Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 64 (2008) 1058–1063

Synthesis, optical and electroanalytical characterizations of a thiacalix[4](*N*-phenylazacrown-5)ether–BODIPY ionophore

Viktor Csokai,[a] Mihály Kádár,[b,c,d] Diem Lan Ha Mai,[c,d] Olívia Varga,[d,f] Klára Tóth,[b,c,d] Miklós Kubinyi,[e,f,g] Alajos Grün[a] and István Bitter[a,g,*]

[a] *Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[b] *Research Group of Technical Analytical Chemistry of Hungarian Academy of Sciences, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[c] *Department of Inorganic Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[d] *Department of Analytical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[e] *Department of Physical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[f] *Department of Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[g] *Chemical Research Center, Hungarian Academy of Sciences, PO Box 17, H-1525 Budapest, Hungary*

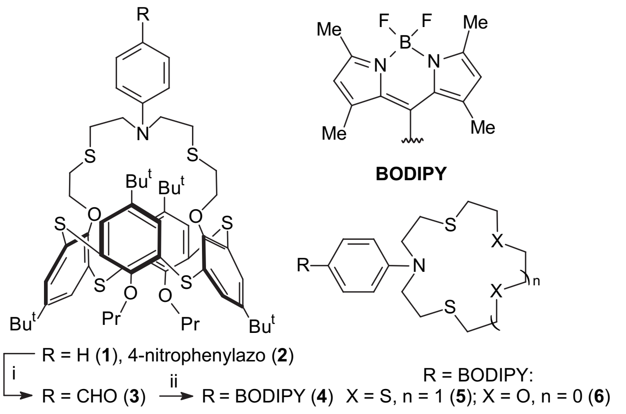
Received 1 February 2007; revised 8 June 2007; accepted 28 June 2007
Available online 10 July 2007

Dedicated to Professor Cs. Szántay on the occasion of his 80th birthday

Abstract—Novel fluorogenic 1,3-alt thiacalix[4](*N*-phenylazacrown-5)ether ionophore has been synthesized by conjugation of the *N*-phenyl group with borondipyrromethene (BODIPY) fluorophore moiety. The ionophore exhibits pronounced off–on type fluorescent responses to some transition metal ions, in particular to Cu^{2+}. In a PVC membrane electrode, distinct Ag^+ selectivity was observed in potentiometric transduction.

1. Introduction

Over the last decades a large number of supramolecules combining the unique properties of calixarenes (CA) and crowns have been described[1,2] and applied in analytical and separation chemistry.[3,4] Recently, calix[4](aza)crowns have attracted great interest due to the easy and versatile derivatization of the nitrogen atom in the crown ring. N-alkylation provides a convenient route to the introduction of various side chains, most frequently additional binding sites or sensing (chromo/fluorophore) units.[5–11] Due to synthetic difficulties associated with the selective base-promoted cyclization of thiacalix[4]arenes (TCA4),[12,13] the respective TCA4-crown counterparts have remained unexplored for years. Our recent method, utilizing the mild and selective Mitsunobu cyclization of TCA4 with glycols, opened an easy way of accessing various distal *O*,*S*,*N*-monocrowns (e.g., **1** in Scheme 1), which otherwise have not been available.[14–16] Among them, in particular, the chromogenic TCA4-O_2,S_2,*N*-crown-5 derivative **2** (Scheme 1) gave optical responses toward some transition metal ions in a preliminary UV–vis spectroscopic study.[16]



Scheme 1. Crowned BODIPY dyes **4**–**6** and the synthesis of **4**. Reagents and conditions: (i) $POCl_3$/DMF; (ii) (a) 2,4-dimethylpyrrole, TFA, DCM, rt; (b) chloranil, DIPEA, rt; (c) $BF_3 \cdot Et_2O$.

The design and synthesis of fluorescent chemosensors are a particularly attractive field of supramolecular chemistry due to the simplicity and high detection limit of the

---

Keywords: Thiacalix[4]crowns; Complexation; BODIPY; Fluorescence; Ion selectivity; ISE.

* Corresponding author. Tel.: +36 1 463 1379; fax: +36 1 463 3648; e-mail: ibitter@mail.bme.hu

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.06.116

fluorescent signals.[17] Besides the development of fluorosensors for main group I and II metal ions,[17a] great progress has been made in the synthesis of fluoroionophores for heavy and transition metal ions working under UV excitation with different mechanisms (PET, ICT, etc.) as off–on or on–off type chemosensors.[18]

Recently, the excellent luminescent properties of BODIPY[19a] (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) derivatives have aroused constantly growing interest. BODIPY dyes can be excited with visible light and possess enhanced (photo)chemical stability, relatively high fluorescent quantum yields showing narrow absorption and emission bands with high peak intensities.[19b] In addition, the structural modification of the dipyrromethene unit allows the generation of dyes with tunable spectral characteristics.[20] These unique properties have been utilized in developing a large number of BODIPY-based chemosensors targeting metal cations of biological relevance.[21]

Among the binding sites of probes, cyclic (crowns) or linear oligoethylene glycol ligating groups are particularly attractive, where the selectivity of complexation can be modified by the number and quality of donor atoms.[21a–c,i,j] In this series, two calix[4]crown ether–BODIPY dyes are also to be mentioned, where the fluorophore was introduced either in the upper rim[21h] or in the azacrown ring through a phenyl group.[21e] Similar or other examples have not been described yet in thiacalixarene chemistry. As part of our ongoing work to expand the number and utility of TCA4-crown ether ionophores,[16,22,23] herein we report on the preparation, optical and electroanalytical investigations of a TCA4-(*N*-phenylazacrown-5)–BODIPY dye **4**.

2. Results and discussion

The synthesis of **4** was straightforward from 1,3-alt TCA4-*N*-phenylazacrown **1**[16] following the literature protocol (Scheme 1). The binding site of **4** is similar to those of the crown–BODIPY counterparts **5**[21i] and **6**[21a] as far as the quality and position of donor atoms are concerned. The ligating atoms, however, are located in different rings in respect of size, flexibility, and steric environment, therefore the comparison of cation sensing properties may provide valuable information on the scope and limit of ion sensing by thiacalixcrown fluorophores.

2.1. Spectroscopic characterization and metal ion binding properties of ligand 4

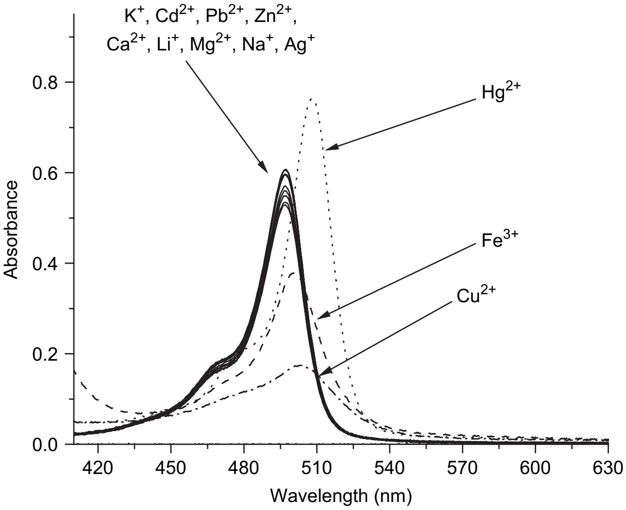


Figure 1. UV–vis spectra of **4** upon addition of 40 equiv of metal salts ([**4**]$=10^{-5}$ M in MeCN).

Receptor **4** shows an absorption spectrum with an absorption pattern typical for BODIPY chromophores. In MeCN, a strong S_0–S_1 transition with a maximum at 497 nm and a shoulder at the shorter wavelength side are observed. No long wavelength charge transfer (CT) absorption is present. Protonation with TFA did not affect the $\lambda_{\max}$ value, only the absorbances decreased slightly indicating the absence of donor–acceptor interaction in the ground state due to the sterically demanding methyl groups forcing the molecules into a twisted conformation. Upon addition of an excess of mono- and divalent metal ions (Li^+, Na^+, K^+, Ag^+, Mg^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+}) and Fe^{3+}, the absorption spectrum of **4** changed only in response to Cu^{2+}, Hg^{2+}, and Fe^{3+}. In the case of Cu^{2+} and Fe^{3+} ions, hypochromic spectra with slightly red-shifted $\lambda_{\max}$ values were obtained, whilst an enhancement of absorbance and 15–20 nm red-shift were detected with Hg^{2+} (Fig. 1).

The changes of the fluorescence emission spectrum were similar to the absorption spectrum. Ligand **4** displayed a weak emission from the locally excited (LE) state of the fluorophore around 520 nm shaped like a mirror image of the absorption spectrum. However, significant emission enhancement characteristic of PET off–on type chemosensors occurred upon protonation with TFA (Fig. 2).

As was expected, strong chelation-induced emission enhancements with some band shifts of **4** were observed on addition of Cu^{2+}, Fe^{3+} (2, 3 nm blue-shift), and Hg^{2+} (8 nm red-shift), while the other ions caused scarcely discernible change of fluorescence (Fig. 3). It is noteworthy, however, that by increasing the excess of Cu^{2+} from 4 to 40 equiv, the emission was enhanced to some extent affording an unstable equilibrium with a relatively rapid fluorescence decay.

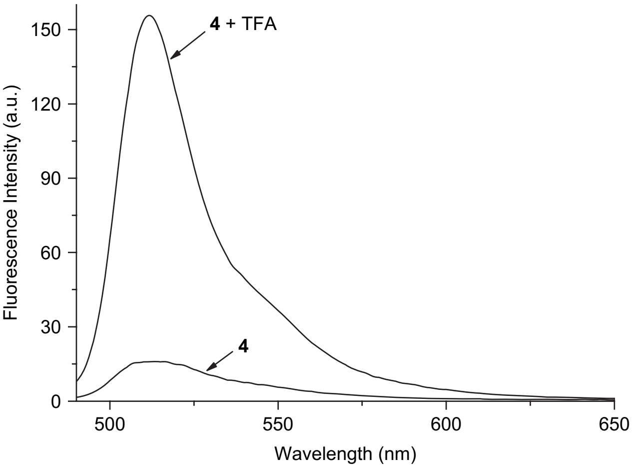


Figure 2. Fluorescence emission spectra of **4** upon protonation with excess of TFA. [**4**]$=4.5\times10^{-6}$ M, [**4**]/[TFA]$=2.6\times10^{4}$, $\lambda_{exc}=470$ nm.

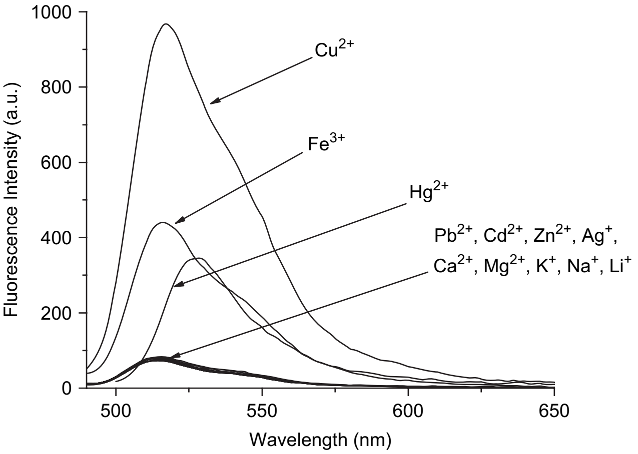


Figure 3. Fluorescence emission spectra of **4** upon addition of 40 equiv of metal salts (Cu^{2+}: 4 equiv). [**4**]$=10^{-5}$ M in MeCN, $\lambda_{exc}=490$ nm.

Anyway, the largest, about 11.8-fold fluorescence enhancement, was achieved with only 4 equiv of Cu^{2+}, while 40 equiv of Fe^{3+} and Hg^{2+} ions led to much lower effects (Fig. 4).

Fluorescence titration experiments with Cu^{2+}, Fe^{3+}, and Hg^{2+} salts afforded a similar series of spectra (illustrated for Cu^{2+} in Fig. 5), which allowed calculation of the log K_s values of complexation from the Benesi–Hildebrand plots applied for 1:1 stoichiometry (Table 1).

Surprisingly, ligand **4** possessing suitable complexing site for thiophilic cations, did not give noteworthy fluorescent response even to 40 equiv of Ag^+ (FEF 1.3). In turn, competitive fluorescence measurements revealed that the emission intensity of the Cu^{2+} complex dramatically decreased in the presence of Ag^+ (Fig. 6) exhibiting FEFs $\phi/\phi_0=8.7$ ($Cu^{2+}/Ag^+=1:1$) and 3.9 ($Cu^{2+}/Ag^+=1:10$) versus 69 (Cu^{2+} alone). This observation means that **4** strongly binds with Ag^+ but it cannot cause a notable fluorescent change in the receptor. At the same time, the complexation of Cu^{2+} is restricted resulting in much lower fluorescence enhancements.

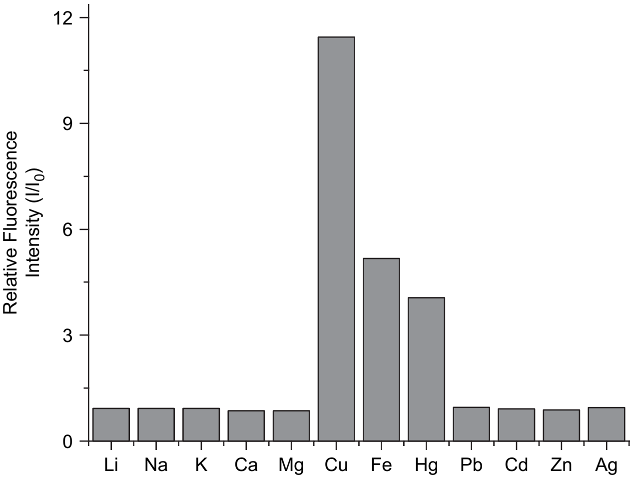


Figure 4. Relative fluorescence intensities of **4**/M^{n+} system (Cu^{2+}: 4 equiv, other ions: 40 equiv).

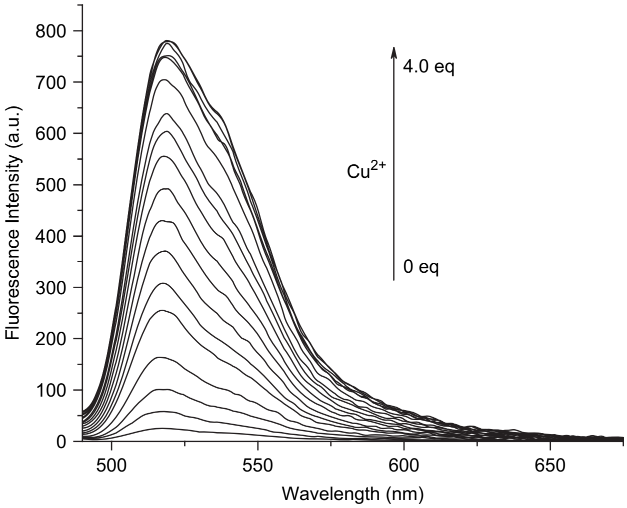


Figure 5. Fluorescence titration of **4** with $Cu(ClO_4)_2$.

The question is, why the Ag^+ complex fluoresces so weakly? Although it is not clear at this point, we assume that the silver ion possessing low positive charge density can be included by the thiacalixarene cavity as well, where it is stabilized by cation–π interaction and coordination with the sterically accessible hetero atoms. Thus, the Ag^+ cation being rather far from the central nitrogen atom cannot induce efficient PET leading to significant FE.

Table 1. Characteristic photophysical and complexation data of **4**/M^{n+} system

4/M^{n+}	$\lambda_{abs}/\varepsilon\times10^3$	λ_{em}	ϕ_f[a]	FEF	log K_s
4	497/76.0	521	0.0016	1	—
Cu^{2+}	502/46.1[b]	517	0.30[b]	185	—
Cu^{2+}	497/64.5[c]	518	0.11[c]	69	4.40
Fe^{3+}	501/54.9	519	0.19	119	4.06
Hg^{2+}	508/94.7	529	0.062	38	4.38

[a] Measured at 488 nm in MeCN relative to Rhodamine 6G perchlorate ($\phi_f=0.76$ in water),[24] error: ±5–10%; 40 equiv of metal salt was used.
[b] The absorption and emission values rapidly decreased in few minutes.
[c] Four equivalents of Cu^{2+}.

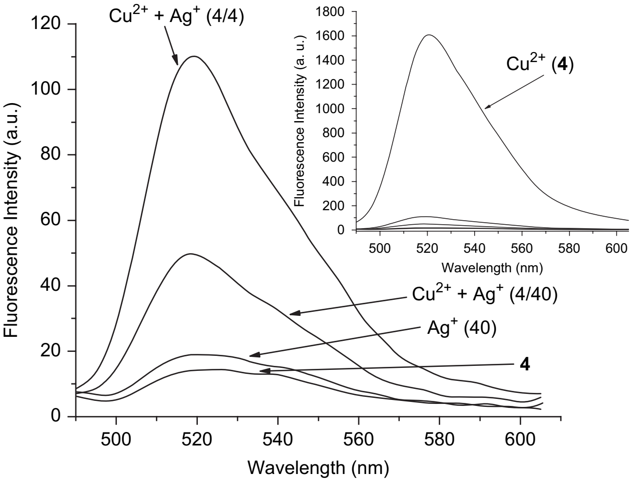


Figure 6. Changes of fluorescence intensity of **4** on addition of Ag^+ (40 equiv), $Cu^{2+}+Ag^+$ (4/4 and 4/40 equiv). [**4**]$=10^{-5}$ M in MeCN, $\lambda_{exc}=488$ nm. Inset: intensity changes relative to Cu^{2+} (4 equiv).

2.2. Evaluation of the fluorescent sensing properties of 4 as compared to phenylazacrowns 5 and 6

NS_4 ligand **5** comprising a 1-aza-4,7,10,13-tetrathia-15-crown-5 unit is claimed to strongly bind with cations in MeCN in the order of Hg^{2+} ($\log K_s$>5.75, ϕ_f=0.59, FEF=5900)>Cu^{2+} ($\log K_s$=5.39, ϕ_f=0.25, FEF=2500)> Ag^+ ($\log K_s$=4.79, ϕ_f=0.22, FEF=2200).[21i] In contrast, *NS_2O* ligand **6** comprised of 1-aza-4,10-dithia-7-oxa-12-crown-4 complexing site (Scheme 1) is claimed to bind as strongly with Fe^{3+} as with Cu^{2+} (FEF>500) in MeCN, but remarkable selectivity was disclosed in MeOH (FEF>500 for Fe^{3+} and ≈10 for Cu^{2+}).[21a]

Our *NS_2O_2* ligand **4** is reminiscent of both in respect of the type, position, and the number of donor atoms, thereby similar sensing features result. However, ligand **4** differs from **5** and **6** concerning the size and flexibility of the crown binding site, which offers a less efficient chelation environment for each ion, however, the weaker complexation resulting in lower sensitivity (FEFs) is associated with noteworthy Cu^{2+} selectivity (Table 1). Unfortunately, the sensing is severely interfered by Ag^+ significantly decreasing the FEFs. This effect may be due to the thiacalixarene scaffold capable of including the silver ion in the cavity, accordingly the Cu^{2+} binding capacity of the crown site is restricted.

2.3. Experiments in membrane phase. Evaluation of the potentiometric selectivities of ligands 1, 2, and 4

Before trying to develop a fluorescent optode, first the ion selectivities of **4** (with reference molecules **1** and **2**) were investigated in a membrane phase. Therefore, plasticized PVC membrane-based ISEs were fabricated using DOS and *o*-NPOE plasticizers, respectively, and the potentiometric ion-selectivity values with respect to Cu^{2+} ($\log K^{pot}_{Cu,M}$) were determined (Table 2). We supposed, this simple and rapid method would help to elucidate how the ionophoric properties would alter in an optode membrane of the same composition.

The potentiometric measurements revealed that the ligand **4**-based ISEs do not give selective responses to Cu^{2+} irrespective of the plasticizer used. Instead, remarkable Ag^+ selectivity was observed, which was further improved when DOS was replaced by *o*-NPOE (Table 2). In particular, the parent ligand **1**-based electrode exhibits extremely high $\log K_{Ag}$ value (+13.97) that exceeds those of our recent TCA4-crown-based potentiometric sensors utilized for the determination of Ag^+ in the sub-nanomolar range.[23] The Ag^+ selectivities of **2** and **4** are also rather high, but significantly lower than that of **1** due to the electron-withdrawing chromophore groups, which reduce the electron density of the central nitrogen atom, thereby allowing Ag^+ to move away from the crown site resulting in weaker potentiometric responses.

Table 2. Potentiometric selectivities of **1**-, **2**- and **4**-based PVC membrane electrodes (*o*-NPOE)

M^{n+}	$\log K^{pot}_{Cu,M}$			
	1	**2**	**4**	Blank
Cu^{2+}	0	0	0	0
Li^+	−1.60	−1.05	−0.28	+0.78
Na^+	−0.58	−0.32	+0.20	+1.58
K^+	+2.33	+3.56	+2.77	+4.55
Ca^{2+}	−1.32	−0.66	−0.26	+0.10
Mg^{2+}	−1.05	−0.25	−0.36	+0.39
Zn^{2+}	−0.46	−0.24	+0.34	+0.40
Cd^{2+}	−1.57	−0.86	−0.60	+0.31
Pb^{2+}	−0.23	−0.94	+0.99	+0.89
Ag^+	+13.97[a]	+8.93[b]	+8.84[c]	−0.27

$[M^{n+}]$=0.1 M in 0.05 M NaOAc/AcOH buffer, pH 5.56, blank: without ionophore.

[a] +11.10 (DOS).

[b] +8.39 (DOS).

[c] +3.64 (DOS).

Preliminary studies with potential PVC optode membranes (thickness 3–4 μm) prepared from **4** and DOS (*o*-NPOE was assumed to quench fluorescence) were carried out in a flow-through cell. We established that **4** strongly fluoresces due to the low polarity of DOS affording restricted PET. Accordingly, on exposure to the flowing solution of Ag^+, only weak fluorescence enhancements were observed (18–20% in the range 10^{-3}–10^{-6} M). Other ions including Cu^{2+} gave no FE. Presently, more polar plasticizers that cannot quench the fluorescence and facilitate the PET process are being tried to find more appropriate conditions for fabricating fluorescent optodes.

3. Conclusion

A novel thiacalix[4](*N*-phenylazacrown-5)ether ionophore coupled with BODIPY fluorescent signaling group (**4**) was synthesized and its optical characteristics were studied in the presence of a series of metal salts. The fluorescent emission spectra revealed an off–on type PET process upon complexation of Cu^{2+}, Hg^{2+}, and Fe^{3+} ions with a preference for Cu^{2+}. The sensitivity of **4**, however, did not reach those of the respective crown ether–BODIPY counterparts **5** and **6**. In addition, a sever Ag^+ interference attributable to the thiacalixarene scaffold was observed decreasing the sensitivity of Cu^{2+} sensing in a competitive process. Plasticized PVC membrane electrodes fabricated from **4** exhibited high potentiometric Ag^+ selectivities over Cu^{2+}.

4. Experimental

4.1. General

Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ at 500/125 MHz on a Bruker Avance DRX-500 spectrometer. ESI mass spectrum was taken in the positive mode using an API-2000 type mass spectrometer. UV–vis spectra were taken on a UNICAM UV4-100 spectrophotometer, the fluorescence spectra were recorded on a Perkin–Elmer LS 50B luminescent spectrometer supplied with an FL WinLab 3.0™ software. Precoated silica gel plates (Merck 60 F_{254}) were used for analytical TLC and Kieselgel 60 for column chromatography. All chemicals were of reagent grade and used without further purification. Compounds **1** and **2** were prepared as described earlier,[16] while the formylation of **1** to **3** and the synthesis of **4** were conducted following literature analogy.[21a]

4.2. Potentiometric measurements

Membrane composition: 2 mg ligand, 60 mg PVC powder, 120 mg plasticizer (dioctyl sebacate (DOS) or *o*-nitrophenyl octyl ether (*o*-NPOE)), and lipophilic anionic site (sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate) 50 mol % with respect to the ligand. The membrane disc (*d*=7 mm) was incorporated into a Philips IS-560 electrode body using 10^{-3} M $CuCl_2$ inner filling solution. The indicator electrodes, thus prepared, were connected with an Ag/AgCl double-junction reference electrode (Metrohm 1098-0013) in a multi-channel pH-meter (Lawson Labs.) and the potentiometric selectivity coefficients were determined by the separate solution method from the EMF data measured in buffered 0.1 M solutions of metal chloride or nitrate salts.

4.3. Thiacalix[4](*N*-phenylaza-*S*$_2$-crown-5)ether–BODIPY dye (4)

Aldehyde **3** (0.3 g, 0.28 mmol), 2,4-dimethylpyrrole (0.1 g, 1.06 mmol), and TFA (three drops) in dichloromethane (50 ml) were allowed to react at ambient temperature for 1 h followed by treatment with chloranil (0.08 g, 0.75 mmol), DIPEA (3 ml), and $BF_3 \cdot Et_2O$ (3 ml) to afford **4** (0.15 g, 40%) as orange solid after column chromatography on silica (hexane/AcOEt=8:2).

Mp >250 °C; IR (KBr) (characteristic frequencies): 2962, 2872, 1612, 1545, 1525, 1511, 1471, 1440, 1309, 1266, 1196, 1088, 984 cm^{-1}; ^{1}H NMR δ 7.34 (s, 4H, Ar*H*), 7.33 (s, 4H, Ar*H*), 7.05 (d, 2H, *J*=8.5, Ar*H*), 6.67 (d, 2H, *J*=8.5, Ar*H*), 5.98 (s, 2H, pyrrole C*H*), 4.00 (t, 4H, *J*=8.5, OC*H*$_2$), 3.73 (t, 4H, *J*=8.0, OC*H*$_2$), 3.28 (t, 4H, *J*=7.5, OC*H*$_2$), 2.57 (br, 4H, NC*H*$_2$), 2.55 (s, 6H, C*H*$_3$), 2.25 (t, 4H, *J*=8.5, SC*H*$_2$), 1.49 (s, 6H, C*H*$_3$), 1.31 (s, 18H, ^{t}Bu), 1.27 (s, 18H, Bu^t), 0.84 (p, 4H, C*H*$_2$), 0.62 (t, 6H, *J*=7.5, C*H*$_3$); ^{13}C NMR δ 156.6, 156.5, 155.0, 147.4, 146.1, 146.0, 143.1, 142.7, 132.2, 129.3, 128.4, 127.6, 127.4, 125.8, 122.7, 121.0, 117.5 (Ar), 77.3, 69.9, 67.2 (O*C*H$_2$), 50.7 (N*C*H$_2$), 34.4, 34.3 (*C*(CH$_3$)$_3$), 31.7, 31.6 (C(*C*H$_3$)$_3$), 32.1 (S*C*H$_2$), 21.7 (*C*H$_2$), 14.7, 14.6 (*C*H$_3$), 10.0 (*C*H$_3$); ESI-MS (KCl doping): 1354.5 [M+K]$^+$, monoisotopic mass (1315.55). Anal. Calcd for $C_{73}H_{92}BF_2N_3O_4S_6$ (1316.73) C 64.59, H 7.04, N 3.19, S 14.61; found C 64.35, H 7.09, N 3.14, S 14.52%.

Acknowledgements

Financial support from the Hungarian Scientific Research Foundation (OTKA No. T 046055, T 046403, and T 042546) is gratefully acknowledged.

References and notes

1. Casnati, A.; Ungaro, R.; Asfari, Z.; Vicens, J. *Calixarenes 2001*; Asfari, M., Boehmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 2001; pp 365–384.
2. Ungaro, R.; Arduini, A.; Casnati, A.; Pochini, A.; Ugozzoli, F. *Pure Appl. Chem.* **1996**, *68*, 1213–1218.
3. Ludwig, R. *Fresenius' J. Anal. Chem.* **2000**, *367*, 103–128.
4. Thuéry, P.; Nierlich, M.; Lamare, V.; Dozol, J. F.; Asfari, Z.; Vicens, J. *J. Inclusion Phenom. Macrocycl. Chem.* **2000**, *36*, 375–408.
5. Ikeda, A.; Tsudera, T.; Shinkai, S. *J. Org. Chem.* **1997**, *62*, 3568–3574.
6. Kim, J. S.; Yu, I. Y.; Suh, I.-H.; Ra, D. Y.; Kim, J. W. *Synth. Commun.* **1998**, *28*, 2937–2944.
7. Kim, J. S.; Shon, O. J.; Lee, J. K.; Lee, S. H.; Kim, J. Y.; Park, K.-M.; Lee, S. S. *J. Org. Chem.* **2002**, *67*, 1372–1375.
8. Kim, J. S.; Shon, O. J.; Rim, J. A.; Kim, S. K.; Yoon, J. *J. Org. Chem.* **2002**, *67*, 2348–2351.
9. Kim, J. S.; Shon, O. J.; Ko, J. W.; Cho, M. H.; Yu, I. Y.; Vicens, J. *J. Org. Chem.* **2000**, *65*, 2386–2392.
10. Kim, J. S.; Shon, O. J.; Sim, W.; Kim, S. K.; Cho, M. H.; Kim, J.-G.; Suh, I.-H.; Kim, D. W. *J. Chem. Soc., Perkin Trans. 1* **2001**, 31–36.
11. Kim, J. S.; Shon, O. J.; Yang, S. H.; Kim, J. Y.; Kim, M. J. *J. Org. Chem.* **2002**, *67*, 6514–6518.
12. Grün, A.; Csokai, V.; Parlagh, Gy.; Bitter, I. *Tetrahedron Lett.* **2002**, *43*, 4153–4156.
13. van Leeuwen, F. W. B.; Beijleveld, H.; Kooijman, H.; Spek, A. L.; Verboom, W.; Reinhoudt, D. N. *Tetrahedron Lett.* **2002**, *43*, 9675–9678.
14. Bitter, I.; Csokai, V. *Tetrahedron Lett.* **2003**, *44*, 2261–2265.
15. Csokai, V.; Grün, A.; Bitter, I. *Tetrahedron Lett.* **2003**, *44*, 4681–4684.
16. Csokai, V.; Bitter, I. *Supramol. Chem.* **2004**, *16*, 611–619.
17. (a) *Fluorescent Chemosensors for Ion and Molecular Recognition*; Czarnik, A. W., Ed.; ACS Symposium Series 538; American Chemical Society: Washington, DC, 1993; (b) Czarnik, A. W. *Acc. Chem. Res.* **1994**, *27*, 302–308; (c) Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, *24*, 197–202; (d) de Silva, A. P.; Gunaratne, H. Q. N.; Gunlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566; (e) Martinez-Máñez, R.; Sancanón, F. *Chem. Rev.* **2003**, *103*, 4419–4476.
18. (a) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Coord. Chem. Rev.* **2000**, *205*, 59–83; (b) Rurack, K. *Spectrochim. Acta, Part A* **2001**, *57*, 2161–2195.
19. (a) BODIPY® is a registered trademark of Molecular Probes Inc., Eugene, OR, U.S.A.; (b) Haugland, R. P. *Handbook of Fluorescent Probes and Research Chemicals*, 9th ed.; Molecular Probes: Eugene, OR, U.S.A., 2002.
20. Rohand, T.; Baruah, M.; Qin, W. W.; Boens, N.; Dehaen, W. *Chem. Commun.* **2006**, 266–268.
21. Recent examples: (a) Bricks, J. L.; Kovalchuk, A.; Trieflinger, C.; Nofz, M.; Büschel, M.; Tolmachev, A. I.; Daub, J.; Rurack, K. *J. Am. Chem. Soc.* **2005**, *127*, 13522–13529; (b) Yamada, K.; Nomura, Y.; Citterio, D.; Iwasawa, N.; Suzuki, K. *J. Am. Chem. Soc.* **2005**, *127*, 6956–6957; (c) Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2005**, *127*, 10464–10465; (d) Basarić, N.; Baruah, M.; Qin, W. W.; Metten, B.; Smet, M.; Dehaen, W.; Boens, N. *Org. Biomol. Chem.* **2005**, *3*, 2755–2761; (e) Malval, J.-P.; Leray, I.; Valeur, B. *New J. Chem.* **2005**, *29*, 1089–1094; (f) Wu, Y. K.; Peng, X. J.; Guo, B. C.; Fan, J. L.; Zhang, Z. C.; Wang, J. Y.; Cui, A. J.; Gao, Y. L. *Org. Biomol. Chem.* **2005**, *3*, 1387–1392; (g) Moon, S. Y.;

Cha, N. R.; Kim, Y. H.; Chang, S.-K. *J. Org. Chem.* **2004**, *69*, 181–183; (h) Cha, N. R.; Moon, S. Y.; Chang, S.-K. *Tetrahedron Lett.* **2003**, *44*, 8265–8268; (i) Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968–969; (j) Kollmannsberger, M.; Rurack, K.; Resch-Genger, U.; Rettig, W.; Daub, J. *Chem. Phys. Lett.* **2000**, *329*, 363–369.

22. Csokai, V.; Grün, A.; Balázs, B.; Simon, A.; Tóth, G.; Bitter, I. *Tetrahedron* **2006**, *62*, 10215–10222.
23. Szigeti, Zs.; Malon, A.; Vigassy, T.; Csokai, V.; Grün, A.; Wygladacz, K.; Ye, N.; Xu, C.; Chebny, V. J.; Bitter, I.; Rathore, R.; Bakker, E.; Pretsch, E. *Anal. Chim. Acta* **2006**, *572*, 1–10.
24. Olmsted, J. *J. Phys. Chem.* **1979**, *83*, 2581–2584.