Synthesis of a new 2,6-bis-(oxazole)pyridine ligand as a sensitiser for luminescent Ln (III) complexes

Paula M.T. Ferreira, José A. Martins, Elisabete M.S. Castanheira, Miguel F. Ferreira, Goreti Pereira.

\textit{a} Centro de Química (CQ-UM), University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; \textit{b} Centro de Física (CFUM), University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

pmf@quimica.uminho.pt

The lanthanides emission is due to $f-f$ transitions which are spin and parity forbidden. However to overcome this limitation organic ligands has been used as sensitizers. Recently, several bis(oxazolines)pyridine ligands were used as sensitizers in highly luminescent Ln(III) complexes.\textsuperscript{1} In our research group we have developed a new and efficient method for the synthesis of oxazole derivatives from $N$-acyl-threonines.\textsuperscript{2} Herein we report the synthesis and application of a new 2,6-(bis-oxazole)pyridine derivative as a ligand for Ln(III) ions. The synthesis of the organic sensitiser involved the synthesis of a bis-threonine (1) which was dehydrated with Boc$_2$O and DMAP followed by treatment with TMG (2). Compound 2 was brominated with NBS (3) and treated with a 2% solution of DBU to give the corresponding bis-oxazole (4) in a good yield (Scheme 1).

![Scheme 1](image1)

Compound 4 was used for complexation with Eu(III) and Tb(III) ions and the photophysical properties of these complexes in acetonitrile were investigated. Normalized absorption and luminescence spectra of solutions (1×10$^{-4}$ mol.dm$^{-3}$) of [3:1] complexes of compound 4 with Eu(III) (dashed line) and Tb(III) (solid line) ions, in acetonitrile are shown in Figure 1. The Ln(III) luminescence was obtained through excitation of the 2,6-bis-(oxazole)pyridine moiety that acts as sensitiser.

**Acknowledgments:** This work was funded by Foundation for Science and Technology (FCT) and FEDER through CQ-UM, CFUM, National NMR Network (Bruker 400), research project PTDC/QUI/81238/2006 (cofinanced by FCT and FEDER/COMPETE) and PhD grant of G.P. SFRH/BD/38766/2007 and of M.F.F. SFRH/BD/63994/2009.
