Synthesis, Time-Resolved Luminescence, NMR Spectroscopy, Circular Dichroism and Circularly Polarised Luminescence Studies of Enantiopure Macrocyclic Lanthanide Tetraamide Complexes

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Abstract: The syntheses and properties of a series of lanthanide complexes (Ln = Eu, Tb, Dy, Yb) of C_4 symmetric chiral tetraamide ligands based on 1,4,7,10-tetraazacyclododecane are reported. The configuration of the chiral centre at carbon in the amide substituent (CH_2NHCO-CH(Me)Ar) determines the helicity of the derived complex and the configuration of the macrocyclic ring. The enantiopure lanthanide complexes do not undergo Δ/Λ interconversion in the temperature range 220 to 320 K and three complexes have been characterised by X-ray crystallography, revealing nine-coordination about the lanthanide ion (Ln = Eu, Dy) with a monocapped square-antiprismatic coordination geometry. The terbium complexes are highly emissive in aqueous solution following excitation into the aryl chromophore (e.g. for [Tb·(*R*)-**7a**]$^{3+}$ $\varphi H_2O = 0.49$; $\varphi D_2O = 0.81$) and all of the lanthanide complexes exhibit strong circularly polarised luminescence. The ytterbium complexes (e.g. [Yb·(*S*)-**5b**]$^{3+}$) shows a strong near-IR CD and circularly polarised luminescence (CPL) associated with the $^2F_{5/2} - {}^2F_{7/2}$ transition. Overall, these emissive complexes allow control in modulating both the frequency and the polarisation of emitted light in aqueous solution.

Keywords: chirality · circular dichroism · luminescence · lanthanides · macrocyclic ligands

Introduction

Recent years have witnessed a renaissance in lanthanide complexation chemistry, driven by the need for tailored complexes for use in magnetic resonance imaging,[1] targeted radiotherapy[2] and luminescent analyses.[3] Following early work that has established the structural requirements for formation of kinetically robust complexes in aqueous media, various ligand substructures can be identified that are appropriate for modification and elaboration. These include the terpyridyl complexes originally examined by Hemmila et al.,[4] the bipyridyl cryptands of Lehn et al.,[5] several calixarene derivatives by Reinhoudt et al.,[6] and the versatile series of ligands derived from 1,4,7,10-tetraazacyclododecane (cyclen).[7] Ligands of this latter class have been studied intensively lately, with the octadentate tetraacetate derivative (′dota′) **1**, being generally regarded as the archetypal ligand forming kinetically stable lanthanide complexes.[8] In the lanthanide complexes of ′dota′ and its achiral carboxamide analogues, **2**, there are two structurally independent elements of chirality defined by the pendant arm N-C-C-O and ring N-C-C-N torsion angles. The pendant arms may thus be arranged in either a clockwise (Δ) or anticlockwise (Λ) manner and the twelve-membered ring may adopt two enantiomeric conformations in the complex, given as $\lambda\lambda\lambda\lambda$ or $\delta\delta\delta\delta$, following Corey's original classification.[9] Interconversion between these isomers occurs relatively quickly in solution on the NMR timescale, with the nature of the major isomer being a function of lanthanide ion size.[10] For the ′middle-lanthanide′ ions, a regular square-antiprismatic geometry is adopted in aqueous solution with a ninth site being occupied by a bound water molecule.

Chiral lanthanide complexes are of some interest as discriminating luminescent probes in biological media. They are generally not appropriate for examination by circular dichroism—examining ground-state chirality—because of the very low molar extinction coefficients associated with Laporte-forbidden f–f transitions. However, they are well suited to an examination of excited-state chirality using

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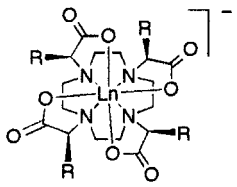
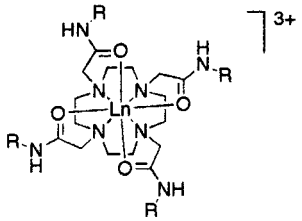
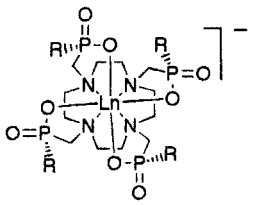


1 a) R = H
b) R = Me
c) R = $CH_2CH_2CO_2^-$



2 e.g. R = Me

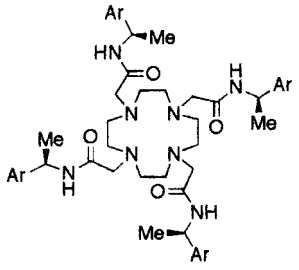


3 a) R = Bn
b) R = Me
c) R = Bu

readily undergo interconversion of the Δ/Λ isomers and exist as one predominant isomer in solution. We herein report further studies and present fuller details that define the luminescence and structural properties of the Eu, Dy and Tb complexes of **4** and the *para*-substituted derivatives **5**, **6** and **7**. Details of certain chiroptical properties are defined that render such complexes attractive models on which to base the design of responsive and functional chiral lanthanide probes.

circularly polarised luminescence (CPL).[11] This is the emission analogue of circular dichroism, requiring relatively emissive complexes for its observation, with g_{em} values of $\geq 10^{-4}$. In order to be useful as a probe that may report on interactions with other chiral molecules or macromolecules, a single enantiomer of an emissive complex is desirable that is conformationally rigid on the timescale of the luminescence emission lifetime. This is of the order of milliseconds for shielded complexes of Eu and Tb, and microseconds for Nd and Yb. In seeking a suitable lanthanide complex for use as a chiral probe, it is likely to be important to freeze-out intramolecular fluxionality as well as obviating intermolecular exchange mechanisms. For the complexes based on cyclen, inhibiting arm rotation in solution will prevent the Δ/Λ helical interconversion that is most likely to determine the overall rotatory power in emission.

The introduction of a chiral centre in the pendant arm α to the ring N, as in **1b** and **1c**, does inhibit arm rotation, but the Eu and Tb complexes exist as a mixture of square-antiprismatic and twisted square-antiprismatic diastereomers (ca. 4:1 for R = Me[12] or $CH_2CH_2CO_2$[13] specifying an *RRRR* configuration at each stereogenic carbon centre). In the related chiral phosphinate complexes, for example **3**, one diastereoisomer does predominate in solution with a twisted square-antiprismatic structure observed for complexes of **3a** with La, Eu, Gd, Y and Yb.[14] However whilst the *RRRR* and *SSSS* complexes do form selectively in solution, it has so far proved difficult to resolve these complexes, limiting their use to studies involving circularly polarised excitation.[15] We have recently reported that the introduction of a stereogenic centre δ to the ring N not only imparts sufficient conformational rigidity to the complex so as to inhibit arm-rotation, but also leads to formation of one isomer only in solution, that is an enantiopure complex. Thus in the lanthanide complexes of the chiral tetraamide, **4**, at least three of the essential requirements necessary to allow an exploration of the feasibility of such complexes as chiral luminescent probes are in place: such complexes are kinetically stable in aqueous media, do not



(R)- **4a** Ar = Ph
(S)- **4b** Ar = Ph

(R)- **5a** Ar = *p*-Br-Ph
(S)- **5b** Ar = *p*-Br-Ph

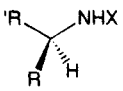
(S)- **6** Ar = *p*-CN-Ph

(S)-**7** Ar = *p*-CO_2Me-Ph

Results and Discussion

Ligand and complex synthesis and characterisation

Tetraalkylation of 1,4,7,10-tetraazacyclododecane was achieved by reaction with five equivalents of the appropriate enantiopure α-chloroamide **8a**, **8b**, **9c, 9d**, **10d** and **11c** in DMF at 60 °C in the presence of potassium carbonate. The α-chloroamides were prepared by acylation of the corresponding α-arylethylamine with chloroethanoyl chloride, having



(*R*)- **8a** : R = Ph, R' = Me, X = $COCH_2Cl$
(*S*)- **8b** : R = Me, R' = Ph, X = $COCH_2Cl$

(*R*)-**9a** : R = *p*-Br-Ph, R' = Me, X = H
(*S*)-**9b** : R = Me, R' = *p*-Br-Ph, X = H
(*R*)-**9c** : R = *p*-Br-Ph, R' = Me, X = $COCH_2Cl$
(*S*)-**9d** : R = Me, R' = *p*-Br-Ph, X - $COCH_2Cl$

(*S*)-**10a** : R = Me, R' = *p*-Br-Ph, X = COMe
(*S*)-**10b** : R = Me, R' = *p*-CN-Ph, X = COMe
(*S*)-**10c** : R = Me, R' = *p*-CN-Ph, X = H
(*S*)-**10d** : R = Me, R' = *p*-CN-Ph, X = $COCH_2Cl$

(*S*)-**11a** : R = Me, R' = *p*-CO_2H-Ph, X = H
(*S*)-**11b** : R = Me, R' = *p*-CO_2Me-Ph, X = H
(*S*)-**11c** : R = Me, R' = *p*-CO_2Me-Ph, X = $COCH_2Cl$

first established that the enantiomeric purity of the primary amine was $\geq 98\%$ *ee* by using the NMR chiral solvating agent, O-acetylmandelic acid.[17] The intermediates **10b** and **11b** were prepared in a sequential sequence from **9a**: acetylation of **9a** followed by cyanation (CuCN, DMF) and selective amide hydrolysis (1 M HCl, 15 h, 60 °C) afforded the nitrile **10c**. Acid hydrolysis of **10a** under more forcing conditions (6 M HCl, 105 °C, 18 h) yielded the amino acid **11a** from which the methyl ester **11b** was formed by standard esterification. The tetra-N-substituted ligands **4**, **5**, **6** and **7** were purified by recrystallisation from acetonitrile following column chromatography on neutral alumina. Metal complexation involved heating the ligand with the appropriate lanthanide trifluoromethanesulfonate (triflate) salt in dry acetonitrile and the complexes were purified by recrystallisation from acetonitrile as the triflate or trifluoroacetate salts. Enantiomeric complexes showed mirror image optical rotations and uv circular dichroism spectra: thus $[Tb\cdot(R)\text{-}\mathbf{4}]^{3+}$ in methanol gave a rotation $[\alpha]_D^{20} = +104.2$ ($c = 2.21$, MeOH), while the (*S*)-enantiomer gave $[\alpha]_D^{20} = -104.2$ ($c = 0.14$, MeOH). The CD spectra of the enantiomeric complexes, (Figure 1), were also

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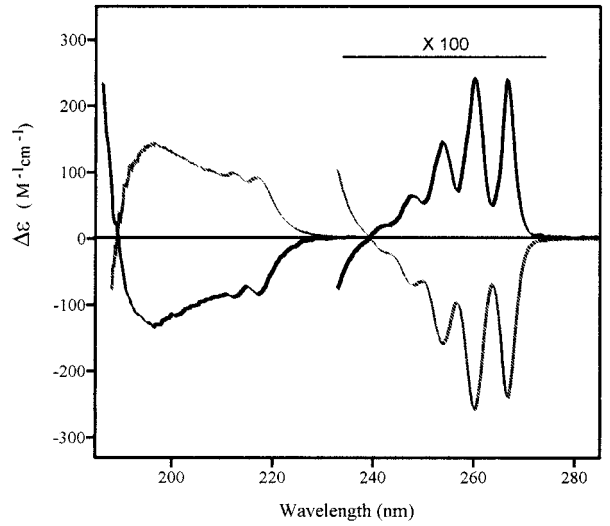

Figure 1. Circular dichroism spectra of the UV region for $[Tb\cdot(S)\text{-}\mathbf{4}]^{3+}$ (bold) and $[Tb\cdot(R)\text{-}\mathbf{4}]^{3+}$ in methanol (293 K).

equal in magnitude and opposite in sign with no evidence for the exciton coupling between the aryl chromophores that characterised the behaviour of the related series of 1-naphthyl substituted complexes. [18] With the corresponding *p*-substituted phenyl complexes a more marked crossover was noted at 195 nm, for example with $[Eu\cdot(R)\text{-}\mathbf{5}]^{3+}$ and $[Yb\cdot(R)\text{-}\mathbf{7}]^{3+}$ (Figure 2). However, variable-temperature spectra led to no

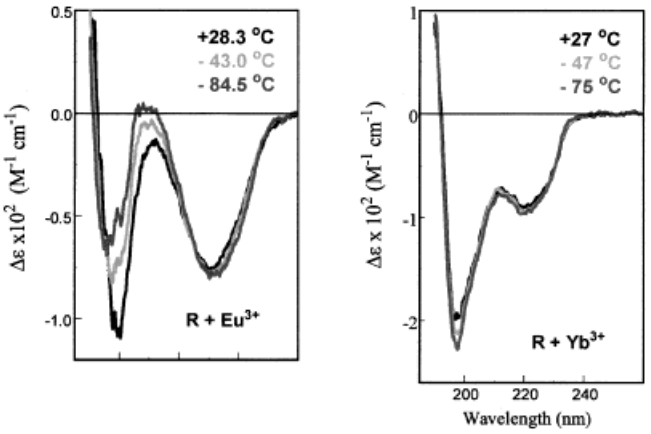

Figure 2. Variable-temperature CD spectra of the UV region for $[Eu\cdot(R)\text{-}\mathbf{7}]^{3+}$ (temperatures from top to bottom: 28.3, −43.0 and −84.5 °C) and $[Yb\cdot(R)\text{-}\mathbf{5}]^{3+}$ (temperatures from top to bottom: 27, −47.0 and −75 °C) in methanol (293 K).

increase in the intensity of this transition ruling out any exciton-coupling in these cases also. No significant change in these CD spectra was observed in the presence of up to a fifty-fold excess of sodium hydrogencarbonate or disodium hydrogenphosphate.

Proton NMR spectra for europium complexes (293 K, 200 or 250 MHz, CD_3OD) of ligands **4** to **8** were very similar in form, revealing the presence of four resonances for the pseudo-axial ($\delta_H = +27.5$ and -8.43 for $[Eu\cdot\mathbf{4}]$) and the pseudo-equatorial macrocyclic ring protons ($\delta_H = -8.93$ and -3.50 for $[Eu\cdot\mathbf{4}]$). Varying the temperature over the range 318 to 200 K led to some shifting of the position of these resonances and linewidths were greater at lower temperatures. Both of these effects are expected to occur as a consequence of the temperature dependence of the paramagnetic susceptibility. No additional resonances were observed over this temperature range, consistent with the presence of only one stereoisomeric complex (S/N 100:1 at 293 K) with time-averaged C_4 symmetry, that does not appear to be in exchange, on the NMR timescale, with other stereoisomers.

The europium complex $[Eu\cdot(R)\text{-}\mathbf{4}]$ $(CF_3CO_2)_3$ crystallised in the chiral space group $P2_12_12_1$ with the asymmetric unit comprising the europium ligand complex, four trifluoroacetate counterions, two CH_3CN molecules and a single hydronium ion. The enantiomeric complex $[Eu\cdot(S)\text{-}\mathbf{4}](CF_3SO_3)_3$ crystallised in the same space group but with three triflate anions, nine water molecules of crystallisation and three acetonitrile molecules. The dysprosium complex $[Dy\cdot(S)\text{-}\mathbf{4}](CF_3SO_3)_3$ is isostructural with the (*S*)-europium complex (Table 1), and also contained three molecules of CH_3CN in the unit cell. For all three complexes (Figure 3), the twelve-membered ring adopts the square [3333] conformation, and the relative rotational orientation of the N_4 and C_4 planes around the C_4 axis was 37°, consistent with a slightly distorted square-antiprismatic geometry that characterises many of the

Table 1. Crystal data and structure refinement for the complexes $[Eu\cdot(R)\text{-}\mathbf{4a}]^{3+}$, $[Eu\cdot(S)\text{-}\mathbf{4b}]^{3+}$ and $[Dy\cdot(S)\text{-}\mathbf{4b}]^{3+}$.[a]

Parameter	$[Eu\cdot(R)\text{-}\mathbf{4a}]^{3+}$	$[Eu\cdot(S)\text{-}\mathbf{4b}]^{3+}$	$[Dy\cdot(S)\text{-}\mathbf{4b}]^{3+}$
T [K]	150	150	150
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
symmetry	orthorhombic	orthorhombic	orthorhombic
a [Å]	14.9659(1)	15.7764(2)	15.7679(4)
b [Å]	18.4204(1)	20.4123(2)	20.3133(4)
c [Å]	24.9210(1)	21.7840(2)	21.7304(4)
U [Å^3]	6870.2(1)	7015.1(1)	6960.2(3)
Z	4	4	4
formula	$C_{60}H_{73}EuF_{12}N_{10}O_{13}$	$C_{57}H_{75}EuF_9N_{11}O_{14}S_3$	$C_{57}H_{78}DyF_9N_{11}O_{14}S_3$
M_r	1522.24	1557.42	1570.98
R_1	0.030	0.051	0.042
wR_2	0.090	0.120	0.117

[a] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179152. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail. deposit@ccdc.cam.ac.uk).

lanthanide complexes of 'dota', **1a**[19] and related tetraamide complexes.[20] The ninth coordination site is occupied by a water molecule and the $Eu-OH_2$ bond length is very similar to those previously reported for nine-coordinate europium aqua complexes,[20,21] irrespective of the overall charge on the complex. The smaller ionic radius of Dy^{3+} gives rise to slightly shorter Ln–N and Ln–O bond lengths compared to those in the europium complexes (Table 2). For $[Eu\cdot(R)\text{-}\mathbf{4a}]^{3+}$, the mean N-C-C-N torsion angle was +58.6°, while the N-C-C-O angle averaged −30.3°. These two torsion angles define the absolute configuration of the 12-N_4 ring ($\delta\delta\delta\delta$) and the left-handed helicity ($\Lambda(-)$) of the pendant arm lay-out respectively. Therefore in $[Eu\cdot(S)\text{-}\mathbf{4b}]^{3+}$, the complex is left-

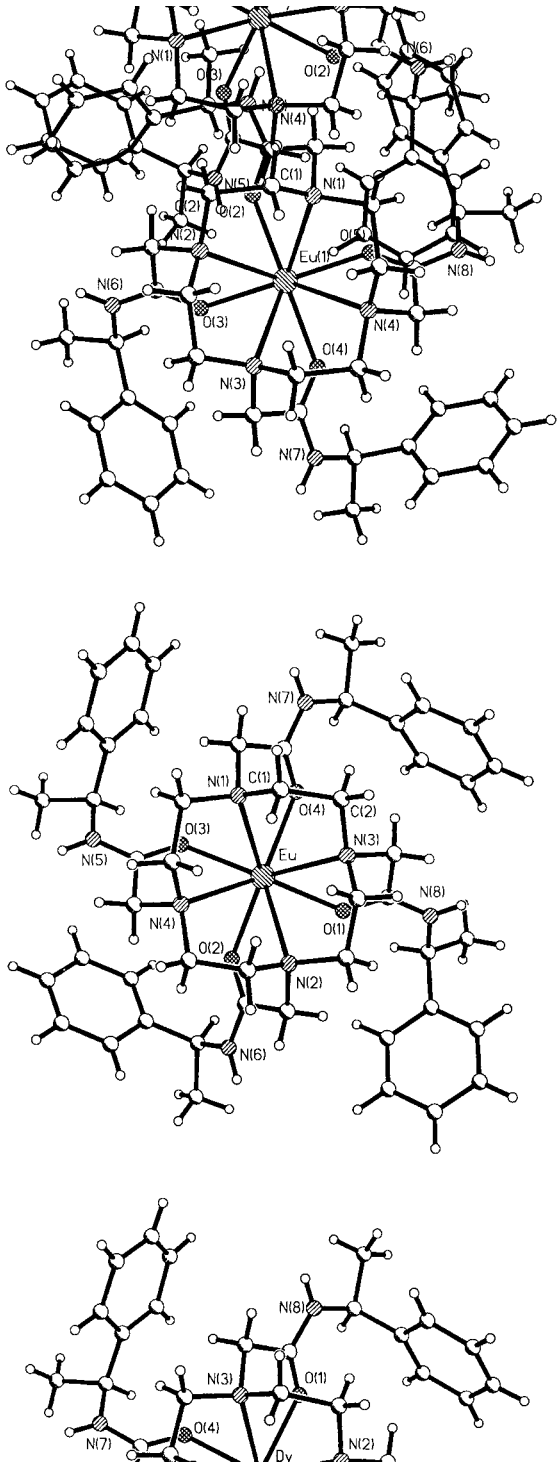

Figure 3. View down the C_4 axis (containing the Ln-OH_2 bond) of the chiral complexes $[Eu\cdot(R)\text{-}\mathbf{4}]^{3+}$ (top), $[Eu\cdot(S)\text{-}\mathbf{4}]^{3+}$ (middle) and $[Dy\cdot(S)\text{-}\mathbf{4}]^{3+}$ (bottom).

Table 2. Relevant bond lengths [Å] in the complexes $[Eu\cdot(R)\text{-}\mathbf{4a}]^{3+}$, $[Eu\cdot(S)\text{-}\mathbf{4b}]^{3+}$ and $[Dy\cdot(S)\text{-}\mathbf{4b}]^{3+}$.

Parameter	$[Eu\cdot(R)\text{-}\mathbf{4}]^{3+}$	$[Eu\cdot(S)\text{-}\mathbf{4}]^{3+}$[a]	$[Dy\cdot(S)\text{-}\mathbf{4}]^{3+}$
Ln–N(1)	2.694(3)	2.638(5)	2.657(5)
Ln–N(2)	2.717(3)	2.713(5)	2.648(5)
Ln–N(3)	2.688(3)	2.678(5)	2.609(4)
Ln–N(4)	2.696(3)	2.684(5)	2.676(5)
Ln–OH_2(1)	2.435(2)	2.437(4)	2.421(4)
Ln–O(2)	2.374(3)	2.348(4)	2.382(4)
Ln–O(3)	2.352(2)	2.364(4)	2.307(4)
Ln–O(4)	2.384(3)	2.381(5)	2.326(4)
Ln–O(5)	2.358(2)	2.430(4)	2.342(4)

[a] Mean N-C-C-N torsion angles are +58.6, −58.5 and −58.6° for $[Eu\cdot(R)\text{-}\mathbf{4a}]^{3+}$, $[Eu\cdot(S)\text{-}\mathbf{4b}]^{3+}$ and $[Dy\cdot(S)\text{-}\mathbf{4b}]^{3+}$ respectively. The mean N-C-C-O dihedral angles were −30.3, +31.9 and +29.7° in the same order.

handed in the ring configuration ($\lambda\lambda\lambda\lambda$) and possesses right-handed (Δ) helicity in the pendant arm lay-out.

The europium-bound water molecule is hydrogen-bonded to an oxygen atom of the counterion in both $[Eu\cdot(R)\text{-}\mathbf{4}](CF_3CO_2)_3$ and $[Eu\cdot(S)\text{-}\mathbf{4}](CF_3SO_3)_3$ (Figures 4 and 5). In

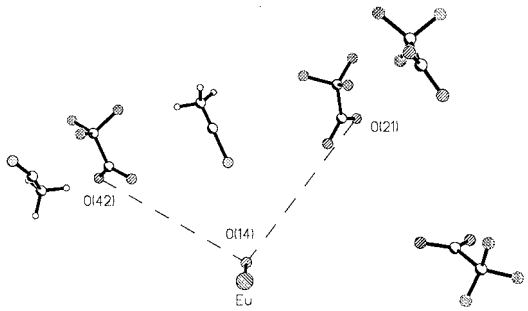

Figure 4. Relationship between the bound water molecule and the trifluoroacetate and acetonitrile solvent molecules in the crystal lattice of $[Eu\cdot(R)\text{-}\mathbf{4}](CF_3CO_2)_3$.

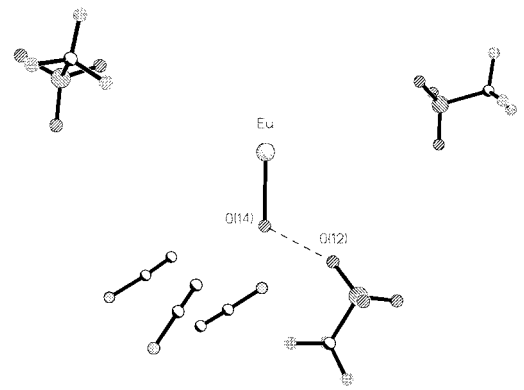

Figure 5. Arrangement of the europium-bound water molecule and the trifluoromethanesulfonate and acetonitrile solvent molecules in the crystal lattice of $[Eu\cdot(S)\text{-}\mathbf{4}](CF_3SO_3)_3$ (O(14)···O(12) distance is 2.785(5) Å).

the former case hydrogen bonding occurs between each hydrogen atom of the water molecule and two different trifluoroacetate counterions (O···O distances are 2.831(5) and 2.832(5) Å). In the latter case a single triflate counterion is hydrogen-bonded to a bound-water hydrogen atom, and an acetonitrile molecule is oriented with its nitrogen atom close to the other relatively acidic hydrogen of the bound water molecule.

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Luminescence behaviour in water

The aryl chromophore in the lanthanide complexes of **4**–**8** may act as an antenna, facilitating the delayed emission from the bound lanthanide ion following intramolecular energy transfer from the excited aryl triplet. The metal-based emission lifetimes and quantum yield were measured in H_2O and D_2O (Table 3). As expected with the Eu complexes, quantum yields were low due to the efficient deactivation of the aryl singlet excited state associated with photoinduced electron transfer to the readily reduced europium centre ($Eu^{3+/2+} = -0.35$ V). However, the introduction of an electron-withdrawing group in the phenyl ring disfavours this electron (or charge) transfer process, as the HOMO energy is lowered. Accordingly the *p*-CO_2Me substituted complex [Eu·(*R*)-**8**]$^{3+}$ has a much higher quantum yield (0.12 in D_2O) than the parent complex [Eu·(*R*)-**4**]$^{3+}$, with the *p*-cyano-substituted complex showing intermediate behaviour. Of course other factors do contribute to the measured quantum yield φ_{obs} [Eq. (1)], where φ_{ISC}, φ_{ET} and φ_{Ln} denote quantum yields for the intersystem crossing, energy transfer and lanthanide emission steps respectively. The triplet energies of toluene, 4-carboxymethyltoluene and 4-cyanomethyltoluene fall in the series 346, 320 and 316 kJ mol^{-1}. Given that a more efficient energy transfer step might be anticipated to occur to the $^5D_1$ and/or $^5D_0$ Eu excited states (at 224 and 207 kJ mol^{-1} respectively) as the energy gap narrows, then the fact that the cyano-substituted complex is over ten times less emissive than the carboxymethyl analogue (Table 3), suggests that this factor is not so significant.

Table 3. Luminescence data[a] for cationic lanthanide complexes of **4a**, **5a**, **6a** and **7a** (293 K, pH 6).[b]

Parameter	τ_{H_2O}	τ_{D_2O}	φ_{H_2O}	φ_{D_2O}
[Tb·**4a**]$^{3+}$	1.74	3.45	0.29	0.48
[Eu·**4a**]$^{3+}$	0.58	2.44	0.6×10^{-3}	3×10^{-3}
[Yb·**4a**]$^{3+}$[c]	0.0007	0.0062	–	–
[Eu·**5a**]$^{3+}$	0.64	2.57	n.d.	n.d.
[Tb·**5a**]$^{3+}$	1.66	3.09	–	–
[Yb·**5a**]$^{3+}$	0.0008	0.0075	–	–
[Tb·**6a**]$^{3+}$	1.69	3.03	0.25	0.41
[Eu·**6a**]$^{3+}$	0.57	2.27	2.7×10^{-3}	1.1×10^{-2}
[Tb·**7a**]$^{3+}$	1.75	3.13	0.49	0.81
[Eu·**7a**]$^{3+}$	0.58	2.44	0.029	0.12

[a] Lifetimes are given in milliseconds, and quantum yields are absolute values independent of excitation wavelength in the range 240 to 280 mm. The counterion is trifluoromethanesulfonate. [b] After correcting for the quenching effect of the NH and 'unbound' OH oscillators, each complex has one bound water molecule. [c] The (*R*)-1-naphthyl analogue gave $\tau_{H_2O} = 0.83$ µs, $\tau_{D_2O} = 5.00$ µs.

$$\varphi_{obs} = \varphi_{ISC}\varphi_{ET}\varphi_{Ln} \quad (1)$$

The lifetimes of the set of europium complexes change very little with the nature of the *para* substituent, and the related terbium lifetimes were similarly independent of the nature of the aryl *para* substituent. With both sets of complexes in aqueous media the metal emission lifetime is primarily determined by the efficiency of vibrational quenching of the $^5D_0$ (Eu) and $^5D_4$ (Tb) excited states by proximate OH oscillators. The number of bound (one) and closely diffusing OH oscillators presumably varies very little as a function of the aryl *para* substituent. Notwithstanding the quenching effect of the single bound water molecule, the complex [Tb·(*R*)-**7**]$^{3+}$ is remarkably emissive in water and overall quantum yields of 0.49 and 0.81 (λ_{exc} 270 nm) were measured in H_2O and D_2O respectively.

The lifetimes of the excited states of [Yb·(*R*)-**4**]$^{3+}$ and [Yb·(*R*)-**5**]$^{3+}$ were also measured in H_2O and D_2O and were consistent with an overall hydration state of one.[22] The ytterbium ion is intrinsically more sensitive to non-radiative quenching by OH oscillators as a consequence of the smaller energy gap between the lowest emissive state and the highest non-emissive level. For Yb^{3+} complexes, this value is 10200 cm^{-1} compared to 12500 cm^{-1} for Eu^{3+} and 14800 cm^{-1} for Tb^{3+}, allowing energy transfer to lower vibrational levels of the OH manifold where the Franck–Condon overlap factor is greater.

Metal-based circular dichroism and circularly polarised luminescence

Circular dichroism associated with f–f transitions in lanthanide ions in a chiral environment is rather weak and therefore difficult to observe.[23, 24] Near-IR circular dichroism is seldom reported with chiral lanthanide complexes, but the C_4-synthetic complexes [Yb·(*R*)-**4**]$^{3+}$ and [Yb·(*R*)-**5**]$^{3+}$ gave rise to an observable CD signal, centred around 980 nm, associated with the magnetic-dipole allowed $^2F_{5/2} - {}^2F_{7/2}$ transition (Figure 6). The transition exhibits rich fine structure associated with the $(2J+1)$ components, of each level, but no detailed interpretation has been attempted. A dissymmetry factor, g_{em}^{995}, of 0.18 was calculated.

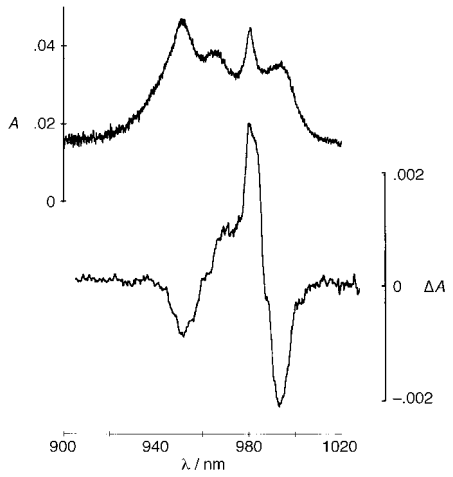

Figure 6. Near infrared circular dichroism spectrum of [Yb·(*R*)-**4a**]$^{3+}$ (293 K, MeOH).

Circularly polarised luminescence (CPL) is the emission analogue of circular dichroism and probes the chirality of the excited state.[11] Metal-based CPL was observed for [Yb·(*R*)-**4**]$^{3+}$ and with the *para*-bromo derivative [Yb·(*R*)-**5**]$^{3+}$ (Figure 7). Again, complex fine structure is expected as a consequence of the large number of allowed transitions. The

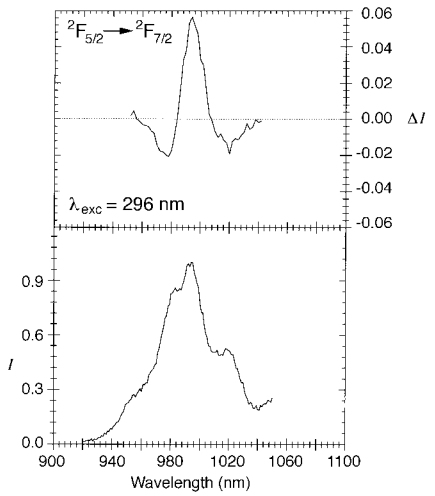

Figure 7. Near-infrared circularly polarised luminescence of [Yb·(*R*)-**5a**]$^{3+}$ and its enantiomer (293 K, λ_{exc} 250 nm, D_2O). *I* = intensity in arbitrary units.

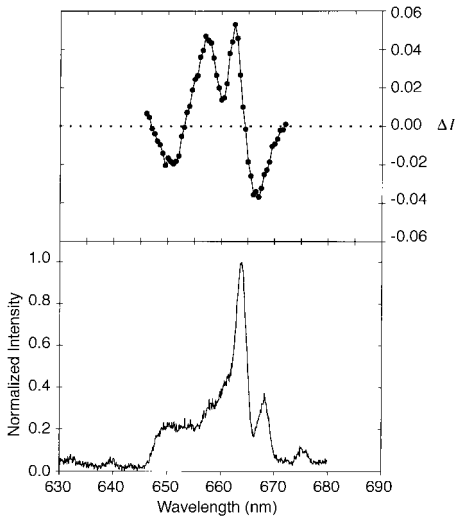

Figure 9. Total emission (lower trace) and circularly polarised emission (upper) for the $^4F_{9/2} - {}^6H_{11/2}$ transition of [Dy·(*R*)-**4a**]$^{3+}$ following excitation at 457.9 nm (293 K, D_2O).

enantiomeric spectra shown in Figure 7 represent the first examples of near-IR CPL observed for a lanthanide complex. The corresponding dysprosium complexes also are rather weakly luminescent because of efficient vibrational quenching. The small energy gap between the emissive state and the ground state in Dy^{3+} complexes (7850 cm^{-1}) leads to particularly efficient energy transfer to the third vibrational level of OH oscillators in water,[25] and C–H oscillators also contribute significantly to non-radiative excited-state deactivation. Weak luminescence and metal-based CPL emission was observed with [Dy·(*R*)-**4a**]$^{3+}$ following direct laser excitation at 457.9 nm. The strongest emission arose from the $^4F_{9/2} - {}^6H_{13/2}$ transition but this was very weakly polarised (Figure 8). The magnetic-dipole allowed $^4F_{9/2} - {}^6H_{11/2}$ transition was also apparent at approximately 660 nm, but displayed a strong

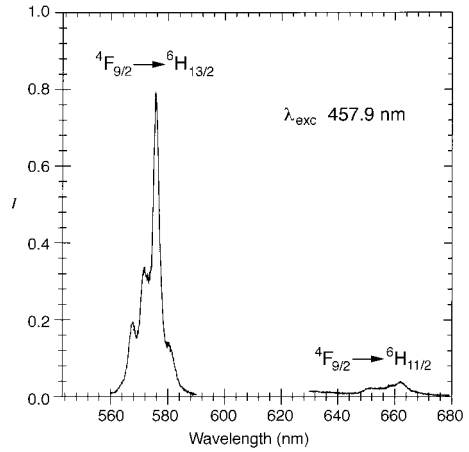

Figure 8. Total emission spectrum for [Dy·(*R*)-**4a**]$^{3+}$ following excitation at 457.9 nm (293 K, D_2O). *I* = intensity in arbitrary units.

circularly polarised emission with dissymmetry factors of $g_{em}^{657} = 0.35$ and $g_{em}^{667} = -0.41$ (Figure 9).

The terbium complexes of **4a**, **5a**, **6a**, and **7a** are much more emissive in protic solvents than the corresponding Yb, Dy or Eu complexes and gave rise to quite intense circularly polarised emission following either direct excitation (λ_{exc} = 380 or 488 nm) of the lanthanide ion or indirect sensitisation through the proximate aryl group (Figure 10). Enantiomeric

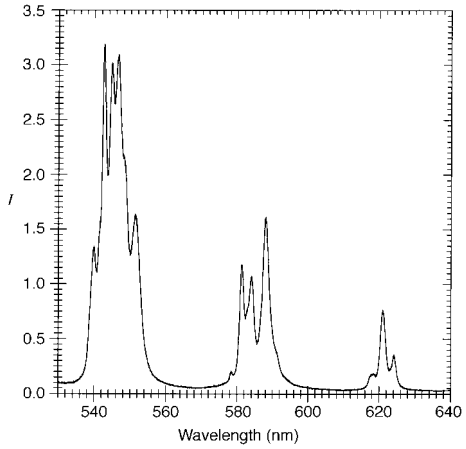

Figure 10. Total emission spectrum for [Tb·(*S*)-**4b**]$^{3+}$ following excitation at 488 nm (H_2O, 293 K). *I* = intensity in arbitrary units.

complexes gave rise to mirror image circularly polarised luminescence spectra,[16] and the largest dissymmetry factors were observed for the magnetic-dipole allowed transitions $^5D_4 - {}^7F_5$ and $^5D_4 - {}^7F_3$ (Figure 11). For the (*S*)-complex, values of $g_{em}^{548} = +0.27$ associated with the $\Delta J = -1$ transition, $g_{em}^{582} = +0.06$ for the $\Delta J = 0$ and $g_{em}^{624} = +0.26$ for the $\Delta J = +1$ transition. Circularly polarised emission from europium complexes has often been found to be much weaker than that from the corresponding terbium complexes.[8, 11, 26] The splitting of the ^7F_n levels of Eu^{3+} ions, associated with ligand crystal field effects, is much less than that for Dy^{3+} or Tb^{3+}, and simpler spectra are obtained which are more amenable to structural interpretation. A relatively strong $^5D_0/{}^7F_0$ transition was observed in the emission spectrum of [Eu·(*S*)-**7b**] at 579 nm that is characteristic of complexes with a

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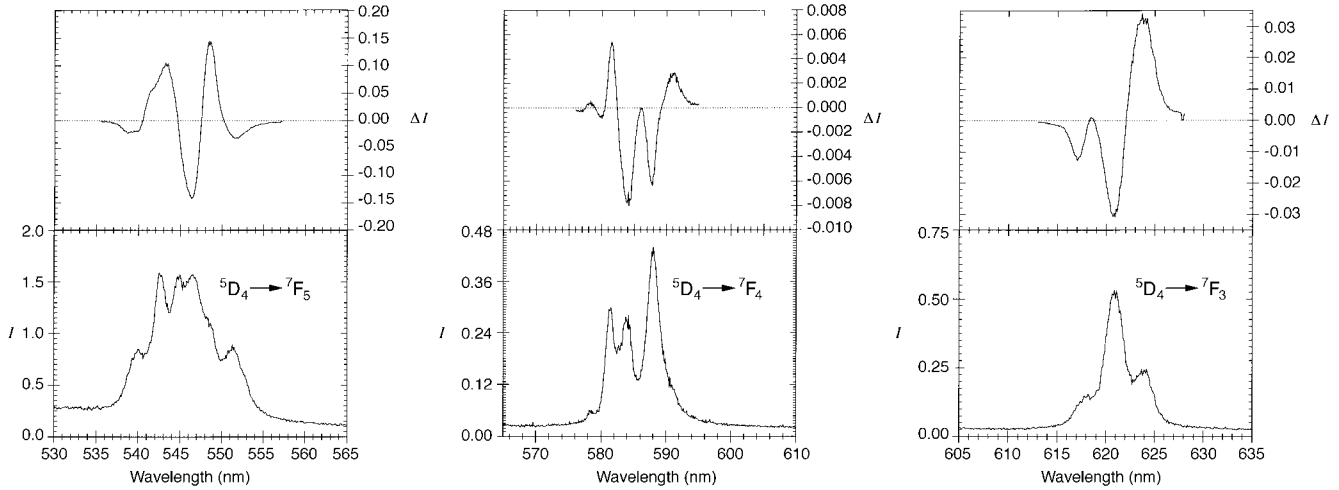

Figure 11. Total luminescence spectra (lower) and CPL spectra (upper) for the $^5D_4-{}^7F_5$ (left), the $^5D_4-{}^7F_4$ (center) and the $^5D_4-{}^7F_3$ transition (right) of $[Tb\cdot(S)\text{-}\mathbf{4b}]^{3+}$ (293 K, H_2O).

strong axial perturbation[24, 27] in C_n or C_{nv} symmetry. This transition carried no CPL as it is electric but not magnetic-dipole allowed in C_4 symmetry. The $\Delta J = 1$ transition, being magnetic-dipole allowed, was associated with a (circularly) polarised emission. Two components were observed (588 (A) and 593 nm (E)) (Figure 12) consistent with the C_4 symmetry

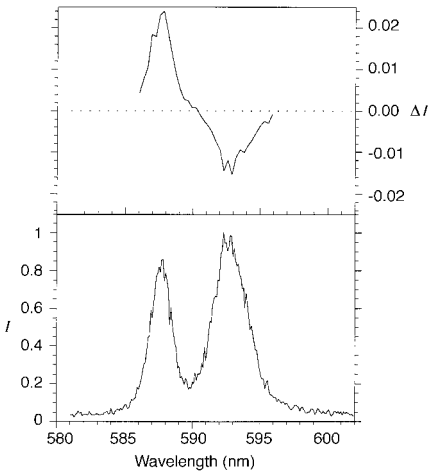

Figure 12. Total emission (lower) and circularly polarised luminescence spectrum (upper) for the $^5D_0-{}^7F_1$ transition in $[Eu\cdot(R)\text{-}\mathbf{7b}]^{3+}$ (D_2O, 293 K). I = intensity in arbitrary units.

of the complex, with modest g_{em} values of $+0.05$ and -0.03 respectively. The hypersensitive $\Delta J = 2$ transition gave a g_{em} value of $+0.12$ (E) and the $\Delta J = 3$ and $\Delta J = 4$ transitions gave g_{em} values of $+0.40$ (668 nm—the highest energy component) and -0.11 (687 nm). Other components of these transitions gave zero or near-zero g_{em} values. The same form of CPL spectra were recorded for the analogous europium complexes of **4b**, **5b** and **6b**, although they were generally less intense. The sign of the CPL emission was independent of the polarisation of the incident light: excitation with left-, right- or plane-polarised light gave rise to the same CPL spectra for a given complex. In addition, the europium complexes could be excited either directly into the $^7F_0-{}^5D_0$ transition using a rhodamine dye laser at 579.8 nm, through the relatively strong ($\varepsilon = 2.8$) metal-centred absorption at 390 nm, or indirectly through the aryl chromophore *without* changing the sign and relative intensity of the emitted light. For example, excitation of $[Eu\cdot(S)\text{-}\mathbf{7b}]^{3+}$ in D_2O at 270 nm with a conventional unpolarised uv light source leads to population of the aryl singlet then, following inter-system crossing to the triplet state, energy transfer occurs leading to population of the emissive $^5D_0$ excited europium state. The resultant emitted light is polarised in a sense which is determined by the helicity (Δ/Λ) of the metal complex, which is controlled in turn by the absolute configuration at the remote chiral centre at carbon. The sign of the observed CPL was the same for all of the europium and terbium complexes studied here and is also the same for the corresponding 1- and 2-naphthyl derivatives. Such behaviour is consistent with the adoption of a structure in each lanthanide complex that possesses the same absolute configuration in the helicity of the pendant arms (*R* at carbon gives a Λ configuration in the complex) and of the macrocyclic ring configuration (*R* at carbon gives $\delta\delta\delta\delta$ in the complex). Given that both sets of enantiopure metal complexes are available, the chiral lanthanide complexes in aqueous solution serve to modulate both the frequency and the polarisation of the emitted light in a controllable manner.[18] The efficiency with which they do this is a sensitive function of the nature of the lanthanide (for example, Tb complexes with quantum yields up to 0.81 in D_2O) and the precise transition which is observed.

Experimental Section

Luminescence and absorbance spectra

Ultraviolet absorbance spectra were recorded on a Unicam UV2-100 spectrometer using Unicam Vision Software Version 2.11. Fluorescence spectra were recorded on a Perkin-Elmer LS50B spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier tube and operated using FL Winlab Version 1.10 software. Quartz fluorescence cuvettes of pathlength 1 cm were employed.

Phosphorescence emission and excitation spectra were recorded on 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 spectra were obtained with slit widths (half-height bandwidth) of 10 nm (excitation) and 2.5 nm (emission).

Lifetimes were measured by using the same instrument and were obtained 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. The phosphorescence decay curves were fitted to an equation of the form $I(t) = I(0)\exp(-t/\tau)$ using a curve fitting program (Kaleidagraph software on an Apple Macintosh or Excel on a PC), 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 values were reproducible to at least ± 0.06 ms and independent of concentration over the range examined (abosrbance range 0.05 – 0.5). Details of the measurements of lifetimes for Yb complexes have been reported elsewhere.[22]

Luminescence quantum yields, ϕ, were measured according to the procedure described by Haas and Stein,[28] using $[Ru(2,2'\text{-bipyridyl})]^{2+}$ ($\phi = 0.028$ in H_2O)[29] and quinine sulfate ($\phi = 0.546$ in 0.5 mol dm^{-3} H_2SO_4)[30] as standards for Eu^{3+} and Tb^{3+} complexes respectively.

Circularly polarised luminescence spectra obtained at Michigan were recorded following excitation of the $^7F_6 \rightarrow {}^5D_4$ transition of Tb^{3+} using the 488 nm line of a Coherent Innova 70 argon-ion laser. Excitation of Eu^{3+} (at 579.76 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 nm 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 %.

Synthesis and characterisation

Reactions requiring anhydrous or inert conditions were carried out using Schlenk-line techniques under an atmosphere of dry argon. 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 visualised under UV (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, or on silica (Merck Silica Gel 60, 230 – 400 mesh).

Infra-red spectra were recorded on a Perkin-Elmer 1600 FT spectrometer using GRAMS Analyst software. Oils were examined as thin films and solids incorporated into KBr discs as stated. ^1H and $^{13}C\{^1H\}$ NMR spectra were acquired using a Brüker AC250 spectrometer operating at 250.13 and 62.9 MHz respectively. Spectra were referenced internally relative to *tert*-butanol (1 drop; $\delta_H = 0$; $\delta_C = 31.3$) for paramagnetic complexes or to the residual protio-solvent resonances which are reported relative to TMS. All chemical shifts are given in ppm and coupling constants are in Hz. Mass spectra were recorded on a VG 7070E spectrometer operating in DCI (ammonia) or FAB (glycerol matrix) mode. Electrospray mass spectra were recorded on a VG Platform II (Fisons instrument) operating in positive- or negative-ion mode as stated. FAB and accurate mass spectra were recorded at the EPSRC Mass Spectrometry Service at Swansea. Optical rotations were measured at the EPSRC National Chiroptical Spectroscopy Centre at Kings College, London on a Perkin-Elmer 141 polarimeter, calibrated with sucrose solutions, 10 mg cm^{-3} ($[\alpha_D] = 66.6$).

(*R*)-*N*-2-chloroethanoyl-1-phenylethylamine (**8a**): Chloroacetylchloride (0.78 mL, 9.9 mmol) in dry diethyl ether (20 mL) was added dropwise to a stirred solution of (*S*)-α-methylbenzylamine (1.1 mL, 8.3 mmol) and triethylamine (1.4 mL, 9.9 mmol) in dry diethyl ether (30 mL) at $-20\,^\circ C$. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The resulting white precipitate was dissolved in water (60 mL) and the organic layer washed with hydrochloric acid (0.1 mol dm^{-3}, 50 mL), water (3×30 mL), dried (K_2CO_3) and the solvent removed in vacuo to yield a white solid. Recrystallisation from diethyl ether yielded white needles (0.95 g, 60 %). M.p. 95 – 96 °C. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.41 - 7.34$ (m, 5H, Ar), 6.82 (br s, 1H, NH), 5.18 (m, 1H, CH), 4.11 (d, $^2J(H, H) = 15.1$ Hz, 1H, CH_2), 4.08 (d, $^2J(H, H) = 15.1$ Hz, 1H, CH_2), 1.58 (d, $^3J(H, H) = 6.7$ Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 165.0$ (CO), 142.4 (q-Ar), 128.8 (*m*-Ar), 127.6 (*p*-Ar), 126.1 (*o*-Ar), 49.2 (CHN), 42.6 (CH_2), 21.7 (CH_3); IR (KBr): $\tilde{\nu} = 3265$ (N – H), 1652 cm^{-1} (C=O); MS (DCI): *m*/*z* (%): 198 (100) $[M^+]$; $C_{10}H_{12}ClNO$ (197.5) (%): calcd C 60.8, H 6.12, N, 7.08; found C 60.6, H 6.15, N 6.90.

The enantiomeric compound **8b** was prepared similarly and gave identical spectroscopic characterisation.

1,4,7,10-Tetrakis-[(*R*)-1-(1-phenyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane (**4a**): A solution of **8a** (5.5 g, 27.8 mmol) in dry *N*,*N*-dimethylformamide (5 mL) was added to a stirred mixture of 1,4,7,10-tetraazacyclododecane (0.96 g, 5.6 mmol) and fine mesh anhydrous potassium carbonate (3.8 g, 27.8 mmol) in dry *N*,*N*-dimethylformamide (60 mL) under an argon atmosphere. The reaction mixture was heated at 60 °C for 48 h. The solvent was removed by distillation in vacuo and the resulting brown oil was extracted into dichloromethane (40 mL), washed with water (3×40 mL) and brine (40 mL), dried (K_2CO_3) and the solvent removed in vacuo to yield a yellow oil. The product was purified by alumina column chromatography (gradient elution from dichloromethane to 2 % methanol-dichloromethane). Recrystallisation from acetonitrile adding hexane yielded white needles (1.4 g, 31 %). M.p. 120 – 122 °C (decomp); $R_f = 0.34$ (br) (Al_2O_3; 10 % CH_3OH-CH_2Cl_2; I_2 and UV detection); ^1H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.38 - 7.33$ (m, 20H, Ar), 7.13 (d, $^3J(H, H) = 8.2$ Hz, 4H, NH), 5.20 (m, 4H, CH), 2.97 (br s, 8H, CH_2CO), 2.60 (br s, 16H, ring-CH_2), 1.56 (d, $^3J(H, H) = 7$ Hz, 12H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 170.2$ (CO), 143.6 (q-Ar), 129.1 (*m*-Ar), 127.8 (*p*-Ar), 126.7 (*o*-Ar), 59.3 (CH_2CO), 53.5 (ring-CH_2), 48.7 (CHN), 21.9 (CH_3); IR (thin film): $\tilde{\nu} = 3293$ (N – H), 1659 cm^{-1} (C=O); MS (ES +): *m*/*z* (%): 839 (100) $[M + Na^+]$, 817 (63) $[M^+]$; $C_{48}H_{64}N_8O_4$ (817.09) (%): calcd C 70.6, H 7.89, N 13.7; found C 70.1, H 7.88, N 13.9.

1,4,7,10-Tetrakis-[(*S*)-1-(1-phenyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane (**4b**): This compound was prepared following a method similar to that for **4a** using 1,4,7,10-tetraazacyclododecane (0.96 g, 5.6 mmol) and fine mesh anhydrous potassium carbonate (3.8 g, 27.8 mmol) in dry *N*,*N*-dimethylformamide (60 mL) and **8b** (5.6 g, 27.8 mmol) in dry *N*,*N*-dimethylformamide (10 mL). The product was recrystallised from acetonitrile and isolated as white needles (1.46g, 37 %). Characterisation data are the same as those reported for **4a**. $C_{48}H_{64}N_8O_4$ (817.09) (%): calcd C 70.6, H 7.90, N 13.7; found: C 70.6, H 8.01, N 14.0.

[Dy · 4a](CF$_3$SO$_3$)$_3$: Dysprosium(III) triflate (0.116 g, 0.19 mmol) and trimethylorthoformate (2 mL) were heated at reflux in dry acetonitrile (2 mL) for 2 h. A solution of ligand **4a** (0.155 g, 0.19 mmol) in dry acetonitrile (1 mL) was added and the solution heated at reflux for a further 18 h. The solution was concentrated and added dropwise with stirring to diethyl ether (100 mL). The resulting white solid was filtered, dried in vacuo and recrystallised from acetonitrile to give white needles (0.18 g, 65 %), m.p. > 250 °C; $R_f = 0.15$ (br) (SiO_2; 30 % CH_3OH-$CH_3CO_2NH_4$); ^1H NMR (250 MHz, CD_3OD, 25 °C): $\delta = 246.6$ (br s, 4H, ring-H_{eq}), 108.6 (br s, 4H, ring-H_{ax}), 58.3 (br s, 4H, ring-H_{eq}), 8.4 – 6.7 (m, 20H, Ar), −3.1 (br s, 4H, CH), −7.1 (s, 12H, CH_3), −125.0 (br s, 4H, CH_2CO), −129.2 (br s, 4H, CH_2CO), −386.6 (br s, 4H, ring-H_{ax}); IR (solid): $\tilde{\nu} = 3256$ (br) (N – H), 1626 cm^{-1} (C=O); MS (ES +): *m*/*z* (%): 1276 (15) $[M^{3+} + (CF_3SO_3^-)_2]^+$, 564 (100) $[M^{3+} + (CF_3SO_3^-)]^{2+}$, 326 (15) $[M^{3+}]$; $C_{51}H_{64}DyF_9N_8O_{13}S_3$ (1426.78) (%): calcd C 42.9, H 4.52, N 7.85; found C 42.8, H 4.52, N 7.56.

[Dy · 4b](CF$_3$SO$_3$)$_3$: This complex was prepared similarly using dysprosium(III) triflate (0.373 g, 0.61 mmol) and trimethylorthoformate (5 mL) in dry acetonitrile (2 mL) and the ligand **4b** (0.5 g, 0.61 mmol) in dry acetonitrile (1 mL). Recrystallisation from acetonitrile yielded white

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needles (0.54 g, 62%). Characterisation data are the same as those reported for [Dy·**4a**]$(CF_3SO_3)_3$. $C_{51}H_{64}DyF_9N_8O_{13}S_3\cdot H_2O$ (1426.78) (%): calcd C 42.4, H 4.60, N 7.76; found C 42.6, H 4.47, N 7.85.

[Eu·4a](CF$_3$SO$_3$)$_3$: This complex was prepared following a method similar to that for the dysprosium complex using europium(III) triflate (0.17 g, 0.28 mmol) and trimethylorthoformate (2 mL) in dry acetonitrile (1 mL) and the ligand **4a** (0.225 g, 0.28 mmol) in dry acetonitrile (1 mL). Recrystallisation from acetonitrile yielded white needles (0.27 g, 68%), m.p. >250 °C; R_f = 0.2 (br) (SiO_2; 30% CH_3OH-$CH_3CO_2NH_4$); ^{1}H NMR (200 MHz, CD_3OD, 25 °C): δ = 27.5 (s, 4H, ring-H_{ax}), 4.32–4.26 (m, 20H, Ar), 2.14 (br s, 4H, CH), −1.17 (d, ^3J(H, H) = 6.3 Hz, 12H, CH_3), −3.50 (d, ^2J(H, H) = 12.5 Hz, 4H, ring-H_{eq}), −8.44 (br s, 4H, ring-H'_{ax}), −8.93 (d, ^2J(H, H) = 13.0 Hz, 4H, ring-H'_{eq}), −16.0 (d, ^2J(H, H) = 15.5 Hz, 4H, CH_2CO), −16.4 (d, ^2J(H, H) = 15.6 Hz, 4H, CH_2CO); ^{13}C{^{1}H} NMR (62.9 MHz, CD_3OD, 25 °C): δ = 189.0 (CO), 142.3 (q-Ar), 127.9 (*m*-Ar), 127.2 (*p*-Ar), 124.3 (*o*-Ar), 110–107 (br, ring-CH_2), 90.0 (br, *C*H_2CO), 85–83 (br, ring-CH_2), 47.1 (CHN), 21.7 (CH_3); IR (solid): $\tilde{\nu}_{max}$ = 3249 (br) (N–H), 1620 cm^{-1} (C=O); MS (ES+): *m*/*z* (%): 1267 (20) [M^{3+} + 2($CF_3SO_3^-$)]$^+$, 559 (100) [M^{3+} + ($CF_3SO_3^-$)]$^{2+}$, 323 (20) [M^{3+}]; $C_{51}H_{64}EuF_9N_8O_{13}S_3\cdot 2H_2O$ (1416.24) (%): calcd C 42.2, H 4.72, N 7.72; found C 42.3, H 4.64, N 7.64.

[Eu·4b](CF$_3$SO$_3$)$_3$: This complex was prepared similarly from ligand **4b**. Recrystallisation from acetonitrile yielded white needles (0.61 g, 69%). Characterisation data are the same as those reported for [Eu·**4a**]$(CF_3SO_3)_3$; $C_{51}H_{64}EuF_9N_8O_{13}S_3$ (1416.24) (%): calcd C 43.3, H 4.55, N 7.91; found: C 43.0, H 4.52, N 7.95.

[Pr·4a](CF$_3$SO$_3$)$_3$: This complex was obtained by an analogous method using praseodymium(III) triflate (0.3 g, 0.51 mmol) and the ligand **4a** (0.42 g, 0.51 mmol). Recrystallisation from acetonitrile yielded white needles (0.4 g, 56%), m.p. >250 °C; ^{1}H NMR (250 MHz, CD_3OD, 25 °C): δ = 22.25 (br s, 4H, ring-H_{eq}), 11.05 (br s, 4H, ring-H_{ax}), 9.28 (br s, 4H, ring-H_{eq}), 5.86–5.62 (m, 20H, Ar), 3.82 (br s, 4H, CH), −0.57 (s, 12H, CH_3), −4.83 (br s, 4H, CH_2CO), −8.10 (d, ^2J(H, H) = 9.1 Hz, 4H, CH_2CO), −42.98 (br s, 4H, ring-H_{ax}). IR (solid): $\tilde{\nu}$ = 3230 (br) (N–H), 1620 cm^{-1} (C=O); MS (ES+): *m*/*z* (%): 553.5 (100) [M^{3+} + ($CF_3SO_3^-$)]$^{2+}$; $C_{51}H_{64}F_9N_8O_{13}PrS_3$ (1405.19) (%): calcd C 42.5, H 4.76, N 7.77; found C 42.7, H 4.61, N 7.64.

[Tb·4a](CF$_3$SO$_3$)$_3$: This complex was prepared using terbium(III) triflate (0.15 g, 0.24 mmol) and the ligand **4a** (0.20 g, 0.24 mmol) using a similar procedure. Recrystallisation from acetonitrile yielded white needles (0.178 g, 52%), m.p. >250 °C; IR (solid): $\tilde{\nu}$ = 3269 (br) (N–H), 1620 cm^{-1} (C=O); MS (ES+): *m*/*z* (%): 1274 (10) [M^{3+} + 2($CF_3SO_3^-$)]$^+$, 563 (100) [M^{3+} + ($CF_3SO_3^-$)]$^{2+}$, 325 (30) [M^{3+}]; [α]$_D$ = +104.2 (*c* = 2.211 in CH_3OH) $C_{51}H_{64}F_9N_8O_{13}S_3Tb.H_2O$ (1423.21) (%): calcd: C 42.0, H 4.70, N 7.68; found C 41.9, H 4.48, N 7.60.

[Tb·4b](CF$_3$SO$_3$)$_3$: This complex was obtained similarly using ligand **4b** (0.30 g, 0.37 mmol) and terbium triflate (0.22 g, 0.37 mmol). Recrystallisation from acetonitrile yielded white needles (0.284 g, 54%). Characterisation data are the same as those reported for [Tb·**4a**]$(CF_3SO_3)_3$, [α]$_D$ = −104.2 (*c* = 0.144 in CH_3OH); $C_{51}H_{64}F_9N_8O_{13}S_3Tb$ (1423.21) (%): calcd C 43.0, H 4.53, N 7.87; found C 43.4, H 4.58, N 7.78.

[Yb·4a](CF$_3$SO$_3$)$_3$: This complex was prepared from ytterbium(III) triflate (0.15 g, 0.24 mmol) and ligand **4a** (0.2 g, 0.24 mmol) by the method described above. Recrystallisation from acetonitrile yielded white needles (0.21 g, 61%), m.p. >250 °C; ^{1}H NMR (250 MHz, CD_3OD, 25 °C): δ = 102 (br s, 4H, ring-H_{ax}), 18.2 (br s, 4H, ring-H_{eq}), 14.8 (br s, 4H, ring-H_{eq}), 4.80–1.83 (m, 20H, Ar), −1.42 (s, 4H, CH), −4.73 (s, 12H, CH_3), −28.8 (s, 4H, CH_2CO), −34.5 (s, 4H, ring-H_{ax}), −66.5 (br s, 4H, CH_2CO); IR (solid): $\tilde{\nu}$ = 3249 (br) (N–H), 1620 cm^{-1} (C=O); MS (ES+): *m*/*z* (%): 568 (100) [M^{3+} + ($CF_3SO_3^-$)]$^{2+}$, 494 (50) [M^{3+}]; $C_{51}H_{64}F_9N_8O_{13}S_3Yb$ (1437.32) (%): calcd C 41.6, H 4.65, N 7.61; found C 41.6, H 4.41, N 7.30.

***(R)*-*N*-2-chloroethanoyl-(4-bromophenyl)ethylamine** (**9c**): A solution of (*R*)-1-(4-bromophenyl)ethylamine **9a** (0.5 g, 2.5 mmol) and triethylamine (0.44 mL, 3.1 mmol) in anhydrous diethyl ether (100 mL) was cooled to −10 °C. Chloroacetyl chloride (0.24 mL, 3.0 mmol) was added dropwise with vigorous stirring, the temperature being maintained between −10 and 0 °C. Water (100 mL) was added and the ether layer separated, washed with HCl (0.1M, aq, 200 mL) followed by water (2 × 100 mL) and finally dried over potassium carbonate. Removal of solvent under reduced pressure, followed by crystallisation of the off-white solid residue from diethyl ether led to the required compound as colourless needle-like crystals. Yield: 0.58 g (83%). M.p. 115–118 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.60 (d, ^3J(H, H) = 7.0, 3H, CH_3), 4.14 (d, ^4J(H, H) = 2.3, 2H, CH_2), 5.17 (p, ^3J(H, H) = 7.2, 1H, CH), 6.90 (br s, 1H, NH), 7.29 (d, ^3J(H, H) = 8.4, 2H, Ar-H), 7.57 (d, ^3J = 8.3, 2H, Ar-H); ^{13}C{^{1}H} (62.9 MHz, $CDCl_3$, 25 °C): δ = 22.1 (CH_3), 43.1 (CH), 49.3 (CH_2), 121.7 (ArC_1), 128.4 (ArC-H), 132.3 (ArC-H), 142.1 (ArC-Br), 165.7 (C=O); IR (solid): $\tilde{\nu}_{max}$ = 1642 cm^{-1} (C=O). (*S*)-*N*-2-chloroethanoyl-(4-bromophenyl)ethylamine (**9d**) was prepared in a similar manner to its enantiomer **9c**, starting from (*S*)-1-(4-bromophenyl)ethylamine **9b**.

1,4,7,10-tetrakis-[(*R*)-1-(4-bromophenyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane (**5a**): A solution of the chloroamide **9c** (656 mg, 2.37 mmol) in dry dimethylformamide (5 mL) was added to a mixture of 1,4,7,10-tetraazacyclododecane (95 mg, 0.55 mmol), caesium carbonate (776 mg, 2.48 mmol) and potassium iodide (183 mg, 1.1 mmol). The mixture was heated at 75 °C under argon for 18 h, after which the solvent was removed under reduced pressure. The residue was taken into dichloromethane (50 mL) and the solution washed with water (2 × 50 mL) and dried over potassium carbonate. The red-brown residue obtained upon removal of the solvent was recrystallised from acetonitrile, leading to the required compound as a colourless solid. Yield: 0.32 g (52%). M.p. 188–190 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.45 (d, ^3J(H, H) = 7.0, 12H, CH_3), 2.57 (br s, 16H, CH_2 of ring), 2.92 (s, 8H, NCH_2CO), 5.06 (p, ^3J(H, H) = 7.2, 4H, MeCH), 6.96 (d, ^3J(H, H) = 8.0, 4H, NH), 7.16 (d, ^3J(H, H) = 8.4, 8H, Ar-H), 7.42 (d, ^3J(H, H) = 8.4, 8H, Ar-H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.9 (CH_3), 48.2 (CH), 53.5 (CH_2 ring), 59.3 (NCH_2CO), 121.4 (ArC_1), 128.5 (ArC-H), 132.0 (ArC-H), 142.8 (ArC-Br), 170.4 (C=O); IR (solid): $\tilde{\nu}_{max}$ = 1642 cm^{-1} (C=O); $C_{48}H_{60}Br_4N_8O_4\cdot H_2O$ (1146.16) (%): calcd C 50.10, H 5.43, N 9.74; found C 49.75, H 5.22, N 9.58. The enantiomeric compound **5b** was prepared similarly using **9d** in place of **9c** and gave identical spectroscopic data. $C_{48}H_{60}Br_4N_8O_4$ (1128.15)(%): calcd C 50.90, H 5.34, N 9.89; found C 50.47, H 5.29, N 9.64.

[Eu·5b](CF$_3$SO$_3$)$_3$: A solution of europium trifluoromethanesulfonate (26.5 mg, 0.044 mmol) in anhydrous acetonitrile (1 mL) was added to a solution of ligand **5b** (50 mg, 0.044 mmol) in hot acetonitrile (1 mL) and the solution heated at 60 °C for 1 h. The solvent was removed under reduced pressure, the residue taken up into the minimum volume of acetonitrile and added dropwise to a large volume (100 mL) of diethyl ether in a centrifuge tube. The resulting fine solid was separated and recrystallised from acetonitrile. M.p. >250 °C; ^{1}H NMR (250 MHz, CD_3OD, 25 °C): δ = 28.12 (s, 4H, ring H_{ax}), 7.23 (s, 8H, aryl H), 6.78 (s, 8H, aryl H), 4.63 (br s, 4H, *CH*CH_3), 1.47 (s, 12H, CH*C*H_3), −1.43 (s, 4H, ring H_{eq}), −5.22 (br s, 4H, ring $H_{ax'}$), −6.56 (br s, 4H, ring $H_{eq'}$), −12.25 (s, 4H, NCH_2CO), −12.75 (s, 4H, NCH_2CO); IR (solid): $\tilde{\nu}$ = 1622 cm^{-1} (C=O); MS (ES+): *m*/*z* (%): 715 (75) [M^{3+} + $CF_3SO_3^-$]$^{2+}$, 641 (25) [M^{3+} + e^-]$^{2+}$, 428 (26) [M^{3+}]. The enantiomeric complex [Eu·**5a**]$(CF_3SO_3)_3$ was prepared similarly and gave identical spectroscopic data.

[Tb·5b](CF$_3$SO$_3$)$_3$: This complex was prepared similarly. IR (solid): $\tilde{\nu}$ = 1625 cm^{-1} (C=O); MS (ES+): *m*/*z* (%): 719 (100) [M^{3+} + $CF_3SO_3^-$]$^{2+}$, 644 (20) [M^{3+} + e^-]$^{2+}$.

[Yb·5a](CF$_3$SO$_3$)$_3$: This complex was obtained using a similar procedure. IR (solid): $\tilde{\nu}_{max}$ = 1632 cm^{-1}. $C_{51}H_{60}Br_4F_9N_8O_{13}S_3Yb\cdot 5H_2O$ (1839.00) (%): calcd C 33.24, H 3.83, N 6.08; found C 33.38, H 3.34, N 5.87. The enantiomeric complex [Yb·**5b**]$(CF_3SO_3)_3$ was prepared similarly; found C 33.07, H 3.36, N 6.10.

***(S)*-*N*-ethanoyl-1-(4-bromophenyl)ethylamine** (**10a**): A solution of (*S*)-1-(4-bromophenyl)ethylamine **9a** (0.5 g, 2.5 mmol) and triethylamine (0.44 mL, 3.1 mmol) in anhydrous diethyl ether (100 mL) was cooled to −10 °C. Acetyl chloride (0.21 mL, 3.0 mmol) was added dropwise with vigorous stirring, the temperature being maintained between −10 and 0 °C. After allowing the mixture to warm to room temperature, water (100 mL) was added and the diethyl ether layer separated, washed with HCl (0.1M, aq, 200 mL) followed by water (2 × 100 mL) and finally dried over potassium carbonate. The off-white solid residue obtained after evaporation of the solvent was recrystallised from diethyl ether, leading to the required compound as colourless needle-like crystals. Yield: 0.58 g (83%); m.p. 127–130 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.40 (d, ^3J(H, H) = 6.9, 3H, *CH*$_3$CH), 1.93 (s, 3H, CH_3CO), 5.00 (p, ^3J(H, H) = 7.1, 1H, CH), 6.23 (d, ^3J(H, H) = 7.2, 1H, NH), 7.14 (d, ^3J(H, H) = 6.5, 2H, Ar-H), 7.40 (d, ^3J(H, H) = 6.6, 2H, Ar-H); IR (solid): $\tilde{\nu}$ = 1645 cm^{-1} (C=O).

(*S*)-*N*-ethanoyl-1-(4-cyanophenyl)ethylamine (**10b**): Copper(I) cyanide, $Cu_2(CN)_2$, (0.93 g, 5.2 mmol) was added to a solution of **10a** (1.20 g, 4.96 mmol) in dry, degassed dimethylformamide (10 mL) and the suspension stirred vigorously at 180 °C (bath temperature) for 48 h. A clear solution was obtained. The solvent was removed under reduced pressure and the residue taken into hydrochloric acid (aq, 6 M, 20 mL) in a well-ventilated fume hood. The resulting clear, red-brown solution was extracted with dichloromethane (5 × 50 mL) and the organic extracts subsequently washed with water (100 mL) to give a colourless solution. The solvent was removed under reduced pressure to yield the required compound as a colourless solid. Yield: 0.71g (76 %). M.p. 187–189 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.46$ (d, $J =$ 7.0, 3H, CH_3CH), 1.99 (s, 3H, CH_3CO), 5.11 (p, J(H, H) = 7.4 Hz, 1H, CH), 5.90 (d, J(H, H) = 6.9 Hz, 1H, NH), 7.40 (d, ^3J(H, H) = 8.0 Hz, 2H, ArH), 7.60 (d, ^3J(H, H) = 7.9 Hz, 2H, ArH); ^{13}C{^{1}H} NMR ($CDCl_3$): 22.4 (CH_3CH), 23.6 (CH_3CO), 49.3 (CH), 111.2 (CN), 119.4 (ArC_1), 127.4 (ArCH), 132.9 (ArCH), 149.9 (Ar*C*-CN), 170.2 (C=O); IR (solid): $\tilde{\nu} = 2227$ (CN), 1637 cm^{-1} (C=O).

(*S*)-1-(4-cyanophenyl)ethylamine (**10c**): Compound **10b** (0.6 g, 3.2 mmol) was taken into HCl (2 M aq, 10 mL) and stirred at 100 °C for 18 h. Selective hydrolysis of the acetamide group in the presence of the nitrile was monitored by means of IR spectroscopy ($\tilde{\nu}_{CO} = 1637$ cm^{-1} in the amide). The pH was then raised to 13 by addition of KOH pellets and the aqueous solution extracted with dichloromethane (3 × 20 mL). The organic extracts were combined, dried over potassium carbonate and the solvent removed under reduced pressure to give the required compound as a colourless oil. Yield: 0.23 g (50 %). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.31$ (d, $^3J =$ 6.8, 3H, CH_3), 1.57 (br s, 2H, NH_2), 4.13 (q, ^3J(H, H) = 6.5 Hz, 1H, CH), 7.42 (d, ^3J(H, H) = 8.4 Hz, 2H, ArH), 7.55 (d, ^3J(H, H) = 8.1 Hz, 2H, ArH); IR (solid): $\tilde{\nu} = 2232$ cm^{-1} (CN).

(*S*)-*N*-2-chloroethanoyl-(4-cyanophenyl)ethylamine (**10d**): A solution of the amine **10c** (0.20 g, 1.37 mmol) and triethylamine (0.29 mL, 2.05 mmol) in anhydrous diethyl ether (60 mL) was cooled to −10 °C. Chloroacetyl chloride (0.14 mL, 1.75 mmol) was added dropwise with vigorous stirring, the temperature being maintained between −10 and 0 °C. Water (100 mL) was added and the diethyl ether layer separated, washed with HCl (0.1 M, aq, 200 mL) followed by water (2 × 100 mL) and finally dried over potassium carbonate. Removal of solvent under reduced pressure, followed by crystallisation of the off-white solid residue from ether, led to the required compound as colourless needle-like crystals. Yield: 0.25 g (82 %). M.p. 75–78 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): 1.52 (d, ^3J(H, H) = 7.0 Hz, 3H, CH_3), 4.05 (d, ^4J(H, H) = 1.5 Hz, 2H, CH_2), 5.12 (p, J(H, H) = 7.4 Hz, 1H, CH), 6.91 (d, ^3J(H, H) = 9.1 Hz, 1H, NH), 7.40 (d, ^3J(H, H) = 8.1 Hz, 2H, ArH), 7.62 (d, ^3J(H, H) = 8.6 Hz, 2H, ArH); IR (solid): $\tilde{\nu} =$ 2228 (CN), 1644 cm^{-1} (C=O).

1,4,7,10-tetrakis-[(*S*)-1-(4-cyanophenyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane (**6**): A solution of the chloroamide **10d** (250 mg, 1.13 mmol) in dry dimethylformamide (5 mL) was added to a mixture of 1,4,7,10-tetraazacyclododecane (45 mg, 0.26 mmol), caesium carbonate (369 mg, 1.18 mmol) and potassium iodide (87 mg, 0.52 mmol). The mixture was heated at 75 °C under argon for 18 h, after which the solvent was removed under reduced pressure. The residue was taken into dichloromethane (50 mL) and the solution washed with water (2 × 50 mL) and dried over potassium carbonate. The red-brown residue obtained upon removal of the solvent was recrystallised from acetonitrile, leading to the required compound as a colourless solid. Yield: M.p. 190–195 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.46$ (d, ^3J(H, H) = 7.1 Hz, 12H, CH_3), 2.67 (br, 16H, CH_2 ring), 3.03 (s, 8H, NCH_2CO), 5.09 (p, J(H, H) = 7.1 Hz, 4H, CH), 7.40 (d, ^3J(H, H) = 8.7 Hz, 8H, ArH), 7.57 (d, ^3J(H, H) = 8.1 Hz, 8H, ArH); ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 21.7$ (CH_3), 48.4 (CH), 53.0 (CH_2 ring), 58.8 (NCH_2CO), 110.6 (CN), 118.7 (ArC_1), 126.9 (ArCH), 132.3 (ArCH), 149.3 (ArC-CN), 170.3 (C=O); IR (solid): $\tilde{\nu} = 2226$ (CN), 1664 cm^{-1} (C=O); MS (ES$^+$): m/z (%): 939.4 (100) $[M + Na^+]$.

[Eu · 6](CF$_3$SO$_3$)$_3$: This complex was prepared as described for [Eu · **5a**](CF$_3$SO$_3$)$_3$. M.p. >250 °C; ^{1}H NMR (250 MHz, CD_3OD, 25 °C): $\delta =$ 28.33 (br s, 4H, ring H_{ax}), 7.50 (s, 8H, aryl H), 6.94 (s, 8H, aryl H), 4.92 (br s, 4H, C*H*CH$_3$), 1.58 (s, 12H, CHC*H*$_3$), −1.36 (br s, 4H, ring H_{eq}), −5.43 (br s, 4H, ring $H_{ax'}$), −7.05 (br s, 4H, ring $H_{eq'}$), −12.15 (s, 4H, NCH_2CO), −12.98 (s, 4H, NCH_2CO); IR (solid): $\tilde{\nu} = 2240$ (CN), 1624 cm^{-1} (C=O).

[Tb · 6](CF$_3$SO$_3$)$_3$: This complex was prepared similarly. M.p. >250 °C; IR (solid): $\tilde{\nu} = 2236$ (CN), 1628 cm^{-1} (C=O).

(*S*)-4-(1-aminoethyl)benzoic acid (**11a**): Compound **10b** (0.7 g, 3.7 mmol) was taken into HCl (6 M, aq) and heated at 110 °C for 75 h. The water was removed under reduced pressure to give a colourless solid, namely the hydrochloride salt of the desired compound, in quantitative yield. ^{1}H NMR (250 MHz, D_2O, 25 °C): $\delta = 1.15$ (d, ^3J(H, H) = 6.9 Hz, 3H, CH_3), 4.02 (q, ^3J(H, H) = 6.9 Hz, 1H, CH), 7.06 (d, ^3J(H, H) = 8.2 Hz, 2H, ArH), 7.53 (d, ^3J(H, H) = 8.2 Hz, 2H, ArH); ^{13}C{^{1}H} NMR (62.9 MHz, CD_3OD, 25 °C): $\delta = 23.41$ (CH_3), 54.6 (CH), 130.6 (ArCH), 134.0 (ArCH), 134.9 (ArC_1), 147.0 (Ar*C*-CO_2H), 171.6 (CO_2H); IR (solid): $\tilde{\nu} = 1703$ cm^{-1} (C=O).

(*S*)-Methyl-4-(1-aminoethyl)benzoate ester (**11b**): Concentrated hydrochloric acid (two drops) was added to a solution of **11a** in methanol (5 mL). The mixture was heated at reflux for 18 h after which, upon cooling, the required compound precipitated as its hydrochloride salt. ^{1}H NMR (250 MHz, CD_3OD, 25 °C): $\delta = 1.44$ (d, ^3J(H, H) = 7.0 Hz, 3H, CH_3), 3.68 (s, 3H, CO_2CH_3), 4.35 (q, ^3J(H, H) = 7.0 Hz, 1H, CH), 7.39 (d, ^3J(H, H) = 8.3 Hz, 2H, ArH), 7.88 (d, ^3J(H, H) = 8.2 Hz, 2H, ArH); ^{13}C{^{1}H} NMR (62.9 MHz, CD_3OD, 25 °C): $\delta = 23.5$ (CH_3), 54.6 (CH), 55.5 (CO_2CH_3), 130.8 (ArCH), 133.8 (ArCH), 134.2 (ArC_1), 147.3 (Ar*C*-CO_2Me), 170.3 (*C*O$_2$Me); IR (solid): $\tilde{\nu} = 1716$ cm^{-1} (C=O).

Methyl [*N*-2-(chloroethanoyl)-4-(*S*)-(1-aminoethyl)] benzoate (**11c**): This compound was prepared as described for **10d**, starting from **11b** · HCl (0.63 g, 3.5 mmol), triethylamine (1.14 mL, 8.0 mmol) and chloroacetyl chloride (0.30 mL, 3.8 mmol). Yield: 0.79 g (89 %). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.56$ (d, ^3J(H, H) = 7.0 Hz, 3H, C*H*$_3$CH), 3.92 (s, 3H, CO_2CH_3), 4.08 (d, ^4J(H, H) = 1.3 Hz, 2H, CH_2), 5.18 (p, ^3J(H, H) = 7.3 Hz, 1H, CH), 6.85 (d, ^3J(H, H) = 7.5 Hz, 1H, NH), 7.39 (d, ^3J(H, H) = 8.3 Hz, 2H, ArH), 8.03 (d, ^3J(H, H) = 8.2 Hz, 2H, ArH); ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$, 25 °C): 22.3 (*C*H$_3$CH), 43.2 (CH), 49.7 (CH_2), 52.8 (CO_2CH_3), 126.7 (ArCH), 130.0 (ArC_1), 130.7 (ArCH), 148.2 (Ar*C*-CO_2Me), 165.8 (CONH), 167.3 (CO_2Me).

1,4,7,10-tetrakis-[(*S*)-1-(4-cyanophenyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane (**7**): This compound was prepared as described for **5a** starting from **11c** (0.50 g, 1.96 mmol) and 1,4,7,10-tetraazacyclododecane (77 mg, 0.45 mmol), in the presence of caesium carbonate (657 mg 2.1 mmol) and potassium iodide (150 mg, 0.9 mmol). Yield: 220 mg (46 %). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.46$ (d, ^3J(H, H) = 6.9 Hz, 12H, C*H*$_3$CH), 2.56 (br s, 16H, CH_2 ring), 2.94 (s, 8H, NCH_2CO), 3.89 (s, 12H, CO_2CH_3), 5.13 (p, ^3J(H, H) = 7.1 Hz, 4H, CH), 7.17 (d, ^3J(H, H) = 8.0 Hz, 4H, NH), 7.33 (d, ^3J(H, H) = 8.1 Hz, 8H, ArH), 7.93 (d, ^3J(H, H) = 8.1 Hz, 8H, ArH); ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 22.1$ (*C*H$_3$CH), 48.9 (CH), 52.8 (CO_2CH_3), 53.4 (ring CH_2), 59.6 (NCH_2CO), 126.9 (ArCH), 129.7 (ArC_1), 130.5 (ArCH), 149.2 (Ar*C*-CO_2Me), 167.4 (CO_2Me), 170.6 (CONH); MS (ES+): m/z (%): 1049 (60) $[M + H^+]$. IR (solid): $\tilde{\nu} = 1712$, 1682 (C=O ester), 1641 cm^{-1} (C=O amide).

[Eu · 7](CF$_3$SO$_3$)$_3$: This complex was prepared as described above for the complexes of **5b**. M.p. >250 °C; ^{1}H NMR (250 MHz, CD_3OD, 25 °C): $\delta =$ 25.94 (s, 4H, ring H_{ax}), 5.16 (s, 8H, aryl H), 4.54 (s, 8H, aryl H), 2.28 (s, 4H, C*H*CH$_3$), 1.98 (br s, 12H, CHC*H*$_3$), −1.04 (s, 12H, CO_2CH_3), −3.95 (br s, 4H, ring H_{eq}), −7.92 (br s, 4H, ring-$H_{ax'}$), −9.22 (4H, br s, ring $H_{eq'}$), −15.4 (br s, 4H, NCH_2CO), −16.0 (br s, 4H, NCH_2CO); IR (solid): $\tilde{\nu} = 1728$ (C=O ester), 1620 cm^{-1} (C=O amide); MS (ES+): m/z (%): 1499 (5) $[M^{3+} + (CF_3SO_3^-)_2]^+$, 1350 (3) $[M^{3+} + (CF_3SO_3^-) + e^-]^+$, 676 (100) $[M^{3+} + CF_3SO_3^-]^{2+}$, 600 (55) $[M^{3+} + e^-]^{2+}$, 400 (38) $[M^{3+}]$; $C_{59}H_{72}EuF_9N_8O_{21}S_3 \cdot 2H_2O$ (1684.33) (%): calcd C 42.07, H 4.55, N 6.65; found C 41.99, H 4.27, N 6.29.

[Tb · 7](CF$_3$SO$_3$)$_3$: This complex was obtained similarly. IR (solid): $\tilde{\nu} = 1732$ (C=O ester), 1624 cm^{-1} (C=O amide); MS (ES+): m/z (%): 1508 (4) $[M^{3+} + (CF_3SO_3)_2]^+$, 1359 (1) $[M^{3+} + CF_3SO_3^- + e^-]^+$, 680 (100) $[M^{3+} + CF_3SO_3^-]^{2+}$, 605 (12) $[M^{3+} + e^-]^{2+}$, 404 (45) $[M^{3+}]$; $C_{59}H_{72}F_9N_8O_{21}S_3Tb \cdot H_2O$ (1672.32) (%): calcd C 42.35, H 4.46, N 6.70; found C 42.26, H 4.29, N 6.48.

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