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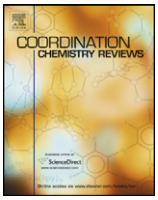

Review

NIR-emissive erbium–quinolinolate complexes

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ABSTRACT

Studies addressed to a deep understanding of the structure/property relationship on the near infrared (NIR)-emissive erbium–quinolinolate complexes, which are of interest for low-cost photonic systems, are reviewed. The role of the 8-quinolinolate ligand (Q), which studies also as sensitizer to overcome the weak absorptivity of lanthanide ion, is discussed. Synthetic and structural aspects are reported to revise the old assumption that these complexes are analogous in structure to AlQ_3 and to point out the specificity of the lanthanide coordination chemistry. In fact depending on reaction conditions, species with high coordination numbers and differing for nuclearity and stoichiometry have been isolated and fully characterized. In some instances it has been shown that coordinated water molecules directly bounded to the emitting erbium ion definitely represent the most effective quenchers for the luminescence at 1.5 μm. Additionally, the combined optical and structural investigation of water-free Er–quinolinolate complexes, allows one to conclude that the C–H groups sitting in the Er^{3+} inner coordination sphere represent a very severe limit to the near-infrared emission yield. Implementation of structural/spectroscopic data into a theoretical model based on Förster's energy transfer resonant theory provides a comprehensive analysis of the near infrared emission quenching in erbium complexes useful to predict the quenching effects in luminescent lanthanide-complexes from the measurements of the vibrational absorption spectrum of the compound, the lanthanide radiative lifetime, and the minimum distance between the emitting ion and the quenchers. On that basis, in order to significantly improve the near-infrared emission yield, ligands which do not bear NH, CH or OH groups at a distance shorter than 7–8 Å from the emitting ion are required. At the same time high sensitization efficiency of near-infrared emission and population saturation of trivalent erbium is achieved in these complexes, photoexcited into the absorption band of the quinolinolate sensitizer. It is concluded that a fully halogenated quinolinolate ligand can be an optimal candidate to improve the luminescent properties of erbium complexes.

1. Introduction

Since the first report by Tang and Van Slyke [1–3] which showed that AlQ_3 (Q = 8-quinolinolate) is a valued green emitter for OLED (organic emitting diodes), extensive work has been performed to improve the properties of organic light emitting devices based on "small molecules" (low molecular weight molecule-OLEDs), toward the development of flat panel displays and other emitting devices [4–6]. Emission from AlQ_3 is due to an intra-ligand transition which is strongly enhanced by ligand coordination to the metal ion. This transition involves HOMO–LUMO ligand π-orbitals, where the phenoxide moiety gives a predominant contribution to the HOMO,

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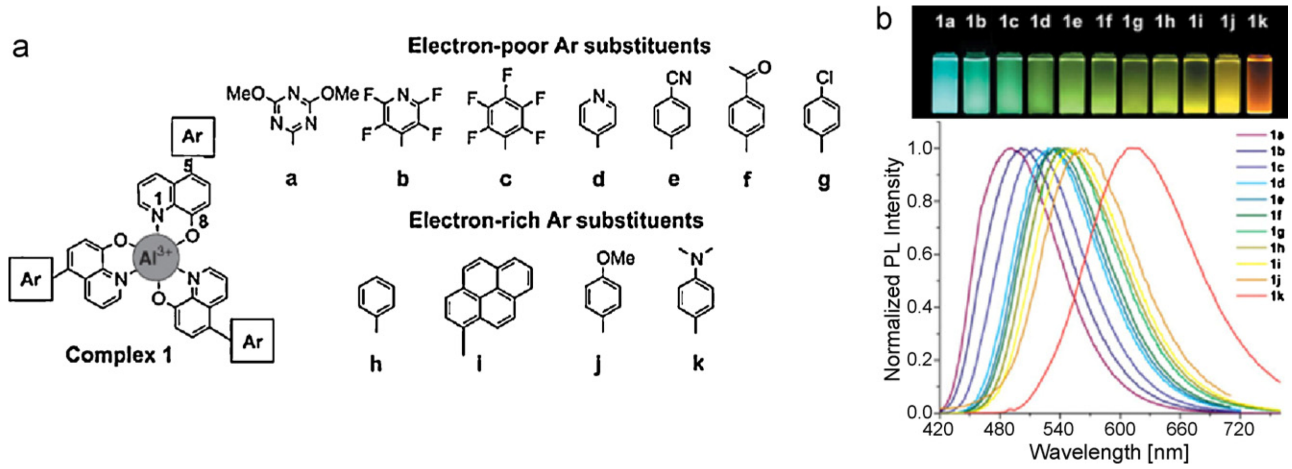


Fig. 1. Structure of some aluminium(III) quinolinolates (a) and their corresponding photoluminescence and emission spectra in CH_2Cl_2 solution (b). Reprinted with permission from Ref. [8]. Copyright 2004 Wiley-VCH.

while the pyridyl moiety to the LUMO. The HOMO–LUMO transition can be tuned by introducing suitable substituents at the phenoxide and/or pyridyl ring. In particular it is predictable that an electron-withdrawing group at C-5, C-7 of the phenoxide ring will induce a blue shift (pushing down the HOMO energy), while an electron-donating group at the same positions will induce a red shift (pushing up the HOMO energy). Similar influences on the LUMO energy can be achieved by proper substitution at the pyridyl ring. In these last years, many efforts have been made to improve the luminescence properties of this class of emitting molecules and to “fine-tuning” the emission wavelength by varying the metal ion or the nature and the position of the substituents on the ligands [2,7,8]. As an example an impressive blue to red tuning of the emission of aluminium tris-8-quinolinolate complexes has been achieved on varying the electron donating properties of substituents at C-5 of Q, as shown in Fig. 1. Moreover the AlQ_3 complex is neutral, stable, suitable to be processed by vacuum thin film deposition, and shows electron-transport properties, as required to be used for efficient OLED.

In the earlier 1990s [9,10], lanthanide ions were proposed as luminescent materials for electroluminescent devices, because their metal-based line-like emission is long-lived and can be considered as nearly monochromatic. The unique properties of lanthanide ions are relatable to their [Xe] $4f^n$ electronic configurations. The 4f electrons being shielded by the 5s and 5p electrons, are little affected by the crystal field or similar effects, in contrast to the behavior of d-levels. For this reason metal-based line-like absorption/emission spectra are observed. The 4f electrons of the ions can be placed in any of the 4f orbitals and this gives rise to many spectroscopic terms and energy levels. Lanthanides with energetically close f-levels [M(III) = Nd, Pr, Ho, Er, Tm, Yb) give rise to emission in the NIR region. The Nd^{3+}, Er^{3+}, Yb^{3+} (and, in part, Pr^{3+}), NIR-emitting ions, have recently gained much popularity because, besides their several potential applications in telecommunications and biomedical analysis, recent advances in electronics and detector technology allow the detection of weak NIR emission by means of readily available and low cost devices [11–17]. Among the NIR-emitting lanthanide ions, Er^{3+} plays a special role in telecom technologies, since it displays a sharp emission occurring at the wavelength of 1.55 μm (0.8 eV), thus covering a spectroscopic window in which glass optical fibers show high transparency (the so-called third-communication window). Doped silica fibers such as EDFAs (Erbium Doped Fiber Amplifiers) are at the heart of the optical amplification technology used in the long-haul communication systems operating in the 1.5-μm spectroscopic window. Also Yb^{3+}, Pr^{3+} and Nd^{3+}, are being used as dopants in optical amplifiers since they can strengthen the signal in the first and second-communication windows, at 1 μm and 1.33 μm wavelengths. A disadvantage of this technology stems from the weak absorptivity of lanthanide ions, being f–f transitions symmetry forbidden, and their very low solubility in all inorganic matrices, resulting in long and expensive amplifiers. To overcome these problems metal complexes where the metal is coordinated to an organic ligand, which can work also as sensitizer, are employed to realize a new generation of low-cost optical amplifiers in the centimeter-length scale, featuring superior optical and mechanical figures of merit, and suitable for the fabrication of photonic integrated circuits [18,19].

Among the several complexes extensively investigated as emitting materials in the last decade, the potential of lanthanide–quinolinolates as low cost emitting materials in the near-infrared region followed the demonstration of the first electrically excited IR emitter based on the erbium complex [20–28], formerly supposed to be formulated as ErQ_3, in analogy with the structurally characterized AlQ_3. Despite the interest of physicists into these compounds, since recently, literature lacked completely in optimized synthetic procedures, and the structures of lanthanide quinolinolates were not available. Photoluminescent studies on this and similar complexes have shown lifetimes much shorter than the natural radiative lifetime of the Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. The unexpectedly short lifetime (in the 2 μs range) and the low quantum yield were ascribed to the presence of CH of the Q-ligand and OH groups of solvent (including water) eventually present in the solvent and supposed to be the most important IR quenchers. This implied that in ErQ_3 the ligand was unable to protect the ion from further coordination by solvent or moisture. The reason of the low quantum yield claimed for a quantitative understanding of IR quenching mechanisms in these materials and several contributions have been provided to help to clarify this point [29–35]. This has led in some instances to questionable assignments of the deactivation mechanisms affecting the luminescence properties of lanthanide quinolinolates. Therefore, a detailed understanding of the structure/property relationship was strongly demanded. The aim of this review is, by using the NIR emitting erbium–quinolinolates as a case study, to point out how experimental data based on well documented synthetic strategies and characterization, including structural data, are of crucial importance for the interpretation of the photophysical properties to achieve a reliable structure/property relationship, which is required to provide guidelines to design lanthanide complexes with improved luminescence efficiency.

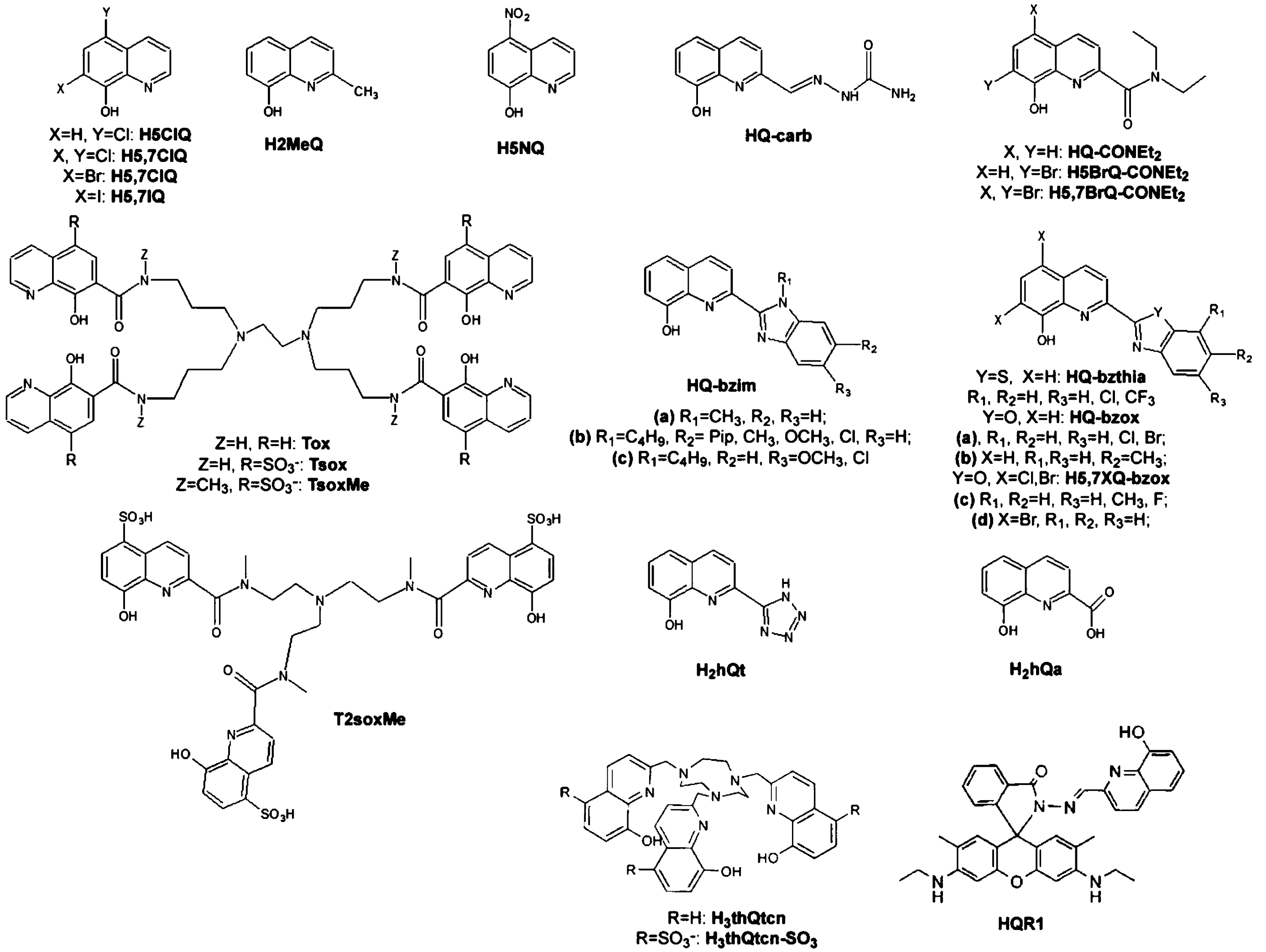


Chart 1. Some quinolinol derivatives used to prepare luminescent complexes with lanthanide ions.

2. Synthesis and characterization of NIR-emissive lanthanide–quinolinolate complexes

In this section, the coordination chemistry of quinolinolates with Er^{3+} is reviewed. In addition, compounds with other lanthanide ions which are similar in some aspects and can be useful as reference to assess and explain the photophysical properties of this class of emitting molecules, are included.

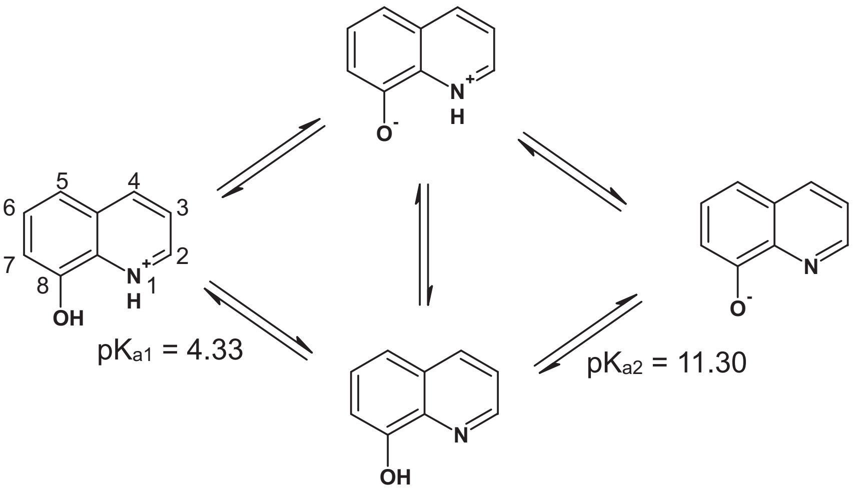
Quinolinol (Q) ligands, for long known as efficient extraction agents toward trivalent lanthanide ions [36–39], are in addition suitable “antenna” ligands and for these reasons have been extensively employed to prepare lanthanide-containing materials for electroluminescent (EL) applications [20–28]. Photophysical applications of this class of compounds developed earlier than their chemistry were fully investigated. Sophisticated physical measurements on samples with LnQ_3 stoichiometry and assumed to be structurally analogs to AlQ_3, gave rise to ambiguous interpretations of the photophysical properties of these compounds.

Besides the parent 8-quinolinol (HQ), several other quinolinol derivatives, either bidentate or multidentate, have been employed so far (see Chart 1). In particular, dihalo-substituted quinolinols have been tentatively used to improve the emission efficiency by reducing the number of CH quenching groups in the complex, and derivatives bearing additional functionalities are used to improve the properties of the compound obtained, including the “shell-type” protection to the ion from water molecules (the main luminescence quencher in the NIR), the carrier transport and antenna capacities as well as the processability [29–31,40–51].

The quinolinol ligand undergoes several protic equilibria in solution, involving neutral, anionic and protonated forms (Scheme 2.1). A tautomeric equilibrium also exists which leads to the zwitterionic form bearing the proton on the nitrogen atom of the pyridine ring. The acidic character of the ligand is remarkably affected by the presence of substituents, and increases when electron-withdrawing groups are located in the *para*- and *ortho*-positions with respect to the phenolic group. Electron-donating groups, such as a methyl substituent, on the pyridine ring, on the other hand, increase the pK values of both the dissociations [52]. As an example, the pK_a values for some 8-quinolinols are reported in Table 2.1.

Table 2.1
pK_a values of some quinolinol derivatives (**HQ** = 8-quinolinol; **H5,7ClQ** = 5,7-dichloro-8-quinolinol; **H5,7BrQ** = 5,7-dibromo-8-quinolinol; **H2MeQ** = 2-methyl-8-quinolinol) [51].

Ligand	pK_{a1}	pK_{a2}
HQ	4.33	11.30
H5,7ClQ	1.70 ± 0.02	8.90 ± 0.02
H5,7BrQ	1.00 ± 0.02	8.95 ± 0.02
H2MeQ	4.45	11.63



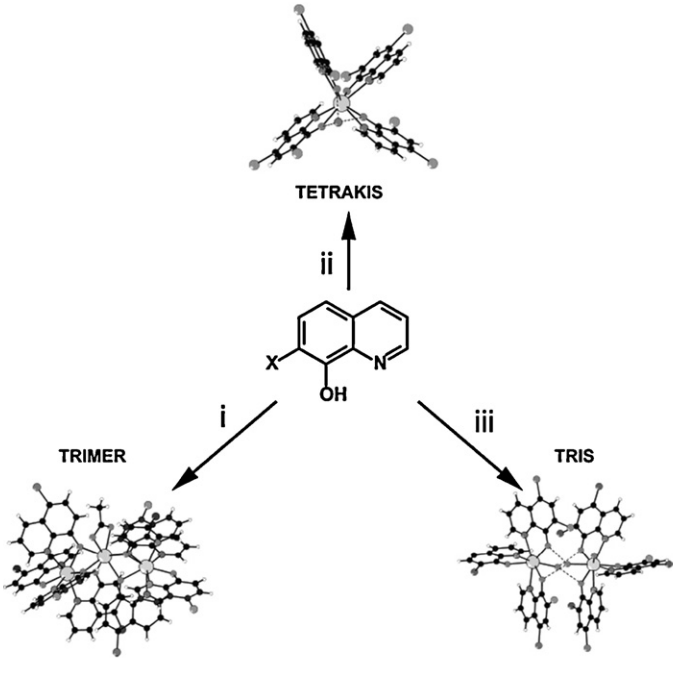
Scheme 2.1. Protic equilibria of 8-quinolinol.

2.1. *Complexes with bidentate 8-quinolinols*

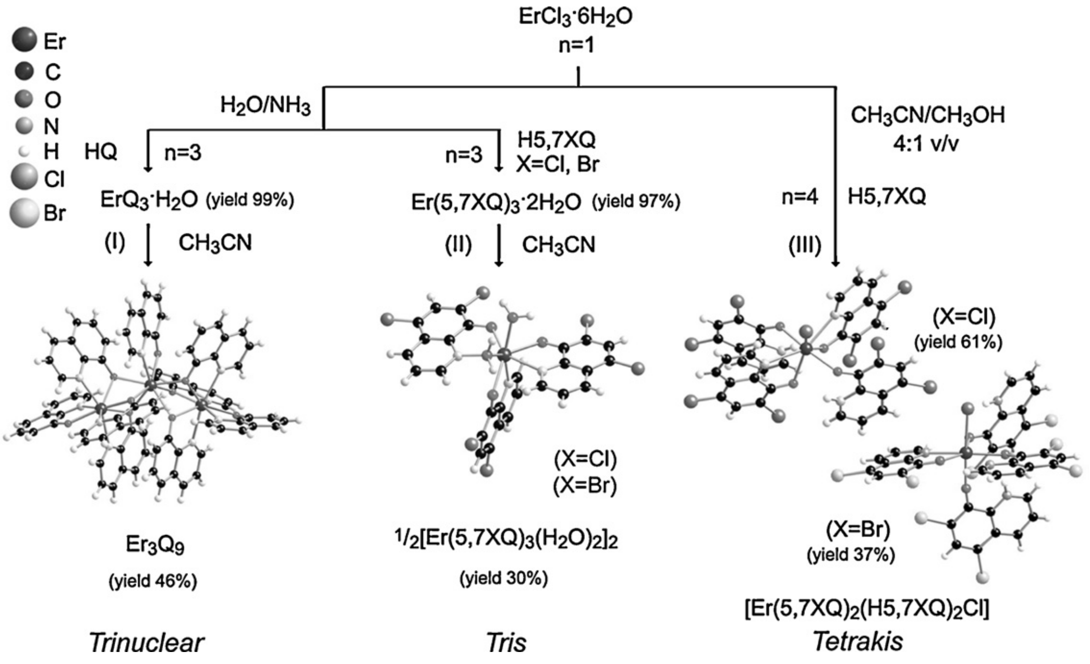
Going back to the hystorical development of chemical studies on lanthanide quinolinato compounds, the first report by Pirtea goes back to 1936 [53]. In the light of previous results on the structure of quinolinolates of trivalent metals [54] the author assumed a tris-chelated octahedral structure for La**Q**$_3$. Since then, several papers have reported controversial assumptions on the stoichiometry of complexes with 8-quinolinol (**HQ**) and its derivatives [20–33,36–39]. One of the most frequently used literature procedure for the preparation of these complexes was described by Aly et al. [37]. According to this synthetic method, an ethanolic solution of HQ is added to a solution of lanthanide nitrate in water. The crude product, which precipitates after addition of a slight excess of ammonia solution, corresponds to 1:3 metal-to-ligand ratio. In 2001, Khreis et al. [28] reported a study on the emission properties of Yb**Q**$_3$ used as emitting centre in an electroluminescence device (OLED). The complex was prepared following a slightly different method in which a water solution of lanthanide chloride is slowly added to a solution of the ligand in methanol/water mixture without addition of a base.

Van Deun and co-workers [55] deeply reinvestigated commonly used literature synthetic procedures and showed that the reaction products of lanthanide salts with HQ and some halo-derivatives, consist of a mixture of species having different stoichiometries rather than a single product. One of the identified species contains three lanthanide ions bridged by the Q ligands (“trimeric” complexes of general formula $Ln_3Q_8^+$), and is the predominant product when using 8-quinolinol and 5-chloro-8-quinolinol as ligands either following a slight altered version of the method described by Aly et al. [37] and the method reported by Khreis et al. [28]. Instead, by using 5,7-dihalo-quinolinol ligands (H5,7XQ, X = Cl, Br, I), mixtures of the dimeric *tris* $[Ln(5,7XQ)_3(H_2O)_2]_2$ (consisting of two *tris* complex units linked by hydrogen bond interactions) and *tetrakis* ($NH_4[Ln(5,7XQ)_4]$) complexes with 1:3 and 1:4 metal-to-ligand ratio have been obtained employing a different synthetic route in which ammonium acetate and an excess of the ligand in acetone were added to the lanthanide chloride solution (see Scheme 2.2). In conclusion the work by Van Deun et al. demonstrated that this class of compounds actually possesses a rich structural chemistry and that the nature of the products obtained strongly depends on the reaction conditions (solvent, pH) and on the ligand. However, the reported improved methods, aimed at obtaining pure products, have proven to be successful only in the case of saline *tetrakis*-type compounds, while the isolation of pure “trimeric” and *tris* species was taken as unfeasible. Moreover, in the case of compounds with the unsubstituted 8-quinolinolate, water molecules are directly bounded to the lanthanide ion and this is detrimental for near-infrared emission efficiency as discussed in Section 3.

A reinvestigation on the preparation and characterization of lanthanide (Er, Yb, Nd, Gd) compounds with **HQ** and **H5,7XQ** (X = Cl, Br) ligands has been independently carried out by our group [56–58]. As a result of these studies, water-free, neutral and pure products suitable to be processed for optical devices, following well-defined synthetic methods, have been isolated. Depending on the reaction conditions, three different kinds of neutral erbium complexes in high yields are obtained, as summarized in Scheme 2.3. Apparently small differences in the reactions’



Scheme 2.2. Summary of synthetic procedures to obtain lanthanide quinolinolate compounds as reported by Van Deun et al. [55]: (i) “Trimeric” species are formed only when X = H, in the absence of small cations. (ii) *Tetrakis* species can be formed for X = H or a halogen. Na^+ counterions give pure species. NH_4^+ gives mixtures. (iii) *Tris* species are formed for X = halogen and with as few cations as possible. Adapted with permission from Ref. [55]. Copyright 2004 American Chemical Society.



Scheme 2.3. Reaction scheme of erbium salt with quinolinolate ligands as reported in Ref. [56]. Reprinted with permission from Ref. [57]. Copyright 2007 Wiley-VCH.

conditions produce different products: (i) the water-free, “pure” *trinuclear* complex $Er_3\mathbf{Q}_9$ obtained when $\mathbf{Q}$ is the unsubstituted ligand deprotonated by NH_3 either in water or ethanol/water mixtures; (ii) the *tris* dimeric complexes where the mononuclear unit consists of $[Er(\mathbf{5,7XQ})_3(H_2O)_2]$ [X = Cl and Br] where the ion is octacoordinated to three deprotonated ligands and to two water molecules, obtained with the same method as (i); (iii) the *tetrakis* mononuclear $[Er(\mathbf{5,7XQ})_2(\mathbf{H5,7XQ})_2Cl]$ [X = Cl and Br] complexes, where only two of the four coordinated ligands are deprotonated, obtained by mixing the erbium chloride with **H5,7XQ** in organic solvents (CH_3CN/CH_3OH 4:1) without addition of a base. The different behavior of the parent quinolinolate and of the 5,7-halo substituted is relatable to electronic and steric effects induced by the presence of halo substituents at the phenoxide ring.

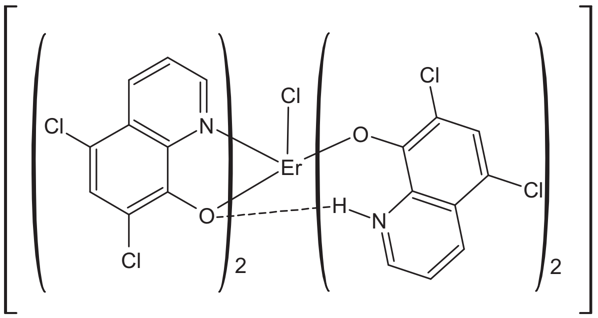
As shown the trinuclear and *tris* species achieve the octacoordination around the lanthanide ion, while the *tetrakis* type complexes take the rather unusual coordination number of 7 (coordination is provided by two bis-chelating, two monodentate ligands and one chloride). Structural evidence show that in the trinuclear $Er_3\mathbf{Q}_9$ molecule each metal presents a distorted anti-prismatic geometry with the two outer metals bound by four nitrogen and four oxygen atoms whereas the inner erbium is co-ordinated by a nitrogen and seven oxygen atoms. The capability of $\mathbf{Q}$ to work as bridging ligand allows the erbium ion to achieve the preferred coordination number 8, also in the presence of only three ligand molecules per ion. Spectroscopic results and ESI-mass data on $Er_3\mathbf{Q}_9$ in solution show that the trinuclear structure is preserved in solution. In this complex a “shell-type” protection to the ion from water or solvent molecules is achieved as further supported by photophysical results (see related section) which are similar in solution and in the solid state. Noteworthy these studies have definitively demonstrated that the compound with $Er\mathbf{Q}_3$ stoichiometry obtained through literature methods, is not structurally analog to $Al\mathbf{Q}_3$, as wrongly assumed in the past, but rather the trinuclear species above described. Accordingly, several studies, and also the formula of the product reported in the Sigma Aldrich catalogue, need to be corrected [59].

Strict control of several parameters such as pH, temperature, solvents and reaction times is required to ensure the completion of the reaction and the formation of the desired product with high purity and high yields; otherwise, a mixture of products results. For example in aqueous solution, the use of the weak base NH_3 to deprotonate the quinolinol ligand is preferable with respect to a strong base, such as NaOH, which often leads to impure products. This may be ascribed to a possible direct coordination of the OH^- group to the lanthanide ion or to a nucleophilic attack on the 2 position of the pyridine ring forming 2-hydroxycarbostyril [60]. Moreover, trivalent lanthanide cations are strong Lewis acids, displaying the tendency to form insoluble hydroxides and oxides (Ln_2O_3), even at rather low pH. In fact, Er^{3+} hydroxides or oxides precipitate from perchlorate solution at pH 6.61 ($K_{sp} = 4.1 \times 10^{-24}\ mol^5\ l^{-5}$) [61].

By comparing our results affording the trinuclear species with those reported in Ref. [54] on the same reaction in water, it may be suggested that the crude products are the same and correspond to $Ln_3\mathbf{Q}_9$ in agreement with analytical results (metal to ligand ratio 1:3; and ESI-mass corresponding to $Ln_3\mathbf{Q}_8^+$). Instead the formation of crystals characterized as $NH_4[Er_3\mathbf{Q}_8Cl(OH)]\cdot 4C_4H_8O_2$ in Ref. [55], obtained by using ethanol as solvent and short reaction times, may be tentatively ascribed to the precipitation of an ionic intermediate before the reaction has gone to completion in organic solvents where the salts are less soluble.

Conversely, the formation of a mononuclear *tris* species instead of the trinuclear complex when using the dihalo-substituted 8-quinolinol ligands, is ascribable to the steric hindrance of the halogen atom in the 7 position of the quinoline ring which prevents the bridging arrangement, as stated in Refs. [55,57].

Tetrakis complexes, where two ligands are in the anionic form and the other ones are “zwitterionic” (see Scheme 2.4), were obtained in the absence of a base thanks to the increased acidity of the dihalo-substituted 8-quinolinols (due to the presence of electron-withdrawing groups especially on the 5-position of the phenoxy-ring) with respect to the unsubstituted one [52], so that partial ligand deprotonation immediately takes place upon addition of the Er^{3+} salt. It can be inferred that the formation of the “zwitterionic” complex from the reaction mixture under neutral conditions undergoes competitive prototropic equilibria between the different forms of the quinolinol (see Scheme 2.4), strongly

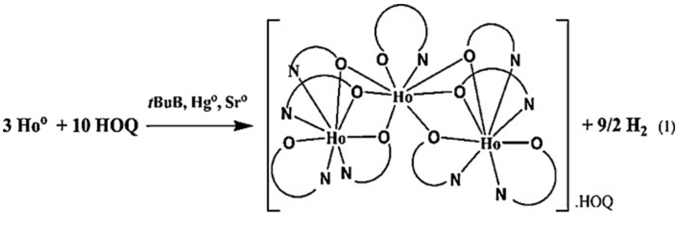


Scheme 2.4. Structure of the *tetrakis* [Er(**5,7ClQ**)$_2$(**H5,7ClQ**)$_2$Cl] complex [57], with two ligands in the anionic form and two as zwitterions. Dashed line indicates hydrogen bonding.

influenced by the presence of the metal ion. These equilibria involve both the quinolinolium (**H$_2$5,7XQ$^+$**) and the quinolinolate (**5,7XQ$^-$**) ions along with the zwitterionic form of the ligand, although the acidic character of the lanthanide ion probably shifts the equilibrium toward the protonated form. The tautomeric rearrangement of the neutral quinolinol in the complex is probably due to the preference of the strong Lewis acid Ln^{3+} for anionic oxygen donor atoms.

Following the synthetic procedures described in Scheme 2.3, the Nd^{3+} and Yb^{3+} quinolinolates as well as Gd^{3+} corresponding complexes have been also prepared [58]. The compounds obtained in water, namely the *trinuclear* and the *tris* complexes, were isolated as pure products in high yields. Noteworthy *tetrakis* complexes of neodymium, as well as of other metals belonging to the first half of the series of lanthanides (Ce–Eu) have not been obtained. *Tetrakis* complexes seem to be achievable starting from the mid-term of the series, the Gd^{3+} ion, at the border between the "light" and the "heavy" lanthanides [62]. This behavior may be ascribed to the "lanthanide contraction" effect. In fact lanthanide ions of the first half of the series have larger ionic radii and prefer coordination numbers higher than 7 as found in *tetrakis* species.

Shortly after the demonstration of the existence of a "pure" trinuclear structure for Ln^{3+} 8-quinolinolate [56], Deacon et al. [63] reported on the synthesis and structural characterization of Ho$_3$**Q**$_9$·**HQ**, which is isostructural with Er$_3$**Q**$_9$. This compound was obtained according to a synthetic procedure remarkably different from those described above, by reacting 8-quinolinol with holmium metal in the presence strontium metal and metallic mercury at 190 °C under vacuum in a 1,3,5-tri-*tert*-butylbenzene flux (see Scheme 2.5). This pseudo-solid-state synthetic approach, based on the direct reaction of metals in their elemental state with the **HQ** ligand at elevated temperatures in the presence of an inert flux, was also applied to obtain the heterobimetallic Ln$_2$Ca**Q**$_8$ (Ln = Nd, Eu) complexes and LaCo$_2$**Q**$_7$ [64]. Similar trinuclear structures of lanthanide/alkaline earth heterobimetallic species with ligand **H2MeQ**, of general formula [Ln$_2$Mg(**2MeQ**)$_8$] (Ln = Eu, Gd, Tb, Er), obtained by a rearragement reaction between the two **2MeQ**-complexes of Ln^{3+} and Mg^{2+} at 200–300 °C in a 1,2,4,5-tetramethylbenzene (TMB) flux have been very recently reported [65]. However, several byproducts are obtained using this synthetic procedure which does not seem easily controllable and does not lead to well defined products.



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Scheme 2.5. Synthesis of Ho$_3$**Q**$_9$·**HQ**. Reprinted with permission from Ref. [63]. Copyright 2005 Wiley-VCH.

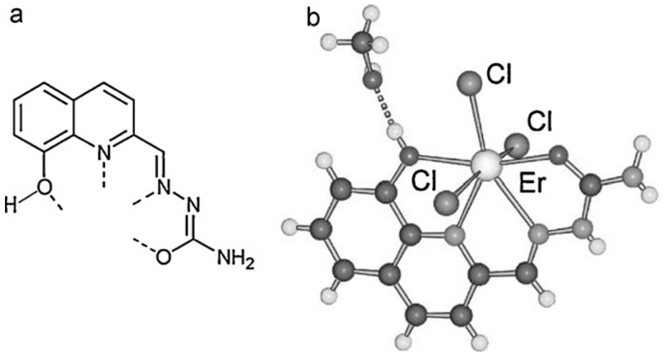


Fig. 2. Ligand **HQ-carb** coordination mode (a) and structure of the [(**HQ-carb**)ErCl$_3$] complex (b). Adapted with permission from Ref. [42]. Copyright 2005 Royal Chemical Society.

2.2. Complexes with multidentate ligands based on 8-quinolinol

The reported examples show that the reaction of 8-quinolinol and its derivatives with lanthanide metals affords a variety of complexes different for nuclearity and stoichiometry. In order to improve the coordination properies of 8-quinolinolate derivatives to lanthanide(III) ions several authors are investigating the coordination ability of new ligands, where the efficiency of the quinolinolate as antenna ligand is maintained and the introduction of additional donor groups is aimed to improve its binding capability to saturate the metal coordination. This strategy seems suitable to favor the formation of stable complexes, since lanthanide coordination chemistry, mainly ruled by steric reasons rather than orbital directionality, is often an "entropy driven" process which takes advantage of complexation with a chelating ligand resulting in a decrease in hydration of the lanthanide ion, with a positive entropy change (chelating effect) [16]. Moreover such multidentate ligands should provide efficient shielding of the lanthanide emitter from the intrusion of external quenchers in the first coordination sphere.

In Fig. 2, the erbium(III) complex [(**HQ-carb**)ErCl$_3$] with the tetradentate **HQ-carb** ligand (Chart 1), the semicarbazone of 8-hydroxy-quinoline-2-carbaldehyde, is shown. This complex has been prepared by reacting **HQ-carb** with one equivalent of erbium(III) triflate in the presence of an excess of potassium chloride, or directly from the ligand and erbium(III) chloride. Given that, in the absence of a base, the phenolic group of the quinoline moiety remains protonated, three chloride either fill the Ln^{3+} coordination sphere and balance the metal 3+ charge. In this case the use of a ligand with several donor sites (four) did not lead to controllable products since 2:1 ligand-to-metal complexes or mixtures of 1:1 and 2:1 or dimeric species can be also found [42].

Ligand **HQR1**, see Chart 1, bears a rhodamine group, and has been proposed as a promising antenna ligand with two chromophoric units. An ytterbium(III) complex was prepared in methanol solution by the reacting (**HQR1**) with 1 equivalent of Yb(NO$_3$)$_3$·5H$_2$O. Upon coordination, the rhodamine 6G moiety of the ligand change its forms from a closed and non-fluorescent spirolactam-ring tautomer to a ring opened tautomer while the 8-quinolinol unit, even in the absence of a base, loses a proton, leading to the formation of a tetradentate ligand. In this case a 1:2 metal to ligand complex was obtained where the Yb^{3+} ion is chelated by two ONNO tetradentate units from two **QR1**$^-$

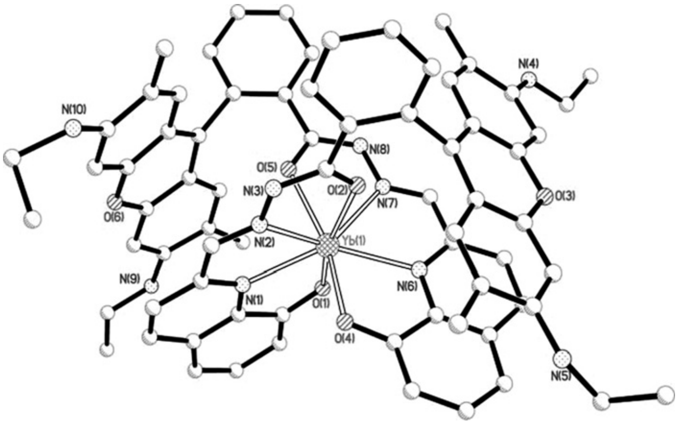


Fig. 3. Molecular structure of the cationic $[Yb(\mathbf{QR1})_2]^+$ with the atomic-numbering scheme. The anions, solvent molecules and hydrogen atoms are omitted for clarity. Reprinted with permission from Ref. [43]. Copyright 2009 Royal Chemical Society.

ligands fulfilling the coordination environment of the central lanthanide ion. Unfortunately, crystals of this compound, formulated as $[Yb(\mathbf{QR1})_2]NO_3{\cdot}CH_3OH{\cdot}H_2O$ were obtained after two weeks of slow solvent evaporation in a very low yield, and the collateral formation of a 1:1 complex, could not be definitely ruled out [43]. The molecular structure of the $[Yb(\mathbf{QR1})_2]^+$ cation complex is reported in Fig. 3.

On the other hand, the use of tridentate instead of tetradentate ligands can lead to better control of the nuclearity of complexes. In fact, by using **HQ-CONEt$_2$**, **H5BrQ-CONEt$_2$** and **H5,7BrQ-CONEt$_2$** ligands of Chart 1, mononuclear, water-free, 1:3 metal to ligand ratio lanthanide complexes were obtained [44]. These complexes were prepared by reaction with appropriate hydrates of lanthanide(III) salts in methanol at 55 °C using potassium carbonate as base. The red product obtained after slow evaporation of the solvent, extraction with dichloromethane and subsequent crystallization showed to be the neutral Ln(**Q-CONEt$_2$**)$_3$ (Ln = Yb, Eu, Er, Nd) complex. In this case the three tridentate ligands effectively saturate the lanthanide ion providing nine-coordination. The structure of the erbium compound Er(**Q-CONEt$_2$**)$_3$·K(SO$_3$CF$_3$) is shown in Fig. 4. However, yellow side products of general formula LnL_nX_m ($X = Cl, SO_3CF_3$; $n + m = 3$) also form in this reaction, but they can be removed from the desired product thanks to differences in solubility.

Another interesting class of ligands based on 8-quinolinol to obtain lanthanide complexes with sensitized NIR-luminescence has been rather recently studied by Shavaleev et al. [45,46]. The idea beyond this is once again to extend the coordination site of 8-quinolinol by attachment of a chromophoric substituent (benzimidazole **HQ-bzim**, or benzothiazole/benzoxazole **HQ-bzthia/HQ-bzox/H5,7Q-bzox**, see Chart 1), bearing an additional donor site, in the 2-position of the Q-ring in order to obtain 3:1 complexes. This approach revealed to be successful and *tris* complexes of the early lanthanides (La^{3+}–Gd^{3+}) were obtained with ligands **HQ-bzim(a–c)** in rather high yields from ethanol/water solutions starting from $LnCl_3{\cdot}nH_2O$ and using NaOH as a base. Elemental and X-ray structural analyses confirmed the formulation of the complexes as [Ln(**Q-bzim**)$_3$]·nH$_2$O containing up to three molecules of crystallization water. In all of the structures, the lanthanide ion was nine-coordinate, with a tricapped trigonal prism coordination environment, by three ligands arranged in an "up–up–down" fashion around the metal center. However, the lanthanide ion is preferentially bound to the 8-quinolinolate moiety, while bonding to the benzimidazole (bzim) group is relatively weak, and this is reflected in longer Ln–N(bzim) bond lengths [45]. Similar results were obtained by using benzoxazole-substituted ligands (**HQ-bzox/H5,7XQ-bzox**, Chart 1). *Tris* Nd^{3+} and Yb^{3+} complexes were obtained as air- and moisture-stable intensely colored dark red solids from THF/water solutions starting from a stoichiometric 3:3:1 molar ratio of the ligand, base (NaOH or NEt_4OH), and $LnCl_3{\cdot}nH_2O$). The formation of mixed metal complexes containing both sodium and lanthanide was observed by using NaOH instead of the organic noncoordinating base NEt_3 [46].

When using **HQ-bzim(a–c)** ligands no satisfactory result was achieved with the synthesis of complexes of the heavier (Tb^{3+}–Yb^{3+}) and smaller lanthanide ions whereas the ytterbium(III) complex with ligand **H5,7BrQ-bzox** displays a structural arrangement in which only two ligands coordinate in a tridentate fashion while the other one is coordinated to the metal only through the phenolate oxygen allowing a water molecule entering the coordination sphere. This results in the formation of an hydrated species, [Yb(κ^3-**5,7BrQ-bzox**)$_2$(κ^1-**5,7XQ-bzox**)H$_2$O]. On the other hand, complexes with the "light" neodymium(III) ion always have a water free nine-coordinated "pure" *tris* structure [Nd(κ^3-**Q-bzox**)$_3$] and [Nd(κ^3-**5,7XQ-bzox**)$_3$]. Also in this case the different coordination behavior among ions belonging to the first or second half of the lanthanide series may be ascribable to the so-called lanthanide contraction. The structures of Nd^{3+} and Yb^{3+} complexes with the deprotonated **5,7BrQ-bzox**$^-$ ligand are reported in Fig. 5.

Very recently, a similar synthetic strategy aimed at obtaining 1:3 lanthanide complexes involving dianionic tridentate Q-derivatives (8-hydroxy-quinoline-2-carboxylic acid, **H$_2$hQa**, and 2-(1H-tetrazol-5-yl)quinoline-8-ol **H$_2$hQt**, Chart 1) has been reported [47]. It is proposed that dianionic ligands afford a better control of the coordination sphere and of the solubility and produce ionic complexes with potential application in the design of lanthanide-based iono-gels and ionic liquids [66]. Carboxylate and tetrazolate groups have been chosen as substituents in the 2-position of the quinoline ring to provide an appropriate additional binding site for the lanthanide ion. In fact, carboxylates have been widely used in lanthanide chemistry to yield water stable complexes [67], whereas tetrazolate groups, which can be considered convenient analogues of carboxylates, can be also used to tune the photophysical properties of lanthanides in podates or self-assembled complexes [68]. Syntheses were made by reacting a solution of $Ln(CF_3SO_3)_3$ (Ln = Nd, Er, Yb,) in water with 3 equivalents of ligand (**H$_2$hQa/H$_2$hQt**) at pH 12 adjusted by addition of aqueous KOH (1 M). Crystals of homoleptic tris-anionic tris-ligand complexes of general formulas [Ln(**hQa**)$_3$]K$_3$ and [Ln(**hQt**)$_3$]K$_3$ were obtained after crystallization from a mixture of methanol/diisopropylether. These complexes display a nine-coordinated structure where the dianionic ligand coordinates in a tridentate fashion through the 8-quinolinolate unity and the carboxylate (**hQa^{2-}**) or tetrazolate (**hQt^{2-}**) groups and adopts an

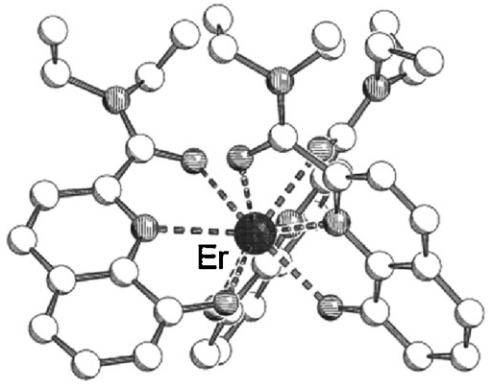


Fig. 4. Structure of Er(**Q-CONEt$_2$**)$_3$. Reprinted with permission from Ref. [44]. Copyright 2007 Royal Chemical Society.

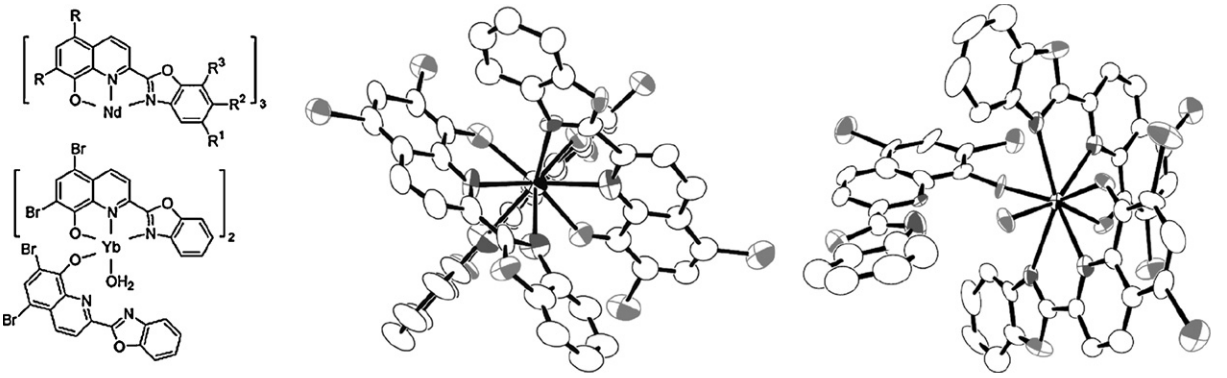


Fig. 5. Coordination and molecular structure of [Nd(κ^3-**5,7BrQ-bzox**)$_3$] (left) and of [Yb(κ^3-**5,7BrQ-bzox**)$_2$(κ^1-**5,7BrQ-bzox**)H_2O] (right). Adapted with permission from Ref. [46]. Copyright 2009 American Chemical Society.

helical arrangement. K^+ counterions interact with ligand O, N donor sites probably playing a role in the *syn* or *anti* conformation of the complex in the crystal lattice. When using triethylamine (Et_3N) as base instead of NaOH with ligand **H_2hQa**, only partial ligand deprotonation is observed affording [Nd(**$H_{1/2}$hQa**)$_3$]$_2$(Et_3NH)$_3$·Et_3NH CF_3SO_3. This compound, reported in Fig. 6, consists of two *tris* Nd complexes connected to form a dimer through hydrogen bonding between the three H atoms of the partially deprotonated ligand and the six phenol oxygen atoms. Protonation of the quinoline O donor site does not prevent coordination to the lanthanide ion.

More structurally elaborated polydentate ligands such as 8-quinolinol based podates (**Tsox** and **T2soxMe**, Chart 1) [48–50] were also proposed to obtain NIR-emitting lanthanide complexes with improved stability, kinetic inertness and water solubility, suitable to be used as molecular bioprobes. Unfortunately, although the authors claim the formation of 1:1 Ln:ligand chelates in water under controlled pH, no molecular structure is available as all the complexes were only studied in solution by means of UV–Vis titrations.

Mazzanti et al. [51] reported on the design and synthesis of tripodal 8-quinolinolate ligands based on 1,4,7-triazacyclononane (**H_3thQtcn**, **H_3thQtcn-SO_3**, Chart 1). Lanthanide (Nd, Er, Yb) complexes of the triply deprotonated ligand **thQtcn^{3-}** were prepared by mixing equimolar amounts of the Ln^{3+} triflate salt and of the ligand **H_3thqtcn** in methanol followed by slow diffusion of a 1 M KOH solution at 4 °C. Elemental analyses of all complexes are consistent with the presence of analytically pure 1:1 metal:ligand [Ln(**thqtcn**)] species. The isostructural structures of neodymium and ytterbium complexes show that the metal ion is nine-coordinated by the nine donor atoms of the ligand: three nitrogen atoms from the 1,4,7-triazacyclononane ring, three nitrogen and three oxygen atoms from the 8-quinolinolate units. The quinolinolate pendant arms bind the metal in a helical fashion, saturating its coordination sphere and preventing the intrusion of water molecules. The isostructurality of the neodymium and the ytterbium complexes indicates that the ligand **thqtcn^{3-}** is flexible enough to encapsulate lanthanide ions of different size. See Fig. 7a. While fully deprotonated species with the **thQtcn^{3-}** anion precipitate at pH > 5, at lower pH partially protonated species are observed. The crystal structure of the ytterbium(III) complex obtained at pH < 5, reveals a dimeric structure {[Yb(**$H_{1.5}$thqtcn**)]$^{3/2+}$}$_2$ similar to that of the above described [Nd(**$H_{1/2}$hQa**)$_3$]$_2$$^{3-}$, consisting of two equivalent monomeric complexes of the partially protonated **$H_{1.5}$thqtcn$^{1.5+}$** bridged by hydrogen bonds between the oxygen atoms of the deprotonated phenol group and the OH of the protonated ones (Fig. 7b).

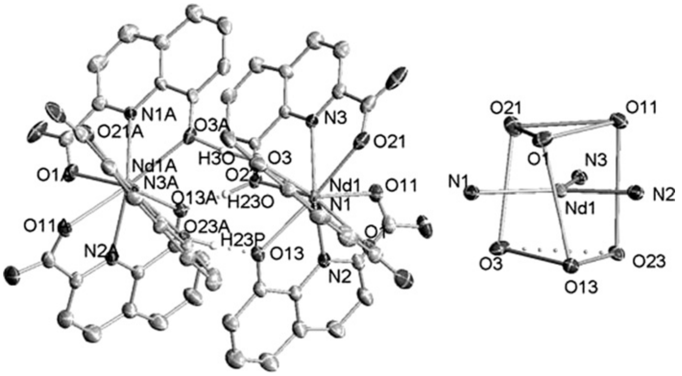


Fig. 6. ORTEP view of the anion [Nd(**$H_{1/2}$hQa**)$_3$]$_2$$^{3-}$ and coordination polyhedron. Atoms labelled A and P are *C*2-symmetry related. The ellipsoids are shown at the 30% probability level. Reprinted with permission from Ref. [47]. Copyright 2010 Royal Chemical Society.

Polydentate Q-derivatives have been also used to prepare homo- and heteronuclear multimetallic edifices. Albrecht et al. [69] succeeded in synthesize, isolate and characterize NIR-luminescent homodinuclear Yb/Yb and heterodinuclear Yb/Al helicates based on the 8quinolinol chromophore (Fig. 8).

These multimetallic edifices were obtained by a self-assembled synthesis from the ligand and lanthanide triflate in a 2:3 ratio (homodinuclear) and lanthanide triflate, $AlCl_3·xH_2O$ and the ligand in a 1:1:3 ratio (heterodinuclear) in the presence of K_2CO_3 as a base. Crystal suitable for X-ray analysis were obtained from methanol/THF/chloroform/ether solvent mixture in the case of Yb/Yb complex which show a helicoidal structural arrangement encapsulating K^+ ions in the cavities (see Fig. 8b). It was inferred that self-assembly of the homobimetallic helicates is templated by a potassium cation through a rare K^+–π interaction of C=C η^2-bond type.

In the light of the reviewed results, it can be underlined that lanthanide quinolinolates show a rich coordination chemistry but obtaining pure products is a difficult item. This is relatable on one side to the ligand features (presence of acid/base equilibria affected by electronic and steric factors induced by the substituents at the quinolinolate-rings) and on the other side to the peculiarities of the chemical properties of lanthanide ions related to their acid character, lanthanide contraction, ionic nature of the bonding. As a consequence it is very difficult to control the several factors which govern these reactions. In any case strict pH control is required. As reminded these ligands can coordinate lanthanide ions as protonated or partially protonated ligands leading to products with different stoichiometries. Weak non-coordinating bases, such as NH_3 or triethylamine seem to be preferable instead of common hydroxides to deprotonate the ligand to avoid OH^- coordinating to the lanthanide ion or reacting with the ligand. Moreover, given the

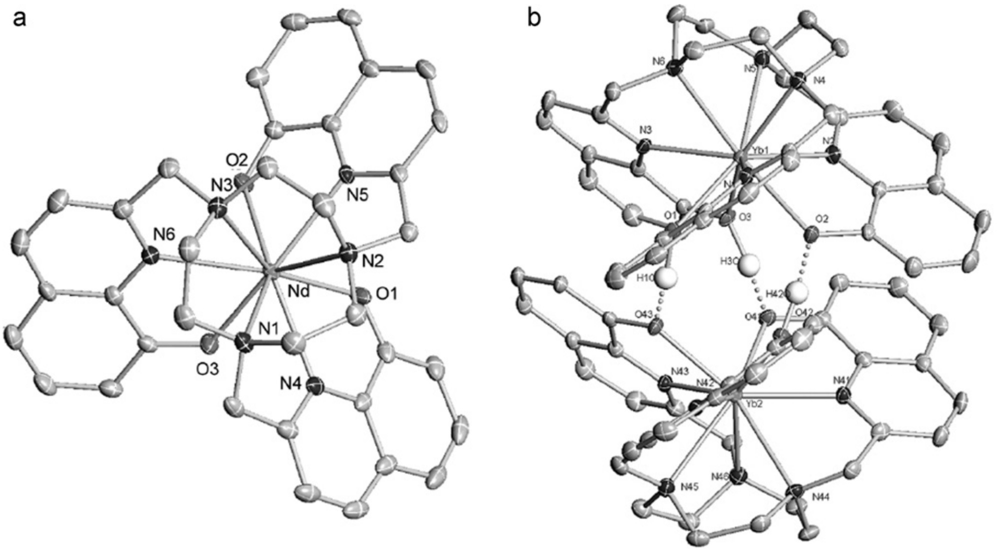


Fig. 7. Structure of Nd(**thqtcn**) (a) and $\{[\mathrm{Yb}(\mathbf{H_{1.5}thqtcn})]^{3/2+}\}_2$ (b) at the 30% probability level. Reprinted with permission from Ref. [51]. Copyright 2009 American Chemical Society.

diffuse radial dispersion of the core-like f orbitals, the complexation reaction is not governed by orbital directionality. Thus the nature of the coordination sphere, and consequently complex geometry, is controlled by a subtle interplay between electrostatic interactions (i.e. minimization of repulsive terms), chelating effects and steric constraints [70,71]. Differences in the crystallization enthalpy of complexes with different stoichiometries and structural arrangements (depending, for example, on π–π interactions, and hydrogen bonding) affect the course of the reactions.

3. Photo-physical properties

In the earlier 1990s, Lehn [72] coined the term “antenna” to denote the absorption, energy transfer, emission sequence involving distinct absorbing (the ligand) and emitting (the lanthanide ion) components in luminescent lanthanide complexes which work as *light conversion molecular devices* (LMCDs). This two-step excitation process allows one to achieve a large excited-state population using light fluences ($\mathrm{J/cm^2}$) four to five orders of magnitude lower than those required for bare ions and allows overcoming the weak absorptivity of lanthanide ions [73,74]. Scheme 3.1 shows, as an example for the erbium case, a simplified energy level scheme illustrating the energy transfer processes [6,75,76]. After optical excitation in the Near-UV ligand singlet excited states S_1 can either decay to the ground state S_0, or to triplet states T_n through an intersystem crossing (ISC) mechanism enhanced by heavy atom effect. Excited triplets can subsequently populate the upper levels of the lanthanide ion *via* resonance energy transfer (RET) [77] which can occur either *via* Dexter [78] or Förster [79] mechanisms, depending on total angular momentum variation (ΔJ) undergone by the lanthanide ion [80]. Following a fast excited-state ion relaxation, the radiative decay ${}^{(2S+1)}\Gamma_J \rightarrow {}^{(2S+1)}\Gamma_J$, yields the NIR emission of Ln^{3+} [81–84].

In a simplified model, the *overall* (or *absolute*) *luminescence quantum yield* Φ_{tot} of sensitised luminescence from a lanthanide complex can be written:

$$\Phi_{\mathrm{tot}} = \eta_{\mathrm{ISC}}\eta_{\mathrm{ET}}\Phi_{\mathrm{Ln}} = \eta_{\mathrm{sens}}\Phi_{\mathrm{Ln}} = \eta_{\mathrm{sens}}\tau_{\mathrm{obs}}/\tau_{\mathrm{rad}} \qquad (3.1)$$

where Φ_{Ln} is the *intrinsic quantum yield* for direct excitation of the lanthanide ion, η_{ISC} represents the efficacy of the intersystem crossing process and η_{ET} is the effectiveness of the ${}^3\pi\pi^*$–Ln

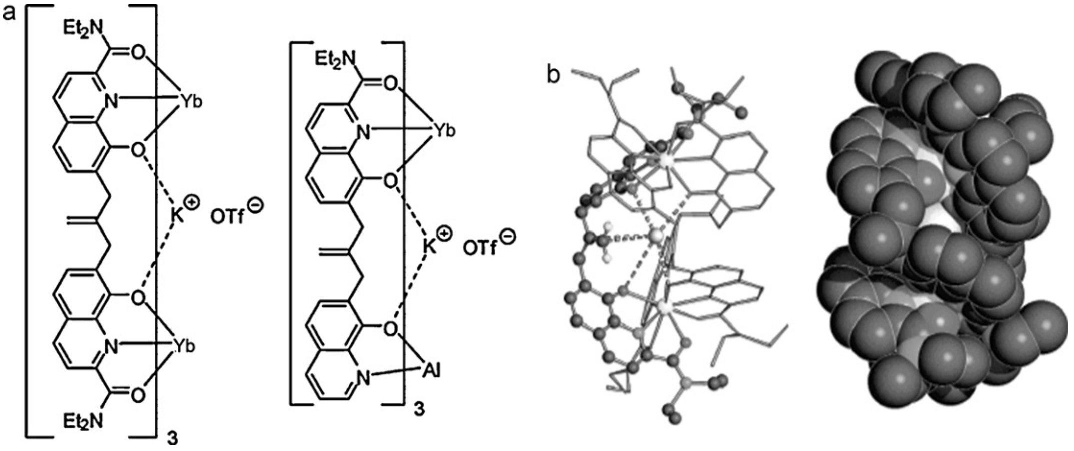
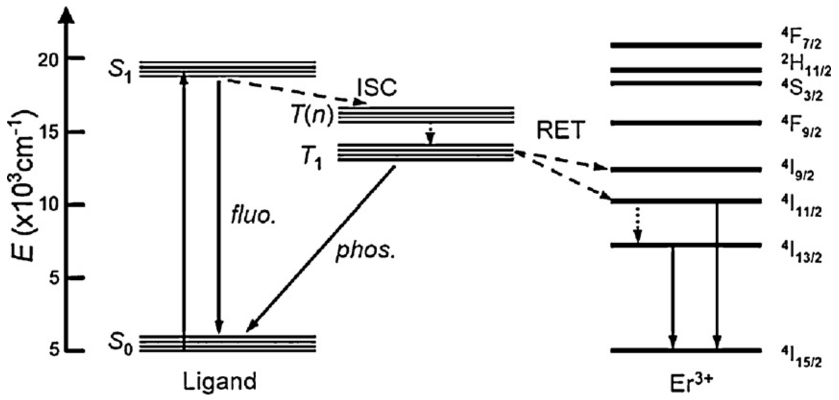


Fig. 8. (a) Homo-(Yb/Yb) and heterodinuclear (Yb/Al) complexes with 8-quinolinol based multidentate ligand. (b) Molecular structure of the cation of Yb/Yb complex. H-atoms (except the two vinylic H in a) as well as triflate and water are omitted for clarity. Color code: Yb, yellow; K, blue; N, green; O, red, C, black. Left: the ligand exhibiting an unusual alkene–potassium coordination is shown as ball and stick model. Right: space-filling model showing the helical arrangement of the ligands around the Yb···K···Yb axis. Adapted with permission from Ref. [69]. Copyright 2007 American Chemical Society.



Scheme 3.1. Jablonski diagram illustrating the two-step excitation process for erbium in quinolinolate complex. Dashed arrows represent non-radiative relaxation mechanisms. According to information available on 8-quinolinolate and similar N-heterocycles [7,85], the first excited singlet state S_1 and the fundamental triplet state (T_1) correspond to π–π* transitions, whereas a triplet state involving transition from a nonbonding (n) to a π* state (T(n)) lies in energy between S_1 and T_1.

(ligand-to-metal) transfer. These latter terms can be combined in the sensitization efficiency parameter η_{sens}. Φ_{Ln} is severely limited by several competitive non-radiative decay processes undergone by the emitting lanthanide ion (see further in the text) and depends on the ratio between the rate constants of radiative ($\kappa_{\text{rad}} = 1/\tau_{\text{rad}}$) and excited state deactivation ($\kappa_{\text{obs}} = 1/\tau_{\text{obs}}$) processes. τ_{obs} is the observed NIR decay time of a lanthanide compound and τ_{rad} is the "natural" radiative lifetime of a given lanthanide ion in the absence of radiationless deactivation [16,71,86,87]. Only the *overall quantum yields* Φ_{tot} and luminescence lifetimes τ_{obs} can be directly measured and reliable values are found in the literature whereas the other terms of Eq. (3.1) are often difficult to be determined and only rough estimations are reported in most cases (see next paragraphs).

In summary, the light output of luminescent materials based on lanthanide complexes essentially depends on: (i) the absorption of the antenna unit, (ii) the efficiency of the two-step $^1S^* \rightarrow {}^3T^* \rightarrow Ln^*$ sensitization process and (iii) the luminescence efficiency of the metal ion, affecting the emission lifetime.

3.1. NIR luminescence

Photoluminescence spectra of NIR emitting quinolinolate complexes, excited in the less energetic absorption band of the Q ligand (assigned to a π–π* transition), are reported in Fig. 9 [47]. As shown, three emission bands are observed for Nd^{3+} (near 880, 1060 and 1330 nm and assigned to $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions, respectively), while the Yb^{3+} and Er^{3+} complexes are characterized by a single band, centered around 980 nm, $^2F_{5/2} \rightarrow {}^2F_{7/2}$, and 1530 nm, $^4I_{13/2} \rightarrow {}^4I_{15/2}$, respectively.

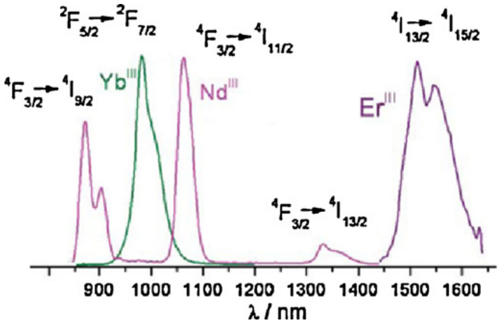


Fig. 9. Emission spectra in the NIR region ($\lambda_{\text{exc}} = 371$ nm) of Ln(**hQt**)$_3$K$_3$ (Ln = Nd, Er, Yb) complexes. Adapted with permission from Ref. [47]. Copyright 2010 Royal Chemical Society.

The moderate broadening and partial resolution (*Stark lines*) of these bands are ascribable to a partial removal of the degeneracy of 4f levels into $2J+1$ terms by crystal field effect, which makes f–f transitions slightly allowed. The fine structure arising from this Stark splitting may be used as a tool to probe the metallic environment, since the spectroscopic shape depends on the symmetry of complexes, and becomes broader as the symmetry lowers. Noteworthy the spectroscopic breadth may allow one to obtain high gain bandwidth for optical amplification in laser systems [6,16,57,83–90].

As an example, the 1.5 μm emission and absorption spectra of two erbium *tetrakis* complexes of general formula [Er(**5,7XQ**)$_2$(**H5,7XQ**)$_2$Cl] (X = Cl, Br), showing differences in the fine structure relatable to different coordination geometries, are reported in Fig. 10.

The emission properties of erbium quinolinolates, being the most studied in view of the interest of their applications [6,19–23],

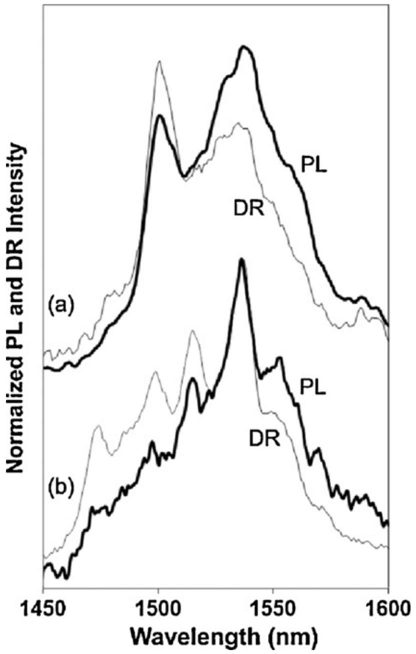


Fig. 10. Comparison of photoluminescence (PL, bold line) and absorption (diffuse reflectance, DR, thin line) spectra originating from Er^{3+} $^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ transitions of *tetrakis* [Er(**5,7ClQ**)$_2$(**H5,7ClQ**)$_2$Cl] (a) and [Er(**5,7BrQ**)$_2$(**H5,7BrQ**)$_2$Cl] (b) showing different fine structures relatable to structural arrangement. Adapted with permission from Ref. [57]. Copyright 2007 Wiley-VCH.

Table 3.1
Summary of literature photophysical parameters of erbium quinolinolates.

Ref.	Compound	τ_{obs} (solvent) (μs)	Φ_{tot} (%)	τ_{rad} (ms)	Φ_{Ln} (%)[a]	η_{sens}
[32]	“Er**Q**$_3$”	2.9 (DMSO-d_6)		8 ms[b]	0.03	
[55]	Na[Er$_3$**Q**$_8$Cl(OH)]	1.6 (DMSO)	–	–		–
[91,92]	Er$_3$**Q**$_9$	2.20 (DMSO)[c]	3.90×10^{-2}	4.35[d]	0.05	0.77
		2.2 (solid state)[c]				
	[Er(**5,7ClQ**)$_2$(**H5,7ClQ**)$_2$Cl]	2.15 (DMSO)	3.85×10^{-2}	4.50[d]	0.05	0.80
[57]	[Er(**5,7XQ**)$_3$(H_2O)$_2$] (X = Cl, Br)	~0.1 (DMSO)				
[49]	[Er**H2Tsox**]$^{3-}$	1.39 (D_2O)	5.4×10^{-3}			
		0.23 (H_2O)	3.7×10^{-5}	0.66 (aqua ion)[e]		<0.01
	[Er**H2TsoxMe**]$^{3-}$	2.31 (D_2O)	7.1×10^{-3}			
		0.67 (H_2O)	4.0×10^{-5}	0.66 (aqua ion)[e]		<0.01
[50]	Er-**T2soxMe**	2.55 (D_2O)	3.5×10^{-3}			
		0.24 (H_2O)	–			
[44]	Er(**HQ-CONEt$_2$**)$_3$	1.5 (solid state)	1.2×10^{-2}	5 ms[g]	0.03	0.40
	Er(**H5BrQ-CONEt$_2$**)$_3$	2.3 (solid state)[f]	2.1×10^{-2}[f]	5 ms[g]	0.05	0.45
	Er(**H5,7BrQ-CONEt$_2$**)$_3$	4.05 (solid state)	3.3×10^{-2}	5 ms[g]	0.08	0.41
[51]	[Er(**thQtcn**)]	1.17 (solid state)	4.32×10^{-3}	0.66 (aqua ion)[e]		0.024
	[Er(**thQtcn-SO$_3$**)]	– (H_2O)[h]	$<2 \times 10^{-3}$[h]	5 ms[g]	0.023	0.19
		0.642(D_2O)	5.7×10^{-3}			
[47]	Er(**hQa**)$_3$K$_3$	0.479 (solid state)	5.1×10^{-3}	5 ms[g]	0.01	0.51
	Er(**hQt**)$_3$K$_3$	0.375 (MeOH)	1.9×10^{-3}			
		0.623 (solid state)	5.9×10^{-3}	5 ms[g]	0.01	0.49
		0.471 (MeOH)	2.0×10^{-3}			

[a] Values calculated from Eq. (3.1).

[b] Average value from literature data.

[c] Although there are two inequivalent coordination sites in the *trinuclear* complex, nearly single-component decay is observed within the available dynamic range. This nearly single-exponential behavior can be explained considering that Er–Er energy migration within an Er$_3$Q$_9$ molecule occurs in the 10-ns time scale much faster than the Er non-radiative decay time; as a result, Er excitations are effectively delocalized over the three metal ions and experience only a coordination configuration average [56].

[d] Experimentally determined from spectroscopic data.

[e] Value taken from Ref. [93].

[f] Measurements performed on impure sample.

[g] Inferred value for erbium quinolinolates [92,94], see Section 3.3.

[h] Er^{3+} luminescence too weak to accurately determine photophysical parameters.

seem suitable to be discussed as a case study to point out the several aspects related to the photophysical processes.

Magennis et al. [32] performed the first study on time-resolved photoluminescence of “ErQ$_3$” reporting an observed emission lifetime in DMSO-d_6 solution of $\tau = 2$ μs. Further studies [44,47–49,55–57,91,92] have confirmed that the emission lifetimes of erbium quinolinolates fall in the microsecond range in organic/deuterated solvents, and are even shorter (<1 μs) in water solution. A summary of literature photophysical parameters of erbium quinolinolates is reported in Table 3.1.

3.2. Non-radiative deactivation mechanisms

Several non-radiative deactivation processes (quenching effects) can severely limit the emission quantum yield of lanthanide complexes, leading to observed luminescent lifetimes (τ_{obs}) which are shortened at times, at least three orders of magnitude lower than the Ln^{3+} radiative lifetime (τ_{rad}). In the cases under discussion, the efficiency of Er^{3+} luminescence suffers from quenching phenomena mainly due to resonance energy transfer (RET) [77] from the emitting lanthanide ion to the oscillating C–H and O–H groups present in the surrounding (*deactivation via vibrational excitation*). From a classic viewpoint the resonance energy transfer (RET) process, explained by T. Förster in the 1940s–1950s [79], could be summarized in three basic steps: (i) excited donor acts as oscillating dipole; (ii) acceptor molecules interact with this oscillating field; (iii) excitation transfer occurs from donor to acceptor without photon emission through a multipolar–dipolar interaction mechanism through space. This mechanism is strongly dependent on the distance (r) between the donor, namely the emitting lanthanide ion, and the acceptor, that is the oscillating O–H or C–H group, and this relationship is proportional to r^{-6}. Moreover, it depends on the relative orientations of donor and acceptor transition dipole moments and on the spectroscopic overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor (*resonance condition*). The energy gap of the radiative (f–f) transition matches well the energy of the vibrational overtones of O–H and C–H groups (with vibrational quanta $\nu = 2$ and $\nu = 3$) which therefore act as efficient quenchers [95]. Since the vibrational transition probability is inversely proportional to the vibrational quantum number ν (Franck–Condon theory), quenching *via* vibrational excitation drastically decreases for superior harmonics of deactivating oscillators. Water molecules are undoubtedly the most powerful deactivators for NIR-luminescence, especially in the case of erbium emission at 1.5 μm, since the first overtone of the H–O–H vibration falls around 1.42 μm. See Fig. 11 where the energy gaps of emitting levels of NIR-emissive lanthanide ions are compared to the energy of CH, NH and OH vibrational modes. This finds experimental evi-

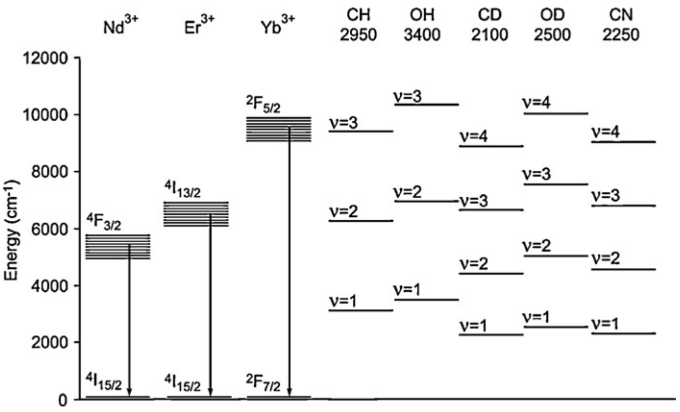


Fig. 11. Energy gaps of emitting levels of NIR-emissive lanthanide ions compared to the energy of vibrational modes of C–H, O–H, C–D, O–D, C–N bonds and their superior harmonics.

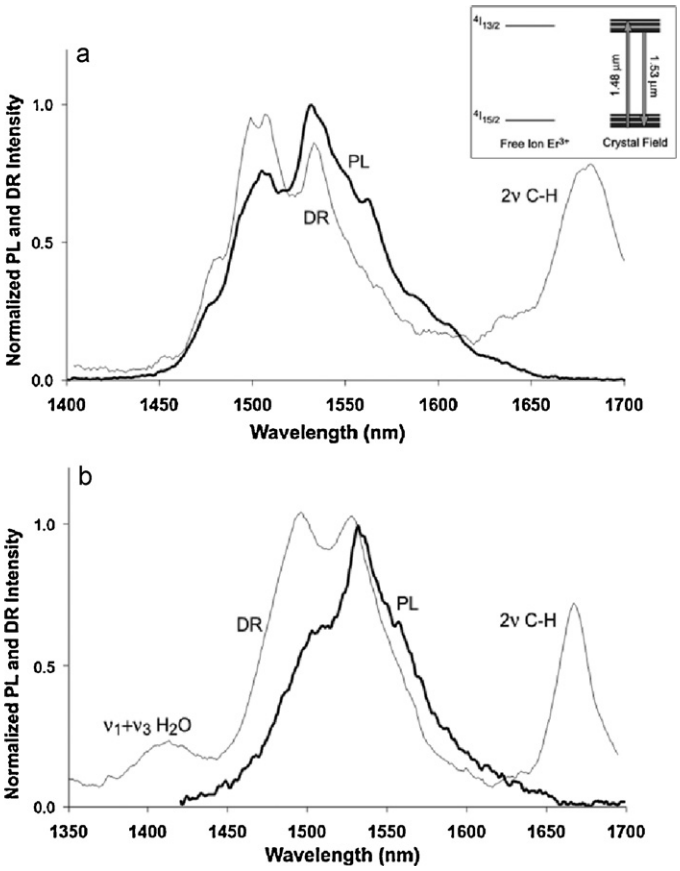


Fig. 12. Continuous wave (CW) photoluminescence (PL, thick line) and diffuse reflectance (DR, thin line) spectra of Er_3**Q**$_9$ (a) and [Er(**5,7BrQ**)$_3$(H_2O)$_2$] (b) in the 1400–1700 nm region. Absorption bands due to 2ν symmetric stretching vibration of C–H groups (~1670 nm) and combination symmetrical–antisymmetric stretching $\nu_1 + \nu_3$ of coordinated water molecules (~1420 nm) are assigned. In the inset a scheme of the energy levels of Er^{3+} in a local crystal/ligand field, is shown.

dence through the comparison of the emission lifetimes ~0.1 μs *versus* 2.2 μs of [Er(**5,7ClQ**)$_3$(H_2O)$_2$], bearing two water molecules in the inner coordination sphere, and of [Er(**5,7ClQ**)$_2$(**H5,7ClQ**)$_2$Cl] a water free complex of the same ligand. Moreover, the entity of such quenching effect depends on the number of H_2O molecules in the surrounding of the lanthanide ion, and the comparison of luminescence lifetimes and quantum yields measured in H_2O and D_2O has been used as a tool to identify the coordination sphere of hydrated lanthanide ions [49–51,96,34,97]. Substitution of C–H and O–H bonds with C–D and O–D bonds, often improves NIR luminescence lifetimes, see the examples reported in Table 3.1.

In Er_3**Q**$_9$, where the coordination sphere is completely saturated by the ligands, the role of water in quenching phenomena is definitely ruled out and non-radiative deactivation processes can be only ascribed [98] to the ligand CH groups in the vicinity of the metal ion. In Fig. 12, the diffuse reflectance (DR) and photoluminescence (PL) spectra in the NIR region of Er_3Q_9 and [Er(**5,7BrQ**)$_3$(H_2O)$_2$] are reported. Structural and spectroscopic data have allowed one to evaluate quantitatively the rate of the Förster's vibrational deactivation [91] of erbium luminescence in Er_3Q_9 through oscillating C–H groups at a distance r from the emitting ion, from the determination of the erbium and CH absorption cross-section, the overlap integral between the erbium emission and CH absorption spectra, and the distances and angles between the emitting metal ion and each C–H bond. The results obtained definitively demonstrate that the non-radiative lifetime of excited erbium ions falls in the microsecond timescale if coupled to CH vibrations, in agreement with experimentally determined lifetimes. In addition, by applying the Förster's theory in a continuous medium approximation, $R_{\min}$, i.e. the minimum distance between the lanthanide ion and the acceptors, where the discrete distribution has been replaced by a homogeneous one, has been calculated. It is concluded that in order for CH deactivation not to affect the lanthanide emission at all, $R_{\min}$, should be larger than 30 Å. However, even a distance of at least 7–8 Å between the emitting ion and the nearest neighbouring C–H groups should provide a significant improvement of the NIR-luminescence lifetime (decay about two orders of magnitude slower) as further confirmed by theoretical studies performed with *ab initio* calculations [99,100]. These conclusions give support to strategies based on the substitution of hydrogen atoms with halogens in the ligand, providing decay times inversely proportional to the CH density (number of hydrogen atoms) in the complex. Significant enhancement of near-IR emission by halogen substitution in lanthanide complexes has been claimed by some authors [29–31,44], and the emission lifetime found for dibromo-substituted Er(**H5,7BrQ-CONEt$_2$**)$_3$ in the solid state is the longest reported so far for erbium quinolinolates (see Table 3.1). Such improvement has not been observed in the case of [Er(**5,7ClQ**)$_2$(**H5,7ClQ**)$_2$Cl] [92]. Anyway, the increase in luminescence lifetimes is not particularly relevant taking into account that the values obtained so far fall in the microsecond timescale. Combined experimental and theoretical studies will help to better quantify these as well as other aspects such as a more efficient ligand to metal energy transfer for halo-substituted ligands in affecting the luminescence lifetimes [30,31].

3.3. Ligand to metal sensitization efficiency

Ligand-to-metal sensitization quantum yield, η_{sens}, is a key parameter for the design of luminescent lanthanide complexes since it critically influences the *overall emission quantum yield* (see Eq. 3.1). Several relaxation steps are involved in the sensitization of the lanthanide ion, including the mixing between ligand singlet and triplet states (intersystem crossing, ISC), and resonance energy transfer (RET) from the triplet state to the ion. These processes compete with other external relaxation mechanisms such as triplet oxygen quenching [102–3, or internal intraligand charge-transfer [45] which may lead to low overall quantum yields. Therefore, for obtaining high lanthanide luminescence efficiencies upon excitation of the antenna it is then necessary to design and select suitable ligands ensuring high sensitization efficiencies.

Enhancement of spin–orbit coupling due to the heavy-atom effect associated with the lanthanide ions is expected to result in acceleration of the ISC process and to efficient η_{ISC} [85]. Ligand-to-metal energy transfer (η_{ET}) depends on the distance as well as on the energy overlap between the sensitizer and the lanthanide ion. For efficient lanthanide ion sensitization, the triplet states of the ligand must be closely matched to or slightly above, the metal ion's emitting resonance levels, but not so close that thermal back energy transfer competes effectively with Ln^{3+} emission [6,103–106]. Typically, an energy gap of 1500 cm^{-1} should be recommended to prevent this detrimental phenomenon.

Quinolinol ligands are good "light harvesters" and possess good photosensitising properties toward the NIR emissive lanthanide ions, since, in addition to broad absorption and emission bands in the visible region, have triplet state energies (at about 18000 cm^{-1}) matching well the accepting energy levels of the 4f orbitals of Er^{3+} as well as for Nd^{3+} and Yb^{3+} while are unsuitable for the resting lanthanide ions, as shown in Fig. 13 [26,30,31,107]. The introduction of substituents on the quinoline ring allows the fine tuning of ligand triplet states leading to a better ligand-metal (Er^{3+}, Nd^{3+}, Yb^{3+}) energy overlap (calculated in the framework of the Dexter theory) of chloro- and bromo-substituted quinolinolates with respect to

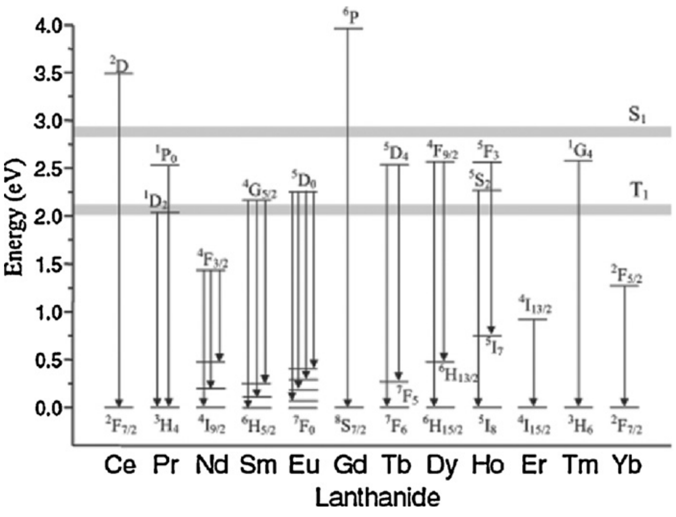


Fig. 13. Schematic energy level diagram showing the emissive levels of the lanthanides, and the singlet and triplet energies of the quinolinolate ligands. Reprinted with permission from Ref. [26]. Copyright 2004 Wiley-VCH.

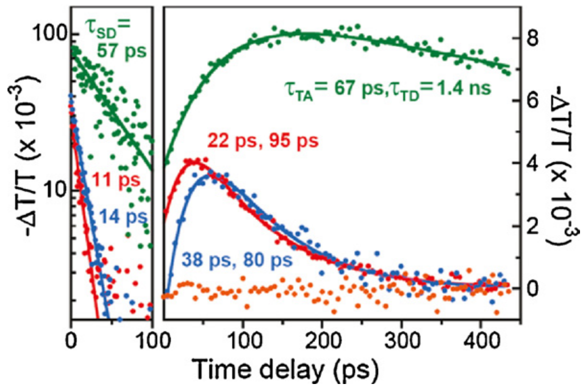


Fig. 15. Excited-state absorption dynamics of metal complexes photopumped by subpicosecond pulses centered at 392 nm wavelength. The dynamics is reconstructed by differential transmission ($\Delta T/T$) measurements *versus* probe-to-pump time delay. Left panel: Resonant response, probed at 392 nm (singlet dynamics). Right panel: Nonresonant response probed in 570–650 nm spectroscopic window by broadband pulses (triplet dynamics). Dots: Experimental data. Solid lines: Model curves best fitting to experimental data. Time constants of excited-state processes are indicated: singlet-decay time (τ_{SD}) in left panel, triplet activation (τ_{TA}), and decay (τ_{TD}) time in right panel. Color code is the same as in Fig. 14. Adapted with permission from Ref. [112]. Copyright 2010 American Chemical Society.

unsubstituted ones and therefore to increased emission quantum yields [30,31].

η_{sens} is usually calculated from Eq. (3.1) through Φ_{tot} and Φ_{Ln}. The *intrinsic quantum yield* value depends on the radiative lifetime τ_{rad} and can be experimentally determined from spectroscopic data (absorption cross-section) through the Strickler–Berg equation [108]. However, despite the fact that the importance of the radiative lifetime τ_{rad} in assessing the photophysical properties of emitting lanthanide complexes is well recognized, only few values have been experimentally determined, while in most cases only estimated values are provided. Radiative lifetimes depend on several parameters, including the refractive index of the medium (n) and the coordination environment [86], and literature data may vary widely. As an example, Er^{3+} radiative lifetimes ranging from 0.66 ms (aqua ion) [93] to 14 ms (Er^{3+}-doped silica fiber) [109] are reported, however a value of 4–5 ms seems to be the most reasonable for erbium complexes (for $n \approx 1.5$) [91,92,110,111]. From available data on erbium emission lifetimes and quantum yields, reported in Table 3.1, values of η_{sens} ranging from a few percents to 80% are inferred in erbium quinolinolates.

The high values found for erbium sensitization efficiency up to inversion threshold [92] in Er_3Q_9 and [Er(**5,7ClQ**)$_2$(**H5,7ClQ**)$_2$Cl] have been confirmed by the results of time-resolved studies on the intraligand and ligand to-metal excited-state temporal dynamics [112]. Time-resolved photoluminescence measurements have shown ultrafast ligand singlet decay times (fluorescence) of ~20 ps in erbium quinolinolates whereas, in the case of the corresponding Gd^{3+} complex with the Q ligand, where lanthanide sensitization is suppressed, a value of ~60 ps is estimated from fitted curves reaching up to the 10 ns scale in AlQ_3, as expected given the negligible heavy atom effect of the Al^{3+} ion which do not favour ISC (Fig. 14). This suggests efficient ISC and ligand to metal RET rates in erbium quinolinolates as further confirmed by excited state absorption (ESA) experiments showing ultrafast ligand excited triplet rise times following singlet decay and subsequent triplet depopulation in the 80–100 ps range. These results are to be compared with those of the Gd^{3+} reference compound where triplet activation (τ_{TA}) is slower and triplet decay time (τ_{TD}) is more than one order of magnitude longer (1.4 ns) than in erbium complexes, while no triplet signal is observed for AlQ_3 (Fig. 15). Ligand to metal energy transfer rates retrievable from triplet decay times ($\kappa_{\text{ET}} = 1/\tau_{\text{TD}}$) in erbium quinolinolates are exceptionally efficient if compared to literature data of *m*-terphenyl-based complexes functionalized

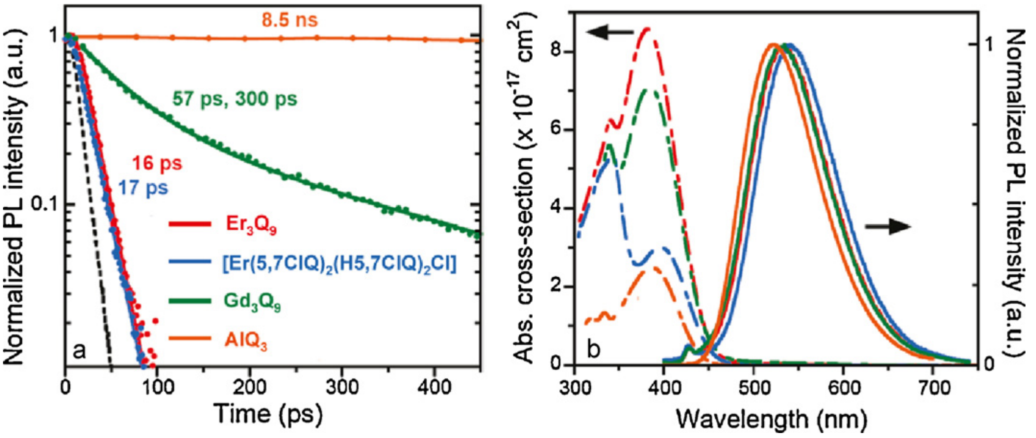


Fig. 14. (a) Normalized temporal decay traces of photoluminescence (PL) intensity of metal complexes excited in the lowest absorption band of the Q ligand (380 nm). Characteristic decay times are indicated for single and double (Gd^{3+}) exponential decay curves best fitting to experimental data and (b) absorption and emission spectra in diluted anhydrous dimethylsulfoxide solutions. Dashed lines: Absorption cross-section spectra (left scale). Solid lines: Normalized photoluminescence (PL) spectra excited by a cw source at 380 nm wavelength (right scale). Adapted with permission from Ref. [112]. Copyright 2010 American Chemical Society.

with a triphenylene antenna chromophore [102]. Parallel triplet decay pathways such as oxygen quenching are much slower than ligand-to-metal energy transfer, and can only marginally influence lanthanide-ion sensitization efficiency in erbium quinolinolates [101,102].

Moreover, triplet activation times are systematically shorter than singlet decay times suggesting a two-step, intraligand relaxation of photoexcitations involving an intermediate $T_{(n)}$ state through enhanced $S_1 \rightarrow T_{(n)}$ ISC and subsequent $T_{(n)} \rightarrow T_1$ conversion (see Scheme 3.1).

It is then possible to conclude that quinolinol ligands are extremely efficient antenna ligands toward the erbium ion and this property is retained when incorporating the complex in vacuum-deposited thin-films, doped spin-coated IR polymer films and doped polymer microparticles [90]. Ligand excited states can be easily modulated through the introduction of suitable substituents which can increase molar absorptivity enhancing the light harvesting power [41] or extend the absorption range into the visible [43,46] or can even enhance metal sensitization through improved ligand-metal energy overlap [29–31]. Similar experiments on corresponding complexes with the other NIR-emitting lanthanide ions, will help to reach a full understanding of the sensitization processes.

4. Conclusions and perspectives

The reviewed combined studies on the chemical and photophysical properties of NIR luminescent erbium-8-quinolinolato complexes, show that a satisfactory understanding of structure/property relationship has been reached. The ligand has shown to: (i) work as antenna chromophore which sensitizes the ion by efficient intramolecular energy transfer; (ii) form stable complexes to protect the ion from further coordination by undesired molecules containing IR quenchers (mostly H_2O); (iii) provide numbers and charges suitable to saturate the preferred coordination number of the ion when forming charge-neutral complex (this is important for processing which requires neutral species, for example, vacuum thin film deposition). It is also known that these ligands have the potential for electrical pumping. Unfortunately these favorable properties are still not sufficient to make these ligands ideal candidates since they contain CH groups, which are capable of lowering the luminescence efficiency by vibrational deactivation. Thus, hydrogen atoms in the quinolinolato ring must be properly substituted (with deuterium or halogen atoms) in order that a significant improvement of luminescence efficiency of this class of complexes can be reached. Additional molecular design criteria for the complexes are required to obtain materials with mechanical properties suitable to be employed as glasses, films or polymers in the desired devices. The vacuum thin film deposition is currently employed and requires neutral complexes, whereas the doping of complexes into pure silica sol–gel glasses seems promising since this improves stability of the complexes and provides shielding from the atmospheric agents. However the silica host matrix is not transparent in the range ~1000 to 2000 nm due to the absorbance of Si–OH residues or eventual CH groups of unreacted alkoxysilane precursors and thus is not suitable for erbium derivatives, although promising for ytterbium or neodymium-based NIR emitting materials. However we can predict the fast development of processing procedures following methods used for similar cases, such as by using modified silicates as the host matrix to link complexes covalently.

As a final comment studies in lanthanide chemistry will improve scientific expertise in this field and this is important due to the crucial role of these metals in several high-tech applications (including defense technologies, such as radar, lasers, and night vision equipments). In particular lanthanide coordination chemistry will produce knowledge useful for several aspects including recycling lanthanide-based materials and improvement of separation–purification methods. This may help to face the problems related to the supply of these metals. The commercial value of lanthanides is growing, but their supply is limited by export tariffs and quotas imposed by China, which is the main producer for these metals, and further tightened export quotas are expected. China is conscious of the relevance of these valuable resources, and is promoting research involving numerous scientists both in Industry and at Universities. These efforts have allowed one to reach important results as testified by the recent book titled “Rare Earth Coordination Chemistry” edited by C. Huang, from Peking University [17], and collecting contributions mostly from Chinese scientists spanning from basic knowledge to applications (magnetic resonance imaging contrast agents for diagnosis, chemosensors and bioimaging probes). These achievements will stimulate further competition and cooperation with scientists from other countries.

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