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Near-infrared (NIR) luminescent homoleptic lanthanide Salen complexes $Ln_4(Salen)_4$ (Ln = Nd, Yb or Er)[†]

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The series of homoleptic tetranuclear $[Ln_4(L)_2(HL)_2(NO_3)_2(OH)_2] \cdot 2(NO_3)$ (Ln = Nd, 1; Ln = Yb, 2; Ln = Er, 3; Ln = Gd, 4) have been self-assembled from the reaction of the Salen-type Schiff-base ligand H_2L with $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Nd, Yb, Er or Gd), respectively (H_2L : *N*,*N'*-bis(salicylidene) cyclohexane-1,2-diamine). The result of their photophysical properties shows that the strong and characteristic NIR luminescence for complexes 1 and 2 with emissive lifetimes in microsecond ranges are observed and the sensitization arises from the excited state (both ¹LC and ³LC) of the Salen-type Schiff-base ligand with the flexible linker.

1. Introduction

Recent startling interest for polynuclear Ln³⁺ complexes with the unusual photophysical and magnetic properties, is stimulated by the continuously expanding need for luminescent¹ and magnetic materials.² However, the synthesis is often problematic due to the high coordination numbers and the flexible coordination geometries adopted by the Ln³⁺ ions.³ In fact, the challenge to resolve the problem is strengthened because the construction of the polynuclear Ln³⁺ complexes is distinctively affected by a variety of factors, such as the character of organic ligands,⁴ the nature of counter anions⁵ and the reaction conditions.⁶ From the viewpoint of self-assembly of the polynuclear Ln³⁺ complexes with good photophysical properties, this requires that the strong lightharvesting of the organic chromophores, the effective energy transfer from the chromophores to the Ln3+ ions and the minimization of non-radiative processes of the Ln³⁺ are achieved,⁷ besides completely avoiding or decreasing the luminescent quenching effect arising from OH-, CH- or NH-oscillators around the Ln3+ ion.8

Compared to the amount of effort on the photophysical behavior of 3d–4f heteronuclear complexes from compartmental

Salen-type Schiff-base ligands,⁹ the photophysical properties of polynuclear lanthanide Salen complexes have not been researched nearly as extensively, especially the limited singlecrystal X-ray diffraction study has been reported for those classic complexes.¹⁰ Nonetheless, in the formation of the series of binuclear triple-decker,¹¹ trinuclear triple-decker,¹² trinuclear tetra-decker¹³ or pentanuclear tetra-decker lanthanide complexes,¹⁴ different Salen-type Schiff-base ligands with rigid linkers have been used, and their photophysical properties should be further enhanced, despite the chromophores with rigid linkers absorbing at longer wavelength. Moreover, the selfassembly from LnX_3 (X⁻ = OAc⁻ or CF₃SO₃⁻) with the Salentype Schiff-base ligands with the flexible linkers usually gives the formation of polymeric lanthanide coordination complexes, not the discrete polynuclear lanthanide complexes.¹⁵ In particular, the recent report of discrete binuclear or tetranuclear homoleptic lanthanide Salen complexes¹⁶ revealed that the pure Salen-type Schiff-base ligand without the outer O₂O₂ moiety could coordinate with the Ln³⁺ ions in quadridentate and bidentate modes, while the self-assembly process is complicated, anion-dependent and strictly relative to the detailed reaction conditions. To the best of our knowledge, no report of the self-assembly of polynuclear lanthanide complexes from flexible hexadentate Salentype Schiff-base ligands with the outer O2O2 moiety has been documented. Herein, starting from the Salen-type Schiff-base ligand H_2L ($H_2L = N, N'$ -bis(3-methoxy-salicylidene)cyclohexane-1,2-diamine) with the flexible linker, the richness of its coordination modes $((L)^{2-}$ and $(HL)^{-}$ modes, as shown in Scheme 1) endows the formation of series of homoleptic tetranuclear $[Ln_4(L)_2(HL)_2(NO_3)_2(OH)_2] \cdot 2(NO_3)$ (Ln = Nd, 1; Ln = Yb, 2; Ln = Er, 3; Ln = Gd, 4) under similar reaction conditions. The sensitization and the energy transfer for the NIR luminescence of the Ln^{3+} ions in the homoleptic tetranuclear $Ln_4(Salen)_4$ complexes are discussed.

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Scheme 1 Molecular structures and bonding modes of Salen-type Schiff-base ligands for polynuclear or polymeric lanthanide complexes.

2. Experimental

All chemicals were commercial products of reagent grade and were used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on a Nicolet Nagna-IR 550 spectrophotometer in the region 4000-400 cm⁻¹ using KBr pellets. ¹H NMR spectra were recorded on a JEOL EX270 spectrometer with SiMe₄ as internal standard in CD₃CN at room temperature. ESI-MS was performed on a Finnigan LCQDECA XP HPLC-MS_n mass spectrometer with a mass to charge (m/z)range of 4000 using a standard electrospray ion source and MeCN or MeOH as solvent. Electronic absorption spectra in the UV/Vis region were recorded with a Cary 300 UV spectrophotometer, and steady-state visible fluorescence, PL excitation spectra on a Photon Technology International (PTI) Alphascan spectrofluorometer and visible decay spectra on a pico-N₂ laser system (PTI Time Master). The quantum yield of the visible luminescence for each sample was determined by the relative comparison procedure, using a reference of a known quantum yield (quinine sulfate in dilute H₂SO₄ solution, $\Phi_{em} =$ 0.546). NIR emission and excitation in solution were recorded by PTI QM4 spectrofluorometer with a PTI QM4 Near-Infrared InGaAs detector.

Syntheses

H₂**L** (**H**₂**L**: *N*,*N*-bis(3-methoxy-salicylidene)cyclohexane-1,2diamine). To a stirred solution of an equimolar mixture of *cis*and *trans*-1,2-diaminocyclohexane (6.0 mL, 50 mmol) in absolute EtOH (20 mL), *o*-vanillin (15.0 g, 100 mmol) was added, and the resulting mixture was refluxed for 5 h. After cooling to room temperature, the insoluble yellow precipitate was filtered and was recrystallized using absolute EtOH to give a pale yellow polycrystalline solid. Yield: 13.6 g, 71%. Calc. for C₂₂H₂₆N₂O₄: C 69.09, H 6.85, N 7.32%; found: C, 69.01, H, 6.94, N, 7.26%. IR (KBr, cm⁻¹): 3455 (b), 3058 (w), 2933 (w), 2862 (w), 2597 (w), 1619 (s), 1588 (w), 1470 (s), 1418 (m), 1345 (w), 1251 (vs), 1196 (w), 1168 (w), 1144 (w), 1085 (m), 1036 (w), 984 (m), 953 (w), 894 (w), 849 (m), 776 (w), 731 (m), 668 (w), 616 (w), 595 (w), 568 (w), 516 (w), 467 (w), 422 (w). ¹H NMR (400 MHz, CD₃CN): δ (ppm) 13.84 (s, 2H, -OH), 8.24 (s, 2H, -CH=N), 6.85 (d, 2H, -Ph), 6.78 (d, 2H, -Ph), 6.72 (t, 2H, -Ph), 3.86 (s, 6H, MeO-), 3.32 (m, 2H, -Ch), 1.92 (m, 4H, -Ch), 1.58 (m, 4H, -Ch).

Synthesis of $[Nd_4(L)_2(HL)_2(NO_3)_2(OH)_2] \cdot 2(NO_3)$ (1). To a stirred solution of H₂L (0.115 g, 0.3 mmol) in absolute MeCN (10 mL), Et₃N (100 µL) and a solution of Nd(NO₃)₃·6H₂O (0.3 mmol, 0.117 g) in absolute MeOH (10 mL) were added, respectively. The resultant mixture was refluxed for 2 h, and the clear pale yellow solution was then cooled to room temperature and filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and the pale yellow microcrystal products of 1 were obtained in a few weeks. For 1: Yield: 0.118 g, 67%. Anal. Calc. for C88H100N12O30Nd4: C, 44.36; H, 4.23; N, 7.05%; found: C, 44.15; H, 4.37; N, 7.01%. IR (KBr, cm⁻¹): 3402 (b), 3065 (w), 2938 (m), 2857 (w), 1648 (s), 1615 (m), 1556 (m), 1503 (m), 1452 (vs), 1384 (m), 1355 (w), 1283 (s), 1237 (w), 1221 (s), 1169 (m), 1144 (w), 1098 (w), 1075 (m), 1058 (w), 1019 (w), 946 (w), 902 (w), 847 (m), 783 (w), 742 (m), 659 (w), 605 (w), 561 (w), 491 (w), 470 (w), 433 (w). ¹H NMR (400 MHz, CD₃CN): δ (ppm) 14.58 (s, 4H), 14.17 (s, 4H), 10.10 (t, 4H), 9.40 (t, 4H), 8.61 (d, 4H), 8.36 (d, 4H), 7.59 (m, 4H), 6.53 (m, 4H), 5.48 (m, 12H), 4.66 (m, 12H), 4.02 (m, 4H), 3.80 (m, 4H), 1.70 (s, 6H), 1.31 (s, 6H), 1.16 (m, 3H), 1.03 (m, 3H), -0.10 (m, 4H), -0.42 (m, 4H), -0.81 (m, 4H), -1.23 (m, 4H), -1.83 (m, 4H), -2.65 (m,4H), -2.90 (m, 4H), -5.68 (m, 4H). ESI-MS (in MeCN) m/z: 2320.78 (100%), $[M - NO_3]^+$; 1129.38 (45%), $[M - (NO_3)_2]^{2+}$; 745.94 (4%), [M - (NO₃)₃ + (MeCN)]³⁺ and 554.22 (11%), [M -(NO₃)₄ + (MeCN)₂]⁴⁺; ESI-MS (in MeOH) *m*/*z*: 2320.78 (100%), $[M - NO_3]^+$; 1129.38 (41%), $[M - (NO_3)_2]^{2+}$, 742.94 (5%), $[M - (NO_3)_2]^{2+}$, 742.94 (5%) $(NO_3)_3$ + (MeOH)]³⁺ and 549.71 (10%), $[M - (NO_3)_4$ + $(MeOH)_{2}^{4+}$

Synthesis of $[Yb_4(L)_2(HL)_2(NO_3)_2(OH)_2] \cdot 2(NO_3)$ (2). The complex 2 was prepared in the same way as 1 except that Yb(NO₃)₃·6H₂O (0.3 mmol, 0.126 g) was used instead of Nd(NO₃)₃·6H₂O (0.3 mmol, 0.117 g). For 2: Yield: 0.109 g, 58%. Anal. Calc. for C₈₈H₁₀₀N₁₂O₃₀Yb₄: C, 42.31; H, 4.04; N, 6.73%; found: C, 42.18; H, 4.17; N, 6.66%. IR (KBr, cm⁻¹): 3411 (b), 3065 (w), 2936 (m), 2861 (w), 1653 (s), 1618 (m), 1560 (m), 1505 (m), 1476 (vs), 1384 (m), 1360 (w), 1291 (s), 1236 (w), 1229 (s), 1168 (m), 1143 (w), 1100 (w), 1078 (m), 1060 (w), 1042 (w), 1022 (w), 949 (w), 903 (w), 847 (m), 782 (w), 738 (m), 695 (w), 660 (w), 613 (w), 561 (w), 502 (w), 482 (w), 448 (w). ESI-MS (in MeCN) m/z: 2435.98 (100%), [M - NO₃]⁺; 1186.98 (41%), [M - $(NO_3)_2$ ²⁺; 784.34 (6%), $[M - (NO_3)_3 + (MeCN)]^{3+}$ and 583.02 (13%), $[M - (NO_3)_4 + (MeCN)_2]^{4+}$; ESI-MS (in MeOH) m/z: 2435.98 (100%), $[M - NO_3]^+$; 1186.98 (40%), $[M - (NO_3)_2]^{2+}$; 748.00 (8%), [M - (NO₃)₃ + (MeOH)]³⁺ and 578.51 (14%), [M - $(NO_3)_4 + (MeOH)_2]^{4+}$.

Synthesis of $[Er_4(L)_2(HL)_2(NO_3)_2(OH)_2] \cdot 2(NO_3)$ (3). The complex 3 was prepared in the same way as 1 except that Er(NO₃)₃·6H₂O (0.3 mmol, 0.124 g) was used instead of Nd(NO₃)₃·6H₂O (0.3 mmol, 0.117 g). For **3**: Yield: 0.113 g, 61%. Anal. Calc. for C₈₈H₁₀₀N₁₂O₃₀Er₄: C, 42.71; H, 4.07; N, 6.79%; found: C, 42.58; H, 4.17; N, 6.76%. IR (KBr, cm⁻¹): 3414 (b), 3066 (w), 2940 (m), 2860 (w), 1652 (s), 1618 (m), 1558 (m), 1504 (m), 1469 (vs), 1383 (m), 1357 (w), 1288 (s), 1240 (w), 1227 (s), 1169 (m), 1146 (w), 1100 (w), 1078 (m), 1060 (w), 1043 (w), 1025 (w), 964 (w), 949 (w), 903 (w), 844 (m), 783 (w), 740 (m), 695 (w), 659 (w), 611 (w), 561 (w), 502 (w), 481 (w), 443 (w). ESI-MS (in MeCN) m/z: 2412.86 (100%), [M - NO₃]⁺; 1175.43 (40%), $[M - (NO_3)_2]^{2+}$; 776.63 (3%), $[M - (NO_3)_3 + (MeCN)]^{3+}$ and 577.24 (17%), $[M - (NO_3)_4 + (MeCN)_2]^{4+}$; ESI-MS (in MeOH) m/z: 2412.86 (100%), [M - NO₃]⁺; 1175.43 (42%), [M - $(NO_3)_2$ ²⁺; 773.63 (5%), $[M - (NO_3)_3 + (MeOH)]^{3+}$ and 572.73 $(15\%), [M - (NO_3)_4 + (MeOH)_2]^{4+}.$

Synthesis of $[Gd_4(L)_2(HL)_2(NO_3)_2(OH)_2] \cdot 2(NO_3)$ (4). The complex 4 was prepared in the same way as 1 except that Gd(NO₃)₃·6H₂O (0.3 mmol, 0.121 g) was used instead of Nd(NO₃)₃·6H₂O (0.3 mmol, 0.117 g). For 4: Yield: 0.117 g, 64%. Anal. Calc. for C₈₈H₁₀₀N₁₂O₃₀Gd₄: C, 43.41; H, 4.14; N, 6.90%; found: C, 43.26; H, 4.25; N, 6.85%. IR (KBr, cm⁻¹): 3414 (b), 3065 (w), 2938 (m), 2860 (w), 1651 (s), 1617 (m), 1556 (m), 1504 (m), 1457 (vs), 1384 (m), 1365 (w), 1289 (s), 1243 (w), 1224 (s), 1170 (m), 1144 (w), 1098 (w), 1075 (m), 1058 (w), 1044 (w), 1023 (w), 961 (w), 947 (w), 903 (w), 855 (m), 782 (w), 740 (m), 692 (w), 660 (w), 608 (w), 560 (w), 498 (w), 477 (w), 434 (w). ESI-MS (in MeCN) m/z: 2372.82 (100%), [M - NO₃]⁺; 1155.41 (39%), [M - $(NO_3)_2^{12+}$; 763.29 (7%), $[M - (NO_3)_3 + (MeCN)]^{3+}$ and 567.23 (13%), $[M - (NO_3)_4 + (MeCN)_2]^{4+}$; ESI-MS (in MeOH) *m/z*: 2372.82 (100%), $[M - NO_3]^+$; 1155.41 (43%), $[M - (NO_3)_2]^{2+}$; 760.28 (5%), $[M - (NO_3)_3 + (MeOH)]^{3+}$ and 562.75 (15%), $[M - (NO_3)_3 + (MeOH)]^{3+}$ $(NO_3)_4 + (MeOH)_2]^{4+}$.

X-ray crystallography

 (3·3H₂O) of suitable dimensions were mounted onto thin glass fibers. All the intensity data were collected on a Bruker SMART CCD diffractometer (Mo-K α radiation and $\lambda = 0.71073$ Å) in Φ and ω scan modes. Structures were solved by direct methods followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques against F² using SHELXL-97.¹⁷ All other non-hydrogen atoms were refined with anisotropic thermal parameters. Absorption corrections were applied using SADABS.¹⁸ Hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. In each of complexes 1–3, the three water solvates are disordered with each O atom occupying two sets of positions, and the H atoms are not added. Crystallographic data and refinement parameters for the complexes are presented in Table 1. CCDC reference number 854306–854308 for 1·3H₂O, 2·3H₂O and 3·3H₂O, respectively.

3. Results and discussion

Synthesis and characterization

From reaction of the deprotonated L^{2-} and equimolar amount of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Nd, Yb, Er or Gd) in MeOH–MeCN, series of four homoleptic $[Ln_4(L)_2(HL)_2(NO_3)_2(OH)_2] \cdot 2(NO_3)$ complexes (Ln = Nd, 1; Ln = Yb, 2; Ln = Er, 3; Ln = Gd, 4) are obtained. Similar to the good solubility of the Salen-type Schiffbase ligand H_2L in common organic solvents except for water, the four complexes 1–4 are also soluble in absolute MeCN or MeOH, which should be due to the use of the Salen-type Schiffbase ligand H_2L with the flexible linker and the charge of the two components ($[Ln_4(L)_2(HL)_2(NO_3)_2(OH)_2]^{2+}$ and NO_3^{-}) in each of the four complexes.

The series of four complexes 1–4 were well characterized by EA, FT-IR, ¹H NMR and ESI-MS. In the FT-IR spectra, the characteristic strong absorptions of the v(C=N) vibration at 1648–1653 cm⁻¹ for complexes 1–4, are slightly blue-shifted by the range of 29-34 cm⁻¹ relative to that of the free Salen-type Schiff-base ligand H_2L (1619 cm⁻¹) upon coordination of the Ln³⁺ ions. The two additional strong characteristic absorptions at 1452-1476 cm⁻¹ and 1283-1291 cm⁻¹ for the series of complexes 1-4 were observed, which are tentatively attributed to $v(NO_3^{-})$. As to the room temperature ¹H NMR spectrum in CD₃CN of complex 1, large shifts (δ from 14.58 to -5.68 ppm and 14.17 to -2.90 ppm) of two sets of the proton resonances of the L^{2-} ligands endowed from the observed $(L)^{2-}$ and $(HL)^{-}$ modes in the molecular structure are observed due to the Nd³⁺induced shift, significantly spread in relation to those of the free H_2L ligand (δ from 13.84 to 1.58 ppm). The ESI-MS spectra of the series of four complexes (1-4) in MeCN or MeOH display similar patterns and exhibit two strong mass peaks assigned to the major species {[Ln₄(L)₂(HL)₂(NO₃)₂(OH)₂]· NO_3 ⁺ and $[Ln_4(L)_2(HL)_2(NO_3)_2(OH)_2]^{2+}$, and two fragments to $[Ln_4(L)_2(HL)_2(NO_3)(OH)_2(S)]^{3+}$ and $[Ln_4(L)_2(HL)_2(OH)_2(S)_2]^{4+}$ (S = MeCN or MeOH) for complexes 1–4, respectively. These observations further indicate that the discrete homoleptic tetranuclear unit retains in the respective dilute MeCN or MeOH solution.

X-ray quality crystals of $1 \cdot 3H_2O$, $2 \cdot 3H_2O$ or $3 \cdot 3H_2O$ of the series of four complexes 1-4 were obtained, and the table of selected crystal properties are given in Table 1. For complex

Compound	1 ⋅ 3H ₂ O	2 ·3H ₂ O	3 ⋅3H ₂ O
Empirical formula	C ₈₈ H ₁₀₆ N ₁₂ O ₃₃ Nd ₄	$C_{88}H_{106}N_{12}O_{33}Yb_4$	$C_{90}H_{106}N_{12}O_{33}Er_4$
Formula weight	2436.81	2552.01	2528.89
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P\bar{1}$
a/Å	14.4121(9)	14.4240(12)	14.4573(13)
b/Å	14.7205(9)	14.4630(11)	14.5690(13)
c/Å	14.7927(10)	14.633(2)	14.707(2)
α (°)	110.087(2)	111.254(2)	111.567(2)
β (°)	104.020(2)	104.137(2)	102.880(2)
γ (°)	108.7390(10)	107.6990(10)	107.5400(10)
V/A^3	2562 5(3)	2485 0(4)	2544 9(5)
Z	1	1	1
$\rho/g \text{ cm}^{-3}$	1.579	1.705	1.650
Crystal size/mm	$0.32 \times 0.27 \times 0.23$	$0.33 \times 0.26 \times 0.22$	$0.30 \times 0.26 \times 0.24$
μ (Mo-K α)/mm ⁻¹	2.076	3.814	3.347
Data/restraints/parameters	8717/1/619	8624/1/618	8852/1/618
Quality-of-fit indicator	1.095	1.044	1.020
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0752$	$R_1 = 0.0390$	$R_1 = 0.0394$
	$wR_2 = 0.1978$	$wR_2 = 0.0956$	$wR_2 = 0.0990$
R indices (all data)	$R_1 = 0.1150$	$R_1 = 0.0532$	$R_1 = 0.0576$
	$wR_2 = 0.2431$	$wR_2 = 0.1044$	$wR_2 = 0.1114$

Table 1 Crystal data and refinement for complexes $1 \cdot 3H_2O$, $2 \cdot 3H_2O$ and $3 \cdot 3H_2O$

1·3H₂O, the structural unit is composed of one cation $[Nd_4(L)_2(HL)_2(NO_3)_2(OH)_2]^{2+}$, two free NO₃[−] anions, and three solvate H₂O molecules. As shown in Fig. 1, for the cationic $[Nd_4(L)_2(HL)_2(NO_3)_2(OH)_2]^{2+}$ part lying about an inversion centre, two equivalent Nd₂L(HL) moieties are bridged by two μ-O phenoxide atoms (O6 and O6a) of two Salen-type Schiff-base (HL)[−] ligands with O₄ tetradentate mode (as shown in Scheme 1) and two O atoms (O9 and O9a) of two coordinated μ₃-OH[−] groups, resulting in the formation of a homoleptic cyclic tetranuclear (Nd₄(Salen)₄) host structure. In each of two equivalent Nd₂L(HL) moieties, two Nd³⁺ (Nd1 and Nd2) ions with different



Fig. 1 Perspective drawing of the cationic part in complex $1.3H_2O$; free anions, H atoms and solvates are omitted for clarity. Selected bond length (Å) and angles (°): Nd1–N1, 2.553(9); Nd1–N2, 2.477(8); Nd1–O2, 2.382(6); Nd1–O3, 2.434(6); Nd1–O5a, 2.569(7); Nd1–O6a, 2.437(7); Nd1–O9, 2.414(7); Nd1–O9a, 2.419(6); Nd2–O1, 2.706(7); Nd2–O2, 2.441(6); Nd2–O3, 2.433(6); Nd2–O4, 2.712(7); Nd2–O6, 2.526(7); Nd2–O7, 2.361(7); Nd2–O8, 2.653(8); Nd2–O9, 2.445(6) and Nd2–O11, 2.489(9). Nd1…Nd2, 3.6407(10); Nd1…Nd2a, 3.9781(8); Nd1…Nd1a, 3.8757(11) and Nd2…Nd1a, 3.9782(8). N1–Nd1–N2, 64.2(3); O2–Nd1–O3, 68.2(2); O1–Nd2–O4, 140.2(2); O2–Nd2–O3, 67.3(2); O7–Nd2–O8, 63.0 (2) and O9–Nd2–O6, 68.7(2). Symmetry transformation used to generate equivalent atoms: a: -x + 1, -y + 2, -z + 1.

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coordination environments are also linked by two µ-O phenoxide atoms (O2 and O3) of one Salen-type Schiff-base (L)²⁻ ligand with N_2O_4 hexadentate mode and one O atom (O9) of the coordinated μ_3 -OH⁻ group. The unique inner Nd³⁺ ion (Nd1) is eight-coordinate and bound by the N2O2 core of the Salen-type Schiff-base (L)²⁻ ligand in addition to two O atom (O5a of MeOgroup and O6a of µ-O phenoxide atom) from the Salen-type Schiff-base (HL)- ligand and two O atoms of two coordinated μ_3 -OH⁻ groups. Meanwhile the outer Nd³⁺ ion (Nd2) is ninecoordinate; in addition to the seven oxygen atoms from the two outer O₂O₂ moieties of the two Salen-type Schiff-base ligands, where four O atoms (two of MeO- groups and two of phenoxide atoms) are from the Salen-type Schiff-base $(L)^{2-}$ ligand and three O atoms (one of MeO- groups and two of phenoxide atoms) from the Salen-type Schiff-base (HL)⁻ ligand, it completes its coordination environment with one O atom from the monodentate NO₃⁻ anion and one O atom from the coordinated μ_3 -OH⁻ group. The unique Nd…Nd distances are different, with the distances of 3.6407(10) and 3.8757(11)-3.9782(8) Å for Nd1… Nd2, Nd1…Nd1a and Nd2…Nd1a, respectively, in which each of the Nd1...Nd2 separations in the equivalent Nd2L(HL) moieties is slightly shorter than that (Nd1…Nd1a or Nd2…Nd1a separation) between two equivalent Nd₂L(HL) moieties. For the inner Nd³⁺ ion (Nd1 or Nd1a), the Nd–O bond length (2.414(7)– 2.419(6) Å; O atoms from coordinated μ_3 -OH⁻ group) or the Nd-N bond lengths (2.477(8)-2.553(9) Å) are in the range of the Nd-O bond lengths (2.382(6)-2.569(7) A) with O atoms from the phenoxo groups. For the outer Nd³⁺ ion (Nd2 or Nd2a), the nine Nd-O bond lengths also depend on the nature of the oxygen atoms, varying from 2.361(7) to 2.712(7) Å, in which the bond lengths (2.653(8)-2.712(7) Å) from the oxygen atoms of MeOgroups are distinctively longer than those (2.361(7)-2.526(7) A or)2.489(9) A and 2.445(6) A) from the phenoxo oxygen atoms, monodentate NO₃⁻ anion or coordinated μ_3 -OH⁻ group. It is interesting to note the presence of an "apical" triply bridged μ_3 -OH⁻ group for each of the two central O atoms (O9 or O9a), which could be shown from the reasonable directionality of the interactions with three Nd³⁺ ions. Furthermore, as to the cationic $[Nd_4(L)_2(HL)_2(NO_3)_2(OH)_2]^{2+}$ part, the charge should be balanced by the protonation of one (N4 or N4a) of the imino nitrogen atoms for two of the four deprotonated Salen-type Schiff-base (L)²⁻ ligands, which endows the formation of two strong intramolecular H-bond interactions with the short N4– H4…O7 distance (2.575(17) Å) shown in Fig. 1s.† The three solvate H₂O molecules and the two free NO₃⁻ anions of complex 1·3H₂O are not bound to the framework and they exhibit no observed interactions with the host structure.

It is worth noting that the homoleptic cyclic tetranuclear $(Nd_4(Salen)_4)$ host structure in complex $1 \cdot 3H_2O$ is distinctively different from the reported structures of binuclear tripledecker,¹¹ trinuclear triple-decker,¹² trinuclear tetra-decker¹³ or pentanuclear tetra-decker lanthanide complexes¹⁴ based on the Salen-type Schiff-base ligands with the rigid linkers, which should be due to the use of the flexible Salen-type Schiff-base ligand H_2L with the outer O_2O_2 moiety for complex $1 \cdot 3H_2O$. On the other hand, the formation of homoleptic cyclic tetranuclear $(Nd_4(Salen)_4)$ framework in complex $1 \cdot 3H_2O$ appears to be NO_3^- anion-dependent since the use of other LnX_3 (X⁻ = OAc⁻ or CF₃SO₃⁻) in the self-assembly with the Salen-type Schiff-base ligands with the flexible linkers usually results in the formation of polymeric lanthanide coordination complexes.¹⁵ It is of special interest to compare the self-assembly of complex 1.3H₂O with that of the reported Tb₄(Salen)₆ complex.¹⁶ Although the similar tetranuclear framework is obtained necessarily from the Salentype Schiff-base ligands with flexible linkers, the character of the Salen-type Schiff-base ligand H₂L with both the inner N₂O₂ core and the outer O_2O_2 moiety in complex $1.3H_2O_2$, instead of the pure Salen-type Schiff-base ligand without the outer O2O2 moiety in the reported Tb₄(Salen)₆ complex¹⁶ endows the unusual formation of NO3- anion-dependent homoleptic cyclic tetranuclear (Nd₄(Salen)₄) framework in complex $1.3H_2O$. Single-crystal X-ray diffraction analyses indicated that both complex $2 \cdot 3H_2O$ and $3 \cdot 3H_2O$ are isomorphous with complex $1 \cdot 3H_2O$, as shown in Fig. 2 and 3, and the similar strong intramolecular H-bond interactions with the short N4-H4...07 distances (2.605(11) Å for $2 \cdot 3H_2O$ and 2.602(11) Å for $3 \cdot 3H_2O$) are observed in Fig. 2s and 3s,† respectively. The effect of



Fig. 2 Perspective drawing of the cationic part in complex $2 \cdot 3H_2O$; free anions, H atoms and solvates are omitted for clarity.



Fig. 3 Perspective drawing of the cationic part in complex $3 \cdot 3H_2O$; free anions, H atoms and solvates are omitted for clarity.

lanthanide contraction causes the slight variation of the detailed structures.

Photophysical properties

The photophysical properties of the ligand H_2L and complexes 1-4 have been examined in dilute MeCN solution at room temperature or 77 K, and summarized in Table 2 and Fig. 4-6. As shown in Fig. 4, the similar ligand-centered solution absorption spectra (225-227, 267-268 and 339-342 nm) of complexes 1-4 in the UV-visible region are observed and are redshifted upon the coordination of the Ln³⁺ ions as compared to that (221, 259 and 332 nm) of the ligand H_2L or $(L)^{2-}$ in MeCN or in MeOH (shown in Fig. 4s[†]). The molar absorption coefficients of complexes 1-4 in all the lowest energy bands are almost four orders of magnitude larger than that of the ligand H₂L due to the involvement of four chromophores. For complexes 1-3, the similar residual visible emission bands (*ca.* 505 nm and $\tau < 1$ ns, almost undetectable) and low quantum yields ($\Phi_{\rm em} < 10^{-5}$) in dilute absolute MeCN solution at room temperature are observed. While photoexcitation of the antennae at the range of 230–500 nm (λ_{ex} = 402 nm for 1 or 385 nm for 2), as shown in Fig. 5, gives rise to the characteristic emissions of the Nd³⁺ ion $(4F_{3/2} \rightarrow 4I_{J/2}, J = 9, 11, 13)$ and the Yb³⁺ ion (${}^{2}F_{5/2} \rightarrow 2F_{7/2}$) in the NIR region. For complex 1, the emissions at 909, 1085 and 1365 nm can be respectively assigned to $4F_{3/2} \rightarrow 4I_{9/2}, 4F_{3/2} \rightarrow$ $4I_{11/2}$ and $4F_{3/2} \rightarrow 4I_{13/2}$ transitions of the Nd³⁺ ion, and the emission at 1022 nm can be attributed to the ${}^{2}F_{5/2} \rightarrow 2F_{7/2}$ transition of the Yb³⁺ ion for complex 2. Moreover, unlike complex 1 or 2, the characteristic NIR emission of the Er^{3+} ion for complex 3 is too weak to be detected. The ligand H_2L or the complex 4 also does not exhibit the NIR luminescence under the same conditions, and just have the typical luminescence ($\lambda_{em} =$ 361, $\tau=1.21$ ns and $\phi=0.23\times10^{-3};$ $\lambda_{em}=479$ nm, $\tau=1.56$ ns and $\phi = 0.25 \times 10^{-3}$ for the ligand H₂L or $\lambda_{em} = 505$ nm, $\tau = 0.74$ ns and $\phi = 0.64 \times 10^{-3}$ for 4) of the Salen-type Schiff-base ligand in the visible region, as shown in Fig. 6. It is worth noting that for complex 1 or 2, the similar excitation spectrum ($\lambda_{ex} = 385$ and 403 nm for 1 or $\lambda_{ex} = 402$ nm for 2) monitored at the respective strongest NIR emission peak ($\lambda_{em} = 1085$ nm for 1 or $\lambda_{em} =$ 1022 nm for 2) or the visible emission peak ($\lambda_{em} = 505$ nm) of

Table 2 The photophysical properties of the H_2L and complexes 1–4 at 1×10^{-5} M in absolute MeCN solution at room temperature or 77 K

Compound	Absorption $\lambda_{ab}/nm (\log[e/dm^3 mol^{-1} cm^{-1}])$	Excitation λ_{ex}/nm	Emission $\lambda_{\rm em}/{\rm nm}~(\tau,~\Phi imes~10^3)$
H_2L	221 (0.24), 259 (0.11), 332 (0.03)	303, 321, 370	361 (1.21 ns, 0.23), 479 (1.56 ns, 0.25)
1	227 (0.74), 268 (0.31), 342 (0.11)	385, 403(sh)	909 (1.39 μs), 1085 (s, 1.41 μs), 1365 ^a
2	225 (0.76), 268 (0.33), 339 (0.11)	307(sh), 357, 402(sh)	1022 (13.22 µs)
3	226 (0.82), 267 (0.35), 339 (0.12)		
4	226 (0.83), 267 (0.35), 339 (0.12)	290(sh), 350, 397	505 (0.74 ns, 0.64) 487 (2.4 ns, 77 K), 543 (6.2 ms, 77 K)

^a Due to the limitations of the instrument, we were unable to measure the lifetime of the NIR luminescence above 1300 nm. ^b The emission is too weak to be detected.



Fig. 4 UV-Vis spectra of the ligand H_2L and complexes 1–4 in MeCN solution at 1×10^{-5} M at room temperature.



Fig. 5 NIR emission and excitation spectra of complexes 1 and 2 in MeCN solution at 1×10^{-5} M at room temperature.

complex 4, clearly show both the NIR emissions originate from the same π - π * transitions of the H₂L Schiff-base ligand for complexes 1 and 2, suggests that the energy transfer from the antenna to the Ln³⁺ ions takes place efficiently.¹⁹ Moreover, for complexes 1 and 2, the respective NIR luminescent decay curves



Fig. 6 Visible emission and excitation spectra of the ligand H_2L and complex 4 in MeCN solution at 1×10^{-5} M at room temperature.

obtained from time-resolved luminescent experiments can be fitted mono-exponentially with time constant of microseconds (1.41 µs for 1 at 1085 nm and 13.22 µs for 2 at 1022 nm), and the intrinsic quantum yield Φ_{Ln} (0.564% for 1 or 0.661% for 2) of the Ln³⁺ emission may be estimated by $\Phi_{Ln} = \tau_{obs}/\tau_0$, where τ_{obs} is the observed emission lifetime and τ_0 is the "natural lifetime", *viz* 0.25 ms and 2.0 ms for the Nd³⁺ and Yb³⁺ ions, respectively,²⁰ The relatively smaller NIR intrinsic quantum yields of complexes 1 and 2 compared with those of trinuclear triple-decker¹² or pentanuclear tetra-decker lanthanide (Nd³⁺ or Yb³⁺) complexes¹⁴ based on the Salen-type Schiff-base ligand with the rigid linker should be as a result of the partially luminescent quenching effect by the OH-vibrators from coordinated µ₃-OH⁻ groups around the Ln³⁺ ions, in spite of the involvement of more chromophores.

As a reference compound, complex **4** allows the further study of the antennae luminescence in the absence of energy transfer, because the Gd³⁺ ion has no energy levels below 32 000 cm⁻¹, and therefore cannot accept any energy from the antennae excited state.²¹ In dilute MeCN solution at 77 K, complex **4** displays the strengthened antennae fluorescence compared with that ($\lambda_{em} =$ 505 nm, $\tau = 0.74$ ns and $\phi = 0.65 \times 10^{-3}$) at room temperature under the same conditions, which shows higher luminescent intensity ($\lambda_{em} = 487$ nm and 543 nm) and distinctively longer luminescence lifetimes (2.4 ns and 6.2 ms). This result shows that the sensitization of the NIR luminescence for complexes **1–2** should arise from both the ¹LC (20534 cm⁻¹) and the ³LC (18416 cm⁻¹) excited state of the Schiff-base ligand H₂L at low temperature. If the antennae luminescence lifetime of complex 4 is to represent the excited-state lifetime in the absence of the energy transfer, the energy transfer rate $(k_{\rm ET})$ in the complexes 1 and **2** can thus be calculated from $k_{\rm ET} = 1/\tau_{\rm q} - 1/\tau_{\rm u}$,²² where $\tau_{\rm q}$ is the residual lifetime of the luminescent emission undergoing quenching by the respective Ln^{3+} ion, and τ_u is the unquenched lifetime in the reference complex 4, so the energy transfer rates for the Nd³⁺ and Yb³⁺ ions in complexes 1 and 2 may all be estimated to be above 5×10^8 s⁻¹, which could well imply the reason for the effective energy transfer for complexes 1 and 2. Furthermore, from the viewpoint of the energy level match, in spite of the effective energy transfer also taking place in complex 3, the larger energy gap between the energy-donating ³LC level (18 416 cm⁻¹) and the emitting level (${}^{4}I_{13/2}$) of Er³⁺ ion than those of complexes 1 and 2 results in the great non-radiative energy loss during the energy transfer, which should be the reason for the weak and unobservable luminescence in the range of 800-1800 nm for complex 3.23 As to the relatively higher quantum efficiency of 2 (0.661%) than that of 1 (0.564%), besides the smaller energy gap (${}^{2}F_{5/2}$, 9785 cm⁻¹) of Yb³⁺ ion in complex 2 than that $({}^{4}F_{3/2}, 9217 \text{ cm}^{-1})$ of the Nd³⁺ ion in complex 1, the excited state of the Nd³⁺ ion in complex 1 is more sensitive to quenching by the distant C-H or N-H oscillators of the Salentype Schiff-base ligand H₂L and the O-H oscillators of the coordinated µ3-OH- groups around the Ln3+ ions.24 Furthermore, the sensitivity of the NIR luminescent intensities to different solvents for complexes 1 and 2 becomes apparent when the determined solvent is changed from MeCN to CD₃CN or CD₃OD. In CD₃CN or CD₃OD, the typical emission bands of Nd³⁺ ion assigned to the $4F_{3/2} \rightarrow 4I_{J/2}$ (J = 9, 11 or 13) transitions for complex 1 and the emission band of Yb³⁺ ion attributed to the ${}^{2}F_{5/2} \rightarrow 2F_{7/2}$ transition for complex 2 are also observed, which indicates that the two complexes with the discrete homoleptic tetranuclear units can be stabilized in different solvents (MeCN or MeOH), consistent with those found from the results of ESI-MS. Moreover, for either complex 1 or 2, the relative strongest emission intensities (ca. 1085 nm for complex 1 and ca. 1022 nm for complex 2) in CD₃CN and CD₃OD are higher (almost 1.8 times for 1 and 1.5 times for 2 in CD₃CN; 2.6 times for 1 and 3.7 times for 2 in CD_3OD) than those for the two complexes in MeCN when using solutions with their concentrations adjusted to give the same absorbance values at ca. 276 nm. The observed changes following the deuteration of solvents may be relative to an interaction of the solvents (MeCN or MeOH from the dissociated fragments with the loss of coordinated NO₃⁻ anions shown in ESI-MS data) with the Ln³⁺ ions.^{9d}

4. Conclusion

Through the self-assembly of the flexible hexadentate Salen-type Schiff-base ligand H_2L with $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Nd, Yb, Er or Gd), series of homoleptic cyclic tetranuclear $[Ln_4(L)_2(HL)_2(NO_3)_2(OH)_2] \cdot 2(NO_3)$ (Ln = Nd, 1; Ln = Yb, 2; Ln = Er, 3; Ln = Gd, 4) are obtained under similar reaction conditions. The results of their photophysical studies show that more Salen-type Schiff-base ligands may work as antennae or chromophores for the sensitization of NIR luminescence of Nd³⁺ and Yb³⁺ ions, and the characteristic NIR luminescence with emissive lifetimes in the microsecond range, arises from the excited state (both ¹LC and ³LC) of the ligand due to the effective intramolecular energy transfer in complexes **1** and **2**. Moreover, the energy level match between the excited states (³LC) of the chromophores to the corresponding Ln^{3+} ion's exciting state is required for the enhancement of NIR luminescence, in addition to avoiding or decreasing the luminescent quenching effect arising from OH-, CH- or NH-oscillators around the Ln^{3+} ion. The specific design of polynuclear complexes from the flexible Salen-type Schiff-base ligands in facilitating the NIR sensitization is now under way.

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