Conducting Polymers Incorporating Tungsten-Capped Calixarenes

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Calixarenes are highly versatile scaffolds for the design of 3-D cavities,[1] and have found wide utility in host−guest chemistry and molecular recognition.[2] The ability of calixarenes to selectively bind various cations at their lower rim has been widely utilized in the design of both small molecule[3] and polymeric sensory materials.[4] However, despite the numerous examples of calixarene inclusion complexes with organic molecules in the hydrophobic pocket, this binding mode has largely been unexplored with regard to sensors.[1,5,6] As part of our continued interest in conjugated polymer-based sensors[7] we endeavored to make conducting polymeric materials containing conformationally rigid metallocalixarene repeat units. In pursuing this system we considered that the communication between the polymer and the calixarene moiety could be mediated via a transition metal center.

Calixarenes **1a**−**c** were prepared by literature methods.[8,9] Compound **1c** was chosen because of its ability to form a strong host−guest complex with *p*-xylene.[9] When calixarenes **1a**−**c** were refluxed with $WOCl_4$ in toluene overnight followed by addition of **2** and 2 equiv of TMS-Cl, the corresponding tungsten catecholate complexes **3** were obtained in high yield as red crystalline solids (Scheme 1). As expected, the ^{1}H NMR spectra of **3** exhibit two different sets of signals due to the nonequivalent aromatic protons of the calixarene moiety.[10] As the geometry of the polymer precursors was essential for our studies, we determined the X-ray structure of complex **3c**.[11] The important feature of the obtained structure is that the four adamantyl groups form a large deep conical cavity with an ellipsoid base capped by the metal center.

Stille coupling of complexes **3a**−**c** with tributylstannyl ethylenedioxythiophene (Bu_3Sn-EDOT) in refluxing toluene produced **4a**−**c** in reasonable yields (Scheme 1). Complexes **4a**−**c** are dark red-brown crystalline compounds stable in air in the solid state for months. The substitution of the iodine atoms by EDOT results in a downfield shift in the NMR signals of the catecholate protons by more than 0.7 ppm. The hydrogen atoms remote to the substitution site remain largely unaffected. Dark red crystals of **4a** were obtained by slow diffusion of hexane into a solution of **4a** in CH_2Cl_2.[12] The X-ray structure of **4a** (Scheme 1) clearly demonstrates that the tungsten atom has a distorted octahedral configuration. A particular feature is that the phenolic rings of the calixarene trans to the catecholate are substantially distorted from the usual cone conformation with the two phenyl rings being practically coplanar.[13] The other two phenolic oxygens of the calixarene moiety occupy mutually axial positions. The O(4)−W(1)−O(6) angle is 104.5(2)°, while the O(3)−W(1)−O(5) angle is 164.3(2)° as expected for mutually trans ligands in a six-coordinate metal complex. The axial tungsten−oxygen bond distances of 1.951(6) Å (W(1)−O(3)) and 1.910(6) Å (W(1)−O(5)) are longer than the equatorial bond distances of (W(1)−O(4) = 1.867(5) Å and W(1)−O(6) = 1.848(5) Å. The near-linear W−O−C angle of the equatorial phenolates indicates greater p-orbital hybridization of the oxygen lone pairs. Hence back-bonding is likely responsible for the shorter W−O bonds. The EDOT-phenylene torsion angles are 35.7(13)° and 18.4(15)°.

Oxidative electrodeposition of complexes **4** was performed under nitrogen in CH_2Cl_2/0.1 M $Bu_4N^+PF_6^-$ using interdigitated microelectrodes and the potentials were referenced to external Fc/Fc^+. Repeated cycling between −0.2 and 0.7 V (50 mV/s) of a 0.5 μmol solution of **4** resulted in the anodic deposition of polymeric films.[14] While polymer poly**4a** deposited films readily (15−20 cycles), the same process with **4c** required a higher number of scans (up to several hundred) due to slower film growth. This slow rate can be attributed to the bulky adamantyl groups in poly**4c** that create steric repulsions, large voids, and higher solubility oligomers. Complex **4b** showed deposition properties intermediate between the other two analogues.

As expected for a highly delocalized polymer, the cyclic voltammograms of poly**4a**−**c** in the oxidative region exhibit broad waves.[15,16] Poly**4a**−**c** also display a tungsten-centered reduction wave at ca. −1.1 V. This redox activity is unaffected by the polymerization process as evident from the cyclic voltammetry data of the monomeric and polymeric forms (cf. **4a**: $E_{1/2}$ = −1.130 V vs poly**4a**: $E_{1/2}$ = −1.117 V).[17] The current of the tungsten reduction wave relative to the polymer oxidation wave depends on the film thickness. Thicker films display a reduction in the tungsten-centered electroactivity relative to that of the polymer. This effect has been previously observed when the metal center's electroactivity is not matched to that of the polymer.[18] Slow electrochemical kinetics limit the diffusion of charge within

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(11) X-ray structure data for **3c**·$CHCl_3$: $C_{78}H_{70}Cl_{12}I_2O_6W$, *I*2/*a*, a = 26.574(4) Å, b = 10.2177(15) Å, c = 28.363(7) Å, $\alpha = \gamma = 90°$, β = 92.702(2)°, V = 7693(2) Å^3, Z = 4. See Supporting Information for full details.

(12) X-ray structure data for **4a**·CH_2Cl_2: $C_{48}H_{36}Cl_4O_{10}S_2W$, $P\bar{1}$, a = 12.279(3) Å, b = 12.373(4) Å, c = 15.036(4) Å, α = 77.306(5)°, β = 85.491(5)°, γ = 78.231(5)°, V = 2180.3(10) Å^3, Z = 2.

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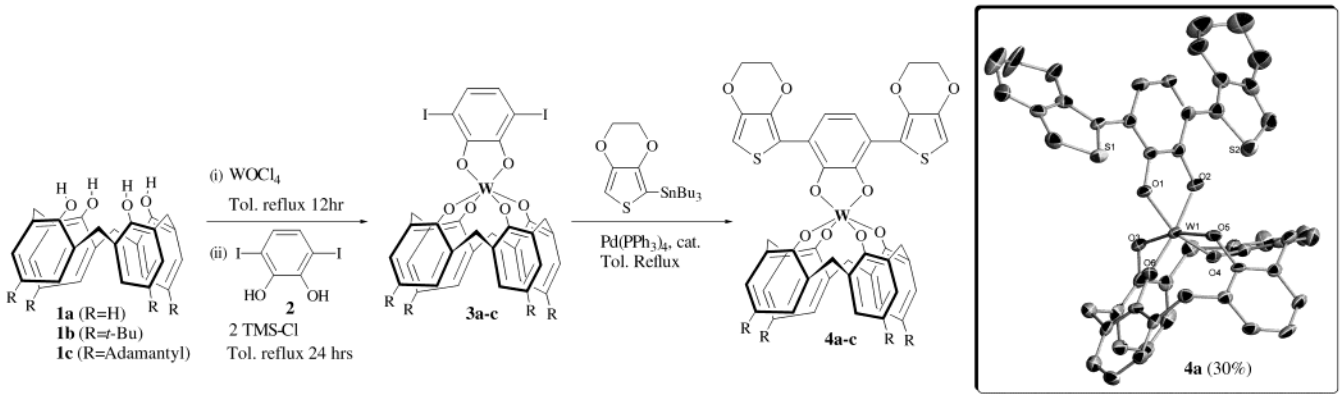
Scheme 1



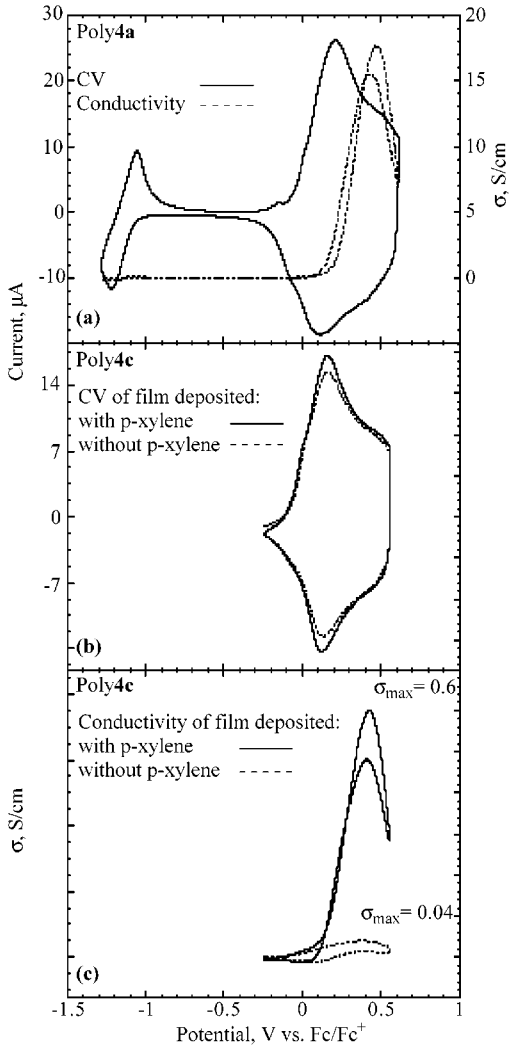


Figure 1. Cyclic voltammetry and in situ conductivity measurements in 0.1 M TBA + PF_6^-/CH_2Cl_2 using a 5 μm interdigitated microelectrode. Sweep rates are 50 mV/s for cyclic voltammograms and 10 mV/s with 40 mV offset potential for conductivity measurements.

the film and the electroactivity associated with the metal center is lost. This interpretation is consistent with conductivity studies, which show that oxidation of the polymer backbone results in formation of highly conductive materials (poly**4a** σ = 15.5 S/cm),[19] while there is no detectable conductivity associated with the metal's electroactivity (Figure 1a).

As mentioned previously, we chose **4c** with pendant adamantyl groups to impart specific recognition of xylene. As a result, we have investigated the effect of added *p*-xylene on **4c**'s electropolymerization. When electropolymerized in the presence of 2 mM *p*-xylene the polymeric films showed 10 times greater conductivity than films deposited in the absence of *p*-xylene under the same conditions. Surprisingly, despite this conductivity difference the CV's of the two films were nearly identical (Figure 1b,c). The *p*-xylene effect on conductivity of poly**4c** likely originates from either specific complexation inside the cavity or a change in the polymer morphology.[20] Electropolymerization of **4c** in the presence of 2 mM toluene did not result in a change of conductivity of the polymer compared to poly**4c** obtained under identical conditions. Similarly, poly**4a** and poly**4b** showed essentially no changes in conductivity when polymerized in the presence of 2mM *p*-xylene. Hence the effect is specific to poly**4c** and *p*-xylene. Curiously, poly**4c** polymerized in the absence of *p*-xylene did not show a significant change in conductivity with *p*-xylene exposure.

In summary, we have prepared highly conductive polymers containing conformationally rigid W(VI)-capped calixarenes. The conductivity of these materials can be influenced by added *p*-xylene and we are pursuing the application of these materials as sensors for aromatic analytes.

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Supporting Information Available: Synthesis and characterization of compounds **3a**−**c** and **4a**−**c** (PDF); X-ray structural information for **3c** and **4a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The narrow ranges of high conductivity relative to related structures (ref 16) may be the result of a more electronically localized structure. The film thickness used in conductivity calculations was determined by using the profilometery technique. The absolute conductivity values were determined using the methods of Zotti [(a) Zotti, G.; Schiavon, G. *Synth. Met.* **1990**, *39*, 183. (b) Schiavon, G.; Sitran, S.; Zotti, G. *Synth. Met.* **1989**, *32*, 209] and have been confirmed in our laboratory to be accurate within a factor of 2 (ref 18).

(20) Although **1c** forms a strong 1:1 complex with *p*-xylene (ref 9), we have not observed any NMR evidence for *p*-xylene complexation with **3c** or **4c**. Nevertheless, the possibility of *p*-xylene binding inside the calixarene cavity cannot be excluded.