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A new calix[4]azacrown ether based boradiazaindacene (Bodipy): selective fluorescence changes towards trivalent lanthanide ions

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Abstract

We report on the synthesis and photophysical properties of a new calix[4]azacrown derivative, capped with two amide bridges, in the cone conformation bearing two boradiazaindacene (Bodipy) groups at the narrow rim. Its binding properties towards trivalent lanthanide ions such as La³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Er³⁺ and Yb³⁺ were investigated by using spectroscopic techniques. With respect to fluorescence intensity changes upon trivalent lanthanide ion complexation, calix[4]azacrown ether based Bodipy showed higher selectivity towards Yb³⁺ ion over other ions. Presence of proximal two amide groups in calix[4]azacrown ether based Bodipy were observed to play an important role in exhibiting its lanthanide ion binding.

Keywords : Calixcrown, Bodipy, Lanthanide ions, Fluorescence probe, Recognition, Chemosensor.

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1. Introduction

The design and synthesis of fluorescent chemosensors have received considerable interest in supramolecular chemistry due to the simplicity and high detection limit of the fluorescent signals [1]. Especially, the investigation of specific chemosensors for the efficient detection of lanthanide ions is one of the most important issues because of their impacts on our environments and chemical significances [2,3]. Lanthanide ions have been widely used in chemical and biological applications as probes and labels [4-6]. Furthermore, these ions are very poor light absorbers, thus, their luminescent states by direct excitation are inefficient. In order to overcome these limitations, many lanthanide (III) chelates have been designed containing 'antenna effect' [7,8]. The macrocyclic chelating agents including cryptands, [9] calixarene, [10] cyclodextrins [11] and crown-ether derivatives, [12] are commonly used to sensitize luminescence towards lanthanide ions. The fluorophore (signaling moiety) makes possible the detection of metal cations through a light signal, whereas the chelating agents (ionophore) linked to the fluorophore is responsible for the selectivity and cation binding efficiency of the chemosensor. Among the fluorophores, boradiazaindacene (Bodipy) are well known fluorescent dyes that have applications in many different areas such as, ion sensing and signaling, fluorescent labeling of biomolecules, fluorescent stains, energy transfer cassettes, light harvesting systems due to their high quantum yields, large extinction coefficients and narrow emission bands [13-15]. In the design of chemosensors, attention should be paid to both recognition of ionophore and signaling of fluorophore moieties. The signaling moiety converts the data into a signal expressed as the differences in the photophysical characteristics of the chemosensor. These differences are due to the perturbation by the bound cation of photochemical transactions such as electron, charge and/or energy transfer, excimer or exciplex formation. Calixarenes are cyclic oligomers made of

several phenolic units bounded with methylene bridges [16,17] and are regarded as the third generation of host molecules because of their inclusion ability to cations, anions, and neutral molecules [18-22]. Calix[4]arenes can be easily functionalized both at the phenolic OH groups (lower rim) and, after partial removal of tert-butyl groups, at the para positions of the phenol rings (upper rim) [23,24]. The vast majority of these modified calixarenes exist in the cone conformation in which there is a cavity suitable for reception of different ionic and neutral species [25]. Since the first report of calixcrown ether derivatives, [26] considerable interest has been dedicated to the design and synthesis of calixcrowns and their use in some chemical applications such as catalysis, ion selective electrodes and liquid supported membranes [27]. Although a large number of works exists on the crown ether and cryptand-based photo-induced electron transfer (PET), those on calizazacrowns are limited [28,29]. Compared to the number of reports on the binding of metal cations with calixazacrown fluoroionophores, reports on the binding of trivalent lanthanide ions are still limited [30-32]. From this point of view calixazacrown ionophore based boradiazaindacene (Bodipy) units is at the center of interest. With this in mind, we set out to synthesis of the calixazacrown ionophore based boradiazaindacene (Bodipy) and explore its metal binding properties towards La^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Er^{3+} and Yb^{3+} .

2. Experimental Section

2.1. Materials

All of the reagents used in this study were obtained from Merck (Germany) or Sigma-Aldrich (USA) and used without further purification. CH_2Cl_2 was distilled from $CaCl_2 \cdot$ MeOH over Mg and stored over molecular sieves. Acetonitrile was dried from CaH_2 and stored under N₂ over molecular sieves (4 A °). Other commercial grade solvents were distilled, and then stored over molecular sieves (Aldrich; 4 A °, 8–12 mesh). Thin layer chromatography (TLC) was performed

using silica gel on glass TLC plates (silica gel H, type 60, Merck). All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

2.2. Apparatus

¹H and ¹³C NMR spectra were obtained using a Varian 400 MHz spectrometer operating at 400 MHz. IR spectra were recorded on a Perkin–Elmer spectrum 100 FTIR spectrometer (ATR). Absorbance spectra are collected by a Perkin Elmer Lambda 25 UV-vis spectrophotometer using quartz cells of 1.0 cm path length. Fluorescence measurements are carried out in a PerkinElmer LS 55 spectrofluorimeter. The fluorescence spectra are recorded in a 1 cm quartz cuvette at room temperature. The excitation and emission slits are set at 5 nm. Elemental analyses were performed using a Leco CHNS-932 analyzer. An Orion 410A+ pH meter was used for the pH measurements. Melting points were determined on a Gallenkamp apparatus. Moreover, the solutions of Bodipy-metal ion were mixed by Kudos Ultrasonic Cleaner 53 kHz.

2. 3. Synthesis

Starting calixarene compounds 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrahydroxycalix[4]arene (2), 25,26,27,28-tetrahydroxycalix[4]arene (3), 25,27,-di-(methoxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene (4) and calix[4]arene (ethyleneamido)crown (5) were synthesized according to literature procedures [17,23,24]. 8-{4-(Chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (1) was prepared by using modified procedure as follow. Final product (6) was synthesized for the first time according to the following described procedure:

2.3.1. Synthesis of 8-{4-(Chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (1)

To a stirred solution of 2,4-dimethyl-3-ethylpyrrole (2.5 mL) in dry dichloromethane (100 mL), 4-(chloromethyl)benzyl chloride (1.875 g, 10 mmol) was added drop wise at room temperature and under N₂. The solution was heated and stirred to 60° C for 2 h. After the cooling of the solution, triethylamine (TEA) (5 equiv.) was added to the residual solid, the mixture was stirred at room temperature for 30 min under N₂, and boron trifuoride diethyl etherate (7 equiv.) was then added. The solution was stirred at 60 °C for 2 h and the final residue was purified by column chromatography (petrolium ether-EtOAc; in 8:1 ratio) and obtained to redden an adhesive material. ¹H NMR [400 MHz, CDCl₃]: δ (ppm) 7.41 (d, 2H, ArH), 7.18 (d, 2H, ArH) 4.63 (s, 2H, CH₂), 2.44 (s, 6H CH₃) 2.21 (q, 4H, CH₂) 1.27 (s, 6H, CH₃) 0.89 (t, 6H, CH₃).¹³C NMR [100 MHz, CDCl₃]: δ (ppm); 153.81, 139.42, 138.42, 136.12, 135.81, 132.83, 130.62, 129.02, 128.78, 45.59, 17.07, 14.43, 12.43, 11.62. Anal.Calc. for (%) C₂₄H₂₈N₂ClBF₂: C, 67.23; H, 6.58; N, 6.53; Found: C, 66.82; H, 6.98; N, 6.12.

2.3.2. Synthesis of Bodipy-calix[4]azacrown (6)

Calix[4]arene(ethyleneamido)crown (5) (0.5 mmol) were refluxed with NaH (2.1 mmol) in anhydrous CH₃CN (30 mL) for 2.5 h. To this mixture, the solution of 8-{4-(Chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-sindacene (1) (1.5 mmol) in anhydrous mixture of CH₃CN/DMF (20:5 mL) in the presence of catalytic amount of NaI were added dropwise for 1 h. and then additionally refluxed for 72 h. After filtration, the solution was evaporated to dryness. The residue was washed with water. Then, the product was recrystallized from CH₂Cl₂ and MeOH. ¹H NMR [400 MHz, CDCl₃]: δ (ppm) 8.81 (t, 2H, NH), 7.71, (d, 2H, ArH), 7.42 (d, 2H, ArH), 7.17 (d, 4H, ArH), 7.03 (d, 4H,

ArH), 6.82 (t, 2H, ArH), 6.77 (t, 2H, ArH), 5.41 (s, 4H, CH₂), 4.57 (s, 4H, ArOCH₂), 4.17 (d, 4H, J_{AB} = 13.3, ArCH₂Ar), 3.50-3.55 (m, 8H, ArCH₂Ar, NHCH₂), 2.50 (s, 6H CH₃) 2.22 (q, 4H, CH₂) 1.20 (s, 6H, CH₃) 0.86 (t, 6H, CH₃). ¹³C NMR [100 MHz, CDCl₃]: δ (ppm); 166.60, 152.77, 151.11, 149.79, 138.88, 138.12, 136.09, 135.13, 133.81, 131.90, 130.96, 129.27, 128.97, 128.11, 127.84, 127.33, 125.27, 73.21, 71.96, 46.61, 31.17., 18.11, 15.32, 12.57, 11.11. FTIR (ATR) (characteristic frequencies): 3352, 2964, 2931, 1688, 1459, 1251, 1095 cm⁻¹; Anal.Calc. for (%) C₈₂H₈₆N₆O₆B₂F₄: C, 73.00; H, 6.42; N, 6.23; Found: C, 73.09; H, 6.38; N, 6.17.

3. Results and Discussion

3.1. Synthesis and characterization

The synthesis of a new calix[4]arene derivative is given in Scheme 1. For the synthesis of calix[4]azacrown containing two boradiazaindacene (Bodipy) functional units on the narrow rim (6), the parent calixarene compounds 5,11,17,23-Tetra-tert-butyl-25,26,27,28tetrahydroxycalix[4]arene (2),25,26,27,28-tetrahydroxycalix[4]arene 25,27,-di-(3). (methoxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene (4) and calix[4]arene (ethyleneamido)crown (5) were prepared according to published literature procedures [17,23,24]. Corresponding 4-chloromethyl phenyl boradiazaindacene (Bodipy) derivative (1) was synthesized according to modified literature method as mentioned Scheme 1 or follows [33]. In order to access the cassette compound bearing Bodipy (1) synthetically, 4-(chloromethyl)benzoyl chloride was condensed with 2,4-dimethyl-3-ethylpyrrole and was then treated with boron trifluoride diethyl etherate in dry dichloromethane. The required starting compounds *p*-tertbutylcalix [4] arene (2) and debutylated calix [4] arene (3) which was obtained from the dealkylation of *p*-tert-butylcalix[4]arene was synthesized according to literature procedure [23] and then 25,27,-di(methoxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene (4) were obtained in

satisfactory yields by refluxing debutylated calix[4]arene (3) with bromomethyl acetate with K₂CO₃ in CH₃CN for 48 h as described previously. When diester derivative of calixarene (4) was interacted with ethylene diamine in CH₂Cl₂ at room temperature for 24 h, it was converted into calix[4]arene (ethyleneamido)crown (5) which could be isolated by recrystallization from the methanol-dichloromethane solvent mixture. The structures of (1) and (6) were established by the analysis of their ¹H and ¹³C NMR spectra as well as Fourier Transform Infrared FTIR (ATR) and elemental analyses. In the ¹H NMR spectrum, it was determined that the pair of doublets at δ 4.17 $(J_{AB} = 13.3 \text{ Hz})$ and 3.55 $(J_{AB} = 13.1 \text{ Hz})$ for ArCH₂Ar protons that could be correlated with the ¹³C NMR signal at δ 31.17. The high field doublet around δ 3.55 was assigned to the equatorial protons of methylene groups, whereas the low field signal around δ 4.17 was assigned to the axial protons of calixarene scaffold for compound (6). These data suggested that compound (6) possessed a cone structure. Calixazacrown based bodipy (6) exhibited prominent signals at δ 8.81 for amide protons, also this amide group could be correlated with the ${}^{13}C$ NMR signal at δ 166.60, around 7.71 ppm and 7.42 ppm for aromatic protons of two bodipy fragments, while signals for aromatic protons of calixarene scaffold appeared around δ 7.17-6.77 as two doublets and two triplets. The ArOCH₂- protons were seen around δ 4.57 while –NHCH₂ protons were hidden because of the overlapped peaks with the equatorial protons of methylene groups. In addition to above signals caliazate converses based bodipy (6) also showed one singlet around δ 5.41, δ 2.50 and δ 1.20 corresponding to the -OCH₂ and -CH₃ (2,4- position of pyrrole ring) protons of bodipy fragments on the narrow rim, respectively. Furthermore, one quartet assigned to the CH₃CH₂- and one triplet assigned to the CH₃CH₂- appeared at δ 2.22 and δ 0.86 for bodipy fragments of compound (6), respectively. All other data were in agreement with the proposed structures of (**6a-d**). In the ¹³C NMR spectra of compound **6**, it is obvious that compound **6** is symmetrical and therefore the number of signals observed in the ¹³C NMR is lesser than the

number of C atoms in the related compound **6**. But in the ¹³C NMR for compound **6**, two signals are hidden because of the overlapped peaks. In the FTIR spectra, the formation of calixazacrown based bodipy (**6**) have been confirmed by the appearance of the characteristic amide bands (N-C=O) at about 1688 cm⁻¹.

Please insert here Scheme 1

3.2. Lanthanide Recognition Studies

We investigated the recognition ability of receptor (6) for lanthanide metal ion such as La^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Er^{3+} and Yb^{3+} . Firstly, the changes of color in solution were detected for target molecules under Uv-lamp at 365 nm. When the colorless lanthanide solutions in methanol were added to the turquoise solution of compound (6) in methanol, the color transformed to green or the brightness of colour increased. However, there was no remarkable color change upon the addition of La^{3+} metal ion. As shown in **Fig. 1**, the color change of compound (6) upon the addition of lanthanide ions is visible to under Uv-lamp. These color variations may be attributed to photophysical differences of target complex compounds such as luminescence (fluorescence or phosphorescence). So, the fascinating optical properties of lanthanide ions are well-known due to the different luminescent transitions of trivalent ions [34].

Please insert here Fig. 1.

The cation binding properties of compound (6) were investigated by UV–vis, fluorescence, FTIR and ¹H NMR spectroscopy. The absorption spectra of the compound (6) are presented in Fig. 2. Compound (6) shows an absorption spectrum with an absorption pattern typical for Bodipy

chromophores. The absorption spectra of compound (6) $(1 \times 10^{-6} \text{ M})$ show typical absorption bands at 255, 288, 331, 530 nm. These absorption bands correspond to π - π * transition of the aromatic moieties and Bodipy fragments of calixarene backbone, respectively [31,35]. The absorption spectra are similar to that of the compound (6) with one strong peak at 530 nm. Upon addition of La^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Er^{3+} and Yb^{3+} ions to the solution of compound (6), the absorption spectra of (6) changed in response to all metal cations. Among the metal cations, considerable an enhancement of absorbance for compound (6) which is attributed to the formation of the (6)-Yb³⁺ or (6)-Dy³⁺ complexes were observed a peak at 390 nm in the form of shoulder and a sharp peak 530nm upon addition of Dy^{3+} and Yb^{3+} . When compound (6) is complexed with Dy^{3+} or Yb^{3+} , the original peak at 530 nm is increased and a new broad absorption band appeared at 490-500 nm. The intense absorption band of conjugated system around 330 nm is given a bathochromic shift in presence of Dy^{3+} or Yb^{3+} and the bands are appeared around 390 nm. The conjugation between ligand and lanthanide ions is caused to charge transfer to metal ion from the π - system that the changes in the absorption band may be due to expansion of π -conjugated system by Dy^{3+} or Yb^{3+} and occurrence of donor-acceptor charge transfer (CT) in the large π conjugate system with the conjugation of the Bodipycalix[4]azacrown ether units. On the other hand, the strong band of (6)-Gd (III) around 290 nm can be ascribed to f-f intra-configurational electron transitions of gadolinium complexes or the absorption spectra of the coordinated chromophoric ligands [34]. The new absorption band and increasing original peak appeared at longer wavelengths indicating that Dy^{3+} or Yb^{3+} accept more charge from the compound (6). Furthermore, the most intense band around 530 nm can be attributed to a strong S_0 - S_1 transition.

Please insert here Fig. 2.

The fluorescence intensity of free ligand (6) and the changes in its fluorescence intensity in the presence of the lanthanide cations are shown in Fig. 2. Upon addition of lanthanide cations to solutions of compound (6), the maximum emission of compound (6) at 530 nm was enhanced by all of the lanthanides and no shift of the fluorescence maximum was observed for lanthanide cations except for Yb^{3+} . However, slightly change between 490-500 nm and the largest increasing at 530 nm in the fluorescence intensity were observed for Yb^{3+} (Figure 3). It might be anticipated that this effect is related to the blocking of the carbonyl groups of two amide bridges by metal ion complexation. This is not surprising result. Because, in literature trivalent cations as Yb^{3+} , are effectively bound by the amide groups [36,37]. Photoinduced electron transfer (PET) from the electron-donating amide functional groups and oxygen atoms to the Bodipy units of the calixarene is decreased or stopped. It known that lanthanide ions have a large lability and high co-ordination number between 8 and 12 in solution medium. So, the multi-dentate chelating agents contain anionic groups, amides, carboxylates, and/or O and N donor atoms are preferred for lanthanide complexation due to ion-dipole bonding with little covalent character. Nonbonding electrons of nitrogen atoms can be given to metal ion as more easy when compared with oxygen due to its higher electronegativity. Non-bonding electrons of oxygen atoms can carry out the weaker coordination bonds with metal ion. Although the non-bonding electrons of oxygen are difficultly given to metal ions, it can make to co-ordination bonds with lanthanide ions owing to their high co-ordination and hard nature of lanthanide ions [3,36-38]. Furthermore, it is known that diamide derivatives of calix[4]arenes form stable complexes with lanthanide ions, alkali and transition metals due to the presence of a cavity formed by donor atoms of phenol, ether and amide groups [39,40]. Upon complexation with Yb³⁺, the carbonyl group of two amide bridges donates its lone electron pairs to the empty orbital of the Yb³⁺ and a large chelation enhanced fluorescence (CHEF) is observed because the chelation abrogates the PET process [3]. The

increased affinity in complexation for Yb³⁺ can be explained by the fact that there is an important role played by the carbonyl groups having π -electron system and electron-donor nitrogen atoms. In there, the Bodipy-terminal of the calix-derivative behaves as an antenna unit capable of light harvesting (by the binding of analyte). Metal cation binding to the potential chelate group (calix[4]azacrown) are caused these changes in fluorescence spectra. Moreover, these phenomena may reflect the "hard and soft acids and bases" concept introduced by Pearson [41]. According to hard soft acid base principle, lanthanide ions belong to hard acid groups, which have strong affinity for electron-donor groups as carbonyl groups. As this environment exists due to the presence of π -bonds containing functionalities, where cation- π interactions favor the complexation with the more polarizable trivalent lanthanide ions. As mentioned above for absorption spectra, the formation of large π conjugate system is beneficial to increasing the plane structure of the molecule which could make the fluorescence emission easy.

Please insert here Fig. 3.

The excitation spectra of the lanthanide cation complexes are shown in Fig. 4, which matches its absorption spectrum well. While excitation of compound (6) give a curve with four different humps at 450 nm emission, the addition of Yb^{3+}/Dy^{3+} gives graphs with more intensity excitation due to energy transfer. This clearly indicated that the luminescence process was sensitized by the two Bodipy units attached to distal position of phenyl rings. Excitation of compound (6) resulted in a broad band centered on 288 nm, as has been observed earlier for similar calixarenes. These excitation values are assigned to the fluorescence resulting from the π , π^* singlet excited state of the aromatic moieties. The origin of the fluorescence was established by recording excitation spectra, which resembled the absorption spectra of the ligand.

Please insert here Fig. 4.

To confirm calix[4]azacrown-Bodipy (6) as an ion-selective fluorescence receptor for Yb^{3+} ions the effect of competing lanthanide ions was determined. Compound (6) (1 μ M in methanol) was treated with 20 equiv. Yb^{3+} in the presence of other lanthanide ions (20 equiv in methanol), respectively. As shown in Fig. 5, the presence of other lanthanide ions on the detection of Yb^{3+} ions had generally a minor effect or competing ions had practically no effect on the emission peak at 530 nm.

Please insert here Fig. 5.

For complexation ratio between compound (6) and Yb³⁺ ion, we carried out Job's plot experiment by varying the concentrations of both compound (6) and Yb³⁺ ion (see Fig. 6). The maximum point at the mole fraction of ~ 0.49 indicates that a typical 1:1 (ligand:metal) complexation performs in this case.

Please insert here Fig. 6.

To gain more information about the conformation of compound (6) and the binding mode of the Yb^{3+} in complex formation, ¹H NMR studies of the Yb^{3+} complex with compound (6) were performed (Fig. 7). Compound (6) showed changes of the chemical shifts in DMSO- d_6 . The symmetrical cone conformation of free compound (6) is preserved in the Yb^{3+} complex as

indicated by the presence of two AB spin systems for the methylene protons (4.18 and 3.62 ppm) of the calixarene skeleton. Compared to free compound (**6**), pronounced downfield shifts were observed for methylene protons adjacent to the amide nitrogen and the methylene protons of CH_2 -NHCO. And also, the amide protons of the two arms attached to opposite (distal) phenyl rings were downfield shifted and broadened. This interaction was also supported by FTIR (ATR) spectra. The amide (NHCO) stretching vibration in compound (**6**) was shifted from 1688 to 1744 cm⁻¹ after the forming complex of compound (**6**) with Yb³⁺ in the FTIR (ATR) spectra of the compound (**6**) and its Yb³⁺ complex. These data supported that the possible interaction between crown linkage of calixarene and Yb³⁺ was occurred.

Please insert here Fig. 7.

4. Conclusion

In conclusion, the synthesis and trivalent lanthanide (La^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Er^{3+} and Yb^{3+}) ion recognition abilities of novel calizazacrown ether appended Bodipy fluorescent probe (**6**) were studied. The spectroscopic data indicated that the new compound was in the cone conformation. The fluorescence of compound (**6**) was increased upon complexation of particular trivalent lanthanide ios and this increasing is probably due to an intramolecular energy transfer process. Furthermore, from the obtained fluorescence data, it was observed that compound (**6**) was effective structure for Yb^{3+} lanthanide ion. Additionally, the selectivity experiments demonstrated the Yb^{3+} recognition by compound (**6**) was not affected by the presence of other metal cations such as La^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} and Er^3 . These results also suggested that two carbonyl groups of the crown ring may allow some degree of selectivity in sensing lanthanides with very similar ionic radii from those with either larger or smaller radii. Furthermore, the

complex mechanism could be easily changed depending on the concentration of fluorophore, temperature of solution medium, pH, solvent, metal ion characteristic. Finally, this type of receptors seems to be promising in design of chemical sensors, ion-binding processes, phase-transfer catalysts, solid-state sensors, and etc.

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Graphical Abstract

A new calix[4]azacrown ether based boradiazaindacene (Bodipy): selective

fluorescence changes towards trivalent lanthanide ions

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RESEARCH HIGHLIGHT

- ► Calix[4]azacrown ether based boradiazaindacene (Bodipy) were synthesized.
- ► The spectroscopic data indicated that the new compound was in the cone conformation.
- ► Spectrofluorometric studies of both ligand and lanthanide ions were carried out.
- ► Lanthanides recognition ability of calix[4]azacrown were investigated.

Sincerely yours, With Regards M. BAYRAKCI

FIGURE CAPTIONS



Scheme 1. Synthetic route of preparation of compound (1) and Bodipy-calix[4]azacrown (6) (i) Dry CH_2Cl_2 , 60 °C, 2 h, under N_2 ; (ii) Triethylamine, borontrifuoride diethyl etherate, 60 °C, 2 h under N_2 ; (iii) AlCl₃, phenol, toluene, rt, 3 h; (iv) Bromomethylacetate, K₂CO₃, CH₃CN, reflux, 48 h; (v) Ethylenediamine, CH₂Cl₂, rt, 24 h; (vi) NaH, NaI, dry CH₃CN, reflux, 72 h.



Fig. 1 The increasing and change in the brightness of colour of compound (6) (1 μ M) in methanol induced by addition of 20 equiv. of lanthanide nitrate (Yb³⁺, Gd³⁺, Dy³⁺, Er³⁺, Tb³⁺ and La³⁺).



Fig. 2. Absorption spectra of compound (6) $(1 \cdot 10^{-6} \text{ M})$ and its complexes $(\text{La}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Er}^{3+} \text{ and } \text{Yb}^{3+})$ in MeOH



Fig. 3. Fluorescence spectra of the compound (6) in methanol $(1 \ \mu M)$ in the absence and presence of various lanthanide cations. Added cation ion concentrations were 20 μM . Excitation: 400 nm



Fig. 4. Excitation spectra of compound (6) in methanol $(1 \ \mu M)$ in the absence and presence of various lanthanide cations (emmission: 425 nm)



Fig. 5. Compound (6) concentration was set at 1 μ M and the concentration of Yb³⁺-competing lanthanide cations was 20 μ M, respectively. (The fluorescence intensity was at 530 nm)







Fig. 7. ¹H NMR spectra of the complex and compounds. (a) Yb³⁺ complex; (b) compound (6); (c) compound (1)



RESEARCH HIGHLIGHT

► Calix[4]azacrown ether based boradiazaindacene (Bodipy) were synthesized by the reaction between calix[4]arene (ethyleneamido)crown and chloromethyl Bodipy in the cone conformation

► Spectrofluorometric studies of both ligand and lanthanide ions were carried out.

► Lanthanides recognition abilities of calix[4]azacrown ether based boradiazaindacene towards trivalent lanthanide ions such as La^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Er^{3+} and Yb^{3+} were investigated by UV, NMR, FTIR (ATR) and fluorescence spectroscopy.

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