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Polyterthiophene π-conjugated by organomolybdenum complex (II): electropolymerization of *erythro*-[(η^5-C_5H_5)$_2$$Mo_2$-$(O)_2$(μ-O){μ-$\eta^2$:$\eta^2$-C(Ph)≡C[$C_4HS(C_4H_3S\text{-}2)_2$-2,5]}]

Dong Hyun Kim [a], Deog-Su Park [b], Yoon-Bo Shim [b], Sung Chul Shin [a,*]

[a] *Department of Chemistry and Division of Applied Life Science, Research Institute of Natural Science, Gyeongsang National University, Chinju 660-701, South Korea*

[b] *Department of Chemistry, Pusan National University, Pusan, 609-735, South Korea*

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Abstract

Terthiophene, to which the organomolybdenum oxide cluster complex is π-conjugated, *erythro*-[(η^5-C_5H_5)$_2$$Mo_2(O)_2$(μ-O){μ-$\eta^2$:$\eta^2$-C(Ph)≡C[$C_4HS(C_4H_3S\text{-}2)_2$-2,5]}] (**2**) was prepared by treatment of *erythro*-[(η^5-C_5H_5)$_2$$Mo_2(CO)_4${μ-$\eta^2$:$\eta^2$-C(Ph)≡C[$C_4HS(C_4H_3S\text{-}2)_2$-2,5]}] (**1**) with air in the presence of trimethylamine *N*-oxide in 1:1 MeCN–CH_2Cl_2. The structure of **2** was identified by spectroscopic methods and elemental analysis. CV of **2** in TBAP–CH_2Cl_2 solution exhibits three discrete electrode processes. Two reversible processes, at $E_{pa} = 0.89$ and 1.08 V, are associated with the oxidation of the cluster core to the radical cation, $[Mo_2core]^{\bullet +}$ and dication, $[Mo_2core]^{2+}$, respectively. Irreversible process at $E_{pa} = 1.30$ V can be assigned to the terthiophene moiety. Electrochemically active, polymer film of **2** shows an electrochromic switching between shiny purple (undoped) and transparent blue (doped), which is sharply discerned form the color contrast of the typical polythiophenes as well as **1**. Such a unique electrochormism can be ascribed to the direct π-electronic interaction between the conjugated organomolybdenum cluster and the polythiophene backbone. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Conducting polymers; Cyclic voltammetry; Electrochromism; Electrochemistry; Clusters; Oligothiophenes

1. Introduction

The modification of the electrode surface with a conducting polymer appended by a specific functional group is one of the most effective and versatile methods used for the chemical derivatization of a surface, in that it allows the deposition of insoluble polymers, a uniform coating on an irregular surface, and easy electrochemical control of the film thickness [1]. Electrodes immobilized with conducting polymers appended by transition metal complexes have attracted attention because these electrode materials can lead to the development of new types of heterogeneous catalysts in electrochemical processes [1–5], photoelectrochemical devices [6–8] and sensors [9–19]. More recently, there has been growing interest in a new class of redox active π-conjugated metallopolymers [20,21]. This class of materials, in which the metal is coordinated directly to the conjugated backbone of the polymer, can show an electronic interaction between the electroactive metal centers and the polymer backbone. The π-conjugated polymers combined by the complexes have been suggested as new models for investigation of electron-transfer chemistry, optoelectrochemistry and electrocatalysis [22,23]. Transition-metal and organotransition metal cluster complexes are important in fields concerned with electrochemical processes, which have shown rapid development [24]. The immobilization of the conducting polymer π-conjugated by the redox-active organometallic cluster should endow an electrode with unique properties, which are impossible to get via either organic or simple inorganic functionalities. Nevertheless, such electrodes have not been actively investigated by now [25,26]. We are currently

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* Corresponding author. Fax: +82-591-7610244.

E-mail address: scshin@nongae.gsnu.ac.kr (S.C. Shin).

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engaged in the design of the electrodes modified by new conducting polymers bearing redox active, nonclassical organometallic cluster complexes in well-defined structural environments [25,26].

In this paper, we report the synthesis and the electrochemical polymerization of *erythro*-$[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph){\equiv}C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}]$ (**2**), in which the $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph){\equiv}C\}]$ organomolybdenum oxide cluster is π-conjugated onto the 3′-position of the terthiophene. To the best of our knowledge, this is the first example of the electrochromism resulted from the electronic interaction between the π-conjugated cluster unit and the polymer backbone. This type of electrochromic switching should be significant, since the variation of the organometallic cluster unit can provide an alternative way of color tuning, which is impossible to get via either organic or dative functionalities.

2. Experimental

2.1. Materials

The starting *erythro*-$[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph){\equiv}C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}]$ (**1**) was prepared by the literature method [25]. All other chemicals and solvents were purchased from commercial suppliers and used without further purification. Column chromatography was performed on Kiesel gel 60 (230–400 mesh).

2.2. Measurements

Melting point was uncorrected. ^{1}H- (500 MHz) and ^{13}C- (125.7 MHz) NMR spectra in $CDCl_3$ were recorded on a Bruker DRX 500 spectrometer using $SiMe_4$ as an internal standard. Infrared spectrum was taken on a Hitachi 270–50 spectrometer with KBr disc and UV–vis absorption spectra were obtained by a Gilford RESPONSE™ spectrophotometer. Mass spectrum and elemental analysis were taken, respectively, at Central Laboratory of Gyeongsang National University.

2.3. Preparation

2.3.1. *Erythro*-$[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph){\equiv}C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}]$ (2)

To the starting cluster **1** (0.78 g, 1 mmol), dissolved in MeCN–CH_2Cl_2 (1:1) (150 ml), was added an excess of freshly sublimed trimethylamine *N*-oxide (0.23 g, 3 mmol). The dark red solution was stirred at room temperature whilst air was gently bubbled through the solution for 7 days, more solvent being added as necessary. The solvent was removed under reduced pressure and purified by a column chromatography. Elution with CH_2Cl_2 gave a reddish brown band due to **1** (0.58 g, 74%). Further elution with ethyl acetate gave a yellow band which, on removal of the solvent, afforded yellow solids, *erythro*-$[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph){\equiv}C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}]$ (**2**) (0.07 g, 10%). Mp. 176°C. ν cm^{-1}: 880. δ_H: 5.90 (s, 5H), 6.02 (s, 5H), 6.74–7.19 (m, 12H). δ_c: 109.94, 113.93, 124.32, 125.07, 125.97, 126.78, 126.93, 127.04, 127.19, 128.17, 128.58, 135.66, 137.12, 143.12, 147.8. *m*/*z*: 718 [M$^+$]. Anal. Calc. for $C_{30}H_{22}Mo_2O_3S_3$: C, 50.14; H, 3.09; S, 13.38. Found: C, 50.19; H, 3.10; S, 13.40%.

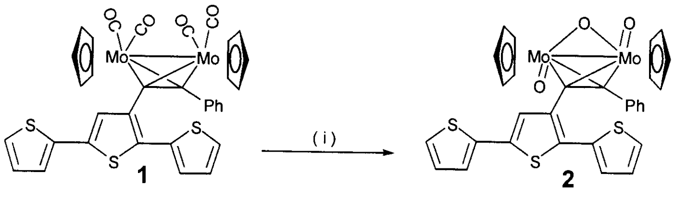
2.4. Electrochemistry

The electrochemical and spectroelectrochemical experiments were performed in CH_2Cl_2, which was purified and dried by distillation from CaH_2 prior to use. Tetrabutylammonium perchlorate (TBAP) (0.1 M) was used as a supporting electrolyte; it was recrystallized twice from ethanol and dried in vacuo at 100°C for 5 days. The concentration of the solutions of **2** was 1.5 mM. Cyclic voltammetric (CV) experiments were performed by a Pine Instrument's Bipotentiostat, Model AFRDE4. A platinum disc (2 mm outside diameter) was used as a working electrode, a platinum wire as a counter, and Ag/AgCl wire as a reference electrode; this was internally calibrated vs. the chemical redox couple of ferrocene/ferrocenium [27]. Electropolymerization was accomplished by repeatedly cycling an electrode potential between the limits 0.00 and 0.50 V at a potential scan rate 100 mV s^{-1}, using a platinum sheet as a counter electrode and Ag/AgCl wire as a reference electrode. Where require for spectroelectrochemical measurement, the polymer film was grown on an indium tin oxide (ITO)-coated glass slide. The cell was placed in the probe beam of a Perkin–Elmer Lamda 900 spectrophotometer, and the applied potential was controlled by a EG&G model 264A polarographic analyzer. All solvents were argon-purged prior to the experiments, and any subsequent electrochemical manipulations were conducted under an argon blanket.

3. Results and discussion

3.1. Preparation

The monomeric cluster, *erythro* - $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph){\equiv}C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}]$ (**2**), was prepared, as shown in Scheme 1. The starting cluster **1** was treated with air in 1:1 MeCN–CH_2Cl_2 in the presence of trimethylamine *N*-oxide at room temperature for 7 days to give **2** in 10% yield. It appears slightly unstable to light and air in solid state, and in convenient organic solutions is slowly decomposed. A number of attempts to prepare the derivatives of **2** having an alkyl or hydrogen substituent on an acetylenic bridge were failed because the clusters were poorly produced and suffered from rapid decomposition to give an intractable mixture. The inefficient production of the $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(R){\equiv}CR\}]$ clusters, without an electron withdrawing substituent on either cyclopentadienyl ligand or an acetylenic bridge, has been reported recently [28]. Spectroscopic data for **2** are given in Section 2. In the IR spectrum, the carbonyl stretching bands of the starting carbonyl cluster disappear and the band of Mo=O appears at 880 cm^{-1} [29]. The ^1H-NMR spectrum shows the resonances of the two cyclopentadienyl ligands at 5.90 and 6.02 ppm, respectively, and aromatic resonances in the range of 6.74–7.19 ppm. In the ^{13}C-NMR spectrum, the carbonyl carbon resonances of **1** disappear. These NMR spectral data fall into the range of those previously reported for the analogous dimolybdenum oxides [28].



Scheme 1. Reagents and conditions: (i) *ex*-Me_3NO, $MeCN{-}CH_2Cl_2$, air purged, 7 days.

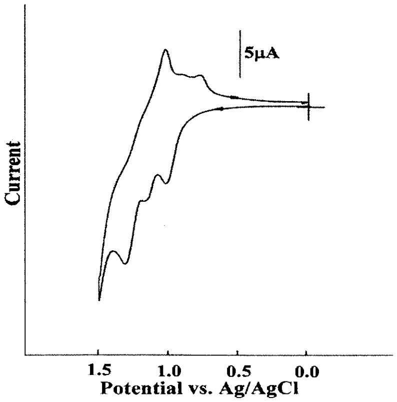


Fig. 1. Single-sweep CV of **2**. Scan rate: 100 mV s^{-1}.

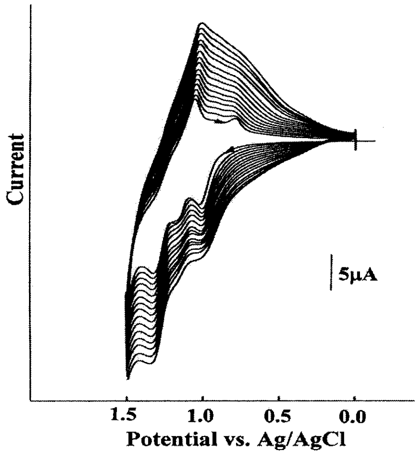


Fig. 2. Electropolymerization of **2** by 15 repeated potential scans. Scan rate: 100 mV s^{-1}.

3.2. *Electrochemistry*

The CV recorded for 1.5 mM of **2** in a 0.1 M $TBAP{-}CH_2Cl_2$ solution exhibits three discrete electrode processes (Fig. 1). By comparison with the redox property of **1** as a reference compound [25], two quasi-reversible electrode processes, at $E_{pa} = 0.89$ and 1.08 V, are associated with the oxidation of the cluster core to the radical cation, $[Mo_2core]^{\bullet +}$ and dication, $[Mo_2core]^{2+}$, respectively. Complex **1** shows two reversible redox peaks, at $E_{pa} = 0.47$ and 0.85 V, respectively [25]. The irreversible anodic peak, at $E_{pa} = 1.30$ V, can be assigned to the oxidation of the terthiophene moiety to produce the polymer film. The CVs of heterocyclic monomers for the electropolymerization generally show highly irreversible redox waves due to the deposition of the electrochemically active polymer film on the electrode surface. Fig. 2 shows the CV recorded for the 1.5 mM solution of **2** during the 15 repeated potential cycling from 0.0 to 1.5 V. The anodic peaks are gradually broadened and the redox processes of the cluster core coalesced with that of the polythiophene as the number of potential cycling increased. The shiny purple film of the polymer begins to form on the electrode as the potential went over $+1.30$ V. No substantial peak shift of the monomer is observed during the potential cycling, demonstrating that the monomer is essentially kept intact. Fig. 3(a) shows the CV recorded for the polymer-grown-electrode after the transfer of the electrode to the blank supporting electrolyte solution. The oxidation peak of the polythiophene backbone appears at ca. $E_{pa} = +0.95$ V, which is composed broad unresolved waves, indicating a high degree of delocalization [30]. In this case, the oxidation peaks of the cluster core shown in Fig. 1 are unresolved and buried into the oxidation peak of the polythiophene backbone on the polymer-coated electrode. The reduction peak responsible to the dimolybdenum cluster core reveals at $E_{pa} = -0.31$ V, as shown in Fig. 3(b). The fact that the reduction peak is originated from the dimolybdenum cluster core is confirmed by comparison with the CV recorded for **2**. Applying the negative potential to the cell containing **2** reveals a very small peak at $E_{pa} = -0.33$ V, which is attributed to the reduction process of the dimolybdenum cluster core of **2** (not shown). Upon both the redox cycling and the potential stepping of the film, the polymer is highly electroactive and electrochromic, switching between

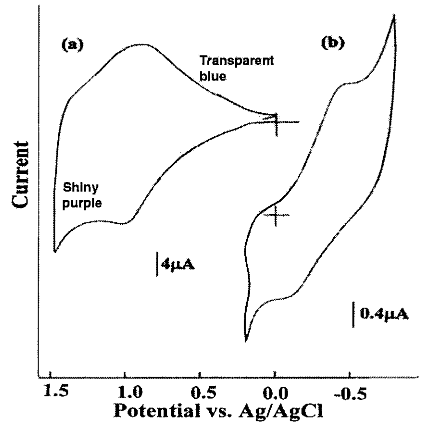


Fig. 3. CV of an electrode modified by polymer film of **2**. Scan rate: 100 mV s^{-1}.

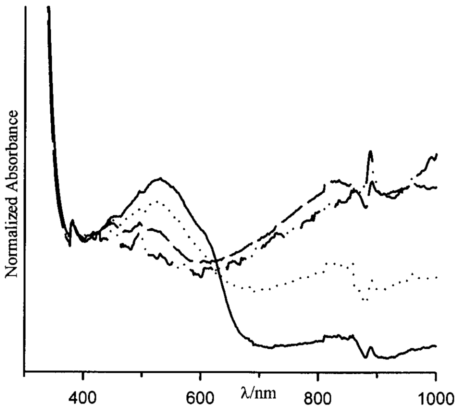


Fig. 4. Near infrared spectra of polymer film grown on ITO in 0.0 V (solid line), 0.7 V (dotted line), 1.0 V (dashed line), 1.5 V (dot–dot–dashed line). Intensities were normalized in order to optimally fit the graphs.

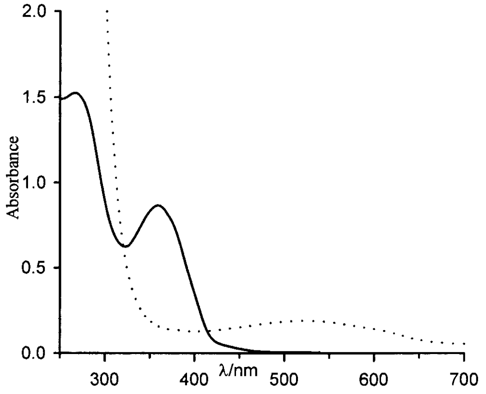


Fig. 5. Absorption spectra of **2** and its neutral polymeric film deposited on ITO glass.

shiny purple (undoped) and transparent blue (doped). The redox activity of the polymer film is found to be rather stable, exhibiting essentially the same CV curve after 50 repeated scans between − 0.0 and 1.5 V in a blank electrolyte solution. The electrochromism of electrochemically-synthesized, alkyl substituted and unsubstituted polythiophenes shows mainly red (undoped)-blue (doped) color constrast, and **1** exhibits red–brown (undoped)–green (doped) contrast. Generally, the color contrast of the conducting polymer is significantly affected by an effective conjugation length and a substituent type as well as the regiochemistry of substitution of the starting oligomers [31]. The doped–undoped color contrast of the present polymer film demonstrates that the directly-conjugated organomolybdenum cluster moiety has dramatic change over the electrochromic property of the polythiophene as a result of the π-electronic interaction between both components. The electrodes, on which the polythiophene directly conjugated by a dative complex of transition metals is deposited, reveal the different electrochromisms, depending upon metal type, as a result of the π-electron communication between the metal and the conjugated backbone [32,33]. To the best of our knowledge, this is the first example of the electrochromism of the conducting polymer π-conjugated by an organometallic cluster complex. This type of electrochromism should be significant, since the variation of the organometallic cluster conjugated into the π-backbone could provide a way of color tuning over a wide range due to the direct electronic interaction between both the components.

The optoelectronic behavior of the polymer film grown on ITO glass during the doping was investigated, as shown in Fig. 4. The π–π* absorption band of the undoped film appreciably decreases at 0.70 V, and the long wave-length transition of the corresponding cluster core is buried into a new, large broad absorption band which appears in a range of above 600 nm. When the polymer film is further oxidized at the peak potential 1.50 V, the π–π* absorption band nearly disappears and the low energy broad band becomes stronger. Such optoelectronic behavior may be attributed to the formation of special electronic states, like polarons and bipolarons, which is generally observed for the doped conducting polymers [34,35].

3.3. Absorption spectra

Fig. 5 shows the absorption spectra of **2** and its neutral polymer film deposited on ITO glass. The absorption spectrum of **2** in $CHCl_3$ exhibits a moderately intense, high energy transition at 269 nm and an intense, lower energy transition at 369 nm. The high-energy band is attributed to the π–π* localized excitation of the thiophene ring [36] while the lower energy band is attributed to the π–π* transition in the conjugated π-system [37]. The lower energy transition is red-shifted 56 nm from that of **1** [25]. This red shift indicates that the distortion of the planarity of the terthiophene π-system of **2**, caused by a steric hindrance between the bulky cluster unit at the 3′-position of the central thiophene and the sulfur atoms of the adjacent two thiophenes in their anti conformation, is smaller than that of **1**, which contributes to the appreciable red shift. In contrast, the amount of the red shift of the $\pi-\pi^*$ localized excitation, caused by such a lengthening of the conjugation, cannot be evaluated because of its transition of the high energy UV region below 250 nm. The absorption spectrum of the polymer film of **2**, electrochemically immobilized on ITO glass, exhibits an unusually broad band, ranging from 350 to 650 nm and a broad near-IR band above 800 nm. This type of broad absorption over a visible range is often observed for the solid-state films of the π-conjugated polymers [38–40]. Although there may be many factors that influence the broadening of the absorption band of the structurally related polymer films in solid-state, the band broadening has been mainly ascribed to the strong intermolecular charge transfer and the multitude of the excited state configuration in closely contacted solid-state of the polymer molecules [25,38,41,42]. The origin of the near-infrared band of the polymer film, which is not observed from the spectrum of the monomer either in solution or in solid state, is unclear at present. Such a very long-wavelength absorption is of interest, owing to its potential applications in the chemical use of solar energy, since a major fraction of the solar radiation that reaches the earth's surface is in the near-infrared ranges [43,44].

4. Conclusion

Terthiophene, to which the organomolybdenum oxide cluster is π-conjugated, *erythro*-$[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph){\equiv}C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}]$ (**2**) was prepared by treatment of *erythro*-$[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(Ph){\equiv}C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}]$ (**1**) with air in the presence of trimethylamine *N*-oxide. The CV of **2** shows the deposition of electroactive polymeric film on the electrode surface. The electrochemical property of the conventional polythiophene is dramatically changed by the π-conjugation of the organomolybdenum cluster complex as a result of the direct π-electronic interaction between the polymer backbone and the cluster unit; the polymer-coated electrode shows a unique electrochromic switching between shiny purple (undoped) and transparent blue (doped).

Acknowledgements

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