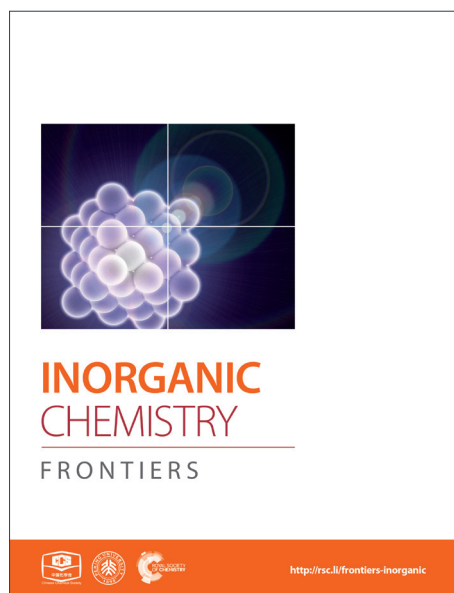
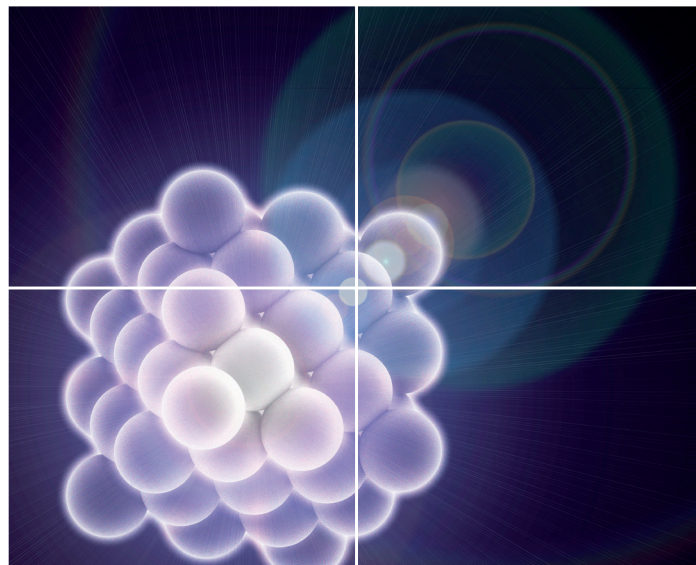


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COMMUNICATION

A bis(1H-pyridin-2-one)salen Eu(III) complex for vapoluminescent sensing

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A bis(1H-pyridin-2-one)salen Eu(III) complex shows strong sensitized luminescence with quantum yield of 28% and vapoluminescent sensing of acid–base vapour on a fabricated device.

Luminescent lanthanide complexes have received considerable attention because of their highly desirable applications such as lighting, display, sensing, and biomedical imaging.¹ Due to the low absorption coefficients of trivalent lanthanide ions, organic ligands with chromophoric groups are required to populate the lanthanide emitting states through energy transfer, which is known as sensitization. In the past decades, a large variety of ligands (eg., phosphine oxides,² β -diketonates,³ dipicolinates,⁴ salen derivatives,⁵ cyclen derivatives,⁶ and cryptands⁷) have been developed to construct emissive lanthanide complexes especially Eu(III) complexes (featuring saturated red emission), some of which showed chemical sensings.^{6b,6c,7c} Although these excellent sensing performances in aqueous solution are of great significance, we believe that the exploitation of lanthanide complexes for gas sensing would be an increased necessity, because most lanthanide complexes possess excellent solubility in methanol and ethanol, which facilitates the fabrication of thin film device.

Vapoluminescence is luminescence vapochromic phenomenon that much promising for the detection of harmful chemical gases.⁸ Recently, there are increasing interest in acid–base gas-responsive luminescent materials because of their application not only as sensors but also as display devices.⁹ However, structurally characterized materials remain rare. By design of a bis(1H-pyridin-2-one)salen ligand, 3,3'-[ethane-1,2-diylbis(azanylylidene)bis(methanylylidene)]bis(1H-pyridin-2-one) (H_2L , Fig. 1a), here we report a mononuclear Eu(III) complex and its luminescence switching triggered by acid–base vapour. Previously, the O donors of the N_2O_2 salen ligands are

invariably the phenol hydroxyl oxygen atom.^{5,10} This is the first time to employ the ketone carbonyl oxygen atom as salen O donor, which may provide lanthanide complexes with novel optical properties.¹¹

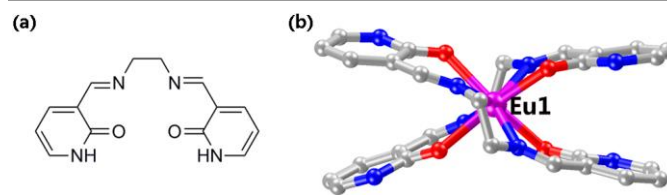


Fig. 1 (a) The H_2L ligand. (b) The mononuclear structure of **1**.

Solvothermal reaction of H_2L with $EuCl_3 \cdot 6H_2O$ in a butanol solution at 75 °C results in the formation of colourless polyhedral crystals of $[Eu(H_2L)_2 \cdot (H_2O)_2 Cl_3]$ (**1**). Single-crystal X-ray analysis of complex **1** at 80 K reveals that it crystallizes in the monoclinic space group Cc . The asymmetric unit contains only one crystallographically independent Eu(III) ion. The Eu(III) ion is eight-coordinate and adopts D_{2d} 8,18,12-dodecahedron geometry (Fig. S4).¹² The sites in axial are covered by two sets of chelating NN donor units in a criss-cross fashion [Eu–N in the range of 2.524–2.625 Å], while the sites at the equator are occupied by four ketone carbonyl oxygen atoms [Eu–O in the range of 2.296–2.342 Å]. Thanks to the kink of ethylenediimine spacer, two H_2L ligands can clasp each other around one Eu(III) ion, thus forming a mononuclear structure (Fig. 1b). It should be noted that the ligands (H_2L) retain the neutral keto form in the complex. The valence requirements of the mononuclear complex are satisfied by the presence of three uncoordinated chloride ions. Each complex molecule is associated with others through hydrogen bonding of all N–H donors to chlorine and water medium (Fig. S5). Three different kinds of hydrogen bonding interactions of $N \dots O$, $N \dots Cl$, and

O...Cl fall into in the range of 2.65–2.68 Å, 3.05–3.10 Å, and 2.74–3.10 Å respectively.

Fig. 2 presents the reflectance spectra of the H₂L ligand and complex **1**. The absorption band of complex shows a little red shift compared to that of ligand, but both contain three peaks in regard to n→σ*, π→π*, and n→π* transitions. The π→π* and n→π* absorption peaks of complex **1** are located at 332 and 381 nm, respectively. The appearance of the n→σ* transition at 247 nm reveals the unique electronic property of bis(1H-pyridin-2-one)salen ligand. The excitation spectrum of complex **1** exhibits one broad band peaking at 367 nm (Fig. 3a), corresponding to the mixed π→π* and n→π* transitions of H₂L ligand. This suggests the particularly efficient sensitization of Eu(III) ion by bis(1H-pyridin-2-one)salen ligand.

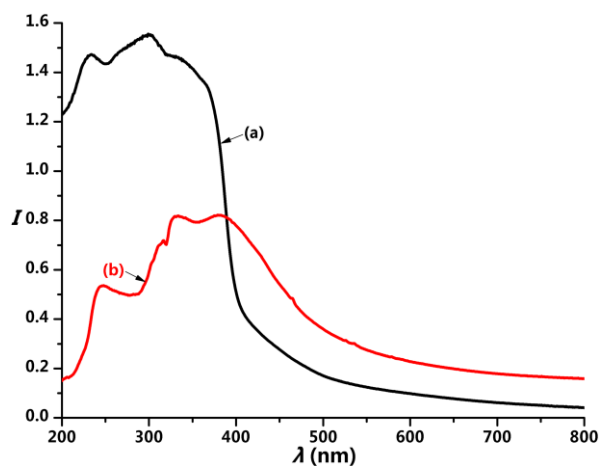


Fig. 2 Reflectance spectra of (a) the H₂L ligand and (b) complex **1**.

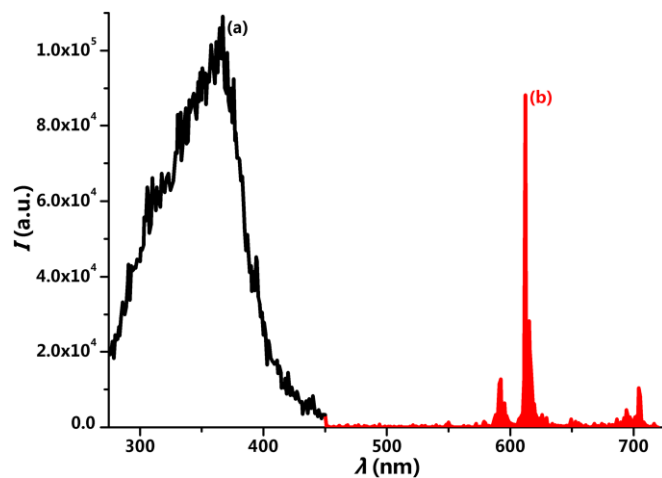


Fig. 3 Solid-state excitation (a) and emission (b) spectra of complex **1**.

After excitation at 367 nm, complex **1** exhibits the characteristic emission of Eu(III) ion (Fig. 3b). The sharp emission lines are attributed to the f–f transitions of ⁵D₀→⁷F_J (J = 0–4), where the ⁵D₀→⁷F₂ transition at 613 nm dominates the spectrum. The luminescence decay curve of complex **1** fits a single-exponential function with a lifetime of 813±1 μs as monitoring the ⁵D₀→⁷F₂ emission line, in agreement with the

single Eu(III) site. The quantum yield was measured to be 28% by absolute integrating-sphere method.

The bis(1H-pyridin-2-one)salen ligand has poor solubility in ordinary organic solvents, but it becomes good soluble in methanol and ethanol after complexation of Eu(III) ion. The deposition from a methanol solution (10 μM) of complex **1** onto a glass substrate by the spin-coating method leads to a transparent and homogeneous thin film. Upon excitation at 365 nm, interestingly, the photoluminescence of the film could be switched between green and red by exposure to acid–base vapour (Fig. 4). When the red-emissive film was exposed to hydrogen chloride (HCl) vapour, it changed into green emission immediately. After subsequent exposure of it to triethylamine (Et₃N) vapour, the red emission was recovered in ten seconds. As can be seen in Fig. 5 and Fig. S6, the red emission peak at 613 nm is corresponding to the sensitized Eu(III) emission, and the green emission band around 467 nm is from the ligand. The acid–base vapour-induced luminescence switching is ascribed to the dissociation of complex structure by protonating the imine nitrogen and ketone carbonyl oxygen atoms under acidic gas environment and the recomplexation of Eu(III) ion by neutralizing the proton under basic gas environment.

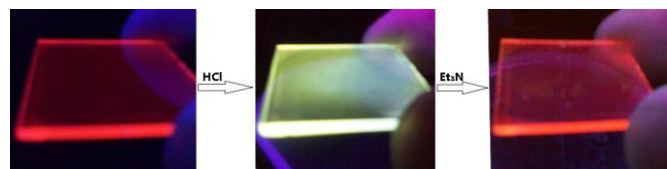


Fig. 4 Photographs of film during the exposure to HCl–Et₃N vapour.

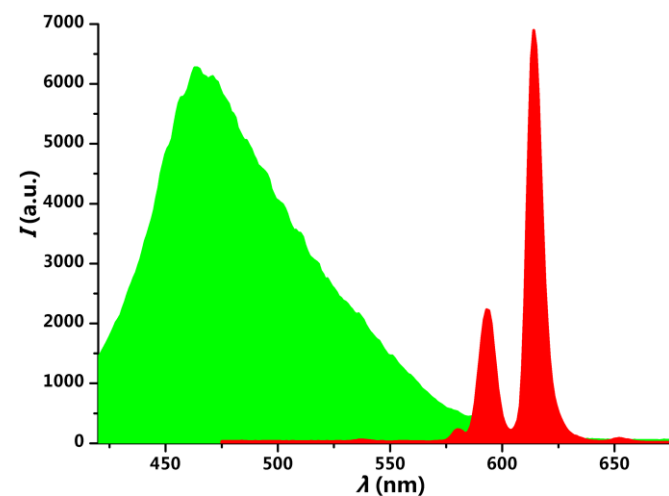


Fig. 5 Spectral changes before and after exposure to HCl–Et₃N vapour. Original Eu(III) complex (red area), after exposure to HCl vapor (green area).

To examine the reversibility and response time, we treat the film alternately with HCl gas and Et₃N vapour. After eight HCl–Et₃N cycles, the film can still return to the strong red emission (Fig. 6), but with growing response times no more than half a minute. These results demonstrate that complex **1** is an excellent substrate for acid–base gas sensing. The slower response may be due to the increased disorder of molecular

arrangement and the gradual accumulation of triethylamine hydrochloride in film during the cycles.

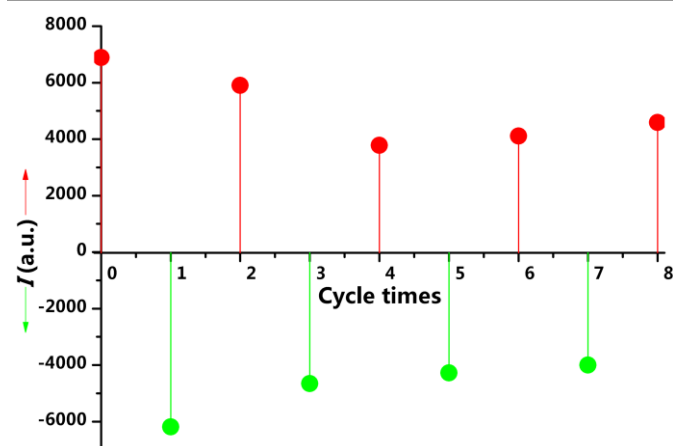


Fig. 6 Responses of luminescence intensities at 466 nm (green ring) and 613 nm (red ring) of film during HCl-Et₃N vapour exposure cycles.

Conclusions

In summary, we design the first bis(1H-pyridin-2-one)salen ligand, and succeed in obtaining a mononuclear Eu(III) complex. The photophysical studies show the particularly efficient sensitization of Eu(III) ion by the bis(1H-pyridin-2-one)salen ligand. The thin film device fabricated by the Eu(III) complex possesses excellent vapoluminescent sensing performance towards acid–base vapour.

Experimental

Synthesis of complex 1

H₂L (27 mg, 0.1 mmol), EuCl₃·6H₂O (20 mg, 0.055 mmol), and n-BuOH solvent (2 mL) was placed in a 20 mL vial. After three minutes of ultrasound, the sealed sample was heated at 75 °C for 1 day, and then cooled to room temperature. The resulting colourless crystals were filtered off and dried in air. Yield (based on H₂L): 84%. IR (KBr, cm⁻¹): 3336 (w), 3082 (w), 2910 (w), 2853 (w), 2782 (w), 2738 (w), 1653 (vs), 1595 (vs), 1548 (s), 1465 (s), 1423 (s), 1344 (s), 1226 (s), 1115 (w), 1060 (m), 1029 (w), 927 (m), 898 (w), 774 (s), 650 (m), 599 (s), 526 (m), 450 (w). Elemental analysis (%): calcd for C₂₈H₃₀Cl₃EuN₈O₆ (832.92): C 40.34, H 3.83, N 13.41; found: C 40.20, H 3.75, N 13.64.

Crystallography analysis

Single-crystal X-ray diffraction data of complex 1 was collected on an Agilent Technologies Gemini A System (Cu K α , $\lambda = 1.54178 \text{ \AA}$) at 80 K. The data was processed using CrysAlis. The structure was solved by direct methods and refined by full-matrix least-squares cycles on F^2 . Crystal data for complex 1: C₂₈H₃₀Cl₃EuN₈O₆, $M = 832.92$, Monoclinic, space group Cc , $a = 15.4368(13)$, $b = 18.1268(7)$, $c = 13.4833(8) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 119.572(8)^\circ$, $\gamma = 90^\circ$, $V = 3281.4(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.686 \text{ g cm}^{-3}$. The final refinement converges to final $R = 0.0601$ and $wR =$

0.1437 with 6399 parameters from 10667 independent reflections ($I > 2\sigma(I)$). The goodness of fit on F^2 was 1.022. CCDC reference number 1414545.

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Notes and references

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Electronic Supplementary Information (ESI) available: Materials and instruments, IR spectrum, powder XRD pattern, luminescence decay profile, emission spectrum of the protonated free ligand, and additional diagrams. See DOI: 10.1039/c000000x/

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