Conducting Pseudopolyrotaxanes: A Chemoresistive Response via Molecular Recognition

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Pseudorotaxanes are host–guest systems comprised of a cyclic molecule whose cavity is pierced by a compatible linear molecule. In pseudopolyrotaxanes, the polymer chain may function either as the cyclic host or as the linear guest. In both cases, the physical properties of the pseudopolyrotaxane and its parent polymer are dramatically different. In the case of self-assembling π-donor/π-acceptor systems, a driving force for this complexation is charge transfer interactions. Although many polyrotaxanes and pseudopolyrotaxanes have been reported,[1] there have been no investigations into pseudopolyrotaxanes derived from conducting polymers. Conducting polymers exhibit highly sensitive resistivities and can vary by multiple orders of magnitude as a result of environmental influences.[2] This sensitivity allows the design of conducting polymer-based sensory materials wherein the resistivity and or redox potential can vary as a function of stimuli generated from host–guest interactions. Herein we report a novel polythiophene-based conducting pseudopolyrotaxane that exhibits both a *reversible* attenuation in conductivity and an anodic shift in redox potential in the presence of a π-deficient 4,4′-bipyridyl guest.

Our design of conducting pseudopolyrotaxanes is based in part on Stoddart's demonstration that bis(*p*-phenylene)-34-crown-10 (BPP) forms self-assembled complexes with π-deficient guest molecules such as paraquat (**5**).[3] We therefore synthesized **1**, which when in a trans conformation produces a host cavity similar in size and shape to that of BPP.

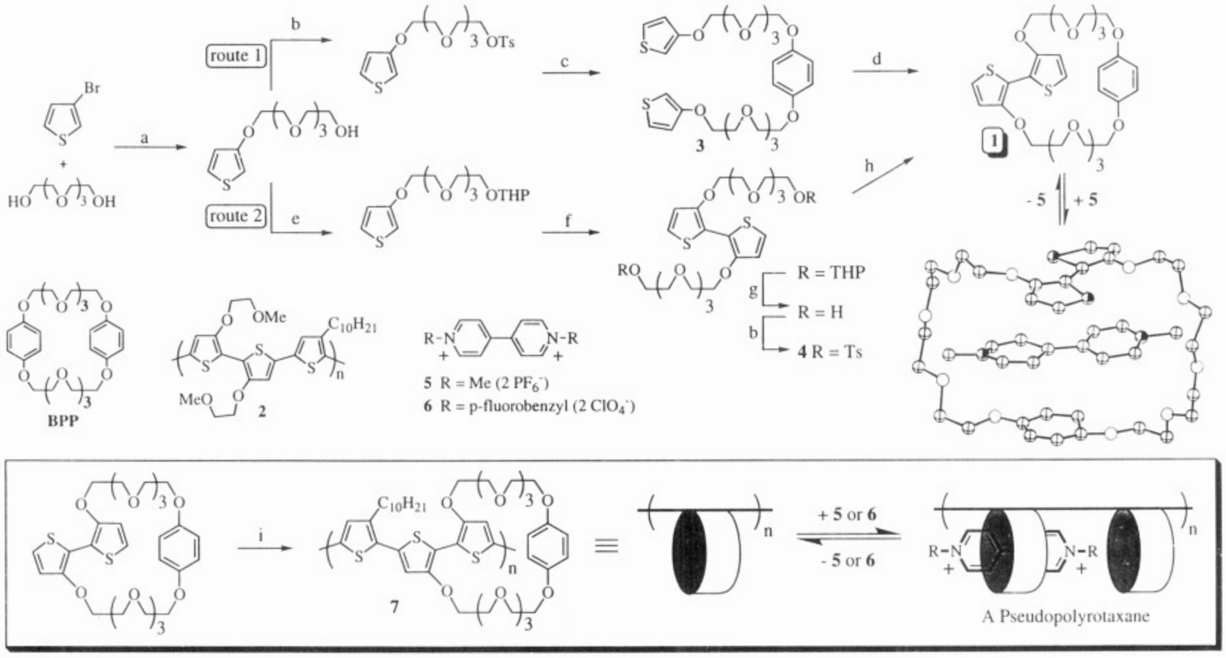
We prepared **1** by two independent synthetic routes (Scheme 1). In route 1, the macrocycle is established by $Fe(acac)_3$ oxidative coupling of the dilithio species of **3**.[4] The alternate approach (route 2) produces the bithiophene unit prior to macrocyclization of **4** via a cesium ion-templated Williamson ether synthesis. Route 1 is slightly more efficient and produced macrocycle **1** in an 8.1% overall yield.

The ability of **1** to form self-assembled complexes with **5** was confirmed by the chemical shifts observed in the ^1H NMR upon 1:1 mixing of the two substrates in MeCN-d_3. A bimolecular complex of **1** and **5** was crystallized and structurally characterized. The ORTEP drawing shown in Scheme 1 confirms the ability of **1** to mimic BPP as an isostructural synthetic receptor for **5**. We have also investigated **6** (Scheme 1), a guest with stronger acceptor properties, and qualitatively found that it binds to **1** more strongly than **5**.[5]

The macrocyclic polymer **7** was prepared via palladium-catalyzed cross-coupling of the organozinc derivative of **1** with 2,5-dibromo-3-decylthiophene. The polymer is isolated in >98% yield, and the M_n was determined by GPC to be 6500 g/mol relative to polystyrene standards (PDI = 2.8). Obtaining reasonable molecular weights requires complete dilithiation of **1**, and our best conditions involved lithiation in the presence of LiCl with sonication to help prevent insoluble lithium aggregates. For comparative purposes, we synthesized a nonmacrocyclic model polymer, **2**, by an analogous protocol (M_n = 12 000, PDI = 2.1).

To ascertain the sensory properties emanating from the macrocyclic structure of **7**, we conducted investigations in parallel with **2**. However, **2**'s ability to model **7** is not ideal since it exhibits somewhat different properties. Most importantly, **2** exhibits a lower bandgap than **7** (λ_{max} = 522 and 510 nm, respectively). The larger bandgap of **7** is most likely due to a twisting of the polymer's backbone caused by the conformational restrictions imposed on it by the macrocycle. Consistent with the physical properties of

Scheme 1[a]



[a] (a) *t*-BuOK, 0.2 equiv of CuI, pyridine, reflux (69%); (b) *p*-tosCl, pyridine, 0 °C (95% route 1; 77% route 2); (c) 0.5 equiv of hydroquinone, K_2CO_3, acetone, DMF, reflux (95%); (d) (1) 2 equiv of BuLi, THF, 0 °C; (2) 2 equiv of $Fe(acac)_3$, THF, reflux (13%); (e) dihydropyran, $pyrH^+Tos^-$, $MeCl_2$ (90%); (f) (1) BuLi, THF, 0 °C; (2) $Fe(acac)_3$, THF, reflux (69%); (g) $pyrH^+Tos^-$, MeOH (100%); (h) 0.5 equiv of hydroquinone, Cs_2CO_3, DMF, 50 °C (17%); (i) (1) 2 equiv of BuLi, 10 equiv of LiCl, THF, 0 °C, sonicate; (2) 2.2 equiv of $ZnCl_2$, THF; (3) 1 equiv of 3-decyl-2,5-dibromothiophene, 3% $Pd(PPh_3)_4$ (>98%).

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pseudopolyrotaxanes, **7** becomes soluble in MeCN on addition of **5** or **6**, whereas no such behavior is observed for **2**.

We anticipated that pseudorotaxane formation with π-deficient guests would produce an anodic shift in the redox potential of **7**.[6] Such a feature can, in principle, perform a sensory function. However, a conducting polymer-based sensor can also utilize changes in resistivity as a highly sensitive probe to detect a chemical species.[7,8] Such chemoresistive effects have the added advantage of requiring minimal electronics to produce a measurable response. Electrochemical studies were performed using two interdigitated microelectrode devices interconnected by thin films of the polymer of interest.[9,10] When configured in a transistor mode, a small potential difference between the electrodes results in a drain current proportional to the relative conductivity as a function of electrochemical potential.[10] The same device with no potential difference between the electrodes was used to record the cyclic voltammogram.

The electrochemical studies of both polymers were performed under ambient conditions in a 1:1 MeCN–water solution with $LiClO_4$ as the electrolyte. As anticipated, pseudopolyrotaxane formation of **7** with guest **6** (45 mM) produces an anodic shift (99 mV) in the peak oxidation potential of **7**. Commensurate with this effect is a 52% decrease in the maximum drain current (Figure 1). These changes in both the redox potential and the maximum drain current are completely reversible and revert back to their original state when **6** is rinsed away by immersing the electrode in clean MeCN. Surprisingly, the redox potential was unaffected by **5**. The differences observed between **5** and **6** illustrate the selectivity of the system and are undoubtedly a combined result of differences in binding affinities, electron deficiencies, and conformational requirements. The cyclic voltammogram of polymer **2** (25 mV/s) revealed its intrinsic oxidation potential to be 137 mV lower than that of **7**. On exposure to 45 mM **6**, polymer **2** exhibits a smaller anodic shift (40 mV) in the peak oxidation potential and only a slight decrease in maximum drain current (ca. 7%). The fact that **7** exhibits a more dramatic chemoresisitve response in spite of its higher oxidation potential clearly demonstrates that the effects are a direct result of host–guest complexation. We propose that in the oxidized (conducting) state of the pseudopolyrotaxane, the electron-deficient sites of "pseudorotaxification" produce a significant degree of charge localization which results in reduced mobility of the positively charged carrier species. This reduction in carrier mobility is the primary factor contributing to the observed decrease in conductivity.

These results demonstrate the first example of a conducting pseudopolyrotaxane as well as the first demonstration of the use of molecular recognition to induce *reversible* changes in the conductivity of a conducting polymer.[8] Combining conducting polymers with synthetic molecular receptors opens vast opportunities for the design of molecule-based sensory devices and can be applied to produce chemoresistive materials capable of detecting a variety of chemical entities.

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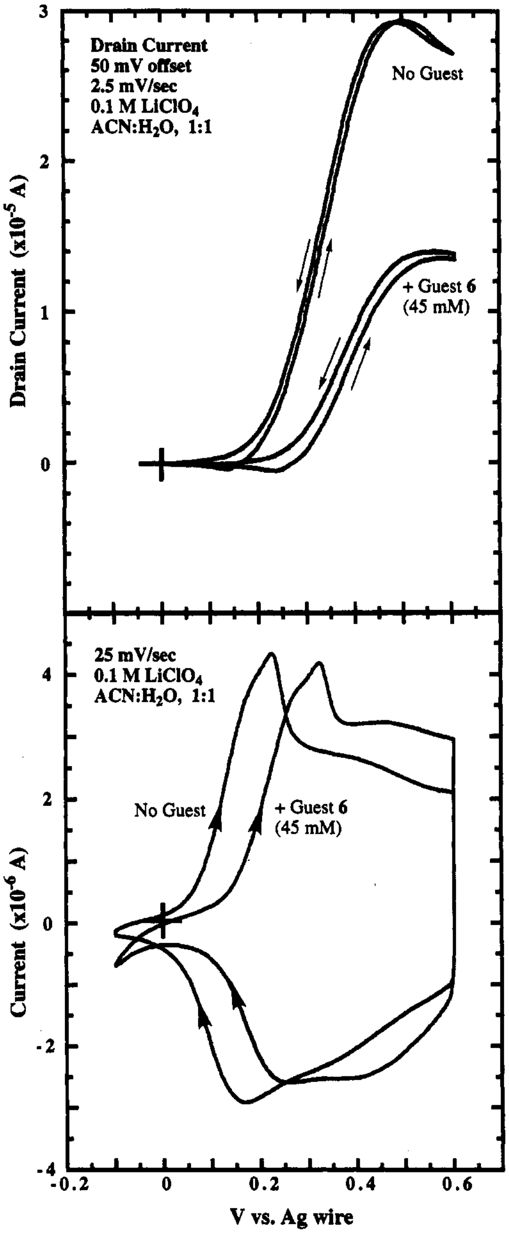

Figure 1. CV and corresponding drain current for polymer **7** in the absence and presence of guest **6**.

Supplementary Material Available: Full experimental details and characterization for the compounds reported (8 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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(1) For a recent review of polyrotaxanes, see: Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11.

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

(3) (a) Allwood, B. L.; Spencer, N.; Shahriari-Zavareh, H; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1064. (b) Amabilino, D. B.; Parsons, I. A.; Stoddart, J. F. *Trends Polym. Sci. (Cambridge, U. K.)* **1994**, *2*, 146 and references therein.

(4) We have previously reported similar methodology in the synthesis of crown ether-containing bithiophenes. Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214.

(5) ^{1}H NMR binding studies show that **1** has a greater binding affinity for **6** over **5** based on the chemical shifts observed for the phenyl protons of **1** on addition of 1.0 equiv of guest ($\Delta\delta = -0.425$ ppm (**5**:1); -0.621 ppm (**6**:1)).

(6) Complexation-induced shifts in the redox potential of pseudorotaxanes has been previously reported. See: Bernardo, A. R.; Stoddart, J. F.; Kaifer, A. E. *J. Am. Chem. Soc.* **1992**, *114*, 10624.

(7) Thackeray, J. W.; Wrighton, M. S. *J. Phys. Chem.* **1986**, *90*, 6674.

(8) Other conducting polymer-based sensors have been reported; however, most are chemically irreversible or require a secondary chemical or electrochemical process to return back to their original state. For recent reviews, see: (a) Zotti, G. *Synth. Met.* **1992**, *51*, 373. (b) Swager, T. M.; Marsella, M. J. *Adv. Mater.*, in press.

(9) The devices used in this study were obtained from AAI-ABTECH and had an interelectrode spacing of 10 μm.

(10) These electrochemical devices have been used extensively by the group of Wrighton in the study of conducting polymers. See: (a) Kittlesen, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 7389. (b) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869 and references therein.