

Luminescence behaviour of cadmium, lead, zinc, copper, nickel and lanthanide complexes of octadentate macrocyclic ligands bearing naphthyl chromophores

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The luminescence behaviour of two macrocyclic ligands incorporating naphthyl fluorophores has been studied in water and acetonitrile. The ligands 1,4,7-tris(methylcarbamoylmethyl)-10-(2-naphthylmethylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane, **1** and 1,4,7,10-tetrakis(2-naphthylmethylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane, **2**, exhibit distinctive luminescence behaviour in the presence of quenching (*e.g.*, Pb^{II}, Cu^{II} and Ni^{II}) and non-quenching ions (*e.g.*, Cd^{II} and Zn^{II}). The protonated tetranaphthyl ligand forms a well-defined excimer in which excimer emission is a sensitive probe of solvent polarity. The naphthyl group serves as an antenna for energy transfer to the phosphorescent bound europium ion and amide N–H coupling provides a significant deactivation mechanism for the excited Eu ⁵D₀ state.

Introduction

The study of luminescent chemosensors has been the focus of a good deal of current research effort. Of particular interest has been the design of conjugate chemosensors which are able selectively to signal the presence of ionic species in aqueous solution.^{1,2} The fluorescent reporter groups are often simple naphthyl³ or anthryl groups⁴ which have been linked to polyamine ionic receptors. In solution, fluorescence quenching occurs *via* intramolecular photoinduced electron transfer from nitrogen to the excited aryl group. Intermolecular quenching of anthryl or naphthyl fluorescence by amines is well known^{5,6} and is predicted from the Weller equation.⁷ In the presence of certain metal ions that can bind to the nitrogen lone pairs, enhanced fluorescence is observed. Complexation of the nitrogen lone pairs raises the amine oxidation potential, so that it can no longer reduce the aryl excited S₁ state. This effect has been termed chelation enhanced fluorescence, and pH sensors and ion-sensors, most operating with modest selectivity, have been reported based upon this principle. In seeking to refine these methods what is required is the coupling of more selective ionic or molecular receptors to suitable lumophores, and in particular devising receptors that can operate in aqueous media, or at an aqueous interface in neutral or acidic conditions. This is a first step towards their development for clinical or environmental monitoring applications.

N-Substituted octadentate ligands based on the 1,4,7,10-tetraazacyclododecane ring are predisposed to bind large metal ions that favour a coordination number of eight. Not only does the macrocyclic ring adopt the same rigid quadrangular [3333] conformation in the ligand as in the metal complex, but all the nitrogen substituents may also be directed above the N₄ plane. This has been observed with the protonated ligands **3a** and **3b** in which a hydrogen-bonding network stabilises the ligand in a conformation that is predisposed to accept metal ions.^{8,9} Such ligands show excellent selectivities for cations which prefer a square-antiprismatic geometry such as calcium,¹⁰ (*e.g.*, with **3e**) the lanthanides (*e.g.*, Eu, Gd, Tb, Dy¹¹ with **3a**, **3c** and **3d**) and the toxic metal ions Cd²⁺ and Pb²⁺ (with **3c**).¹² With the tetraamide ligand **3c**, excellent selectivity (> 10¹⁰) over zinc ions has been found as expressed by the ratio of the 1:1 metal complex stability constants measured in water. With this in mind, two 12-N₄ based tetraamide ligands, **1** and **2**, bearing one or four naphthyl groups have been prepared and the effect of complex formation on their luminescence properties studied.

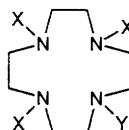
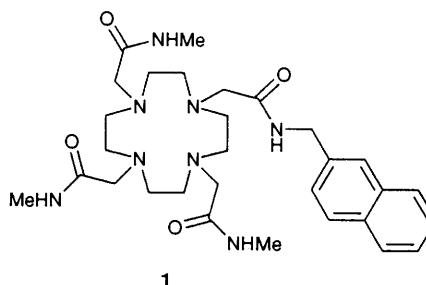
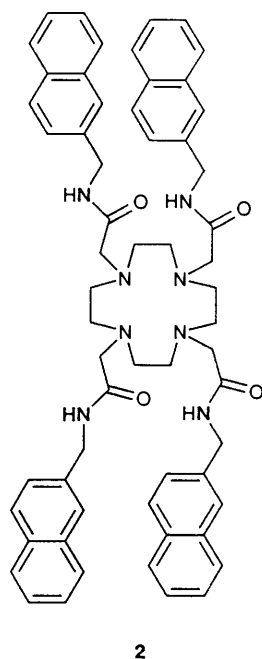
Results and discussion

The monoamide ligand was prepared following selective protection of one of the ring nitrogens using a molybdenum tricarbonyl moiety¹³ (Scheme 1). Thus reaction of 1,4,7,10-tetraazacyclododecane with Mo(CO)₆ in dibutyl ether followed by alkylation of the zero-valent molybdenum complex with *N*-(2-naphthylmethyl)-2-chloroethanamide in DMF yielded the monosubstituted 12-N₄ intermediate. Subsequent reaction with 3 equivalents of 2-chloro-*N*-methylethanamide in DMF in the presence of caesium carbonate gave the desired tetraamide **1** [$\lambda_{\text{max}}(\text{abs}) = 276 \text{ nm}$ ($\epsilon = 5.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), $\lambda_{\text{em}} = 336 \text{ nm}$ in MeCN] which was purified by chromatography on neutral alumina. The tetraamide ligand **2** [$\lambda_{\text{max}} = 276 \text{ nm}$ (CH₃CN), $\epsilon = 2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$] was prepared in 71% yield by direct reaction of 1,4,7,10-tetraazacyclododecane with *N*-(2-naphthylmethyl)-2-chloroethanamide in DMF in the presence of caesium carbonate. This tetranaphthylamide ligand, unlike the mononaphthyl ligand **1** was rather insoluble in common solvents as a neutral species, but dissolved readily in a wide range of solvents (*e.g.*, THF, CH₂Cl₂, MeOH, H₂O) when protonated by adding one or more equivalents of an acid such as trifluoroacetic acid, acetic acid, CF₃SO₃H or HPF₆.

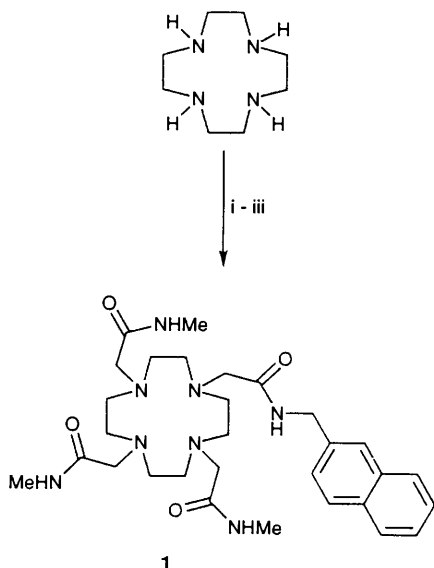
Fluorescence of **2**

The fluorescence emission spectrum of **2** (5 $\mu\text{mol dm}^{-3}$ in CH₃CN) in the presence of added protons ($\geq 30 \mu\text{mol dm}^{-3}$ CF₃CO₂H) revealed not only the expected monomer emission at 337 nm but also a broad band at 401 nm that is typical of the structureless emission of a naphthyl excimer (Fig. 1). The relative intensity of the monomer and excimer emission bands was independent of ligand concentration in the range 0.5–50 $\mu\text{mol dm}^{-3}$, and was also insensitive to the nature of the acid used (HPF₆, CF₃CO₂H or CF₃SO₃H). Such behaviour is consistent with formation of an intramolecular excimer whose formation requires the juxtaposition ($\leq 3.5 \text{ \AA}$) of two naphthyl groups in the protonated ligand.

The relative intensity of the excimer and monomer emission bands ($I_{\text{ex}}/I_{\text{em}}$), was found to be a sensitive function of solvent polarity (Figs. 1 and 2). There is a reasonable correlation between the percentage of excimer emission and solvent polarity, as measured by Reichardt's normalised $E_{\text{T}}(30)$ scale.¹⁴ The more polar solvents, with a high E_{T} value, gave the most excimer emission. Such behaviour may be contrasted with that



- 3 a;** X = Y = CH₂PBnO₂⁻
b; X = CH₂CO₂⁻, Y = H
c; X = CH₂CONH₂ = Y
d; X = Y = CH₂CO₂⁻ (dota)
e; X = Y = CH₂CONMe₂



Scheme 1 i, Mo(CO)₆, Bu₂O; ii, DMF, ClCH₂CONHCH₂-2-Np, Cs₂CO₃; iii, Cs₂CO₃, DMF, ClCH₂CONHMe

observed with a bis-pyrenyl functionalised calixarene wherein monomer emission was stronger with more polar solvents.¹⁵ It is perhaps more reminiscent of the behaviour of a tetrapyrenyl 18-crown-6 tetraamide wherein excimer emission was observed to be most intense in more polar solvents.¹⁶ It is not clear precisely how solvation of the protonated form of **2** favours excimer formation, but given the fact that nearly 90% excimer emission was observed in water, it does seem likely that in the more polar solvents both pairs of naphthyl rings may be involved in excimer formation.

Effect of added metal ions on fluorescence of **1**

(i) **In MeCN.** Addition of five equivalents of anhydrous zinc or cadmium triflates to a solution of the mononaphthyl ligand **1** in MeCN (2×10^{-5} mol dm⁻³) at 20 °C led to a twofold

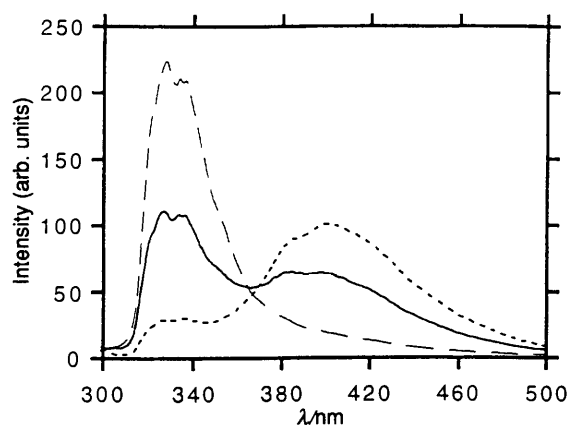


Fig. 1 Corrected fluorescence emission spectra for **2** in MeCN (—), THF (---), and water (····). [**2**] = 0.005 mmol dm⁻³, [CF₃CO₂H] = 0.25 mmol dm⁻³, λ_{exc} = 270 nm.

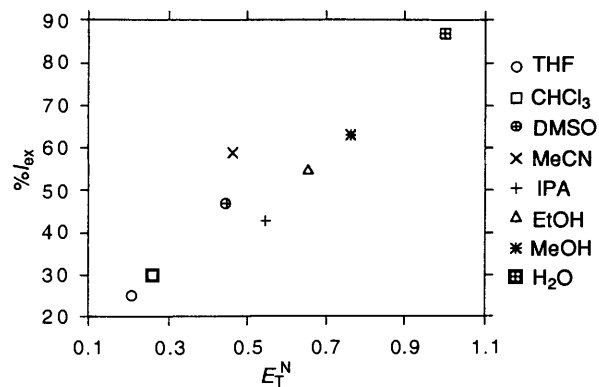


Fig. 2 Variation of excimer emission intensity (%*I*_{ex}) with the normalised *E*_T solvent polarity parameter

increase in the intensity of the naphthyl fluorescence. A similar effect, but to a lesser extent (50% fluorescence enhancement)

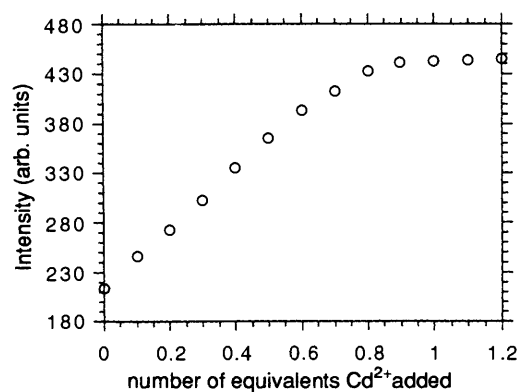


Fig. 3 Effect of adding $\text{Cd}(\text{CF}_3\text{SO}_3)_2$ on the fluorescence emission intensity of **1** ($\lambda_{\text{em}} = 337 \text{ nm}$, CH_3CN , $[\mathbf{1}] = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$)

Table 1 Fluorescence quantum yields for ligand **1** and selected isolated triflate complexes^a (293 K, H_2O)

Species	Solvent	$\Phi_{\text{fl}}(\text{rel})$
1	CH_3CN	1.39
1 ^b	H_2O	3.10
$[\text{Zn}\cdot\mathbf{1}]^{2+}$	CH_3CN	1.48
$[\text{Tb}\cdot\mathbf{1}]^{3+}$	CH_3CN	1.18
$[\text{Eu}\cdot\mathbf{1}]^{3+}$	CH_3CN	0.20
$[\text{Zn}\cdot\mathbf{1}]^{2+}$	H_2O	3.3
$[\text{Tb}\cdot\mathbf{1}]^{3+}$	H_2O	2.1
$[\text{Eu}\cdot\mathbf{1}]^{3+}$	H_2O	0.49

^a Fluorescence quantum yields are quoted relative to the value for naphthalene in CH_3CN ($\Phi_{\text{fl}} = 0.29$). $[\mathbf{1}] = [\mathbf{1}\cdot\text{M}]^{n+} = 10^{-6} \text{ mol dm}^{-3}$. ^b In water the ligand is diprotonated at this ligand concentration; $\text{pH} = 5.5$.

was observed when 50 equivalents of $\text{CF}_3\text{CO}_2\text{H}$ were added to **1** in the same solvent. This behaviour is consistent with a 'chelation enhanced fluorescence effect'.^{1,2,6} When the nitrogen lone pairs are bound, either to a proton or to a metal ion, it is more difficult for an electron to be promoted from an N 'p' orbital to the acceptor π orbital and quenching of the naphthyl excited singlet occurs less efficiently. The increase in the fluorescence intensity (I_{fl}) was directly proportional to the concentration of added metal ion. Thus when $\text{Cd}(\text{CF}_3\text{SO}_3)_2$ was added to **1** in MeCN, I_{fl} was a maximum when the ratio of ligand to added Cd ions was unity (Fig. 3) consistent with formation of a strong 1:1 complex.

Different behaviour was noted following addition of 5 equivalents of Pb^{II} ions. A reduction in fluorescence intensity ($\lambda_{\text{em}} = 336 \text{ nm}$) of 25% was observed accompanied by a 250% increase in absorbance at 270 nm. A sample of the analytically pure $[\text{Pb}\cdot\mathbf{1}]^{2+}$ complex displayed an intense band at 258 nm ($\epsilon = 1.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in the same solvent. In this case the 'chelation enhanced fluorescence' effect is less significant than the quenching effect of the proximate 'heavy atom'. The closeness of the lead ion to the naphthyl chromophore enhances singlet-triplet intersystem crossing and promotes non-radiative deactivation of the naphthyl excited singlet state. Similar behaviour in the presence of Pb^{II} ions has been observed with a monoanthryl linked 18- N_4O_2 cycle in methanol solution.¹⁷

Copper(II) and nickel(II) ions are also well known to quench excited states,¹⁸ and addition of 5 equivalents of copper(II) triflate to **1** in MeCN caused an immediate 95% reduction in ligand fluorescence intensity (Fig. 4). For purposes of comparison, addition of copper triflate to pure naphthalene under the same conditions (solvent, concentration) caused a 20% reduction in fluorescence intensity. The quenching effect of

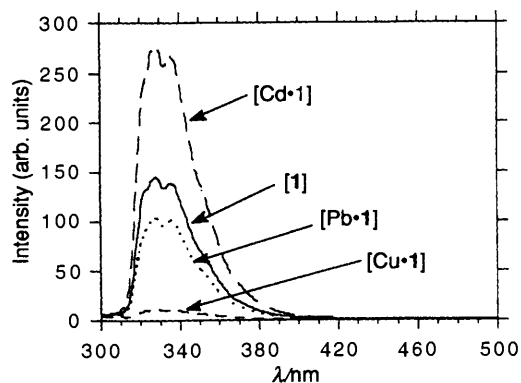


Fig. 4 Corrected fluorescence emission spectra for **1** in the presence of excess metal ions: (i) free ligand **1** (—); (ii) (---) Cd^{2+} ; (iii) (···) Pb^{2+} ; (iv) (-·-·-) Cu^{2+} . ($[\mathbf{1}] = 2 \times 10^{-5} \text{ mol dm}^{-3}$ in CH_3CN , $[\text{M}(\text{CF}_3\text{SO}_3)_2] = 10^{-4} \text{ mol dm}^{-3}$; $\lambda_{\text{exc}} = 270 \text{ nm}$, 293 K, excitation and emission slit widths = 5 nm).

added copper ions can be considered to occur either by means of an energy-transfer mechanism involving electron exchange with a low-lying empty 'd' orbital,¹⁹ or by a Cu^{II} to naphthyl electron-transfer process which requires stabilisation of the resultant Cu^{III} complex. In this case the former mechanism is perhaps the more likely. Addition of nickel triflate in MeCN had a similar effect: addition of 5 equivalents caused a 65% reduction in I_{fl} .

For all of these divalent ions (Pb, Cd, Zn, Cu and Ni) the forward rate of metal binding in MeCN was too fast to allow the estimation of relative rates of complexation. In two cases (Zn and Pb) the cationic complexes were isolated and the luminescence behaviour of the analytically pure complexes was the same as that of the complexes generated *in situ*.

(ii) **In water.** In water the fluorescence emission intensity for the ligand and its metal complexes was significantly greater than in acetonitrile (Table 1). For the ligand, this is explained by protonation of two of the ring nitrogens (the first two $\text{p}K_a$ are at *ca.* 11 and 10)¹⁰ and given the presence of two bifurcated hydrogen bonds in the 12- N_4 ring, there is a lesser tendency for electron-transfer quenching of the naphthyl excited singlet. The rates of complexation of **1** by added metal ions were also somewhat slower in water, and could be monitored in real time by changes in the fluorescence spectrum. The higher free energy of activation in water compared with acetonitrile is understandable given that encounter of a protonated ligand with a charged ion is coulombically inhibited and deprotonation at nitrogen prior to complex formation is necessary at least for the ions favouring 8-coordination (Pb, Cd and lanthanides). At a ligand concentration of $20 \mu\text{mol dm}^{-3}$, reaction with $200 \mu\text{mol dm}^{-3}$ of added metal triflates (*i.e.*, pseudo-first-order conditions) was still too fast to measure with the available instrumentation, but when 5 equivalents were added the rates were sufficiently slow to allow the calculation of comparative observed rate constants (Table 2) at a constant pH of 5.5.

Addition of copper triflate again rapidly caused almost complete (*ca.* 95%) quenching of the naphthyl fluorescence emission. However addition of nickel triflate had very little effect: after 5 min less than a 1% diminution in I_{fl} was observed, compared with a 92% decrease at the same time point for copper. This behaviour provides a good example of distinguishing between Cu^{II} and Ni^{II} ions in aqueous solution,¹⁸ based on their relative rates of complexation with the ligand, notwithstanding the fact that both are intrinsically quenching ions. The addition of lead triflate caused a decrease in I_{fl} of 60% under parallel conditions (Table 2 and Fig. 5). This is a proportionately larger decrease than that observed in MeCN,

Table 2 Effect of added divalent metal ions^a on naphthyl fluorescence emission^b with the [12]-N₄ mononaphthyl ligand **1** (293 K, H₂O)

Metal ion	$k_{\text{obs}}/10^{-2} \text{ s}^{-1}$	Comment
Cd ²⁺	1.27	Fluorescence enhancement observed
Zn ²⁺	0.02	Fluorescence enhancement observed
Ni ²⁺ ^c	<0.0001	Only 1% decay of fluorescence observed after 5 min
Cu ²⁺	1.14	>95% fluorescence quenching
Pb ²⁺	5.00	Rapid fluorescence quenching to 40% of original I_{fl}

^a [1] = $2 \times 10^{-5} \text{ mol dm}^{-3}$; [M²⁺] as the triflate salt = $10^{-4} \text{ mol dm}^{-3}$. At metal concentrations of greater than 1 mmol dm^{-3} , changes in fluorescence intensity were too fast to be monitored accurately (except for nickel). ^b The emission at 337 nm was observed ($\lambda_{\text{exc}} = 270 \text{ nm}$). ^c In CH₃CN under similar conditions, a 65% reduction in I_{fl} was observed within 30 s of addition of nickel trifluoromethanesulfonate.

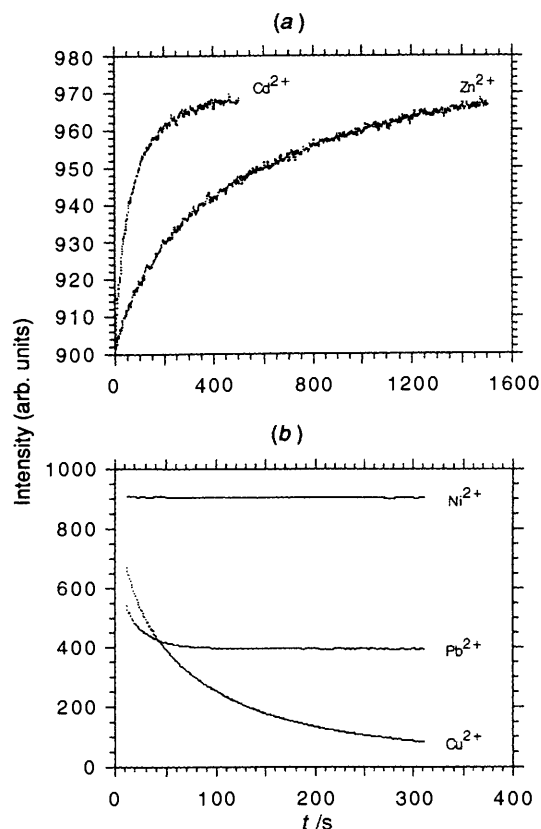


Fig. 5 Effect of adding metal trifluoromethanesulfonate salts (5 equiv.) on the fluorescence emission intensity of ligand **1** in water (a) M = Cd^{II}, Zn^{II}; (b) M = Ni^{II}, Pb^{II} and Cu^{II}: (293 K, [1] = $2 \times 10^{-5} \text{ mol dm}^{-3}$ pH 5.5)

and simply relates to the fact that the change from a diprotonated ligand to [Pb·1] gives a proportionately smaller 'chelation enhanced fluorescence effect' so that the 'heavy-atom' quenching effect of the lead ion is more marked. Binding of the lead ion was the fastest of all the ions studied and may be correlated to the high avidity¹² of the 8-coordinating tetraamide ligand for this heavy metal ion.

The cadmium complex of such tetraamides is also reputed to be very stable and complexation of both the cadmium and lead ions by **3c** has been reported to proceed at pH 1.¹² Complexation of Cd ions by **1** in water was four times slower than with lead, but was quite distinctive in that a fluorescence enhancement was observed (Fig. 5). This 'chelation enhanced fluorescence effect' was also observed upon addition of zinc triflate, although at a reduced rate (Table 2 and Fig. 5).

Behaviour of the tetranaphthyl ligand **2** to added cations

Addition of an excess of zinc triflate to the protonated ligand **2** in MeCN ([2] = $2 \times 10^{-5} \text{ mol dm}^{-3}$, [Zn²⁺] = 100×10^{-5}

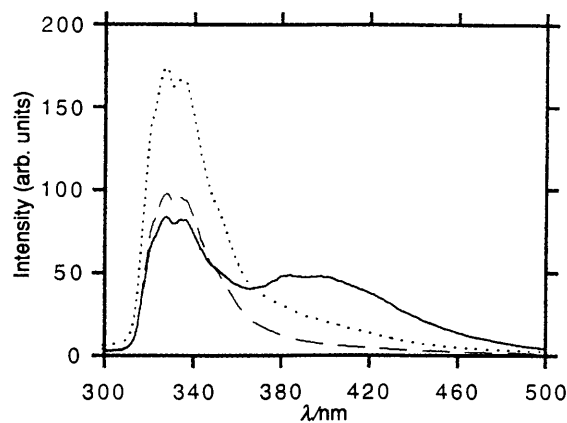


Fig. 6 Corrected fluorescence emission spectra ($\lambda_{\text{exc}} = 270 \text{ nm}$) for **2** (—), [Pb·2] (---), and [Cd·2] (····) in MeCN, each at $0.005 \text{ mol dm}^{-3}$ in the presence of 0.1 mol dm^{-3} of CF₃CO₂H

mol dm^{-3}), caused *no* significant change in the excimer emission intensity over a period of at least 6 h. When cadmium triflate was added to the protonated ligand ([1] = $5 \mu\text{mol dm}^{-3}$, [H⁺] = $50 \mu\text{mol dm}^{-3}$) the monomer emission ($\lambda_{\text{em}} = 336 \text{ nm}$) increased immediately and the excimer emission ($\lambda_{\text{em}} = 404 \text{ nm}$) also decayed quickly. The rates of monomer emission and excimer decay were identical, and a first-order dependence of these rates on ligand and cadmium concentration (for up to 1 equivalent of Cd²⁺) was observed (see the Experimental section, and Fig. 8 for further details). In the more polar solvents MeOH and H₂O, the rate of excimer decay was at least ten times slower and addition of an excess of acid also reduced this rate.

This pattern of behaviour is consistent with the formation of a 1:1 complex, [Cd·1]²⁺, involving expulsion of the ring protons. In the complex there is simultaneous coordination of each amide carbonyl oxygen { $\nu_{\text{CO}}(\text{MeOH})$: 1 1672 cm⁻¹; [Cd·1]²⁺ 1641 cm⁻¹}. The cadmium complex was prepared independently (in the absence of acid) and gave a fluorescence emission spectrum identical with that of the complex prepared *in situ* (Fig. 6). Thus the complex is 8-coordinate in solution with all of the nitrogen and amide carbonyl oxygens bound to the Cd ion. This coordination type may be contrasted with that found for the zinc complexes of **1** and **2**. In each case two carbonyl stretching frequencies were observed both in the solid state (KBr disc) and in solution (MeOH), e.g., for [Zn·1], $\nu_{\text{CO}} = 1665$ and 1636 cm^{-1} for free and bound carbonyls, respectively. Such behaviour is consistent with 6-coordination for the smaller zinc ion, leaving two amide carbonyls unbound in the complex.

The excimer emission of the protonated ligand was quenched even more rapidly by addition of Pb^{II} ions (with little effect on the monomer emission), and the rate of decay showed a similar dependence on solvent, [H⁺] and [2] to that found with Cd^{II} ions (Fig. 6). At a ligand concentration of $5 \mu\text{mol dm}^{-3}$ and in the presence of 20 equivalents of CF₃CO₂H in MeCN, addition of lead triflate ($10 \mu\text{mol dm}^{-3}$) caused excimer quenching with

Table 3 Fluorescence quantum yields^a ([M·2] = 5 μmol dm⁻³, CH₃CN, 293 K)

Complex ^b	$\phi_{\text{fluor}}^{\text{rel}}$
[2·H ₂] ²⁺	1.04
[Tb·2] ³⁺	0.96
[Eu·2] ³⁺	0.12
[Y·2] ³⁺	1.21
[Cd·2] ²⁺	0.88
[Pb·2] ²⁺	0.31

^a Values are relative to naphthalene [$\phi_{\text{fluor}} = 0.29$ (MeCN)].

^b Counterion is CF₃SO₃⁻ or CF₃CO₂⁻ (no dependence on anion).

an observed rate constant of $7.9 \times 10^{-3} \text{ s}^{-1}$, compared to $6.8 \times 10^{-3} \text{ s}^{-1}$ for the corresponding reaction with cadmium triflate. Complexation of lead could be further distinguished from cadmium by the appearance of an intense UV band [λ_{max} 260 nm (MeCN), $\epsilon = 2.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$]. Notwithstanding the higher absorbance of the lead complex in this region of the UV spectrum, the naphthyl fluorescence quantum yield for [Pb·1]²⁺ was significantly lower than that of other metal complexes and of the protonated ligand (Table 3). In this case, it is likely again that there is a heavy-atom effect enhancing singlet to triplet intersystem crossing and hence non-radiative deactivation of the naphthyl singlet excited state. That this effect is intramolecular was demonstrated by adding 10 equivalents of the anionic complex [Pb·3d]²⁻ (3d is the octadentate ligand, DOTA) to the protonated ligand in MeOH: no diminution of the excimer emission was observed.

The quenching of excimer emission by lead ions was also monitored in the presence of increasing quantities of added zinc ions. At a ligand concentration of 5 μmol dm⁻³ in MeCN and in the presence of 100 μmol dm⁻³ of acid (CF₃CO₂H), excimer quenching was still observed and the equilibrium fluorescence spectrum matched that of the isolated lead complex. The effect of added zinc was to slow down the rate at which this equilibrium was reached. Thus in the absence of added zinc ([2] = 5 μmol dm⁻³, [Pb]²⁺ = 50 μmol dm⁻³) excimer emission was completely quenched (*i.e.*, lead complexation had occurred) within 3 min. In the presence of 10, 20 and 50 equivalents of added zinc ions, the rate of formation of the lead complex slowed to 10, 20 and 45 min, respectively. Parallel 'fixed interference' experiments carried out with a zinc background following cadmium complexation showed a more marked interference effect. The rate of excimer quenching by added cadmium was 10 times slower in the presence of 10 equivalents of added zinc, and at higher added zinc concentrations, total excimer quenching was not observed. Evidently the ligand binds lead most avidly, and with good selectivity over zinc. Several other added ions (*e.g.*, Na⁺, K⁺, Mg²⁺) showed no interfering effect whatsoever on lead and cadmium binding even when in 100-fold excess.

Europium and terbium complexes

In principle the naphthyl group may function as an antenna chromophore, sensitising the metal-based luminescence of the bound lanthanide ion. With europium the energy of the emissive excited Eu ⁵D₀ state lies 47 kJ mol⁻¹ below that of the excited naphthyl triplet. Thus if the naphthyl triplet can be populated significantly, then energy transfer may occur to the bound europium ion leading to metal-based luminescence.

Tetraamide lanthanide complexes of 12-N₄ ligands have recently been reported¹¹ and in a crystal structure of the europium complex of the primary amide, 3c, the europium was 9-coordinate with the ninth site occupied by a solvent molecule, *e.g.*, H₂O. The complexes of both Tb and Eu with 1 and 2 were isolated, and the observation of a single carbonyl stretching

Table 4 Lifetimes of the excited states of [Eu·1] and [Eu·2] and the effect of H/D exchange

Complex	Solvent	τ/ms	k/ms^{-1}
[Eu·1]	H ₂ O	0.58	1.72
	D ₂ O	2.40	0.42
	CH ₃ CN	0.85	1.18
	CH ₂ CN ^{a,c}	1.90	0.53
	CH ₃ OH	0.67	1.49
	CD ₃ OD	2.07	0.48
[Eu·2]	H ₂ O	0.59	1.69
	D ₂ O	2.40	0.42
	CH ₃ CN ^b	1.02	0.98
	CH ₃ CN ^{a,b}	1.80	0.56
	CH ₃ OH ^b	0.74	1.35
	CD ₃ OD ^b	2.11	0.47

^a After N-H/N-D exchange, following dissolution of the complex in D₂O followed by drying of the complex *in vacuo* (< 10⁻² mmHg, 60 °C, 3 h). ^b Quantum yields for europium phosphorescence were as follows: [Eu·2] in CD₃OD, 0.12 × 10⁻²; in CD₃OD 0.38 × 10⁻²; in CH₃CN 0.19 × 10⁻²; and in CH₃CN after H/D exchange 0.27 × 10⁻². ^c No significant change in τ was found in CD₃CN.

frequency at 1643 cm⁻¹ in each case [*cf.*, 1660 cm⁻¹ for unbound amide (KBr or MeOH)] confirmed that the ion was bound by all of the ligand nitrogen and oxygen atoms.

Only very weak metal luminescence was observed with the terbium complexes in MeCN for a range of excitation wavelengths, $\lambda_{\text{exc}} = 250\text{--}300 \text{ nm}$. This may be due to an efficient back-energy transfer process from the excited metal to the naphthyl group [Tb ⁵D₄ = 244 kJ mol⁻¹, $E_{\text{T}}(\text{Np}) = 253 \text{ kJ mol}^{-1}$], as has been reported with several terbium-bipyridyl complexes.^{19,20} In water the terbium luminescence was ten times more intense, albeit still weak. This may reflect the differential solvation of the excited state. In water the naphthyl triplet-state free energy may be slightly changed so that back-energy transfer to the ligand becomes less efficient although still operative.

Strong metal-based luminescence with the europium complexes was observed (Table 4), and the characteristic ⁵D₀ to ⁷F_J ($\Delta J = 0, 1, 2, 3, 4$) transitions could be discerned clearly (Fig. 7). Both spectra are remarkably similar reflecting the similarity of their immediate coordination environment. This is particularly notable in the $\Delta J = 2$ transition at *ca.* 618 nm. This transition is electric-dipole allowed and is hypersensitive, so that the emission intensity is a sensitive function of ligand polarisability. Indeed the observed spectra are very similar in form to that observed for [Eu·DOTA].

The excited-state lifetimes have been measured in protiated and deuteriated solvents (Table 4). The difference in excited state lifetime (τ) between H₂O and D₂O was expected, as it is well known that energy transfer to the O-H vibrational manifold of a coordinated water molecule affords an effective non-radiative deexcitation pathway which is absent in D₂O. Using the conventional Horrocks' analysis²¹ [eqn. (1)], this

$$q = 1.05 (k_{\text{H}_2\text{O}} - k_{\text{D}_2\text{O}}) \quad (1)$$

allows an estimation of the apparent hydration state, (q), of the complex, where $k = 1/\tau =$ rate of depopulation of the excited state.

For [Eu·1] and [Eu·2] this analysis gave q values of 1.37 and 1.33, respectively. These are higher than the values expected given that one water molecule only is bound to europium in the related more hydrophilic complex [Eu·3c].¹¹ The reason for the discrepancy was apparent when lifetimes were recorded in methanol and in MeCN. When measurements of lifetimes were compared for dried samples of [Eu·1] and [Eu·2] in MeCN and

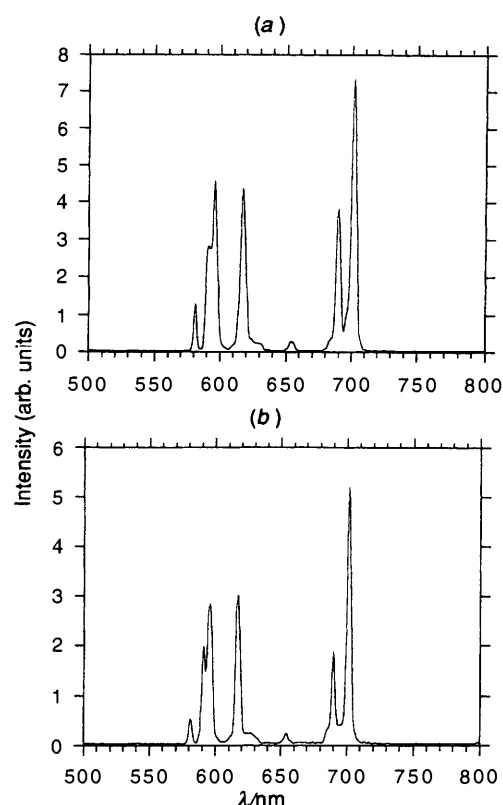


Fig. 7 Phosphorescence emission spectrum of (a) [Eu-1] (D_2O , λ_{exc} 270 nm); (b) [Eu-2] (D_2O , λ_{exc} 270 nm) showing the characteristic metal based 5D_0 to 7F_J transitions ($\Delta J = 0$ to 4)

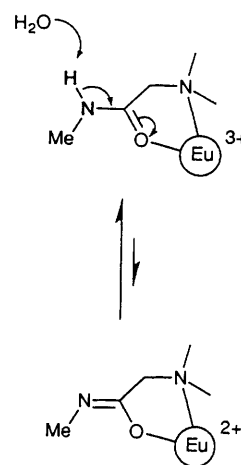
in MeCN after H/D exchange of the amide NH hydrogens (*i.e.*, after dissolution in D_2O), it was found that the lifetime after H/D exchange was significantly longer. Enhanced phosphorescence emission intensities were also noted following H/D exchange. A similar NH/ND exchange occurred rapidly in deuteriomethanol and the lifetimes in the deuteriated solvent were appreciably longer than those found in CH_3OH (Table 4). This behaviour is consistent with a deactivation of the excited Eu 5D_0 state through coupling to amide NH vibrational levels. Such a deactivation mechanism is much less efficient for amide N–D vibrations. Such an effect has not been reported before for an amide-bound europium complex although the effect has been noted with a 7-coordinate ligand based on 12- N_4 where the single ring secondary amine underwent rapid NH/D exchange and led to lengthening of the excited-state lifetime.²²

It was also noted that this rapid (< 20 s) NH/ND exchange occurred *only* with the europium complex. Monitoring of the 1H NMR spectrum of the related yttrium complex of 2, showed that amide NH/ND exchange occurred quite slowly (*i.e.*, the amide NH resonance was still apparent in D_2O 6 h after dissolution of the complex), and similar slow NH/ND exchange was found with the zinc(II) complex of 1. This may be ascribed to the ease of reduction of the europium complex (Eu^{III} to Eu^{II}), so that in the likely H/D exchange mechanism (Scheme 2) the europium centre acts as a charge sink promoting amide enolisation.

The rate constant for depopulation of the europium excited state in water may be partitioned as the sum of the different contributions [eqn. (2)], where k_{nat} = natural luminescence

$$k_{H_2O} = k_{nat} + k_{nr} + k_{OH} + k_{NH} \quad (2)$$

rate constant for emission, k_{nr} = rate constant for non-radiative



Scheme 2

deactivation, k_{OH} = rate constant for energy transfer to coordinated OH oscillators and k_{NH} = rate constant for energy transfer to proximate NH oscillators. If $k_{D_2O} = k_{nat} + k_{nr}$, then eqn. (3) holds.

$$k_{H_2O} - k_{D_2O} = k_{OH} + k_{NH} \quad (3)$$

In the absence of an NH/ND effect and assuming that $q = 1$ (as is suggested by the X-ray analysis),¹¹ then $k_{H_2O} = 1/1.05 = 0.95$ (ms)⁻¹ [from eqns. (1) and (3)]. From this it follows that for [Eu-1] (see Table 4) $1.72 - 0.42 = 0.95 + k_{NH}$; $k_{NH} = 0.35$ (ms)⁻¹ = 350 s ⁻¹.

A similar analysis for [Eu-2], gives $k_{NH} = 320$ s ⁻¹, and using the lifetime data for the behaviour of the complex in CH_3CN prior to and after amide H/D exchange, a value for $k_{NH} = 420$ s ⁻¹ is calculated. Certainly this analysis allows only an estimate of the relative contribution of coupling of the amide NH oscillators ($\nu_{NH} = 3250$ cm ⁻¹) to the Eu 5D_0 emissive state, but the agreement between the two values for the two complexes is reasonable.

Effect of added β -cyclodextrin on luminescence

Collisional deactivation of aryl excited states may be inhibited by binding the aromatic moiety within the cavity of an appropriately sized cyclodextrin. When bound within the cyclodextrin, the aryl group is shielded from solvent vibrational quenching and an enhanced fluorescence emission intensity may be observed.²³ In aqueous solution, the fluorescence characteristics of ligand 1 and selected complexes were examined in the presence of varying concentrations of β -cyclodextrin. This cyclodextrin is well known to form relatively stable complexes with simple naphthyl derivatives ($\log K \approx 10^4$). The ligand itself showed an increase in fluorescence emission (Table 5), and the effect was greater for both higher concentrations of ligand or of added cyclodextrin. At higher concentrations of added CD or of ligand, at equilibrium more of the ligand naphthyl groups will be bound consistent with this observation. A similar variation in I_{fl} with concentration was noted for both the zinc and the more weakly fluorescent europium complexes of 1; the europium complex gave slightly the higher increase. With [Eu-1], the main naphthyl excited-state deactivation pathway is likely to involve a charge-transfer transition mechanism of energy capture by the easily reduced Eu^{3+} ion. This is not likely to be significantly changed by CD complexation; indeed changes in the metal-based luminescence, although showing an enhancement in the presence of the added CD, were not as pronounced as the changes in naphthyl fluorescence intensity.

Table 5 Effect of added β -cyclodextrin on the fluorescence of **1** and its complexes^a (H₂O, 293 K)

Species ($c/\mu\text{mol dm}^{-3}$)	Added β -CD (equiv.)	% increase in I_{fl}
[1] (7.3)	50	10
[1] (18.2)	10	4
[1] (18.2)	50	18
[Zn· 1] ²⁺ (7.3)	50	9
[Eu· 1] ³⁺ (7.3)	50	16
[Zn· 1] ²⁺ (18.2)	50	16
[Eu· 1] ³⁺ (18.2)	50	25
[Zn· 1] ²⁺ (18.2)	10	4
[Eu· 1] ³⁺ (18.2)	10	8

^a Monitoring fluorescence emission at 336 nm; intensity enhancement values quoted are the mean of four separate experiments ($\pm 10\%$).

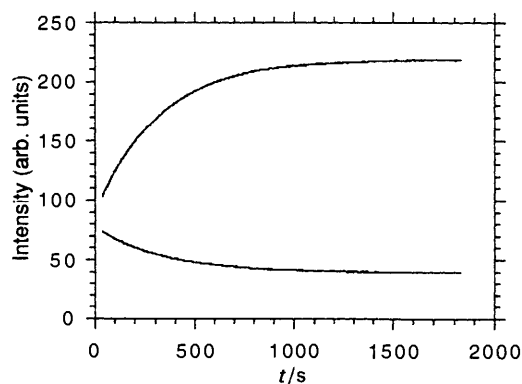


Fig. 8 Increase in monomer emission (337 nm) and decay in excimer emission (401 nm) for ligand **2** (MeCN, [**2**] = 5×10^{-6} mol dm⁻³, [CF₃CO₂H] = 10^{-4} mol dm⁻³), following addition of Cd(CF₃SO₃)₂ (5×10^{-5} mol dm⁻³). Under these conditions pseudo-first-order kinetics are followed, and the data were fitted to an equation of the form $I(t) = c - A \exp(-kt)$ for the increase in monomer emission, giving $k = 3.1 \times 10^{-3}$ s⁻¹ (correlation coefficient = 0.999 95). Excimer decay was fitted to a curve of the form $I(t) = c + A \exp(-kt)$, giving $k = 2.95 \times 10^{-3}$ s⁻¹ ($R = 0.999$ 92).

The increases in I_{fl} may simply be due to suppression of solvent collisional deactivation. Parallel experiments were attempted with ligand **2** and its complexes in aqueous solution, but addition of β -cyclodextrin (up to 100-fold excess over complex at 2×10^{-5} mol dm⁻³), caused no changes at all in I_{fl} . In this case the proximity of three adjacent naphthyl groups in the ligand and its complexes prevents the close approach of the cyclodextrin molecule to a given naphthyl group.

In summary, the protonated ligand **2** is predisposed to form an intramolecular excimer whose visible fluorescence emission is a sensitive probe of solvent polarity that may be distinctively quenched by the presence of Cd^{II} and Pb^{II} ions. The mononaphthyl ligand **1** in water binds copper selectively compared with nickel and also shows a pronounced difference in its behaviour towards other metal ions. Lead is bound most avidly followed by copper, cadmium and zinc. The distinctive luminescence changes that occur on binding of these different ions in solution may allow the *selective* signalling of their presence.

Experimental

Solvents were dried from an appropriate drying agent and water was purified by the Milli Q system. Acetonitrile for luminescence was HPLC grade, with negligible absorbance at 270 nm. Column chromatography was carried out using neutral alumina (Merck Aluminium Oxide 90, 70–230 mesh) pretreated with EtOAc. IR spectra were recorded with a Perkin-Elmer 1600 FT spectrometer with GRAMS Analyst operating software. ¹H and ¹³C spectra were obtained with a Bruker AC250 operating at 250.13 and 62.90 MHz, respectively. The ¹H–¹H COSY was acquired on a Varian VXR400. Mass spectra were recorded with a VG7070E spectrometer, with samples for desorption chemical ionisation being presented as solutions in CHCl₃ using ammonia as the impinging gas. Electrospray mass spectra were recorded at the EPSRC Mass Spectrometry Service Centre, University of Wales, Swansea, using a VG Quattro II triple quadrupole spectrometer.

Luminescence measurements

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. Spectra were acquired with excitation and emission slit widths of 2.5 nm following excitation at 270 nm. Solution absorbances at this wavelength were 0.1 or lower. Spectra 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 cm³ 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 M²⁺, was 100 μ l. 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.

The rates of metal complexation were examined by monitoring the fluorescence intensity at 337 nm (for monomer emission) or 401 nm (excimer) at intervals of 1 s (for the aqueous solutions) or every 0.2 s (for the solutions in acetonitrile). The resulting growth or decay curves were examined using Kaleidagraph software, as exemplified by the effect of Cd²⁺ on the tetranaphthyl ligand **2** (Fig. 8).

The Eu^{III} and Tb^{III} phosphorescence emission and excitation spectra were acquired using the same instrument operating in time-resolved mode, with a delay time of 0.1 ms and a gate time of 10 ms. The most highly resolved emission spectra were obtained using excitation and emission slit widths of 10 and 2.5 nm respectively, following pulsed excitation at 270 nm. Phosphorescence excitation spectra were acquired by monitoring emission at 619 nm for Eu^{III} and 545 nm for Tb^{III}.

Quoted lifetimes (τ) are the average values of at least five separate measurements, each of which is obtained by monitoring the emission intensity at 619 nm ($\lambda_{ex} = 270$ nm) after 20 different delay times. Slit widths of 15 nm were used and the gate time was 0.1 ms. The phosphorescence decay curves were fitted to an equation of the form $I(t) = I(0) \exp(-t/\tau)$ using a curve-fitting program. High correlation coefficients were observed in each case (typically 0.999 or higher). Lifetimes were found to be independent of concentration.

When monitoring the effect of added β -cyclodextrin (Aldrich) on the zinc and europium complexes of ligand **1**, the following procedure was used.

A solution of the complex in water was prepared (3.64×10^{-5} mol dm⁻³), and a 1.5 cm³ aliquot was diluted with 1.5 cm³ of water and its fluorescence emission spectrum was recorded. A second 1.5 cm³ sample was added to 1.5 cm³ of a solution of

β -cyclodextrin in water (1.82×10^{-3} mol dm $^{-3}$), and the fluorescence emission spectrum recorded. As a control, the spectrum of the initially prepared sample was recorded again, and it was found that the enhancements in fluorescence emission intensity were highly reproducible and the mean of four measurements is given ($\pm 2\%$).

Synthesis

2-Naphthylmethylamine. To a solution of 2-cyanonaphthalene (2.5 g, 16 mmol) in THF (5 cm 3) was added borane-THF (1.0 mol dm $^{-3}$; 80 cm 3) and the mixture heated to reflux for 48 h. The excess of borane was destroyed with methanol after which the solvent was removed under reduced pressure and the residue heated to reflux in 6 mol dm $^{-3}$ HCl for 4 h. Removal of water gave a brown residue, to which was added aqueous base (20% KOH, 30 cm 3) giving a yellow emulsion. The mixture was extracted with dichloromethane (2×40 cm 3) and the extracts dried over K $_2$ CO $_3$ and evaporated to give a yellow-brown solid (2.1 g, 84%). Mp 58–60 °C (lit.,²⁴ 59–60 °C), $\delta_{\text{H}}(\text{CDCl}_3)$ 1.63 (2 H, br s, NH $_2$), 4.08 (2 H, s, CH $_2$), 7.46–7.52 and 7.79–7.88 (7 H, m, C $_{10}$ H $_7$); $\delta_{\text{C}}\{^1\text{H}\}(\text{CDCl}_3)$: 46.6 (s, CH $_2$), 125.0, 125.6, 125.9, 126.1, 127.8, 128.2 (singlets, aromatic C), 132.6, 133.6, 140.9 (singlets, quaternary aromatic C); m/z (DCI): 158 (100%, M $^+$ + 1), 157 (M $^+$); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3345, 3048, 2905, 2833, 1560, 1464, 1381, 1310, 1037, 829 and 738.

Chloro-*N*-(2-naphthylmethyl)ethanamide. Triethylamine (1.56 g, 15 mmol) was added to a solution of 2-naphthylmethylamine (2.0 g, 12.7 mmol) in dry dichloromethane (80 cm 3). The solution was cooled to -10 °C and chloroethanoyl chloride (1.7 g, 15 mmol) was added dropwise, the temperature being maintained below 0 °C. The mixture was then allowed to warm to room temperature and washed with aqueous HCl (0.1 mol dm $^{-3}$; 2×40 cm 3) followed by water (2×40 cm 3). The solution was dried over K $_2$ CO $_3$ and the solvent removed under reduced pressure to give a pale-brown solid (2.3 g, 78%). Mp 98–101 °C, $\delta_{\text{H}}(\text{CDCl}_3)$ 4.18 (2 H, s, ClCH $_2$), 4.70 (2 H, d, $^3J = 6$ Hz, CH $_2$ NH), 7.42–7.55 and 7.78–7.90 (7 H, m, C $_{10}$ H $_7$); $\delta_{\text{C}}\{^1\text{H}\}(\text{CDCl}_3)$ 42.7 (s) and 44.0 (s) (ClCH $_2$ and NHCH $_2$), 125.7 (s), 126.1 (s), 126.5 (s), 127.7 (s), 128.7 (s), (aromatic C), 132.8 (s), 133.3 (s) and 134.7 (s) (quaternary aromatic C); m/z (DCI) 253 (7.9%, M + NH $_4^+$ for ^{37}Cl), 251 (23.5, M + NH $_4^+$ for ^{35}Cl), 236 (35.1, M $^+$ + 1 for ^{37}Cl) and 234 (100, M $^+$ + 1 for ^{35}Cl); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3269, 3053, 2934, 1650, 1538, 1423, 1261, 1239, 1030, 823 and 752.

1,4,7,10-Tetrakis(2-naphthylmethylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane (2). To a solution of 1,4,7,10-tetraazacyclododecane (60 mg, 0.35 mmol) in dry dimethylformamide was added anhydrous caesium carbonate (570 mg, 1.75 mmol) and chloro-*N*-(2-naphthylmethyl)ethanamide (410 mg, 1.75 mmol). The mixture was stirred at 70 °C for 12 h. The solids were separated off by centrifuge and washed with water (5×5 cm 3) followed by methanol (3×5 cm 3) to leave a white solid (240 mg, 71%). Mp 245 °C (decomp.), $\delta_{\text{H}}(\text{CDCl}_3)$ containing 10 μl of trifluoroacetic acid) 3.18 (24 H, v br, ring CH $_2$ and NCH $_2$ CO), 4.25 (8 H, s, NHCH $_2$ C $_{10}$ H $_7$), 7.26–7.61 (28 H, overlapping multiplets, aromatic H) and 7.95 (4 H, br s, CONH); $\delta_{\text{C}}\{^1\text{H}\}(\text{CDCl}_3)$ containing 10 μl trifluoroacetic acid) 44.1 (s, C $_{10}$ H $_7$ -CH $_2$ NH), 50.8 (br, NCH $_2$ CH $_2$ N ring), 55.8 (s, NCH $_2$ CO), 125.4, 126.1, 126.6, 127.0, 128.2, 129.0 (singlets, aromatic C), 133.2, 133.7, 134.8 (singlets, quaternary aromatic C) and 165.1 (s, C=O); m/z (DCI) 961 (M $^+$ + 1); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3267, 3052, 2844, 1674, 1600, 1530, 1447, 1369, 1238, 1106, 827, 745 and 578 (Found: C, 73.25; H, 6.9; N, 11.5. C $_{60}$ H $_{64}$ N $_8$ O $_4$ ·H $_2$ O requires C, 73.62; H, 6.75; N, 11.45%).

Chloro-*N*-methylethanamide. Dichloromethane (80 cm 3) was added to an aqueous solution (40% w/w) of methylamine (15.5 g, 0.2 mol MeNH $_2$) containing 8 g of sodium hydroxide and the mixture stirred vigorously with cooling to -10 °C.

Chloroethanoyl chloride (25 g, 0.22 mol) was added dropwise such that the temperature did not rise above 0 °C. After addition, the mixture was allowed to warm to room temperature and the organic layer was separated, washed with aqueous HCl (1 mol dm $^{-3}$; 2×30 cm 3) followed by water (2×50 cm 3) and dried over potassium carbonate. Removal of solvent under reduced pressure gave a white, crystalline solid (7.5 g, 33%). Mp 42–44 °C (lit.,²⁵ 45–46 °C), $\delta_{\text{H}}(\text{CDCl}_3)$ 2.88 (3 H, d, $^3J = 4.5$ Hz, NHCH $_3$), 4.05 (2 H, s, ClCH $_2$) and 6.61 (1 H, br, CONH); $\delta_{\text{C}}(\text{CDCl}_3)$ 26.5 (NCH $_3$), 42.5 (CH $_2$ Cl) and 166.8 (C=O); m/z (CI): 127 (32, M + NH $_4^+$ for ^{37}Cl); 125 (100, M + NH $_4^+$ for ^{35}Cl), 110 (30, M $^+$ + 1 for ^{37}Cl) and 108 (94, M $^+$ + 1 for ^{35}Cl) (Found: C, 33.1; H, 5.5; N, 12.65. C $_3$ H $_6$ ClNO requires C, 33.49; H, 5.58; N, 13.02%).

1-(2-Naphthylmethylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane. 1,4,7,10-Tetraazacyclododecane (0.88 g, 5.12 mmol) and molybdenum hexacarbonyl (1.34 g, 5.12 mmol) in dibutyl ether (40 cm 3) were heated under reflux (160 °C) for 2 h to give a bright yellow precipitate of the 1,4,7,10-tetraazacyclododecane-tricarbonylmolybdenum complex, which was filtered under argon and dried under vacuum. The yellow complex (1.65 g, 4.7 mmol) and anhydrous potassium carbonate (excess) were taken up in degassed dry dimethylformamide (30 cm 3) and chloro-*N*-(2-naphthylmethyl)ethanamide (1.10 g, 4.7 mmol) added under argon. The mixture was heated to 75 °C under an atmosphere of argon for 3 h. The solvent was distilled off under vacuum and the residue taken up in aqueous HCl (1 mol dm $^{-3}$). The resulting brown suspension was stirred open to the air for 15 h. The pH of the solution was raised to 14 with potassium hydroxide pellets, with cooling. The dark green precipitate formed was separated by centrifuge and extracted with dichloromethane (3×30 cm 3) to give a pale yellow solution. Removal of solvent under reduced pressure gave a pale yellow oil (0.70 g, 40%); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.42–2.70 (16 H, overlapping multiplets, NCH $_2$ CH $_2$ N ring), 3.27 (2 H, s, NCH $_2$ CO), 4.65 (2 H, d, $^3J = 5.8$ Hz, C $_{10}$ H $_7$ -CH $_2$ NH), 7.45–7.86 (7 H, overlapping multiplets, C $_{10}$ H $_7$) and 8.50 (1 H, br, CONH); $\delta_{\text{C}}\{^1\text{H}\}(\text{CDCl}_3)$ 43.1, 45.5, 46.4, 46.9 (singlets, CH $_2$ in ring), 53.1 (s, C $_{10}$ H $_7$ -CH $_2$ NH), 58.9 (s, NCH $_2$ CO), 125.7, 126.0, 126.1, 126.2, 127.4, 127.9, 128.1 (singlets, aromatic C), 132.3, 133.1, 136.0 (singlets, quaternary aromatic C) and 171.5 (s, C=O); m/z (DCI) 370 (100%, M $^+$ + 1); 199 (30.9, [C $_{10}$ H $_7$ -CH $_2$ NH-COCH $_3$] $^+$) and 173 (protonated unsubstituted cycle).

1,4,7-Tris(methylcarbamoylmethyl)-10-(2-naphthylmethylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane (1). The monosubstituted cycle (200 mg, 0.54 mmol) and anhydrous caesium carbonate (620 mg, 1.9 mmol) were taken up in dry dimethylformamide (3 cm 3) and chloro-*N*-methylethanamide (200 mg, 1.9 mmol) added. The mixture was stirred at 70 °C under argon for 24 h. Caesium salts were removed by centrifuge and the solvent removed under vacuum to give a brown oil. The product was purified by alumina column chromatography (gradient elution from dichloromethane to 3% methanol-dichloromethane, $R_f = 0.4$ in 10% methanol-dichloromethane) and was isolated as a colourless glassy solid (135 mg, 43%). $\delta_{\text{H}}(\text{CDCl}_3)$ 2.65–2.76 (25 H, overlapping multiplets, br, NCH $_2$ CH $_2$ ring and NHCH $_3$), 3.08 (4 H, s, NCH $_2$ CONHMe), 3.12 (2 H, s, NCH $_2$ CONHMe), 3.32 (2 H, s, NCH $_2$ -CONHCH $_2$ C $_{10}$ H $_7$), 4.63 (2 H, d, $^3J = 4.4$ Hz, C $_{10}$ H $_7$ -CH $_2$ NH) and 7.42–7.85 (7 H, overlapping multiplets, C $_{10}$ H $_7$); $\delta_{\text{C}}\{^1\text{H}\}(\text{CDCl}_3)$ 22.4 (s, NHCH $_3$), 25.9 (s, NHCH $_3$), 43.3 (s, C $_{10}$ H $_7$ -CH $_2$ NH), 52.3 (br, CH $_2$ in ring), 57.8 (s, NCH $_2$ CO), 58.0 (s, NCH $_2$ CO), 58.2 (s, NCH $_2$ CO), 125.9, 126.0, 126.2, 126.4, 127.6, 127.7, 128.4 (singlets, aromatic C), 132.6, 133.2, 136.0 (singlets, quaternary aromatic C), 170.1 and 170.7 (singlets, C=O); m/z (DCI) 583 (13.8%, M $^+$ + 1), 442 (100, M $^+$ - 2[CH $_2$ CONHMe]) and 386 (66.0, M $^+$ - [CH $_2$ CONHCH $_2$ -C $_{10}$ H $_7$]); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3250, 3073, 2960, 2945, 2828, 1657,

1562, 1441, 1401, 1358, 1302, 1310, 1239, 1159, 1106, 1024, 995, 807 and 665.

Complex formation for ligand 2

[Eu-2]³⁺·(CF₃SO₃⁻)₃. Europium triflate (16 mg, 26 μmol) was dissolved in dry dimethylformamide (1 cm³) and trimethylorthoformate added (10 μl). The mixture was heated at 70 °C for 1 h and then transferred by steel cannula to a suspension of the tetranaphthyl ligand (26 mg, 26 mmol) in dry dimethylformamide (1 cm³). Heating was continued for a further 30 min, during which time a yellow solution formed, with no solid remaining. Solvent and volatile material were removed under reduced pressure and the residue taken up in acetonitrile. The resulting solution was filtered, concentrated to a volume of 0.2 cm³ and added dropwise to a large excess of diethyl ether in a centrifuge tube, with vigorous shaking between additions. The complex precipitated as an off-white solid, which was separated from the ether by centrifuge and dried under a stream of argon (18 mg, 43%). $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3473, 3111, 2935, 2878, 1628, 1509, 1435, 1388, 1254, 1226, 1165, 1086, 1031, 822, 757 and 639 (Found: C, 48.75; H, 4.55; N, 7.4. C₆₀H₆₄EuN₈O₄(CF₂SO₃⁻)₃ requires C, 48.49; H, 4.11; N, 7.18%); m/z (ESMS) 1012 (M⁺).

The terbium, yttrium, cadmium and lead complexes of ligand 2 were prepared by a similar procedure.

[Tb-2]³⁺·(CF₃SO₃⁻)₃. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ as for [Eu-2] [Found: C, 48.35; H, 4.57; N, 7.25. C₆₀H₆₄N₈O₄Tb(CF₃SO₃⁻)₃ requires C, 48.28; H, 4.09; N, 7.15%]; m/z (ESMS): 1119 (M⁺).

[Y-2]³⁺·(CF₃SO₃⁻)₃. $\delta_{\text{H}}(\text{CD}_3\text{OD}; ^1\text{H}-^1\text{H COSY})$ 2.20 (4 H, m, axial CH₂CH₂ ring), 2.30 (4 H, d, ²J = 14 Hz, equatorial CH₂CH₂ ring), 2.57 (4 H, d, ²J = 14 Hz, equatorial CH₂CH₂ ring), 2.64 (4 H, d, ²J = 17 Hz, NCH₂CO), 2.95 (4 H, d, ²J = 17 Hz, NCH₂CO), 3.34 (4 H, m, axial CH₂CH₂ ring), 4.58 (8 H, d, ³J = 3 Hz, C₁₀H₇CH₂NH) and 7.38–7.90 (28 H, m, aromatic H); $\delta_{\text{C}}(\text{CD}_3\text{OD})$ 46.1 (s, C₁₀H₇CH₂NH), 56.2, 57.1 (CH₂CH₂), 64.1 (NCH₂CO), 126.8, 128.1, 129.0, 129.3, 130.4 (singlets, aromatic C), 134.6, 135.0, 135.9 (singlets, quaternary aromatic C) and 177.3 (C=O); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ as for [Eu-2] [Found: C, 49.9; H, 4.5; N, 7.4. C₆₀H₆₄N₈O₄Y(CF₃SO₃⁻)₃ requires C, 50.53; H, 4.28; N, 7.48%]; m/z (ESMS) 1049 (M⁺).

[Cd-2]²⁺·(CF₃SO₃⁻)₂. $\delta_{\text{C}}\{^1\text{H}\}(\text{CD}_3\text{OD})$ 45.0 (s, C₁₀H₇CH₂NH), 52.9 (br s, CH₂CH₂ ring), 56.5 (s, NCH₂CO), 127.2, 127.5, 127.8, 128.9, 129.7 (aromatic C), 134.4, 135.0, 137.2 (quaternary aromatic C) and 173.8 (C=O); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3295, 3109, 3058, 2859, 1645, 1559, 1281, 1249, 1160, 1029, 817, 755 and 637; m/z (ESMS) 1223 [M + 1 + (CF₃SO₃)⁺, 1073 (M⁺) [Found: C, 53.3; H, 4.75; N, 7.8. C₆₀H₆₄N₈O₄Cd·(CF₃SO₃⁻)₂·H₂O requires C, 53.60; H, 4.76; N, 8.07%].

[Pb-2]²⁺·(CF₃SO₃⁻)₂. $\delta_{\text{C}}\{^1\text{H}\}(\text{CD}_3\text{OD})$ 44.9 (s, C₁₀H₇CH₂NH), 52.0, 54.4 (CH₂CH₂ ring), 58.0 (NCH₂CO), 127.2, 127.6, 129.0, 129.8 (singlets, aromatic C), 134.4, 135.0, 137.1 (singlets, quaternary aromatic C) and 173.7 (C=O); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3290, 3106, 3055, 2856, 1640, 1559, 1279, 1247, 1163, 1089, 1029, 815, 754 and 637; m/z (ESMS) 1317 (M⁺ + CF₃CO₃⁻)⁺, 1168 (M⁺) [Found: C, 49.0; H, 4.3; N, 7.2. C₆₀H₆₄N₈O₄Pb·(CF₃SO₃⁻)₂·3H₂O requires C, 48.98; H, 4.61; N, 7.37%].

Complex formation for ligand 1

[Eu-1]³⁺·(CF₃SO₃⁻)₃. Europium triflate (29 mg, 48 μmol) was dissolved in dry acetonitrile (1 cm³) and trimethylorthoformate added (10 μl). The mixture was heated under argon at 60 °C for 15 min and then transferred by steel cannula to a solution of the mononaphthyl ligand 1 (28 mg, 48 mmol) in dry acetonitrile (1 cm³). Heating was continued for a further 15 min, after which the solvent and volatile material were removed under reduced pressure. The yellow glassy solid obtained was dissolved in the minimum amount of acetonitrile and added dropwise to a large excess (5 cm³) of diethyl ether in

a centrifuge tube, with vigorous shaking between additions (Whirlimix). The complex precipitated as a fine, microcrystalline solid (29 mg, 50%). $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3304, 3135, 2953, 2881, 1643, 1585, 1465, 1417, 1363, 1281, 1225, 1165, 1087, 1029, 638 and 517; m/z (ESMS) 734 (M⁺).

The terbium and zinc complexes were prepared by a similar procedure.

[Tb-1]³⁺·(CF₃SO₃⁻)₃. $\nu_{\max}/\text{cm}^{-1}$ as for Eu³⁺ complex. m/z (ESMS) 741 (M⁺).

[Zn-1]²⁺·(CF₃SO₃⁻)₂. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3333, 3127, 2942, 2867, 1665, 1636, 1575, 1475, 1413, 1256, 1177, 1095, 1035, 643 and 519; m/z (ESMS): 703 (M⁺).

Preparation of metal triflates

Lead triflate. Trifluoromethanesulfonic acid (3 cm³) was carefully added to lead(II) chloride (1.0 g, 3.6 mmol) in a two-necked flask fitted with a nitrogen bubbler. A steady stream of nitrogen was passed through the suspension and the mixture was warmed to 60 °C for 30 min. Anhydrous diethyl ether was added with cooling to 0 °C and the white solid removed by filtration and washed with more diethyl ether (4 × 20 cm³). The solid was extracted into acetonitrile, the solution filtered and the solvent removed under reduced pressure to give a white solid (1.5 g, 83%). $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3446, 1634, 1263, 1180, 1034, 646, 582 and 518 (Found: C, 4.7; H, 0.4. C₂F₆O₆PbS₂·H₂O requires C, 4.69; H, 0.38%).

Cadmium triflate. Similarly prepared from cadmium chloride, but yields were very low.

Terbium triflate. Obtained by a similar procedure using the acetate but, in this case, it was essential to use a minimum volume of diethyl ether as the metal triflate itself has substantial solubility in this solvent. Residual acetic acid was removed by heating the crude solid to 50 °C under vacuum (0.01 mmHg) for 72 h. Recrystallisation from acetonitrile provided the metal triflate as an analytically pure white solid.

Europium triflate. Prepared by a procedure similar to that previously described for lanthanum triflate. Trifluoromethanesulfonic acid (1 cm³) was added to a suspension of Eu₂O₃ in water. Excess oxide was added to bring the pH to 6–7. The undissolved oxide was removed by filtration through a 0.45 μm (Millipore) filter and the water removed under reduced pressure. The resulting white solid was dried at 160 °C under vacuum (0.01 mmHg). Yield = 1.6 g (71%). $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3452, 1663, 1640, 1256, 1174, 1029, 640, 581 and 523 (Found: C, 5.6; H, 1.05. C₃EuF₉O₉S₃·3H₂O requires C, 5.51; H, 0.92%).

Yttrium triflate. Prepared similarly. Zinc triflate and copper(II) triflate are commercially available (Aldrich) and were used as supplied.

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