

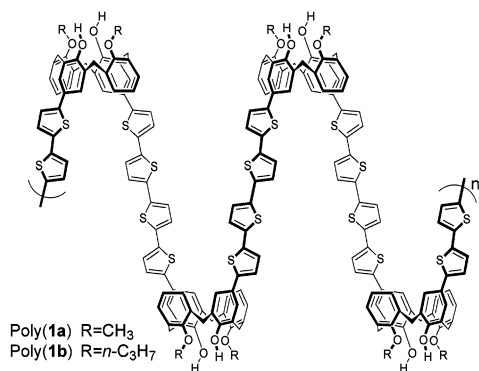
A Proton-Doped Calix[4]arene-Based Conducting Polymer

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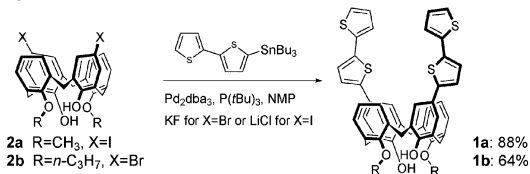
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Calix[4]arenes have long presented one of the most versatile platforms for supramolecular assemblies¹ and molecular recognition.² They undergo dramatic geometric changes involving phenol ring flips between cone, partial cone, and 1,3-alternate conformational isomers,^{1a} and they also can be fashioned to undergo smaller changes such as pinched-cone to pinched-cone hinge movements that vary the distance between two opposite phenol rings.³ For these reasons, we have been intrigued to develop segmented conjugated polymers wherein calix[4]arene units are the flexible and insulating bridges between individual organic electroactive segments. The use of electroactive segments has been demonstrated as a viable route to conducting materials,⁴ and it is understood that the spatial relationship of the electroactive segments is a critical determinant of their electronic, optical, and optoelectronic properties.⁵ We report herein proton-doped segmented polymers, Poly(**1a**) and Poly(**1b**), based upon a calix[4]arene scaffold. The cone conformation of the calix[4]arenes creates a zigzag orientation of the polymer segments, and these dynamic and porous materials are attractive candidates for the design of sensing⁶ and actuating materials.⁷



The phenol groups in monomers **1a** and **1b** display intramolecular hydrogen bonding that enforces the desired cone conformation and facilitate electropolymerization.⁸ Compounds **2a** and **2b** were synthesized as previously reported.⁹ Efficient cross-coupling reactions with these halo-phenols proved to be challenging. Attempts to obtain **1a** and **1b** under common Pd(PPh₃)₄ conditions were slow (4–5 days), poor-yielding (less than 40%), and gave large amounts of the homocoupling byproduct, quarterthiophene. Attempts to protect the phenol with acyl or trimethylsilyl¹⁰ groups prior to coupling reaction resulted in either mixtures of conformational isomers or poor yields due to steric crowding at the lower rim. Optimized cross-coupling reaction conditions were eventually accomplished by utilizing new synthetic methods developed by Fu and co-workers as shown in Scheme 1.^{11,12} Catalytic Pd₂dba₃/P(*t*Bu)₃ in the presence of inorganic salts (KF for –Br and LiCl for –I) afforded monomers **1a,b** in improved yields (64–90%) and reduced

Scheme 1



reaction times (1–2 days). The desired cone conformation was confirmed for these calix[4]arenes by proton and carbon NMR.¹³

Electropolymerizations were performed in CH₂Cl₂ containing 1 mM of monomer **1a** or **1b** and 0.1 M (*n*Bu)₄NPF₆ by repeated cycling of the electrode between –0.4 and 0.8 V at a scan rate of 100 mV/s.¹⁴ Negative shifts of the oxidation current onset after the first scan indicate the formation of the electroactive quarterthiophene *p*-dihydroquinone redox system that has been previously reported.¹⁵ The cyclic voltammogram (CV) of Poly(**1a**) and Poly(**1b**) exhibit two redox waves at $E_1^{1/2} \approx 0.22$ V and $E_2^{1/2} \approx 0.45$ V. No waves were found at negative potentials, thereby indicating that the polymer is fully reduced with the $E_1^{1/2}$ wave. Oxidation at voltages higher than $E_2^{1/2}$ leads to decomposition of the polymer. However, Poly(**1a**) and Poly(**1b**) are very stable for more than 1000 cycles in ambient atmosphere if the potential sweep is kept below $E_2^{1/2}$. Previous studies of metal/organic hybrid materials with this same electroactive system showed similar results.^{8,16,17} The similarity of the electrochemistry of Poly(**1a**) and Poly(**1b**) provides indirect evidence that the cone conformation exhibited by the monomers in solution is also present in the polymers. Most importantly the greater steric bulk of the *n*-propyl groups in Poly(**1b**) dramatically reduces its conformational flexibility and should prevent conformational changes in the polymerization. We have further determined by ¹H NMR that the cone conformation persists in the CD₂Cl₂ electrolyte solutions.

Although the charge is localized by the segmented conjugated backbone, the relatively high maximum conductivity of 6.6 S/cm was determined by in situ conductivity measurements in CH₂Cl₂ electrolyte.¹⁷ The conductivity of films of Poly(**1a**) and Poly(**1b**) showed intriguing characteristics in CH₃CN electrolyte and dropped to less than 1% of the initial value with repeated cycling over –0.20–0.95 V. A similar drop was not observed in CH₂Cl₂, and we considered that the difference was due to the reactivity of CH₃CN. We subsequently found that polymer films that had experienced the conductivity decay in CH₃CN can be transformed to materials with conductivities of the same magnitude as those analyzed in CH₂Cl₂ with the addition of trifluoroacetic acid (TFA) (see Figure 1). On the basis of this behavior, we believe that the decrease of conductivity in CH₃CN is due to the deprotonation of the phenolic protons in the oxidized state, which will not happen in CH₂Cl₂ due to the very high acidity of this solvent's conjugate acid. This behavior is illustrated in Figure 2.

The acid dependence of Poly(**1a**) and Poly(**1b**)'s conductivity is similar to the strong pH conductivity dependence of polyaniline which is said to be acid dopable.¹⁸ Oxidation of the fully reduced

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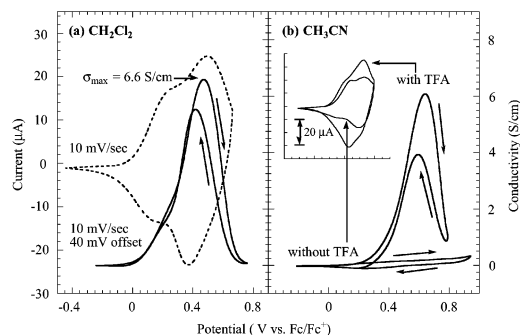


Figure 1. CV (dashed line in (a) and small plot in (b)) and in situ conductivity measurements (solid lines in the large plots) of Poly(**1a**) on 5 μm interdigitated microelectrodes under different conditions: (a) 0.1 M $(n\text{Bu})_4\text{NPF}_6$ in CH_2Cl_2 and (b) 0.1 M $(n\text{Bu})_4\text{NPF}_6$ in CH_3CN with or without 0.5 M trifluoroacetic acid (TFA).

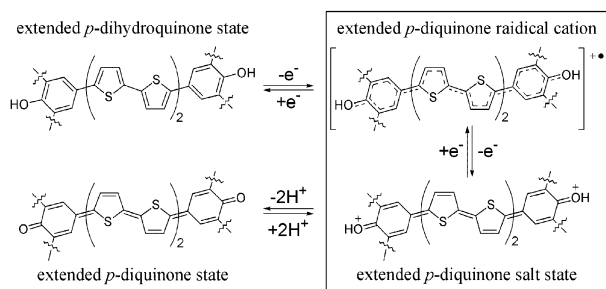


Figure 2. Different oxidation states of the conductive conjugated system in Poly(**1a**) and Poly(**1b**).

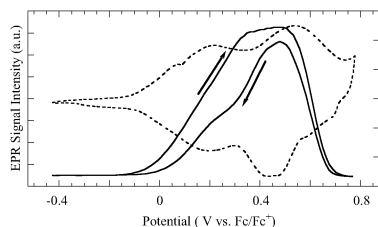


Figure 3. In situ EPR spectroscopy (solid line) and CV (dashed line) of films of Poly(**1a**) on Pt wire electrode in $\text{CH}_2\text{Cl}_2/(n\text{Bu})_4\text{NPF}_6$.

“extended *p*-dihydroquinone” state under conditions that do not allow deprotonation gives a high conductivity. Infrared studies support the presence of the protonated and deprotonated quinones in **1a**. A new intense band at 1578 cm^{-1} is observed for material oxidized in CH_2Cl_2 , and a band at 1596 cm^{-1} is found for material oxidized in CH_3CN solution with small amounts of pyridine. Similar to polyaniline,¹⁶ protonation is expected to shift the $\text{C}=\text{O}$ stretching frequency to lower energy. To further support our assignment of the two different oxidation processes shown in Figure 2, we conducted in situ EPR experiments in CH_2Cl_2 .¹⁷ These investigations, shown in Figure 3, reveal an increase in spin density as Poly(**1a**) undergoes the first oxidation, which is consistent with a one-electron oxidation and a build-up of the extended *p*-diquinone radical cation state. We observed a decrease in the spin density throughout the second oxidation consistent with formation of *p*-diquinone salt. Similar to the emeraldine state of polyaniline, the oxidized protonated state is much more conductive than the conjugate base *p*-diquinone state. However, Poly(**1a**) and Poly-

(**1b**) are very different from polyaniline because they have a segmented structure that imposes greater localization of the carriers. The conductivity of such a system can be considered to result from rapid self-exchange between discrete units and should exhibit a maximum when there are equal amounts of oxidized and reduced states (i.e., $E_1^{1/2}$ and $E_2^{1/2}$).¹⁹ This behavior is readily apparent in Figure 1a wherein the conductivity shows an inflection at $E_1^{1/2}$ and reaches a maximum at $E_2^{1/2}$. Hence, electron exchange between radical cations (1+) and *p*-diquinone salts (2+) shown in Figure 2 produces the highest conductivity.

In summary, we have synthesized electroactive calix[4]arene polymers that require protonation to be highly conductive. Our continuing studies are directed toward related sensory and actuating materials.

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Supporting Information Available: Detailed description of experimental procedures, synthetic preparations, and key CV measurements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) NMR signals of bridge $-\text{CH}_2$ indicate the conformation of calix[4]arene: a pair of doublets between 3.0 and 4.5 ppm in proton NMR with $\Delta\delta$ around 0.9 ppm and one carbon NMR signal at 31 ppm is consistent with all the cone conformation calix[4]arenes.
- (14) All the potentials are referenced to Fc/Fc^+ . Standard three-electrode setup was used for all electrochemical studies: Pt button or ITO/glass working electrode, Pt coil counter electrode, and Ag/Ag^+ reference electrode. Ferrocene is used as an external standard.
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