Ground and excited state chiroptical properties of enantiopure macrocyclic tetranaphthyl lanthanide complexes: controlled modulation of the frequency and polarisation of emitted light

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Circular dichroism spectroscopy has revealed that strong exciton coupling occurs between adjacent pairs of 1-naphthyl chromophores in the chiral sodium, calcium and europium complexes of the macrocyclic tetraamide $L^{1a/b}$. In constitutionally isomeric complexes involving a 2-naphthyl linkage, $L^{2a/b}$, intramolecular excimer formation is observed by fluorescence emission spectroscopy as being strongest in the protonated ligand itself. The terbium and europium complexes show a well-defined circularly polarised luminescence that is independent of the nature of excitation: UV excitation at 300 nm *via* the proximate naphthyl antennae in $[Tb.L^{1a}]^{3+}$ and $[Tb.L^{1b}]^{3+}$ followed by intramolecular energy transfer results in mirror-image circularly polarised emission spectra. The lanthanide complex serves to modulate both the frequency and polarisation of the incident light in a controlled manner.

Lanthanide complexes of *N*-substituted octadentate ligands derived from 1,4,7,10-tetraazacyclododecane have been studied intensively in recent years.[1] The octadentate acetate,[2] phosphinate[3] and carboxamide[4] derivatives form kinetically robust complexes that are suitable for applications as contrast agents for magnetic resonance imaging,[5] for targeted radiotherapy[6a] and as luminescent probes in biochemical analyses.[6b] In complexes of dota† or its achiral carboxamide derivatives, there are two structurally independent elements of chirality associated with ring NC—CN and pendant arm NC—CO torsion angles. Thus the ring may adopt two enantiomeric conformations in the complex (λλλλ or δδδδ in each five-ring chelate following Corey and Bailar's original classification[7]) and the pendant arms may be arranged in either a clockwise (Δ) or anti-clockwise (Λ) fashion. In the lanthanide complexes there are then two enantiomeric pairs of diastereoisomers, which may interconvert in solution *via* pendant arm rotation or ring inversion[8] (Fig. 1). The major stereoisomer found in solution (M_1 or M_2) possesses a regular square-antiprism structure (twist angle *ca.* 40°), whereas the minor isomer (m_1 or m_2) adopts a twisted square antiprism structure (twist angle *ca.* 29°). Support for these models of solution behaviour has come from numerous crystal structures and dipolar analysis of appropriate Yb complexes.[9] Thus, in the middle lanthanide complexes of dota, or of the tetraacetamide (CONHMe) derivative, the observed major isomer in solution is M_1 (and its enantiomer M_2) and the ratio of M : m is 4 : 1 for $[Eudota]^-$ and *ca.* 3.5 : 1 for the NMe secondary amide derivative.[10]

The introduction of a chiral centre β to the ring nitrogen imparts considerable extra-rigidity into the complex, inhibiting arm rotation in particular.[3] We have recently also observed that the introduction of a stereogenic centre δ to the ring N imparts considerable conformational rigidity to the complex and leads to formation of an enantiopure complex. In the Eu, Tb and Yb complexes of L^{1c}, for example, the configuration of the chiral centre in the amide moiety determined both the macrocyclic ring configuration and the helicity of the

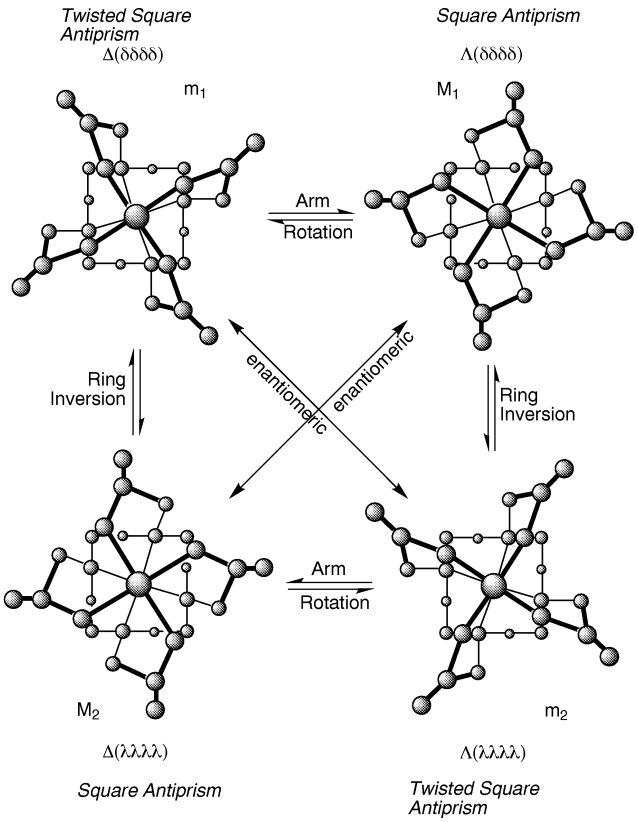
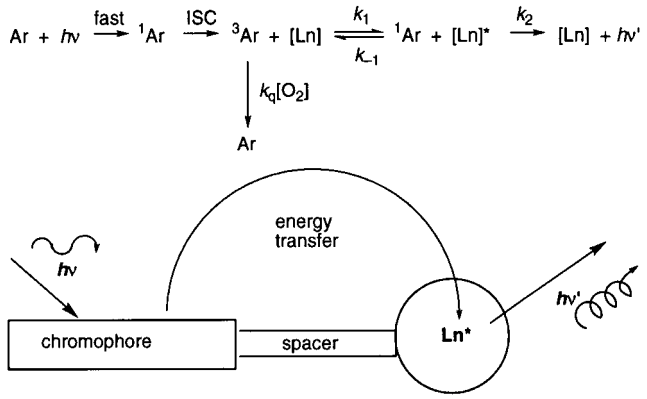


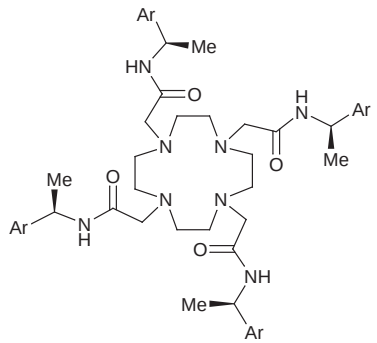
Fig. 1 Schematic representation of the isomers of complexes of dota and related tetraamides, showing the possible exchange mechanisms

† Dota is 1, 4, 7, 10-tetraazacyclododecane tetraacetate



Scheme 1

layout of the *N*-substituents.[11] Given that these complexes are also static with respect to isomer exchange on the timescale for the metal-based emission (*i.e.* milliseconds for Eu or Tb), they are particularly attractive candidates for further study due to the ease of introduction of different substituents at the chiral centre. In particular, different chromophores can be integrated into the complex at the chiral centre, allowing a detailed study of the ligand-based ground-state (circular dichroism) and metal-based excited-state (circularly polarised luminescence) properties to be undertaken. A particular motivation for the work described herein has been the desire to devise a lanthanide complex that may function to modulate both the frequency and chirality of incident light. Thus in Scheme 1, excitation of the complex at the absorption wavelength of the organic chromophore with plane-polarised light may be followed by intramolecular energy transfer to the emissive lanthanide state, which in turn emits light with a frequency and polarisation that is a function of the metal ion and its local helicity.



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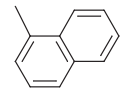
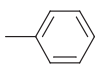
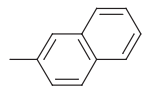
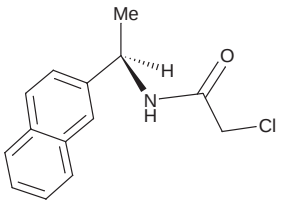


(R)-L^{1c} Ar =



(R)-L^{2a} Ar =





(R)- 2a

Accordingly, we have prepared a series of structurally related tetranaphthylamide complexes, substituted in the 1 or 2 position of the naphthyl ring ([Ln.L^1] and [Ln.L^2], Ln = Eu, Tb, Yb), and examined their chiroptical behaviour in solution. Details of the Yb complexes will be reported elsewhere. Studies of the ground-state properties involved circular dichroism, while the lanthanide excited state was probed using cicularly polarised luminescence spectroscopy.[12]

Results and Discussion

Ligand and complex synthesis and characterisation

Tetraalkylation of 1,4,7,10-tetraazacyclododecane (cyclen) was achieved by reaction with five equivalents of the appropriate α-chloroamide **2a**–**2d** in DMF at 60 °C, in the presence of potassium carbonate. The tetra-*N*-substituted ligands L^{1a}, L^{1b}, L^{2a} and L^{2b} were purified by recrystallisation from acetonitrile following column chromatography on neutral alumina. Metal complexation involved heating the appropriate lanthanide trifluoromethane sulfonate (triflate) salt with trimethyl *ortho*-formate in dry MeCN for 2 h prior to ligand addition, to ensure that adventitious moisture was removed. After heating for up to 18 h, the complexes were purified by recrystallisation from acetonitrile.

The proton NMR spectra of (*R*)-[Eu.L^{1a}]$^{3+}$ (298 K, CD_3OD, 250 MHz) revealed the presence of only four resonances for the macrocyclic ring: at 26.2 and −8.36 ppm for the pseudo-axial protons, and at −4.11 and −9.58 ppm for the corresponding ring equatorial protons. Varying the temperature over the range 200 to 310 K led to some shifting and broadening of the resonances (as expected for the temperature dependence of the lanthanide paramagnetism) but no further resonances could be discerned (*S*/*N* *ca.* 100 : 1). Such behaviour is consistent with the formation of a single C_4-symmetric complex that is not in exchange, on the NMR timescale, with other stereoisomers. Similar behaviour has been observed with [Eu.L^{1c}]$^{3+}$, with the complex adopting C_4 symmetry in solution (by NMR) and in the solid state[11] (X-ray).

The sodium complex of L^{1a} crystallised as its triflate salt from acetonitrile. In the crystal, X-ray analysis revealed that the mean N—C—C—N torsion angle was −60.2, while the N—C—C—O angle averaged −39.2°. These two torsion angles define the absolute configuration of the five chelates in the 12-N_4 ring (λλλλ) and the left-handed helicity [Λ (−)] of the pendant arm lay-out, respectively (Fig. 2). The relative rotational orientation of the N_4 and O_4 planes around the four-fold axis determines the twist angle: in the case of [Na.L^{1a}]$^+$ the angle was 28° so that the eight-coordinate complex adopts a twisted square-antiprismatic structure (*viz.* Scheme 1), similar to that found in eight-coordinate complexes of tetraphosphinate-12 N_4 ligands.[13] This twisted structure is more open than the alternative square-antiprism (ideal twist angle is 45°) and permits octadentate coordination while minimising steric interactions. The four naphthyl groups are inclined in a near orthogonal relationship to one another with interplanar angles varying from 77° to 83° and are steeply inclined to the O_4 plane.

Circular dichroism studies

Circular dichroism spectra for L^{1a}/L^{1b} and L^{2a}/L^{2b} and their europium complexes were recorded in methanol. Enantiomeric ligands and europium complexes gave mirror-image CD, spectra consistent with the presence of a single chiral stereoisomer in solution (Fig. 3 and 4). For a given absolute configuration at carbon, the sign of the circular dichroism of the 1-naphthyl ligands and its complexes was opposite to that of the 2-naphthyl substituted ligand and its complexes. With L^{2a}/L^{2b}, the bands at 280 and 305 nm (shoulder) were assigned to the ^1L_a and $^1L_{1b}$ 2-naphthyl $\pi \rightarrow \pi^*$ transitions.[14] The

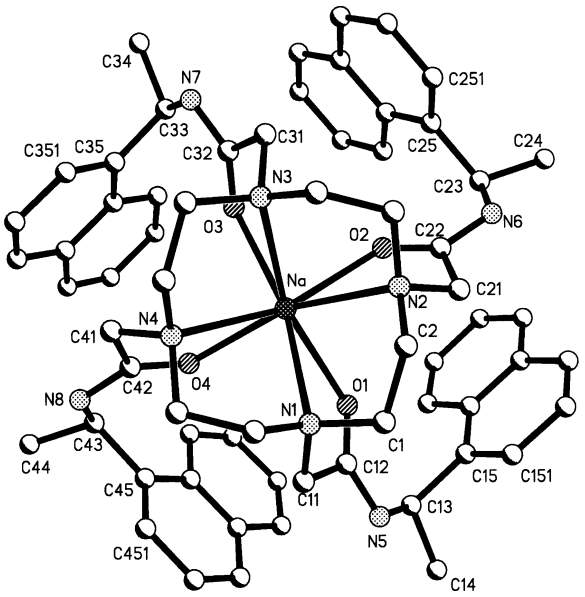


Fig. 2 Views down the C_4 axis of (*R*)-[Na.L^{1a}] in the crystal showing the left-handed lay-out of the pendant arms and the (λλλλ) ring configuration (data deposited at CCDC previously as 182/549)[41]

CD bands at higher energy (Fig. 5) were assigned to the ^1B_b (225 nm) and ^1C_b (210 nm) transitions.[14] Confirmation of this assignment was provided by a variable temperature study (+21 to −83 °C), which revealed little or no change in intensity in these features for the ligands L^{2a}/L^{2b}.

Upon addition of two equivalents of potassium chloride to a methanol solution of $L^{2a/b}$ a distinctive bisignate profile was discerned (Fig. 5), in which the relative intensity of the bands at 220 and 230 nm increased as the temperature was lowered. Such behaviour is consistent with exciton coupling of negative chirality between the proximate naphthyl chromophores[15] (at 190 K $\Delta\lambda = 10$ nm; $g_{abs}(220) = +2.5 \times 10^{-3}$, $g_{abs}(230) = -4.0 \times 10^{-3}$). In the corresponding calcium complex (Fig. 5), the exciton coupling was only revealed at low temperature

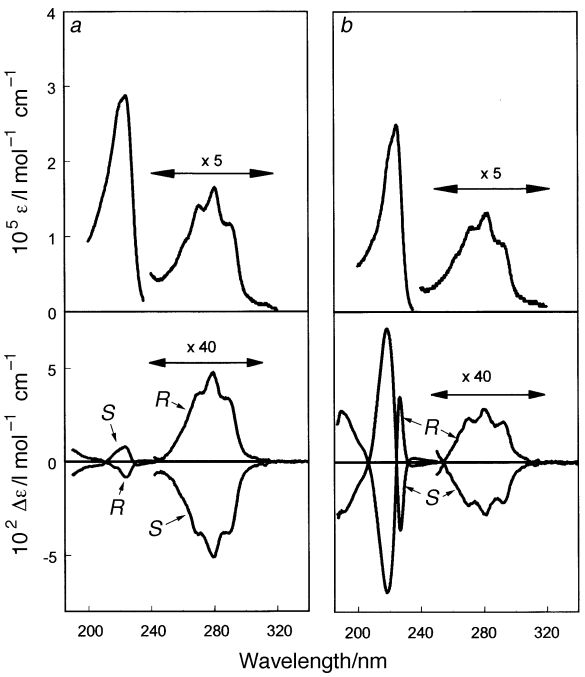


Fig. 3 CD spectra of the *R* and *S* enantiomers of (*a*) L^{1a} and (*b*) [Eu.L^{1a}]$(CF_3SO_3)_3$ in MeOH at 293 K showing the bisignate profile primarily associated with exciton coupling of the naphthyl ^1B_b bands in the Eu complex

(−86 °C) and in $[Eu.L^{2a}]^{3+}$ the CD spectrum showed a *very* small bisignate feature that was slightly enhanced on lowering the temperature (Fig. 5). At room temperature, addition of two equivalents of NaCl or NaOAc to L^{2a} had little effect on the CD spectrum, which resembled that of the Ca^{2+} complex at this temperature.

Exciton coupling between closely spaced, non-conjugated chromophores is often found in the solid state,[16] in ordered polymers[17] and in microheterogeneous media.[18] Well-defined examples in solution of intramolecular exciton coupling generally involve either chromophores possessing large oscillator strengths such as porphyrins,[18] phthalocyanines[19] and squaraines[20] or occur in conformationally relatively rigid systems such as steroids, biaryls and helicenes.[21–23] Indeed the exciton-coupled CD method has been shown to be a very useful probe for establishing absolute configuration and detecting small conformational changes. In metal-coordination chemistry, the exciton-coupling method has been studied in detail in the ubiquitous C_3-symmetric tris-chelate coordination complexes formed by bidentate ligands (*e.g.*, bipyridines and *o*-phenanthrolines)[22,24] as well as in certain chiral tetrahedral complexes.[25]

No examples have previously been reported of exciton coupling in C_4-symmetric, eight-coordinate complexes. In C_4 symmetry, the three exciton coupling modes are expected to give rise to four transitions: one A, one B and two (degenerate) E transitions. The A and E modes are electric- and magnetic-dipole allowed (z, R_z and x, y, R_x, R_y, respectively), whereas the B mode is neither ED nor MD allowed. Therefore, in strict C_4 symmetry, equal and opposite circular dichroism may be expected in two coupling modes only. In the case of $[EuL^{1a}]^{3+}$, three transitions are observed, with the most intense, higher energy, bisignate couplet (Fig. 3), attributed to exciton coupling of the naphthyl ^1B_b bands.

With L^{1a} and L^{1b}, ligand enantiomers gave mirror-image CD spectra (Fig. 3). At room temperature no sign of exciton coupling was evident but at −86 °C a bisignate profile was observed (Fig. 6), with a crossover at 222 nm. Similar exciton coupling of positive chirality was induced at room temperature by addition of two equivalents of $CaCl_2$ or NaCl to (*R*)-L^{1a}: as the temperature was lowered, the intensity of the bisignate CD profile was enhanced consistent with an

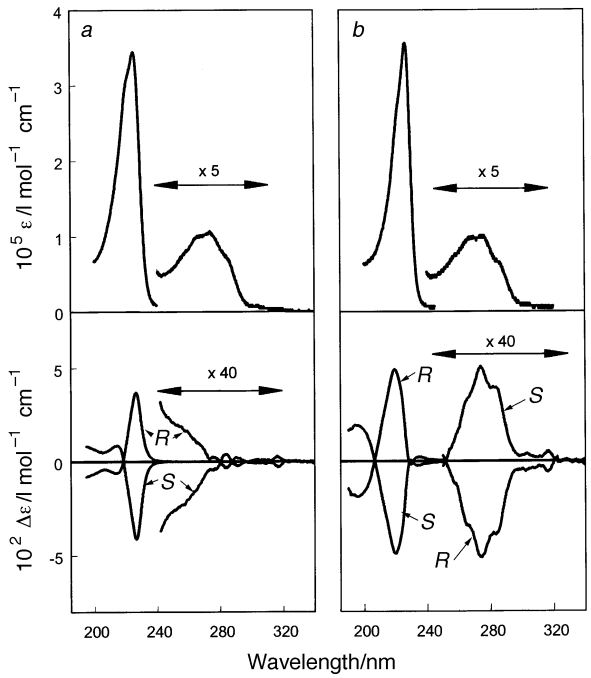


Fig. 4 CD spectra of the *R* and *S* enantiomers of (*a*) L^2 and (*b*) [Eu.$L^{2a/b}$]$(CF_3SO_3)_3$ in MeOH at 293 K

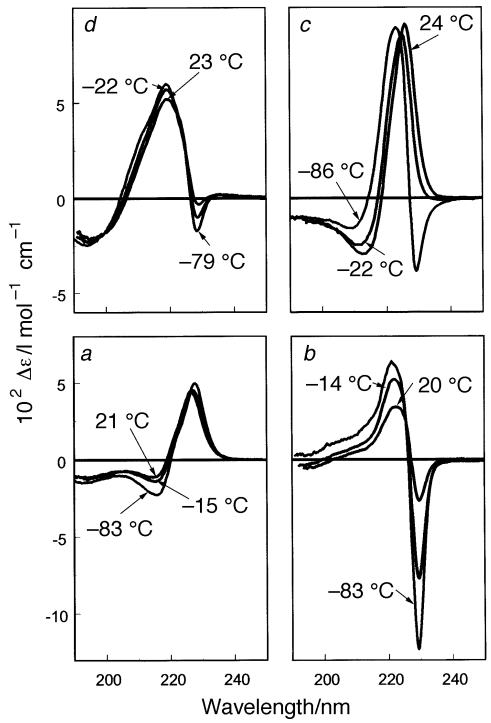


Fig. 5 CD spectra in MeOH for (*a*) (*R*)-L^{2a} as the free ligand, in the presence of two equivalents of (*b*) KCl and (*c*) $CaCl_2$ and (*d*) in $[Eu.L^{2a}](CF_3SO_3)_3$ as a function of temperature

increased population of a metal complex in which the naphthyl chromophores are oriented appropriately for exciton coupling. At room temperature $[Na.L^{1a}]^+$ gave rise to a Davydov splitting of 10 nm with $g_{abs}(219) = -2.2 \times 10^{-3}$ and $g_{abs}(229) = +1.4 \times 10^{-3}$. Crystallographic studies on $[Na.L^{1a}]^+$ had revealed that the dihedral angles between the planes of adjacent pairs of naphthyl chromophores were 81.3°, 80.9°, 82.7° and 77.1°. Given that the magnitude of exciton coupling is zero when the dihedral angle between the chromophores is 0° or 180° and is maximised when the angle is *ca.* 70°,[14] the right-handed orientation of the naphthyl groups in $[Na.L^{1a}]^+$ is well-suited to efficient coupling of the electric dipole transition moments along the long axis of the naphthyl chromophores. Methanolic solutions of (*S*)-L^{1b} in the presence of NaCl or NaOAc at room temperature gave rise to mirror-image CD spectra that were independent of the nature of the anion, with a bisignate profile typical of negative chirality.

The nine-coordinate europium complexes (*R*)-$[Eu.L^{1a}]^{3+}$ and (*S*)-$[Eu.L^{1b}]^{3+}$ displayed large exciton coupling at room temperature of positive and negative chirality, respectively (*e.g.*, for $[Eu.L^{1a}]^{3+}$: $g_{abs}(219) = -7.8 \times 10^{-3}$; $g_{abs}(229) = +3.5 \times 10^{-3}$). Analysis of the solution NMR spectra of (*R*)-$[EuL^{1a}]^{3+}$ and (*R*)-$[EuL^{2a}]^{3+}$ revealed that the paramagnetically shifted 12-N_4 ring resonances occurred at 26.2 ($H_{ax.}$), −4.11 ($H_{eq.}$), −8.36 ($H_{eq'}$) and −9.58 ($H_{ax'}$) ppm in the former case and at 25.6, −4.19, −7.83 and −9.33 ppm in the latter. Given that the diastereotopic NCH_2CO methylene protons resonated at −16.3/−16.7 and −16.0/−15.5 ppm in each complex and bearing in mind the steep distance dependence (from the Eu centre) of the shifted proton, it is certain that the ring and side chains are adopting a very similar conformation in both complexes. Therefore, the observation of positive chirality with a right-handed orientation of the strongly exciton-coupled naphthyl groups in (*R*)-$[EuL^{1a}]^{3+}$, but negative chirality in the very weakly coupled naphthyl groups in (*R*)-$[EuL^{2a}]^{3+}$, is most likely to reflect a change in the relative orientation of the ^1B_b transition moments in the coupled naphthyl chromophores.

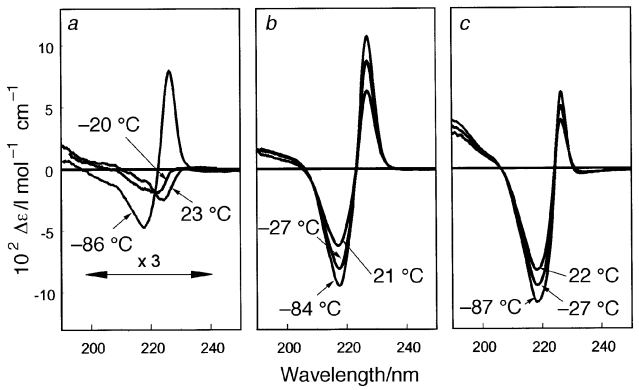


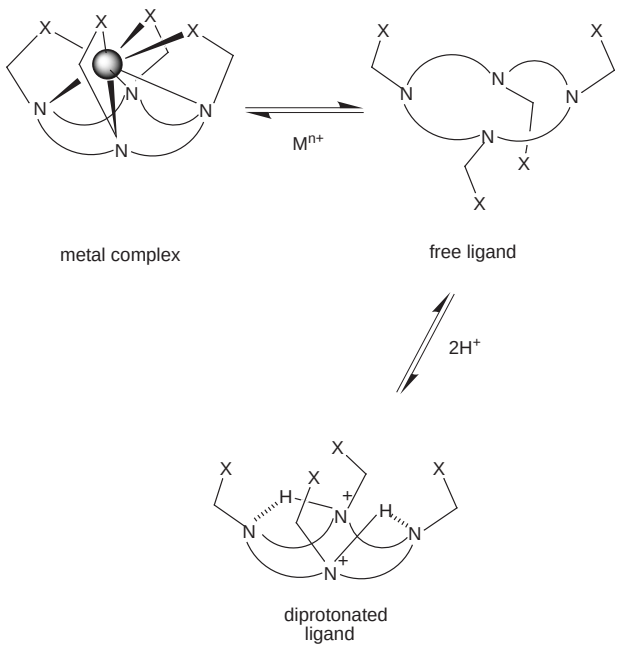
Fig. 6 CD spectra in MeOH for (*a*) (*R*)-L^{1a} as the free ligand, (*b*) in the presence of two equivalents of $CaCl_2$ and (*c*) in $[Eu.L^{1a}](CF_3SO_3)_3$ as a function of temperature

Metal complexes of tetraamide derivatives of 1,4,7,10-tetraazacyclododecane tetraacetate have been studied in some detail in the past,[26] and typically the lanthanide complexes have a nine-coordinate structure with a monocapped square antiprismatic structure[11] and an overall stability β_{ML} of the order of 10^{11} in aqueous media. The corresponding sodium and calcium complexes adopt eight-coordinate structures[26] with binding affinities (β_{ML}) of *ca.* 10^5 and 10^7, respectively, in aqueous media,[27] although this is dependent upon the nature of the amide substitution.[28] The slightly asymmetric exciton coupling bands seen in the CD profiles of the nine-coordinate Eu complexes, together with the presence of a third, weaker, higher energy transition (Fig. 3), contrast with the symmetric profiles observed for the eight-coordinate sodium and calcium complexes. This may simply reflect the presence of pure C_4 symmetry in the Na and Ca complexes, whereas the nine-coordinate Eu complex (usually a slightly distorted monocapped square antiprism about Eu) may possess a lower symmetry in solution, so that other transitions become allowed. Alternatively, the distribution and asymmetry of the bands observed with $[EuL^{1a}]^{3+}$ may reflect the slightly differing degree of configuration interaction between transitions of different energy, as has been observed in exciton-coupled systems in pure C_3 symmetry.[23b]

It is known from ^{13}C and IR studies that in the weak ($\beta_{ML} < 10^3$) complexes of potassium with such ligands, the amide oxygen does not bind to the ion in competitive media (*e.g.*, H_2O–MeOH).[26,27] Therefore, the observation that room temperature exciton coupling was observed only in the potassium 'complex' of L^{2a}/L^{2b} may be related to the fact that the ligand adopts a rather different structure in the complex. While the N_4 ring most probably binds the K^+ ion, the absence of amide ligation may allow the naphthyl chromophores in the *N*-pendant arms enough conformational mobility to align themselves sufficiently closely to undergo exciton coupling. In the free ligand L^{2a}/L^{2b}, it is likely that there is a square [3333] ring conformation, but with the 1,7 and 4,10 pairs of nitrogen substituents oriented above and below the 12-N_4 ring plane,[29] precluding strong exciton coupling (Scheme 2).

Ligand-based luminescence

In methanol and acetonitrile solution, the ligands L^{1a} and L^{2a} both exhibited a fluorescence emission band at 338 nm characteristic of the naphthyl singlet excited state. Aqueous solutions of the protonated complex[4] $[H_2.L^{2a}]^{2+}$ (acid is required for solution), obtained at pH 3, revealed formation of an additional structureless band at 400 nm whose intensity was independent of concentration in the range 2×10^{-5} to 10^{-6} mol dm^{-3}. Such behaviour is consistent with formation of an intramolecular excimer.[30] With excitation at 270 nm ($A_{270} = 0.08$), the excimer/monomer intensity ratio was >3 : 1, suggesting that two pairs of excimers may exist simultaneously.



Scheme 2

Under the same conditions, $[H_2.L^{1a}]^{2+}$ at pH 3 showed less than 15% of the broad excimer band at 400 nm. The formation of the excimer—observed only upon protonation—requires that the naphthyl groups be aligned in a plane-parallel orientation, approximately 3.5 Å apart. In the free ligand (Scheme 2) the *N* substituents are too far apart to interact, but on protonation, the formation of two bifurcated hydrogen bonds requires that the ligand adopts a structure with the four substituents disposed on the same face of the ring. Reported crystal structures of protonated 12-N_4(cyclen) based ligands have also revealed this orientation.[13]

Weak excimer emission from proximate naphthyl chromophores has been reported in poly(2-naphthyl-Ala) in degassed DMF, whereas excimer emission was absent for the constitutionally isomeric poly(1-naphthyl-Ala).[31] Some excimer emission has also been observed in poly(1-naphthylmethyl glutamate).[32]

The europium complexes $[Eu.L^{2a}]^{3+}$ and $[Eu.L^{2b}]^{3+}$ also exhibited some excimer formation in aqueous solution. The excimer/monomer intensity ratio was *ca.* 0.4, significantly less than that found in the protonated complex and consistent with a change in orientation of the naphthyl groups in the square-antiprismatic complex.[11] No evidence for excimer formation in water was found on inspection of the fluorescence emission spectra of $[Eu.L^{1a}]^{3+}$or $[Eu.L^{1b}]^{3+}$. In the latter case, the fact that *strong* exciton coupling occurs instead, *proves* that the naphthyl groups are oriented with a dihedral angle closer to 70° than the 0° or 180° required for excimer formation.

Metal-based luminescence and circularly polarised luminescence

Phosphorescent emission was observed with the europium and terbium complexes of L^{1a} and L^{2a} following indirect excitation at 270 nm into the proximate naphthyl chromophore. Relatively weak emission was observed with $[Eu.L^{1a}]^{3+}$, due to the competitive charge transfer mechanism of energy capture by the europium ion. Measured lifetimes in H_2O and D_2O ($[Eu.L^{1a}]^{3+}$: $\tau_{H_2O} = 0.53$, $\tau_{D_2O} = 2.70$ ms; $[Eu.L^{2a}]^{3+}$: $\tau_{H_2O} = 0.52$, $\tau_{D_2O} = 2.08$ ms) are consistent with a solution structure in which there is one metal-bound water molecule in each case.[11,33] For both of the corresponding terbium complexes, strong emission was observed only by degassing the sample. Under deoxygenated conditions, emission was relatively intense and for $[Tb.L^{1a}]^{3+}$ an overall quantum yield of 0.12 was measured ($\lambda_{exc} = 274$ nm), with $\tau_{H_2O} = 1.67$ ms and $\tau_{D_2O} = 3.35$ ms. In these terbium complexes, as studied in detail recently in related terbium complexes bearing an amide-linked naphthyl chromophore,[34] competitive back-energy transfer from the emissive $^5D_4$ Tb excited state to the naphthyl triplet (at *ca.* 250 kJ mol^{-1}) occurs, allowing competitive quenching of the aryl triplet by molecular oxygen (Scheme 1).

Metal-based circularly polarised emission was observed under degassed conditions in water with $[Tb.L^{1a}]^{3+}$ and $[Tb.L^{1b}]^{3+}$, following indirect sensitisation, using excitation at 300 nm into the naphthyl chromophores. The strong magnetic-dipole character of the $^5D_4 \rightarrow {}^7F_5$ transition (544 nm) gave rise to dissymmetry factors of $g_{em}(544) = +0.17$ and -0.17 for (*R*)-$[Tb.L^{1a}]^{3+}$and (*S*)-$[Tb.L^{1b}]^{3+}$ respectively (Fig. 7). The sign and magnitude of the observed circularly polarised luminescence (CPL) in this transition were almost identical to those seen in the tetraphenylamide analogue $[Tb.L^{1c}]^{3+}$ obtained by direct excitation of the terbium ion.[11] The observed CPL was *independent* of the polarisation of the incident light and is likely to be determined by the helicity of the pendant arms around the metal centre. As both the ^7F_J and $^5D_4$ levels are extensively split by ligand crystal fields, a

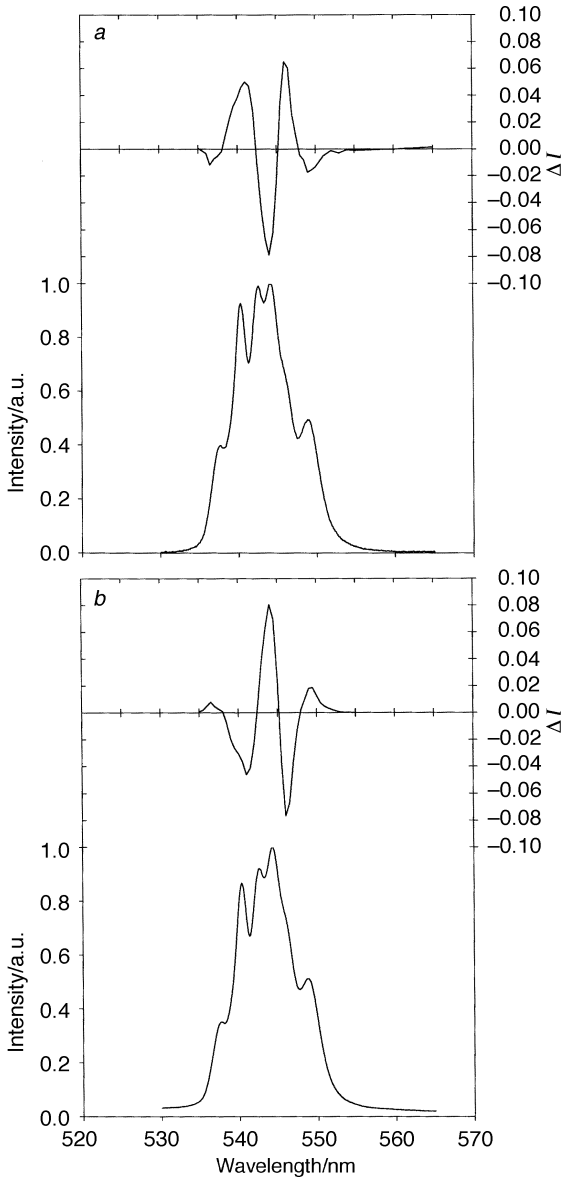


Fig. 7 Total emission (lower trace) and circularly polarised emission (upper trace) for (*a*) $[Tb.L^{1b}](CF_3SO_3)_3$ and (*b*) $[Tb.L^{1a}](CF_3SO_3)_3$ following UV excitation of the proximate naphthyl chromophore at 300 nm (293 K, degassed MeCN), showing the $^5D_4 \rightarrow {}^7F_5$ transitions

number of components to each transition arise, giving fairly complex CPL spectra that are not ideally suited to full spectral interpretation.

What is very clear from these experiments is that *the lanthanide complex serves to modulate both the frequency and the polarisation of the incident light*. Excitation with a simple UV source at 300 nm led to a circularly polarised emission at 545 nm whose handedness was determined by the absolute configuration of the chiral terbium complex. Although there have been reports of CPL from undefined protein and amino acid terbium complexes following sensitisation from Trp and Tyr residues,[12,35] this system is the first example where both complex enantiomers are accessible and in which there is control over the polarisation of the light emission (Scheme 1).

Control over the frequency of light emission in well-defined lanthanide complexes is more straightforward and replacement of Tb by Eu ($\lambda_{em} = 616$ nm, *inter alia* for example) or Yb ($\lambda_{em} = 980$ nm)[36] allows this to occur. Excitation into the charge transition at 390 nm in $[Eu.L^{1a}]^{3+}$ and $[Eu.L^{1b}]^{3+}$ gave rise to fairly weak mirror-image CPL spectra in MeOH (Fig. 8). These are the first CPL spectra of well-defined Eu^{3+} complexes of C_4 symmetry. As expected, the $^5D_0 \rightarrow {}^7F_0$ transition is relatively strong in the emission spectrum: this is characteristic of complexes with a strong axial perturbation. The phenomenon was noticed by Blasse and Bril[37] for the C_{4v} site of Eu^{3+} doped in Sr_2TiO_4 (where the intensity of the $^5D_0 \rightarrow {}^7F_0$ transition is greater than that of the magnetic-dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition) and was explained by the presence of the axial term (proportional to the Y^{10} spherical harmonic) in the crystal field expansion. This term occurs in the C_n and C_{nv} groups, but not in the corresponding dihedral groups (D_n and D_{nd}) where the $^5D_0 \rightarrow {}^7F_0$ transition is therefore forbidden.[37]

More surprising at first sight is the observation that the $^5D_0 \rightarrow {}^7F_0$ transition carries no CPL. This is explained by the fact that the crystal field term is of *odd* parity. It cannot therefore mix the $^7F_1$ and $^7F_0$ states, both of which arise from the same f^6 configuration, and which would be required to give magnetic-dipole intensity to the $^5D_0 \rightarrow {}^7F_0$ transition.[38] Thus the $^5D_0 \rightarrow {}^7F_0$ transition is *electric*- but not magnetic- dipole allowed in C_4 symmetry and so shows no CPL.

The magnetic-dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition shows strong CPL (Fig. 8). For (*R*)-$[Eu.L^{1a}]^{3+}$, the g_{em} factors were -0.12 (A) and $+0.18$ (E) . The hypersensitive $\Delta J = 2$ transition, which is comparatively weak, gave a g_{em} of -0.1 (E) and the $\Delta J = 3$ and 4 transitions gave g_{em} values of -0.3 and ($+0.11$ and 0), respectively. The isomeric 2-naphthyl Eu complexes had slightly smaller overall quantum yields, but the qualitative appearance of the spectra and the g_{em} values were essentially identical to those of the 1-naphthyl-derived complexes. In particular, the sign of the observed CPL was the same for (*R*)-$[Eu.L^{1a}]^{3+}$ and (*R*)-$[Eu.L^{2a}]^{3+}$, consistent with the adoption of a structure in the complex that has the same absolute configuration in the helicity of the pendant arms and the macrocyclic ring.

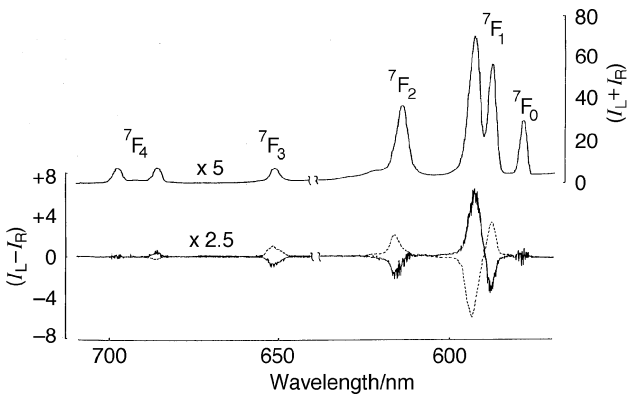


Fig. 8 Total luminescence ($I_L + I_R$) and circularly polarised luminescence ($I_L - I_R$) spectra of $[Eu.L^{1a}](CF_3SO_3)_3$ (solid line) and $[Eu.L^{1b}](CF_3SO_3)_3$ (dashed line) in methanol (λ_{exc} 390 nm, 293 K, 2×10^{-3} mol dm^{-3})

Experimental

General procedures and characterisation techniques

Reactions requiring anhydrous or inert conditions were carried out using Schlenk-line techniques under an atmosphere of dry argon. Anhydrous solvents when required were freshly distilled over the appropriate drying agent. Water was purified by the 'Purite$_{STILL}$ plus' system.

Thin layer chromatography was carried out on neutral alumina plates (Merck Art 5550) or silica plates (Merck 5554) and detection was made following irradiation at 254 nm or by staining with iodine. Column chromatography was carried out using neutral alumina (Merck Aluminium Oxide 90, activity II–III, 70–230 mesh) pre-soaked in ethyl acetate.

Melting points were measured with a Köfler block and are uncorrected. Infra-red spectra were recorded on a Perkin-Elmer 1600 FT spectrometer with GRAMS Analyst software and a Graseby-Specac "Golden Gate" Diamond ATR accessory spectrometer. Oils were examined as thin films and solids incorporated into KBr discs as stated.

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, a Varian VXR 200 operating at 200 MHz for ^1H and a Varian VXR 400 operating at 400 MHz for ^1H spectra. Two-dimensional spectra were run on the Varian VXR 200. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced internally relative to *tert*-butanol (1 drop; δ_H 0; δ_C 31.3) for paramagnetic complexes or to the residual protio-solvent resonances, which are reported relative to teramethylsilane. Reported coupling constants are in Hz.

Mass spectra were recorded on a VG 7070E spectrometer operating in the DCI (ammonia) or FAB (glycerol matrix) mode. Electrospray mass spectra were recorded on a VG Platform II (Fisons Instruments) operating in positive or negative ion mode as stated. FAB and accurate mass spectra were recorded by the EPSRC Mass Spectrometry Service at Swansea.

Luminescence and absorption spectra

Ultraviolet absorbance spectra were recorded on a Unicam UV/VIS UV2-100 spectrometer with Unicam Vision Software version 2.11. Fluorescence spectra were recorded on a Perkin-Elmer LS50B spectrofluorimeter using FL Winlab version 1.10 software, equipped with a Hamamatsu R928 photomultiplier tube using quartz fluorescence cuvettes of 1 cm pathlength.

Phosphorescence emission and excitation spectra were recorded on the LS50B operating in time-resolved mode with a delay time of 0.1 ms and a gate time of 10 ms. Emission spectra were corrected for the wavelength dependence of the photomultiplier tube and the most highly resolved spectra were obtained with slit widths (half-height bandwidth) of 10 nm (excitation) and 2.5 nm (emission). The spectrometer automatically corrects the phosphorescence excitation spectra through a reference photomultiplier tube and the spectra were obtained by monitoring the emission at 590 or 619 nm for Eu^{3+} and 545 nm for Tb^{3+} complexes.

Luminescence quantum yields, ϕ, were measured according to the procedure described by Haas and Stein,[39] using [Ru(2,2′-bipyridyl)]$^{2+}$ ($\phi = 0.028$ in H_2O)[40] and quinine sulfate ($\phi = 0.546$ in 0.5 mol dm^{-3} H_2SO_4)[40] as standards for Eu^{3+} and Tb^{3+} complexes, respectively.

Lifetimes were measured on a Perkin-Elmer LS50B spectrofluorimeter using in-house software, written by Dr. A. Beeby (University of Durham). Reported lifetimes, τ, are the average of at least three separate measurements calculated by monitoring the emission intensity at 590 or 619 nm for Eu^{3+} and 545 nm for Tb^{3+} complexes after at least 20 different delay times covering two or more lifetimes. The gate time was 0.1 ms and slit widths of 15 nm and 5 nm or less were employed for Eu^{3+} and Tb^{3+} complexes, respectively. The phosphorescence decay curves were fitted by an equation of the form $I(t) = I(0)\exp(-t/\tau)$ using a curve fitting program (Kaleidagraph software on an Apple Macintosh), where $I(t)$ is the intensity at time t after the excitation flash, $I(0)$ the initial intensity at $t = 0$ and τ is the phosphorescence lifetime. High correlation coefficients were observed; τ measurements were reproducible to at least ± 0.06 ms and were independent of concentration over the range examined ($0.05–0.5 \times 10^{-5}$ mol dm^{-3}).

Circularly polarised luminescence spectra were recorded at Michigan Technological University or at the University of Glasgow. Excitation of the $^7F_6 \rightarrow {}^5D_4$ transition of Tb^{3+} was accomplished with the 488 nm line of a Coherent Innova 70 argon ion laser. Excitation of the Eu^{3+} (560–581 nm) was accomplished by using a Coherent 599 tunable dye laser (0.03 nm resolution) using the argon ion laser as a pump source. The laser dye used in the measurement was Rhodamine 110 in ethylene glycol. Calibration of the emission monochromator (and subsequently the dye laser) was accomplished by passing scattered light from a low power He-Ne laser through the detection system. The error in the dye laser wavelength was assumed to be equal to the resolution of the emission detection. The optical detection system consisted of a photoelastic modulator (PEM, Hinds Int.) operating at 50 kHz and a linear polariser, which together act as a circular analyser, followed by a long pass filter, focusing lens and a 0.22 m double monochromator. The emitted light was detected by a cooled EM1-9558QB photomultiplier tube operating in photon counting mode. The output pulses from the photomultiplier tube were passed through a variable gain amplifier/discriminator and input into a specially built differential photon counter. The 50 kHz reference signal from the photoelastic modulator was used to direct the incoming pulses into two separate counters, an up-counter, which counts every photon pulse and thus is a measure of the total luminescence signal $I = I_{left} + I_{right}$, and an up/down counter, which adds pulses when the analyser is transmitting left circularly polarised light and subtracts when the analyser is transmitting right circularly polarised light. This second counter provides a measure of the differential emission intensity $\Delta I = I_{left} - I_{right}$. The differential photon counter allows for the selection of a time window for counting, which is centred around the maximum in the modulation cycle. For the measurements reported here, the window was set to 50%.

Details of the X-ray structural analysis of (*R*)-[Na.L^{1a}](CF_3SO_3) have been deposited previously at the CCDC (ref. 182/549).[41]

Synthesis of ligands and lanthanide complexes

2-Chloro-*N*-[(*R*)-2-naphthyl]ethylethanamide, 2a. (*R*)-1-(2-Naphthyl)ethylamine (5 g, 29.2 mmol) and triethylamine (4.88 cm^3, 35.0 mmol) were dissolved in dry diethyl ether (60 cm^3) held at $-20\,^{\circ}C$ and a solution of chloroacetyl chloride (2.79 cm^3, 35.0 mmol) in dry diethyl ether (30 cm^3) was added. The mixture was stirred for 2 h and water (50 cm^3) was added. The organic layer was separated, washed successively with dilute aqueous hydrochloric acid (0.1 mol dm^{-3}, 40 cm^3) and water (2×40 cm^3), then dried (K_2CO_3), filtered and solvent removed under reduced pressure to yield a colourless solid. The product was recrystallised from diethyl ether and isolated as white needles (5.57 g, 77%): mp 114–115 °C; ν_{max} (solid)/cm^{-1} 3256 (N—H), 1646 (C=O); δ_H(250 MHz; $CDCl_3$) 7.88–7.75 (4H, m, Ar), 7.52–7.43 (3H, m, Ar), 6.94 (1H, br s, NH), 5.32 (1H, m, CH), 4.12 (1H, d, ^2J 15.1, CH_2), 4.04 (1H, d, ^2J 15.0, CH_2), 1.64 (3H, d, ^3J 7.0, CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 165.7 (CO), 140.3 (Ar), 133.7 (Ar), 133.4 (Ar), 129.3 (Ar), 128.5 (Ar), 128.2 (Ar), 127.0 (Ar), 126.7 (Ar), 125.2 (Ar), 125.0 (Ar), 49.9 (CH), 43.3 (CH_2), 22.2 (CH_3); *m/z* (DCI) 248 (100%, MH^+). (Found: C, 67.8; H, 5.67; N, 5.66%. $C_{14}H_{14}ClON$ requires C, 67.8; H, 5.69; N, 5.65%).

2-Chloro-*N*-[(*S*)-2-naphthyl]ethylethanamide, 2b. The title compound was prepared following a method similar to that for **2a** using (*S*)-1-(2-naphthyl)ethylamine (5 g, 29.2 mmol) and triethylamine (4.9 cm^3, 35.1 mmol) in dry diethyl ether (100 cm^3) and reacting with a solution of chloroacetyl chloride (2.79 cm^3, 35.1 mmol) in dry diethyl ether (50 cm^3). The product was recrystallised from diethyl ether and isolated as white needles (4.7 g, 65%). Characterisation data are the same as those reported for **2a**. (Found: C, 67.9; H, 5.76; N, 5.67%. $C_{14}H_{14}ClON$ requires C, 67.8; H, 5.69; N, 5.65%).

1, 4, 7, 10 - Tetrakis - [(*R*) - 1 - (1 - naphthyl)ethylcarbamoyl - methyl]-1,4,7,10-tetraazacyclododecane, (*R*)-L^{1a}. 1,4,7,10-Tetraazacyclododecane (0.39 g, 2.3 mmol) and fine mesh anhydrous potassium carbonate (1.6 g, 11.3 mmol) were added to dry *N*,*N*-dimethylformamide (30 cm^3) and a solution of 2-chloro-*N*-[(*R*)-1-naphthyl]ethylethanamide (2.8 g, 11.3 mmol) in dry *N*,*N*-dimethylformamide (10 cm^3) added. The mixture was heated with stirring at 60 °C for 48 h. Solvent was removed under reduced pressure and the residue treated with dichloromethane (40 cm^3) and water (40 cm^3). The organic layer was separated, washed successively with water ($2 \times 40 cm^3$) and saturated aqueous brine (40 cm^3) and then dried (K_2CO_3), filtered and solvent removed to yield a pale yellow oil. The oil was purified by chromatography on neutral alumina (gradient elution from 100% CH_2Cl_2 to 2% MeOH–CH_2Cl_2). The product was recrystallised from acetonitrile and isolated as colourless needles (1.1 g, 45%): mp 195–196 °C; R_f (Al_2O_3; 10% CH_3OH–CH_2Cl_2; I_2 and UV detection) 0.57; ν_{max} (thin film)/cm^{-1} 3281 (N—H), 1656 (C=O); δ_H (250 MHz; $CDCl_3$) 7.97–7.68 (4H, m, Ar), 7.75–7.68 (8H, m, Ar), 7.51–7.29 (16H, m, Ar), 6.65 (4H, d, ^3J 8, NH), 5.86 (4H, m, CH), 2.44 (8H, br s, CH_2CO), 1.82–1.60 (16H, m, ring CH_2), 1.62 (12H, d, ^3J 6.7, CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 169.8 (CO), 138.5 (qAr) 134.4 (qAr), 131.8 (qAr), 129.4 (Ar), 129.1 (Ar), 127.1 (Ar), 126.5 (Ar), 125.8 (Ar), 124.0 (Ar), 123.4 (Ar), 58.5 (CH_2CO), 53.7 (ring CH_2), 44.4 (CHN), 20.8 (CH_3); *m/z* (ES+) 1040 (15%, MNa^+), 1018 (100%, MH^+); $[\alpha]^{20}_D + 27.4°$ (*c.* 0.767 g(100 cm^3 solvent)$^{-1}$ in MeOH). (Found: C, 74.5 H, 7.00; N, 10.5%. $C_{64}H_{72}N_8O_4 \cdot H_2O$ requires C, 74.3; H, 7.20; N, 10.8%).

1, 4, 7, 10 - Tetrakis - [(*S*) - 1 - (1 - naphthyl)ethylcarbamoyl - methyl]-1,4,7,10-tetraazacyclododecane, (*S*)-L^{1b}. The title compound was prepared following a method similar to that for (*R*)-L^{1a} using 1,4,7,10-tetraazacyclododecane (0.77 g, 4.4 mmol) and fine mesh anhydrous potassium carbonate (3.0 g, 22.2 mmol) in dry *N*,*N*-dimethylformamide (30 cm^3) and 2-chloro-*N*-[(*S*)-1-naphthyl]ethylethanamide [(*S*)-**2b**] (5.5 g, 22.2 mmol) in dry *N*,*N*-dimethylformamide (10 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (3.0 g, 67%). Characterisation data are the same as those reported for (*R*)-L^{1a}: $[\alpha]^{20}_D -28.4°$ (c. 0.668 in MeOH). (Found: C, 74.7; H, 7.30 N, 11.0%. $C_{64}H_{72}N_8O_4.H_2O$ requires C, 74.3; H, 7.20; N, 10.8%).

1, 4, 7, 10 - Tetrakis - [(*R*) - 1 - (2 - naphthyl)ethylcarbamoyl - methyl]-1,4,7,10-tetraazacyclododecane, (*R*)-L^{2a}. The title

compound was prepared following a method similar to that for (*R*)-L^{1a} using 1,4,7,10-tetraazacyclododecane (0.765 g, 4.4 mmol) and fine mesh anhydrous potassium carbonate (3.0 g, 22.2 mmol) in dry *N*,*N*-dimethylformamide (30 cm^3) and 2-chloro-*N*-[(*R*)-1-naphthyl]ethylethanamide[42] (5.5 g, 22.2 mmol) in dry *N*,*N*-dimethylformamide (10 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (1.1 g, 24%): mp 182–183 °C; R_f (Al_2O_3; 10% CH_3OH–CH_2Cl_2; I_2 and UV detection) 0.43; ν_{max} (thin film)/cm^{-1} 3281 (N—H), 1656 (C=O); δ_H (250 MHz; $CDCl_3$) 7.84–7.75 (16H, m, Ar), 7.51–7.40 (12H, m, Ar), 7.00 (4H, d, ^3J 7.6, NH), 5.32 (4H, m, CH), 2.83 (8H, br s, CH_2CO), 2.52 (16H, br s, ring CH_2), 1.59 (12H, d, ^3J 6.8, CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 170.3 (CO), 141.1 (qAr), 133.7 (qAr), 133.0 (qAr), 128.8 (Ar), 128.2 (Ar), 128.0 (Ar), 126.7 (Ar), 126.4 (Ar), 125.4 (Ar), 125.1 (Ar), 59.0 (CH_2CO), 53.8 (ring CH_2), 48.6 (CHN), 21.7 (CH_3); *m*/*z* (ES+) 1040 (60%, MNa^+), 529 (100%, MK^+H^+). (Found: C, 74.1; H, 7.06; N, 11.0%. $C_{64}H_{72}N_8O_4 \cdot H_2O$ requires C, 74.3; H, 7.20; N, 10.8%).

1, 4, 7, 10 - Tetrakis - [(*S*) - 1 - (2 - naphthyl)ethylcarbamoyl - methyl]-1,4,7,10-tetraazacyclododecane, (*S*)-L^{2a}. The title compound was prepared following a method similar to that for L^{1a} using 1,4,7,10-tetraazacyclododecane (0.65 g, 3.8 mmol) and fine mesh anhydrous potassium carbonate (2.6 g, 18.9 mmol) in dry *N*,*N*-dimethylformamide (30 cm^3) and 2-chloro-*N*-[(*S*)-2-naphthyl]ethylethanamide [(*S*)-**2b**][42] (4.7 g, 18.9 mmol) in dry *N*,*N*-dimethylformamide (10 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (1.23 g, 32%). Characterisation data are the same as those reported for (*R*)-L^{2a}. (Found: C, 73.5; H, 7.08 N, 10.8%. $C_{64}H_{72}N_8O_4 \cdot 2H_2O$ requires C, 73.0; H, 7.27; N, 10.6%).

[Eu.L^{1a}]$(CF_3SO_3)_3 \cdot H_2O$. Europium(III) triflate (0.058 g, 0.98 mmol) and trimethylorthoformate (1 cm^3) were heated at reflux in dry acetonitrile (2 cm^3) for 1 h and a solution of (*R*)-L^{1a} (0.1 g, 0.98 mmol) in dry acetonitrile (1 cm^3) added. The solution was heated under reflux for 18 h and concentrated to a volume of 0.5 cm^3. The solution was added dropwise, with stirring, to dry diethyl ether (100 cm^3). The resultant solid was recrystallised from acetonitrile and isolated as white needles (0.05 g, 31%), mp >250 °C; ν_{max} (thin film)/cm^{-1} 3261 (N—H), 1619 (C=O); δ_H (250 MHz; CD_3OD) 26.2 (4H, s, ring H_{ax}), 7.49 (8H, s, Ar), 6.07 (4H, s, Ar), 5.53 (4H, s, Ar), 4.88 (4H, s, Ar), 4.48 (4H, s, Ar), 3.10 (4H, s, Ar), 2.23 (4H, br s, CH), −1.24 (12H, br s, CH_3), −4.11 (4H, br s, ring H_{eq}), −8.36 (4H, br s, ring H_{ax}), −9.58 (4H, br s, ring H_{eq}), −16.3 (4H, br s, CH_2CO), −16.7 (4H, br s, CH_2CO); $\delta_C\{^1H\}$ (62.9 MHz; CD_3OD) 188.1 (CO), 138.2 (Ar), 133.2 (Ar), 129.4 (Ar), 128.3 (Ar), 127.8 (Ar), 127.2 (Ar), 124.4 (Ar), 123.1 (Ar), 121.0 (Ar), 107.4–105.6 (br, ring CH_2), 89.4 (CH_2CO), 73.9 (br, ring CH_2), 42.8 (CHN), 21.2 (CH_3); *m*/*z* (ES+) 1467 {100%, $[M^{3+} + 2(CF_3SO_3^-)]^+$}. (Found: C, 49.2; H, 4.54; N, 6.72%. $C_{67}H_{72}EuF_9N_8O_{13}S_3 \cdot H_2O$ requires C, 49.2; H, 4.56; N, 6.85%).

[Eu.L^{1b}]$(CF_3SO_3)_3 \cdot H_2O$. The title compound was prepared following a method similar to that given above using europium(III) triflate (0.118 g, 0.2 mmol) and trimethyl *ortho*-formate (2 cm^3) in dry acetonitrile (2 cm^3) and the ligand (*S*)-L^{1b} (0.2 g, 0.2 mmol) in dry acetonitrile (2 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (0.5 g, 31%). Characterisation data are the same as those reported for $[Eu.L^{1a}]^{3+}$. (Found: C, 49.6; H, 4.61; N, 6.69%. $C_{67}H_{72}EuF_9N_8O_{13}S_3 \cdot H_2O$ requires C, 49.2; H, 4.56; N, 6.85%).

[Eu.L^{2a}]$(CF_3SO_3)_3 \cdot 4H_2O$. The title compound was prepared following a method similar to that described above using europium(III) triflate (0.12 g, 0.2 mmol) and trimethyl *ortho*-formate (1 cm^3) in dry acetonitrile (2 cm^3) and the ligand (*R*)-L^{2a} (0.2 g, 0.2 mmol) in dry acetonitrile (2 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (0.13 g, 40%): mp >250 °C; ν_{max} (solid)/cm^{-1} 3260br (N—H), 1620 (C=O); δ_H (250 MHz; CD_3OD) 25.6 (4H, s, ring H_{ax}), 5.86 (4H, s, Ar), 5.66 (4H, s, Ar), 5.49 (8H, s, Ar), 5.00 (4H, s, Ar), 4.88 (4H, s, Ar), 3.89 (4H, s, Ar), 2.09 (4H, br s, CH), −1.16 (12H, br s, CH_3), −4.19 (4H, br s, ring H_{eq}), −7.83 (4H, br s, ring H_{ax}), −9.33 (4H, br s, ring H_{eq}), −15.5 (4H, br s, CH_2CO), −16.0 (4H, br s, CH_2CO); $\delta_C\{^1H\}$ (62.9 MHz; CD_3OD) 188.8 (CO), 139.5 (qAr), 132.8 (qAr), 132.3 (qAr), 128.2 (Ar), 128.0 (Ar), 127.7 (Ar), 127.0, (Ar), 123.3 (Ar), 121.8 (Ar), 121.0 (Ar), 106.4 (br, ring CH_2), 89.7 (CH_2CO), 74.6 (br, ring CH_2), 47.3 (CHN), 22.3 (CH_3); *m*/*z* (ES+) 1467 {10%, $[M^{3+} + 2(CF_3SO_3^-)]^+$}, 659 {100%, $[M^{3+} + CF_3SO_3^-]^{2+}$}. (Found: C, 47.8; H, 4.70; N, 6.29%. $C_{67}H_{72}EuF_9N_8O_{13}S_3 \cdot 4H_2O$ requires C, 47.7; H, 4.78; N, 6.64%).

[Eu.L^{2b}]$(CF_3SO_3)_3 \cdot H_2O$. The title complex was prepared following a method similar to that described above using europium(III) triflate (0.058 g, 0.1 mmol) and trimethyl *ortho*-formate (1 cm^3) in dry acetonitrile (2 cm^3) and the ligand (*S*)-L^{2b} (0.1 g, 0.1 mmol) in dry acetonitrile (2 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (0.15 g, 47%). Characterisation data are the same as those reported for [Eu.L^{2a}]. (Found: C, 49.0; H, 4.49; N, 6.63%. $C_{67}H_{72}EuF_9N_8O_{13}S_3 \cdot H_2O$ requires C, 49.2; H, 4.56; N, 6.85%).

[Gd.L^{1a}]$(CF_3SO_3)_3 \cdot H_2O$. The title compound was prepared following a method similar to that given above using gadolinium(III) triflate (0.13 g, 0.21 mmol) and trimethyl *ortho*-formate (2 cm^3) in dry acetonitrile (3 cm^3) and the ligand (*R*)-L^{1a} (0.21 g, 0.21 mmol) in dry acetonitrile (2 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (0.17 g, 51%): mp >250 °C; ν_{max} (solid)/cm^{-1} 3256br (N—H), 1620 (C=O); *m*/*z* (ES+) 661 {100%, $[M^{3+} + CF_3SO_3^-]^{2+}$} (Found: C, 49.0; H, 4.50; N, 6.37%. $C_{67}H_{72}F_9GdN_8O_{13}S_3 \cdot H_2O$ requires C, 49.0; H, 4.55; N, 6.83%).

[Tb.L^{1a}]$(CF_3SO_3)_3 \cdot 4H_2O$. The title compound was prepared following a method similar to that given above using terbium(III) triflate (0.03 g, 0.05 mmol) and trimethyl *ortho*-formate (1 cm^3) in dry acetonitrile (2 cm^3) and the ligand (*R*)-L^{1a} (0.05 g, 0.05 mmol) in dry acetonitrile (2 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (0.04 g, 49%): mp >250 °C; ν_{max} (solid)/cm^{-1} 3262br (N—H), 1614 (C=O); *m*/*z* (ES+) 1474 {10%, $[M^{3+} + 2(CF_3SO_3^-)]^+$}, 662 {100%, $[M^{3+} + CF_3SO_3^-]^{2+}$}. (Found: C, 47.4; H, 4.58; N, 6.53%. $C_{67}H_{72}F_9N_8O_{13}S_3Tb \cdot 4H_2O$ requires C, 47.5; H, 4.76; N, 6.61%).

[Tb.L^{1b}]$(CF_3SO_3)_3 \cdot 5H_2O$. The title compound was prepared following a method similar to that described above using terbium(III) triflate (0.03 g, 0.05 mmol) and trimethyl *ortho*-formate (1 cm^3) in dry acetonitrile (2 cm^3) and the ligand (*S*)-L^{1b} (0.05 g, 0.05 mmol) in dry acetonitrile (2 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (0.04 g, 47%). Characterisation data are the same as those reported for [Tb.L^{1a}]. (Found: C, 46.7; H, 4.63;

N, 6.34%. $C_{67}H_{72}F_9N_8O_{13}S_3Tb \cdot 5H_2O$ requires C, 47.0; H, 4.82; N, 6.54%).

$[Yb.L^{1b}](CF_3SO_3)_3 \cdot 2H_2O$. The title compound was prepared following a method similar to that described above using ytterbium(III) triflate (0.09 g, 0.15 mmol) and trimethyl *ortho*-formate (1 cm^3) in dry acetonitrile (2 cm^3) and the ligand (*S*)-L^{1b} (0.15 g, 0.15 mmol) in dry acetonitrile (2 cm^3). The product was recrystallised from acetonitrile and isolated as white needles (0.11 g, 44%): mp $>250\,^{\circ}C$; ν_{max} (solid)/cm^{-1} 3262br (N—H), 1620 (C=O); δ_H (250 MHz; CD_3OD) 102 (4H, br s, ring H_{ax}), 17.8 (4H, br s, ring H_{eq}), 14.7 (4H, br s, ring H_{eq}), 3.80–1.62 (28H, m, Ar), −1.15 (4H, s, CH), −4.97 (12H, s, CH_3), −29.1 (4H, s, CH_2CO), −34.7 (4H, s, CH_2CO), −66.6 (4H, br s, ring H_{ax}); *m/z* (ES+) 1487 {15%, $[M^{3+} + 2(CF_3SO_3^-)]^+$}, 669 {100%, $[M^{3+} + CF_3SO_3^-]^{2+}$}. (Found: C, 48.0; H, 4.39; N, 6.50%. $C_{67}H_{72}F_9N_8O_{13}S_3Yb \cdot 2H_2O$ requires C, 48.1; H, 4.58; N, 6.70%).

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