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A Conducting Poly(cyclophane) and Its Poly([2]-catenane)

Davide L. Simone and Timothy M. Swager*

Department of Chemistry and Center for Materials Science
and Engineering, Massachusetts Institute of Technology
77 Massachusetts Avenue, Cambridge, Massachusetts 02139

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There has been great interest devoted to the development of multicomponent arrays that undergo inter- and intramolecular electron transfer via an exergonic gradient. Dyads, triads, and higher-order arrays have been synthesized in attempts to mimic and better understand the photosynthetic reaction center[1] and toward the realization of molecular-based storage devices.[2] Catenane and rotaxane architectures consisting of electron-rich and electron-poor aromatic units are ideal substrates for investigation because they exhibit charge-transfer characteristics that facilitate electron migration.[3] Recently, a transition metal-based [2]-catenane has been reported that exhibits migration via an intramolecular gradient;[1a] however, research into conductive poly([2]-catenanes) has gone undeveloped.[4] Herein, we report the synthesis and electrochemical study of an electrically conducting poly([2]-catenane).

We have focused our investigations on macrocycle **3** and its [2]-catenane **4** (Scheme 1). The choice of this system is largely based on previous work of Stoddart who showed the base BPP34C10 cyclophane unit (compound **2** without iodo-groups) to bind dialkylated-4,4′-bipyridiniums producing rotaxanes and catenanes.[3b,5] We prepared macrocycle **3** in two steps from **1**. The cyclization of bistosylate **1** with a diiodohydroquinone derivative forms the strategically functionalized diiodo crown ether, **2**. Coupling of **2** with (3,4-ethylenedioxy)-thiophene groups affords the highly fluorescent, electropolymerizable **3**.

To probe **3**'s ability to bind electron-deficient guests, we undertook Stern−Volmer fluorescence quenching experiments with (*N*,*N*′-dimethyl-4,4′-bipyridinium) bis-hexafluorophosphate, paraquat, as the quenching analyte. The addition of paraquat to **3** in CH_3CN resulted in the formation of a deep-green colored solution on account of a charge-transfer absorption band at $\lambda = 589$ nm ($\epsilon = 204$ $M^{-1}cm^{-1}$). The association stability constant (K_a) was determined in CH_3CN by monitoring the diminished emission intensity at $\lambda = 392$ nm ($\lambda_{ex} = 360$ nm) with increasing analyte concentration. The linear Stern−Volmer behavior of the 1:1 complex gave a rather large K_a value of 2930 ± 30 M^{-1} ($\Delta G^o \approx -4.8$ kcal/mol), indicative of the highly electron-donating nature of the thiophene−phenylene−thiophene aromatic scaffold. For comparison BPP34C10 displays a K_a of 730 M^{-1} in acetone.[5] It seems likely that the extended structure and electron-donation provided by the thiophene moieties contributes to this larger binding constant.

The self-assembly of [2]-catenane **4** follows from the cyclization of the trication derived from **3a** that is bound in the macrocycle of **3**. As expected, the tetracationic cyclophane portion of **4** quenches the fluorescence of the crown ether component. The deep-green [2]-catenane complex exhibits a charge-transfer absorption at $\lambda = 626$ nm ($\epsilon = 1230$ M^{-1} cm^{-1}), which is red-shifted relative to the paraquat:**3** complex indicating greater intimacy between donor and acceptor in the [2]-catenane.

The crystal structure obtained for **4**[6] (Scheme 1) supports an interlocked π-stacked geometry. The bipyridinium aromatic units are situated in electronically unique environments as illustrated by the inner bipyridinium aromatic positioned within the tetracationic cyclophane cavity and the outer bipyridinium aromatic on the outer periphery of the cavity. The centroid-centroid distances between aromatic rings in the complex are ~3.4 Å, indicative of strong $\pi-\pi$ stacking interactions between aromatic units.[7] The [2]-catenane complex exhibits hydrogen bonding between the α- and β-bipyridinium aromatic protons and crown ether oxygen atoms as well as edge-to-face interactions between aromatic subunits. The distance between the central oxygen atom attached to the crown ether linkage and the α-bipyridinium protons is 2.51 Å. The edge-to-face distance between the inside hydroquinone ring protons and the *p*-xylyl spacers is 2.93 Å. The torsion angle between the thiophene−phenylene planes is 21.6°, orienting the thiophene ring 3,4-ethylenedioxy bridge within the receptor cavity. Surprisingly, the twist allows for a stabilizing interaction between the 3-position ether oxygen atom of the thiophene ring and β-bipyridinium protons, with a distance of 2.86 Å. Within the unit cell, complementary π-stacking between molecules persists with centroid−centroid distances of 3.47 Å.

The electrochemical polymerization of macrocyclic monomer **3** and [2]-catenane **4** proceeds via two propagating sites centered at the 5-position of the 3,4-ethylenedioxythiophene functionality. As the voltage is cycled to a positive potential of 0.35 V vs Fc/Fc^+, the oxidation of monomer **3** ($E_{p,m}$) occurs, indicating formation of radical-cationic species that can then propagate via radical combination forming dimers, trimers, etc. Further oxidative cycling leads to polymer formation as evident by an oxidation peak growing in at a lower positive potential. This lowering of the oxidative peak ($E_{p,p}$) for poly(**3**) versus monomer **3** is indicative of the former's ability to stabilize cations via delocalization. The acyclic dimethoxyphenylene derivative of **3** has been synthesized by Reynolds and exhibits a $E_{p,m} = 0.46$ V.[8] The lower $E_{p,m}$ for **3** can be attributed to the stabilizing π-donation imparted by the neutral hydroquinone aromatic to the oxidized thiophene-phenylene-thiophene backbone.[3b] The electropolymerizations are performed such that the resulting polymer is deposited on a 2 μm interdigitated electrode[9] allowing in situ conductivity measurements.[10] The cyclic voltammogram and conductivity profile for poly(**3**) in Figure 1A displays a peak oxidation for the polymer, $E_{p,p} = 0$ V and a maximum conductivity of 11 S/cm at 0.2 V vs Fc/Fc^+.[11]

The $E_{p,m}$ of monomer **4** occurs at 0.43 V vs Fc/Fc^+, indicating that it is slightly more difficult to oxidize than **3**. This is expected due to the repulsive nature of the resulting radical-cation stacked above the inner-dicationic portion of the bipyridinium cyclophane. The $E_{p,p}$ for poly(**4**), 0.07 V vs Fc/Fc^+, is also shifted to a less

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[9] Electrodes fabricated with the following dimensions: 2 μm interdigit spacing, 99 gaps, 0.2005 cm electrode length, 0.04 cm electrode width.

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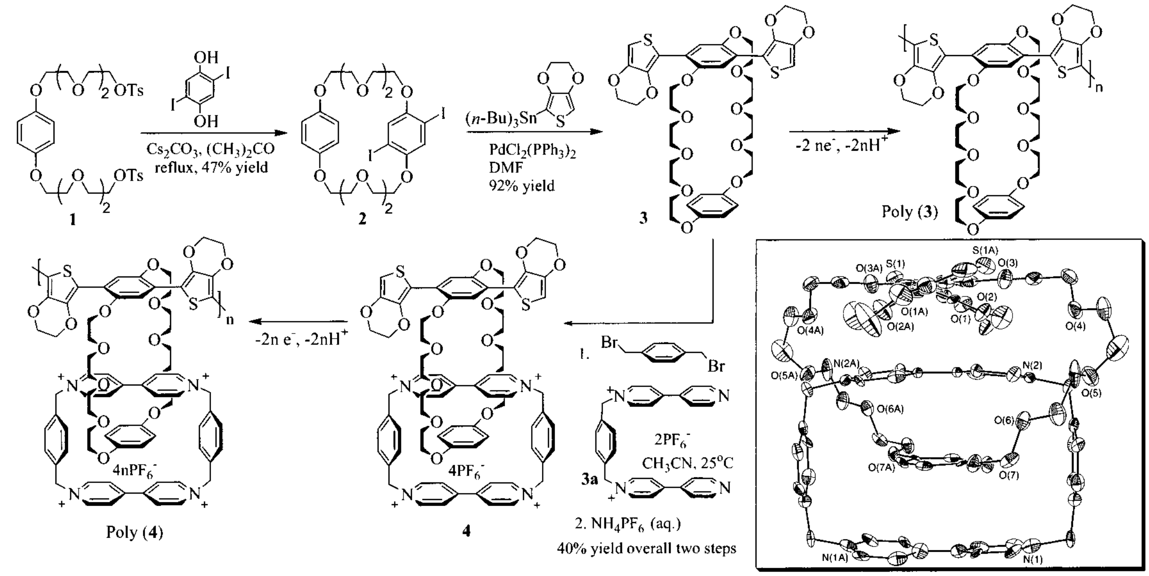
Scheme 1



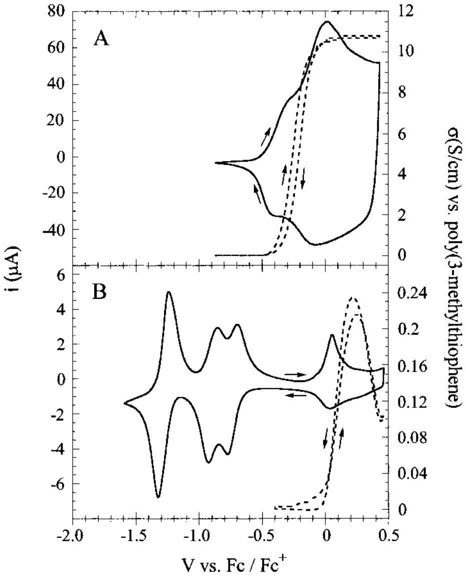


Figure 1. Cyclic voltammogram (—) and conductivity profile (– – –) for (A) poly(**3**) (0.1 M TBA ClO_4^- in CH_3CN and (B) poly(**4**) (0.1 M TBA ClO_4^-/0.1 M TBA PF_6^- (7:3) in CH_3CN), (50 mV/sec for the cv, 10 mV/sec and 40 mV offset for the conductivity profile).

positive potential than its monomer (Figure 1B). The similarity between $E_{p,p}$ for poly(**4**) and poly(**3**) is not surprising considering the small difference in oxidation potential of their respective monomers.

The three-peak reduction potentials observed for the tetracationic cyclophane portion of poly(**4**) are identical to those for monomer **4**. This behavior suggests that the neutral polymer backbone has the same electronic influence on the tetracation as the thiophene−phenylene−thiophene aromatic in **4.** The multiple reduction peaks are indicative of the energetic inequality between the inner- and outer-bipyridinium aromatics. This non-equivalence has been observed by Stoddart and Kaifer with the BPP34C10 derived [2]-catenane.[3b] The first one electron reduction of poly(**4**), $E_{p,r1} = -0.77$ V, occurs at the more electropositive outer-bipyridinium, followed by a one-electron reduction of the inner-bipyridinium at $E_{p,r2} = -0.93$ V. A final two-electron reduction, $E_{p,r3} = -1.32$ V, yields a neutral cyclophane. The greater electron affinity (first reduced) for the outer-bipyridinium than for the inner-bipyridinium leads to the formation of an electrochemical energy gradient within the polymer repeat unit.

The conductivity profile for poly(**4**) rapidly leads to a maximum value of 0.2 S/cm at 0.12 V vs Fc/Fc$^+$, which decays quickly thereafter. In contrast, the profile for poly(**3**) (Figure 1A), shows that oxidation of the polymer backbone occurs over a broad range of potentials without decay. The sharp parabolic nature for the conductivity profile of poly(**4**), as well as the calculated +1 charge per repeat unit reflects a more localized electronic state with characteristics similar to a redox conductor (i.e., each repeat unit acts as a discrete entity) but with a σ_{max} much larger than a typical redox conductor.[12] The optimum rate of electron transfer in the material is realized when the ratio of neutral and oxidized repeat units is 1:1. The tetracationic portion of poly(**4**) does not show any detectable redox conductivity upon reduction of the bipyridinium units.

Spectroelectrochemical investigations of poly(**3**) and poly(**4**) films revealed similar absorption characteristics. In their neutral (insulating) form, the λ_{max} for poly(**3**) was 527 nm (2.35 eV) and poly(**4**) 542 nm (2.29 eV). When oxidatively doped, both displayed a longer wavelength band appearing between 767 and 796 nm (1.62−1.56 eV), indicative of new states formed within the band gap upon reaching a conductive state. Further lower energy absorptions occur at higher oxidation potentials leading to an absorption at >1100 nm (>1.13 eV) owing to the formation of free carriers.[8] The films differ in that poly(**4**) requires higher oxidation potentials to reach its conductive state than does poly(**3**).

Receptor **3**'s penchant for associating with electron-deficient aromatics has also prompted us to investigate the assembly of rotaxane architectures with other conductive acceptor polymers. Further studies into the electronic properties of poly(**4**) are now underway.

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Supporting Information Available: Spectral data, cyclic voltammetry data, characterization for all synthesized compounds, and crystallographic data for **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Non-uniform film coverage on the interdigitated electrodes required a correction factor in the form of a poly(3-methylthiophene) standard to be applied to the conductivity values calculated (see Kingsborough, R. P.; Swager, T. M. *Adv. Mater.* **1998**, *10*, 1100). Detailed calculations are reported in the Supporting Information.

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