# Syntheses, structures, and photoluminescence of 1-D lanthanide coordination polymers†

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Five new lanthanide 1-D coordination polymers are reported which are formed from flexible salen type Schiff-base ligands $H_2L$ and $H_2L'$ ($H_2L = N$,$N^1$-ethylene bis(salicylideneimine); $H_2L' = N$,$N^1$-bis(3-methoxysalicylidene)ethylene-1,2-diamine). The polymeric structures are formed by bridging neutral $H_2L$ units in the case of $\{[Ln_2L_2(CF_3SO_3)(H_2L)_4(MeOH)]\cdot CF_3SO_3\}_n$ (Ln = Eu (**1**), Nd (**2**) and Er (**3**)), and by acetate ($OAc^-$) groups in $[Yb_2(L)_2(OAc)_2(MeOH)_2]_n$ (**4**) and $\{[Tb_3(L')_2(OAc)_5]\cdot Et_2O\cdot (MeOH)_{0.5}\}_n$ (**5**). The structures of **1–5** were determined by single crystal X-ray crystallographic studies and the luminescence properties of **1** and **5** in MeOH solution were determined.

## Introduction

There is currently considerable interest in the rational design and synthesis of coordination framework materials prepared from multifunctional organic ligands and lanthanide ions since they have potential applications related to luminescence, magnetism, gas absorption and sensing.[1] Control over the lanthanide coordination environment, and therefore a coordination framework is challenging due to high coordination numbers and flexible coordination geometries that are encountered in Ln(III) chemistry.[2] In addition, the structures and compositions of lanthanide frameworks are often significantly influenced not only by ligand structures but also by counterions and reaction conditions.[1,3] The majority of Ln(III) coordination polymers reported so far have employed polydentate rigid ligands, such as multicarboxylic acids, pyridine $N$-oxide-based ligands, carboxyphenyl porphyrin and various other macrocyclic ligands.[4] It is interesting to note that while more flexible ligands featuring S, N or O atom donors have been employed in the construction of d-block transition metal frameworks relatively few studies involving more flexible linkers with lanthanides have been reported.[5]

Schiff-base ligands are among the most widely studied chelators for metal ions owing to their relatively easy synthesis and their versatility in the formation of stable complexes. Our research has recently focused on the use of multidentate Schiff-base ligands for the preparation of new luminescent lanthanide complexes.[6] Although the first X-ray crystal structure of a lanthanide coordination polymer from the reaction of the neutral ligand $H_2L$ (Scheme 1) with La(NO$_3$)$_3$ hydrate was reported by Xie in 1999[7] there are relatively few reports of lanthanide coordination polymers which employ salen type Schiff-base ligands.[8] We recently reported that under
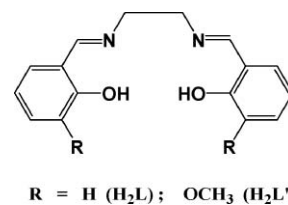


**Scheme 1** Schiff-base ligands $H_2L$ and $H_2L'$.

R = H ($H_2L$) ; OCH$_3$ ($H_2L'$)

neutral conditions the products from reactions of $LnX_3\cdot nH_2O$ (X = $OAc^-$, $NO_3^-$ and $Cl^-$) with $H_2L$ (salen) were highly dependant on the nature of the anion $X^-$. When X = acetate ($OAc^-$) the neutral binary species $Tb_4L_6$ was formed.[6a] However, when X = $Cl^-$ or $NO_3^-$ simple dinuclear complexes of formula $(XLnL)_2(\mu\text{-}H_2L)$ are formed in which a neutral salen molecule ($H_2L$) acts a simple bridge between two metal centers. In this report we describe further examples of Ln(III) 1-D coordination polymers. These materials fall into two categories. Firstly, complexes in which a neutral $H_2L$ salen group bridges between metal centers through phenolic–OH groups; $\{[Ln_2L_2(CF_3SO_3)(H_2L)_4(MeOH)(H_2O)]\cdot CF_3SO_3\}_n$ (Ln = Eu (**1**), Nd (**2**) and Er (**3**)). Secondly, complexes in which 1-D coordination polymers are created by the use of acetate ($OAc^-$) groups which bridge between both bimetallic and trimetallic Ln(III) clusters $[Yb_2(L)_2(OAc)_2(MeOH)_2]_n$ (**4**) and $\{[Tb_3(L')_2(OAc)_5]\cdot Et_2O\cdot (MeOH)_{0.5}\}_n$ (**5**). Interestingly the reaction conditions used for the synthesis of these materials are critical and involve the use of $Et_3N$ in refluxing MeOH. The use of stronger bases often result in the formation of Ln(OH) species.

## Experimental section

### General considerations

All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. The Schiff-base ligands tend to be slightly unstable with respect to rearrangements or hydrolysis under the reaction conditions, especially in the presence of air. The reactions are therefore conducted under an inert atmosphere. After coordination to lanthanide ions the Schiff-base ligand is far more stable in air, especially at room

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temperature. The metal complexes can therefore be crystallized in air at this stage of the procedure. Metal salts, triethylamine and other solvents were purchased from Aldrich and used directly without further purification. Schiff-base ligands $H_2L$ and $H_2L'$ were prepared according to well-established procedures.[9] Physical measurements: IR: Nicolet IR 200 FTIR spectrometer. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. Satisfactory microanalytical data (C, H, N) was obtained for all compounds. Absorption spectra were obtained on a BECKMAN DU 640 spectrophotometer, excitation and visible emission spectra on a QuantaMaster PTI fluorimeter.

## Synthesis of complexes 1-5

$\{[Eu_2L_2(CF_3SO_3)(H_2L)_4(MeOH)]\cdot CF_3SO_3\}_n$ (1). Triethylamine (2 mL of a 0.1 M MeCN solution) was added to a solution of $H_2L$ (0.027 g, 0.10 mmol) and $Eu(CF_3SO_3)_3$ (0.060 g, 0.10 mmol) in MeOH (25 ml). The resulting solution was stirred and heated under reflux for one day. The solution was then cooled to room temperature and filtered. The filtrate was allowed to evaporate in the air. Yellow single crystals of **1** were formed after two weeks. Yield (base on $H_2L$): 0.011 g (30%). m. p. > 300 °C (dec.). ESI-MS (MeOH) $m/z$: 955 ($[Eu_2L_2(H_2L)_4]^{2+}$). IR ($CH_3OH$, $cm^{-1}$): 3464(s), 2998 (m), 2949 (m), 2835 (m), 1634 (s), 1536 (w), 1470 (m), 1442 (m), 1397 (w), 1343 (w), 1278 (s), 1254 (s), 1225 (m), 1172 (m), 1111 (w), 11086 (w), 1029 (s), 759 (m), 641 (m).

$\{[Nd_2L_2(CF_3SO_3)(H_2L)_4(MeOH)]\cdot CF_3SO_3\}_n$ (2). The procedure was the same as that for **1** using $Nd(CF_3SO_3)_3$. Yellow single crystals of **2** were formed after two weeks. Yield (base on $H_2L$): 0.012 g (33%). m. p. > 300 °C (dec.). ESI-MS (MeOH) $m/z$: 947 ($[Nd_2L_2(H_2L)_4]^{2+}$), 1088 ($[Nd_2L_2(HL)]^+$), 1237 ($[Nd_2L_2(H_2L)(CF_3SO_3)]^+$). IR ($CH_3OH$, $cm^{-1}$): 3358 (m), 3174 (m), 3011 (m), 1629 (s), 1535 (w), 1470 (m), 1442 (m), 1401 (w), 1339 (w), 1274 (s), 1245 (s), 1170 (s), 1029 (s), 755 (m), 632 (m).

$\{[Er_2L_2(CF_3SO_3)(H_2L)_4(MeOH)]\cdot CF_3SO_3\}_n$ (3). The procedure was the same as that for **1** using $Er(CF_3SO_3)_3$. Yellow single crystals of **3** were formed after two weeks. Yield (base on $H_2L$): 0.015 g (40%). m. p. > 306 °C (dec.). 1284 ($[Er_2L_2(H_2L)(CF_3SO_3)]^+$). IR ($CH_3OH$, $cm^{-1}$): 3312 (m), 3008 (m), 1631 (s), 1539 (w), 1472 (m), 1445 (m), 1396 (w), 1341 (w), 1276 (s), 1251 (s), 1168 (s), 1017 (s), 756 (m), 630 (m).

$[Yb_2L_2(OAc)_2(MeOH)_2]_n$ (4). The procedure was the same as that for **1** using $Yb(OAc)_3\cdot 4H_2O$ (0.035 g, 0.10 mmol). Yellow single crystals of **3** were formed after two weeks. Yield 0.058 g (55%). m. p. > 295 °C (dec.). ESI-MS (MeOH) $m/z$: 1002 ($[Yb_2L_2(OAc)(MeOH)_2]^+$). IR ($CH_3OH$, $cm^{-1}$): 3411 (s), 1634 (s), 1548 (s), 1454 (m), 1409 (m), 1335 (w), 1286 (w), 1237 (w), 1217 (w), 1074 (w), 951 (w), 739 (m), 677 (m).

$\{[Tb_3(L')_2(OAc)_5]\cdot Et_2O\cdot (MeOH)_{0.5}\}_n$ (5). Triethylamine (2 mL of a 0.1 M MeCN solution) was added to a solution of $H_2L'$ (0.033 g, 0.10 mmol) and $Tb(OAc)_3\cdot 4H_2O$ (0.034 g, 0.10 mmol) in MeOH (20 ml). The resulting solution was stirred and heated under reflux for one day. The solution was then cooled to room temperature and filtered. Diethylether was allowed to diffuse slowly into this solution at room temperature and yellow single crystals were formed in three weeks. Yield (base on

$Tb(OAc)_3\cdot 4H_2O$): 0.025 g (50%). m. p. > 315 °C (dec.). ESI-MS (MeOH) $m/z$: 1425 ($[Tb_3L'(HL')(OAc)_5]^+$). IR ($CH_3OH$, $cm^{-1}$): 3101 (s), 2884 (m), 1638 (s), 1548 (s), 1454 (m), 1417 (m), 1342 (w), 1221 (m), 1168 (w), 1082 (w), 951 (w), 678 (m).

## X-Ray Crystallography

Data were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 153 K. Absorption corrections were applied using GAUS-SIAN. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.[10] Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[11]

## Results and discussion

In the presence of the weak base $Et_3N$, reactions of Schiff-base ligands $H_2L$ and $H_2L'$ with $Ln(CF_3SO_3)_3$ (Ln = Eu, Nd and Er), $Yb(OAc)_3\cdot 4H_2O$ and $Tb(OAc)_3\cdot 4H_2O$ in refluxing MeOH produced yellow solutions from which compounds **1–5** may be isolated as yellow crystalline solids in 30–50% yields. The solid state structures of **1–5** were determined by single crystal X-ray crystallographic studies. Crystallographic data for all polymers are presented in Table 1 and selected bond lengths and angles are given in Table 2–6.

### Neutral Salen Bridged 1-D Polymers

Complexes **1–3** are isomorphous and have the general formula $\{[Ln_2L_2(CF_3SO_3)(H_2L)_4(MeOH)]\cdot CF_3SO_3\}_n$ (Ln = Eu (**1**), Nd (**2**) and Er (**3**)). The compounds crystallize in the triclinic space group $P\bar{1}$ with two $Ln^{3+}$ ions, two $L^{2-}$ ligands, four neutral $H_2L$ groups, two $CF_3SO_3^-$ anions and one coordinated MeOH molecule per asymmetric unit. A view of the central $Eu_2$ structure of **1** is shown in Fig. 1. Each Eu(1) ion is coordinated to a deprotonated salen group ($L^{2-}$) and two neutral salen ligands ($H_2L$) while Eu(2) is coordinated to three salen ligands and one $L^{2-}$. Eu(1) and Eu(2) are bridged by a neutral salen ligand with a separation of 10.171 Å, forming a 1-D polymeric structure. The central $O_2N_2$ binding pocket of each $L^{2-}$ group is in an approximately planar arrangement. The non bridging, neutral $H_2L$ groups bind *via* one phenolic OH group leaving the other OH group of the ligand not bound to a metal. Both metal centers have coordination numbers of 8. Eu(1) also bears a coordinated $CF_3SO_3^-$ group *via* an oxygen atom while Eu(2) bears a single coordinated MeOH molecule. In complexes **1–3**, the average distance for the Ln-O(phenolic) interactions (2.380 Å **1**, 2.448 Å **2**, 2.319 Å **3**) and Ln-N (2.611 Å **1**, 2.682 Å **2**, 2.548 Å **3**) are comparable to those found in the literature.[6,12] The Ln-Ln distances in **2** (10.210 Å) and **3** (10.041 Å) are similar to that observed in **1**. A view of the 1-D polymeric chain-like structure of **1** is shown in Fig. 2. The 1-D polymeric structure is formed by a zig-zag chain of alternating $Eu^{3+}$ ions and $H_2L$ (salen) ligands which bridge as neutral ligands between the metal centers (Scheme 2, type **II**).

**Table 1** Crystal data and structure refinement for compounds **1–5**

|  | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Formula | $C_{99}H_{96}F_6N_{12}O_{19}S_2Eu_2$ | $C_{99}H_{96}F_6N_{12}O_{19}S_2Nd_2$ | $C_{99}H_{96}F_6N_{12}O_{19}S_2Er_2$ | $C_{38}H_{42}N_4O_{10}Yb_2$ | $C_{50.5}H_{60}N_4O_{19.5}Tb_3$ |
| Fw | 2239.92 | 2224.48 | 2270.52 | 1060.84 | 1511.78 |
| Cryst syst. | Triclinic | Triclinic | Triclinic | Orthorhombic | Monoclinic |
| Space group | P1 | P1 | P1 | $Pbca$ | $P2_1/c$ |
| $a/Å$ | 9.5068(19) | 9.5105(19) | 9.3209(19) | 17.117(3) | 15.194(3) |
| $b/Å$ | 14.029(3) | 14.286(3) | 14.000(3) | 20.590(4) | 20.024(4) |
| $c/Å$ | 17.803(4) | 17.870(4) | 17.577(4) | 22.583(5) | 20.223 |
| $\alpha$ (°) | 83.56(3) | 82.99(3) | 84.07(3) | 90 | 90 |
| $\beta$ (°) | 89.28(4) | 89.68(4) | 89.09(2) | 90 | 111.40(3) |
| $\gamma$ (°) | 84.18(3) | 83.67(3) | 84.48(3) | 90 | 90 |
| $V/Å^3$ | 2347.2(8) | 2395.1(8) | 2270.8(8) | 7959(3) | 5729(2) |
| Z | 1 | 1 | 1 | 8 | 4 |
| $D_c/g\,cm^{-3}$ | 1.585 | 1.542 | 1.660 | 1.771 | 1.753 |
| $T/K$ | 153(1) | 153(1) | 153(1) | 153(1) | 153(1) |
| $F(000)$ | 1138 | 1132 | 1148 | 4144 | 2968 |
| $\mu/mm^{-1}$ | 1.458 | 1.203 | 1.974 | 4.731 | 3.738 |
| $\theta$ range, deg | 1.76-25.00 | 2.98-25.00 | 2.94-25.00 | 2.93-25.00 | 1.76-25.00 |
| reflns meas | 13282 | 15839 | 14053 | 13346 | 15917 |
| reflns used | 13282 | 15839 | 14053 | 7006 | 10058 |
| params | 1118 | 1118 | 1118 | 488 | 704 |
| R $^a$($I > 2\sigma(I)$) | $R_1 = 0.0727$ | $R_1 = 0.0737$ | $R_1 = 0.0681$ | $R_1 = 0.0447$ | $R_1 = 0.0455$ |
|  | $wR_2 = 0.1848$ | $wR_2 = 0.1771$ | $wR_2 = 0.1594$ | $wR_2 = 0.1105$ | $wR_2 = 0.1178$ |
| R $^a$(all data) | $R_1 = 0.1153$ | $R_1 = 0.1185$ | $R_1 = 0.1117$ | $R_1 = 0.0643$ | $R_1 = 0.0558$ |
|  | $wR_2 = 0.2242$ | $wR_2 = 0.2076$ | $wR_2 = 0.1853$ | $wR_2 = 0.1307$ | $wR_2 = 0.1272$ |
| S | 1.109 | 1.114 | 1.100 | 1.135 | 1.061 |

$^a$ $R_1 = \sum \|F_o\| - \|F_c\|/\sum\|F_o\|$. $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$, where $P = (F_o^2 + 2F_c^2)/3$.

**Table 2** Selected bond lengths (Å) and angles (°) for **1**. Symmetry operator $(1 + x, y, 1 + z)$ generates equivalent atoms marked with "#"

| Eu(1)-O(2B) | 2.30(2) | Eu(1)-O(1B) | 2.377(16) |
|---|---|---|---|
| Eu(1)-O(2E)#1 | 2.392(16) | Eu(1)-O(1) | 2.404(18) |
| Eu(1)-O(1C) | 2.431(18) | Eu(1)-O(3) | 2.482(8) |
| Eu(1)-N(1B) | 2.58(2) | Eu(1)-N(2B) | 2.70(2) |
| Eu(2)-O(2D) | 2.325(18) | Eu(2)-O(1E) | 2.348(18) |
| Eu(2)-O(2C) | 2.380(19) | Eu(2)-O(1D) | 2.400(17) |
| Eu(2)-O(2F) | 2.439(19) | Eu(2)-N(2D) | 2.59(3) |
| Eu(2)-O(9) | 2.561(14) | Eu(2)-N(1D) | 2.59(2) |
| O(2B)-Eu(1)-O(1B) | 156.1(6) | O(2B)-Eu(1)-O(2E)#1 | 95.2(7) |
| O(1B)-Eu(1)-O(2E)#1 | 71.5(6) | O(2B)-Eu(1)-O(1) | 83.9(7) |
| O(1B)-Eu(1)-O(1) | 109.6(6) | O(2E)#1-Eu(1)-O(1) | 72.3(6) |
| O(2B)-Eu(1)-O(1C) | 74.4(7) | O(1B)-Eu(1)-O(1C) | 83.5(6) |
| O(2E)#1-Eu(1)-O(1C) | 79.2(6) | O(1)-Eu(1)-O(1C) | 142.2(7) |
| O(2B)-Eu(1)-N(1B) | 133.7(7) | O(1B)-Eu(1)-N(1B) | 69.3(6) |
| O(2E)#1-Eu(1)-N(1B) | 119.8(6) | O(1)-Eu(1)-N(1B) | 80.1(6) |
| O(1C)-Eu(1)-N(1B) | 136.8(6) | O(2B)-Eu(1)-N(2B) | 68.2(7) |
| O(1B)-Eu(1)-N(2B) | 134.2(7) | O(2E)#1-Eu(1)-N(2B) | 141.2(6) |
| O(1)-Eu(1)-N(2B) | 71.3(6) | O(1C)-Eu(1)-N(2B) | 125.0(6) |
| N(1B)-Eu(1)-N(2B) | 65.8(7) | | |

**Table 3** Selected bond lengths (Å) and angles (°) for **2**. Symmetry operator $(1 + x, y, 1 + z)$ generates equivalent atoms marked with "#"

| Nd(1)-O(2B) | 2.387(17) | Nd(1)-O(2E)#1 | 2.429(16) |
|---|---|---|---|
| Nd(1)-O(1C) | 2.436(15) | Nd(1)-O(1B) | 2.439(15) |
| Nd(1)-O(1) | 2.513(17) | Nd(1)-O(3) | 2.544(7) |
| Nd(1)-N(1B) | 2.668(19) | Nd(1)-N(2B) | 2.694(18) |
| Nd(2)-O(2D) | 2.409(17) | Nd(2)-O(1E) | 2.435(13) |
| Nd(2)-O(1D) | 2.456(15) | Nd(2)-O(2F) | 2.473(14) |
| Nd(2)-O(2C) | 2.498(16) | Nd(2)-O(9) | 2.636(11) |
| Nd(2)-N(2D) | 2.637(19) | Nd(2)-N(1D) | 2.74(2) |
| O(2B)-Nd(1)-O(2E)#1 | 98.3(6) | O(2B)-Nd(1)-O(1C) | 73.9(6) |
| O(2E)#1-Nd(1)-O(1C) | 80.6(5) | O(2B)-Nd(1)-O(1B) | 159.2(6) |
| O(2E)#1-Nd(1)-O(1B) | 71.0(5) | O(1C)-Nd(1)-O(1B) | 86.6(6) |
| O(2B)-Nd(1)-O(1) | 85.7(6) | O(2E)#1-Nd(1)-O(1) | 72.1(6) |
| O(1C)-Nd(1)-O(1) | 143.1(5) | O(1B)-Nd(1)-O(1) | 106.9(6) |
| O(2B)-Nd(1)-N(1B) | 133.7(6) | O(2E)#1-Nd(1)-N(1B) | 118.0(6) |
| O(1C)-Nd(1)-N(1B) | 136.0(5) | O(1B)-Nd(1)-N(1B) | 66.1(6) |
| O(1)-Nd(1)-N(1B) | 79.9(5) | O(2B)-Nd(1)-N(2B) | 67.5(6) |
| O(2E)#1-Nd(1)-N(2B) | 142.1(6) | O(1C)-Nd(1)-N(2B) | 124.2(5) |
| O(1B)-Nd(1)-N(2B) | 131.7(5) | O(1)-Nd(1)-N(2B) | 71.9(5) |
| N(1B)-Nd(1)-N(2B) | 66.3(6) | | |

## 1-D Polymers with Acetate ($OAc^-$) Bridges

**Yb$_2$.** The reaction of $Yb(OAc)_3\cdot4H_2O$ with salen in the presence of $Et_3N$ in refluxing MeOH produces the 1-D polymeric material $[Yb_2(L)_2(OAc)_2(MeOH)_2]_n$ (**4**) in 55% yield. The compound crystallizes in the orthorhombic space group $Pbca$ with two unique Yb atoms, two $L^{2-}$ anions, two $OAc^-$ groups and two coordinated MeOH molecules per asymmetric unit. A view of the central Yb$_2$ unit of **4** is shown in Fig. 3. Each $Yb^{3+}$ ion is bound by the $N_2O_2$ cavity of a deprotonated salen ligand ($L^{2-}$) and is 8-coordinate. Yb(1) ion has two coordinated MeOH molecules and is linked to Yb(2). The shorter distance Yb(1)-Yb(2) is 3.948 Å. The longer distance between these two ions, bridged

by a single $OAc^-$ unit is 6.467 Å. A view of the resulting 1-D framework structure is shown in Fig. 4. The average distances for Yb–O (phenolic) (2.292 Å) and Yb–N (2.533 Å) bonds are comparable to those found in the literature.[6,12] In **4**, the salen ligand displays two bonding modes with $Yb^{3+}$ ions: (a) type **I** Scheme 2, and (b) coordinating with two $Yb^{3+}$ ions by the $N_2O_2$ set to one $Yb^{3+}$ and to the other *via* a phenolic oxygen atom, respectively (Scheme 2, type **III**).

**Tb$_3$.** Reaction of the methoxy substituted salen derivative $H_2L'$ with $Tb(OAc)_3\cdot4H_2O$ in the presence of $Et_3N$ in refluxing MeOH produces the 1-D polymeric compound $\{[Tb_3(L')_2(OAc)_5]\cdot Et_2O\cdot(MeOH)_{0.5}\}_n$ (**5**). A view of the central

**Table 4** Selected bond lengths (Å) and angles (°) for **3**. Symmetry operator (1 + x, y, 1 + z) generates equivalent atoms marked with "#"

| | | | |
|---|---|---|---|
| Er(1)-O(2B) | 2.263(7) | Er(1)-O(2E)#1 | 2.334(7) |
| Er(1)-O(1C) | 2.345(6) | Er(1)-O(1) | 2.356(7) |
| Er(1)-O(1B) | 2.353(7) | Er(1)-O(3) | 2.383(5) |
| Er(1)-N(1B) | 2.493(9) | Er(1)-N(2B) | 2.597(8) |
| Er(2)-O(2D) | 2.262(7) | Er(2)-O(1E) | 2.253(6) |
| Er(2)-O(1D) | 2.307(7) | Er(2)-O(2C) | 2.321(7) |
| Er(2)-O(2F) | 2.386(8) | Er(2)-N(2D) | 2.483(9) |
| Er(2)-O(9) | 2.513(7) | Er(2)-N(1D) | 2.611(9) |
| O(2B)-Er(1)-O(2E)#1 | 96.2(2) | O(2B)-Er(1)-O(1C) | 74.1(2) |
| O(2E)#1-Er(1)-O(1C) | 79.5(2) | O(2B)-Er(1)-O(1) | 83.0(3) |
| O(2E)#1-Er(1)-O(1) | 73.7(2) | O(1C)-Er(1)-O(1) | 142.4(2) |
| O(2B)-Er(1)-O(1B) | 153.3(2) | O(2E)#1-Er(1)-O(1B) | 69.0(2) |
| O(1C)-Er(1)-O(1B) | 81.1(2) | O(1)-Er(1)-O(1B) | 112.1(2) |
| O(2B)-Er(1)-N(1B) | 135.9(3) | O(2E)#1-Er(1)-N(1B) | 116.8(3) |
| O(1C)-Er(1)-N(1B) | 137.0(3) | O(1)-Er(1)-N(1B) | 79.5(3) |
| O(1B)-Er(1)-N(1B) | 70.3(3) | O(2B)-Er(1)-N(2B) | 69.1(3) |
| O(2E)#1-Er(1)-N(2B) | 143.1(3) | O(1C)-Er(1)-N(2B) | 124.7(2) |
| O(1)-Er(1)-N(2B) | 71.1(3) | O(1B)-Er(1)-N(2B) | 135.7(3) |
| N(1B)-Er(1)-N(2B) | 66.9(3) | | |

**Table 5** Selected bond lengths (Å) and angles for **4**. Symmetry operator (0.5 + x, y, z) generates equivalent atoms marked with "#"

| | | | |
|---|---|---|---|
| Yb(1)-O(1) | 2.207(5) | Yb(1)-O(3) | 2.299(5) |
| Yb(1)-O(2) | 2.341(5) | Yb(1)-O(7) | 2.434(5) |
| Yb(1)-O(5) | 2.446(5) | Yb(1)-O(8) | 2.496(5) |
| Yb(1)-N(1) | 2.543(6) | Yb(1)-N(2) | 2.551(6) |
| Yb(2)-O(4)#1 | 2.244(5) | Yb(2)-O(1B) | 2.281(5) |
| Yb(2)-O(2B) | 2.339(5) | Yb(2)-O(5) | 2.432(5) |
| Yb(2)-O(2) | 2.460(5) | Yb(2)-O(6) | 2.489(5) |
| Yb(2)-N(2B) | 2.497(6) | Yb(2)-N(1B) | 2.540(6) |
| O(1)-Yb(1)-O(2) | 148.90(17) | O(1)-Yb(1)-N(1) | 72.02(19) |
| O(2)-Yb(1)-N(1) | 138.68(19) | O(1)-Yb(1)-N(2) | 138.2(2) |
| O(2)-Yb(1)-N(2) | 71.58(19) | N(1)-Yb(1)-N(2) | 67.1(2) |
| O(1B)-Yb(2)-O(2B) | 149.71(18) | O(1B)-Yb(2)-O(2) | 75.11(17) |
| O(2B)-Yb(2)-O(2) | 77.55(17) | O(1B)-Yb(2)-N(2B) | 139.3(2) |
| O(2B)-Yb(2)-N(2B) | 70.32(19) | O(2)-Yb(2)-N(2B) | 144.23(18) |
| O(1B)-Yb(2)-N(1B) | 72.3(2) | O(2B)-Yb(2)-N(1B) | 137.94(19) |
| O(2)-Yb(2)-N(1B) | 139.91(19) | N(2B)-Yb(2)-N(1B) | 67.9(2) |

**Table 6** Selected bond lengths (Å) and angles (°) for **5**

| | | | |
|---|---|---|---|
| Tb(1)-O(2) | 2.227(5) | Tb(1)-O(3) | 2.376(5) |
| Tb(1)-N(1) | 2.506(6) | Tb(1)-N(2) | 2.518(6) |
| Tb(2)-O(3) | 2.411(5) | Tb(2)-O(6) | 2.425(5) |
| Tb(2)-O(5) | 2.544(5) | Tb(2)-O(4) | 2.552(5) |
| Tb(3)-O(7) | 2.232(5) | Tb(3)-O(6) | 2.395(5) |
| Tb(3)-N(3) | 2.491(7) | Tb(3)-N(4) | 2.514(7) |
| O(2)-Tb(1)-O(9) | 103.4(2) | O(2)-Tb(1)-O(3) | 146.22(18) |
| O(9)-Tb(1)-O(3) | 85.89(19) | O(2)-Tb(1)-N(1) | 72.9(2) |
| O(9)-Tb(1)-N(1) | 83.6(2) | O(3)-Tb(1)-N(1) | 140.87(19) |
| O(2)-Tb(1)-N(2) | 140.40(19) | O(3)-Tb(1)-N(2) | 72.91(18) |
| N(1)-Tb(1)-N(2) | 68.1(2) | O(3)-Tb(2)-O(6) | 146.90(17) |
| O(14)-Tb(2)-O(5) | 130.95(17) | O(17)-Tb(2)-O(5) | 129.20(16) |
| O(3)-Tb(2)-O(5) | 89.56(17) | O(6)-Tb(2)-O(5) | 63.00(17) |
| O(12)-Tb(2)-O(5) | 72.65(17) | O(15)-Tb(2)-O(5) | 140.05(17) |
| O(14)-Tb(2)-O(4) | 129.98(16) | O(17)-Tb(2)-O(4) | 134.70(16) |
| O(3)-Tb(2)-O(4) | 62.69(15) | O(6)-Tb(2)-O(4) | 87.65(16) |
| O(12)-Tb(2)-O(4) | 137.09(17) | O(15)-Tb(2)-O(4) | 75.60(16) |
| O(5)-Tb(2)-O(4) | 64.49(16) | | |

Tb$_3$ core of **5** is shown in Fig. 5. The central Tb$_3$ core of this material contains two L′$^{2-}$ groups bound to the two terminal Tb$^{3+}$ ions *via* the conventional N$_2$O$_2$ binding pocket as well as one chelating acetate and are 8-coordinate. The central Tb ion (Tb(2)) is coordinated to 10 oxygen atoms. Each L′$^{2-}$ group binds Tb(2) with a bridging phenolic O atom as well as one of its OMe groups.
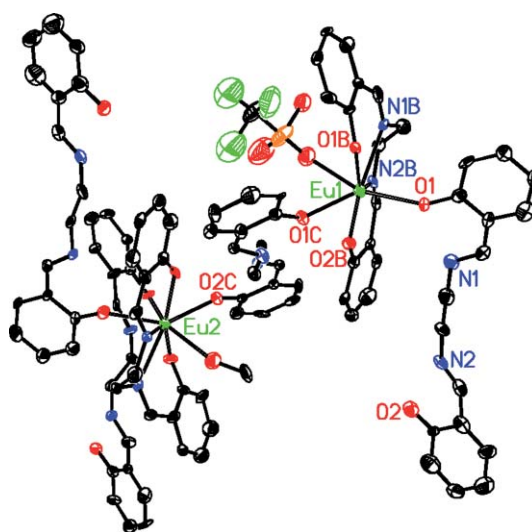


**Fig. 1** A view of the molecular structure of **1**. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 50% probability level.
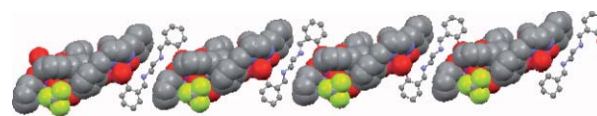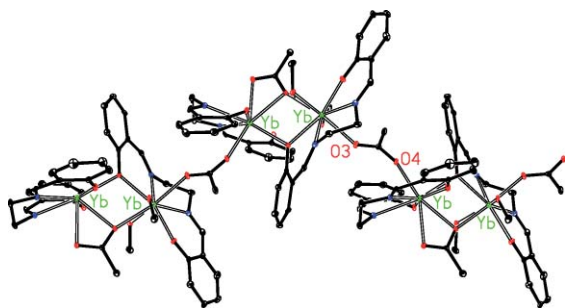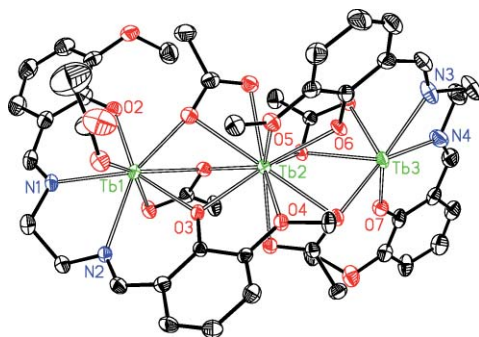


**Fig. 2** A view of the 1-D polymeric chain in **1**.
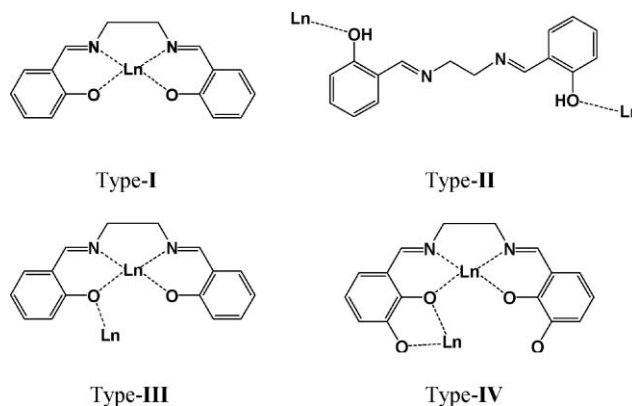


**Scheme 2** Four bonding modes for Schiff-base ligands with Ln$^{3+}$ ions in **1–5**.
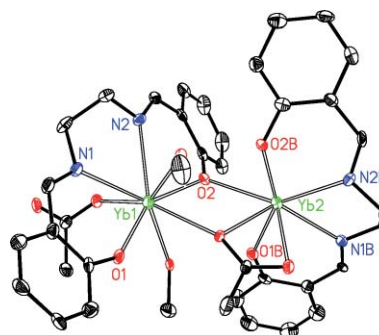


**Fig. 3** A view of the molecular structure of **4**. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 50% probability level.

**Fig. 4** A view of the 1-D polymeric chain in **4**.



**Fig. 5** A view of the molecular structure of **5**. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 50% probability level.

There are also two chelating OAc⁻ anions each of which bridges to a terminal Tb³⁺ ion *via* one O atom. In turn, each terminal Tb³⁺ ion bears a chelating OAc⁻ group which also bridges to the central Tb ion *via* one O atom. The 1-D polymeric framework is completed by OAc⁻ units which link the Tb₃ clusters. (Fig. 6) The Tb–Tb distances within the central Tb₃ cluster are similar at 3.709 Å and 3.719 Å for Tb(1)-Tb(2) and Tb(2)-Tb(3) respectively. The average distances for Tb–O (phenolic) (2.344 Å), Tb–O(methoxy) (2.549 Å) and Tb–N (2.507 Å) are comparable to those found in the literature.[6,12] As expected, the average Tb–O (phenolic) distance is significantly shorter than the average Tb–O (methoxy) distance and reflects the difference between the two different oxygen atoms involved. In this case the modified salen ligand H₂L′ bears two extra -OMe groups and has only one overall bonding mode. This involves coordination to two Tb³⁺ ions by the N₂O₂ core plus two O atoms - one from a phenolic group and one from an OMe unit (Scheme 2, type **IV**).
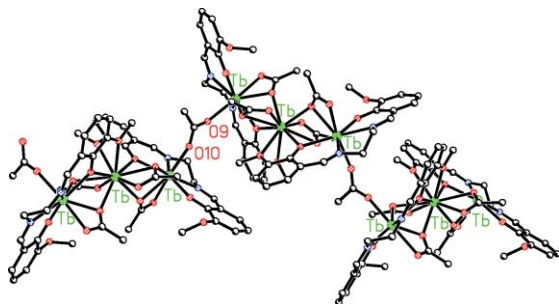


**Fig. 6** A view of the 1-D polymeric chain in **5**.

We have also probed the nature of these compounds in solution using high resolution ESI mass spectrometry studies.

As expected, in solution the 1-D polymeric structures of the complexes break down into smaller, more soluble units. Thus the ESI mass spectra of complexes **1–3**, **4** and **5** show [Ln₂L₂(H₂L)₄]²⁺, [Yb₂L₂(OAc)(MeOH)₂]⁺ and [Tb₃L′(HL′) (OAc)₅]⁺ fragments, respectively.

**Luminescence Studies**

The photophysical properties of the Eu(III) compound **1** and Tb(III) compound **5** were studied in MeOH. The free H₂L and H₂L′ ligands exhibit absorption bands in their uv-vis spectra (*i.e.* 216, 255 and 316 nm for H₂L and 218, 260, 286, 323 and 413 nm for H₂L′). These bands are red-shifted upon metal ion coordination in both **1** and **5** (Fig. 7). The emission and excitation spectra of both H₂L and **1** are shown in Fig. 8. Excitation of the absorption band at 366 nm in the free ligand H₂L produces a broad emission band at $\lambda_{max} = 455$ nm. Excitation of the ligand centered absorption band at 271 nm in **1** results in visible emission bands for the Eu³⁺ ion (⁵D₀→⁷Fⱼ transitions, j = 1, 2, 3 and 4). The fluorescence of **1** is very weak with quantum yield $(\Phi_{em})$[13] less than 10⁻³. The emission and excitation spectra of both H₂L′ and **5** are shown in Fig. 9. Excitation of the absorption band at 361 nm in the free ligand H₂L′ produces a broad emission band at $\lambda_{max} = 490$ nm. Excitation of the ligand centered absorption band at 340 nm in **5** results in typical visible emission bands for the Tb³⁺ ion (⁵D₄ → ⁷Fₙ transitions, n = 6, 5, 4 and 3). The fluorescence quantum yield $(\Phi_{em})$[14] for **5** is 0.21.
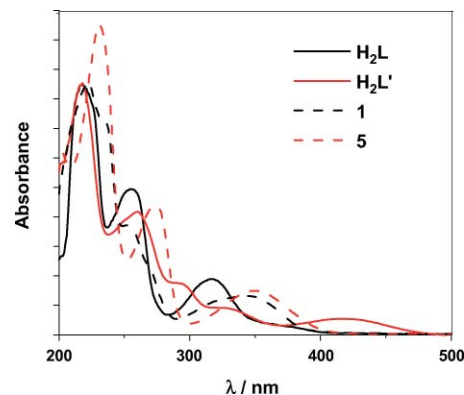


**Fig. 7** UV-Vis spectra of free ligands (H₂L and H₂L′), **1** and **5** in CH₃OH. (Concentrations: ~10⁻⁶ M).



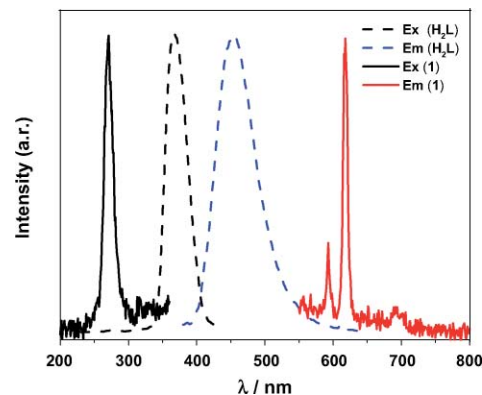**Fig. 8** The excitation and emission spectra of free H₂L (---) and **1** (—).
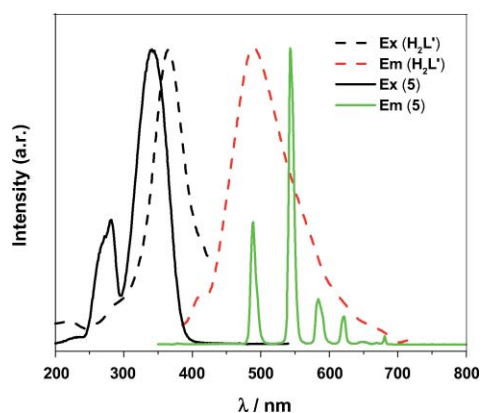
**Fig. 9** The excitation and emission spectra of free $H_2L'$(---) and **5**(—).

## Conclusions

Five 1-D coordination lanthanide polymers with Schiff-base ligands $H_2L$ and $H_2L'$ have been prepared, and structurally characterized. The stoichiometry and structures of these compounds are dependent on the Schiff-base ligand employed in their syntheses as well as the nature of the anion present ($CF_3SO_3^-$ *vs.* $OAc^-$). In **1–3**, the flexible neutral salen ligand ($H_2L$) acts as a bridge or linker in the formation of 1-D coordination frameworks, while $CF_3SO_3^-$ is merely a counter anion. In **4** and **5**, acetate ($OAc^-$) is employed as a linker in the formation of such frameworks. In **1** and **5** both sets of ligand frameworks enable the materials to display luminescence of the lanthanide(III) ions *via* the antenna effect.

## Acknowledgements

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