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Synthesis, Complexation and Photophysics in Protic Solvents of Lanthanide Complexes of Novel Calix[4]arene Polycarboxylic-2,2′-bipyridine Mixed Ligands

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Two novel *cone* calix[4]arene ligands 11a and 11b bearing two iminodiacetic chelating units and two C^6 or C^5 substituted 2,2′-bipyridine chromophores in diametral position at the lower rim were synthesized. These ligands form complexes with lanthanide ions in methanol solution whose stability ($4.5 < \log K_{ass} < 6.2$) depends on the substitution pattern (C^6 or C^5) of the 2,2′-bipyridine units. Contrary to that observed with other neutral calixarene ligands, the luminescence properties of the Eu^{3+} and Tb^{3+} complexes are not very much affected by the type of the 2,2′-bipyridine chromophore. Luminescence lifetimes ($0.31\,ms < \tau < 1.1\,ms$) and quantum yields ($0.017 < \phi < 0.130$) are higher for Terbium compared with the corresponding Europium complexes.

Keywords: Calixarenes; Europium; Terbium; Photophysics; Luminescence; Ionizable ligands

INTRODUCTION

Calixarenes have been extensively used as hosts for the complexation of lanthanide ions [1–3]. Since the early report by our group on the ability of calix[4]arene tetramide $\mathbf{L_1}$ to form luminescent complexes with lanthanide ions (especially Tb^{3+}) (Fig. 1) [4], several groups have tried to synthesize new ligands with improved photophysical properties [5]. The tetramide $\mathbf{L_1}$, like cryptands [6,7], is able to encapsulate lanthanide ions and shield them from the counterions and the solvent.

However, this system suffers a low molar absorptivity and in, the case of Eu^{3+} complexes, a poor luminescence quantum yield is observed, which is attributed to the efficient deactivation of the ligand centered excited states, by accessible ligand-to-metal charge-transfer states. In order to increase the molar absorptivity, calix[4]arenes bearing 2,2′-bipyridine (bipy) moieties attached at the lower rim through the C^6 carbon (*ortho* position to the pyridine nitrogen) $\mathbf{L_2}$ [8] or via the C^5 carbon (*meta* position to the pyridine nitrogen) $\mathbf{L_3}$ [9] were synthesized and their luminescent properties studied [8–11].

In order to increase the stability of the complexes with lanthanide ions, we synthesized a series of ligands bearing chelating groups of different nature such as amide-bipyridine or amide-phenantroline [8] or having a macrobicyclic structure [12]. For solubility reasons, in most of these cases, the luminescence measurements were performed in acetonitrile. Reinhoudt's group has extensively exploited calix[4]arene triacid derivatives bearing different types of chromophores on the fourth pendant arm to prepare and study neutral luminescent lanthanide complexes in methanol and water solution [13–15]. It is well known [15–17] that polyamino-polycarboxylic acid ligands form strong complexes with hard metal cations including lanthanides but additional chromophoric units are needed for the complexes to be luminescent. In this paper, we report the synthesis and the photophysical

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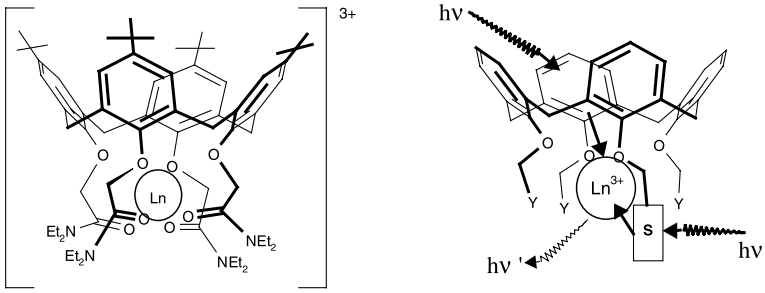
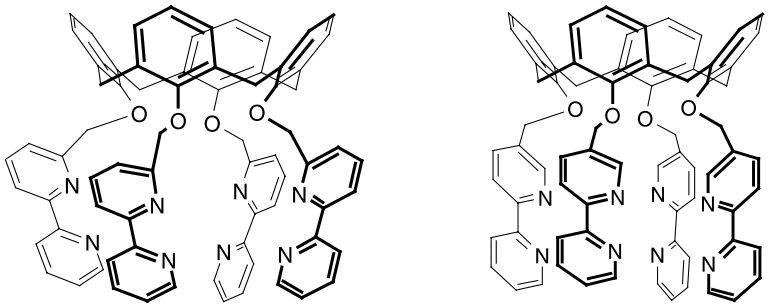


(a) $[Ln \subset \mathbf{L_1}]^{3+}$ (b)

FIGURE 1 (a) Complex of ligand $\mathbf{L_1}$ with a lanthanide (III) metal ion and (b) antenna effect in calix[4]arene lanthanide complexes: S = sensitiser; Y = binding group.



$\mathbf{L_2}$ $\mathbf{L_3}$

properties in methanol of two novel calixarene ligands bearing two iminodiacetic acid moieties and two bipyridine chromophores, in distal positions.

EXPERIMENTAL SECTION

Melting points were determined with an electrothermal melting point apparatus in a capillary sealed under nitrogen. ^{1}H- and ^{13}C NMR spectra were recorded with a Bruker AMX400 (^{1}H: 400 MHz), AC300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) spectrometers of the Centro Interdipartimentale di Misure (CIM) of the University of Parma using Me_4Si as internal standard. Mass spectra were obtained either with a Finnigan MAT SSQ710 spectrometer (DCI using methane as ionizing gas) or with a ZMD MICROMASS spectrometer (ESI, methanol/dichloromethane = 9/1). All solvents were purified with standard procedure; dry solvents were obtained by literature methods and stored over molecular sieves. Analytical thin layer chromatography (TLC) was performed on precoated silica gel plates (SiO_2, Merck, 60 F_{254}) or on precoated reverse-phase plates (RP-18, Merck, $F_{254}S$), while silica gel 60 (SiO_2, Merck, particle size 0.040–0.063 mm, 230–240 mesh) or LiChroprep® (RP-18, Merck, particle size 0.025–0.040 mm) were used for preparative flash column chromatography. 25,26,27,28-Tetrahydroxycalix[4]-arene (**1**) [18] and *N*,*N*-bis[(*tert*-butoxycarbonyl)-methyl]-2-bromoethylamine (**7**) [19] were prepared as described in the literature. 6-Bromomethyl-2,2′-bipyridine (**8a**) was synthesized according to Ref. [8]. 5-Bromomethyl-2,2′-bipyridine (**8b**) [20] was obtained by photochemical bromination with NBS in CCl_4 of 5-methyl-2,2′-bipyridine which was obtained by Kröhnke from the reaction of pyridacylpyridinium iodide [21] and methacroleine [22]. Absorption spectra were measured in MeOH (Carlo Erba, spectrofluorimetric grade) at room temperature (22°C) with a Perkin–Elmer Lambda 5 UV–Vis spectrophotometer. For the steady state luminescence experiments, a Spex Fluorolog II spectrofluorimeter equipped with a Hamamatsu R928 phototube was employed. Corrected luminescence spectra were obtained by applying corrections in the range 500–820 nm, owing to the wavelength dependence of the phototube response. Relative luminescence intensities (ϕ) were evaluated by using optically diluted samples (absorbance 0.15 at the excitation wavelength) from the area of the luminescence spectra on an energy scale and with reference to an optically matched (at the excitation wavelength) luminescence standard; both $Ru(bpy)_3Cl_2$ ($\phi = 0.028$ in air-equilibrated water [23]) and quinine sulphate ($\phi = 0.546$ in 1N H_2SO_4 [6]) were employed. Luminescence lifetimes on the ms time scale were obtained with a Perkin–Elmer LS50B luminescence spectrometer. The experimental uncertainty on the absorption and luminescence maxima is 2 and 1 nm, respectively, that

for the ϕ and τ values is 10%. Titration experiments were performed starting from 1×10^{-5} M MeOH solutions of the ligands containing stoichiometric amounts of tetrabutylammonium hydroxide (Merck) with respect to the number of the acidic protons of the ligands, at constant ionic strength $I = 0.01$ M in Et $NClO_4$. The UV–Vis spectra were recorded after each of the 25 additions of a 10^{-3} M methanol solution of lanthanide salts (as Cl^-, Fluka) (M/L = 0.1/25). The changes of the absorption spectra were reasonably consistent with a 1:1 association process. The association constants were evaluated by using the absorbance points at selected wavelengths and according to a fitting procedure based on Eq. (1) [24,25]

$$I = I_0 + \frac{\Delta I}{2S_0}\left[K_{\text{diss}} + X + S_0 - \sqrt{(K_{\text{diss}} + X + S_0)^2 - 4XS_0}\right] \quad (1)$$

where I, I_0 and ΔI are absorbance values, $K_{\text{diss}} = 1/K_{\text{ass}}$, and X and S_0 are the titrant and substrate concentrations, respectively. The values given in the Table I are the arithmetic means of at least two independent determinations.

25,27-Bis(cyanomethoxy)calix[4]arene (2)

To a stirred solution of calix[4]arene **1** (3.0 g, 7.1 mmol) in acetone (100 ml), K_2CO_3 (3.9 g, 28.3 mmol) was added, followed, after 30 min at reflux under nitrogen atmosphere, by NaI (4.20 g, 28.3 mmol) and α-chloroacetonitrile (2.14 g, 28.3 mmol). The reaction mixture was then refluxed overnight, filtered through a Celite pad and rinsed three times with CH_2Cl_2. The solvent of the combined filtrates was removed under reduced pressure, the residue triturated with EtOH, and purified by recrystallization from EtOH.

Yield: 75%. Mp: 220–222°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.12 (d, 4H, ArH, $J = 7.5$ Hz); 6.78 (m, 4H, ArH); 6.75 (d, 4H, ArH, $J = 7.5$ Hz); 5.98 (s, 2H, ArOH); 4.84 (s, 4H, CH_2CN); 4.25 (d, 4H, $ArCH_2Ar$ ax, $J = 13.6$ Hz); 3.51 (d, 4H, $ArCH_2Ar$ eq, $J = 13.6$ Hz). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm): 152.3, 151.2 (s, Ar-*ipso*); 133.15, 129.17 (s, Ar-*ortho*); 129.7, 127.8 (d, Ar-*meta*); 125.9, 119.4 (d, Ar-*para*); 116.3 (s, CN); 60.6 (t, *C*H_2CN); 30.8 (t, $ArCH_2Ar$). MS (CI) m/z: 502.4 (M^+) 100%.

25,27-Bis(cyanomethoxy)-26,28-bis(benzyloxy)calix[4]arene (3)

To a solution of compound **2** (2.10 g, 4.1 mmol) in dry DMF (30 ml), benzyl bromide (2.10 g, 12.3 mmol) and NaH (0.41 g, 10.3 mmol 60% suspension in oil) were added. The reaction mixture was stirred at room temperature under nitrogen for 4 h and then quenched by slow addition (CAUTION!) of a 2N HCl solution (25 ml). The organic layer was separated, washed twice with H_2O (2 × 30 ml) and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the product was crystallized from cold CH_3OH.

Yield: 85%. Mp: 182–183°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.45–7.37 (m, 10H, Ph); 7.16 (d, 4H, ArH, $J = 7.4$ Hz); 7.04 (t, 2H, ArH, $J = 7.4$ Hz); 6.33 (t, 2H, ArH, $J = 6.4$ Hz); 6.25 (d, 4H, ArH, $J = 6.4$ Hz); 4.84, 4.70 (s, 4H each, CH_2Ph and CH_2CN); 4.36 (d, 4H, $ArCH_2Ar$ ax, $J = 13.7$ Hz); 3.15 (d, 4H, $ArCH_2Ar$ eq, $J = 13.7$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 155.2, 154.7 (s, Ar-*ipso*); 137.2 (s, Ph-*ipso*); 137.0, 133.0 (s, Ar-*ortho*); 128.9 (d, Ph); 129.7, 128.1 (d, Ar-*meta*); 125.1, 123.2 (d, Ar-*para*); 116.7 (s, CN); 78.5 (t, *C*H_2Ph); 58.2 (t, *C*H_2CN); 31.6 (t, $ArCH_2Ar$). MS (CI) m/z: 683.2 (MH^+) 100%.

25,27-Bis(2-aminoethoxy)-26,28-bis(benzyloxy)calix[4]arene (4)

To a solution of compound **3** (1.65 g, 2.42 mmol) in dry THF (50 ml), a 1 M solution of BH_3 in THF (48.4 ml, 48.4 mmol) was added. The reaction was refluxed under nitrogen atmosphere for 5 h, then cooled with an ice-bath and quenched by slow addition (CAUTION!) of a 2N HCl solution (100 ml). The resulting solution was heated at 85°C for 3 h and, after removal of the solvent under reduced pressure, 30 ml of H_2O were added. The water phase was adjusted at basic pH with NaOH and extracted with CH_2Cl_2. The organic layer was then dried over $MgSO_4$, the filtrate concentrated under *vacuum* and compound **3** crystallized from ethyl ether.

Yield: >95%. Mp: 190°C (dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.42–7.35 (m, 10H, Ph); 7.04 (d, 4H, ArH, $J = 7.4$ Hz); 6.89 (t, 2H, ArH, $J = 7.4$ Hz); 6.31 (t, 2H, ArH, $J = 7.4$ Hz); 6.21 (d, 4H, ArH, $J = 7.4$ Hz); 4.79 (s, 4H, CH_2Ph); 4,34 (d, 4H, $ArCH_2Ar$ ax, $J = 13.3$ Hz); 3.95 (t, 4H, $ArOCH_2$, $J = 7.3$ Hz); 3.08 (d, 4H, $ArCH_2Ar$ eq, $J = 13.3$ Hz); 2.85 (t, 4H, CH_2NH_2, $J = 7.3$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 157.1 and 152.1 (s, Ar-*ipso*); 137.0 (s, Ph); 136.4 and 133.5 (s, Ar-*ortho*); 130.1 and 129.4 (d, Ar-*meta*); 128.8 (d, Ph); 78.0 (t, *C*H_2Ph); 76.8 (t, O*C*H_2CH_2N); 41.4 (t, $OCH_2C$$H_2$N); 31.1 (t, $ArCH_2$-Ar). MS (CI) m/z: 691 (MH^+) 100%.

*(**4**)·(HCl)*$_2$. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.40–7.32 (m, 10H, Ph); 7.08 (d, 4H, ArH, $J = 7.5$ Hz); 6.96 (t, 2H, ArH, $J = 7.5$ Hz); 6.26 (t, 2H, ArH, $J = 7.5$ Hz); 6.12 (d, 4H, ArH, $J = 7.5$ Hz); 4.98 (s, 4H, CH_2Ph); 4.35 (t, 4H, OCH_2CH_2N, $J = 7.3$ Hz); 4.05 (d, 4H, $ArCH_2Ar$ ax, $J = 13.7$ Hz); 3.26 (t, 4H, OCH_2CH_2N, $J = 7.3$ Hz); 2.94 (d, 4H, $ArCH_2Ar$ eq, $J = 13.7$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 156.1 and 152.1 (s, Ar-*ipso*); 136.0 (s, Ph-*ipso*); 135.5 and 132.9 (s, Ar-*ortho*); 130.3 and 128.9 (d, Ph); 129.4 and 127.9 (d,

Ar-*meta*); 123.6 and 123.2 (d, Ar-*para*); 78.5 (t, *C*H_2Ph); 71.2 (t, OCH_2CH$_2$NH$_2$); 39.5 (t, OCH$_2$CH_2NH$_2$); 30.9 (t, ArCH_2Ar).

25,27-Bis{2-[*N*,*N*-bis(*tert*-butyloxycarbonylmethyl)amino]ethoxy}-26,28-bis(benzyloxy)calix[4]arene (5)

To a stirred solution of compound **4** (1.9 g, 2.7 mmol) in dry CH_3CN (225 ml), DIPEA (4.7 ml, 27 mmol) and *tert*-butyl bromoacetate (2.67 g, 13.7 mmol) were added. The reaction was refluxed under nitrogen atmosphere for 20 h and, after removal of the solvent under reduced pressure, the residue was quenched with water (150 ml) and extracted with CH_2Cl_2 (200 ml). The separated organic layer was washed with water (200 ml) and dried over $MgSO_4$. CH_2Cl_2 was distilled off and the residue crystallized with cold MeOH.

Yield: 65%. Mp: 97–99°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.39–7.29 (m, 10H, Ph); 6.80–6.69 and 6.39–6.28 (m, 6H each, ArH); 5.13 (s, 4H, CH_2Ph); 4.24 (d,4H, ArCH_2Ar ax, $J = 13.5$ Hz); 3.87 (t, 4H, OCH_2CH$_2$N, $J = 7.3$ Hz); 3.42 (s, 8H, CH$_2$NCH_2CO); 3.12 (t, 4H, CH_2NCH$_2$CO, $J = 7.3$ Hz); 2.99 (d, 4H, ArCH_2Ar eq, $J = 13.5$ Hz); 1.43 (s, 36H, CCH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 170.4 (s, C = O); 155.6 and 155.5 (s, Ar-*ipso*); 137.9 (s, Ph-*ipso*); 136.4 and 133.9 (s, Ar-*ortho*); 130.0 and 128.5 (d, Ar-*meta*); 127.8 (d, Ph); 122.0 (d, Ar-*para*); 80.7 (s, *C*CH$_3$); 76.0 (t, *C*H$_2$Ph); 72.4 (t, OC H$_2$CH$_2$N); 55.9 (t, NC H$_2$CO); 53.9 (t, OCH$_2$C H$_2$N); 31.2 (t, ArCH$_2$Ar); 28.1 (q, CC H$_3$). MS (CI) m/z: 1147.5 (MH^+) 100%.

25,27-Bis{2-[*N*,*N*-bis(*tert*-butyloxycarbonylmethyl) amino]ethoxy}calix[4]arene (6)

Indirect synthesis: In a Schlenk tube compound **5** (1.4 g, 1.22 mmol) was dissolved in *tert*-butanol (70 ml) and then $Pd(OH)_2$ (0.35 g, 25% (w/w) on charcoal) and cyclohexene (7 ml) were added. The reaction mixture was heated for 24 h and then filtered on a Celite bed. The filter was accurately rinsed with CH_2Cl_2, the filtrates combined and the solvent removed under reduced pressure. Product **6** was obtained by crystallization of the crude product from CH_3OH. Yield: >95%.

Direct synthesis: To a stirred solution of compound **1** (0.3 g, 0.71 mmol) in dry acetonitrile (20 ml), K_2CO_3 (0.12 g, 0.85 mmol) and *N*,*N*-bis[(*tert*-butyloxycarbonyl)methyl]-2-bromoethylamine **7** (0.65 g, 1.86 mmol) were added. The reaction mixture was refluxed under nitrogen atmosphere for 14 h and the solvent removed under reduced pressure. The residue was treated with a 1N HCl solution (50 ml) and extracted with dichloromethane (2 × 50 ml). The combined organic extracts were washed with water, dried over $MgSO_4$ and the solvent removed under vacuum. The residue was treated several times with ethyl ether (30 ml) and each time the solvent removed at reduced pressure, till a white solid formed.

Yield: 93%. Mp: 138–139°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.42 (s, 2H, ArOH); 7.04 (d, 4H, ArH-*meta*, $J = 7.6$ Hz); 6.82 (d, 4H, ArH-*meta*, $J = 7.6$ Hz); 6.67 (t, 2H, ArH-*para*, $J = 7.6$ Hz); 6.65 (t, 2H, ArH-*para*, $J = 7.6$ Hz); 4.32 (d, 4H, ArCH_2Ar ax, $J = 13.1$ Hz); 4.13 (t, 4H, OCH_2CH$_2$N, $J = 6.5$ Hz); 3.63 (s, 8H, CH$_2$NCH_2CO); 3.35 (t, 4H, CH_2NCH$_2$CO, $J = 6.5$ Hz); 3.35 (d, 4H, ArCH_2Ar eq, $J = 13.1$ Hz); 1.43 (s, 36H, CCH_3). ^{13}C NMR ($CDCl_3$, 25 MHz) δ (ppm): 170.9 (s, C = O); 153.6 and 152.5 (s, Ar-*ipso*); 133.3 and 128.4 (s, Ar-*ortho*); 139.1 and 128.7 (d, Ar-*meta*); 125.3 and 119.1 (d, Ar-*para*); 81.2 (s, *C*CH$_3$); 76.0 (t, OC H$_2$CH$_2$N); 57.1 (t, NC H$_2$CO); 54.6 (t, OCH$_2$C H$_2$ N); 31.6 (t, ArCH$_2$Ar); 28.4 (q, CC H$_3$). MS (CI) m/z: 967.7 (MH^+) 100%.

25,27-Bis{2-[*N*,*N*-bis(*tert*-butyloxycarbonylmethyl)amino]ethoxy}-26,28-bis(2,2′-bipyridyl-6-methoxy)calix[4]arene (9a)

A sample of compound **6** (0.29 g, 0.3 mmol) and NaH (0.036 g, 0.9 mmol, 60% suspension in oil) in dry DMF (4 ml) was stirred at 40°C under nitrogen for 30 min. The reaction mixture was then cooled to room temperature and 6-bromomethyl-2,2′-bipyridine **8a** (0.23 g, 0.9 mmol) was added in three portions at 1 h intervals. Three hours after the last addition, the reaction was quenched with 2 ml of CH_3OH (CAUTION!) and then the solvent removed under reduced pressure. Compound **9a** was obtained by column chromatography of the residue (RP-18, eluent: CH_3OH–CH_2Cl_2 20:1).

Yield: 48%. Mp: 64–65°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.63 (d, 2H, H6′bpy, $J = 4.8$ Hz); 8.32 (d, 2H, H3′bpy, $J = 7.7$ Hz); 8.13 (d, 2H, H3bpy, $J = 7.9$ Hz); 7.86 (t, 2H, H4bpy, $J = 7.9$ Hz); 7.73 (d, 2H, H5bpy, $J = 7.9$ Hz); 7.64 (t, 2H, H4′bpy, $J = 7.7$ Hz); 7.22 (dd, 2H, H5′bpy, $J = 7.7$ and 4.8 Hz); 6.89 (d, 4H, *H*ArOCH$_2$CH$_2$-*meta*, $J = 7.3$ Hz); 6.79 (t, 2H, *H*ArOCH$_2$CH$_2$-*para*, $J = 7.3$ Hz); 6.34 (t, 2H, *H*ArOCH$_2$bpy-*para*, $J = 7.4$ Hz); 6.26 (d, 4H, *H*ArOCH$_2$bpy-*meta*, $J = 7.4$ Hz); 5.46 (s, 4H, OCH_2bpy); 4.33 (d, 4H, ArCH_2Ar ax, $J = 13.6$ Hz); 3.81 (t, 4H, OCH_2CH$_2$N, $J = 7.5$ Hz); 3.35 (s, 8H, CH$_2$NCH_2CO); 3.08 (d, 4H, ArCH_2Ar eq, $J = 13.6$ Hz); 3.00 (t, 4H, CH_2NCH$_2$CO, $J = 7.5$ Hz); 1.37 (s, 36H, CCH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 170.3 (s, C = O); 157.7 (s, C2bpy); 156.6 (s, C2′bpy); 156.2 and 154.9 (s, Ar-*ipso*); 155.4 (s, C6bpy); 148.8 (d, C6′bpy); 137.1 (d, C4bpy); 136.7 (d, C4′bpy); 136.1 and 133.7 (s, Ar-*ortho*); 128.7 and 127.8 (d, Ar-*meta*); 123.8 (d, C5bpy); 123.4 (d, C5′bpy); 122.2 (d, C3bpy); 122.0 (d, C3′bpy); 121.4

and 119.6 (d, Ar-*para*); 80.7 (t, OCH_2bpy); 77.0 (s, CCH_3); 72.5 (t, OCH_2CH_2N); 55.9 (t, NCH_2CO); 53.9 (t, OCH_2CH_2N); 31.3 (t, $ArCH_2Ar$); 28.0 (q, CCH_3). MS (CI) m/z: 1303.2 (MH^+) 100%.

25-{2-[*N*,*N*-bis(*tert*-butyloxycarbonylmethyl)amino]ethoxy}-26,28-bis(2,2′-bipyridyl-6-methoxy)-27-hydroxycalix[4]arene (10)

Compound **10** was obtained as a side-product in the preparation of compound **9a** after column chromatography.

Yield: 15% (not optimized). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.66 (dd, 1H, H6′bpy, $J = 4.8$ and 1.9 Hz); 8.41 (d, 1H, H3′bpy, $J = 7.8$ Hz); 8.38 (d, 1H, H3bpy, $J = 7.9$ Hz); 8.25 (d, 1H, H5bpy, $J = 7.9$ Hz); 7.98 (t, 1H, H4bpy, $J = 7.9$ Hz); 7.77 (td, 1H, H4′bpy, $J = 7.8$ and 1.9 Hz); 7.27 (dd, 1H, H5′bpy, $J = 7.8$ and 4.8 Hz); 7.17 and 7.09 (2d, 4H, *H*ArOCH$_2$bpy-*meta* and *H*ArOH-*meta*, $J = 7.5$ and 7.4 Hz); 6.98 and 6.76 (2t, 2H, *H*ArOCH$_2$bpy-*para* and *H*ArOH-*para*, $J = 7.5$ and 7.4 Hz); 6.50–6.40 (m, 6H, *H*ArOCH$_2$CH$_2$); 5.26 (s, 2H, OC*H*$_2$bpy); 4.37 and 4.35 (2d, 4H, ArC*H*$_2$Ar ax, $J = 13.0$ and 13.6 Hz); 3.77 (t, 4H, OC*H*$_2$CH$_2$N, $J = 7.2$ Hz); 3.32 and 3.21 (2d, 4H, ArC*H*$_2$Ar eq $J = 13.6$ and 13.0 Hz); 3.27 (s, 8H, CH$_2$NC*H*$_2$CO) 2.88 and 2.78 (2t, 4H, C*H*$_2$NCH$_2$CO, $J = 7.2$ Hz); 1.36 (s, 36H, CC*H*$_3$). MS (CI) m/z: 1135.2 (MH^+) 100%.

25,27-Bis-2-[*N*,*N*- bis(*tert*-butyloxycarbonyl methyl)amino]ethoxy-26,28-bis(2,2′bipyridyl-5-methoxy)calix[4]arene (9b)

Compound **9b** was obtained from compound **6** and 5-methyl-2,2′-bipyridine using the same procedure reported previously for **9a**. After quenching the reaction with H_2O (10 ml), a white precipitate formed which was filtered on a Buchner funnel and purified by column chromatography (neutral Al_2O_3: eluent hexane/ethyl acetate/triethylamine 9:3:0.5).

Yield: 35%. Mp: 149–150°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.82 (d, 2H, H6bpy, $J = 1.6$ Hz); 8.66 (dd, 2H, H6′bpy, $J = 4.0$ and 1.1 Hz); 8.48 (dd, 2H, H3′bpy, $J = 7.4$ and 0.8 Hz); 8.37 (d, 2H, H3bpy, $J = 8.1$ Hz); 7.80 (td, 2H, H4′bpy, $J = 7.4$ and 1.1 Hz); 7.76 (dd, 2H, H4bpy, $J = 8.1$ and 1.6 Hz); 7.28 (ddd, 2H, H5′bpy, $J = 7.4$, 4.0 and 0.8 Hz); 6.98 (d, 4H, *H*ArOCH$_2$CH$_2$-*meta*, $J = 7.2$ Hz); 6.87 (t, 2H, *H*ArOCH$_2$CH$_2$-*para*, $J = 7.2$ Hz); 6.23 (t, 2H, *H*ArOCH$_2$bpy-*para*, $J = 7.1$ Hz); 6.10 (d, 4H, *H*ArOCH$_2$bpy-*meta*, $J = 7.1$ Hz); 5.35 (s, 4H, OC*H*$_2$bpy); 4.20 (d, 4H, ArC*H*$_2$Ar ax, $J = 13.6$ Hz); 3.84 (t, 4H, OC*H*$_2$CH$_2$N, $J = 6.8$ Hz); 3.52 (s, 8H, CH$_2$NC*H*$_2$CO); 3.26 (t, 4H, C*H*$_2$NCH$_2$CO, $J = 6.8$ Hz); 3.02 (d, 4H, ArC*H*$_2$Ar eq, $J = 13.6$ Hz); 1.39 (s, 36H, CC*H*$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 170.4 (s, C = O); 156.0 (s, C2bpy); 154.8 (s, C2′bpy); 151.5 and 149.3 (s, Ar-*ipso*); 150.8 (d, C6bpy); 148.9 (d, C6′bpy); 141.5 (d, C4 and C4′bpy); 137.1 and 136.9 (s, Ar-*ortho*); 133.1 (s, C5bpy); 129.0 and 127.5 (d, Ar-*meta*); 123.5 (d, C3bpy); 122.5 (d, C3′bpy); 122.3 (d, C5′bpy); 121.3 and 120.1 (d, Ar-*para*); 80.8 (t, OCH_2bpy); 73.0 (s, CCH_3); 72.6 (t, OCH_2CH_2N); 55.7 (t, NCH_2CO); 54.1 (t, OCH_2CH_2N); 31.2 (t, $ArCH_2Ar$); 28.0 (q, CCH_3). MS (CI) m/z: 1303.4 (MH^+) 100%.

25,27-Bis{2-[*N*,*N*- bis(hydroxycarbonyl methyl)amino]ethoxy}-26,28-bis(2,2′bipyridyl-6-methoxy)calix[4]arene (11a)

To a cooled (0°C) solution of compound **9a** (0.16 g, 0.12 mmol) and triethylsilane (0.96 ml, 0.6 mmol) in dry CH_2Cl_2 (3 ml), trifluoroacetic acid (1.40 ml, 18.0 mmol) was added dropwise. The reaction was stirred overnight at room temperature and then the solvent removed under reduced pressure. The residue was treated with ethyl ether, hexane and chloroform and each time the solvent removed under reduced pressure. The product was first obtained by crystallization with hexane and then recrystallized from CH_3OH and ethyl ether.

Yield: 48%. Mp: 156–158°C; ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm): 8.72 (d, 2H, H6′bpy, $J = 4.3$ Hz); 8.39 (d, 2H, H3′bpy, $J = 7.9$ Hz); 8.26 (d, 2H, H3bpy, $J = 7.7$ Hz); 8.17 (dd, 2H, H4′bpy, $J = 7.9$ and 6.8 Hz); 7.97 (t,2H, H4bpy, $J = 7.7$ Hz); 7.62 (dd, 2H, H5′bpy, $J = 6.8$ and 4.3 Hz); 7.52 (d, 2H, H5bpy, $J = 7.7$ Hz); 6.67–6.66 (m, 6H, *H*ArOCH$_2$CH$_2$); 6.48–6.42 (m, 6H, *H*ArOCH$_2$bpy); 5.30 (s, 4H, OC*H*$_2$bpy); 4.25 (t, 4H, OC*H*$_2$CH$_2$N, $J = 7.7$); 4.22 (d,4H, ArC*H*$_2$Ar ax, $J = 13.6$ Hz); 3.83 (s, 8H, CH$_2$NC*H*$_2$CO); 3.66 (t, 4H, C*H*$_2$NCH$_2$CO, $J = 7.7$ Hz); 2.98 (d, 4H, ArC*H*$_2$Ar eq, $J = 13.6$ Hz). MS (ESI) m/z: 1079.2 (MH^+) 100%.

*Tetrasodium salt of **11a***. The salt was obtained by titration of a solution of **11a** with NaOH in methanol. ^{1}H NMR (CD_3OD, 300 MHz) δ (ppm): 8.62 (d, 2H, H6′bpy, $J = 4.5$ Hz); 8.23 (d, 2H, H3′bpy, $J = 7.8$ Hz); 8.02 (d, 2H, H3bpy, $J = 7.6$ Hz); 7.98 (t, 2H, H4bpy, $J = 7.6$ Hz); 7.81 (t, 2H, H4′bpy, $J = 7.8$ Hz); 7.67 (d, 2H, H5bpy, $J = 7.6$ Hz); 7.37 (dd, 2H, H5′bpy, $J = 7.8$ and 4.5 Hz); 6.79–6.66 (m, 6H, *H*ArOCH$_2$CH$_2$); 6.39 (s, 6H, *H*ArOCH$_2$bpy); 5.31 (s, 4H, OC*H*$_2$bpy); 4.25 (d, 4H, ArC*H*$_2$Ar ax, $J = 13.2$ Hz); 4.16 (t, 4H, OC*H*$_2$CH$_2$N, $J = 7.5$ Hz); 3.18 (t, 4H, C*H*$_2$NCH$_2$CO, $J = 7.5$ Hz); 3.10 (s, 8H, CH$_2$NC*H*$_2$CO); 2.87 (d, 4H, ArC*H*$_2$Ar eq, $J = 13.2$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 179.3 (s, C = O); 158.3 (s, C2bpy); 157.7 (s, C2′bpy); 157.3 (s, C6bpy); 156.4 and 155.6 (s, Ar-*ipso*); 150.1 (d, C6′bpy); 139.1 (d, C4bpy); 138.6 (d, C4′bpy); 137.1 and 135.8 (s, Ar-*ortho*); 129.7 and 129.1 (d, Ar-*meta*); 126.3 (d, C5bpy); 125.1 (d, C5′bpy); 123.8 (d, C3bpy); 123.5 (d, C3′bpy); 123.1 and 121.4 (d, Ar-*para*); 78.9 (t, OCH_2bpy); 72.9 (t, OCH_2CH_2N); 62.2 (t, NCH_2CO); 56.7 (t, OCH_2CH_2N); 32.1 (t, $ArCH_2Ar$).

25,27-Bis-2-[*N*,*N*-bis(hydroxycarbonylmethyl) amino]ethoxy-26,28-bis(2,2′-bipyridyl-5-methoxy)calix[4]arene (11b)

Compound **11b** was obtained from **9b** following the same procedure described for **11a**.

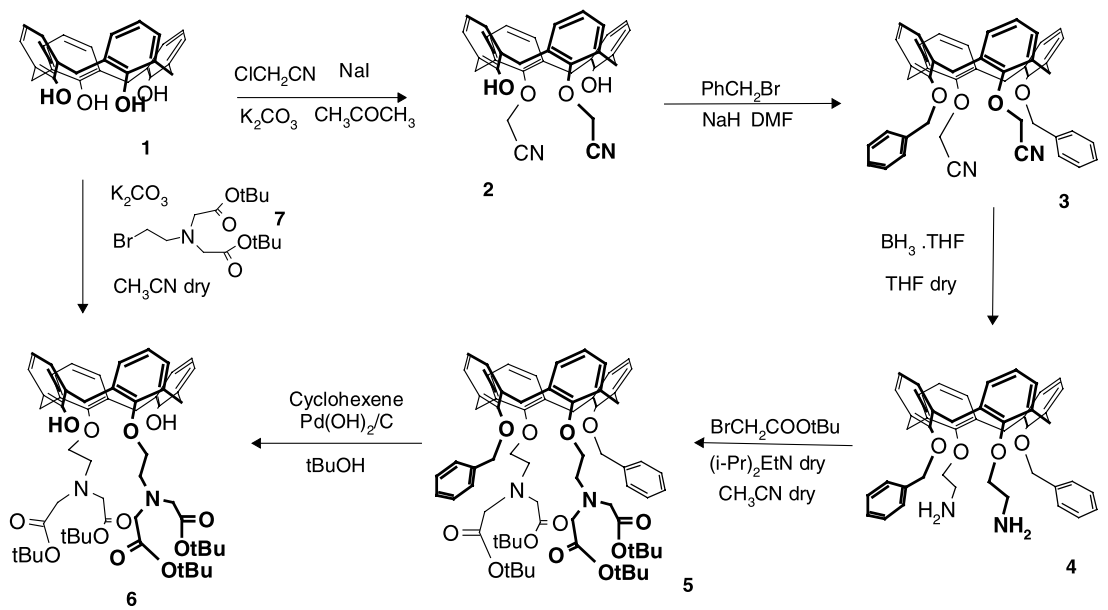
Yield: 90%. Mp: 115–117°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.88 (d, 2H, H6bpy, $J = 1.5$ Hz); 8.77 (dd, 2H, H6′bpy, $J = 5.2$ and 1.6 Hz); 8.51 (dd, 2H, H3′bpy, $J = 7.9$ and 1.0 Hz); 8.40 (d,2H, H3bpy, $J = 8.1$ Hz); 8.25 (td, 2H, H4′bpy, $J = 7.9$ and 1.6 Hz); 8.10 (dd, 2H, H4bpy, $J = 8.1$ and 1.5 Hz); 7.22 (ddd, 2H, H5′bpy, $J = 7.9$, 5.2 and 1.0 Hz); 6.61 (s, 6H, HAr); 6.59 (s, 6H, HAr); 5.24 (s, 4H, OCH_2bpy); 4.23 (t, 4H, OCH_2CH$_2$N, $J = 7.9$ Hz); 4.20 (d, 4H, ArCH_2Ar ax, $J = 13.6$ Hz); 3.93 (s, 8H, CH$_2$NCH_2CO); 3.66 (t, 4H, CH_2NCH$_2$CO, $J = 7.9$ Hz); 3.09 (d, 4H, ArCH_2Ar eq, $J = 13.6$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 171.5 (s, C = O); 156.9 (s, C2bpy); 155.5 (s, C2′bpy); 152.7 (d, C6bpy); 152.1 (d, C6′bpy); 151.1 and 147.9 (s, Ar-*ipso*); 142.8 (d, C4bpy); 142.0 (d, C4′bpy); 136.7 (s, C5bpy); 136.2 and 135.9 (s, Ar-*ortho*); 129.9 (d, Ar-*meta*); 127.0 (d, C3bpy); 124.3 (d, C3′bpy); 124.2 (d, Ar-*para*); 123.2 (d, C5′bpy); 74.6 (t, OC H$_2$bpy); 70.9 (t, OC H$_2$CH$_2$N); 56.9 (t, NC H$_2$CO); 55.4 (t, OCH$_2$C H$_2$N); 32.2 (t, ArCH$_2$Ar). MS (CI) m/z: 1079.3 (MH$^+$) 100%.

RESULTS AND DISCUSSION

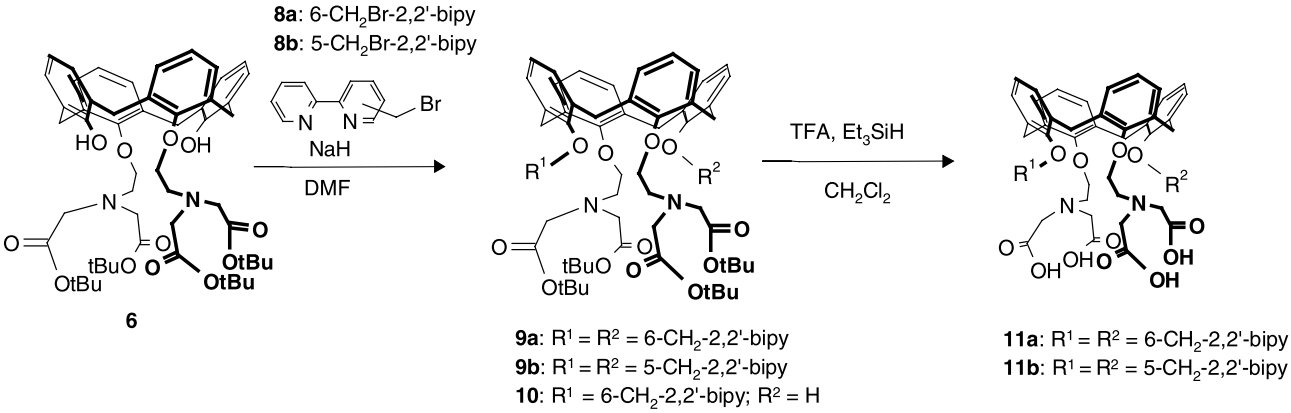
Synthesis of the Ligands

In order to introduce the two iminodiacetic acid moieties at the lower rim of a calix[4]arene, we first developed a protective–deprotective procedure (Scheme 1), which exploits the selective 1,3-dialkylation of calix[4]arenes [26] and gives compound **6** in 40% overall yield.

The presence of the iminodiacetate groups in the ^{1}H NMR spectrum of compound **6** is proved by the absorbance of the methylene and butyl protons of the CH$_2$COO*t*-Bu group at $\delta = 3.63$ and 1.43, respectively, while the removal of benzyl groups is also evidenced by the appearance of the phenolic OH protons at $\delta = 7.42$ which exchange with D$_2$O. Alternative to this route, we developed a direct synthesis of compound **6** from **1** using *N*,*N*-bis[(*tert*-butyloxycarbonyl)methyl]-2-bromoethylamine **7**. This compound is not commercially available, but can be easily synthesized in two steps from ethanolamine according to a literature procedure [19]. Reaction of calix[4]arene **1** with K_2CO_3 and 2.6 equiv. of **7** in refluxing acetonitrile gives compound **6** in nearly quantitative yields and therefore this direct synthesis is much more efficient and highly preferable to the indirect one. Compound **6** is an interesting intermediate, useful for the synthesis of a variety of water-soluble ligands for metal ions [27]. For the purpose of this work we needed to introduce a proper bipyridine chromophore able to coordinate Tb(III) and Eu(III) and give an efficient *antenna effect*. Compound **6** was therefore alkylated with 6-bromomethyl- (**8a**) or 5-bromomethyl (**8b**)-2,2′-bipyridine in dry DMF using NaH as base. In order to avoid a fast decomposition of the alkylating agents, calixarene **6** was first reacted at 50°C for 30 min with a slight excess (3 equiv.) of NaH and then three portions (1 equiv. each) of bromomethylpyridine **8** were added at 1 h intervals. Compounds **9a** and **9b** were isolated from the reaction mixture by column chromatography in 48 and 35% yield, respectively. In the reaction with the



SCHEME 1



SCHEME 2

TABLE I Spectroscopic and photophysical results

	Absorption		Emission		
	$\log K_{ass}$*	λ_{max}†, nm ($10^{-4} \times \epsilon$, $M^{-1}cm^{-1}$)	λ_{max}‡, nm	τ, ms	ϕ¶
[Eu ⊂ **11a**]$^{3+}$	5.4	311 (0.57)	616	0.31	0.050
[Tb ⊂ **11a**]$^{3+}$	4.5	311 (0.85)	541	1.14	0.130
[Gd ⊂ **11a**]$^{3+}$	5.4	311 (0.63)	450§,‖	0.49§	–
[Eu ⊂ **11b**]$^{3+}$	5.9	301 (2.6)	612	0.71	0.017
[Tb ⊂ **11b**]$^{3+}$	6.2	301 (2.5)	542	1.1	0.127
[Gd ⊂ **11b**]$^{3+}$	6.1	301 (2.5)	441§,‖	0.52§	–

Solvent MeOH, 22°C. * Evaluated by spectrophotometric titration and according to a 1:1 process ($I = 0.01$ M in Et_4NClO_4), $\sigma = \pm 0.1$. † Longest wavelength absorption band maximum. ‡ Highest intensity peak of the luminescence profile. ¶ Upon excitation at the shortest wavelength maximum, and with reference to luminescence standard, see text. § From 77 K measurements. ‖ Broad band maximum.

6-bromomethylpyridine **8a**, the product of mono-alkylation **10** was also isolated (15%) (Scheme 2).

Both compound **9a** and **9b** show a similar structure in chloroform solution, as evidenced by their ^{1}H NMR spectra. The calixarene is in a distorted "flattened cone" structure where two aromatic nuclei are bent inside the cavity of the macrocycle, since their protons are shielded at $\delta = 6.3 - 6.2$. The subsequent hydrolysis of the *tert*-butyl esters **9** was performed in dry CH_2Cl_2 with an excess of trifluoroacetic acid (TFA) and triethylsilane and the resulting acids **11a** and **b** were easily isolated in nearly quantitative yields. Compounds **11a** and **b** are insoluble in chloroform, slightly soluble in basic water solution but well soluble in methanol both as tetracid and tetrasodium salt. Upon addition of 4 equiv. of solid NaOH to a CD_3OD solution of **11a** and **b**, most of the chemical shifts of the protons of the 2,2′-bipyridine (bpy) units and of the calixarene remain unchanged. On the other hand, significant upfield shifts of 0.8 ppm (from 3.83 to 3.10 ppm) and 0.6 ppm (from 3.66 to 3.10 ppm) are experienced by the NCH_2CO and OCH_2CH_2N protons of the iminodiacetic units of **11a** and **b**, thus suggesting that they are present as zwitter-ions.

Complexation and Luminescence Studies

To a MeOH solutions of ligands **11a** and **b**, 4 equiv. of a tetrabutylammonium hydroxide solution were first added, thus obtaining the corresponding salts. Then titrations with concentrated terbium, europium and gadolinium chlorides were carried out and the changes of absorption spectra were used both for determining the nature of the association process and estimating the association constants. Table I lists the evaluated 1:1 association constants, K_{ass} (see "Experimental section"), and the absorption and luminescence data for the complexes. For all the metal ions studied, ligand **11b** shows higher values of $\log K_{ass}$ than **11a**.

Figures 2 and 3 show the spectrophotometric results obtained in the Tb^{3+} titration of 1×10^{-5} M solutions of **11a** and **11b**, respectively. The free ligands **11a** and **11b** show an absorption maximum λ_{max} around 285 nm while their lanthanide complexes present a significant bathochromic shift to 311 and 301 nm, respectively (Table I), indicating bipyridine coordination to the cation. It may be noted that for **11a** as compared to **11b**, a larger bathochromic shift is accompanied by a less intense

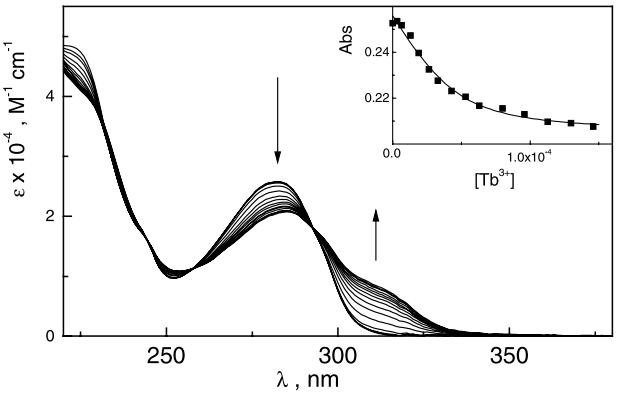


FIGURE 2 Titration of a 1×10^{-5} M solution of **11a** with Tb^{3+}. The inset shows the analysis of the absorbance ($\lambda = 311$ nm), versus [Tb^{3+}], see text.

absorption (see the ϵ values, Table I). This suggests some differences in the coordination geometry. It may well be that for **11a** the bipy C^6 linkages to the lower rim of the calix[4]arene inhibit, for steric reasons, the simultaneous coordination of both nitrogen atoms of each bipy moiety to the metal ion. The luminescence properties of Tb^{3+} and Eu^{3+} complexes of compounds **11a** and **b** in MeOH solution are collected in the Table I. Spectroscopic data for the analogous complexes of Gd^{3+}, that are expected not to exhibit metal-centred luminescence [6], were also obtained. Considering the highly competing nature of the methanol solvent, the luminescence properties of **11a** and **11b** with Eu^{3+} or Tb^{3+} metal ions are reasonably good [6]. Contrary to that observed with neutral bipyridine containing calixarene ligands in acetonitrile [8,9], terbium complexes give rise to longer lifetimes (τ) and luminescent quantum yields (ϕ) than the corresponding europium complexes also in the case of C^5 bipyridine ligand **11b**. Therefore, it seems that for this class of ionizable ligands the substitution pattern (C^6 or C^5) of the 2,2′-bipyridine units has more influence on their association constants than on their luminescence properties.

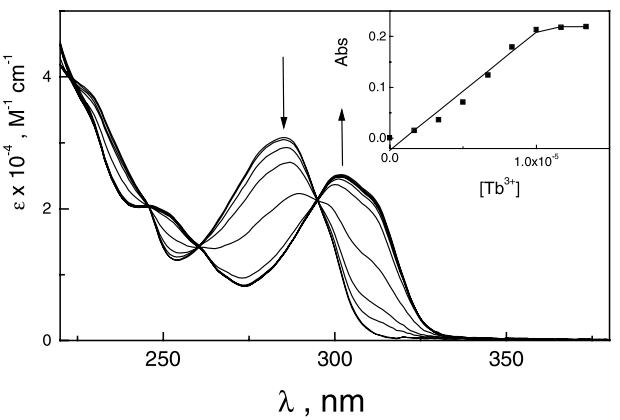


FIGURE 3 Titration of a 1×10^{-5} M solution of **11b** with Tb^{3+}. The inset shows the analysis of the absorbance ($\lambda = 301$ nm), versus [Tb^{3+}], see text.

In conclusion, we have shown, for the first time, that iminodiacetic units can be attached at the lower rim of calix[4]arenes in the *cone* conformation, thus offering the possibility of exploiting the strong chelating ability of these units for hard metal ion complexation [27]. Although we did not completely succeed in obtaining water-soluble luminescent lanthanide complexes using ionizable calix[4]arene ligands, we were able to perform our complexation and photophysical studies in a protic solvent, such as methanol.

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