Construction of a crystalline 14-metal Zn–Nd rectangular nanocluster with a dual-emissive response towards metal ions†

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A crystalline 14-metal Zn–Nd cluster \([\text{Zn}_{6}\text{Nd}_{8}\text{L}_{2}\text{OAc}_{20}\text{O}_{2}\text{(NO}_{3})_{4}\text{OC}_{2}\text{H}_{5}_{4}]\) (I) was constructed using a flexible Schiff base ligand with long-chain \((\text{CH}_{2})_{2}\text{O}(\text{CH}_{2})_{2}\text{O}(\text{CH}_{2})_{2}\text{backbone. 1 exhibits a nanoscale}\) rectangular structure \((10 \times 14 \times 18 \text{ Å})\). Besides the visible ligand-centered emission, 1 displays typical NIR luminescence of Nd\(^{3+}\). Interestingly, 1 shows both a ligand-centered and lanthanide fluorescence response towards metal ions, especially to K\(^+\) and Co\(^{2+}\) at the ppm level.

Introduction

A fluorescence response towards various analytes such as metal ions, acid radical anions and small molecules has recently gained considerable attention for its potential application in biology, medicine and environment.\(^1\)-\(^3\) For example, the fluorescence detection of potassium (K\(^+\)) is essential to biomedical diagnosis since potassium plays a central role in the human body. Recently, many crown ethers and cryptands have been used in the study of fluorescent K\(^+\) sensors.\(^4\)-\(^6\) However, the results of the fluorescence intensity-based response may be easily affected by some factors such as the power of the light source and the concentration of the analyte. Recently, dual-emissive probes with two emission bands have been designed to make the response more accurate by the self-calibration of the fluorescence signals.\(^7\)-\(^14\) For example, some dual-emissive probes such as fluorescent organic compounds,\(^14\)-\(^15\) nanoparticles,\(^16\),\(^17\) and d-block metal complexes\(^18\),\(^19\) have been used for this purpose in biologic imaging.

Lanthanide complexes are particularly attractive for the fluorescent response, due to their unique emission properties such as large Stokes shifts, high colour purity and long luminescence lifetimes. For example, near-infrared (NIR) luminescent lanthanide complexes with Nd\((m)\), Yb\((m)\) and Er\((m)\) ions have potential application in bioassays because biological tissues are transparent in this spectral range \((900–1600 \text{ nm})\). So far, many visible luminescent lanthanide complexes with Eu\((m)\) and Tb\((m)\) ions have been used as sensors to detect analytes.\(^20\)-\(^24\) For example, a Tb\((m)\) complex with 18-crown-6 ligand has been used for the time-gated luminescence detection of K\(^+\) ion.\(^25\) However, there are very few reports on the dual-emissive probes based on lanthanide complexes. Recently, Chi et al. first reported the detection of water in organic solvents using a dual-emissive Eu\((m)\)-based metal–organic framework (MOF) encapsulating carbon-based dots (CDs), where both red light emission from Eu\(^{2+}\) ions and blue light emission from CDs show response to the water.\(^26\) For the NIR luminescent lanthanide complexes, besides the lanthanide luminescence around 900–1600 nm, they can exhibit ligand-centered emission in the visible region. Dual-emissive probes based on emissions from both lanthanide ion and organic ligand may have some advantages in the detection of target objects, due to the difference between the emissions in their lifetimes, wavelengths and band shapes.

Compared with the visible luminescence of lanthanide ions such as Eu\((m)\) and Tb\((m)\), the NIR lanthanide luminescence is much far apart from the ligand-centered emission (usually at near 500 nm). Thus, the purpose of our research is to design dual-emissive lanthanide-based probes with both visible ligand-centered emission and NIR lanthanide luminescence. It is known that, some metal chromophores with d-block transition-metal ions such as Zn\((m)\), Ru\((m)\), Pt\((m)\) and Cd\((m)\) may not only show strong visible emission, but also can act as sensitizers for the NIR lanthanide luminescence (“antenna effect”). Our current research has focused on the luminescent response of d-4f nanoclusters towards various analytes.\(^27\),\(^28\) Here, one crystalline 14-metal Zn–Nd cluster \([\text{Zn}_{6}\text{Nd}_{8}\text{L}_{2}\text{OAc}_{20}\text{O}_{2}\text{NO}_{3})_{4}\text{OC}_{2}\text{H}_{5}_{4}]\) (I) was prepared using a long-chain Schiff base ligand \(N,N^{'},N^{{''}}\text{bis}(3\text{-methoxysalicylidene})[1,2\text{-bis(ethoxy)ethane}]-1,6\text{-diadime (H}_{2}\text{L, Scheme 1). The length of H}_{2}\text{L is about 24 Å, which is much longer than most of other reported flexible Schiff
Results and discussion

Synthesis and crystal structure of 1

The Schiff-base ligand $H_2L$ was prepared from the reaction of 2-[2-(2-amion-ethoxy)-ethoxy]ethylamine and 2-hydroxy-3-methoxy-benzaldehyde, according to well established procedures. The reaction of $H_2L$ with $\text{Zn(OAc)}_2\cdot2\text{H}_2\text{O}$ and $\text{Nd(NO}_3)_3\cdot6\text{H}_2\text{O}$ gave a yellow solution, and 1 was obtained by the diffusion of diethyl ether into the solution as pale yellow crystalline solid. As shown in Fig. 1, the crystal structure of 1 is centrosymmetric. Six $\text{Zn}^{2+}$ and eight $\text{Nd}^{3+}$ ions are linked together by two Schiff base ligands, twenty $\text{OAc}^-$, two $\text{O}^{2-}$ and four $\text{NO}_3^-$ anions. The $\text{Zn(n)}$-$\text{Nd(m)}$ distances are from 3.706 Å to 3.897 Å. The $\text{OAc}^-$, $\text{O}^{2-}$ and $\text{NO}_3^-$ anions exhibit $\mu_2$, $\mu_3$ and $\mu_5$ coordination modes with the metal ions, respectively. All $\text{Nd}^{3+}$ ions are surrounded by O atoms from the Schiff base ligands and anions. Six $\text{Nd}^{3+}$ ions are nine-coordinated with single cap square antiprism geometry, while another two are ten-coordinated with pseudo-bicapped square-antiprismatic geometry. In 1, $\text{Zn}^{2+}$ ions show tetrahedral, triangular bipyramidal and octahedron geometries. For the Schiff base ligands in 1, their N atoms coordinate to two six-coordinated $\text{Zn}^{2+}$ ions, and the phenoxide and methoxy O atoms bind to four $\text{Nd}^{3+}$ ion, while the backbone O atoms do not coordinate to the metal ions. The $\text{Zn}$–$\text{N}$, $\text{Zn}$–$\text{O}$, $\text{Nd}$–$\text{N}$ and $\text{Nd}$–$\text{O}$ bond lengths are 2.082 Å–2.099 Å, 1.906 Å–2.444 Å, 2.916 Å–2.970 Å and 2.395 Å–2.666 Å, respectively.

The luminescence properties of 1 were studied in $\text{CH}_3\text{CN}$ and the solid state. The UV-vis absorption spectra show that the absorption bands of 1 are red-shifted compared with those of the free $H_2L$ (Fig. 3). Upon the excitation in ligand absorption band at 355 nm, 1 exhibits typical NIR luminescence of $\text{Nd}^{3+}$. The overall NIR emission quantum yield ($\Phi_{\text{em}}$) of 1 is estimated to be 31.8%. The energy transfer efficiency ($\eta_{\text{hf}}$) from the free ligand $H_2L$ (Fig. 3) to metal ions $\text{Cr}^{3+}$, $\text{Mn}^{2+}$, $\text{Fe}^{3+}$, $\text{Co}^{3+}$, $\text{Ni}^{2+}$, $\text{Cu}^{2+}$, $\text{Zn}^{2+}$, $\text{Cd}^{2+}$, $\text{Ag}^+$, $\text{Mg}^{2+}$, $\text{Sr}^{2+}$, $\text{Al}^{3+}$, $\text{Li}^+$, $\text{Na}^+$ and $\text{K}^+$ (metal acetates) have been investigated in DMF. Interestingly, the addition of metal ions results in different intensity changes of the emissions. For example, the addition of all metal ions decreases the lanthanide luminescence of 1. The addition of metal ions $\text{K}^+$, $\text{Li}^+$, $\text{Na}^+$, $\text{Ag}^+$, $\text{Mg}^{2+}$, $\text{Al}^{3+}$, $\text{Cr}^{3+}$ and $\text{Sr}^{2+}$ increases the ligand-centered emission, but the addition of

![Scheme 1](image)

Scheme 1: Long-chain Schiff base ligand $H_2L$. The reaction of $H_2L$ with $\text{Zn(OAc)}_2\cdot2\text{H}_2\text{O}$ and $\text{Nd(NO}_3)_3\cdot6\text{H}_2\text{O}$ gave a yellow solution, and 1 was obtained by the diffusion of diethyl ether into the solution as pale yellow crystalline solid. As shown in Fig. 1, the crystal structure of 1 is centrosymmetric. Six $\text{Zn}^{2+}$ and eight $\text{Nd}^{3+}$ ions are linked together by two Schiff base ligands, twenty $\text{OAc}^-$, two $\text{O}^{2-}$ and four $\text{NO}_3^-$ anions. The $\text{Zn(n)}$-$\text{Nd(m)}$ distances are from 3.706 Å to 3.897 Å. The $\text{OAc}^-$, $\text{O}^{2-}$ and $\text{NO}_3^-$ anions exhibit $\mu_2$, $\mu_3$ and $\mu_5$ coordination modes with the metal ions, respectively. All $\text{Nd}^{3+}$ ions are surrounded by O atoms from the Schiff base ligands and anions. Six $\text{Nd}^{3+}$ ions are nine-coordinated with single cap square antiprism geometry, while another two are ten-coordinated with pseudo-bicapped square-antiprismatic geometry. In 1, $\text{Zn}^{2+}$ ions show tetrahedral, triangular bipyramidal and octahedron geometries. For the Schiff base ligands in 1, their N atoms coordinate to two six-coordinated $\text{Zn}^{2+}$ ions, and the phenoxide and methoxy O atoms bind to four $\text{Nd}^{3+}$ ion, while the backbone O atoms do not coordinate to the metal ions. The $\text{Zn}$–$\text{N}$, $\text{Zn}$–$\text{O}$, $\text{Nd}$–$\text{N}$ and $\text{Nd}$–$\text{O}$ bond lengths are 2.082 Å–2.099 Å, 1.906 Å–2.444 Å, 2.916 Å–2.970 Å and 2.395 Å–2.666 Å, respectively.

The luminescence properties of 1 were studied in $\text{CH}_3\text{CN}$ and the solid state. The UV-vis absorption spectra show that the absorption bands of 1 are red-shifted compared with those of the free $H_2L$ (Fig. 3). Upon the excitation in ligand absorption band at 355 nm, 1 exhibits typical NIR luminescence of $\text{Nd}^{3+}$. The overall NIR emission quantum yield ($\Phi_{\text{em}}$) of 1 is calculated to be 2.2% ($\Phi_{\text{em}} = \tau/\tau_0$, $\tau = 250$ μs, the natural lifetime of $\text{Nd}^{3+}$). The overall NIR emission quantum yield ($\Phi_{\text{em}}$) of 1 is 0.7%. The energy transfer efficiency ($\eta_{\text{hf}}$) from the free ligand $H_2L$ (Fig. 3) to metal ions $\text{Cr}^{3+}$, $\text{Mn}^{2+}$, $\text{Fe}^{3+}$, $\text{Co}^{3+}$, $\text{Ni}^{2+}$, $\text{Cu}^{2+}$, $\text{Zn}^{2+}$, $\text{Cd}^{2+}$, $\text{Ag}^+$, $\text{Mg}^{2+}$, $\text{Sr}^{2+}$, $\text{Al}^{3+}$, $\text{Li}^+$, $\text{Na}^+$ and $\text{K}^+$ (metal acetates) have been investigated in DMF. Interestingly, the addition of metal ions results in different intensity changes of the emissions. For example, the addition of all metal ions decreases the lanthanide luminescence of 1. The addition of metal ions $\text{K}^+$, $\text{Li}^+$, $\text{Na}^+$, $\text{Ag}^+$, $\text{Mg}^{2+}$, $\text{Al}^{3+}$, $\text{Cr}^{3+}$ and $\text{Sr}^{2+}$ increases the ligand-centered emission, but the addition of
others decreases the emission (Fig. 5, 6 and S5, S6†). It is found
that the addition of K+ and Co2+ ions causes a more rapid
decrease of the lanthanide luminescence intensity than the
addition of other metal ions. For example, the emission inten-
sities at 1061 nm of
\[ \text{1} \]
are decreased about 50% when the
concentrations of added K+ and Co2+ solutions are 255
m
M and
109
m
M, respectively (Fig. 5 and S5†). Compared with other
metal ions, the addition of K+ (or Co2+) ion also leads to a more
rapid enhancement (or decrease) of the ligand-centered emis-
sion. For example, with the addition of 60 μM K+ (or 44 μM Co2+)
ion, the ligand-centered emission intensity at 494 nm is
increased by one time (or decreased by a half) (Fig. 6 and S6†).
These results indicate that, compared with other metal ions, 1
shows high sensitivity to K+ and Co2+ ions through both
lanthanide and ligand-centered fluorescent response.

The intensity changes for both lanthanide and ligand-
centered emissions of 1 and the concentrations of the added
metal ions show a linear relationship. Thus, the emission
quenching and enhancement efficiencies (Ksv) of 1 can be
calculated by using
\[ K_{sv} = \frac{\left( I_0/I \right)}{[A]} \]
(Stern–Volmer equation). Here, I0 and I are the emission intensities of 1 at 1065 (or 494) nm before and after the addition of metal ion, respectively [A] is the concentration of added metal ion. The Ksv values for the lanthanide and ligand-centered emission sensing of 1 towards metal ions are shown in Fig. 7 and 8. For the lanthanide luminescence, the Ksv values of 1 to K+ and Co2+ ions are 17.2 × 103 M⁻¹ and 12.7 × 103 M⁻¹, respectively. While, for the ligand-centered emission, the Ksv values of 1 to K+ and Co2+ ions are 9.4 × 103 M⁻¹ and 58.7 × 103 M⁻¹, respectively. All these Ksv values to K+ and Co2+ ions are greater than corresponding values to other metal ions. The limits of detection (LOD) of 1 to metal ions can be estimated by the signal-to-noise ratio (S/N = 3), using
\[ \text{LOD} = \frac{3\sigma}{K_{sv}} \]
where σ is the standard deviation. For

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**Fig. 3** UV–visible absorption spectra of the free Schiff base ligand H2L and 1 in CH3CN.

**Fig. 4** Excitation and emission spectra of 1 in CH3CN at room temperature (λex = 355 nm).

**Fig. 5** Lanthanide luminescent response of 1 (60 μM) to the addition of K(OAc) in DMF (λex = 355 nm).

**Fig. 6** Ligand-centered fluorescent response of 1 (60 μM) to the addition of K(OAc) in DMF (λex = 355 nm).

**Fig. 7** Lanthanide luminescence quenching efficiencies (Ksv) of 1 towards metal cations.
the lanthanide (or ligand-centered) emission sensing, the LOD data of 1 to K+ and Co2+ ions are calculated to be 3.67 μM (or 1.87 μM) and 4.96 μM (or 2.97 μM), respectively. These results indicate that 1 show both lanthanide and ligand-centered fluorescent response to these metal ions at the ppm level.

The underlying principles of fluorescence response of sensors towards metal ions are so-called chelation enhancement of the quenching emission (CHEQ) and chelation-enhanced fluorescence chelation-enhanced fluorescence (CHEF) effects. These effects are determined by a series of transduction mechanisms based on energy transfer and charge transfer processes. The added metal ions may affect the energy transfer and charge transfer processes in different ways, resulting in various CHEQ and CHEF effects to the emissions of 1. For example, d-block metal ions Co2+, Mn2+, Fe3+, Ni2+, Cr3+ and Cu2+ ions have d–d transitions due to their unfilled d electronic configurations. Thus, these metal ions may consume the excitation energy of lanthanide ions through f → d energy transfers, resulting in the decrease of lanthanide luminescence. In addition, the added metal ions may affect the ligand-to-metal energy transfer process because of their perturbation to the electronic structure and excited state of the ligand, leading to various intensity changes of the lanthanide luminescence and ligand-centered emission of 1. As shown in Fig. 8, differing from the addition of other 3d metal ions Co2+, Cu2+, Mn2+, Fe3+, Ni2+ and Zn2+, which decreases the ligand-centered emission of 1, the addition of Cd2+ ion increases the ligand-centered emission. This may be explained by the presence of the ligand-to-metal charge transfer (LMCT) transition resulted by the addition of metal ion.

It is found that, the intensity changes of visible and NIR emissions of 1 are not proportional to the radii of added metal ions (Fig. S7†). In fact, the interaction between the added metal ions and 1 plays a key role in both lanthanide and ligand-centered fluorescent response. For example, K+ ion has been reported to be easy to form some intermolecular interaction such as cation–π interaction with macrocyclic compounds and framework complexes due to its suitable ionic size. The interaction between the added metal ions and 1 was investigated by UV-vis titration measurement (Fig. S8†). As shown in Fig. 9, the addition of K+ ion results in a red-shift of the absorption bands of 1, which confirms the formation of intermolecular interaction between K+ ion and the complex.

Experimental

Synthesis of the crystalline cluster

[Zn6Nd4L2(OAc)20(O)2(NO3)4(OC2H5)4] (1)

Zn(OAc)2·2H2O (0.30 mmol, 0.0666 g), Nd(NO3)3·6H2O (0.40 mmol, 0.1800 g) and H2L (0.10 mmol, 0.0417 g) were dissolved in 10 mL EtOH, 2 mL MeOH and 2 mL DMF at room temperature, and a solution of triethylamine in EtOH (0.01 mol L−1, 2 mL) was then added. The resulting solution was heated under reflux for 30 min. It was filtered at room temperature. The yellow crystalline product of 1 was obtained by the slow diffusion of diethyl ether into the filtrate at room temperature after three weeks. The product was collected and dried in the oven at 120 °C for two hours. Yield: 0.0672 g (32%). Mp > 155 °C (dec.). Elemental analysis: found: C, 28.85; H, 3.71; N, 2.63%. Calc. for C100H152N8O72Zn6Nd8: C, 28.84; H, 3.68; N, 2.69%. IR (cm−1): 1624 (s), 1552 (s), 1450 (m), 1408 (m), 1397 (m), 1367 (m), 1277 (s), 1164 (s), 1150 (w), 1082 (m), 1021 (m), 983 (m), 904 (s), 877 (m), 839 (m), 795 (m), 747 (m), 673 (m).

Crystallography

X-ray data were collected for 1 on a Smart APEX CCD diffractometer at 190 K in the θ-2θ mode with monochromated Mo Kα radiation. The direct method (SHELX 97 program) was used to solve the structures. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included but not refined. The selected bond lengths and angles for the structure of 1 are listed in Table S1†.

1: C100H152N8O72Zn6Nd8, triclinic, space group P1, a = 14.1791(12), b = 15.7934(13), c = 18.0200(15) Å, α = 108.2630(10)°, β = 96.2280(10)°, γ = 108.4170(10)°, V = 3538.5(5) Å3, Z = 1, Dc = 1.954 g cm−3, μ(Mo Kα) = 3.971 mm−1, F(000) = 2044, T = 190 K. R1 = 0.0314, wR2 = 0.1021, GOF = 1.129.
Conclusions

In conclusion, one crystalline 14-metal Zn–Nd complex 1 was constructed using a flexible Schiff base ligand with long-chain (CH$_2$)$_2$O(CH$_2$)$_2$O(CH$_2$)$_2$ backbone. 1 has nanoscale rectangular molecular size (10 × 14 × 18 Å). Upon the excitation of absorption bands, 1 exhibits visible ligand-centered and NIR lanthanide emissions. The addition of K$^+$, Li$^+$, Na$^+$, Ag$^+$, Mg$^{2+}$, Al$^{3+}$ and Cr$^{3+}$ ions increases the intensity of ligand-centered emission of 1, however, the addition of Co$^{2+}$, Cu$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ ions decreases the intensity. While, the addition of metal ions decreases the lanthanide luminescence of 1. Compared with other metal ions, 1 shows high sensitivity to K$^+$ and Co$^{2+}$ ions at the ppm level through both lanthanide and ligand-centered fluorescent response. Further studies focused on the dual-emissive response of lanthanide-based clusters to other analytes are in progress.

Conflicts of interest

There are no conflicts to declare.

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