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Calix[4]pyrrole-Based Heteroditopic Ion-Pair Receptor That Displays Anion-Modulated, Cation-Binding Behavior

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Abstract: A new ditopic ion-pair receptor **1** was designed, synthesized, and characterized. Detailed binding studies served to confirm that this receptor binds fluoride and chloride ions (studied as their tetraalkylammonium salts) and forms stable 1:1 complexes in $CDCl_3$. Treatment of the halide-ion complexes of **1** with Group I and II metal ions (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, and Ca^{2+}; studied as their perchlorate salts in CD_3CN) revealed unique interactions that were found to depend on both the choice of the added cation and the precomplexed anion. In the case of the fluoride complex $[\mathbf{1}\cdot F]^-$ (preformed as the tetrabutylammonium (TBA^+) complex), little evidence of interaction with the K^+ ion was seen. In contrast, when this same complex (i.e., $[\mathbf{1}\cdot F]^-$ as the TBA^+ salt) was treated with the Li^+ or Na^+ ions, complete decomplexation of the receptor-bound fluoride ion was observed. In sharp contrast to what was seen with Li^+, Na^+, and K^+, treating complex $[\mathbf{1}\cdot F]^-$ with the Cs^+ ion gave rise to a stable, receptor-bound ion-pair complex [Cs·**1**·F] that contains the Cs^+ ion complexed within the cup-like cavity of the calix[4]pyrrole, which in turn was stabilized in its cone conformation. Different complexation behavior was observed in the case of the chloride complex $[\mathbf{1}\cdot Cl]^-$. In this case, no appreciable interaction was observed with Na^+ or K^+. In addition, treating $[\mathbf{1}\cdot Cl]^-$ with Li^+ produces a tightly hydrated dimeric ion-pair complex $[\mathbf{1}\cdot LiCl\cdot(H_2O)]_2$ in which two Li^+ ions are bound to the crown moiety of the two receptors. In analogy to what was seen in the case of $[\mathbf{1}\cdot F]^-$, exposure of $[\mathbf{1}\cdot Cl]^-$ to the Cs^+ ion gives rise to an ion-pair complex [Cs·**1**·Cl] in which the cation is bound within the cup of the calix[4]pyrrole. Different complexation modes were also observed when the binding of the fluoride ion was studied by using the tetramethylammonium and tetraethylammonium salts.

Keywords: anion recognition · calix[4]pyrroles · cation modulation · ditopic receptor · ion pairs · receptors

Introduction

The design, synthesis, and application of ditopic receptors, molecular systems that can bind both anionic and cationic guests, represents a current challenge in supramolecular chemistry. These receptor systems are particularly attractive because of their potential applications in various fields including salt solubilization,[1] extraction,[2] trans-membrane ion-transport agents,[3] and as recognition elements in chemosensors[4] or logic gates.[5] To date, a number of systems containing two different binding sites within a single molecular framework have been reported.[6–8] Most of these systems possess heterotopic binding domains, such as a crown-ether and an amide functionality.[9,10] However, to the best of our knowledge, only a limited number of systems containing spatially separated anion- and cation-recognition motifs have been reported. Such systems are of interest because they might allow for a fine-tuning of the recognition properties by appropriate placement of the ion binding sites within suitably preorganized scaffolds. In the limit, this might allow for the specific binding of a particular ion-pair species in preference to ostensibly similar salts combinations. However, the design features that regulate the specifics of ion-pair binding remain poorly understood. Recently, we reported a calix[4]pyrrole-based ion-pair receptor that displayed three different ion-pair binding modes with Cs^+-ion salts, namely solvent bridged, contact, and host separated (shared).[11,12] Herein, we report a new ion-pair receptor, specifically a calix[4]pyrrole core that is covalently linked to a *m*-dibenzo-[26]crown-8 subunit through phenyl spacers.[13] This system, receptor **1**, displays ion-pair binding features that are very different from what has been observed so far. Specifically, receptor **1** was found to act as an anion-modulated, cation-selective ion-pair receptor in $CDCl_3$ and CD_3CN, displaying selectivity for specific cation and anion combinations within a series of closely related salts of alkali and alkaline earth metals. As detailed below, ^1H NMR spectroscopic studies revealed that receptor **1** binds the fluoride and chloride ions

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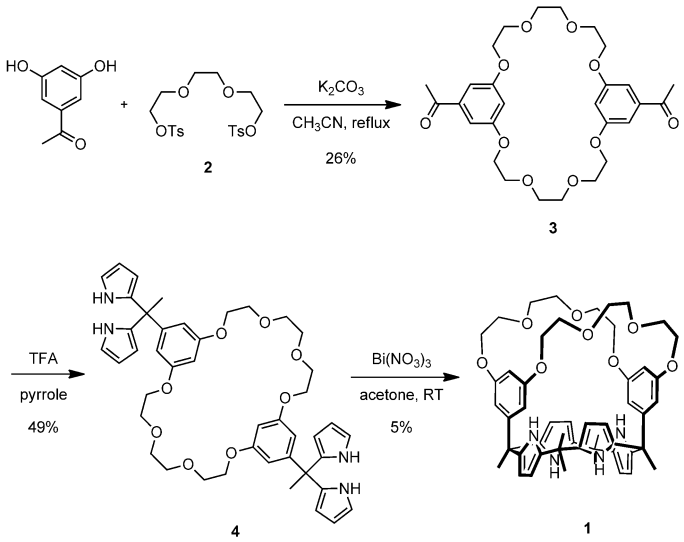
(as the corresponding tetraalkylammonium salts) strongly and forms stable 1:1 complexes in $CDCl_3$ and CD_3CN. Treatment of the resulting anion-bound complexes with Group I or II metal ions (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, and Ca^{2+} as their perchlorate salts in CD_3CN) gave rise to spectral features that were found to depend on both the choice of the cation and the nature of the initially complexed anion. Receptor **1** also interacts with tetramethylammonium fluoride (TMAF) and tetraethylammonium fluoride (TEAF) in $CDCl_3$. It forms a contact ion pair with TMAF in which the ammonium ion is bound to the crown moiety, but stabilizes a receptor-stabilized ion-pair complex in the case of the ostensibly similar TEAF salt. Presumably, this reflects the fact that the relatively smaller cation (tetramethylammonium vs. tetraethylammonium) is bound more strongly by the crown-ether moiety.

Results and Discussion

The synthesis of the receptor **1** was accomplished as shown in Scheme 1. The ditosylated triethylene glycol **2** was reacted with 3,5-dihydroxy acetophenone to afford the corresponding macrocyclic bisketone **3** in 26% yield.[14]



Scheme 1. Synthesis of receptor **1**.

Reaction of **3** with pyrrole and TFA at 60°C produced the corresponding dipyyromethane **4** in 49% yield.[15] Lewis acid catalyzed condensation of **4** with acetone afforded the desired receptor **1** in low yield (5%). Attempted condensation with other acids, such as BF_3, also gave the desired product **1**, albeit in the same low yield. On the other hand, because each of the steps could be carried out easily, useable quantities of material were readily obtained. The structure of receptor **1** was confirmed by standard spectroscopic means and by single-crystal X-ray diffraction analysis, as shown in Figure 1. The structure reveals that the calix[4]pyrrole moiety of the free host **1** adopts a partial cone conformation (Figure 1a). In the solid state, on the other hand, the CsF complex of the receptor **1** was found to exist in the form of a receptor-shared ion-pair complex (Figure 1b). The fluoride ion is tightly held inside the cavity, while the caesium cation is mainly bound within the calix[4]pyrrole "cup" of the cone that is formed upon anion binding and interacts with two oxygen atoms on the crown moiety. The net result is a receptor-separated ion-pair complex [Cs·**1**·F].

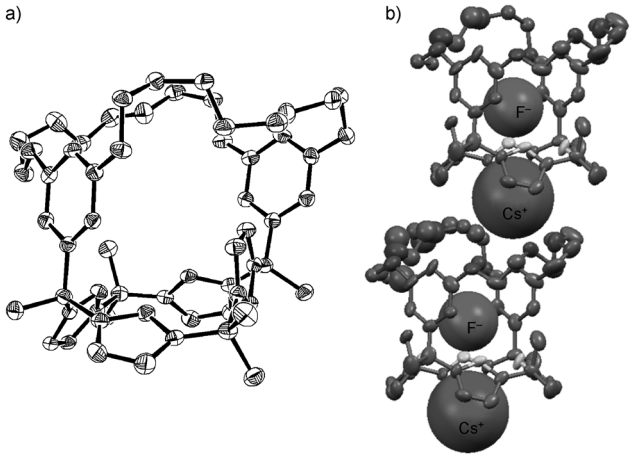


Figure 1. Single-crystal X-ray structures of a) free host **1** (solvent is not shown, the elipsodal probability is 50%) and b) CsF complex of receptor **1** ([Cs·**1**·F]), and view of the 3D-packing arrangement. Note that the cesium cation resides within the cup of the calix[4]pyrrole and half of the ether moiety, which adopts a cone-like conformation.

The single-crystal structure of the LiCl complex of the receptor **1** reveals completely different structural features. As shown in Figure 2, two molecules of the Cl^--bound complex formed with receptor **1** and LiCl associate to form a dimeric structure that is connected by two Li^+ ions, each of which is bound by four oxygen atoms. One water molecule was bound between Li^+ and Cl^- by the separated distance of 4.7 Å (the O–Cl distance was 3.11 Å and the O–Li^+ dis-

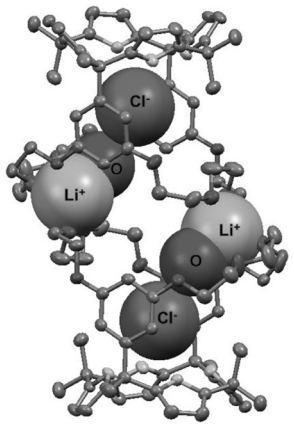
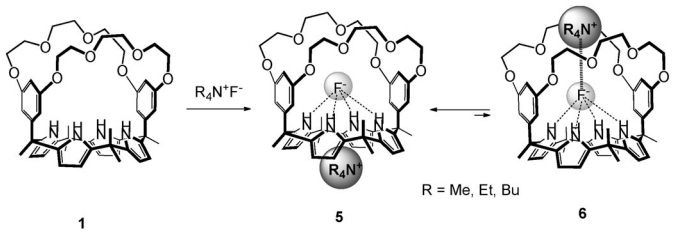


Figure 2. Single-crystal X-ray structures of dimeric complex of receptor **1** ([**1**·LiCl(H_2O)]$_2$). Note that the two crown moieties of chloride-bound receptors hold two lithium ions to form a dimeric hydrated ion-pair complex.

tance was 1.92 Å). Although complicating the overall arrangements of the crown moiety, this system is best described as a water-separated dimeric ion-pair complex [{**1**·LiCl·(H_2O)}$_2$].

The ion-recognition properties of receptor **1** and its ability to bind ion-pair salts in $CDCl_3$ were investigated by ^{1}H NMR spectroscopy. Significant chemical-shift changes were observed when the receptor **1** was subjected to titration with the fluoride ion (as its tetrabutylammonium salt; see the Supporting Information, Figure S9). In the course of reaching saturation, the signals of the pyrrole N–H protons move significantly downfield, while the signals of the β-pyrrolic and ArH protons move slightly upfield. These spectral changes are interpreted in terms of conformational locking. However, they could reflect the presence of a weak anion–π interaction as well. The protons on the crown-ether subunits were also shifted to slightly lower field, an effect that is likewise ascribed to conformational locking. On the basis of this analysis, we conclude that the receptor-separated ion-pair complex **5** (Scheme 2) is being formed. The addition of



Scheme 2. Proposed binding modes of receptor **1** with tetraalkylammonium fluoride in $CDCl_3$. Receptor-shared ion-pair complex **5** and contact ion-pair complex **6**.

other anions (Cl^-, CH_3COO^-, NO_3^-, $H_2PO_4^-$, or HSO_4^-, all as their respective TBA^+ salts) was also found to induce similar changes in the chemical shifts of receptor **1**, as recorded in $CDCl_3$. Particularly large chemical-shift changes in the pyrrole N–H signal were observed when either chloride or acetate ions were added. In contrast, relatively modest changes were observed in the case of dihydrogen phosphate, hydrogen sulfate, and nitrate ions. These observations lead to the conclusion that these last anions are not bound strongly to receptor **1** under these solution-phase conditions.

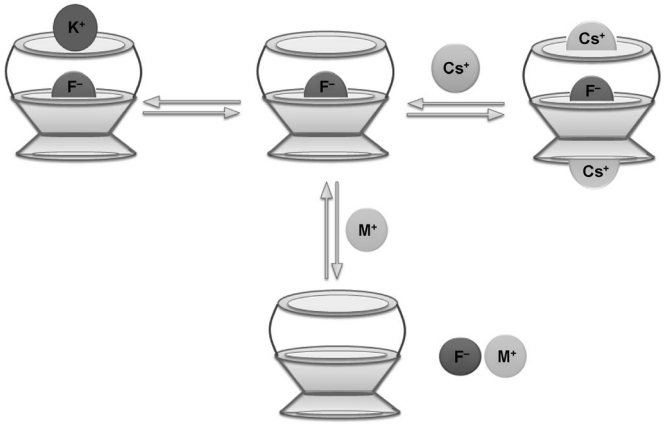
Downfield shifts in the signals corresponding to the protons on the crown-ether moiety were also observed, findings that are consistent with interactions with the counter cations. To further assess the possible effects of the counter cation, ^{1}H NMR-spectroscopic titrations of receptor **1** with several alkylammonium salts, including TEAF and TMAF, were carried out (see the Supporting Information, Figures S10 and 11). Upon titration with TEAF, two new signals, corresponding to the anion-bound pyrrole N–H, appeared at $\delta = 12.35$ and 11.72 ppm. However, these signals disappeared upon addition of excess TEAF, and a new signal, corresponding to the typical fluoride-ion-bound N–H protons, appeared at $\delta = 12.64$ ppm as a doublet ($J_{HF} = 42$ Hz). These seemingly unusual spectroscopic findings can be explained by assuming the concomitant formation of two different ion-pair complexes, namely **5** and **6**, as shown in Scheme 2. The complex formed at an early stage of the titration is thought to be the contact ion-pair complex **6** in which the TEAF binds to the cavity. This complex is not thermodynamically stable and, thus, converts to the more stable receptor-shared ion-pair complex **5** in which the ammonium counter cation interacts with the crown-ether moiety.

In this last complex **5**, the cation interacts with the cavity-bound anion. In complex **6**, produced early on in the titration, the N–H resonance is observed at $\delta = 11.72$ ppm, a chemical-shift value that is consistent with the presence of pyrrole N–H–anion hydrogen bonds that are weakened owing to anion–cation interactions involving the centrally cobound cation. Upon conversion to **5**, the N–H signals in question move to lower field, finally appearing at $\delta =$ 12.64 ppm, as noted above. Such spectral changes are consistent with the formation of a species characterized by strong N–H–anion interactions, as would be expected for the receptor-shared ion-pair complex **5**.

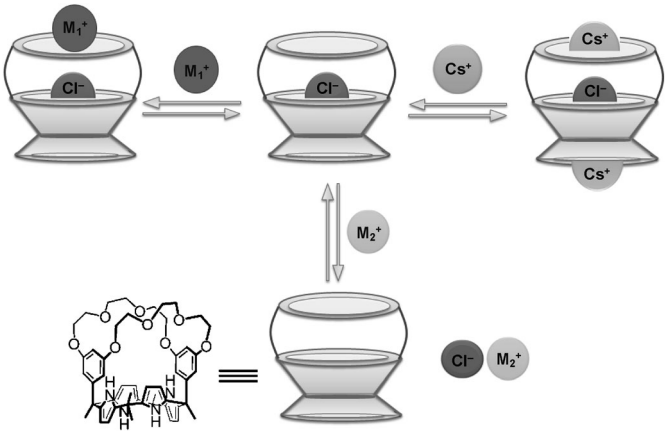
^{1}H NMR titrations of receptor **1** with TMAF resulted in spectral changes similar to those of the addition of TEAF. However, unlike TEAF, spectral features corresponding to a small quantity of contact ion pair (i.e., **6**) remained, even after the addition of an excess (10 equiv) of TMAF. These observations provide support for the notion that the relatively smaller tetramethylammonium ion, in contrast to the tetraethylammonium ion, allows for better interactions with the crown moiety. Such findings are consistent with the expectation that this smaller cation can be better accommodated by the crown-ether moiety. Relative to what was seen with TEAF, this favors formation of **6** over **5**, although the last is still the dominant species by the time ten equivalents of F^- have been added to the solution (as inferred from the integration data). Since ^{1}H NMR-spectroscopic titrations with various ammonium salts proved consistent with the formation of contact ion-pair complexes, we also examined the cation-recognition properties of the preformed supramolecular anion–host ensembles [**1**·X]$^-$ (X = F^- or Cl^-; as the TBA^+ salt). These preformed anion complexes were treated with various Group I metal ions. First, the fluoride-bound complex [**1**·F]$^-$ was treated with various Group I metal ions, as well as with Ca^{2+} and Mg^{2+} (as their respective perchlorate salts). Owing to limited solubility of the salts in chloroform, [D_3]acetonitrile was used as the solvent. Upon addition of the Cs^+ ion (as its perchlorate salt) to the ensemble [**1**·F]$^-$, the signals corresponding to the fluoride-bound pyrrole N–H protons shifted slightly upfield, while those of the crown-ether moiety remained unchanged (see the Supporting Information, Figure S12). A similar trend was observed upon the addition of the K^+ ion; however, in this case, the signal of the pyrrole N–H protons remained unchanged. Upon cation addition, the signal of the pyrrole β-protons were shifted to slightly lower field as compared to the corresponding signals for the complex [**1**·F]$^-$.

The results above are most easily rationalized by the Cs^+ being bound to the cup of the cone-shaped calix[4]pyrrole through cation–π interactions. Concurrent fluoride-ion binding by the pyrrole N–H protons results in the formation of a receptor-shared ion-pair complex [Cs·**1**·F]. The K^+ ion is expected to stabilize weaker cation–π interactions; thus, it was expected to form a complex that is less well ordered, but one in which both the anion and cation are associated with the receptor through the cup of the calixpyrrole rather than through the crown ether (i.e., [K·**1**·F]). Support for this conclusion stems from the observation of broadened but split N–H signals at about $\delta = 12.78$ ppm ($J = 234$ Hz), which is in analogy to what was seen for complex **5** discussed above.

Interestingly, the use of other cations, including Li^+, Na^+, Ca^{2+}, and Mg^{2+}, serves to engender decomplexation of the bound fluoride ion, as inferred from crown-ether signals that resemble those of the uncomplexed form. The presence of N–H resonances at about $\delta = 8.24$ ppm, as seen in the absence of an added salt, indicated that coulombic interactions between these latter cations and the fluoride ion under these solution-phase conditions is stronger than those provided by the four N–H–F hydrogen bonding motifs. A summary of the results observed with the fluoride ion is presented in Scheme 3. It was further observed that when the receptor–chloride complex $[\mathbf{1}\cdot Cl]^-$ (TBA^+ salt) was treated with various alkaline-metal ions (as their perchlorate salts), different changes were seen than in the case of the corresponding fluoride-ion complex. When the preformed complex $[\mathbf{1}\cdot Cl]^-$ was treated with excess Cs^+ ions, a typical upfield shift of the hydrogen-bonded pyrrole N–H proton resonances and downfield shifts in the crown-ether signals were observed (see the Supporting Information, Figure S13). These results are consistent with one Cs^+ ion being bound within the cup of the calix[4]pyrrole (present in its anion-stabilized cone conformation). Addition of Na^+ ion resulted in complete decomplexation of the bound chloride ion from the complex. In contrast, the addition of Li^+, K^+, Ca^{2+}, and Mg^{2+}, (all as the corresponding perchlorate salts) induced only partial decomplexation of the bound chloride complex. The decomplexation was greater in the case of Ca^{2+} and Mg^{2+} than with Li^+ and K^+, as inferred from the relative integrals of the N–H signals at about $\delta = 11.3$ and 8.22 ppm (bound and unbound forms, respectively). A summary of the experimental findings and the proposed interactions of the prebound chloride-ion complex with cations of alkali and alkaline earth metals is shown in Scheme 4.



Scheme 3. Schematic representation of the proposed binding modes of anion complex $[\mathbf{1}\cdot F]^-$ (TBA^+ salt) that were observed in the presence of various metal ions in acetonitrile. The metal ions were used in the form of their respective perchlorate salts. $M^+ = Li^+$, Na^+, Mg^{2+}, Ca^{2+}.



Scheme 4. Schematic representation of the proposed binding modes of anion complex $[\mathbf{1}\cdot Cl]^-$ (TBA^+ salt) that were observed in the presence of various metal ions in acetonitrile. The metal ions were used in the form of their respective perchlorate salts. $M_1^+ = K^+$ and Li^+; $M_2^+ = Na^+$, Mg^{2+}, Ca^{2+}.

Conclusion

We have demonstrated that the benzocrown-ether-capped ion-pair receptor **1**, which contains both cation and anion binding sites within a single overall framework, supports the formation of two different ion-pair complexes that were observed depending on the nature of the cation. The receptor–fluoride complex $[\mathbf{1}\cdot F]^-$ forms a receptor-shared ion-pair complex in which the Cs^+ ion is bound to the cup of the calix[4]pyrrole, as inferred from spectroscopic studies carried out in [D_3]acetonitrile. Decomplexation of the bound fluoride ion was observed when $NaClO_4$, $LiClO_4$, $Ca(ClO_4)_2$, and $Mg(ClO_4)_2$ were added to solutions of $[\mathbf{1}\cdot F]^-$ in [D_3]acetonitrile (TBA^+ salt). The receptor-bound chloride complex $[\mathbf{1}\cdot Cl]^-$ displayed different cation-binding properties than the analogous fluoride-ion complex $[\mathbf{1}\cdot F]^-$. In this case, addition of $CsClO_4$ resulted in the formation of a cup-bound ion-pair complex, as well as a crown-ether-bound contact ion-pair complex. While complete decomplexation was observed upon addition of $NaClO_4$, only partial decomplexation of the bound chloride was achieved upon treatment with K^+, Ca^{2+}, and Mg^{2+}. Thus, the present results serve to underscore the emerging impression that the ion-pair-recognition properties of appropriately designed ditopic receptors can be highly specific. Moreover, the results presented

herein lead us to suggest that these binding properties can be specifically tuned through appropriate synthetic modifications to the receptor framework, and that the nature of the cobound cation and anion plays a major role in defining the structure of the resulting ion-pair complex. These findings have important implications for the design of new ion-recognition systems.

Experimental Section

^{1}H NMR spectra were recorded on 400 MHz NMR spectrometers by using TMS as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; br s, broad singlet; d, doublet; t, triplet; m, multiplet. ^{13}C NMR spectra were proton decoupled and recorded on 150 and 100 MHz NMR spectrometers by using TMS as the internal standard. All other chemicals and solvents were purchased from commercial sources and were used as such, unless otherwise noted. Column chromatography was performed over silica gel. ITC titration was performed by using HPLC grade acetonitrile.

Synthesis and spectral characterization of bisketone (3): K_2CO_3 (1.82 g, 1.32 mmol) and ditosylated triethylene glycol **2** (0.300 g, 3.29 mmol) were added to a solution of 3,5-dihydroxy acetophenone (0.500 g, 3.29 mmol) in acetonitrile (50 mL). Then, the mixture was heated at reflux for 56 h. At that point, the reaction was deemed complete and the reaction mixture was filtered. CH_2Cl_2 (20 mL) and aqueous HCl (5%, 15 mL) were added to the filtrate, . The resulting mixture was extracted with CH_2Cl_2 (3×50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel; CH_2Cl_2/EtOAc = 2:1) to yield compound **3** as a white solid (0.46 g, 26%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.08$ (d, $J =$ 2.3 Hz, 4H), 7.06 (t, 2H, $J = 2.3$ Hz), 4.12 (t, 8H, $J = 4.7$ Hz), 3.86 (t, 8H, $J = 4.7$ Hz), 3.74 (s, 8H), 2.53 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.7$, 160.0, 138.9, 107.0, 106.6, 71.0, 69.6, 67.7, 26.7 ppm; MALDI-TOF: *m/z* calcd for $C_{28}H_{36}O_{10}+H$: 533.23, $C_{28}H_{36}O_{10}+Na$: 555.23; found: 533.09 $[M+H]^+$, 555.07 $[M+Na]^+$.

Synthesis and spectral characterization of bis(5-(1,1-di(1H-pyrrol-2-yl)ethyl)-1,3-phenylene)-[26]crown-8 (4): Bisketone **3** (0.377 g, 0.71 mmol), pyrrole (7 mL), and TFA (0.526 mL, 7.1 mmol) were mixed and heated at reflux (ca. 60 °C) for 24 h. After this time, the reaction was deemed complete and the reaction mixture was cooled to room temperature. At this point, CH_2Cl_2 (5 mL) and TEA (1 mL) were added and the resulting mixture was extracted with CH_2Cl_2 (3×50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel; CH_2Cl_2/EtOAc = 2:1) to yield compound **4** as a brown, gummy thick liquid (0.266 g, 49%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.77$ (br s, 4H), 6.61–6.59 (m, 4H), 6.33 (t, 2H, $J = 2.5$ Hz), 6.30 (d, $J = 2.5$ Hz, 4H), 6.14–6.12 (m, 4H), 5.97–5.96 (m, 4H), 3.97 (t, 8H, $J = 2.8$ Hz), 3.77 (t, 8H, $J =$ 5.0 Hz), 3.68 (s, 8H), 1.97 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 159.7, 149.6, 137.1, 116.8, 108.2, 106.9, 106.1, 99.6, 70.8, 69.6, 67.3, 44.9, 28.8 ppm; MALDI-TOF: *m/z* calcd for $C_{44}H_{52}N_4O_8+3H$: 767.38; found: 767.42 $[M+3H]^{3+}$.

Synthesis and spectral characterization of the bis(1,3-phenylene)-[26]crown-8-capped calix[4]pyrrole (1): Compound **4** (0.33 g, 0.43 mmol), acetone (50 mL), and $Bi(NO_3)_3{\cdot}5H_2O$ (0.075 g, 25% mol) were mixed and the reaction mixture was stirred at room temperature for 4 h. After filtration of the reaction mixture, a saturated solution of KOH (10 mL) was added to the filtrate, which was extracted with CH_2Cl_2 (3×50 mL). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel; CH_2Cl_2/EtOAc = 1:1) to yield compound **1** as a white solid (0.018 g, 5%).^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.18$ (br s, 4H), 6.39 (s, 2H), 6.13 (d, $J = 2.14$ Hz, 4H), 5.98 (t, 4H, $J = 2.7$ Hz), 5.88 (t, 4H, $J = 2.7$ Hz), 3.99–3.94 (m, 8H), 3.83–3.82 (m, 4H), 3.69–3.61 (m, 12H), 1.89 (s, 6H), 1.65 (s, 6H), 1.51 ppm (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.3$, 151.6, 138.8, 136.8, 106.9, 104.7, 102.7, 100.3, 70.5, 69.8, 67.0, 45.4, 34.9, 32.7, 29.7, 29.1, 27.0 ppm; MALDI-TOF: *m/z* calcd for $C_{50}H_{60}N_4O_8+H$: 845.44 ; found: 845.48 $[M+H]^+$.

Acknowledgements

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