Three resorcin[4]arene-based lanthanide-coordination polymers with multifunctional photoluminescence sensing properties†

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By utilizing a novel octacarboxylate-functionalized resorcin[4]arene as organic linkers, three lanthanide-coordination polymers, namely, \([\text{[CH}_3\text{H}_2\text{NH}_2\text{][Ln}_2\text{(HL)(H}_2\text{O)}_7\text{]}\cdot 2\text{H}_2\text{O (Ln = Tb (1), Eu (2) and Gd (3))}, \text{H}_8\text{L} = 2.8,14,20\text{-}\text{tetra}-\text{pentyl}-\text{4,6,10,12,16,18,22,24}\text{-}\text{octa}-\text{carboxymethoxy}\text{-resorcin[4]arene}\text{]}

Introduction

Currently, probing hazardous chemicals, such as volatile organic compounds and metal ionic pollutants is of great importance because it is highly critical in the fields of biology, physiology, pharmacology and environmental sciences. In light of the impacts that hazardous chemicals have on human health and the environment, developing effective technologies for the sensing of volatile organic compounds and metal ionic pollutants are therefore of global importance and highly necessary. It needs to be mentioned that fluorometric techniques offer relative ease of use, technical simplicity, and wide applicability, and would likely be preferred during sensing of volatile organic compounds and metal ionic pollutants if available.

Emerging as a class of luminescent materials, lanthanide-coordination polymers (Ln-CPs) have afforded a great opportunity in terms of molecular sensing because of their exceptional fluorescence features with narrow emission bands, long emission lifetimes, and high luminescent quantum efficiencies. So far, fluorescent Ln-CPs have been successfully employed for luminescent sensing of harmful volatile organic compounds, ionic pollutants, pH value, gas and biomarker molecules with a turn-on-type luminescent process. Most recently, some progress has been achieved in development of turn-on-type Ln-CP luminescent sensors that were utilized to monitor local concentration fluctuations of environmentally hazardous chemicals. However, single Ln-CP luminescent sensors that discriminate volatile organic compounds and metal ionic pollutants through different response types remain exceedingly rare. Thus, it is an active and challenging research field to develop new luminescent Ln-CPs.

Among all lanthanide elements, Tb3+ and Eu3+ could show intense characteristic green and red emissions, respectively, when they are excited by energy transfer from an "antenna" linker to Ln3+ cations under UV irradiation. Remarkably, during the probing process the bright color changes of green or red could even be observed by the naked eye directly. On the other hand, introduction of suitable organic chromophoric sensitizers into Ln-CPs will significantly enhance the light absorption ability and increase the luminescent brightness of Ln3+ cations by "antenna effect". In this regard, resorcin[4]arenes are particularly attractive because of their bodies and rims with various substituents, thus yielding a great diversity of ligands. Thus far some metal–organic frameworks with fascinating structures and properties have been synthesized by applying the resorcin[4]arene-based ligands. Remarkably, carboxylate-functionalized resorcin[4]arene ligands have been proven to exhibit strong "antenna effects" in building luminescent Ln-CPs.

Based on above consideration, we herein report three Ln-CPs, namely, \([\text{[CH}_3\text{H}_2\text{NH}_2\text{][Ln}_2\text{(HL)(H}_2\text{O)}_7\text{]}\cdot 2\text{H}_2\text{O (Ln = Tb (1), Eu (2) and Gd (3))}, \text{H}_8\text{L} = 2.8,14,20\text{-}\text{tetra}-\text{pentyl}-\text{4,6,10,12,16,18,22,24}\text{-}\text{octa}-\text{carboxymethoxy}\text{-resorcin[4]arene}

† Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format, TGA, PXRD, luminescent spectra and tables. CCDC 1581287–1581289. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ra09777a
Synthesis of H₈L

The precursor 1,3-bis[(methoxycarbonyl)methoxy]benzene (L₁) was synthesized according to the literature procedure. ²⁸ A mixture of L₁ (2.56 g, 10.0 mmol) and hexaldehyde (1.0 g, 10 mmol) in dichloromethane (30 mL) was stirred at ice bath for 0.5 h with dropwise addition of BF₃·OEt₂ (6 mL). Then the mixture was stirred at room temperature overnight. The mixture was transferred to a big sealed container (50 mL) with DMF (20 mL) for 24 h or by ultrasound treatment for 1 min. Subsequently, the small beaker was taken out from the container and quickly sealed, and the emission spectra were measured by using the solid samples. The initial emission spectrum of the solid sample was measured in a solid sample holder before exposure to DMF vapor. Each suspension was transferred to a cuvette and tested by a doublebeam UV-vis spectrophotometer. Thermogravimetric (TG) data were conducted on a Perkin-Elmer Model TG-7 analyzer under nitrogen gas. Luminescent spectra were performed on a FLS920 Edinburgh Fluorescence Spectrometer.

Synthesis of H₈L ligand

Fourthly, the mixture was transferred to a big sealed container (15 mL) and heated at 100 °C for 3 days. Colorless crystals of 1 were achieved in a 35% yield based on Tb³⁺ after cooling the reactor to room temperature. Anal. calcd. for C₆₆H₉₄Eu₂NO₃₃ (Mr = 1733.34): C, 45.73; H, 5.46; N, 0.80. Found: C, 45.66; H, 5.88; N, 0.85. IR data (KBr, cm⁻¹): 3750(s), 3369(m), 2929(w), 2857(m), 1578(w), 1508(w), 1427(w), 1387(s), 1298(w), 1257(m), 1188(s), 1119(w), 1071(m), 939(s), 908(s), 852(s), 775(s), 725(m), 680(m), 582(s), 510(s), 413(s).

Synthesis of [(CH₃)₃NH][Tb₂(HL)(H₂O)₃]·2H₂O (1)

A mixture of H₈L (27.0 mg, 0.1 mmol) and TbCl₃·6H₂O (18.0 mg, 0.048 mmol) was dissolved in a mixed solution of DMF (2 mL) and water (6 mL). Then the suspension was transferred into a Teflon-lined autoclave (15 mL) and heated at 100 °C for 3 days. Colorless crystals of 1 were achieved in a 35% yield based on Tb³⁺ after cooling the reactor to room temperature. Anal. calcd. for C₆₆H₉₄Eu₂NO₃₃ (Mr = 1733.34): C, 45.73; H, 5.46; N, 0.80. Found: C, 45.66; H, 5.88; N, 0.85. IR data (KBr, cm⁻¹): 3750(s), 3369(m), 2929(w), 2857(m), 1711(m), 1583(w), 1507(w), 1454(w), 1427(w), 1373(m), 1331(m), 1298(w), 1257(m), 1189(m), 1119(w), 1071(m), 939(s), 908(s), 852(s), 775(s), 725(m), 680(m), 582(s), 510(s), 413(s).

Synthesis of [(CH₃)₃NH][Gd₃(HL)(H₂O)₆]·2H₂O (3)

2 and 3 were synthesized in a similar procedure as 1, in which TbCl₃·6H₂O was replaced by EuCl₃·6H₂O (17 mg, 0.048 mmol) and GdCl₃·6H₂O (18.0 mg, 0.048 mmol), respectively. Colorless crystals of 2 and 3 were achieved in 39% and 42% yields, respectively, based on Ln³⁺ cations. Anal. calcd. for C₆₆H₉₄Eu₂O₃₃ (Mr = 1733.34): C, 45.73; H, 5.46; N, 0.80. Found: C, 45.66; H, 5.88; N, 0.85. IR data (KBr, cm⁻¹): 3750(s), 3369(m), 2929(w), 2857(m), 1711(m), 1583(w), 1507(w), 1454(w), 1427(w), 1373(m), 1331(m), 1298(w), 1257(m), 1189(m), 1119(w), 1071(m), 939(s), 908(s), 852(s), 775(s), 725(m), 680(m), 582(s), 510(s), 413(s).

Luminescent sensing experiments

Before luminescent determination, the samples of Ln-CPs were ground into powder. Then the suspension was prepared by introducing the powder sample (3 mg) of Ln-CPs into each volatile organic compounds solvent (3 mL) or stock solutions (1 × 10⁻² M, 3 mL) of MCl₃ by ultrasound treatment for 1 min. Each suspension was transferred to a cuvette and tested by luminescent spectrum.

Measurement for luminescent sensing of DMF vapor

A small beaker (10 mL) with the samples (10 mg) was placed into a big sealed container (50 mL) with DMF (20 mL) for 24 h or 10 min. Subsequently, the small beaker was taken out from the container and quickly sealed, and the emission spectra were measured by using the solid samples. The initial emission spectrum of the solid sample was measured in a solid sample holder before exposure to DMF vapor.

X-ray crystallography

Crystallographic data for 1–3 were determined on an Oxford Diffraction Gemini R Ultra diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct method and refined on F² by full-
Tables S2

[H2N(CH3)2]+ cation is included as a counter cation to balance nine oxygen atoms from three HL7 and three coordinated water molecules. Tb2 is coordinated by 2.648(17) spheres. The Tb

nated water molecules in a distorted tricapped trigonal prism

[(CH3)2NH2][Gd2(HL)(H2O)7] 2H2O( 1 ),[(CH3)2NH2][Eu2(HL)(H2O)7] 2H2O( 2 ) and [(CH3)2NH2][Gd2(HL)(H2O)7]-2H2O (3)

1–3 are isostructural and crystallize in the same triclinic space group P1. Herein, we will only describe the structure of 1 in detail (Fig. S1†). One of the most striking features of such Ln-CPs is the presence of numerous coordinated waters around the Ln3+ centers. The asymmetric unit of 1 consists of two Tb3+ cations, one HL7− anion, seven coordinated water molecules, one [H2N(CH3)2]+ cation, and two lattice water molecules (Fig. 1a). Two Tb3+ cations exhibit different coordination spheres. Tb1 is in a distorted square antiprism geometry, surrounded by eight oxygen atoms from two different HL7− anions and three coordinated water molecules. Tb2 is coordinated by nine oxygen atoms from three HL7− anions and four coordinated water molecules in a distorted tricapped trigonal prism sphere. The Tb−O bond distances vary from 2.300(14) to 2.648(17) Å, which are within the normal range. One [H2N(CH3)2]+ cation is included as a counter cation to balance the negative charge. Seven carboxylates of each HL7− anion are involved in coordination with five Tb3+ cations. It is noticeable that two HL7− anions form a sandwich-like unit via sharing two Tb1 cations (Fig. 1b). Further, adjacent sandwich-like units are interconnected by Tb2 cations to give a unique two dimensional sandwich-based layer (Fig. 1c).

**Results and discussion**

Crystal structural descriptions of [(CH3)2NH2][Tb3(HL)(H2O)7]-2H2O (1), [(CH3)2NH2][Eu2(HL)(H2O)7]-2H2O (2) and [(CH3)2NH2][Gd2(HL)(H2O)7]-2H2O (3)

Fig. 1 (a) Coordination environments of Tb3+ cations in 1. (b) View of the sandwich unit of 1. (c) Top view of the unique 2D sandwich-based network of 1.

Luminescent properties

Solid state emission spectra of the free H8L and 1 and 2 were determined at room temperature. For the free H8L, the emission peak at 366 nm (λex = 315 nm) corresponds to the π→π* or π→n transitions, as shown in Fig. S2.† When excited at 295 nm, 1 emits characteristic emission peaks at 488, 543, 584, and 623 nm, which could be ascribed to 5D4 → 7Fj (j = 6–3) transitions of the Tb3+ cations (Fig. 2a). The most intense emission at 543 nm is attributed to the 5D4 → 7F3 transition of the Tb3+ cations, resulting in an intense green emission output in the solid state. Similarly, 2 exhibits characteristic transitions of the Eu3+ cations upon excitation at 318 nm. As depicted in Fig. 2b, the emission peaks at 579, 593, 614, 651, and 698 nm correspond to the 5D0 → 7Fj (j = 0–4) transitions of the Eu3+ cations. Notably, the emission spectrum of 2 is mainly dominated by the 5D0 → 7F2 transition, which is more intense than others, leading to intense red luminescence. The bright colors also demonstrate that HL7− acts as an excellent “antenna” linker in the effectively transfer energies to Tb3+ and Eu3+ metals.

Another critical luminescence characteristic of Ln-CPs is the lifetime, which refers to the average time that a molecule stays in its excited state before emitting a photon. Hence, the lifetime values of the excited states 5D4 (Tb3+) and 5D0 (Eu3+) of 1 and 2 were monitored with 543 and 614 nm, respectively (Fig. S3†). The observed luminescent decay profiles correspond to single exponential functions, with the lifetimes of τ = 0.730 ms for 1 and τ = 1.242 ms for 2. Moreover, the ligand-centered emission is not detected, thus implying the existence of an efficient ligand-to-metal energy-transfer process in these Ln-CPs.

To better understand the energy transfer process, the UV-vis absorption spectrum of 3 was determined in methanol solution at room temperature. The wavelength of the absorbance edge is about 312 nm, indicating that HL7− has a singlet state (S1) energy level of 32 051 cm−1 (Fig. S4a†). The phosphorescent spectrum of 3 was also recorded at 77 K to estimate the triplet state (T1) energy level of HL7−, and obtained the T1 energy level of 22 675 cm−1 (Fig. S4b†). According to Reinhoudt’s empirical rule, the energy transfer from ligand to metal will become effective when the energy gap between S1 and T1 of the organic
Luminescent recognition of DMF

Most recently, volatile organic compounds sensing has gained considerable interest in fundamental research due to their potential applications in optical devices, environmental monitoring, and separation.\textsuperscript{43,44} To explore the potential applications in this field, luminescent responses of 1 and 2 after incubation in various volatile organic compounds, including chloroform, dichloromethane, ethanol, acetonitrile, tetrahydrofuran, ether, cyclohexane, methanol and DMF, were studied in detail. As shown in Fig. 3, the corresponding luminescence curves still show the four characteristic emission peaks, and only the relative $^5D_4 \rightarrow ^7F_5$ or $^5D_0 \rightarrow ^7F_2$ transition intensities of 1 and 2 were monitored under the perturbation of various volatile organic compounds. Particularly, DMF triggers a superior luminescent turn-on effect for 1 and 2, while other volatile organic compounds have no significant effect on the emission. Moreover, the inset photographs shows that only DMF can obviously enhance the emission colors of 1 and 2, which leads to brighten under UV light. This finding suggests that 1 and 2 are potential sensing materials for DMF with an excellent selectivity.

The obvious emission intensity enhancement of 1 and 2 by displacement in DMF encouraged us to further explore the potential applications of them for probing DMF vapor. In order to test the performance of 1 and 2 as DMF vapor sensor, an in situ solid-state luminescent sensor setup was designed and used (Fig. S5†). The luminescence response of 1 and 2 after incubation for 24 h under DMF vapor were measured and the results are plotted in Fig. 4. The observation indicates 1 and 2 still exhibit a clear enhancement effect. Besides good sensitivity, fast response is also an important criterion for a good sensor. Hence, the solid state emission spectra of 1 and 2 were further determined after exposed in DMF vapor for 10 minutes. Clearly, the response rate of the sensor is quite fast with 88.9% and 89.7% (the relative $^5D_4 \rightarrow ^7F_5$ or $^5D_0 \rightarrow ^7F_2$ transition intensities) of enhancement achieved compared that after 24 h, rendering 1 and 2 potential sensors for turn-on-type detection of DMF vapor. Moreover, PXRD patterns of 1 and 2 in DMF vapor are nearly identical to the simulated one, suggesting they are stable in the luminescent sensing process (Fig. S6†).

The emission intensity of the Ln$^{3+}$ is well-known to rely on the energy transfer efficiency from the ligand to the Ln$^{3+}$ center.\textsuperscript{45} Meanwhile, the interactions with the O–H bond of coordinated water may lead to quenching of Ln$^{3+}$ luminescence.\textsuperscript{46} DMF has a more strong coordination ability compared to other volatile organic compound. When coordinated waters are partially replaced by DMF, the O–H bonds surrounding the Ln$^{3+}$ centers may leave fewer and thus enhance Ln$^{3+}$ emission. Hence, we infer that the marked enhancement of their emission intensities in response to DMF is likely caused by the displacement of coordinated water molecules by DMF molecules.

Selective sensing of Fe$^{3+}$ ion

Metal ion sensing and detection play a significant role in environment and life science.\textsuperscript{46–48} In this study, we also investigated
luminescent 1 and 2 to sense metal ionic pollutants. The crystalline samples were simply soaked in aqueous solutions of MCl₂ [M = Na⁺, K⁺, Ca²⁺, Cd²⁺, Zn²⁺, Mn²⁺, Ni²⁺, Mg²⁺, Co²⁺, Al³⁺, Cu²⁺, Cr³⁺, Fe²⁺, and Fe³⁺; 1 × 10⁻² M] for luminescence studies. As depicted in Fig. 5, the corresponding luminescence curves still show the four characteristic emission peaks, and only the relative ⁵D₄ → ⁷F₅ or ⁵D₅ → ⁷F₂ transition intensities for 1 and 2 were monitored under the perturbation of various cations. Interestingly, Fe³⁺ exhibits a pronounced quenching effect on the luminescence of 1 and 2, while other metal ions have no significant effect with the exception of Fe²⁺ or Cr³⁺, which can weaken the luminescence to some extent. Moreover, the inset photographs show that only Fe³⁺ can completely quench the emission colors of 1 and 2, which leads to the dark under UV light. The above phenomenon indicate that 1 and 2 may be considered as a promising luminescent probe for Fe³⁺ ions.

To further prove the luminescence quenching by Fe³⁺ ion, concentration-dependent luminescence studies for 1 and 2 were carried out in the presence of Fe³⁺ ion. As demonstrated in Fig. 6, the emission intensity for the suspension of 1 and 2 sharply declines with the increase of Fe³⁺ concentration from 0 to 5000 μM. At the Fe³⁺ content of 5 × 10⁻³ M, the fluorescence intensity of 1 and 2 completely disappeared. Quantitatively, the Stern-Volmer equation I₀/I = 1 + Kₛv[M] can be used to describe this quenching effect, where the values I₀ and I represent the luminescent intensities of 1 without and with addition of Fe³⁺, respectively, [M] is the concentration of Fe³⁺, and Kₛv is the quenching constant. Based on the quenching experimental data, the Kₛv value is calculated to be 1.545 × 10⁴, suggesting a strong quenching effect on the luminescence of 1. The calculated linear correlation coefficient (R) in the Kₛv curve of 1 with addition of Fe³⁺ is 0.99685, demonstrating that the quenching effect of Fe³⁺ on the luminescence of 1 fits the Stern-Volmer model. The suspension of 2 also exhibits the similar selective sensing of Fe³⁺ ion. The calculated Kₛv value is 3.93 × 10⁴ based on the Stern-Volmer equation, demonstrating a quenching effect on the fluorescence of 2. Besides, a good linear relationship is achieved with the coefficient of 0.96502 (Fig. S7†).

To understand the mechanism of the fluorescence quenching effect of 1 and 2 toward Fe³⁺ ions the UV/vis absorption data of 1 and 2 and varied metal ions were carried out. The UV/vis absorption spectra show that the wide absorption band from 260 to 400 nm of Fe³⁺ covers the range of absorption bands of 1 and 2, and is much more stronger than those of other metal ions (Fig. S8†). This means that the UV/vis absorption of Fe³⁺ upon excitation may prevent the absorption of 1 and 2, and result in the decrease or quenching of the luminescence.⁵⁹,⁷⁰

Conclusions

In summary, we reported three Ln-CPs assembled with a new octacarboxylate-functionalized resorcin[4]arene ligand and Ln³⁺ cations. 1 and 2 emit intense characteristic red and green emission colors. The photophysical properties demonstrated that H₄L is well suited for the sensitization of Tb³⁺ and Eu³⁺ emissions thanks to the favorable energy level of its triplet state. 1 and 2 could be employed as potential turn-on-type fluorescent sensors for DMF and turn-off-type luminescent probe for Fe³⁺ ion.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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