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# Lanthanide(III) Complexes of Bis-semicarbazone and Bis-imine-Substituted Phenanthroline Ligands: Solid-State Structures, Photophysical Properties, and Anion Sensing

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*Dedicated to Professor Kenneth N. Raymond on the occasion of his 70th birthday*

**Abstract:** Phenanthroline-based hexadentate ligands  $L^1$  and  $L^2$  bearing two achiral semicarbazone or two chiral imine moieties as well as the respective mononuclear complexes incorporating various lanthanide ions, such as  $La^{III}$ ,  $Eu^{III}$ ,  $Tb^{III}$ ,  $Lu^{III}$ , and  $Y^{III}$  metal ions, were synthesized, and the crystal structures of  $[ML^1Cl_3]$  ( $M = La^{III}$ ,  $Eu^{III}$ ,  $Tb^{III}$ ,  $Lu^{III}$ , or  $Y^{III}$ ) complexes were determined. Solvent or water molecules act as coligands for the rare-earth metals in addition to halide anions. The big  $Ln^{III}$  ion exhibits a coordination number (CN) of 10, whereas the corre-

sponding  $Eu^{III}$ ,  $Tb^{III}$ ,  $Lu^{III}$ , and  $Y^{III}$  centers with smaller ionic radii show CN = 9. Complexes of  $L^2$ , namely  $[ML^2Cl_3]$  ( $M = Eu^{III}$ ,  $Tb^{III}$ ,  $Lu^{III}$ , or  $Y^{III}$ ) ions could also be prepared. Only the complex of  $Eu^{III}$  showed red luminescence, whereas all the others were nonluminescent. The emission properties of the Eu derivative can be applied as a photophysical signal for sensing various

anions. The addition of phosphate anions leads to a unique change in the luminescence behavior. As a case study, the quenching behavior of adenosine-5'-triphosphate (ATP) was investigated at physiological pH value in an aqueous solvent. A specificity of the sensor for ATP relative to adenosine-5'-diphosphate (ADP) and adenosine-5'-monophosphate (AMP) was found.  $^{31}P$  NMR spectroscopic studies revealed the formation of a  $[EuL^2(ATP)]$  coordination species.

**Keywords:** chirality • crystal structures • lanthanides • phosphate ions • sensors

## Introduction

Lanthanide complexes have gained significant importance over recent decades due to their potential photophysical,<sup>[1]</sup> magnetic,<sup>[2]</sup> and redox properties.<sup>[3–8]</sup> As new materials, they are valuable building blocks for light-emitting devices<sup>[9]</sup> or as contrasting agents<sup>[10]</sup> in medicinal diagnostics. In particular, their molecular-sensing properties<sup>[11]</sup> make them highly attractive with promising applications in bioanalytical chemistry. With this interest, the coordination chemistry of a series of semicarbazone-based tetradentate<sup>[12]</sup> and pentaden-

tate ligands<sup>[13]</sup> and their corresponding transition-metal<sup>[14–15]</sup> and lanthanide(III) complexes have been studied extensively. Furthermore, the search for new chelators with enhanced stability and higher donor numbers are considered to have paramount importance for the formation of coordination complexes of lanthanides for new applications. In this context, the hexadentate ligand  $L^1$  developed by Palenik and co-workers<sup>[16]</sup> has been already reported as a chelator for thorium(III)<sup>[16]</sup> and cerium(III).<sup>[17]</sup> On the basis of our related earlier studies with pentadentate pyridine bis-semicarbazone ligand A (Scheme 1), we were interested in investigating  $L^1$  as a platform for the coordination of lanthanide(III) ions. A novel related ligand  $L^2$ , with L-valinamide bound as an imine group, and the respective lanthanide complexes were synthesized. The aim was to obtain complexes with a helical structure of the organic ligand that wraps electronically ("Lewis acidic") and geometrically unsaturated metal centers.

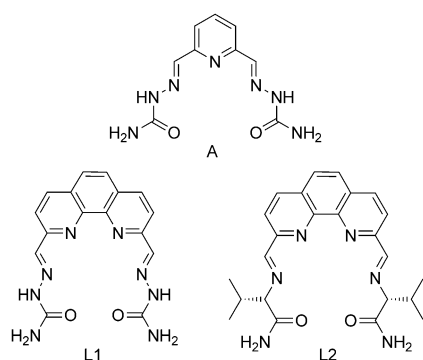
In the recent decade, studies on the recognition, detection, and extraction of anions<sup>[18]</sup> has gained great interest among researchers. Motivation behind such anion-recognition studies lies in an immense amount of implications in biology,<sup>[19]</sup> medicine,<sup>[20]</sup> catalysis,<sup>[21]</sup> molecular assembly, and host-guest chemistry.<sup>[22]</sup> Among the anions, the phosphate ion possesses a unique importance as a major component of our genes.<sup>[23]</sup> It plays a pivotal role in various physiological

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Scheme 1. The pentadentate ligand A and hexadentate ligands  $L^1$  and  $L^2$  discussed in this study.

events.<sup>[24,25]</sup> As an example, the ATP is cleaved into AMP, ADP, and pyrophosphate and acts as an universal energy source.<sup>[26,27]</sup> ATP deficiency causes ischemia, Parkinson's disease, and hyphoglycaemia.<sup>[28]</sup> Consequently, the sensing of phosphate ions is important and much effort has been devoted to the development of luminescent molecular probes. For this purpose, chromogenic<sup>[29]</sup> and fluorogenic<sup>[30]</sup> receptors are considered to be powerful monitoring tools, and several fluorescent chemosensors have been reported. In this respect, lanthanide complexes<sup>[31]</sup> have been investigated for their well-defined and intense luminescence. Reports on the detection of phosphate ions in aqueous media is rare.<sup>[32]</sup> Through our aim of searching for new fluorometric sensors that can detect phosphate anions in aqueous solution at neutral pH with high sensitivity and selectivity, a series of lanthanide complexes of  $L^1$  and  $L^2$  were synthesized and were investigated for their fluorescent properties. Interestingly  $[\text{Eu}L^2\text{Cl}_3]$  was the only complex obtained as strong red-emitting luminescent material, all the other complexes were non-luminescent. Consequently, the luminescent europium complex was tested as a sensor for anions.

## Results and Discussion

The bis-semicarbazone  $L^1$  and the bis-imine  $L^2$  ligands were synthesized as chelators for lanthanide(III) ions (Scheme 1). Ligand  $L^1$  was obtained by simple imine condensation<sup>[14–17]</sup> of phenanthroline dialdehyde and semicarbazide, and ligand  $L^2$  with the imine-connected L-valinamide moiety was obtained by following the synthetic procedure described in the Experimental Section. Both ligands were thoroughly characterized.

Upon treating  $L^1$  or  $L^2$  with  $\text{LnCl}_3$  in a 1:1 ratio, the respective mononuclear complexes  $[\text{La}L^1\text{Cl}_3]$ ,  $[\text{Eu}L^1\text{Cl}_3]$ ,  $[\text{Tb}L^1\text{Cl}_3]$ ,  $[\text{Lu}L^1\text{Cl}_3]$ ,  $[\text{Y}L^1\text{Cl}_3]$ ,  $[\text{Eu}L^2\text{Cl}_3]$ ,  $[\text{Tb}L^2\text{Cl}_3]$ ,  $[\text{Lu}L^2\text{Cl}_3]$ , and  $[\text{Y}L^2\text{Cl}_3]$  were obtained under dilute conditions from methanol at elevated temperature. All the  $[\text{ML}^1\text{Cl}_3]$  complexes ( $\text{M}=\text{La}^{\text{III}}$ ,  $\text{Eu}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$ ,  $\text{Lu}^{\text{III}}$ , and  $\text{Y}^{\text{III}}$ ) are highly soluble in DMSO and DMF, whereas they are sparingly or insoluble in other solvents such as methanol or

acetonitrile. Complexes  $[\text{ML}^2\text{Cl}_3]$  are soluble in a broad variety of different solvents, including water. Although we were successful in obtaining crystals for the  $L^1$  complexes, our repeated attempts failed in the case of the  $L^2$  complexes.

The  $^1\text{H}$  NMR spectra of ligand  $L^1$  in  $[\text{D}_6]\text{DMSO}$  and of complexes  $[\text{ML}^1\text{Cl}_3]$  in  $[\text{D}_7]\text{DMF}$  depict sharp resonances (Figure 1), with the exception of complex  $[\text{Tb}L^1\text{Cl}_3]$ , which showed paramagnetic shifting and line broadening. Due to its low solubility,  $L^1$  can only be recorded in  $[\text{D}_6]\text{DMSO}$ . IR and NMR spectroscopic, mass-spectrometric, and elemental analysis revealed the formation of 1:1-type ligand/lanthanide(III) ion complexes.

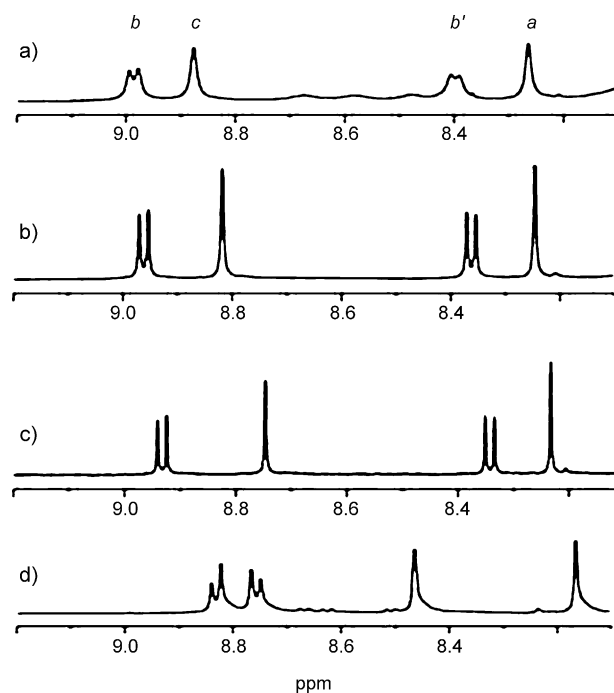


Figure 1.  $^1\text{H}$  NMR spectra of complexes a)  $[\text{Lu}L^1\text{Cl}_3]$ , b)  $[\text{Y}L^1\text{Cl}_3]$ , and c)  $[\text{La}L^1\text{Cl}_3]$  in  $[\text{D}_7]\text{DMF}$  and d) ligand  $L^1$  in  $[\text{D}_6]\text{DMSO}$  ( $L^1$  is insoluble in DMF).

**Structure of complexes of  $L^1$ :** X-ray quality crystals of  $[\text{Ln}L^1\text{Cl}_3]$  for complexes “ $[\text{La}L^1]$ ”, “ $[\text{Tb}L^1]$ ”, “ $[\text{Lu}L^1]$ ”, and “ $[\text{Y}L^1]$ ” were obtained from DMSO/DMF upon diffusion of diethyl ether. Complex  $[\text{Eu}L^1]$  was obtained from aqueous methanol. Ligand  $L^1$  acts as a hexadentate platform and wraps the central lanthanide metal ion. In addition to chloride ions, solvent molecules such as DMSO, DMF, or water acted as coligands, depending on the solvent of crystallization. Chloride anions dissociate and open-up space for the coordination of the solvent molecules on both sides of the ligand platform. The europium(III) complex with  $L^1$  exhibited coordination of water molecules, whereas the other complexes were crystallized from nonaqueous solvents such as DMF or DMSO. The obtained crystal structures are almost isostructural.

In the lanthanum(III) and yttrium(III) complexes, ligand  $L^1$  behaves as a hexadentate ligand that encapsulates the respective metal ion in its cleft (Figure 2). However, due to

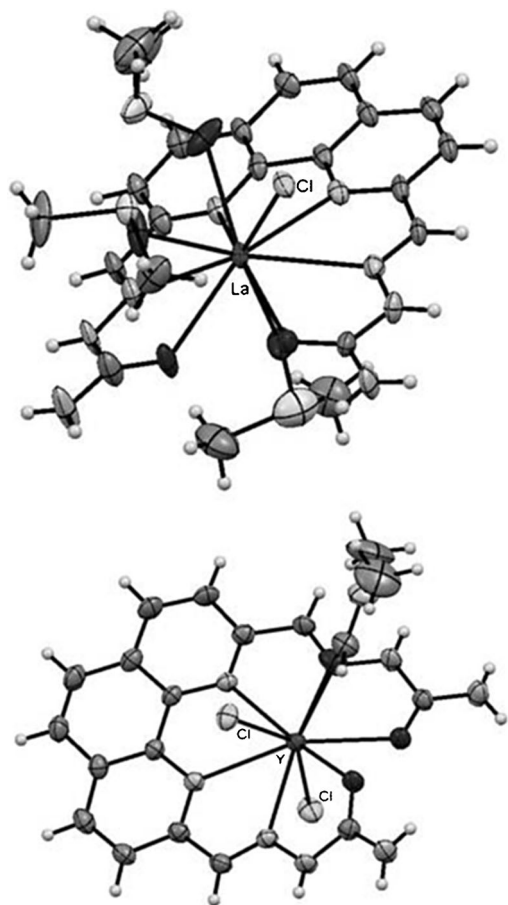


Figure 2. ORTEP diagrams of the ions  $[LaL^1Cl(dmsO)_3]^{2+}$  (top) and  $[YL^1(dmf)Cl_2]^+$  (bottom).

the different sizes of the metal ions, additional coordination sites for coligands are available. In case of the lanthanum(III) complex, one chloride ion and two DMSO molecules are bound to the metal center from the upper side, an additional DMSO molecule coordinates from below, thus resulting in a coordination number of 10. Thus, a salt of the dication  $[LaL^1Cl(dmsO)_3]^{2+}$  is present in the crystal. This dication dimerises in the solid by intermolecular hydrogen bonding between the semicarbazone units (Figure 3). In case of the yttrium(III) complex, less space is available at the metal center (Figure 2). Two chloride ions are bound from opposite sides of the ligand platform in addition to one DMF molecule, thus resulting in CN=9. In the europium(III) complex, ligand  $L^1$  wraps around the metal center in a hexadentate fashion, two water molecules coordinate from one side, and another water molecule from the other side of the ligand, thus leading to CN=9. All three chloride anions are dissociated and are located outside the coordination sphere of the metal. Thus, the  $[EuL^1(H_2O)_3]^{3+}$  ion is present as a

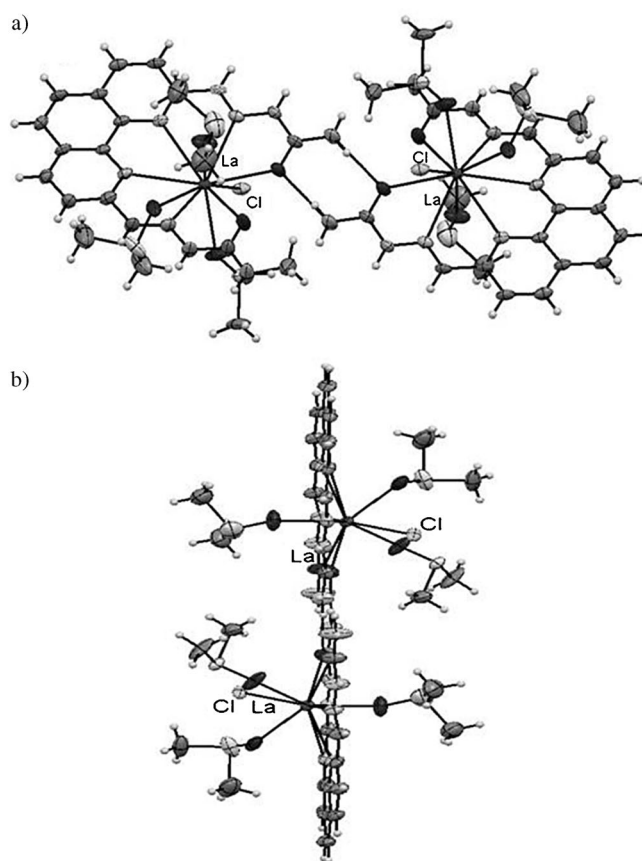


Figure 3. Intermolecular  $NH\cdots O$ -mediated dimer of  $[LaL^1Cl(dmsO)_3]^{2+}$ : a) top and b) side views.

trication (Figure 4). The terbium(III) and lutetium(III) complexes (Figures 5 and 6, respectively) were crystallized from DMF, and similar binding to the yttrium derivative, in which chloride ions bind from opposite sides and one DMF molecule is observed.

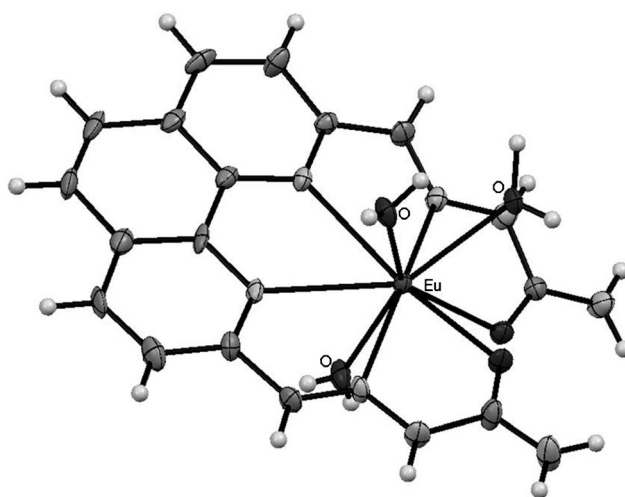


Figure 4. ORTEP diagram of complex ion  $[EuL^1(H_2O)_3]^{3+}$  crystallized from methanol. (The lattice solvent molecules and anions have been removed for clarity.)

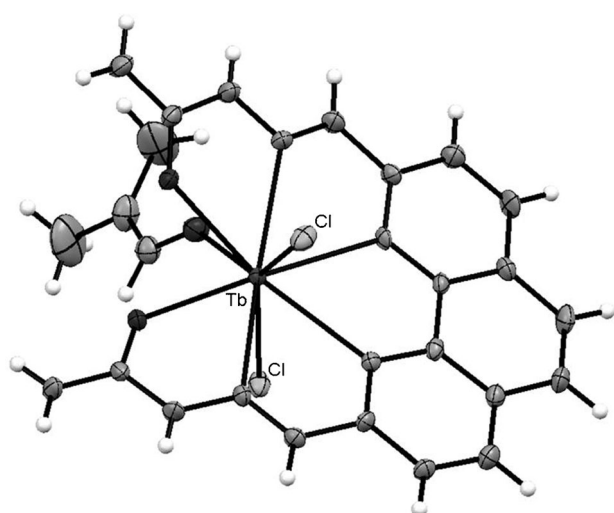


Figure 5. ORTEP diagram of  $[\text{TbL}^1(\text{dmf})\text{Cl}_2]^+$ . (The lattice DMF molecule and  $\text{Cl}^-$  ions have been removed for clarity.)

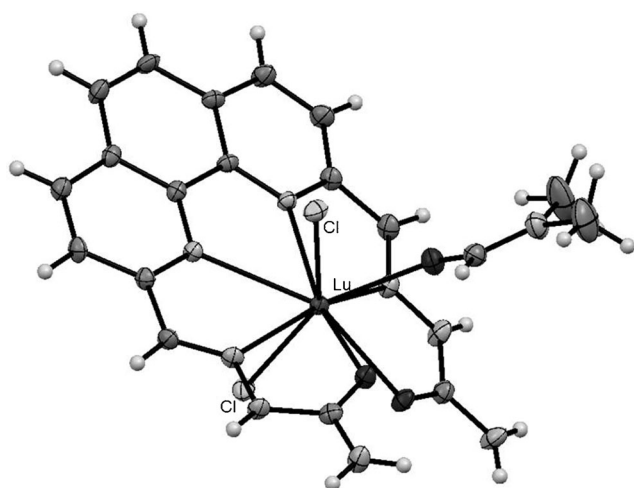


Figure 6. ORTEP diagram of complex ion  $[\text{LuL}^1(\text{dmf})\text{Cl}_2]^+$ . (The DMF molecule and noncoordinated  $\text{Cl}^-$  ions have been removed.)

Selected structural parameters derived from the crystal structures of complexes of  $\text{L}^1$  are depicted in Table 1. Relative to the corresponding reported values for pyridine-based pentadentate ligand  $\text{A}$ ,<sup>[13,14]</sup> the present hexadentate  $\text{L}^1$  provides a larger space to accommodate a range of large metal ions. Assuming that the  $\text{N}_{\text{aza}} \cdots \text{N}_{\text{aza}}$  distance is a measure of the cavity provided by the ligand for metal encapsulation, this distance is longer for the large lanthanum(III) ion and shortest for the lutetium(III) complex (5.33 and 5.09 Å, respectively). This outcome illustrates that the ligand  $\text{L}^1$  has the flexibility to adjust to metal ions with different sizes.

Due to different levels of dissociation in the tricationic  $[\text{EuL}^1(\text{H}_2\text{O})_3]^{3+}$ , dicationic  $[\text{LaL}^1(\text{dmsO})_3\text{Cl}]^{2+}$ , and monocationic  $[\text{YL}^1\text{Cl}_2(\text{dmsO})]^+$ ,  $[\text{TbL}^1\text{Cl}_2(\text{dmsO})]^+$ , and  $[\text{LuCl}_2(\text{dmsO})]^+$  complex ions in the solid state, the degree of dissociation was studied in solution. Accordingly, molar conductance values were 80.52, 100.3, 84.03, 75.03, and 82.83S

Table 1. Comparison of selected structural parameters of  $\text{Ln}^{\text{III}}$  complexes of  $\text{L}^1$  with different coligands (i.e., DMSO, DMF, and chloride).

	$[\text{LaL}^1]$	$[\text{EuL}^1]$	$[\text{TbL}^1]$	$[\text{LuL}^1]$	$[\text{YL}^1]$
$\text{N}^{\text{Py}}-\text{M}^{[\text{a}]}$	2.915(7)	2.647(5)	2.659(4)	2.617(3)	2.649(3)
	2.871(6)	2.670(5)	2.618(4)	2.575(3)	2.612(3)
$\text{N}-\text{M}^{[\text{a}]}$	2.775(7)	2.614(5)	2.638(4)	2.608(3)	2.623(3)
	2.785(7)	2.635(5)	2.610(4)	2.660(3)	2.595(3)
$\text{O}_2-\text{M}^{[\text{a}]}$	2.672(6)	2.381(5)	2.544(3)	2.536(2)	2.541(2)
		2.406(6)	2.377(3)	2.330(2)	2.357(2)
$\text{Cl}-\text{M}^{[\text{a}]}$	2.898(2)	— <sup>[b]</sup>	2.665(1)	2.663(1)	2.646(1)
			2.721(1)	2.598(9)	2.704(1)
$\text{N}_{\text{Aza}} \cdots \text{N}_{\text{Aza}}^{[\text{a}]}$	5.33(1)	5.161(8)	5.182(6)	5.091(4)	5.147(4)
$\text{N}^{\text{Py}}-\text{M}-\text{O}^{\text{ox}}^{[\text{a}]}$	5.365(9)	5.066(7)	5.041(5)	4.991(3)	5.027(4)
	5.396(9)	4.942(7)	4.966(5)	4.864(4)	4.938(4)
CN	10	9	9	9	9

[a] Given in Å. [b] Not applicable. Aza = azamethine nitrogen, CN = coordination number, Py = pyridine, ox = oxygen atom attached to urea unit.

$\text{mol cm}^{-2}$  for complexes  $[\text{MLCl}_3]$  ( $\text{M} = \text{La}^{\text{III}}, \text{Eu}^{\text{III}}, \text{Tb}^{\text{III}}, \text{Lu}^{\text{III}}$ , and  $\text{Y}^{\text{III}}$ ). A comparative study with respective trichloride lanthanide salts suggests the presence of 1:3  $\text{M}^{3+}/\text{X}^-$  electrolytes in solution, although this full dissociation was not observed in the crystal.

**Circular dichroism:** Figure 7a represents the circular dichroism (CD) spectra of  $\text{L}^2$  and the prepared lanthanide complexes in DMSO, and the respective CD spectra of the lanthanide complexes in HEPES buffer (pH 7.4) are shown in Figure 7b. Unfortunately, ligand  $\text{L}^2$  is insoluble in water; thus, the CD spectrum in aqueous solution could not be recorded.

Due to the chiral  $\text{sp}^3$  carbon center in the side chains of  $\text{L}^2$ , there is no full conjugation. The CD spectrum of  $\text{L}^2$  shows a dominant positive signal at  $\lambda = 265$  nm and a negative cotton effect at  $\lambda = 292$  nm. Formation of  $[\text{EuL}^2\text{Cl}_3]$ ,  $[\text{TbL}^2\text{Cl}_3]$ ,  $[\text{LuL}^2\text{Cl}_3]$ , and  $[\text{YL}^2\text{Cl}_3]$  results in a decrease of optical intensity, with almost none observed for the europium(III) complex (Figure 7a). The biggest ion, europium(III), might enforce the coordination of the ligand in a more-or-less planar fashion without helical twisting. The CD behavior in Figure 7b in HEPES buffer at pH 7.4 indicates that the configuration at the metal center is the same in all complexes.

**Luminescence spectral investigations:** The ligand  $\text{L}^1$ ,  $[\text{LnL}^1]$  complexes, and the  $[\text{EuL}^2]$  complex show distinct differences in their luminescent behavior. Figure 8a shows the luminescence spectra of ligand  $\text{L}^1$  and the respective lanthanide complexes in DMSO. These spectra reveal only ligand-centered emission. Though europium and terbium are known for their luminescence properties, the absence of metal-centered luminescence in the case of the  $\text{L}^1$  complexes indicates that metal-induced emission is not active here ( $\lambda = 364$  nm). Probably, the NH deactivation process inhibits the emission of europium, whereas the triplet state of the ligand lies too low for sensitizing in the case of terbium.

Luminescence spectra of  $\text{L}^2$  and its complexes in DMSO are depicted in Figure 8b. Upon excitation at  $\lambda = 355$  nm

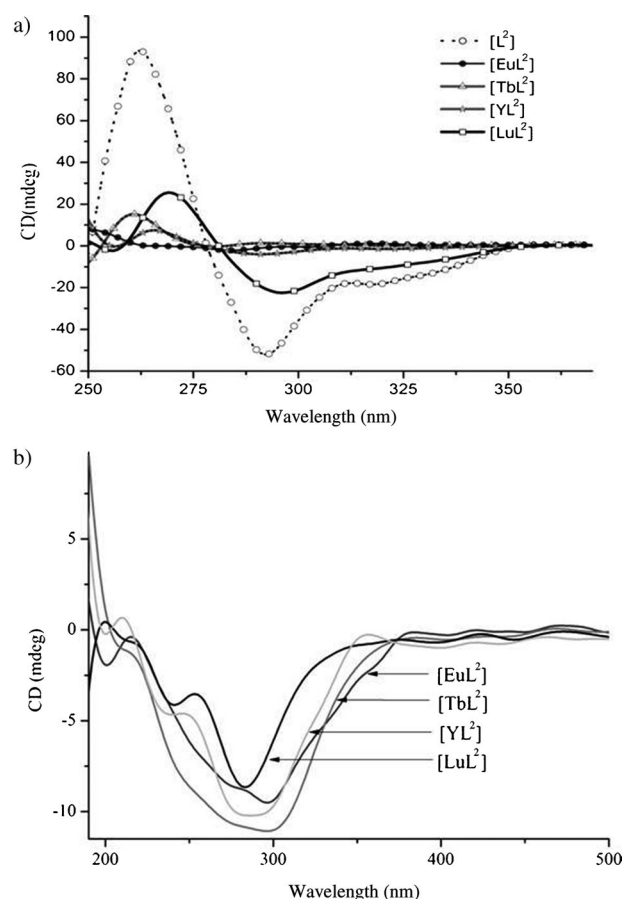


Figure 7. CD spectra of  $L^2$  and its complexes at a concentration of  $1 \times 10^{-4}$  M in DMSO (top) and in HEPES buffer pH 7.4 (bottom). HEPES = 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid.

$[EuL^2Cl_3]$  reveals a typical strong “red emission” both in the solid state and solution (even in water). Surprisingly, all the other complexes of  $L^2$  are nonluminescent. The characteristic strong and intense red emission observed at  $\lambda = 615$  nm is attributable to a  $J=2$  transition ( $^5D_0 \rightarrow ^7F_2$ ).<sup>[33]</sup> Figure 8c illustrates the excitation and emission spectra of complex  $[EuL^2]$  in HEPES buffer.

A comparison of characteristics of  $L^1$  and  $L^2$  reveals that the former possesses NH groups and conjugation on the semicarbazone pendant arms. Metal-centered luminescence is found in  $[EuL^2Cl_3]$ , which might be due to the substitution of the quencher NH group by a  $sp^3$  carbon atom. Although the terbium(III) ion is known for its green emission, the absence of fluorescence shown by  $[TbL^2]$  may be attributed to a low-lying triplet state of the ligand unfavourable for energy transfer to the terbium ion.

As described above, the  $[EuL^2]$  complex exhibits a strong red emission. This finding, in addition with the proposed Lewis acidity of the complex, was the inspiration to apply the system to the sensing of various anions. Accordingly, a detailed investigation was carried out using  $I^-$ ,  $Br^-$ ,  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $CH_3COO^-$ ,  $HPO_4^{2-}$ , and  $SO_4^{2-}$  ions (Figure 9a). Emission spectra in the bar diagram (Figure 9b) indicate that the addition of all mononegative anions results

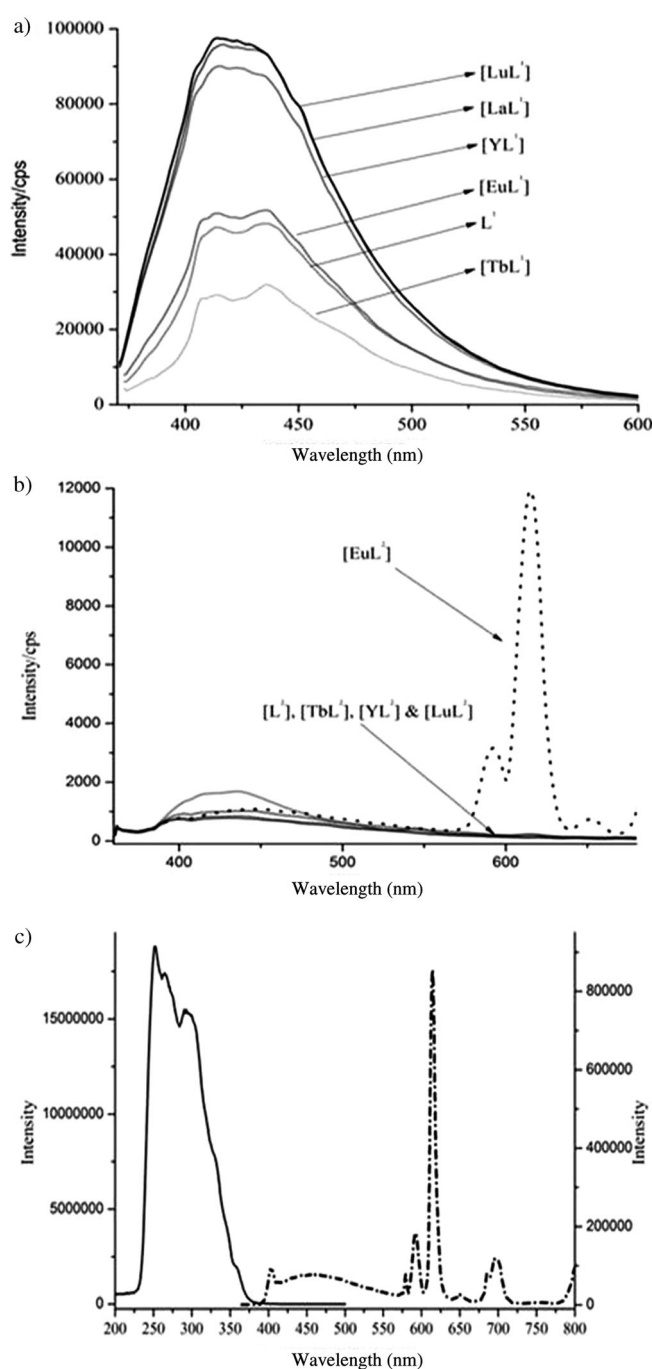


Figure 8. Emission spectra of a) ligand  $L^1$  and its complexes ( $\lambda_{exc} = 361$  nm) and b)  $L^2$  and its complexes ( $\lambda_{exc} = 355$  nm) ( $[DMSO] = 1 \times 10^{-5}$  M). c) Excitation and emission spectra of complex  $[EuL^2]$  in HEPES buffer pH 7.4.

in a relative emission with a factor of 0.87–1.13 with respect to the parent  $[EuL^2Cl_3]$  complex. The quenching of the emission by  $HPO_4^{2-}$  ions was remarkable.

Subsequently, the study was extended to sensing of ATP, ADP, and AMP anions. Only ATP quenched the emission with a distinguishable response (Figure 10). On the basis of this outcome, a systematic fluorescence titration was carried out and the respective binding constants for the  $HPO_4^{2-}$  and

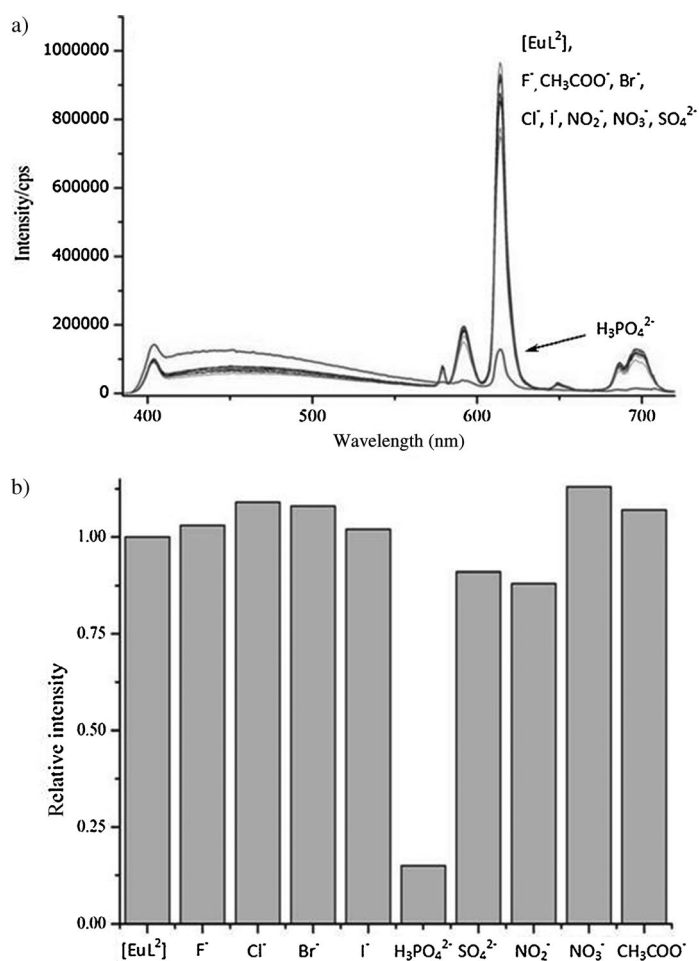


Figure 9. a) Change in the emission spectra of  $[\text{EuL}^2\text{Cl}_3]$  ( $2 \times 10^{-5} \text{ M}$ ) upon the addition of ten equivalents of various anions (as the potassium or sodium salts) using HEPES buffer pH 7.4. b) Respective bar diagrams that show the relative luminescence intensity ( $\lambda_{\text{exc}} = 615 \text{ nm}$ ) of  $[\text{EuL}^2\text{Cl}_3]$ .

ATP anions were  $\log K_b = 4.15 \pm 0.1$  and  $4.40 \pm 0.1 \text{ M}^{-1}$ , respectively (Figure 11), as derived from the linear fit (inset Figure 11). This data clearly indicates that the ATP anion binds more strongly relative to the  $\text{HPO}_4^{2-}$  ion. The tripotassium  $\text{Eu}^{3+}$  metal centre preferably interacts with the anion, thus possessing higher negative charge.

To ascertain the formation of the  $[\text{EuL}^2]/\text{ATP}$  complex, a mixture of 1:1  $[\text{EuL}^2\text{Cl}_3]$  and the ATP disodium salt was studied by ESI mass-spectrometric analysis. However, no well resolved spectra were obtained due to a poor signal-to-noise ratio. However, characteristic broad peaks were observed in the region of  $[\text{EuHL}^2\text{Cl}_2\text{ATP}]^-$  ( $m/z$  1162.8; calcd: 1160.2) and  $[\text{EuNaL}^2\text{Cl}_2\text{ATP}]^-$  ( $m/z$  1183.1; calcd: 1182.0).

In addition,  $^{31}\text{P}$  NMR spectroscopic analysis showed three distinguishable sharp resonances at  $\delta = -5.88$ ,  $-9.85$ , and  $-20.91 \text{ ppm}$  for ATP in the free state. The signals broaden and shifted to  $\delta = -7.86$ ,  $-39.80$ , and  $-74.39 \text{ ppm}$  upon binding with the europium(III) center (Figure 12). This behavior effected all three phosphorus signals, thus indicating that each phosphate unit of ATP is located close to the pa-

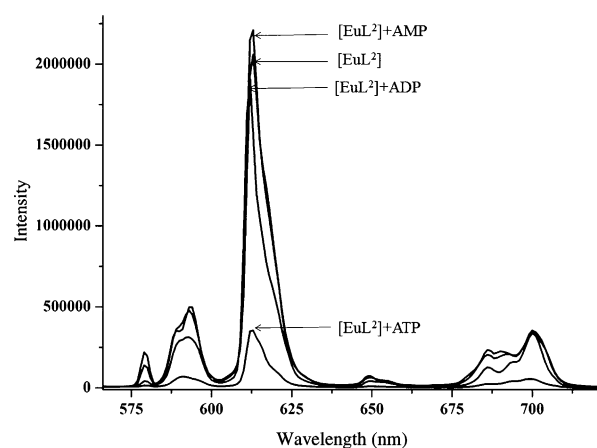


Figure 10. Emission spectra of  $[\text{EuL}^2\text{Cl}_3]$  (concentration =  $2 \times 10^{-5} \text{ M}$ ) against ATP/AMP/ADP (10 equiv) in HEPES buffer pH 7.4. ATP = adenosine-5'-triphosphate, AMP = adenosine-5'-monophosphate, ADP = adenosine-5'-diphosphate.

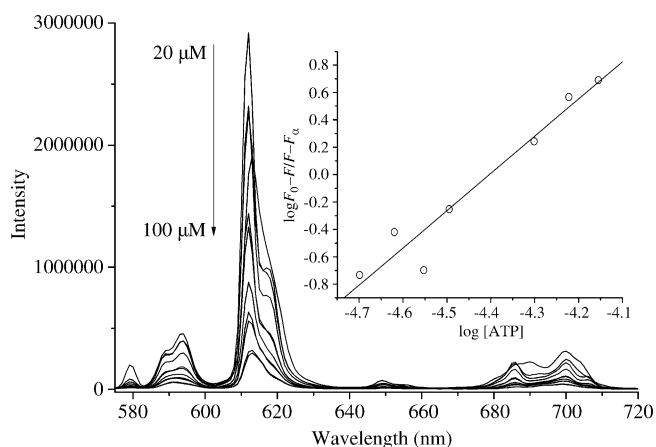


Figure 11. Changes in the emission of  $[\text{EuL}^2\text{Cl}_3]$  (concentration =  $2 \times 10^{-5} \text{ M}$ ) on successive additions of different molar equivalents of ATP (20–100  $\mu\text{M}$ ;  $\lambda_{\text{exc}} = 355 \text{ nm}$ ; HEPES buffer pH 7.4). The inset shows the binding-constant determination of ATP to  $[\text{EuL}^2\text{Cl}_3]$ .

ramagnetic europium(III) center. A similar observation by Ziessel and co-workers<sup>[34]</sup> supports the binding of ATP. A tentative structure for the interaction of ATP with  $[\text{EuL}^2\text{Cl}_3]$  can be proposed (Figure 13).<sup>[35]</sup>

## Conclusion

We have synthesized phenanthroline-based hexadentate ligands  $\text{L}^1$  and  $\text{L}^2$ . A series of lanthanide complexes incorporating lanthanum(III), europium(III), terbium(III), lutetium(III), and yttrium(III) trichlorides were prepared. The crystal structures obtained for the  $[\text{LnL}^1\text{Cl}_3]$  complexes gave some understanding of the geometry and indicated similar structural behavior for the  $[\text{LnL}^2\text{Cl}_3]$  complexes. The hexadentate ligand  $\text{L}^1$  with lanthanide(III) ions unveils that despite the tight wrapping of the ligand by the metal ions, space is left for coordination of coligands in the solid state. Conductivity measurements suggest that the chloride ion

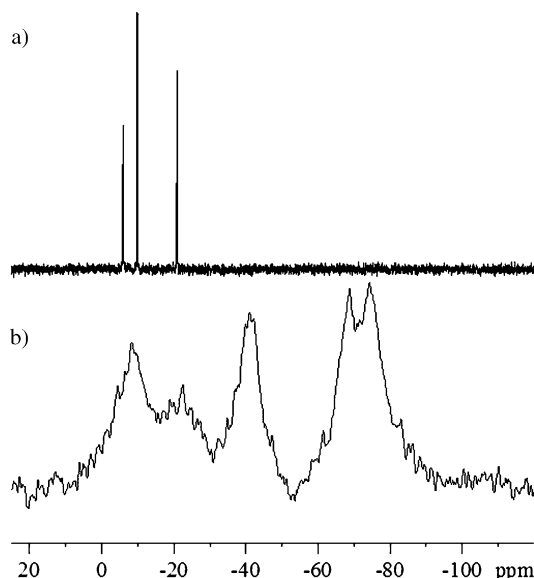


Figure 12.  $^{31}\text{P}$  NMR spectra of a) ATP and b) ATP in the presence of  $[\text{EuL}^2\text{Cl}_3]$ .

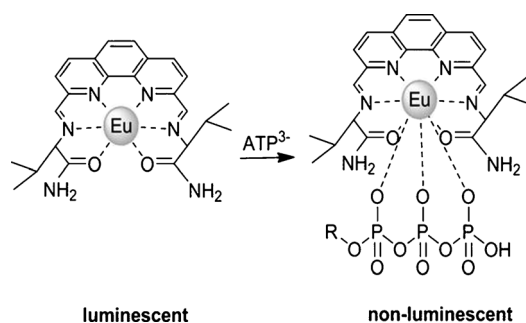


Figure 13. Proposed binding mode of ATP with the  $\text{Eu}^{\text{III}}$  complex.

fully dissociates in solution. However, in the solid state, some of the halide ions bind to the metal centers and monocation, dication, and trication complexes are observed.

The ligand  $\text{L}^1$  and its lanthanide complexes show ligand-centered emissions. Among the lanthanide complexes obtained from  $\text{L}^2$ , only  $[\text{EuL}^2\text{Cl}_3]$  shows a strong red emission. Complex  $[\text{EuL}^2\text{Cl}_3]$  incorporates a  $\text{sp}^3$  chiral carbon atom in the side arms and was a strong red emitter. This luminescence property was meticulously probed for the sensing of a series of anions. Most of the studied anions do not show a significant influence on the luminescence properties of the complex. However, a strong response was detected for the hydrogenphosphate ion, and on the basis of this finding, a high specificity for ATP over ADP or AMP could be detected in water at a physiological pH value of 7.4. A reasonable model for the binding of ATP can be suggested following NMR spectroscopic studies. However, this model does not give a sufficient explanation for the effective luminescence quenching. Regarding the association constant for ATP binding, some effective total quenching seems to be present. These results are promising in regard to the application of these lanthanide complexes to sensing biologically relevant anionic species.

## Experimental Section

**Materials and general methods:** All the chemicals were purchased from Aldrich & Co. and ABCR GmbH & Co. KG. Elemental analysis of the complexes was carried out by using a varioEL from Elementar. IR spectra were recorded from KBr pellets (1% w/w) on a Perkin–Elmer spectrum GX FTIR spectrophotometer. Electronic spectra were recorded on a Shimadzu UV 3101PC spectrophotometer. All the electronic spectra were scanned at  $\lambda = 200\text{--}1200\text{ nm}$ . Mass-spectrometric analysis was performed by using the positive ESI technique on a Waters Q ToF micro mass spectrometer for all these complexes upon dissolving in  $\text{CH}_3\text{OH}$ .  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance 500 MHz FT-NMR spectrometer. The chemical shifts for proton resonances are reported in ppm ( $\delta$ ) relative to TMS. In the case of  $^{31}\text{P}$  NMR spectroscopy, 20% hydrophosphoric acid dissolved in  $\text{D}_2\text{O}$  was used as an external standard. The conductance measurements were carried out using a digital conductivity meter Digicell from Systronics Vadodara. Emission spectra were recorded using an Edinburgh Instruments model Xe-900, and all the spectra recorded are reported herein after applying emission correction. The slit sizes for emission and excitation are adjusted as 3.0/3.0 nm.

**Crystal-structure determination:** Suitable single crystals of each compound were selected from the mother liquor, immersed in paratone oil, and then mounted immediately onto the tip of a glass fiber. Intensity data for all the three crystals were collected using  $\text{MoK}\alpha$  ( $\mu = 0.71073\text{ \AA}$ ) radiation on a Bruker Smart Apex diffractometer equipped with CCD area detector at 100 K. The data integration and reduction were processed with SAINT software. An empirical absorption correction was applied to the collected reflections with SADABS. The structures were solved by direct methods using SHELXTL and were refined on  $F^2$  by means of the full-matrix least-squares technique and using the program SHELXL-97. The lattice solvent molecule (DMF) present in the case of complex  $[\text{LuL}^1]$  was highly disordered and their contribution to the diffraction data has been removed by using the SQUEEZE subroutine as implemented in PLATON. Refinement of  $[\text{LuL}^1]$  by using the modified reflection-data set apparently improved the  $R$  factor. All nonhydrogen atoms were refined anisotropically till convergence was reached. Hydrogen atoms attached to the organic moieties were either located from the difference Fourier map or stereochemically fixed in all the three complexes.

### Ligand synthesis

**Phenanthroline-2,9-dialdehyde:** A previously reported synthetic procedure was used to synthesize this compound.<sup>[36]</sup>

**Ligand  $\text{L}^1$ :** Semicarbazide hydrochloride (0.02 mol, 2.230 g) dissolved in methanol (200 mL) was added to a suspension of phenanthroline-2,9-dialdehyde (0.01 mol, 2.362 g) in methanol (400 mL) with stirring at room temperature. Upon completion of this addition, the resultant clear solution was allowed to continue stirring. During the reaction, formation of a precipitate occurred and stirring was continued for more than 70 h to accomplish the precipitation. The resulting yellow precipitate was separated by filtration, washed with cold methanol, and dried (yield: 80%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ , 500 MHz):  $\delta = 11.01$  (s, 2H), 8.60–8.73 (dd,  $J = 8\text{ Hz}$ , 4H), 8.35 (s, 2H), 8.08, (s, 2H), 6.88 ppm (s, 4H);  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ , 500 MHz):  $\delta = 121.30, 127.47, 129.23, 137.39, 139.61, 140.39, 153.59, 156.81\text{ ppm}$ ; IR (KBr):  $\tilde{\nu} = 3428$  (st), 1707 (st), 1575 (s), 1152  $\text{cm}^{-1}$  (m); MS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{N}_8\text{O}_2^+$ : 351.13; found: 351.58; UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 302 (40620), 317 (36040), 344 (37200), 362 (26720), 497 nm ( $22\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$ ); elemental analysis (%) calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_8\text{O}_2 \cdot 4\text{HCl}$ : C 38.73, H 3.66, N 22.58; found: C 38.87, H 4.32, N 22.08.

**2,2'-(2E,2'E)-2,2'-[(1,10-Phenanthroline-2,9-diyl)bis(methanylylidene)]-bis(hydrazin-1-yl-2-ylidene)]bis(3-methylbutanamide) ( $\text{L}^2 \cdot \text{H}_2\text{O}$ ):** A mixture of triethylamine (0.0418 mL) and L-valinamide hydrochloride (0.002 mmol, 0.305 g) dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL) was added dropwise to 1,9-diformyl-1,10-phenanthroline (0.0001 mmol, 0.0236 g) dissolved in  $\text{CH}_2\text{Cl}_2$  (100 mL) with stirring. The resultant yellow solution was heated to reflux on an oil bath at  $50^\circ\text{C}$  for more than 72 h. The resulting mixture was extracted with a saturated solution of brine ( $3 \times 100\text{ mL}$ ). The solvent was removed under vacuum and the resultant yellow product was isolat-



ed (yield: 70 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 8.78 (s, 2H), 8.48, 8.49 (d,  $J$  = 8 Hz, 2H), 8.38, 8.39 (d,  $J$  = 8 Hz, 2H), 7.94 (s, 2H), 5.74 (s, 2H) 6.68 (s, 2H), 3.88 (d,  $J$  = 6 Hz, 2H), 2.45 (m,  $J$  = 7 Hz, 2H), 1.07 ppm (dd,  $J$  = 7 Hz, 12H); IR (KBr):  $\tilde{\nu}$  = 3380 (br), 1678 (s), 1508 (s), 1140  $\text{cm}^{-1}$  (s); UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 260 (32170), 267 (31530), 291 (32240), 321 (17910), 335 (14230), 355 nm ( $2730 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); MS (ESI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{28}\text{N}_6\text{O}_2$ : 433.33, 455.51; found: 433.55  $[\text{M} + \text{H}]^+$ , 455.55  $[\text{M} + \text{Na}]^+$ ; elemental analysis (%) for  $\text{C}_{24}\text{H}_{28}\text{N}_6\text{O}_2 \cdot \text{H}_2\text{O}$ : C 63.98, H 6.71, N 18.65; found C 63.76, H 6.89, N 17.80.

**General procedure for the preparation of metal complexes:** Ligand  $\text{L}^1$  or  $\text{L}^2$  (0.001 mmol) was dissolved in methanol (200 mL) and stirred continuously until a suspension was formed. Lanthanide trichloride salt (0.001 mmol) dissolved in methanol (50 mL) was added gradually to the reaction mixture, which was heated for 6 h at 60 °C using an oil bath with constant stirring. A slow change from light yellow to reddish brown of the reaction mixture was generally observed for almost all the metal complex preparations. The reaction mixture was cooled to room temperature. A negligible amount of precipitate formed during this cooling process was removed upon filtration and the clear yellow solution obtained as the filtrate was evaporated under vacuum.

**[LaL $^1$ Cl $_3$ ]:**  $\text{L}^1$  (0.01 mmol, 0.248 g) and  $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$  (0.01 mmol, 0.186 g) were used (yield: 85 %).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ , 500 MHz):  $\delta$  = 12.93 (s, 4H,  $\text{NH}_2$ ), 8.89 (d,  $J$  = 8.4 Hz, 2H), 8.60 (s, 2H), 8.29 (d,  $J$  = 8.4 Hz, 2H), 8.19 (s, 2H), 7.51 ppm (sbr, 2H, NH); IR (KBr):  $\tilde{\nu}$  = 3133 (br), 1662 (s), 1533 (s), 1145  $\text{cm}^{-1}$  (s); UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 302 (48510), 317 (42180), 344 (42180), 361 nm ( $3940 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); MS (ESI):  $m/z$  calcd for  $[\text{LaC}_{16}\text{H}_{14}\text{Cl}_2\text{N}_8\text{O}_2]^+$ : 558.97, 489.03; found: 557.33  $[\text{LaLCl}_2]^+$ , 487.08  $[\text{LaL}]^{3+}$ ; elemental analysis (%) calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_8\text{O}_2\text{LaCl}_3 \cdot 3\text{H}_2\text{O}$ : C 29.58, H 3.10, N 17.25; found: C 29.54, H 3.30, N 17.02.

Crystal data for  $\text{C}_{24}\text{H}_{38}\text{Cl}_3\text{LaN}_6\text{O}_6\text{S}_4$ : FW = 908.12;  $T$  = 110 K; yellow plates, dimension =  $0.34 \times 0.23 \times 0.14$  mm; triclinic; space group:  $P\bar{1}$ ;  $a$  = 9.1582(6),  $b$  = 14.0440(10),  $c$  = 16.4080(11) Å;  $\alpha$  = 68.7070(10),  $\beta$  = 83.6190(10),  $\gamma$  = 77.8510(10)°;  $V$  = 1920.9(2) Å $^3$ ;  $Z$  = 2; reflections collected = 14675;  $\theta_{\text{min}}$  = 2.28°,  $\theta_{\text{max}}$  = 28.15°;  $\rho_{\text{calcd}}$  = 1.570  $\text{g cm}^{-3}$ ;  $F(000)$  = 916;  $\mu$  = 1.584  $\text{mm}^{-1}$ ;  $\lambda(\text{MoK}\alpha)$  = 0.71073 Å;  $R_1$  = 0.0775,  $wR_2$  = 0.2140; GOF = 1.036.

**[EuL $^1$ Cl $_3$ ]:**  $\text{L}^1$  (0.01 mmol, 0.350 g) and  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.01 mmol, 0.366 g) were used (yield: 80 %).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ , 500 MHz): broad features; IR (KBr):  $\tilde{\nu}$  = 3403, 1667, 1627, 1555, 1503, 1154  $\text{cm}^{-1}$ ; UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 302 (32700), 317 (28590), 345 (29020), 362 (21240) (sh), 465 nm ( $45 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) (sh); MS (ESI):  $m/z$  calcd for  $[\text{EuC}_{16}\text{H}_{14}\text{Cl}_2\text{N}_8\text{O}_2]^+$ : 573.20, 537.75; found: 573.25  $[\text{EuL}^1\text{Cl}_2]^+$ , 537.25  $[\text{EuL}^1\text{Cl}]^{2+}$ ; elemental analysis (%) for  $\text{C}_{16}\text{H}_{14}\text{N}_8\text{O}_2\text{EuCl}_3 \cdot 3\text{H}_2\text{O} \cdot 2\text{HCl}$ : C 26.12, H 3.01, N 15.23; found: C 26.30, H 2.71, N 14.75.

Crystal data for  $\text{C}_{32}\text{H}_{50}\text{Cl}_6\text{Eu}_2\text{N}_{16}\text{O}_{15.50}$ : FW = 1423.50; light-red crystals; dimensions =  $0.32 \times 0.21 \times 0.12$  mm; triclinic; space group:  $P\bar{1}$ ;  $a$  = 13.9416(16),  $b$  = 14.0352(16),  $c$  = 14.0849(16) Å;  $\alpha$  = 101.106(2),  $\beta$  = 105.264(2),  $\gamma$  = 96.967(2)°;  $V$  = 2565.3(5) Å $^3$ ;  $Z$  = 2;  $\theta_{\text{min}}$  = 1.50°,  $\theta_{\text{max}}$  = 28.30°;  $\rho_{\text{calcd}}$  = 1.843  $\text{g cm}^{-3}$ ;  $F(000)$  = 1412;  $\mu$  = 2.813  $\text{mm}^{-1}$ ;  $\lambda(\text{MoK}\alpha)$  = 0.71073 Å;  $R_1$  = 0.0557,  $wR_2$  = 0.1293; GOF = 1.212.

**[TbL $^1$ Cl $_3$ ]:**  $\text{L}^1$  (0.01 mmol, 0.35 g) and  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  (0.01 mmol, 0.373 g) were used (yield: 82 %).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ , 500 MHz): only broad signals are observed; IR (KBr)  $\tilde{\nu}$  = 3377 (s), 1667 (s), 1625 (s), 1543 (s), 1502 (s), 1154  $\text{cm}^{-1}$  (s); UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 298 (20720), 318 (15610), 344 (15710), 362 (12050), 326 nm ( $14320 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); MS (ESI):  $m/z$  calcd for  $[\text{TbC}_{16}\text{H}_{14}\text{Cl}_2\text{N}_8\text{O}_2]^+$ : 578.99, 543.359, 507.366; found: 579.38  $[\text{TbL}^1\text{Cl}_2]^+$ , 544.02  $[\text{TbLCl}]^{2+}$ , 509.05  $[\text{TbLCl}]^{3+}$ ; elemental analysis (%) for  $\text{C}_{16}\text{H}_{26}\text{Cl}_3\text{N}_8\text{O}_8\text{Tb}$ : C 26.55, H 3.62, N 15.48; found: C 26.32, H 4.00, N 15.25.

Crystal data for  $\text{C}_{26.50}\text{H}_{38.50}\text{Cl}_3\text{N}_{11.50}\text{O}_{5.50}\text{Tb}$ : FW = 871.46;  $T$  = 223(2) K; light-yellow crystals; dimensions =  $0.10 \times 0.10 \times 0.03$  mm; triclinic; space group:  $P\bar{1}$  (No.2);  $a$  = 10.5843(2),  $b$  = 11.0206(2),  $c$  = 17.1032(3) Å;  $\alpha$  = 92.469(1),  $\beta$  = 104.384(1),  $\gamma$  = 110.637(1)°;  $V$  = 1789.59(6) Å $^3$ ;  $Z$  = 2;  $T$  = 223(2) K; reflections measured = 15919;  $\theta_{\text{min}}$  = 4.11°,  $\theta_{\text{max}}$  = 27.85°;  $\rho_{\text{calcd}}$  = 1.617  $\text{g cm}^{-3}$ ;  $F(000)$  = 876;  $\mu$  = 2.254  $\text{mm}^{-1}$ ;  $\lambda(\text{MoK}\alpha)$  = 0.71073 Å;  $R_1$  = 0.0471,  $wR_2$  = 0.1091; GOF = 1.059.

**[LuL $^1$ Cl $_3$ ]:**  $\text{L}^1$  (0.01 mmol, 0.074 g) and  $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.01 mmol, 0.106 g) were used (yield: 86 %).  $^1\text{H}$  NMR ( $\text{DMF}$ , 500 MHz):  $\delta$  = 13.94, (s,  $\text{NH}_2$ ), 8.99, 8.97 (d,  $J$  = 10 Hz, 2H), 8.8 (s, 2H), 8.41, 8.39 (d, 2H), 8.26 (s, 2H) 8.03 ppm (br, NH); IR (KBr):  $\tilde{\nu}$  = 3316, 3160 (s), 1688, 1630 (s), 1537 (s), 1154  $\text{cm}^{-1}$  (s); UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 302 (50290), 317 (43610), 344 (43610), 362 nm ( $32400 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); MS (ESI):  $m/z$  calcd for  $[\text{LuC}_{16}\text{H}_{14}\text{Cl}_2\text{N}_8\text{O}_2]^+$ : 595.00; found: 595.15  $[\text{LuL}^1\text{Cl}_2]^+$ ; elemental analysis (%) for  $\text{LuC}_{16}\text{H}_{14}\text{Cl}_3\text{N}_8\text{O}_2$ : C 32.36, H 3.6, N 18.68; found: C 30.42, H 2.23, N 17.74.

Crystal data for  $\text{C}_{25}\text{H}_{35}\text{Cl}_3\text{LuN}_{11}\text{O}_5$ : FW = 850.96,  $T$  = 110(2) K; yellow block crystals, dimensions =  $0.4 \times 0.28 \times 0.24$ ; triclinic; space group:  $P\bar{1}$ ;  $a$  = 10.4885(6),  $b$  = 10.8713(6),  $c$  = 17.0447(10) Å;  $\alpha$  = 92.4170(10),  $\beta$  = 104.1410(10),  $\gamma$  = 110.5430(10)°;  $V$  = 1747.17(17) Å $^3$ ;  $Z$  = 2; reflections measured = 6248;  $\theta_{\text{min}}$  = 2.22°,  $\theta_{\text{max}}$  = 28.24°;  $\rho_{\text{calcd}}$  = 1.618  $\text{g cm}^{-3}$ ;  $F(000)$  = 848;  $\mu$  = 3.105  $\text{mm}^{-1}$ ;  $\lambda(\text{MoK}\alpha)$  = 0.71073 Å;  $R_1$  = 0.0250,  $wR_2$  = 0.0775; GOF = 1.118.

**[YL $^1$ Cl $_3$ ]:**  $\text{L}^1$  (0.01 mmol, 0.248 g) and  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (0.01 mmol, 0.1526 g) were used (yield: 80 %).  $^1\text{H}$  NMR ( $[\text{D}_7]\text{DMF}$  500 MHz):  $\delta$  = 13.84 (s, 4H,  $\text{NH}_2$ ), 8.99, 8.97 (d,  $J$  = 10 Hz, 4H), 8.84 (s, 4H), 8.39, 8.37 (d,  $J$  = 10 Hz, 4H), 7.99 ppm (brs, 2H, NH); IR (KBr):  $\tilde{\nu}$  = 3148 (s), 1661, 1623 (s), 1534, 1503 (s), 1146  $\text{cm}^{-1}$  (s); UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 302 (44960), 317 (38890), 344 (39060), 361 nm ( $28890 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); MS (ESI):  $m/z$  calcd for  $[\text{LuC}_{16}\text{H}_{14}\text{Cl}_2\text{N}_8\text{O}_2]^+$ : 508.97; found: 507.417  $[\text{YLCl}_2]^+$ ;  $\text{C}_{16}\text{H}_{22}\text{Cl}_3\text{N}_8\text{O}_6\text{Y} \cdot 4\text{H}_2\text{O}$ : C 31.11, H 3.59, N 18.14; found: 31.34, H3.87, N 17.45.

Crystal data for  $\text{C}_{26.50}\text{H}_{38.50}\text{Cl}_3\text{N}_{11.50}\text{O}_{5.50}\text{Y}$ : FW = 801.45;  $T$  = 223(2) K; yellow crystals; dimensions =  $0.30 \times 0.15 \times 0.10$  mm; triclinic, space group:  $P\bar{1}$  (No.2)  $a$  = 10.5722(2),  $b$  = 11.0110(2),  $c$  = 17.0896(4) Å;  $\alpha$  = 92.570(1),  $\beta$  = 104.207(1),  $\gamma$  = 110.761(1)°;  $V$  = 1784.16(6) Å $^3$ ;  $Z$  = 2, reflections measured = 15654;  $\theta_{\text{min}}$  = 4.12°,  $\theta_{\text{max}}$  = 27.90°;  $\rho_{\text{calcd}}$  = 1.492  $\text{g cm}^{-3}$ ;  $F(000)$  = 824;  $\mu$  = 1.913  $\text{mm}^{-1}$ ;  $\lambda(\text{MoK}\alpha)$  = 0.71073 Å;  $R_1$  = 0.0539,  $wR_2$  = 0.1418; GOF = 1.058.

**[EuL $^2$ Cl $_3$ ] $\cdot 3\text{H}_2\text{O}$ :** A mixture of  $\text{L}^2 \cdot \text{H}_2\text{O}$  (0.01 mmol, 0.045 g) and  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.01 mmol, 0.0366 g) in methanol was heated to reflux at 70 °C for 8 h with constant stirring to give an orange-red solution. The reaction mixture was evaporated at room temperature by rotatory evaporation (yield: 83 %). IR (KBr):  $\tilde{\nu}$  = 3274 (s), 1667 (s), 1507 (s), 1140  $\text{cm}^{-1}$  (s); UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 289 (27890), 321 (13980), 336 (9930), 357 (3080) 433 (377), 571 nm ( $159 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); MS (ESI):  $m/z$  calcd for  $[\text{EuC}_{24}\text{H}_{28}\text{Cl}_2\text{N}_6\text{O}_2]^+$ : 655.09; found: 655.38  $[\text{EuL}^2\text{Cl}_2]^+$ ; elemental analysis (%) calcd for  $\text{C}_{24}\text{H}_{34}\text{Cl}_3\text{EuN}_6\text{O}_5$ : C 38.70, H 4.60, N 11.28; found: C 38.42, H 4.58, N 11.64.

**[TbL $^2$ Cl $_3$ ] $\cdot 3\text{H}_2\text{O}$ :**  $\text{L}^2$  (0.01 mmol, 0.045 g) and  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  (0.01 mmol, 0.037 g) were used (yield: 82 %). IR (KBr):  $\tilde{\nu}$  = 3154 (s), 1667 (s), 1507 (s), 1137  $\text{cm}^{-1}$  (s); UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 289 (27336), 322 (14074), 334 (11273), 356 (2998), 435 (206), 583 nm ( $163 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); MS (ESI):  $m/z$  calcd for  $[\text{TbC}_{24}\text{H}_{28}\text{Cl}_3\text{N}_6\text{O}_2\text{Na}]^+$ : 721.24; found: 721.44  $[\text{TbL}^2\text{Cl}_3 + \text{Na}]^+$ ; elemental analysis (%) calcd for  $\text{C}_{24}\text{H}_{36}\text{Cl}_3\text{N}_6\text{O}_6\text{Tb}$ : C 37.44, H 4.71, N, 10.92; found: C 37.93, H 4.73, N 11.09.

**[LuL $^2$ Cl $_3$ ] $\cdot \text{H}_2\text{O} \cdot \text{MeOH}$ :**  $\text{L}^2$  (0.02 mmol, 0.090 g) and  $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.02 mmol, 0.079 g) were used (yield: 80 %)  $^1\text{H}$  NMR (DMSO, 500 MHz):  $\delta$  = 9.57 (s, 2H), 9.37 (s, 2H), 9.11, 9.10 (d,  $J$  = 8 Hz, 2H), 8.97 (s, 2H), 8.63, 8.61 (d,  $J$  = 10 Hz, 2H), 8.36 (s, 2H), 8.02 (s, 2H), 4.75, 4.74 (d,  $J$  = 7 Hz, 2H), 2.77 (m,  $J$  = 7 Hz, 2H), 1.15, 1.17 (d,  $J$  = 7 Hz, 6H), 1.24, 1.25 ppm (d,  $J$  = 7 Hz, 6H); IR (KBr):  $\tilde{\nu}$  = 3374 (s), 1674 (s), 1508 (s), 1140  $\text{cm}^{-1}$  (s); UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 267 (39480), 290 (40090), 321 (20790), 333 (16800), 356 nm ( $3460 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); MS (ESI):  $m/z$  calcd for  $[\text{LuC}_{24}\text{H}_{28}\text{ClN}_6\text{O}_2]^+$ : 642.14; found: 641.78  $[\text{LuL}^2\text{Cl}]^{2+}$ ; elemental analysis (%) calcd for  $\text{C}_{25}\text{H}_{34}\text{Cl}_3\text{LuN}_6\text{O}_4$ : C 39.31, H 4.49, N 11.0; found: C 39.86, H 4.07, N 11.13.

**[YL $^2$ Cl $_3$ ] $\cdot 2\text{H}_2\text{O} \cdot \text{MeOH}$ :**  $\text{L}^2$  (0.02 mmol, 0.09 g) and  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (0.02 mmol, 0.061 g) were used (yield: 86 %)  $^1\text{H}$  NMR (DMSO, 500 MHz):  $\delta$  = 9.68 (s, 2H), 9.30 (s, 2H), 9.11, 9.10 (d,  $J$  = 8 Hz, 2H), 8.97 (s, 2H), 8.62, 8.61 (d,  $J$  = 8 Hz, 2H), 8.367 (s, 2H), 8.02 (s, 2H), 4.77, 4.78 (d,  $J$  = 7 Hz, 2H), 2.67 (m,  $J$  = 7 Hz, 2H), 1.18, 1.20 (d,  $J$  = 7 Hz, 6H), 1.22, 1.24 ppm (d,  $J$  = 7 Hz, 6H); IR (KBr):  $\tilde{\nu}$  = 3151 (s), 1670 (s), 1508 (s), 1140  $\text{cm}^{-1}$  (s); UV/Vis (DMSO):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 269 (26600), 288 (28070), 319 (14340), 336 (10740), 356 (3050), 556 nm ( $191 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ); MS

(ESI):  $m/z$  calcd for  $[\text{YC}_{24}\text{H}_{28}\text{Cl}_2\text{N}_6\text{O}_2]^+$ : 591.07; found: 591.28  $[\text{YL}^2\text{Cl}_2]^+$ ; elemental analysis (%) for  $\text{C}_{25}\text{H}_{36}\text{Cl}_3\text{YN}_6\text{O}_5$ : C 43.15, H 5.21, N 12.08; found: C 43.78, H 5.73, N 11.95.

CCDC-854035 ( $[\text{LaL}^1\text{Cl}_3]$ ), 848589 ( $[\text{EuL}^1\text{Cl}_3]$ ), 855107 ( $[\text{TbL}^1\text{Cl}_3]$ ), 854034 ( $[\text{LuL}^1\text{Cl}_3]$ ), and 855108 ( $[\text{YL}^1\text{Cl}_3]$ ) 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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