

Luminescence Properties of the Europium(III) Complex of the Octadentate Polypyridyl Ligand 1,1'-bis[bis(2-pyridylmethyl)aminomethyl]-3,3'-biisoquinoline

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An europium(III) complex of the potentially octadentate polypyridyl ligand 1,1'-bis[bis(2-pyridylmethyl)aminomethyl]-3,3'-biisoquinoline (L^1) has been prepared. Irradiation with UV light of the compound $[Eu(L^1)]Cl_3 \cdot 3H_2O$ in water solution led to a metal-centred luminescence. The luminescence lifetimes in water and D_2O at 296 K were 0.75 and 1.35 ms, respectively. From these data the average number of coordinated water molecules was calculated to 0.6.

Over the past decade there have been numerous reports of Eu^{III} complexes that display a metal-centred luminescence in aqueous solution.¹ Such complexes might find use as luminescent labels in biological systems (fluoro-immunoassay)^{2,3} and for this application a high efficiency of converting incident (UV) photons to emitted (VIS) photons is crucial. The requirements that largely govern this efficiency are (a) the ligand includes highly absorbing chromophores (antennae), (b) the energy transfer from the ligand-centred excited states to the metal centre is fast and efficient, (c) water is excluded from the first coordination sphere of the metal ion. Recently,⁴ the preparation and the photophysical properties of the Eu^{III} complex of the podand type ligand L^2 (Fig. 1) was reported. It was shown that the energy transfer only from the bipyridine chromophore, not the pyridine chromophores, was efficient and luminescence lifetimes measurements in water and CH_3OH solutions of $[Eu(L^2)]Cl_3$ (**2**) revealed that on average 0.5 solvent ligands are present in the first coordination sphere. In order to enhance the absorption intensity of the chromo-

phore acting as the antenna, a 3,3'-biisoquinoline chromophore has been introduced in place of the bipyridine chromophore giving the compound L^1 (Fig. 1). The preparation of an europium(III) complex of L^1 is reported here along with its luminescence properties in aqueous solution.

Experimental

Materials. The compound 1,1'-bis(bromomethyl)-3,3'-biisoquinoline was prepared by literature methods.⁵ Bis(2-pyridylmethyl)amine was obtained from Nepera and distilled prior to use. $EuCl_3 \cdot 6H_2O$ (99.9%) and trimethyl orthoformate were obtained from Aldrich.

Preparations

1,1'-bis[bis(2-pyridylmethyl)aminomethyl]-3,3'-biisoquinoline (L^1). Bis(2-pyridylmethyl)amine (0.45 g, 2.26 mmol), 1,1'-bis(bromomethyl)-3,3'-biisoquinoline (0.50 g, 1.13 mmol) and Na_2CO_3 (2 g) were added to acetonitrile (1 l). The mixture was stirred and refluxed for one week then cooled to room temperature and filtered. The filtrate was evaporated to dryness. The brown solid was washed with small portions of acetonitrile (3×3 ml) and then redissolved in acetonitrile (100 ml) under warming and added dropwise to a solution of $CuSO_4 \cdot 5H_2O$ (0.65 g, 2.6 mmol) in water (20 ml). The resulting blue precipitate $[Cu_2(SO_4)_2(L^1)] \cdot 7H_2O$ was filtered off and washed with water, ethanol and diethyl ether and air-dried (0.5 g). Calc. for $C_{44}H_{52}N_8Cu_2S_2O_{15}$: C, 47.01; H, 4.66; N, 9.97; Cu, 11.30. Found: C, 47.02; H, 4.34; N, 9.86;

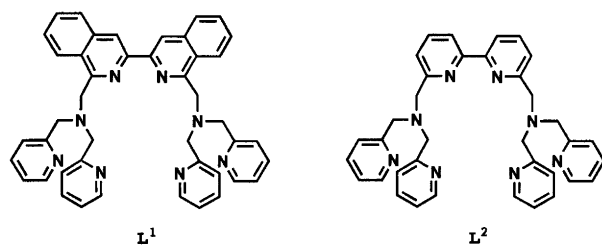


Fig. 1. Structural formulae of the compounds L^1 and L^2 .

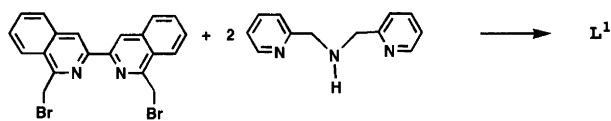
Cu 11.11. For decomplexation the complex was stirred with a mixture of 12 M NH_3 (25 ml) and CH_2Cl_2 (25 ml). The mixture was stirred until the aqueous phase was blue and clear. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2×25 ml). The combined organic extracts were dried (Na_2SO_4) and the solvent evaporated leaving a pale-brown product (400 mg, 52%). Calc. For $\text{C}_{44}\text{H}_{38}\text{N}_8$: C, 77.85; H, 5.64; N, 16.51. Found: C, 76.88; H, 5.54; N, 16.21. UV (CH_3OH , $\lambda_{\text{max}}/\text{nm}$, $\epsilon_{\text{max}}/10^3 \text{ M}^{-1} \text{ cm}^{-1}$). (330, 22.0), (312, 26.3), (254, 60.2). $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): δ 3.91 (s, 8 H), 4.36 (s, 4 H), 7.05 (t, J 6.2 Hz, 4 H), 7.38–7.45 (m, 6 H), 7.53 (t, J 7.6 Hz, 4 H), 7.59 (t, J 7.6 Hz, 2 H), 7.86 (d, J 8.1 Hz, 2 H), 8.16 (d, J 8.4 Hz, 2 H), 8.42 (d, J 4.5 Hz, 4 H), 8.74 (s, 2 H).

$[\text{Eu}(\text{L}^1)]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ (**1**). $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (43 mg, 0.12 mmol) and trimethyl orthoformate (1.5 ml, 14 mmol) was added to acetonitrile (20 ml). The mixture was refluxed for 2 h. Then L^1 (80 mg, 0.12 mmol) was added and the mixture was refluxed for additional 1 h. The solvent was evaporated off and the white residue was redissolved in ethanol (10 ml). The solution was filtered and the complex was reprecipitated by addition of diethyl ether (100 ml). The product was washed with diethyl ether and air-dried (100 mg). For recrystallization the product was dissolved in ethanol (1 ml) and reprecipitated by vapour diffusion of diethyl ether into the solution (62 mg, 52%). Calc. For $\text{C}_{44}\text{H}_{44}\text{N}_8\text{EuCl}_3\text{O}_3$: C, 53.32; H, 4.47; N, 11.30; Cl, 10.73. Found: C, 54.01; H, 4.62; N, 11.23; Cl, 10.60. UV (CH_3OH , $\lambda_{\text{max}}/\text{nm}$, $\epsilon_{\text{max}}/10^3 \text{ M}^{-1} \text{ cm}^{-1}$). (327, 17.2), (260, 58.3).

Other physical measurements. Optical absorption spectra were recorded on a Perkin–Elmer Lambda 17 spectrophotometer. NMR spectra were recorded on a Varian 400 MHz spectrometer. The luminescence spectra and decays were recorded on a Perkin–Elmer LS 50 spectrofluorimeter. The decays were analyzed with a least-squares fitting program. The luminescence quantum yields were obtained as described by Haas⁶ using $[\text{Ru}(\text{bpy})_3]^{2+}$ as a standard ($\Phi = 0.028$ in aerated water⁷). Elemental analyses of C, H, N and Cl were made at the H. C. Ørsted Institute, University of Copenhagen.

Results and discussion

Syntheses. In the syntheses of L^1 the functionalized 3,3'-biisoquinoline was alkylated in reasonable yield with two equivalents of bis(2-pyridylmethyl)amine as shown in Scheme 1. The starting material 1,1'-bis(bromomethyl)-3,3'-biisoquinoline is only sparingly soluble in



Scheme 1. Synthesis of L^1 .

acetonitrile and this necessitated a long reaction time. A very convenient way to purify L^1 is to complex with copper(II) sulfate, giving the complex $[\text{Cu}_2(\text{SO}_4)_2(\text{L}^1)] \cdot \text{aq}$ followed by decomplexation with 12 M NH_3 , a method used in the preparation of L^2 .⁸ In the preparation of **1**, the crystal water in the starting material, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, was removed by refluxing with trimethyl orthoformate before addition of L^1 . In this way the possible formation of hydroxo and/or polynuclear complexes was avoided.

Absorption spectra. The absorption spectrum in CH_3OH of the compound L^1 is shown in Fig. 2. The absorption band at 254 nm is a mixture of pyridine- and biisoquinoline-centred absorptions, and the bands at 312 and 330 nm are biisoquinoline-centred. An absorption spectrum of **1** in CH_3OH is shown in Fig. 2, and a red shift of the biisoquinoline-centred bands is seen. Such redshifts are commonly observed.¹ From the spectrum of the **1** in water (Fig. 2) the presence of free ligand is clearly seen. The dissociation of **1** is therefore more pronounced in aqueous solution than in CH_3OH , showing that water molecules are more strongly bound to the europium ion than CH_3OH molecules. Precipitation of L^1 from aqueous solution of **1** was observed at complex concentration above $\sim 5 \times 10^{-5} \text{ M}$. The absorption spectrum of **1** in CH_2Cl_2 solution matches closely with the spectrum in CH_3OH . The solvent CH_2Cl_2 is not expected to promote any significant dissociation, so the similarity between the spectra in CH_2Cl_2 and CH_3OH indicates that no substantial dissociation of **1** occurs in CH_3OH either.

Luminescence. Compound **1** is highly luminescent in the solid state and in aqueous solution. The emission spectrum consists of several sharp peaks originating from decays from the $^5\text{D}_0$ excited state to the $^7\text{F}_J$ ($J=0-6$) ground-state manifold, the most intense at 613 nm. The

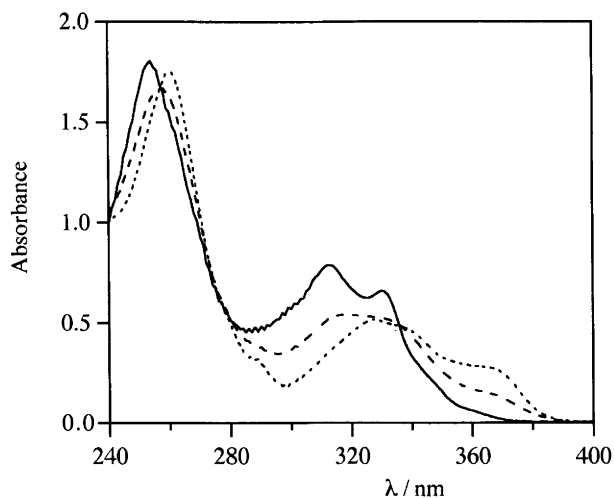


Fig. 2. Optical absorption spectra of L^1 in CH_3OH (—) and of **1** in CH_3OH (···) and in water (---), $C = 3.00 \times 10^{-5} \text{ M}$.

excitation spectrum of **1** in water ($\lambda_{\text{analysis}}=613$ nm) is shown in Fig. 3. From comparison with the absorption spectrum of **1** in CH_3OH it is seen that the relative intensity of the band at 260 nm in the excitation spectrum is lower than in the absorption spectrum. Both the biisoquinoline and the pyridine chromophores absorb at 260 nm (see above), so the lower relative intensity at 260 nm in the excitation spectrum could be due to an inefficient energy transfer from the excited pyridine chromophores to the metal centre. This behaviour was indeed observed in the case of **2**.⁴ From luminescence lifetime measurements ($\lambda_{\text{analysis}}=613$ nm) in water and D_2O at 296 K, which were 0.75 and 1.35 ms, respectively, the number of coordinated water molecules could be estimated by the use of the Horrocks formula [eqn. (1)].^{9,10}

$$n_{\text{H}_2\text{O}} = k(1/\tau_{\text{H}_2\text{O}}^{296} - 1/\tau_{\text{D}_2\text{O}}^{296}) \quad (1)$$

Here $\tau_{\text{H}_2\text{O}}^{296}$ and $\tau_{\text{D}_2\text{O}}^{296}$ denote the emission lifetime at 296 K in H_2O and D_2O solution, respectively, k is a constant, 1.05, empirically determined for Eu^{III} . Use of eqn. (1) gives $n_{\text{H}_2\text{O}}=0.6$. The value of $n_{\text{H}_2\text{O}}$ is considered to have an uncertainty of ± 0.5 , so the complex **1** could in aqueous solution have either zero or one metal-bonded water molecule. The decays were monoexponential. However, multiexponential decays with rather similar rate constants could occur, but the number of data (20) did not allow such fits. With this reservation in mind, it can be concluded that once the metal ion is coordinated to the biisoquinoline group it is (almost) fully wrapped by the pyridine groups. The emission quantum yields are dependent on the irradiation wavelength. Irradiation at 375 nm gave $\Phi=0.042$ in water at room temperature. At this wavelength only the biisoquinoline chromophore is excited, not the pyridine chromophores (see discussion above). Furthermore, the presence of free ligand in the solution does not interfere with the quantum yield measurements, since the free ligand does not absorb at the excitation wavelength (Fig. 2). The emission quantum yield is close to the emission quantum yield determined for **2** (0.046).⁴ The much lower emission quantum yield at $\lambda_{\text{ex}}=260$ nm, $\Phi=0.009$, could be due to two reasons. Firstly, the free ligand does absorb at that wavelength, and secondly, the pyridine groups are also irradiated. We have found in the case of **2** that irradiation of the pyridine chromophores does not lead to a substantial metal-centred emission, and this could be the case as well for **1**. This is also in accordance with the conclusion made from comparison of the excitation and absorption spectra (see above).

In conclusion, the ligand **L**¹, as **L**², efficiently wraps the metal centre, thereby excluding water molecules from the first coordination sphere of the metal. The experimental data indicate that only the biisoquinoline chromo-

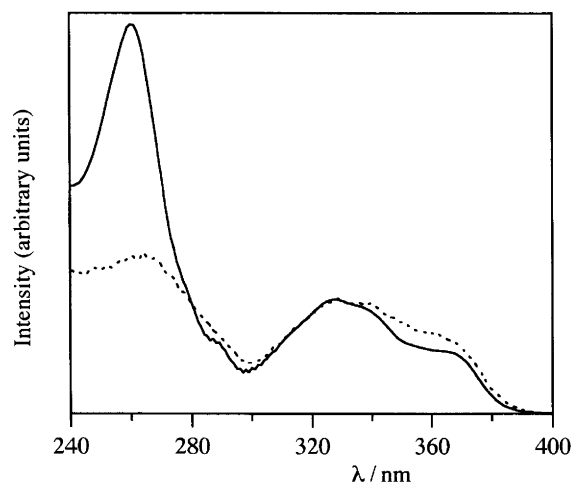


Fig. 3. Excitation spectrum (---, $\lambda_{\text{em}}=613$ nm) of **1** in water at 296 K. For comparison the absorption spectrum (—) of **1** in CH_3OH is shown.

phore, and not the pyridine chromophores, acts as the antenna. The pyridine groups serve only to shield the metal centre from the solvent molecules. The energy of the excitation photons has been lowered, an advantage for the possible application in fluoroimmunoassay. The absorption efficiency of the antenna has been enhanced in comparison with **L**². However, one major drawback in this system is the low solubility of the free ligand in water which promotes the dissociation of the europium(III) complex.

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