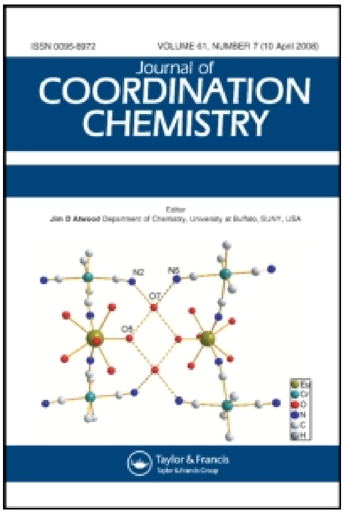

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A 3,3'-bhsoquinoline-2,2'-dioxide with two dibenzoylmethane side-arms, and its luminescent europium (iii) complexes

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NOTE

A 3,3′-BIISOQUINOLINE-2,2′-DIOXIDE WITH TWO DIBENZOYLMETHANE SIDE-ARMS, AND ITS LUMINESCENT EUROPIUM (III) COMPLEXES

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C-alkylation of dibenzoylmethane by 1,1′-*bis*(bromomethyl)-3,3′-biisoquinoline-2,2′-dioxide leads to an acyclic ligand capable of forming europium (III) complexes in its neutral or ionized forms. The neutral 1:1 complex with $EuCl_3$ showed red fluorescence when irradiated at 330 nm, with the strongest emission line at 614 nm; the quantum yield was 0.05. The ionized ligand forms complexes with EuCl(II) and $CF_3SO_3Eu(II)$ with very similar fluorescence spectra, except for unexpectedly low quantum yields.

Keywords: 3,3′-Biisoquinoline-2,2′-dioxide; dibenzoylmethane; europium; fluorescence

INTRODUCTION

Lanthanide cations form strongly fluorescent complexes with 1,3-diketones in their ionized form,[1] and with heterocyclic *N*-oxides.[2] Our interest in light-converting supramolecular devices based on the Absorption Energy Transfer Emission process led us to consider the combination of both 1,3-diketones and heterobiarylic *N*,*N*-dioxides as sensitizers for lanthanide emission with the aims of better quantum yields and possible formation of dinuclear lanthanide complexes. Such luminescent materials may be of interest as fluorescent markers for advanced medical diagnostics based on labelled monoclonal antibodies.[3]

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EXPERIMENTAL

General Procedures

All chemicals were purchased form Fluka or Aldrich and were used as received, except for methylene chloride which was distilled over CaH_2. NMR spectra were recorded on a Varian Gemini 200 MHz instrument in $CDCl_3$ solution with TMS as internal standard. IR spectra were recorded on a Beckman spectrometer, and MS on an Intectra AMD-604 spectrometer. Fluorescence spectra were recorded on a spectrofluorimeter constructed by *Jasny*.[4] Quantum yields and luminescence lifetimes were measured as in ref. 5. Microanalyses were carried out by the Institute of Organic Chemistry, Polish Academy of Sciences.

Synthesis of the Ligand (L)

1,1′-Bis(bromomethyl)-3,3′-biisoquinoline-2,2′-dioxide (0.948 g, 2 mmol), dibenzoylmethane (0.896 g, 4 mmol) and cesium carbonate anhydrous (1.3 g, 4 mmol) were placed in methylene chloride (300 cm^3) and stirred at room temperature for three days. Inorganic solids were filtered off and the filtrate evaporated under reduced pressure. The residue was chromatographed on silica (Merck 60, 230–400 mesh) with 5% MeOH in methylene chloride as eluent. The product was crystallized from methylene chloride-diethyl ether to give colourless crystals. Yield: 0.503 g, 33%.

Synthesis of $EuLCl_3.H_2O$

The ligand (0.038 g, 0.05 mmol) in MeCN (5 cm^3) was treated with an equimolar amount of anhydrous $EuCl_3$ (0.013 g, 0.05 mmol), and the solution was stirred at 60°C for two hours. The clear yellow solution was treated with diethyl ether to precipitate the product. Yield: 0.044 g, 86%. The product was recrystallized from MeCN by vapour diffusion with diethyl ether.

Synthesis of $EuLH_{-2}Cl.H_2O$ and its Trifluoromethanesulfonate Analogue

The ligand (0.038 g, 0.05 mmol) and anhydrous $EuCl_3$ (0.013 g, 0.05 mmol), or $Eu(SO_3CF_3)_3$ (0.030 g, 0.05 mmol) were mixed in MeCN (5 cm^3) and the calculated amount of a methanolic solution of LiOMe (0.1 mmol) was added. A white precipitate was filtered off, and into the filtrate was added diethyl ether by vapour diffusion. The complexes slowly separated and were isolated as above. Both complexes were obtained in *ca* 45% yield.

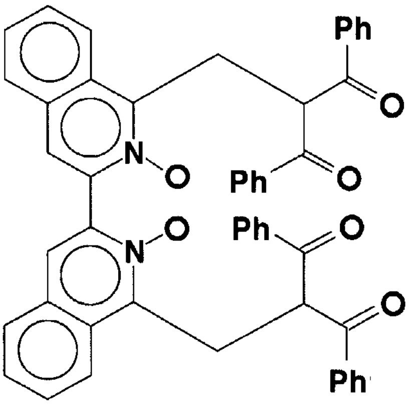
TABLE I Spectroscopic data and analyses for the compounds

L	IR (KBr, cm^{-1}) $\nu_{C=O}$ 1690, $\nu_{N\text{-}O}$ 1262. ^{1}HNMR ($CDCl_3$, δ), 4.10(d,4H, J = 6.95 Hz, 2 × CH_2), 6.79(t, 2H, J = 6.96 Hz, 2 × **CH**-CH_2), 7.10–8.40(m, 20H, aromatic protons). MS (EI, 70 eV) 761[M^+ + 1],783[M^+ + Na]. *Anal.* Calc. (%): C, 77.50; H, 5.09; N, 3.93. Found: C, 77.31; H, 4.83; N, 4.98.
$EuLCl_3.H_2O$	IR (KBr, cm^{-1}) $\nu_{C=O}$ 1690, $\nu_{N\text{-}O}$ 1260. Fluorescence (MeCN, λ_{exc} = 330 nm) 579, 594, 615 s, 622, 653, 703 nm. *Anal.* Calc.(%): C, 55.87; H, 3.88; N, 2.83. Found: C, 57.79; H, 3.78; N, 2.78.
$EuLH_{-2}Cl.H_2O$	IR (KBr, cm^{-1}) $\nu_{C=O}$ 1670, $\nu_{N\text{-}O}$ 1200. Fluorescence (MeCN, λ_{exc} = 330 nm), 592, 615 s, 653, 703 nm. Anal. Calc. C, 62.12; H,4.17; N, 3.05; found C, 62.04; H, 2.97; N, 3.01.
$EuLH_{-2}CF_3SO_3.H_2O$	IR (KBr, cm^{-1}) $\nu_{C=O}$ 1680, $\nu_{N\text{-}O}$ 1200. Fluorescence (MeCN, λ_{exc} = 330 nm) 580, 594, 615 s, 653, 702 nm. Anal. Calc. (%) C,54.64; H, 3.71; N, 2.71. Found: C, 56.59; H, 3.67; N, 2.68

RESULTS AND DISCUSSION

We selected 3,3′-biisoquinoline-2,2′-dioxide as the host ligand to which two dibenzoylmethane residues are attached. 3,3′-Biisoquinoline-2,2′-dioxide is a particularly efficient sensitizer for Eu(III) emission,[5] it was hoped to increase the performance of the whole assembly by introducing the two additional photoactive units.

1,1′-*Bis*(bromomethyl)-3,3′-biisoqiunoline-2,2′-dioxide[5] reacted with dibenzoylmethane in the presence of cesium carbonate in methylene chloride to give the ligand.[6] A Eu(III) complex with the neutral ligand formed in MeCN solution at elevated temperatures. The dibenzoylmethane residues could be ionized in the complex upon addition of a calculated amount of a strong base.



All complexes are easily soluble in acetonitrile. Their fluorescence spectra were recorded at room temperature in MeCN. The complex with the neutral ligand displayed several bands at 581, 593, 613 (the strongest), 620, 653 and 703 nm, when irradiated at 330 nm, with a quantum yield for Eu(III) emission of 0.05. Complexes of the anionic ligand had very similar fluorescence characteristics with bands at 581, 593, 615 (the strongest), 653 and 702 nm.

It has already been found that 1,1′-dimethyl-3,3′-biisoquinoline-2,2′-dioxide forms a 2:1 complex with $EuCl_3$ that displays outstanding photoactive features.[5] Its quantum yield was found to be 0.25 in MeCN. In the present case, the efficiency of one 3,3′-biisoquinoline-2,2′-dioxide unit accounts for only 0.05 conversion efficiency of absorbed UV light in the 1:1 complex with $EuCl_3$. The side arms remain photochemically inactive, since they are not expected to participate in coordination to Eu(III). However, when the side arms are charged by treatment with base, they are supposed to be ion-paired with Eu(III). In this way, there was an additional contribution expected in the energy transfer from the excited state of the 1,3-diketonate units to the Eu(III) cation. Surprisingly, the quantum yields for the emission of the Cl^- and $CF_3SO_3^-$ complexes were 0.003 and 0.028, respectively. Molecular models show that six-coordination around Eu(III) by doubly ionized ligand is difficult, due to steric crowding involving the two bulky dibenzoylmethane units. Therefore it is likely that binding at Eu(III) cation is not particularly efficient. Future design will involve longer side-arms of the same type that should be able to enclose the lanthanide cation more efficiently.

Acknowledgments

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