A NIR luminescent octanuclear Zn(II)–Nd(III) nanocluster \( \text{1} \) was constructed by the use of a salen-type Schiff base ligand. \( \text{1} \) exhibits a lanthanide luminescent response to Que with high sensitivity. The quenching constant of Que to the lanthanide emission is \( 2.6 \times 10^4 \text{ M}^{-1} \), and the detection limit of \( \text{1} \) to Que is 2.5 \( \mu \text{M} \). The response behavior of \( \text{1} \) to Que is not affected by the existence of some potential interferents such as biomolecules.

**Results and discussion**

**Synthesis and crystal structure of the Zn(II)–Nd(III) nanocluster**

The salen-type Schiff base ligand \( \text{H}_4\text{L} \) was synthesized from the reaction of 2,3-dihydroxybenzaldehyde and 4-methoxy-phenylelenediamine (ESI†). \( \text{1} \) was synthesized from the reaction of \( \text{H}_4\text{L} \) with \( \text{Nd(OAc)}_3 \cdot 4\text{H}_2\text{O} \) and \( \text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O} \). The molecular dimensions of \( \text{1} \) are about 1.1 \( \times \) 1.6 \( \times \) 1.8 nm (Fig. 1). In \( \text{1} \), six Zn(II) and two Nd(III) ions are coordinated with four Schiff base ligands. Four Zn(II) ions are located in the \( \text{N}_2\text{O}_2 \) cavities of the

![Scheme 1](image_url)
Schiff base ligands with a square based pyramidal geometry, while other two \( \text{Zn(n)} \) ions are coordinated with phenolic oxygen atoms of the ligands with a tetrahedral geometry. Each \( \text{Nd(n)} \) ion is bound to two \( \text{O}_2\text{O}_2 \) donor sets of the ligands, and the coordination number is eight. Each \( \text{Nd(n)} \) ion is surrounded by eight O atoms from three Schiff base ligands, one \( \text{OAc}^- \) anion and one solvent molecule \( \text{EtOH} \) (or DMF). The neighboring \( \text{Nd(n)} \) ions not only bind to the \( \text{N}_2\text{O}_2 \) donor sets of the ligands but also to their \( \text{O}_2\text{O}_2 \) sets. In Fig. 2, one image of scanning electron microscopy (SEM) displays the crystalline nature of 1, and in energy dispersive X-ray (EDX) spectroscopy the molar ratio of \( \text{Zn}/\text{Nd} \) is about 3, consistent with its structure. The measured powder XRD pattern of \( \text{ZnNd} \) is similar to the simulated one, while other two \( \text{Zn(II)} \) ions are coordinated with phenolic oxygen atoms which help the formation of metal ions in the structure (Fig. S7†). Upon the excitation in ligand-centered absorption band, 1 displays the NIR luminescence of \( \text{Nd(III)} \) (\( ^{4}\text{F}_{3/2} \rightarrow ^{4}\text{I}_{5/2} \) transitions, \( j = 9, 11 \) and 13) at 880, 1064 and 1337 nm (Fig. 3). The emission lifetime (\( \tau \)) is 5.6 \( \mu \)s (Fig. S8†), so the intrinsic quantum yield (\( \Phi_{\text{Ln}} \)) of \( \text{Nd(III)} \) is calculated to be 2.2\%, using equation \( \Phi_{\text{Ln}} = \tau/\tau_0 \) (\( \tau_0 = 250 \mu \)s, the natural lifetime of \( \text{Nd(III)} \)). The whole luminescence quantum yield (\( \Phi_{\text{em}} \)) of 1 is 0.14\%, thus, the energy transfer efficiency (\( \eta_{\text{sens}} = \Phi_{\text{em}}/\Phi_{\text{Ln}} \)) from the Schiff base ligands to \( \text{Nd(III)} \) ions can be calculated as 6.4\%.11

The NIR luminescent sensing behaviour of 1 to Que was studied in \( \text{CH}_3\text{CN} \). The results show that, as the concentrations of added Que increase, the intensities of lanthanide luminescence of 1 are decreased gradually (Fig. 4). The quenching constant (\( K_{\text{SV}} \)) of Que to the lanthanide emission is calculated to be 2.6 \( \times \) 10^5 \( \text{M}^{-1} \), by using Stern–Volmer equation. Also, the limit of detection (LOD = 3\( \sigma/K_{\text{SV}} \)) (ref. 33) of 1 to Que is obtained to be 2.5 \( \mu \)M, which is among the lowest ones reported for the

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Schiff base ligands with a square based pyramidal geometry, while other two \( \text{Zn(n)} \) ions are coordinated with phenolic oxygen atoms of the ligands with a tetrahedral geometry. Each \( \text{Nd(n)} \) ion is bound to two \( \text{O}_2\text{O}_2 \) donor sets of the ligands, and the coordination number is eight. Each \( \text{Nd(n)} \) ion is bounded to the \( \text{N}_2\text{O}_2 \) donor sets and \( \text{Zn-N} \) are 2.28–2.52 Å, 1.91–2.08 Å and 1.99–2.18 Å, respectively. Intramolecular \( \pi-\pi \) stacking interactions exist between the phenyl rings of Schiff base ligands (distances: 3.371 Å to 3.750 Å), which helps the formation of 1. Compared with other reported d-4f complexes with similar salen-type conjugated Schiff base ligands, the \( \text{Zn(n)} \) ions in 1 are not only bound to the \( \text{N}_2\text{O}_2 \) donor sets of the ligands but also to their \( \text{O}_2\text{O}_2 \) sets. In Fig. 2, one image of scanning electron microscopy (SEM) displays the crystalline nature of 1, and in energy dispersive X-ray (EDX) spectroscopy the molar ratio of \( \text{Zn}/\text{Nd} \) is about 3, consistent with its structure. The measured powder XRD pattern of 1 is similar to the simulated one generated from the crystal structure, indicating the purity of the solid product (Fig. S3†). Thermogravimetric analysis indicates that 1 loses about 3\% weight before 100 °C, due to the escaping of uncoordinated solvent molecules such as \( \text{MeOH}, \text{EtOH} \) and \( \text{H}_2\text{O} \) in the sample. 1 starts to decompose from about 180 °C (Fig. S4†), which is also confirmed by the melting point measurement (see Experimental section).

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Photophysical properties and NIR luminescent response to Que

The free \( \text{H}_4\text{L} \) has three bands at 214 nm, 276 nm and 339 nm, which are assigned to \( \pi \rightarrow \pi^* \) or \( \pi \rightarrow \pi^* \) transitions associated with imine and phenyl functions of the Schiff base ligand. These bands are red-shifted in 1 due to the disturbance of metal ions in the structure (Fig. S7†). Upon the excitation in ligand-centered absorption band, 1 displays the NIR luminescence of \( \text{Nd(III)} \) (\( ^{4}\text{F}_{3/2} \rightarrow ^{4}\text{I}_{5/2} \) transitions, \( j = 9, 11 \) and 13) at 880, 1064 and 1337 nm (Fig. 3). The emission lifetime (\( \tau \)) is 5.6 \( \mu \)s (Fig. S8†), so the intrinsic quantum yield (\( \Phi_{\text{Ln}} \)) of \( \text{Nd(III)} \) is calculated to be 2.2\%, using equation \( \Phi_{\text{Ln}} = \tau/\tau_0 \) (\( \tau_0 = 250 \mu \)s, the natural lifetime of \( \text{Nd(III)} \)). The whole luminescence quantum yield (\( \Phi_{\text{em}} \)) of 1 is 0.14\%, thus, the energy transfer efficiency (\( \eta_{\text{sens}} = \Phi_{\text{em}}/\Phi_{\text{Ln}} \)) from the Schiff base ligands to \( \text{Nd(III)} \) ions can be calculated as 6.4\%.

The NIR luminescent sensing behaviour of 1 to Que was studied in \( \text{CH}_3\text{CN} \). The results show that, as the concentrations of added Que increase, the intensities of lanthanide luminescence of 1 are decreased gradually (Fig. 4). The quenching constant (\( K_{\text{SV}} \)) of Que to the lanthanide emission is calculated to be 2.6 \( \times \) 10^5 \( \text{M}^{-1} \), by using Stern–Volmer equation. Also, the limit of detection (LOD = 3\( \sigma/K_{\text{SV}} \)) (ref. 33) of 1 to Que is obtained to be 2.5 \( \mu \)M, which is among the lowest ones reported for the

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**Fig. 1** The crystal structure of 1 (Zn(II): green; Nd(III): blue).

**Fig. 2** The image of scanning electron microscopy (a) and energy dispersive X-ray spectroscopy (b) of 1.

**Fig. 3** The excitation (\( \lambda_{\text{em}} = 1064 \text{ nm} \)) and NIR lanthanide emission (\( \lambda_{\text{ex}} = 370 \text{ nm} \)) spectra of 1 (30 \( \mu \)M) in \( \text{CH}_3\text{CN} \).

**Fig. 4** The quenching of NIR luminescence of 1 (30 \( \mu \)M) to the addition of Que with different concentrations in \( \text{CH}_3\text{CN} \).
fluorescent detection of Que so far. It is noticeable that, the shapes of NIR emission peaks of 1 are same before and after the addition of Que (Fig. 4). Meanwhile, conductivity study confirms that 1 is neutral in CH3CN, in accordance with the crystal structure. These results suggest that 1 is stable during the sensing experiments.

To assess the response selectivity of 1 to Que in biological system, we investigated its sensing behaviour to potential biomolecule interferents such as apigenin (Api), flavanone (Fla), naringin (Nar), hesperidin (Hes), phloroglucinol (Phl), daidzein (Dai), hydroquinone (Hyd), resorcinol (Res) and puerarin (Pue) (Scheme S1†). Compared to Que, the addition of these biomolecules causes much smaller changes to the lanthanide emission of 1 (Fig. 5 and S9†). For instance, the lanthanide emission quenching of 1 caused by 60 μM biomolecules is less than 30% (Fig. S9†), indicating the sensing selectivity of 1 to Que. Additionally, the response behaviour of 1 to Que in the presence of the interferents was examined. The results show that the quenching of the lanthanide emission of 1 aroused by Que is not affected by the existence of the interferents (Fig. 6). The luminescence selectivity of 1 to Que was further confirmed by the step-by-step addition of the interferents. For instance, the luminescence decreases slowly when Api is added twice firstly (Fig. 7). While, it decreases fast by the subsequent addition of equal amount of Que. This trend happens again in the following additions of Api and Que, suggesting the high selectivity of 1 to Que even in the existence of the interferents.

In 1, the Schiﬀ base ligands can absorb and transfer energy to Nd(III) ions, resulting in the lanthanide luminescence ("antenna effect", Scheme 2). It is noticeable that, Que has a much higher absorption coefﬁcient at λex = 370 nm than 1 (1.18 × 10^5 M⁻¹ cm⁻¹ vs. 0.21 × 10^5 M⁻¹ cm⁻¹, Fig. 8 and S7†). Thus, the added Que can compete with 1 for the energy absorption at λex, resulting in the quenching of lanthanide luminescence ("inner ﬁlter effect", Scheme 2). As shown in Fig. 8, the absorptions of biomolecule interferents at λex are much weaker than Que, and they have little effect on the lanthanide luminescence of 1. The "inner ﬁlter effect" of Que to the lanthanide luminescence can be conﬁrmed by comparing the quenching constants of Api and other biomolecule interferents. The absorption coefﬁcient of Api at λex is 0.15 × 10^5 M⁻¹ cm⁻¹, which is higher than those of other interferents (less than 0.07 × 10^5 M⁻¹ cm⁻¹) (Fig. 8), thus, Api can absorb
more light energy than other interferents. Unsurprisingly, Api also shows larger $\kappa_{\text{St}}$ value ($0.44 \times 10^4$ M$^{-1}$) than other interferents (less than $0.13 \times 10^4$ M$^{-1}$), demonstrating the “inner filter effect” to the lanthanide luminescence. Furthermore, the addition of Que results in the quenching of visible ligand-centered emission of 1 at 545 nm (Fig. S10†). This is also due to the decrease of excitation energy of Schiff base ligands caused by the “inner filter effect” of Que.

Experimental

Materials and general methods

All chemical materials were obtained from commercial sources and directly used without further purified. The Schiff base ligand and the lanthanide complex were synthesized using Schlenk system. Elemental analyses were performed on a EURO EA3000. Melting points were obtained on an XT-4 electrothermic micromelting point apparatus. IR spectra of the Schi ligand and the lanthanide complex were measured on a FTIR-650 spectrometer. $^{1}H$ NMR spectrum of the ligand was obtained using AVANCE III AV500 at 298 K. The mass spectrum (ESI) was measured by a standard instrument corrections. The wavelength range is 200 nm–600 nm. The NIR emission and excitation spectra of the complex were carried out on a FLS 980 fluorimeter. Liquid nitrogen cooled Ge PIN diode detector is used to detect the NIR emissions (800 nm–1700 nm). An integrating sphere is used to obtain the quantum yield, and the luminescence lifetime is obtained by using the attached storage digital oscilloscope. Systematic errors are deducted through the standard instrument corrections.

Crystallography

The X-ray data of the complex were collected by a Smart APEX CCD diffractometer (Mo $K\alpha$ radiation). The structure was solved using SHELX 97 program with direct method. The empirical absorption was corrected by SADABS program. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated by geometrical methods and refined isotropically. The CCDC number of 1 is 2102148 (see www.ccdc.cam.ac.uk/data_request/cif). The bond lengths and angles are displayed in Table S1.†

For 1: $C_{97}H_{86}N_{10}O_{32}Zn_{6}Nd_{2}$, monoclinic ($P2_{1}/n$), $a = 20.327(15)$, $b = 23.139(16)$, $c = 25.376(19)$ $\AA$, $\alpha = 90^\circ$, $\beta = 94.941(13)^\circ$, $\gamma = 90^\circ$, $V = 11 891(15)\AA^{3}$, $D_{c} = 1.444 \text{ g cm}^{-3}$, $\mu (\text{Mo } K\alpha) = 2.118 \text{ mm}^{-1}$, $T = 190 \text{ K}$, $Z = 4$, $F(000) = 5176$, GOF = 1.163, $R_{1} = 0.0913$, $wR_{2} = 0.1995$.

Conclusions

In conclusion, an octanuclear Zn(II)–Nd(III) cluster 1 was synthesized from a salen-type Schiff base ligand. The molecular sizes of 1 are $1.1 \times 1.6 \times 1.8$ nm. It shows NIR lanthanide emission, which can be decreased gradually by the addition of Que. The emission quenching of 1 is due to the “inner filter effect” of Que. The limit of the detection of 1 to Que is 2.5 $\mu$M, and its luminescent response behaviour is not affected by the existence of some potential biomolecule interferents.

Conflicts of interest

There are no conflicts to declare.

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