Designing Conducting Polymer-Based Sensors: Selective Ionochromic Response in Crown Ether Containing Polythiophenes

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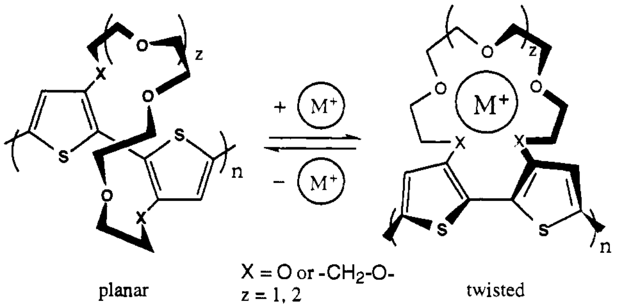
A molecule-based sensor must elicit a measurable response in reaction to a specific stimulus. Ion-selective crown ether dyes are an established example of a molecular sensory component.[1] We are working to expand the scope of measurable responses to include chemically induced resistance changes in organic conducting polymers. It is well-known that twisting a conducting polymer's backbone from planarity can result in a conductivity drop as high as 10^5 or greater.[2] Hence, conductivity changes in conducting polymers provide a large dynamic range which, if harnessed effectively, can result in very sensitive sensory materials. Toward this goal, we have been designing conducting polymers that undergo stimulus-induced conformational changes. The desired end result is a reversible modulation in the conductivity of the system, a response which can be easily monitored and miniaturized.[3] Conducting polymer-based sensors have been reported previously.[4] However, most are chemically irreversible and cannot detect a time dependent signal in real time, and none utilize an approach that can be easily modified to detect any chemical species. Herein we report crown ether containing polythiophenes which undergo large band gap changes in response to alkali metal ions.

Substituted polythiophenes are an ideal choice for a sensory material due to their ease of structural modification, high conductivity, and environmental stability.[5,6] In addition, recent studies have shown the conductivity of these materials to be highly sensitive to the nature and regiospecificity of the side chains, indicating that small conformational changes may produce large effects.[5,7] As conceptualized in Scheme I, our goal is to control conformational preferences of the macrocycle and cause rotation about the bithiophene axis. In the case that the uncomplexed polymer is capable of maximizing long-range conjugation, metal complexation will force a rotation of the thiophene rings in order to accommodate maximum chelationwhich reduces π-orbital overlap[8].

Total synthesis of the polymers is shown in Scheme II. Two routes to monomer **4** were investigated which utilize copper-catalyzed alkoxylation to directly attach the terminal oxygens of the polyether tether to the 3-position of the thiophene rings. While the conversion of **3** to **4** is low, conversion of **1** proceeds smoothly to give **2**, z = 1 and 2, in 33% and 36% yields, respectively. Treatment of the dilithio species of **2** in DME with copper(II) chloride gave the desired macrocycle **4** in approximately 20% yield. This coupling reaction fails in both THF and diethyl ether.

Scheme I



For monomer **9**, a methylene spacer between the bithiophene and the polyether chain is introduced. The methylene spacer has the effect of increasing the size of the macrocyclic cavity and also prevents electron donation from the macrocycle's oxygen to the thiophene ring.

The relative association constants of the monomers were measured for K^+, Na^+, and Li^+ using standard picrate extraction techniques.[9] The binding constants for all monomers were on the order of 10^3 times lower than that observed for K^+ with 18-crown-6, with monomer **4** binding approximately twice as effectively as the methylene-spaced monomer **9**. We attribute the poor binding ability of the monomers to their inherent flexibility.[10]

Polythiophenes have been synthesized by both electrochemical and chemical oxidation as well as through chemical coupling reactions.[5] We chose to produce polymers by chemical coupling reactions since these methods are better suited for producing materials which can be characterized by standard solution chemical methods. In our initial studies we were not concerned with production of high molecular weight polymers since it is well-known that the electronic structure of polythiophenes is determined at low degrees of polymerization.[11] In the case of polymer **6** we introduced a new polymerization method whereby the dilithiated monomer **5** is formed and then reacted with $Fe(acac)_3$ to produce the homopolymer **6**. In this Fe(III) polymerization, insoluble $Fe(acac)_2$ is separated by filtration to produce materials free of the iron salts which typically plague $FeCl_3$ oxidative polymerizations. After precipitation of **6** in methanol, the degree of polymerization of the soluble (low molecular weight) portion was determined to be 10 thiophene units long by ^1H NMR integration of the two doublets resulting from the disubstituted thiophene end groups. We have also made use of Stille coupling methodology in the synthesis of copolymers.[12] In this case, the dilithio species of **5** and **10** are reacted *in situ* with trimethyltin chloride and then subjected to palladium-catalyzed cross-coupling with 5,5′-dibromo-2,2′-bithiophene. The molecular weights produced in this procedure were most likely solubility limited since these copolymers precipitated during the course of the reaction. The molecular weights as determined by GPC relative to polystyrene standards were determined to be 2800, 3700, 2000, and 1900 for polymers **7**, **8**, **11**, and **12**, respectively. However, the absolute molecular weights may be higher since the absolute molecular weight determined by NMR

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(2) *Handbook of Conducting Polymers*; Skotheim, T. J., Ed.; Dekker: New York, 1986.

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(4) (a) Thackeray, J. W.; Wrighton, M. S. *J. Phys. Chem.* **1986**, *90*, 6674. (b) For a recent review, see: Zotti, G. *Synth. Met.* **1992**, *51*, 373.

(5) See: Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

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(8) Similar conformational changes have been reported for 4,4′-bipyridine-derived macrocycles. Gourdon, A. *New. J. Chem.* **1992**, *16*, 953.

(9) For experimental procedure, see: Koenig, K. E.; Lein, G. M.; Stuckler, P.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553. K_a for monomers **4** and **9** are as follows: **4** (**z = 1**): $K_a = 8.6 \times 10^4$ (K^+); 2.8×10^5 (Na^+); 1.2×10^5 (Li^+); **4** (z = **2**): $K_a = 1.1 \times 10^5$ (K^+); 2.3×10^5 (Na^+); 1.9×10^5 (Li^+); **9** (z = **1**): $K_a = 7.5 \times 10^4$ (K^+); 1.7×10^5 (Na^+); 9.2×10^4 (Li^+); **9** (z = **2**): $K_a = 1.8 \times 10^5$ (K^+); 1.4×10^5 (Na^+); for Li^+, so little salt was extracted from the aqueous layer that an accurate measurement of K_a was not possible.

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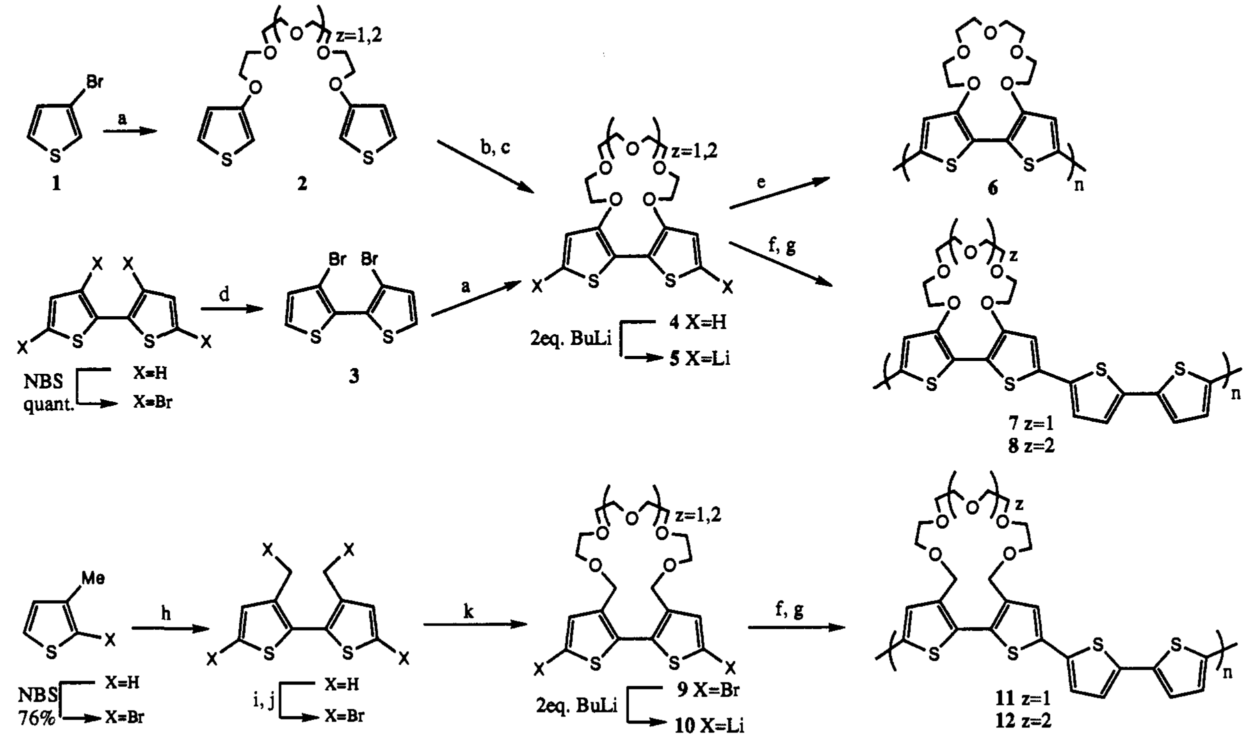
Scheme II[a]



[a] (a) $CuOCH_2(CH_2OCH_2)_{n+2}CH_2OCu$, *tert*-butyl alcohol, lutidine, 80 °C (yield **1** → **2** z = 1, 32.5%; z = 2, 36%; **3** → **4** 0–9.3%); (b) 2 equiv of BuLi, DME, 0 °C. (c) $CuCl_2$, DME, room temperature (yield b + c; z = 1, 19%; z = 2, 21%); (d) Zn^0, HOAc, 1-propanol, reflux (59%); (e) $Fe(acac)_3$, THF, reflux; (f) Me_3SnCl, THF; (g) 5,5′-dibromo-2,2′-bithiophene, $PdCl_2(AsPh_3)_2$, THF, reflux; (h) 0.5 equiv of Mg^0, 0.5% $NiCl_2dppp$, Et_2O, 0 °C (98%); (i) 2 equiv of NBS, DMF/MeOH (95%); (j) NBS, benzoyl peroxide, AIBN, benzene, reflux (78%); (k) $MOCH_2(CH_2OCH_2)_{n+2}CH_2OM$ for z = 1, M = Na^+, DME (55%); for z = 2, M = K^+, THF (18%).

Table I. Ionochromic Response of Polymers

		$\Delta\lambda_{max}$ (nm)		
polymer	λ_{max} (nm)	K^+	Na^+	Li^+
6	497	22	91	46
7	510	10	63	15
8	524	45	30	13
11	434	−4	3	3
12	432	1	3	4

end group analysis for **6** shows the true molecular weight to be almost double that determined by GPC (1800 vs 960).

The sensitivity of effective conjugation length to different side chains is apparent from comparison of the λ_{max} of the pure polymers (Table I). Polymers **6**, **7**, and **8** show a higher λ_{max} than polymers **11** and **12**, indicating that the conformational restrictions are greater when the methylene spacer is incorporated between the thiophene ring and the polyether tether. Comparison of the λ_{max} of **7** with that of its homologue **6** suggests that there is some degree of twisting imposed by the polyether tether in the uncomplexed state since the λ_{max} is decreased by incorporating the nonsterically hindered unsubstituted bithiophene unit. This effect is similar to the decrease in band gap observed when a vinylene spacer is introduced into the backbone of the sterically crowded poly(3,4-di-*tert*-butoxythiophene).[13]

Ionochromic effects were measured in 0.1 M salt solutions in acetonitrile, and the results are shown in Table I.[14] Polymers **6**, **7**, and **8** show large shifts in λ_{max} with the appropriate ion, and because the shift occurs in the visible region, a dramatic color change is observed. As anticipated from the binding preferences of their crown ether analogs, polymers **6** and **7** show the largest shift for sodium, and **8** is most responsive to potassium. The large magnitude of the shift despite the low binding constants is ascribed to the additive effect of destroying conjugation at several points along a highly conjugated system. This is supported by the fact that copolymer **7**, in which the number of twisting sites has been reduced, shows a smaller shift than its corresponding homopolymer, **6**. The observed differences between ions result from the varying degree of rotation imposed on the bithiophene unit by the ligand's distinct conformational requirements for each metal. We do not disregard the fact that electrostatic variations between the complexed and uncomplexed systems may play a role; however, at this time we do not attempt to quantify the individual conformational and electrostatic perturbations. The poor ionochromic activity of polymers **11** and **12** is not surprising considering their poor binding affinity (which results in failure of the twist-inducing mechanism) and the loss of electrostatic interaction between the terminal oxygens of the polyether tether and polymer backbone.

We have demonstrated an ionochromic response in conducting polymers in the solution state. Future investigations will explore the behavior of these materials in their conducting (oxidized) state, and microelectrode sensory devices will be fabricated. By the implementation of known molecular recognition principles, the design demonstrated herein can be expanded to produce conducting polymers which are responsive to many chemical entities.

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Supplementary Material Available: Full experimental details and characterization for the compounds reported (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; See any current masthead page for ordering information.

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[13] Van Dort, P. C.; Pickett, J. E.; Blohm, M. L. *Synth. Met.* **1991**, *41–43*, 2305.

[14] Although the onset of absorbance defines the true band gap, we chose to measure λ_{max}, which can be more precisely determined.