Photophysical studies of *m*-terphenyl-sensitized visible and near-infrared emission from organic 1:1 lanthanide ion complexes in methanol solutions

PERKIN 2
KEYNOTE

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The luminescence properties of several 1:1 lanthanide ion (Sm^{3+}, Tb^{3+}, Dy^{3+}, Pr^{3+}, Nd^{3+}, Ho^{3+}, Tm^{3+} and Yb^{3+}) complexes based on the *m*-terphenyl-containing ligands 1–3 have been studied in methanol solutions. The organic complexes show their typical luminescence in the visible (Sm^{3+}, Tb^{3+}, Dy^{3+} and Pr^{3+}) and in the near-infrared (Nd^{3+}, Er^{3+} and Yb^{3+}) region of the electromagnetic spectrum. The degree of shielding of the lanthanide ions from high-energy quenching modes of the solvent by the acyclic ligand 3 is less than the shielding by the macrocyclic ligands 1 and 2.

Not only the high-energy vibrational modes of the solvent quench the luminescent state, but also the C–H modes of the organic ligand, and even O–D and C–D modes can contribute significantly to the quenching. In general, the high-energy vibrational O–H and C–H modes are most efficient in luminescence quenching, but the quenching is strongly dependent on the magnitude of the energy gap between the lowest luminescent state and a lower-lying state. Luminescence at longer wavelengths can be quenched relatively easily because of the smaller energy gaps, rendering all quenching pathways, especially quenching by the remaining C–H modes in the partially deuterated ligand, efficient. When the energy gap is resonant with (an overtone of) a vibrational mode, *i.e.* O–H, C–H, O–D or C–D, the luminescence is very efficiently quenched by these modes and can even be extinguished. For instance: Ho^{3+} luminescence was not observed because the ${}^5S_2 \rightarrow {}^5F_5$ transition is resonant with the C–H vibrational mode, deuteration is less effective than expected for Pr^{3+} because the energy gap is resonant with the first overtone of the C–D vibration, and Nd^{3+} is efficiently quenched by the deuterated solvent because the energy gap is resonant with the first overtone of the O–D vibration.

Introduction

The luminescence properties of lanthanide ions are of special interest for various applications,[1] amongst others in fluoroimmunoassays (FIAs), in optical amplifiers and in lasers. Luminescent labels can be used for analysis in biological media as an alternative to radioimmunoassays,[2] because handling and disposal of radiolabeled substances are avoided. FIAs are relatively inexpensive and their luminescence can be measured relatively easily and rapidly. Lanthanide ion complexes are especially of interest because they exhibit long luminescence lifetimes and large Stokes shifts (relative to biological substances), rendering separation of the luminescence signal from the background fluorescence and scattering relatively easy.[3] The main drawback of lanthanide ions is their low absorption coefficients, resulting in inefficient direct excitation.[4] One way to solve this problem is to use polyaromatics as sensitizers, taking advantage of the generally high extinction coefficients of these molecules.[5] The sensitizer absorbs the excitation energy efficiently, transfers it to the lanthanide ion and this results in lanthanide ion luminescence (see Fig. 1). This process can be realized by either the direct coordination of sensitizer molecules to a lanthanide ion[1d] or by the covalent attachment of sensitizer molecules to an organic ligand which is able to complex a lanthanide ion.[6–8]

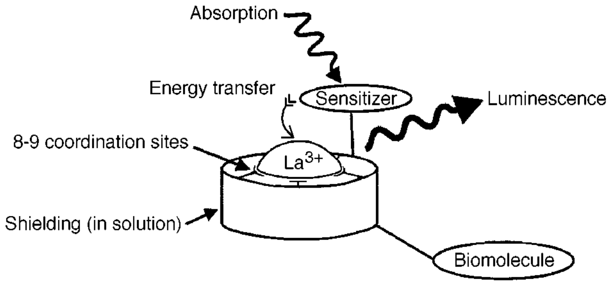

Fig. 1 Fluoroimmunoassay (FIA), showing the energy absorption by a sensitizer molecule (antenna), followed by the energy transfer to the lanthanide ion resulting in lanthanide ion luminescence

The luminescence of lanthanide ions is also used in optical amplifiers which operate according to the laser principle (**l**ight **a**mplification by **s**timulated **e**mission of **r**adiation, see Fig. 2).[1] A laser pump is used to bring the lanthanide ion to an excited state, which is followed by a relatively fast relaxation to a lower luminescent state. Due to interaction with the incoming data signal, *i.e.* a photon with a frequency that matches the lasing level, the lanthanide ion is stimulated to emit its energy in the form of light with the same phase and frequency as the incoming signal, hence the signal is amplified. Net emission occurs when the number of sites in the excited state is larger than the number of sites in the ground state (population inversion). Two basic configurations are the three- and four-level lasers. In a three-level laser the lasing transition is between an excited state and the ground state. The excited state is populated by

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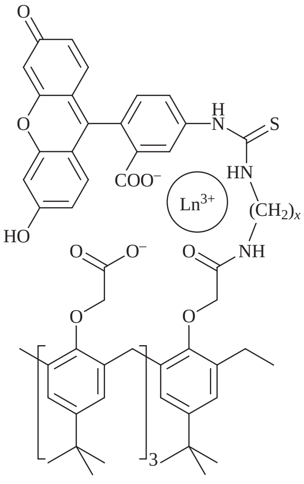
excitation to a somewhat higher level, followed by fast non-radiative decay. In a four-level laser the lasing transition is between two energy states higher in energy than the ground state. The higher of the two energy states of the lasing transition is populated in a similar way to the three-level laser and the lower is depopulated by fast non-radiative decay to the ground state. The latter phenomenon makes the population inversion inherently easier to achieve in a four-level laser.

Two telecommunication windows are commonly used for long-distance communication, one at 1.3 μm using neodymium or praseodymium emission and one at 1.5 μm using erbium emission. Drawbacks of the silica fibers that are frequently used for optical data transport are the low lanthanide ion concentration that can be used, leading to long and expensive amplifiers, and the relatively difficult fabrication process. These are the reasons for the current research interest in the possible application of luminescence originating from lanthanide ions complexed by organic and/or polymer systems.[9]

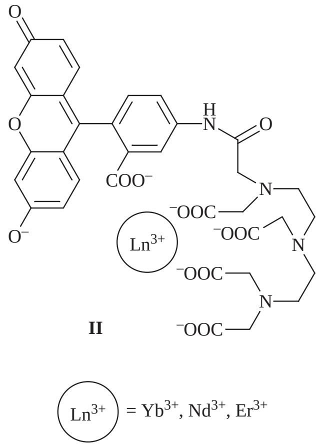
Although the two applications seem very different, the basic requirements for a molecular-based system are more or less the same. The requirements are: (i) formation of kinetically inert complexes, which can be obtained by designing polydentate ligands that (completely) encapsulate the trivalent lanthanide ion, (ii) shielding from quenching moieties like O–H groups from water molecules, (iii) efficient excitation, which can be accomplished by an antenna molecule with a high extinction coefficient and an efficient energy transfer to the lanthanide ion, (iv) long lifetimes of the excited state of the lanthanide ion, which not only implies that quenchers like O–H groups are removed from the first coordination shell but also that the encapsulating ligand provides no or minimal pathways for non-radiative decay, and (v) in the case of an FIA system a tissue- or organ-specific biomolecule should be covalently attached.

The positions of the luminescence bands in the electromagnetic spectrum are characteristic for a specific lanthanide ion. This means that one organic ligand that is capable of complexing different lanthanide ions can serve various applications operating at different wavelengths, just by changing the complexed lanthanide ion. Luminescence in the visible region of the spectrum is mostly applied in FIAs, however, the interest in using lanthanides that emit at longer wavelengths is growing since sensitization can be performed at longer wavelengths, thereby preventing the competitive excitation of organic chromophores. On the other hand, the near-infrared (NIR) part of the spectrum is especially important for optical data transmission. The luminescence properties of the lanthanide ions will be discussed in the order of the following groups (see also Fig. 3):[10] Group 1: Lanthanide ions that luminesce strongly in the visible wavelength region (Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+}); Group 2: Lanthanide ions that exhibit weak luminescence in the visible part of the spectrum (Pr^{3+}, Ho^{3+} and Tm^{3+}); Group 3: Lanthanide ions that emit in the NIR (Pr^{3+}, Nd^{3+}, Dy^{3+}, Er^{3+} and Yb^{3+}).[11]

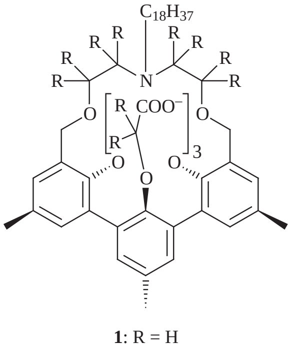
Whereas numerous examples of luminescent 1:1 organic Eu^{3+} and Tb^{3+} complexes in organic solvents have been reported,[1] luminescence originating from complexes with other lanthanide ions in organic solvents has seldom been reported. β-Diketonates are most commonly used for the complexation of lanthanide ions, and luminescence has been reported for Sm^{3+} (590 nm) and Dy^{3+} (570 nm) complexes in the visible part of the electromagnetic spectrum,[12] and for Nd^{3+} complexes (1060 nm) in the near-infrared.[13] Dicarboxylic acids were also used for 3:1 complexation of lanthanide ions, giving rise to Sm^{3+}, Dy^{3+}, Pr^{3+} (595 nm) and Tm^{3+} (780 nm) luminescence.[14] To the best of our knowledge, in the visible part of the electromagnetic spectrum only Sm^{3+} and Dy^{3+} luminescence has been observed for 1:1 complexes based on crown ethers[15] and calix[4]arenes.[16] Recently, NIR emission has been reported originating from tetraaza-macrocycle-based Yb^{3+}[17] and Nd^{3+}[18] complexes in organic solutions and of Yb^{3+} complexed by proteins.[19] Recently, we[7] (system **I**) and others[8] (system **II**) have reported the sensitized NIR emission of polydentate ligands with a covalently attached sensitizer.



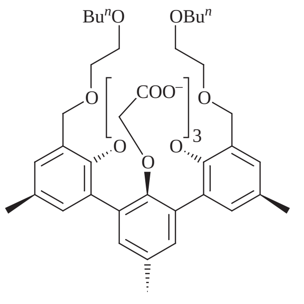
I, *x* = 3,6



In this paper a study is presented of organic 1:1 lanthanide ion complexes which give sensitized luminescence in organic solvents in both the visible and the near-infrared parts of the electromagnetic spectrum. In particular the effect of substituting C–H for C–D groups has been investigated. The *m*-terphenyl-based organic ligands **1**–**3**, the synthesis of which was described in previous papers,[20] were complexed with lanthanide ions that are known to exhibit luminescence.[4] The photophysical properties of the corresponding Eu^{3+} complexes have been reported previously,[20] and they show an increase in luminescence lifetime by a factor of 1.5 upon deuteration of the ligand in **1·Eu^{3+}**, to give **2·Eu^{3+}**. Moreover, we have shown that one solvent molecule is coordinated in the first coordination sphere of **1** and **2**. The degree of shielding from the solvent decreased when the acyclic ligand **3** was the complexing agent, leading to the coordination of two molecules of methanol to the Eu^{3+} ion. However, the distances between the C–H groups of the ligand and the Eu^{3+} ion in **3·Eu^{3+}** are larger than in **1·Eu^{3+}** and **2·Eu^{3+}**, leading to reduced quenching by ligand **3**. Despite the two coordinating solvent molecules the luminescence lifetime of **3·Eu^{3+}** in CH_3OH is equal to the lifetime of **1·Eu^{3+}** in CH_3OH within experimental error.[20b] These photophysical studies are



1: R = H
2: R = D



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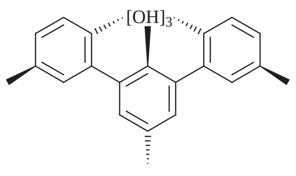

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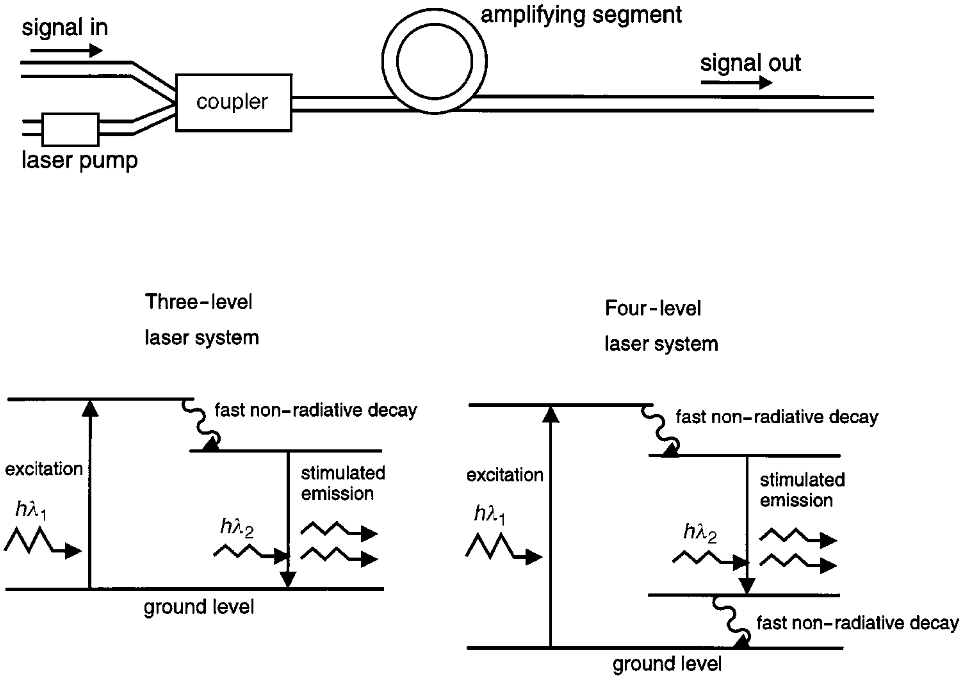

Fig. 2 Schematic presentation of part of the telecommunication network and transitions involved in a three-level and four-level laser energy diagram

now extended to complexes of the known luminescent lanthanide ions and we have concentrated our studies in particular on the elucidation of the various quenching pathways. The hypothesis is that the increase in luminescence intensity and lifetime resulting from ligand deuteration will be more pronounced when the energy gap between the luminescent state and a lower-lying state is small, since lower overtones of the vibrational modes are able to match the energy gap.[21] Our ultimate goal is the optimization of the encapsulating ligand leading to luminescence properties that can be applied in the field of polymer-based optical amplifiers that operate in the near-infrared. Therefore, we are mainly interested in this part of the electromagnetic spectrum and in the possible application of this part of the spectrum in immunoassays and for optical amplification.

Results and discussion

Synthesis

The lanthanide ion complexes were synthesized according to the synthetic pathways we published previously for **1·Eu**$^{3+}$, **2·Eu**$^{3+}$ and **3·Eu**$^{3+}$.[20] The complexes were characterized by FAB mass spectrometry,[22] elemental analysis[23] and infrared spectroscopy (Tables 2–4) which showed that 1 : 1 complexes were obtained upon three-fold deprotonation of the ligands.

Photophysical studies

The model compound **4** was used for a first indication of the energy of the triplet states of the ligands **1**–**3**. The emission spectrum of a deaerated 10^{-4} M solution of **4** [2,6-bis(2′-hydroxy-5′-methylphenyl)-4-methylphenol] in methanol–ethanol (3 : 1), recorded after excitation at 287 nm, is dominated by fluorescence with a peak maximum at approximately 365 nm. Upon cooling to 77 K the fluorescence spectrum shows a small blue shift to 350 nm, with a concomitant approximately 20-fold decrease in intensity. Additionally, a band appears with a 0→0 transition around 425 nm, which is attributed to the phosphorescence of the *m*-terphenyl moiety. These spectral features are in good agreement with the observed phosphorescence 0→0 band at 437 nm determined for *m*-terphenyl in ethanol by Chakravorti *et al.*[24] and the triplet state energy of 2.88 eV (= 421 nm) derived from energy transfer measurements in benzene by Kira and Thomas.[25]

The emission spectrum of a deaerated solution of **1·Eu**$^{3+}$ in methanol–ethanol (3 : 1) at 77 K, recorded after excitation at 287 nm, shows a weak shoulder at approximately the same wavelength as **4**, *i.e.* 425 nm, implying that the ligand has the same triplet state. The energy of this triplet state is 23 500 cm^{-1}, which is for example ~3000 cm^{-1} higher than the emissive $^5D_4$ level of Tb^{3+} and ~6500 cm^{-1} higher than the emissive $^5D_0$ level of Eu^{3+}. The emission intensity of the solution of **1·Eu**$^{3+}$ at room temperature increases by approximately 22% upon deaeration which indicates that the energy transfer is relatively slow, in the order of 10^7 s^{-1}. Due to the fact that the *m*-terphenyl moieties in **1·Eu**$^{3+}$ and **3·Eu**$^{3+}$ have very similar conformations[26] and the fact that the triplet state of the rigid macrocycle **1** is equal to the triplet state of the 'flexible' compound **4** within the experimental error, we assume the triplet state of **3** also to be close to 23 500 cm^{-1}.

The photophysical studies described below were performed using 10^{-4} M solutions of the lanthanide ion complexes in [$^2H_4$]methanol or non-deuterated methanol.[27] Details of the experimental approach are given in ref. 20.

Luminescence properties of Group 1 complexes

Samarium. The excitation spectra, depicted in Fig. 4(*a*), were recorded by detection of the most intense Sm^{3+} emission at 590 nm. The occurrence of sensitized emission is obvious from the spectra, which further show the weak absorption band of the Sm^{3+} ion at 403 nm. The emission intensity decreases in the order **3·Sm**$^{3+}$ > **2·Sm**$^{3+}$ > **1·Sm**$^{3+}$ > Sm(NO$_3$)$_3$, a trend which is also shown by the emission spectra recorded after excitation at 287 nm [Fig. 4(*b*)]. The Sm^{3+} complexes show two intense emission bands at 590 and 640 nm, and two weaker bands at 560 and 700 nm. The more intense luminescence of **3·Sm**$^{3+}$ may be a result of the 1.3 times higher absorption coefficient of the acyclic ligand and/or of the less efficient quenching by the acyclic ligand compared to the macrocyclic ligands. The latter is supported by the lifetime measurements[28] that were performed on these solutions, showing the longest lifetime of 90 μs for **3·Sm**$^{3+}$ (Table 1). The intensity difference between the deuterated and the non-deuterated complex is explained in terms of

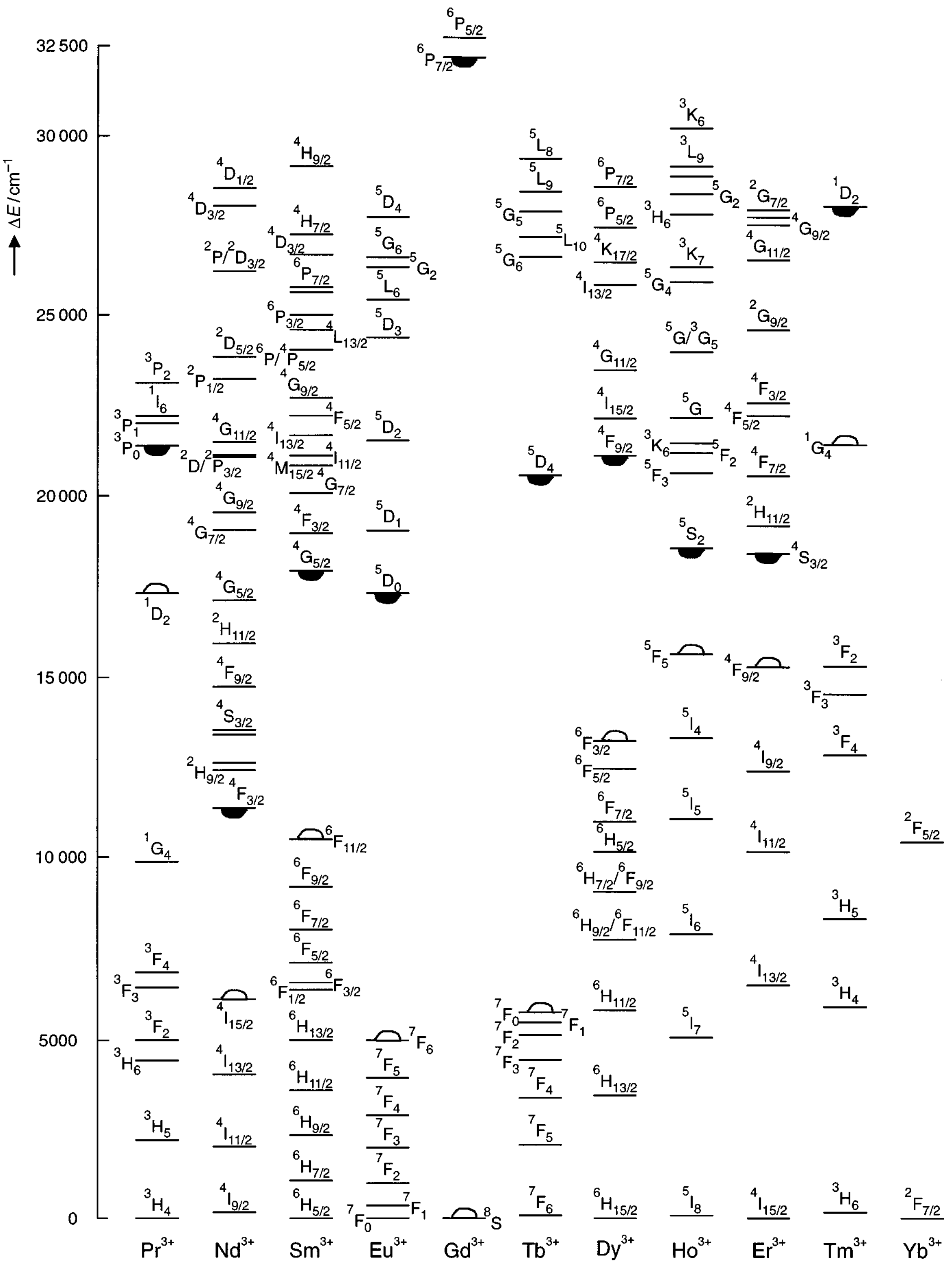

Fig. 3 Energy level diagram for the lanthanide ions in aqueous solutions; ▾ represent the lowest luminescent level, ⌓ represent the highest level of the ground state. Reproduced from *J. Chem. Phys.*, 1975, **62**, 208 with the kind permission of the American Institute of Physics.

the less efficient quenching by the deuterated ligand due to the smaller number of C–H high-energy vibrational modes.[29] This is supported by the lifetime increase by a factor of 1.5 upon deuteration of the Sm^{3+} complex (Table 1).

The luminescence intensity of all the complexes is significantly decreased when the more efficiently quenching, non-deuterated methanol (data not shown) is used as solvent. The intensity is approximately three times lower for the macrocyclic ligands, and approximately 10 times lower for the acyclic ligand. The more pronounced decrease for **3·Sm**$^{3+}$ is the result of the coordination of more, probably two strongly quenching solvent molecules to the lanthanide ion instead of one in the case of the macrocyclic ligands, as was also observed for Eu^{3+}.[20b]

The lifetimes of the different Sm^{3+} complexes dissolved in non-deuterated methanol are equal within experimental error. However, these lifetimes are more or less equal to the shortest lifetime that can be measured with the maximally attainable modulation frequency with the mechanical chopper (4000 Hz) and may thus be even shorter. As a consequence, quenching by the high-energy vibrational solvent modes may be larger than is

Table 1 Lifetimes and deactivation rate constants of 10^{-4} M solutions of lanthanide ion complexes, after excitation of the ligand at 287 nm[a]

	$\tau_{CD_3OD}/\mu s$	$\tau_{CH_3OH}{}^{b}/\mu s$	k^{c} ms^{-1}	
1·Sm^{3+}	54	≈40	6	Sm^{3+} : C–H$^{lig\,d}$
2·Sm^{3+}	80	≈40	⩾12	**2·Sm^{3+}** : (O–H + C–H)^{solv}
3·Sm^{3+}	90	≈40	⩾14	**3·Sm^{3+}** : (O–H + C–H)^{solv}
1·Tb^{3+}	2780	2520	<0.02	Tb^{3+} : C–H$^{lig\,d}$
2·Tb^{3+}	2910	2770	0.02–0.04	**2·Tb^{3+}** : (O–H + C–H)^{solv}

[a] The experimental error was ⩽10% which was determined from duplicate or triplicate measurements. [b] ≈40 µs is the maximally attainable modulation frequency with the mechanical chopper (4000 Hz). [c] *k* is the rate constant of quenching of the excited state of the lanthanide ion. The column on the far right gives the responsible modes. [d] Of the macrocyclic ligand.

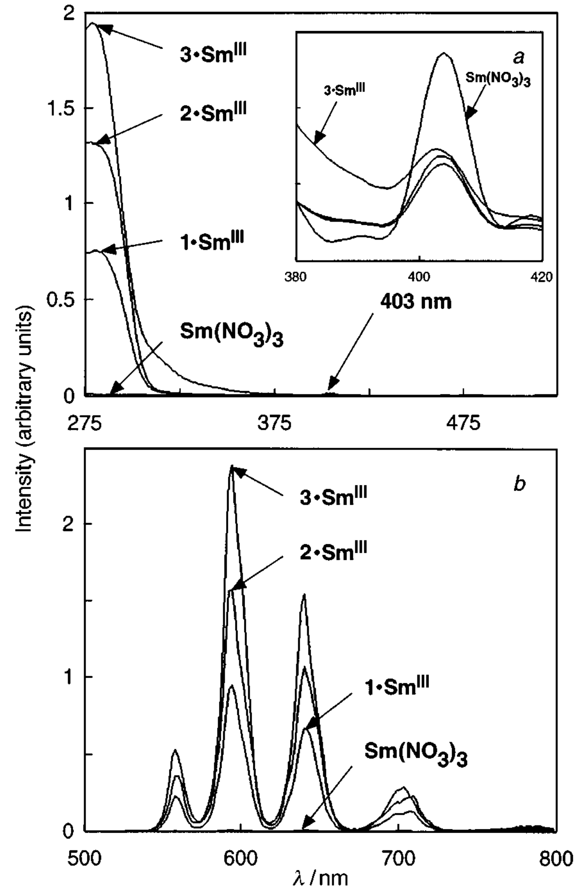

Fig. 4 (*a*) Excitation spectra detected at 590 nm and (*b*) emission spectra after excitation at 287 nm, both of 10^{-4} M solutions of **1·Sm^{3+}**, **2·Sm^{3+}**, **3·Sm^{3+}** and Sm(NO$_3$)$_3$ in [^{2}H$_4$]methanol

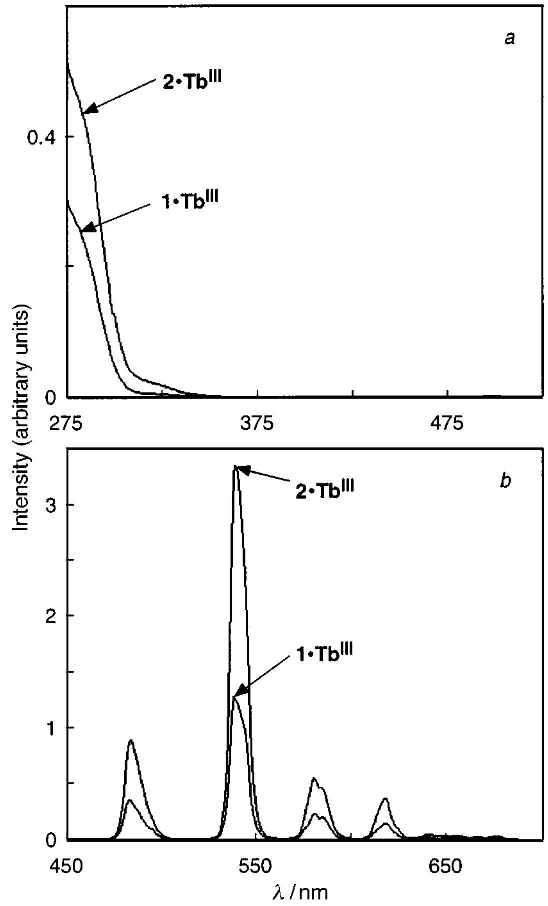

Fig. 5 (*a*) Excitation spectra detected at 540 nm and (*b*) emission spectra after excitation at 300 nm, both of 10^{-4} M solutions of **1·Tb^{3+}** and **2·Tb^{3+}** in [^{2}H$_4$]methanol

indicated by the rate constants of quenching, $k_{2\text{-}Sm^{3+}}{}^{solv}$ ⩾12 ms^{-1} and $k_{3\text{-}Sm^{3+}}{}^{solv}$ ⩾14 ms^{-1}. For example, the rate constant of quenching $k_{2\text{-}Sm^{3+}}{}^{solv}$ is calculated by taking the difference of the reciprocal lifetimes in CD$_3$OD and CH$_3$OH, respectively. Because of the use of CH$_3$OH and CD$_3$OD the rate constants of quenching include the contributions of both the O–H and the C–H modes. These contributions can in principle be unravelled by also using CH$_3$OD and CD$_3$OH as solvents. However, this has not been done for the focus of this paper lies more on the quenching by the encapsulating ligands. Compared to the Eu^{3+} complexes[20a] (order 0.5 ms^{-1}) these rate constants are quite high. This can be related to the smaller energy gap between the lowest luminescent excited state, $^4G_{5/2}$, and the highest ground state, $^6F_{11/2}$, of Sm^{3+} ($\Delta E_{Sm^{3+}}$ ≈7400 cm^{-1} compared to $\Delta E_{Eu^{3+}}$ ≈12 300 cm^{-1}, see Fig. 3). Therefore, lower overtones of the high-energy vibrational modes are able to match the energy gap of Sm^{3+}, resulting in more efficient quenching of the luminescent state.[21] This is also indicated by the calculated rate constants for quenching by the C–H modes of the ligand, 6 ms^{-1} for the macrocyclic Sm^{3+} complexes and 0.25 ms^{-1} for the analogous Eu^{3+} complexes.[20a]

Based on these lifetimes and the assumption that one methanol coordinates to the lanthanide ions complexed by **1** and **2**, the $q_{methanol}$ factor in the 'Horrocks equation'[30] was estimated to be $q_{methanol}$ ≈0.05–0.1 for Sm^{3+} ions in methanol solutions. This low value, compared to 2.1 for Eu^{3+} and 8.4 for Tb^{3+},[1] also indicates the more efficient quenching of the Sm^{3+} luminescence. In their review article, Ermolaev and Sveshnikova[31] estimated the rate constant for quenching per O–H oscillator as 18 ms^{-1} for Sm^{3+}. This value is equal to the reciprocal value of $q_{methanol}$ (in ms) and consequently lies within the range of the estimation made for these Sm^{3+} complexes.

Terbium.[32] The excitation spectra of the Tb^{3+} complexes in [^{2}H$_4$]methanol show that UV excitation [Fig. 5(*a*)] leads to sensitized emission of Tb^{3+}. The emission spectra, depicted in Fig. 5(*b*), show the typical Tb^{3+} luminescence with an intense emission band at 540 nm, and three weaker bands at 485, 580 and 615 nm. The luminescence intensity increased by a factor of approximately two upon ligand deuteration as the result of reduced quenching by the ligand.

Lifetime measurements show a slight lifetime increase upon ligand and solvent deuteration (Table 1). This indicates that

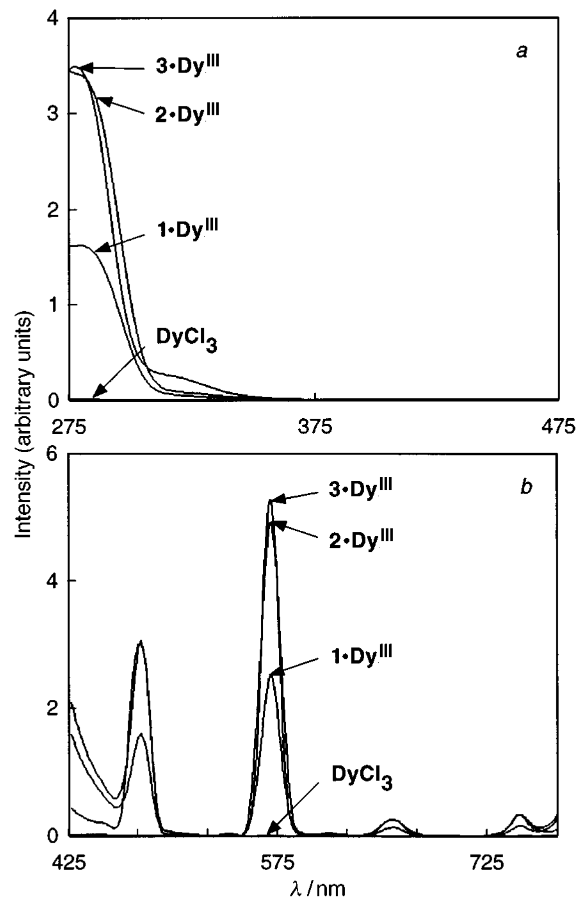

Fig. 6 (*a*) Excitation spectra detected at 570 nm and (*b*) emission spectra after excitation at 287 nm, both of 10^{-4} M solutions of **1·Dy**$^{3+}$, **2·Dy**$^{3+}$, **3·Dy**$^{3+}$ and $DyCl_3$ in [$^2H_4$]methanol

quenching by the C–H modes of the organic ligand is less important in the luminescence quenching of Tb^{3+} complexes ($k_{\mathrm{C-H}}^{\mathrm{lig}}$ <0.02 ms^{-1}) compared to the Sm^{3+} complexes ($k_{\mathrm{C-H}}^{\mathrm{lig}}$ = 6 ms^{-1}) and Eu^{3+} complexes ($k_{\mathrm{C-H}}^{\mathrm{lig}}$ = 0.25 ms^{-1}).[20a] The less efficient quenching is the result of the larger energy gap between the lowest luminescent excited state, $^5D_4$, and the highest ground state, $^7F_0$, for the Tb^{3+} ions ($\Delta E_{\mathrm{Tb}^{3+}}$ ≈14 200 cm^{-1} compared to $\Delta E_{\mathrm{Eu}^{3+}}$ ≈12 300 cm^{-1} and $\Delta E_{\mathrm{Sm}^{3+}}$ ≈7400 cm^{-1}, see Fig. 3).[21] Moreover, quenching by the O–H high-energy vibrational modes of the solvent is inefficient, indicated by the low quenching rate constant ($k_{\mathrm{O-H+C-H}} = 0.03$ ms^{-1} for Tb^{3+} and $k_{\mathrm{O-H}} = 0.59$ ms^{-1} for Eu^{3+}). The 'Horrocks equation' with $q_{\mathrm{methanol}} = 8.4$ for Tb^{3+} ions in methanol solutions[1] was used for an approximation of the number of solvent molecules in the first coordination sphere of the Tb^{3+} ions, giving (0.2–0.3 ± 0.5).[33] This number is smaller than was determined for the analogous Eu^{3+} complexes, and might be the result of the smaller ionic radius of the Tb^{3+} ion (0.923 Å compared to 0.950 Å for Eu^{3+}, due to the so-called 'lanthanide ion contraction').[34] This results in a more 'compact' complex that leaves apparently less space in the first coordination sphere of the lanthanide ion for solvent coordination. However, it should be noted that the accuracy of the 'Horrocks equation' is low for small numbers of coordinating water molecules as is indicated by the error of ± 0.5.[35]

Dysprosium. The excitation spectra of **3·Dy**$^{3+}$ in [$^2H_4$]methanol differ only slightly from those of the macrocyclic complexes, probably as the result of symmetry changes or the lower solubility of **1·Dy**$^{3+}$ and **2·Dy**$^{3+}$ in methanol [Fig. 6(*a*)]. A direct comparison of the luminescence properties of the acyclic and the macrocyclic Dy^{3+} complexes is thus not possible. The emission spectra [see Fig. 6(*b*)] show two intense emission bands at 475 and 570 nm, and two weak bands at 655 and 745 nm. The luminescence of the deuterated complex is approximately two times more intense compared to the non-deuterated complex, due to the less efficient quenching by the ligand.[36] The relative intensities of the two intense emission bands at 475 and 570 nm are not the same for the acyclic and the macrocyclic complexes, also indicating that the emission spectra cannot be compared directly. The intensity variation is probably the result of changes in the symmetry around the lanthanide ion.[37] For the Sm^{3+} and Eu^{3+} complexes, no significant influence of the symmetry of the ligands on the luminescence properties was observed. The luminescence at 570 nm of the macrocyclic complexes was too weak for meaningful lifetime measurements, whereas the lifetime of the luminescent $^4F_{9/2}$ state of the acyclic complex **3·Dy**$^{3+}$ dissolved in [$^2H_4$]methanol could be determined as 79 μs.[38]

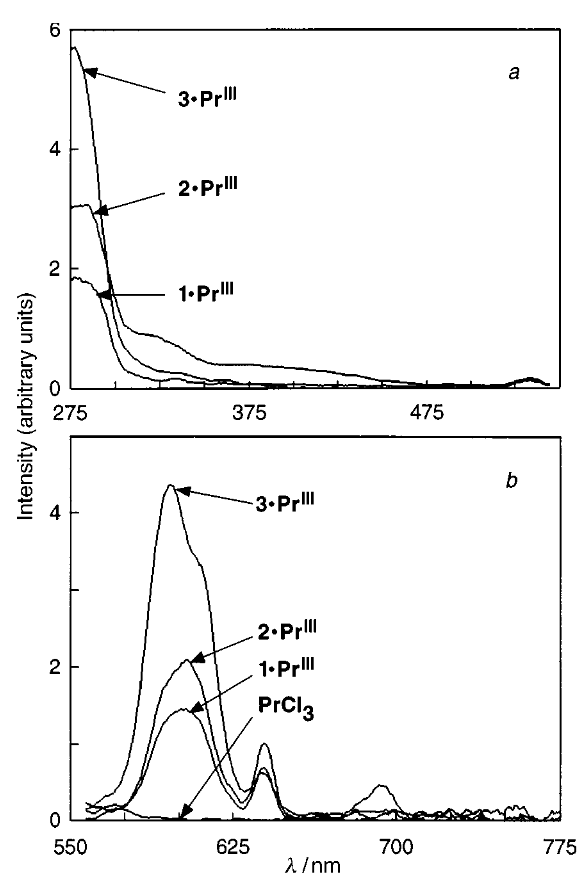

Fig. 7 (*a*) Excitation spectra detected at 594 nm and (*b*) emission spectra after excitation at 287 nm, both of 10^{-4} M solutions of **1·Pr**$^{3+}$, **2·Pr**$^{3+}$, **3·Pr**$^{3+}$ and $PrCl_3$ in [$^2H_4$]methanol

The energy difference between the lowest luminescent excited state, $^4F_{9/2}$, and the highest ground state, $^6F_{3/2}$, of the Dy^{3+} ions ($\Delta E_{\mathrm{Dy}^{3+}}$ ≈7850 cm^{-1}, see Fig. 3) is somewhat larger than for Sm^{3+} ($\Delta E_{\mathrm{Sm}^{3+}}$ ≈7400 cm^{-1}),[10,21,39] leading to slightly less efficient quenching of the Dy^{3+} luminescence. The luminescence of the Sm^{3+} and Dy^{3+} complexes is quenched more efficiently compared to the Eu^{3+} and Tb^{3+} complexes ($\Delta E_{\mathrm{Eu}^{3+}}$ ≈12 300 cm^{-1} and $\Delta E_{\mathrm{Tb}^{3+}}$ ≈14 200 cm^{-1}) because the energy gaps of Sm^{3+} and Dy^{3+} are smaller and can be matched by a lower overtone of a vibrational mode.[21]

Luminescence properties of Group 2 complexes

The luminescence properties of the lanthanide ions that weakly emit light in the visible part of the spectrum were only studied in [$^2H_4$]methanol. The luminescence in non-deuterated methanol was always very weak or not detectable. Consequently, deactivation by the high-energy vibrational solvent modes could not be studied for these complexes.

Praseodymium. The excitation spectra of solutions of **1·Pr**$^{3+}$, **2·Pr**$^{3+}$ and **3·Pr**$^{3+}$ in [$^2H_4$]methanol were recorded by detecting the most intense signal at 595 nm and show a significant increase in luminescence intensity upon excitation in the UV region, *i.e. via* the ligand [Fig. 7(*a*)]. The emission spectra [Fig. 7(*b*)] show an intense luminescence band at 595 nm, corresponding to the $^3P_0 \rightarrow {}^3F_2/{}^3H_6$ transitions, whereas two weak signals are present at 640 and 695 nm. The acyclic complex **3·Pr^{3+}** shows the highest luminescence intensity, most probably due to the less efficient quenching by the ligand due to the relatively long distance between the C–H modes of the ligand and Pr^{3+}.[40] Also the 1.3 times higher absorption coefficient of **3** (compared to **1** and **2**) may contribute to the enhanced intensity. The lifetimes of the luminescent $^3P_0$ states of the Pr^{3+} complexes are < 40 μs, and are more or less equal to the shortest lifetime that can be measured with the maximally attainable modulation frequency with the mechanical chopper (4000 Hz). Therefore, conclusions cannot be drawn.

Despite the smaller energy gap between the lowest luminescent excited state, $^3P_0$, and the highest ground state, $^1D_2$, of Pr^{3+} ($\Delta E_{Pr^{3+}}$ ≈4100 cm^{-1}, see Fig. 3) compared to the Group 1 complexes, the luminescence is enhanced only 1.4 times upon ligand deuteration. Based on the results of Stein and Würzberg,[21] we hypothesized that the effect of ligand deuteration on the luminescence intensity should be larger for lanthanide ions with a small energy gap. However, we did not observe this, probably as a result of the magnitude of the energy gap (4100 cm^{-1}), which is more or less resonant with the first overtone of the C–D vibration (ν_{C-D} ≈2100–2200 cm^{-1}). In this case C–H for C–D substitution is less effective for increasing the luminescence intensity, because the C–D vibration is also relatively efficient in quenching the Pr^{3+} luminescence. Moreover, the expected increase in luminescence upon deuteration of the ligand might be obscured by the efficient quenching by the remaining C–H modes that are abundantly present within the 'quenching distance' of the Pr^{3+} ion.

Holmium. The only weak luminescence for the Ho^{3+} complexes (data not shown) is most likely the result of the magnitude of the energy gap between the luminescent state, $^5S_2$, and the highest lower-lying state, $^5F_5$ ($\Delta E_{Ho3^{+}}$ ≈3000 cm^{-1}, see Fig. 3), which is resonant with a C–H vibration (ν_{C-H} ≈2900–3100 cm^{-1}).

Thulium. The Tm^{3+} complexes do not show detectable luminescence. The energy of the emissive $^1D_2$ level is too high (≈27 800 cm^{-1}) for sensitized population by the *m*-terphenyl-based ligands (triplet energy ≈23 500 cm^{-1}).

Luminescence properties of Group 3 complexes

Praeseodymium. Pr^{3+} ions do not only exhibit luminescence in the visible part of the spectrum, but also at 1.3 μm, originating from the $^1G_4 \rightarrow {}^3H_5$ transition.[14] Unfortunately, we were not able to detect any luminescence of this wavelength upon ligand excitation at 287 nm, and laser excitation using the argon lines between 400 and 500 nm. The energy gap between the $^1G_4$ state and the highest ground state, $^3F_4$ ($\Delta E_{Pr^{3+}}$ ≈3000 cm^{-1}, see Fig. 3), is resonant with a C–H vibration, rendering efficient quenching by these high-energy vibrational modes.

Neodymium. The two most important luminescence bands of Nd^{3+} for application in optical amplifiers are situated at 1060 and 1350 nm, corresponding to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition and the $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition, respectively.[4c] Optical amplifiers and lasers, based on inorganic matrices, that operate at these wavelengths have been developed.[42] The excitation spectra, depicted in Fig. 8(*a*), were recorded using solutions of **1·Nd^{3+}**, **2·Nd^{3+}** and **3·Nd^{3+}** in [$^2H_4$]methanol and detection at 1060 nm. In contrast with all other lanthanide ion complexes, the emission intensity after excitation in the UV part of the electromagnetic spectrum is the lowest for **3·Nd^{3+}** and most intense for **2·Nd^{3+}**. This was also established by the emission spectra of the same solutions, after ligand excitation at 287 nm, depicted in Fig. 8(*b*). The emission spectra clearly show the emission bands at 1060 nm, whereas for **2·Nd^{3+}** the luminescence band at 1350 nm was easily detectable. The low intensity of **3·Nd^{3+}** is probably the result of the presence of two solvent molecules in the first coordination sphere of the Nd^{3+} ion compared to one for **1·Nd^{3+}** and **2·Nd^{3+}**, despite the deuterated solvent. The energy gap of the $^4F_{3/2} \rightarrow {}^4I_{15/2}$ transition is small ($\Delta E_{Nd^{3+}}$ ≈5300 cm^{-1}, see Fig. 3) and more or less resonant with the first overtone of the O–D vibration (ν_{O-D} ≈2400 cm^{-1}). This also explains why the luminescence lifetime of **3·Nd^{3+}** in [$^2H_4$]methanol is relatively short (0.74 μs).[43]

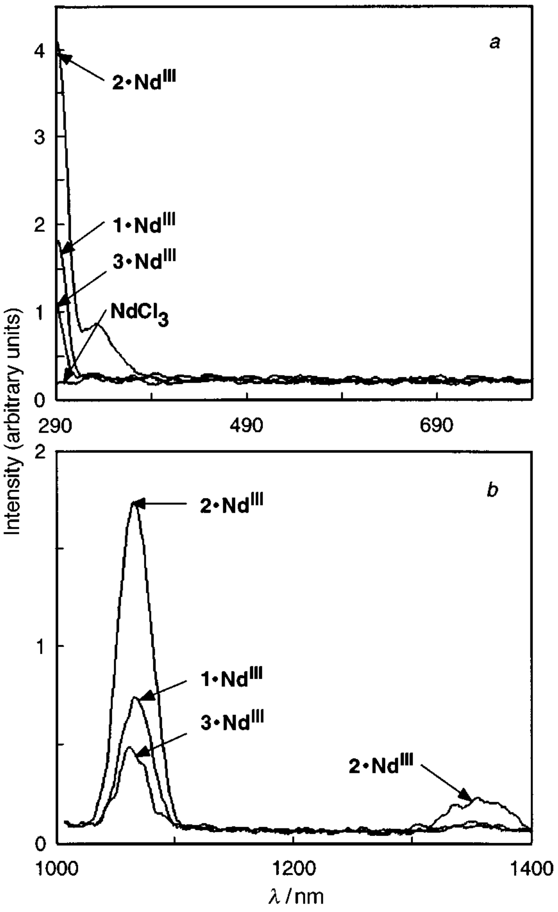

Fig. 8 (*a*) Excitation spectra detected at 1060 nm and (*b*) emission spectra after excitation at 287 nm, both of 10^{-4} M solutions of **1·Nd^{3+}**, **2·Nd^{3+}**, **3·Nd^{3+}** and NdCl$_3$ in [$^2H_4$]methanol

The luminescence intensity at 1060 nm is increased by a factor of 2.3 upon partial deuteration of the macrocyclic ligand, indicating less efficient quenching by the deuterated ligand. The large increase shows that quenching by high-energy vibrational modes is important for Nd^{3+} due to the small energy gap between the $^4F_{3/2}$ state and the lower-lying state, $^4I_{15/2}$. Lifetime measurements of the macrocyclic complexes ($\tau_{1\cdot Nd^{3+}}$ = 0.79 μs and $\tau_{2\cdot Nd^{3+}}$ = 0.89 μs) give a rate constant for quenching by the C–H modes of the ligand of $k_{C-H}{}^{lig}$ = 142 ms^{-1} (compared to $k_{C-H}{}^{lig}$ = 6 ms^{-1} for Sm^{3+}). This implies that the quenching of Nd^{3+} by the ligand C–H modes is very efficient.

The measured lifetimes are relatively long compared to values reported in the literature, *i.e.* Nd^{3+} complexed by EDTA (0.48 μs) and in deuterated solutions (0.15 μs in D_2O and 0.48 μs in CD_3OD).[18] This also indicates that quenching by O–D vibrations is an important deactivation pathway for excited Nd^{3+} ions.

Erbium. Luminescence studies performed on the Er^{3+} complexes **1·Er^{3+}**, **2·Er^{3+}** and **3·Er^{3+}** in the solid phase (dispersed in KBr tablets) and dissolved in DMF and [^{2}H]*n*-butanol showed the typical 1.54 μm emission band at room temperature. The luminescence lifetime of the complexes dispersed in KBr tablets is short (τ_{KBr} <0.5 μs), probably due to concentration

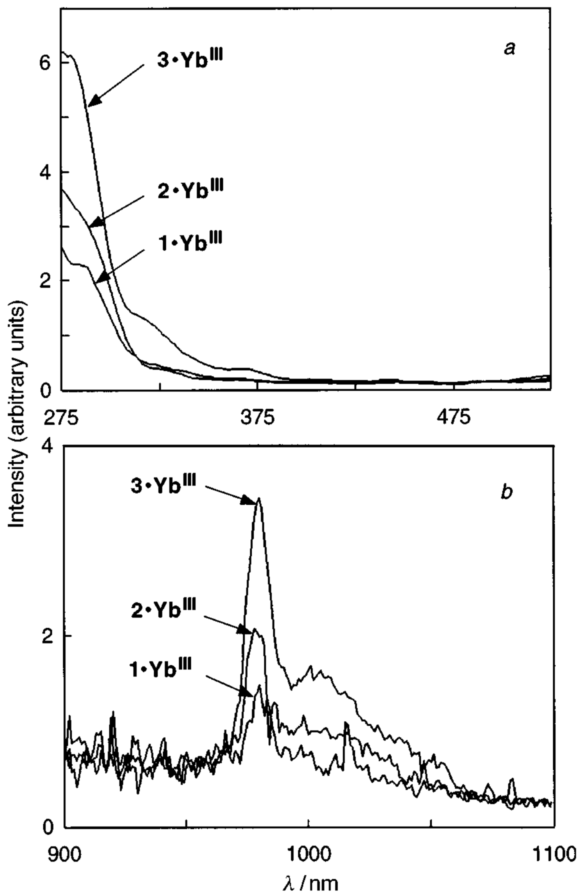

Fig. 9 (*a*) Excitation spectra detected at 984 nm and (*b*) emission spectra after excitation at 287 nm, both of 10^{-4} M solutions of **1·Yb**$^{3+}$, **2·Yb**$^{3+}$ and **3·Yb**$^{3+}$ in [^{2}H$_4$]methanol

quenching, whereas in [^{2}H]*n*-butanol a lifetime of 0.8 μs was observed for all complexes. From these experiments it became clear that the effect of partial deuteration was still obscured by the remaining high-energy vibrational C–H modes of the ligand. The 1 : 1 organic Er^{3+} complexes are especially interesting for application in optical amplification because the emission band is relatively wide (full width at half maximum is 70 nm), thereby permitting high gain. For further details on the Er^{3+} complexes see ref. 11.

Ytterbium. The Yb^{3+} ions are often used as codopants in lasers and optical amplifiers because of their relatively broad absorption (with a relatively high absorption coefficient) and emission band at 980 nm and the possibility of transfering this energy to other lanthanide ions, like Pr^{3+},[44] Er^{3+} [45] and Tm^{3+}.[46] The excitation spectra of solutions of **1·Yb**$^{3+}$, **2·Yb**$^{3+}$ and **3·Yb**$^{3+}$ in [^{2}H$_4$]methanol after detection at 984 nm are depicted in Fig. 9(*a*). The more soluble, acyclic complex **3·Yb**$^{3+}$ shows the highest intensity. However, a direct comparison with the macrocyclic complexes is not possible, due to the low solubility of the macrocyclic Yb^{3+} complexes. The emission spectra of these solutions [Fig. 9(*b*)], after ligand-mediated excitation at 287 nm, clearly show the emission band at 980 nm, corresponding to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition, and a broad band at 1005 nm. This latter band may be the result of splitting of the energy levels of the Yb^{3+} ion as a consequence of ligand field effects and/or the presence of more than one species in solution. Also in this case the effect of ligand deuteration is obvious from the emission spectra, showing an increase in luminescence upon ligand deuteration. The efficient quenching by the high-energy vibrational modes is also established by the increase in luminescence lifetime from 16 to 24 μs upon ligand deuteration in [^{2}H$_4$]methanol, giving a rate constant of $k_{\text{C–H}}{}^{\text{lig}} = 21$ ms^{-1}. The lifetime of **3·Yb**$^{3+}$ in [^{2}H$_4$]methanol was determined to be 14 μs. To the best of our knowledge, the longest lifetime ever reported for a 1 : 1 organic Yb^{3+} complex dissolved in D$_2$O is 10 μs.[17]

Conclusions

Near-infrared and visible luminescence originating from organic solutions of 1 : 1 lanthanide ion *m*-terphenyl-based complexes was observed and the effect of ligand deuteration was investigated in detail. By making use of one type of organic ligand, luminescent materials operative at several wavelengths are accessible just by varying the lanthanide ion. All lanthanide ions studied (except HO^{3+} and Tm^{3+}) showed sensitized emission *via* the *m*-terphenyl part of the organic ligand. The highly efficient lanthanide luminescence obtained in this way may be useful for diagnostic (multi-label) applications and for use in optical amplifiers.

The quenching by high-energy vibrational C–H and/or O–H modes surrounding the lanthanide ion is relatively efficient for all complexes, except for the macrocyclic Tb^{3+} complexes. Generally, quenching is more efficient when the energy gap between the luminescent excited state and a lower-lying level is smaller. However, the lifetime increase as a result of ligand deuteration does not show a straightforward relationship with the magnitude of the energy gap due to other operative quenching pathways. The concentration of high-energy vibrational C–H modes in the organic environment remains relatively high upon partial deuteration and this sometimes obscures the effect of deuteration. When the energy gap is resonant with the first overtone of a C–D or O–D vibration, quenching by these vibrations becomes of the same order of magnitude as quenching by the remaining C–H vibrations. Discrimination between different quenching processes is thus no longer possible.

Overall it can be concluded that apart from O–H quenching, other (high-energy) vibrational modes, *e.g.* O–D, C–D and C–H, can contribute significantly to luminescence quenching. This becomes especially important for shielded lanthanide ions with a relatively small energy gap between the luminescent state and a lower-lying level. Solvent and ligand deuteration is nevertheless always beneficial to some extent which leads to the conclusion that fully deuterated complexes should live even longer.

Experimental

Synthesis

The synthesis of the tricarboxylic acid precursor was reported previously.[20] Mass spectra were recorded with a Finnigan MAT 90 spectrometer using *m*-NBA (*m*-nitrobenzyl alcohol) as a matrix, unless otherwise stated.[22] IR spectra were obtained using a Biorad 3200 or a Nicolet 5SXC FTIR spectrophotometer. Elemental analyses[23] were performed using a Carlo Erba EA1106 instrument. The Ln^{3+} content was determined by destroying the ligand in the presence of concentrated nitric acid and concentrated perchloric acid. The remaining acids were evaporated, the salts dissolved in Q$_2$ water, followed by the addition of an acetate buffer to keep the pH at 5–5.5, and a drop of pyridine was added. After heating to 60 °C a titration with an aqueous solution of 0.01 M EDTA (ethylenediamine tetraacetate) was carried out using xylenol orange as an indicator.

General procedure for the complexation of Ln^{3+}. The corresponding triacid[20] (100 mg) was dissolved in MeOH (2 ml), after which three equivalents of Et$_3$N were added using a microsyringe. Subsequently a solution of LnCl$_3$·6H$_2$O in a minimal amount of MeOH (1 ml) was added in one portion. For the preparation of the Sm^{3+} and Ho^{3+} complexes, Ln(NO$_3$)$_3$·5H$_2$O salts were used.

A. Macrocyclic complexes were prepared according to the general procedure using macrocyclic triacid (100 mg, 0.11 mmol), Et$_3$N (46 μl, 0.33 mmol) and LnX$_3$·*n*H$_2$O (40 mg, 0.12 mmol). The complex precipitated immediately as an off-white solid upon addition. The reaction mixture was stirred for an

Table 2 FABMS spectroscopic data for the $(M + H)^+$ peak of cyclic lanthanide ion complexes of **1** and **2** in PEG-200 unless otherwise stated

	1				**2**			
	Calcd.	Found[a]			Calcd.	Found[a]		
Pr^{3+}	1015.4	1015.0	956.5	898.8	1028.5	1028.2	968.5	908.1
Nd^{3+}	1017.4	1017.8	959.4	—	1031.5	1031.2	971.5	911.5
Sm^{3+}	1025.4	1025.5[b]	967.4	—	1039.5	1039.4[b]	979.4	919.4
Tb^{3+}	1032.4	1032.5	974.5	916.5	1046.5	1047.0	986.9	926.2
Dy^{3+}	1036.4	1036.2[c]	979.3	919.3	1051.5	1051.4[b]	991.4	929.4
Ho^{3+}	1038.4	1038.0	994.3	922.4	1052.5	1052.5[b]	992.4	932.4
Tm^{3+}	1042.4	1042.5	984.4	926.3	1056.5	1056.4	996.6	936.5
Yb^{3+}	1047.4	1047.4[d]	989.4	931.3	1061.5	1061.4[d]	1001	941.3

[a] The mass spectra show fragmentation peaks due to the scission of one and/or two pendant arms $[C(R_2)_2COO^-]$. [b] In *m*-NBA–PEG-200. [c] M^+. [d] In MB.

Table 3 Elemental analysis data for the cyclic and acyclic lanthanide ion complexes of **1** and **3**

	1						**3**			
	$H_{calcd.}$	H_{found}	$N_{calcd.}$	N_{found}	$Ln_{calcd.}$	Ln_{found}	$H_{calcd.}$	H_{found}	$Ln_{calcd.}$	Ln_{found}
Pr^{3+}	6.96	6.21	1.38	1.09	13.9	14.5	5.76	5.59	15.8	16.2
Nd^{3+}	6.93	6.44	1.38	1.09	14.2	15.4	5.74	5.84[a]	16.1	*b*
Sm^{3+}	6.99	*b*	1.37	*b*	14.7	13.5	5.70	5.63	16.7	16.3
Tb^{3+}	6.93	*b*	1.36	1.10	15.4	17.2	5.64	5.57	17.4	18.7
Dy^{3+}	6.81	6.10	1.35	1.11	15.7	16.1	5.62	5.45	17.8	16.3
Ho^{3+}	6.89	*b*	1.35	*b*	15.9	15.3	5.61	5.68	18.0	16.9
Tm^{3+}	6.86	*b*	1.34	*b*	16.2	15.1	5.58	5.71	18.3	17.1
Yb^{3+}	6.83	*b*	1.34	*b*	16.5	13.4	5.56	5.58	18.7	18.2

[a] $+1H_2O$. [b] No satisfactory analysis was obtained.

additional 15 min and concentrated (to ≈3 ml), after which the precipitated complex was filtered off. The product was purified by refluxing it in CH_3CN for 3 h, after which it was concentrated (to ≈3 ml) and cooled to 0 °C. The product was filtered off and washed once with cold CH_3CN (≈3 ml).

B. Acyclic complexes were prepared in the same way using acyclic triacid (100 mg, 0.13 mmol), Et_3N (55 μl, 0.40 mmol) and $LnX_3 \cdot nH_2O$ (50 mg, 0.14 mmol). The reaction mixture was stirred overnight, followed by evaporation of the organic solvent and subsequent addition of some water. The complex was extracted with CH_2Cl_2 and the organic layer was dried over $MgSO_4$. In all cases the complexes were obtained as slightly yellow solids in almost quantitative yield.

FAB mass spectrometric and infrared spectroscopic data, and elemental analysis data for the lanthanide complexes **1·Ln**$^{3+}$, **2·Ln**$^{3+}$ and **3·Ln**$^{3+}$ are reported in Tables 2–4.

Table 4 Infrared vibration frequencies for the lanthanide ion complexes of **1**–**3** in cm^{-1}

	1	**2**				**3**
	$\nu_{C=O}$	$\nu_{C=O}$	$\nu_{C–D}$			$\nu_{C=O}$
Pr^{3+}	1616	1624	2212	2154	2101	1642
Nd^{3+}	1623	1617	2208	2154	2101	1637
Sm^{3+}	1616	1610	2205	2156	2098	1604
Tb^{3+}	1608	1601	2205	2154	2095	1608
Dy^{3+}	1606	1603	2205	2154	2094	1608
Ho^{3+}	1614	1610	2204	2154	2095	1606
Tm^{3+}	1610	1606	2206	2154	2094	1654
Yb^{3+}	1610	1607	2204	2154	2094	1602

Photophysical studies

Steady state luminescence measurements were performed with a PTI (Photon Technology International, Inc.) Alphascan spectrofluorimeter. For excitation a 75 W quartz–tungsten–halogen lamp followed by a SPEX 1680 double monochromator was used. A PTI 0.25 m single monochromator was used for separation of the emitted light, which was detected at an angle of 90° from the excitation light. The signal from the Hamamatsu R928 photomultiplier was fed to a photon counting interface. For measurements in the phase-resolved mode (used for the Sm^{3+}, Tb^{3+}, Dy^{3+} and Pr^{3+} complexes), the excitation beam was modulated in intensity by means of a mechanical chopper. The excitation beam was modulated in intensity at a frequency of 30–400 Hz for the long-lived complexes (Tb^{3+}) and at a frequency up to 4000 Hz for the short-lived complexes (Sm^{3+}, Dy^{3+}, Pr^{3+}). The modulated luminescence signal was subsequently analyzed with a Stanford Research SR530 lock-in amplifier. The frequency dependence of the phase shift and demodulation of the luminescence signal was fitted to well-known expressions applied for phase-resolved luminescence data.[28] For time-resolved luminescence measurements (used for the Nd^{3+} and Yb^{3+} complexes), an Edinburgh Analytical Instruments LP900 system was used, which consisted of a pulsed Xe-lamp (μs-pulsed output) followed by a 0.25 m monochromator for excitation and another 0.25 m monochromator, used for the separation of light, positioned at an angle of 90° with respect to the first one. The luminescence lifetimes were determined with an LTB MSG400 nitrogen laser (pulse duration 500 ps, $\lambda = 337$ nm). The luminescent photons were transferred into electric signals by means of a North Coast EO817P liquid nitrogen-cooled germanium detector, and fed to a Tektronix fast digital oscilloscope.

Because of the sensitivity of the luminescence lifetimes and intensities to the water content of the solutions, methanol was dried over molecular sieves (3 Å) prior to use and the lifetimes and luminescence spectra were recorded using freshly prepared samples.

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