Organic LETTERS

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# Calix[4]tetrahydrothiophenopyrrole: A Ditopic Receptor Displaying a Split Personality for Ion Recognition

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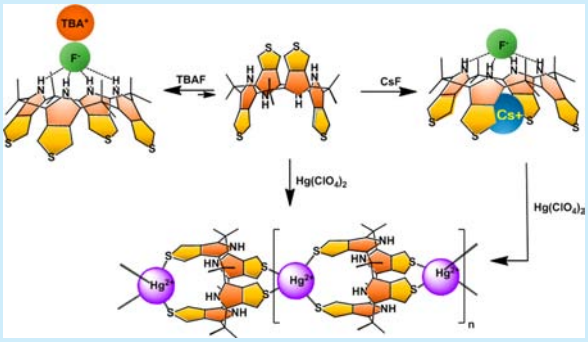
Supporting Information

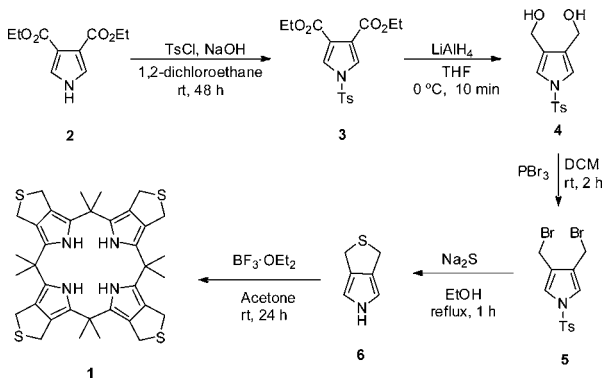
**ABSTRACT:** A calix[4]pyrrole fused with 2,5-dihydrothiophene, possessing both a deep, $\pi$-electron-rich pocket upon anion binding and chelating ligands on the periphery, was developed. The receptor selectively forms an ion-pair complex with CsF through H-bonding and a cation$-\pi$ interaction. In the process, it adopt a conformationally fixed cone conformation. The receptor displays exceptionally high affinity toward the Hg(II) ion and forms stable complexes while maintaining a rigid 1,3-alternate conformation. This metal ion-induced conformational locking is unprecedented in calix[4]pyrrole chemistry.




The design and synthesis of smart receptors that are capable of sensing various environmentally and chemically important anions has become an area of increasing interest in supramolecular and molecular recognition chemistry owing to the key role played by anions in numerous chemical and biological processes.[1] Considerable efforts have been devoted to improve selectivity and affinity toward the desired guest molecules. Among the various anion receptors reported to date,[2] calix[4]pyrroles are known to be efficient for anionic species, and many modified systems have been developed.[3,4] These modifications typically focus on either the $\beta$-pyrrolic positions or the *meso*-positions.[4,5] The strapped systems generally have superior affinity and guest selectivity. Introduction of substituents on the $\beta$-pyrrolic positions usually decreases the anion affinity because of destabilizing steric interactions incurred upon anion binding followed by conformational changes.[6] Currently, there are few calix[4]pyrrole-based anion receptors that contain a bicyclic pyrrole.[7] A good ion-pair receptor must possess functionalities that recognize both cations and anions with high affinity.[8] There have been numerous reports detailing efforts to improve the anion affinity of the calix[4]pyrrole platform compared with relatively few attempts to improve its cation binding affinity. We considered it likely that the introduction of chelating functions on the periphery of calix[4]pyrroles could serve to enhance their cation-binding capability. Recently, it was established that octamethylcalix[4]-pyrrole can form an ion-pair complex with cesium halide salts.[9] In these systems, the cation is believed to be held inside the cone-shaped cavity through a cation$-\pi$ interaction that is maximized by the proper cone angle. However, the cation$-\pi$ interaction is weaker than the H-bonding interaction and results in a reduced binding affinity for the ion-pair complex compared to what might otherwise be possible. We report here a calix[4]pyrrole with fused 2,5-dihydrothiophene subunits at the $\beta$-pyrrolic carbons. This system (**1**) proved to be a Hg(II)-selective receptor, as well as a selective ion-pair receptor for CsF.

The synthesis of receptor **1** was achieved according to Scheme 1. Diethyl pyrrole-3,4-dicarboxylate **2** was obtained from the reaction of *p*-tosylmethylisocyanide and diethyl fumarate in the presence of potassium *tert*-butoxide and 18-crown-6 in dry THF.[10,11] After N-protection using tosyl chloride, the ester

**Scheme 1. Synthesis of Receptor 1**

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functions of **3** were reduced to diol **4** with LAH. Conversion to the dibromo compound **5** followed by cyclization with sodium sulfide in boiling ethanol afforded the dihydrothiophenopyrrole **6** directly in moderate yield. Acid catalyzed condensation of **6** in the presence of acetone gave the desired calix[4]dihydrothiophenopyrrole **1** in 14% yield. Receptor **1** was characterized by spectroscopic means, as well as by single-crystal X-ray diffraction analysis.

A diffraction grade crystal was obtained by slow evaporation of chloroform in methanol. In the resulting single-crystal structure of **1**, the receptor is seen to adopt a 1,2-alternate conformation wherein the two solvent molecules (MeOH) are bound to two adjacent pyrrolic N−H protons (Figure 1).

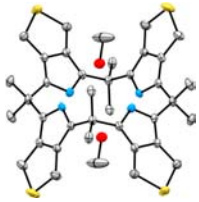

**Figure 1.** Single-crystal structure of **1**·$(CH_3OH)_2$. Two molecules of methanol are H-bonded to two N−H's each. H-atoms were removed for clarity. Displacement ellipsoids are scaled to the 50% probability level.

The preliminary anion binding ability of **1** toward various anions ($F^-$, $Cl^-$, $Br^-$, $I^-$, $CH_3COO^-$, $H_2PO_4^-$, $ClO_4^-$, $CN^-$, $NO_3^-$, $HSO_4^-$, and $ClO_4^-$, studied as their tetraalkyl ammonium salts) were investigated through $^1$H NMR spectroscopic titrations carried out in $CDCl_3$. The receptor displays a very strong affinity for the fluoride anion. The pyrrole N−H's of **1** resonate at $\delta$ = 7.00 ppm. A singlet for methylene protons ($H_a$ and $H_b$) at $\delta$ = 3.97 ppm is also seen (see Supporting Information (SI)). The appearance of only one signal for $H_a$ and $H_b$ was attributed to the fast conformational motion of **1** on the $^1$H NMR time scale at rt. Upon addition of ca. 1.0 equiv of tetrabutylammonium fluoride (TBAF), a large downfield shift in the pyrrole N−H signals ($\Delta\delta$ = 5.0 ppm) is observed. This supports the proposal that receptor **1** interacts strongly with the fluoride anion. Although no splitting of the *meso*-methyl protons or the $H_a$ and $H_b$ signals was observed, a slight upfield shift in the $H_a$ and $H_b$ peaks was noted ($\Delta\delta$ = 0.04 ppm). Furthermore, changes in the spectrum are evident upon addition of ca. 1.0 equiv of TBAF that are consistent with the fluoride anion forming a 1:1 complex with receptor **1**.

However, initial addition of TBAF resulted in significant peak broadening. Disappearance of the N−H signal was also observed upon the addition of ca. 1.0 equiv of TBAF. These findings are interpreted in terms of the **1**·TBAF complex undergoing fast complexation−decomplexation kinetics in the solution phase. The single resonance line seen for the methylene protons supports the proposed conformational flexibility of the complex. The fact that no chemical shift changes corresponding to the tetrabutyl ammonium cation were seen is interpreted in terms of the countercation ($TBA^+$) forming a loose ion pair with the complex as suggested schematically in Figure 2.

The interaction of receptor **1** with tetraethylammonium fluoride (TEAF) was also investigated using $^1$H NMR spectroscopic titrations carried out in $CDCl_3$. These studies revealed dramatic differences relative to TBAF. As shown in Figure 3, the pyrrole N−H signal is shifted further downfield ($\Delta\delta$ = 5.45 ppm) compared with what is seen in the presence of

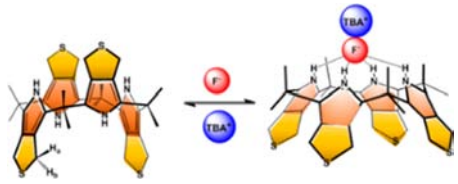

**Figure 2.** Schematic representation of electrostatic interactions that may stabilize the nonion paired complex obtained when receptor **1** is treated with TBAF in $CDCl_3$.

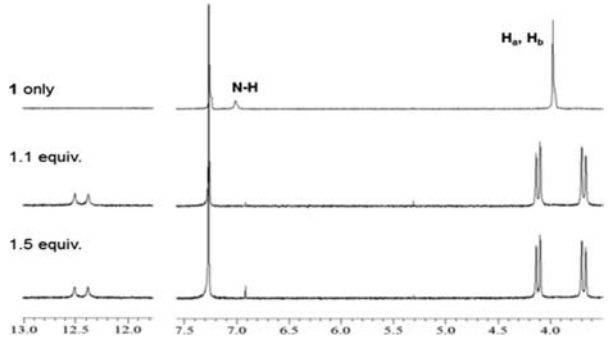


**Figure 3.** Partial $^1$H NMR spectra recorded during the titration of receptor **1** (3.03 mM) with TEAF in $CDCl_3$.

TBAF ($\Delta\delta$ = 5.00 ppm). In the presence of TEAF, the methylene protons ($H_a$ and $H_b$) appeared at $\delta$ = 4.12 and 3.68 ppm as two doublets ($J$ = 11.2 Hz). This was attributed to tight ion-pair binding resulting in conformational locking of the complex into a cone conformation. Further support for the fixed conformation of the TEAF complex came from the split *meso*-methyl protons at $\delta$ = 1.87 and 1.71 ppm (originally appearing as a singlet at $\delta$ = 1.54 ppm; see SI). The changes in the spectrum are essentially complete upon the addition of ∼1.0 equiv of TEAF. The resonances corresponding to the tetraethylammonium ($TEA^+$) cation moved downfield as the concentration of TEAF increased (SI). This observation is explained by the fact that the $TEA^+$ cation becomes encapsulated within the deep-concave cavity, formed as a result of convergent H-bonding of the pyrrole N−H's with the anion.[7] Further support for the conclusion that the fluoride anion from TEAF is bound more strongly than that from TBAF came from the observation that the N−H resonance of **1** is split into a doublet ($J_{H-F}$ = 38.4 Hz) at rt in the presence of TEAF. The appearance of a doublet is presumably due to the coupling of the bound fluoride anion and the N−H protons. These differences in cation-dependent binding affinities are attributed to the limited size of the extended concave cavity, which can better accommodate the smaller tetraethylammonium ($TEA^+$) cation compared with the rather larger tetrabutylammonium ($TBA^+$) cation.

Receptor **1** also displayed moderate affinity toward the chloride anion. When a $CDCl_3$ solution of **1** was subjected to titration with TBACl, complete saturation is reached upon the addition of >10 equiv of the anion with significant downfield shifts in the pyrrole N−H signals being observed (SI). These observations support the suggestion that **1** has a lower affinity for the chloride anion than for the fluoride anion. Nevertheless, in analogy to what was seen for the fluoride anion, the chloride anion binding affinity of **1** was also enhanced when TEACl, rather than TBACl, was used as the chloride anion source. This was corroborated by the downfield shift of the pyrrole N−H signal ($\Delta\delta_{N-H}$ = 3.9 ppm). In contrast to what was observed for


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TEAF, upon exposure to TEACl, the singlet for the $H_a$ and $H_b$ protons became broadened and shifted only slightly upfield ($\delta$ = 0.05 ppm). The signal for the *meso*-methyl protons also broadens and appears at ca. $\delta$ = 1.89 ppm in the presence of excess TEACl. As the concentration of TEACl increases, the signals corresponding to the ethyl group of the $TEA^+$ cation gradually shift to lower field. Such observations are consistent with the $TEA^+$ cation interacting more strongly with the $\pi$-rich cavity than $TBA^+$. The result is a tight, 1:1 ion-pair complex ($Cl^-\cdot\mathbf{1}\cdot TEA^+$).

A significant downfield shift of the pyrrole N−H signal was also observed upon titration with TEABr ($\Delta\delta_{N-H}$ = 2.96 ppm upon addition of 5.0 equiv) as compared with TBABr ($\Delta\delta_{N-H}$ = 0.8 ppm upon addition of 10.0 equiv; see SI). On the other hand, both $CH_3COO^-$ and $H_2PO_4^-$ interact very weakly with receptor **1** with almost no changes in the chemical shifts being observed upon exposure to the $I^-$, $CN^-$, $NO_3^-$, $HSO_4^-$, and $ClO_4^-$ anions ($TBA^+$ salts).

The significant peak broadenings as well as the substrate-dependent disappearance of the N−H signal during the course of the NMR spectral titrations of **1** with fluoride and chloride salts precluded the use of this method for quantitative determination of the binding affinities. Therefore, to quantify the anion binding affinity as well as determine the thermodynamic parameters for the complexation with various anions, isothermal titration calorimetry (ITC) experiments were performed in chloroform at 25 °C (see SI). In contrast to NMR techniques, ITC methods provide information on the energetics of the binding event without the need for a structural probe.[12] The thermodynamic parameters obtained from the ITC analyses revealed that chloride anion binding is almost entirely driven by enthalpy (see SI). In contrast, bromide binding is entropically unfavorable, resulting in an overall lower Gibb's free energy change and lower binding affinity. As expected, relatively high affinities were observed for the tetraethylammonium chloride and bromide salts compared with the corresponding tetrabutyl ammonium salts. For example, the association constant for chloride binding is increased by ∼15-fold in the case of the $TEA^+$ salt vs the $TBA^+$ salt. Almost no interaction between **1** and TBABr is observed by ITC. However, a weak affinity for TEABr is observed ($K_a$ = 233 $M^{-1}$).[7]

Because receptor **1** possesses a deep electron-rich cavity and sulfur ligands that can coordinate with metal cations, we investigated the ion-pair binding properties of **1**. Initially, the ion-pair recognition ability of **1** was explored using solid−liquid extraction experiments in chloroform with salts such as CsF, CsCl, and $CsClO_4$. A suspension of **1** with 5 equiv of each salt in $CDCl_3$ was sonicated for 1 h. Then, the $^1H$ NMR spectra were recorded using the soluble portion of the mixture. In the case of CsF, the spectra clearly revealed two different sets of distinguishable signals corresponding to the free host **1** and the ion-pair complex [**1·CsF**] (see SI). A large downfield shift of the N−H proton ($\Delta\delta$ = 4.97 ppm) was observed with concurrent splitting to a doublet ($J$ = 34.9 Hz). The methylene proton ($H_a$ and $H_b$) signals split into two doublets ($J$ = 11.5 Hz). Furthermore, the *meso*-methyl groups were also split into two singlets appearing at $\Delta\delta$ = 1.89 and 1.68 ppm, respectively. Such splitting is attributed to the formation of a tight ion-pair complex where the conformation of receptor **1** is fixed in the cone conformation. The slight upfield shift of the $\beta$-pyrrolic protons is consistent with the existence of a cation−$\pi$ interaction.[9] These observations also support the suggestion that the cone angle of the deep cavity, cup-like conformation formed by anion binding is well suited for accommodating the $Cs^+$ cation (Figure 4). Due to this

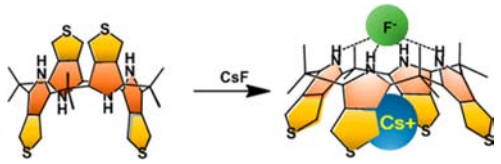


**Figure 4.** Schematic representation of the proposed CsF complex of **1**.

conformational locking, the methylene protons ($H_a$ and $H_b$) become diastereotopic. On this basis, we suggest that receptor **1** can selectively form a tight ion-pair complex with CsF. Due to the limited solubility of CsF in chloroform even after a prolonged sonication time, only 30% of **1** was associated with CsF. On the other hand, neither CsCl nor $CsClO_4$ was found to form a receptor-shared ion-pair complex under the solid−liquid extraction conditions.

To complement the solid−liquid extraction experiments, the possible formation of ion-pair complexes was also studied in organic solution. For these studies, a $CDCl_3$ solution of **1** was titrated against CsF dissolved in $CD_3OD$. Upon the addition of 1.0 equiv of CsF, evidence for formation of a tight ion-pair complex was seen in the $^1H$ NMR spectra (SI). Two doublets ($J$ = 11.5 Hz) appeared at $\delta$ = 3.75 and 4.04 ppm, corresponding to the methylene ($H_a$ and $H_b$) resonances. Two singlets were also identified at $\delta$ = 1.89 and 1.68 ppm corresponding to the *meso*-methyl resonance. On this basis, we conclude that the CsF strongly binds to receptor **1** resulting in a fixed conformation on the NMR time scale. Likewise, when **1** was subjected to titration with CsCl under identical conditions, binding occurred with conformational changes but to a lesser extent. Upon addition of an increasing amount of CsCl, two doublets ($J$ = 11.7 Hz) at $\delta$ = 3.75 and 4.04 ppm, corresponding to the $H_a$ and $H_b$ resonances, and two singlets at $\delta$ = 2.05 and $\delta$ = 1.65 ppm, corresponding to the *meso*-methyl signals, were observed. The splitting of $H_a$ and $H_b$ and the *meso*-methyl groups upon complexation with CsF and CsCl, but not with TBAF and TBACl, is consistent with **1** being a more effective ion-pair receptor rather than an anion receptor.

Cation binding studies carried out in the solution phase revealed that **1** is an excellent metal ion receptor. When **1**, dissolved in $CDCl_3$, was subjected to titration with the $Hg^{2+}$ ion (dissolved in $CD_3OD$ and studied as the $ClO_4^-$ salt), the methylene protons were split into two doublets appearing at $\delta$ = 5.46 and 4.68 ppm ($J$ = 15.0 Hz), respectively, upon addition of ∼2.0 equiv of $Hg^{2+}$. A white precipitate was instantly formed during the titration. In contrast to what was seen in the case of CsF binding, a significant downfield shift of the signal for the $H_a$ and $H_b$ was seen, a finding attributed to the chelation of $Hg^{2+}$ to the S-atoms. The fact that the signal for the *meso*-methyl groups appears as a singlet at 1.68 ppm is consistent with a 2:1 binding stoichiometry ($Hg^{2+}$/receptor). The diastereotopic nature of the $H_a$ and $H_b$ signals and the single *meso*-methyl resonance also supports the suggestion that receptor **1** is complexed to two $Hg^{2+}$ cations while in the 1,3-alternate conformation (see SI).

The observed homotopic nature of all the *meso*-methyl groups is taken as evidence that the $Hg^{2+}$−receptor complex derived from **1** adopts a 1,3-alternate conformation. The two $Hg^{2+}$ cations serve to lock the conformation into a 1,3-alternate fashion, and the immediate solid precipitation indicates intermolecular complexation to form a polymeric structure (Figure 5). Treatment of the preformed [**1**·CsF] complex with $Hg^{2+}$ (as its $ClO_4^-$salt) resulted in complete decomplexation of the bound CsF and formation of the insoluble Hg(II) complex. This observation reinforces the notion that receptor **1** reacts with


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**Figure 5.** Schematic view of the oligomeric complex formed with Hg(II).

Hg(II) to form a stable complex in near-irreversible fashion (see SI). Other cations, such as $Li^+$, $Na^+$, $K^+$, $Cs^+$, $Sr^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Pb^{2+}$, $Mg^{2+}$, $Zn^{2+}$, and $Cd^{2+}$, were not found to interact with receptor **1**, as inferred from the results of $^1$H NMR spectroscopic titration experiments (SI).

To obtain insights into $Hg^{2+}$ binding in the solid state, the powder X-ray diffraction (XRD) patterns of **1** and **1**·$(Hg^{2+})_2$ were recorded (Figure 6). The PXRD profile for the **1**·$(Hg^{2+})_2$

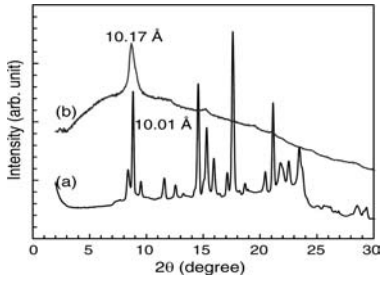


**Figure 6.** XRD patterns of (a) free host **1** and (b) after addition of $Hg(ClO_4)_2{\cdot}3H_2O$ (2 equiv).

complex is significantly broadened. Yet, there is a distinct peak at ~10.17 Å (roughly corresponding to the molecular dimension of receptor **1**; see SI). In contrast to the crystalline nature of **1**, the **1**·$(Hg^{2+})_2$ complex exhibits significant amorphous (disordered) character. This is attributed to the formation of oligomers or amorphous polymeric structures in the solid state.[13]

To the best of our knowledge, this is the first example of cation-induced locking of the calix[4]pyrrole framework in a 1,3-alternate conformation. Our results support the suggestion that calix[4]pyrroles not only have value as ion pair receptors but also could emerge as excellent cation binding systems provided suitable chelating ligands are installed around the calixpyrrole periphery. To the extent this proves true, it could allow for the construction of new coordination-based materials, including metal−organic frameworks (MOFs), based on calixpyrroles.

## ■ ASSOCIATED CONTENT

### Supporting Information

Single crystal X-ray data and solution phase spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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(13) X-ray diffraction (XRD) data were collected with Cu K$\alpha$ radiation on a Rigaku R-AXIS-IV X-ray imaging plate detector.