Luminescence from Lanthanide(3+) Ions in Solution

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An overview of recent work dealing with luminescence properties in solution of complexes of the lanthanide(3+) ions Nd^{3+}, Eu^{3+}, Tb^{3+}, Er^{3+} and Yb^{3+} in which an organic chromophore is attached to the metal centre as a sensitizer is given. The various factors that influence the metal-centred luminescence lifetime and intensity are discussed and illustrated with own results and recent literature examples. The VIS emitting metal ions Eu^{3+} and Tb^{3+} require sensitizers that absorb light in the UV or near UV range whereas VIS absorbing sensitizers can be used for the NIR emitting ions Nd^{3+}, Er^{3+} and Yb^{3+}. The latter type of complexes is currently of great interest because of potential applications as luminescent markers in biological systems.

Introduction

Complexes of the trivalent lanthanide ions (Ln^{3+}) that display a metal-centred luminescence in solution have attracted an increased attention in the recent years owing to their potential use as luminescent tags in biological systems e.g. fluoroimmunoassays.[1] The emission from the excited state Ln^{3+} ions is characterized by narrow emission bands in the NIR to UV range and long emission lifetimes, up to milliseconds, characteristic of the individual metal ion. The energy levels, $^{(2S+1)}L_J$, of selected Ln^{3+} ions are shown in Figure 1.[2] These characteristics are caused by the parity forbidden, and in many cases spin forbidden, nature of the $4f \rightarrow 4f$ transitions and the fact that the 4f electrons, being effectively shielded by 5p and 6s electrons, are not involved in chemical bonding.

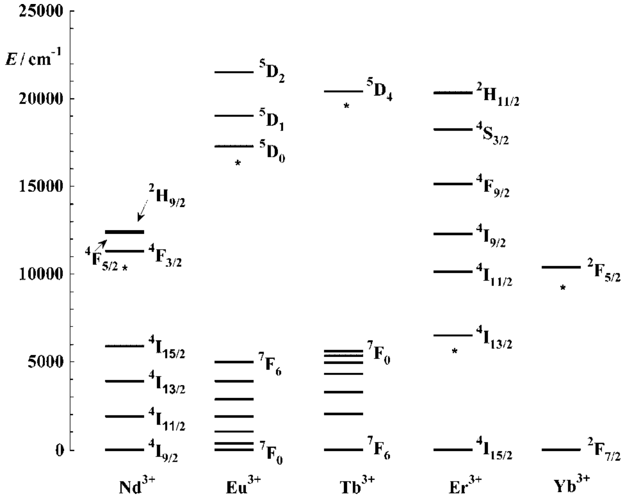
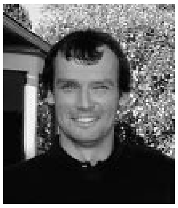


Figure 1. Lower energy levels of selected lanthanide(3+) aqua ions.[2] The luminescent level is marked with an asterisk.

Concerning potential applications of such complexes the parity-forbidden nature of the $4f \rightarrow 4f$ transitions is a major draw back. The $4f \rightarrow 4f$ transitions have very low molar absorption coefficients ($\varepsilon < 1\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$), and population of



Anders Døssing was born in 1962 in Denmark and received his Ph.D. degree in 1990 from the University of Copenhagen in chemistry under the supervision of Prof. Peter Andersen in the field of hydroxo-bridged, dinuclear chromium(III) complexes. In 1991 he did postdoctoral work in Prof. Peter C. Ford's group at University of California, Santa Barbara where he investigated the photophysical properties of polynuclear copper(I) complexes. In 1992–1994 he worked with Prof. Hans Toftlund at Odense University (Denmark) in the field of lanthanide-polypyridyl complexes. In 1994 he returned to University of Copenhagen as an Assistant Professor and in 1997 he became an Associate Professor.

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the excited state(s) of the emitting metal ion by direct excitation is consequently inefficient. One way to overcome this problem is to include a highly absorbing chromophore in the ligand coordinated to the metal centre, which is illustrated in the Jablonski diagram in Figure 2. The chromophore absorbs efficiently the excitation energy followed by an energy transfer to the metal centre, and finally a metal-centred, sensitized luminescence occurs. Such a process, where light is harvested by a strongly absorbing chromophore (or sensitizer), is usually referred to as the "antenna effect". The energy transfer from the chromophore to the metal centre in principle can take place either from the singlet excited state S_1 or from the triplet excited state T_1 after an intersystem crossing. It is, however, generally believed that the energy transfer in most cases occurs from T_1 rather than from S_1.[3] Competitive to the intersystem crossing and the subsequent energy transfer is fluorescence, phosphorescence and thermal decay to the ground state S_0. The energy transfer is mediated by two mechanisms. The first is the so-called Förster mechanism,[4] a dipole−dipole mechanism that operates through space with a chromophore–metal distance (r) dependence of r^{-6} and displays a strong dependence on spectral overlap between emission spectrum of the chromophore (T_1) and the absorption spectrum of the metal centre. The selection rule for this mechanism is $\Delta J = 2$, 4, 6. The second is the Dexter mechanism,[5] where energy transfer is mediated through orbitals with ΔJ being 0 or 1 ($0 \leftrightarrow 0$ excluded) and with a distance dependence of e^{-r}. It follows, that the energy difference between T_1 of the chromophore and ${}^{2S'+1}L'_{J'}$ of the metal centre should not be too large with the energy of T_1 being the higher in energy. On the other hand, a too small energy gap will lead to back energy transfer from ${}^{2S'+1}L'_{J'}$ to T_1 and possible bimolecular quenching of T_1 by dioxygen (vide infra).

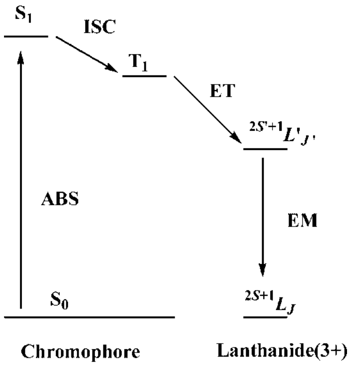


Figure 2. Jablonski diagram illustrating the absorption (ABS) of incident light on the sensitizing chromophore followed by intersystem crossing (ISC) from the singlet (S_1) to the triplet state (T_1) on the chromophore and energy transfer (ET) to the ${}^{2S'+1}L'_{J'}$ level on the lanthanide(3+) centre from which deactivation to the ground state ${}^{2S+1}L_J$ by emission of light (EM) occurs.

The metal centre being in the excited state ${}^{2S'+1}L'_{J'}$ as a result of energy transfer from the chromophore can undergo radiative or nonradiative deactivation to the ground state ${}^{2S+1}L_J$. The latter is promoted by the high-frequency vibrational modes of coordinated X–H oscillators, such as coordinated water or amine ligands (ν_{OH} = 3300–3500 cm^{-1}, ν_{NH} = 3100–3300 cm^{-1}). The extent of this nonradiative deactivation pathway, which results in luminescence quenching, is inversely proportional to the energy gap between the excited state and the ground state manifold. By inspection of Figure 1 it is seen that the energy gap between ${}^5D_0$ and ${}^7F_6$ in Eu^{3+} of 12300 cm^{-1} matches the 2nd vibrational overtone of an O–H oscillator. For Tb^{3+} a gap of 14800 cm^{-1} matches the 3rd overtone, and the vibrational deactivation is therefore less efficient owing to a smaller Frank-Condon overlap between the two wavefunctions. Going to Er^{3+} with an energy gap of only 6500 cm^{-1}, the emission is effectively quenched by coordinated water ligands. The spacing between the vibrational levels in X–D oscillators is smaller than in X–H oscillators and vibrational luminescence quenching is accordingly much less pronounced and can often be neglected. This has been done by Horrocks,[6] who proposed a correlation (1) to estimate the number of coordinated water ligands coordinated to the metal centre, n_{H_2O}, with an alleged uncertainty of 0.5.

$$n_{H_2O} = A\ (k_H - k_D) \tag{1}$$

Here k_H and k_D are the first-order rate constant (in ms^{-1}) for deactivation of the excited state metal in water and D_2O solution, respectively, and A an empirically determined constant being 1.05 ms, 4.2 ms and 0.9 µs for Eu^{3+}, Tb^{3+} and Yb^{3+}, respectively (for Yb^{3+} k_H and k_D should be in units of µs^{-1}). Correlation (1) can be extended to work in methanol solution. The number of coordinated methanol ligands can be estimated by measuring the rate constants in CH_3OH and CD_3OD solution and by use of values of A that are twice the above mentioned, since a methanol ligand only contains one O–H oscillator compared to two in a water ligand. A later and more sophisticated treatment of this subject by Parker[7] has resulted in the modified correlation (2):

$$n_{H_2O} = A'\ (k_H - k_D - B) \tag{2}$$

Here the term B accounts for interaction between the metal centre and outer sphere O–H oscillators. Values for A' in aqueous solution are 1.2 ms, 5 ms and 1.0 µs and for B 0.25 ms^{-1}, 0.06 ms^{-1} and 0.2 µs^{-1} for Eu^{3+}, Tb^{3+} and Yb^{3+}, respectively. The uncertainty of n_{H_2O} in correlation (2) is believed to be smaller than in correlation (1). Attempts to make similar expressions for complexes including other oscillators were made by Parker.[7]

Recently,[8] on the basis of a study of luminescence lifetimes in aqueous solution with 25 Eu^{3+} complexes of ligands not containing any X–H oscillators, Horrocks has proposed correlation (3):

$$n_{H_2O} = 1.11\ \text{ms}\ (k_H - k_D - 0.31\ \text{ms}^{-1}) \tag{3}$$

This result in combination with Parkers work[7] that included other X–H oscillators in a series of macrocyclic complexes, gives correlation (4) for Eu^{3+} complexes of ligands containing hydroxo, amine and amide oscillators coordinated to the metal centre:

$$n_{H_2O} = 1.11\ \text{ms}\ (k_H - k_D - 0.31\ \text{ms}^{-1} + 0.45\ \text{ms}^{-1}\ n_{OH} + 0.99\ \text{ms}^{-1}\ n_{NH} + 0.075\ \text{ms}^{-1}\ n_{O=CNH}) \qquad (4)$$

For Nd^{3+} correlation (5) has been proposed by Faulkner[9a]

$$n_{H_2O} = 130\ \text{ns}\ (k_H - k_D) - 0.4 \qquad (5)$$

with the rate constants in ns^{-1}. Kimura[9b] proposed for Sm^{3+} and Dy^{3+} correlation (6):

$$n_{H_2O} = Ak_H - B \qquad (6)$$

with A being $0.026\ \text{ms}^{-1}$ and $0.024\ \text{ms}^{-1}$ and B being 1.6 and 1.3 for Sm^{3+} and Dy^{3+}, respectively. Obtaining noninteger values of n_{H_2O} by use of the correlations above is not necessarily wrong, since there could be several more or less aquated species coexisting in solution. In summary, a complex that efficiently converts incident light (UV or VIS) to metal-centred, emitted light (VIS or NIR) should fulfil the following conditions: (i) The ligand includes a highly absorbing chromophore, (ii) energy transfer from the ligand-centred excited states is fast and efficient, (iii) X–H oscillators are excluded from the first coordination sphere of the metal, (iv) the complex is thermodynamically stable and kinetically inert. In the following a brief overview of lanthanide complexes that display VIS and NIR luminescence will be given.

VIS Emitters

The most intense emitters in the VIS range among the Ln^{3+} ions are Eu^{3+} and Tb^{3+} with the weaker ones being Sm^{3+} and Dy^{3+}. The energy of the emitting state in Eu^{3+}, $^5D_0$, is ca. 17300 cm^{-1} and in Tb^{3+}, $^5D_4$, is ca. 20500 cm^{-1} as seen in Figure 1. The energy of the triplet state of the sensitizer has, as mentioned above, to be larger and useful sensitizers for Eu^{3+} and Tb^{3+} centred emission should consequently absorb in the UV or near UV range. Heteroaromatic compounds such as bipyridine, phenanthroline, quinoline, terpyridine or benzimidazole have been used in this regard.[10–15] Numerous complexes of the above mentioned compounds have been isolated in the solid state and structurally characterized. However, these compounds coordinate only weakly to the Ln^{3+} ions and the complexes dissociate readily in coordinating solvents such as water or alcohols. This obstacle can be overcomed by incorporating the chromophores as part of larger chelating ligands with podand, macrocyclic or cage type structure. Examples of such ligands are shown in Figure 3 (**1**–**7**). Apart from including the heteroaromatic sensitizers, these ligands more or less exclude solvent molecules from the first coordination sphere, which, as mentioned above, suppresses the nonradiative deactivation pathway.

A widely used ligand structure is based on the cyclic amine 1,4,7,10-tetraazacyclododecane (cyclen) with neutral or anionic donors such as $\text{-CH}_2\text{COO}^-$ attached as pendant arms to the nitrogen atoms.[16] The ligand DOTA (**8**) forms complexes of very high thermodynamic and kinetic stability. Concerning the influence of the radius of the Ln^{3+} ion on the thermodynamic stability of such complexes, a study by Sherry[17] showed that the Ln^{3+} ions with an ionic radius less than 0.94 Å (Gd^{3+} or later) are more stable. By including UV absorbing sensitizers in the pendant arm(s), sensitized emission from the metal centre has been observed in numerous cases. One interesting example of this was reported by Parker et al.[18] who attached a phenanthridine chromophore to the cyclen unit as seen in **9**. In the Tb^{3+} and Eu^{3+} complexes of **9** a pH and oxygen concentration dependence of the intensity of the metal-centred emission was observed. The pH dependence was explained in terms of protonation equilibria involving the nitrogen atom in the sensitizing phenanthridine chromophore.

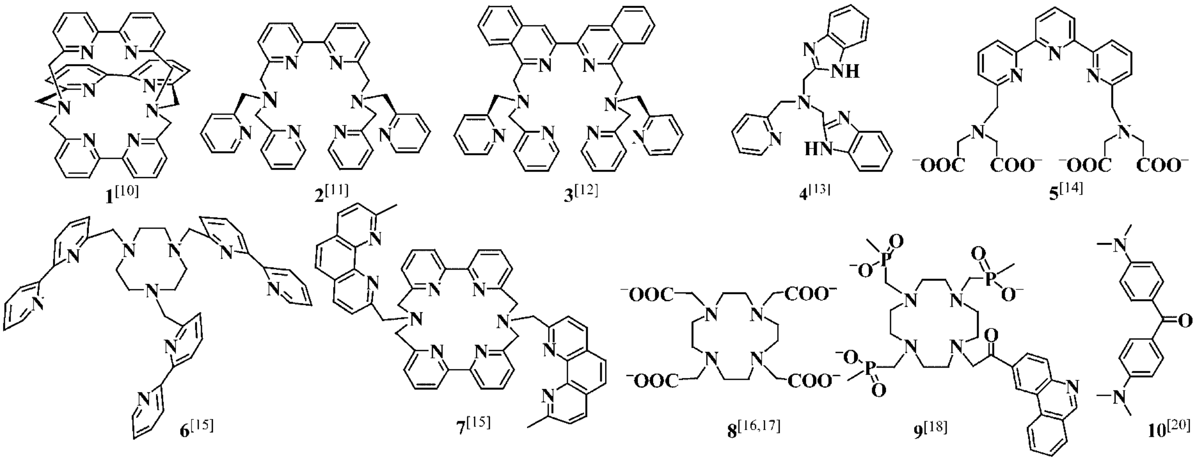


Figure 3. Structure of different ligands.

In the use of the Eu^{3+} ion as the emitter there is a major draw back resulting from its redox properties. It is well known that the Eu^{3+} ions is the lanthanide ion most readily reduced to the oxidation state 2+ with the standard electrode potential $E^\circ_{Eu^{3+}/Eu^{2+}} = -0.35$ V in aqueous solution.[19] The second most readily reduced ion is the Sm^{3+} ion with $E^\circ_{Sm^{3+}/Sm^{2+}} = -1.5$ V.[19] In the case of Eu^{3+}, electron transfer from the excited state (S_1) chromophore to the metal centre might then compete with the intersystem crossing (and subsequent energy transfer) with a reduction of the Eu^{3+} to Eu^{2+} as a result. An *rough* estimate of the free energy of the excited-state electron transfer, ΔG°_{el}, can be found by use of correlation (7):

$$\Delta G^\circ_{el} = FE^\circ_{sens^+/sens} - FE^\circ_{Eu^{3+}/Eu^{2+}} - E_{sens*} \qquad (7)$$

Here $E^\circ_{sens^+/sens}$ is the standard electrode potential for sens$^+$/sens couple, E_{sens*} the energy of the excited state of the sensitizer and F the Faraday constant. A small correction term for charge redistribution has been omitted. As a result of the intramolecular electron transfer, a LMCT excited state will be populated from which a nonradiative deactivation to the ground state is likely to occur. To suppress this deactivation pathway, the sensitizing chromophores should have high values of $E^\circ_{sens^+/sens}$, namely, they should be difficult to oxidize. One way achieving that could be done by attaching electron withdrawing substituents to the aromatic rings.

Returning to the energy gap between the sensitizer T_1 state and the acceptor state(s) of the metal centre Latva et al.[14] has systematically studied the emission quantum yield of a large series of Tb^{3+} and Eu^{3+} complexes of heteroaromatic ligands with T_1 energies in the range 18 600–27 000 cm^{-1}. They found that in the case of Eu^{3+} there was no clear correlation between the T_1 energy and the emission quantum yield. It was concluded that the Eu^{3+} centre is able to accept energy, not only with the $^5D_0$ level but also with the higher ^5D_J levels. In the case of Tb^{3+} there was a clear correlation between the emission quantum yield and the T_1 energy. With an energy gap between the T_1 state and the $^5D_4$ state larger than 1850 cm^{-1} the quantum yields were found in the range 0.12–0.58. Below 1850 cm^{-1}, the quantum yields dropped dramatically to 0.01 or less. One possible explanation for this behaviour is that with small energy gaps, back energy transfer from the metal centre to the sensitizer might occur with a reduction of the emission quantum yield as a result. However, in the case of a small energy gap the energy transfer from the sensitizer T_1 state to dioxygen, which is present in the solution, might compete with the energy transfer to the metal centre efficiently. Again, this resulted in a reduction of the metal-centred emission quantum yield. An example of this phenomenon was observed in the Tb^{3+} complex of the Lehn-cryptand (**1**). Here, the T_1 state of the bipyridine chromophore has an energy of 21 600 cm^{-1}. A temperature dependence of the emission quantum yield and a bimolecular quenching of the metal-centred emission by dioxygen was observed[10] with a second-order rate constant $k_q = 3.9 \times 10^6$ M^{-1} s^{-1}. This was interpreted in terms of back energy transfer.

The sensitizing chromophores in the ligands **1**–**7** and **9** require irradiation at $\lambda < 400$ nm. A very interesting example of an Eu^{3+} complex that displays a metal-centred luminescence at irradiation wavelengths *above* 400 nm was recently reported by Verhoeven et al.[20] The coordinatively unsaturated tris(β-diketonate) complex [Eu(fod)$_3$] (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione) forms in the non-coordinating solvent benzene a 1:1 complex with Michler's ketone [4,4′-bis(dimethylamino)benzophenone, **10**). The compound **10** is a so-called push-pull chromophore, and an intense absorption band at 350 nm ($\varepsilon \approx$ 16 000 cm^{-1} M^{-1}) has some charge-transfer character, where electron density is moved from the dimethylamino groups to the carbonyl group. The formation of a bond between the carbonyl oxygen atom on **10** and the Eu^{3+} centre yielding [Eu(fod)$_3$(**10**)] results in a bathochromic shift of this charge-transfer band to 414 nm. Irradiation of such a solution with light gave intense red luminescence at wavelengths up to 450 nm with an emission quantum yield of 0.17 in an aerated solution. From phosphorescence measurements of the complex [Gd(fod)$_3$(**10**)] the triplet energy of coordinated **10** was estimated to be 19 600 cm^{-1}, which is only 2300 cm^{-1} above the $^5D_0$ level on Eu^{3+} centre. However, the bond between the carbonyl oxygen and the metal centre is so weak that it is broken in coordinating solvents, which limits the potential applications of this system.

Ln^{3+} complexes of the cage ligand **1** were among the early systems to be investigated.[10] Luminescence lifetime measurements revealed by use of correlation (1) the presence of 2–3 water molecules coordinated to the metal centre in aqueous solution. A later[21] crystal structure determination of the Tb^{3+} complex of **1** showed an open structure (Figure 4) with bond lengths to the bipyridine groups A, B and C being 2.90, 2.55 and 2.74 Å, respectively. Tb^{3+}–bipyridine bond lengths fall typically in the range 2.5–2.6 Å,[22,23] so the cavity size in **1** is obviously too large. Furthermore, a water molecule and a chloride anion are coordinated to the metal centre. This prompted us to investigate Ln^{3+} complexes of the related and more flexible podand type ligand **2**.[11] The ligand **2** can be imagined to be the result of hydrogenolysis of the 2,2′ C–C bonds in two of the bipyridine groups. Therefore, the more flexible ligand **2** should enclose the metal centre more efficiently than **1**. Single crystals of the Gd^{3+} complex of **2** were grown from an ethanol solution and the structure is shown in Figure 5.[11a] It is seen that one of the pyridine groups is dangling uncoordinated, and that two chloride anions are coordinated to the metal centre. Therefore, the complex cation should be formulated as [Gd(**2**)Cl$_2$]$^+$. Moreover, the complex cation is chiral with the nitrogen atoms N1–N2–N3–N4–N5–N6 forming a helix. The unit cell contains two complex cations of opposite chirality. In collaboration with J. Legendziewicz's group more detailed studies of the luminescence properties of Ln^{3+} complexes of **2** have been done.[11b,11d] From the phosphorescence spectrum of [Gd(**2**)Cl$_2$]$^+$ in CH_3OH solution at 77 K the energy of the T_1 state in the bipyridine chromophore was found to be 21 900 cm^{-1}.[11b] In water or CH_3OH solution the Eu^{3+} and Tb^{3+} complex of **2** displays luminescence on irradiation with UV light. In the case Eu^{3+} the energy of $^5D_0 \rightarrow {}^7F_0$ transition depends on the ligand field, and the presence of more than one peak is therefore indicative of more than one species in the solution. A close scrutiny of the $^5D_0 \rightarrow {}^7F_0$ transition at 77 K in the solid state and in various solvents shows indeed the presence of two components in water and in CH_3OH solution (Figure 6).[11b] In CH_3CN solution and in the solid state the stoichiometry of the complex is likely to be $[Eu(\mathbf{2})Cl_2]^+$, and in water and CH_3OH solution a partly solvatized species, such as $[Eu(\mathbf{2})Cl(CH_3OH)]^{2+}$, is present as well. In agreement with this, luminescence lifetime measurements in CH_3OH and CD_3OD gave in each solvent two luminescence lifetimes τ_1 and τ_2, and by use of correlation (1) it was found that the two species contains 0.0 and 0.6 coordinated CH_3OH molecules, respectively. Investigations of the Tb^{3+} complex of **2** indicated that back energy transfer took place.[11d]

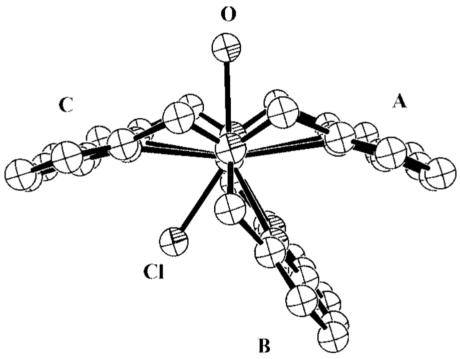


Figure 4. ORTEP drawing of the cation $[Tb(\mathbf{1})(OH_2)Cl]^{2+}$ prepared by Lehn et al.[21] viewed along the axis comprised by the two aliphatic nitrogen atoms. Drawn using coordinates taken from Cambridge Crystallographic Database. Tb–N bond lengths are 2.90 Å (A), 2.55 Å (B) and 2.74 Å (C).

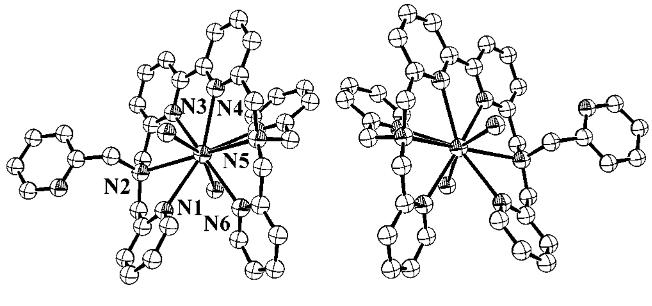


Figure 5. ORTEP drawing of the two complex cations in the unit cell of $[Gd(\mathbf{2})Cl_2]Cl{\cdot}2H_2O{\cdot}½EtOH$ prepared by Døssing et al.[11a]

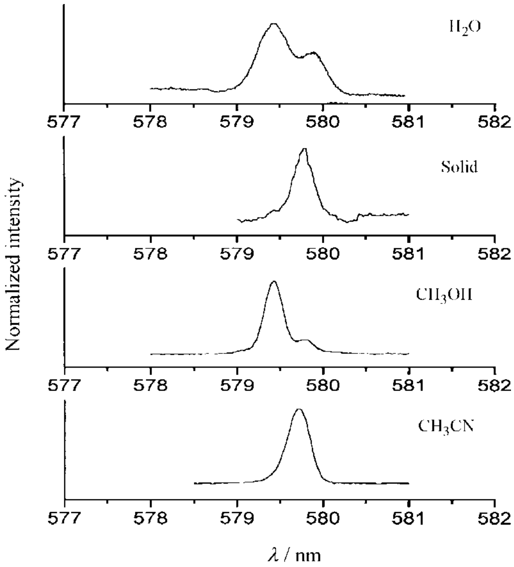


Figure 6. $^5D_0 \rightarrow {}^7F_0$ emission spectra of $[Eu(\mathbf{2})Cl_2]Cl{\cdot}1.5H_2O$ in different solvents at 77 K (λ_{ex} = 320 nm) Redrawn from ref.[11b] with permission from Elsevier.

Complexes of La^{3+} are diamagnetic and the structure and dynamics of such complexes in solution can conveniently be studied by use of NMR spectroscopy. The complex $[La(\mathbf{2})]Cl_3{\cdot}4H_2O$ has been studied in CD_3OD and CD_3CN solution, and the ^1H NMR spectrum in the latter solvent is shown in Figure 7 along with the assignment obtained by help of two-dimensional COSY spectroscopy.[11c] The figure shows that the four pyridine groups exist in two pair-wise equivalent groups and that the bipyridine group is symmetric. The presence of six methylene groups that give rise to the three AX spin systems (α1, α2), (β1, β3) and (β2, β4) of equal intensity shows that the pyridine rings 1 and 3 (and, 2 and 4) are symmetry related, and the complex ion has therefore twofold symmetry. The ^1H NMR spectrum of $[La(\mathbf{2})]Cl_3{\cdot}4H_2O$ in CD_3OD is very similar except for a number of additional low-intensity peaks, which shows the existence of an other species in low concentration. This is not surprising, since this is also the case in Eu^{3+} complexes of **2** in methanol solution (see Figure 6). At higher temperatures the peaks corresponding to the protons in the four pyridine groups are broadened, which indicates that a slow interchange between the two pairs of symmetric pyridine groups takes place. Moreover, the peaks corresponding to the α1 and α1′ protons broadens. No broadening was observed for the peaks corresponding to the protons in the bipyridine group. From the two-dimensional EXSY spectrum showed in Figure 8 the presence of the cross peaks between the four protons in the pyridine groups clearly confirms the interchange. Moreover, cross peaks between primed and unprimed protons in the methylene groups are present. The exchange rates in CD_3CN solution were measured in the temperature range 270–315 K with the first-order rate constant, k, for the interconversion at 300 K being 1.78(5) s^{-1} with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ being 69(1) kJ mol^{-1} and –9(2) J·mol^{-1}·K^{-1}, respectively. In CD_3OD solution the behaviour was similar with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ being 71(2) kJ·mol^{-1} and 4(6) J·mol^{-1}·K^{-1}, respectively. The pseudo-first-order rate constants for substitution of unidentate ligands in the first coordination sphere of the

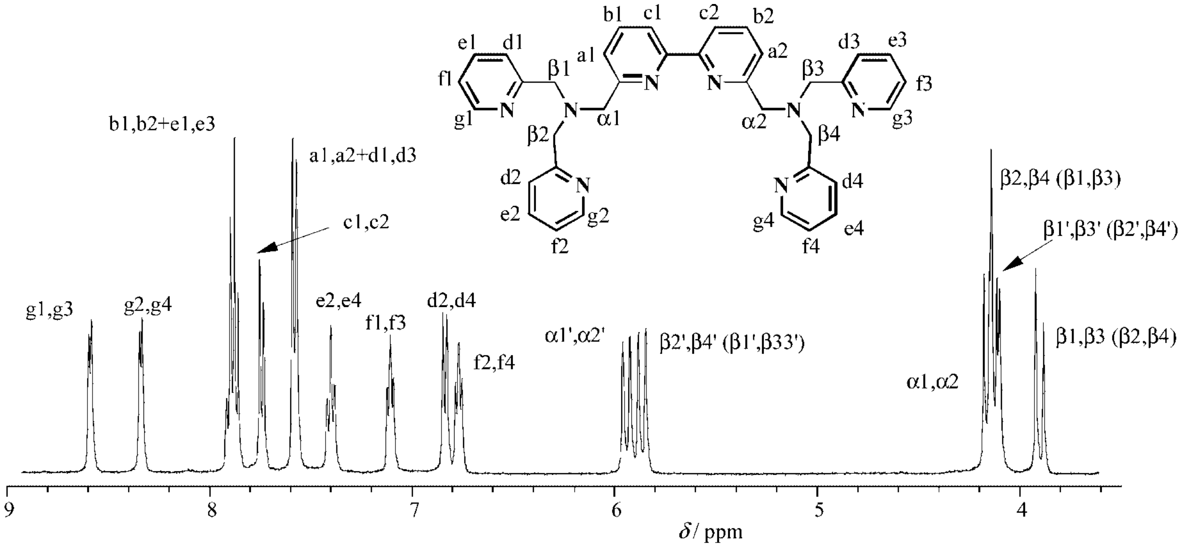


Figure 7. One dimensional ^{1}H NMR spectrum of [La(**2**)]Cl$_3$·4H$_2$O in CD$_3$CN solution at 298 K with assignments. The primed and unprimed methylene protons refer to chemically and magnetically inequivalent protons bound to the same carbon atom. For reasons of clarity the La^{3+} centre has been omitted in the labelling figure.

lanthanide(3+) ions have been found in the range 10^5–10^9 s^{-1},[24] several orders of magnitude higher than the interconversion rate, *k*. The interconversion process is therefore unlikely to be either an exchange between dangling (uncoordinated) and coordinated pyridine groups or a solvento/chloro ligand exchange but rather a concerted twist. With twofold symmetry the cation could be chiral having a C_2 axis or achiral having a mirror plane. The interconversion is in the first case a conformational change during which the chirality changes and in the second case a mirror-image conformational change through a plane orthogonal to the symmetry plane of the complex. The NMR spectroscopic data did not allow any distinction between the two cases.

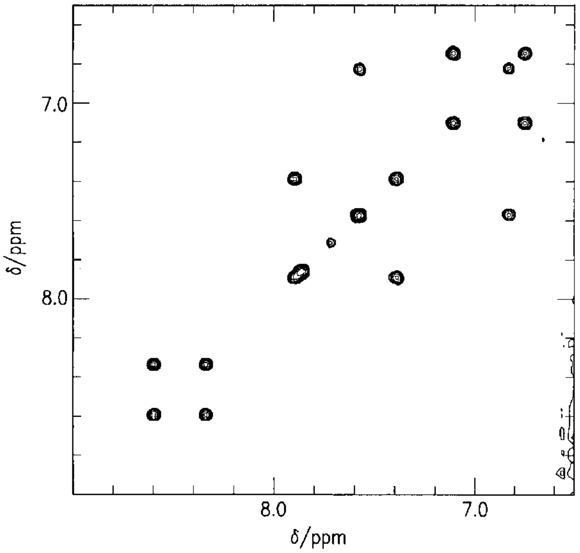


Figure 8. The EXSY spectrum recorded of [La(**2**)]Cl$_3$·4H$_2$O in CD$_3$CN solution at 300 K in the range 6.6–9.0 ppm with an exchange delay of 1.0 s.

One way to clarify if a solution of a luminescent Ln^{3+} complex consists of a racemic mixture of two interconverting enantiomers is by use of circularly polarized (CP) excitation light. A racemic mixture may on excitation with CP light be enantiomerically enriched in the excited state. The metal centre may subsequently display a circularly polarized luminescence (CPL). An excellent review of this technique has been given by J. P. Riehl.[25] The requirement for the detection of a CPL signal is, however, that the rate of the racemization in the excited state (which is probably very close to the racemization rate in the ground state) is slower than the rate of the decay from the metal-centred excited state. In collaboration with J. P. Riehl, Tb^{3+}, Eu^{3+} and Dy^{3+} complexes of **2** have been studied by this technique.[11d] A CPL signal was indeed seen for the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition in the Dy^{3+} complex in aqueous solution at room temperature. The $^4F_{9/2}$ excited state lifetime was found to be 10 µs under such conditions. In the cases of Tb^{3+} and Eu^{3+} with the much longer excited state lifetimes in H$_2$O (1.53 ms and 0.78 ms) no CPL was detected.

In conclusion, CH$_3$CN solutions of complexes between **2** and Ln^{3+} ions consist of interconverting enantiomers of [Ln(**2**)Cl$_2$]$^+$ species with **2** being heptadentate as shown in Figure 5 for Ln^{3+} = Eu^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} and octadentate in the case of the larger La^{3+} ion. In water and CH$_3$OH solution solvento ligands partly displace the chloro ligands.

NIR Emitters

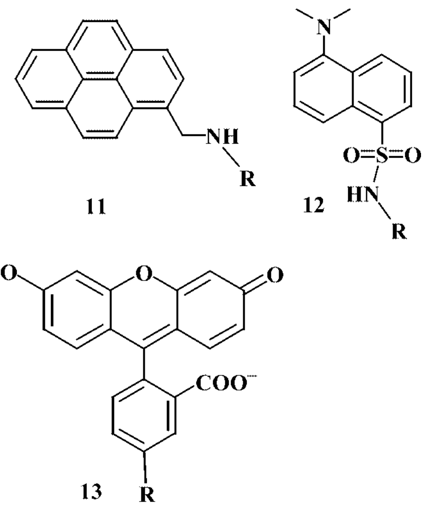
The Ln^{3+} ions emitting in the NIR range are Nd^{3+}, Er^{3+}, and Yb^{3+}. For Nd^{3+} the typical emission lines are located around 890 nm ($^4F_{3/2} \rightarrow {}^4I_{9/2}$), 1060 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) and 1350 nm ($^4F_{3/2} \rightarrow {}^4I_{13/2}$), for Er^{3+} around 1540 nm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) and for Yb^{3+} around 980 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$). For many reasons luminophores based on the three metal ions have attracted large interest in the recent years. One reason is that this gives the opportunity to use sensitizers that absorb in the VIS range. This gives an advantage in their use as luminescent tags in biological systems compared to tags based on Eu^{3+} and Tb^{3+}, since biological tissue is more transparent to VIS excitation light than UV excitation light, and since cheap light sources such as diode lasers can be used then. Although this review deals with luminescence in solution, in this context it should be mentioned that the Nd^{3+} and Er^{3+} ions complexed by organic groups and doped in polymer waveguides may find use as optical amplifiers of 1300 nm and 1500 nm light, respectively, two standard wavelengths used in telecommunication.[26]

There are some drawbacks in the use of luminophores based on the three above mentioned Ln^{3+} ions. Firstly, the luminescence intensities are low and the luminescence lifetimes are short, typically in the range 10^{-7}–10^{-5} s, which is about 3 orders of magnitude lower than lifetimes in Eu^{3+} and Tb^{3+} complexes. Secondly, the low energy gap between the emitting level and the ground state manifold on the metal centre has the result, that the luminescence is quenched, not only by O–H or N–H oscillators directly bound to the metal centre, but also unbound C–H oscillators nearby, with an r^{-6} distance dependence. The energy gap in Er^{3+} is 6500 cm^{-1} which is resonant with the 1st overtone of the C–H oscillator ($\nu \approx 2950\ cm^{-1}$ in aliphatic groups), but the quenching can be somewhat reduced by deuteration ($\nu_{CD} \approx 2200\ cm^{-1}$). To illustrate this, it was shown by Parker[7] that each CH_2COO^- pendant arm in **8** contributes by 13000 s^{-1} to the first-order deactivation rate constant of the complex [Yb(**8**)]$^-$, while the contribution in the corresponding Eu^{3+} complex is 45 s^{-1}.

Metal-centred emission from the three above-mentioned lanthanide ions can be sensitized by UV absorbing chromophores such as bipyridine,[9] terpyridine,[27] pyrene[28] **(11)** or dansyl[29] (**12**) (see Figure 9). The accepting energy level(s) on the metal ions Nd^{3+} and Er^{3+} are therefore located higher than the emitting level. However, the most interesting aspects are connected with the use of sensitizers that absorb in the VIS range. Therefore, the following will deal with such ligands.

As light harvesters absorbing in the VIS range, the chromophore fluorescein **13** (Figure 9) has been used extensively. Fluorescein absorbs strongly around 500 nm (depending of the nature of the solvent) with $\varepsilon \approx 80000\ \text{M}^{-1}cm^{-1}$ and is widely used as a (green) fluorescent probe in biology.[30]

Reinhoudt et al. described one of the first systems where a Nd^{3+} or Er^{3+} ion is bound to a ligand that is covalently bound to a VIS absorbing organic sensitizer.[31] The metal complexes of **14** in which fluorescein is attached to a calix[4]arene ring (Figure 10) displayed NIR luminescence in CD_3OD and dimethyl sulfoxide (dmso) solution. The luminescence intensity was found to depend on the spacer length with the highest luminescence intensity with the C_3 spacer ($x = 3$). In the case of Er^{3+}, only the fluorescein sensitized the emission whereas in the Nd^{3+} case, also the UV absorbing calix[4]arene moiety was able to sensitize the emission. In another study, a fluorescein chromophore was attached to the chelating ligand diethylenetriaminepentaacetic acid (**15**).[32] This ligand forms 1:1 metal complexes and NIR luminescence of such complexes in aqueous solution was observed. The emission intensity for the Yb^{3+} was found to be much lower than for the Nd^{3+} and Er^{3+} complexes. To explain this we must look at Figure 1, which shows that the two latter ions have several higher lying accepting states above the emitting level and thus a better spectral overlap with the T_1 state (located at 15900 cm^{-1}) of the fluorescein chromophore. The emission was, however, found to be quenched by dissolved molecular dioxygen, and this shows that the energy transfer is rather inefficient. A more efficient energy transfer was observed in metal complexes of **16**,[33] where the binding site of the metal ion is much closer to the sensitizer than in **15**. The attached iminodiacetic acid groups ensures a thermodynamic and kinetic stability of the 1:1 complexes that equals the corresponding EDTA complexes, and NIR emission was observed in aqueous solution. Moreover, the NIR emission is *not* quenched by dissolved dioxygen. The Yb^{3+} complex of **16** is so long-lived (1.91 µs in water), that it is possible to distinguish it from background fluorescence from organic groups in biological systems. Systems with fluorescein (**17**)[34] or its derivatives (**18, 19**)[35] attached to a terphenyl moiety have been studied by Reinhoudt and van Veggel. In the ligands **18** and **19** the two VIS absorbing chromophores (lissamine and Texas Red, respectively) absorb strongly in the near-UV to VIS range with absorption maxima at 568 nm ($\varepsilon = 8.8\times10^4\ \text{M}^{-1}cm^{-1}$) and 590 nm ($\varepsilon = 8.5\times10^4\ \text{M}^{-1}cm^{-1}$), respectively. They were found to be able to sensitize emission from the Nd^{3+} ion in [D$_6$]dmso solution with luminescence lifetimes close to 2 µs. The triphenylmethane derivative xylenol orange (**20**) is widely used as an indicator for complexometric determination of metal ions. It has been reported that 1:1 complexes with the Ln^{3+} ions were formed, and interestingly, it is able to sensitize emission



11 **12** **13**

Figure 9. Structure of different chromophores that absorb in the UV range (**11** and **12**) and VIS range (**13**).

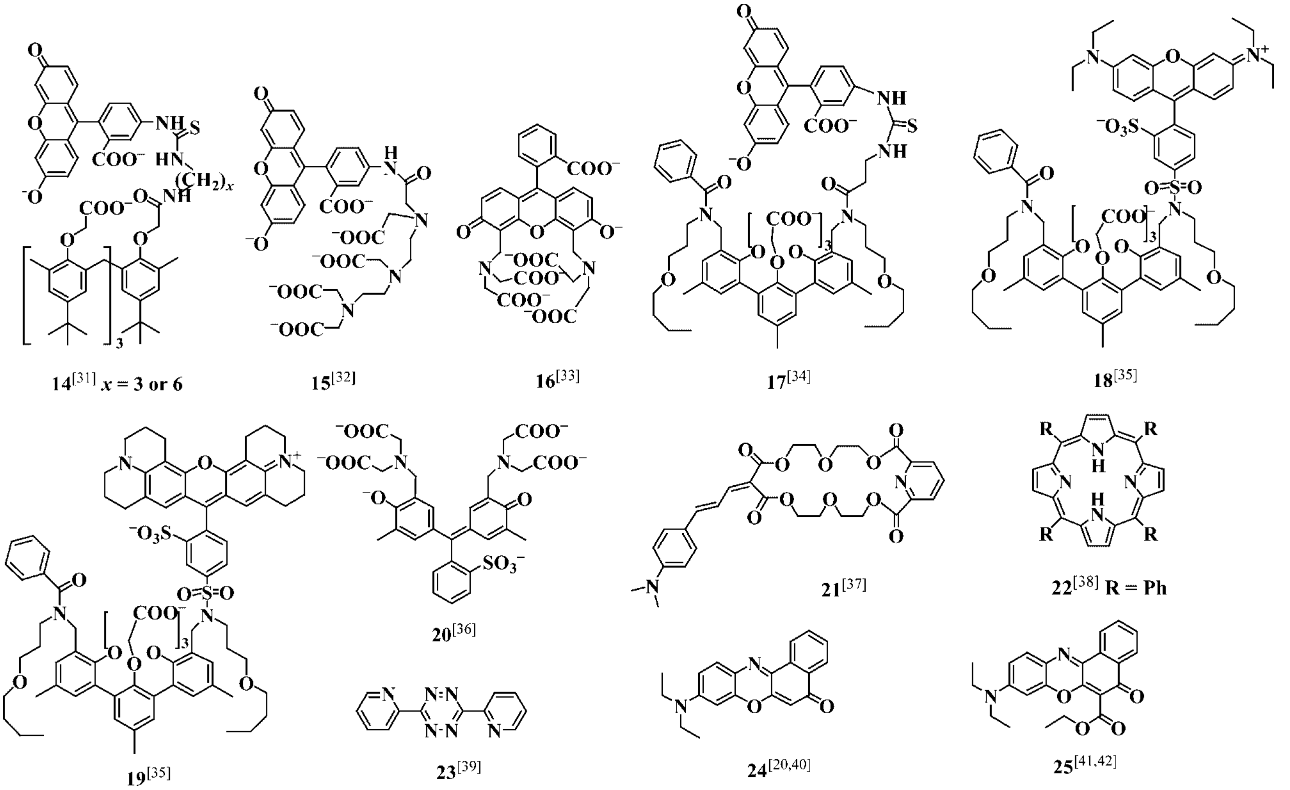


Figure 10. Structure of different VIS absorbing ligands.

from the Nd^{3+} and Yb^{3+} ions.[36] In ligand **21** an oligoene sensitizer is incorporated in a crown ether. The Er^{3+} complex of **21** absorbs VIS light between 400 and 600 nm and displays NIR luminescence in dmso solution.[37] Boncella reported the isolation and structural characterization of tetraphenylporphyrinate, tpp, (**22**, R = Ph) Ln^{3+} complexes capped with multidentate additional ligands such as the tridentate hydridotris(1-pyrazol)borate (tp).[38] The intense Soret bands of the porphyrin group and the low lying T_1 state makes the porphyrin group suitable as sensitizer for the NIR emitting Ln^{3+} ions. The complexes were found to be stable in the solid state in air, but they are sensitive to hydrolysis during which cleavage of the Ln–N bond occurs. The crystal structure of [Yb(tpp)(tp)] is shown in Figure 11, and it is seen that the cavity size of the porphyrin ring is too small for the metal ion to fit in. The ligand field caused the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition to be split into multiple bands in the [Yb(tpp)(tp)] complex. The coordinatively unsaturated complex $[Ln(tta)_3]$ [Htta = thenoyl(trifluoro)acetone] been found to form complexes with the potentially bis-bidentate bridging imine ligand 3,6-bis(2-pyridyl)tetrazin, bptz (**23**).[39] The crystal structure of a dinuclear complex $[\{Yb(tta)_3\}_2(\mu\text{-bptz})]$ is shown in Figure 12. The Yb^{3+}, Er^{3+} and Nd^{3+} complexes have an absorption band around 500 nm and exhibit NIR luminescence in CH_2Cl_2 solution.

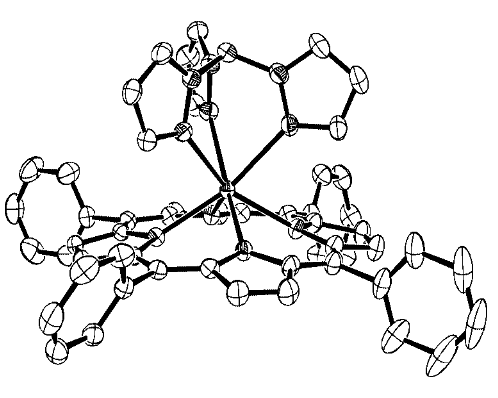


Figure 11. ORTEP drawing of the complex [Yb(tpp)(tp)] prepared by Boncella et al.[38] Drawn using coordinates taken from Cambridge Crystallographic Database. For abbreviations see text.

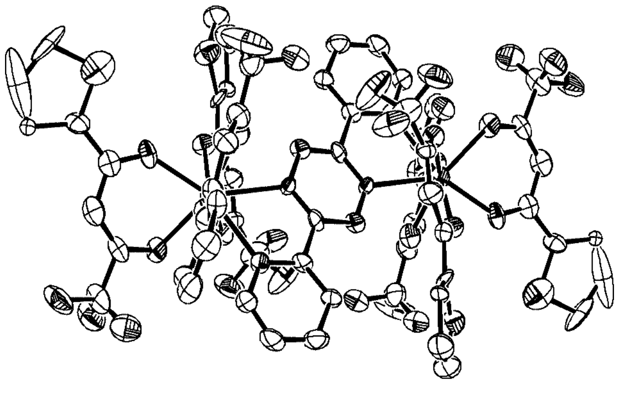
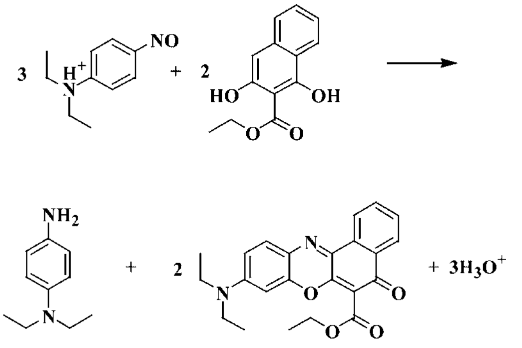


Figure 12. ORTEP drawing of the dinuclear complex $[\{Yb(tta)_3\}_2(\mu\text{-bptz})]$ prepared by Ward et al.[39] Drawn using coordinates taken from Cambridge Crystallographic Database. For abbreviations see text.

The compound **24** (Nile Red) is a highly fluorescent laser dye.[40] It is, like **10**, a push-pull chromophore with a strong solvent polarity dependence on the absorption and emission band maxima. The position of the absorption maximum has been found in a wide range moving from 484 nm in pentane to 629 nm in trifluoroacetic acid with values of ε around 35000 $\text{M}^{-1}\text{cm}^{-1}$,[40a] and the compound has thus been used as a polarity probe in chemical and biophysical environments. This solvatochromic effect has its origin in the fact that the dipole moment in the first excited state is significantly higher than in the ground state.[40b,40c] Verhoeven[20] found that **24** forms a complex (through the carbonyl oxygen atom) in benzene solution with the lewis acids [Ln(fod)$_3$], and that coordinated **24** was able to sensitize NIR emission for Ln = Er or Yb. The complex formation is, however, weak and does not occur in more coordinating solvents. In our laboratory we have tried to circumvent this obstacle by using the derivative of Nile Red **25**. This compound, along with a whole range of other Nile Red derivatives, was first described by Meng and co-workers,[41] and it was conveniently prepared as shown below (Scheme 1).



Scheme 1.

The compound **25** is able to form chelate metal complexes as shown in Figure 13 with an increased stability compared to the complexes of **24**. Preliminary experiments[42] showed indeed the complex formation between Ln^{3+} ions and **25** even in coordinating solvents such as CH$_3$CN or CH$_3$OH as seen in Figure 14. From an CH$_3$CN solution of La(OSO$_2$CF$_3$)$_3$ and **25** single crystals of [La(**25**)$_2$(OSO$_2$CF$_3$)$_3$(OH$_2$)$_2$] were grown. A crystal structure determination showed that **25** does coordinate bidentately to the metal centre (Figure 13). The luminescence properties of the Nd^{3+}, Er^{3+}, and Yb^{3+} complexes of **25** are under current investigation.

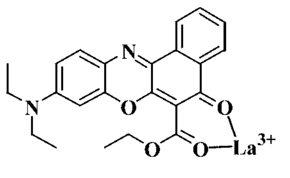


Figure 13. Structure of the [La(**25**)]$^{3+}$ chelate complex.

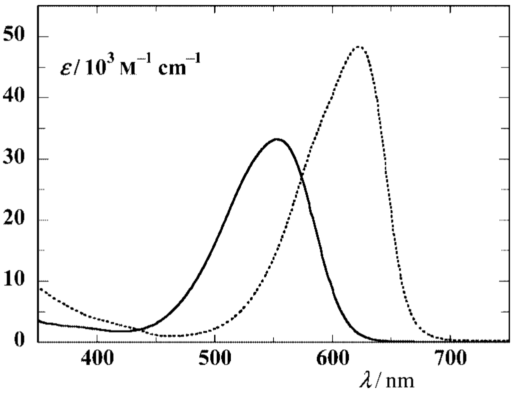


Figure 14. Absorption spectra of 1.05×10^{-5} M **25** (—) and 1.05×10^{-5} M **25**/1.12×10^{-4} M La(CF$_3$SO$_3$)$_3$ (···) in CH$_3$CN solution at 295 K.

Outlook

Despite the fact that the detection of NIR light requires specialized equipment, it seems very interesting to develop luminescent probes based on the NIR emitting metal ions Nd^{3+}, Er^{3+} and Yb^{3+}. However, the very low overall quantum yields (typically 10^{-4}–10^{-3}) of the metal-centred emission from complexes of the three metal ions in solution has been a disadvantage. The efficiency of the energy transfer from the VIS-absorbing to the metal centre is a bottleneck in that regard, and a better understanding of the mechanism for the energy transfer is needed in order to optimize the ligand design. It is crucial that the ligand enclose the metal centre efficiently so that water molecules are excluded from its first coordination sphere, and that the complex is stable in solution. Moreover, deuteration of the ligand, in proximity to the metal centre, increases the quantum yield significantly. Thus there is much room for improvement of the ligand design, and there are definitely many challenges ahead for synthetic chemists.

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