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Tris(tropolonato)phenanthroline Lanthanide(III) Complexes as Photochemical Devices

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The tris-tropolonato erbium(III) complexes [Er(hino)$_3$(phen)] and [{Er(hino)$_3$}$_2$(pdon)] (H-hino = 2-hydroxy-6-isopropylcyclohepta-2,4,6-trien-1-one; phen = 1,10-phenanthroline; pdon = 1,10-phenanthroline-5,6-dione) have been prepared by reaction of [Er(hino)$_3$]$_n$ with the appropriate chelating ligand in alcoholic solution. The complexes were characterized by elemental analyses, TG, ESI MS, ^{1}H NMR, and IR spectroscopy, also by comparison with the properties of the analogous Eu^{III} and Yb^{III} complexes. The ESI-MS spectroscopy of the complex with the ditopic ligand pdon parallels the other physico-chemical data (IR, NMR), confirming the occurrence of a dinuclear entity. All the investigated Er^{III} complexes show efficient NIR emissions at about 1550 nm upon excitation at 355 nm in the UV ligand absorption band, emerging as possible candidate as active material for the realization of plastic amplifiers for telecommunications.

Introduction

Lanthanide complexes with distinct magnetic and optical properties are currently of interest for use in applications involving the fabrications of novel materials, both as active layer in optoelectronic devices and probes in biological systems.[1–5]

Among a wealth of stimulating applications the recent developments of (i) new phosphors for lighting,[6] (ii) high-efficiency electroluminescent devices for light-emitting diodes,[7] (iii) contrast agents for medical magnetic resonance imaging,[8] (iv) NMR shift reagents for cations for transport processes of alkali metal ions through biological membranes,[9] (v) luminescent probes for analytes,[10] (vi) labels for proteins and amino acids,[11] (vii) light-emitting sensors in fluoroimmunoassays,[12] (viii) tags for time-resolved luminescent microscopy,[13] (ix) magnetically addressable liquid crystals,[14] (x) magnetic alloys for refrigeration,[15] (xi) precursors for superconducting materials,[16] (xii) specific redox reagents for chemical transformation[17] or molecular-based information storage,[18] and (xiii) acidic catalysts for sophisticated organic transformations[19,20] or for the cleavage of phosphodiester bridges in RNA[21] fully justify the efforts made to control the metallic sites and to selectively introduce lanthanides into organized assemblies. For more than two decades, systematic investigations of the subtle interplay between the structural control of the coordination sphere and the associated metal-centred electronic properties have led to the design of lanthanide-containing devices whose function can be judiciously addressed and tuned.

The use of optical properties of these metal ions are quite attractive and promising. However, these photophysical properties of these ions depend markedly on their environment. To optimize efficient emissions, for instance, chromophoric ligands have been often employed to transfer absorbed energy efficiently to the appropriate lanthanide ion.

Remarkably, these ligands must be capable of protecting the lanthanide(III) centre from solvent molecules, which can quench emission.

A variety of multidentate cyclic and acyclic ligands, designed to encapsulate the lanthanide ions, have been synthesized and successfully used. Thus, using ligands with appropriate coordination geometry, and/or coordinating anions, it is possible to obtain suitable structure quite effective in keeping solvent and water molecules away from lanthanide(III) centres.

The design and synthesis of lanthanide complexes with charged and/or neutral chelating organic ligands offers the possibility to obtain stable compounds with quite particular optical properties. A relevant aspect of this research consists in the possibility to optimize these properties of a particular lanthanide(III) ion by suitable choice of ligands.

The recent interest towards Organic Light-Emitting Diodes (OLED) based on organolanthanide complexes[22] stems on the fact of the observed peculiar mechanism of

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emission in regions different according to the lanthanide. Specifically the ligand acting as antenna, absorbs the light, and then transfers the energy towards the coordinate metal ion (Er^{3+}), poorly absorbing in the visible, while efficiently emitting in the near infrared (NIR) region. With the aim to enhance the luminescence efficiency of these materials, the accurate choice of peculiar ligands assumes crucial relevance due to both the window of use and the stability. Quite recently, a versatile approach to the development of lanthanide complexes that emit in the NIR based on tropolone (H-L_T) as ligand has been found.[23] Upon deprotonation, tropolones can be used as seven-membered ring, bidentate oxygen-donor chelators that allow direct coordination of the chromophoric group to the Ln^{III} cation. Their hard Lewis base character is suitable for forming strong bonds with Ln^{III}. Furthermore, tropolone has a good electronic structure to act as an antenna because the energy of its triplet state (16800 cm^{-1}) is compatible for efficient energy transfer to the low accepting levels of several Ln^{III} ions that emit in the NIR such as Nd^{III}, Er^{III}, Ho^{III}, and Tm^{III}. In the past, $[Ln(L_T)_3]$ and $M[Ln(L_T)_4]$ ($M = NH_4^+, Na^+$) complexes have been prepared.[24] Upon changing the counterion to K^+, the complexes $K[Ln(L_T)_4](dmf)$ have been prepared and fully characterized also by X-ray diffraction investigations.[23] In these complexes the coordination around the lanthanide cation has been described as a distorted dodecahedron. Quantitative luminescence measurements indicated that the tropolonato ligands are able to sensitize several lanthanide cations that emit in the NIR domain.[23]

Other studies have been successfully carried out on tris-β-diketonato lanthanide complexes containing also functionalized dipyridine or phenanthroline ligands that are known as very good sensitizers and many excellent papers have been published consequently.[25] In particular, the addition of the phenanthroline ligand acts to saturate the coordination number of Ln^{III} ions and also to improve the fluorescence intensity, volatility and stability of the Ln^{III} complexes[26]

In order to enhance the optical properties we have used as ligand 2-hydroxy-4-isopropylcyclohepta-2,4,6-trien-1-one (4-isopropyltropolone, also known as hinokitiol or β-thujaplicin) (H-hino) and prepared the tris-tropolonato complexes $[Er(hino)_3(phen)]$, and $[\{Er(hino)_3\}_2(pdon)]$ by reaction of H-hino with $ErCl_3\cdot 6H_2O$ and 1,10-phenanthroline or 1,10-phenanthroline-5,6-dione in methanol, respectively, in the presence of NaOH. Furthermore, 1,10-phenanthroline-5,6-dione was successfully used as appropriate ditopic ligand for dinuclear lanthanide complexation. In fact, it permits to coordinate two lanthanide(III) ions in the opposite side of the molecule by the N_2 and O_2 donor atoms allowing an interesting interaction between the two coordinated metal ions. In particular, $[\{Er(hino)_3\}_2(pdon)]$ was obtained following a procedure similar to that employed for the phenanthroline analogue. The complexes were characterized by ^1H NMR, ESI MS and IR spectroscopy and elemental analysis, moreover a photophysical characterization in solution was performed. All the complexes display an absorption in the UV region, while the subsequent emission in the NIR region (≈ 1550 nm) is quite interesting and comparable with the best emitter compounds up to now reported. This paper reports the physicochemical properties arising from this molecular aggregation.

Results and Discussion

Synthesis of the Complexes

The tris-tropolonato lanthanide(III) complexes of Er^{III}, Eu^{III}, and Yb^{III} have been prepared accordingly to Scheme 1.

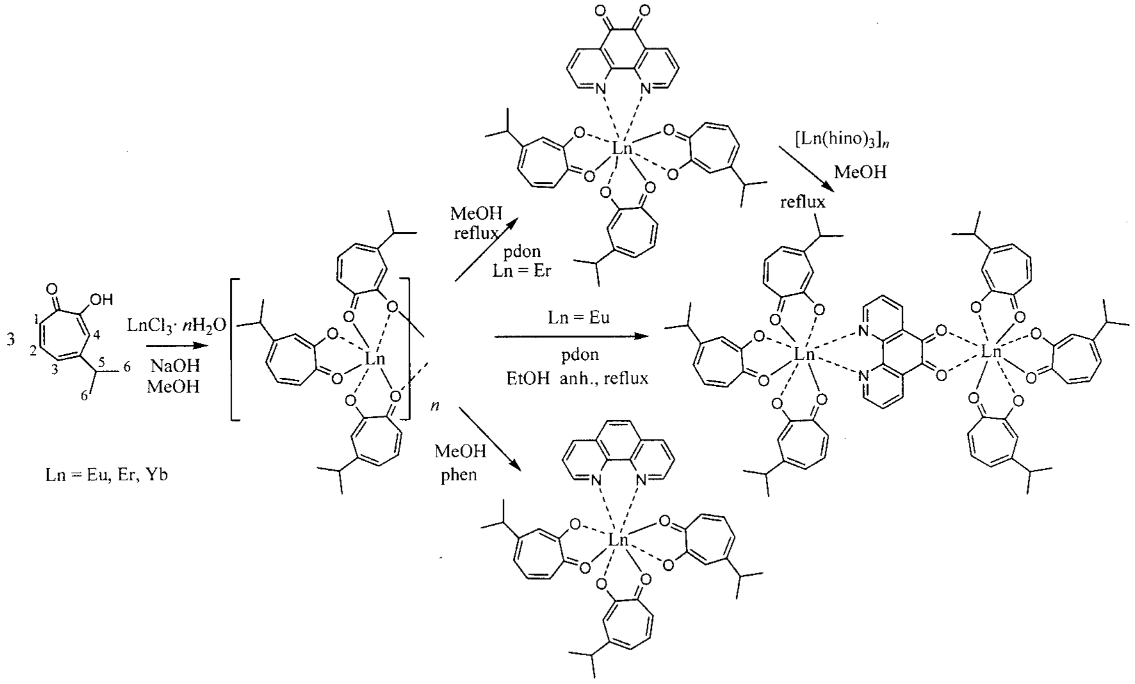
In particular the tris-tropolonato Ln^{III} complexes obtained by reaction of a methanolic solution of 4-isopropyltropolone (H-hino) with NaOH and the appropriate lanthanide(III) trichloride hexahydrate and recovered from a water/methanol solution, show only trace of water or methanol according to elemental analyses and thermogravimetric and IR investigations. Furthermore, the complexes are stable in air for long periods of time. We suppose that, in order to complete the high coordination number required by these lanthanides(III) ions, the complexes are in the form $[Ln(hino)_3]_n$ (n = 2 or 3). NMR spectra in CD_3OD or $CDCl_3$ show in fact the correct pattern [shifted depending on the paramagnetism of lanthanide(III) metal ion] of the tropolonato ligand with very small amount of free water. Only the $[Eu(hino)_3]_n$ complex in $(CD_3)_2SO$ shows a double pattern of the tropolonato ligand, indicating the different role of the oxygens bridging the Eu^{III} ions.

This is not a very surprising result; many β-diketonate complexes, for instance, can loose a solvent molecule coordinated to the central metal ion giving rise to an easy oligomerization through oxygen bridges of the chelating ligands. The lack of quenching in the fluorescence of these complexes (vide postea) is an additional proof of the absence of water in the coordination environment of the erbium(III) ion.

This dimeric or trimeric complexes can easily turn into the monomeric one in the presence of the chelating ligand 1,10-phenanthroline. The resulting complex $[Er(hino)_3(phen)]\cdot H_2O$ is soluble in a variety of solvents, such as MeOH, EtOH, $CHCl_3$, CH_2Cl_2, CH_3CN, DMSO, but insoluble in H_2O and *i*PrOH. The IR spectra of the complex show the characteristic strong absorption bands at (cm^{-1}) 1588 (νC=O), 1504 (νAr, C=C), 1239–1240 (νC–O). Thermogravimetric analyses indicate a 1.71% weight loss at 92 °C, in agreement with the loss of one non-coordinated water molecule. Again the presence of water only in the crystalline framework and not directly bonded to the central metal ion is proved by the photophysical behaviour (vide postea).

The complex appears to be monomeric with the metal ion in an octacoordinated environment.

A further functionalization of the periphery of the chelating nitrogen-containing ligands was introduced in order to allow them to serve as dinucleating ligands towards equal



Scheme 1.

or different lanthanide(III) ions. 1,10-Phenanthroline-5,6-dione (pdon) is a suitable ditopic ligand: it contains two well separated coordinating sites, one containing two nitrogen atoms and one containing two oxygen atoms, both suitable for lanthanide(III) complexation. Thus, the reaction of $[Er(hino)_3]_n$ with pdon in anhydrous methanol in a 1:1 molar ratio under reflux affords $[Er(hino)_3(pdon)]\cdot 0.2H_2O$ with the lanthanide(III) ion coordinated to the two nitrogen atoms of the functionalized phenanthroline. In fact, ^1H NMR experiments performed in CD_3OD of diamagnetic yttrium and lutetium complexes[27] $[Ln(hino)_3(pdon)]$ show a significant downfield proton shift of CH-N (from 8.95 to 9.12 ppm) and the corresponding upfield shift of CH-C=O (from 8.55 to 8.45 ppm) with respect to the free pdon. This mononuclear complex, by reaction of $[Er(hino)_3]_n$ in anhydrous methanol in a 1:1 ratio under reflux gives rise to the homodinuclear $[\{Er(hino)_3\}_2(pdon)]\cdot H_2O$. Elemental and thermogravimetric analyses of the mononuclear and dinuclear complexes agree with the proposed formulations, whereas IR spectra show nearly the same pattern, with the characteristic strong absorption bands at (cm^{-1}) 1688–1689 (νC=O, pdon), 1588 (νC=O), 1504–1505 (νAr, C=C), 1239–1240 (νC–O). The NMR spectra of $[Er(hino)_3(pdon)]\cdot 0.2H_2O$ and $[\{Er(hino)_3\}_2(pdon)]\cdot H_2O$ in $(CD_3)_2SO$ have the same pattern as well, but in the spectrum of the dinuclear complex, the peaks related to the protons of 4-isopropyltropolone are of double intensity (with respect to the pdon proton intensity) compared to those present in the spectrum of the mononuclear complex, therefore showing the presence of six 4-isopropyltropolonate units to one of 1,10-phenanthroline-5,6-dione in the dinuclear complex.

It must be noted that, under anhydrous conditions, using the precursor $[Eu(hino)_3]_n$ and pdon in a 1:1 molar ratio, only the homodinuclear complex $[\{Eu(hino)_3\}_2(pdon)]$ was obtained. This complex, shows the same IR spectrum as that of the related Er^{III} complexes above reported, but a different NMR pattern system, in which the peaks of the two $Eu(hino)_3$ units are shifted each other, as inferred by 2D COSY and NOESY experiments: peaks at $\delta = 7.32$ (4-H), 6.81 (1-H), 5.94 (3-H), 4.51 (2-H), 2.37 (5-H), 0.86 (6-H) are related to one 4-isopropyltropolonate unit, and peaks at $\delta = 4.86$ (3′-H), 3.49 (4′-H), 3.28 (1′-H), 3.09 (2′-H), 1.33 (5′-H), 0.08 (6′-H) to the other unit, while the signals at $\delta = 8.97$, 8.36, and 7.65 correspond to the protons of 1,10-phenanthroline-5,6-dione.

Population of gas phase ions generated by ESI-MS was studied to prove the presence of polynuclear complexes. The structural assignments of such ions are supported by their characteristic isotopic distributions particularly affected by the presence of erbium and europium atoms ($^{166}Er/^{167}Er/^{168}Er$ of 1:1.5:1.25) ($^{151}Eu/^{153}Eu$ of 1:1.1) and exact mass measurements.

The spectra of $[Ln(hino)_3(phen)]$ and $[Ln(hino)_3(pdon)]$, (Ln = Er and Eu) parallel each other and shows a fragmentation pattern consistent with the proposed formulation. In particular, it is interesting to note that, under the experimental conditions used for the spectra acquisition (1% HCOOH in $MeCN/H_2O$, 1:1 solution), the detected peaks are due to species ranging from $[Ln(hino)_2]^+$ to $[Ln(hino)_3(H\text{-}hino)_3]^+$, $[Ln(hino)(L)]^{\cdot +}$, and $[Ln(hino)_3(L)]^+$ (L = phen, pdon). Thus, while for $[Er(hino)_3(phen)]$ the parent peak is clearly detectable at the appropriate *m*/*z* value, the

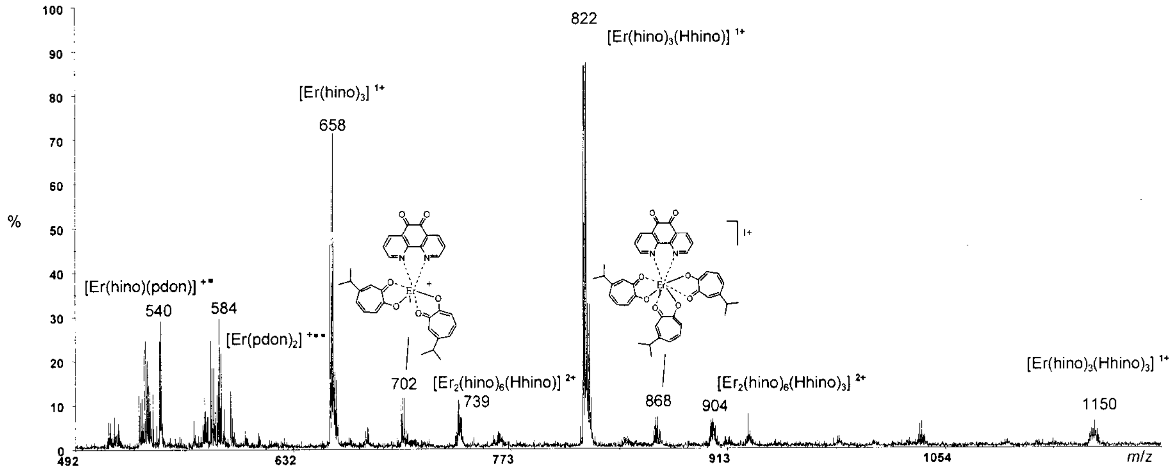


Figure 1. ESI mass spectrum in the positive mode of the methanolic solution of [Er(hino)$_3$(pdon)].

parent peak of the dinuclear complex [{Ln(hino)$_3$}$_2$(pdon)] was not detected probably owing to the particular experimental condition adopted.

As an example, the mass spectrum of [{Eu(hino)$_3$}$_2$(pdon)] is reported in Figure 1; the most relevant species present in solution are indicated. The obtained data clearly show the rearrangement of the starting complex, this favouring the formation of complexes with a progressively higher number of tropolonato ligands about the central metal ion. This is certainly due to the high affinity of this particular α-diketone towards lanthanide(III) ions.

Photophysical Properties

All the investigated Er^{III} complexes in anhydrous DMSO dilute solution display strong and broad UV absorption band due to transitions between the electronic states of the organic ligand. On the contrary the UV/Vis absorption peaks arising from transition between the Er^{3+} ground and excited states are only barely recognizable because of their small oscillator strength. In particular, as shown in Figure 2 (A) for the [Er(hino)$_3$(pdon)] complex, only the $^2H_{11/2}$–$^4I_{15/2}$ transition gives rise to a detectable absorption peak at 520 nm.

Upon optical excitation in the absorption bands of the ligand, the characteristic Er^{3+} emission due to the transition $^4I_{13/2}$–$^4I_{15/2}$ can be easily observed [Figure 2, (A)] indicating that an efficient energy-transfer process between the ligand and the manifold of Er^{3+} excited state takes place. The quantum yield (QY) of the IR emission is nearly the same of the corresponding peak observed in a [Er(Q)$_3$][28] (HQ = 8-hydroxyquinoline), i.e. of the order of few 10^{-4}, in agreement with the data reported for similar tropolonate-based complexes.[23] The emission bandwidth is about 60 nm, significantly larger than the corresponding one in Er-doped silica, suggesting a high inhomogeneous disorder of Er^{3+} surroundings, which hinder any possible differences among different complexes.

Deeper insight about the processes involved in the IR emission of these complexes can be obtained from time-resolved measurements. In such a way it is possible to evaluate independently the efficiency of the ligand→Er^{3+} energy transfer and the efficiency of the Er^{3+} photoluminescence (PL) quenching processes. Indeed, the PL intensity immediately after the excitation pulse [PL(t = 0)] depends only on the efficiency of the energy transfer, because the quenching of the Er^{3+} excited states occurs in a relatively long timescale. On the other hand, the lifetime of the Er^{3+} PL is strongly affected by the presence of non-radiative decay channels but is not related to the efficiency of Er^{3+} excitation processes that take place within few ns. In Figure 3 the PL decay trace is showed for the [Er(hino)$_3$(pdon)] complex with the corresponding fit obtained using a single exponential function. The found lifetime (τ_{tot}) for the [Er(hino)$_3$(pdon)] complex is 2.12 µs, while it is not possible to observe any PL rise time. This confirms that the excitation of the Er^{3+} is extremely fast. The agreement between experimental and fitted data is perfect indicating that all the Er^{3+} ions experiment the same mean local environment. Quite similar measurements have been obtained for all the studied complexes, and the corresponding lifetimes and PL efficiencies are reported in Table 1.

Because the radiative lifetime (τ_{rad}) of the Er^{3+} $^4I_{13/2}$–$^4I_{15/2}$ transition is around 10 ms,[29] i.e. about 10^4 time longer the PL-detected decay time, the origin of the low efficiency of the 1550 nm emission has to be ascribed completely to the presence of fast quenching processes as usual for all the Er^{3+} complexes. Indeed the $^4I_{13/2}$–$^4I_{15/2}$ transition is nearly resonant with both the first overtone of the O–H stretching vibration and the second overtone of the C–H one. By contrast the indirect excitation pathway of the Er^{3+} ion seems to be rather efficient because: i) no 1550 µm PL rise time is detectable, at least in the employed timescale, and ii) the QY evaluated from the ratio between radiative and total PL lifetime (QY = τ_{tot}/τ_{rad}) and that obtained from the comparison of the integrated PL of tropolone-based complexes and of [Er(Q)$_3$] are in good agreement. As a confirmation, it should be pointed out that in all considered complexes the distance between the Er atom and the closest H atom (C–H bond), belonging to phenanthroline ligand, has been

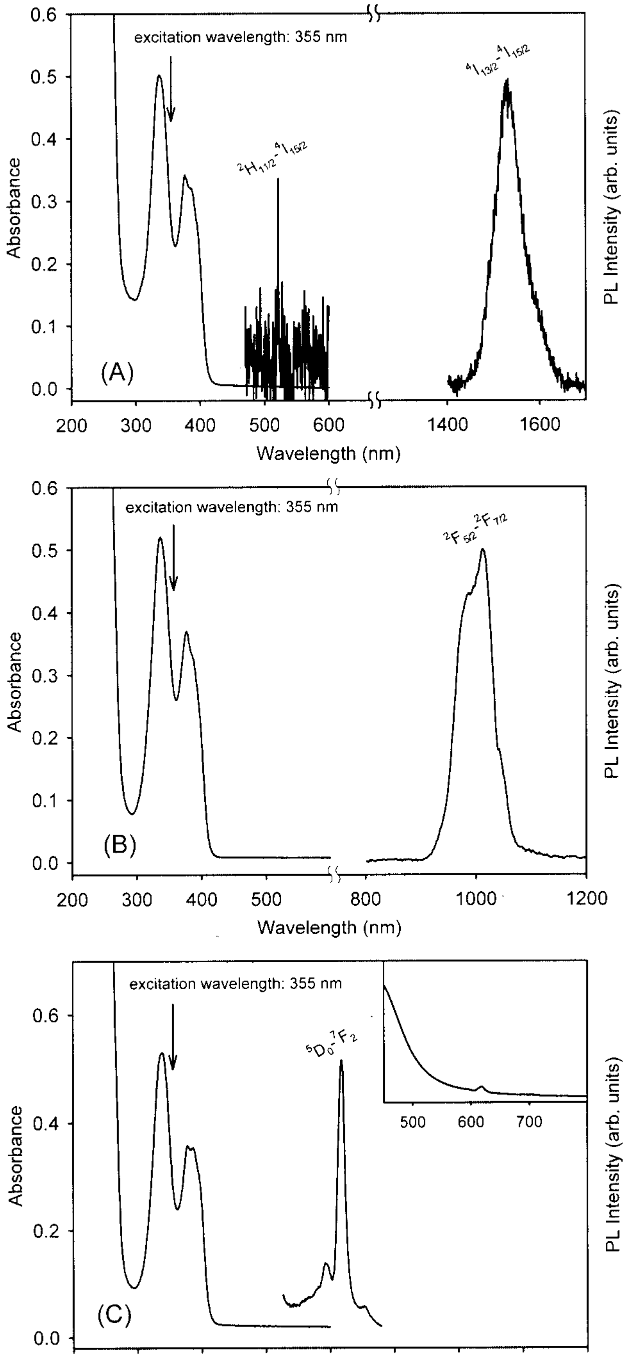


Figure 2. Absorption (left) and emission (right) spectra of the $[Er(hino)_3(pdon)]$, $[Yb(hino)_3]_n$ and $[Eu(hino)_3]_n$ complexes in DMSO at room temperature [(A), (B), and (C)] respectively. The absorption spectrum in the region of the $^2H_{12/2}$–$^4I_{15/2}$ Er^{3+} transition (520 nm) has been multiplied by 100. In the panel (C) the broad PL from the ligand has been subtracted (the recoded spectrum is reported in the inset).

evaluated, from molecular modelling calculations, near to 0.41 nm; hence accounting for a reduced PL in NIR region.

It is interesting to outline that the measured PL decay times ($\tau > 2.10$ µs) are systematically longer in the studied complexes than in $[Er(Q)_3]$ ($\tau = 1.80$ µs), while the PL ($t = 0$) is larger in this reference complex (see Table 1). This behaviour can be tentatively explained assuming that the bond length between the ligand and the rare earth ion are longer in the tropolone-based complexes than in $[Er(Q)_3]$, because both Er^{3+} excitation and PL quenching involve energy-transfer processes which strongly depend on the distance (R) between donor and acceptor moieties (the transfer rate is proportional $1/R^6$ or to e^{-R} for the Förster and Dexter mechanisms, respectively). Moreover, also the ability of the synthesized complexes to shield the Er^{3+} ion from water molecules should be rather good, being the O–H vibration of these latter another source of non-radiative decay channels.

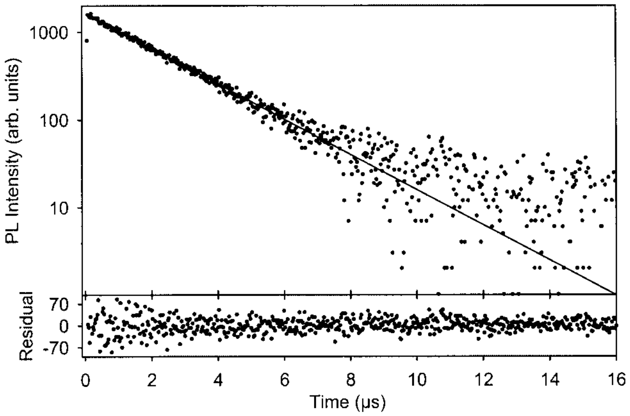


Figure 3. PL decay trace of the $[Er(hino)_3(pdon)]$ complex in DMSO (dots) recorded at 1550 nm complex at room temperature. The continuous line is the fit obtained with a single exponential function. The PL lifetime is 2.12 µs.

Table 1. Main optical data of the studied Er^{III} complexes. All the reported efficiencies have been normalized to the values of $[Er(Q)_3]$ which has been set to 100.

	Lifetime	Relative transfer efficiency	Relative total efficiency
$[Er(Q)_3]$	1.80 µs	100	100
$[\{Er(hino)_3\}_2(pdon)]$	2.11 µs	107	125
$[Er(hino)_3(pdon)]$	2.12 µs	91	108
$[Er(hino)_3(phen)]$	2.15 µs	106	127
$[Er(hino)_3]_n$	2.15 µs	91	108

In Figure 2 (B, C) also typical absorption/emission spectra of the $[Yb(hino)_3]_n$ and $[Eu(hino)_3]_n$ complexes have been reported. In the case of Yb^{III} complexes, upon the excitation of the ligand at 355 nm, the emission at around 1 µm due to the $^2F_{5/2}$–$^2F_{7/2}$ rare-earth transition is rather strong. Even if quantitative measurements have been not performed, the QY of these complexes is about two order of magnitude larger than in the corresponding Er^{III} complexes. The $^2F_{5/2}$–$^2F_{7/2}$ PL decay is again a single exponential with a lifetime as long as 70–80 µs, which suggest the lack of any efficient quenching process in agreement with the observed high emission efficiency. On the contrary in the Eu^{III} complexes the sharp emission of the lanthanide at 615 nm, even if still detectable, is extremely week and partially overlapped to the low energy tail of the ligand PL

[Figure 2 (C)]. In particular, in the tropolone-based complexes only the first Eu^{3+} optical transition ($^5D_0$–$^7F_2$) is nearly resonant with the first triplet excited state of the ligand at about 16800 cm^{-1} (595 nm). However, due to its small oscillator strength, this transition can not be excited efficiently via energy transfer.

Conclusions

The erbium(III) derivatives $[Er(hino)_3]_n$, $[Er(hino)_3(phen)]$, $[Er(hino)_3(pdon)]$, and $[\{Er(hino)_3\}_2(pdon)]$ containing the tropolonato moiety and designed to test the IR emission on varying the chemical surrounds at the metal(III) ion were synthesized and characterized by IR, NMR, thermogravimetry, and both absorption and emission spectroscopy. The PL efficiency at 1550 nm has been measured for the whole series; values larger than that for $[Er(Q)_3]$ were observed, even though they were still affected by quenching due to the relatively short distances between the C–H bonds and the Er atom. However the longer lifetimes with respect to the $[Er(Q)_3]$ complex indicate that in tropolone complexes the number of such short distances should be diminished and and/or their values have been augmented, encouraging to design new ligands where H atoms are placed more far away. The absence of water molecules coordinated to europium(III) ion in $[Eu(hino)_3]_n$ is remarkable and somewhat unexpected. Owing to this and the high stability in the solid state and the easy formation of the phenanthroline adduct $[Eu(hino)_3(phen)]$, it is an excellent starting complex for the preparation of more sophisticated tropolonato-containing complexes.

Experimental Section

Materials: The solvents, the inorganic and organic compounds and the lanthanide chloride hydrates were commercial products, supplied by Aldrich, Riedel-de Haën, Carlo–Erba, or Fluka. They were used as received, without further purification. 4-Isopropyltropolone is a TCI-GR product.

Preparation of $[Ln(hino)_3]$ (Ln = Er, Yb, Eu): To a methanolic (40 mL) solution of 4-isopropyltropolone (H-hino) (0.3 mmol), NaOH in methanol was added in a 1:1 ratio. Then $LnCl_3\cdot 6H_2O$ (Ln = Er, Yb, Eu) (0.1 mmol) was added, and the resulting solution was stirred for 4 h. The solution was reduced in volume and water was added. The precipitate formed was collected by filtration, washed with water and dried in vacuo.

$[Er(hino)_3]_n$: IR (cm^{-1}): $\tilde{\nu}$ = 1588 (νC=O), 1504 (νAr, C=C), 1239 (νC–O). $C_{30}H_{33}ErO_6$ (656.83): calcd C 54.86, H 5.06; found C 54.80, H 5.17. ^1H NMR $[(CD_3)_2SO$, paramagnetic]: δ = 7.45, 5.45, 3.48, 1.39, 1.07, 0.31, –1.26, –2.83, –3.63, –3.90, –7.34, –10.25 ppm.

$[Yb(hino)_3]_n$: IR (cm^{-1}): $\tilde{\nu}$ = 1588 (νC=O), 1505 (νAr, C=C), 1241 (νC–O). $C_{30}H_{33}O_6Yb$ (662.61): calcd. C 62.29, H 5.75; found C 60.91, H 5.74. ^1H NMR $[(CD_3)_2SO$, paramagnetic]: δ = 13.06, 8.34, 7.21, 6.57, 5.97, 5.03, 3.28, 2.77, 0.79, 0.63, –0.05, –1.17, –3.42, –7.46, –9.20 ppm.

$[Eu(hino)_3]_n$: IR (cm^{-1}): $\tilde{\nu}$ = 1588 (νC=O), 1504 (νAr, C=C), 1239 (νC–O). $C_{30}H_{33}EuO_6$ (641.53): calcd. C 56.17, H 5.19; found C 55.92, H 5.02. ^1H NMR $[(CD_3)_2SO$, paramagnetic]: δ = 7.28, 6.79, 5.90, 5.87, 4.82, 4.47, 3.46, 3.09, 2.29, 1.28, 0.78, 0.01 ppm.

Preparation of $[Er(hino)_3(phen)]$: To a methanolic solution of 4-isopropyltropolone (40 mL, 0.3 mmol), NaOH in methanol was added in a 1:1 ratio. Then $ErCl_3\cdot 6H_2O$ (0.1 mmol), was added. The resulting solution was added to a methanolic solution (20 mL) of 1,10-phenanthroline (phen) (0.1 mmol) and stirred for 4 h. The solution was reduced in volume and water was added. The precipitate formed was collected by filtration, washed with water and dried in vacuo.

$[Er(hino)_3(phen)]\cdot 1H_2O$: IR ($cm^{-1}$): $\tilde{\nu}$ = 1588 (νC=O), 1504 (νAr C=C), 1240 (νC–O). $C_{42}H_{43}ErN_2O_7$ (855.05): calcd. C 59.00, H 5.07, N 3.28; found C 59.14, H 4.88, N 3.00. These values are in agreement with thermogravimetric data. ^1H NMR $[(CD_3)_2SO$, paramagnetic]: δ = 9.09, 8.49, 7.99, 7.77, 0.38, –1.34, –2.84, –3.17, –3.77, –7.58, –10.53 ppm.

Preparation of $[Er(hino)_3(pdon)]$: $Er(hino)_3$ in anhydrous methanol (40 mL) was added to 1,10-phenanthroline-5,6-dione dissolved in anhydrous methanol (20 mL) in a 1:1 molar ratio, and the resulting solution was refluxed overnight. After refluxing, a brown precipitate appears, that was centrifuged off. The clear solution was evaporated to dryness and the solid was washed with diethyl ether, filtered and dried in vacuo.

$[Er(hino)_3(pdon)]\cdot 0.2H_2O$: IR ($cm^{-1}$): $\tilde{\nu}$ = 1588 (νC=O), 1504 (νC=C Ar), 1240 (νC–O). $C_{42}H_{39.1}ErN_2O_{8.2}$ (870.32): calcd. C 57.00, H 4.67, N 3.17; found C 56.52, H 4.56, N 2.91. ^1H NMR $[(CD_3)_2SO]$, paramagnetic: δ = 8,96, 8.36, 7.65, 4.02, 0.37, –1.35, –2.85, –3.85, –7.63, –10.54 ppm.

Preparation of $[\{Er(hino)_3\}_2(pdon)]$: $Er(hino)_3$ in anhydrous methanol was added to $[Er(hino)_3(pdon)]$ dissolved in anhydrous methanol in a 1:1 molar ratio, and the solution was refluxed for 1 day. The solution was reduced in volume and diethyl ether was added. The precipitate now formed was collected by filtration and dried in vacuo.

$[\{Er(hino)_3\}_2(pdon)]\cdot H_2O$: IR ($cm^{-1}$): $\tilde{\nu}$ = 1588 (νC=O), 1505 (νC=C, Ar), 1239 (νC–O). $C_{72}H_{74}Er_2N_2O_{15}$ (1541.85): calcd. C 56.09, H 4.84, N 1.82; found C 55.48, H 4.71, N 1.66. ^1H NMR $((CD_3)_2SO)$, paramagnetic: δ = 8.97 (2 H, pdon), 8.36 (2 H, pdon), 7.66 (2 H, pdon), 3.14, 1.05, 0.34, –1.29, –2.82, –3.69, –3.88, –7.46, –10.42 ppm.

Preparation of $[\{Eu(hino)_3\}_2(pdon)]$: $Eu(hino)_3$ dried in vacuo at 100° was dissolved in anhydrous ethanol and 1,10-phenanthroline-5,6-dione in anhydrous ethanol was added in a 1:1 molar ratio. The solution was refluxed for 3 h under nitrogen, then it was reduced in volume. Diethyl ether was added and the precipitate formed was filtered and dried in vacuo.

$[\{Eu(hino)_3\}_2(pdon)]$: IR (cm^{-1}): $\tilde{\nu}$ = 1588 (νC=O), 1503 (νC=C Ar), 1239 (νC–O). $C_{72}H_{72}Eu_2N_2O_{14}$ (1493.24): calcd. C 57.91, H 4.86, N 1.88; found C 56.79, H 4.59, N 2.21. ^1H NMR $[(CD_3)_2SO$, paramagnetic]: δ = 8.97 (2 H, pdon), 8.36 (2 H, pdon), 7.65 (2 H, pdon), 7.32 (4-H), 6.81 (1-H), 5.94 (3-H), 4.86 (3′-H), 4.51 (2-H), 3.49 (4′-H), 3.28 (1′-H), 3.09 (2′-H), 2.37 (5-H), 1.33 (5′-H), 0.86 (6-H), 0.08 (6′-H) ppm.

Physico-Chemical Measurements: Elemental analyses were carried out with a Fison 1108 analyzer. IR spectra were recorded as KBr pellets with a Mattson FTIR spectrometer. NMR spectra (^1H, ^{13}C) were recorded with a Bruker AMX300 spectrometer equipped with direct and inverse broad-band multinuclear probes. The T_1 longitudinal relaxation times and the mixing times of NOESY experiments of the paramagnetic europium complex were measured using the standard inversion recovery pulse sequence. All ESI-MS spectra measurements were performed with a LCQ mass spectrometry (Finnigam) in methanol solutions of the samples (10^{-5} M) eluted with MeCN/H_2O (1:1) solution with 1% of HCOOH. The water content in the prepared samples was evaluated by thermal analysis curves using a Netzsch STA 429 thermoanalytical equipment. The tests were performed under nitrogen (flux rate 250 mL/min; heating rate 5 °C min^{-1}) and in air under the same conditions. Neutral alumina (Carlo–Erba product) was used as reference material.

All the optical characterizations have been performed in anhydrous DMSO dilute solution. As reference, also [Er(Q)$_3$] [tris(8-hydroxyquinolinato)erbium(III)] solutions, which is currently the benchmark for non-fluorinated organolanthanide and coordination complexes, have been prepared. UV/Vis absorption measurements have been done with a Cary 50 (Varian) spectrophotometer. NIR photoluminescence (PL) measurements have been carried out by exciting the samples with the third harmonic of a pulsed ND:YAG laser (λ_{exc} = 355 nm, pulse duration ca. 10 ns, repetition rate 20 kHz, power ca. 1 mW). The laser beam was focused on the samples with a cylindrical lens (spot dimension about 7×0.5 mm^2) in order to minimize the complex degradation. The PL emission was detected with a Hamamatsu R5509-73 photomultiplier (or with a Spex 2000 CCD in the case of emissions in the visible) coupled with a Cornerstone (Oriel) monochromator (bandwidth 20 nm). The PL spectra and PL decay traces have been recorded in photon counting mode with a Ortec 9353 multichannel scaler. The overall time resolution is better than 30 ns.

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