

Photoactive Eu(III) and Tb(III) Complexes of Calix[4]arenes with Pyridine-*N*-oxide Pendant Groups

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(Received: 4 December 1990)

Abstract. Two calix[4]arenes with four 2-pyridylmethyl-1-oxide pendant groups at the lower rim have been synthesized, and their Tb(III) and Eu(III) complexes are fluorescent upon UV light excitation at 312 nm. The complexes are not stable in aqueous solution, completely losing their luminescent properties.

Key words. Lanthanide calix[4]arene complexes, luminescence spectra.

1. Introduction

Calixarenes are a class of hydrophobic macrocyclic receptors composed of phenolic units linked by methylene bridges [1]. The versatility of these compounds has been demonstrated by a variety of functionalizations at the lower rim (phenolic OH groups), such as ester [2], keto [3], amide [4], and 2-pyridylmethyl derivatives [5, 6], providing a vast number of interesting ligands with desirable properties.

It has been reported recently that calix[4]arenes may be functionalized at the hydroxyl groups to form tetrakis-[(2-pyridylmethyl)oxy]calix[4]arenes in the fixed cone conformation [5].

Our interest in luminescent lanthanide macrocyclic complexes involving heterocyclic *N*-oxides [7] prompted us to synthesize the tetrakis-[(2-pyridylmethyl-1-oxide)oxy] derivatives shown in Chart I as potential photoactive ligands for the formation of luminescent complexes with lanthanide cations. They combine the preorganization of the calix[4]arene skeleton in the fixed cone conformation with the proclivity of convergent pyridine-*N*-oxide ligating groups to act as effective sensitizers for the emission of lanthanide ions. To date there have been only a few reports on lanthanide complexes with calixarenes [8].

2. Experimental

The tetrakis-[(2-pyridylmethyl)oxy]calix[4]arene precursors ($Z = \text{CMe}_3, \text{H}$) were synthesized according to a reported procedure [5].

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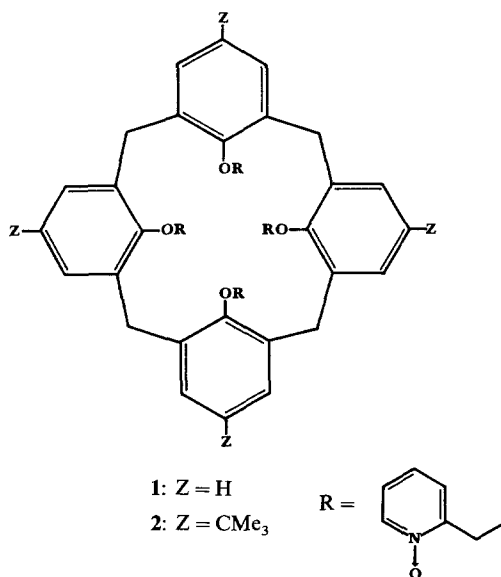


Chart I. Calix[4]arenes with 2-pyridylmethyl-1-oxide pendant groups.

Proton NMR spectra were recorded on a Bruker AC 250 or AM 500 spectrometer using CDCl₃ as solvent, with Me₄Si as the internal standard. Positive ion FAB mass spectra were obtained on a Kratos MS 50 double-focusing mass spectrometer, equipped with a standard FAB source, using 3-nitrobenzylalcohol as a matrix.

MCPBA OXIDATION OF 25,26,27,28-TETRAKIS[(2-PYRIDYLMETHYL)OXY]CALIX[4]ARENES: GENERAL PROCEDURE

Each calix[4]arene (0.1 mmol) was dissolved in anhydrous chloroform (5 mL) and treated at 0°C with MCPBA (0.8 mmol). The reaction mixture was stirred for 2 h, then the solvent was evaporated. The residue was washed with Et₂O to leave the crude tetra-*N*-oxide, which was dissolved in CHCl₃ (20 mL) and stirred with anhydrous K₂CO₃ for 0.5 h to remove residual acids. Filtration and evaporation gave the pure ligand, which was stored in a vacuum desiccator over P₂O₅.

25,26,27,28-TETRAKIS[(2-PYRIDYLMETHYL-1-OXIDE)OXY]CALIX[4]ARENE 1

72% yield; ¹H NMR (500 MHz) δ 3.30 and 4.61 (ABq, *J* = 14.2 Hz, ArCH₂Ar, 8 H), 5.40 (s, OCH₂Py—O, 8 H), 6.58–6.67 (m, ArH, 12 H), 7.20 (td, *J* = 6.4, 1.4 Hz, Py—O, 4 H), 7.40 (t, *J* = 7.7 Hz, Py—O, 4H), 8.26 (d, *J* = 7.7 Hz, Py—O, 4 H), and 8.33 (d, *J* = 6.4 Hz, Py—O, 4 H); FAB(+) MS, *m/z* 853 (M + 1).

Anal. Calcd. for C₅₂H₄₄N₄O₈: C, 73.22; H, 5.20; N, 6.57. *Found*: C, 73.19; H, 5.29; N, 6.48.

5,11,17,23-TETRA-*t*-BUTYL-25,26,27,28-TETRAKIS[(2-PYRIDYLMETHYL-1-OXIDE)OXY] CALIX[4]ARENE **2**

83% yield; $^1\text{H NMR}$ (250 MHz) δ 1.10 (s, CMe_3 , 36 H), 3.15 and 4.45 (ABq, $J = 12.7$ Hz, ArCH_2Ar , 8 H), 5.22 (s, $\text{OCH}_2\text{PY-O}$, 8 H), 6.87 (s, ArH , 8 H), 7.01 (t, $J = 7.3$ Hz, Py-O , 4 H), 7.12 (td, $J = 6.9, 2.0$ Hz, Py-O , 4 H), 7.90 (dd, $J = 7.7, 1.8$ Hz, Py-O , 4 H), and 8.26 (d, $J = 6.2$ Hz, Py-O , 4 H); FAB (+) MS, m/z 1078 ($\text{M} + 1$).

Anal. Calcd. for $\text{C}_{68}\text{H}_{76}\text{N}_4\text{O}_8$: C, 75.81; H, 7.11; N, 5.20. *Found*: C, 75.76; H, 7.02; N, 5.15.

PREPARATION OF LANTHANIDE COMPLEXES OF **1**

Solutions of ligand **1** (0.1 mmol) in MeCN (2 mL) and lanthanide salt ($\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 0.1 mmol) in absolute EtOH (2 mL) containing triethyl orthoformate (0.5 mL) were mixed together to give the desired complexes, which precipitated instantly in almost quantitative yield. They were filtered off, washed with MeCN, and dried in vacuum over P_2O_5 . The complexes were poorly soluble in most organic solvents.

1-EuCl₃ Complex: IR (KBr) 1465, 1240 cm^{-1} ; FAB (+) MS, m/z 1076 ($\text{M} - \text{Cl}$).

Anal. Calcd. for $\text{C}_{52}\text{H}_{44}\text{N}_4\text{O}_8 \cdot \text{EuCl}_3$: C, 56.20; H, 3.99; N, 5.04.
Found: C, 56.10; H, 3.93; N, 4.98.

1-TbCl₃ Complex: IR (KBr) 1450, 1230 cm^{-1} ; FAB (+) MS, m/z 1084 ($\text{M} + 1 - \text{Cl}$).

Anal. Calcd. for $\text{C}_{52}\text{H}_{44}\text{N}_4\text{O}_8 \cdot \text{TbCl}_3$: C, 55.85; H, 3.96; N, 5.01.
Found: C, 55.79; H, 3.93; N, 4.96.

3. Results and Discussion

Tetrakis[2-pyridylmethyl-1-oxide]oxy]calix[4]arenes **1** and **2** were obtained in good yield by oxidation of the appropriate precursors with an excess of *m*-chloroperbenzoic acid (MCPBA) in CHCl_3 solution at 0°C . Their positive ion FAB mass spectra display prominent molecular ion peaks, and the $^1\text{H NMR}$ pattern of the bridging methylenes is commensurate with a fixed cone conformation in solution [9].

Treatment of **1** with one equivalent of lanthanide salt[Eu(III) or Tb(III)] in MeCN solution in the presence of triethyl orthoformate [10] produced the corresponding complexes in a nearly quantitative yield. FAB (+) MS evidence and microanalytical data are consistent with a 1 : 1 stoichiometry of the complexes.

The absorption spectra of Tb(III) and Eu(III) complexes with **1** in MeOH are practically identical, and consist of one broad band with a maximum at 263 nm. When compared with the spectrum of the free ligand, they exhibit a small (*ca* 400 cm^{-1}) shift to shorter wavelength.

The luminescence spectra of these complexes have been recorded on a Jasnys spectrofluorimeter [11]. The spectra were calibrated for spectral response of the detection system. The fluorescence spectrum of the Eu(III) complex (Figure 1) displays five distinct lines at 580, 592, 616 (the strongest one), 654, and 700 nm. The

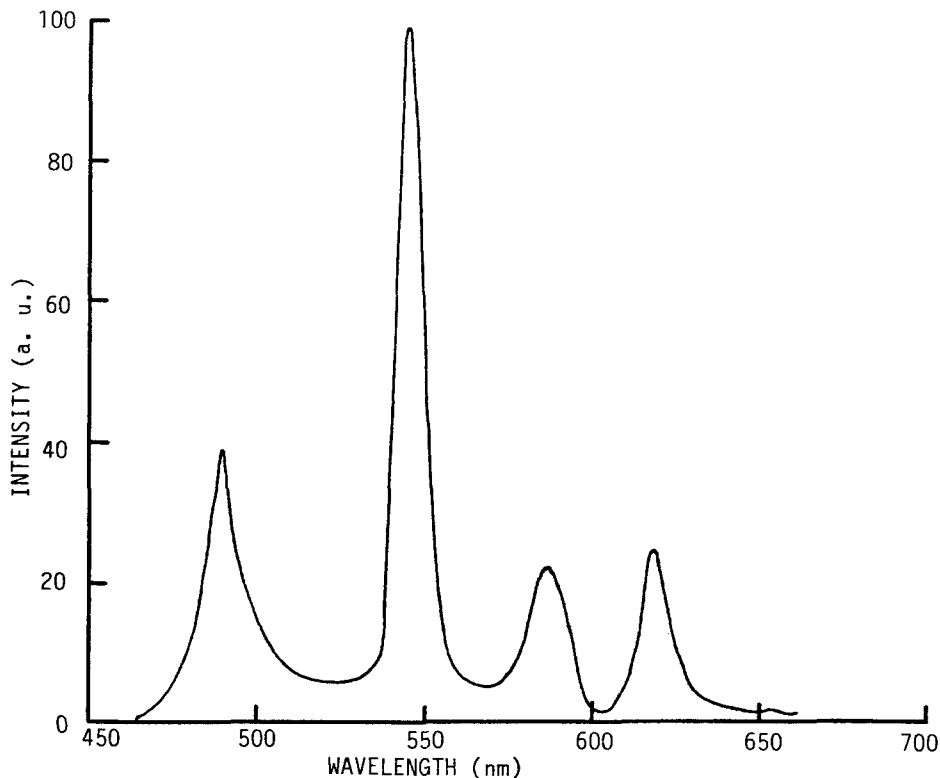


Fig. 1. Corrected fluorescence spectrum of $1 \cdot \text{TbCl}_3$ in MeOH.

spectrum of the Tb(III) complex (Figure 2) shows four lines at 490, 544 (the strongest one), 587, and 618 nm.

The quantum yields of the luminescence have been measured using the $(3,3'$ -dimethyl-1,1'-biisoquinoline-2,2'-dioxide) $_2 \cdot \text{EuCl}_3$ complex for comparison, for which the quantum yield in MeCN solution was found to be 25% [7b]. The evaluated quantum yields for the conversion of the absorbed light (excitation at 312 nm) into lanthanide cation visible luminescence was 0.003 and 0.002 for the Eu(III) and Tb(III) complexes, respectively. The estimated error of quantum yield measurements was $\pm 30\%$.

Unfortunately, these complexes totally lost their luminescence upon addition of water, indicating their modest stability in aqueous medium. These results may suggest that the hydrophilic cavity defined by the ethereal oxygens and by the converging pyridine-*N*-oxide groups is unable (perhaps too small) to encapsulate and tightly bind lanthanide cations, and to preserve them from interaction with water.

Future work will be directed to the design and synthesis of modified calixarenes that might display better binding of the lanthanide cations, to be useful as potential candidates for fluorimetric immunoassays [12].

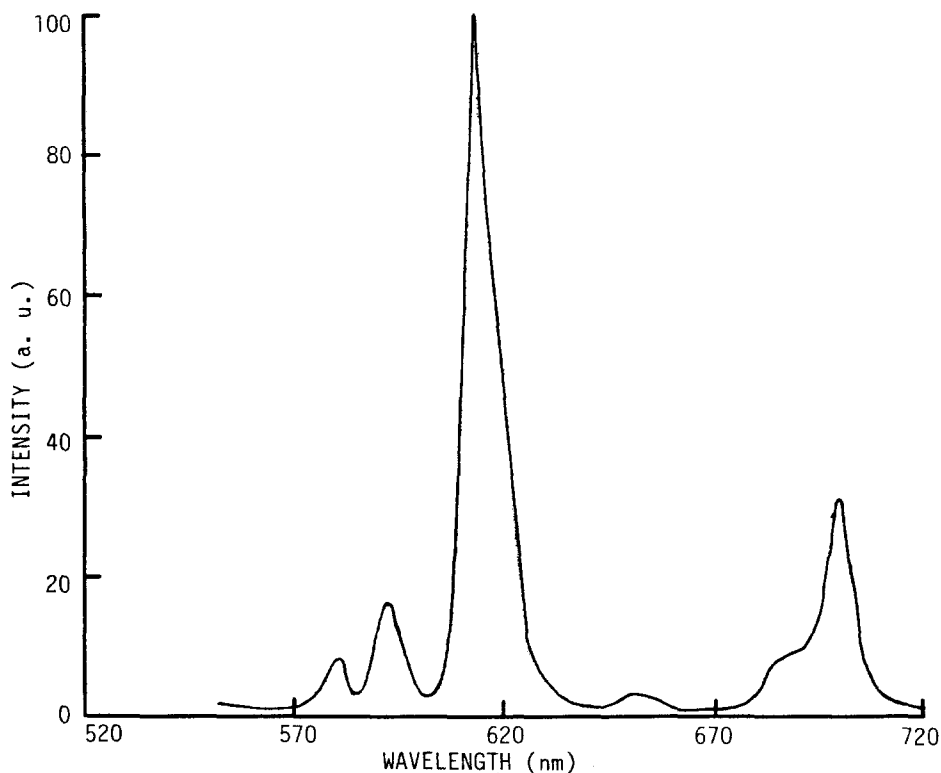


Fig. 2. Corrected fluorescence spectrum of $1 \cdot \text{EuCl}_3$ in MeOH.

Acknowledgement

This work was supported by the Italian Ministry of Education and by grants CPBR 3.20 and CPBP 1.19 from the Polish Academy of Sciences.

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