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Anion Responsive TTF-Appended Calix[4]arenes. Synthesis and Study of Two Different Conformers

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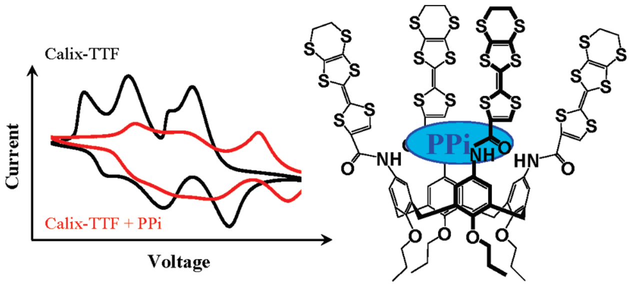

Two new *cone*- and *1,3-alternate*-calix[4]arenes (***cone*-1** and ***1,3-alt*-1**), bearing four modified TTF (tetrathiafulvalene) substituents on the upper rim, have been synthesized. The binding ability of these two sets of conformers for various anions, including F^-, Cl^-, Br^-, I^-, PF_6^-, ClO_4^-, HSO_4^-, CH_3COO^-, $H_2PO_4^-$, and $HP_2O_7^{3-}$, was tested in organic media by monitoring the changes in their UV/vis and ^{1}H NMR spectra as a function of added anion, as well as via cyclovoltammetry (CV) (all anions studied as their respective TBA salts). On the basis of the present findings, we propose that incorporation of four TTF units within an overall calix[4]arene-based recognition framework produces a preorganized receptor system that displays a modest preference for the pyrophosphate ($HP_2O_7^{3-}$) anion.

Introduction

Calix[4]arenes are well-known building blocks with a storied history in supramolecular chemistry. They have been extensively studied on their own, but have likewise been frequently used as molecular scaffolds for the construction of more elaborate host systems.[1] There are many examples in the literature, where substituted calixarenes are used for cation complexation studies.[2] On the other hand, the use of calix[4]arene-based receptors for anion recognition is relatively rare.[3] However, the importance of anions in biological and environmental systems provides an incentive to explore this aspect of calix[4]arene chemistry.[4]

For practical applications, a good receptor should display easy detectable optical and/or electrochemical signals and undergo readily discernible changes in these signals after binding a given guest species. These design criteria make systems based on tetrathiafulvalene (TTF) attractive. TTF is a good electrochemical response element due to its strong π-donating ability and the good reversibility. It displays when subject to stepwise oxidation to form stable radical cation ($TTF^{\bullet+}$) and dication (TTF^{2+}) species.[5] In addition, TTF-based systems typically display an optical response

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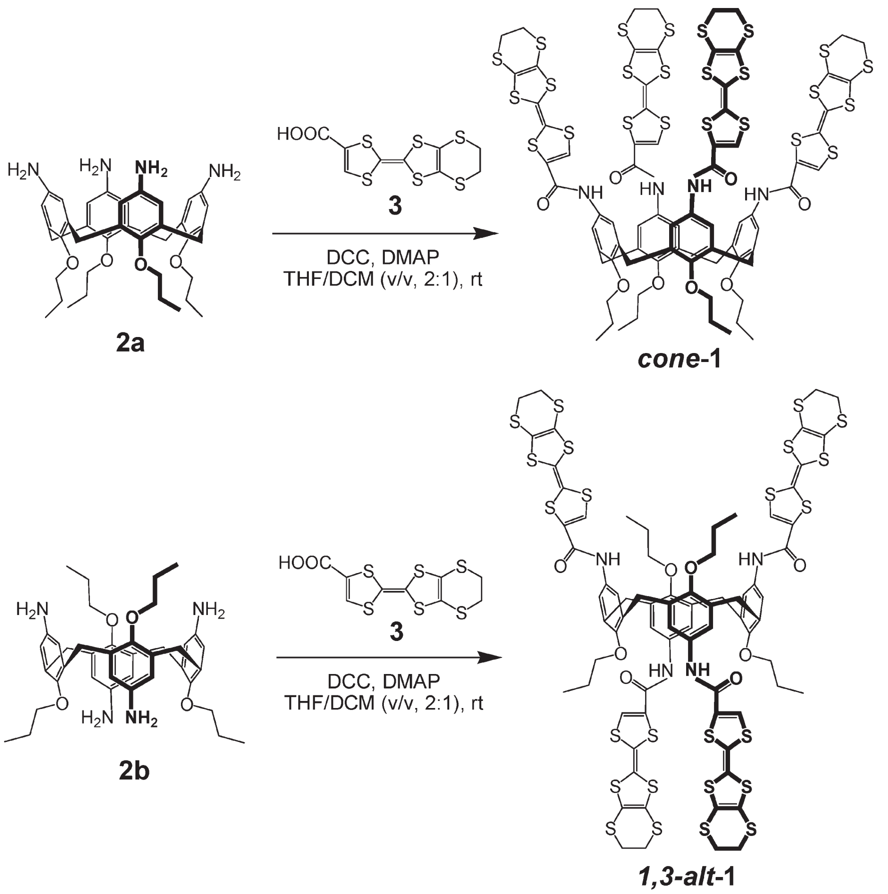
SCHEME 1. Synthetic Routes to *cone*-1 and *1,3-alt*-1



driven by inter/intramolecular charge transfer interactions, with the specifics depending on the coordinated guest species.[6,7] To date, several research groups have worked to create and study electroactive TTF-calix[4]arene architectures.[8,9] Several of these systems have been used for cation recognition.[8] However, TTF anchored calix[4]arenes for anion recognition have yet to be extensively explored.[9] Here, we report two new *cone*- and *1,3-alternate*-calix[4]arenes bearing modified TTF subunits on their respective upper rims (***cone*-1** and ***1,3-alt*-1**, respectively). We have studied the anion binding properties of these systems in organic media by monitoring substrate-induced changes in their UV/vis and ^{1}H NMR spectra, as well as in their electrochemical features by use of CV. The test anions (studied as their tetrabutylammonium (TBA) salts) in question included F^-, Cl^-, Br^-, I^-, PF_6^-, ClO_4^-, HSO_4^-, CH_3COO^-, $H_2PO_4^-$, and $HP_2O_7^{3-}$, with the latter displaying a particularly noteworthy response.

Results and Discussion

cone- and *1,3-alternate*-calix[4]arene derivatives bearing modified TTF pendants were prepared by the synthetic routes outlined in Scheme 1. Briefly, the tetraaminotetrapropylcalix[4]arene derivatives (**2a** and **2b**) and the TTF monoacid (**3**) were prepared by using procedures reported earlier.[10] The ***cone*-1** (30% yield) and ***1,3-alt*-1** (20% yield) targets were then obtained via amide coupling by reacting **2a** (or **2b**) with **3** in the presence of DCC and DMAP in THF/DCM.[10] The conformation and overall chemical structures of ***cone*-1** and ***1,3-alt*-1** were confirmed by using ^{1}H NMR and ^{13}C NMR spectroscopy, as well as via MALDI-TOF MS and FT-IR methods (Supporting Information). The ^{1}H NMR spectrum of ***cone*-1** shows two pairs of doublet at δ 4.36 (4H) and 3.11 (4H) for the ArCH_2Ar protons and a ^{13}C NMR peak at δ 31.4 for the ArCH$_2$Ar carbon. In contrast, ***1,3-alt*-1** displays a typical singlet ^{1}H NMR peak at 3.65 ppm for the ArCH_2Ar protons and a ^{13}C NMR peak at 38.5 ppm for the ArCH$_2$Ar carbon.

Initial studies of the ability of ***cone*-1** and ***1,3-alt*-1** to bind anions were made by monitoring the spectral changes in the

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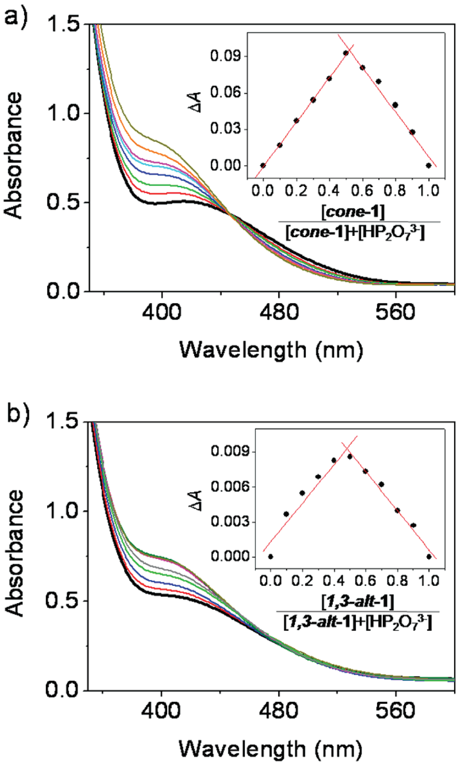

FIGURE 1. UV/vis absorption spectral changes and Job plot of (a) ***cone*-1** and (b) ***1,3-alt*-1** (0.05 mM, respectively) in CH_2Cl_2. Spectra shown were recorded in the presence of (a) 0, 0.2, 0.4, 1.0, 2.0, 5.0, 10.0, 30.0 equiv and (b) 0, 1.0, 2.0, 3.0, 4.0, 30.0, 50.0, 70.0 equiv of $HP_2O_7^{3-}$ (as its TBA salt). Inset: Job plot measured at 406 nm.

UV/vis spectra seen upon the addition of TBA salts of various anions, such as F^-, Cl^-, Br^-, I^-, PF_6^-, ClO_4^-, HSO_4^-,CH_3COO^-, $H_2PO_4^-$, and $HP_2O_7^{3-}$, in CH_2Cl_2 (Figure S1, Supporting Information). Both ***cone*-1** and ***1,3-alt*-1** displayed strong and broad absorption bands centered at 303 and 415 nm, respectively (Figure S2, Supporting Information). The strong absorption band is ascribed to a localized TTF transition, whereas the broader feature is thought to reflect an intramolecular charge-transfer (ICT) transition involving a TTF (donor)–carbonyl (acceptor) interaction.[7] Addition of 10 equiv of anion salt to a solution of ***cone*-1** or ***1,3-alt*-1** was found to give rise to blue shifts in the lower energy absorption feature in the case of F^-, Cl^-, CH_3COO^-, $H_2PO_4^-$, and $HP_2O_7^{3-}$ ions. These changes, which are mainly ascribed to a suppression of the ICT (intramolecular charge transfer) interaction, were not seen in the case of the Br^-, I^-, PF_6^-, ClO_4^-, and HSO_4^- ions.

Among the anions tested, $HP_2O_7^{3-}$ gave rise to the greatest changes in the UV/vis spectrum. It was thus inferred that this anion is bound most strongly among the test anions used in this study, a conclusion supported by NMR spectroscopic analyses and CV studies (vide infra). Figure 1 illustrates the detailed UV/vis absorption changes for ***cone*-1** and ***1,3-alt*-1** as a function of increasing [$HP_2O_7^{3-}$] in CH_2Cl_2. Upon addition of $HP_2O_7^{3-}$ ions to a solution of ***cone*-1**, the absorption band at 415 nm gradually blue-shifts with an isosbestic point centered at 446 nm (Figure 1a). As shown in Figure 1a, the Job plot reveals features consistent with the formation of a 1:1 complex (***cone*-1**:$HP_2O_7^{3-}$). From a structural point of view, it is conceivable that the $HP_2O_7^{3-}$ ion is encapsulated by a cavity composed of the calix[4]arene and four TTF amide linkers to form an intermolecular H-bonding array. Unfortunately, all efforts to obtain X-ray diffraction grade crystals of this putative complex proved unsuccessful. Nevertheless, from an operational perspective it is important to note that readily discernible spectral changes were obtained in the case of the $HP_2O_7^{3-}$ anion. This means ***cone*-1** shows a high affinity for the pyrophosphate anion, a biologically important species for which bona fide receptor systems are rare.[11]

TABLE 1. Binding Constants (K_a, M^{-1}) of *cone*-1 and *1,3-alt*-1 for F^-, Cl^-, CH_3COO^-, $H_2PO_4^-$, and $HP_2O_7^{3-}$ Ions in CH_2Cl_2 As Determined from Absorption Spectroscopic Titrations

	K_a [M^{-1}][a]	
anion[b]	receptor ***cone*-1**	receptor ***1,3-alt*-1**
$HP_2O_7^{3-}$	4.7×10^4	9.2×10^3
$H_2PO_4^-$	3.1×10^4	5.5×10^3
F^-	2.6×10^3	1.6×10^4
Cl^-	2.8×10^3	–[c]
CH_3COO^-	1.8×10^4	9.5×10^3

[a] Estimated errors are < 20%. [b] Anions were used in the form of their Bu_4N^+ (TBA) salts. [c] No reliable fit could be obtained, presumably due to the formation of a mixture of 1:1 and 1:2 complexes (Figure S10, Supporting Information).

Receptor ***1,3-alt*-1** also showed progressively blue-shifted absorptions upon the addition of $HP_2O_7^{3-}$ ions. However, in this case a distinct isosbestic point was not seen (Figure 1b). Such an observation leads us to suggest that complexation of ***1,3-alt*-1** with $HP_2O_7^{3-}$ ions either produces a complex that is relatively unstable or produces one with a binding stoichiometry more complex than 1:1.[12] We also found that the apparent binding constant for $HP_2O_7^{3-}$ was smaller in the case of ***1,3-alt*-1** than in the case of ***cone*-1** (Table 1). The binding constants were obtained under the assumption of 1:1 stoichiometry. The difference in conformation-based binding behavior can be explained in terms of a negative allosteric effect being operative in the case of ***1,3-alt*-1**. Specifically, formation of an initial 1:1 complex induces a conformational change in the second binding site, rendering it less suitable for the binding of a second anion.[13]

Similar results were observed upon the addition of the F^-, Cl^-, CH_3COO^-, and $H_2PO_4^-$ ions to a solution of ***cone*-1** or ***1,3-alt*-1** (Figures S3–S10, Supporting Information). The binding constant (K_a) of each conformation for these anionic species was obtained via standard anion titration experiments.[14] The results obtained are summarized in Table 1. In accord with the above rationale, ***cone*-1** displays a higher binding affinity for most anions than does ***1,3-alt*-1**.

To obtain further support for the assignment of the observed UV/vis spectral changes to anion binding events, ^1H NMR spectral experiments were carried out in $CDCl_3$/DMSO-d_6 (9:1, v/v). The ^1H NMR spectra recorded for

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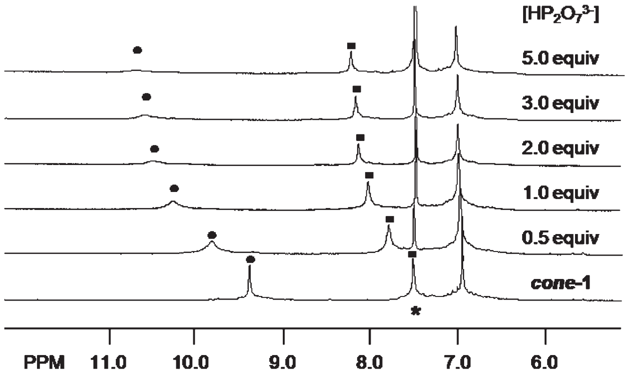

FIGURE 2. Partial ^{1}H NMR titration spectra (300 MHz) recorded in $CDCl_3$/DMSO-d_6 (v/v, 9:1) of ***cone*-1** upon the addition of increasing concentrations of the $HP_2O_7^{3-}$ anion (as the TBA salt). The peaks are marked as follows: ●, NH; ■, C=C—H of TTF unit; and $\ast$, $CDCl_3$.

***cone*-1** upon the addition of increasing quantities of the $HP_2O_7^{3-}$ anion are shown in Figure 2. The $-NH$ peak was first seen to shift downfield ($\Delta\delta$ = 1.45 ppm at 5.0 equiv) and then disappear after more than 5.0 equiv had been added. The $-C{=}CH$ protons of the TTF unit were also seen to undergo a downfield shift ($\Delta\delta$ = 0.98 ppm at 5.0 equiv), leading us to infer that the $-C{=}CH$ proton also takes part in H-bonding interactions with the bound $HP_2O_7^{3-}$ anion. Quantitative ^{1}H NMR spectroscopic titrations were carried out (Figure S13, Supporting Information). The resulting data were then used to obtain binding constants by employing Wilcox' nonlinear method[15] and fitting the binding profiles to a 1:1 complex stoichiometry. The binding constants (K_a, M^{-1}) were determined to be $HP_2O_7^{3-} = 2.5 \times 10^2$, $H_2PO_4^- = 2.3 \times 10^2$, and $F^- = 1.2 \times 10^2$ M^{-1} for ***cone*-1** and $F^- = 2.1 \times 10^2$, $HP_2O_7^{3-} = 1.6 \times 10^2$, $H_2PO_4^- = 1.4 \times 10^2$ M^{-1} for ***1,3-alt*-1**, respectively. This trend is in good agreement with what was inferred from the absorption spectroscopic experiments described above.

TABLE 2. Maximum Displacement ($\Delta E_{1/2}$) in the Fourth Redox Potential of Receptors *cone*-1 and *1,3-alt*-1 Observed upon the Addition of 1.0 Equiv of the TBA Salts of the Indicated Anions in Distilled CH_2Cl_2 Solution

	$\Delta E_{1/2}$ (mM)				
receptors	$HP_2O_7^{3-}$	$H_2PO_4^-$	F^-	CH_3COO^-	Cl^-
***cone*-1**	453	217	236	214	33
***1,3-alt*-1**	163	171	265	40	26

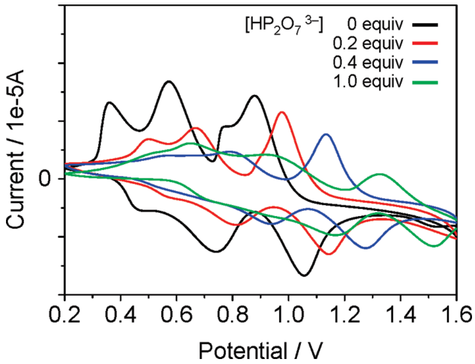

FIGURE 3. CVs of ***cone*-1** (in distilled CH_2Cl_2 solution, 0.5 mM) recorded upon addition of increasing quantities of $HP_2O_7^{3-}$ ions. Reference electrode = AgCl/Ag; supporting electrolyte = $TBAPF_6$.

The redox characteristics of both ***cone*-1** and ***1,3-alt*-1** were studied in $TBAPF_6/CH_2Cl_2$ solution, using CV (Pt electrodes vs Ag/AgCl). Both receptors show four couples (i.e., redox peaks; Figure S14, Supporting Information), presumably reflecting a splitting in the first and second redox waves. Since the four TTF units present in ***cone*-1** and ***1,3-alt*-1** are in the same chemical environment, as inferred from symmetry considerations and their respective NMR spectra, these multiredox processes are attributed to a strong intramolecular interaction between the pendant TTF moieties. It is known that a broadening or a splitting of the first oxidation wave can be induced when multiple TTF units are covalently linked via a short, flexible tether. Presumably, this linking leads to an electronic stabilization of the radical cation formed initially by a neighboring TTF unit.[16] However, a splitting in the second redox wave is rare because adjacent TTF^{2+} units, produced by a two-electron oxidation, would be subject to repulsive electrostatic interactions, reducing the chance for overlap.[17] The split signal associated with the second redox process seen in the present instance may be ascribed to the constraint enforced by the parent calix[4]arenes. The short linker $-CONH-$ between the calix and the TTF moieties is expected to keep the cationic forms of the latter produced via electro-oxidation locked in a rigid environment (preventing expulsion altogether and even keeping the TTF^{2+} species from diffusing apart to a significant extent). The result is an enforced through-space interaction between the redox-active TTF subunits. Consistent with this suggestion is the finding that ***cone*-1** displays a larger splitting in the CV than does its ***1,3-alt*-1** congener, as would be expected given the more preorganized binding cavity present in receptor ***cone*-1** than in ***1,3-alt*-1**.

The addition of F^-, $H_2PO_4^-$, and $HP_2O_7^{3-}$ to ***cone*-1** and ***1,3-alt*-1** in CH_2Cl_2 solution induced notable changes in the redox features (Table 2), while other anions produce little or no change, as determined by CV. Upon titration of anions, the first two set of peaks were seen to undergo an anodic shift then flatten, whereas in contrast, the next set of redox waves was seen to retain reversibility, even in the presence of a large excess of added anions (Figure 3). In general, cathodic shifts in the redox potentials are seen when anions are added to TTF-based redox-responsive receptors; this is because the bound anion serves to stabilize the positively charged TTF moiety produced upon oxidation.[6c,9a] In fact, such a cathodic shift was observed by Batail et al. in the case of a simple TTF-CONHMe system upon exposure to anions.[18]

In our case, the large anodic shift is attributed to electron transfer from the propoxybenzenamine part of the molecule to the TTF moiety, something that makes the TTF moiety more easily oxidized. In the presence of a bound anion, this process is suppressed or inhibited; as a consequence, the

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redox potential increases. To the best of our knowledge, this is the first example of TTF-based receptors for anions that undergoes an anodic, as opposed to cationic, shift in the redox potential upon anion binding. Multiwave, substrate-induced responses in the case of anion receptors are also very rare.[6] Finally, the magnitude of the observed anodic perturbations, up to 453 mV in the case of pyrophosphate, are, to the best of our knowledge, the highest recorded so far for ligands based on TTF units.[19]

Conclusions

We have prepared two new TTF-calix[4]arene derivatives, namely ***1,3-alt*-1** and ***cone*-1**. The latter isomer represents a particularly attractive system that permits anion recognition via both photophysical and electrochemical means in CH_2Cl_2 solution. This system incorporates four redox-active TTF units onto the upper rim of a conformationally defined calix[4]arene. This produces a preorganized cavity that interacts with anions, particularly the $HP_2O_7^{3-}$ ion, via intermolecular H-bonds. ***cone*-1** represents a rare example of a TTF-functionalized calix[4]arene derivative that has been applied for the purpose of anion recognition and the first such receptor to display anodic perturbations in its CV in the presence of anions.

Experimental Section

Ttetraamino-tetrapropylcalix[4]arene derivatives (**2a** and **2b**)[10b] and TTF monoacid (**3**)[10a] were prepared according to literature procedures.

Synthesis of *cone*-1. A suspension of **2a** (0.26 g, 0.04 mmol), **3** (0.74 g, 2.2 mmol), DCC (0.49 g, 2.4 mmol), and DMAP (0.29 g, 2.4 mmol) in dry THF/CH_2Cl_2 (1:2, v/v) was stirred under nitrogen for 5 days at room temperature. After the solvent was evaporated, CH_2Cl_2 (100 mL) and water (100 mL) were added, and the organic layer was separated. The CH_2Cl_2 layer was dried by anhydrous $MgSO_4$. After removal of the solvents, the crude product was purified over silica gel, using CH_2Cl_2/hexanes (v/v, 1:3) as the eluent, to yield ***cone*-1** as a dark orange solid (0.2 g, 30%). Mp 232−235 °C. IR (deposit from DCM solution on a NaCl plate, cm^{-1}) 3390, 2913, 1638, 1539, 1452. MALDI-TOF MS *m*/*z* (M^+) calcd 1933.8292, found 1933.0134. ^1H NMR (DMSO-d_6, 400 MHz) δ 9.83 (s, 4 H), 7.68 (s, 4 H), 6.98 (s, 8 H), 4.36 (d, 4 H, $J = 11.9$ Hz), 3.78 (t, 8 H, $J = 7.9$ Hz), 3.38 (s, 16 H), 3.11 (d, 4 H, $J = 11.9$ Hz), 1.89−1.83 (m, 8 H), 0.95 (t, 12 H, $J = 7.4$ Hz). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 157.2, 153.3, 134.9, 134.7, 132.8, 126.2, 120.5, 116.4, 113.5, 104.5, 77.0, 31.3, 30.1, 23.3, 10.8 ppm.

Synthesis of *1,3-alt*-1. Compound ***1,3-alt*-1** was synthesized by using a method used to produce ***cone*-1**. The ***1,3-alt*-1** product was obtained as a brilliant orange solid in 20% yield. Mp 212−225 °C. IR (deposit from DCM solution on a NaCl plate, cm^{-1}) 3390, 2922, 2360, 1635, 1536, 1214. MALDI-TOF MS *m*/*z* (M^+) calcd 1933.8292, found 1933.0509. ^1H NMR (DMSO-d_6, 400 MHz) δ 9.29 (s, 4 H), 7.43 (s, 4 H), 7.22 (s, 8 H), 3.60 (s, 8 H), 3.48 (t, 8 H, $J = 6.5$ Hz), 3.35 (s, 16 H), 1.60−1.64 (m, 8 H), 0.85 (t, 12 H, $J = 7.4$ Hz). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 157.4, 153.8, 134.8, 134.1, 132.8, 126.1, 121.7, 116.7, 113.5, 104.6, 72.9, 38.5 30.2, 23.0, 10.4 ppm.

Materials and Methods

General Instrumentations and Reagents. UV/vis absorption spectra were recorded on a S-3100 spectrophotometer (Scinco). NMR spectra were recorded with Varian-400 and Varian-300 MHz. All reagents and anhydrous solvents were of commercial quality. CH_2Cl_2 for the spectra studies was HPLC reagent grade and free of fluorescent impurities. All anion salts, including the tetrabutylammonium (TBA) salts of F^-, Cl^-, Br^-, I^-, PF_6^-, ClO_4^-, HSO_4^-, CH_3COO^-, $H_2PO_4^-$, and $HP_2O_7^{3-}$, were used as received.

UV/Vis Spectroscopic Method. Stock solutions of anion TBA salts (0.01 M) and receptors ***cone*-1** and ***1,3-alt*-1** were prepared in CH_2Cl_2. Titration experiments were performed with 0.05 mM solutions of receptors and involved adding various concentrations of anion salts in CH_2Cl_2.

CV Method. Electrochemical measurements were performed with a CHI 624C potentiostate. All electrochemical measurements were carried out in a one-compartment cell under a nitrogen atmosphere at 25 °C, equipped with a Pt disk working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode with a special salt bridge. The working electrode surface was carefully polished with basic Al_2O_3−water slurry, washed with MeOH, and sonicated in a H_2O−MeOH−CH_3CN 1:1:1 mixture at 40 °C for 15 min prior to use. All potentials were recorded in dichloromethane (DCM) and are quoted relative to Ag/AgCl, and were calibrated with useofdecamethylferrocene ($E_{1/2} = 0.46$ V). The supported electrolyte was a 0.10 M DCM solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$).

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Supporting Information Available: ^1H NMR, ^{13}C NMR spectra, and MALDI-TOF MS data for ***cone*-1** and ***1,3-alt*-1** and supplementary data of UV/vis absorption, ^1H NMR spectra, and CV studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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