COMMUNICATION

Chiroptical features and luminescence behaviour of macrocyclic tetra(4-quinolyl)-complexes: surprising absence of exciton coupling

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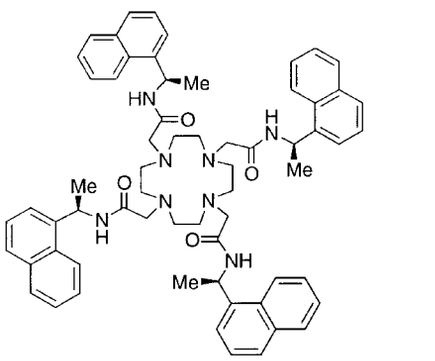
The C_4-symmetric (*S*)-tetra(4-quinolyl) tetraamide derivative of dota has been prepared. The sodium complex has been characterised by X-ray crystallography and although the quinolyl groups are appropriately oriented for exciton coupling in the solid-state, in solution no evidence for coupling was found for the free ligand nor its protonated, Na, Ca or Eu complexes. Instead, excimer formation was observed in emission consistent with a coplanar arrangement of the quinolyl groups.

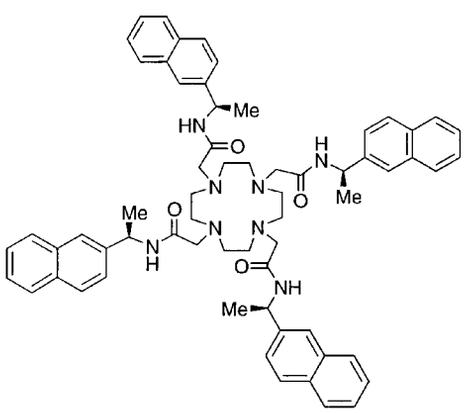
Introduction

The phenomenon of exciton coupling between non-conjugated chromophores held in proximity is frequently reported in chiral ordered polymers,[1] in micro-heterogeneous media[2] and in the solid-state.[3] Among the multitude of examples in solution, intramolecular exciton coupling typically occurs either in conformationally constrained systems—such as biaryls, steroids or helicenes[4–6]—or with chromophores possessing a high oscillator strength, such as phthalocyanines and porphyrins.[7,8] In addition, exciton coupling has been studied intensively in the octahedral, C_3-symmetric tris-chelate complexes formed by transition metal ions with bipyridine and 1,10-phenanthridine ligands.[5,9] Recently, we reported the first example of exciton coupling in a C_4-symmetric system:[10,11] in the free ligand (*S*)-L^1 at low temperature, and in its sodium, calcium and europium complexes at ambient temperature, exciton coupling of negative chirality was observed for the naphthyl ^1B_b bands around 220 nm. This observation was consistent with the structure of $[Na(R)\text{-}L^1]^+$ in the solid state, which revealed that the dihedral angles between the planes of adjacent pairs of naphthyl chromophores were *ca.* 80°—allowing efficient coupling of the electric dipole transition moments along the long axis of the naphthyl chromophores.[3] With the constitutionally isomeric 2-naphthyl ligand, markedly different behaviour was observed: no evidence for exciton coupling was found for the free ligand nor for its sodium complex in MeOH at any temperature and a small bisignate profile for the Ca^{2+} and Eu^{3+} complexes was only revealed at lower temperatures. The observation of positive chirality in the very weakly coupled naphthyl groups of (R)-$[ML^2]$ (M = Ca, Eu) suggested a radical change in the relative orientation of the ^1B_b naphthyl transition moments compared to L^1 and its complexes. This was consistent with the detection of intramolecular excimer formation for $[H_2L^2]^{2+}$ and $[EuL^2]^{3+}$, that was absent for $[EuL^1]^{3+}$.[11]

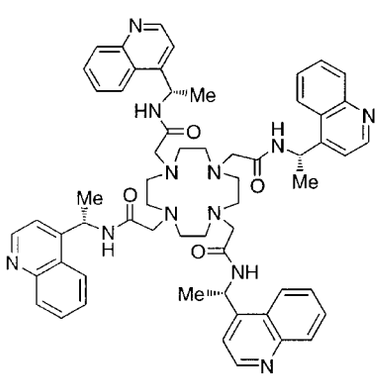
Following these studies, we elected to perturb the structure of L^1 in a minor way and set out to examine the chiroptical behaviour in the free and bound-state of the 4-substituted quinolyl analogue of L^1, *i.e.* L^3. No previous examples of exciton coupling between similar quinolyl chromophores had been reported, nor are there examples of intramolecular excimer formation with quinolines.



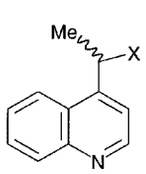
L^1



L^2



L^3



1 X = OH
2 X = OMs
3 X = N_3
4 X = NH_2

Results and discussion

Reaction of racemic 1-(4′-quinolyl)ethanol, **1**, with MsCl

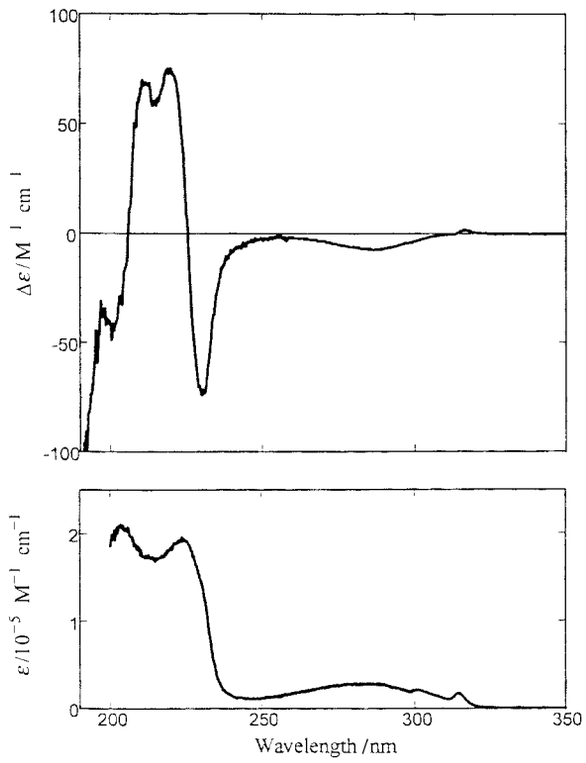


Fig. 1 Circular dichroism and absorption spectrum of L^3 (293 K, MeOH).

(Et_3N, $^iPr_2N$, CH_2Cl_2) yielded the mesylate **2** in 80% yield and subsequent addition of sodium azide (DMF, 60 °C) followed by transfer hydrogenation ($N_2H_4{\cdot}OH_2$; MeOH; $Pd(OH)_2$-C) gave the racemic amine **4**. Resolution of the amine with (*SS*)-tartaric acid (aqueous EtOH) afforded (*S*)-**4** as a pale yellow oil with an enantiomeric purity of ≥96%, as determined by ^1H NMR analysis using the chiral solvating agent (*R*)-*O*-acetylmandelic acid in $CDCl_3$.[12] Four equivalents of (*S*)-**4** were coupled with 1,4,7,10-tetraazacyclododecanetetraacetic acid (dota), (edc, HOBt, $^iPr_2NEt$, THF–H_2O, 0→20 °C), to afford a low yield of L^3 which was isolated by crystallisation from MeCN–Et_2O (20 : 1) as a colourless solid (mp > 250 °C; $[\alpha]_D^{20} = -156.6$ [*conc.* 0.22, MeOH]). The ^1H NMR spectrum of L^3 (CD_3OD, 293 K) was consistent with a species possessing time-averaged C_4 symmetry in solution (*e.g.* H(2) and H(3) resonated at 8.77 and 7.32 ($J = 4.5$ Hz)), as clean doublets, and the ring CH_2CO and CH_2N protons resonated at similar shifts to those observed for L^2 in CD_3OD (rather than L^1). The absorption spectrum of L^3 in methanol revealed intense bands at 200, (^1C_b) and 225 nm (^1B_b), together with less intense bands in the near-uv at 280 (^1L_a) and 315 nm (^1L_b).[13] The CD spectrum at ambient temperature (Fig. 1) revealed an apparent bisignate profile—with a negative band at 232 nm and a positive band at 223 nm which were 30% of the intensity of the bands seen with L^1 . In addition a weak negative band at 285 and a very weak positive band at 320 nm could be discerned. Variable temperature studies, over the range 190–290 K, showed that the bands at 232 and 223 nm *reduced* in intensity to a differing extent as the temperature was lowered. Such behaviour is not consistent with the changes expected when exciton coupling occurs, for which similar increases in intensity of the bisignate profile are expected, as the temperature is lowered. No changes in the form or intensity of the CD and absorption spectra were observed in the presence of up to 1 mM NaCl or KCl. Addition of excess $CaCl_2$ also had no observable effect on the CD spectrum in the region 200–260 nm (MeOH or H_2O–MeOH), although the intensity of the weak CD band at 285 nm reduced by 80% and the sign of the CD band at 315 nm was changed to weakly positive.

Below pH 4, reversible protonation of the quinoline moiety occurred, characterised by a shift in the ^1B_b band of 10 nm to 235 nm, with isosbestic points at 230 and 292 nm. The CD spectrum shifted to the red to a similar extent with the positive band at 230 nm reducing in intensity by ~10%, while the 240 nm band decreased in intensity by a factor of three. The fluorescence emission spectrum of L^3 was also recorded as a function of pH over the range 11 to 2. Between pH 11 and 8, a structured emission band was observed at 370 nm together with a very broad band at 430 nm whose relative intensity was independent of concentration. Under strongly acidic conditions (pH < 2.5), this broad band had virtually disappeared, and a single broad emission band at 385 nm was apparent, consistent with the shift in the π* level to lower energy that accompanies protonation. Over the intermediate pH range 3 to 6, a rather complex pH dependence was observed, characterised by the appearance of a new broad emission band at 415 nm which was not evident below pH 2.4. Taken together, this emission behaviour is characteristic of excimer formation at pH values above 7, involving the diprotonated ligand $[H_2L^3]^{2+}$. The first two protonations of L^3 fall in the range 10.5 to 12,[14] and below pH 5 successive protonation of the quinolyl groups and remaining ring nitrogens will occur. Coulombic repulsion dictates that quinolyl groups which are *trans*-disposed will protonate first, such that intermediate formation of a symmetric tetraprotonated ligand may occur—which could be associated with the formation of the 415 nm band over the pH range 6 to 3. Under higher acid concentrations, ring and quinoline N protonation compete and excimer formation is inhibited by charge repulsion. Examples of fluorescent and non-fluorescent exciplex formation with 2-substituted quinolines have been reported previously,[15] but the singular report of excimer formation in quinolyl systems is restricted to a low temperature study of quinoline itself.[16]

In MeOH solution, addition of excess $CaCl_2$ gave an emission spectrum with a monomer band at 365 nm and a less intense broad band at 430 nm was apparent as a shoulder. The europium complex of L^3 was generated *in situ* by addition of one equivalent of anhydrous $Eu(CF_3SO_3)_3$ to a methanolic solution of the ligand. The complex was characterised by electrospray mass spectrometry (*m/z* = 1470 $[EuL^3(CF_3SO_3)_2]^+$; 1321 $[EuL^3(CF_3SO_3)]^+$; 661 $[EuL^3(CF_3SO_3)_2]^{2+}$ and 391 $[EuL^3]^{3+}$) and by the characteristic europium emission and metal-based circularly polarised luminescence spectra which very closely resembled those reported for (*S*)-$[EuL^1]^{3+}$ and (*S*)-$[EuL^2]^{3+}$.[11] The pH dependence of the fluorescence emission in $[EuL^3]^{3+}$ was also examined, and in the pH region 11 to 6 a structured emission band at 370 nm was observed together with a very broad band at 425 nm which reduced in intensity below pH 6. Even at pH 2 a broad feature was observed around 405 nm, together with a broadened monomer band shifted to 360 nm. With $[EuL^2]^{3+}$, excimer formation had also been observed in aqueous media, which was *absent* with the 1-substituted isomeric complex, $[EuL^1]^{3+}$. Thus the *solution* behaviour of L^3—in the protonated form and in its complexes with Ca^{2+} and Eu^{3+}—resembles that found for L^2, notwithstanding their different constitution.

It therefore came as a surprise to find that the complex $[NaL^3]^+$† was almost isostructural with $[NaL^1]^+$ (Fig. 2), in which the aryl groups (in the solid state) are appropriately aligned for exciton coupling to occur—as had been observed with $[NaL^1]^+$ in solution at room temperature.[11] In the case of $[NaL^3]^+$, one chloride counteranion, a single well-ordered water molecule and three molecules of acetonitrile were present in the asymmetric unit. One of the CH_3CN molecules was included by the cleft defined by the quinoline groups, and the closest CH · · · Na distance was 3.38(1) Å, (Fig. 2).

In conclusion, no evidence for exciton coupling has been found in solution for L^3 and its metal complexes, so there remain no well-defined reports of exciton coupling involving quinolyl chromophores. This surprising behaviour—bearing in mind the properties shown by the tetranaphthyl analogue[11]—indicates that in solution the ligand and its complexes prefer to adopt a conformation which allows the quinolyl groups to be co-planar, in turn, giving rise to intramolecular excimer formation.

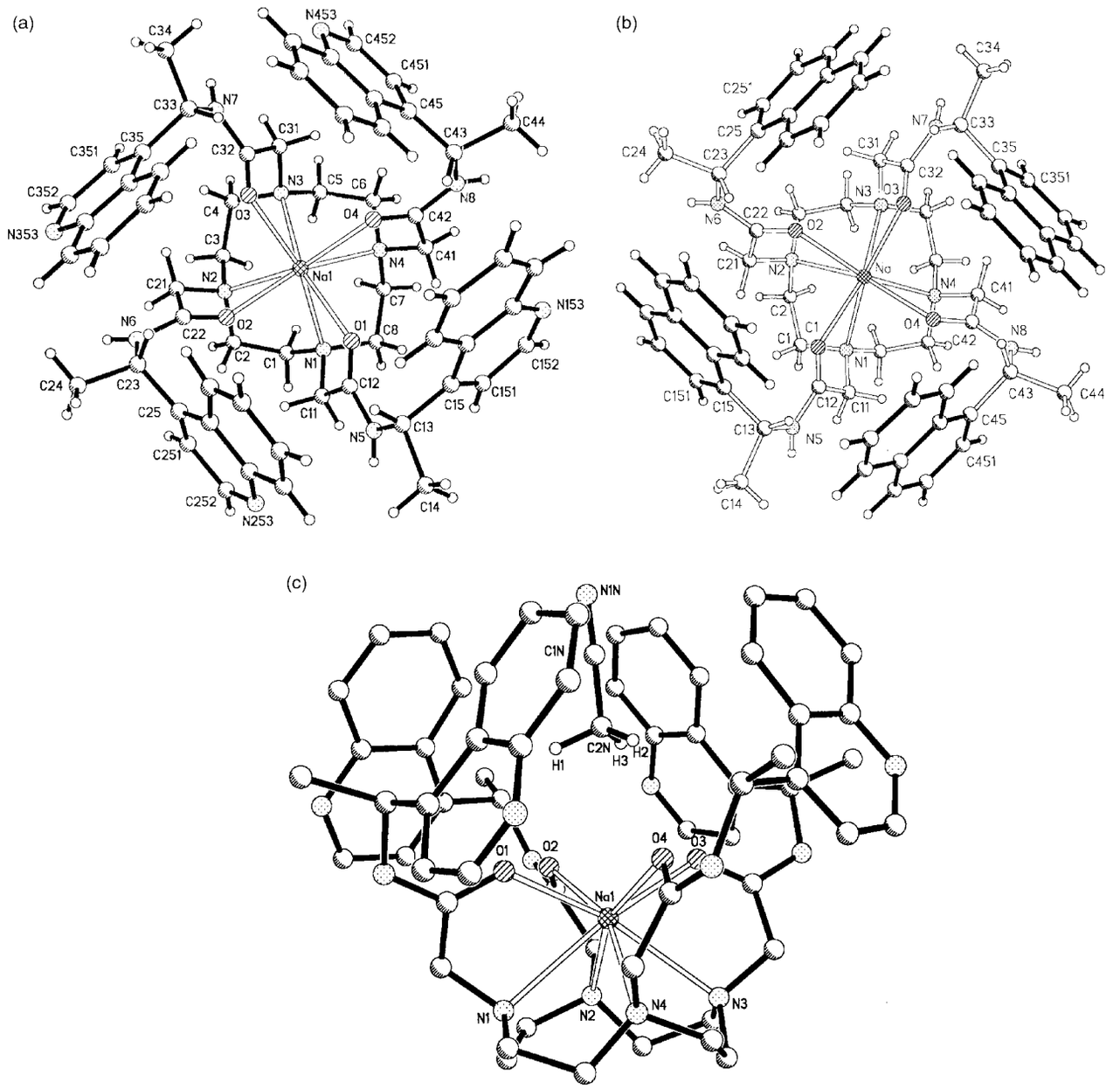


Fig. 2 Crystal structure of (*S*)-[NaL^3]$^+$ (a) compared to (b) (*R*)-[NaL^1]$^+$; in the former case the mean twist angle is 36° and the geometry about the sodium ion is slightly twisted square antiprismatic [$\Delta(\delta\delta\delta\delta)$]. (c) The included CH_3CN molecule in [NaL^3]$^+$.

Acknowledgements

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Notes and references

† *Crystal data* for $C_{64}H_{76}ClN_{14}NaO_5$, $M = 1179.83$, orthorhombic, $P2_12_12_1$, $a = 12.057(1)$, $b = 14.675(2)$, $c = 34.231(4)$ Å, $U = 6057(1)$ Å^3, $D_c = 1.294$ g cm^{-3}, $T = 150(2)$ K, crystal size = $0.25 \times 0.15 \times 0.10$ mm^3, $\lambda = 0.6875$ Å, $Z = 4$, $\mu = 0.13$ mm^{-1}. Data were collected at the Daresbury SRS on station 9.8, which is equipped with a SMART-CCD diffractometer. A wavelength setting of 0.6875 Å was calibrated using a standard ruby crystal. Data were collected using an ω scan width of 0.45° due to the uniform broadness of all the reflection profiles. The exposure time was 1 second and a crystal-detector distance of 5 cm was used. Exponential incident beam decay was corrected for by SADABS,[17] and the structure was solved using the SHELX program 'half baked', an application particularly suited to macromolecules or where data extending to atomic resolution are not available. This program uses the Shake and Bake principle of real-reciprocal space recycling to optimise the atom peaklist and also economises on computer time by maximising the normalised structure factors used. The coordinates of the complex and one solvent molecule were yielded by this solution.

The eight-coordinate sodium complex has a twisted square antiprismatic geometry where the mean N–Na–O twist angle is 36°. This complex is similar to the previously determined chiral sodium tetranaphthylamide complex derived from cyclen.[11] A chloride counterion, one well-ordered water molecule and three molecules of acetonitrile are also present in the asymmetric unit. As can be seen from Fig. 2(c), one of the acetonitrile molecules is inserted into the groove defined by the quinoline groups, the nearest solvent hydrogen being 3.38(1) Å from the metal atom. This provides a stabilising effect and the lower thermal motion in these particular solvent molecule atoms is reflected in the reduced values of their thermal parameters. The fact that this molecule is not crystallographically isostructural with its tetranaphthylamide analogue cannot be ascribed to any structure determining intermolecular interactions or conformational changes between the two complexes. One must assume that this is because of the presence of a relatively bulky trifluoroacetate counterion in the lattice of the quinoline crystal structure.

The refinement of 8734 data against 757 parameters by full-matrix least-squares[18] on F^2 converged at $R = 0.104$, $wR_2 = 0.281$ with $I > 2\sigma(I)$. All of the non-hydrogen atoms, except those on the dis-

ordered acetonitrile solvent molecule, were refined with anisotropic displacement parameters and the hydrogen atoms were placed in calculated positions. The disappointing refinement is reflected in the poor structural precision, however the data were collected from a small sample that displayed poor crystallinity. Nevertheless, the absolute structure was determined reliably, $x = -0.1(2)$, verifying the molecule to be the *S* diastereomer.

CCDC reference number 188/187. See http://www.rsc.org/suppdata/p2/1999/2415 for crystallographic files in .cif format.

1 J. H. Perlstein, in *Electrical Properties of Polymers*, ed. D. Seaner, Academic Press, New York, 1982, pp. 59–91.
2 T. Nishimi, M. Tachikawa, T. Meada, Y. Ishikawa and T. Kunitake, *Chem. Lett.*, 1994, 331; D. G. Whitten, *Acc. Chem. Res.*, 1993, **26**, 502.
3 N. Harada and K. Nakanishi, *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*, University Science Books, Mill Valley, CA, 1983; G. E. Ficken, *J. Photogr. Sci.*, 1973, **21**, 11.
4 K. Liang, M. S. Farahat, J. Perlstein, K.-Y. Law and D. G. Whitten, *J. Am. Chem. Soc.*, 1997, **119**, 830.
5 S. F. Mason, *Molecular Optical Activity and the Chiral Discriminations*, Cambridge University Press, Cambridge, 1982.
6 J. Canceill, A. Collet, G. Gotarelli and P. Palmieri, *J. Am. Chem. Soc.*, 1987, **109**, 6454.
7 S. Matile, N. Berova, K. Nakanishi, J. Fleischhauer and R. W. Woody, *J. Am. Chem. Soc.*, 1996, **118**, 5798.
8 A. Harriman, V. Heitz and J.-P. Sauvage, *J. Phys. Chem.*, 1993, **97**, 5940.
9 S. F. Mason and B. J. Heart, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 949.
10 R. S. Dickins, J. A. K. Howard, J. M. Moloney, D. Parker, R. D. Peacock and G. Siligardi, *Chem. Commun.*, 1997, 1747.
11 R. S. Dickins, J. A. K. Howard, C. L. Maupin, J. M. Moloney, D. Parker, R. D. Peacock, J. P. Riehl and G. Siligardi, *New J. Chem.*, 1998, 891.
12 D. Parker and R. J. Taylor, *Tetrahedron*, 1987, **46**, 5451; D. Parker, *Chem. Rev.*, 1991, **91**, 1441.
13 J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 484.
14 R. Kataky, K. E. Matthes, P. E. Nicholson, D. Parker and H.-J. Buschmann, *J. Chem. Soc.*, *Perkin Trans. 2*, 1990, 1425.
15 G. A. Epling and K.-Y. Lin, *J. Heterocycl. Chem.*, 1984, **21**, 1205.
16 R. P. Blaunstein and R. S. Gant, *Photochem. Photobiol.*, 1973, **18**, 347.
17 G. M. Sheldrick (1996), SADABS, Program for the correction of area detector data, University of Göttingen, Germany.
18 Bruker Analytical X-ray Instruments (1998) SHELX96. Suite of programs for the data reduction, solution and refinement of crystal structures.

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