Ionoresistivity as a Highly Sensitive Sensory Probe: Investigations of Polythiophenes Functionalized with Calix[4]arene-Based Ion Receptors

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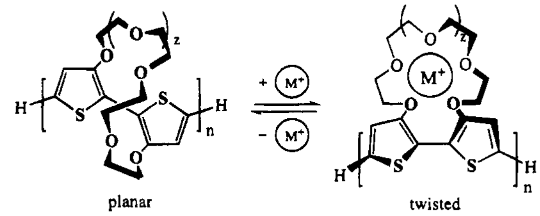
Abstract: Herein we report the synthesis, optical, and electrochemical properties of a calix[4]arene-substituted polythiophene which demonstrates ion selective voltammetric, chromic, fluorescent, and resistive responses. The ionochromic response of this polythiophene on exposure to Na^+ shows an increased effective conjugation length of the polymer backbone. Despite this, Na^+ induces a large positive shift in the potential at which the polymer is oxidized (>+100 mV) commensurate with a large decrease in conductivity (>99%). Although the calix[4]arene-substituted polythiophene exhibits no changes in the UV–vis spectrum and only minimal changes in the voltammetric responses on exposure to Li^+ or K^+, there are large decreases in relative conductivities (69% and 47%, respectively). Thus, although the sensory properties of this polymer are expressed via several measurable entities, the ionoresistive response is clearly the most sensitive. This sensitivity originates from the cooperative nature of carrier transport in a CP and is thus inherent in chemoresistive CPs.

Introduction

Receptor-based conducting polymers (CPs) are one class of materials that have been successfully utilized in the development of molecule-based sensory materials.[1–5] The reversible binding of an analyte by such a CP can produce perturbations in the chemical structure, oxidation state, and/or solid state ordering of the system resulting in voltammetric, ionochromic, and chemoresistive responses.[1–5] The vast body of research on CPs teaches that conductivity, or equivalently resistivity, is the component most sensitive to a polymer's chemical state and/or organization.[6] In the immediately preceding paper in this issue, we have demonstrated chemoresistive behavior in polythiophenes functionalized with a cyclophane-based receptor and found that perturbations to the CP which are not consistently detected via cyclic voltammetry (CV) are readily and reliably detected by changes in conductivity. Our goal is to design additional sensory materials and explore new perturbations resulting from binding of a specific analytes to receptor sites covalently attached to the polymer. An advantage of this design is that the sensory mechanism functions via reversible molecular recognition events, thereby allowing a completely reversible response such that, in the absence of analyte, the sensory material returns back to its original unperturbed state. As articulated in the preceding paper in this issue, we propose that there is an inherent sensitivity gain in receptor-based chemoresistive CPs. In this paper, we further demonstrate the utility of this approach in the design of ionoresistive materials. We report herein a polythiophene functionalized with calix[4]arene-based receptors which shows reversible, ion-specific voltammetric, chromic, fluorescent, and resistive responses. Our results conclusively demonstrate our assertion that ionoresistivity, which is a property of a collective assembly, can display a much greater sensitivity to analyte-induced perturbations than other more localized properties.

Results and Discussion

a. Design of Polythiophene Receptors. Central to our design of chemo- and ionosensitive CPs is the covalent attachment of a molecular recognition site to the polymer backbone.[1,2,7] Our earlier work in ionoresponsive CPs utilized simple crown ether based polythiophenes which undergo ion-induced conformational changes as shown.[1] Despite relatively low binding constants of the bithiophene-based receptor monomers (**1a**, $n = 1$, $z = 1$; **1b**, $n = 1$, $z = 2$) (K_a = ca. 10^5),[1] these polymers demonstrated a large ion-induced decrease in absorption wavelength ($\Delta\lambda_{max} = -91$ nm) consistent with the twisting mechanism shown:



In an effort to further optimize sensitivity and selectivity, we have substituted a 1,3-dimethylcalix[4]arene into the polyether tether to produce bithiophene receptor **3**. The choice of **3** was based in part on reports that calixarene-based ion receptors display some of the highest known binding affinities for alkaline

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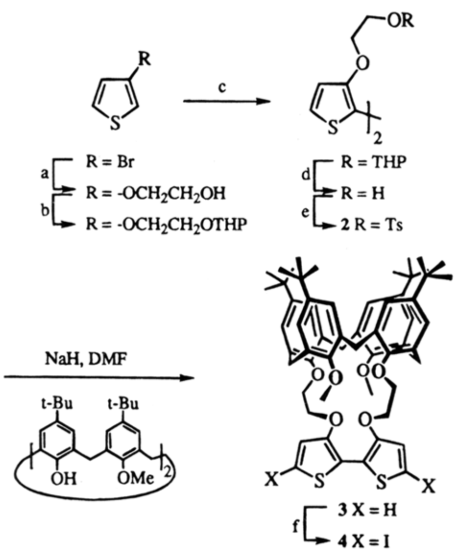
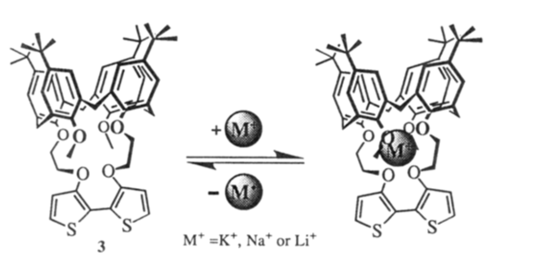
Scheme 1[a]



[a] (a) Reference 13; (b) DHP, PPTS (89%); (c) (1) *n*-BuLi, THF, −10 °C; (2) $Fe(acac)_3$, THF, reflux (64%); (d) MeOH, PPTS (100%); (e) *p*-TosCl, pyridine, 0 °C (78%); (f) $Hg(OAc)_2$, I_2 (59%).

metal salts.[8,9] These enhancements are in accord with the fact that the calixarene group provides a highly preorganized architecture.[10,11] Thus, we have affixed the calixarene-based receptor directly to the polymer backbone such that ion binding will both compete for oxygen lone pairs which delocalize into the π system of the polymer as well as induce conformational changes in the polymer's backbone. These two features were expected to produce an ionoresistive effect on the basis of the following observations: (1) CPs with nonplanar conformations are known to exhibit lower conductivities than their planar counterparts,[6] and (2) decreased donation by lone pairs coupled with electrostatic repulsions will impede cationic carrier mobility by increasing the potential required to oxidize the occupied binding sites.[2,12] Additional support for these premises comes from our previous investigations which have demonstrated both an ionochromic response in crown ether based polythiophenes and chemoresistive effects derived from binding of cationic organic guests into conducting pseudopolyrotaxanes.[1,2,7] As such, we anticipated that the complex formed by incorporation of an ion into the six oxygen cavity of **3** would produce the necessary conformational and electrostatic perturbations required to induce an ionoresistive response.



b. Synthesis and Characterization of Monomers and Polymers. Receptor **3** was synthesized in six steps from commercially available 3-bromothiophene (Scheme 1). 3-(2-Hydroxyethoxy)thiophene could be readily prepared from literature procedures.[13] THP protection of the hydroxy group allowed for selective lithiation at the 2-position of the thiophene ring using stoichiometric *n*-butyllithium. Direct oxidative coupling of the organolithium species with $Fe(acac)_3$, followed by deprotection of the THP moiety, afforded 3,3′-bis(hydroxyethoxy)bithiophene, which could then be converted to its ditosylate (**2**). Finally, **3** could be readily obtained via reaction of **2** with tetra-*p*-*tert*-butyl-26,28-dimethoxycalix[4]arene using NaH in DMF.

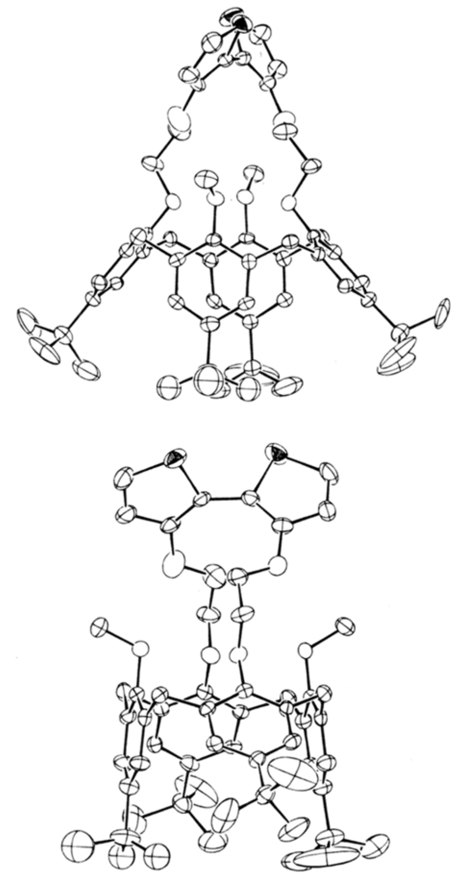


Figure 1. ORTEP drawings showing two views of compound **3**. The thermal ellipsoids are plotted at the 30% probability level.

Structural assignments by NMR spectroscopic methods were complicated by **3**'s fluxional behavior. This behavior suggests the existence of several diasteriomeric conformers and only minor simplifications were observed when **3** was heated to 80 °C in benzene-d_6. The structure of **3** was confirmed by X-ray crystallography, and the ORTEP drawing is shown in Figure 1. The crystallographic studies also show **3** to crystallize in a single chiral conformation with a 68° dihedral angle between the thiophenes, thereby inducing a helical twisting of the polyether tether connecting the bithiophene to the calix[4]arene.

In spite of multiple conformations, **3** displays ionophoric properties with good selectivity and relatively high association constants. Indeed even the highly twisted conformation which was characterized crystallographically showed a well defined oxygen-rich binding site. The relative association constants (K_a) of **3** were measured for K^+, Na^+, and Li^+ using standard picrate extraction techniques.[14] These results in comparison with **1a,b** and 18-crown-6 are shown in Table 1. These studies showed **3** to best accommodate Na^+, exhibiting a K_a for Na^+ ap-

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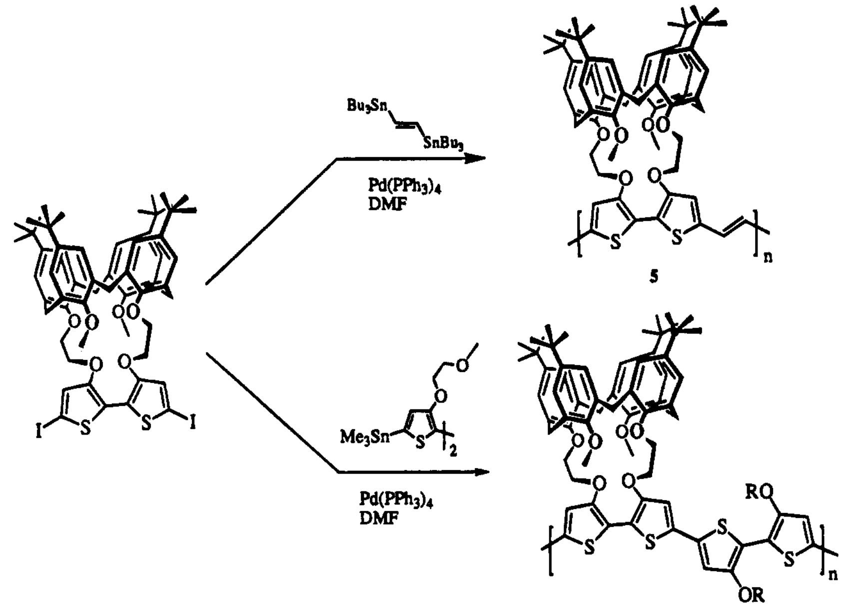
Scheme 2



6 R = -CH2CH2OCH3

Table 1. Comparison of Alkali Metal Picrate Binding of 18-Crown-6 with Bithiophene Ionophores **1** and **3**

	K_a		
monomer	K^+	Na^+	Li^+
18-crown-6[a]	2.0×10^8	2.3×10^6	1.9×10^5
1a	8.6×10^4	2.8×10^5	1.2×10^5
1b	1.1×10^5	2.3×10^5	1.9×10^5
3	7.3×10^5	7.6×10^7	1.9×10^6

[a] Measurements of this known ionophore were included as a point of reference for the K_a's of bithiophene-based monomers.

proximately 270 times greater than we had previously reported for **1a**.[1] Additionally, **3** exhibits good discriminating characteristics and binds to Na^+ 40 times stronger than Li^+ and ≈100 times stronger than K^+. Due to its stronger binding properties, we have focused on **3** for our continuing studies.

Iodination of **3** using $Hg(OAc)_2$ and I_2 affords monomer **4** in high yield, which can be copolymerized using Stille cross-coupling methodologies (Scheme 2).[15,16] Seeking to avoid a highly twisted backbone resulting from steric crowding of the bulky calixarene groups, we separated neighboring calixarenes by synthesizing a vinylene copolymer (**5**). Introduction of a vinylene spacer into the backbone of poly(3,4-di-*tert*-butoxythiophene) was previously reported as a successful way to minimize steric crowding of the side chains, thus lowering the bandgap of the corresponding vinylene copolymer.[17]

Polymer **5** was synthesized by a Stille-type cross-coupling procedure reported previously by ourselves and others using bis(tributylstannyl)ethylene as a monomer.[18,19] This method proceeds to give high molecular weight polymers (Table 2). We also synthesized polymer **6** by copolymerization of **4** with the electron-rich 3,3′-bis(methoxyethoxy)bithiophene in order to lower the potential at which the polymer is oxidized. This strategy was found to be successful in similar systems and has been discussed in detail.[7] As can be seen in Table 2, the incorporation of 3,3′-bis(methoxyethoxy)bithiophene is again effective at lowering the potential at which the polymer is oxidized.

Table 2. Properties of Polymers **5** and **6**

polymer	M_n	PDI	λ_{max} (nm)	E_{pa} (vs Ag wire)
5	47 000	1.6	500	1.05 V
6	22 000	1.7	498	0.57 V

Table 3. Ionochromic Response of Polymers **5** and **6**

		$\Delta\lambda_{(max)}$ (nm)		
polymer	$\lambda_{(max)}$ (nm)	K^+	Na^+	Li^+
5	498	−8	−24	0
6	500	0	[−20, +36, +80][a]	0

[a] Broad absorbance with three poorly defined peaks at 480, 536, and 580 nm ($\Delta\lambda_{onset}$ = +32 nm). See Figure 2.

c. Ion Selective Optical Properties. The ionochromic properties of both **5** and **6** were measured in THF (0.5 mM salt), and the results are shown in Table 3. The most striking result is the near perfect selectivity of this property for Na^+ in both polymers. As can be seen in Table 3, no measurable shifts were detected for Li^+ and only a minor shift for K^+ is observed for **5** even though these ions bind **3** with reasonably high K_a's. The all thiophene containing polymer **6** displays a visible red shift upon exposure to Na^+. Thus, it can be inferred that incorporation of Na^+ into the binding sites forces a rotation about the bithiophene axis which results in increased π-orbital overlap. This effect is opposite to what we had previously observed in related systems containing simple tetra- and penta(ethylene oxide) tethers (**1a,b**),[1] and reflects, as was suggested in our crystal structure of **3**, that the bithiophene receptor is dominated by nonplanar conformations. The strong binding of Na^+ is required to force a planar conformation in these materials. Given these behaviors, we were surprised to find that **5** displays a dramatic visible blue shift with Na^+ complexation.

An explanation of the differences between **5** and **6** may lie in the fact that the energy differences between several diastereomeric conformers of **3** are small and are highly influenced

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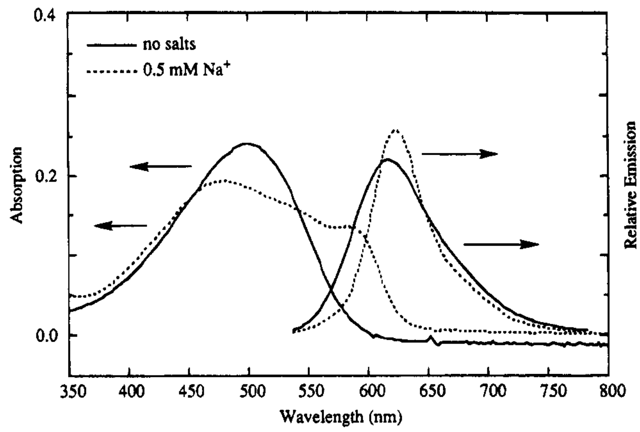

Figure 2. Absorption and relative emission spectra for polymer **6** in THF in both the absence and presence of Na^+ (0.5 mM).

by substitution at the 5,5′-positions of the bithiophene. Due to the absences of obvious steric demands by either polymer, we believe the differences are likely the result of both steric and electronic factors. Depending on the initial conformation of **3**, it is possible that binding of Na^+ will either increase or decrease the dihedral angle between the thiophene rings. Since we are targeting polymers which demonstrate a decreased conductivity on exposure to analyte, it would be intuitively more desirable to utilize a system which exhibits a blue shift with ion binding. Ideally, the combination of a decreased conjugation length and the electrostatic perturbations between the ion and polymer should produce the greatest ionoresistive response.

Given the above criteria, polymer **5** would be expected to give the largest sensory responses. Unfortunately, **5** is oxidized only at a high potential and displays low stability in its oxidized (doped) state which precludes a study of its chemoresistive properties. This problem is solved by the lower potential at which polymer **6** is oxidized, and **6** displays stable and reversible electrochemical behavior. Although **6** demonstrates an increased conjugation length on exposure to Na^+, we expected an ionoresistive response arising strictly from electrostatic contributions to be significant. Such a result is precedented, since in our preceding paper we have demonstrated chemoresistive effects in macrocycle-based polythiophenes resulting principally from electrostatic perturbations.

Given polymer **6**'s stability we endeavored to further investigate its optical properties as a function of Na^+ concentration with fluorescence and absorption measurements. It has been reported that the emission of CPs can be dominated by chromophores which produce local minima in the band structure.[20,21] Such processes require energy migration through the polymer backbone to a chromophore which presents a local minima. Recent results from this laboratory have demonstrated this as a method for enhancing the response of a fluorescent chemosensor.[22] In this regard we were particularly interested in **6**'s emission as a function of Na^+ concentration (Figure 2), since Na^+ complexation results in increased conjugation and thus a local minima in the band structure.

The effects were less pronounced than other fluorescence-based polymer sensors,[22] however the emission peak does shift to slightly lower energy ($\Delta\lambda_{max} = 6$ nm). More significantly was the commensurate narrowing of the emission peak and broadening of the absorption band in the Na^+-complexed material relative to the uncomplexed material. The broad absorption implies that Na^+ complexation produces a greater distribution of effective conjugation lengths. The narrowed emission indicates an increased efficiency of the fluorescence at planarized (lower bandgap) sites. This latter feature is afforded by the increased number of planar segments induced by Na^+ complexation. In contrast, the greater fractions of the uncomplexed repeating units restrict energy migration and emission occurs from a broader distribution of local bandgaps associated with different conformational domains. In this case, the broadening of the emission peak reflects the inability of energy to migrate to true minima in the overall band structure.

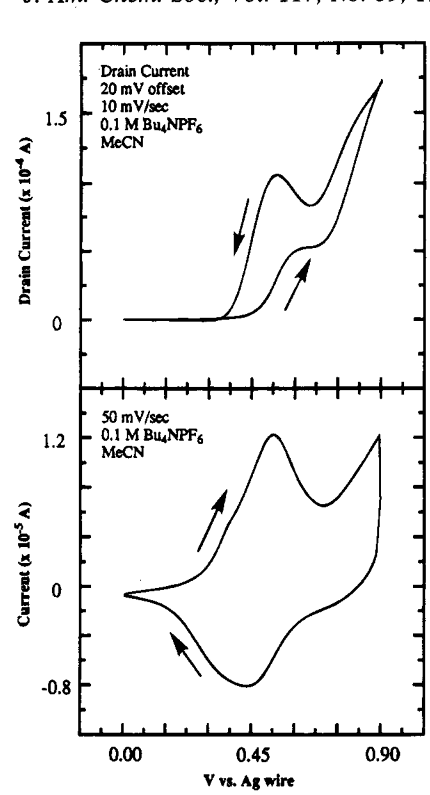

Figure 3. CV and corresponding I_d-V_g for polymer **6** in the absence of alkali metal ions.

d. Electrochemical and Ionoresistive Studies. Electrochemical studies were performed in MeCN (0.1 M Bu_4NPF_6) using devices produced by solution casting films of **6** onto interdigitated platinum microelectrodes having interelectrode spacing of 10 μm.[23] Cyclic voltammetry (CV) and relative conductivity measurements (as measured from the I_d-V_g characteristic) were performed exactly as described in the immediately preceding paper in this issue.[24,25] To allow for direct comparison between conductivity and redox activity, the same potential range was used for both the CV and I_d-V_g characteristics.

Figure 3 shows the CV and corresponding I_d-V_g measurements of polymer **6** in alkali metal free electrolyte solution. There are several features of the I_d-V_g characteristic which are not typical of CPs. As is generally observed for polymers which can be oxidized to high levels, the conductivity goes through a maximum.[25] Hysteresis is common in these systems; however, it is generally in the form of lower conductivities on the reduction wave.[25] In contrast, the conductivity maximum associated with reduction of the oxidized form of **6** is larger.

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Table 4. Voltammetric and Resistive Response of Polymer **6** to Different Ions

salt	$\Delta E_{p,a}$ (vs Ag wire) (mV)	decrease in $I_{d\,(max)}$ (%)
K^+	0	47
Na^+	>100	>99
Li^+	−20	69

This is most likely a result of a nonplanar polymer conformation in its neutral state. Oxidation of the polymer backbone induces a more planar conformation, allowing greater carrier mobility (and thus higher conductivity). As such, a higher conductivity is observed as **6** is reduced from its more planar, oxidized state to its neutral state. The reproducibility of this result in consecutive scans indicates that, once **6** is reduced back to its neutral state, it returns to its original nonplanar conformation.

In addition to **6**'s unusual hysteresis, the I_d-V_g characteristic also demonstrates the onset of a second region of high relative conductivity. While it is common for CPs to display multiple redox peaks in the CV, the I_d-V_g characteristic is typically limited to a single region of peak conductivity.[25] As shown in Figure 3, it appears that the first conductivity maximum of **6** corresponds to the first oxidation wave, with the conductivity leveling off or dropping slightly (depending upon the sample) as this oxidation wave approaches completion. A second oxidation wave beginning at ≈0.7 V is accompanied by an additional onset of increased conductivity. Hence, the observed I_d-V_g for the electrochemical oxidative doping of **6** shows two regions of electrochemical activity which produce two discrete windows of peak conductivity. It should be noted that the stability of the polymer in MeCN above 0.7 V is poor, and electrochemical activity is dramatically reduced upon repeated scanning. As a result of this instability, the ionoresistive and voltammetric measurements of the remainder of our studies were conducted between 0 and 0.7 V.

The ion-promoted voltammetric and resistive responses of **6** were measured as the change in the voltage associated with the peak anodic current flow ($E_{p,a}$) and change in $I_{d\,(max)}$, respectively, upon exposure to a 0.5 mM salt solution and the results are summarized in Table 4. Representative Na^+- and Li^+-promoted voltammetric and resistive properties of **6** are illustrated by the I_d-V_g characteristics and commensurate CVs shown in Figures 4 and 5 for Na^+ and Li^+, respectively. Although these responses vary slightly from device to device, due to deviations in the homogeneity of the film thickness and morphology, representative data demonstrating the general trends are shown.

The potential at which **6** is oxidized experiences a large positive shift on exposure to Na^+ (Figure 4). The magnitude and direction of this shift is opposite to what would be expected, based upon purely conformational effects, considering that the ionochromic response indicated increased conjugation in the presence of Na^+. We therefore attribute the voltammetric effect to be due to both the reduced ability of Na^+ complexed oxygens to function as electron-donating groups and electrostatic factors. Exposure to K^+ produces no voltammetric response, and exposure to Li^+ produces only a minimal response. This most likely reflects the poorer binding affinity observed for these ions with monomer **3**.

As anticipated from its voltammetric response, films exposed to Na^+ salt solutions exhibited a very large (>99%) decrease in peak conductivity (as measured by $I_{d\,(max)}$). This decrease reflects a lower limit since the residual current in Figure 4 (top) appears to be a Faradaic current which is always present in I_d-V_g scans but is usually so small as to be undetected in higher conductivity samples. As indicated by our optical studies, this

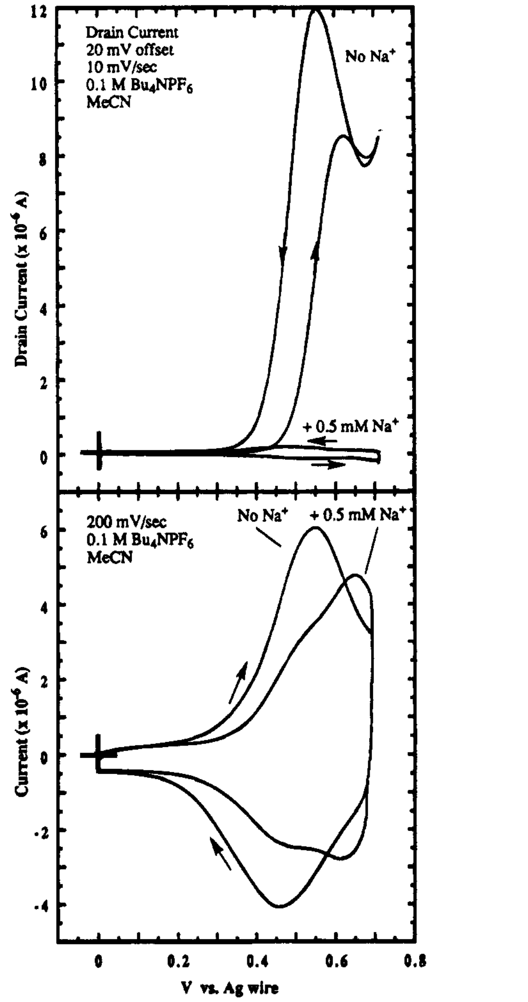

Figure 4. CV and corresponding I_d-V_g for polymer **6** in the absence and presence of Na^+.

decrease occurs despite a more planar backbone in the Na^+-complexed case.

Surprisingly, rinsing the neutral Na^+-containing films with fresh MeCN does not return the polymer to its original state. We discovered, however, that the Na^+ bound within the polymer can be removed by holding the polymer in Na^+-free electrolyte at +0.7 V for ca. 0.5 h. Monitoring I_d during this time shows a steady increase of the polymer's conductivity back to its original value. This behavior reflects a smaller K_a for the oxidized form of **6** due to electrostatic repulsion between cation and cationic carrier species. This is supported by our other results in which we also demonstrated a potential dependence in K_a for pseudorotaxane formation.[7] Both the CV and drain current of films which have been "oxidatively purged" free of Na^+ revert to essentially their original state.

Perhaps the greatest illustration of the sensitivity of the ionoresistive response is the significant decrease in peak conductivity observed for **6** in Li^+ and K^+ solutions. While the conformational and electrostatic perturbations brought on by these ions produce only minor changes in the voltammetric response and absolutely no change in the UV−vis spectrum, the ionoresistive effect is large (Table 4 and Figure 5). Significantly, the decrease in conductivity appears to correlate with the corresponding K_a of **3**.

These results indicate that localization of carriers via electrostatic repulsions resulting from analyte-occupied binding sites represents a powerful approach to chemoresistive materials. Additionally, we have shown that the ionoresistive response has a lower threshold of sensitivity than both voltammetric and

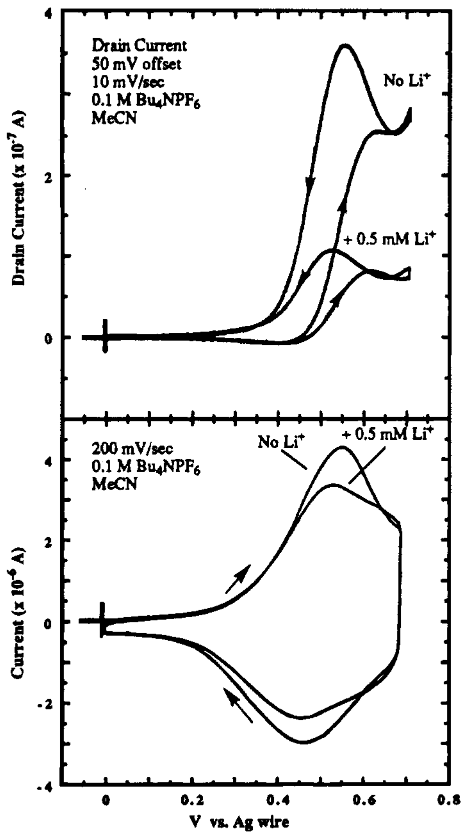

Figure 5. CV and corresponding I_d-V_g for polymer **6** in the absence and presence of Li^+.

optical methods. Reemphasizing that which was articulated in the immediately preceding paper in this issue, the potential at which a polymer is oxidized and its UV−visible spectra are determined by localized regions within a CP. Therefore, minor perturbations in the electronic structure may not induce significant changes in these characteristics. In contrast, conductivity (in the ideal case) reflects the electronic structure of the entire collective assembly. As such, there arises the inherent amplification of chemoresistive response to analyte-promoted perturbations. We have utilized molecular recognition events to trigger these perturbations and successfully demonstrated an ionoresistive material.

Summary

We have designed an ion-responsive sensory material based on a calix[4]arene-substituted polythiophene. This polymer demonstrates ionochromic, voltammetric, fluorescent, and ionoresistive responses to Na^+. The receptor moiety of the polymer appears to exist in several diasteromeric conformations which are highly sensitive to further functionalization of the bithiophene at the 5,5′-positions. As a result, the ionochromic response varies significantly between different polymers containing this receptor.

Polymer **6** demonstrates the predicted Na^+-promoted positive shift in the voltammetric response commensurate with a decrease in conductivity, despite the fact that Na^+ complexation induces an increased effective conjugation length. This implies that electrostatic factors dictate the observed properties of these materials and that conformational perturbations play a much lesser role. Results herein reinforce the concept that chemoresistivity in CPs possesses the inherent ability to amplify the detection of perturbations occurring within a polymer with respect to other commonly measured entities (e.g., CV and UV−visible spectra). As such, minimal perturbations inflicted upon the CP by molecular recognition events, in this case Li^+ and K^+ complexations, can produce dramatic chemoresistive effects. Future work will focus on tuning these materials to be more analyte selective, as well as focus on maximizing the amplification effect.

Experimental Section

General Procedures. Air and moisture-sensitive reactions were carried out in over-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon. THF was distilled from sodium-benzophenone ketyl or used directly from Aldrich Kilo-Lab metal cylinders. Pyridine was dried over molecular sieves prior to use. Reagents were used as received from Aldrich unless otherwise noted. $Fe(acac)_3$ was purchased from Jansen and stored under dry nitrogen. 3-(2-Hydroxyethoxy)thiophene,[13] 5,11,17,23-tetra-*tert*-butyl-25,26,27,-28-tetrahydroxycalix[4]arene,[26] 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene,[27] and 3,3′-bis(methoxyethoxy)-2,2′-bithiophene[7] were synthesized according to literature procedures. NMR spectra were recorded with a Bruker AC-100 (100 MHz), AC-250 (250 MHz), AMX-500 (500 MHz), or a Varian Gemini (200 MHz) instrument in $CDCl_3$ unless otherwise noted. GPC was performed on a Rainin HPXL solvent delivery system with a RI-1 refractive index detector and three Waters Ultrastyragel columns (10^4, 10^3, and 500 Å). Molecular weights are reported relative to polystyrene standards. UV−vis absorption spectroscopy was performed on an Olis spectrophotometer with a Cary-14 spectrophotometer conversion upgrade or a Hewlett Packard 8452A diode array spectrophotometer. Melting points were determined on a ThomasHoover or a MelTemp II device. The emission spectroscopy was performed using optically dilute samples in four-sided quartz cells. Emission measurements were performed using a Photon Technology International spectrofluorimeter operating with a Ushio Xenon short arc lamp powered by a Photon Technology International LPS-220 arc lamp supply and using a Photon Technology International 710 photomultiplier detector system. Binding constants were determined according to literature procedures.[14] Electrochemical measurements were carried out using a Pine Model RDE 3 bipotentiostat. The data were recorded on a Macintosh IIci using LabVIEW 2 (National Instruments). Microelectrode devices used in these studies were obtained from AAI-ABTECH and had an interelectrode spacing of 10 μm. All potentials were controlled relative to an isolated silver wire quasielectrode. CVs obtained by this electrochemical setup were checked for accuracy by using ferrocene samples as a reference compound in the same electrolyte medium used for the electrochemical studies. The ferrocene $E_{1/2}$ was found to be consistently at +0.14 V. Electrochemical measurements were carried out under ambient conditions in MeCN, 0.1 M Bu_4NPF_6.

Preparation of THP-Protected 3-(2-Hydroxyethoxy)thiophene (I). 3-(2-Hydroxyethoxy)thiophene (13.91 g, 96.6 mmol) was combined with dihydropyran (9.74 g, 116 mmol) in 100 mL of dichloromethane. To this was added 0.2 g of pyridinium *p*-toluenesulphonate (PPTS). The solution was stirred overnight. $MgSO_4$ was added, and the mixture was filtered and concentrated. The cloudy liquid was chromatographed (silica gel under nitrogen pressure, hexane) to give the pure product in 89% yield. ^1H NMR ($CDCl_3$, 100 MHz): δ 1.5−1.8 (m, 6H), 3.5−4.2 (m, 6H), 4.68 (dd, 1H, J = 3.4, 3.4 Hz), 6.28 (dd, 1H, J = 1.5, 3.1 Hz), 6.8 (dd, 1H, J = 1.5, 5.2 Hz), 7.18 (dd, 1H, J = 3.1, 5.2 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 19.05, 25.89, 30.98, 62.67, 66.23, 70.07, 98.04, 99.43, 120.13, 125.06, 158.10. Anal. Calcd for $C_{11}H_{16}SO_3$: C, 57.89; H, 7.02. Found: C, 57.19; H, 7.17. HRMS: calcd 229.0898, obsd 229.0892.

Preparation of THP-Protected 3,3′-Bis(2-hydroxyethoxy)-2,2′-bithiophene (II). Compound **I** (5.77 g, 25.3 mmol) in anhydrous THF containing TMEDA (2.84 g, 25.3 mmol) was slowly treated at −10 °C with *n*-butyllithium (15 mL of 1.7 M solution, 25.3 mmol) under an atmosphere of argon. After stirring for 40 min the solution was transferred via cannula to a refluxing mixture of $Fe(acac)_3$ (8.94 g, 25.3 mmol) in THF under an atmosphere of nitrogen. After refluxing overnight the mixture was filtered through a bed of silica gel and

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concentrated in vacuo. The red residue was chromatographed (silica gel, hexane with increasing amounts of ether) to give a white solid in 64% yield. Mp: 83 °C. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 1.3−1.9 (m, 12H), 3.4−4.2 (m, 12H), 4.68 (dd, 2H, J = 3.4, 3.4 Hz), 6.9 (d, 2H, J = 5.6 Hz), 7.0 (d, 2H, J = 5.6 Hz). Anal. Calcd for $C_{22}H_{30}S_2O_6$: C, 58.15; H, 6.61. Found: C, 58.03; H, 6.89. HRMS: calcd 454.1484, obsd 454.1484.

Preparation of 3,3′-Bis(2-hydroxyethoxy)-2,2′-bithiophene (III). Bithiophene **II** (3.00 g, 6.6 mmol) was stirred overnight at 55 °C in 30 mL of methanol containing 0.05 g of PPTS. The green solution was filtered through silica gel to remove the PPTS and concentrated in vacuo. The residue was taken up in chloroform and washed with water to remove the green color. The organic layer was dried with $MgSO_4$, filtered and concentrated in vacuo to give 100% product. Mp: 119 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.46 (t, 2H, J = 6.6 Hz), 3.97 (m, 4H), 4.23 (m, 4H), 6.87 (d, 2H, J = 5.6), 7.14 (d, 2H, J = 5.6). ^{13}C NMR (DMSO-d_6, 50 MHz): δ 60.0, 72.7, 73.5, 113.2, 116.1, 121.3, 151.1.

Preparation of 3,3′-Bis(4-(*p*-toluenesulfonyl)-1,4-dioxabutyl)-2,2′-bithiophene 2. Compound **III** (1.89 g, 6.61 mmol) in 20 mL of dry pyridine was treated at ice-bath temperature with p-toluenesulfonyl chloride (2.65 g, 13.9 mmol). The mixture was placed in a freezer overnight and then poured into cold 5% HCl with vigorous stirring. The mixture was stirred for several hours and then filtered. The solid was washed with water. The product was isolated as a light tan material in 78% yield. Mp: 173−5 °C. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 2.42 (s, 6H), 4.26 (m, 4H), 4.39 (m, 4H), 6.72 (d, 2H, J = 5.5 Hz), 7.01 (d, 2H, J = 5.5 Hz) 7.28 (d, 4H, J = 8.2), 7.78 (d, 4H, J = 8.2). ^{13}C NMR (50 MHz): δ 21.4, 69.0, 69.6, 113.5, 116.7, 123.0, 128.0, 130.4, 132.2, 145.3, 150.9. Anal. Calcd for $C_{26}H_{26}S_4O_8$: C, 52.53; H, 4.38. Found: C, 52.71; H, 4.66. HRMS: calcd 594.0511, obsd 594.0503.

Preparation of Bithiophene Macrocycle 3. 5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (2.00 g, 2.96 mmol) was placed in a flask containing NaH (234 mg, 9.77 mmol) suspended in 700 mL of anhydrous THF and 20 mL of dry DMF under an atmosphere of nitrogen. The mixture was refluxed for 1 h. Then ditosylate **1** (1.76 g, 2.96 mmol) in 60 mL of dry DMF was added dropwise while the system was maintained at reflux. The mixture was refluxed for 5 days. After cooling, the THF was removed under vacuum. The residue was dissolved in dichloromethane and extracted with water to remove DMF. The solution was dried with $MgSO_4$, filtered, and concentrated in vacuo. The remaining DMF was removed by high vacuum. The crude solid was chromatographed (silica gel, 10% ether in hexane) to give a white solid in 59% yield. Overall yield from commercially available 3-bromothiophene was 23%. The decomposition point is 300 °C. ^{1}H NMR (250 MHz): δ 0.78 (s), 0.98 (s), 1.04 (s) 1.16−1.25 (br m), 1.29 (s), 1.30 (s), 2.13 (s), 3.00−3.28 (br m), 3.31 (s), 3.53 (s), 3.62−3.65 (br m), 3.72−3.93 (br m), 4.07−4.15 (br m), 4.25−4.42 (br m), 4.65 (br m), 6.45 (s), 6.68 (s), 6.83−7.21 (br m) [^{1}H integration: 0.78−1.30 (53% of H), 3.0−4.67 (31% of H), 6.4−7.3 (16% of H)]. ^{13}C NMR (62.5 MHz): δ 29.72, 30.28, 30.43, 30.80, 32.77, 33.07, 33.29, 37.12, 37.99, 57.22, 61.09, 61.17, 71.12, 71.29, 71.91, 72.26, 112.88, 118.32, 119.46, 119.81, 123.05, 123.39, 123.77, 124.39, 124.68, 124.84, 125.25, 125.61, 130.96, 131.24, 132.51, 133.14, 134.31, 135.11, 143.57, 143.83, 144.03, 144.37, 145.17, 152.29, 153.69, 154.24, 154.46. Anal. Calcd for $C_{58}H_{70}S_2O_6$: C, 75.16; H, 7.56. Found: C, 75.06; H, 7.91. HRMS: calcd (MW + Na) 949.4512, found (MW + Na) 949.4548.

Preparation of Compound 4. A mixture of **3** (0.5 g, (0.54 mmol) and $Hg(OAc)_2$ (0.34 g, 1.08 mmol) was allowed to stir in CH_2Cl_2 for 1 h followed by the portionwise addition of I_2 (0.27 g, 1.08 mmol). The reaction was allowed to stir for an additional 1 h. The solution was filtered through a short pad of silica and concentrated in vacuo. The crude was chromatographed (silica gel, Et_2O:hexane (1:1)), isolated, and recrystallized from EtOAc to give a white solid in 59% yield. Mp > 250 °C. The ^{1}H and ^{13}C NMR are, similar to those of **3**, complex; however, the reduction in integration in the aromatic (δ 6.4−7.3) region is consistent with the loss of the 5,5′-hydrogens of the bithiophene moiety. ^{1}H NMR (250 MHz): δ 0.82 (br s), 0.89 (br s), 0.95 (br s), 1.06 (br s), 1.20 (br s), 1.28 (br s), 1.33 (br s), 2.05 (s), 3.00−4.14 (br m) 4.31 (br m), 4.62 (br m), 6.48 (br s), 6.71 (br s), 7.09 (br m), 7.10 (br m), 7.24 (br m). ^{13}C NMR (62.5 MHz): δ 30.52, 31.10, 31.60, 33.75, 34.10, 37.91, 38.78, 58.01, 62.01, 71.32, 72.34, 72.75, 73.32, 124.61, 125.23, 125.53, 126.02, 126.46, 128.60, 129.77, 130.04, 131.70, 131.95, 132.84, 133.23, 133.94, 135.07, 135.87, 144.46, 144.70, 146.11, 153.11, 154.34, 154.84, 155.32. HRMS: calcd (MW + Na) 1201.2445, found 1201.2481.

Preparation of Copolymer 5. To a Schlenk flask containing **4** (225 mg, 0.191 mmol) and approximately 3 mol % $Pd(PPh)_4$ in 3 mL of DMF was added bis(tributylstannyl)ethylene (116 mg, 0.191 mmol) via syringe. The reaction was heated with stirring at 100 °C for 24 h. The resulting polymer was precipitated in MeOH, filtered, and then washed rigorously with MeOH, EtOH, Et_2O, and finally hexanes. The polymer was dried overnight under reduced pressure. A total of 105 mg of the red polymer was recovered (58% yield). ^{1}H NMR (250 MHz): δ 0.80−1.5 (m, 52% of H) 3.1−4.7 (m, 30% of H), 6.5 (br s, 2% of H), 6.7−7.2 (m, 16% of H); ^{13}C NMR (125 MHz): δ 31.09−31.61, 33.76, 34.11, 58.11, 62.09, 72−73, 119−121, 124.6−126.5, 131.72−131.99, 132.99−133.27, 135.14−135.93, 138−140, 144−145, 146.02, 153.12, 154−155; Anal. Calcd for $(C_{60}H_{70}S_2O_6)_n$: C, 75.74; H, 7.43. Found: C, 73.99; H, 7.71. λ_{max} = 498 nm.

Preparation of Copolymer 6. To a Schlenk flask containing 0.0534 g (0.169 mmol) of 3,3′-bis(methoxyethoxy)-2,2′-bithiophene and dry LiCl (1.7 mmol) dissolved in 2 mL of THF was added 2.1 equiv of BuLi (1.06 mL, 1.6 M solution) dropwise at 0 °C. The reaction was allowed to stir at 0 °C for 0.5 h. The organolithium species generated was then quenched with trimethyltin chloride (0.372 mmol) dissolved in the minimum amount of THF required to facilitate transfer. This solution was transferred via canula into a solution of **4** (0.200 g, 0.169 mmol) and 3 mol % $Pd(PPh_3)_4$ dissolved in 2 mL of DMF. The reaction was heated and purged with dry argon to remove THF. The reaction was then allowed to stir overnight at 100−110 °C. The resulting polymer was precipitated in MeOH, filtered, washed with additional MeOH, and then washed with Et_2O until no color was removed in the wash. ^{1}H NMR (250 MHz): δ 0.81−1.33 (m, 44% of H), 3.11−4.48 (m, 38% of H), 4.7 (m, 2% of H), 6.48 (br s, 2% of H), 6.71 (br s, 2% of H), 6.89−7.14 (12% of H). ^{13}C NMR (125 MHz): δ 31.07−31.60 (m), 33.56−34.01(m), 37.94, 58.01 (m), 59.38, 62.12, 65.82, 71.30−71.54 (m), 72.24−73.07 (m), 112.49 (br), 114.41 (br), 115.97 (br), 124.56−126.44 (m), 131.70−135.96 (m), 144.36−146.04 (m), 151.82, 153.10, 154.43, 154.91−155.27 (m). Anal. Calcd for $(C_{72}H_{84}S_4O_{10})_n$: C, 69.87; H, 6.84. Found: C, 67.69; H, 6.85. λ_{max} = 500 nm.

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Supporting Information Available: Text giving full reports of X-ray structure determination for compound **3** and ^{1}H NMR spectroscopic plots for compounds **3**, **4**, **5**, and **6** (20 pages). This material is contained in many libraries on microfiche, immediately following this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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