Photochemical investigations of functionalised 1,4,7,10-tetraazacyclododecane ligands incorporating naphthyl chromophores

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The fluorescence properties of two macrocyclic ligands incorporating bis-(β-naphthyl amide) groups, –$CH_2CON(CH_2C_{10}H_7)_2$, as fluorophores, have been studied in water and acetonitrile. The ligands exhibit distinctive luminescence behaviour in the presence of quenching (*e.g.* Pb^{2+}, Ni^{2+}, Cu^{2+} and Eu^{3+}) and non-quenching ions (*e.g.* Zn^{2+} and Cd^{2+}). Excimer-to-monomer intensity ratios are affected to differing extents, as are the total integrated fluorescence intensities. The behaviour is contrasted to that reported previously for related ligands containing 'isolated' naphthyl units. The luminescence properties of the terbium complex of one of these earlier ligands, containing just one naphthalene group, have been studied in detail. Naphthyl-sensitised metal emission is observed but a nanosecond laser flash photolysis study reveals that back energy transfer to the naphthyl triplet state provides a facile deactivation mechanism for the metal excited state.

Introduction

The detection of ionic and molecular species through their effect on the fluorescence of suitable organic molecules is an increasingly active area of research.[1–3] That metal ions may have a profound influence on fluorescence has been known for over a century but only over the past 20 years has a rational approach to the design of fluorescent chemosensors been pursued. The recent systems differ from their predecessors in that the receptor or host is not an intrinsic part of the fluorophore: the two may be separated by several atoms and the resulting molecule may have properties characteristic of both of the isolated entities. The term 'supramolecular' is often applied in describing such systems.[4]

Many of the systems which have been studied to date are made up of simple fluorescent aryl groups, as reporter units, linked to polyamine or polyoxa ionic receptors.[1,2] The basis of their operation lies in the fact that the binding of a metal ion may disfavour the rate of amine-to-aryl photoinduced electron transfer as a quenching process, by perturbing the amine oxidation potential, with a resulting enhancement of the fluorescence intensity. Conversely, binding of inherently quenching metal ions results in a reduction of the fluorescence. The further development of such systems lies in the pursuit of two important goals, namely a search for more selective ionic or molecular receptors which may be coupled to suitable lumophores and, secondly, the extension of the applicability of such systems to allow their use in aqueous media or at an aqueous interface in neutral or acidic conditions. It is only with the attainment of these objectives that development for clinical or environmental monitoring applications becomes realistic.

Other desirable features have also become apparent. For example, it has long been recognised that practicable fluorescence detection of metal ions or other species is favoured if the emission or excitation spectrum can be monitored at two different wavelengths, the intensities of which are perturbed to differing extents on binding of the analyte. This then allows detection and quantification to be achieved through the measurement of the ratio of the intensities at these two wavelengths.[5] This avoids a number of problems associated with detection by the monitoring of absolute emission intensities, such as variations in illumination intensity and detection efficiency and the problem of varying amounts of other species absorbing at the excitation wavelength, which serve to reduce the fluorescence intensity.

N-Substituted octadentate ligands based on the 1,4,7,10-tetraazacyclododecane ring adopt a quadrangular [3333] conformation and are predisposed to bind large metal ions that favour a coordination number of eight. Such behaviour is not just confined to systems such as the well known tetracarboxylate ligand DOTA.†[6] Ligands bearing four amide groups, such as **5** and **6**, show related coordination properties. Such ligands are particularly versatile, forming complexes of high stability with a number of different metal ions, especially those which prefer a square antiprismatic geometry. Thus, ligand **5** has been found to display a marked preference for Ca^{2+} over alkali metal ions (log K_{ML} for the Ca^{2+} complex is 6.80 at 298 K, 0.1 M NMe_4NO_3),[7] whilst complexation of lanthanides by **6** has been investigated.[8] A stability constant of 10.05 has been measured for the gadolinium complex (298 K, 0.1 M $NaNO_3$). This ligand also binds strongly the toxic metal ions Cd^{2+} and Pb^{2+}, with a lower limit of 19 for log K_{ML}.[8b] In terms of stability constants, high selectivity over zinc is observed. Importantly, these values apply to aqueous solution and, indeed, for lead and cadmium, complexes were fully formed even at pH 0.3.

With these points in mind, a series of $12N_4$-based polyamide ligands has been prepared bearing one or more naphthyl groups in differing arrangements (**1**–**4**). The effect of metal complexation on the fluorescence properties of the naphthyl groups has been investigated. The behaviour of ligands **1** and **2** towards a number of different metal ions has been reported previously.[9] Here, we report some further observations on the fluorescence properties of these compounds together with the behaviour of the hexadentate ligand **3** and the octadentate ligand **4** in aqueous and non-aqueous solutions, and the characteristic perturbations of fluorescence which occur following metal binding.

Closely related to these studies is the study of stable water-soluble luminescent lanthanide complexes.[10,11] These compounds are of growing interest because the long lifetime of emission allows time-resolved detection procedures to be employed, allowing discrimination against short-lived background fluorescence when used as probes or labels in biological systems.[12] In order to overcome the problem of the

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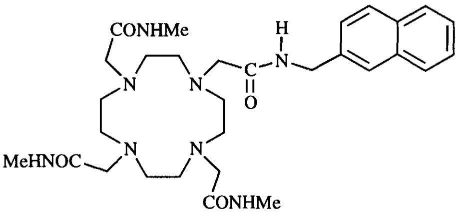
† DOTA = 1,4,7,10-tetraazacyclododecanetetraacetate.



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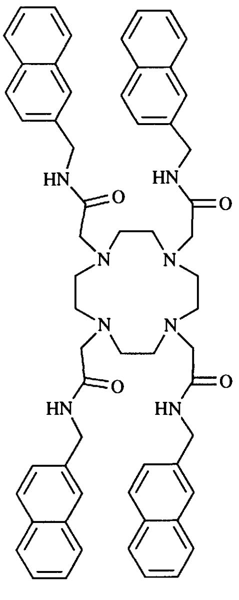

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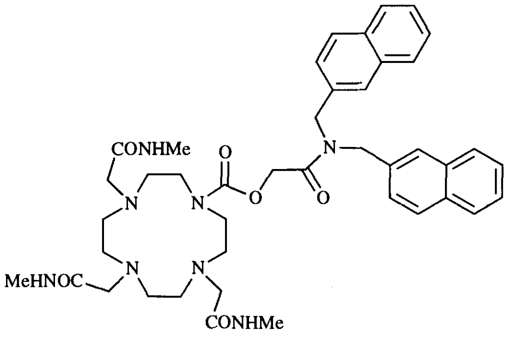

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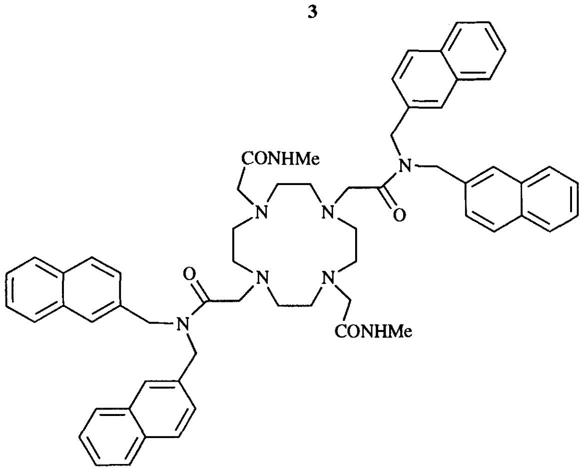

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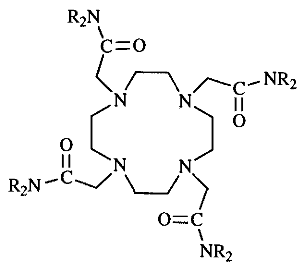
low molar absorptivities of the lanthanide ions, the ligands need to incorporate an 'antenna' group, whose function is to sensitise the metal emission through an energy transfer process.[4] The current work presents an opportunity to investigate the behaviour of a naphthyl moiety as such a sensitising group and the results with terbium are described in detail here.

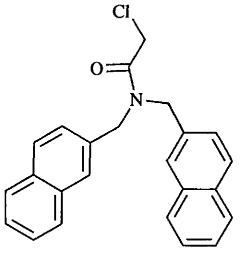


5 R = Me

6 R = H

Ligand synthesis

The preparation of ligands **1** and **2** has been described previously.[9] The introduction of a bis-naphthyl fragment onto $12N_4$, as in **3** and **4**, necessitated the preparation of the bis-naphthyl amide **7**. The bis-naphthyl imine **8** was prepared in quantitative yield by reaction of 2-(aminomethyl)naphthalene with 2-naphthaldehyde. Reduction of the imine with $NaBH_4$ gave the bis-naphthyl amine **9** in high yield. Subsequent acylation with chloroacetyl chloride provided the required compound **7**.



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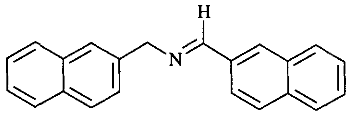

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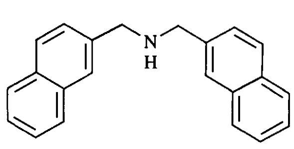

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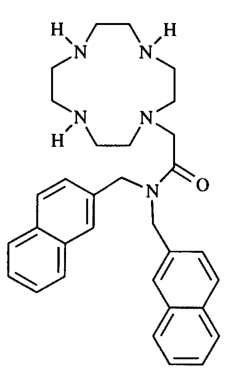
Alkylation of the $Mo(CO)_3$ complex of 1,4,7,10-tetraazacyclododecane with the bis-naphthyl chloroamide **7** was expected to proceed in the usual manner to provide the intermediate monoalkylated system **10**. Over a dozen such monoalkylation reactions have been successfully undertaken with a variety of α-haloamides. However, a most curious reaction was found to occur in this case: compound **11** was isolated where there had been an apparent insertion of 'CO_2' giving a carbamate. Moreover, the reaction was reproducible. The mechanism of this curious reaction remains unclear. One possible explanation would involve the migration of one of the carbonyl groups of $[12N_4 \cdot Mo(CO)_3]$ to the nitrogen of the ring. However, this still requires a second oxygen atom, the source of which is uncertain, but could possibly arise from trace water. Potassium carbonate is used as the base in this reaction and could conceivably be a



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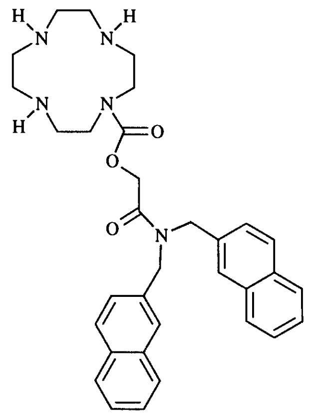

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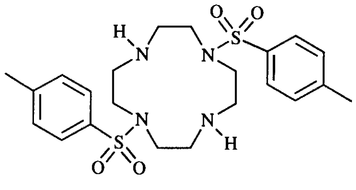
source of CO_2. On the other hand, 1.5 equivalents was used and so the product of reaction with H^+ should be HCO_3^- with no further reaction to give CO_2. A possible means of determining whether a carbonyl group of the $Mo(CO)_3$ moiety is involved would be to prepare $[12N_4{\cdot}Mo(^{13}CO)_3]$ and examine whether or not the ^{13}C nucleus becomes incorporated into the carbamate.

There is a second possibility, which assumes that the *N*-alkylation reaction had not occurred initially. It has been reported that carbamates R_2NCOOR' can be obtained from secondary amines R_2NH on treatment with CO, O_2 and an alcohol R'OH in the presence of platinum and the iodide ion.[13] This bears some relation to the present instance, where an amine, O_2 and a source of CO are present during oxidative work-up, together with an alkyl halide. Of course, such an analogy would require that the combination of Mo and Cl^- could function in a similar manner to Pt and I^- and, on the basis of the literature mechanism, this seems unlikely. Moreover, the cited reaction requires the use of high pressures of CO and O_2. Irrespective of the mechanism of the reaction, compound **11** was the product and reaction with 3 equivs. of $MeNHCOCH_2Cl$ led to compound **3**, the purification of which proved to be straightforward using silica column chromatography.

Ligand **4** is related to **2** in that it contains four naphthyl groups, but, in this case, they are arranged as two pairs bound to *trans*-related nitrogen atoms of the ring. The synthesis of such a system requires the selective protection of two such *trans*-related nitrogens allowing the other two to be alkylated first, either with **7** or with $MeNHCOCH_2Cl$. Desreux *et al.* have reported that reaction of $12N_4$ with two equivalents of toluenesulfonyl chloride in pyridine leads exclusively to the *trans*-functionalised compound **12**.[14] The tosyl groups can subsequently be removed using, for example, concentrated H_2SO_4 or HBr–AcOH or by means of a dissolving metal reduction.



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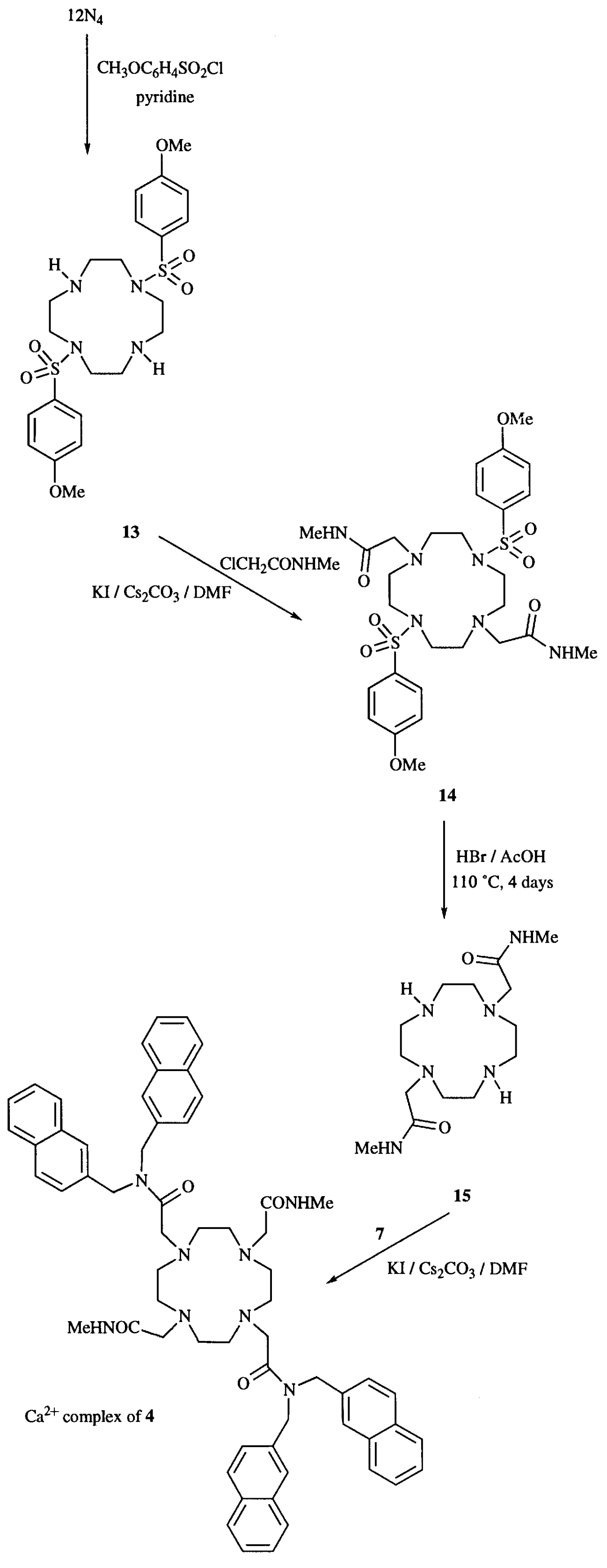
With this in mind, compound **13** (Scheme 1) was prepared by an analogous procedure using 4-methoxybenzenesulfonyl chloride. This compound is likely to display some advantage over **12** in that the 4-methoxybenzenesulfonamides are generally more sensitive to acid cleavage than the tosyl analogues.



Scheme 1 Synthetic procedure for the preparation of ligand **4**

Compound **13** was alkylated with $MeNHCOCH_2Cl$ as shown in Scheme 1. Deprotection was subsequently achieved by treatment with a 33% solution of HBr in AcOH at 110 °C for 4 days: the use of lower temperatures and shorter reaction times had in this case failed to provide complete removal of the sulfonamides.

Reaction of the bis-amide **15** with the bis-naphthyl chloroamide **7** was carried out in dimethylformamide in the presence of caesium carbonate, in the expectation that the desired ligand **4** would be formed. Potassium iodide was added in an attempt to catalyse the reaction and the product was purified by silica column chromatography. Curiously, the compound isolated was the Ca^{2+} complex of the required ligand, with iodide as the counterion, as shown by the elemental analysis (C, H, N, I, Ca) and the positive ion electrospray mass spectrum, which consistently displayed a 100% peak at 515 (mass of $[42.Ca]^{2+}$ = 1030). This is a remarkable result and seemed to suggest that the ligand had leached out trace Ca^{2+} from the silica during chromatography. The kinetics of dissociation must be very slow, perhaps reflecting the steric bulk of the four naphthyl groups and the restricted rotation about the N–C(O) bonds at room temperature. This latter point was clearly apparent from the variable temperature ^1H NMR spectra of the compound in $[^2H_6]$DMSO (400 MHz). At 25 °C, four broad signals, each of relative intensity 2, were observed between 4.4 and 5.2 ppm due to the non-equivalence of the four sets of $NCH_2C_{10}H_7$ protons. By 70 °C, the resonances had coalesced to give a single signal at 4.81 ppm. Similarly, two resonances were observed for the $NCH_2CON(CH_2C_{10}H_7)_2$ protons at low temperature, but these had also coalesced by 70 °C. Removal of the calcium was achieved through treatment with acid to induce dissociation, followed by re-complexation by DOTA, which forms a water-soluble complex of exceptionally high thermodynamic stability with Ca^{2+} [log K_{ML} = 17.2 (H_2O, 298 K)[6a]].

The metal complexes were prepared by reaction of the ligand with the appropriate metal triflate salt in solution in CH_3CN at 50 °C. Complexation occurred very rapidly under these conditions and the complexes were isolated, where required, by precipitation from diethyl ether in a similar manner to that described previously.[9]

Results and discussion

Luminescence behaviour

Europium complexes. The luminescence properties of the europium complexes of **1** and **2** have been discussed previously.[9] The naphthyl group does serve as an antenna chromophore for Eu^{3+}, but the quantum yields of metal emission following excitation at 270 nm were low. This behaviour almost certainly reflects the fact that Eu^{3+} is able to quench the naphthyl excited singlet state efficiently, through an electron transfer mechanism involving transient formation of Eu^{2+}. Such a process is favoured by the relative ease of reduction of Eu^{3+} to Eu^{2+} and also accounts for the low quantum yields of the naphthyl fluorescence in these compounds. Indeed, a study of intermolecular quenching of this type has been carried out and a bimolecular quenching rate constant of 7.2×10^9 dm^3 mol^{-1} s^{-1} was reported in CH_3CN.[15]

The europium complexes of the bis-naphthyl containing ligands **3** and **4** were also prepared by a similar procedure. Bearing in mind that these ligands emit strongly at around 400 nm (the excimer band) and that the free Eu^{3+} ion displays one of its strongest absorption bands at 397 nm (ε *ca.* 3 dm^3 mol^{-1} cm^{-1}), the overlap integral for energy transfer from the naphthyl excimer to the bound europium ion should be high. On this basis, one might expect the europium complexes of these ligands to show more intense metal emission than $[Eu\cdot\mathbf{1}]^{3+}$ and $[Eu\cdot\mathbf{2}]^{3+}$. Unfortunately, this did not prove to be the case. The most likely explanation is that the electron transfer quenching pathway is too fast relative to excimer formation and subsequent energy transfer to the metal. Again, the total fluorescence emission intensity was greatly reduced.

It is appropriate to mention here a further interesting feature which was observed for the europium complexes. This relates to the metal excited-state lifetimes. Luminescence lifetimes were longer in D_2O than in H_2O, as expected, since it is well known that energy transfer to the O–H vibrational manifold of a coordinated water molecule provides an efficient non-radiative deactivation pathway which is negligible in D_2O. However, use of the conventional Horrocks analysis [eqn. (1)][16] indicated

$$q = A_{Ln}(k_{H_2O} - k_{D_2O}) \quad A_{Tb} = 4.2 \quad A_{Eu} = 1.05 \quad (1)$$

hydration states (q) of 1.37 and 1.33 for $[Eu\cdot\mathbf{1}]^{3+}$ and $[Eu\cdot\mathbf{2}]^{3+}$, respectively, significantly higher than expected given that one water molecule only is bound to europium in the related, more hydrophilic complex $[Eu\cdot\mathbf{6}]^{3+}$.[8a] This apparent discrepancy was shown to arise from an N–H/N–D exchange process. It was concluded that there exists an additional deactivation mechanism for the excited europium $^5D_0$ state through coupling to amide N–H vibrational levels.[17] Such a de-excitation pathway will be much less efficient for amide N–D bonds owing to their lower vibrational stretching frequencies. Dissolution of the complexes in D_2O results in rapid N–H/N–D exchange, probably mediated by the ability of the Eu^{3+} to accept charge readily. Thus, the measured hydration state of the europium complex is higher than that which would arise solely from the substitution of a bound H_2O molecule by D_2O.

Terbium complexes. The terbium complexes of **1** and **2** displayed only very weak emission in acetonitrile solution following excitation of the naphthyl groups at 270 nm. In water, the terbium luminescence was about 10 times more intense for a solution of the same absorbance, although still extremely weak. However, degassing of the solutions resulted in an enormous increase in the intensity of the metal luminescence. It is well established that dissolved molecular oxygen has little direct effect on the excited states of the lanthanide ions.[18] On the other hand, the naphthyl triplet state will be susceptible to rapid quenching by molecular oxygen. Bearing in mind the small energy gap between the emissive Tb $^5D_4$ state (244 kJ mol^{-1}) and the triplet naphthyl level (255 kJ mol^{-1} is the literature value for naphthalene itself), this behaviour could be tentatively ascribed to a back energy transfer process from the metal emissive state to the naphthyl triplet, which is subsequently quenched by molecular oxygen. There are a number of examples of the occurrence of such an effect with other sensitising chromophores.[19,20] Since the back energy transfer process would require thermal activation, a marked temperature dependence would be expected.

A nanosecond laser flash photolysis study was undertaken for $[Tb\cdot\mathbf{1}]^{3+}$ in order to investigate in more detail the possibility of such a thermally activated back energy transfer process. A xenon chloride excimer laser (308 nm) was used to excite the sample. The duration of each laser pulse was 20 ns, during which time the triplet level of the naphthyl group is populated to a significant extent, allowing the triplet state to be probed by transient absorption spectroscopy. The transient absorption was investigated over a range of wavelengths (360–430 nm) and the maximum found to be 410 nm. This is close to the literature value for λ_{max}^{T-T} of naphthalene of 415 nm.[21a] Neither ground state naphthalene nor terbium absorb at this wavelength, and hence the rate of triplet deactivation can be probed by monitoring the decay of this absorption band, following the excitation pulse. A small modification of the instrumental set-up also allowed the decay of the terbium luminescence (490, 545 and 590 nm) to be monitored on the same timescale.

A degassed solution of $[Tb\cdot\mathbf{1}]^{3+}$ in water (10^{-3} M) at room temperature was examined in this way. The terbium luminescence showed an initial rapid rise over a few microseconds followed by a slow decay over several milliseconds (see Figs. 1 and 2 showing the behaviour in ethanol). The profile could be fitted to the sum of two exponentials with good residuals, and acquisition of data on short, intermediate and long timescales (corresponding to 1, 10 and 100 μs per division on the oscilloscope) allowed two rate constants to be extracted. The rate constant, k_1^{Tb}, for the initial rapid growth of the emission had a value of about 2.7

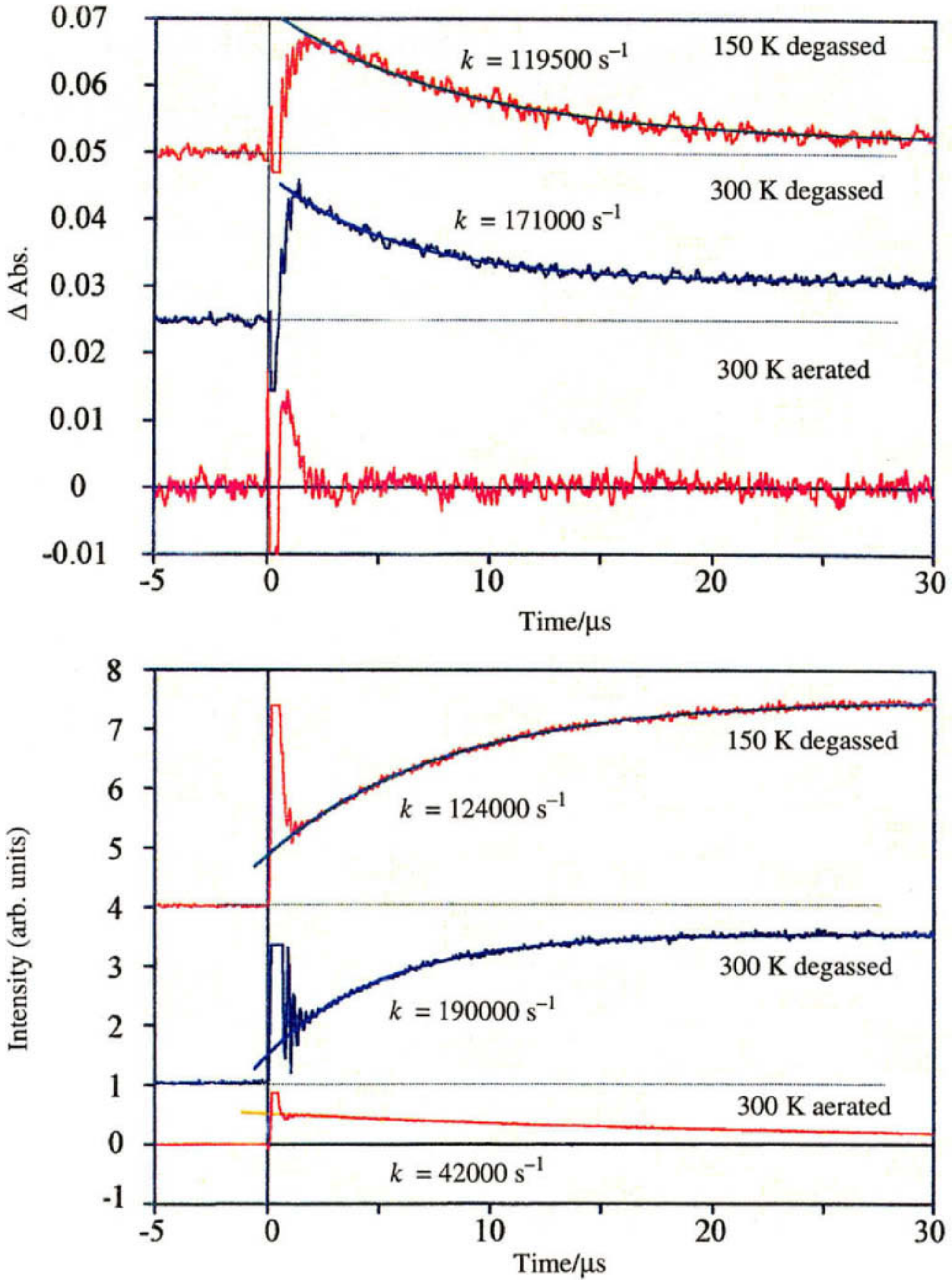


Fig. 1 Growth and initial fast decay of the triplet naphthyl absorbance at 410 nm (upper) and the grow-in of the terbium luminescence at 490 nm (lower) on a microsecond timescale for $[\mathrm{Tb}\cdot\mathbf{1}]^{3+}$ in ethanol following pulsed laser excitation at 308 nm

$(\pm 0.1) \times 10^5$ s^{-1} ($\tau = 3.7$ µs) whilst the rate constant, k_2^{Tb}, for the slow decay was 1.3 $(\pm 0.1) \times 10^3$ s^{-1} ($\tau = 0.75$ ms).

The naphthyl triplet absorption, on the other hand, displayed a rapid decay over the first few microseconds, with k_1^{Np} about 2.5 $(\pm 0.1) \times 10^5$ s^{-1}. The similarity of this value to the rate of growth of the terbium emission is strong evidence in support of an energy transfer process from the triplet state of the naphthyl group to the terbium. Following this initial fast decay, the triplet naphthyl was observed to decay over a much longer timescale with a rate constant, k_2^{Np}, of 1.5 $(\pm 0.1) \times 10^3$ s^{-1}, which is close to the decay constant found for the terbium decay. This observation can be interpreted in terms of formation of triplet naphthalene by energy transfer from the terbium excited state. In other words, an equilibrium is set up between the triplet naphthyl state and the terbium $^5D_4$ excited state, with the result that both decay at the same rate. The rapid growth of ^{3}Np through intersystem crossing from the excited singlet state occurred on a timescale which was too fast to monitor using the available instrumentation. The possibility of direct energy transfer from the singlet state to the metal could not be investigated for the same reason.

The effect of oxygen on these four rate constants was examined by studying the behaviour in the presence of a known pressure of air. Assuming that at atmospheric pressure, $[O_2] = 0.29 \times 10^{-3}$ M in water,[21b] the concentration of dissolved oxygen was estimated at a number of different pressures of air. The rate of the initial fast decay of ^{3}Np was increased on introduction of oxygen, reflecting the fact that there is now an additional pathway for ^{3}Np deactivation, namely quenching by oxygen, the significance of which increases as the oxygen concentration rises. In the presence of a quenching species, the observed first-order rate constant, k_{obs}, for depopulation of an emitting or absorbing state is given by eqn. (2) where k_{f}^0 is

$$k_{\mathrm{obs}} = k_{\mathrm{f}}^0 + \Sigma k_i^{\mathrm{nr}} + k_{\mathrm{Q}}[\mathrm{Q}] \qquad (2)$$

the natural radiative rate constant in the absence of other deactivating processes and Σk_i^{nr} is the sum of the first-order

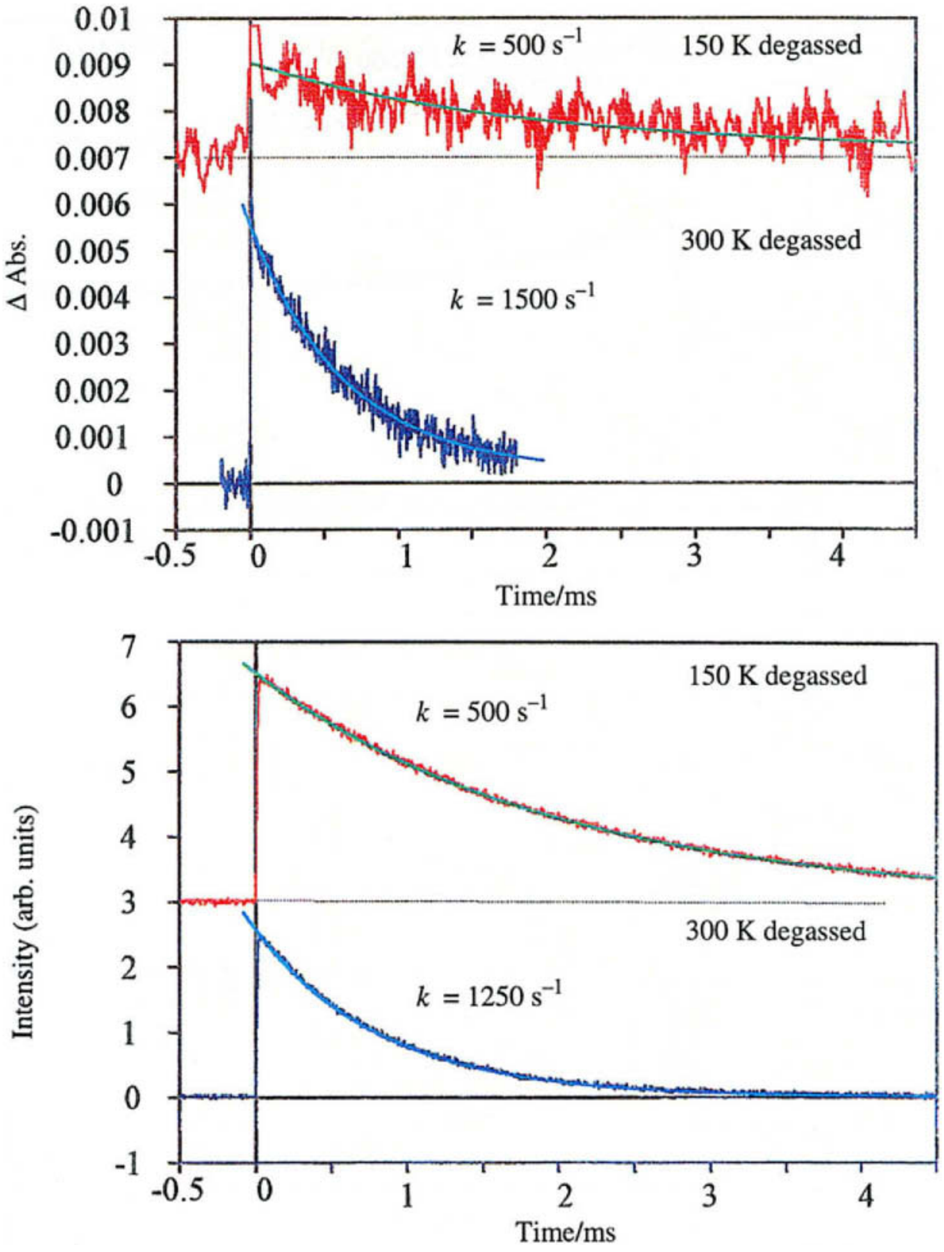


Fig. 2 Decay of the triplet naphthyl absorbance at 410 nm (upper) and of the terbium luminescence at 490 nm (lower) on a millisecond timescale for $[Tb{\cdot}1]^{3+}$ in ethanol following pulsed laser excitation at 308 nm

rate constants for competitive non-radiative deactivation processes. The quenching species is denoted Q and k_Q is the second-order rate constant for bimolecular quenching by Q. Thus, a plot of the observed rate constant of deactivation against the concentration of the quencher Q should yield a straight line of gradient k_Q. The k_1^{Np} values were plotted against the O_2 concentration and a linear relationship was indeed observed. A value of 1.3 (±0.1) × 10^9 dm^3 mol^{-1} s^{-1} was obtained for the second-order rate constant for the quenching process. A similar analysis has been carried out for the rate constants, k_1^{Tb}, associated with the growth of the terbium emission (Fig. 3). A k_Q value of 1.4 × 10^9 dm^3 mol^{-1} s^{-1} was determined in this case. The similarity of these values is again consistent with terbium sensitisation by the ^{3}Np state. The values are similar to the literature k_Q values for oxygen quenching of the triplet state of free naphthalene.[21b] The rate constant for the decay of the terbium emission was also increased on introduction of oxygen: k_2 = 26 000 s^{-1} at equilibrium with air at atmospheric pressure, compared with a value of 1340 s^{-1} in a degassed solution. This is good evidence for the back energy transfer process. The observation noted earlier, namely that (at atmospheric pressure) the intensity of the terbium emission in water was about 10 times that detected for an equi-absorbant solution in acetonitrile, is consistent with these results concerning the effects of oxygen. The equilibrium concentration of oxygen in aerated water is much lower than

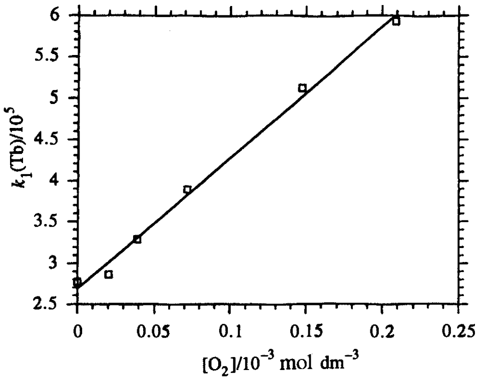


Fig. 3 Effect of oxygen on the rate constant, k_1, for the growth of terbium emission following laser excitation at 308 nm and detection at 490 nm

in MeCN (the values are 0.27×10^{-3} and 2.1×10^{-3} M, respectively, at 25 °C) and so deactivation of the naphthyl triplet state occurs more rapidly in the organic solvent.

As pointed out above, the back energy transfer process is likely to require thermal activation as the triplet state of the naphthyl group is expected to be of slightly higher energy than the Tb $^5D_4$ state. Thus, one would expect the extent of back energy transfer to be reduced as the temperature is lowered. Of course, at low temperatures, the efficiency of other non-radiative deactivation pathways for both the terbium excited state and the ^{3}Np will also be diminished and so a decrease in the rate constants would be expected. A variable temperature study was undertaken to examine these photophysical properties in more detail. Ethanol was used as the solvent for this work as it allows a large range of temperatures to be examined in fluid solution. The range 150–330 K was investigated.

The growth and decay profiles at 150 and 300 K are shown in Figs. 1 and 2. The rate constant for decay of the terbium luminescence is seen to be reduced from $1.2\,(\pm 0.1) \times 10^3\ s^{-1}$ at 300 K to $500\,(\pm 50)\ s^{-1}$ at 150 K and the decay of the long-lived ^{3}Np shows a similar pattern, with a reduction in k_2 from 1.5 $(\pm 0.1) \times 10^3$ to $500\,(\pm 50)\ s^{-1}$. Again, decay profiles which are common to both the metal and the ^{3}Np are consistent with formation of the latter through back energy transfer from the terbium excited state. A further feature is also apparent from these decay curves. Although the amount of ^{3}Np initially formed is about the same at both temperatures (initial triplet–triplet absorbance is approximately equal for the two profiles in Fig. 1), at later times after the flash, there is much less ^{3}Np at 150 K, as shown by the smaller triplet absorbance at 150 K compared with 300 K in Fig. 2. This indicates that the back energy transfer is indeed a thermally activated process: reduction of the temperature from 300 to 150 K is seen to reduce substantially its significance.

The ratio of the amount of ^{3}Np present at long time intervals (*i.e.* that which is formed by energy transfer from terbium) to the amount produced initially (by intersystem crossing from the singlet), as measured by the absorbances, is a useful measure of the extent to which the back energy transfer is occurring. This ratio is effectively the equilibrium constant K for the back energy transfer process. The variation of K with temperature should allow the enthalpy change, ΔH^0, of the energy transfer process to be estimated through application of the van't Hoff isochore. The gradient of a plot of ln K *vs.* $1/T$ at a given temperature provides the value of ΔH^0 at this temperature. Since ΔH^0 is often only weakly temperature-dependent, such a plot may approximate to a straight line. An analysis of this type was carried out on the flash photolysis data and the result is shown in Fig. 4. The plot does indeed give a reasonable straight line and the enthalpy change ΔH^0 for the back energy transfer process is estimated from the gradient to be 4.5 kJ mol^{-1}. Using literature values for the triplet level of naphthalene and the energy of the excited terbium level, an energy gap of 11 kJ mol^{-1} would be predicted, although it should be noted that this refers to ΔG^0 rather than to ΔH^0. The value of ΔG^0 at 298 K is estimated to be 2.5 kJ mol^{-1} using the ln K value at this temperature. Of course, one would not expect perfect agreement with the literature estimate as the naphthyl triplet energy in $[Tb{\cdot}\mathbf{1}]^{3+}(aq)$ will inevitably differ from that of naphthalene itself.

Effect of β-cyclodextrin

Cyclodextrins are able to form non-covalently bound adducts with a very large number of organic molecules containing aryl groups. Simple naphthyl derivatives are most suited to complex formation with β-cyclodextrin, where the resulting adducts in water typically display association constants of the order of 10^2–10^3 M^{-1}. It has been frequently observed that binding of an aromatic moiety within the cavity of an appropriately sized cyclodextrin inhibits deactivation of the aryl excited states.[22,23] When bound within the cyclodextrin, the aryl group is shielded from solvent vibrational quenching and has less conformational freedom so that non-radiative deactivation processes such as internal conversion are disfavoured. Under such circumstances, an enhanced fluorescence emission intensity may result.

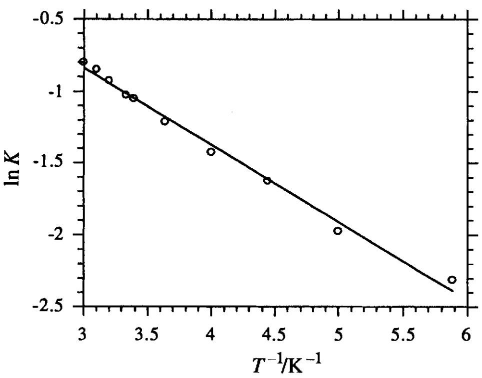


Fig. 4 Plot of ln K *versus* $1/T$ where K is the equilibrium constant for the back energy transfer process as determined from the triplet absorbances at short and long time intervals after the excitation flash

The effect of β-cyclodextrin on the luminescence properties of $[Tb{\cdot}\mathbf{1}]^{3+}$ has been examined. Binding of this cyclodextrin to $[Tb{\cdot}\mathbf{1}]^{3+}$ in degassed aqueous solution (18.2 μM and in the presence of 50 equivalents of the CD) led to a significant increase in the fluorescence emission intensity of the naphthyl fluorophore. The increase of 13% is of a similar magnitude to that previously observed for the zinc complex of ligand **1**[9] and can be interpreted in terms of reduced non-radiative deactivation of the excited singlet state. Of more interest, however, is the much larger rise of 44% in the intensity of the metal emission, together with a significant lengthening of the luminescence lifetime (from 0.67 to 0.85 ms). These observations would appear to indicate that there is a reduction in the efficiency of the back energy transfer deactivation process on binding to the cyclodextrin. It is not the energy transfer process itself which will be affected here, but rather the fact that the triplet naphthyl formed as a result of the back energy transfer is subject to a reduced degree of non-radiative deactivation, in a similar manner to the singlet state. Enhanced phosphorescence is indeed commonly observed for aryl groups included inside cyclodextrins at room temperature.[22,23] Indeed, the effect on phosphorescence is generally more marked than for fluorescence, partly because triplet–triplet annihilation, a common phosphorescence quenching channel, is greatly suppressed on binding to the cyclodextrin. Thus, the lifetime of the ^{3}Np will be increased and, since the Tb $^5D_4$ state is in equilibrium with the ^{3}Np as deduced from the flash photolysis studies above, this increase should also be reflected in a lengthening of the terbium lifetime and an enhancement of the metal luminescence intensity. Indeed, the results of this experiment serve to reinforce the conclusions drawn earlier concerning this equilibrium.

Characteristics of the terbium emission spectra

The terbium emission spectrum showed bands at the wavelengths expected for the transitions normally observed (Fig. 5). However, there are some notable differences compared with the spectra of some related complexes incorporating phosphinate $[-CH_2P(R)O_2^-]$ as opposed to amide coordinating arms.[11] First, the $J = 6$ band shows substantially enhanced intensity relative to the $J = 5$ band when compared with the tetraphosphinate complexes. Actually, it is well known that the $J = 6$ band is sensitive to the metal environment[12] and so this observation is not altogether surprising. A more interesting point is the difference in the fine structure. Here, the $J = 6$ and $J = 5$ bands do not display any sign of splitting, in complete

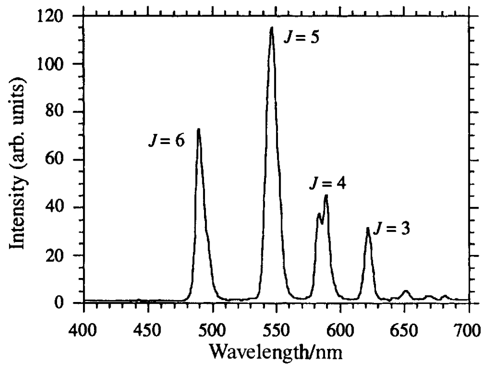


Fig. 5 Metal luminescence emission spectrum of [Tb·**1**]$^{3+}$ in D_2O (degassed) following excitation at 270 nm (excitation and emission monochromator band passes of 2.5 nm were employed). The bands arise from $^5D_4 \rightarrow {}^7F_J$ transitions; the *J* values of the bands are labelled on the spectrum

contrast to the phosphinate complexes. Since fine structure is reduced upon moving to higher symmetry, this observation could be interpreted in terms of higher symmetry in the tetraamide complexes compared with the tetraphosphinates and may reflect the change from a square antiprismatic geometry for the former[8] to the inverted square antiprismatic structure of the latter.[24,25] The emissive quantum yield of [Tb·**1**]$^{3+}$ in degassed ethanol solution at 295 K was determined to be 0.11 by means of the fluorimeter (using quinine sulfate as the standard). This compares to emission which was barely detectable using the same instrument under aerated conditions.

Fluorescence of the free ligands

The fluorescence properties of ligands **1** and **2** have been described previously.[9] As expected, ligand **1** displayed the characteristic fluorescence of a naphthyl group (λ_{max} = 337 nm) on excitation at 270 nm. In contrast, a solution of the protonated ligand **2** in acetonitrile showed, in addition to the usual naphthyl emission, a second broad unstructured band centred at about 400 nm and attributable to naphthyl excimer emission. The proportion of excimer emission showed a sensitive dependence on the polarity of the solvent, being almost negligible in the least polar solvents such as THF, but accounting for almost 90% of the total emission in water. For both of the ligands and also for their complexes, it was noted that the total integrated fluorescence intensities were substantially higher in water than in acetonitrile, typically by a factor of 2 or more, although no explanation was provided at the time.

Studies using degassed solutions have shown that these observations are probably related to the effect of dissolved molecular oxygen. The extent to which quenching by oxygen can compete with fluorescence and other non-radiative processes depends on the relative magnitude of $k_Q[O_2]$ compared with k_f (where k_f is the observed decay rate constant in the absence of oxygen). The bimolecular rate constant for quenching by O_2, k_Q, is of the order 10^{10} dm^3 mol^{-1} s^{-1} in most organic solvents. Moreover, for typical organic solvents in equilibrium with air at 760 mmHg pressure (*i.e.* 0.21 atm O_2), the concentration of dissolved oxygen, $[O_2]$, is usually about 2×10^{-3} M. Thus, the rate of quenching by oxygen is of the order of 2×10^7 s^{-1}. Consequently, singlet states with decay rate constants (k_f) of the order of 10^8–10^9 s^{-1} will not be efficiently quenched under such conditions. Many commonly encountered fluorescent compounds have lifetimes in the range 1–10 ns, such that no significant differences in fluorescence intensity are observed upon degassing solutions of such compounds. Naphthalene is rather more unusual in this respect as it has a particularly long singlet lifetime of about 100 ns; *i.e.* $k_f \approx 10^7$ s^{-1}. As this is of the same order of magnitude as $k_Q[O_2]$, significant quenching by oxygen is to be expected. Indeed, upon degassing a solution of the protonated ligand **1** in acetonitrile, the fluorescence intensity increased three-fold, in line with this prediction. In fact, the difference in fluorescence intensities between aerated and degassed solutions allows an approximate estimate of the fluorescence lifetime (τ_f) for compound **1** to be obtained through application of the Stern–Volmer equation [eqn. (3)] where φ_f and $\varphi_f{}^Q$ are the quantum

$$\frac{\varphi_f}{\varphi_f{}^Q} = 1 + \tau_f k_Q[Q] \qquad (3)$$

yields in the absence and in the presence of the quenching species and [Q] is the concentration of the quencher. Since φ_f (degassed) $\approx 3\varphi_f$ (aerated) and $[O_2] = 1.9 \times 10^{-3}$ M (in MeCN at 760 mmHg pressure) then, using a k_Q value of 2.7×10^{10} dm^3 mol^{-1} s^{-1}, we can crudely estimate τ_f to be 39 ns which is close to the value of 47 ns reported for 2-methylnaphthalene.

The relevance to the solvent dependence of the fluorescence lies in the fact that the equilibrium concentration of O_2 in water at atmospheric pressure is much smaller than in acetonitrile, as noted above. In water, $[O_2] = 0.27 \times 10^{-3}$ M at atmospheric pressure (25 °C).[21b] Thus, $k_Q[O_2]$ is only of the order of 3×10^{-6} s^{-1} in water such that quenching by molecular oxygen is much less significant in this solvent. This then probably accounts for the higher fluorescence intensities observed in aqueous solution, although of course there may be other effects contributing as well.

Compounds **3** and **4** were prepared in the hope that they would exhibit excimer emission. This did indeed prove to be the case: in addition to the usual fluorescence band (λ_{max} 337 nm), these compounds displayed a second, longer wavelength band (λ_{max} 397–401 nm) typical of a naphthyl excimer. The ratio of excimer to monomer emission intensities (I_{ex}/I_m) is a useful parameter in such systems. Here it was found to be independent of concentration in a given solvent (for concentrations < 10^{-4} M) which is indicative of intramolecular excimer formation, as expected: an excited state naphthyl group in the $-N(CH_2C_{10}H_7)_2$ unit is able to interact with the other naphthyl group in its ground state to form the excited dimer. For aromatic groups linked by several methylene units, it has generally been found that excimer emission is most likely to be observed when there are three CH_2 groups between the two aryl groups.[26] This reflects the requirement for the aryl groups to adopt a mutually plane–parallel arrangement, with an optimum interplanar distance of 3.5 Å.[27] This conclusion was also expected to apply in the present instance, where there are again three atoms in the linking chain, although of course one of them is now the nitrogen of the amide. The observation of intense excimer emission vindicates this prediction. Significant excimer emission is also a feature of related bis-naphthyl amines, although most work has dealt with the α-substituted compounds.[28]

In subsequent discussions, the ratio of the maximum fluorescence intensity of the excimer (between 390 and 401 nm) to that at 337 nm is used as a measure of I_{ex}/I_m. This is not strictly correct, as the two bands overlap to some extent. However, the overlap is small at these two wavelengths and so the approximation is largely justified for the discussions which ensue.

Solutions of **3** and **4** in aerated acetonitrile displayed I_{ex}/I_m values of about 1.4 (from the corrected emission spectra, Fig. 6). Degassing of the solutions resulted in a net increase in the fluorescence intensity, as expected, but the excimer band increased to a greater extent, leading to an I_{ex}/I_m ratio of 2.3. This is consistent with the original observations of Hirayama, who found that oxygen had a more pronounced effect on the excimer than on the monomer in the fluorescence spectra of diphenyl and triphenyl alkanes.[29] In this instance, there are two possible reasons for the greater increase in the excimer band. First, excimer emission is generally longer lived than monomer emission. For example, a value of 143 ns has been measured

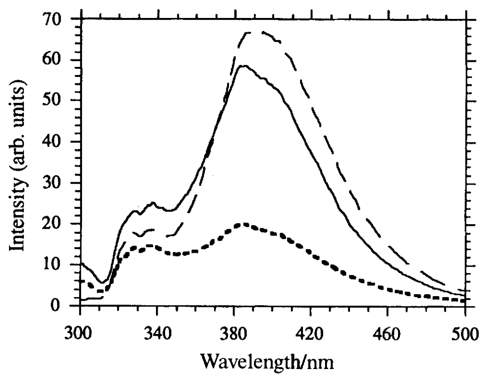
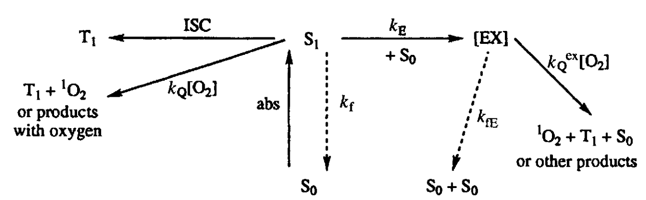


Fig. 6 Fluorescence emission spectrum of ligand **3** in degassed acetonitrile (solid line), aerated acetonitrile (dotted line) and in water (dashed line) at a concentration of 10^{-5} M. Ligand **4** displayed similar behaviour

for the intermolecular excimer formed by 1,6-dimethylnaphthalene,[30] which compares with 47 ns for τ_f of monomer 2-methylnaphthalene.[21] As outlined above, the effect of quenching by molecular oxygen is more significant for excited states having long decay lifetimes and will therefore be more significant for the excimer than for the monomer. Secondly, oxygen quenching of the monomer will also result in a decrease in excimer intensity (in addition to the monomer) as this process will be in competition with excimer formation (Scheme 2). In fact, if we consider $^{\beta}$Np–(CH$_2$)$_3$–$^{\beta}$Np as a possible model compound, the rate constant for excimer formation, k_E, has a value of 2.4×10^8 s^{-1}, which compares with 5×10^7 s^{-1} for $k_Q[O_2]$ at 760 mmHg and a value of k_f for monomer naphthalene of 2.13×10^7 s^{-1}.[21] These values indicate that the removal of monomer quenching is likely to have a more significant effect on the intensity of monomer fluorescence than on the extent of excimer formation and so the increase in I_{ex}/I_m probably arises solely from the first explanation, namely the longer lifetime of the excimer.



Scheme 2 Quenching effect of molecular oxygen on excimer and monomer emission

In solution in water, the I_{ex}/I_m ratio had a higher value of about 3.5 for both **3** and **4** and also for the model compound **8**. According to the discussion above, a higher I_{ex}/I_m ratio would be expected in water compared with acetonitrile (under aerated conditions), simply on the basis of the lower oxygen content of water compared with organic solvents under 760 mmHg pressure of air. Actually, the effect here of changing from acetonitrile to water must be more profound than simply a change in oxygen concentration alone since I_{ex}/I_m is still rather higher in aerated water than in degassed acetonitrile (the values are about 3.5 and 2.3, respectively). The reasons for this are unclear. Intensity measurements on a nanosecond timescale would be required in order to investigate the effect of solvent on the lifetimes of the monomer and excimer and the rate of excimer formation, k_E. It is possible that a hydrophobic effect leads to excimer formation being favoured in water relative to CH_3CN (the emission maxima were at 396 and 391 nm, respectively) which might be reflected in an increase in k_E in water.

In the case of the protonated tetranaphthyl ligand **2**, the value of I_{ex}/I_m in aerated acetonitrile was 0.6. Upon degassing of this solution, the total fluorescence intensity was substantially increased, as expected in light of the above discussions concerning the quenching effect of oxygen on naphthalene fluorescence. However, it is interesting to note that in this case, degassing barely had any effect whatsoever on the I_{ex}/I_m ratio, in complete contrast to the bis-naphthyl compounds **3** and **4**. The reason for this intriguing difference is not certain, but it would appear to indicate that in the present instance, there is relatively little difference in the lifetimes of the monomer and excimer. Clearly, decay measurements on a nanosecond timescale at 337 and 401 nm would be required to confirm or disprove this possibility. However, we note that where data are available, intermolecular excimers generally exhibit lifetimes which are substantially shorter than those of their intramolecular analogues. An example is provided by pyrene, where the intermolecular excimer has a lifetime of 67 ns compared with 140 ns for the intramolecular case in 2-pyr-CH(CH$_3$)–CH$_2$–CH(CH$_3$)-2-pyr. It does not seem unreasonable to suppose that the excimer in ligand **2** may show behaviour more akin to an intermolecular excimer than the intramolecular systems of **3** and **4** (it does, after all, have a large number of atoms intervening between each pair of naphthyl groups). This might then account for the different observations concerning the effect of oxygen on I_{ex}/I_m.

What these observations do serve to highlight is that the sensitive dependence of the excimer emission intensity on the solvent, which is observed for ligand **2** (*e.g.* I_{ex}/I_{em} increases from 0.6 to 3.3 on going from MeCN to H_2O), cannot be attributed to the differing equilibrium concentrations of oxygen. In this case, it is not completely clear why the solvent should have such a profound effect. The lack of any significant changes in the excimer emission wavelength in the various solvents seems to rule out an effect of selective stabilisation of the excimer in the more polar solvents. One possible explanation is that the more polar solvents disfavour intramolecular hydrogen bonding, perhaps allowing the molecule to adopt the desired conformation for excimer formation. Intramolecular hydrogen bonding between the amide groups might be expected to increase the activation energy required for two adjacent naphthyl groups to adopt the conformation required for excimer formation. This would be reflected in a reduction in k_E such that the excimer emission loses out to monomer emission. A somewhat related viewpoint is that the solvophobic naphthyl groups are forced closer together in polar solvents to give a larger contribution from excimers. Similar behaviour is seen in solvent effects on polymer molecules.[31] The lack of variation of I_{ex}/I_{em} over a 100-fold concentration range (5×10^{-7}–5×10^{-5} M) suggests that intermolecular effects are absent. On the other hand, aggregation cannot be completely ruled out as there is always the possibility of a critical aggregation concentration at values lower than the range examined.

Effect of metal ions

Addition of metal ions such as Cd^{2+} and Zn^{2+} to ligand **1** in MeCN resulted in an enhancement of the fluorescence intensity as described previously. This behaviour may be interpreted in terms of the increase in the oxidation potential of the amine nitrogen atoms on binding to the metal, which serves to reduce the competitive effect of amine-to-aryl photoinduced electron transfer as a deactivation pathway for the aryl excited singlet state. As expected, quenching ions such as Pb^{2+}, Cu^{2+} and Ni^{2+} caused large diminutions in the fluorescence intensity. Metal binding was effectively instantaneous in MeCN, but was slower in water, in which the rates differed markedly for the different metal ions.

Binding of Cd^{2+} and Pb^{2+} (and also the trivalent lanthanide ions) to the protonated ligand **2** in acetonitrile resulted in loss of the excimer emission, presumably reflecting a change in geometry to one in which the naphthyl groups are unable to attain the plane–parallel conformation required for excimer

Table 1 Effect of metal ions (5 equivs.) on the excimer-to-monomer intensity ratio (I_{ex}/I_m) and on the total fluorescence intensity (I_{total}) for ligand **3** (10 μM)

	Acetonitrile solution		Aqueous solution	
	I_{ex}/I_m[a]	I_{total} (%)[b]	I_{ex}/I_m[a]	I_{total}[b]
Free ligand	1.41	100	3.34	100
Zinc	1.40	119	*c*	*c*
Cadmium	1.31	106	3.47	97
Lead	1.20	64	2.68	61
Nickel	1.03	63	*d*	*d*
Copper	0.85	14	2.32	25
Europium	1.14	25	3.28[e]	90[e]

[a] The ratio of the maximum emission intensities of excimer and monomer was used, as obtained from the corrected emission spectra. [b] I_{total} is the total emission intensity expressed as a percentage of that measured for the free ligand. [c] No effect observed. [d] Binding of nickel was very slow; complexation of the other metals was effectively instantaneous in both solvents. [e] Probably an intermolecular effect.

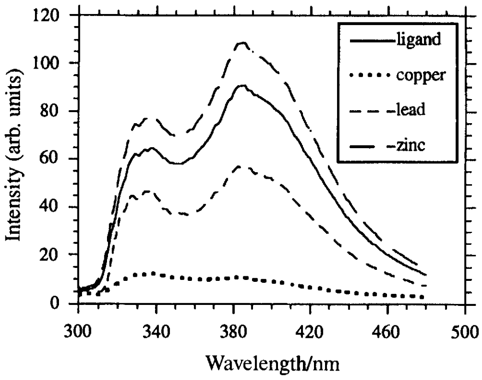


Fig. 7 Fluorescence spectrum of ligand **3** in CH_3CN (10 μM) and after addition of 5 equivs. of metal triflates (M = Zn^{2+}, Pb^{2+} and Cu^{2+})

formation. Binding of Cd^{2+} could be distinguished from Pb^{2+} in that the former gave rise to a significant increase in the monomer intensity in such a way that the total integrated fluorescence intensity was barely affected. A change in both monomer and excimer intensities is an attractive feature as it allows detection to be achieved through the measurement of the ratio of the intensities at the two wavelengths, with the accompanying advantages described earlier.

The concept of exploiting a ratio of emission intensities was also in mind for the ligands **3** and **4**. Here, the bis-naphthyl moiety is extrinsic to the metal-binding part of the system and so structural changes on metal binding would not be expected to have a significant effect on I_{ex}/I_m. However, it was noted above that the lifetime of a naphthyl excimer is likely to be substantially longer than that of the monomer (*i.e.* $k_{fE} < k_f$), with the result that excimer emission displays a more sensitive dependence on the presence or absence of quenching species. Thus, one might reasonably expect the binding of suitable quenching ions to have a more significant effect on the excimer band than on the monomer emission, in such a way that I_{ex}/I_m is reduced. By the same token, complexation of an enhancing ion [which reduces the efficiency of the photoelectron transfer (PET) process] may be expected, at least in principle, to have a more significant effect on the excimer, especially if k_{ET} has a value intermediate between that of k_f and k_{fE}. Of course, in both cases, the total fluorescence intensity should also be affected, providing a further parameter which may be monitored.

The effect of adding 5 equivalents of a number of different metal triflate salts to ligand **3** in CH_3CN (10^{-5} M) was investigated. The results are shown in Table 1 where the I_{ex}/I_m ratios before and after complexation are given, together with the changes in the total fluorescence intensity I_{total} expressed as a percentage of the initial intensity. Some of the spectra are shown in Fig. 7. It is clear that the quenching ions, Cu^{2+}, Pb^{2+}, Ni^{2+} and Eu^{3+}, do indeed result in a reduction of the total fluorescence intensity in a manner which resembles, at least qualitatively, the behaviour of **1**.[9] Again, Cu^{2+} is the most efficient quencher and Pb^{2+} and Ni^{2+} cause similar changes to one another (*ca.* 36% reduction). However, in addition to these changes in I_{total}, the I_{ex}/I_m ratios are also affected to differing extents. Thus, binding of a given metal ion is characterised by a unique pair of values for the parameters I_{ex}/I_m and I_{total}. For all of these quenching ions, the I_{ex}/I_m value is reduced on metal binding. This fulfils the prediction above, namely that the excimer emission is expected to be affected to a greater extent than that of the monomer in the presence of a quenching species owing to its longer lifetime. The trend in I_{ex}/I_m follows that of I_{total} to some extent, but not precisely. For example, nickel and lead both induce similar changes in I_{total} (37 and 36% reductions, respectively) but the former causes a significantly larger decrease in I_{ex}/I_m. Europium, on the other hand, has a proportionately larger effect on the total intensity than on the excimer : monomer ratio. These differing observations probably arise from the relative rates of quenching (be it through electron or energy transfer, as for Cu^{2+} say, or through enhanced intersystem crossing, *e.g.* for lead), monomer emission k_f, excimer formation k_E and excimer emission k_{fE}. Thus, one can envisage one extreme where the quenching rate constant is intermediate between k_f and k_{fE}, in which case I_{ex} will be reduced to a significantly greater extent than I_m. This would be reflected in a substantial decrease in I_{ex}/I_m, without the total emission intensity being affected to the same extent. This is perhaps the case for Ni^{2+}. On the other hand, if the quenching rate constant is much larger than both k_f and k_{fE} then a large decrease in I_{total} would be expected but the effect on the monomer will be almost as large as the effect on the excimer, such that I_{ex}/I_m is not greatly affected. This probably accounts for the behaviour of europium. It has been found that the bimolecular rate constant, k_Q, for quenching of the first excited singlet state of naphthalene by Eu^{3+} ions in CH_3CN has a value of 7.2×10^9 dm^3 mol^{-1} s^{-1}.[15] The local concentration [Q] of Eu^{3+} is high in the complex and so quenching is likely to compete very efficiently with both monomer and excimer fluorescence (k_f *ca.* 2×10^7 s^{-1}, k_{fE} *ca.* 7×10^6 s^{-1} for possible model compounds). Thus, quenching will cause a substantial fall in I_{total} with relatively little discrimination between excimer and monomer, such that I_{ex}/I_m is not affected to such a large extent.

Zinc causes a modest increase in I_{total}, consistent with a 'chelation enhanced fluorescence effect'. This is rather less pronounced than for compound **1** in CH_3CN, which probably reflects a proportionately smaller PET deactivation in **3** compared with **1**. This may be related to the fact that the ring nitrogen nearest to the naphthyl groups in **3** is a carbamate nitrogen, which will have a much higher oxidation potential than the corresponding amine nitrogen in **1**. Indeed, the carbamate nitrogen lone pair is delocalised into the neighbouring carbonyl group and so will not be available for binding to the metal. Moreover, the naphthyl amide C=O is now too far from the cycle to act as a donor to the bound metal. Thus, **3** is only a hexadentate ligand and this will of course disfavour binding of the larger ions such as lead and europium, which prefer octacoordination. However, this does not seem to be a problem in acetonitrile: binding of all six of the metal ions investigated, including lead and europium, occurred very rapidly (within the time required to record the spectrum).

Very rapid binding was also observed for most of the metal ions in aqueous solution: equilibrium had again been attained before the spectra could be acquired. This contrasts with the behaviour of **1**, where metal binding was substantially slower in water than in CH_3CN.[9] There are probably two contributing factors to the faster rates of complexation in water for **3**

Table 2 Effect of metal ions (5 equivs.) on I_{ex}/I_m and on I_{total} for ligand **4** in CH_3CN (5 mM)

	I_{ex}/I_m [a]	I_{total} (%) [b]
Free ligand **4**	1.66	100
Copper	1.25	58
Lead	1.04	69
Europium	0.79	40

[a] The ratio of the maximum emission intensities of excimer and monomer was used, as obtained from the corrected emission spectra. [b] I_{total} is the total emission intensity expressed as a percentage of that measured for the free ligand.

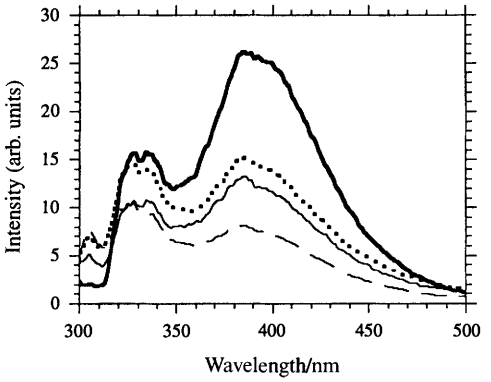


Fig. 8 Corrected fluorescence emission spectra of ligand **4** in acetonitrile at a concentration of 5 μM (▬▬) and the spectra 72 h after addition of Pb^{2+} (· · ·), Cu^{2+} (——) or Eu^{3+} (– – –) (as their triflate salts, 5 equivs.)

compared with **1**. First, since one of the ring nitrogen atoms of **3** is incorporated into a carbamate, the pK_a values of this ligand are likely to be somewhat lower than those of **1** with the result that the deprotonation required prior to metal binding may occur more readily in the former. Secondly, the bis-naphthyl unit of **3** is further away from the metal binding site than the naphthyl group in **1**, so that there is less steric hindrance to the approach of the metal ion in **3**. As in the case of ligand **1**, nickel was found to bind only very slowly in aqueous solution, in complete contrast to all of the other metal ions investigated: only a 10% reduction in I_{total} was observed over 30 min. Europium appeared not to bind at all in aqueous solution. This is probably not surprising bearing in mind the high affinity of lanthanide ions for water molecules as ligands and the fact that **3** is only a hexadentate and charge-neutral ligand (protonated in water). Binding of Cu^{2+} and Pb^{2+} in aqueous solution induced similar changes to those observed in acetonitrile. (Of course, the I_{ex}/I_m ratio is higher than in MeCN, both before and after complexation, owing in part to the lower concentration of dissolved oxygen). Both the total fluorescence intensity and the I_{ex}/I_m values were affected and to extents which were dependent on the identity of the metal ion (Table 1). Binding of zinc gave rise to no detectable effect: the chelation enhanced fluorescence effect was small in MeCN and will be smaller still in water, owing to the fact that the ligand is initially protonated under these conditions.

Conclusions

Ligand **3** is of significance for a number of reasons. There appear to have been no previous studies on the use of a 'built in' excimer for fluorescence detection of metal ions or other species. Where excimer emission has been exploited, it is normally through some form of geometrical change affecting the relative positions or orientations of a pair of aryl groups. Whilst the changes in I_{ex}/I_m are not as large in the present system as those in some previously reported compounds[32] (or indeed for ligand **2**[9]), it is important to note that the extent to which I_{ex}/I_m is affected shows a sensitive and reproducible dependence on the identity of the metal ion. The total fluorescence intensity (as measured by the area under the fluorescence spectrum) is also affected to differing extents (in a similar manner to **1**). Thus, there are two parameters characterising the binding of a specific metal ion. This should allow, in principle, the simultaneous detection of two different metal ions (*e.g.* Pb^{2+} and Cu^{2+} in aqueous solution). In this respect, **3** offers a significant advantage over **1**. A further point relates to the fact that the system operates effectively in aqueous solution and, importantly, at a very fast rate. This is a property which is clearly desirable in any practical system.

The behaviour of ligand **4** to added metal ions was also investigated. Unfortunately, for this compound, metal binding was extremely slow, even in solution in MeCN. Several days were required for equilibrium to be attained, even for lead. This slow rate of binding probably reflects the steric hindrance of the two bulky bis-naphthyl groups to the approach of the metal ion, coupled with the restricted rotation about the tertiary amide bonds. Such behaviour is consistent with the kinetic inertness noted for the Ca^{2+} complex formed initially during the synthesis of the ligand, where metal ion dissociation is hindered for the same reasons. The observed effects of Cu^{2+}, Pb^{2+} and Eu^{3+} are shown in Table 2 and Fig. 8. The pattern is somewhat different to that of **3**. This could be due to the differing distance dependencies of the quenching rates: the naphthyl groups in **4** are closer to the metal binding site than in **3**.

In conclusion, the present work has extended our previous observations[9] concerning the fluorescence of naphthyl substituted amide derivatives of 1,4,7,10-tetraazacyclododecane and their metal complexes. The use of a bis-naphthyl amide fragment, $-CH_2CON(CH_2C_{10}H_7)_2$, allows the preparation of ligands whose fluorescence spectra are characterised by excimer emission in addition to the usual monomer naphthyl band. The ratio of excimer to monomer intensities is affected to differing extents following complexation of different metal ions, as is the total fluorescence intensity. For ligand **3**, metal complexation is very rapid even in aqueous solution. The terbium complex of ligand **1** displays naphthyl sensitised metal emission, but the minimal difference in energy between the metal excited state and the naphthyl triplet results in a particularly efficient back energy transfer process from the metal to the chromophore, which serves to reduce dramatically the lifetime and intensity of the metal emission under ambient conditions at atmospheric pressure.

Experimental

General

Reactions requiring an inert atmosphere or anhydrous conditions were carried out under a dynamic atmosphere of dry, oxygen-free nitrogen or argon using standard Schlenk line techniques. Solvents were dried from an appropriate drying agent where required and water was purified by the Milli Q system. Acetonitrile for luminescence was HPLC grade, with negligible absorbance at 270 nm. Preparative column chromatography was carried out using Merck Silica Gel 60 (230–400 mesh). Dichloromethane for chromatography was HPLC or Analar® grade; other eluants were distilled prior to use. Analysis by HPLC was performed by means of a Varian 9010/9065 Polychrom system using a Technicol Hypersil 5ODS reverse-phase column.

IR spectra were recorded using a Perkin-Elmer 1600 FT spectrometer with GRAMS Analyst operating software. Variable temperature NMR spectra were recorded on a Varian VXR-400. All other NMR spectra were acquired using a Brüker AC250 spectrometer operating at 250.13 and 62.9 MHz for ^1H and $^{13}C\{^1H\}$ measurements, respectively. Spectra were referenced internally to residual protio-solvent resonances and are reported relative to tetramethylsilane (δ 0). All chemical shifts (δ) are quoted in ppm and coupling constants (J) in Hz. Mass spectra (CI and DCI) were recorded using a VG 7070E spectrometer with samples for desorption chemical ionisation being presented as solutions in chloroform using ammonia as the impingent gas. Fast-atom-bombardment spectra were obtained at the EPSRC Mass Spectrometry Service Centre, University of Wales, Swansea using *m*-nitrobenzyl alcohol as the matrix. Electrospray mass spectra were recorded at the University of Durham using a VG platform spectrometer.

Luminescence and transient absorption measurements

Ground-state UV absorbance spectra were recorded using an ATI Unicam UV-2 spectrometer. Fluorescence spectra were obtained with a Perkin-Elmer LS50B spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier tube. Metal luminescence emission and excitation spectra were recorded using the same instrument operating in time-resolved mode, with a delay time of 0.1 ms and a gate time of 10 ms. In both cases, emission spectra were acquired following excitation at 270 nm and were corrected for the wavelength dependence of the photomultiplier tube.

The effect of metal ions was investigated by addition of a solution of the metal triflate to 3 cm^3 of a solution of the ligand in the same solvent. In each case, the concentration of the metal triflate solution was first adjusted such that the volume of solution to be added, containing the required number of equivalents of M^{2+}, was 100 μl (1 μl = 1 mm^3). The addition thus results in a constant dilution (of only 3.3%) which is the same for all the metals and which has a negligible effect on the fluorescence intensity.

In the case of the flash photolysis study, the sample was excited by pulses of laser radiation of wavelength 308 nm, produced by a Lambda Physik EMG101 xenon chloride excimer laser. Maximum pulse energy at the sample was of the order of 1 mJ, with a pulse duration of 20 ns. The triplet state of the naphthyl group produced on laser excitation was observed by absorption spectroscopy (410 nm) at right angles to the exciting pulse. Light from a 100 W tungsten filament lamp was focused onto the sample. The attenuated light emerging was focused onto a Bentham TM300 monochromator (set at 410 nm) and the intensity measured using a Hamamatsu R928 photomultiplier tube. The output was fed into a Tektronix TDS 320 digital storage oscilloscope triggered by a photodiode. Data was transferred to a PC for analysis. The transient decay was observed after about 10 consecutive laser pulses in order to increase the signal-to-noise ratio. The observed signals were converted to a plot of absorbance *versus* time. At the wavelength used (410 nm), ground-state naphthalene does not absorb and so the profile obtained represents the decay of the triplet naphthalene with time.

The experimental set-up for observation of the laser-induced metal luminescence was similar except that the lamp was disconnected and the optics set up so as to optimise the collection of luminescence. The monochromator was set to the wavelengths of the strongest emission bands of terbium (490, 545 and 590 nm).

Low temperature spectra were acquired using a variable temperature liquid nitrogen cryostat, Oxford Instruments model DN1704, controlled by an Oxford Instruments ITC 4 temperature controller. In recording spectra at temperatures exceeding 295 K, a thermostatted water bath was used, which rapidly circulated warm water through a channel bored into the cuvette holder. Ethanol was chosen as the solvent for temperature studies as its freezing point is sufficiently low for a large range of temperatures to be available in fluid solution (the range 150–330 K was examined).

Synthesis

The preparation of ligands **1** and **2** and their europium and terbium complexes has been reported previously.[9]

***N*-(2′-Naphthylmethyl)-2-naphthylmethanimine 8.** 2-Naphthylmethylamine (460 mg, 2.93 mmol) was dissolved in absolute ethanol (50 cm^3) and a solution of 2-naphthaldehyde (460 mg, 2.93 mmol) in absolute ethanol (10 cm^3) was added. The mixture was heated at reflux for 2 h, during which time a pale yellow crystalline solid precipitated. On cooling, the solid was separated, washed with cold ethanol and dried under vacuum (630 mg, 70%), mp 177–178 °C. δ_H(CDCl$_3$) 5.16 (2 H, s, $C_{10}H_7C\mathit{H}_2N$), 7.51–8.21 (14 H, overlapping multiplets, aromatic H) and 8.72 (1 H, s, $C_{10}H_7C\mathit{H}{=}N{-}$); $\delta_C\{^1H\}$(CDCl$_3$) 65.9 (s, $C_{10}H_7\mathit{C}H_2N$), 124.6, 126.3, 126.7, 127.2, 127.9, 128.4, 128.6, 128.9, 129.2, 129.3 and 130.9 (singlets, aromatic C), 133.5, 134.0, 134.9 and 138.0 (singlets, quaternary aromatic C) and 162.9 (s, $C_{10}H_7\mathit{C}H{=}N{-}$); *m*/*z* (DCI) 296 (100, $M^+ + 1$) and 156 (22, $C_{10}H_7CH{=}NH_2{}^+$); ν(KBr)/cm^{-1} 3047m (Ar–H str), 2865m and 2806w (HC–H str), 1636s (C=N str), 1507m, 1299s, 866m, 829s, 745s and 477s (Found: C, 89.2; H, 5.8; N, 5.0. $C_{22}H_{17}N$ requires C, 89.5; H, 5.8; N, 4.8%).

***N*,*N*-Bis(2-naphthylmethyl)amine 9.** The imine (0.58 g, 1.97 mmol) was taken into absolute ethanol (30 cm^3) and sodium borohydride (0.16 g, 4.2 mmol) was added to the stirred suspension. The mixture was heated under reflux for 2 h, during which time a yellow solution was formed. The solvent was removed under reduced pressure and the residue taken up into dichloromethane (25 cm^3) and washed with aqueous base (KOH, 1 M, 3 × 15 cm^3). The solution was dried over K_2CO_3 and the solvent removed under reduced pressure leaving a pale yellow solid (470 mg, 81%), mp 82–83 °C. δ_H(CDCl$_3$) 1.91 (1 H, br s, NH), 4.11 (4 H, s, $C_{10}H_7C\mathit{H}_2N$), 7.52–7.63 (6 H, overlapping multiplets, aromatic H) and 7.90–7.96 (8 H, overlapping multiplets, aromatic H); $\delta_C\{^1H\}$(CDCl$_3$) 53.7 (s, $C_{10}H_7\mathit{C}H_2N$), 126.0, 126.5, 127.0, 127.1, 128.2 and 128.5 (singlets, aromatic C), 133.2, 133.9 and 138.3 (quaternary aromatic C); *m*/*z* (DCI) 298 (100, $M^+ + 1$), 156 (17, $C_{10}H_7CH_2NH^+$) and 141 (21, $C_{10}H_7CH_2{}^+$); ν(KBr)/cm^{-1} 3447m (N–H str), 3050m (Ar–H str), 2814m and 2770w (HC–H str), 1507m, 1433m, 1360w, 1095m, 863m, 815s, 746s and 478s.

Chloro-*N*,*N*-bis(2-naphthylmethyl)ethanamide 7. The bisnaphthyl amine (470 mg, 1.58 mmol) was dissolved in dry dichloromethane (20 cm^3) and triethylamine (350 cm^3, 2.5 mmol) was added. The solution was stirred under argon with cooling to −10 °C and chloroacetylchloride (200 cm^3, 2.5 mmol) was added dropwise, the temperature being maintained below 0 °C. On warming to room temperature, the solution was washed with HCl(aq) (1 M, 3 × 10 cm^3) followed by water (3 × 10 cm^3), dried over anhydrous K_2CO_3 and the solvent removed under reduced pressure, leaving a pale brown oil (530 mg, 89%). δ_H(CDCl$_3$) 4.24 (2 H, s, $ClCH_2$), 4.71 (2 H, s, $C_{10}H_7C\mathit{H}_2NCO$), 4.87 (2 H, s, $C_{10}H_7C\mathit{H}_2NCO$) and 7.40–7.90 (14 H, overlapping multiplets, aromatic H); $\delta_C\{^1H\}$(CDCl$_3$) 42.1 (s, $ClCH_2$), 49.3 (s, $C_{10}H_7\mathit{C}H_2NCO$), 50.9 (s, $C_{10}H_7\mathit{C}H_2$-NCO), 124.9, 125.6, 126.6, 126.9, 127.2, 127.7, 128.3, 129.2 and 129.6 (singlets, aromatic C), 133.4, 133.6, 133.8, 133.9 and 134.4 (singlets, quaternary aromatic C) and 167.9 (C=O); *m*/*z* (DCI) 376 (9, $M^+ + 1$ for ^{37}Cl), 374 (26, $M^+ + 1$ for ^{35}Cl), 340 (100, $[M^+ - Cl + H] + 1$) and 141 (18, $C_{10}H_7CH_2{}^+$); ν(KBr)/cm^{-1} 3053m (Ar–H str), 2942m and 2868w (HC–H str), 1657s (C=O str), 1453s, 1370s, 1271m, 1209m, 942m, 816s and 753s.

Bis(2-naphthylmethyl)carbamoylmethyl 1,4,7,10-tetraazacyclododecane-1-carboxylate 11. The molybdenum tricarbonyl complex of 1,4,7,10-tetraazacyclododecane (430 mg, 1.23 mmol) was taken into dry degassed dimethylformamide (25 cm^3) with anhydrous potassium carbonate (250 mg, 1.8 mmol) and chloro-*N*,*N*-bis(2-naphthylmethyl)ethanamide was added under argon. The mixture was heated at 80 °C under argon for 3 h, during which time a brown solution was obtained. The solvent was removed under reduced pressure and the residue taken up into HCl(aq) (1 M, 30 cm^3) and stirred open to the air for 18 h. The brown solid formed was separated by centrifuge and extracted with dichloromethane. The resulting yellow solution was washed with aqueous base (KOH, 1 M, 3 × 25 cm^3), dried over anhydrous potassium carbonate and the solvent removed under reduced pressure leaving a yellow oil (550 mg, 40%). The purity of the product at this stage, as judged by HPLC, was poor. An attempt at purification by reverse-phase HPLC proved unsatisfactory and the compound was therefore used in the next step without futher purification. $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 2.67–2.84 (12 H, br, overlapping multiplets, $\mathrm{CH_2}$ ring), 3.03 (7 H, br, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{NCO_2}$ and N–H), 4.72 (2 H, s, $\mathrm{NCO_2CH_2CO}$), 4.92 (2 H, s, $\mathrm{C_{10}H_7C}\mathit{H}_2\mathrm{N}$), 4.95 (2 H, s, $\mathrm{C_{10}H_7C}\mathit{H}_2\mathrm{N}$) and 7.51–7.98 (28 H, overlapping multiplets, aromatic H); $\delta_{\mathrm{C}}\{^1\mathrm{H}\}(\mathrm{CDCl_3})$ 43.3 ($\mathrm{NH}\mathit{C}\mathrm{H_2CH_2NHCH_2CH_2NCO_2}$), 43.8 ($\mathrm{NHCH_2}\mathit{C}\mathrm{H_2NHCH_2CH_2NCO_2}$), 45.1 ($\mathrm{NH}\mathit{C}\mathrm{H_2CH_2CO_2}$), 49.5 ($\mathrm{C_{10}H_7}\mathit{C}\mathrm{H_2N}$), 50.4 ($\mathrm{C_{10}H_7}\mathit{C}\mathrm{H_2N}$), 51.6 ($\mathrm{NHCH_2}\mathit{C}\mathrm{H_2CO_2}$), 63.9 ($\mathrm{NCO_2}\mathit{C}\mathrm{H_2}$), 124.5, 125.1, 125.8, 126.0, 126.5, 127.1, 127.4, 128.4, 129.7, 130.0, 132.9, 133.5, 133.8 and 134.1 (aromatic C), 156.6 ($\mathrm{N}\mathit{C}\mathrm{O_2}$) and 170.3 ($\mathrm{N}\mathit{C}\mathrm{OCH_2}$); *m*/*z* (DCI) 414 (20, $\mathrm{M^+} - [\mathrm{C_{10}H_7CH_2}] + \mathrm{H} + 1$), 356 (45, $\mathrm{M^+} - [(\mathrm{C_2H_4N})_4\mathrm{C{=}O}] + \mathrm{H} + 1$), 340 (100, $\mathrm{M^+} - [(\mathrm{C_2H_4N})_4\mathrm{CO_2}] + \mathrm{H} + 1$), 199 [33, $(\mathrm{C_2H_4N})_4\mathrm{C{=}O^+}$] and 141 ($\mathrm{C_{10}H_7CH_2{}^+}$); ν(thin film)/cm^{-1} 3052m (Ar–H str), 2935m and 2846m (HC–H str), 1703m (carbamate C=O str), 1655s (amide C=O str), 1466m, 1370m, 1222w and 817m.

Bis(2-naphthylmethyl)aminocarbonylmethyl 4,7,10-tris(methylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane-1-carboxylate 3. The monoalkylated derivative **11** (200 mg, 0.36 mmol) was dissolved in anhydrous dimethylformamide (2 cm^3) and anhydrous caesium carbonate (472 mg, 1.45 mmol) was added, followed by chloro-*N*-methylethanamide (156 mg, 1.45 mmol). The mixture was heated at 80 °C under argon for 18 h. Removal of solvent under reduced pressure gave a brown oil, which was purified by silica column chromatography [gradient elution from $\mathrm{CH_2Cl_2}$–MeOH–$\mathrm{NH_3}$ (aq. 0.88) = 55:45:0 to 50:45:5; $R_{\mathrm{f}} = 0.6$ (55:45:5)] giving a colourless solid (40 mg, 15%), mp 180 °C (decomp). $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 2.66 (8 H, br s, $\mathrm{CH_2CH_2}$ ring), 2.75–2.79 (9 H, overlapping doublets, $\mathrm{CONHC}\mathit{H}_3$), 3.05–3.07 (4 H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2NCO_2CH_2}$ and 2 H, $\mathrm{NC}\mathit{H}_2\mathrm{CONHMe}$), 3.20 (4 H, s, $\mathrm{NC}\mathit{H}_2\mathrm{CONHMe}$), 3.49 (4 H, br, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{NCO_2}$); 4.56 (2 H, s, $\mathrm{NCO_2CH_2CON}$), 4.83 ($\mathrm{C_{10}H_7C}\mathit{H}_2\mathrm{N}$), 4.89 ($\mathrm{C_{10}H_7C}\mathit{H}_2\mathrm{N}$) and 7.29–7.95 (14 H, overlapping multiplets, aromatic H; and 3 H, br, $\mathrm{CON}\mathit{H}\mathrm{Me}$ overlapping with aromatic H); $\delta_{\mathrm{C}}\{^1\mathrm{H}\}(\mathrm{CDCl_3})$ 28.6 ($\mathrm{CONH}\mathit{C}\mathrm{H_3}$), 47.0 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2NCH_2CH_2NCO_2}$), 48.6 ($\mathrm{NCH_2CH_2NCH_2CH_2NCO_2}$), 54.0 (s, $\mathrm{N}\mathit{C}\mathrm{H_2CH_2NCO_2}$), 54.3 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2NCO_2}$), 59.3 (s, $\mathrm{N}\mathit{C}\mathrm{H_2CONHMe}$), 62.9 ($\mathrm{CO_2}\mathit{C}\mathrm{H_2CON}$), 124.9, 125.0, 126.5, 126.8, 127.1, 127.4, 128.4, 129.4 and 129.9 (singlets, aromatic C), 133.3, 133.6, 134.0 and 134.4 (singlets, quaternary aromatic C), 157.0 (s, $\mathrm{N}\mathit{C}\mathrm{O_2CH_2}$), 168.1 [s, $(\mathrm{C_{10}H_7CH_2})_2\mathrm{N}\mathit{C}\mathrm{O}$], 171.4 and 171.5 (singlets, MeNHCO); *m*/*z* (ES +) 790 (5, $[\mathrm{M} + \mathrm{Na^+}]^+$), 768 (100, $[\mathrm{M} + 1]^+$); ν(KBr)/cm^{-1} 3319m (N–H str), 3054w (Ar–H str), 2938m and 2817m (HC–H str), 1702s (carbamate C=O str), 1663 (amide I) and 1533 (amide II) [Found (FAB, NOBA matrix): M$^+$ 767.4246 (0.6 ppm). $\mathrm{C_{42}H_{55}N_8O_6}$ requires M, 767.4245].

Complexes of the carbamate ligand 3. These were prepared in solution in acetonitrile without isolation using a 10% excess of the appropriate metal triflate salt and were characterised by electrospray mass spectroscopy (positive ion detection mode): $\mathrm{Cu^{2+}}$ 978 $\{3, [\mathrm{M^{2+}} + (\mathrm{CF_3SO_3{}^-})]^+\}$; 829 $\{8, [\mathrm{M^{2+}} + \mathrm{e^-}]^+\}$; 415 (100, $\mathrm{M^{2+}}$). $\mathrm{Zn^{2+}}$ 980 $\{6, [\mathrm{M^{2+}} + (\mathrm{CF_3SO_3{}^-})]^+\}$; 416 (100, $\mathrm{M^{2+}}$). $\mathrm{Pb^{2+}}$ 1122 $\{6, [\mathrm{M^{2+}} + (\mathrm{CF_3SO_3{}^-})^+\}$; 487 (100, $\mathrm{M^{2+}}$).

1,7-Bis(4-methoxybenzenesulfonyl)-1,4,7,10-tetraazacyclododecane 13. A procedure similar to that described previously for the preparation of the *p*-toluenesulfonyl analogue (**12**) was employed.[14] A solution of 1,4,7,10-tetraazacyclododecane (1.29 g, 7.5 mmol) in dry pyridine (12 cm^3) was added dropwise to a solution of 4-methoxybenzenesulfonyl chloride (3.10 g, 15 mmol) in pyridine (30 cm^3) over a period of 15 min, with cooling to 0 °C. The mixture was allowed to warm to room temperature and stirred for a further 2 h. The pyridine was removed under reduced pressure and the yellow residue treated with water (30 cm^3) and the resulting suspension stirred at room temperature for 1 h. The solid was separated by filtration, washed with water (3 × 30 cm^3) followed by saturated aqueous potassium carbonate solution (3 × 30 cm^3) and finally methanol (3 × 30 cm^3). (Yield 3.1 g, 81%). Mp >250 °C. $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 3.28 (8 H, br, $\mathrm{HNC}\mathit{H}_2\mathrm{CH_2NSO_2Ar}$), 3.52 (8 H, br, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{NSO_2Ar}$), 4.00 (6 H, s, $\mathrm{OCH_3}$), 7.15 (4 H, d, ^3J 8.9, Ar) and 7.85 (4 H, d, ^3J 8.9, Ar); $\delta_{\mathrm{C}}\{^1\mathrm{H}\}(\mathrm{CDCl_3})$ 49.2 (s, $\mathrm{OCH_3}$), 52.3 (s, $\mathrm{N}\mathit{C}\mathrm{H_2CH_2NSO_2Ar}$), 55.7 (s, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2NSO_2Ar}$), 114.4 (s, *meta* C), 128.5 (s, C–OMe), 129.5 (s, *ortho* C), 163.9 (s, C–$\mathrm{SO_2}$); *m*/*z* (ESMS, positive ion) 513 (55, $\mathrm{M^+} + 1$), 535 (17, $\mathrm{M} + \mathrm{Na^+}$), 551 (6, $\mathrm{M} + \mathrm{K^+}$); ν(KBr)/cm^{-1} 3447m (N–H str), 3170w (Ar–H str), 2978m and 2937m (HC–H str), 1597s, 1496s, 1339s, 1258s, 1157s, 1095m, 1016m, 701s and 561s [Found: M$^+$ (CI): 513.1840. $\mathrm{C_{22}H_{33}N_4S_2O_6}$ requires *M* 513.1842].

1,7-Bis(4-methoxybenzenesulfonyl)-4,10-bis(methylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane 14. 2-Chloro-*N*-methylethanamide (580 mg, 5.40 mmol) was added to a suspension of the disulfonamide **13** (1.1 g, 2.15 mmol) in dry dimethylformamide (10 cm^3) containing anhydrous caesium carbonate (1.76 g, 5.40 mmol) and potassium iodide (714 mg, 4.30 mmol). The mixture was heated at 75 °C under an atmosphere of argon for 48 h. [The progress of the reaction was readily monitored by alumina TLC: the R_{f} values (5% methanol–dichloromethane) of the starting material and the monoalkylated and dialkylated compounds were 0.4, 0.6 and 0.8, respectively.] The solvent was removed under reduced pressure and the residue taken into dichloromethane and filtered. Removal of solvent from the resulting yellow solution gave a brown residue which was purified by silica column chromatography (gradient elution from dichloromethane to 3% methanol–dichloromethane, $R_{\mathrm{f}} = 0.4$ in 5% methanol–dichloromethane), giving a colourless solid (1.19 g, 84%), mp 112–115 °C. $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 2.87 (6 H, d, ^3J 4.9, $\mathrm{CONHC}\mathit{H}_3$), 2.95 (8 H, br, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 3.12 (8 H, br, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{N}$), 3.25 (4 H, s, $\mathrm{NC}\mathit{H}_2\mathrm{CONHMe}$), 7.00 (4 H, d, ^3J 8.8, Ar), 7.69 (4 H, d, ^3J 8.8, Ar); $\delta_{\mathrm{C}}\{^1\mathrm{H}\}(\mathrm{CDCl_3})$ 26.2 (s, $\mathrm{CONH}\mathit{C}\mathrm{H_3}$), 50.7 (s, $\mathrm{OCH_3}$), 55.8 and 56.0 (singlets, $\mathrm{NCH_2CH_2N}$), 58.7 (s, $\mathrm{N}\mathit{C}\mathrm{H_2CONHMe}$), 114.8 (s, *meta* C), 129.2 (s, C–OMe), 129.7 (s, *ortho* C), 163.5 (s, C–$\mathrm{SO_2}$) and 171.8 ($\mathit{C}\mathrm{ONHMe}$); *m*/*z* (ES +) 655 (100, $\mathrm{M^+} + 1$) and 677 (80, $\mathrm{M} + \mathrm{Na^+}$); ν(KBr)/cm^{-1} 3395m (N–H str), 3076w (Ar–H str), 2943m and 2841m (HC–H str), 1662s (C=O str), 1596s, 1497m, 1335s, 1261s, 1155s, 1093m, 1023m, 699s and 558s (Found: C, 49.0; H, 6.4, N, 12.2. $\mathrm{C_{28}H_{42}N_6S_2O_8{\cdot}2H_2O}$ requires C, 48.7; H, 6.7; N, 12.2%).

1,7-Bis(methylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane 15. A solution of hydrogen bromide in acetic acid (33%, 30 cm^3) was added to **14** (2.0 g, 3.06 mmol) in the presence of phenol (2.88 g, 30.6 mmol) and the mixture was heated at 110 °C for 48 h. A further 20 cm^3 of HBr–AcOH was then added and heating continued for a further 48 h. The resulting brown solution was added dropwise to a large excess of diethyl ether in a large centrifuge tube. The solid which precipitated was separated by centrifuge, washed with diethyl ether, dried under reduced pressure and taken up into water. The pink solution obtained was filtered and passed down an anion exchange column (Amberlite IRA 400 in OH$^-$ form). The basic fractions collected were combined and the water removed by freeze-drying giving an oily solid. ^{13}C NMR spectra indicated that the required compound was present, but contaminated with a significant proportion of monoamide. Separation was achieved by selective precipitation of the diamide from toluene, giving a colourless solid (300 mg, 31%), mp 95–98 °C. $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 2.45 (2 H, br s, NH amine), 2.65 (16 H, br, $\mathrm{CH_2CH_2}$ ring), 2.81 (6 H, d, ^3J 4.8, $\mathrm{CONHC}H_3$), 3.17 (4 H, s, $\mathrm{NCH_2CO}$) and 7.51 (2 H, br d, ^3J 4.8, $\mathrm{CON}H\mathrm{Me}$); $\delta_\mathrm{C}\{^1\mathrm{H}\}(\mathrm{CDCl_3})$ 26.6 (s, $\mathrm{CONH}C\mathrm{H_3}$), 46.6 (s, $\mathrm{NH}C\mathrm{H_2CH_2NCH_2CO}$), 54.1 (s, $\mathrm{NHCH_2}C\mathrm{H_2NCH_2CO}$), 60.3 (s, $\mathrm{N}C\mathrm{H_2CO}$), 172.7 (s, $C\mathrm{ONHMe}$); *m*/*z* (DCI) 315 (100, $\mathrm{M}^+ + 1$); ν(KBr)/cm^{-1} 2941m and 2835m (H–H str), 1654s (C=O str), 1560s, 1465m, 1406m, 1281w, 1068m, 975m, 786w [Found: M + (CI): 315.2508. $\mathrm{C_{14}H_{31}N_6O_2}$ requires *M* 315.25085].

1,7-Bis[*N*,*N*-bis(2-naphthylmethyl)carbamoylmethyl]-4,10-bis(methylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane: $\mathbf{Ca^{2+}}$ complex $\mathbf{[Ca{\cdot}4]^{2+}(I^-)_2}$. A solution of the bis-naphthyl chloroamide **7** (232 mg, 0.62 mmol) in dry dimethylformamide (1 cm^3) was added to a solution of the *trans*-diamide **15** (96 mg, 0.31 mmol) in dimethylformamide (1 cm^3) in the presence of anhydrous caesium carbonate (250 mg, 0.77 mmol) and potassium iodide (103 mg, 0.62 mmol). The mixture was heated at 75 °C under an atmosphere of argon for 48 h. The solvent was removed under reduced pressure and the residue taken into dichloromethane and filtered. Removal of solvent gave a brown oil which was purified by column chromatography on silica (gradient elution from dichloromethane to 2% $\mathrm{NH_3(aq)}$–18% methanol–80% dichloromethane, $R_\mathrm{f} = 0.5$ by TLC under these conditions). The product was further purified by precipitation from chloroform–ethanol giving a fine off-white solid which proved to be the calcium complex of the required ligand as its iodide salt (40 mg, 10%), mp > 250 °C. $\delta_\mathrm{H}([^2\mathrm{H}_6]\mathrm{DMSO}$, 363 K, 400 MHz) 2.48 (8 H, br, $\mathrm{NC}H_2\mathrm{CH_2N}$ ring), 2.57 (6 H, d, ^3J 4.4, $\mathrm{CONHC}H_3$), 2.83 (8 H, br, $\mathrm{NCH_2C}H_2\mathrm{N}$ ring), 3.33 (4 H, s, $\mathrm{NCH_2CO}$), 3.73 (4 H, s, $\mathrm{NCH_2CO}$), 4.82 (8 H, s, $\mathrm{C_{10}H_7C}H_2\mathrm{N}$), 7.38–7.92 (28 H, overlapping multiplets, Ar–H) and 8.62 (2 H, d, ^3J 4.4, $\mathrm{CON}H\mathrm{Me}$); $\delta_\mathrm{C}\{^1\mathrm{H}\}(\mathrm{CDCl_3}$, 298 K) 27.0 ($\mathrm{CH_3}$), 49.5 (br, $\mathrm{C_{10}H_7}C\mathrm{H_2N}$), 51.1 ($\mathrm{N}C\mathrm{H_2CH_2N}$), 53.3 ($\mathrm{NCH_2}C\mathrm{H_2N}$), 57.3 ($\mathrm{N}C\mathrm{H_2CO}$), 58.0 ($\mathrm{N}C\mathrm{H_2CO}$), 124.7, 126.0, 126.4, 127.1, 127.5, 128.4, 128.6, 129.6, 130.0, 132.5, 133.5, 133.7 and 133.9 (aromatic C), 174.4 (C=O) and 174.6 (C=O); *m*/*z* (ES +) 1156 (5, $[\mathrm{M^{2+} + I^-}]^+$) and 515 (100, $\mathrm{M^{2+}}$); ν(KBr)/cm^{-1} 3223m (N–H str), 3103m (Ar–H str), 2985m and 2851m (HC–H str), 1643s (C=O str), 1616s, 1309m, 1234m, 1093m, 999m, 817m and 754m (Found: C, 56.9; H, 5.0; Ca, 3.1; I, 19.7; N, 8.4. $\mathrm{C_{62}H_{68}CaI_2N_8O_4{\cdot}H_2O}$ requires C, 57.2; H, 5.4; Ca, 3.1; I, 19.5%; N, 8.6).

1,7-Bis[*N*,*N*-bis(2-naphthylmethyl)carbamoylmethyl]-4,10-bis(methylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane 4. Dilute aqueous acid (HCl, 0.01 M, 3 cm^3) was added to the calcium complex obtained as above (15 mg, 0.012 mmol) followed by methanol (1 cm^3). The mixture was stirred at room temperature for 18 h and an excess of DOTA was added. The pH was raised slowly to 13 by the dropwise addition of KOH (0.1 M aq). Extraction into dichloromethane (3 × 5 cm^3) and removal of solvent under reduced pressure gave a colourless residue (4 mg, 35%). $\delta_\mathrm{H}(\mathrm{CDCl_3})$ 2.55 (16 H, br, $\mathrm{CH_2}$ ring), 2.67 (6 H, d, ^3J 4.6, $\mathrm{CONHC}H_3$), 3.32 (4 H, br s, $\mathrm{NCH_2CO}$), 3.47 (4 H, br s, $\mathrm{NCH_2CO}$), 4.64 (4 H, br s, $\mathrm{C_{10}H_7C}H_2\mathrm{N}$), 4.86 (4 H, br s, $\mathrm{C_{10}H_7C}H_2\mathrm{N}$) and 7.35–7.91 (28 H, overlapping multiplets, aromatic H); *m*/*z* (ES +) 1012 (5, $[\mathrm{M + Na^+}]^+$), 990 (12, $[\mathrm{M + H^+}]^+$) and 496 (30, $[\mathrm{M + 2\,H^+}]^{2+}$); ν(KBr)/cm^{-1} 3210m (N–H str), 3115m (Ar–H str), 2969m and 2843m (HC–H str), 1643s (C=O str), 1313m, 1085m, 990m and 754m.

Complexes of the bis-naphthyl ligand 4. These were prepared in solution in acetonitrile without isolation, using a 10% excess of the appropriate metal triflate and were characterised by electospray mass spectroscopy (positive ion detection): $\mathrm{Cu^{2+}}$ 526 (70, $\mathrm{M^{2+}}$), $\mathrm{Pb^{2+}}$ 598 (80, $\mathrm{M^{2+}}$), $\mathrm{Eu^{3+}}$ 1140 (12, $[\mathrm{M^{3+} + 2e^-}]^+$).

Metal triflate salts. These were prepared as previously reported.[9]

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