescent CDs and Eu^{3+} into MOF-253 materials to form Eu^{3+}/CDs@MOF-253. The as-prepared Eu^{3+}/CDs@MOF-253 not only remains the excellent optical properties of CDs and Eu^{3+} but also can be developed an ultrasensitive and highly selective sensor for Hg^{2+} ions with a wide response range (0-150 μM) and a very low detection limit of 13 nM. Furthermore, it has been successfully applied in the detection of Hg^{2+} ions in environmental water samples. It is envisioned that various MOFs incorporated with fluorescent center would be synthesizes in similar way and could be applied in sensing target analytes.

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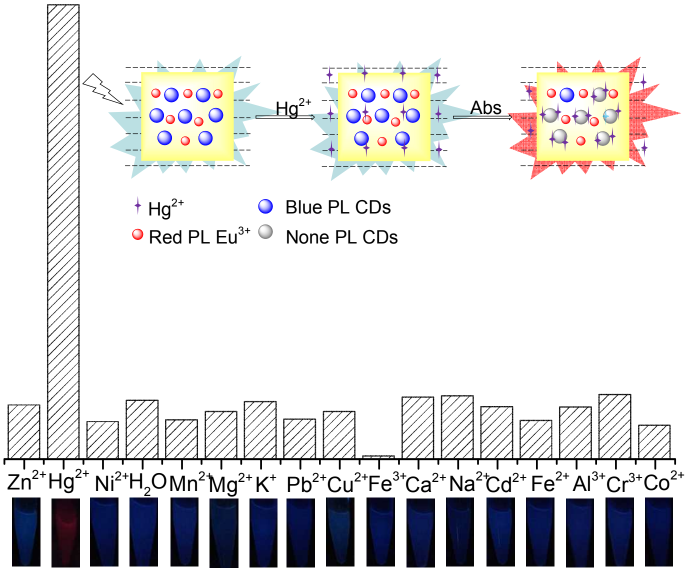

A novel ratiometric and colorimetric PL probe has been designed and prepared to detect Hg^{2+} in aqueous environment by encapsulating excellent PL CDs and Eu^{3+} into MOF-253.