Near-infrared (NIR) luminescent homoleptic linear tetranuclear \([\text{Ln}_4((\text{OH})_2-\text{Salophen})_4]\) (\(\text{Ln} = \text{Nd} \text{ or } \text{Yb}\)) complexes self-assembled from the dihydroxylated Salophen ligand

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Sensitization for NIR luminescence

A B S T R A C T

Through self-assembly of the (\(\text{OH})_2-\text{Salophen}\) \(\text{H}_4\text{L}\) (\(\text{H}_4\text{L} = N, N'-\text{bis}(3\text{-hydroxyl salicylidene})\text{benzene-1,2-diamine}\)) with \(\text{LnCl}_3 \cdot 6\text{H}_2\text{O}\) (\(\text{Ln} = \text{La}, \text{Nd}, \text{Yb}, \text{Er} \text{ or } \text{Gd}\)), series of \([\text{Ln}_4((\text{OH})_2-\text{Salophen})_4]\)-arrayed complexes \([\text{Ln}_4(\text{H}_4\text{L})_2(\text{L})_2(\text{EtOH})_2]\) (\(\text{Ln} = \text{La}, 1; \text{Ln} = \text{Nd}, 2; \text{Ln} = \text{Yb}, 3; \text{Ln} = \text{Er}, 4 \text{ or } \text{Ln} = \text{Gd}, 5\)) were obtained, respectively. The result of their photophysical properties shows that the strong and characteristic NIR luminescence for complexes 2-3 with emissive lifetimes in microsecond ranges is observed, and the sensitization arises from the excited state (1LC) of the (\(\text{OH})_2-\text{Salophen}\) ligand despite the luminescent quenching with OH-oscillators around the \(\text{Ln}^{3+}\) ions.

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Luminescent polynuclear \(\text{Ln}^{3+}\) complexes are currently of considerable interest due to their potential use in materials science [1] and biological systems [2]. However, the control on their molecular structures is synthetically challenging due to the variable coordination numbers and the flexible coordination geometries of the \(\text{Ln}^{3+}\) ions [3]. On the other hand, the nature of counter-anions [4] and the reaction conditions [5] have the distinctive effects on the construction of the polynuclear \(\text{Ln}^{3+}\) complexes besides the character of the selected organic ligands [6]. Further from the viewpoint of the enhancement of their photophysical properties, it is required that both the energy level’s match between the excited states of the organic chromophore and the ground state \((1\text{LC})\) of the (\(\text{OH})_2-\text{Salophen}\) ligand despite the luminescent quenching with OH-oscillators around the \(\text{Ln}^{3+}\) ions [7].

Compared with the amounts of d and/or f-block complexes based on the typical Salen-type Schiff-base ligands [9], few examples on the complexes from the hydroxyl-modified Salen ligands are reported. In fact, the introduction of single or multiple hydroxyl groups on the Salen-type Schiff-base ligands endows the multi-dentate coordination and the complicated charge balance modes in the formation of their complexes. For example, with the solely hydroxyl group on the linkers of Salen-type Schiff-base ligands, the obtained \(\text{Nd}_2\text{O}_3\)-quinquidentate OH-Salen ligands gave discrete cyclic \(\text{Zn}_2\text{Ln}_2\) [10] or homoleptic \(\text{Ln}_2\)-

- arrayed complexes [11], respectively. As to the \((\text{OH})_2-\text{Salen}\) ligands \((\text{H}_4\text{L})_0\) with two hydroxyl groups at the \(\text{Ln}^{3+}\) ion [7], and the complete avoiding or decreasing of the luminescent quenching effect arising from \(\text{OH}\)-, \(\text{CH}\)- or \(\text{NH}\)-oscillators around the \(\text{Ln}^{3+}\) ions [8] are realized.

As shown in Scheme 1, reaction of o-phenylenediamine with 2,3-dihydroxybenzaldehyde in 1:2 molar ratio afforded the dihydroxylated (\(\text{OH})_2-\text{Salen}\) ligand \(\text{H}_4\text{L}\). Further through the self-assembly of \(\text{H}_4\text{L}\) with \(\text{LnCl}_3 \cdot 6\text{H}_2\text{O}\) (\(\text{Ln} = \text{La}, \text{Nd}, \text{Yb}, \text{Er} \text{ or } \text{Gd}\)) within the molar ratio of 1:1, series of homoleptic linear tetranuclear \([\text{Ln}_4((\text{OH})_2-\text{Salophen})_4]\)-arrayed complexes were obtained, respectively.

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The (OH)$_2$-Salophen ligand H$_4$L and its five complexes 1–5 were well characterized by EA, FT-IR, $^1$H NMR and ESI-MS. As to the room temperature $^1$H NMR spectrum (Fig. 1S) in DMSO-$_d_6$ of antiferromagnetic [La$_4$((OH)$_2$-Salophen)$_4$]-arrayed complex 1, the disappearance of the easily deprotonated intramolecular resonance-assisted hydrogen bonded (RAHB) O–H–N proton resonances ($\delta = 13.35$ ppm) of the free H$_4$L ligand while the retention of two kinds of down-field shifted free OH-based proton resonances ($\delta = 9.45$ and 6.29 ppm) are observed, respectively. Especially, the ESI-MS spectra (Fig. 2S) of the free hydrogen bonded (RAHB) O atom (O16 or O8) from the almost linear tetranuclear host structure are different, where the free Yb–Yb separation (Yb2–Yb3, 3.827(3) Å) between two Yb$_2$(Ln)(H$_2$L) portions is slightly longer than that (3.582(4)–3.602(4) Å for Yb1–Yb2 or Yb3–Yb4) in each of portion. The solvate DMF molecule of 3·DMF, contributes to the stability of the structure, while exhibits no observed hydrogen-bonding interactions with the framework. It is worth noting the linear tetranuclear [Yb$_4$(OH)$_2$-Salophen)$_4$] host structure in 3·DMF is distinctly different from binuclear triple-decker Ln$_3$(Salen)$_2$ [18] and trinuclear triple-decker Ln$_3$(Salen)$_3$ complexes [19] from the typical quadridentate Salen-type Schiff-base ligands, and also incomparable to trinuclear triple-decker Ln$_3$(Salen)$_3$ [19] and pentanuclear tetra-decker Ln$_6$(Salen)$_6$ [20] and hexadentate Salen-type Schiff-base ligands with the two –OMe groups, where the charge balance just depends on the counter-ions while not the mixed (L)$^{4+}$ and (H$_2$L)$_2^{-}$ coordination modes of four (OH)$_2$-Salophen ligands in 3·DMF. As to the bulk purity of the four polycrystaline samples 2–5, it is convincingly established by PXRD measurements. As shown in Fig. 3S, for each of the four samples, the peak positions of the measured pattern closely match those of the simulated 3·DMF, confirming that they are really isostructural and a single phase is formed for each complex. Moreover, TGA of the four polycrystaline samples 2–5 shows the similar weight loss patterns, as shown in Fig. 4S, where a gradual weight loss (about 5%) occurs in the range of 80–140 °C, probably indicative of the loss of two coordinated EtOH molecules, and the frameworks decompose at ca. 250 °C with an observed abrupt weight loss.

The photophysical properties of the ligand H$_4$L and complexes 2–5 have been examined in dilute MeCN at room temperature or 77 K, and summarized in Table 3S, Figs. 2 and 5–7S. As shown in Fig. 5S, the almost identical ligand-centered while red-shifted absorptions (236–240, 310–312 and 418–422 nm) of complexes 2–5 as compared to that (228, 280 and 336 nm) of the free H$_4$L ligand in the UV–visible region are
observed, and the molar absorption coefficients in all the lowest energy bands (418–422 nm) are almost four orders of magnitude larger than that (336 nm) of the ligand H4L, due to the involvement of four chromophores. For complexes 2–3, the similar residual visible emissions (λem = 484 nm, τ = 1 ns and Φem < 10−5) in dilute absolute MeCN solution at room temperature are observed, while photo excitation at the range of 510–500 nm (λex = 426 nm for 2 or λex = 423 nm for 3), as shown in Fig. 2, gives rise to the characteristic emissions of Nd3+ ion (909, 1086 and 1366 nm, τF3/2 = 4P3/2, J = 9, 11, 13) for complex 2 and Yb3+ ion (982 nm, τH2F2 = 2P3/2) for complex 3 in the NIR region, respectively. Unlike that for complex 2 or 3, the characteristic NIR emission of the Er3+ ion for complex 4 cannot be observed. Further based on the results of time-resolved luminescent experiments, the two luminescent decay curves (Fig. 6S) can be fitted monoexponentially with time constants of microseconds (1.05 μs for 2 or 117.9 μs for 3), and the intrinsic quantum yields Φex (0.42% for 2 or 0.59% for 3) of the Ln3+ emissions may be estimated by Φex = τabs/τobs, where τabs is the observed emission lifetime and τobs is the “neutral lifetime” viz. 0.25 ms and 2.0 ms for the Nd3+ and Yb3+ ions [23], respectively.

It is of particular interest to explore the energy transfer process on the NIR emission for complexes 2–4. As a suitable reference compound [24], the [D4a(H2O)2-Salophen]4⁺-based complex 5 in dilute MeCN solution just exhibits antenna fluorescence at room temperature (λem = 484 nm and τ = 1.71 ns as shown in Fig. 7S) or even 77 K (λem = 471 nm, τ = 6.26 ns and λem = 550 nm, τ = 12.58 ns as shown in Table 3S), which shows that the sensitization of the NIR luminescence for complexes 2–4 should arise from the LC (18182 cm−1) excited state of H4L ligand especially at low temperature [25]. Further from the viewpoint of the energy level match, the larger energy gap (ΔE = 11572 cm−1) between the 4C excited state of H4L ligand and the first emitting level (4F7/2, 6610 cm−1) of the Er3+ ion in complex 4 leads to the greater nonradiative energy loss, which should be the reason to its weak and unobservable NIR characteristic emission. As to the higher intrinsic quantum yield Φex (0.59%) of the Yb3+ emission for 3 than that (0.43%) of the Nd3+ emission for 2, although the energy gap (ΔE = 6925 cm−1) in 2 is smaller than that (ΔE = 7782 cm−1) of 3, it should be resulted from the quantity (4F7/2, J = 9, 11, 13) of accepting energy levels of the Nd3+ ion while only one (3P5/2) of the Yb3+ ion. Moreover, the excited state of the Nd3+ ions in 2 with the smaller energy gap is more sensitive to luminescent quenching especially with the nearby O–H oscillators of partially deprotonated [H4L]7− and coordinated EOH around the Nd3+ ions. It is worth noting that the NIR intrinsic quantum yields of both complexes 2–3 are relatively smaller than those of Ln4(Salen)4 [20] or Ln4(Salen)2 [21] complexes based on the typical Salen-type Schiff-base ligands, which should be primarily due to the use of the rigid linker for complexes 2–3 while not flexible linkage with the NIR sensitization from both 3LC and 14C excited states of the ligand.

In conclusion, on the basis of self-assembly of the dicarboxyl-modified (OH)2-Salophen ligand H4L with LnCl3·6H2O, the mixed (L4− and (H4L)7− coordination modes induce the formation of anion-independent linear tetranuclear [Ln4((OH)2-Salophen)4]14−-arrayed complexes [Ln4(H4L)2(L2)2(EOH)2]3− (1–5). Moreover, the result of their photophysical studies shows that the (OH)2-Salophen ligand may work as antennae for the sensitization of the characteristic NIR luminescence of Nd3+ and Yb3+ ions despite the luminescent quenching with the OH-oscillators around the Ln3+ ions. The specific design of polynuclear Ln3+ complexes from the flexible (OH)2-Salen ligands by further deep deprotonation in facilitating the NIR sensitization is now under way.

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Appendix A. Supplementary data

The coordination modes for the common (OH)2-Salen ligand (H4L0) or the (OH)2-Salophen ligand (H4L) in Schemes 1–2, the crystallographic data for 3–DMF in Tables 1–25, the photophysical properties of H4L and complexes 2–5 in Table 3S, and the 1H NMR spectra of H4L and complexes 1, the ESI-MS spectra, PXRD patterns and TGA results of complexes 1–2, UV-visible absorption spectra of H4L and complexes 2–5, luminescent decay profiles for complexes 2–3 and visible emission and excitation spectra of H4L and complex 5 in Figs. 1–7S. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jinorgbio.2014.08.009. These data include MOL files and InChIKey of the most important compounds described in this article.

References


Fig. 2. NIR emission and excitation spectra of complexes 2 and 3 in MeCN solution at 2 × 10−3 M at room temperature.