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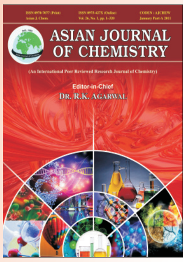

Anion Recognition of Two Calix[4]pyrrole-BODIPY Sensors Containing Different Steric Groups

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The anion recognition properties of *meso*-octaethyl and *meso*-tetracyclohexyl calix[4]pyrrole-based boradiazaindacenes (BODIPY) sensors (compound **2** and **3**) were investigated by absorption and fluorescence spectra. The results showed that both sensors effectively gave dual responses for F^- through color changes and fluorescence quenching. Compared with *meso*-octamethylcalix[4]pyrrole-BODIPY sensor compounds **1**, **2** exhibited a higher selectivity for F^- and compound **3** showed rather weaker bonding interactions with tested anions, which can be ascribed to their steric hindrance effect of different *meso*-alkyl groups of calix[4]pyrrole.

Keywords: Anion recognition, Calix[4]pyrrole, BODIPY, Steric.

INTRODUCTION

The search for novel and selective anion sensors continues to be a challenging area of supramolecular chemistry[1,2]. Because of the key role of anions in fundamental aspects of chemistry and biology, the development of anion hosts has attracted considerably attention[3-6]. During numerous anion receptors, calix[4]pyrrole, a venerable class of macrocycles, exhibit interesting anion binding characteristics[7-9]. As known, Sessler and co-workers[9,10] firstly discovered that calix[4]pyrrole analogs are effective anion receptors for halids, carboxylates and phosphates by hydrogen bonds. These have led to the synthesis of expanded analogues, the attachment of optical and electrochemical groups and the higher order calix[n]pyrroles (*i.e.*, those where $n > 4$)[11-14]. In these work various functional groups were modified at the different positions including *C*-rim, *N*-rim and *meso*-position, in order to readily predict and rationalize anion binding process. It is evident that the binding strength decreases as the steric bulk of neutral and anionic substrates are increased[15,16]. These findings inspired us to investigate whether calix[4]pyrrole moieties bearing diverse hindrance blocks respond special anions. Therefore, *meso*-octamethylcalix[4]pyrrole, *meso*-octaethylcalix[4]pyrrole and *meso*-tetracyclohexylcalix-[4]pyrrole, were selected with increasing steric bulk at the *meso*-position (Fig. 1). Besides, BODIPY, acting as a fluorescent signaling group[17,18], was introduced at the *C*-rim to readily rationalize anion recognition. In previous work, anion sensing natures of compound **1** have been studied[19]. Herein, we report the synthesis, characterization and anion recognition properties of other novel sensors compound **2** and **3** to reveal the steric hindrance effect at *meso*-position of calix[4]pyrrole.

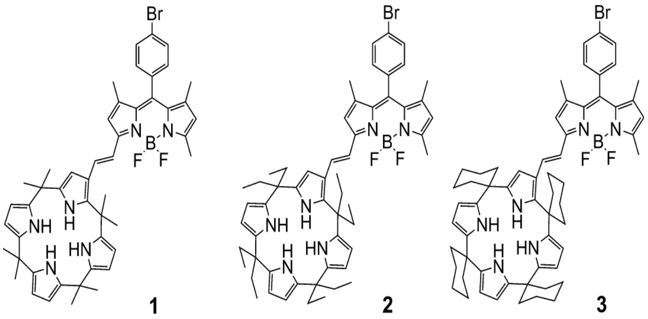

Fig. 1. Structures of sensors compounds **1**, **2**, and **3**

EXPERIMENTAL

All the tetrabutylammonium salts with various anions were purchased from Alfa Aesar and used without further purification. Acetonitrile was chromatographic pure. ^{1}H NMR and ^{13}C NMR spectra were using a Varian INOVA 400 MHz spectrometer. ESI-MS were recorded using a Waters Micromass ZQ-4000 spectrometer. UV-visible spectra were determined using a Perkin Elmer Lambda 35 spectrometer. Fluorescence were recorded on a Perkin Elmer LS55 spectrometer. C, H, N elemental analyses were performed on a Vario-EL.

Sensors compounds **2** and **3** were prepared according to the reported route of sensor[19] compound **1**.

Compound 2: Yield 38 %. m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.60 (m, 30 H, CH_2CH_3), 1.90 (m, 10 H,

CH_2CH_3), 1.42 (s, 6H, CH_3), 2.57 (s, 3H, CH_3), 5.90 (m, 6H, pyrrolic CH), 5.96 (d, J = 3.2 Hz, 2H, pyrrolic CH), 6.37 (s, 1H, NH), 6.87 (s, 1H, NH), 7.14 (s, 2H, 2NH), 7.18-7.21 (m, 4H, 2H for ArH, 1H for vinylic, 1H, CH), 7.59-7.64 (m, 3H, 2H for ArH, 1H for vinylic). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 7.9, 8, 8.7, 14.5, 15, 28.3, 29.1, 29.7, 30.4, 42.8, 43.0, 46.6, 104.3, 104.8, 105.3, 105.9, 119.6, 120.4, 123.0, 132.3, 33.6, 134.5, 135, 135.8, 136.1, 136.4, 136.7, 137.2, 142.7, 152.5. ESI-MS: *m/z* 954.5 $[M + H]^+$. Anal. Calcd. for compound **2** ($C_{56}H_{68}N_6BBrF_2$): C, 70.49; H, 7.20; N, 8.85; found: C, 70.52; H, 7.16; N, 8.88.

Compound 3: Yield 32 %. m.p. > 300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.42 (s, 6H, CH_3), 1.49 (m, 30 H, CH_2), 2 (m, 10H, CH_2), 2.60 (s, 3H, CH_3), 5.88-6 (m, 6H, pyrrolic CH), 5.91-5.94 (m, 2H, pyrrolic CH), 5.96 (d, J = 3.2 Hz, 1H, pyrrolic CH), 6.40 (s, 1H, NH), 6.49 (s, 1H, NH), 7.16 (s, 2H, 2NH), 7.18-7.24 (m, 3H, 2H for ArH, 1H for vinylic), 7.63-7.67 (m, 3H, 2H for ArH, 1H for vinylic). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.7, 14.7, 15, 115.8, 116.9, 117.8, 121,4, 123.3, 129.3, 129.4, 130.1, 132.4, 134.1, 136.5, 138.3, 142.1, 142.4, 142.5, 153.8, 153.8, 155.1, 156.7. ESI-MS: *m/z* 1003.2 $[M + H]^+$. Anal. Calcd. for compound **3** ($C_{60}H_{68}N_6BBrF_2$): C, 71.91; H, 6.84; N, 8.40; found: C, 71.85; H, 6.87; N, 8.38.

RESULTS AND DISCUSSION

The anion sensing properties of sensors compounds **2** and **3** were firstly studied by UV-visible absorptions in CH_3CN, which were recorded from the solutions of both compounds in the absence or presence of anions such as F^-, AcO^-, $H_2PO_4^-$, Cl^-, Br^-, I^-, ClO_4^- and HSO_4^-. Both compound **2** and **3** displayed an intense absorption peak at 590 nm corresponding to charge transfer of the classical BODIPY moiety[20]. Upon addition of various anions to the solution of sensor compound **2**, only F^- induced obvious absorption and color changes from fuchsia to blue in Fig. 2. During UV-visible titrations of compound **2** with F^- in Fig. 3, the absorption maximum at 590 nm decreased and red-shifted to 606 nm. While as for compound **3**, similar absorption and naked eye-detectable color changes were observed not only for F^- but for AcO^-, $H_2PO_4^-$ and Cl^-. By contrast, addition of Br^-, I^-, ClO_4^- and HSO_4^- showed no significant absorption and color change. The different anion sensing responses of compounds **2** and **3** can be ascribed to their distinguishing hindrance effect at the *meso*-position of calix[4]pyrrole.

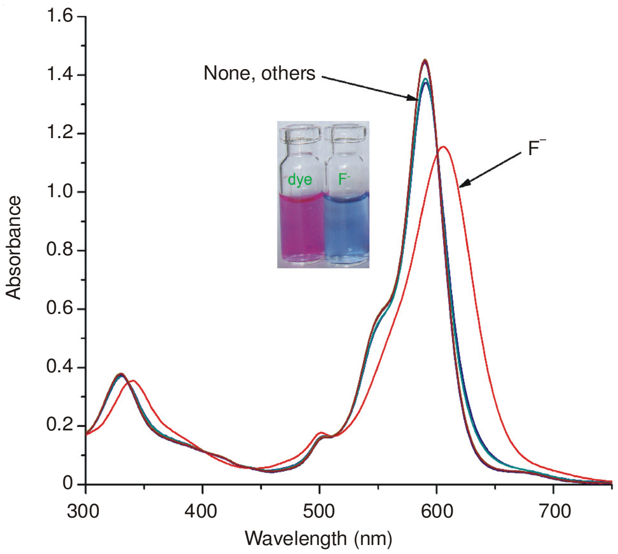

Fig. 2. Changes in the UV-visible absorption spectrum of compound **2** (1×10^{-5} M in CH_3CN) upon addition of various anions (10 equiv. excess); inset: The color changes of compound **2** upon addition of 10 equiv. of F^-

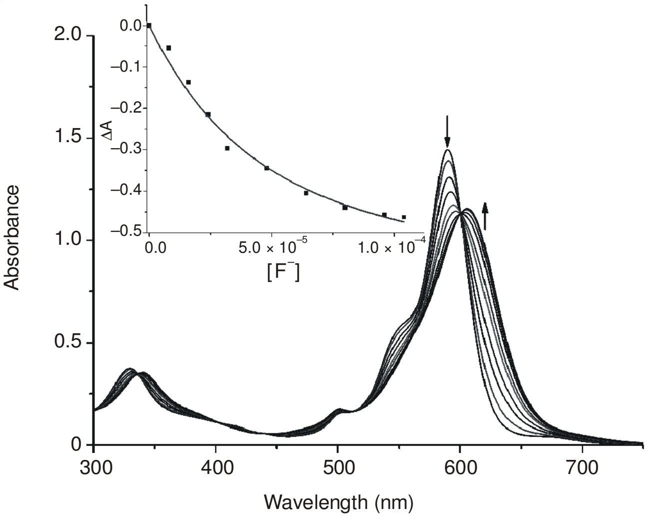

Fig. 3. Changes in the UV-visible absorption spectrum of compound **2** (1×10^{-5} M in CH_3CN) upon addition of F^- from 0 to 1.1×10^{-4} M; inset: non-linear curve fitting as a function of $[F^-]$ monitored at 590 nm

For a further investigation, their association constants were calculated according to[21] 1:1 stoichiometry (Fig. 3) and the values were given in Table-1. The affinity of sensors toward F^- is: **1** > **2** > **3**, which is assigned to the effect of steric hindrance of *meso*-alkyl groups of the calix[4]pyrrole: methyl < ethyl < cyclohexyl. As for sensor compounds **2**, we preclude, the small electron-rich cavity, formed by four pyrrole rings and octaethyl groups, can only allow the approach of the small size of F^-, while exclude other bigger size anions[22]. But as for compound **3**, the fixed and rigid of tetracyclohexyl groups led to a slight open and big cavity, which could easily capture not only smaller F^- but also bigger AcO^-, $H_2PO_4^-$ and Cl^-. These results suggested that the binding strength decreases as the steric alkyl groups at the *meso*-position of calix[4]pyrrole are increased.

TABLE-1
ASSOCIATION CONSTANTS FOR SENSORS COMPOUNDS **2** AND **3** WITH PUTATIVE ANIONS IN CH_3CN AS DETERMINED FROM UV-VISIBLE ABSORPTION CHANGES AT 590 nm

Anion	K (M^{-1}) in CH_3CN		
	1[a]	**2**	**3**
F^-	6.78×10^4	2.87×10^4	8.00×10^3
AcO^-	2.27×10^4	–[b]	5.11×10^3
$H_2PO_4^-$	4.16×10^3	–[b]	2.63×10^3
Cl^-	1.88×10^3	–[b]	8.88×10^2

[a]K values of **1** refer to the reported paper[19]; [b]Changes in the UV-visible spectra were not enough to determine the association constant

Fluorescence titration experiments of both compound **2** and **3** with various anions were also conducted. With gradual addition of F⁻, the fluorescence intensity of compound **2** at 629 nm decreased obviously without any significant changes in the emission wavelength (Fig. 4). Red fluorescence quenching can be ascribed to the occurrence of intramolecule charge transfer (ICT) process from calix[4]pyrrole unit to BODIPY[23]. Slight quenching was observed upon addition of AcO^-, $H_2PO_4^-$ or Cl^-.

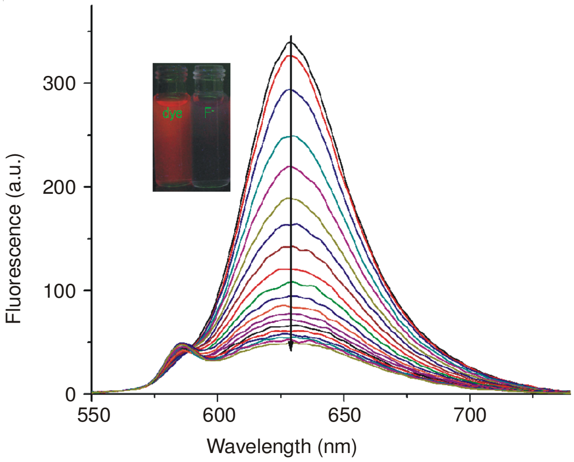

Fig. 4. Changes in the emission spectrum of compound **2** (1×10^{-6} M in CH_3CN) upon addition of F^- from 0 to 5.6×10^{-5} M. Excitation was at 590 nm

Interestingly, in the case of compound **3**, addition of F^- not only induced the decrease of fluorescence intensity, but also produced a slight blue shift about 10 nm (Fig. 5). Similar changes were also observed in the fluorescence titration experiments of compound **3** with AcO^-, $H_2PO_4^-$ and Cl^-. This blue shift could be attributed to a slight twist of the calix[4]pyrrole-BODIPY plane, which can influence the co-planarity of the molecule system, after binding anions in the first excited state[24]. Different affects of octaethyl and tetra-cyclohexyl groups on the cavity should be responsible for their different anion sensing behaviors of compounds **2** and **3** in fluorescence spectra.

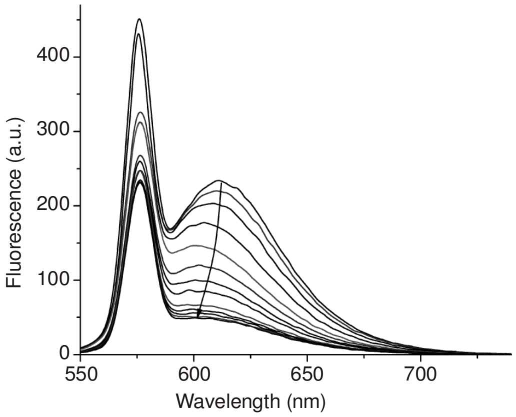

Fig. 5. Changes in the emission spectrum of compound **3** (1×10^{-6} M in CH_3CN) upon addition of F^- from 0 to 1.1×10^{-5} M. Excitation was at 590 nm

Conclusion

In summary, two BODIPY-calix[4]pyrrole sensors were constructed and their significant colorimetric and fluorometric changes were investigated. Sensor compound **2** selectively recognized F^- because of the fitness of the electron-rich cavity with the size of F^-. Nevertheless, sensor compound **3** didn't exhibit good selectivity owing to the fixed and rigid steirc hindrance leading to a slight twist of host plane in the anion binding event. Therefore, such a design by introducing different substituent groups into the *meso*-position of calix[4]-pyrrole skeleton would help tune the inorganic anion sensing ability of calix[4]pyrrole derivatives. Further work to modify at *C*-rim or *N*-rim is under way.

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