

Strong exciton coupling and circularly polarised luminescence in rigid complexes of chiral macrocyclic tetranaphthylamides

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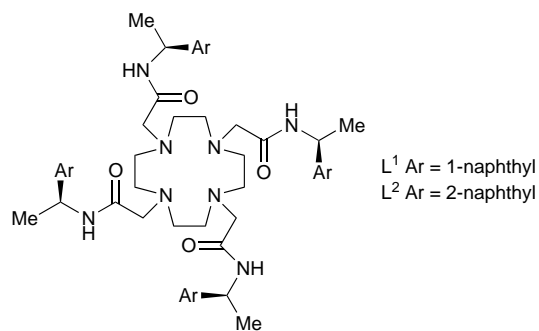
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Strong exciton coupling occurs between adjacent pairs of naphthyl chromophores in the chiral sodium and europium complexes of L¹; in the constitutionally isomeric complexes of L², intramolecular excimer formation is observed and both sets of Eu complexes give a well defined, metal-based circularly polarised emission.

Recently we have been examining the luminescence behaviour of lanthanide complexes of N-substituted octadentate ligands derived from 1,4,7,10-tetraazacyclododecane (cyclen).^{1–4} The chiral europium and terbium complexes of L³ are conformationally rigid and stereochemically homogeneous in solution on the timescale of the metal-centred luminescence (*i.e.* ms), and the remote chiral centre at carbon in the N-substituent determines both the configuration of the macrocyclic ring and the helicity of the array of N-substituents.¹ With this model complex in mind, we have prepared the corresponding enantiomeric pairs of 1- and 2-naphthyl substituted ligands, L¹ and L² and their Eu complexes. A particular motivation for this work has been the consideration that strong exciton coupling between proximate chromophores may be a necessary condition in seeking the efficient population of the enantiomeric (π - π^*) excited states of these lanthanide complexes.



Reaction of (*S*)- or (*R*)-*N*-2-chloroethanoyl-1-(1'-naphthyl)ethylamine with 1,4,7,10-tetraazacyclododecane (dmf, K₂CO₃, 60 °C) afforded the ligands (*S*)- or (*R*)-L¹ (mp 195 °C). The constitutionally isomeric ligand, L², based on 1-(2'-naphthyl)ethylamine was prepared analogously (mp 182 °C). Aqueous solutions of [H₂L²]²⁺, as the trifluoroacetate salt, gave rise to a structureless band in the emission spectrum at 400 nm whose intensity was independent of concentration in the range 10⁻⁴–10⁻⁶ mol dm⁻³. This band was not observed in MeOH or MeCN, so that intramolecular excimer formation⁴ may be favoured by a particularly strong hydrophobic interaction involving expulsion of hydrogen-bonded water molecules from the solvated protonated ligand. In MeOH, the enantiomers of ligand L² gave mirror-image CD spectra. No exciton coupling features were observed for the CD bands at 280 and 310 nm, which were attributed to ¹L_a and ¹L_{1b}

2-naphthyl π - π^* transitions.⁵ In the far-UV region, the apparent bisignate CD spectrum was assigned to naphthyl ¹B_b (225 nm) and ¹C_b (210 nm) transitions, rather than exciton coupling.^{5†} No sign of exciton coupling was evident from the mirror image CD spectra (MeOH) for the enantiomers of L¹, at room temp. (Fig. 1). The CD band at *ca.* 280 nm (¹L_a π - π^*) appeared to mask the ¹L_b 1-naphthyl transition at 305 nm.⁵ However, at -86 °C, a bisignate profile with crossover at 222 nm was observed for the free ligand (*R*)-L¹ and similar exciton coupling was observed at room temp. in the presence of 2 equiv. of Na⁺, K⁺, Ca²⁺. The intensity of the bisignate profile was enhanced on lowering the temperature. Such behaviour is consistent with coupling of the electric dipole transition moments along the long axis of the naphthyl chromophores, and with positive chirality.

The crystal structure (Fig. 2) of the sodium complex of L¹† at 150 K revealed a twisted square-antiprismatic eight-coordinate geometry about the sodium ion [mean Na–O = 2.46(3) Å, Na–N = 2.72(4) Å, twist angle 28° from prismatic geometry]. All four naphthyl rings are steeply inclined to the O₄ coordination plane (angles ranging from 81 to 103°) and are in a near orthogonal relationship to each other. Given that the amplitude of exciton coupling is maximal when the dihedral angle between the two chromophores is *ca.* 70°, and tends to zero as the angle approaches 0 or 180°,⁸ this arrangement of the naphthyl groups is consistent with the observed exciton

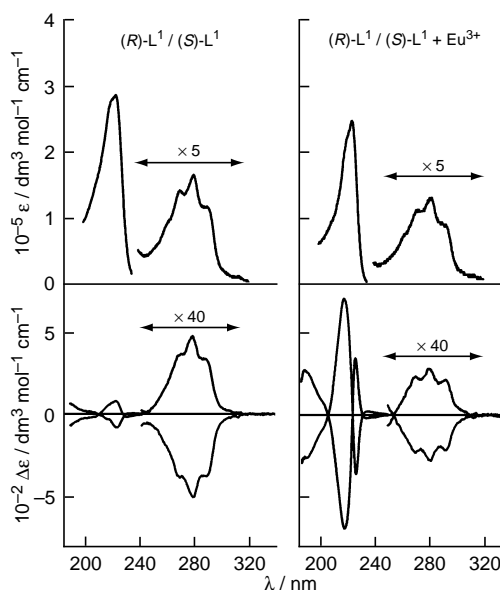


Fig. 1 CD spectra of the enantiomers of L¹ and [EuL¹][CF₃SO₃]₃ in MeOH [293 K; (*R*)-enantiomer is upper trace] showing the bisignate profile in the metal complex associated with exciton coupling of the 1-naphthyl ¹B_b bands

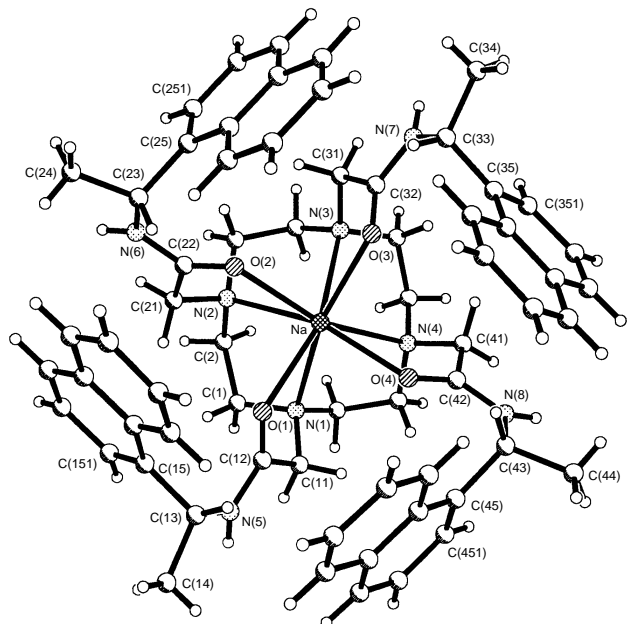


Fig. 2 Structure of the complex $[\text{NaL}^1]\text{CF}_3\text{CO}_2$ in the crystal, showing the octadentate and twisted square-antiprismatic coordination about sodium

coupling: for $[\text{Na}\{(R)\text{-L}^1\}]^+$: $\Delta\lambda = 10 \text{ nm}$; $g_{\text{abs}}(219) = -2.2 \times 10^{-3}$, $g_{\text{abs}}(229) = +1.4 \times 10^{-3}$. Methanolic solutions of $(S)\text{-L}^1$ in the presence of 2 equiv. of NaCl , NaOAc or Na_2HPO_4 gave rise to mirror-image CD spectra, with a bisignate profile typical of negative chirality, and independent of the anion.

Solution NMR studies in CD_3OD of the Eu complexes of L^1 and L^2 , indicated the presence of a single C_4 -symmetric complex, that showed no evidence for exchange broadening in the range 200–320 K (400 MHz). With $[\text{EuL}^2]^{3+}$, there was no evidence for exciton coupling in the solution CD spectrum, and in the fluorescence emission spectrum, an excimer band was evident at 400 nm (40% of the monomer emission intensity) only if water was present. In 100% MeOH, no excimer was discerned, resembling the behaviour shown by the protonated ligand. Formation of an excimer requires the co-planarity of the two aryl groups and their close juxtaposition (3.5 Å): the absence of observed exciton coupling is consistent with this behaviour as the average interchromophoric dihedral angle must be near 0° . In the isomeric complex, $[\text{EuL}^1]^{3+}$, the situation is reversed: no distinct excimer band was observed in the emission spectrum irrespective of the presence of water, and in the CD spectrum (Fig. 1) of $\{(R)\text{-L}^1\}[\text{Eu}]^{3+}$, positive chirality was exhibited with a bisignate profile associated with strong exciton coupling for which $g_{\text{abs}}(219) = -6 \times 10^{-3}$ and $g_{\text{abs}}(229) = +3 \times 10^{-3}$. Excimer emission between proximate naphthyl chromophores has been reported previously, e.g. in poly(1-naphthylmethylglutamate),⁶ and in poly(1-naphthyl-Ala) no evidence for excimer formation was found whereas in the isomer, poly(2-naphthyl-Ala), a weak excimer emission was observed in degassed dmf solutions.⁷

Although these europium complexes are only weakly emissive in their metal-based luminescence spectra following sensitised excitation via the naphthyl antenna $\{[\text{EuL}^1]: \lambda_{\text{exc}} = 280 \text{ nm}$, $\tau_{\text{H}_2\text{O}} = 0.53$, $\tau_{\text{D}_2\text{O}} = 2.7 \text{ ms}$; $[\text{EuL}^2]: \tau_{\text{H}_2\text{O}} = 0.55$, $\tau_{\text{D}_2\text{O}} = 2.1 \text{ ms}\}$ primarily because of competitive photoinduced charge transfer from the excited naphthyl singlet to the Eu^{3+} ion,^{15,16} both gave rise to well defined circularly polarised luminescence (CPL) spectra following excitation into the charge-transfer transition at 390 nm. The unpolarised luminescence is characteristic of Eu in a C_4 environment and the strength of the ${}^5\text{D}_0\text{-}{}^7\text{F}_0$ transition implies

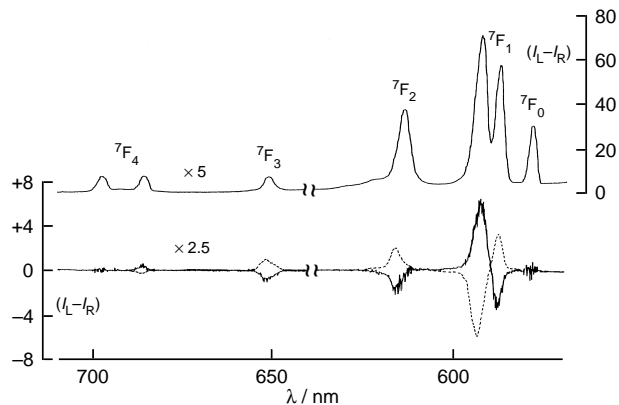


Fig. 3 Total luminescence ($I_L + I_R$) and circularly polarised luminescence spectra ($I_L - I_R$) of $[\text{Eu}\{(R)\text{-L}^1\}]^{3+}$ (solid line) and $[\text{Eu}\{(S)\text{-L}^1\}]^{3+}$ (dashed line) [$\lambda_{\text{exc}} = 395 \text{ nm}$ (Xe lamp), 293 K, MeOH, $2 \times 10^{-3} \text{ mol dm}^{-3}$]

a large axial perturbation. The ${}^5\text{D}_0\text{-}{}^7\text{F}_0$ transition at 580 nm showed no CPL, but for the allowed transitions associated with a change in magnetic dipole, e.g. ${}^5\text{D}_0\text{-}{}^7\text{F}_1$, strong CPL was clearly observed (Fig. 3). For $\{(R)\text{-L}^1\}[\text{Eu}]$, the g_{em} factors are $-0.12(\text{A})$ and $+0.18(\text{E})$ for $\Delta J = 1$, -0.1 for $\Delta J = 2$ (only the E is observed), -0.3 for $\Delta J = 3$ and -0.11 and 0 for $\Delta J = 4$. The enantiomeric Eu complexes gave rise to enantiomeric CPL spectra, and CPL spectra from $[\text{EuL}^2]^{3+}$ were very similar.

In summary, the Eu complex of L^1 gives rise to strong exciton coupling between adjacent pairs of naphthyl chromophores. In the isomeric 2-substituted Eu complex of L^2 , the naphthyl chromophores are aligned almost parallel and excimer formation occurs.

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Footnotes and References

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† Such assignments were confirmed by variable-temperature studies and by the appearance of true exciton coupling (negative chirality with a crossover at ca. 225 nm), on addition of 2 equiv. of KCl to $(R)\text{-L}^2$ (at room temperature) or CaCl_2 (revealed at -86°C). In these latter two cases, the intensities of both bands of the bisignate profile increased as the temperature was lowered. No such behaviour was observed with the free ligand L^2 .

‡ Crystal data for $\text{C}_{68}\text{H}_{75}\text{F}_3\text{N}_9\text{NaO}_6$, $M = 1194.36$, orthorhombic, $P2_12_12_1$, $a = 15.022(1)$, $b = 17.136(1)$, $c = 23.900(1) \text{ \AA}$, $U = 6152.1(8) \text{ \AA}^3$, $D_c = 1.290 \text{ g cm}^{-3}$, $\lambda(\text{Mo-K}\alpha) 0.71073 \text{ \AA}$, $Z = 4$, $\mu = 0.96 \text{ mm}^{-1}$. Data were collected on a SMART at 150(2) K. Refinement of 745 parameters with SHELXL 93, using 7364 observations converged at $R = 0.071$, $wR_2 = 0.171$ for 5660 reflections with $I > 2\sigma(I)$. CCDC 182/549.

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