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Lanthanide-containing luminescent molecular edifices

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Abstract

The first part of this short review focuses on the insertion of luminescent lanthanide ions into molecular compounds. The main requirements for the development of highly luminescent chelates with potential applications in biomedical analysis and time-resolved luminescent microscopy are presented. We then describe the design of adequate macrocyclic receptors with potential applications in nuclear waste management and in the design of liquid crystalline materials. In the latter case, the luminescent properties of the lanthanide ions can be taken advantage of for the determination of the transition temperature. Finally, we turn to self-assembly processes, which allow a fine-tuning of the coordination sphere and, consequently, of the electronic, and associated, properties of the lanthanide ions. Heteropairs of lanthanide ions may be specifically recognized, which leads to the design of bifunctional (bicolour) probes. Moreover, the properties of one metal ion can be controlled by the presence of the other metal ion (either 4f or 3d) when both are inserted into polymetallic edifices.

Keywords: Lanthanide; Luminescence; Macrocycle; Self-assembly; Helicate; Bimetallic; Liquid crystal; Ionic liquid

1. Introduction

Luminescent lanthanide-containing compounds have unusual spectroscopic characteristics, such as narrow, easy-to-recognize emission bands in the visible and near-infrared, as well as long-lived excited states, which make them attractive as alternative probes to organic fluorophores [1] in biomedical analyses. As a consequence, they are being increasingly used as responsive analytical systems, diagnostic tools, for instance in fluoroimmunoassays, enhanced imaging of cancer or in colour-tailored fluorophores for simultaneous detection of multiple targets on DNA strands [2]. Solid-state chemistry also takes advantage of these ions, e.g. in the well known phosphor applications for lighting industry [3], in the engineering of organic electroluminescent devices for light emitting diodes or in the design of up-conversion UV-tunable lasers [4]. More recently, luminescent liquid crystals, emitting either in the visible [5] or in the near-infrared spectral range [6], and coordination polymers [7,8] doped with luminescent lanthanide ions have been proposed.

Due to the very weak oscillator strength of the Laporte's forbidden f–f transitions ($\varepsilon < 10\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$), the lanthanide ions have to be excited by energy transfer from chromophores attached to them, the so-called process of sensitization (or antenna effect). The overall efficiency $\Phi_{\mathrm{L}}^{\mathrm{Ln}}$ of a luminescent lanthanide-containing label is usually given as follows:

$$\Phi_{\mathrm{L}}^{\mathrm{Ln}} = \varepsilon_{\mathrm{L}}(\lambda_{\mathrm{exc}}) \times Q_{\mathrm{L}}^{\mathrm{Ln}} = \varepsilon_{\mathrm{L}}(\lambda_{\mathrm{exc}}) \times \eta_{\mathrm{isc}} \times \eta_{\mathrm{et}} \times Q_{\mathrm{Ln}}^{\mathrm{Ln}} \quad (1)$$

where $\varepsilon(\lambda_{\mathrm{exc}})$ is the molar absorption coefficient at the excitation wavelength and $Q_{\mathrm{L}}^{\mathrm{Ln}}$ the quantum yield of the metal-centred luminescence upon ligand excitation. The latter quantity is the product of three terms: (i) η_{isc}, the efficiency of the intersystem crossing from the singlet to the triplet state of the ligand, which often acts as the main energy feeder for the long-lived excited states of the lanthanide ions [9], (ii) η_{et}, the efficacy of the $^3\pi\pi^*$-to-Ln transfer and (iii) $Q_{\mathrm{Ln}}^{\mathrm{Ln}}$ the intrinsic quantum yield of the lanthanide ion upon direct excitation. The latter is in principle equal to the ratio of the actual lifetime, τ_{obs} divided by the radiative lifetime τ_{rad}:

$$Q_{\mathrm{Eu}}^{\mathrm{Eu}} = \frac{\tau_{\mathrm{obs}}}{\tau_{\mathrm{rad}}} \quad (2)$$

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While τ_{obs} is easily accessible by experimental measurements, τ_{rad} is more difficult to estimate. One has to stress here that this parameter is not compound-independent as often assumed in the literature and that it has to be determined in each specific case, from photophysical data (absorption oscillator strengths and emission intensities). However, in the special case of Eu^{III}, τ_{rad} can be easily determined because the intensity of the purely magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition is independent of the chemical environment of the ion and the following expression holds [10]:

$$k_r = \frac{1}{\tau_{rad}} = A_{MD,0} n^3 \left(\frac{I_{tot}}{I_{MD}}\right) \qquad (3)$$

in which $A_{MD,0} = 14.65\ s^{-1}$ is the spontaneous emission probability of the $^5D_0 \rightarrow {}^7F_1$ transition, n the refractive index of the medium and I_{tot}/I_{MD} is the ratio of the integrated total emission from the $^5D_0 \rightarrow {}^7F_J$ transitions ($J = 0$–6) to the area of the Eu($^5D_0 \rightarrow {}^7F_1$) transition. A good receptor for designing lanthanide-containing luminescent stains must meet several requirements, which are not always brought together easily, a reason why several different synthetic strategies have been (successfully) proposed by various authors. Chemical requirements, such as high thermodynamic stability and kinetic inertness, are now well mastered, while biochemical requirements, especially in case of in vivo use (specific targeting, non-toxicity, easy excretion), are much more difficult to meet. In addition, photophysical prerequisites are quite stringent. The energy transfer process from the ligand to the metal ion is quite complex; Fig. 1 gives a schematic view of it. There is no doubt that the triplet state of the ligand is playing a crucial role. However, discussions in the literature are often oversimplified, considering only one major parameter, the energy difference between the 0-phonon transition of the triplet $^3\pi\pi^*$ state and the luminescent excited state of the Ln^{III} ion. Although this is often the main path of energy flow, as shown in Fig. 2, which represents a modelling of the ligand-to-metal energy transfer in a bimetallic Sm^{III} helicate [9], the singlet $^1\pi\pi^*$ state can also transfer energy onto the metal ion. This happens particularly when short lived metal-centred excited states are involved, which de-activate rapidly to feed the luminescent state(s). Moreover, several excited states of the Ln^{III} ions can accept energy, although symmetry-related selection rules must be met [11]. Finally, complex ligands may posses several feeder $^1\pi\pi^*$ and $^3\pi\pi^*$ states.

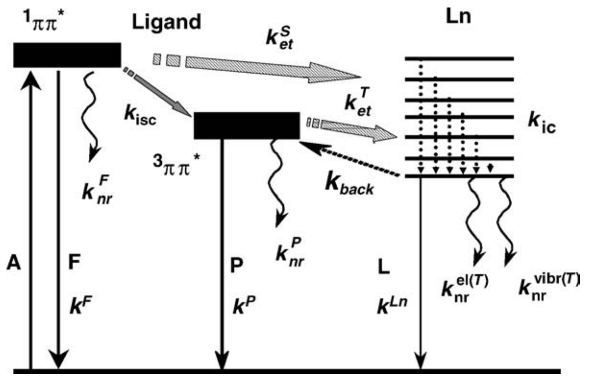


Fig. 1. Simplified diagram showing the energy migration paths in a Ln^{III} complex ($^1\pi\pi^*$, singlet state; $^3\pi\pi^*$, triplet state; A, absorption; F, fluorescence; P, phosphorescence; L, luminescence (either fluorescence or phosphorescence); isc, intersystem crossing; nr, nonradiative; ic, internal conversion; et, energy transfer; back, back transfer; T, temperature-dependent; el, electronic; vibr, vibrational.

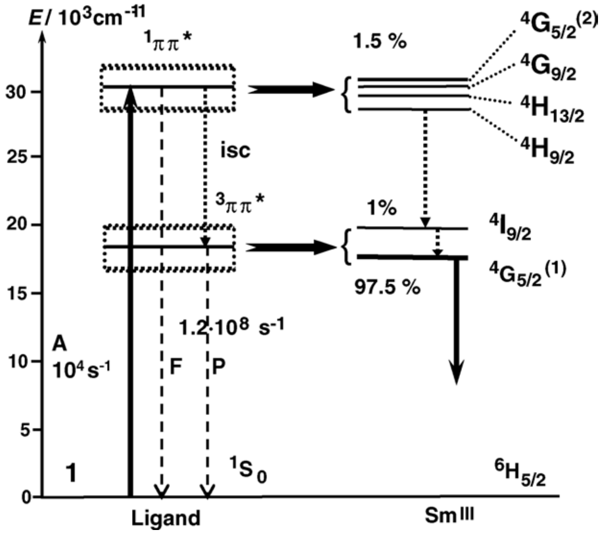


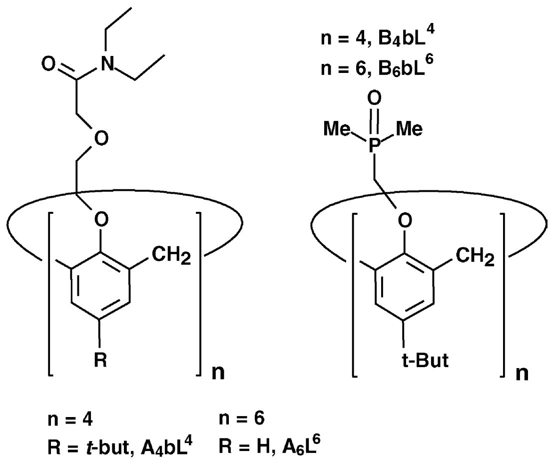
Fig. 2. Modelling of the energy transfer paths in a bimetallic Sm^{III} helicate (redrawn from ref. [9]).

The synthetic strategies tested to meet all the above described requirements include [8] the use of pre-organized macrocyclic receptors [12] or pre-disposed receptors [13,14], leading to an induced cavity; the latter can also be obtained by self-assembly processes [15] or by the use of flexible podands [16]. In the following, we briefly describe some of our recent work on both macrocyclic receptors and self-assembly processes.

2. Macrocyclic chemistry

2.1. Derivatised calixarenes for Ln/An separation

Calixarenes act as versatile blocks in supramolecular and coordination chemistry, since both their wider (lower) and narrower (upper) rims can be easily derivatised to induce specific functionalities [17]. They are currently being used in the design of chemical sensors, catalysts, and as selective ligands for the complexation of d-transition [18] and f-transition [19] metal ions. Furthermore, self-assembly through either π-stacking, H-bonding or coordination interaction leads to elaborate supramolecular structures [20]. In our laboratory, we have been developing model calixarenes for the study of energy migration mechanisms in luminescent lanthanide-containing compounds, and of 4f–4f magnetic interactions [19]. More recently, we have tempted to develop calixarenes



Scheme 1.

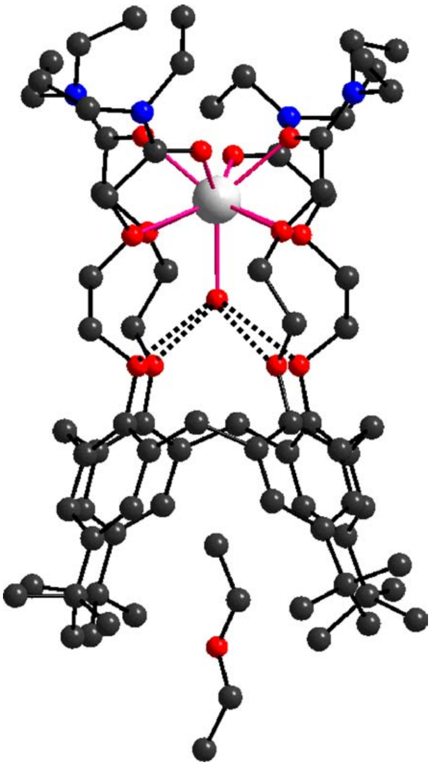


Fig. 3. Molecular structure of $[Lu(A_4bL^4)(H_2O)](CF_3SO_3)_3 \cdot 2Et_2O$ showing the H-bonded water molecule rigidifying the coordination cavity and one diethylether molecule encapsulated into the wider rim (redrawn from ref. [13]).

having 4f–5f separation capabilities and, also, luminescent properties, in order to be able to follow the extraction process by luminescence. With this in mind, we have focused on two series of branched calixarenes, one bearing ether-amide pendant arms ($A_n bL^n$, $n = 4$, 6; see Scheme 1), and the other fitted with phosphanylyl groups ($B_n bL^n$, $n = 4$, 6, 8). These compounds are obtained in fair yields (20–50%) via Williamson synthesis, from the polysodium derivatives of the parent calixarenes and the corresponding brominated arm in case of A or chloro(dimethylphosphinoyl)methane in case of B.

The ether-amide substituent A has been designed so that it can act as a bidentate coordinating unit forming (stable) five-membered chelate rings upon binding to the metal ion. In solution, calixarene A_4bL^4 adopts a cone conformation with a time-averaged C_{4v} symmetry. It reacts with trivalent lanthanide ions to yields stable 1:1 complexes in acetonitrile ($\log K_1 = 9.6$ for Ln = La). The crystal structure of the Lu complex shows that the four ligand arms wrap around the metal ion, forming a protective cavity which is rigidified by the presence of one water molecule, bound to the metal ion and hydrogen-bonded to the phenolic oxygen atoms (see Fig. 3) [13]. The formation of these hydrogen bonds offsets the entropic disadvantage of relatively long pendant arms, which have to organize themselves around the metal ion. Moreover, the hydrophobic cavity formed by the aromatic rings of the calixarene hosts an organic molecule (here diethylether) so that the A_4bL^4 calixarene acts as a mixed inorganic/organic receptor. The experimental results gathered both in the solid state (X-ray diffraction, IR, EPR, luminescence spectra and lifetimes) are consistent with a series of compounds (Eu, Gd, Tb, Lu) displaying a similar structure and solution studies (NMR, luminescence) suggest that this structure is essentially retained in acetonitrile. As far as photophysical properties are concerned, the Eu^{III} and Tb^{III} complexes display the characteristic metal-centred luminescence upon excitation into the ligand levels. The measured quantum yields in acetonitrile remain modest (2% for Eu and 5.8% for Tb), mainly because of a relatively inefficient singlet-to-triplet energy transfer due to a large energy gap ($\approx$10,000 cm^{-1}), but the overall properties of the supramolecular assemblies are interesting.

When the calixarene framework in enlarged in A_6L^6, while removing the *tert*-butyl groups, the situation changes considerably. Indeed, conformational interconversion is now much easier and the formation of 2:1 (Ln:L) complexes with the pendant-arm derivatised receptor is favoured. In fact, molecular mechanics calculations taking into account solvent effects show the conformer with the lowest energy displaying a pinched "chair" conformation of the 1,2,3-alternate type. Three consecutive phenol groups are positioned in such a way that the pendant arms form two predisposed cavities for metal ion co-ordination, each built up of three pendant arms, and extending on opposite sides of the macrocycle. Experimentally, this is substantiated by NMR data in solution, and by the isolation of a 2:1 complex with Eu [21]. The calculated structure of the latter is shown on Fig. 4. It possesses an asymmetrical structure with two 9-co-ordinate Eu ions: one ion (site a) is bound to two phenolic oxygen atoms, three bidentate arms and one monodentate triflate anion; the co-ordination environment of the second ion (site b) is somewhat different, with two water molecules replacing the bonding to the phenolic ether atoms. Therefore, the suggested formulation of the 2:1 complex is $[Eu_2(OTf)_2(A_6L^6)(H_2O)_2]^{4+}$. The coordination environment in site a is comprised of six short

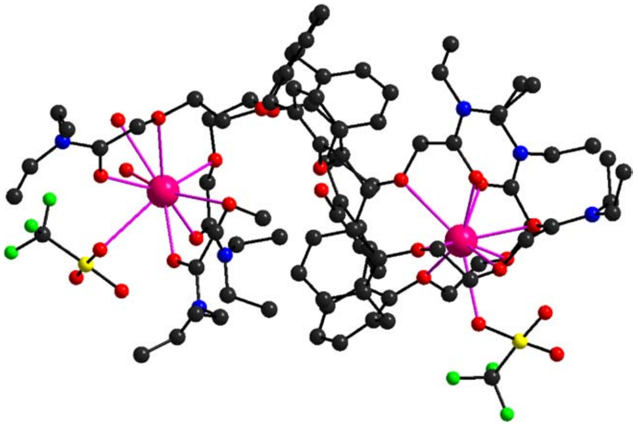


Fig. 4. Calculated structure (molecular mechanics) of the bimetallic complex $[Eu_2(OTf)_2(A_6L^6)(H_2O)_2]^{4+}$ (redrawn from ref. [21]).

bonds (three carbonyl groups, one ether function and the two phenoxide moieties) and three longer bonds (by 13%) involving two ether functions and the triflate anion. The situation for site b is somewhat different in that it features only three short bonds (carbonyl groups) identical to those of site a, all the other distances being 13% longer. It is noteworthy that site a builds a more protective cavity around the metal ion than site b. Moreover, contrary to what was inferred in the ligand design, the phenoxide groups participate more than expected to the bonding (site a), with Ln–O distances comparable to the one with carbonyl functions. The quantum yield of the bimetallic Eu complex is comparable (2.5%) to the one mentioned above for the 1:1 complex with A_4bL^4.

Macrocycle B_4bL^4 also adopts a cone conformation, both in the solid state, as ascertained by X-ray crystallography (Fig. 5) and in solution, as pointed out by NMR data [22]. The phosphanylyl substituent B is a stronger binding unit than the ether-amide moiety A and this is exemplified by the larger stability constants displayed by the La complexes with 1:1 and 1:2 stoichiometry: $\log \beta_1 = 11.4 \pm 1.5$ and $\log \beta_2 = 19.6 \pm 1.8$. An interesting point is that a different structure is obtained for 1:1 complexes depending on their hydration. When the complex is hydrated (Fig. 5), the lanthanide ion sits on top of the cavity and is only coordinated to the four phosphanylyl groups, in addition to five water molecules. Upon dehydration, the lanthanide ion goes into the cavity formed by the pendant arms and is now also coordinated to the phenolic moieties of the calixarene. The phenomenon is reversible, leading to a kind of push–pull movement upon addition or removal of water.

According to its crystal structure, the larger receptor B_6bL^6 forms a kind of triangle with three of the phenyl rings at the vertex and the other three along the sides of the triangle [23]. Adjacent phenyl rings are almost perpendicular, and the conformation can be described as being a distorted alternate in–out cone conformation. However, the structure may also be seen as comprised of four phenyl rings forming a kind of calix[4]arene with two additional aromatic rings positioning themselves between the two halves of the calix[4]arene. It is noteworthy that one phosphanylyl substituent points inside the cavity while its opposite counterpart extends outward, in the prolongation of the phenyl ring plane (Fig. 6). This ligand also forms 1:1 and 1:2 complexes in acetonitrile with trivalent Ln ions, with a stability comparable to the one exhibited by the complexes with the calix[4]arene derivative. Their photophysical properties, however, are improved particularly with respect to the quantum yields obtained for the Eu solutions (1.5–2.5%).

As a conclusion, the two series of investigated ligands present interesting characteristics with respect to Ln^{III} ion complexation. The stoichiometry of the corresponding com-

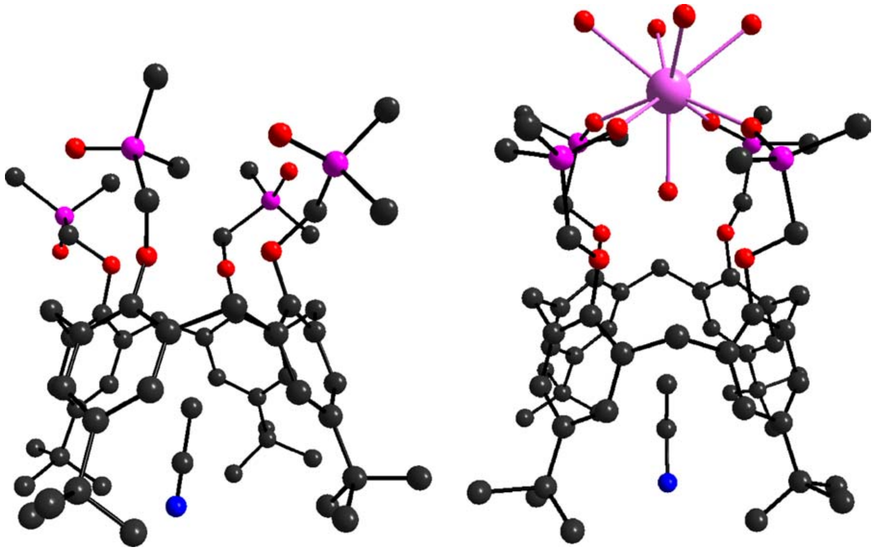


Fig. 5. Molecular structure of (left) $B_4bL^4 \cdot EtCN$ (redrawn from ref. [22]) and (right) $[La(B_4bL^4)(H_2O)_5]^{3+} \cdot (EtCN)$ (unpublished results).

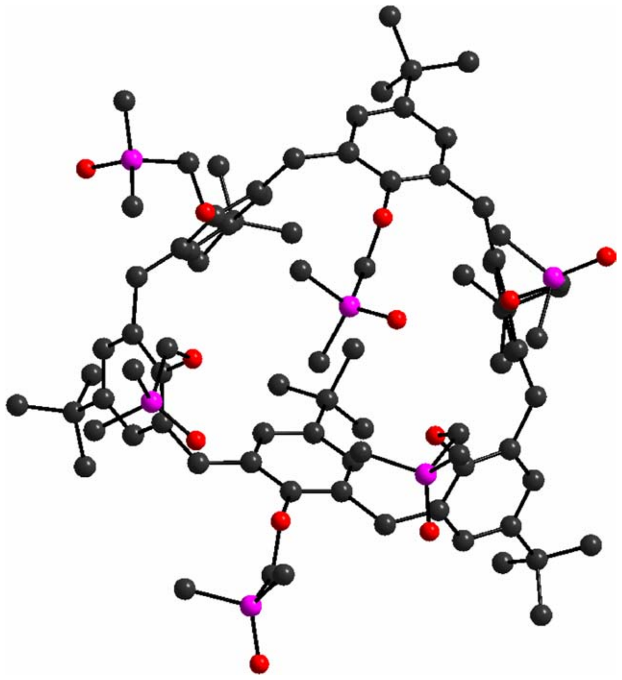


Fig. 6. Top view of the molecular structure of $B_6bL^6 \cdot 13H_2O \cdot 0.5C_7H_8$ (redrawn from ref. [23]).

plexes can be tuned by a suitable choice of the narrower and/or wider rim substituents, and in some cases induced cavities can be formed through hydrogen bonding. Lifetime data of the Ln^{III} excited states reported in Table 1 demonstrate that the inner coordination sphere of the metal ion is saturated and most of the time devoid of coordinated water molecules. The Eu^{III} and Tb^{III} complexes are luminescent, as anticipated, and despite their modest quantum yields, the complexes are luminescent enough to present some analytical interest. Presently, extraction studies are in progress with the B_nbL^n series of ligands. When $n = 4$, 6, preferential extraction of UO_2^{2+} and Th^{IV} nitrates in nitric acid over Ln^{III} ions can be achieved by solutions of these ligands in $CHCl_3$ [24].

Table 1
Lifetimes of the Eu($^5D_0$) and Tb($^5D_6$) excited states and absolute quantum yield upon ligand excitation of the calixarene complexes with Eu and Tb

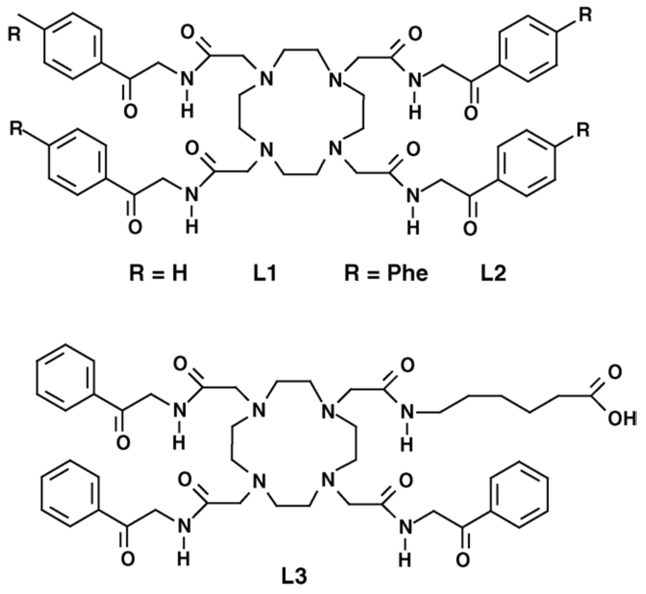
Ligand	Ln	Ln:L	τ (ms)	Q (%)[a]	Reference
A_4bL^4	Eu	1:1	0.73 ± 0.05	2.0	[13]
	Tb	1:1	1.42 ± 0.09	5.8	
A_6L^6	Eu	2:1	1.38 ± 0.02	2.5	[21]
B_4bL^4	Eu	1:1	1.38 ± 0.02	5×10^{-2}	[22]
		1:2	2.25 ± 0.05	7×10^{-2}	
	Tb	1:1	2.13 ± 0.06	2.6	
		1:2	2.71 ± 0.01	3.0	
B_6bL^6	Eu	1:1	1.54 ± 0.06	1.5	[23]
		1:2	2.00 ± 0.06	2.5	
	Tb	1:1	2.06 ± 0.06	4.8	

Acetonitrile solutions at 295 K.
[a] Relative error estimated on quantum yields: 20%.

2.2. *Cyclen-based receptors for sensitizing Ln^{III} luminescence*

Ligands based on the cyclen framework (cyclen is 1,4,7,10-tetra-azacyclododecane) are ideal complexation agents for trivalent lanthanide ions. Besides stabilising the complexes by the macrocyclic effect, they fulfil the requirement of Ln^{III} ions for large co-ordination numbers [25]. The resulting edifices, strongly stable even in aqueous media [26], are therefore particularly appropriate for analytical and/or biomedical uses, for instance as NMR shift reagents, magnetic resonance imaging contrast agents [27], radiopharmaceuticals [28] or as catalysts for the specific cleavage of RNA and DNA [29]. Several luminescent lanthanide-containing chemosensors have been developed, based on cyclen complexes and in which modulation of the emission occurs via ligand or metal-centred processes [30]. The design of such edifices requires a good command of the structural factors influencing their stability and photophysical properties and many structural studies have been reported on complexes with cyclen derivatives bearing pendant arms functionalized by carboxylate, phosphinate or amide co-ordinating groups. In addition, a chromophoric group can easily be attached on one of the amine function of the macrocyclic core [31], which allows one to tune the photophysical properties of the resulting chelates [32].

Since phenacyl and 4-phenylphenacyl chromophores are known to induce efficient energy transfers onto Tb^{III} and Eu^{III} ions [33], we have designed ligands **L1** and **L2** (Scheme 2) incorporating these moieties [34]. They indeed form stable complexes with Ln^{III} ions ($\log K = 12.9 \pm 0.2$ for Eu**L1** in water, for instance) and the luminescence sensitization obtained is quite good. The luminescence of lanthanide ions, such as Sm^{III} and Dy^{III}, is also sensitized (Fig. 7). The next



Scheme 2.

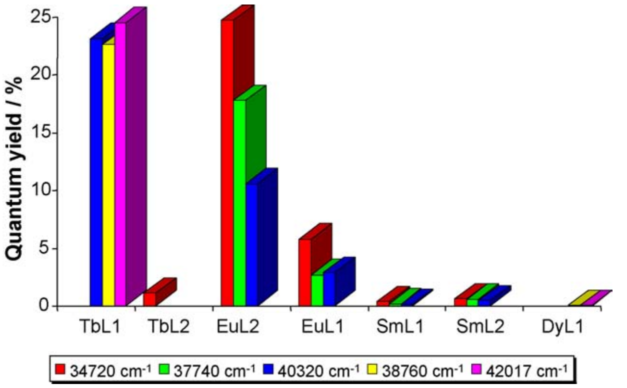
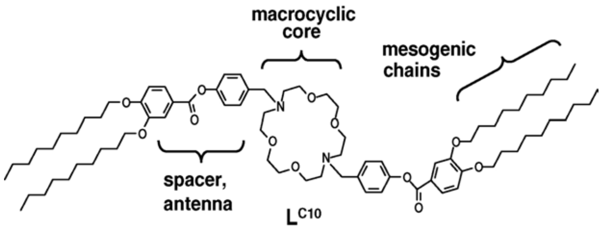


Fig. 7. Quantum yields of the Ln complexes with **L1** and **L2** in aqueous solutions obtained under various excitation conditions into ligand levels.

step has been to replace one of the pendant arm in **L1** by an alkyl chain bearing a carboxylic acid function in **L3** for coupling with biological material. Preliminary photophysical study have demonstrated that the corresponding complexes with Eu^{III} and Tb^{III} transfer efficiently their excitation energy onto the cyanine dye 5 (Cy-5) [35], an acceptor commonly used in homogeneous luminescent immunoassays and in evidencing protein interactions [2].

2.3. A derivatised coronand for generating a luminescent mesophase

Lanthanide-containing liquid crystals are attracting a great deal of research efforts [36] because incorporation of 4f ions into mesogenic phases allows the tailoring of devices taking advantage of the unique optical and magnetic properties of these ions. One specific aspect consists in the preparation of luminescent liquid crystals for LCDs, eliminating the need for photoluminescent sheets acting as filters and which considerably reduce the emission efficiency of the devices. Many phosphors used in lighting devices or displays are based on lanthanide-containing materials emitting narrow bands in the three basic colours, blue (Eu^{II}), green (Tb^{III}) and red (Eu^{III}) [3], because these ions have emission characteristics matching well the physiological response of the eye. There are basically two strategies for designing lanthanide-containing liquid crystals, which are known since 1977 [37]. The first one appears to be quite simple. It consists in doping lanthanide salts or complexes, for instance the highly luminescent β-diketonates, in known cholesteric [37] and nematic [38] phases. Some authors are now also taking advantage of the remarkable properties of room-temperature ionic liquids, some of them displaying mesogenic phases [39]. The other strategy is to synthesize mesogenic or pro-mesogenic ligands leading to mesogenic lanthanide complexes. Initially, it was thought that introducing bulky spherical Ln^{III} ions in mesogenic compounds could disrupt the required order to produce mesophases. However, it turned out that many lanthanide-containing systems are in fact amenable to form liquid crystalline phases [36]. Macrocyclic complexes were among the first reported lanthanide-containing mesogens [40,41]; they often display discotic phases and most of the receptors used are either phtalocyanines or benzoporphyrins [42]. In the former compounds, the lanthanide ion is sandwiched between two macrocycles and it was foreseen that these complexes could act as one-dimensional molecular semiconductors [43].



Scheme 3.

Based on our experience in lanthanide macrocyclic chemistry [25,44–46], we have designed a series of pro-mesogenic ligands derived from the known coronand 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, abbreviated (2,2). The macrocyclic receptors are in fact built from three different synthons: (i) the (2,2) core for Ln^{III} complexation, (ii) two spacers connected to the amine functions which also play the role of antenna for sensitizing the Ln^{III} luminescence and (iii) long mesogenic alkoxy chains with 10, 12 or 16 carbon atoms connected to the spacers. The underlying principle of the synthesis is to firstly resort to a multistep synthesis of the entire substituent, spacer and alkoxy chain, under the form of a bromide or carboxyl, before coupling it with (2,2) [47]. One of these macrocycles is shown in Scheme 3. Although the ligand in itself is non-mesogenic, complexes with lanthanide nitrates display a columnar hexagonal liquid crystalline phase which, in the case of $[Eu(NO_3)_3L^{C10}]\cdot 0.25H_2O$, extends from 85 to 195 °C [5].

Conventional techniques to monitor phase transitions in mesogenic materials rely usually on thermal analyses, polarized light microscopy and small-angle X-ray diffraction. The latter two techniques are required when the exact nature of the mesophase has to be unravelled. On the other hand, when an appraisal of the temperature transition only is needed, differential thermal analysis (DTA) or differential scanning calorimetry (DSC) is sufficient, but subject to hysteresis effects depending on the heating rate. Another, relatively unexplored approach is to resort to changes in luminescence properties. Indeed, specific luminescence intensity and excited state lifetime are expected for each phase, since the lattice parameters, site symmetry and long-range order will alter over the phase transition. These changes are expected to be more pronounced for first-order transitions and will result in discontinuities in the luminescence properties. Since several lanthanide ions display metal-centred luminescence properties, e.g. Eu^{III} and Tb^{III}, we have consequently explored the possibility of determining the temperature of the crystalline-to-liquid crystalline (Cr–LC) phase transitions by monitoring these properties. The Eu^{III} ion is a convenient analytical and structural probe [1,2,48,49] due to both its ground state ($^7F_0$) and most luminescent excited state ($^5D_0$) having a *J* quantum number equal to zero. Until now, only few papers have exploited the Eu^{III} ion to probe liquid crystalline phases. For instance, the degree of disorder around the metal ion in metastable liquid crystals based on europium laurate has been established at very low temperature [50], and second-rank crystal-field parameters have been worked out through analysis of the $^5D_0 \rightarrow {}^7F_1$ transition in order to assess the magnetic anisotropy of europium-containing metallomesogens [51]. Luminescence parameters, such as emission intensity and excited state lifetime, are temperature dependent, and this dependence is usually monotonous. However, when monitored over the crystalline-to-liquid crystalline transition of [Eu(NO$_3$)$_3$L^{C10}]·0.25H$_2$O (and vice versa), the observed changes follow a sigmoid curve [5,52], as shown on Fig. 8. This feature is still seen after correction for the temperature variation measured on a similar complex, but devoid of its mesogenic alkyl arms. In fact, the emission intensity of a Ln^{III} ion is given by the following expression [53]:

$$I(J, J') = \frac{64\pi^4\tilde{\nu}^3}{3h(2J+1)}\left[\frac{n(n^2+2)^2}{9}D_{\mathrm{ED}} + n^3 D_{\mathrm{MD}}\right] \qquad (4)$$

where $I(J, J')$, in s^{-1}, represents the probability of spontaneous emission, $\tilde{\nu}$ the average energy of the transition (cm^{-1}), *h* the Planck's constant (6.63×10^{-27} erg s), $(2J+1)$ the degeneracy of the initial state (1 for Eu($^5D_0$)), while D_{ED} and D_{MD} (esu^2 cm^2) are the contributions from the electric and magnetic dipole operators, respectively. Finally, *n* is the refractive index of the medium, which is known to undergo a non-linear, S-shaped variation over phase transitions. Therefore, a large variation in *n* could be responsible for the observed changes in the luminescence intensity and lifetime on going over the phase transition. In our case, since the $^5D_0 \rightarrow {}^7F_2$ transition is purely electric dipole in nature [53], the second term vanishes and grouping all the constants yields the simplified relationship:

$$I(0, 2) = \frac{n(n^2+2)^2}{9} \times D_{\mathrm{ED}} \times \mathrm{cst} \qquad (5)$$

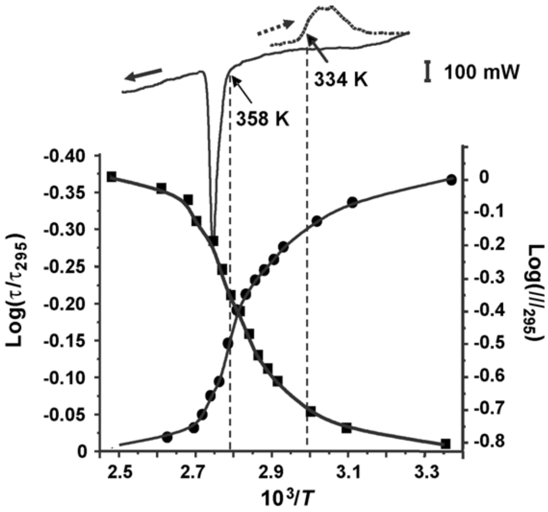


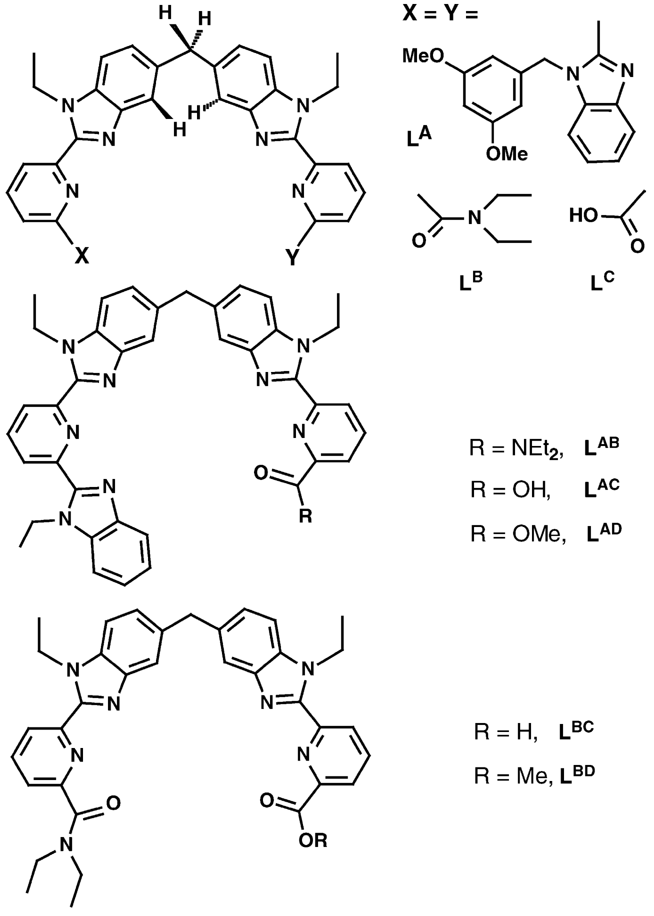
Fig. 8. (Top) DSC traces for the mesogenic complex [Eu(NO$_3$)$_3$(L^{C10})]·0.25H$_2$O (solid line: heating; dotted line: cooling). (Bottom) Variation of the luminescence intensity (right scale, black circles) and of the excited state lifetime (left scale, black squares) over the transition temperature (redrawn from refs. [5,52]).

The variation of the refractive index over the transition temperature has been measured and the intensity and lifetime versus temperature curves corrected accordingly. In fact, the correction amounts for only about 15% of the overall variation and therefore the observed sigmoid temperature-dependence is genuine. Analysis of the residual curve yields a transition temperature in complete agreement with the one determined by the other experimental techniques (DSC, polarized light microscopy, small-angle X-ray scattering). We assign this phenomenon to an effect consecutive to the larger fluxionality of the complex molecules in going from the crystalline to the less-ordered liquid crystalline phase, generating a larger coupling between the phonon density of states and the ^5D_J electronic states. A similar behaviour has also been observed for the Tb^{III} compound. However, only first-order transitions (or transitions generating a thermal effect) can be monitored in this way [52].

3. Self-assembly processes

3.1. Selective recognition of heteropairs of Ln^{III} ions

Molecular recognition, which is the heart of life processes, is often based on self-assembly, an action in which carefully tailored particles spontaneously assemble around the selected guest. Application of these processes in coordination chemistry is relatively recent [54], particularly in lanthanide chemistry [55], but has produced fascinating bi- and tridimensional functional architectures [8]. In coordination chemistry, self-assembly of the host cavity not only relies on the strong ion–dipole bonds to spatially organize the ligands strands but also on the presence of programmed weak non-covalent interactions between these strands. In our laboratories, we have produced a large library of monotopic and ditopic ligands, which self-assemble with Ln^{III} ions to yield monometallic 4f and dimetallic 3d–4f and 4f–4f edifices with predetermined luminescent or magnetic properties [14]. The starting point for the assembly of bimetallic helicates was ditopic, hexadentate ligand **L^{A}** (Scheme 4), which was engineered to build dimetallic edifices in organic solutions, in order to minimize the desolvation energy of the Ln^{III} ions. The resulting helicates are stable in acetonitrile where they display a reverse electrostatic trend with $\log \beta_{23} \approx 20$–22 for the larger La^{III} and Eu^{III} ions and $\log \beta_{23} = 17.5$ for Lu^{III} [56]. Not unexpectedly, they proved to be rather sensitive to hydrolysis and, moreover, the quantum yield of the Eu helicate is extremely small, probably because of the presence



Scheme 4.

of a too low-lying ligand-to-metal charge transfer state [57]. Diethylamido groups were therefore substituted to the terminal benzimidazole moieties to yield ligand $\mathbf{L^{B}}$. Helicates with the latter are more stable than the bimetallic complexes with $\mathbf{L^{A}}$ and less sensitive to hydrolysis, surviving the addition of 3 M water in CH_3CN. Moreover, the quantum yield of the Eu helicate is 40 times larger than the one of $[Eu_2(\mathbf{L^{A}})_3]^{6+}$ and luminescent properties are not altered by the addition of water [15,58]. Hydrolysis of $\mathbf{L^{B}}$ introduced terminal carboxylic acid function in $\mathbf{L^{C}}$ and enabled self-assembly in water, the large hydration enthalpy of the Ln^{III} ions being finally easily overcome. The resulting edifices are the first bimetallic 4f–4f helicates self-assembled in water and they are highly stable [15,59]: the pEu value is around 21 as compared to 25 for $[Eu(dota)]^-$. Moreover, the Ln^{III} ions are well protected from water interaction, resulting in quite long lifetimes of the excited $Eu(^5D_0)$ and $Tb(^5D_4)$ levels (2.1 and 2.5 ms, respectively). The quantum yield of the metal-centred luminescence amounts to 1.3% for the Eu helicate, but is much smaller for the Tb edifice because of a back transfer process. On the other hand, Sm^{III} and Yb^{III} (emitting in the NIR range) are also sensitized [9].

The mechanism of the self-assembly process leading to the exclusive formation of the water-soluble triple-stranded bimetallic helicate $[Eu_2(\mathbf{L^{C}\text{-}2H})_3]$ has been elucidated using a fruitful combination of electrospray mass spectrometry, potentiometry, UV–vis spectrophotometry, luminescence and ^{1}H NMR [60,61]. The final product $[Eu_2(\mathbf{L^{C}\text{-}2H})_3]$ (Eu_2L_3) and two of the intermediate species, $[Eu(\mathbf{L^{C}\text{-}2H})_2]^-$ (EuL_2) and $[Eu_2(\mathbf{L^{C}\text{-}2H})_2]^{2+}$ (Eu_2L_2), could be characterized. The presence of terminal carboxylates in $(\mathbf{L^{C}\text{-}2H})^{\mathbf{2}-}$ significantly reduces the electrostatic repulsions of the coordination sites in the bimetallic moieties compared with the corresponding complexes formed with analogous neutral ligands and thus increases the stability of the helicates. Kinetic investigations carried out in excess of ligand and in excess of Eu^{III}, show that the self-assembly proceeds through either EuL_2 or Eu_2L intermediates depending on the experimental conditions and leads to a key preorganized Eu_2L_2 intermediate by either a “braiding” or a “keystone” mechanism. In the last step, a fast and efficient wrapping of the third ligand strand leads to the targeted Eu_2L_3 helicate (Fig. 9).

A further step was taken rendering the ditopic ligands unsymmetrical, with two coordination units of different strength, in an attempt to selectively recognize heteropairs of lanthanide ions. Ligands $\mathbf{L^{AB}}$, $\mathbf{L^{AC}}$, $\mathbf{L^{AD}}$, $\mathbf{L^{BC}}$ and $\mathbf{L^{BD}}$ were successfully synthesized (Scheme 4) and it turned out that L^{AB} is the ligand with the best selectivity [62]. In the initial design of these ditopic ligands, we expected that the variable affinity of their coordinating units versus the lanthanide ion sizes would lead to the selective incorporation of two different metal ions into triple stranded bimetallic helicates. Two among the three tested ligands effectively lead to selective supramolecular recognition of heteropairs of lanthanide ions. However, contrary to our initial thoughts, the best host, by far, proved to be neutral $\mathbf{L^{AB}}$ and not deprotonated $\mathbf{L^{AC}}$.

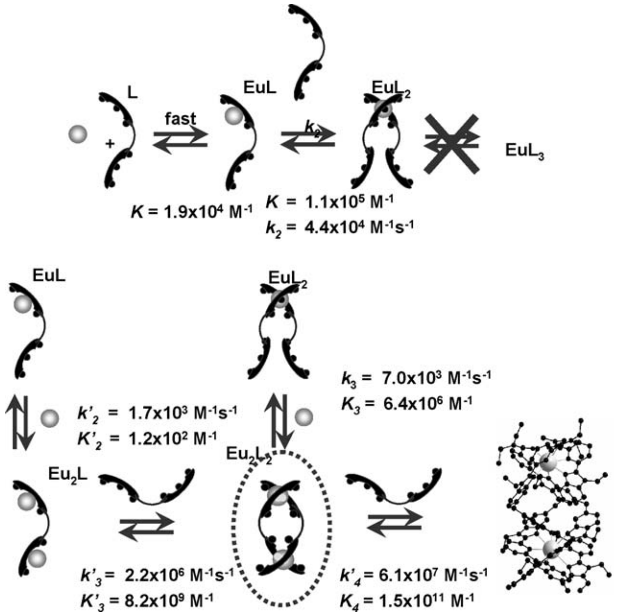


Fig. 9. Self-assembly mechanisms of the triple-stranded helicate [Eu2(Lc-2H)3] (Eu2L3) (redrawn from ref. [60]).

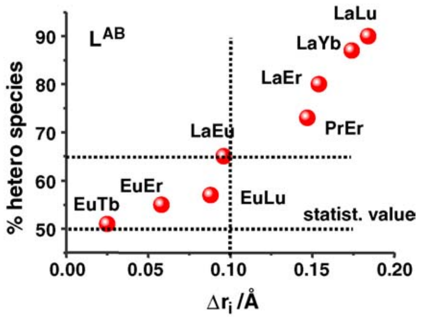
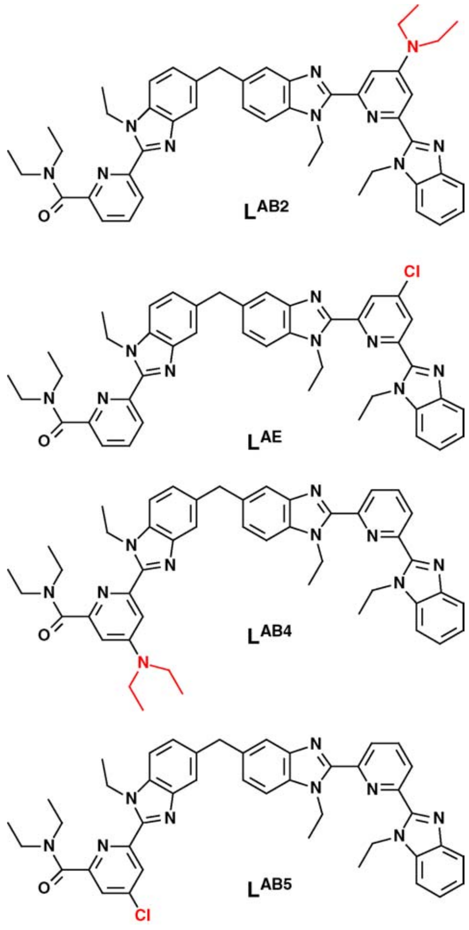


Fig. 10. Percentages of hetero-bimetallic species (as observed by both ^{1}H NMR and ES–MS, from acetonitrile solutions) vs. ionic radii differences (redrawn from ref. [62]).

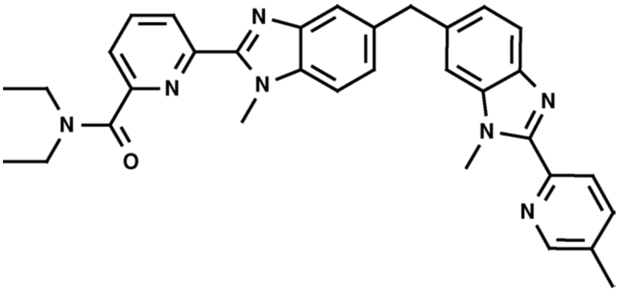
This finding is important since it points to the selectivity being governed by a combination of electrostatic interactions and interstrand interactions. In fact, $\mathbf{L^{AB}}$ forms a majority of head-to-head-to-head (HHH) helicates, which is by far not the case for deprotonated $\mathbf{L^{AC}}$, and a high selectivity is precisely related to this configuration of the complexes. Altogether, remarkable enhancements in the concentration of the heterobimetallic $[\mathrm{LnLn'}(\mathbf{L^{AB}})_3]^{6+}$ species over the statistical distribution are obtained when the ionic radius differences are larger than 0.1 Å, reaching up to 90% for the LaLu pair (Fig. 10). In terms of energy, this translates in differences in ΔG_r (with respect to the statistical situation) remaining modest, between -3 and -10 kJ mol^{-1}, henceforth, the difficulty in planning the adequate ligands. It is noteworthy that the softer tridentate unit, bis(benzimidazoylpyridine) is always bound the larger (softer) lanthanide ion, as ascertained by several crystal structure determinations. The quantum yields of the LaEu, EuEu and EuLu species in acetonitrile amount to 4.2, 2.2 and 0.6%, respectively [63], so that luminescent probes derived from these helicates can be envisaged. Presently, we are investigating the subtle origins of the selectivity towards a given heteropair of Ln$^{\mathrm{III}}$ ions by varying slightly the coordinating strength of the tridentate units (see ligands $\mathbf{L^{AB2}}$, $\mathbf{L^{AE}}$, $\mathbf{L^{AB4}}$, $\mathbf{L^{AB5}}$; Scheme 5). A good understanding of them will allow chemists to master the design of ingenious hosts leading to bimetallic functional edifices [63].

3.2. *Extending the lifetime of NIR-emitting Ln$^{\mathrm{III}}$ ions*

Besides being major components of diode lasers and optical fibers for telecommunication [64], near-infrared lanthanide-based emitters (0.9–1.6 μm) are presently attracting hefty interest in biomedical analysis [65] in view of their potential for non-invasive in vivo imaging. Recently, there have been attempts to use NIR tomography to examine deep tissues, with the idea of developing highly sensitive methods for early detection of cancer [66]. In this respect, receptor-targeted optical imaging of tumors is gaining in interest because hemoglobin has low absorption coefficients above 650 nm while the absorption of water, a major component of biological tissues, diminishes drastically below 900 nm [67]. NIR-luminescent Ln$^{\mathrm{III}}$ ions, such as Nd$^{\mathrm{III}}$ (emitting in three distinct spectral ranges: 0.87–0.92, 1.06–1.09 and 1.32–1.39 μm) or Yb$^{\mathrm{III}}$ (0.98–1.03 μm), although potentially interesting in view of their emission wavelengths, have two intrinsic drawbacks: (i) low sensitization of the metal-centered luminescence due to a small energy gap between their excited and ground state levels, favouring efficient non-radiative processes and (ii) relatively short lifetimes (ns to μs) which limit the efficiency of time-resolved detection. One strategy for extending the NIR emitter lifetime in the millisecond (ms) range controls the population of the Ln$^{\mathrm{III}}$ excited levels through Cr$^{\mathrm{III}}$ → Ln$^{\mathrm{III}}$ energy transfers in bimetallic edifices in which the intrinsic Cr$^{\mathrm{III}}$ lifetime is long. A suitable modification of the ditopic ligands sketched in Scheme 6, allowed us to incorporate Cr$^{\mathrm{III}}$–Ln$^{\mathrm{III}}$ pairs into triple-stranded helicates [8,68]. When Nd$^{\mathrm{III}}$ and Yb$^{\mathrm{III}}$ are inserted into these edifices, efficient energy transfers occur resulting in the population of the Ln$^{\mathrm{III}}$ excited states by the 3d ion. As a result, the NIR-luminescence is now emitted with an apparent lifetime identical to the lifetime of the Cr(^{2}E) level: 0.46(1) ms (Nd, $^4F_{7/2} \rightarrow {}^4I_{9/2}, {}^4I_{11/2}$ transitions) and 2.05(3) ms (Yb) at 10 K; 0.11(2) ms (Nd) and 0.24(2) ms (Yb) at room temperature,



Scheme 5.



Scheme 6.

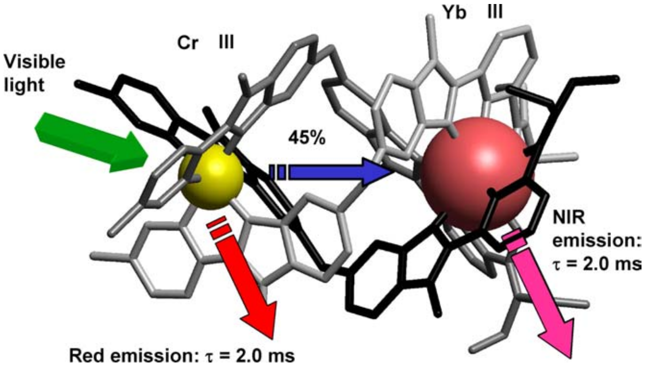


Fig. 11. Extending lifetime of the NIR emission from Yb^{III} in a heterobimetallic Cr–Yb helicate (redrawn after ref. [69]).

meaning that:

$$k_{ET}(CrLn) \ll k_{lum}(Ln) \quad (6)$$

The phenomenon is sketched on Fig. 11.

4. Conclusion

The various examples described above ascertain the wide variety of potential applications that lanthanide luminescence may have in the field of coordination chemistry. The main lesson emerging from the numerous papers published in the field during the last decade is that synthetic procedures are now well at hand to design lanthanide-containing edifices with all the required chemical properties for featuring useful luminescent probes. Modelling is also progressing, but the ultimate ab initio design of highly luminescent lanthanide-containing stains is not yet within reach, given the various parameters involved in the energy transfer. However, the promising topic of NIR emitting probes will certainly have a positive impact on the field. Another point is the availability of ditopic ligands able to self-assemble with a heteropair of lanthanides ions, open the way for elaborate polymetallic functional edfices.

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