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Toward Molecular Muscles: Design and Synthesis of an Electrically Conducting Poly[cyclooctatetrathiophene]

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Conducting polymer electromechanical actuator devices (“molecular muscles”) function via large dimensional changes that occur in the polymer as a result of redox (doping) processes.[1] Thus, the incorporation of counterions and solvating species into the polymer matrix during electrochemical doping drives the expansion process, while the expulsion of counterions and solvating species upon dedoping drives the contraction process. *Such a mechanism defines electromechanical actuation in conducting polymers as a bulk phenomenon of the conducting composite, not an intrinsic property of the individual polymer chains*. In other words, the doping and dedoping of a single, isolated conducting polymer chain would not in itself be expected to elicit a significant muscle-like expansion or contraction. Given the recent interest in single molecule-based devices,[2] we found it an intriguing challenge to pursue the development of conducting polymers specifically designed to function as single molecule electromechanical (EM) actuators. As stated, traditional conducting polymers would be poor candidates for such devices, thus requiring alternate polymer architectures to be explored. Herein we report the synthesis of poly[cyclooctatetrathiophene], **2**, the first [8]annulene-based polymer whose design attempts to satisfy the requirements of a single molecule EM actuator. Additionally, the preliminary molecular modeling, electrochemistry, and electrical conductivity of polymer **2** are presented.

A prerequisite for our design is a polymer repeat unit capable of exhibiting a significant redox-induced conformational change such that the distance between the two points corresponding to main-chain attachment is altered.[3] We propose that, upon oxidation (or reduction) of the homopolymer, the redox-induced conformational changes occurring at each repeat unit will additively contribute to a change in the polymer’s end-to-end distance. This process is synonymous with single molecule EM actuation. It is well-known that the [8]-annulene, cyclooctatetraene, undergoes a significant conformational change from tub-shaped to planar upon a one- or two-electron reduction.[4,5] As illustrated in Scheme 1, such a redox-induced conformational change establishes cyclooctatetraene and related [8]annulenes as ideal candidates for our purposes.

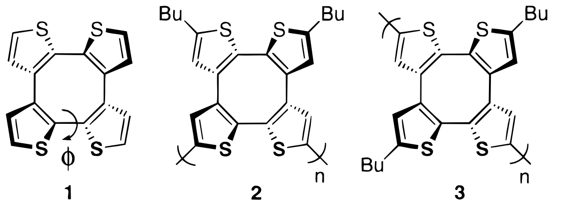
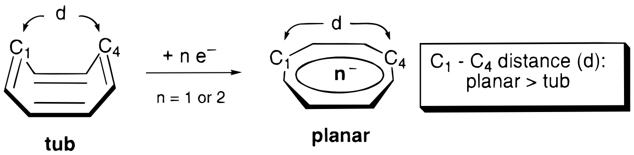


Figure 1. Showing the parent cyclooctatetrathiophene monomer (**1**) and two regioisomers of the related cyclooctatetrathiophene polymers (**2** and **3**).

Scheme 1



To facilitate the incorporation of an [8]annulene into a polymer backbone, we chose to utilize cyclooctatetrathiophene (**1**) as our “masked” [8]annulene subunit. With four peripheral α-positions available on the parent cyclooctatetrathiophene, we envisioned utilizing two sites for the attachment of side chains and the remaining two sites for backbone connectivity. Two regioisomers, polymers **2** and **3**, fit this scenario (Figure 1). Although the backbone of polymer **3** is connected at the α-positions capable of undergoing the largest redox-induced spatial change, this connectivity yields an overall cross-conjugated backbone. For this preliminary study, we chose to utilize the well-established redox behavior of traditional polythiophenes to induce the desired conformational changes and thus chose regioisomer **2** as our initially targeted system.[6]

The synthesis of **1** and its dimer was previously reported by Kauffmann.[7,8] Although the original synthesis works well for the homocoupling of bithiophenes, it is not amenable to the regiospecific synthesis of disubstituted cyclooctatetrathiophenes. Furthermore, preliminary attempts by us to synthesize disubstituted cyclooctatetrathiophenes by cross-coupling two unique 2,2′-bithiophene units at their 3,3′-positions were unsuccessful. Our synthesis of monomer **6** was thus predicated on the well-known ability of thiophenes to undergo highly regiospecific bromination and to participate well in the Ni^0-catalyzed cross-coupling of thienyl Grignards with thienyl bromides.[9] As depicted in Scheme 2, commercially available 2-butylthiophene can be converted into linear tetrathiophene (**4**) via two iterative regiospecific bromination and cross-coupling cycles. The regiospecific bromination of **4** ultimately allows lithium−halogen exchange to occur on dibromide **5** such that Fe(III) oxidative coupling of the resulting dianion provides compound **6** in 48% yield. Deprotonation of the two peripheral α-thienyl positions of monomer **6**, followed by quenching with I_2, provided the requisite diiodo polymer precursor, monomer **7**.

Polymerization of **7** to yield polymer **2** was achieved via Ni^0-catalyzed cross-coupling, as depicted in Scheme 2. ^1H NMR analysis of polymer **2** revealed the complete absence of α-iodo end groups. Ni^0-promoted aryl halide homocoupling[10] and/or Ni^0-catalyzed reduction[11] of α-iodo end groups apparently occurred once cross-coupling had ceased. This result allowed us to obtain the average molecular weight of **2** directly by ^1H NMR end group analysis. Integration of the terminal α-thienyl hydrogens versus the internal β-thienyl hydrogens affords an average repeat corresponding to dodecamers.

A relative measure of the effective conjugation length as a function of molecular weight can be obtained by comparing the UV−vis spectra of monomer **6**, the dimer of **1**, and polymer **2**. The UV−vis of **6** and **2** are shown

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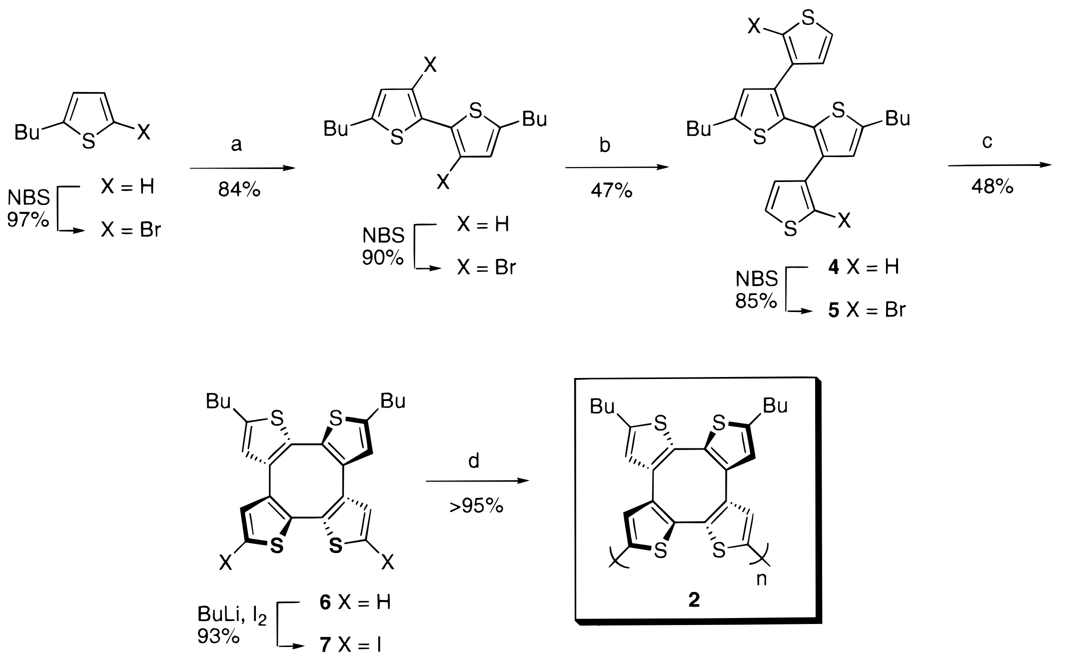
Scheme 2[a]



[a] (a) 0.5 equiv *n*-BuLi, MgBr$_2$, NiCl$_2$(dppp); (b) 3-thienylmagnesium bromide, NiCl$_2$(dppp); (c) *n*-BuLi, FeCl$_3$; (d) 2 equiv *t*-BuLi, MgBr$_2$, NiCl$_2$(dppp).

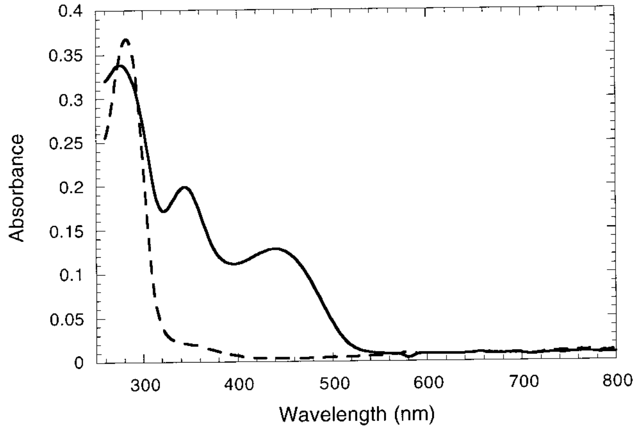


Figure 2. UV−vis spectra of monomer **6** (dashed line) and polymer **2** (solid line).

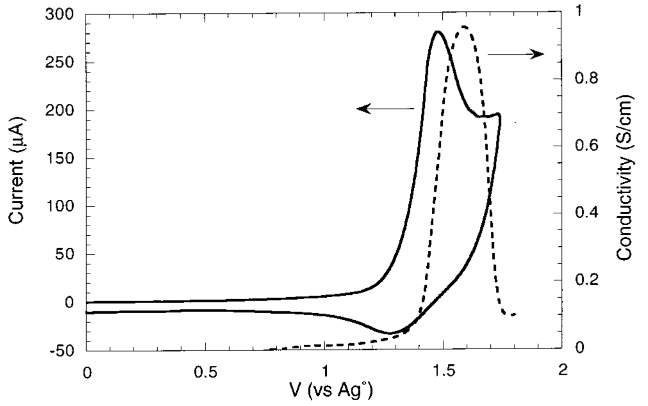


Figure 3. Cyclic voltammogram (CV) of polymer **2** (solid line) and its corresponding conductivity as a function of oxidation state (dashed line).

in Figure 2, and the previously prepared dimer of **1** is reported to have absorbance peaks at 276, 328, and 372 nm.[8] From these data, it is apparent that the effective conjugation length of the polymer exceeds that of the dimer, despite the significant twisting of the π-system (vide infra). The solid-state UV−vis spectra of polymer **2** exhibit slightly broadened absorptions, and only a slight red shift from that observed for the solution spectra, indicating that interchain interactions are small. A band gap of 2.3 eV is estimated from the band edge of the solid-state spectra, a value in good agreement with the range of band gaps reported for other nonplanar polythiophenes.[12]

The conformational consequences of electrochemically oxidizing polymer **2** were examined by calculating the structures of **1**, **1**$^{+1}$, and **1**$^{+2}$ using the AM1 semiempirical method.[13] The calculated redox-induced conformational perturbations are reported herein as a function of the two S−C−C−S dihedral angles, ϕ (Figure 1). To test the validity of the calculations as applied to this system, the calculated value of ϕ for neutral **1** was compared to that experimentally determined by X-ray crystallography. Since the crystal structure of **1** was not previously reported, we prepared **1** using literature procedures and obtained X-ray quality crystals via multiple recrystallizations from benzene/ethanol.[14] It was found that the calculated structure (ϕ = 45.9°) is in good agreement with that obtained experimentally (two unique values, ϕ^1 = 47.6° and ϕ^2 = 46.4°). The calculated structures of **1**$^{+1}$ and **1**$^{+2}$ do indeed predict the desired trend of a conformational change toward a more planar system (ϕ^1 = 31.7° and ϕ^2 = 44.6° for **1**$^{+1}$, and ϕ = 29.7° for **1**$^{+2}$). Given the unique value of ϕ associated with each oxidation state, polymer **2** is predicted to exhibit a redox-dependent attenuation of conformation, which should translate into an overall attenuation of EM actuation.

Both the cyclic voltammetry (CV) and the electrical conductivity of **2** were determined and are shown in Figure 3. The CV of polymer **2** exhibits significant irreversibility when oxidized to potentials beyond that corresponding to its peak conductivity (ca. 1 S/cm at 1.6 V). This result may be due to poor contact with the working electrode, as visible cracking and peeling of the oxidized polymer film were observed (vide infra). This lack of mechanical integrity precluded determination of EM actuation by the traditional bending beam method.[1,15,16]

Although a physical measurement of single-molecule EM actuation could not be obtained at this time, the value of ϕ corresponding to the peak conductivity can be estimated by calculating the structure of the repeat unit at the appropriate oxidation state. From the CV, it can be determined that the charge per repeat unit at 1.6 V is +0.6. Approximating this oxidation state by calculating the structure of both **1**-dimer and **1**-dimer^{+1} reveals a change in the main-chain S−C−C−S dihedral angle from $\phi = 44.1°$ to $\phi = 40.5°$, respectively. Although this approximation underestimates the charge per repeat unit at peak conductivity, it does follow the expected trend predicted by the modeling studies of **1** (vide supra) and confirms that redox-induced conformational changes occur prior to (and possibly *contribute to*) the aforementioned electrochemically induced degradation of polymer **2**. It should be noted that the peak conductivity of polymer **2** (ca. 1 S/cm) is in good agreement with that reported for regiorandom poly(3-alkylthiophene)s, a class of polymers possessing an approximately equal band gap and calculated degree of backbone nonplanarity.[12,17,18]

Herein, our design and synthesis of a novel, electrically conducting poly(cyclooctatetrathiophene) have been reported. As a general class of polymers, such poly([8]-annulene)s are predicted to possess a continuum of redox-tunable conformations and thus potentially serve as single-molecule EM actuators. Studies focused on the synthesis of higher molecular weight poly([8]annulene)s capable of accessing a higher charge per repeat unit are currently underway and will provide additional insight into the development of single-molecule EM actuators. Additionally, utilization of the cyclooctatetrathiophene scaffold as a building block for other novel conjugated macromolecules (such as helical polymers[6,19]) will be the subject of future reports.

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Supporting Information Available: Crystal structure and tables of crystallographic data for compound **1** and a complete Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

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