Polyterthiophene Appended by Organomolybdenum Sulfide Cluster: Electrochemical Synthesis and Electrochemical Properties of Poly[$Mo_2(\mu\text{-}C_5H_5)_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}SC(R)=CS[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}_2$]s

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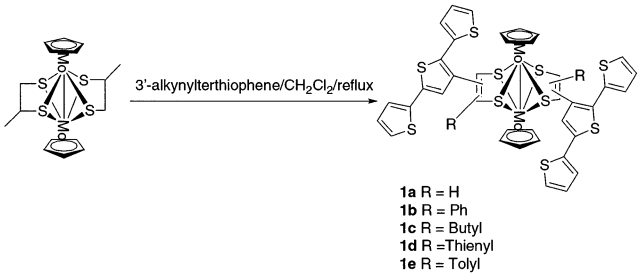
In the past quarter century, structurally modified polythiophenes have been widely investigated since their modification is a powerful method for tuning the electronically conducting properties of these materials. The tuning of these properties allows a number of technological applications utilizing reversible reduction/oxidation properties.[1−3]

More specifically, polythiophene hybrids modified by metal complexes have recently attracted great attention.[4−11] The polythiophene hybrids in which the metal unit is directly conjugated to the backbone of the polythiophene may bring exciting synergistic effects due to the close interaction of the delocalized π-electrons of the backbone with the d-electrons of the metal. Not only are such effects extremely interesting research models to theoretical and experimental scientists, but also they will be a basis for the development of new types of molecular electronic devices. In our efforts to learn the electronic interaction between the organometallic cluster center and the polythiophene backbone, we have recently synthesized a series of terthiophene hybrids appended by redox-active organomolybdenum cluster units and investigated their electrochemistry, including electrochemical polymerization and the physical properties of the resulting polymers.[12,13] Very recently, we found that a series of newly synthesized polythiophene hybrids, poly[$(CpMo)_2\{SC(R)=CS[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}_2$]s (**1**) exhibit unusual electrochromism resulting probably from a synergistic interaction between the molybdenum sulfide cluster unit and the polythiophene backbone. The electrochromism is a reversible color change between electrochemically doped and undoped states and has become a recent focus of research due to applicability to switchable windows and mirrors, active advertising displays, and dynamic camouflage.[14−16] In this communication, we report our preliminary results obtained from the polythiophene hybrids.

Scheme 1



The polythiophene hybrids were synthesized by the electrochemical polymerization of monomeric clusters, $[(CpMo)_2\{SC(R)=CS[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}_2]$s (**1a**−**1e**). Electrochemical polymerization has been popularly used for the preparation of electrochemically active polymer films.[2,3] The monomeric clusters **1a**−**1e** were prepared by the reaction of 3′-(alkynyl)-2,2′:5′,2″-terthiophenes with $(CpMo)_2(SC_3H_6S)_2$ in CH_2Cl_2 and isolated as reddish brown solids by column chromatography in 15−46% yields (Scheme 1). The compositions of the clusters **1a**−**1e** were determined with elemental analysis and the structures were identified from the spectroscopic data (see Supporting Information). Crystals of the cluster **1b** were obtained from benzene/ether solution. The cell parameters are monoclinic, space group $P2_1/n$, a = 17.081(8) Å, b = 18.258(18) Å, c = 18.788(15) Å, β = 115.18(6)°, $F(000)$ = 2480, Dc = 1.535 g cm^{-3}, Z = 4, μ = 0.904 mm^{-1}, $R(R_w)$ = 0.1377(0.3829) for 4854 reflections [$I > 2\sigma(I)$] and 596 parameters. Although the accuracy of the structural parameters is limited because of the disorder of benzene solvate, the atomic connection of the cluster **1b** is clear and characterized as a syn isomer in terthienyl/terthienyl orientation around the molybdenum cluster moiety, as shown in Figure 1. The clusters **1a**−**1e** might be produced as a mixture of a syn isomer and an anti one in terthienyl/terthienyl orientation. Any attempts to separate each isomer as well as to identify their existence by conventional spectroscopic methods were unsuccessful.

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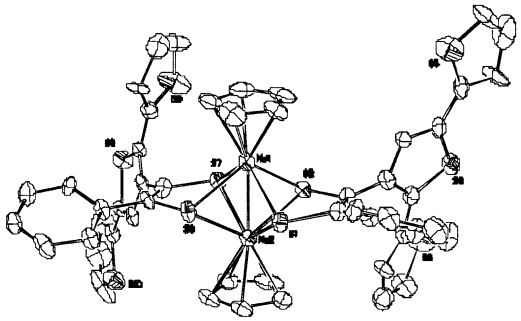

Figure 1. Crystal structure of the cluster **1b** (30% thermal ellipsoid).

Table 1. Cyclic Voltammetry Data for Redox Processes of the Cluster 1a−1e

	$Mo_2^0 \leftrightarrow Mo_2^{+\bullet}$	$Mo_2^{+\bullet} \leftrightarrow Mo_2^{2+}$	thienyl moiety
cluster	Epa/Epc (V)	Epa/Epc (V)	Epa/Epc (V)
1a	+0.39/+0.31	+0.91/+0.81	+1.30/
1b	+0.37/+0.30	+1.10/+1.03	+1.46/
1c	+0.43/+0.35	+1.22/+1.02	+1.39/
1d	+0.44/+0.37	+1.12/+1.10	+1.38/
1e	+0.41/+0.34	+1.16/+1.04	+1.41

Cyclic voltammograms (CVs) of the clusters **1a**−**1e** in CH_2Cl_2 containing 0.1 M tetrabutylammonium phosphate (TBAP) are characterized by three sets of electrode processes. The CV data are listed in Table 1 and a typical CV of the cluster **1c** in the potential range from 0.0 to 1.6 V and scan rate 100 mV s^{-1} is shown in Figure 2a. Two redox waves of the clusters **1a**−**1e** in lower potential ranges, 0.37/0.30−0.44/0.37 and 0.91/0.81−1.22/1.02 V are associated with oxidations of the cluster core to the radical cation, $Mo_2^{\bullet+}$ and dication, Mo_2^{2+}, analogous to the electrochemistry of other Mo cluster systems previously studied by us.[12,13] The CVs of the clusters **1a**−**1e** in a narrower applying sweep window excursed between 0.0 and 1.2 V shows chemical reversibility of both the core processes for generation of $Mo_2^{\bullet+}$ and Mo_2^{2+}. An irreversible wave of each cluster that appeared at higher potential, 1.30−1.41 V, is assigned to the oxidation of the terthienyl moiety.

Potential cycling into this terthienyl wave makes the redox processes of the cluster core sluggish and irreversible, indicating deposition of a polymer film on the electrode surface and electronic interaction in the doped state of the terthienyl π-backbone with the cluster core. Construction of the conducting polymer on an electrode surface hinders an electron transfer between the redox-active subunit and the electrode surface, which leads to a decrease of electrochemical reversibility.[6] The electronic interaction between the p-doped backbone and the metal center also causes the distortion of the metal-centered wave.[17,18]

Polymer films of the clusters **1a**−**1e** were prepared by repetitive potential cycling onto Pt disk electrodes or indium tin oxide (ITO) coated glass electrodes in CH_2Cl_2 containing 0.1 M TBAP. The range of cycling was from 0.0 to 1.5 V and the scan rate 100 mV s^{-1}. A representative CV of **1c** recorded during polymerization by potential cycling five times are shown in Figure 2b. During the growth of the polymer films, the anodic and

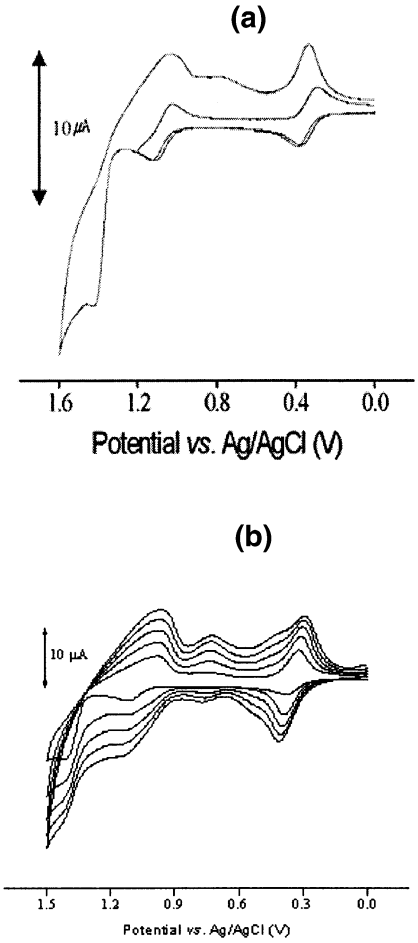

Figure 2. (a) Cyclic voltammograms recorded for 5×10^{-4} M of the cluster **1c** in a 0.1 M TBAP/CH_2Cl_2 solution. (b) CVs recorded during polymerization in a 5×10^{-4} M **1c** containing 0.1 M TBAP/CH_2Cl_2 solution.

cathodic currents of the polymer itself gradually increased and broadened around the monomer oxidation potential due to the extension of the conjugation length and the increase of the amount of the polymer. As the polymerization continues, the separation of the cathodic and anodic peak potential corresponding to the cluster cores was larger, indicating the gradual decrease of the reversibility of the cluster redox processes. The polymer films of all the clusters were smoothly deposited on the electrode surface. The resulting polymer films looked brown and were stable under normal air conditions. The CVs of all the polymer films show the same fashion and are composed of broad irreversible waves, indicating a high degree of delocalization and strong electronic interaction between the cluster core and π-conjugated system of the polythiophene backbone.[17−19] The two cluster core-based processes exhibited for the monomers (at the range of 0.37/0.30−0.44/0.37 and 0.91/0.81−1.22/1.02 V) are both retained by the polymer hybrids. In refractive FT-IR spectra, the Mo−S−Mo band of the monomeric clusters at 437−485 cm^{-1} stays intact, which is generally observed in the bimolybdenum sulfide clusters.[20,21] This IR band together with the two cluster

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Table 2. Colors and CIE *L*a*b Color Coordinates for the Polymer Films in the Neutral and Doped States**

Polymer	neutral				doped			
	color	L*	a*	b*	color	L*	a*	b*
1a		69.91	10.75	24.56		70.52	-0.29	18.40
1b		51.06	14.32	27.56		54.27	6.83	26.53
1c		52.87	18.07	30.81		50.77	-0.48	16.61
1d		61.51	9.06	27.14		46.44	-5.01	10.29
1e		48.84	15.17	22.42		49.51	7.20	20.04

core-based processes of the CVs of the polymers indicates that the cluster cores remain intact.

The films of the polymer hybrids **1a**−**1e** onto an indium tin oxide (ITO) coated glass electrode shows color switching between brown (undoped) and gray (oxidatively doped) to the naked eye. The present color change is a unique electrochromism distinguishable from that of the usual thiophene-based conducting polymers, which appear in various colors in their neutral undoped state and become blue in the doped state.[22] Such a unique electrochromism is interpreted as a result of an electronic synergistic interaction between the molybdenum sulfide cluster unit and the polythiophene π-backbone. The observed colors were quantitatively measured by a spectrocolorimeter and described in CIE 1976 *L*a*b** coordinates.[23] The colors and color coordinates measured in the undoped and doped states are given in Table 2. All the doped polymers exhibit the decreases in the *a** and *b** values, which are measures of the red and yellow components, respectively. The polymer films prepared from the clusters **1b** and **1e** show a small change in the *a** and *b** values. The colors of the polymers were repeatedly switched between their brown and gray states.

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Supporting Information Available: Synthesis of $[Mo_2(\mu\text{-}C_5H_5)_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}SC(R)\!=\!C\ S[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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