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Calix[4]pyrroles with Shortest Possible Strap: Exclusively Selective toward Fluoride Ion

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Supporting Information

ABSTRACT: Four new calix[4]pyrroles with the shortest possible strap so far through ortho-linking of the aromatic unit have been synthesized, including a naphthalene-derived fluorescent receptor. They show exclusive selectivity toward the fluoride ion as confirmed by ^{1}H NMR, isothermal titration calorimetry, and fluorescence spectroscopic study. Anion affinity could also be modulated further via functionalization at the strap. Computational analysis displays calix[4]pyrroles binding to fluoride ion in a very unusual 1,3-alternate conformation where the anion resides on the opposite side of the strap.

The recognition of a guest by a supramolecular host depends on how closely the two partners fit together. One of the most fundamental and first thoughts in this area was the "lock-and-key" concept proposed by Fisher,[1a] which is still a stimulating research area in "host−guest" chemistry. With a given host and guest, the thermodynamic stability of the "host−guest" complex is dependent on host preorganization and complementarity with respect to a specific guest. From the very first report on the anion receptors, the above theory was found to be viable, where it was also found that due to proper size match only one receptor was selective toward the chloride ion.[1b,c] In later studies, Lehn and co-workers followed by various groups explored this phenomenon extensively through their work.[2] Among various classes of anion receptors, pyrrole-based macrocycles are quite popular among chemists, and this class of anion receptors has undergone a vast amount of modification over the decades in search of better selectivity toward a specific anion.[3] A century-old macrocycle, calix[4]pyrrole,[4a] after discovery of its anion-recognition abilities,[4b] also endured an extensive amount of alteration for the same cause. In particular, functionalization has been carried out at its *meso*[5] and *β*-positions,[6] including core modification[7] and core expansion.[8] Further, among the calix[4]pyrrole-based anion-receptor family, single side-strapped calix[4]pyrroles are unique, owing to the large enhancement in their affinity toward anions.[9] However, to the best of our knowledge, there are only two reports that deal with anion affinity and selectivity with regard to variable strap sizes.[9b,c] No insight was found about the minimum length of the strap needed to design these types of receptors and the possible selectivity toward anions it may impart, owing to the small binding domain. In this regard, our effort was to try to synthesize calix[4]pyrrole with the shortest possible strap and explore its consequences on anion binding and selectivity. In these types of systems some interesting things can happen. For example, a shorter binding domain will try to discriminate between the smaller and bigger anions on the basis of their size. This has been schematically illustrated (Figure 1) for calix[4]pyrrole with a large strap (**L**) and a short strap (**S**), both interacting with small and large anions. For **L**, there may not be much selectivity in the interaction between the large and small anions, as the binding domains have enough space to accommodate both types of anions. However, in the case of **S**, owing to steric hindrance caused by the shorter strap, the larger anion may not fit into the binding domain, whereas the smaller anion may not have any such difficulty in binding. This size-imposed discrimination may eventually lead to better selectivity for the smaller anions. However, another event can happen with **S** where an anion can go to the other side of calix[4]pyrrole, i.e., opposite side of the strap, and hence may not display any size-based discrimination between anions.

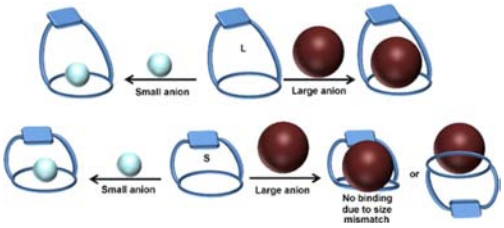

Figure 1. Schematic representation of possible modes of interaction between a long (**L**) and short (**S**) strapped calix[4]pyrrole with a small and a large anion.

In order to achieve **S**-type calix[4]pyrrole, a preliminary structural analysis using Chem3D program (ChemBioOffice 12.0) shows strapped calix[4]pyrrole with one carbon between benzene and calix[4]pyrrole is less likely to result in macrocyclization. Therefore, we intended to prepare strapped

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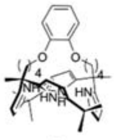
calix[4]pyrroles with two atoms as a bridging unit and for the sake of convenience chosen the $-OCH_2-$ unit as a spacer between the calix[4]pyrrole core and the strapping aromatic unit, e.g., **3**−**6**. In all of the receptors, aromatic units were derived from catechol or its derivatives, like our previously reported receptors **1** and **2**.[10] All strapped calix[4]pyrrole receptors were synthesized by slightly modifying the method we have used previously to synthesize **1** (Scheme 1).[10a] Our attempts to alkylate the dihydroxy aromatic compounds using 1-bromoacetone in dry acetone, in the presence of anhyd potassium carbonate, did not yield the desired products, probably owing to decomposition of 1-bromoacetone at a higher reaction temperature. Although the reaction at rt in acetone resulted in formation of the product, it was always accompanied by some impurities, making the purification very tedious. On the other hand, replacing the solvent with acetonitrile led to satisfactory yields of the diketo compounds. The desired diketo compounds (**7**−**10**) were purified from the crude product by column chromatography with moderate to good yields (42−84%) (Scheme S1, Supporting Information). These diketo compounds were converted to their respective bisdipyrromethanes **11**−**14** using excess pyrrole and TFA at 60 °C with satisfactory yields (45−78%). Finally, condensation of the bisdipyrromethanes in acetone, using catalytic BF_3·etherate, led to the formation of the desired macrocycles after 10 min, as per TLC analysis. Purification of the reaction mixtures using silica gel column chromatography and subsequent washing of the product with methanol led to the desired strapped calix[4]pyrroles **3**−**6** in 18−31% yields. Our attempt to synthesize analogous strapped calix[4]pyrrole from 1,3-dihydroxybezene met with failure in the final macrocyclization step, possibly indicating the strap length is not sufficient for convergent synthesis of calix[4]pyrrole (Scheme S2, Supporting Information). All of the compounds were characterized with standard spectroscopic techniques. Further, the solid-state structure of strapped calix[4]pyrroles **3**, **4** (slow evaporation of ethyl acetate−hexane mixture), and **5** (slow evaporation of dichloromethane−methanol mixture) could be unequivocally ascertained by single-crystal X-ray diffraction analysis (Figure 2). Although so far we did not succeed in obtaining the solid-state structure of **6**, however, we were able to obtain the crystal structure for its precursor **14** by slow evaporation of its chloroform solution (Figure S40, Supporting Information). In all of the crystal structures, macrocycles display a 1,3-alternate orientation of the pyrrole units, and interestingly, the strap resides almost orthogonal to the calix[4]pyrrole cores, not noticed in analogues with a longer strap viz. **1**.[10a] Further, the methylene units are found to be outwardly disposed in all of the crystal structures.



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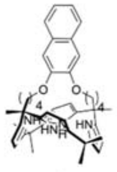

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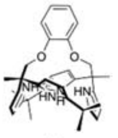

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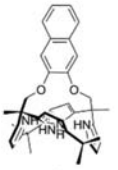

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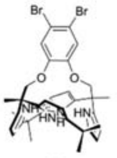

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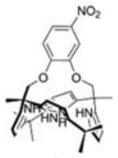

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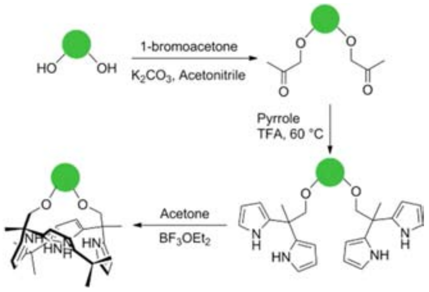
Scheme 1. Schematic Representations of Synthesis of Receptors



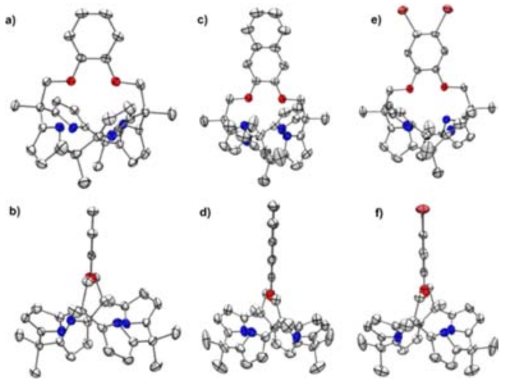


Figure 2. Molecular structures of (a) front and (b) side views of **3**, (c) front and (d) side views of **4**, and (e) front and (f) side views of **5** scaled at 50% probability level. Hydrogen atoms are excluded for clarity. Color code: C, gray; N, blue; O, red; Br, brown.

Preliminary solution-phase anion-binding behavior of **3**−**6** was studied by ^1H NMR titration in CD_3CN with various anions as their tetrabutylammonium (TBA) salts (i.e., F^-, Cl^-, Br^-, I^-, CN^-, HSO_4^-, $H_2PO_4^-$, $CH_3CO_2^-$, N_3^-, NO_2^-, NO_3^-, and ClO_4^-), and the study revealed that the four tested receptors showed interaction only with fluoride ion (Figures S41−47, Supporting Information). To our knowledge, this type of exclusive selectivity toward a particular anion is not reported in calixpyrrole chemistry except for the highly organized cone calix[4]arene diester strapped calix[4]pyrrole[11] and colorimetric sensing of fluoride ion by meso-expanded calix[2]-bispyrrolylethene reported by us recently.[8h] For receptors **3**−**6**, it was found that 1 equiv of anion was sufficient for the complete conversion of free receptors to corresponding receptor−anion complexes. Interestingly, less shift of pyrrolic-NH signals was observed unlike for other strapped calix[4]pyrroles, whereas those in the case of β-pyrrolic-CH signals were almost negligible. This indicates that the hosts possibly undergo very minimal conformation change during complexation, which thus resulted in diminished interaction toward fluoride ion (Figures S41−47, Supporting Information).

In order to evaluate the binding affinities, isothermal titration calorimetry (ITC) was performed in HPLC-grade acetonitrile (with ~0.05% water) for the receptors **3**−**6** with fluoride ion. The binding isotherm was found to follow 1:1 binding stoichiometry in all cases. Binding processes are found to be exothermic in nature, with maximum heat change occurred for **5** upon complexation and followed by **6**, **3**, and **4** (Figures S48−51, Supporting Information). All of the processes were entropically favored owing to the release of water molecules by TBAF upon complexation (as it was used as its trihydrate) and only marginally favored thermodynamically, except for **5**, in which case the binding is favored by enthalpy. Further, the translational and conformational freedom available to the host could also contribute to the change in entropy, and this component is possibly less in the case of **5** owing to the much bulkier bromo groups in the strap, and no binding of chloride ion was observed when TBACl was used. Association constants and thermodynamic parameters are tabulated in Table 1. The data clearly indicate association constants are lower compared to the previously reported strapped calix[4]pyrroles with larger straps,[10] and this may be attributed to the repulsive interaction between lone pairs of oxygen atoms present in the strap and the anion. For example, receptor **3** displayed about two orders and receptor **4** one order weaker association constant with fluoride ion as compared to analogous calix[4]pyrroles with longer strap, **1** and **2**, respectively. On the other hand, association constant of **5** was found to be about 1 order higher when compared with those of **3** and **4**. It showed that the affinity toward fluoride ion could be enhanced further, without compromising on the selectivity, by introducing electron-withdrawing groups onto the benzene moiety of the strap (in **5** and **6**), which probably helps in reducing the repulsion between the lone pairs on oxygen atoms and the anion. In order to prove this further, we tried to synthesize analogous strapped calix[4]pyrrole by replacing the "O"s with methylene moieties in **3**. However, the corresponding bisdipyrromethane did not yield the desired macrocycle, probably owing to nonbonding repulsion between the bridging alkyl chains (Scheme S2, Supporting Information). Further, we could observe that two bromine atoms (in **5**) impart a stronger effect than one nitro group when introduced onto the benzene moiety of the strap (in **6**). Our attempt to synthesize analogous strapped calix[4]pyrrole with two nitro groups on the benzene moiety again could not succeed. In order to minimize the possible error owing to the hygroscopic nature of acetonitrile, we tried to introduce water onto it (0.5%); however, this led to no proper isotherm, probably due to the weak binding nature of these receptors. However, our similar study in analogous receptor **1** already indicated that the presence of water in acetonitrile only reduces the affinity constant marginally.[10] Interestingly, in the case of **5** and **6** endothermic heat flows were noticed upon successive addition of F$^-$ to the host solution, particularly after addition of more than 1 equivt of the anion (Figures S50−51, Supporting Information). This effect was more severe in the case of the latter and may be attributed to possible interaction of released water with the functional groups on the strap, in which case the nitro derivative is expected to exhibit greater hydration owing to hydrogen-bonding interactions.

Table 1. Association Constants (K_a) and Thermodynamic Data Derived from ITC Experiments for the Interactions of Receptors 1−6 with TBAF·3H$_2$O in CH$_3$CN at 303 K

	K_a (M^{-1})	ΔH[b]	$T\Delta S$[b]	ΔG[b]
1[10a]	$1.17 \pm 0.33 \times 10^6$	−6.27	2.16	−8.42
2[10b]	$2.42 \pm 0.68 \times 10^5$	−14.20	−6.50	−7.47
	$2.42 \pm 0.42 \times 10^5$[a]			
3	$3.77 \pm 0.41 \times 10^4$	−0.84	5.45	−6.29
4	$1.57 \pm 0.18 \times 10^4$	−0.68	5.15	−5.83
	$1.16 \pm 0.22 \times 10^4$[a]			
5	$2.01 \pm 0.22 \times 10^5$	−3.77	3.58	−7.34
6	$5.52 \pm 0.40 \times 10^4$	−1.99	4.58	−6.57

[a] Determined by fluorescence spectroscopy. [b] In kcal/mol.

In order to make our receptor fluorescence active, the naphthalene moiety was introduced instead of benzene in receptor **4**. Its anion-binding affinities with various anions were explored using fluorescence spectroscopy. It was found that quenching of fluorescence was observed only in the case of fluoride ion (Figure S52, Supporting Information). Further, the selective affinity of the host toward F$^-$ ion could also be verified by competitive-binding experiments (Figure S53, Supporting Information). However, the amount of quenching was found to be less than that observed in the case of **2**. Job plot analysis for this binding event found to follow 1:1 binding stoichiometry (Figure 3, inset). The association constant (K_a) derived from this quenching experiment is 1.16 × 10^4, which is again found to be less by 1 order of magnitude than that observed for its higher homologue **2**.[10b] On the other hand, the association constants derived for **4** from two methods (fluorescence quenching and ITC) were found to be in good agreement with each other, as noticed in the case of **2**.

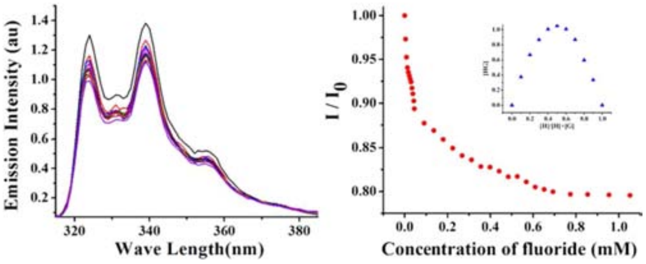


Figure 3. (Left) Fluorescence spectra of **4** in CH$_3$CN (0.04 mM) excited at 310 nm showing the induced changes upon addition of increasing quantities of TBAF·3H$_2$O. (Right) Quenching effect of TBAF·3H$_2$O upon gradual addition to **4**. (Inset) Job plot analysis of **4** vs TBAF·3H$_2$O.

To obtain insight into the possible binding modes, we performed density functional theory (DFT) calculations on the host−anion complexes (fluoride and chloride).[12] The analysis clearly revealed only fluoride ion complexes with the host. Interestingly, the anion resides on the other side of the strap with the calix[4]pyrrole in cone conformation transformed to its 1,3-alternate conformation (Table S1, Supporting Information). In addition, optimization of the complexes with host in 1,2-alternate conformation led to partial cone conformation and was found to be very slightly higher in energy than that with 1,3-alternate conformation. They in turn were found to be more than 4 kcal/mol lower in energy compared to complexes where the host is in reverse cone conformation, i.e., cone away from the strap (Table S1, Supporting Information). To our knowledge, calix[4]pyrrole binding anions in a 1,3-alternate conformation are not known; therefore, we believe the short strap with two electronegative oxygens possibly forces the anion to bind on the opposite side of the strap. This presumption is well supported by the minimal NH shift in the ^{1}H NMR study as well as the weaker binding constants obtained in ITC experiments of the fluoride complexation of these calixpyrroles.

In conclusion, we have synthesized four new strapped calix[4]pyrroles with the shortest possible strap so far. Anion-binding studies revealed that these receptors display exclusive selectivity toward the fluoride ion, albeit weakly compared to the analogous calix[4]pyrroles with a longer strap. This may be attributed to the conformational restriction imposed by the small strap on the calix[4]pyrrole moiety not being able to attain its most favorable cone conformation toward the anion. Therefore, a slightly longer strap may make the host more effective toward the anion, and at present, efforts are underway in this direction. Further, for the first time we demonstrate that incorporation of substituents at the aromatic unit of the strap can also help modulate the anion affinity without compromising the guest selectivity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01866. CCDC nos. for compounds **3**, **4**, **5** and **14** are 1409307, 1409308, 1409309, and 1409310.

Crystallographic data for **3** (CIF)
Crystallographic data for **4** (CIF)
Crystallographic data for **5** (CIF)
Crystallographic data for **14** (CIF)
Detailed synthetic scheme, procedures, NMR, and ITC (PDF)

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Notes

The authors declare no competing financial interest.

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