

Structure Variation and Luminescence Properties of Lanthanide Complexes Incorporating a Naphthalene-Derived Chromophore Featuring Salicylamide Pendant Arms

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A new potentially bridging ligand containing two salicylamide pendant arms separated by a 2,3-dimethoxynaphthalene spacer has been prepared and its coordination chemistry with Ln^{III} ions has been investigated. An analysis of the presented crystal structures indicates that the diversity of these supramolecular structures is mainly dictated by the nature of the metal ions. These compounds represent good examples of tuning crystal structures arising from the flexibility of the ligands and the Ln contraction effect. Luminescence studies showed that the introduction of the methoxyl substituents on

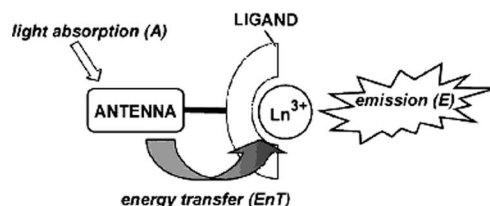
the naphthalene backbone lowers the triplet energy and considerably changes the luminescent behaviors of the Eu^{III} and Tb^{III} complexes, which is very different from the literature data on similar compounds. In the emission spectra of the Tb complex the ligand fluorescence remains relatively important because of the back-energy transfer from the Tb^{III} ion to the ligand, which to the best of our knowledge, may be the first example of salicylamide lanthanide complexes.

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Introduction

Stimulated by potential applications in biochemical sensors and fluoroimmunoassays,^[1] there is intense current interest being shown in the design of lanthanide complexes that exhibit characteristic luminescence properties. The low extinction coefficients (less than 10 dm³ mol⁻¹ cm⁻¹) of the Laporte forbidden f-f transitions of lanthanides necessitates the use of sensitized energy transfer from a suitable absorbing chromophore to influence lanthanide luminescence.^[2] For this process to be efficient, suitable chromophores have been used to act as antennae or sensitizers that can transfer energy to the lanthanide ion indirectly (Scheme 1). In this approach the lanthanide ion is linked by complexation with a ligand that has an organic chromophore capable of absorbing light energy with a higher efficiency than the metal itself. In a subsequent energy transfer process this chromophore acts as a sensitizer of the lanthanide excited state, which can subsequently be deactivated through luminescence. Because of the large spectral gap between antennae excitation (often UV light) and emitted photons (visible to near IR), lanthanide-antenna conjugates have often been

referred to as “molecular devices for wavelength conversion”.^[3] Furthermore, complexation with a ligand provides lanthanides with a certain degree of protection from the surrounding water, hence increasing their luminescence quantum yields. The interest generated by the wide range of applications of luminescent lanthanide complexes^[4] explains why the design of efficient molecular edifices is still an important research goal.



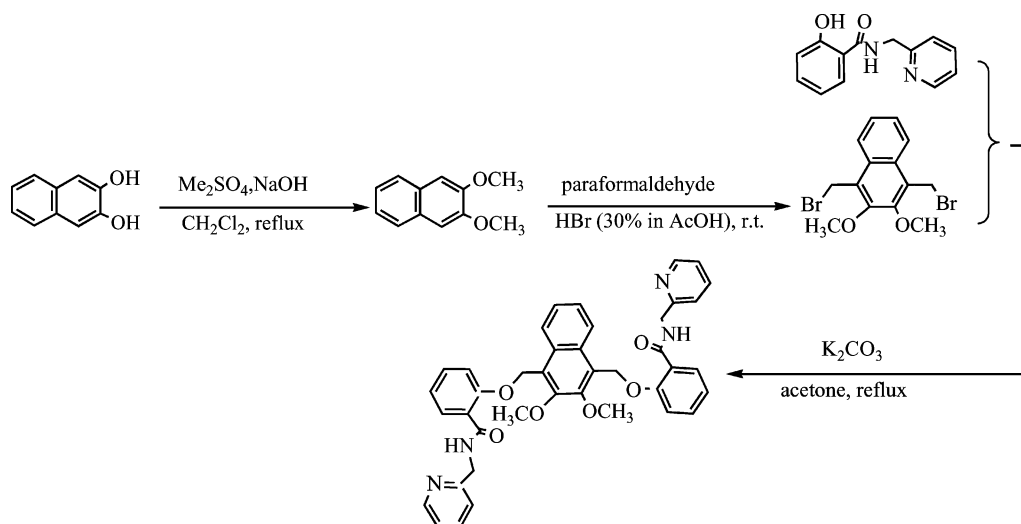
Scheme 1. Sensitization of lanthanide excited states by energy transfer from an antenna.

Recently a significant increase in the research of coordination polymers in which metal ion centers are bridged through organic molecules has been observed, because of the potential applications in optoelectronics, magnetism, and catalysis.^[5–12] Most of the described materials are based on transition metal ions and have multidimensional structures with geometrically simple repeating units from the templating effect of the transition metal ions, which generally show low coordination numbers. Only a few examples of coordination polymers that incorporate lanthanide ions

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Scheme 2. The synthetic route of the ligand **L**.

are known,^[13–20] along with some examples of high-nuclearity lanthanide clusters.^[21–24] However, these large ions achieve high and variable coordination numbers with irregular geometries, leading to potentially highly luminescent coordination polymers with more complicated features. To generate target coordination polymers by design, a judicious choice of ligands provides a way of controlling supramolecular interactions. In general, ligands with certain features, such as rigidity and symmetry, are suitable for obtaining coordination polymers. In an attempt to optimize lanthanide-centered emission in lanthanide-containing polymers and explore the varied possibilities of lanthanide-based coordination polymers, we are systematically studying the structure and the photophysical properties of complexing agents capable of efficiently sensitizing Eu^{III} and Tb^{III} emission while having a polymerizable moiety.^[25,26] Along these lines, we have recently described the fluorescence properties of lanthanide complexes with naphthalene bearing pendant arms of salicylamide moieties.^[27] In order to extend our work in this field we have explored a ligand (Scheme 2) incorporating a naphthalene-derived chromophore featuring salicylamide pendant arms, with the additional interesting characteristics: (1) the high extinction coefficients of the ligand in the near UV/Vis range provide effective absorption of the excitation energy, which promotes a more effective energy transfer to the lanthanide ion; (2) it also maintains flexibility because of the presence of a $-\text{NHCH}_2-$ spacer between the aromatic ring that may bend to require its conformation to coordinate to metal centers; (3) the presence of O and N atoms and aromatic rings may form hydrogen bonds and π - π stacking interactions to extend and stabilize the whole framework series. Hence, diverse supramolecular structures may result from this interesting ligand.

The radii of the Ln cations decrease with increasing atomic number, which imposes evident influences on the coordination geometry and might lead to different types of structure and physical properties. Thus, it was interesting to

examine whether the architecture is maintained across the lanthanides. To date, only a few reports are concerned with the diversity of Ln-based structures controlled by the radii of Ln ions.^[28] We report herein on (i) the diversity of the supramolecular structure of the lanthanide complexes with this new bridging ligand and (ii) the luminescence properties of the resulting complexes formed with ions used in fluoroimmunoassays (Ln = Sm, Eu, Tb, Dy).

Results and Discussion

One of the important issues in determining the framework structures is the geometry of the organic ligands. In our study, the terminal coordinating donors are separated by the naphthalene ring at the *para* position, and two salicylamide arms attached to naphthalene groups are rotationally free and are thus capable of adjusting to match the metal coordination preference. Such a divergent arrangement would favor the formation of polymeric coordination polymers instead of discrete complexes. In addition, bulky coordination arms grafted on the 2,3-dimethoxynaphthalene backbone could result in intra-ligand twisting.

This bidentate spacer ligand, **L**, has been obtained in 78% yield by treating the picolylsalicylamide^[29] with 1,4-bis(bromomethyl)-2,3-dimethoxynaphthalene^[30] in dry acetone in the presence of an excess amount of K₂CO₃. The new ligand gave satisfactory ¹H NMR, IR, and mass spectra, as well as elemental analyses. Treatment of Ln(NO₃)₃·6H₂O with the new ligand in an ethyl acetate/methanol solution yields a series of complexes which, according to combustion analysis, correspond to the formulae [PrL(NO₃)₃(H₂O)CH₃OH]·3/2H₂O, [NdL(NO₃)₃(H₂O)CH₃OH]·1/2CH₃OH, SmL(NO₃)₃(CH₃OH) EuL(NO₃)₃(H₂O), GdL(NO₃)₃(H₂O), TbL(NO₃)₃(H₂O), [DyL(NO₃)₃(H₂O)₂]·CH₃OH, and ErL(NO₃)₃(H₂O)₂·CH₃OH. X-ray quality crystals of all the complexes except TbL(NO₃)₃(H₂O) were obtained after several weeks from vapor diffusion from an

ethyl acetate/methanol solution. Complexation of the arms through the carbonyl functions is reflected by the $\nu(\text{C}=\text{O})$ vibration, which is shifted towards lower energy by ca. 46 cm^{-1} . The complexes are soluble in DMF, DMSO, and methanol, slightly soluble in ethyl acetate, acetonitrile, and acetone, but insoluble in CHCl_3 and ether.

FT-IR Spectra Analyses

The characteristic bands of the carbonyl group belonging to the free ligand are seen at 1657 cm^{-1} and shift to 1611 cm^{-1} upon complexation. Among the spectra of these lanthanide complexes the main differences lie in the signals at 1611 cm^{-1} . The absence of a shoulder around this signal for the Pr^{III} to Tb^{III} complexes indicates the complete coordination of the ligand, while its presence in the Dy^{III} and Er^{III} complexes suggests the incomplete coordination of the ligand, which may be attributed to strong hydrogen bonding. Weak absorptions observed in the range $2900\text{--}2950\text{ cm}^{-1}$ can be attributed to the νCH_2 stretch of the ligand. The broad bands at ca. 3422 cm^{-1} are ascribed to the vibration of the water ligands in the complexes.

Solid-State Structure

Crystal Structure of Type I

Owing to the structural similarity of the Pr^{III} and Nd^{III} complexes, the Pr^{III} complex was selected for investigation in detail. As illustrated in Figure 1, the asymmetric unit of the Pr^{III} complex consists of one crystallographically independent Pr^{III} center. The polyhedron around the Pr^{III} ion is a distorted, bicapped *anti*-square prism with two oxygen atoms (O5, O6) from two carbonyl groups of two separate ligands, six oxygen atoms from three bidentate nitrate groups, one methanol molecule, and one aqua molecule completing the decaordinated sphere. The $\text{Pr}\text{--}\text{O}$ bond distances are in the range $2.387(8)\text{--}2.651(10)\text{ \AA}$. The Pr^{III} centers were extended to form an infinite 1D-chain polymer by the bridging connection of the ligand, **L**, stacking along the crystallographic *c* axis (Figure 2). Although the ligands have an “over and under” conformation, the chains are not helical, rather each metal–ligand chain shows a clear zigzag structure with a $\text{Pr}\text{--}\text{Pr}$ internal angle of 88.64° . The $\text{Pr}\cdots\text{Pr}$ separations between metals linked by the same bridging ligand are ca. $17.6\text{ \AA}$. The separations between alternate Pr^{III} centers (on the same side of the zigzag) are greater (ca. $24.6\text{ \AA}$). It is well known that the most important driving forces in crystal engineering are coordination-bonding and hydrogen-bonding interactions. Extended networks assembled by both coordination and hydrogen bonds are one of the important strategies to construct supramolecular networks.^[31] In principle, higher dimensionality networks can be obtained by the assembly of lower dimensionality polymers (or molecules) via hydrogen-bonding interactions. A series of such compounds has been reported previously.^[32] It is worth noting that significant hydrogen-

bonding interactions exist between the adjacent chains of the Pr^{III} complex (Figure 3). The nitrate groups can interact with the oxygen atoms of the coordinated water forming interesting two-dimensional supramolecular structures. The $\text{O}\cdots\text{O}$ distance [$2.764(5)\text{ \AA}$] and $\text{O}\text{--}\text{H}\cdots\text{O}$ angle (167.58°) are both within ranges of those reported for hydrogen bonds.

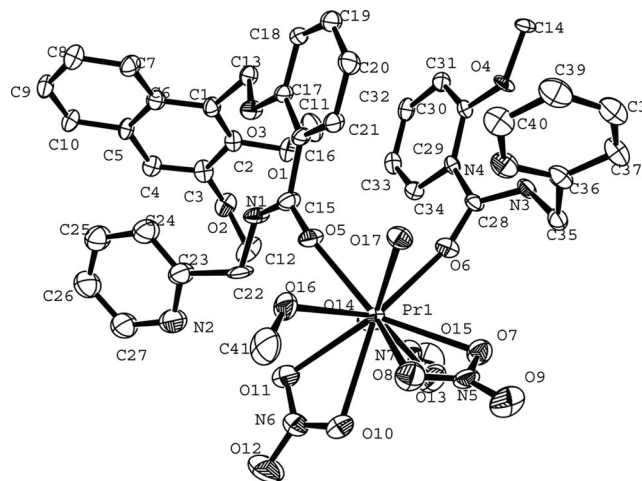


Figure 1. ORTEP drawing of the Pr^{III} complex showing the local coordination environment of the crystallographically independent Pr^{III} center (thermal ellipsoids at 30% probability).

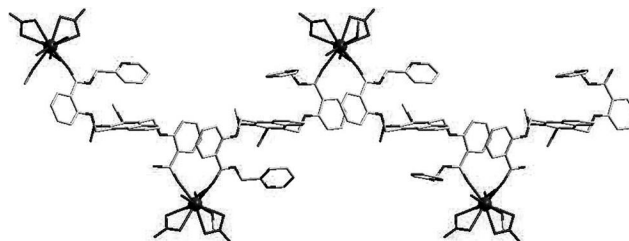


Figure 2. View of the 1D chain of the Pr^{III} complex along the *a* axis (hydrogen atoms are omitted for clarity).

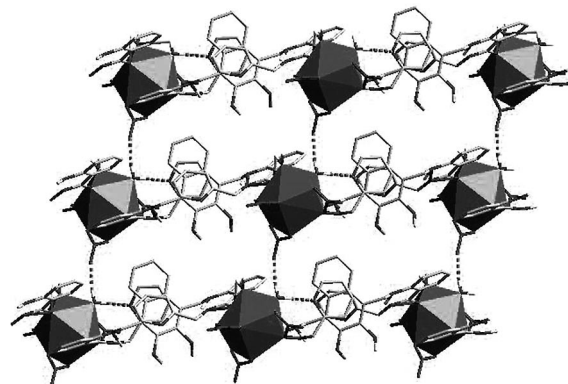


Figure 3. The 2D supramolecular structure of the Pr^{III} complex formed by coordinated water-mediated hydrogen bonds, which are indicated with dashed lines (viewed along the *b* axis).

Crystal Structure of Type II

Once the ligand coordinates with Sm^{III} and Eu^{III} the coordination environment of the metal ions changes dramati-

cally and the coordination number decreases from 10 to 9 for the complexes of Sm^{III} and Eu^{III} . The difference may be ascribed to the larger ionic radius and lower electronic density of Pr^{III} and Nd^{III} compared with Sm^{III} and Eu^{III} , which allows a higher coordination number for the former. The Sm^{III} and Eu^{III} complexes also have similar structures except for the coordinated water molecule that occurs in the Eu^{III} complex instead of the coordinated methanol molecule in the Sm^{III} complex. Hence, we selected the Eu^{III} complex for a detailed description. As shown in Figure 4, the asymmetric unit contains one Eu^{III} ion and two half ligands (from two crystallographically independent ligands) such that all the Eu^{III} ions are crystallographically equivalent. The europium complex of the ligand crystallizes in the monoclinic $P2_1/n$ space group. The coordination polyhedron around the Eu^{III} ion is a distorted, monocapped *anti*-square prism. There is one water molecule and three bidentate nitrate anions completing the nonacoordinate sphere of the europium ion, and the distance to the oxygen atom of the water molecule is $\text{Eu}-\text{O}(16)$ 2.383(6) Å. The other oxygen atoms form bond distances between 2.322(7) and 2.528(7) Å. The ligands coordinate in the bidentate bridging mode. This arrangement of two ligands around the europium ion leads to the structure of a one-dimensional zigzag chain (see Figure S1, Supporting Information) with a $\text{Eu}-\text{Eu}-\text{Eu}$ internal angle of 91.67° . The $\text{Eu}\cdots\text{Eu}$ separations between metals linked by the same bridging ligand are ca. 17.4 Å and the separations between alternate Eu^{III} centers (on the same side of the zigzag) are greater, ca. 25.0 Å, which are very similar to those of the Pr^{III} complex. It is interesting to note that evidence for intermolecular hydrogen bonds was not found. Upon further careful investigation of the structure of the Eu^{III} complex it can be seen that

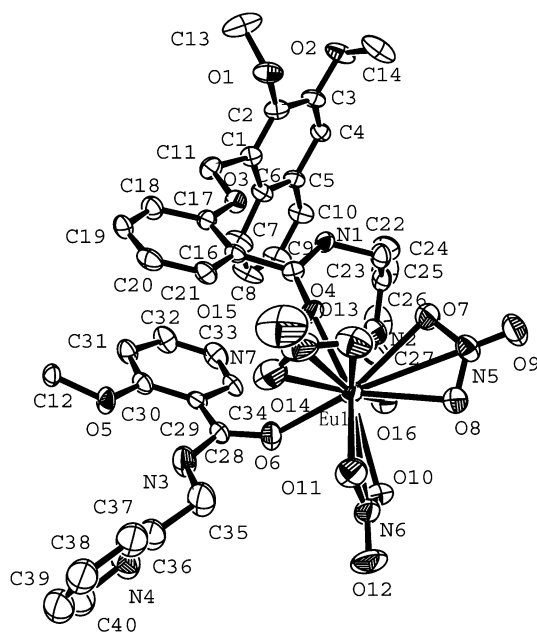


Figure 4. ORTEP drawing of the Eu^{III} complex showing the local coordination environment of the crystallographically independent Eu^{III} center (thermal ellipsoids at 30% probability).

two adjacent chains are interlinked by two kinds of $\pi-\pi$ stacking interactions. The dihedral angle between the benzene rings is 4.22° and the distance between the centroid of each ring is 3.732 Å, while the aromatic $\pi-\pi$ stacking interaction between two parallel pyridine rings is situated at a distance of 3.869 Å (see Figure S2, Supporting Information). In this way, the zigzag polymer chains are connected together and constructed into a three-dimensional supramolecular structure (Figure 5).

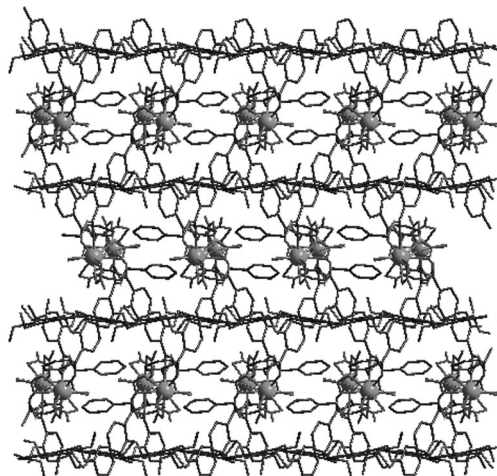


Figure 5. The 3D supramolecular structure of the Eu^{III} complex constructed by $\pi-\pi$ stacking interactions (viewed along the c axis; hydrogen atoms are omitted for clarity).

Crystal Structure of Type III

The molecular structure of colorless $[\text{GdL}(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_\infty]$ displays the following main features: (i) The gadolinium complex crystallizes in the monoclinic $P2_1/c$ space group. The structure consists of neutral molecules in which Gd^{III} is nonacoordinated, bound on one side to six O atoms from the three bidentate nitrate ions and one O atom from the water molecule and on the other side by the two O atoms from **L** (Figure 6). The coordination sphere of the central Gd^{III} ion is similar to that of the Eu^{III} ion. The coordinated salicylamide arms also adopt a *trans-trans* conformation with respect to the naphthalene backbone. Each ligand adopts a bridging mode, in which two oxygen atoms (O5 and O6) act as chelating atoms bonded to crystallographically independent gadolinium ions forming a 1D zigzag chainlike framework (Figure 7) with a $\text{Gd}-\text{Gd}-\text{Gd}$ internal angle of 132.78° , and the $\text{Gd}\cdots\text{Gd}$ separations between metals linked by the same bridging ligand are ca. 18.23 Å. The separations between alternate Gd^{III} centers (on the same side of the zigzag) are larger, ca. 33.5 Å, which is considerably different from that of type I and type II. This implies that the ligand in the Gd^{III} complex has a more extended conformation. (ii) The two salicylamide arms form fold-back angles of about 72.69 and 33.01° with the naphthalene ring. We also note that the naphthalene moieties are slightly puckered with CCC triangles folded by 2° with respect to the naphthalene mean plane. (iii) The two methoxyl substituents on C2 and C5 lying on the same side

of the naphthalene ring also adopt a *trans-trans* arrangement to minimize the intramolecular methoxyl-methoxyl repulsion. (iv) The one-dimensional zigzag chain is self-assembled through hydrogen bonds giving rise to a 3D MOF with hexagonal, chair-conformational cavities (see Figure S3 and S4, Supporting Information). Provided that neither water nor other molecules or ions are present in these cavities their dimensions are worth noting. The inner diameter of each hexagonal pore has been evaluated taking into account the van der Waals radii of the involved atoms.^[33] Particularly, the shorter distance shown in Figure S4 corresponds to an effective free pore opening of about 3.4 Å. This value agrees well with the total free volume of 170.1 Å³ per cell (ca. 3.9% of the crystal volume) determined by using the PLATON program.^[34]

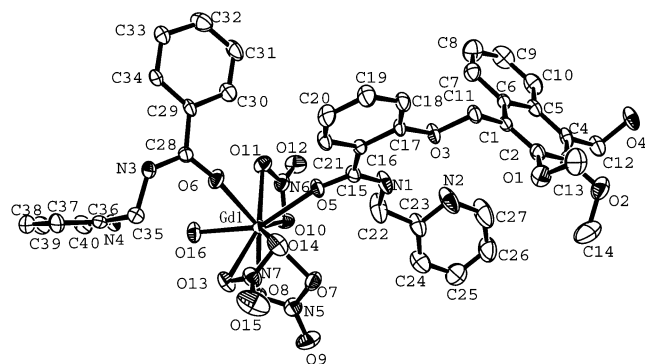


Figure 6. ORTEP drawing of the Gd^{III} complex showing the local coordination environment of the crystallographically independent Gd^{III} center (thermal ellipsoids at 30% probability).

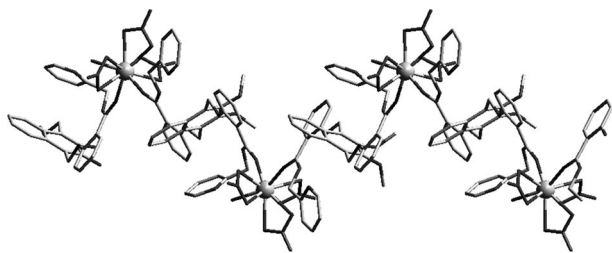


Figure 7. View of the 1D zigzag chain of the Gd^{III} complex along the *a* axis (hydrogen atoms are omitted for clarity).

Crystal Structure of Type IV

Even though the radius of Dy^{III} is only 0.026 Å smaller than that of Gd^{III}, the introduction of Dy during the synthesis results in quite a different product. The ligand coordinates to a single metal center in a monodentate mode, in contrast to the di-monodentate bridging coordination mode observed for the Pr^{III} to the Eu^{III} complexes, possibly because the combination of the bulkier ligand and the smaller ionic radius results in a higher degree of steric crowding. Dy^{III} and Er^{III} complexes are also isomorphous, therefore, only the structure of the Dy^{III} complex will be discussed in detail as a representative. A representative molecular structure plot of the Dy^{III} complex is shown in Figure 8. The Dy^{III} complex crystallizes in the monoclinic space group

P2₁/n. The metal ion is ninefold coordinated and surrounded by three bidentate nitrate groups, two water molecules, and one ligand. The bond distances of Dy–O are in the range 2.318(6)–2.488(8) Å. The Dy^{III} coordination polyhedron is fairly distorted and best described as a monocapped *anti*-square prism with an O atom from the nitrate group lying in the capping position similar to the arrangement observed above. The [DyL(NO₃)₃(H₂O)₂] units self-assemble via intermolecular O16–H41...O6 and O17–H44...O6 hydrogen-bonding interactions where water molecules act as an O–H hydrogen-bond donor to the carbonyl O atoms forming a zigzag chain (Figure 9). These chains are further threaded by O16–H42...O18, O17–H43...N2, and O18–H18...N4 interchain hydrogen-bonding interactions leading to a three-dimensional (3D) supermolecular structure (Figure 10). In addition, the intramolecular N–H...O hydrogen bonds, forming among the carbonyl oxygens, amide nitrogen atoms, and aqua ligands, play a vital role in determining the crystal packing and in the construction of the extended 3D supramolecular network of the Dy^{III} complex.

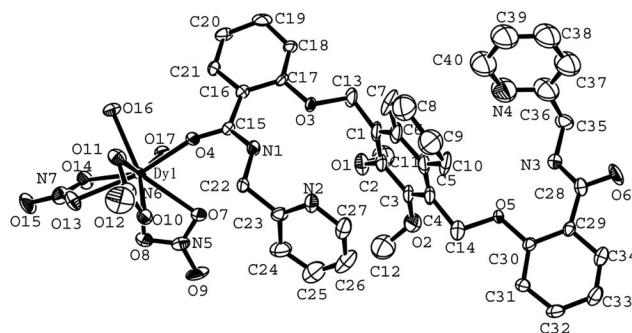


Figure 8. ORTEP drawing of the Dy^{III} complex showing the local coordination environment of the crystallographically independent Dy^{III} center (thermal ellipsoids at 30% probability; crystallization water molecules are omitted for clarity).

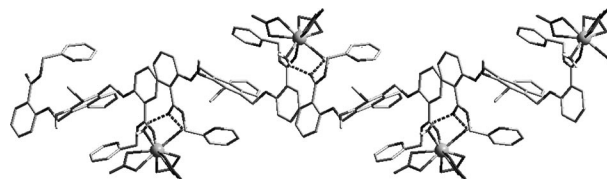


Figure 9. The 1D zigzag chain of the Dy^{III} complex self-assembled by hydrogen bonds between coordinated water and uncoordinated carbonyl oxygen atoms, which are indicated with dashed lines (viewed along the *a* axis; hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

Many lanthanide complexes based on the same ligand usually have similar building blocks due to similar valence shell electron configurations.^[35] However, polymers constructed from Pr^{III} to Gd^{III} and mononuclear Dy^{III} and Er^{III} complexes with the new ligand present different arrays. The only possible explanation for this change might be the templating effect resulting from the different lanthanide ions due to all the complexes crystallized under exactly the same conditions, such as solvent system, temperature, con-

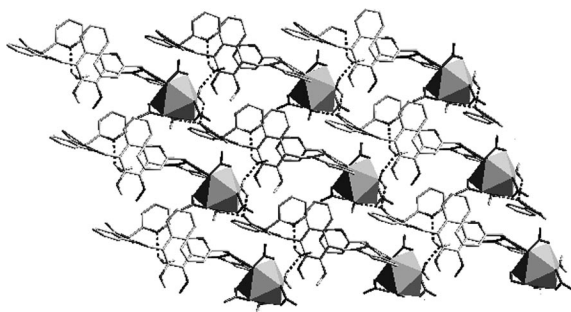


Figure 10. The 3D supramolecular structure of the Dy^{III} complex with methanol oxygen atoms as hydrogen-bond donors and acceptors, which are indicated with dashed lines (viewed along the b axis; hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

centration, and metal-to-ligand ratio. The ligand conformation in these coordination polymers extends due to the lanthanide contraction effect. These results not only imply that the similar metal ions could be separated via self-assembly reactions with appropriate organic ligands but illustrate the caution that one must take in extending the results obtained for one complex to the rest of the lanthanide series. As demonstrated above, complexes of lanthanide ions having the same ligand throughout the series may preserve the same atomic coordination, but need not be isomorphic.

Photophysical Properties of Ligand L and of the Complexes in the Solid State

Photophysical Properties of the Ligand

The investigated ligand presents two strong π - π^* absorptions at 251 and 290 nm, which are attributed to π - π^* ligand transitions centered on the pyridine and salicylamide group, respectively. The other relatively weak band centered at 325 nm can be assigned to the substituted naphthalene

group. Indeed, even though the band at 325 nm has the lowest intensity in the absorption spectrum, it has a high intensity in the excitation spectrum. Complexation with the lanthanide ion induces minor red shifts in the energy of the transitions and a small variation in their intensity (Figure 11 and Table 1). We note that molar absorption coefficients at the maximum of the ligand-centered band for these lanthanide complexes are large (ca. $15000 \text{ L mol}^{-1} \text{ cm}^{-1}$), a favorable condition for an efficient antenna effect.

It is well known that the energy transfer from ligand excited states to the resonance states of the Ln^{III} ion in the complexes can occur in different ways. The favored simplified mechanism involves ligand excitation by the absorption of ultraviolet energy to an excited singlet state, followed by energy migration via nonradiative intersystem crossing to a ligand triplet state [$E1 = E(\text{S1} - \text{T})$] and energy transfer from the triplet state to a resonance state of the Ln^{III} ion, from which the emission occurs [$E2 = E(\text{T}) - E$].^[36]

The ligand has multiple aromatic rings with a semi-rigid skeleton structure, so it is a strong fluorescence substance. Excited by the absorption band at 336 nm, the ligand displays two strong luminescence bands, one at 365 nm assigned to a $^1\pi\pi^*$ state, while the other at 456 nm, which is much weaker, corresponds to an emission from the $^3\pi\pi^*$ state. The ligand-centered luminescence in the Gd^{III} complex (Figure S5) basically displays the same features observed for the free ligand with the singlet band slightly blue-shifted (maximum around 362 nm), thus confirming the suitability of this ligand as a sensitizer for Eu^{III} and Tb^{III} luminescence. In order to both obtain additional information on excited states of the systems studied and to estimate the potential of their luminescent applications, the phosphorescence spectra of the gadolinium complex was also considered (Figure S6). The triplet state of the ligand, which is located at 21930 cm^{-1} is affected by complexation in the Gd^{III} complex and sustains a red shift (-1354 cm^{-1}) up to 20576 cm^{-1} at 77 K in methanol solution. Introduc-

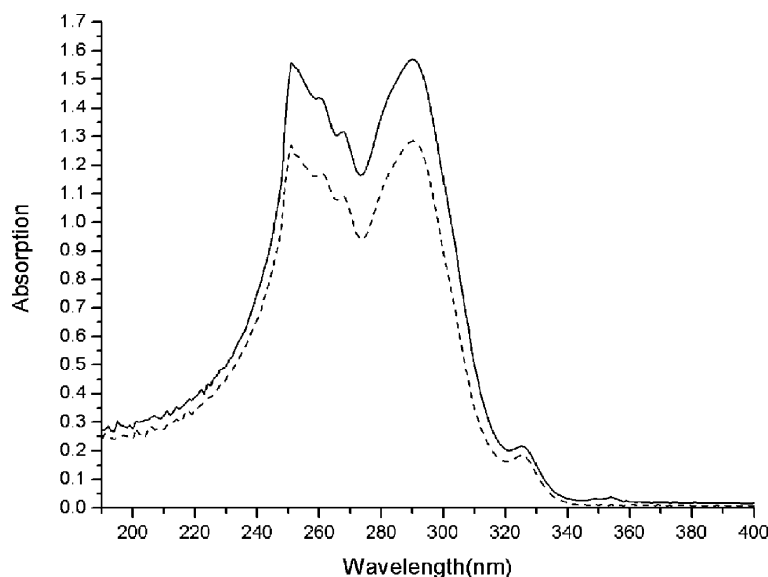
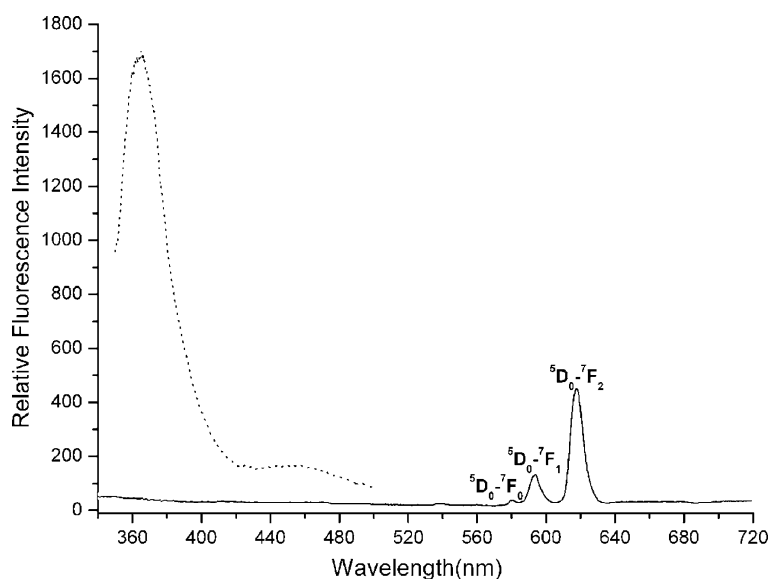


Figure 11. Absorption spectra of the ligand **L** (black dotted line) and its Eu^{III} complex (black solid line).

Table 1. Absorption in ethyl acetate solution (1×10^{-5} mol L $^{-1}$) and emission features in the solid state of L and its Sm^{III}, Eu^{III}, Tb^{III}, and Dy^{III} complexes.

	Absorption		Fluorescence		RFI [a.u.]	Φ (%)	
	$\lambda_{\max}$ [nm]	$\varepsilon \times 10^4$ [L mol $^{-1}$ cm $^{-1}$]	λ_{ex} [nm]	λ_{em} [nm]			
L	251	1.27	336	365	1700	–	–
	290	1.28		456	170.2		
	325	0.18					
[SmL(NO ₃) ₃ (CH ₃ OH)] _∞	251	1.55	325	564	20.35	–	6
	290	1.57		597	24.46		
	325	0.22					
[EuL(NO ₃) ₃ (H ₂ O)] _∞	252	1.49	325	581	38.33	0.23	243
	290	1.51		594	132.7		
	325	0.21		618	450.8		
[TbL(NO ₃) ₃ (H ₂ O)] _∞	251	1.50	325	492	438.4	0.14	428
	291	1.53		546	1216		
	324	0.19		585	76.10		
[DyL(NO ₃) ₃ (H ₂ O) ₂]·CH ₃ OH	251	1.47	325	621	13.49	–	25
	290	1.49		575	70.63		
	325	0.18					

Figure 12. Emission spectrum of L and its Eu^{III} complex in the solid state. Black dotted line: emission spectra of ligand at room temp., $\lambda_{\text{ex}} = 336$ nm; black solid line: emission spectra of the Eu complex at room temp., $\lambda_{\text{ex}} = 325$ nm, excitation and emission slit widths: 2.5 nm.

tion of the methoxyl group to the naphthalene backbone lowers the energy of the triplet state by about 3520 cm $^{-1}$.^[27] The relatively low energy of the triplet state of the ligand may be explained by the large delocalization of the π electrons upon methoxyl substitution. It does not appear that the terminal effect is a likely factor for the observed result, since measurements of the pyridine terminal and benzene terminal (20491 cm $^{-1}$) give a phosphorescence band in almost the same range. The triplet states are much too low in energy to act as sensitizers of the lowest energy excited state of Gd^{III} [$E(^6P_{7/2}) = 32000$ cm $^{-1}$]. The energy gap E_1 is relatively large (about 5467 cm $^{-1}$), which points to an effective intersystem crossing process. To estimate the luminescence efficiency for other lanthanide complexes the energy gap E_2 was also calculated on the basis of the values obtained. The E_2 values are ca. 3276, 2676, 76, and –524 cm $^{-1}$ for the

Sm^{III}, Eu^{III}, Tb^{III}, and Dy^{III} complexes, respectively. The value of 3276 cm $^{-1}$ is near to optimal for the high luminescence intensity of europium complexes according to the published data.^[37] The absence of any residual luminescence of excited ligand states for the Eu complex is evidence of the effective energy transfer from the excited ligand states to the Eu^{III} resonance levels and is in line with this estimation (Figure 12).

Luminescence Properties of the 1:1 Nitrato Complexes in the Solid State

In order to examine the ability of the ligand to act as an antenna group for sensitized luminescence from lanthanides, we measured the luminescence properties of four of

the complexes with **L** (Table 1). Excitation spectra of the lanthanide complexes in the solid state (Ln = Sm, Eu, Tb, or Dy) display only one ligand-centered band with a maximum at ca 30769 cm⁻¹, indicating that the L→Ln energy transfer goes through the triplet state and suggesting that the geometry of the ligand should be very similar regardless of the metal ion considered. The excellent agreement between the absorption and excitation spectra unequivocally shows that in all of the complexes studied the lanthanide ions are excited by ligand-metal intersystem energy transfer from the sensitized substituted naphthalene chromophore.

For the Eu^{III} ion, the energy transfer to the upper ⁵D_J levels (*J* = 1–3) seems to be most efficient when the ligand triplet state is approximately 500 cm⁻¹ more energetic than the specific acceptor level concerned, excitation energy is then transferred to the ⁵D₀ level, which is the predominant emitting state. The emission peaks of the Eu^{III} complex at 579, 592, and 619 nm can be assigned to ⁵D₀→⁷F_J (*J* = 0, 1, 2) transitions of the Eu^{III} ion, respectively, as shown in Figure 12. The intensity of the ⁵D₀→⁷F₀ transition is particularly large, pointing to a C_n (or C_{nv}) point group, which is validated by X-ray analysis of the Eu^{III} complex. Notably, the ⁵D₀→⁷F₂ transition is much more intense than the ⁵D₀→⁷F₁ transition, the intensity ratio of the Eu^{III} complex for $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ indicates the absence of an inversion center at the Eu^{III} site. This is also in agreement with the result of single-crystal X-ray analysis. No obvious emission bands from the ligands are observed, indicating that the ligands transfer the excitation energy efficiently to the Eu^{III} ion. The fluorescence quantum yield, Φ , of the europium nitrate complex in spectroscopic grade ethyl acetate (concentration: 1.0 × 10⁻⁵ mol L⁻¹) was found to be 0.23% with quinine sulfate as reference.^[38] The room-temperature solid-state phosphorescence lifetime of the sample was determined to be 243 μs. This lifetime is shorter than

that commonly observed for aromatic ligands with similar excited triplet-state levels suggesting that one or more non-radiative pathways assist in the deactivation of the excited state and shorten the observed lifetimes. It is known from X-ray structural data that **L** does not encapsulate the entire metal leaving one site ligated with water. Earlier work has established that a weak vibronic coupling between lanthanides and OH oscillators of coordinated water molecules provides a facile path for radiationless de-excitation of the metal ion.^[39] Thus, the lifetimes observed are expected to be shorter because of the direct coordination of water onto the lanthanide ion. It is important to note that the inter-layer π–π stacking interactions between the pyridyl rings and benzene rings of the ligands may favor the reduction of the energy of the π–π* transition to some extent and thus help the photoluminescence.^[40] On the other hand, a quenching mechanism through bonded water molecules and a low-lying charge-transfer state, from the low reduction potential of the Eu^{III} ion and the presence of the electron pairs of the aliphatic nitrogens, may account for the relatively low quantum yield. The direct observation of LMCT transitions in the absorption spectra of the Eu^{III} complex is not possible because of their much smaller extinction coefficients compared with those of the ligand-centered bands.

When Tb^{III} is introduced into the edifices, the luminescence spectra display a mixture of ligand-centred band emission and metal-centred line emissions (Figure 13). Two intense emission bands at 490 and 544 nm correspond to ⁵D₄→⁷F₆ and ⁵D₄→⁷F₅ transitions, respectively, while the weaker emission bands at 584 nm originate from ⁵D₄→⁷F₄ transitions and the typical emission band at 621 nm corresponds to ⁵D₄→⁷F₃ transitions. The ligand fluorescence remains relatively important and may be a result of the energy back transfer from the Tb^{III} ion to the ligand. A large in-

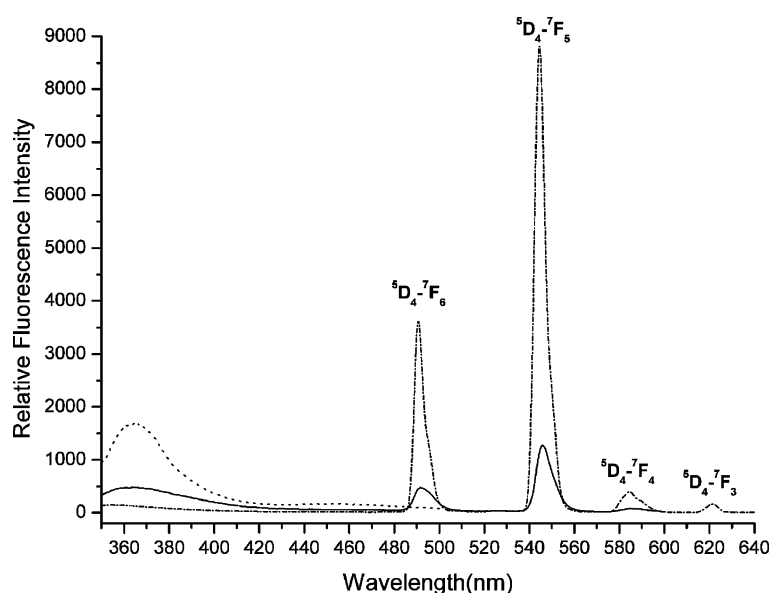


Figure 13. Emission spectrum of **L** and its Tb^{III} complex in the solid state. Dotted line: emission spectra of ligand at room temp.; solid line: emission spectra of the Tb complex at room temp.; short dash dotted line: emission spectra of the Tb complex at 77 K, λ_{ex} = 325 nm, excitation and emission slit widths: 2.5 nm.

crease in the luminescent intensity ratio between the Tb^{III} $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition and the ligand $^1\pi-\pi^*$ transition (from 2.68 to 58.8) is observed when the temperature is lowered to 77 K. This indicates that thermally activated back-energy transfer, which in particular is observed for the Tb^{III} complexes of the bipyridine-based ligands,^[41,42] is rather efficient in the Tb^{III} complex. This result is consistent with the work of Latva et al., who suggested that a fast and irreversible energy transfer to the Tb^{III} ion occurs when an energy gap, $E_2 [E(\text{T}) - E(^5\text{D}_4)]$, is greater than 1850 cm^{-1} .^[42] In the Tb^{III} complex, this energy gap, measured as usual from the ligand phosphorescence spectrum of the Gd^{III} complex [$E(\text{T}) = 20576 \text{ cm}^{-1}$], is estimated to

be 76 cm^{-1} and, consequently, is greatly lower than the threshold value. No transition corresponding to the proper Tb^{III} absorption levels, especially those located at 485 nm and between 340 and 380 nm, is observable in the excitation spectra. This unequivocally shows that an energy transfer process from the substituted naphthalene chromophore to the metal ion is the only photophysical pathway leading to observable luminescence in the sample. The fluorescence quantum yield, Φ , of the terbium nitrate complex in spectroscopic grade ethyl acetate (concentration: $1.0 \times 10^{-5} \text{ mol L}^{-1}$) was found to be 0.14% with eosin as the reference^[43] at room temperature. The room-temperature phosphorescence lifetime of the terbium complex was deter-

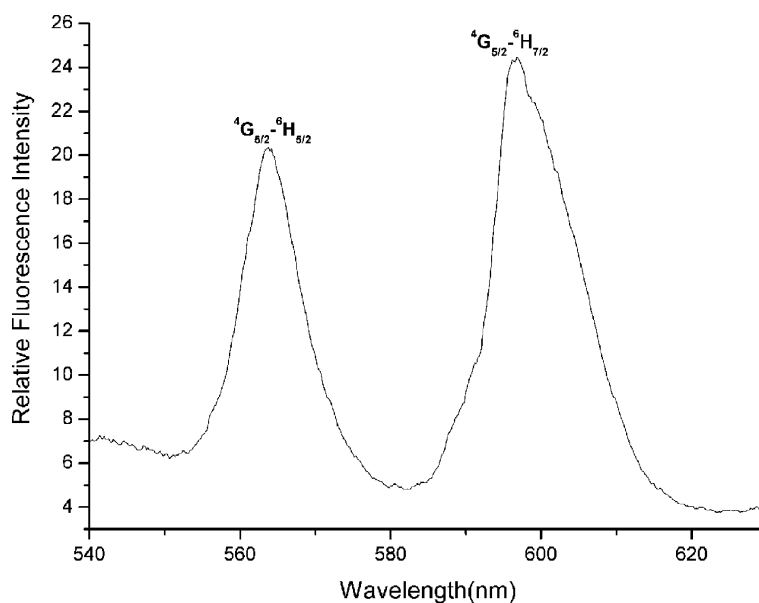


Figure 14. Emission spectrum of the Sm^{III} complex in the solid state at room temp.; $\lambda_{\text{ex}} = 325 \text{ nm}$, excitation and emission slit widths: 2.5 nm.

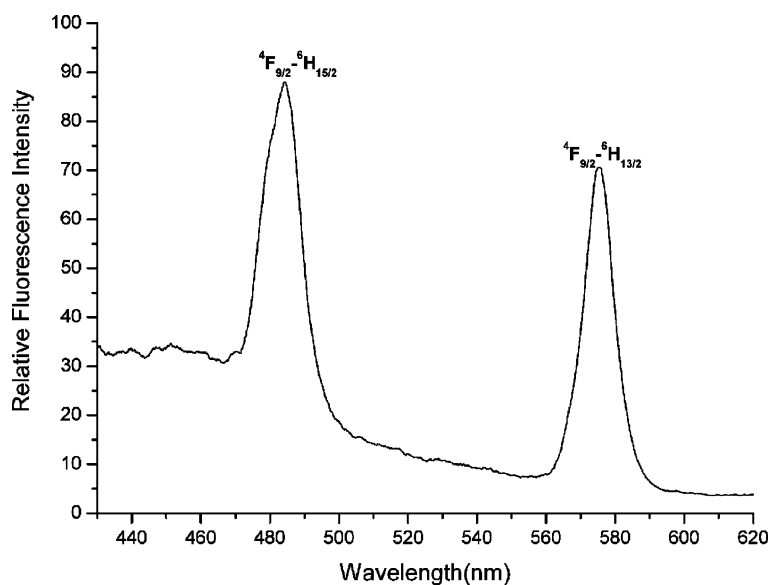


Figure 15. Emission spectrum of the Dy^{III} complex in the solid state at room temp.; $\lambda_{\text{ex}} = 325 \text{ nm}$, excitation and emission slit widths: 2.5 nm.

mined to be 428 μ s. The moderate quantum yield and lifetime may be tentatively attributed to a poor energy match between the donating level of the ligand and the accepting level of the Tb^{III} ion and the high-energy vibrational modes of one coordinated water molecule on quenching the excited state.

In order to demonstrate the capability of antenna-modified ligands as sensitizers for lanthanides other than the commonly used europium and terbium, we extended our work to Sm^{III} and Dy^{III}. The excitation spectra registered at the maximum of the Sm^{III} or Dy^{III} emissions are in line with previous observations for the europium and terbium complexes. Upon excitation at $\lambda_{\text{ex}} = 325$ nm, typical emission spectra of Sm and Dy were detected (Figures 14 and 15). In the case of Sm^{III}, this corresponds to emission lines at 564 and 597 nm, which are assigned to $^4G_{5/2} \rightarrow ^6H_J$ transitions, with $J = 5/2$ and $7/2$, respectively. The relatively strong peak is the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition at 597 nm. The emission spectrum of Dy is composed of two intense lines at 484 and 577 nm, corresponding to $^4F_{9/2} \rightarrow ^6H_J$ transitions with $J = 15/2$ and $13/2$, respectively. Generally, the luminescence spectra of Sm^{III} and Dy^{III} were quite weak. Quantum yields are expected to be very small and their measurements were therefore omitted. The higher sensitivity of samarium- and dysprosium-derived luminescence, in comparison with europium or terbium luminescence, can be explained by the energy gap between the excited luminescent states and the highest J levels of the ground states of these lanthanides. This energy gap is about 7500 cm^{-1} for Sm^{III} and 7800 cm^{-1} for Dy^{III}, that is, considerably smaller than that for Eu^{III} and Tb^{III} ions with values around 12300 cm^{-1} and 14800 cm^{-1} , respectively.^[44] Since OH oscillators act independently ($E_{\text{vib}} = 3657$ cm^{-1} ; symmetric OH stretching mode),^[45] it can be estimated that, in the case of samarium and dysprosium, fewer water molecules are needed to bridge the gap than is the case for europium and terbium (ca. 2 vs. 3–4). Lifetime measurements for both the Sm and Dy complexes are found to be 6 and 25 μ s, respectively, based on a single-exponential fit of the data. This higher water sensitivity explains why lifetimes of Dy^{III} or Sm^{III} luminescence are generally much shorter than those observed with Eu^{III} or Tb^{III}.

Conclusions

We have demonstrated here that the new bidentate naphthalene-bridged space ligand is a useful building block in the construction of polymeric and discrete lanthanide complexes. It is interesting to note that the two salicylamide arms of **L** are somewhat flexible and rotational around the naphthalene group in order to meet the geometrical preference of the metal centers and the structural variation may be a result of the different coordination features of the lanthanide ions. In the structures of the Pr^{III} to Gd^{III} complexes, **L** acts as a di-monodentate bridging ligand to connect two metal ions, but acts as a monodentate ligand in the complexes of Dy^{III} and Er^{III}. Hydrogen-bonding pathways

made possible by the amide functional group as well as the pyridyl group of the ligand are also significant structure directing factors. The introduction of the methoxyl substituents on the naphthalene backbone lowers the triplet energy by about 3520 cm^{-1} , leading to a better match with the acceptor 5D_0 state of the europium ion than the 5D_4 state of terbium. It is worth noting that we first observed the back-energy transfer phenomenon in the Tb^{III} complex of salicylamide derivatives. The behavior of the Eu and Tb complexes, which is very different from the literature data for similar compounds, shows that the physical properties of the lanthanide edifices may be easily tuned by changing the nature of the backbone properties.^[25–27] In conclusion, this work not only demonstrates that the supramolecular structure of lanthanide complexes with a naphthalene-derived chromophore featuring salicylamide pendant arms can be tuned by the nature of metal ions, but also offers interesting perspectives for the development of efficient luminescent stains.

Experimental Section

Synthesis and Characterizations: Solvents and chemicals were used without further purification. Acetone was treated with K_2CO_3 and distilled prior to use. Lanthanide nitrate was prepared from the oxides (99.99%) and nitric acid.^[46] 1,4-Bis(bromomethyl)-2,3-dimethoxynaphthalene and picolylsalicylamide were synthesized as described previously.^[29,30] Ligand **L** was prepared using the method similar to that used by Zhao et al.^[27] with 1,4-Bis(bromomethyl)-2,3-dimethoxynaphthalene instead of 1,4-Bis(chloromethyl)-naphthalene and picolylsalicylamide instead of benzylsalicylamide. Yield 1.042 g (78%); m.p. 161.7 °C. ^1H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 3.89$ (s, 6 H), 4.43 (d, $J = 5.4$ Hz, 4 H, NHCH_2), 5.68 (s, 4 H, OCH_2), 6.91 (d, $J = 9.9$ Hz, 4 H, Ar), 7.15 (t, 2 H, Ar), 7.24–7.56 (m, 8 H, Ar), 7.99–8.02 (m, 4 H, Ar), 8.25–8.27 (m, 2 H, Ar), 8.55 (t, 2 H, NH) ppm. IR (KBr, $\tilde{\nu}$): $\tilde{\nu} = 3415$ (s, NH), 1657 (s, C=O), 1597 (m), 1537 (m), 1469 (m), 1298 (m), 1220 (s), 991 (s), 755 (s) cm^{-1} . Analytical data **L** (668.3): calcd. C 71.84, H 5.43, N 8.38; found C 71.69, H 5.45, N 8.42. ES: $m/z = 669.3$ [$\text{M} + \text{H}$].

Complexes: A solution of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{and Er}$) (0.1 mmol) in a minimum amount of ethyl acetate was added dropwise to a solution of ligand **L** (0.1 mmol) in a minimum amount of ethyl acetate. The mixture was stirred at room temperature for 4 h. Methanol (1 cm^3) was then added and the solution was filtered. Upon standing the filtrate at room temperature for several weeks, $\{\text{PrL}(\text{NO}_3)_3(\text{H}_2\text{O})\text{CH}_3\text{OH}\} \cdot 3/2\text{H}_2\text{O}\}_\infty$, $\{\text{NdL}(\text{NO}_3)_3(\text{H}_2\text{O})\text{CH}_3\text{OH}\} \cdot 1/2\text{CH}_3\text{OH}\}_\infty$, $\{\text{SmL}(\text{NO}_3)_3(\text{CH}_3\text{OH})\}_\infty$, $\{\text{EuL}(\text{NO}_3)_3(\text{H}_2\text{O})\}_\infty$, $\{\text{GdL}(\text{NO}_3)_3(\text{H}_2\text{O})\}_\infty$, $\{\text{DyL}(\text{NO}_3)_3(\text{H}_2\text{O})_2\} \cdot \text{CH}_3\text{OH}$, and $\{\text{ErL}(\text{NO}_3)_3(\text{H}_2\text{O})_2\} \cdot \text{CH}_3\text{OH}$ were obtained in 32–58% yield (based on Ln). The elemental analyses showed that the metal complexes obtained are composed of a 1:1 ratio of Ln to ligand. This ratio was later unequivocally confirmed by X-ray crystallographic analyses. Data for $\{\text{PrL}(\text{NO}_3)_3(\text{H}_2\text{O})\text{CH}_3\text{OH}\} \cdot 3/2\text{H}_2\text{O}\}_\infty$, $\text{C}_{41}\text{H}_{45}\text{N}_7\text{O}_{18.5}\text{Pr}$ (1072): calcd. C 45.91, H 4.23, N 9.14, Pr 13.14; found C 45.72, H 4.21, N 9.17, Pr 13.08. IR (KBr): $\tilde{\nu} = 3378$ (br. s), 2924 (w), 1611 (s, C=O), 1562 (m), 1457 (m), 1309 (s), 1226 (m), 1110 (m), 1028 (m), 755 (m) cm^{-1} . Data for $\{\text{NdL}(\text{NO}_3)_3(\text{H}_2\text{O})\text{CH}_3\text{OH}\} \cdot 1/2\text{CH}_3\text{OH}\}_\infty$, $\text{C}_{41.50}\text{H}_{44}\text{N}_7\text{NdO}_{17.50}$ (1063): calcd. C 46.80, H 4.16, N 9.21, Nd 13.54; found C 46.57, H 4.15, N 9.25, Nd 13.48. IR (KBr): $\tilde{\nu} = 3352$ (br. s), 2928 (m), 1613 (s, C=O),

1564 (m), 1456 (m), 1307 (s), 755 (w) cm^{-1} . Data for $[\text{SmL}(\text{NO}_3)_3 \cdot (\text{CH}_3\text{OH})_\infty]$, $\text{C}_{41}\text{H}_{40}\text{N}_7\text{O}_{16}\text{Sm}$ (1037): calcd. C 47.48, H 3.89, N 9.45, Sm 14.50; found C 47.59, H 3.90, N 9.43, Sm 14.43. IR (KBr): $\tilde{\nu}$ = 3348 (br. s), 2922 (m), 1611 (s, C=O), 1452 (m), 1308 (s), 1222 (m), 1110 (m), 1038 (m), 752 (w) cm^{-1} . Data for $[\text{EuL}(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_\infty]$, $\text{C}_{40}\text{H}_{38}\text{EuN}_7\text{O}_{16}$ (1025): calcd. C 46.88, H 3.74, Eu 14.83, N 9.57; found C 47.06, H 3.71, Eu 14.77, N 9.53. IR (KBr): $\tilde{\nu}$ = 3422 (br. s), 2922 (w), 1611 (s, C=O), 1457 (m), 1304 (s), 1222 (m), 752 (w) cm^{-1} . Data for $[\text{GdL}(\text{NO}_3)_3(\text{H}_2\text{O})_\infty]$, $\text{C}_{40}\text{H}_{38}\text{GdN}_7\text{O}_{16}$ (1030): calcd. C 46.64, H 3.72, Gd 15.27, N 9.52; found C 46.42, H 3.71, Gd 15.21, N 9.48. IR (KBr): $\tilde{\nu}$ = 3350 (br. s), 2928 (m), 1611 (s, C=O), 1480 (m), 1294 (s), 1227 (m), 754 (w) cm^{-1} . Data for $[\text{TbL}(\text{NO}_3)_3(\text{H}_2\text{O})_\infty]$, $\text{C}_{40}\text{H}_{38}\text{N}_7\text{O}_{16}\text{Tb}$ (1032): C 46.57, H 3.71, N 9.50, Tb 15.40; found C 46.38, H 3.69, N 9.46, Tb 15.34. IR (KBr): $\tilde{\nu}$ = 3378 (br. s), 2927 (m), 1611 (s, C=O), 1452 (m), 1308 (s), 1221 (m), 752 (w) cm^{-1} . Data for $[\text{DyL}(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot \text{CH}_3\text{OH}$, $\text{C}_{41}\text{H}_{44}\text{DyN}_7\text{O}_{18}$ (1085): C 45.37, H 4.09, Dy 14.97, N 9.03; found C 45.59, H 4.07, Dy 14.92, N 9.07. IR (KBr): $\tilde{\nu}$ = 3348 (br. s), 2922 (m), 1610 (s, C=O), 1452 (m), 1308 (s), 1222 (m), 1035 (m), 752 (w) cm^{-1} . Data for $[\text{ErL}(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot \text{CH}_3\text{OH}$, $\text{C}_{41}\text{H}_{44}\text{ErN}_7\text{O}_{18}$ (1090): C 45.18, H 4.07, Er 15.34, N 8.99; found C 45.27, H 4.08, Er 15.28, N 9.02. IR (KBr): $\tilde{\nu}$ = 3408 (br. s), 2926 (m), 1610 (s, C=O), 1458 (m), 1224 (m), 1036 (m), 752 (w) cm^{-1} .

Physical Measurements: The metal ions were determined by EDTA titrations using Xylenol Orange as the indicator. C,H,N elemental analyses were performed with an Elementar Vario EL. Melting points were determined with a Kofler apparatus. IR spectra were recorded with a Nicolet FT-170SX instrument using KBr discs in the 400–4000 cm^{-1} region. ^1H NMR spectra were measured with a Varian Mercury plus 300B spectrometer in CDCl_3 solution with TMS as the internal standard. The electronic spectra were recorded with a RF-540 spectrophotometer in an ethyl acetate solution. Fluorescence measurements were made with a Hitachi F-4500 spectrophotometer and a shimadzu RF-540 spectrofluorophotometer equipped with quartz cuvettes of 1 cm path length. An excitation slit of 2.5 nm and an emission slit of 2.5 nm were used for the measurements in the solid state. The 77 K solid-state emission spectra were recorded with solid samples loaded into a quartz tube inside a quartz-walled optical Dewar flask filled with liquid nitrogen. The 77 K solution-state phosphorescence spectra were recorded with solution samples loaded into a quartz tube inside a quartz-walled optical Dewar flask filled with liquid nitrogen in the phosphorescence mode.

X-Ray Crystallographic Analysis of the Complex: A single crystal suitable for detection was selected and subsequently glued to the tip of a glass fiber. The determination of the crystal structure at 25 °C was carried out with an X-ray diffractometer (Bruker Smart-1000 CCD) using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and included in the final cycles of refinement using a riding model. The programs used for structure solution and refinement were SHELXS-97 and SHELXL-97, respectively. The crystallographic data and details of the structure refinement for the complexes are listed in Table S1.

CCDC-662759 (for $[\text{PrL}(\text{NO}_3)_3(\text{H}_2\text{O})\text{CH}_3\text{OH}] \cdot 3/2\text{H}_2\text{O}$), -662760 (for $[\text{NdL}(\text{NO}_3)_3(\text{H}_2\text{O})\text{CH}_3\text{OH}] \cdot 1/2\text{CH}_3\text{OH}$), -669035 (for $[\text{SmL}(\text{NO}_3)_3(\text{CH}_3\text{OH})_\infty]$), -662761 (for $[\text{EuL}(\text{NO}_3)_3(\text{H}_2\text{O})_\infty]$), -662764 (for $[\text{GdL}(\text{NO}_3)_3(\text{H}_2\text{O})_\infty]$), -662762 (for $[\text{DyL}(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot \text{CH}_3\text{OH}$), and -662763 (for $[\text{ErL}(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot \text{CH}_3\text{OH}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystal data and structure refinement, the view of the 1D chain of the Eu^{III} complex, the 3D supramolecular structure of the Eu^{III} complex showing π – π stacking interactions, the 3D supramolecular structure of the Gd^{III} complex, a space-filling diagram of the nanosized holes in the Gd^{III} complex constructed by intermolecular hydrogen bonds, fluorescence of the Gd complex at room temperature and phosphorescence spectra of the Gd complex at 77 K (Table S1, Figures S1–S6, see also the footnote on the first page of this article).

Acknowledgments

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