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Novel calix[4]arene-based receptors with bis-squaramide moieties for colorimetric sensing of anions via two different interaction modes

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ABSTRACT

Novel calix[4]arene-based anion receptors **1–3** with bis-squaramide moieties were designed and synthesized. Their sensing properties with various anions were investigated by UV–vis, ESI-MS, and ^{1}H NMR spectra. The experimental results revealed that there were two types of interaction modes where receptor **1** bound biologically important $H_2PO_4^-$, F^-, and AcO^- ions selectively over other anions in the hydrogen bonding interaction mode, while receptors **2** and **3** displayed deprotonation behavior with basic anions (F^-, AcO^-, and $H_2PO_4^-$) via acid–base interaction mode. Receptors **2** and **3** were proved to be efficient 'naked-eye' sensors for F^- and AcO^- with marked color changes.

Anion plays an important role in a wide range of chemical, biological, and environmental science.[1] Thus, anion recognition as a significant branch of supramolecular chemistry has become an active research field in recent decades.[2] Numerous charge neutral receptors containing polarized N–H fragments such as amides,[3] ureas,[4] thioureas,[5] and pyrroles[6] as excellent hydrogen bond donors have been widely employed in the anion recognition. However, although a number of anion receptors bearing above N–H groups have been studied, there is still a need for developing novel receptors based on N–H binding units to enhance the binding affinity and selectivity for various anions. Thanks to the pioneering work of Costa's[7] and Fabbrizzi's[8] groups, aromatic squaramide moieties containing polarized N–H binding units, whose binding affinity is better than their counterparts of urea binding moieties, have become of great significance in the anion recognition for their strong hydrogen bond donor ability in recent years, and the superiority of squaramide moieties over urea groups as H-bond donors was also supported by further theoretical studies.[7d,e] What is more, recently, it has been reported that squaramide binding units could be applied for potent transmembrane anion transporters, performing much better than thiourea and urea analogues.[9] As strong H-bond donors, squaramide moieties can form stable hydrogen-bond complex with anions; on the other hand, when squaramide moieties with electron-withdrawing groups interact with strong basic anions, such as fluoride (F^-), acetate (AcO^-), or dihydrogenphosphate ($H_2PO_4^-$), they could be deprotonated via acid–base process.[8]

Calix[4]arene has been employed as a popular building platform due to its well preorganized molecular architecture for ionic and molecular recognition.[10] Compared to monotopic calix[4]arene receptors, 1,3-disubstituted ditopic calix[4]arene designed by the introduction of two squaramide moieties could provide better preorganized binding pocket for anion binding so as to possibly achieve better binding affinity and selectivity in anion recognition.[2e] Herein we designed and synthesized bis-squaramide calix[4]arene-based receptors **1**–**3**, where squaramide groups were incorporated on the calix[4]arene to make strong multiple interactions through N–H moieties as well as preorganized binding pocket. The anion binding ability of receptor **1** was expected to be enhanced by the introduction of two squaramide moieties compared to their (thio)urea counterparts. Besides, receptors **2** and **3** with nitrophenyl group attached to the squaramide moiety were designed as a chromogenic unit (typically with electron-withdrawing groups) to achieve colorimetric sensing of anions by 'naked-eye' detection. As noted above, receptor **1** with squaramide moieties could form a stable hydrogen-bond complex with anions, while receptors **2**–**3** with squaramide moieties could be deprotonated by basic anions via acid–base process.

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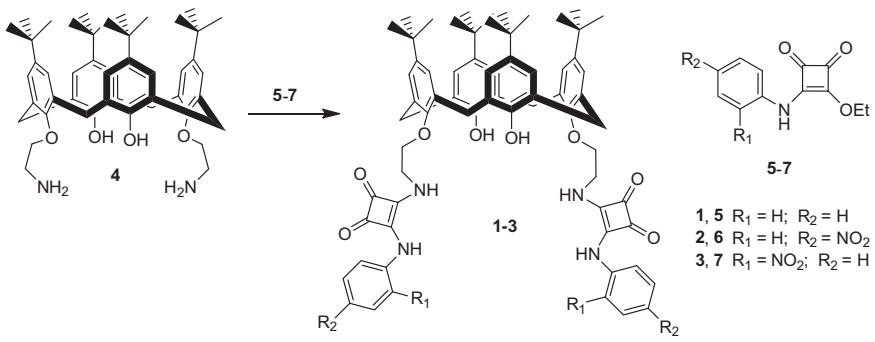
Receptors **1**–**3** based on a lower-rim 1,3-disubstituted calix[4]-arene scaffold were synthesized[11] as shown in Scheme 1. $Zn(OTf)_2$ was chosen as an effective catalyst for the preparation of **1**–**3** from **4** in 73–80% yield developed by Taylor and co-workers.[12] The structures of **1**–**3** were all characterized by ^1H NMR, ^{13}C NMR, and ESI-MS analyses (see Supplementary data). As an example, the ^1H NMR spectra (in DMSO-d_6) of **1** showed two sets of N–H protons (9.76 and 7.99 ppm) assigned to squaramide protons, respectively, and ESI-MS data gave a peak for the $[M+Na]^+$ ion at 1099.75 (m/z).

The single crystal structure of receptor **3** was successfully obtained by slow evaporation of a mixed DMSO/H_2O solution in three weeks. As depicted in Figure 1a, the crystal structure of **3**·H_2O shows monoclinic space groups $P2_1/c$, and the asymmetric unit of 3·H_2O contains one vase-like calix[4]arene moiety skeleton, two *N*-(2-nitrophenyl)-squaramide arms, and one lattice water molecule. The overall conformation of 3·H_2O is similar to the reported 1,3-bridged calix[4]arene derivatives,[13] in which two bridged aromatic rings become more 'vertical' than the other two aromatic rings, and tend to adopt the favored *anti–anti* conformation and head-to-tail packing of squaramide sheets.[14] In receptor **3**, although N–H bonds point to the same direction, the squaramide moieties do not pack in a linear formation as forecasted (Fig. 1b). Intra-molecular interactions (Table S3) are formed between two squaramide moieties through N–H···O hydrogen bonds with the donor–acceptor distance of 2.773(3) Å, while N(5) and N(2) form another two intense intra-molecular bonds (2.634(4) Å for N(5)–H(5)···O(9) and 2.657(3) Å for N(2)–H(2)···O(11)) with the nitro groups of the *ortho*-nitrobenzene. The squaramide moieties connect to the adjacent molecules through the intermolecular N4–H4···O4^i and N5–H5···O4^i (i = x, 1 + y, z) hydrogen bonds, resulting in the formation of a zigzag chain arrangement in the crystals.

The anion binding affinity of receptor **1** with F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, AcO^-, and NO_3^- (tetrabutylammonium as the counter cation) were initially investigated by UV–vis spectra in DMSO due to the solubility issue. For receptor **1** (Fig. 2a), slight bathochromic shifts (8–10 nm) were observed only upon addition of AcO^-, F^-, and $H_2PO_4^-$ ions, respectively, while the addition of other anions (Cl^-, Br^-, I^-, HSO_4^-, and NO_3^-) resulted in negligible changes of **1** in UV–vis spectra. Therefore, UV–vis titration experiments of AcO^-, F^-, and $H_2PO_4^-$ in receptor **1** were conducted further, respectively. The UV–vis titration spectra of $H_2PO_4^-$ in receptor **1** were illustrated in Figure 2b, showing that the peak at 329 nm decreased while the peak at 339 nm increased with slight bathochromic shift. Job's plot of receptor **1** with $H_2PO_4^-$ (Fig. 2b) was carried out to give the 1:1 stoichiometry which was also confirmed by ESI-MS experiment (Fig. S20). Based on UV–vis titration spectra of receptor **1** upon addition of anions F^- (Fig. S10), AcO^- (Fig. S11), and $H_2PO_4^-$, the association constants $\log K_a$ were obtained using non-linear fitting (Table 1) in a 1:1 binding equilibrium model.[4f] These values showed an order of **1** binding with $H_2PO_4^-$ (4.72) > F^- (4.66) > AcO^- (4.34). The best selectivity of **1** toward $H_2PO_4^-$ indicated that the preorganized calix[4]arene scaffold might be more complementary for tetrahedron $H_2PO_4^-$ ion.

In order to confirm the hydrogen binding mode of receptor **1** with AcO^-, F^-, and $H_2PO_4^-$ anions and compare with the reported urea or thiourea derivatives in anion recognition, ^1H NMR titration experiments of receptor **1** with AcO^-, F^-, and $H_2PO_4^-$ in DMSO-d_6 solution were also carried out, respectively. From the titration experiment of receptor **1**, instant and similar downfield shifts were observed with the above three anions. As presented in Figure 3, both squaramide N–H protons peaks at 9.76 and 7.83 ppm of receptor **1** showed large downfield shifts to 11.75 and 9.75 ppm upon addition of $H_2PO_4^-$ ion to host solution, and it indicated clearly that both squaramide N–H participated in the binding in the hydrogen bond interaction mode.[15] In addition, *ortho*-position C–H in the aromatic ring of squaramide at 7.31 ppm and O–H at 7.99 ppm were downfield shifted to 7.58 and 8.32 ppm, respectively, indicating that the complex of **1** and $H_2PO_4^-$ was formed via multiple hydrogen bonds. Besides the association constant obtained from UV–vis titration experiment, the association constants $\log K_a$ based on ^1H NMR titration were calculated using EQNMR software [16] and these values were presented in Table 1. The results demonstrated that receptor **1** formed a stronger hydrogen bond complex with anions ($\log K_a$ in DMSO-d_6, F^-: 3.35, AcO^-: 3.04, and 3.73 for $H_2PO_4^-$) than urea ($\log K_a$ in $CDCl_3$, F^-: 2.86, AcO^-: 2.69, and 2.43 for $H_2PO_4^-$) and thiourea ($\log K_a$ in $CDCl_3$, F^-: 2.68, AcO^-: 1.68, and 2.00 for $H_2PO_4^-$) derivatives reported previously [15] where $\log K_a$ was obtained from ^1H NMR titration, which could be due to the more excellent H-bond donor properties of squaramide moieties even in polar solvent than urea or thiourea moieties.

Sequentially, the anion binding affinity of receptors **2**–**3** with F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, AcO^-, and NO_3^- (tetrabutylammonium as the counter cation) were investigated by UV–vis experiments in DMSO (Fig. 4) as receptor **1** was. In both cases, spectral changes were observed only upon addition of F^-, AcO^-, and $H_2PO_4^-$, in which the addition of $H_2PO_4^-$ caused the smallest spectral change. In receptors **2**–**3**, the nitrophenyl subunit, as a chromophore and electron withdrawing group, caused different results in the anion recognition mode and the colorimetric proprieties of receptors **2**–**3** compared to receptor **1** due to the fact that the electron-withdrawing effect of the nitrophenyl subunits increased the acidity of squaramide N–H protons. The absorbance spectrum of only **2** in DMSO has two bands at 282 and 406 nm ascribed to the highest-energy and the lowest-energy charge transfer transition (Fig. 4a). [8] There are similar two charge transfer transition bands to only **3** at 276 and 431 nm from absorbance spectrum (Fig. 4b). Furthermore, the titrations of F^-, AcO^-, and $H_2PO_4^-$ into receptors **2**–**3** were investigated by UV–vis titration experiments, respectively. Titration of receptor **2** with AcO^- (Fig. 5a) or F^-



Scheme 1. Synthesis of receptors **1**–**3** based on squaramide derivatives **5**–**7**.

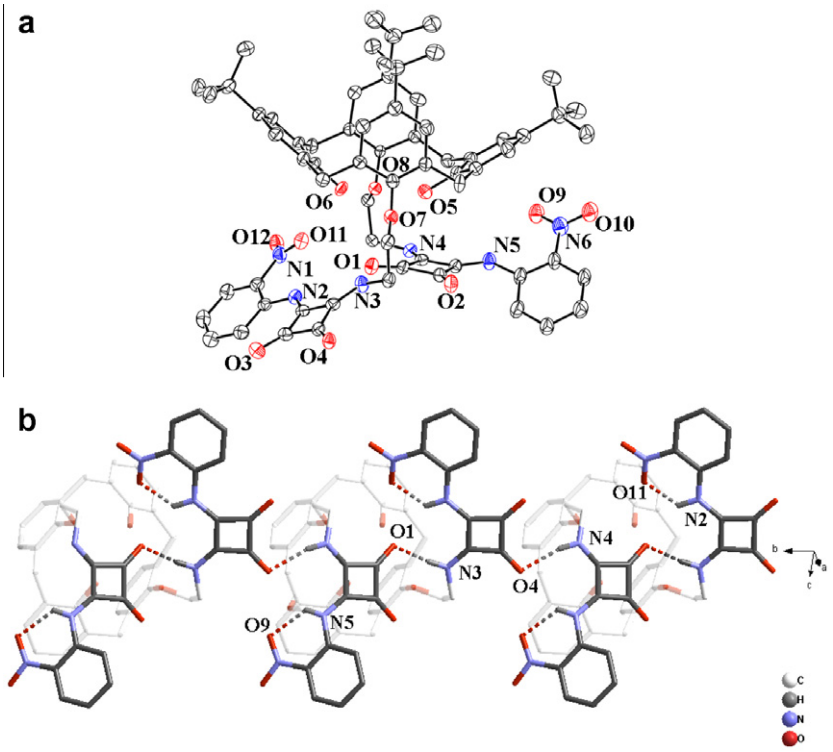


Figure 1. (a) ORTEP view (30% thermal ellipsoids) of the crystal structure of **3**, H_2O. (b) The hydrogen bonds in **3**, H_2O involving the squaramide moieties along *b* axis (H atoms which are not involved in hydrogen bonding and the lattice water molecules are omitted for clarity).

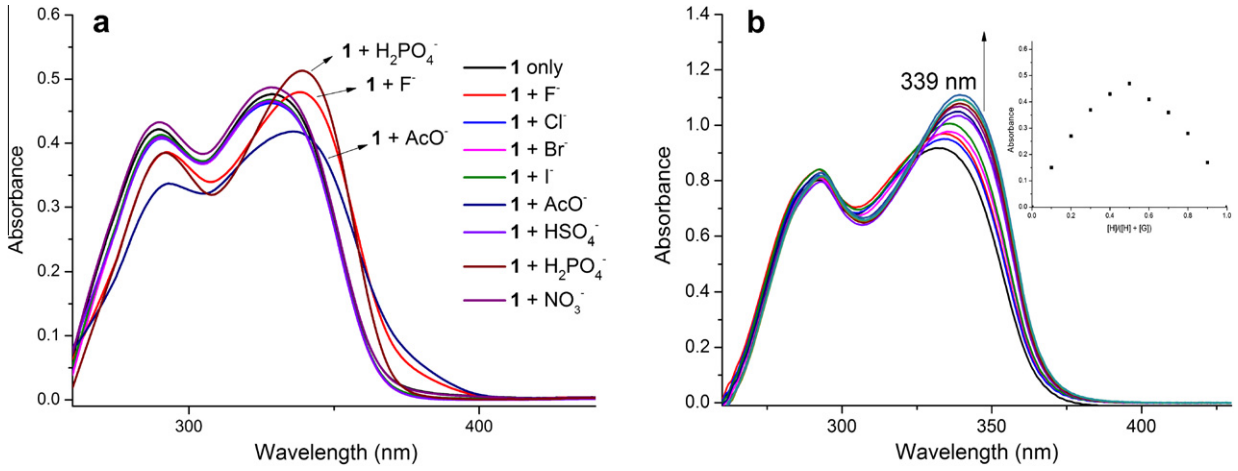


Figure 2. (a) Absorption spectra of **1** (1.0×10^{-5} M) in the presence of various anions (1.0×10^{-4} M) in DMSO. (b) Absorption spectra of receptor **1** (2.0×10^{-5} M) upon addition of $H_2PO_4^-$ (0–2.4×10^{-4} M) in DMSO. Inset: job's plot was constructed based on absorbance changes at 339 nm in the total concentration of 2.0×10^{-5} M.

Table 1
Association constants $\log K_a$ and equilibrium constants $\log K_D$ for receptors **1**–**3** with anions[a]

Anion[b]	1		2	3
	$\log K_a$[c]	$\log K_a$[d]	$\log K_D$[c]	$\log K_D$[c]
F^-	4.66	3.35	9.08	9.01
AcO^-	4.34	3.04	8.77	8.69
$H_2PO_4^-$	4.72	3.73	7.85	7.36

[a] All errors were <15%.
[b] Anions were used as tetrabutylammonium salts.
[c] Determined by UV–vis titration.
[d] Obtained by ^1H NMR titration using EQNMR software.

(Fig. 5b) resulted in notable bathochromic shift from the band at 406 nm to the new band at 536 nm due to the internal charge transfer (ICT) transition.[17] This new ICT band at 536 nm matched well with the absorbance band obtained when **2** was reacted with strong base tetrabutylammonium hydroxide (TBAOH) (Fig. S13), so it was reasonable to propose the acid–base process to give the deprotonated receptor **2** upon addition of F^- or AcO^-. Moreover, the intensity of new ICT band by the addition of $H_2PO_4^-$ ion (Fig. S12) increased much more slightly than F^- or AcO^-, which was consistent with its weaker basicity in solution.[18] ESI-MS technique was employed to support this acid–base interaction mode for receptor 2 with the addition of F^-, AcO^-, or $H_2PO_4^-$ anions, where no corresponding binding complex peak was found. Compared with receptor **2**, very similar experimental results of

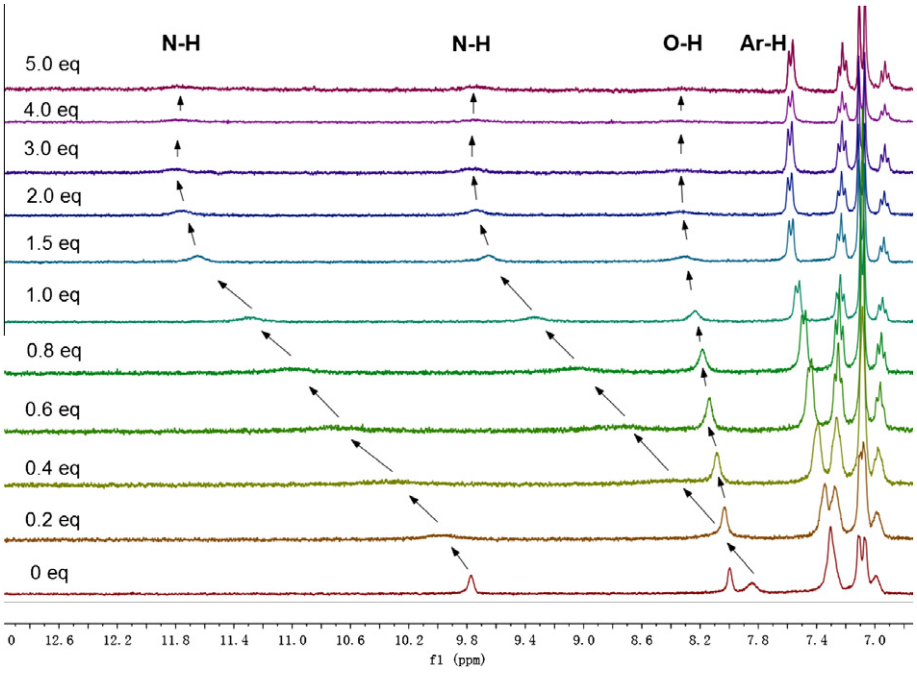


Figure 3. Partial ^{1}H NMR spectra (300 MHz, DMSO-d_6) of receptor **1** (2.0×10^{-3} M) upon addition of $H_2PO_4^-$.

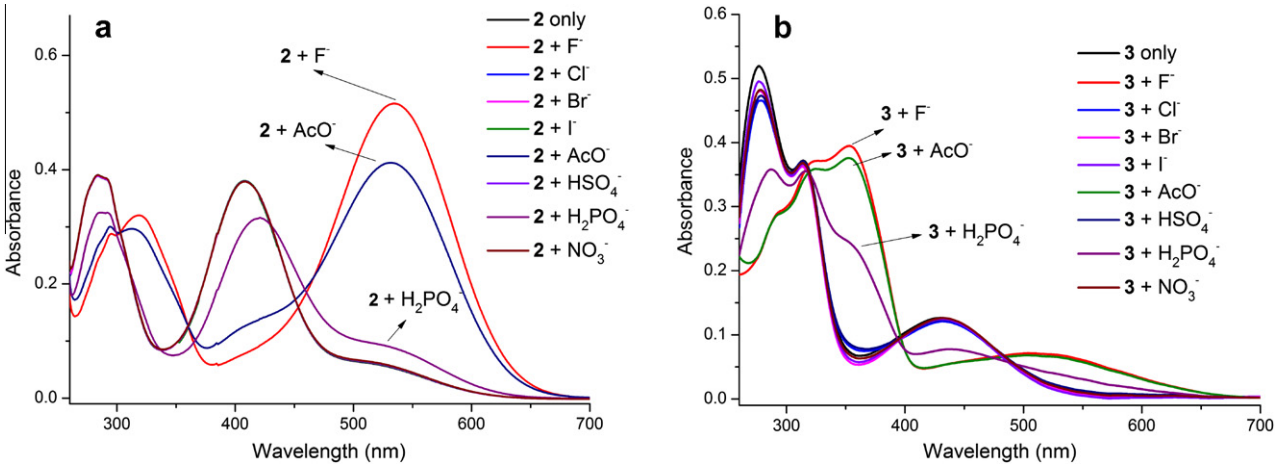


Figure 4. UV–vis absorption spectra of receptors (1.0×10^{-5} M) (a) **2** and (b) **3** with the **s**elected anions (1.0×10^{-4} M) in DMSO.

UV–vis titration were also obtained for receptor **3** upon addition of OH^- (Fig. S17), AcO^- (Fig. 6a), F^- (Fig. 6b), and $H_2PO_4^-$ (Fig. S16). These above-mentioned results strongly indicated a typical Bronsted acid–base reaction for receptors **2**–**3** upon addition of basic anions (F^-, AcO^-, or $H_2PO_4^-$).[17] Fabbrizzi et al reported that squaramide N–H adjacent to nitrophenyl group, which is exactly the same with our case, might be directly deprotonated by basic anions and the resonance formula of the deprotonated squaramide form was given in Scheme 2.[8]

To further investigate the interaction mode of **2** upon addition of Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, F^-, AcO^-, and $H_2PO_4^-$ anions, especially to confirm the acid–base interaction mode with F^-, AcO^-, and $H_2PO_4^-$, ^{1}H NMR experiments were also carried out. The results showed that it was in accordance with UV–vis experimental results, where no noticeable ^{1}H NMR spectral changes of receptor **2** were observed upon addition of Cl^-, Br^-, I^-, HSO_4^-, and NO_3^- anions, but the addition of F^-, AcO^-, and $H_2PO_4^-$ caused obvious ^{1}H NMR spectral changes which agree well with the above experimental results to confirm that receptor **2** underwent the direct deprotonation of N–H adjacent to nitrophenyl group by F^-, AcO^-, and $H_2PO_4^-$ ions in DMSO-d_6 solution (see Supplementary data). Aromatic proton signals of nitrophenyl group in receptor **2** were shifted downfield or upfield, which also supported the typical acid–base interaction mode between receptor and anions. The changes of aromatic protons of nitrophenyl rings linked to squaramide moiety in NMR spectra could be explained by (1) the *through-bond* propagation with the increasing electron density of nitrophenyl rings which caused a shielding effect leading to an upfield shift and (2) the polarization of the C–H bonds within the electrostatic effect causing a downfield shift reported by Fabbrizzi.[17] No effect on the change of O–H protons in this case indicated that O–H groups of calix[4]arene did not participate in the acid–base process (Fig. S23–25).

In general, the deprotonation process of receptor H_2L by basic anions A^- can be associated with a common equilibrium of the following type (Eq. 1):[19]

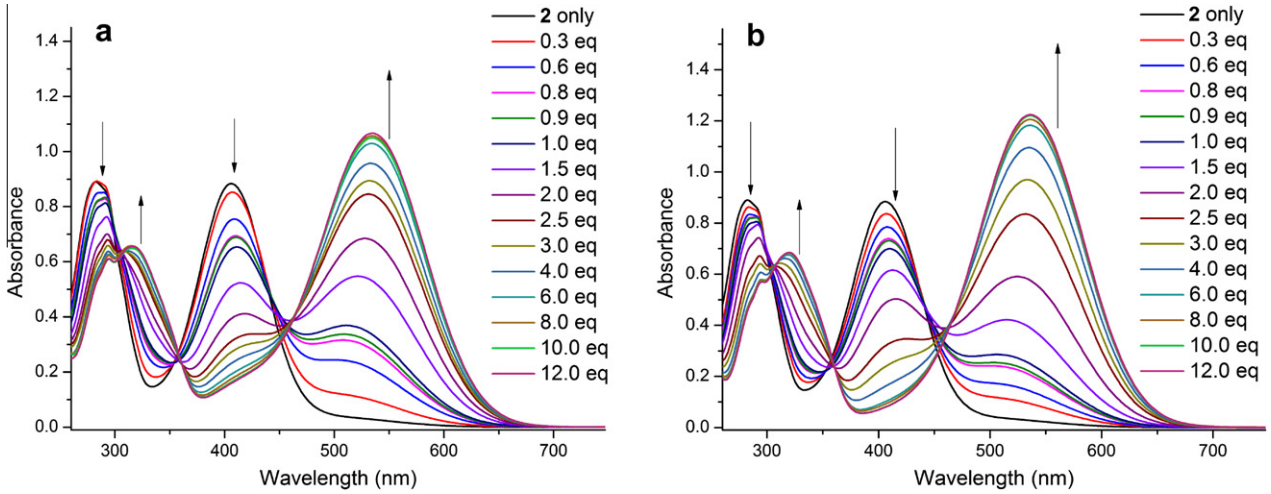


Figure 5. UV–vis absorption spectra of receptor **2** (2.0×10^{-5} M) upon addition of increasing amount (0–2.4×10^{-4} M) of (a) AcO^- and (b) F^- in DMSO.

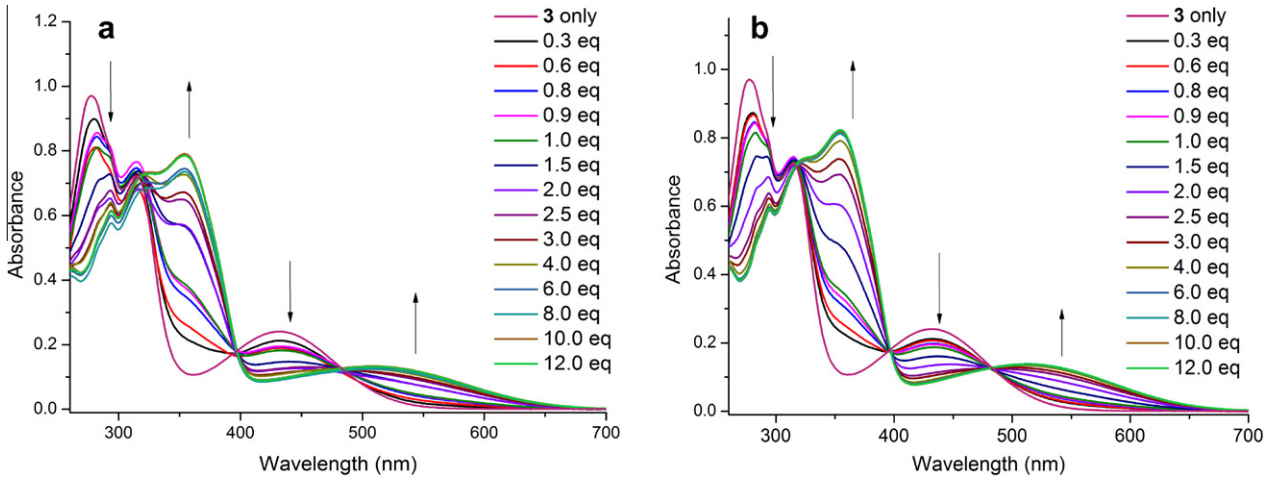
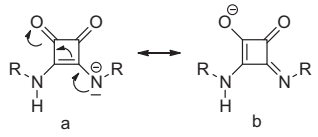


Figure 6. UV–vis absorption spectra of receptor **3** (2.0×10^{-5} M) upon addition of increasing amount (0–2.4×10^{-4} M) of (a) AcO^- and (b) F^- in DMSO.



Scheme 2. Resonance formulae of the deprotonated squaramide-based receptor given by Fabbrizzi.

$$H_2L + 2A^- \rightleftharpoons L^{2-} + 2HA(K_D) \quad (1)$$

Moreover, considering the stable dimers formatted by excess A^-,[19a] the following dimer formation equilibrium (Eq. 2) should be applied in the subsequent step:

$$HA + A^- \rightleftharpoons + HA_2^- \quad (2)$$

This two-step equilibrium can be applied to the N–H deprotonation processes promoted by F^-, AcO^-, and $H_2PO_4^-$ ions which can form relatively stable $[HA_2]^-$ dimers.[18] Moreover, UV–vis titration spectra of **2** and **3** revealed that the process reached a saturation point on addition of 4 equiv of F^- and AcO^- ions (see Supplementary data, Fig. S14, S15, S18 and S19). These observations supported the acid–base process induced by basic anions in an overall 1:4 stoichiometry for H_2L-anion interactions (Eq. 3) obtained by combining (Eqs. 1) and (2):

$$H_2L + 4A^- \rightleftharpoons L^{2-} + 2HA_2^- \quad (3)$$

The equilibrium constants $\log K_D$ of **2** and **3** with F^-, AcO^-, and $H_2PO_4^-$ ions were calculated[20] from UV–vis titration experiments depicted in Table 1, and **2** or **3** showed higher affinity for F^- ion. Different from the hydrogen binding process, it seemed that acid–base process might be solely determined by the anion basicity ($F^- > AcO^- > H_2PO_4^-$)[5c] instead of anion recognition. Besides, in the light of these data, intramolecular H-bonds existing in **3** might prevent the deprotonation process to certain extent of the N–H hydrogen adjacent to the nitrobenzene moiety.[21]

The interaction of **1**–**3** with anions (F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, AcO^-, and NO_3^-, tetrabutylammonium as the counter cation) was further monitored through visual observations in DMSO. Receptor **1** did not give any visual response with anions. The receptor **2** (20 μM) exhibited a unique and instant color change from yellow to purple upon addition of 10 equiv F^- or AcO^- ions, whereas there was no obvious color change upon addition of 10 equiv other anions (Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, and NO_3^-) (Fig. 7). Similarly, receptor **3** also gave a marked color change only upon addition of 10 equiv F^- or AcO^- ions from yellow to light pink under the same conditions. The above 'naked-eye' color changes can be attributed to the deprotonation of the N–H on the squaramide moiety of **2** and **3** induced by the relative stronger basic anions, F^- or AcO^-,[17] compared with a weaker basic anion

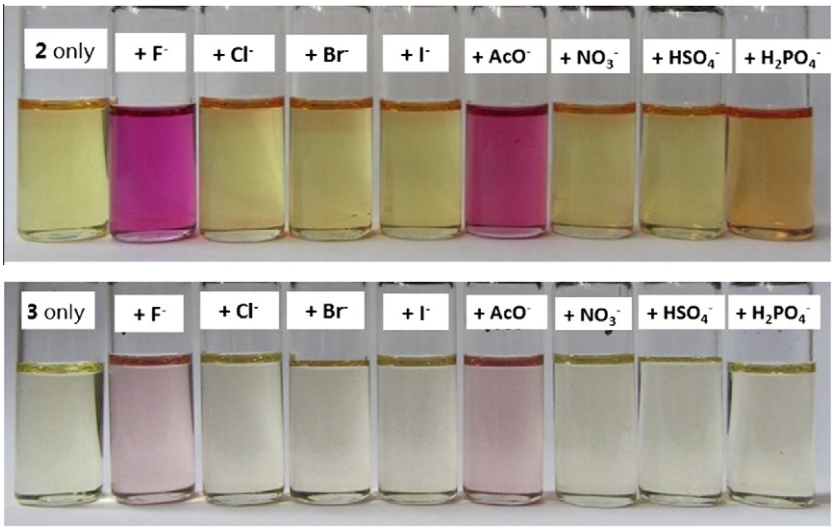


Figure 7. The color changes of receptors **2** (above) and **3** (below) (20 μM) when treated with 10 equiv of various anions in DMSO solutions.

$H_2PO_4^-$ which are in agreement with the results of the UV–vis spectra changes.

In this Letter, we synthesized and discussed the sensing properties of three new calix[4]arene-based anion receptors **1**–**3** with bis-squaramide moieties. The receptor **1** selectively binds biologically important $H_2PO_4^-$, F^-, and AcO^- ions via stronger hydrogen bond interaction than (thio)urea counterparts whereas **2** and **3** are deprotonated by basic anions via acid–base interaction mode. Receptors **2** and **3** exhibit prominent 'naked-eye' color changes with basic anions such as F^- and AcO^- through efficient deprotonation. These results pave a way for the development of designing and studying colorimetric receptors for anions with squaramide moieties. We are currently working on developing novel receptors based on calixarene platform using squaramide moieties to improve the selectivity of anion recognition.

Acknowledgments

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Supplementary data

Supplementary data (general experimental methods, synthetic procedures, ^{1}H NMR, ^{13}C NMR, ESI-MS, UV–vis titration, NMR titration and crystal data) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.11.117.

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