

# A novel colorimetric and fluorometric anion sensor based on BODIPY-calix[4]pyrrole conjugate

Yongjun lv · Jian Xu · Yong Guo · Shijun Shao

Received: 18 January 2011 / Accepted: 1 March 2011 / Published online: 20 April 2011  
© Springer Science+Business Media B.V. 2011

**Abstract** A novel fluorescent anion sensor **1** based on boradiazaindacenes (BODIPY) derivative was synthesized and its absorption and fluorescence properties were investigated in various solvents. **1** exhibited a red shift of absorption spectrum and fluorescence quenching in varying degree in the presence of  $F^-$ ,  $AcO^-$ ,  $H_2PO_4^-$  and  $Cl^-$  due to multiple hydrogen bonding interactions between these anions and calix[4]pyrrole receptor. As an anion sensor in the visible region, **1** displayed the similar selectivity and sensitivity toward anions compared to the parent calix[4]pyrrole. However, **1** can be used as an effective dual responsive optical sensor for  $F^-$  via chromogenical and fluorogenical signals.

**Keywords** Calix[4]pyrrole · BODIPY · Fluorescence · Colorimetric · Anion sensor

## Introduction

Design and synthesis of optical chemosensors capable of selectively recognizing and sensing anions have attracted increasing interest in the last few years, as anions play an important role in medical, biological, and environmental researches [1–5]. Many reported anion receptors generally follow the approach of the covalent attachment of a signaling unit to an anion receptor [6]. Based on this strategy, some chromophores and fluorophores capable of absorbing and emitting in the visible region have been employed to response anion binding by giving rise to colorimetric receptors and fluorometric receptors. Among many signaling fluorophores, BODIPY dyes are very attractive functional groups due to their high extinction coefficients, fluorescence quantum yields, stability against light and chemical reactions, and excitation at approximately 500 nm. Moreover, the parent BODIPY dye can be easily modified to afford a variety of chemosensors, light-harvesting systems, energy transfer cassettes, fluorescent biolabeling reagents, and photodynamic therapy [7, 8]. In spite of this, fluorescent anion sensors based on BODIPY moiety are still relatively rare [9–12]. Therefore, we set out to construct a novel colorimetric and fluorometric anion sensor that contains a fluorescent BODIPY moiety and a calix[4]pyrrole anion binding site. As is well known, calix[4]pyrrole, a class of molecule known for over a century, are effective anion binding agents for halides, carboxylates and phosphates via multiple hydrogen bonding interactions in solution [13–15]. However, the parent calix[4]pyrrole only response anion recognition events in

**Electronic supplementary material** The online version of this article (doi:10.1007/s10847-011-9946-1) contains supplementary material, which is available to authorized users.

Y. lv · J. Xu · Y. Guo · S. Shao (✉)  
Key Laboratory of Chemistry of Northwestern  
Plant Resources and Key Laboratory for Natural Medicine  
of Gansu Province, Lanzhou Institute of Chemical Physics,  
Chinese Academy of Sciences, Lanzhou 730000,  
People's Republic of China  
e-mail: sjshao@licp.cas.cn

S. Shao  
State Key Laboratory for Oxo Synthesis and Selective  
Oxidation, Lanzhou Institute of Chemical Physics,  
Chinese Academy of Sciences, Lanzhou 730000,  
People's Republic of China

Y. lv  
Graduate School of the Chinese  
Academy of Sciences, Beijing 100039,  
People's Republic of China

the ultraviolet region, and these changes are unpredictable and difficult to rationalize. As a result, it is desirable to design calix[4]pyrrole-based sensors by attaching various fluorescent reporter groups such as anthracene, dansyl, rhodamine B, fluorescein, and anthraquinone moieties [16–18], and these systems show relatively short-wavelength absorption and emission spectra changes. To obtain an optical anion sensor in the longer wavelength region, we herein report a novel BODIPY-calix[4]pyrrole conjugate **1** and its spectroscopic properties and particular behaviors of anion recognition and sensing. The target compound **1** and a reference **2** were prepared according to the route shown in Scheme 1.

## Experimental section

### Materials and methods

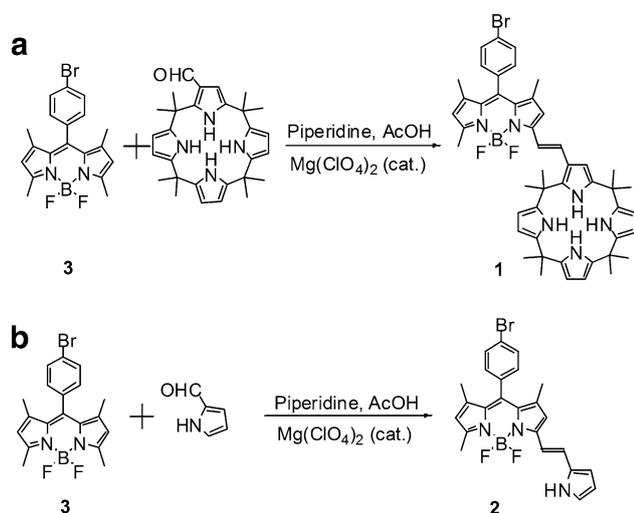
All chemicals were obtained from commercial suppliers and used without further purification.  $\text{CH}_2\text{Cl}_2$  was distilled from NaH, THF was distilled from  $\text{LiAlH}_4$ , and  $\text{CH}_3\text{CN}$  was distilled from  $\text{P}_2\text{O}_5$  prior to use. Silica gel (mesh 200–300) was used for TLC analysis and flash column chromatography. Proton and carbon NMR spectra were performed on a Varian INOVA 400 MHz spectrometer in  $\text{CDCl}_3$  using TMS as the internal standard. HRMS (ESI) studies were carried out using a Bruker Daltonics APEX spectrometer. The emission spectra were recorded on a Perkin Elmer LS55 spectrometer. UV–vis spectra were determined on a Perkin Elmer Lambda 35 spectrometer. FT-IR spectra were performed on a Nexus 870 spectrometer. C, H, N elemental analyses were made on a Vario-EL.

### Synthesis of 3-[2-( $\beta$ -octamethylcalix[4]pyrrolyl)ethenyl]-4,4-difluoro-8-(4-bromo)phenyl-1,5,7-trimethyl-3a,4a-diaza-4-bora-s-indacene (**1**)

Compound **3** (1.00 g, 2.19 mmol) [19] and formylcalix[4]pyrrole (0.88 g, 2.19 mmol) [20] were refluxed in a mixture of toluene (80 mL), piperidine (0.5 mL), glacial acetic acid (0.5 mL), and  $\text{Mg}(\text{ClO}_4)_2$  (cat.). Any water formed during the reaction was removed azeotropically by heating in a Dean-Stark apparatus overnight. After completion of the reaction monitored by TLC, solvents were evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel using eluent ( $\text{CH}_2\text{Cl}_2/\text{Hexane}$ , 1:1). The red colored fraction was collected to afford purple solid **1**. Yield 40%. M.p.  $>300^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.40 (s, 3H,  $\text{CH}_3$ ), 1.44 (s, 3H,  $\text{CH}_3$ ), 1.50 (s, 6H,  $\text{CH}_3$ ), 1.51 (s, 6H,  $\text{CH}_3$ ), 1.53 (s, 6H,  $\text{CH}_3$ ), 1.66 (s, 6H,  $\text{CH}_3$ ), 2.57 (s, 3H,  $\text{CH}_3$ ), 5.84 (d,  $J = 3$  Hz, 1H, pyrrolic CH), 5.88 (d,  $J = 3$  Hz, 1H, pyrrolic CH), 5.91–5.94 (m, 3H, pyrrolic CH), 5.96 (d, 3.2 Hz, 2H, pyrrolic CH), 6.38 (s, 1H, NH), 6.50 (s, 1H, CH), 6.90 (s, 2H, 2NH), 7.16 (s, 1H, NH), 7.18–7.24 (m, 4H, 2H for ArH, 1H for vinylic, 1H, CH), 7.60–7.63 (m, 3H, 2H for ArH, 1H for vinylic).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  14.5, 14.6, 15.0, 28.6, 28.7, 29.3, 29.8, 35.1, 35.2, 35.3, 37.4, 101.8, 102.8, 103.0, 103.1, 103.6, 103.7, 103.8, 114.5, 117.3, 117.8, 120.5, 123.0, 130.3, 130.8, 132.3, 132.8, 134.4, 136.9, 137.2, 137.3, 137.6, 138.1, 138.3, 138.7, 139.2, 139.4, 140.2, 142.7, 152.9, 155.8. FT-IR (KBr): 3406.05, 3104.88, 2966.64, 2924.01, 2865.72, 1602.60, 1544.04, 1508.36, 1488.84  $\text{cm}^{-1}$ . HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{48}\text{H}_{52}\text{BBrF}_2\text{N}_6$  840.3608 ( $\text{M} + \text{H}^+$ ), Found 840.3600. Anal. Calcd. for **1** ( $\text{C}_{48}\text{H}_{52}\text{N}_6\text{BBrF}_2$ ): C, 67.99; H, 7.04; N, 9.37. Found: C, 68.06; H, 6.93; N, 9.37.

### Synthesis of 3-[2-(2-pyrrolyl)ethenyl]-4,4-difluoro-8-(4-bromo)phenyl-1,5,7-trimethyl-3a,4a-diaza-4-bora-s-indacene (**2**)

The procedure is similar to the synthesis of **1**. Compound **3** (1.00 g, 2.19 mmol) reacted with 2-formylpyrrole (0.21 g, 2.19 mmol) to afford black solid **2**. Yield 42%. M.p.  $>300^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.42 (s, 3H,  $\text{CH}_3$ ), 1.43 (s, 3H,  $\text{CH}_3$ ), 2.55 (s, 3H,  $\text{CH}_3$ ), 5.97 (s, 1H, CH), 6.26 (m,  $J = 4.4$  Hz, 1H, pyrrolic CH), 6.45 (m,  $J = 4.4$  Hz, 1H, pyrrolic CH), 6.53 (s, 1H, CH), 6.90 (s,  $J = 4.0$  Hz, 1H, pyrrolic CH), 7.11 (s, 2H, vinylic CH), 7.18 (d,  $J = 8.4$  Hz, 2H, ArH), 7.62 (d,  $J = 8.4$  Hz, 2H, ArH), 8.76 (s, 1H, NH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  14.6, 15.0, 110.9, 112.6, 114.1, 117.6, 120.9, 122.2, 123.2, 126.7, 130.2, 130.5, 132.3, 134.2, 137.4, 141.1, 142.6, 153.7, 154.1. FT-IR (KBr): 3362.70, 2918.33, 2851.39,



**Scheme 1** The synthetic route of compounds **1** and **2**

1603.48, 1541.15, 1496.11  $\text{cm}^{-1}$ . HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{24}\text{H}_{21}\text{BBBrF}_2\text{N}_3$  479.1089 ( $\text{M} + \text{H}^+$ ), Found 479.1092. Anal. Calcd. for **2** ( $\text{C}_{24}\text{H}_{21}\text{N}_3\text{BBBrF}_2$ ): C, 58.91; H, 4.60; N, 8.15. Found: C, 58.85; H, 4.65; N, 8.12.

## Results and discussion

### Design and synthesis of sensors

The “fluorophore-spacer-receptor” format, one of the most popular models to build fluorescent sensors and switches [21, 22], was configured for the design of sensor **1**. In this case, BODIPY unit was a fluorophore, calix[4]pyrrole unit served as an anion binding site, and vinyl fragment acted as a spacer. It was predicted that intramolecular charge transfer (ICT) process would occur from the electron-rich calix[4]pyrrole unit to the electron-withdrawing BODIPY unit [23, 24]. Moreover, this ICT process can be enhanced by the anion coordination of calix[4]pyrrole unit, which would result in changes in absorption and fluorescence spectra [25, 26]. For a control test, compound **2** was synthesized as a reference to study the anion recognition mechanism.

The target compound **1** was prepared by a little modified Knoevenagel reaction in satisfied yields. Intermediate **3** reacted with formyl-calix[4]pyrrole and 2-formylpyrrole to obtain compounds **1** and **2**, respectively.

### Spectroscopic properties of sensors

As shown in Table 1, spectroscopic properties of **1** and **2** were investigated in various solvents. Their absorption maxima showed minor solvent-dependent shifts, indicating a weak ICT character for the lowest electronic excitation in the ground state [27]. Both **1** and **2** displayed an absorption band centered at 586–595 nm having about a 90 nm red shift in comparison to that of the parent BODIPY dye **3**

( $\lambda_{\text{Abs}} = 499 \text{ nm}$ ). This red shift can be attributed to the increased degree of  $\pi$ -electron conjugation of the two compounds due to the attachment of the conjugated pyrrole unit to BODIPY core. The high molar absorption coefficients of **1** and **2** suggested that the long-wavelength of the absorption spectra were ICT bands during  $\text{S}_0 \rightarrow \text{S}_1$  transition.

Fluorescence quantum yields of **1** and **2** were estimated in different solvents using rhodamine B ( $\Phi_f = 0.49$  in EtOH) as a standard [28]. As the solvent polarity increased, the  $\Phi_f$  value became small, which can be assigned to the solvent relaxation of the fluorescent state in the polar solvent. Both **1** and **2** showed identical emission maxima at 600–620 nm, which revealed their similar ICT nature of excited states. The Stokes shift for sensor **1** or **2** was small ( $\Delta_{\text{max}\nu} = 338\text{--}1061 \text{ cm}^{-1}$ ) indicating that there was no obvious difference in the structure of sensor in the ground state  $\text{S}_0$  and in the first excited state  $\text{S}_1$  [29]. However, the fluorescence quantum yield of **1** was smaller than that of **2**, especially in  $\text{CH}_3\text{CN}$ , which may be ascribed to a more efficient ICT process for the system of **1** in the polar solvent.

In a word, both **1** and **2** exhibited almost similar absorption and fluorescence characteristics. These results indicated that, for sensor **1**, the conjugated pyrrole group of calix[4]pyrrole subunit made substantial contributions to its improved spectroscopic properties.

### Anion sensing studies of sensors

The anion binding and sensing properties of sensor **1** were firstly studied by UV–vis spectroscopic techniques. Sensor **1** ( $1 \times 10^{-5} \text{ M}$  in  $\text{CH}_3\text{CN}$ ) itself displayed an intense absorption peak at 587 nm which can be assigned to the ICT absorption band. Upon addition of anions such as  $\text{F}^-$ ,  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$  and  $\text{HSO}_4^-$  (as tetrabutylammonium salts) to the solution of sensor **1**, only

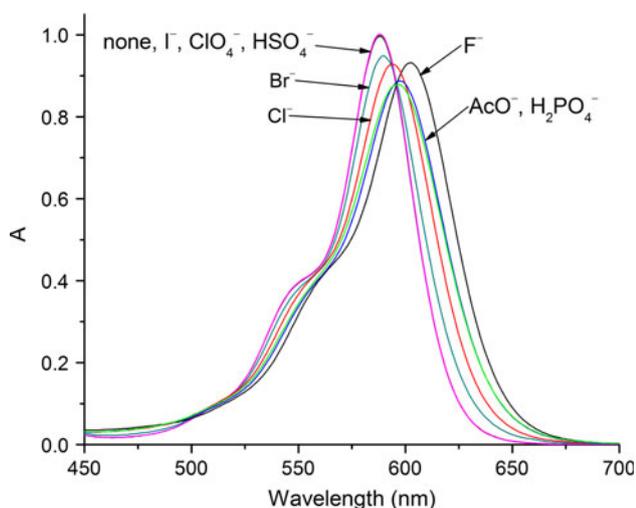
**Table 1** Spectroscopic characteristics of two BODIPY dyes (**1** and **2**) in different solvents

Dyes	Solvent	$\lambda_{\text{Abs}}$ (max/nm)	$\lambda_{\text{em}}$ (max/nm)	$\Delta_{\text{max}\nu}$ ( $\text{cm}^{-1}$ )	$\Phi_f$	$\varepsilon$ ( $\text{M}^{-1}\text{cm}^{-1}$ )
<b>1</b>	$\text{CH}_3\text{CN}$	587	626	1061	0.036	$0.97 \times 10^5$
	EtOH	591	622	843	0.100	$0.86 \times 10^5$
	THF	592	617	684	0.187	$0.79 \times 10^5$
	$\text{CH}_2\text{Cl}_2$	589	617	770	0.200	$1.02 \times 10^5$
	Cyclohexane	589	604	422	0.219	$1.84 \times 10^5$
<b>2</b>	$\text{CH}_3\text{CN}$	586	619	910	0.176	$1.34 \times 10^5$
	EtOH	595	623	755	0.207	$1.12 \times 10^5$
	THF	595	620	678	0.210	$0.88 \times 10^5$
	$\text{CH}_2\text{Cl}_2$	590	613	636	0.249	$1.52 \times 10^5$
	Cyclohexane	590	602	338	0.299	$1.78 \times 10^5$

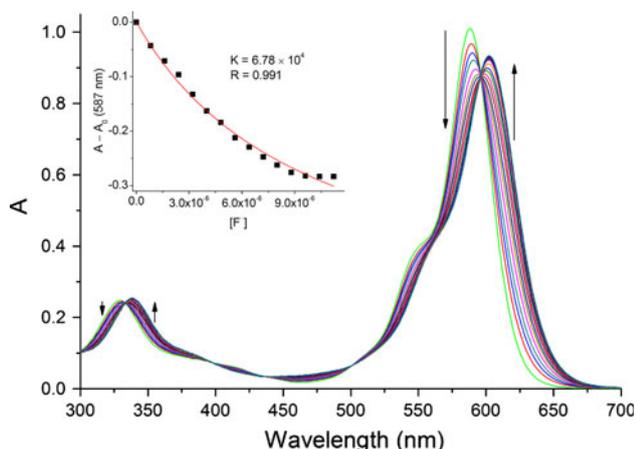
$F^-$ ,  $AcO^-$ ,  $H_2PO_4^-$  and  $Cl^-$  induced obvious absorption spectral changes over other anions tested (Fig. 1).

During the titration of  $F^-$  with a solution of sensor **1** in Fig. 2, the absorption maximum at 587 nm decreased, along with the formation of a new red-shift band centered at 602 nm, which was responsible for simultaneously changing the solution of **1** from fuchsia to blue (Fig. 3). Likewise, a new red-shift absorption band appeared at 597 nm for  $AcO^-$ , at 596 nm for  $H_2PO_4^-$  or 592 nm for  $Cl^-$ , respectively (Fig. S1–S3). Naked eye-detectable color change from fuchsia to purple was observed for  $AcO^-$  and  $H_2PO_4^-$ .

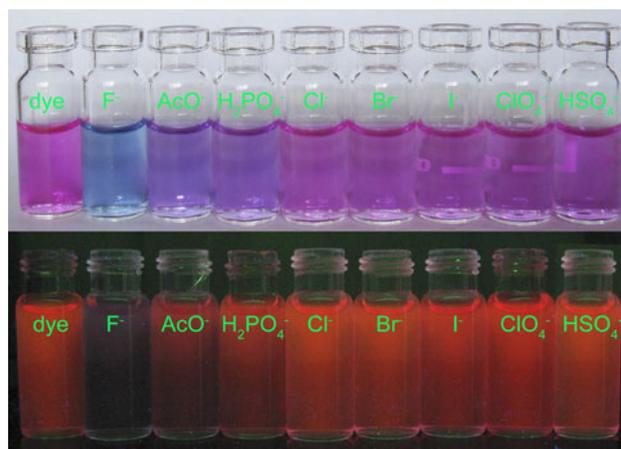
The 1:1 binding stoichiometry of sensor **1** with  $F^-$ ,  $AcO^-$ ,  $H_2PO_4^-$ , and  $Cl^-$  (Fig. 4) was established by Job plot method, respectively. According to 1:1 model, the



**Fig. 1** Changes in the UV–vis absorption spectrum of **1** ( $1 \times 10^{-5}$  M in  $CH_3CN$ ) upon addition of various anions (10 equiv. excess)



**Fig. 2** Changes in the UV–vis absorption spectrum of **1** ( $1 \times 10^{-5}$  M in  $CH_3CN$ ) upon addition of  $F^-$  from 0 to  $1.1 \times 10^{-5}$  mol  $L^{-1}$ . Inset: Nonlinear curve fitting as a function of  $[F^-]$  monitored at 587 nm



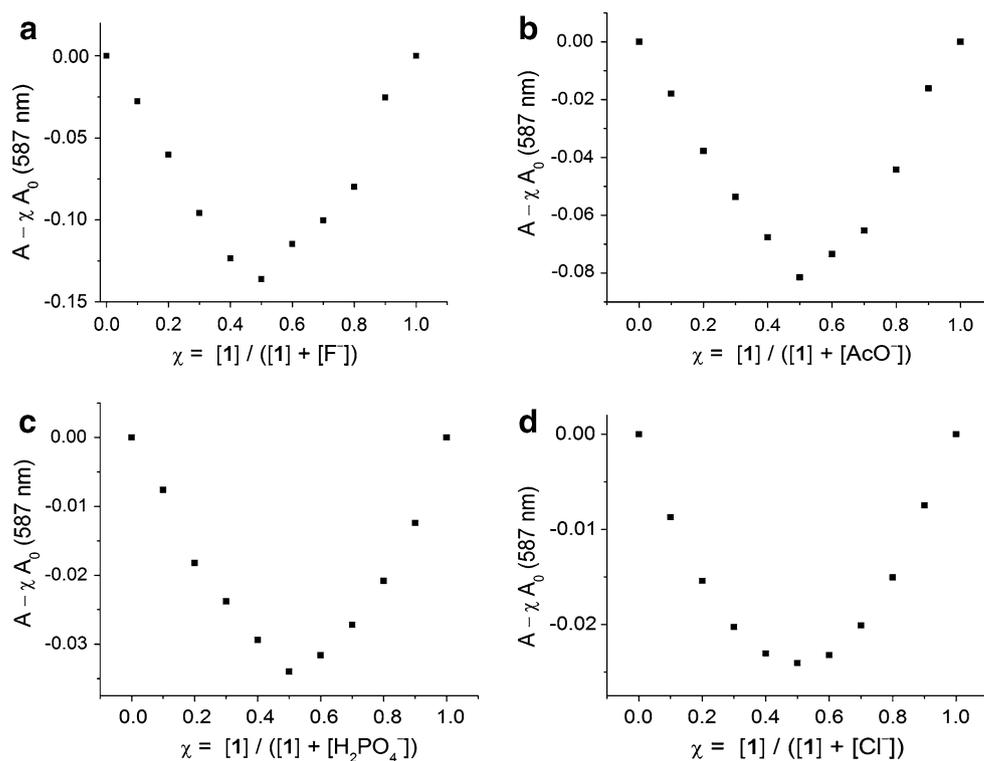
**Fig. 3** The color changes and the fluorescence emission responses of **1** ( $1 \times 10^{-5}$  M in  $CH_3CN$ ) upon addition of various anions (10 equiv. excess)

association constants of sensor **1** interacting with these anions were determined (Figs. 2 and S1–S3 inset) and the values were given in Table 2 [30]. The affinity of sensor **1** toward various anions was:  $F^- > AcO^- > H_2PO_4^- > Cl^- \gg Br^-, I^-, ClO_4^-$  and  $HSO_4^-$ , in consistent with that of the parent calix[4]pyrrole [31]. These results suggested that the anion-sensor complexations formed between sensor **1** and putative anions, which might be based on hydrogen bonds.

For a further investigation, fluorescence titration experiment of sensor **1** ( $5 \times 10^{-6}$  M) with  $F^-$  was conducted in  $CH_3CN$  (Fig. 5). With gradual addition of  $F^-$ , the emission intensity at 626 nm decreased without any significant changes in the emission wavelength, which reflected that there was no obvious structure difference in sensor **1** before and after binding  $F^-$  in the first excited state. Fluorescence quenching can be ascribed to the occurrence of ICT process from calix[4]pyrrole unit upon binding  $F^-$  to BODIPY unit. Quenching was also observed in varying degree upon addition of  $AcO^-$ ,  $H_2PO_4^-$ , and  $Cl^-$  to sensor **1** (Fig. S4–S6). In this stance it can be seen that the addition of  $F^-$  caused the greatest fluorescence quenching, followed by the addition of  $AcO^-$ ,  $H_2PO_4^-$  and  $Cl^-$  (Fig. 3). Using these quenching data and Nonlinear curve fitting, association constants were calculated for sensor **1** interacting with  $F^-$ ,  $AcO^-$ ,  $H_2PO_4^-$  and  $Cl^-$ , as illustrated in Table 2 (Figs. 5 and S4–S6 inset). In general, good agreement was observed between these  $K$  values and those obtained using UV–vis changes. In contrast, addition of  $Br^-$ ,  $I^-$ ,  $ClO_4^-$ , and  $HSO_4^-$  showed no significant fluorescence response.

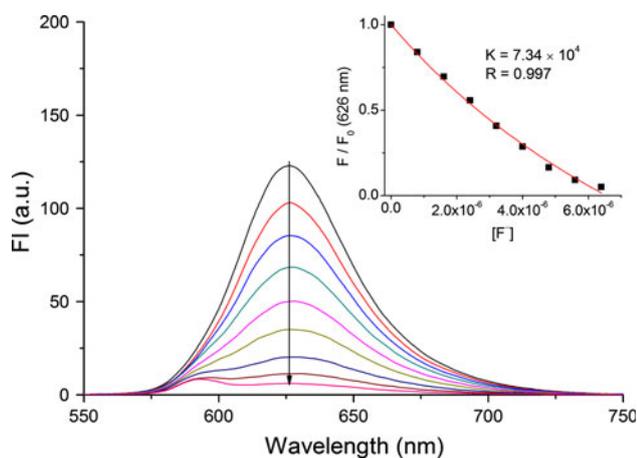
The reversibility of the anion binding process was examined by adding water to the system of sensor **1**, in result, the absorption and fluorescence spectra can revert to the original spectra. This is presumably because water

**Fig. 4** Job plots of sensor **1** with various anions measured by UV–vis spectroscopy at 587 nm in CH<sub>3</sub>CN. [1] + [Anion] = 1 × 10<sup>-5</sup> M



**Table 2** Association constants for sensor **1** with putative anions in CH<sub>3</sub>CN as determined from UV–vis at 587 nm and fluorescence titrations at 626 nm

Anion	$K$ (M <sup>-1</sup> ) determined by absorption changes	$K$ (M <sup>-1</sup> ) determined by fluorescence quenching
F <sup>-</sup>	$6.78 \times 10^4$	$7.34 \times 10^4$
AcO <sup>-</sup>	$2.27 \times 10^4$	$3.42 \times 10^4$
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$4.16 \times 10^3$	$9.11 \times 10^3$
Cl <sup>-</sup>	$1.88 \times 10^3$	$2.59 \times 10^3$

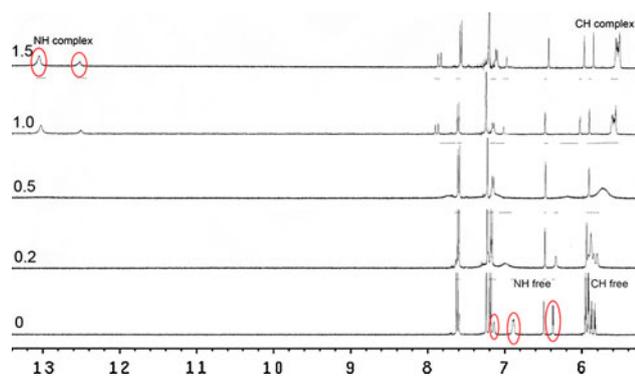


**Fig. 5** Changes in the emission spectrum of **1** ( $5 \times 10^{-6}$  M in CH<sub>3</sub>CN) upon addition of F<sup>-</sup> from 0 to  $6.4 \times 10^{-6}$  M. Inset: Nonlinear curve fitting as a function of [F<sup>-</sup>] monitored at 626 nm. Excitation was at 587 nm

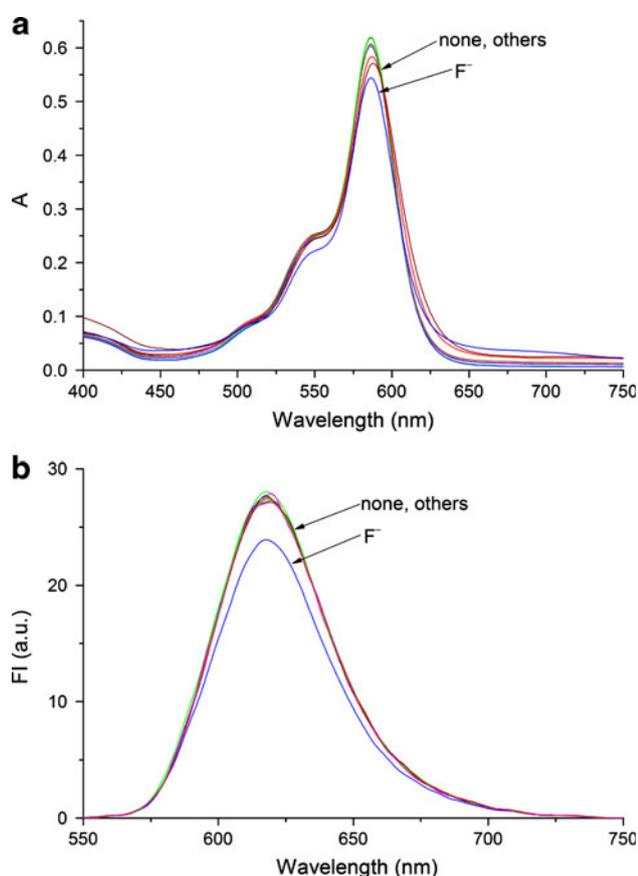
could compete for anion with NH moieties through hydrogen bonding interactions.

In addition, the nature of interactions between sensor **1** and F<sup>-</sup> was evident by means of <sup>1</sup>H NMR titration in CDCl<sub>3</sub>, as shown in Fig. 6. With gradual addition of tetrabutylammonium fluoride to sensor **1**, pyrrolic NH protons resonance broadened and downfield shifted significantly from 6.377, 6.897 and 7.162 to 12.52 and 13.05 ppm, consistent with the formation of anion-sensor hydrogen bonds. Moreover, it was also found that pyrrolic CH protons upfield shifted and split by interaction with fluoride. These results indicated that hydrogen bonding interactions may occur between sensor **1** and F<sup>-</sup> involving calix[4]pyrrole-anion complex.

For a comparison, a control experiment using reference **2** was carried out to investigate whether the interaction of sensor **1** with anions underwent deprotonation under similar experimental conditions. There were no significant absorption and fluorescence changes observed upon addition of various anions tested (Fig. 7). These results indicated that the only one pyrrole unit, as an anion binding site, can not effectively bind anions through deprotonation or hydrogen bonds. In the case of calix[4]pyrrole-based sensor **1**, the pyrrole unit that conjugated to BODIPY fluorophore should cooperate with other three pyrrole units to effectively bind anions through multiple hydrogen bonds. In other words, bearing calix[4]pyrrole unit as an effective and sensitive anion binding unit, **1** can be used as a colorimetric and fluorometric anion sensor.



**Fig. 6**  $^1\text{H}$  NMR spectra of sensor **1** in the presence of 0.2, 0.5, 1.0 and 1.5 equiv. of  $\text{F}^-$ . The NH and  $\beta$ -pyrrolic CH proton resonances in free and complexed sensor **1** are labeled as follows: NH free, CH free, NH complex, and CH complex



**Fig. 7** **a** Changes in the UV–vis absorption spectrum of **2** ( $5 \times 10^{-6}$  M in  $\text{CH}_3\text{CN}$ ) upon addition respective anions (10 equiv. excess). **b** Changes in the emission spectrum of **2** ( $5 \times 10^{-6}$  M in  $\text{CH}_3\text{CN}$ ) upon addition of respective anions (10 equiv. excess). Excitation was at 586 nm by use of 1% T attenuator emission filter

## Conclusion

According to the concept “reporter-spacer-receptor”, numerous sensors can be designed and constructed. Herein,

a new fluorescent anion sensor **1** based on BODIPY-calix[4]pyrrole conjugate was reported, and it can be used as a colorimetric and fluorometric anion sensor especially for  $\text{F}^-$  based on hydrogen bonding interactions. Though the anion binding behavior of sensor **1** toward specific anions was the same as that of the parent calix[4]pyrrole, the introduction of the BODIPY group had a positive effect on the anion sensing properties of calix[4]pyrrole receptor, which allowed the detection of anions via dual optical methods in the visible region. As a result, the recognition of  $\text{F}^-$  gave rise to the fabrication of both color change from fuchsia to blue and fluorescence quenching, which would have a potential application to develop a naked-eye detection material. Further work to that end is in progress.

**Acknowledgments** This work was supported by the National Natural Science Foundation of China (Grant No. 20972170 to S-J. Shao), the open fund of State Key Laboratory of Oxo Synthesis & Selective Oxidation (Grant No. OSSO2008kjk6 to S-J. Shao) and by the Natural Science Foundation of Gansu province (No. 096RJ2A033 to Y. Guo).

## References

- Gale, P.A., Garcia-Garrido, S.E., Garric, J.: Anion receptors based on organic frameworks: highlights from 2005 and 2006. *Chem. Soc. Rev.* **37**, 151–190 (2008)
- Steed, J.W.: Coordination and organometallic compounds as anion receptors and sensors. *Chem. Soc. Rev.* **38**, 506–519 (2009)
- Caltagirone, C., Gale, P.A.: Anion receptor chemistry: highlights from 2007. *Chem. Soc. Rev.* **38**, 520–563 (2009)
- Kubik, S.: Amino acid containing anion receptors. *Chem. Soc. Rev.* **38**, 585–605 (2009)
- Amendola, V., Fabbrizzi, L.: Anion receptors that contain metals as structural units. *Chem. Commun.* **5**, 513–531 (2009)
- Loudet, A., Burgess, K.: BODIPY dyes and their derivatives: synthesis and spectroscopic properties. *Chem. Rev.* **107**, 4891–4932 (2007) and references therein
- Ulrich, G., Ziessel, R., Harriman, A.: The chemistry of fluorescent bodipy dyes: versatility unsurpassed. *Angew. Chem. Int. Ed.* **47**, 1184–1201 (2008)
- Coskun, A., Baytekin, B.T., Akkaya, E.U.: Novel fluorescent chemosensor for anions via modulation of oxidative PET: a remarkable 25-fold enhancement of emission. *Tetrahedron Lett.* **44**, 5649–5651 (2003)
- Ekmekci, Z., Yilmaz, M.D., Akkaya, E.U.: A monostyryl-boradiazaindacene (BODIPY) derivative as colorimetric and fluorescent probe for cyanide ions. *Org. Lett.* **10**, 461–464 (2008)
- Shiraishi, Y., Maehhara, H., Sugii, T., Wang, D., Hirai, T.: A BODIPY-indole conjugate as a colorimetric and fluorometric probe for selective fluoride anion detection. *Tetrahedron Lett.* **50**, 4293–4296 (2009)
- Gale, P.A., Sessler, J.L., Král, V.: Calixpyrroles. *Chem. Commun.* **1**, 1–8 (1998)
- Gale, P.A., Anzenbacher, J.P., Sessler, J.L.: Calix[4]pyrroles II. *Coordination Chem. Rev.* **222**, 57–102 (2001) and references therein
- Lee, C.H., Miyaji, H., Yoon, D.W., Sessler, J.L.: Strapped and other topographically nonplanar calixpyrrole analogues. Improved anion receptors. *Chem. Commun.* **1**, 24–34 (2008)

14. Miyaji, H., Anzenbacher, P.J., Sessler, J.L., Bleasdale, E.R., Gale, P.A.: Anthracene-linked calix[4]pyrroles: fluorescent chemosensors for anions. *Chem. Commun.* **17**, 1723–1724 (1999)
15. Anzenbacher, J.P., Jursíková, K., Sessler, J.L.: Second generation calixpyrrole anion sensors. *J. Am. Chem. Soc.* **122**, 9350–9351 (2000)
16. Miyaji, H., Sato, W., Sessler, J.L.: Naked-eye detection of anions in dichloromethane: colorimetric anion sensors based on calix[4]pyrrole. *Angew. Chem. Int. Ed.* **39**, 1777–1780 (2000)
17. Zhang, X., Xiao, Y., Qian, X.: Highly efficient energy transfer in the light harvesting system composed of three kinds of boron-dipyromethene derivatives. *Org. Lett.* **10**, 29–32 (2008)
18. Nishiyabu, R., Anzenbacher, J.P.: 1,3-Indane-based chromogenic calixpyrroles with push–pull chromophores: synthesis and anion sensing. *Org. Lett.* **8**, 359–362 (2006)
19. Kollmannsberger, M., Rurack, K., Resch-Genger, U., Daub, J.: Ultrafast charge transfer in amino-substituted boron dipyrromethene dyes and its inhibition by cation complexation: a new design concept for highly sensitive fluorescent probes. *J. Phys. Chem. A* **102**, 10211–10220 (1998)
20. Sunahara, H., Urano, Y., Kojima, H., Nagano, T.: Design and synthesis of a library of BODIPY-based environmental polarity sensors utilizing photoinduced electron-transfer-controlled fluorescence ON/OFF switching. *J. Am. Chem. Soc.* **129**, 5597–5604 (2007)
21. Rurack, K., Kollmannsberger, M., Daub, J.: Molecular switching in the near infrared (NIR) with a functionalized boron-dipyromethene dye. *Angew. Chem. Int. Ed.* **40**, 385–387 (2001)
22. Yuan, M., Li, Y., Li, J., Li, C., Liu, X., Lv, J., Xu, J., Liu, H., Wang, S., Zhu, D.: A colorimetric and fluorometric dual-modal assay for mercury ion by a molecule. *Org. Lett.* **9**, 2313–2316 (2007)
23. Miyaji, H., Sato, W., Sessler, J.L., Lynch, V.M.: A ‘building block’ approach to functionalized calix[4]pyrroles. *Tetrahedron Lett.* **41**, 1369–1373 (2000)
24. Nishiyabu, R., Anzenbacher, P.J.: Sensing of antipyretic carboxylates by simple chromogenic calix[4]pyrroles. *J. Am. Chem. Soc.* **127**, 8270–8271 (2005)
25. Coskun, A., Akkaya, E.U.: Ion sensing coupled to resonance energy transfer: a highly selective and sensitive ratiometric fluorescent chenosensor for Ag (I) by a modular approach. *J. Am. Chem. Soc.* **127**, 10464–10465 (2005)
26. Baruah, M., Qin, W., Flors, C., Hofkens, J., Vallée, R.A.L., Beljonne, D., Auweraer, M.V., Borggraeve, W.M.D., Boens, N.: Solvent and pH dependent fluorescent properties of a dimethylaminostyryl borondipyromethene dye in solution. *J. Phys. Chem. A* **110**, 5998–6009 (2006)
27. Casey, K.G., Quitevis, E.L.: Effect of solvent polarity on non-radiative processes in xanthene dyes: rhodamine b in normal alcohols. *J. Phys. Chem.* **92**, 6590–6594 (1988)
28. Almonasy, N., Nepraš, M., Hyková, Š., Lyčka, A., Čermák, J., Dvořák, M., Michl, M.: The synthesis of *N*-derivatives of 3-aminoperylene and their absorption and fluorescence properties. *Dyes Pigment.* **82**, 164–170 (2009)
29. Tian, M., Peng, X., Feng, F., Meng, S., Fan, J., Sun, S.: Fluorescent pH probes based on boron dipyrromethene dyes. *Dyes Pigment.* **81**, 58–62 (2009)
30. Connors, K.A.: *Binding Constants: The Measurement of Molecular Complex Stability.* Wiley, New York (1987)
31. Gale, P.A., Sessler, J.L., Allen, W.E., Tvermoes, N.A., Lynch, V.: Calix[4]pyrroles: *C*-rim substitution and tenability of anion binding strength. *Chem. Commun.* **7**, 665–666 (1997)