Chem. Mater. **1998,** *10,* 3−5

Communications

A Novel Polymeric Metallomacrocycle Sensor Capable of Dual-Ion Cocomplexation

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Received July 15, 1997
Revised Manuscript Received October 22, 1997

We have developed the first electroactive, thiophene-based polymer capable of complexing multiple metal ions, while also being able to detect organic (nonionic) species. These polymer films show characteristic potential shifts for their redox processes upon complexation of a crown ether ring by cations or a transition-metal center with donor molecules. Furthermore, even in the small confines of the metallomacrocylce's core, complexation of one active site does not preclude the sensing abilities of the other.

Recently, a number of examples in the literature have utilized π-conjugated systems as the fundamental components of sensors.[1−10] Electroactive polymer sensors utilizing molecular recognition have been achieved via polypyrroles and polythiophenes that have been equipped with long glyme chains or pendent macrocyclic rings capable of binding a large variety of metal ions and organic guests.[6−10] The working premise behind all of these studies is the high sensitivity shown by the conjugated backbones toward minute perturbations in their respective electronic and steric environments. Previously, we have reported the bithienyl-SALOTH (*N,N′*-bis(salicylidene)-3,4-thiophenediamine) architecture that, when electropolymerized, affords a polythiophene possessing transition-metal ions that are capable of direct electronic communication with the π-backbone.[11] In this system electrochromic properties unique to metal type are obtained for the corresponding polymers. For example, when the metal ion is Cu^{2+}, a deep green to light green transition occurs; however, use of Ni^{2+} yields a more distinct orange-to-green switch. Such a tuning effect shows the broad utility that varied-metal type complexation can instill in a single polymeric foundation.

To increase the sensing range and performance of these polymers, we have appended a crown ether portion to allow coordination of cationic species. We now report polymers capable of complexing two different metal ions simultaneously within each repeat unit. With the transition-metal ion in the bis(salicylidene) core quite sensitive to the presence of σ-donor ligands,[12,13] and a macrocyclic host readily able to bind cations, a single polymeric material is achieved that possesses the ability to detect both electron-rich and electron-deficient species.

Reinhoudt et al. have developed synthetic methods to prepare a number of elegant monomeric macrocycles exhibiting the ability to coordinate multiple ion centers.[14] We have extended this methodology to electroactive, sensing polymers by incorporating a glyme bridge into the SALOTH framework, joining the two phenolic rings. This synthetic transformation was accomplished as shown in Scheme 1, utilizing the "template effect"[15] to position the crown dialdehyde **2** for condensation with the aromatic diamine **1**.[11] Due to the instability of the corresponding Schiff base ligands in solution, we opted to perform both the condensation and subsequent transition-metal ion complexation in the same step to afford the dicomplexed monomers **3**. The template ion (Ba^{2+}) was then removed in high yield by treatment with guanidine sulfate for 1 h, yielding monomers **4**.[16]

Repeated potential cycling between −0.3 and +0.8 V versus Ag/Ag^+ (all further potentials will be referenced versus this reference electrode) of monomer **4** in 0.1 M $TBAClO_4/CH_2Cl_2$ showed both monomer oxidation and electropolymerization to form an electroactive film, **5**. A clean monomer oxidation was observed with an $E_{p,m}$ at +0.73 V while the first return scan showed a substantial reduction at +0.43 V. Repeated scanning

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[16] All monomers gave satisfactory analytical results (e.g., monomer **4** elemental anal. cald: C 54.33; H 3.99; N 3.96; S 13.59. Found: C 54.01; H 4.37; N 3.65; S 13.16). Synthetic details for these compounds as well as other derivatives will be presented in an upcoming full paper.

S0897-4756(97)00500-0 CCC: $15.00

Scheme 1

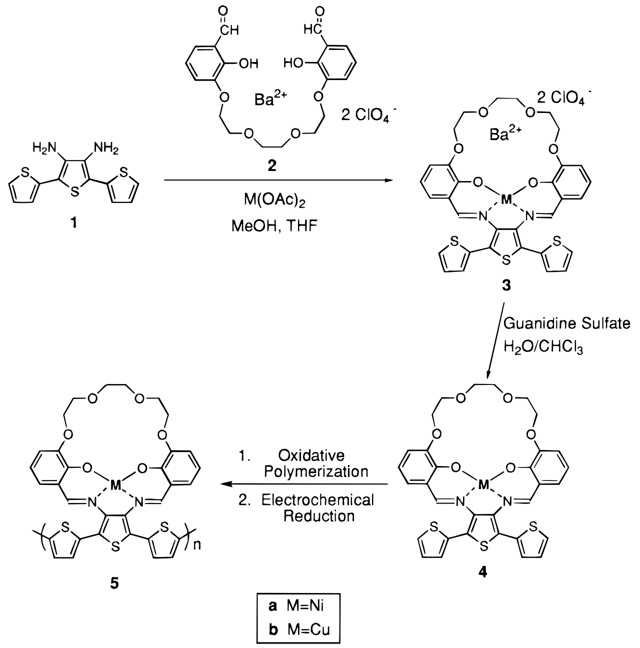

Table 1. Poly(crown−Bth−SALOTH) Redox Potentials (mV vs Ag/Ag$^+$) with Various Alkali and Alkaline Earth Ions[a]

		guest ion				
polymer	redox process	no ion	Li^+	Na^+	Mg^{2+}	Ba^{2+}
5	$E_{p,a}$	480	490	510	590	620
	$E_{p,c}$	360	400	440	430	510
	$E_{1/2}$	420	445	475	510	565

[a] Solutions consisted of 0.1 M $TBAClO_4/CH_3CN$ + 0.05 M of alkali or alkaline cation. $E_{p,a}$ = anodic peak potential, $E_{p,c}$ = cathodic peak potential. Scan rate of 100 mV/s.

to +0.8 V showed rapid growth of the polymer redox at +0.65 and +0.43 V for the oxidation and reduction, respectively. The increased peak current at $E_{p,m}$ observed with repeated scanning is expected for a conducting, polymer film (**5** in Scheme 1) that is forming with a greater surface area than the bare metal electrode.

Polymer films grown on a platinum button (0.02 cm^2) were cycled in monomer-free 0.1 M $TBAClO_4$ solutions also containing 0.05 M of various alkali and alkaline earth perchlorate salts. Shifts in the polymers' redox potentials were discovered for all of the alkali ions studied, and these are shown in Table 1. Such behavior clearly demonstrates the ion-specific effects attributable to this new type of architecture. We also note that the monocations $Li^+$and Na^+ caused a sharpening of the peaks for the various redox processes, possibly due to enhanced ion mobility relative to the alkaline-earth ions. The Li^+ and Na^+ ions could be reversibly exchanged for each other, as evidenced by the ability to place a Li^+-cycled film in Na^+-containing electrolyte and, upon cycling, voltammograms identical with those obtained by sole treatment of a film with an Na^+ electrolyte evolve (or vice versa). On the other hand, incorporation of Mg^{2+} and Ba^{2+} was irreversible[17] showing no change in the cyclic voltammograms upon cycling in solutions containing either of the alkali ions. Coordination of the Ba^{2+} ion resulted in the largest shift of peak potentials with both processes moving in excess of 140 mV higher in potential. A trend in electroactivity seems to appear that is first based upon charge and, subsequently, upon the size of the ion used during switching. As the E values shift anodically, the polymer becomes more difficult to oxidize with the larger and more highly charged cations.

An interesting effect of ion complexation on the polymer's electrochemical performance can be evidenced by the scan rate dependencies of electrochemically grown films. With films exposed solely to noncomplexing electrolytes ($TBAClO_4$), a linear relationship exists between the square root of scan rate and peak current. Such results imply that the associated electrochemical processes are diffusion controlled and are consistent with an observed increasing peak separation with higher scan rates. However, when the polymer is complexed with a small cation (e.g., Li^+, Na^+), little peak separation is encountered with increasing scan rate, and the scan rate (0−400 mV/s) scales linearly with peak current. This suggests that the electroactive sites display surface-confined and non-diffusion-limited behavior when cations are complexed in the polymer crowns and their associated anions are distributed throughout the film. While the exact mechanism by which this ionic assistance operates is unclear, studies utilizing the electrochemical quartz crystal microbalance (EQCM) to probe ion transport in these systems are underway.

In addition to cation-sensing, a very important property of these polymers is their additional capability of detecting neutral organic molecules that can coordinate to the polymers' oxidized transition-metal ions. The electrochemistry of similar nickel-containing coordination complexes has been explored in solvents such as CH_3CN or CH_2Cl_2 where it was found that oxidation of the complexes in the poorly coordinating media leaves the metal centers unstabilized.[12,13] Conversely, the use of solvents possessing high donor numbers (DN, i.e., pyridine, DMF, DMAc, DMSO) has been shown to stabilize such oxidations in analogous Salen and Salophen complexes affording "reversible" redox couples via stabilization of oxidized species through axial solvent ligation.[18−20] Given this precedence, we expected these new polymers to be quite sensitive to the presence of even small amounts of high DN molecules. In fact, an in vivo nitric oxide sensor was recently reported utilizing Fe(III)-containing Salophen molecules.[21] Furthermore, we expected that complexation of the crown ring with a cation would make the transition metal center in the bis(salicylidene) core even less stable when oxidized, and afford a sensor with exceptional detection capabilities.

Figure 1 shows the effect that exposing a **5**−Li^+ surface-modified electrode to a 5 nM pyridine/0.1 M $TBAClO_4$ electrolyte solution for three potentiometric cycles has on the electrochemical behavior of the poly-

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(17) These ions can be removed by immersing the polymer films in solutions containg guanidine sulfute for 1 h; however, large losses in electroactivity were encountered with films decomplexed in this manner.

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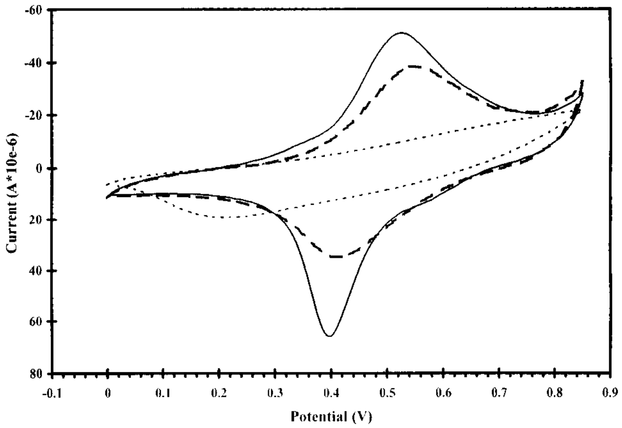

Figure 1. Changes in electroactivity for a **5**−Li^+ film grown on a vitreous-carbon electrode upon exposure to 5 nM pyridine for three potential sweeps. The illustration shows the cyclic voltammograms of the **5**−Li^+ film in Li^+-based electrolyte (—); in a 5 nM pyridine-containing solution (---); and in a Li^+-based electrolyte after pyridine exposure (— — —). (All experiments were conducted in acetonitrile with 0.1 M $TBAClO_4$ and 0.05 M $LiClO_4$ scanning anodically from 0 to +0.85 V at a scan rate of 100 mV/s.)

mer film. Voltammograms in the dilute pyridine solutions show a major loss of electroactivity (>75% for the cathodic process) of the polymer film highlighting the extreme sensitivity of transition-metal ion.[22] This behavior may be attributed to adduct formation between the Lewis base and the transition-metal ion, leading to a loss in interchain electronic interaction. Rinsing and cycling the electrode in a pyridine free Li^+-based electrolyte shows a 50% recovery of electroactivity. Full recovery is not seen here due to remnant pyridine coordination. We believe that one to two pyridine molecules bind to the oxidized metal center to help stabilize the unstable Ni(III) oxidation state. A previous literature report investigated the effects of a pyridine environment on oxidized monomeric bis(salicylidene) metal complexes, and their EPR data supported the formation of such "pyridine-stabilized" species.[23] Similar repression and recovery of electroactivity was also noticed substituting PPh_3 for pyridine as the donor molecule, demonstrating the ability to sense different species. To help elucidate the role of the donor molecule, we are performing studies using a variety of pyridines possessing various electronic configurations and steric environments.

In conclusion we have developed a new polymer sensor based on π-conjugated, coordination complexes endowed with sites for sensing various ionic and nonionic species. The corresponding polymer films were found to reversibly bind small monocations with the accompanying shifts in polymer redox potentials being unique to each ion type. Even at nanomolar concentrations, significant changes in polymer electroactivity were discovered upon coordination of neutral donor molecules to oxidized metal centers of crown-complexed polymer films. Such a system is of interest for developing polymeric sensors capable of detecting a multitude of guests, present at extremely low concentrations and displaying either electron-rich or -deficient natures, based upon electrochemical responses. The coordination of two different transition-metals ions also presents the opportunity to prepare a series of modified electrodes capable of electrocatalyzing a variety of important chemical reactions.[24,25] We are presently exploring these avenues, in addition to investigating the effects that polymer backbone composition imparts on performance.

Acknowledgment. This work was supported by grants from the AFOSR (F49620-96-1-0067) and NSF (CHE 96-29854).

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