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Fast response and highly selective sensing of amine vapors using a luminescent coordination polymer†

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Detecting volatile amines is a significant topic in the quality control of food and medical diagnosis. We report the first Eu-coordination polymer (CP) as a sensory material for the detection of a class of amine vapors with high selectivity and rapid response.

Detection of volatile amine species is of great interest over the last few years because of increasing content found in soil or wastewater as well as in the fields of industrial monitoring and food safety.[1] Various types of analytical tools have been exploited for the detection of amines,[2] in which the fluorescent chemosensor is an expedient detection device because it has many advantages over other sophisticated electrochemical devices, such as a high signal output, simple detection, low cost, and reliability.[3] Coordination polymers (CPs), known as a class of crystalline materials, have been used widely as sensing materials due to tunable pore sizes and functional sites.[4] Several groups have reported their discoveries of CP-sensors aimed at the convenient detection of various small solvent molecules, explosives, and gas molecules,[5,6] but much less success has been achieved in the vapor phase than in solution.[7] The reason is that vapour pressures of common small organic molecules are usually very low at room temperature, so the luminescence detection of these trace volatile vapour molecules is always a significant but challenging task. To the best of our knowledge, no lanthanide based-CPs display excellent selective vapor detection for volatile amines.[8] Compared with main group and transition-metal coordination polymers, lanthanide-based CPs as fluorescent probes are more attractive candidates, thanks to their exceptional luminescence features with sharp and characteristic emissions. On the other hand, it is known that, as sensing fluorescent materials, their selectivity and sensibility are mainly ascribed to host–guest interactions between analytes and frameworks of complexes, so it is important to fully make use of hydrogen bonding, electrostatic force, metal–ligand coordination, and van der Waals interaction. With this in mind, we design and synthesize a highly luminescent active europium-based coordination polymer, which is capable of fast response and highly selective detection of amine vapors.

In the present work, 4-(pyrimidin-5-yl) benzoic acid (HL) with one carbonyl group and two N-donors is used as a tripodal ligand to react with Eu^{3+} ions. A H-bonded three-dimensional Eu-CP as colorless crystals can be readily synthesised by the solvothermal reaction in an acetonitrile/H_2O (6 : 1) mixture at 80 °C for four days, which can be formulated as $\{[EuL_2(H_2O)_3](NO_3)\}$ (**EuL**) based on elemental analysis, the single crystal X-ray study, and TGA analysis. The phase purity of the bulk material was also confirmed by the powder X-ray diffraction pattern (PXRD).

Single crystal X-ray diffraction analysis reveals that **EuL** crystallizes in a triclinic space group $P\bar{1}$ (Table S1, ESI†). Its asymmetric unit contains one crystallographically independent Eu^{3+} ion, two deprotonated $\{L\}^-$ anions, three coordinated water molecules, and one μ_1-$\eta^1\ \eta^1\ \eta^0$ chelating NO_3^- ligand (Fig. 1 and Fig. S1a, ESI†). The Eu^{3+} ion adopts a tricapped trigonal-prismatic geometry with nine oxygen donors: four from carboxylate groups of three different $\{L\}^-$ ligands, two from one NO_3^- ion, and three from coordinated water molecules (Fig. S1b, ESI†). The Eu–O bond lengths range from 2.384(2) to 2.540(3) Å (Table S2, ESI†), which are comparable to those reported for Eu-based complexes.[6b,7a] In two unique $\{L\}^-$ ligands, all nitrogen atoms are non-coordinated as vacant coordination sites, one carboxylate group containing O(1)C(1)O(2) chelates the central Eu^{3+} ion in a μ_1-$\eta^1\ \eta^1$ mode, and the other one containing O(3)C(12)O(4) adopts a μ_2-$\eta^1\ \eta^1$ bridging mode. Eu1 and its adjacent symmetrical Eu1A are twofold bridged by carboxylate groups to form dimer $[Eu_2L_4]$ units (Fig. 1), which are further constructed into a H-bonded 3D framework with one-dimensional rhombic channels of about

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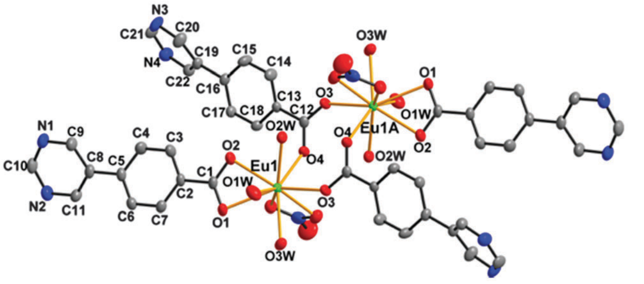


Fig. 1 A dimer building unit [Eu$_2$L$_4$]. Thermal ellipsoids are drawn at the 50% probability level (Eu, green; carbon, gray; nitrogen, blue; and oxygen, red), and hydrogen atoms are omitted for clarity.

12.4×9.9 Å^2 and 7.7×3.8 Å^2 along the *b*-axis (Fig. S2e, ESI†). These hydrogen bonds occur between aqua ligands and non-coordinated N sites of the dangling pyrimidine rings (Table S2, Fig. S2a–d, ESI†). So the motion of the dangling pyrimidine rings is fully restricted with dihedral angles of 33.5° and 40.6° through hydrogen bonds (Fig. S1c, ESI†). These structural characteristics with open N-sites facilitate the interaction between dangling pyrimidine rings and incorporated analytes that is helpful for chemical sensing.

To test the **EuL**'s robustness, TGA and temperature-dependent powder X-ray diffraction patterns (Fig. S3b and S5, ESI†) were obtained. These results indicate that three coordinated water molecules originally bound to Eu^{3+} can be completely removed in the temperature range of 120 to 231 °C, rendering metal building units with open metal sites, its identical framework structure is retained up to 395 °C, which can be identified from the DSC curve and the FTIR pattern of **EuL** after thermal treatment (Fig. S4i, ESI†). Besides, **EuL** is insoluble in water and common organic solvents, its PXRD patterns illustrate its good water/solvent-stability upon treatment with various solvents. Considering all of the above, and inspired by the characteristic bright-red luminescence of **EuL**, those prompt us to examine its ability as a potential sensor material for various solvents. Such high thermal stability and solvent-stability also set a solid foundation for the further study of chemical sensing applications.

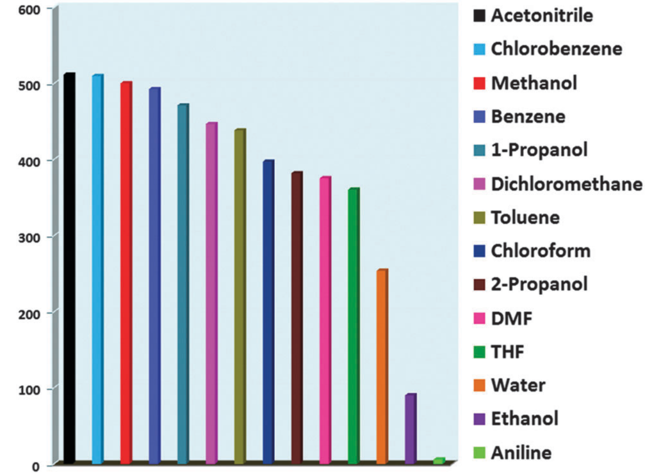
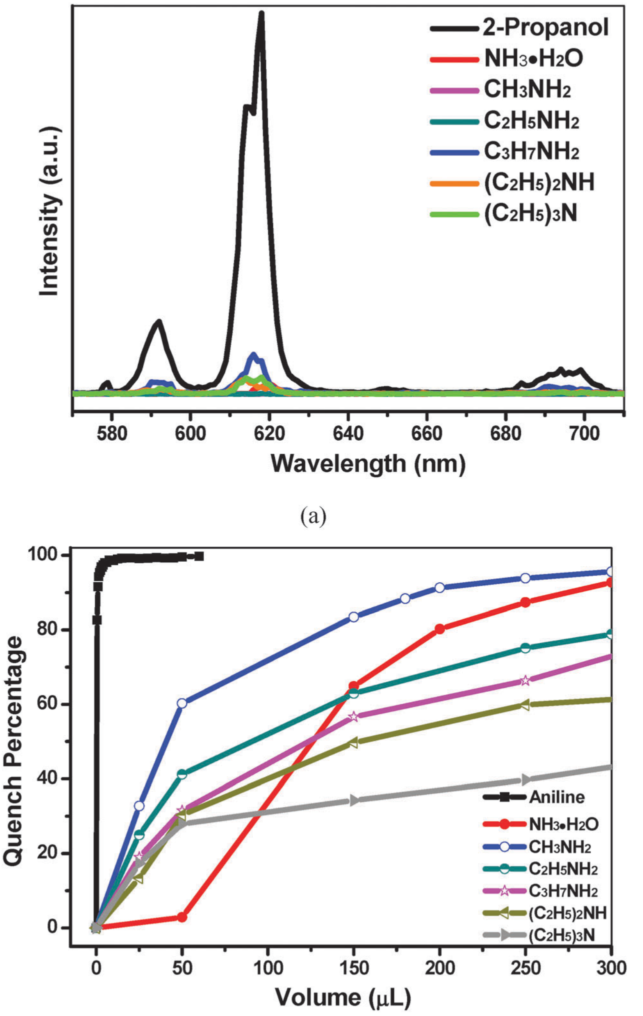


Fig. 2 The $^5D_0 \rightarrow {}^7F_2$ transition (620 nm) intensities of **EuL** in various pure solvents (λ_{ex} = 308 nm).

The solid excitation and photoluminescence (PL) spectra of HL and **EuL** were recorded at room temperature, as shown in Fig. S6 (ESI†). The excitation spectrum of **EuL**, by monitoring the $^7F_0 \rightarrow {}^5D_2$ transition under the characteristic emission (620 nm) of the Eu^{3+} ion, exhibits a strong sharp line with a maximum at 308 nm. When excited at 308 nm, **EuL** exhibits the luminescence bands at 581, 593, 620, 651, and 696 nm, which could be attributed to the characteristic f–f electronic transitions of the Eu^{3+} ion: $^5D_0 \rightarrow {}^7F_J$ (J = 0–4), respectively (the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition dominating the spectra with 0.32 ms luminescence lifetime). A broad emission band ranging from 350 nm to 490 nm, centered at 376 nm is observed, which can be assigned to the π–π^* ligand transition, but it is much weaker than the metal-based red emission. This demonstrates that the organic ligands are capable of significantly sensitizing the luminescence of the Eu^{3+} center, however, it is not completely effective. Further luminescence sensing measurements were performed to investigate the influence of different guest molecules on the luminescence properties of **EuL**. The feature is that its intensities in the PL spectra (Fig. 2 and Fig. S7, ESI†) are strongly dependent on the solvent molecules, particularly in the case of aniline, which exhibits the most significant quenching effect. Such solvent-dependent luminescence properties are of interest for sensing of these small-molecule solvents harmful to human beings. A further detailed study has been carried out on the guest effect of aniline for the luminescence intensities of **EuL**. **EuL** was dispersed in 2-propanol as the standard suspension, while the content of aniline was gradually increased to monitor the emissive response. It was found that the addition of aniline to the 2-propanol suspension of **EuL** led to a significant decrease of its fluorescence intensity (Fig. S8a, ESI†), which almost disappeared at an aniline content of 0.5 μL (166 ppm). The decreasing trend of the fluorescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} at 620 nm *versus* the volume of aniline could be well fitted with a first-order exponential decay (Fig. S8b, ESI†), indicating that fluorescence quenching of **EuL** by aniline is diffusion-controlled.[6a–c] Considering such an excellent selective luminescence quenching effect of **EuL** for aniline, this microporous material will be of interest for detecting other more volatile amines as a potential fluorescence sensor, such as ammonium hydroxide ($NH_3 \cdot H_2O$), methylamine (CH_3NH_2), ethylamine ($C_2H_5NH_2$), propylamine ($C_3H_7NH_2$), *N*,*N*′-diethylamine ($(C_2H_5)_2NH$), and triethylamine ($(C_2H_5)_3N$). Our study shows that all amines act as fluorescence quenchers with apparently differential sensitivity, as illustrated in Fig. 3 and Fig. S10 (ESI†). Aniline is the most effective one in liquid media based on the quenching efficiency (%). The order of quenching efficiency is aniline $> CH_3NH_2 \sim NH_3 \cdot H_2O > C_2H_5NH_2 > C_3H_7NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$.

In order to test the sensing ability and the response rate of **EuL** as a sensor, the luminescence properties and detection behavior upon exposure to the vapors of aforementioned various amines as well as the time-dependent fluorescence quenching profile of each analyte have been investigated (Fig. S11–S14, ESI†). An *in situ* solid-state luminescent sensor setup was designed (Fig. S13, ESI†). The results show that the quenching level of each amine vapor is in accordance with the one in liquid media (Fig. S11 and S12, ESI†).



(a)

(b)

Fig. 3 (a) Suspension-state PL spectra of $^5D_0 \rightarrow {}^7F_2$ transition for **EuL** dispersed in various amine solvents (3 mL) (λ_{ex} = 308 nm). (b) A comparison of the fluorescence quenching percentages of **EuL** in the presence of different amounts of related various amines. The fluorescence quenching percentage is defined as $(I_0 - I)/I_0 \times 100\%$, where I_0 = the original peak maximum intensity (λ_{em} = 620 nm) and I = the maximum intensity after immersing various amines.

Their time-dependent quenching efficiency displays that the fluorescence quenching of aniline reaches a maximum in ten seconds with a quenching percentage of more than 90% (Fig. S14, ESI†). Several factors affect the fluorescence attenuation efficiency of **EuL**, such as energy constraints, the binding strength to the analytes, its porosity, *etc*. But it is well known that the luminescence of lanthanide compounds mainly relies on sensitization by organic ligands, so the efficiency of ligand–metal energy transformation is crucial to determine the emission of Eu^{3+}. To deeply understand the mechanism of the quenching effect of amines, UV-vis absorption spectra of **EuL**, HL as well as various amines have been recorded. It is obvious that the absorption peaks of HL at 205 and 260 nm are almost mantled by the wide absorption peak of aniline and partially overlapped by peaks of other amines, while no other solvents absorb at this wavelength. Upon illumination, there is a competition for excitation energy between the absorption of amines, especially for aniline, and HL, so very little energy will be transferred through the ligand to Eu^{3+} ions, resulting in a decrease (even quenching) in luminescence intensities. This mechanism is consistent with the ones previously proposed by other groups and us.[6a–c] On the other hand, the ability of electron/energy-transfer between guest solvents and ligands also affects the sensitivity of fluorescent sensory materials. The fluorescence responses of the framework are mainly attributed to guest–host interactions and are diffusion-controlled, so the size-effect of guest molecules is an important factor. Guest molecules with large sizes, whose diffusion may be constrained by the channel, would show a weaker effect on the fluorescence property of the framework, in accordance with the above experimental results. We could come to a conclusion that the luminescent **EuL** exhibits not only high solvent-selectivity but also a remarkable size-selectivity for the sensing of various amines.

A new luminescent Eu-CP sensor with high thermal and solvent stability has been successfully prepared based on an appropriate ligand (HL), which not only shows significant selective quenching response for amine vapors, but also exhibits a clearly differential response rate because of pore sieving functions. These inspire us that further studies will be focused on the construction of more luminescent coordination polymers with different pore sizes and functional sites to enhance their recognition selectivity or to direct specific recognition of certain molecules or ions.

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