Tuning the self-assembly and luminescence properties of lanthanide coordination polymers by ligand design[†]

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Two new structure-related tripodal ligands featuring salicylamide pendant arms,

1,3,5-tris{[(2'-furfurylaminoformyl)phenoxyl]methyl}-2,4,6-trimethylbenzene (L¹) and 1,1,1-tris{[(2'-furfurylaminoformyl)phenoxyl]methyl}ethane (L^{II}) have been designed and synthesized with the ultimate aim of self-assembling lanthanide polymers with interesting luminescent properties. Among two series of Ln^{III} nitrate complexes (Ln = Pr, Nd, Sm, Eu, Gd, Tb or Dy) which have been characterized by elemental analyses, XRD, TGA and IR spectra, three new coordination polymers have been determined by X-ray diffraction analysis. The coordination polymer type {[Ln(NO₃)₃(L¹)]·*n*H₂O}_{*n*} possesses an unusual ladderlike double chain which can be further connected through π - π stacking interactions constructing a three-dimensional supramolecular structure. In contrast, the coordination polymer type {[Ln(NO₃)₃(L^{II})]·*n*CH₃OH}_{*n*} displays a (3,3)-connected puckered two-dimensional net with 4·8² topological notation. The photophysical properties of the Sm, Eu, Tb and Dy complexes at room temperature are investigated. The present work substantiates the claim that the supramolecular structure as well as the luminescent properties of the coordination polymer can be tuned by varying either the backbone group or the terminal group of the organic ligand.

Introduction

The construction of coordination polymers has been a field of rapid growth in supramolecular and materials chemistry due to the formation of fascinating structures and their potential applications as new materials.1 So far, most of the work reported in the literature has been focused on the coordination polymers of d-block transition metal elements.² In contrast with transitionmetal complexes, covalence plays a minor role in metal-ligand bonds of lanthanide complexes, and the nature of the coordination sphere is controlled by a tenuous balance between coulombic interactions and ligand steric hindrance.³ The high coordination number and flexible coordination geometry of lanthanide metal ions make it difficult to control the preparation of lanthanide complexes. Therefore, the use of lanthanide ions as nodes for the construction of coordination polymers is more difficult than their d-block metal analogues.4a Recently a few examples have appeared on lanthanide-based frameworks employing polydentate ligands such as sulfoxides,⁴ carboxylates,⁵ pyridones,⁶ lactames,⁷ 4.4'-bipyridine-N.N'-dioxide⁸ and nitrophenolate.⁹ Generally, the polymer topology generated from the self-assembly of inorganic (metal) species and organic ligands can be modified by the chemical structure of the ligands chosen. As we know, the organic ligands serve to tether the metal centers and to propagate the structural information expressed in metal coordination preferences throughout the extended structure, as a result, properties of the organic ligands such as coordination ability, length, geometry, relative orientation of the donor groups and flexibility play a very important role in dictating polymer framework topology. In the long run, this line of research can lead to predictions of the topology and/or the periodicity of crystalline lattices generated from the molecular structures of the participating small building blocks, one can anticipate that the relationship between polymeric structures and physical properties will eventually be elucidated as well.

Judicious choice of ligand is also required to ensure that the chosen lanthanide metal is well shielded from the surrounding environment to prevent quenching of the excited state and enhance its emission. By deliberate incorporation of appropriate multiple absorption groups suitable for energy transfer the tripodal ligands could be used to develop strongly luminescent lanthanide complexes.¹⁰ Owing to the structural features of salicylamide derivatives, their lanthanide complexes have some advantages for luminescence research. First, the ligand featuring salicylamide pendant arms can strongly minimize the probability of solvent molecule coordination (that is especially important for water molecules); second, the high extinction coefficients of the ligand featuring salicylamide pendant arms in the near UV-vis range provide effective absorption of excitation energy which promotes

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^dDepartment of Chemistry, Liaocheng University, Liaocheng, 252000, China † Electronic supplementary information (ESI) available: TGA diagrams, XRD patterns, fluorescence spectra of the Sm and Dy complexes at room temperature, phosphorescence spectra of the Gd complex of ligands L¹ and L¹ at 77 K and selected bond distances (Å) and angles (°) for polymers **1**, **2**, **3** (Fig. S1–S8 and Tables S1–S3). CCDC reference numbers 672449– 672452. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b800217g

more effective energy transfer to the lanthanide ion; third, the presence of O and N atoms and aromatic rings may allow potentially strong hydrogen bonds and π - π stacking interactions to form supramolecular structures. We are interested in how different types of rigid and flexible backbone as well as different terminal coordination sites impact the coordination and supramolecular motifs of a variety of lanthanide complexes based on ligands with salicylamide arms. So far, several attractive supramolecular complexes based on salicylamide derivatives, such as benzylsalicylamide derivatives and also related types of ligand have been used to construct supramolecular complexes.¹¹⁻¹³ However, the coordination chemistry based on five-membered heterocyclic ring containing tridentate ligands, such as L¹ and L^{II} reported herein, which are analogues of the extensive series of ligands studied above, is still unprecedented.

In view of this, we report here the syntheses of two new members of a family of tripodal ligands, namely, 1,3,5-tris{[(2'-furfurylaminoformyl)phenoxyl]methyl}-2,4,6-trimethylbenzene (L¹) and 1,1,1-tris{[(2'-furfurylaminoformyl)phenoxyl]methyl}-ethane (L^u) and describe the syntheses and the luminescence properties of the resulting complexes formed with ions used in fluoroimmunoassays (Ln = Sm, Eu, Tb, Dy). Three polymeric coordination complexes, namely, [Pr(NO₃)₃(L¹)·H₂O]*n* (1), [Nd(NO₃)₃(L^u)·0.5CH₃OH]*n* (2), and [Sm(NO₃)₃(L^u)]*n* (3), based on the two ligands L¹ and L^u, were structurally characterized by single-crystal X-ray diffraction.

Result and discussion

Synthesis and structural analysis of ligands $L^{\rm I}$ and $L^{\rm II}$

The interesting coordination chemistry exhibited by salicylamide derivatives encouraged us to undertake further studies on the design and synthesis of new types of salicylamide ligand. Following this approach, we expand benzene containing salicylamide to furan-containing salicylamide. As shown in Scheme 1, L^{I} and L^{II} , were successfully obtained which are pale white crystalline solids and are soluble in common polar organic solvents such as ethyl acetate, CHCl₃, CH₃OH, and DMF. This potentially facilitates the solution reaction between the ligand and inorganic metal salts. The IR spectra of these ligands showed an –NH absorption band around 3400 cm⁻¹. The strong absorption bands around 1646 cm⁻¹ are consistent with carbonyl absorption, which is comparable to those corresponding bands in known compounds.

Structural analysis of ligand L¹. The 1,3,5-trimethylbenzene spacer exhibits symmetry and plays a crucial role in controlling the steric configuration of the functional groups introduced into its 2,4,6-positions. Namely, the functional groups attached to the 2,4,6-positions are forced to position themselves at the same side of the benzene ring of the spacer, since the *ababab* configuration (a denotes 'above' and b denotes 'below') is the most thermodynamically stable configuration due to the steric repulsion between the neighboring substituents. The structure of L¹ has been fully characterized by infrared spectroscopy, elemental analysis and ¹H NMR. To further confirm the structure of the new ligand, the solid molecular structure of L^{I} was determined using single-crystal X-ray diffraction. The crystal structure of L¹ reveals that the unsymmetric unit contains four crystallographically and conformationally equivalent molecules. As shown in Fig. 1, L^I crystallizes in space group $P2_1/n$. The bridging trimethylbenzene moiety and three furfurylsalicylamide arms are linked together at the *meta* position by a methylene group, which gives rise to ligand L^{I} being asymmetric with an angular backbone driven by the sp³ configuration of the bridging carbon atom. Three arms of the ligand are severely twisted with a ca. 70° dihedral angle between phenyl and the terminal furan moiety attached to the phenyl ring. The dihedral angle between the phenyl rings is 45.19, 68.33 and 78.39°. Such an asymmetric bent organic spacer with divergent properties is potentially useful in the construction of polymeric complexes with photophysical properties. The amide hydrogen atoms (H(11), H(14), H(36)) are hydrogen bonded to the ether oxygen atom (O(3), O(3) \cdots H(14) 1.94(8) Å, N(1)–H(14)···O(3) 134(2)°, and O(3)···N(1) 2.620(17) Å; $O(7), O(7) \cdots H(11) 2.02(5) \text{ Å}, N(3)-H(11) \cdots O(7) 135(17)^{\circ}$, and $O(7) \cdots N(3)$ 2.68(6) Å; O(4), $O(4) \cdots H(36)$ 2.00(3) Å, N(2)- $H(36) \cdots O(4) \ 134(70)^{\circ}$, and $O(4) \cdots N(2) \ 2.705(17) \ \text{Å}$) to provide three hydrogen bonded six-membered rings. It is no doubt noteworthy that the robust intramolecular hydrogen bonds have a template effect and participate in the stabilization of the complete architecture.



Fig. 1 Molecular structure of L^1 (30% probability displacement ellipsoids).



Scheme 1 Schematic illustration of ligands L^{I} and L^{II} .

Table 1	Elemental	analytical	and IR	spectral	data for	the complexes
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	Elemental analyses ^a (%)				IR $(\lambda_{\rm max}/{\rm cm}^{-1})$
	С	Н	Ν	Ln	v(C=O)
PrL ^I (NO ₃) ₃ ·H ₂ O	50.08 (50.01)	4.09 (4.11)	7.26 (7.29)	12.27 (12.22)	1610
$NdL^{I}(NO_{3})_{3}$	50.49 (50.65)	4.00 (3.99)	7.36 (7.38)	12.63 (12.67)	1612
$SmL^{I}(NO_{3})_{3}$	50.27(50.38)	3.97 (3.96)	7.33 (7.34)	13.19 (13.14)	1610
$EuL^{I}(NO_{3})_{3}$	50.19 (50.31)	3.95 (3.96)	7.35 (7.33)	13. 22 (13.26)	1611
$GdL^{I}(NO_{3})_{3}$	50.14 (50.08)	3.94 (3.94)	7.32 (7.30)	13.60 (13.66)	1612
$TbL^{I}(NO_{3})_{3}$	50.09 (50.01)	3.92 (3.93)	7.30 (7.29)	13.84 (13.79)	1613
$DyL^{I}(NO_{3})_{3}$	49.77 (49.85)	3.93 (3.92)	7.25 (7.27)	13.99 (14.05)	1610
$PrL^{II}(NO_3)_3 \cdot 0.5CH_3OH$	47.66 (47.50)	4.01 (4.03)	7.80 (7.82)	13.08 (13.11)	1606
NdL ^{II} (NO ₃) ₃ ·0.5CH ₃ OH	47.43 (47.35)	4.03 (4.02)	7.79 (7.80)	13.42 (13.38)	1607
$\mathrm{Sm}\mathbf{L}^{\Pi}(\mathrm{NO}_3)_3$	47.21 (47.23)	3.88 (3.87)	7.85 (7.87)	14.04 (14.08)	1606
$EuL^{II}(NO_3)_3$	47.09 (47.16)	3.87 (3.86)	7.86 (7.86)	14.16 (14.21)	1606
$GdL^{II}(NO_3)_3$	47.07 (46.92)	3.83 (3.84)	7.80 (7.82)	14.59(14.63)	1607
$\Gamma b L^{\Pi} (NO_3)_3$	46.69 (46.85)	3.84 (3.84)	7.83 (7.81)	14.78 (14.76)	1608
$DvL^{II}(NO_3)_3$	46.58 (46.70)	3.82 (3.83)	7.76 (7.78)	15.00 (15.04)	1607

^{*a*} Data in parentheses are calculated values.

Structural analysis of lanthanide complexes based on tripodal ligands $L^{\rm I}$ and $L^{\rm II}$

Treatment of $Ln(NO_3)_3$ · $6H_2O$ with the new ligands in ethyl acetate–methanol solution in a 1:1 ratio yields a series of complexes which, according to XRD, combustion analysis, and IR exhibit the same structure and correspond to the formula $LnL^{1}(NO_3)_3$ · nH_2O and $LnL^{1}(NO_3)_3$ · nCH_3OH (Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, n = 0, 0.5, 1) respectively. IR and elemental analysis data for all complexes are summarized in Table 1. X-Ray quality crystals of {[$PrL^{1}(NO_3)_3$]· H_2O }n, {[$NdL^{11}(NO_3)_3$]· $0.5CH_3OH$ }n, and [$SmL^{11}(NO_3)_3$]n were obtained after several weeks of slow evaporation of the ethyl acetate–methanol solution. Complexation of the arms through the carbonyl functions is reflected in the v(C=O) vibration which is shifted towards lower energy by *ca.* 36 cm⁻¹. The complexes are soluble in DMF, DMSO and methanol, slightly soluble in ethyl acetate, acetonitrile and acetone, but insoluble in CHCl₃ and diethyl ether.

Structural analysis of $[Pr(NO_3)_3(L^1) \cdot H_2O]_n$ (1). As shown in Fig. 2A-1, each Pr^{III} center in 1 adopts a distorted monocapped square antiprism coordination sphere, which is defined by three oxygen donors from three L¹ ligands and three bidentate coordination nitrate oxygen groups. The Pr–O distances are from 2.398(5) to 2.584(7) Å, which are comparable to the corresponding Pr-O bond lengths found in related complexes. It is worth noting that a surprisingly similar orientation of the three furfurylsalicylamide arms is found between free ligand L^{I} and its complex (Fig. 2A-2) showing that the conformation of ligand L^{I} does not change upon coordination. Each praseodymium(III) center, shown as green large spheres in Fig. 2, connects three ligands of L¹. Similarly, each ligand molecule is connected to three praseodymium atoms. The combination of tripodal L¹ and nona-coordinated praseodymium atoms in two adjacent chains are joined together by sharing the O(8) carbonyl oxygen atom to build up an unusual ladderlike double chain in which one of the ligand arms acts as the middle rungl of the ladder (Fig. 2B) which is distinctly different from previous report by Tang et al.12

It is interesting to note that evidence for intermolecular hydrogen bonding was not found. Upon further careful investigation of the structure of **1** it can be seen that two adjacent chains are interlinked by two kinds of π - π staking interactions. The dihedral angle between benzene rings (C(26), C(27), C(28), C(29), C(30), C(31)) is 0° and the distance between the centroid of each ring is 3.777 Å and 3.736 Å, while the aromatic π - π staking interactions between two parallel furan rings are situated at a distance of 3.786 Å. In this way, the ladder-like polymer double chains are connected together and construct a 3D supramolecular structure (Fig. 2C). It is important to note that such an arrangement may reduce steric hindrance and make the whole framework more stable.

Structural analysis of $[Nd(NO_3)_3(L^{II})]_n$ (2). To confirm the role of different backbone groups in the self-assembly process, L^{II} was used instead of L^{I} to perform the reaction. Compounds 2 and 3 were obtained as crystals by combination of L^{II} with Ln(NO₃)₃·6H₂O in an ethyl acetate-methanol system. Singlecrystal X-ray analysis revealed that they are isomorphous with only very minor differences in their comparative geometries reflecting the normal Ln^{III} contraction effects, thus only 2 is described here in detail. As shown in Fig. 3A-1, the Nd^{III} center lies in a monocapped square antiprism coordination environment defined by nine O-donors from the carbonyl groups of three tridentate ligands L^{II} (O(4), O(6) and O(8)), and six O-donors from three bidentate coordinated nitrate groups (O(10), O(11), O(13), O(14), O(16) and O(17)). Each Nd^{3+} is coordinated to three L^{II} ligands; each L^{II} ligand provides O(4) for one Nd³⁺, O(6) for the second Nd³⁺ and O(8) for the third Nd³⁺, thus each L^{II} ligand is coordinated to three Nd3+ and each Nd3+ is coordinated to three L^{II} ligands to form a 1:1 complex. The Nd³⁺ cation acts as a threeconnecting node linking neighboring Nd3+ cation centers via the ligands, forming a 2D coordination polymer. It is worth pointing out that L^{II} acts as a tridentate bridging spacer in 2 with all three Odonors binding Nd^{III} centers, which is markedly distinct from the coordination behavior of the previous report.¹¹ The only possible explanation for this change might be the templating effect resulting from the different terminal groups due to all the reactions being carried out under exactly the same conditions including solvent system, metal-to-ligand ratio and temperature. In addition, the intramolecular N-H...O hydrogen bonds, formed among the



Fig. 2 (A) ORTEP plot of complex **1** showing the local coordination environment of Pr^{III} with thermal ellipsoids at 30% probability (disordered water molecules are omitted for clarity) and ligand **L**¹ in complex **1** showing a divergent fashion. (B) View of the 1D ladder-like coordination polymer of the Pr^{III} complex with the **L**¹ ligand along the *a*-axis and *c*-axis (hydrogen atoms as well as crystalline water molecules are omitted for clarity). (C) The 3D supramolecular structure of **1** constructed by π – π stacking interactions which are indicated with dashed orange lines (viewd along the *a*-axis, hydrogen atoms as well as crystalline water molecules are omitted for clarity).

carbonyl oxygens, amide nitrogen atoms and nitrate ligands, play a vital role in stabilizing the 2D coordination structure.

It is interesting to note that the ligand L^{II} was arranged with all three salicylamide arms in a gathered-round fashion (Fig. 3A-2)



Fig. 3 (A) ORTEP plot of complex 2 showing the local coordination environment of Nd^{III} with thermal ellipsoids at 30% probability (disordered methanol molecules are omitted for clarity) and ligand L^{II} in complex 2 showing a gathered-round fashion. (B) Schematic description of the (3,3)-connected 2D net with 4.8² topological notation built on the 3-connected organic spacers (T1) and metal centers (T2): the connectors of ligand and Nd atoms are colored in gray and purple, respectively.

which is quite different from L^{II} itself. Each salicylamide arm had a similar conformation and the arm is so long that their terminal groups can "fold back". Three oxygen atoms of the carbonyl groups in the ligand, namely, O4, O6 and O8 are located in the outer part of the whole ligand molecule. This conformation is necessary for the ligand to bind three Nd^{III} ions simultaneously. Overall, the ligands in **2** and **3** were arranged in a virtually identical fashion, with most of the differences due to slight changes in folding at $-CH_2$ - groups or small rotations of C-C bonds which were caused by lanthanide contraction effects.

To deeply understand the nature of the involuted frameworks, a topological approach can be used, *i.e.*, reducing multi-dimensional structures to simple node-and-connection nets. Obviously, in this framework, one Nd^{III} ion is linked with three ligands through carbonyl groups, which could be considered as an inorganic three-connected node (T_1 ; Fig. 3B). Likewise, each L^{II} ligand is connected to three Nd^{III} ions through carbonyl groups, so it could be regarded as an organic three-connected linker (T₂; Fig. 3B). There is one four-membered ring, and two eight-membered rings around the three-connected metal node, thus forming a threeconnected linker. Because the three-connected nodes and threeconnected linkers are arranged in a ratio of Nd/L = 1:1, the short Schläfli symbol of the topology can be expressed as 4.8² (Fig. 3B). Ultimately, this special assembly may be related to the flexible coordination of the lanthanide centers and flexible conformations of the ligand. Thus, polymer 2 affords the (3,3)connected puckered 2D net with 4.8² topological notation.

TGA, XRD and MS studies. To examine the thermal stability of the resulting polymers, thermal gravimetric analysis (TGA) was carried out (Fig. S1 and S2, ESI[†]) on crystalline samples of the

compounds in the range 25-625 °C. The two kinds of complex exhibited very similar mass losses over the entire operating range respectively. The mass decrease of the coordination polymers of L^{I} began at ~188.2 °C, while the coordination polymers of L^{II} showed higher thermal stability with mass remaining constant until \sim 234 °C, at which point decomposition commenced. The X-ray powder diffraction pattern of the decomposition product obtained at 625 °C gave diffraction peaks corresponding to lanthanide oxide and some other minor peaks belonging to unknown compounds. It is obvious that the coordination polymers of L^{II} are thermally more stable than that of L^1 , which could be attributed to the fact that Ln–O bonds are normally much stronger in complexes of L^{II} than in L¹. To explore the other complex structures, with the exception of 1, 2 and 3, powder X-ray diffraction (XRD) of those complexes was investigated. The XRD patterns (Fig. S3 and S4, ESI[†]) of the other complexes showed the main reflections remaining nearly identical with the 1, 2 and 3 samples, respectively, which supported the notion that the two kinds of complexes are isostructural.

To get structural information in solution, we have successfully obtained the positive-ion ESI mass spectra of the coordination polymers of ligands L^{I} and L^{II} in ethyl acetate-methanol solution respectively, although the measurements of their matrix-assisted-laser-desorption ionization (MALDI) mass spectra were unsuccessful. In the ESI mass spectrum of the Gd^{III} complex of ligand L^{II} , 1:1, 1:2, 1:3, 2:3, 3:2 species were detected (Fig. 4). The first two species were observed as $[GdL^{II}(NO_3)_2]^+$ (*m*/*z* 1013.4) and $[GdL^{II}_2(NO_3)_2]^+$ (*m*/*z* 1744.8), in addition, the 3:1 species was observed as a dicationic species $[GdL^{II}_3(NO_3)]^{2+}$ (*m*/*z* 1207.6),

2:3 and 3:2 species were observed as penta-cationic species $[Gd_2L^{II}_3(NO_3)]^{5+}$ (*m*/*z* 516.0) $[Gd_3L^{II}_2(NO_3)_4]^{5+}$ (*m*/*z* 437.0). This observation strongly indicates that the polymeric complexes of the ligands observed in the solid state are maintained in solution too.

The idea behind the use of the two ligands is to explore the coordination chemistry and self assembly principles of tripodal type ligands. There is no doubt that tripodal bridging ligands with three coordination sites are expected to result in more unprecedented coordination polymers with novel topologies. As discussed above, L^{I} herein exhibits a divergent spacer to link metal ions into 1D ladder-like polymeric complexes. In contrast to L^{I} , L^{II} act as a convergent ligand and binds metal ions into the (3,3)-connected puckered 2D net with 4.8² topological notation. These results substantially indicate that the different rigidity of the backbone groups as well as the different aromatic terminal groups play a central role in determining the supermolecular structure of the coordination polymers.

UV-vis spectroscopic studies

As shown in Fig. 5, the absorption spectra of the ligand L^1 in acetonitrile features one main band located at around 294 nm $(\varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}, 11\,800)$ which can be assigned to characteristic $\pi-\pi^*$ transitions centered on the salicylamide units. It is interesting to note that the UV-vis absorption spectrum of L^{II} in acetonitrile is almost the same as that observed for L^1 (293 nm, $\varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$, 9920) which shows that the backbone groups do not substantially affect the electronic properties of the salicylamide moiety. The



Fig. 4 Positive-ion ESI mass spectra measured in ethyl acetate and methanol mixed solution, the inset shows an enlargement around the peaks m/z 1207 and 1747.



Fig. 5 Electronic absorption spectra of L^1 (dotted line) and L^{II} (solid line) in acetonitrile (5 × 10⁻⁵ M).

large molar absorption coefficient for the ligands indicates that the two tripodal ligands have a strong ability to absorb light. When Ln^{3+} was added to an acetonitrile solution of L^{I} or L^{II} , respectively, the absorption spectrum showed little change which proves that the lanthanide ions do not substantially affect the electronic properties of the salicylamide moiety either. But it must be noted that the complexes of L¹ tended to precipitate more easily because of their poor solubility in acetonitrile than those of L^{II} . Weak absorption bands of the Nd complex of L^{II} were also observed at $\lambda = 490$ -550, 550-640, 650-700, 715-775, 775-845 and 845-925 nm, as shown in Fig. 6. The electronic spectra in the visible region of the Nd^{III} complex exhibits alterations in intensity and shifts in position of the absorption bands relative to the corresponding Ln^{III} aquo ions which have been attributed by Jørgensen to the effect of crystal fields upon interelectronic repulsion between the 4f electrons, and is related to covalence in the metal-ligand bond, assessed by Sinha's parameter (δ), and the nephelauxetic ratio (β) .^{14,15} The β value (1.0028) for the Nd^{III} complex is more than unity and the δ value (-0.2134) is negative, suggesting that the Nd³⁺–O bond of the complex has weaker covalency than that of the Nd³⁺ aquo ion.

Sensitization of lanthanide-centered emission by ligands

Upon UV irradiation, the free ligands emit a strong blue luminescence (apparent λ_{max} at *ca.* 463 nm for L¹ and *ca.* 454 nm for L^I that can be easily detected with the naked eye. However, upon complexation this emission is replaced by the typical luminescence color arising from the corresponding lanthanide cation. These colors can also be easily visualized using a standard laboratory UV lamp ($\lambda_{ex} \approx 365$ nm), and no loss in signal intensity over a period of several weeks was observed, indicating good stability of the complexes.

For the Sm^{III} complex of L^{II}, the emission intensity is the weakest, but two characteristic bands can still be observed. They are attributed to ${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{J}$ (J = 5/2, 7/2) transitions (Fig. S5, ESI[†]). The solid state excitation and emission spectrum of the europium complex of L^{II} at room temperature is shown in Fig. 7. The excitation spectrum of the europium complex of L^{II} exhibits a series of sharp lines characteristic of the Eu^{III} energy-level structure, and can be assigned to transitions between the ${}^{7}F_{0,1}$ and ${}^{5}L_{6}$, ${}^{5}D_{2}$ levels¹⁶ which indicates that the Eu^{III} luminescence is not efficiently sensitized by the ligand. There are five characteristic peaks of Eu^{III} shown in the emission spectra which are attributed to ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ (580 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (592 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (616 nm), ${}^5D_0 \rightarrow {}^7F_3$ (648 nm) and ${}^5D_0 \rightarrow {}^7F_4$ (693 nm). The sharpness of the non-degenerate transition (${}^{5}D_{0} \rightarrow {}^{7}F_{0}$) indicates that all the Eu sites in the sample have essentially identical ligand coordination and structural environments. The intensity of the ${}^5D_0 \rightarrow {}^7F_2$ transition (electric dipole) is stronger than that of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition (magnetic dipole), which indicates that the coordination environment of the Eu^{III} ion is asymmetric.¹⁷ For Tb^{III}, the emission intensity is stronger than that of the other three in the same conditions. There are three characteristic peaks shown in Fig. 8 which are assigned to the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 4, 5, 6) transitions. For Dy^{III}, three characteristic bands can be seen in the emission spectra, which are attributed to transitions of 457 nm (${}^{4}I_{15/2} \rightarrow$ ${}^{6}\text{H}_{15/2}$), 481 nm (${}^{4}\text{D}_{9/2} \rightarrow {}^{6}\text{H}_{15/2}$) and 577 nm (${}^{4}\text{D}_{9/2} \rightarrow {}^{6}\text{H}_{13/2}$) (Fig. S6, ESI[†]). Compared with the emission spectra of the four complexes (Table 2), the transition intensity changes in the order $Tb^{III} > Dy^{III} > Eu^{III} > Sm^{III}$ which means that the energy transfer





Fig. 6 Absorption spectra of the Nd^{III} complex (0.02 M acetonitrile solution) showing f–f transitions.



Fig. 7 Room-temperature excitation and emission spectra for europium complex of ligand L^{II} ($\lambda_{ex} = 397$ nm, excitation and emission passes = 2.5 nm) in the solid state with emission monitored at approximately 616 nm.

Table 2 Photophysical data of the complex

		$\lambda_{\max}{}^a/\mathrm{nm}$	τ/ms	Φ^{b} (%)
L	Sm	564 (50.56), 598 (82.57)		
	Eu	593 (138), 619 (498)	0.558	0.82
	Tb	492 (2803), 546 (7434), 580 (389.2)	1.021	5.2
	Dy	482 (2622), 573 (1866)		
L^{II}	Sm	562 (96.5), 97 (117)	0.050	0.3
_	Eu	580 (54,57), 593 (283,6) 618 (536,1), 648 (14,62), 693 (16,17)	1.613	2.6
	Tb	492 (>10 000), 546 (>>10 000), 583 (2099), 590 (1843)	2.014	44
	Dy	457 (76.53), 482 (2622), 573 (1866)	0.069	1.6

^{*a*} Excitation and emission passes = 2.5 nm. Data in parentheses for the relative fluorescence intensity are given in a.u. ^{*b*} Luminescence lifetimes and quantum yield values are reported here with an error of $\pm 15\%$.



Fig. 8 Room-temperature emission for ligand \mathbf{L}^{II} (\neg , $\lambda_{ex} = 326$ nm) and its terbium complex (---, $\lambda_{ex} = 318$ nm) in the solid state (excitation and emission passes = 1 nm), The inset shows the lifetime decay curve of the Tb complex of ligand \mathbf{L}^{II} .

from the organic ligands to Tb^{III} and Dy^{III} is more effective than that to Eu^{III} and Sm^{III} . Furthermore, the intensity of the four complexes based on the L^1 ligand is relatively weak, possibly due to the steric effects of the backbone group, which prevents the salicylamide chromophore of L^1 from being accessible to the Ln^{III} ion reducing the luminescent intensity of the lanthanide ions.

In addition to steady state measurements, the luminescence lifetimes of the Sm(${}^{4}G_{5/2}$), Eu(${}^{5}D_{0}$), Tb(${}^{5}D_{4}$) and Dy(${}^{4}F_{9/2}$) excited states and quantum yield determinations upon ligand excitation for each of the differing complexes were determined with the results also summarized in Table 2. We note that both the luminescence lifetimes and quantum yield values were strongly influenced by the backbone groups. The relatively long luminescence lifetimes and larger quantum yield values are an indication that the tripodal ligand provides a significant level of protection from non-radiative deactivation of lanthanide cations by the solvent molecules which is consistent with the single crystal analysis. In view of the fact that both Φ and τ have diminished by about the same factor, it is evident that the main problem lies in a decrease of sensitization efficiency and not in an increase of non-radiative deactivation of the lanthanide excited state. This is most likely due to insufficient inter-system crossing (ISC) of L^{I} as further supported by the energy transfer discussed below.

Energy transfer between the ligand and Ln^{III}

To demonstrate the energy transfer process, the phosphorescence spectrum of the Gd complex of L^{I} and L^{II} were measured for triplet energy-level data. From the phosphorescence spectra (Fig. S7 and S8, ESI[†]), the triplet energy level (${}^{3}\pi\pi^{*}$) of the Gd complex, which corresponds to its lower wavelength emission edge, is 22727 cm⁻¹ (440 nm) and 24449 cm^{-1} (409 nm) respectively. Because the lowest excited state, ${}^{6}P_{7/2}$ ($E({}^{6}P_{7/2}) = 32\,000 \text{ cm}^{-1}$) of Gd^{III} is too high to accept energy from the ligand, the data obtained from the phosphorescence spectra actually reveal the triplet energy level of ligands in lanthanide complexes. The singlet state energy $({}^{1}\pi\pi^{*})$ level of the ligand is estimated by referencing its absorbance edge, which is $32\,467$ and $32\,258$ cm⁻¹ (308 nm and 310 nm) respectively. In general, the sensitization pathway in luminescent europium complexes consists of excitation of the ligands into their excited singlet states, subsequent intersystem crossing of the ligands to their triplet states, and energy transfer from the triplet state to the ${}^{5}D_{J}$ manifold of the Eu^{III} ions, followed by internal conversion to the emitting ⁵D₀ state. Finally, the Eu^{III} ion emits when a transition to the ground state occurs.¹⁸ Moreover, electron transition from the higher excited states, such as ${}^{5}D_{3}$ (24 800 cm⁻¹), ${}^{5}D_{2}$ (21 200 cm⁻¹), and ${}^{5}D_{1}$ (19 000 cm⁻¹), to ${}^{5}D_{0}$ (17 500 cm⁻¹) becomes feasible by internal conversion, and most of the photophysical processes take place in this orbital. Consequently, most europium complexes give rise to typical emission bands at \sim 581, 593, 614, 654, and 702 nm, corresponding to the deactivation of the ⁵D₀ excited state to the ⁷F_J ground states (J = 0–4). In a similar way, the 4f electrons of the Tb^{III} ion are excited to the 5D_J ion manifold from the ground state. Finally, the Tb^{III} ion emits when the 4f electrons undergo a transition from the excited-state of ${}^{5}D_{4}$ to the ${}^{7}F_{J}$ ground states (J = 6-4). The gap between the ${}^{3}\pi\pi^{*}$ and ${}^{1}\pi\pi^{*}$ states ($\Delta E = {}^{1}\pi\pi^{*} - {}^{3}\pi\pi^{*} = 9740 \text{ cm}^{-1}$ or 7809 cm⁻¹) of ligands is favorable for a relatively efficient intersystem crossing process.¹⁹ Latva's empirical rule²⁰ states that an optimal ligand-to-metal energy transfer process for Ln^{III} needs ($\Delta E = {}^{3}\pi\pi^{*} - {}^{5}D_{J}$) 2500– 4000 cm⁻¹ for Eu^{III} and 2500–4500 cm⁻¹ for Tb^{III}. The triplet energy level of the two salicylamide ligands (22 727 cm⁻¹ and 24 449 cm⁻¹) is higher than the ${}^{5}D_{0}$ level of Eu^{III} (17 500 cm⁻¹) and the ${}^{5}D_{4}$ level of Tb^{III} (20400 cm⁻¹). This therefore supports the observation of stronger sensitization of the terbium complexes than the europium complexes because of the smaller overlap between the ligand triplet and europium ion excited states. It is important to note that the stronger sensitization of the L^{II} complexes than that of L^{I} complexes is mainly due to the higher ${}^{3}\pi\pi^{*}$ energy of L^{II} which depends on the backbone groups.

Experimental

Synthesis of the ligands

L¹. The ligand 1,3,5-tris{[(2'-furfurylaminoformyl)phenoxyl]methyl-2,4,6-trimethylbenzene (L^I) was prepared by the following synthetic route. To a solution of 1,3,5-tris(bromomethyl)-2,4,6trimethylbenzene²¹ (1.31 g, 3.3 mmol) in dry acetone was added K_2CO_3 (0.69 g, 5 mmol) and the mixture stirred and heated for 10 min, furfurylsalicylamide²² (2.39 g, 11 mmol) in 50 ml of acetone was added dropwise over 30 min and the resulting solution stirred and heated to reflux for 12 h. After cooling, the inorganic salts were then separated by filtration and the solvent removed from the filtrate under reduced pressure. The crude product was purified by chromatography on silica, gradient elution from petroleum ether (boiling range: 60-90 °C) to 1:5 petroleum ether-ethyl acetate. 2.32 g, Yield 87%; mp: 158.7 °C. Analytical data, calc. for C48H45N3O9: C, 71.36; H, 5.61; N, 5.20; Found: C, 71.59, H, 5.59, N, 5.18%; IR (KBr, v, cm⁻¹): 3379 (s, NH), 1646 (s, C=O), 1599 (m), 1518 (s), 1469 (m), 1292 (m), 1223 (s), 978 (m), 755 (m). ¹H NMR (CDCl₃, 300 MHz): δ : 2.36 (s, 9H), 4.39 (d, J = 5.2, 6H, NHCH₂), 5.18 (s, 6H, OCH₂), 6.89 (d, J = 3.0, 3H, Ar), 6.09 (t, 3H, Ar), 7.02-7.21 (m, 9H, Ar), 7.50-7.58 (m, 3H, Ar), 8.02 (s, 3H, NH), 8.27–8.31 (dd, 3H, Ar).

L^{II}. The ligand 1,1,1-tris{[(2'-furfurylaminoformyl)phenoxyl]methyl}ethane (L^{II}) was prepared by a similar synthetic route. To a solution of 1,1,1-tris(p-tosyloxymethyl)propane²³ (2.98 g, 5 mmol) in dry DMF was added K₂CO₃ (1.00 g, 7 mmol) and the mixture stirred and heated for 10 min, furfurylsalicylamide (3.08 g, 16.5 mmol) in 50 ml of DMF was added dropwise over 30 min and the resulting solution stirred and heated to reflux for 48 h. After cooling, the inorganic salts were then separated by filtration and the solvent removed from the filtrate under reduced pressure. The crude product was purified by chromatography on silica, gradient elution from petroleum ether to 1:8 petroleum ether-ethyl acetate. 1.75 g, Yield 48%; mp: 126.1 °C. Analytical data, calc. for C₄₂H₄₁N₃O₉: C, 68.93; H, 5.65; N, 5.74; Found: C, 68.74, H, 5.67, N, 5.75%; IR (KBr, v, cm⁻¹): 3406 (s, NH), 1647 (s, C=O), 1601 (m), 1530 (m), 1486 (m), 1295 (m), 1224 (s), 1012 (m), 753 (m). ¹H NMR (CDCl₃, 300 MHz): δ: 0.63 (t, 3H CH₃), 1.35 (m, 2H, CH₂), 4.18 (s, 6H, OCH₂), 4.49 (d, $J = 3.6, 6H, NHCH_2), 6.09-6.12 (m, 6H, Ar), 6.81 (d, J = 5.4, J)$ 3H, Ar), 7.11 (s, 3H, Ar), 7.11-7.15 (t, 3H, Ar), 7.18-7.22 (t, 3H, NH), 7.99-8.02 (dd, 3H, Ar).

Syntheses of the complexes

[LnL¹(NO₃)₃] (Ln = Pr, Nd, Sm, Eu, Gd, Tb or Dy). To a clear solution of L¹ (0.081 g, 0.1 mmol) in ethyl acetate (10 ml) was added Ln(NO₃)₃·5H₂O (0.10 mmol) in 5 ml of ethyl acetate. The resulting solution was left stirring overnight at room temperature to afford a pale white solid which was filtered off, washed three times with ethyl acetate, and dried over CaCl₂ for 1 d to give the product in 70–80% yield. A layer of a solution (10 mL) of ethyl acetate was carefully layered over an 4 mL ethyl acetate solution of L¹ (0.01 mmol, 8.1 mg). Then, an methanol solution (2 mL) of lanthanide nitrate salts was carefully layered over the buffer layer. Pale green crystals appeared after 4–5 weeks and were collected and dried in air after being washed with ethyl acetate.

[LnL^{II} (NO₃)₃] (Ln = Pr, Nd, Sm, Eu, Gd, Tb or Dy). To a clear solution of **L**^{II} (0.073 g, 0.1 mmol) in ethyl acetate (5 ml) was added Ln(NO₃)₃·5H₂O (0.1 mmol) in 5 ml of ethyl acetate. The resulting solution was left stirring overnight at room temperature to afford a pale white solid which was filtered off, washed three times with ethyl acetate, and dried over CaCl₂ for 1 d to give the product in 50–60% yield. One millimole of ligand and 1 equiv. (1 mmol) of the metal nitrates were dissolved in a hot methanol + ethyl acetate (v/v = 1:10) solution to make a concentrated solution. Then the flask was cooled, and the mixture was filtered into a sealed 25–40 ml glass vial for crystallization at room temperature. After about three weeks crystals suitable for analysis were obtained.

Materials and instrumentation

The commercially available chemicals were used without further purification. All of the solvents used were of analytical reagent grade.

The metal ions were determined by EDTA titration using xylenol orange as indicator. C, N and H were determined using an Elementar Vario EL. Melting points were determined on a Kofler apparatus. Thermogravimetric analyses (TGA) were performed with a WCT-2A thermoanalyzer under air atmosphere (25-625 °C) at a heating rate of 10 °C min⁻¹. X-Ray powder diffraction (XRD) patterns were obtained on a Rigaku D/Max-II X-ray diffractometer with graphite-monochromatized Cu-Kα radiation. IR spectra were recorded on a Nicolet FT-170SX instrument using KBr discs in the 400-4000 cm⁻¹ region. ¹H NMR spectra were measured on a Bruker DRX 300 spectrometer in CDCl₃ solution with TMS as internal standard. Electronic spectra were recorded with a Varian Cary 100 spectrophotometer in acetonitrile solution. Mass spectra (electrospray ionization timeof-flight, ESI-TOF, positive mode) were recorded on Mariner ABI Mass spectrometer. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer and a shimadzu RF-540 spectrofluorophotometer equipped with quartz curettes of 1 cm path length with a xenon lamp as the excitation source. An excitation slit of 2.5 or 1 nm and an emission slit of 2.5 or 1 nm were used for the measurements in the solid state. The 77 K solution-state phosphorescence spectra were recorded with solution samples loaded in a quartz tube inside a quartzwalled optical Dewar flask filled with liquid nitrogen in the phosphorescence mode.

Quantum yields were determined by the optically dilute method²⁴ using the following equation:

$$\frac{\phi_{\rm x}}{\phi_{\rm r}} = \frac{A_{\rm r}(\lambda_{\rm r})I_{\rm r}(\lambda_{\rm r})n_{\rm x}^2D_{\rm x}}{A_{\rm x}(\lambda_{\rm x})I_{\rm x}(\lambda_{\rm x})n_{\rm r}^2D_{\rm r}}$$

Here A is the absorbance at the excitation wavelength (λ), I is the intensity of the excitation light at the same wavelength, n is the refractive index, and D is the integrated luminescence intensity. The subscripts "x" and "r" refer to the sample and reference, respectively. In this case, quinine sulfate in 1.0 N sulfuric acid was used as the reference ($\Phi_r = 0.546$).²⁵

The luminescence decays were recorded using a pumped dye laser (Lambda Physics model FL2002) as the excitation source. The nominal pulse width and the linewidth of the dye-laser output were 10 ns and 0.18 cm^{-1} , respectively. The emission of a sample was collected by two lenses into a monochromator (WDG30),

Table 3Crystal data and structure refinement parameters for ligand L^1 and polymers 1, 2 and 3

Compound	Lı	1	2	3
Empirical formula	$C_{48}H_{45}N_3O_9$	$C_{48}H_{47}N_6O_{19}Pr$	C _{42.5} H ₄₃ N ₆ NdO _{18.5}	$C_{42}H_{41}N_6O_{18}Sm$
Temperature/K	293	293	298	294
M	807.84	1152.83	1078.07	1068.16
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c	P2(1)/c	P2(1)/c
a/Å	8.9278(2)	14.395(2)	16.657(7)	16.6382(6)
b/Å	15.1760(4)	17.708(3)	16.373(7)	16.2654(5)
c/Å	31.0232(8)	24.171(4)	18.370(9)	18.6824(6)
β/°	95.2180(10)	106.782(2)	98.696(7)	98.911(2)
$V/Å^3$	4185.86(18)	5898.9(17)	4952(4)	4994.9(3)
Ζ	4	4	4	4
$D_{\rm c}/{ m kg}~{ m m}^{-3}$	1.282	1.298	1.446	1.420
μ/mm^{-1}	0.089	0.896	1.125	1.250
F(000)	1704	2352	2192	2164
Crystal size/mm	$0.45 \times 0.32 \times 0.28$	$0.36 \times 0.32 \times 0.29$	$0.30 \times 0.27 \times 0.25$	$0.15 \times 0.13 \times 0.10$
θ Range for data collection/°	1.88-25.50	1.76-25.00	1.67-25.00	2.21-25.05
Index ranges, hkl	-10 to 10, -18 to 17, -36	-16 to 17, -21 to 19, -28	-19 to 18, -19 to 18, -15	-19 to 15, -19 to 19, -21
	to 37	to 28	to 21	to 22
Reflections collected/unique	22130/7759	30035/10300	25588/8712	22725/8209
$R_{\rm int}$	0.0414	0.0660	0.0901	0.1010
Data/restraints/params	7759/0/702	10300/446/712	8712/616/619	8209/0/578
Goodness-of-fit on F^2	1.015	1.053	1.022	0.964
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0529, wR2 = 0.1263	R1 = 0.0660, wR2 = 0.1431	R1 = 0.0702, wR2 = 0.1880	R1 = 0.0666, wR2 = 0.1198
R indices (all data)	R1 = 0.1135, wR2 = 0.1578	R1 = 0.1672, wR2 = 0.2285	R1 = 0.1548, wR2 = 0.2545	R1 = 0.1788, wR2 = 0.1413

detected by a photomultiplier and processed by a Boxcar Average (EGG model 162) in line with a microcomputer.

X-Ray crystallography

The X-ray diffraction data were collected on a CCD area detector with a graphite-monochromated Mo-K α radiation source ($\lambda =$ 0.71073 Å). All of the structures were solved by direct methods and refined by full-matrix least-squares cycles on F^2 . The coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. The furan ring and crystalline water in complex 1, crystalline methanol in complex 2 exhibit disorder over two positions and were refined isotropically with half site occupancy. Details of crystallographic parameters, data collection and refinements are listed in Table 3. Selected bond distances and angles for polymers 1, 2 and 3 are listed in Tables S1, S2 and S3† respectively. CCDC 6724449 for L¹, CCDC 672450 for 1, CCDC 672451 for 2 and CCDC 672452 for 3.

Conclusions

This study demonstrates that the two tripodal ligands with furfurylsalicylamide arms 1,3,5-tris{[(2'-furfurylaminoformyl)phenoxyl]methyl}-2,4,6-trimethylbenzene (L^{I}) and 1,1,1-tris{[(2'-furfurylaminoformyl)phenoxyl]methyl}ethane (L^{II}) are capable of coordinating lanthanide ions with carbonyl oxygen atoms and generate novel lanthanide coordination polymers. The resulting polymers provide the lanthanide ions with a nona-coordination environment and prevents solvent and water molecules from entering the coordination sphere, effectively resulting in an enhanced sensitization of the lanthanide due to a decrease in the vibronic quenching effect. Luminescence studies also demonstrated that the salicylamide ligands exhibit a good antennae effect with respect to the Tb^{III} ion due to efficient intersystem crossing and ligand-to-metal energy transfer. It is worth noting that the change of backbone as well as terminal groups is a decisive factor in determining the coordination environments of the metal centers, the topologies of the polymeric products as well as luminescence properties.

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