Synthesis and Luminescent Properties of a Eu$^{\text{III}}$ Complex with a Macrocyclic Ligand incorporating 2,2′-Bipyridyl-1,1′-dioxide Units

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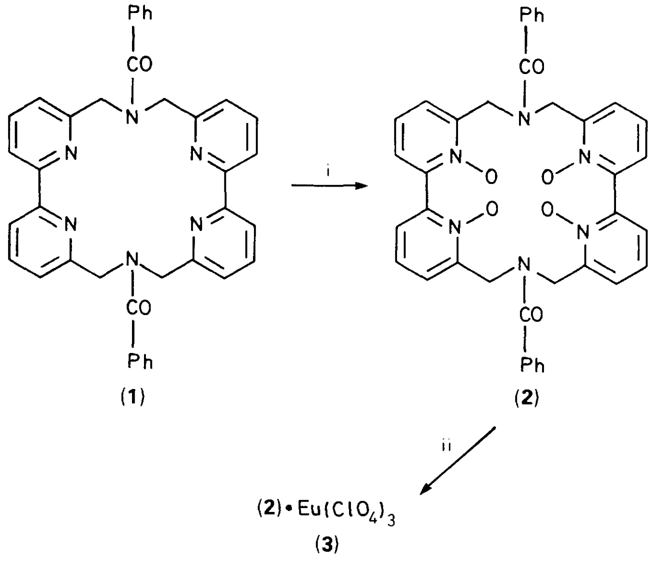
A novel ligand incorporating two 2,2′-bipyridyl-1,1′-dioxide units forms a very stable Eu$^{\text{III}}$ complex, which exhibits very excellent luminescent characteristics in water solution.

Over the past few years there has been great interest in the design, synthesis, and photophysics of luminescent lanthanide cryptates bearing heterocyclic units as potential probes in fluoroimmunoassays.[1]

Since heteroaromatic *N*-oxides form strong and highly luminescent complexes with lanthanide ions,[2] it was logical to introduce them into a macrocyclic structure to achieve greater stability of the lanthanide complexes and good fluorescent properties in water solution.

The initial ligand (**1**) was prepared according to the



Scheme 1. *Reagents and conditions*: i, *m*-ClPhCO$_3$H (10 equiv.), CHCl$_3$, 20 °C, 10 h; ii, Eu(ClO$_4$)$_3$ (1 equiv.), MeCN, 20 °C.

literature,[3] and oxidized with *m*-chloroperbenzoic acid to form the tetra-*N*-oxide (**2**) (82%),† as illustrated in Scheme 1. Compound (**2**), insoluble in MeCN, solubilized instantly in MeCN upon addition of one equivalent of Eu(ClO$_4$)$_3$. Slow evaporation yielded quantitatively a microcrystalline complex (**3**),† whose FAB MS and microanalytical data are consistent with a 1 : 1 formula (Scheme 1).

It turned out that the Eu^{III} complex (**3**), although sparingly soluble in water, showed very bright luminescence in water solution when excited with UV light at 294 nm. The intensity of luminescence did not drop for several months, indicating that the complex is very stable in an aqueous medium.

The fluorescence spectrum of the complex (**3**), recorded in water solution, consists of four lines at 581, 593, 614, and 700 nm, with the strongest one at 614 nm, as shown in Figure 1. The total quantum yield of the luminescence has been evaluated by using the (1,1′-dimethyl-3,3′-bi-isoquinoline-*N*,*N*′-dioxide)$_2$EuCl$_3$ complex[4] as a standard, and was found to be 0.016 (estimated error 3.0%).

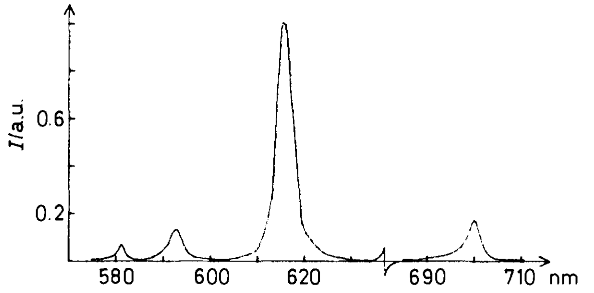


Figure 1. Corrected fluorescence spectrum of the complex (**3**) in water solution. Sample not deoxygenated.

Good luminescent characteristics and excellent stability of the complex (**3**) in water seem to be very promising with respect to its potential applications as a fluorescent probe in fluoroimmunoassays.

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† *Spectroscopic data* for (**2**): ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.94—6.75 (22H, m, aromatic), 4.97—4.13 (8H, m, CH$_2$); UV λ (CHCl$_3$) 273 (ε 19000); FAB(+) MS 667 (*M*H$^+$), 651 (*M*H − O), 635 (*M*H − 2O), 619 (*M*H − 3O), 603 (*M*H − 4O). For (**3**): UV λ (MeCN) 307 (ε 7400); FAB(+) MS 1017 (*M* − ClO$_4$).