



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 ¹H NMR spectra. The experimental results revealed that there were two types of interaction modes where receptor **1** bound biologically important H₂PO₄[−], 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 H₂PO₄[−]) 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.

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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 pyrroles⁶ 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's⁷ and Fabbrizzi's⁸ 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 com-

plex 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 (H₂PO₄[−]), 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 pre-organized 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 synthesized¹¹ 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, ¹³C 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*).

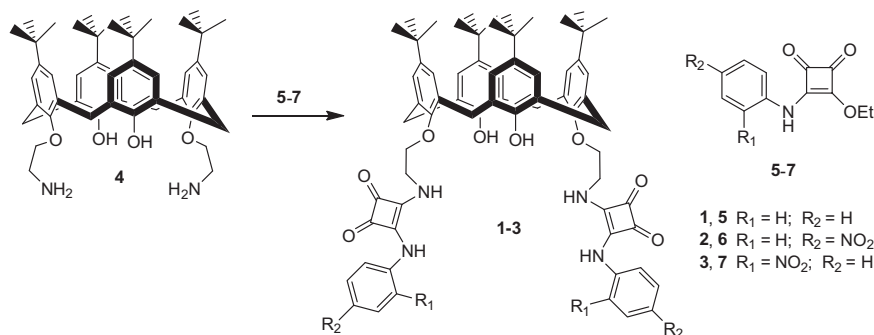
The single crystal structure of receptor **3** was successfully obtained by slow evaporation of a mixed DMSO/H₂O solution in three weeks. As depicted in Figure 1a, the crystal structure of **3**·H₂O shows monoclinic space groups *P*2₁/*c*, and the asymmetric unit of **3**·H₂O contains one vase-like calix[4]arene moiety skeleton, two *N*-(2-nitrophenyl)-squaramide arms, and one lattice water molecule. The overall conformation of **3**·H₂O 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[−], H₂PO₄[−], HSO₄[−], AcO[−], and NO₃[−] (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 H₂PO₄[−] ions, respectively, while the addition of other anions (Cl[−], Br[−], I[−], HSO₄[−], and NO₃[−]) resulted in negligible changes of **1** in UV–vis spectra. Therefore, UV–vis titration experiments of AcO[−], F[−], and H₂PO₄[−] in receptor **1** were conducted further, respectively. The UV–vis titration spectra of H₂PO₄[−] 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 H₂PO₄[−] (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 H₂PO₄[−], 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 H₂PO₄[−] (4.72) > F[−] (4.66) > AcO[−] (4.34). The best selectivity of **1** toward H₂PO₄[−] indicated that the preorganized calix[4]arene scaffold might be more complementary for tetrahedron H₂PO₄[−] ion.

In order to confirm the hydrogen binding mode of receptor **1** with AcO[−], F[−], and H₂PO₄[−] anions and compare with the reported urea or thiourea derivatives in anion recognition, ¹H NMR titration experiments of receptor **1** with AcO[−], F[−], and H₂PO₄[−] 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 H₂PO₄[−] 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 H₂PO₄[−] 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 software¹⁶ 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 H₂PO₄[−]) than urea (log*K*_a in CDCl₃, F[−]: 2.86, AcO[−]: 2.69, and 2.43 for H₂PO₄[−]) and thiourea (log*K*_a in CDCl₃, F[−]: 2.68, AcO[−]: 1.68, and 2.00 for H₂PO₄[−]) derivatives reported previously¹⁵ 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[−], H₂PO₄[−], HSO₄[−], AcO[−], and NO₃[−] (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 H₂PO₄[−], in which the addition of H₂PO₄[−] 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 properties 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 H₂PO₄[−] 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**.

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