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Tetra[2,3-thienylene]: A Building Block for Single-Molecule Electromechanical Actuators

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Abstract: Tetra(2,3-thienylene) is a thiophene-fused [8]annulene capable of undergoing redox-induced dimensional changes. The feasibility of efficiently translating this intrinsic function into a single polymeric electromechanical actuator is investigated by both experiment and density functional theory (B3LYP 6-31G-[d,p]). A study of tetra(2,3-thienylene) and its homodimer reveal that redox-induced conformational change is conserved upon dimerization, a result that implicates similar behavior in the corresponding polymer. Theoretical predictions yield a maximum redox-induced dimensional change of 5.92% per repeat unit for the homodimer. Cyclic voltammetry reveals complete reversibility for the corresponding redox cycle. The latter two facts establish tetra(2,3-thienylene) as a suitable building block for single-molecule electromechanical actuators.

Introduction

All-organic mechanical actuators convert chemical, electrical, or electromagnetic energy into mechanical work. Dubbed "molecular muscles", electromechanical actuators fabricated from redox-active polymers are the most extensively studied systems to date.[1] The accepted actuation mechanism associated with these materials is based on volume changes that result from the uptake or expulsion of counterions during a redox cycle (Figure 1). Such electromechanical actuation in redox-active polymers is a *bulk* property that is not necessarily intrinsic to individual polymer chains. Given the attention paid to molecular devices, it is not surprising that recent efforts have been directed toward the design of single-molecule actuators. Examples of single-molecule chemomechanical[2] and photomechanical[3] actuators have recently been reported. To date, however, there have been no clear demonstrations of single-molecule *electromechanical* actuation in a redox-active polymer. Two factors likely contribute to this. The first is a limited pool of materials satisfying the design requirements of a *molecular* electromechanical actuator.[4,5] The second is the inability of traditional analytical techniques to differentiate between the commensurate *bulk* mechanism (ion intercalation/expulsion) and the *intrinsic* (single-molecule) mechanism.[1,4] Addressing the former limitation, we have proposed tetra[2,3-thienylene] as a building block for molecular electromechanical actuators.[5] Given the latter limitation, we limit our current efforts to predicting the inherent amplitude of intrinsic actuation in isolated poly(tetra[2,3-thienylene]) chains by studying tetra[2,3-thienylene] monomers and dimers.

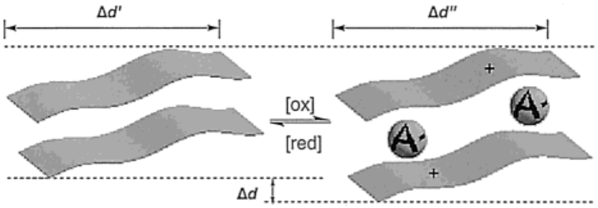
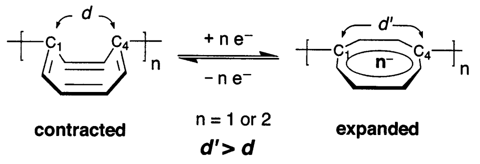


Figure 1. Conceptual illustration of *bulk* electromechanical actuation in a redox-active polymer. Ribbons represent polymer chains, spheres represent counterions, right arrow designates an oxidation of the polymer backbone, and left arrow designates reduction back to neutral. A change in Δ*d* is due to counterion intercalation (left to right) or expulsion (right to left) and does not require a change in individual polymer chain length, as Δ*d*′ and Δ*d*″ may remain equal throughout the process.

Scheme 1



Our design strategy for single-molecule electromechanical actuators targets the redox-induced tub-to-planar conformational change associated with the prototypical [8]annulene, cyclooctatetraene,[6] as the intrinsic unit of actuation.[7] Although tub-to-planar intercoversion of cyclooctatetraene is typically associated with the neutral to 2− aromatic state (a $4n + 2$ number of π-electrons), it should be emphasized that *any nonneutral redox*

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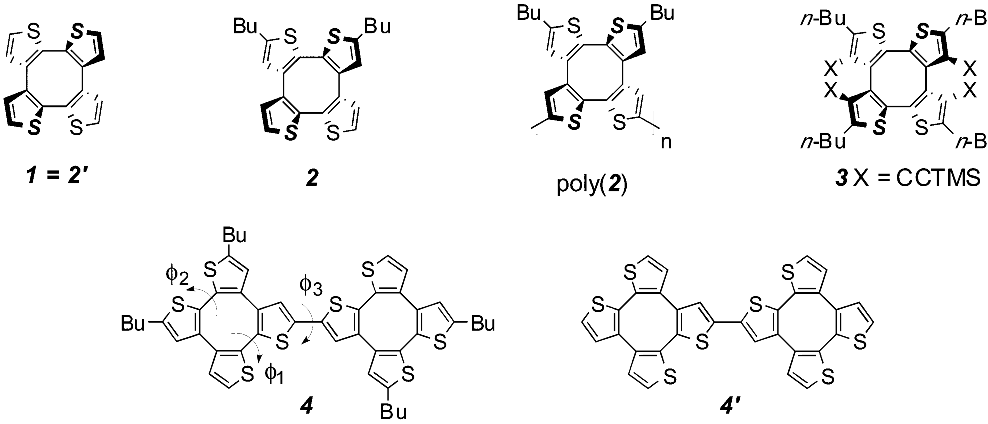
Chart 1



state should promote a redox-induced conformational change. For both the 2± and 1± redox states, delocalization of charge across the [8]annulene π-system is a significant driving force behind conformational change. In theory, poly(cyclooctatetraene) would translate such a redox-induced actuation process (i.e., the tub-to-planar interconversion) occurring at each [8]-annulene repeat unit into an additive dimensional change of the corresponding polymer chain. This design concept is illustrated in Scheme 1. In practice, we selected a derivative of Kauffmann's thiophene-fused [8]annulene, tetra(2,3-thienylene) (compound **1**; see Chart 1),[8] as our building block (specifically, compound **2**).[5] This choice was based on both synthetic considerations and anticipated physical properties. Regarding the latter, it was envisioned that the resulting polymer would possess the favorable redox properties of a polythiophene (relatively stable oxidation states)[9] while retaining the conformational attributes of the prototypical [8]annulene, cyclooctatetraene. The syntheses of all compounds have been previously reported.[5,10]

One caveat to our original design strategy is the unknown effect of thiophene fusion onto an [8]annulene core. Given that the conformational restrictions imposed by the four sterically congested phenyl groups of tetra-*o*-phenylene (also an [8]-annulene) would render it a poor unit of actuation,[11,6] the structure−property consequences of thiophene fusion onto the ideal poly([8]annulene) must be addressed. Herein we report the properties of tetra[2,3-thienylene] that directly impact its performance as an intrinsic unit of electromechanical actuation. Both theoretical and experimental results are reported.

Definitions. For clarity, certain parameters must be defined (refer to Figure 2). The four thiophene rings of tetra(2,3-thienylene) are denoted a−d. Linear poly(tetra[2,3-thienylene])s may possess two points of backbone connectivity at the peripheral α-positions of rings a−b, a−c, or b−c. Polymers of type a−c best translate redox-induced dimensional changes throughout the polymer chain (assuming a linear backbone orientation), while a−b- and b−c-type regioisomers yield a fully conjugated polymer. Compound **4′** is the common dimer for all three regioisomers.

The S−C−C−S dihedral angle, denoted as ϕ, is used as a measure of planarity, with $\phi = 0°$ indicating a planar, D_2-symmetric system. As a point of reference, the X-ray crystal structure of tetra(2,3-thienylene) yields two distinct values of ϕ, $\phi_1 = 47.6°$ and $\phi_2 = 46.4°$.[5] The distance between carbons C_a and C_c (α-carbons of rings a and c, respectively) is denoted as *d*, and any reference to electromechanical actuation implies a change in this value as a function of redox state. There is a direct relationship between the dihedral angle, ϕ, and distance, *d*, such that a decrease in ϕ mandates an increase in *d*, and vice versa. Note that two unique values of ϕ (ϕ_1 and ϕ_2) will be required to describe tetra(2,3-thienylene)s possessing symmetry less than D_2.

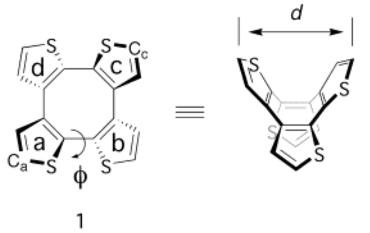


Figure 2. Notations used to describe the parent tetra(2,3-thienylene) scaffold.

To facilitate calculations (density functional theory, DFT),[12] simplified model compounds were used in place of their actual physical counterparts. Specifically, alkyl side chains were omitted from model compounds in all cases. All such hypothetical model compounds are denoted by a prime (′) following their reference number. For clarity, the reference number used is identical to that of the compound which the model is intended to represent (see Chart 1). Excellent agreement between theory and experiment establishes confidence in DFT methods at the B3LYP 6-31G(d, p) level of theory. For example, geometry optimization of compound **2′** yields a D_2 symmetric structure

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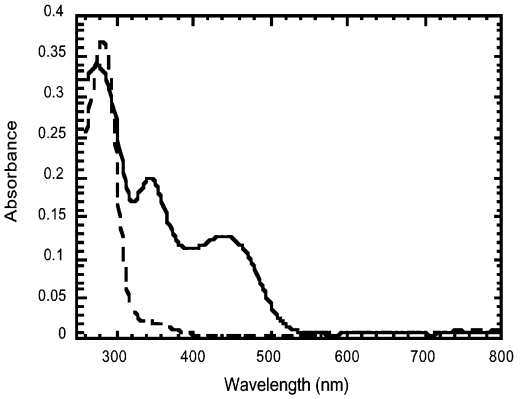

Figure 3. UV−visible overlay spectra of compound **1** (dashed line) and poly(**2**) (solid line). TD DFT calculations predict an onset of absorption of 355 nm for compound **1** (see text).

with $\phi = 49.6°$, in good agreement with experiment (X-ray structural data of compound **1**, vide supra). Furthermore, TD DFT methods on the same geometry-optimized structure yield a calculated band gap ($S_0 - S_1$ transition energy) of 355 nm, a value in good agreement with the broad (350−400 nm) shoulder corresponding to the onset of absorption for compound **1** (note compound $\mathbf{1} = \mathbf{2'}$; see both Chart 1 and Figure 3).

Results

It is well established that the conformational dynamics of [8]annulenes are perturbed dramatically when the steric demands of the parent cyclooctatetraene are increased.[6] For example, the barrier to ring inversion for isopropylcyclooctatetraene (14.8 kcal/mol)[13] increases by more than 30 kcal/mol upon fusion of four phenyl rings (tetra-*o*-phenylene).[11] Given that the conformational dynamics of tetra(2,3-thienylene) directly impacts the range of accessible ϕ values (hence impacting range of actuation), it became critical to determine the effect of thiophene fusion onto the parent [8]annulene.

The inversion barrier of tetra(2,3-thienylene) was experimentally determined as follows. Dimer **4** was prepared from racemic **2** as a mixture of diastereomeric conformers having a maximum number of 10 aromatic signals in the ^{1}H NMR spectrum, coalescing to five signals at temperatures above the inversion barrier. Room-temperature ^{1}H NMR spectra of **4** in either $CDCl_3$ or DMF-d_7 reveal seven of the 10 possible aromatic signals (three are equivalent). At 90 °C in DMF-d_7, all but two signals coalesce. Extrapolation of variable-temperature ^{1}H NMR experiments predicts an inversion barrier of ca. 23.6 kcal/mol. DFT calculations report this value at 29.4 kcal/mol, in reasonable agreement with the (extrapolated) experimentally determined value. Note that the calculated transition-state structure is *not* the planar ($\phi = 0$; D_{2h} symmetry) conformer.

Paquette has demonstrated that comparing redox potentials of differently substituted cyclooctatetraenes provides a qualitative assessment of steric interactions within the [8]annulene.[6,14] To summarize these findings, [8]annulenes were found to become more difficult to reduce to the 2− oxidation state as peripheral steric crowding increased. In the present case, it should follow that the more sterically congested β-substituted derivative, compound **3**, should exhibit higher potentials corresponding to the peak anodic current flow ($E_{p,a}$) than the less hindered counterpart, compound **2**. The observed $E_{p,a}$s for compounds **2** and **3** are 1.01 and 1.36 V, respectively. In both cases, only the 1+ oxidation state is observed within a window from 0 to 1.80 V (ferrocene = 0.52 V). This result differs from both cyclooctatetraene and octamethoxytetraphenylene in that a two-electron redox process is not observed.[3,14,15] Regardless, the difference in $E_{p,a}$ implicates an enhanced range of conformational dynamics in **2** versus that of **3**. Evidently, β-substituents significantly impact the range of redox-induced actuation. This fact has been further supported by studies focusing on didehydro[12]annulene analogues of compound **2**.[16] This observation demonstrates the ability to attenuate the range of actuation via judicious choice of peripheral β-substitution.

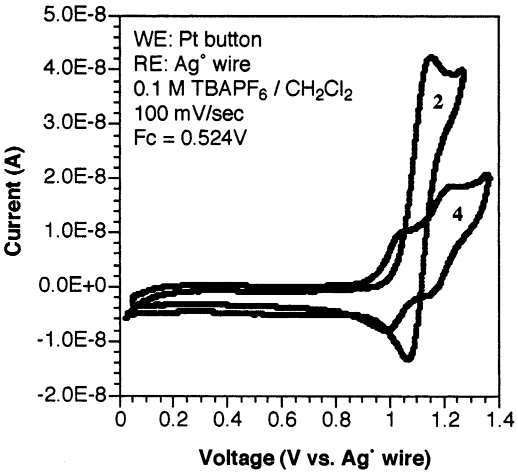

Figure 4. Cyclic voltammograms of compounds **2** and **4**.

As reported, the *solid state* electrochemistry of poly(**2**) is less electrochemically robust than the *solution state* electrochemistry of parent monomer **2**.[5] Regardless, it was determined that poly(**2**) is oxidized to ca. 0.6+ per tetra(2,3-thienylene) repeat unit. Further oxidation of poly(**2**) results in a significant decrease in electrochemical activity upon subsequent cyclic voltammetry. The cause of this decrease in electrochemical activity is unknown; it may be a result of decomposition, poor adhesion to the electrode, or a combination of both.

Electrochemistry of dimer **4** was also examined. In agreement with the aforementioned results, the dimer undergoes two distinct one-electron oxidations to yield an overall 2+ oxidation state (1+ per tetrathienylene unit). The two independent $E_{p,a}$s establish delocalization of the 1+ state over the entire dimer and implicate an actuator that can be attenuated over three oxidation states (**4**, $\mathbf{4}^{1+}$, $\mathbf{4}^{2+}$). The cyclic voltammograms of compounds **2** and **4** are shown in Figure 4. Unlike the solid-state electrochemistry of poly(**2**), the solution state electrochemistry of compounds **2** and **4** is robust and completely reversible. Furthermore, electrochemical polymerization (α-thienyl carbon−carbon bond formation via intermolecular radical coupling) was not observed. This behavior is more characteristic of substituted cyclooctatetraenes than of substituted tetra-*o*-phenylenes. With specific regard to the latter, octamethoxytetraphenylene has been shown to undergo reversible *intramolecular* redox-induced carbon−carbon bond formation.[17]

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Table 1

compound	charge	symmetry	ϕ_1 (deg)	ϕ_2 (deg)	d (Å)	Δd (Å)	Δd (%)
2′	0	D_2	49.5	49.5	6.875		
2′	1+	C_1	34.8	34.8	7.266	0.391	5.69
4′	0	C_2	48.9	49.5	6.898		
4′	1+	C_2	38.6	43.9	7.142	0.244	3.54
4′	2+	C_2	31.4	37.4	7.332	0.434	5.92

Given the fact that crystal structures of $\mathbf{2}^{n+}$ and $\mathbf{4}^{n+}$ ($n = 1$ or 2) have been elusive, DFT geometry optimizations serve as the best currently available method to predict trends regarding redox-induced conformational changes in this series of tetra-[2,3-thienylene]s. Calculations at the B3LYP 6-31G(d, p) level of theory were employed to predict the structures of compounds **2**, $\mathbf{2}^{1+}$, **4**, $\mathbf{4}^{1+}$, and $\mathbf{4}^{2+}$. Key properties are given in Table 1, including charge, symmetry, dihedral angle(s) ϕ_1 (and ϕ_2), distance d, and the corresponding values of Δd in both angstroms and percent change. Regarding the latter property, it should be noted that the planar ($\phi = 0$) conformer is calculated to exhibit a Δd of ca. 20%. This value establishes the maximum range of actuation, albeit an unachievable one (due to the sterics of adjacent β-thienyl hydrogens, as predicted by calculations and implicated by the high barrier to inversion). Although the predicted values of Δd do not approach the theoretical limit, the calculated upper limit of a 5.92% dimensional change is within the range of existing *bulk* organic electromechanical actuators. For comparison, the average percent dimensional change is ca. 10% for *bulk* conducting polymer actuators[1] and ca. 1% for carbon nanotubes.[18]

As can be gleaned from Table 1, calculations corroborate with electrochemical data. Specifically, note the decrease in actuation observed between compound $\mathbf{2'}^{1+}$ and its corresponding dimer, $\mathbf{4'}^{1+}$. The two distinct $E_{\mathrm{p,a}}$s corresponding to $\mathbf{4}/\mathbf{4}^{1+}$ and $\mathbf{4}^{1+}/\mathbf{4}^{2+}$ imply delocalization of the 1^+ charge over both repeat units. Thus, delocalization of charge over any one [8]annulene core of **4** is effectively reduced from that observed in $\mathbf{2}^{1+}$. Given that redox-induced conformational perturbations within the [8]-annulene core are governed primarily by delocalization of charge, alternate manifolds to more widely distribute charge may attenuate the range of corresponding actuation. Calculated optimized geometry of $\mathbf{2'}^{1+}$ and $\mathbf{4'}^{1+}$ reflect this fact, yielding a 5.69% and 3.54% dimensional change, respectively. Note, however, that the latter value is greater than half that of the former. This effective enhancement of actuation in the dimer is also observed in the $\mathbf{4'}^{2+}$ case. Here, charge per repeat unit is 1+, yet the predicted expansion is greater than that of $\mathbf{2'}^{1+}$ (5.92% versus 5.69%, respectively). However, the predicted expansion of $\mathbf{4'}^{2+}$ is less than double that of $\mathbf{4'}^{1+}$. Apparently, the near planar bithiophene unit ($\phi_3 = 2.4°$) formed via the homocoupling of **2** effectively reduces the delocalization of charge within each of the two [8]annulene cores—an observation further validated by the electrostatic potential map of $\mathbf{4'}^{2+}$. Ultimately, the conservation of redox-induced conformational changes from monomer to homodimer implicates similar behavior in the corresponding oligomers and polymer, thus establishing it as a suitable candidate for single-molecule electromechanical actuation.

Conclusions

As stated, the impetus for this study derived from the inherent difficulties associated with discriminating between bulk and single-molecule electromechanical actuation in single (macro)-molecule electromechanical actuators. In an effort to make reliable predictions of redox-induced dimensional changes, electrochemistry and DFT calculations were employed. The key issue to be addressed was the impact of 4-fold thiophene fusion onto an [8]annulene. As discussed, thiophene fusion was a key design requirement, included to impart favorable electronic properties onto the material as a whole; i.e., to emulate a traditional polythiophene conducting polymer backbone. Countering this favorable property is the associated sterics imposed by neighboring thiophene rings. The aforementioned example of octamethoxytetraphenylene serves as the extreme example of a 4-fold annuleno[8]annulene, having properties diametric to its parent [8]annulene, cycoloctatatetraene. These differences are steric in nature, altering both redox chemistry and associated conformational changes. Given the range of properties exhibited by [8]annulenes (in particular, perannuleno[8]annulenes), the design strategy of creating a molecular electromechanical actuator based on a poly[8]annulene cannot be a general one. In this regard, the electrochemical properties of tetra[2,3-thienylene] were examined, and subsequent redox-induced conformational changes were predicted by DFT calculations.

From the data presented, it is evident that tetra[2,3-thienylene] does indeed function as a unit of actuation, and this function is maintained at least to the level of the homodimer. The most significant impact of thiophene fusion is the steric interaction between neighboring β-thienyl hydrogens. Specifically, this interaction prohibits tetra(2,3-thineylene)$^{n+}$ ($n = 1$ or 2) from attaining a planar conformer; one that would be analogous to cyclooctatetraene^{2-}. As a result, the predicted range of actuation is limited to 3.54−5.92% (versus ca. 20% for the planar conformer). Regardless, both **2** and **4** exhibit highly reversible electrochemistry and commensurate, *intrinsic* actuation is predicted. Given that tetra(2,3-thienylene) has been predicted to match our original design prerequisites (i.e., reversible electrochemistry and commensurate dimensional change), we are currently investigating permutations of this system in an effort to maximize the range of actuation. Toward this goal, we have elsewhere reported a thiophene-fused didehydro[12]-annulene as being an excellent candidate for actuation, exhibiting $\Delta d = 19\%$.[16] Confirmation of the aforementioned predictions with analytical measurements of single-molecule actuation is both a continuing effort and a goal.

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Supporting Information Available: Experimental procedures and coordinates for all calculated geometries (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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