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FULL PAPER

Polyterthiophene-bearing pendant organomolybdenum complexes: electropolymerization of *erythro*-[$Mo_2(\mu\text{-}C_5H_5)_2(CO)_4\{\mu\text{-}\eta^2:\eta^2\text{-}C(R)\equiv C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}$]

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Terthiophenes bearing pendant organomolybdenum complexes, *erythro*-[$Mo_2(\eta\text{-}C_5H_5)_2(CO)_4\{\mu\text{-}\eta^2:\eta^2\text{-}C(R)\equiv C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}$] (R = H **1a** or Ph **1b**) were prepared by reaction of [$Mo_2(\eta\text{-}C_5H_5)_2(CO)_4$] with 3′-alkynyl-2,2′ : 5′,2″-terthiophenes. The molecular structures of **1a** and **1b** were identified by spectroscopic methods and X-ray diffraction. Cyclic voltammetry of **1a** and **1b** showed deposition of electroactive polymeric films on the electrode surface. The absorption spectra of **1a**, **1b** and their polymer films are presented.

Great interest has been focused upon rigid π-polymers bearing carbon-rich organometallics. These organometallic polymers are important assemblies for the study of electron-transfer processes,[1] the preparation of organometallic liquid crystals,[2] the construction of nanostructured materials[3] and molecular devices.[4]

Grafting of specific functionalities on the individual rings of heterol conducting polymers can tune their physical properties in a unique way. Although organotransition-metal complexes can modify the properties of conducting polymers in a specific way that may be impossible *via* classical organic functionalities, studies have been restricted to ferrocene derivatives and only a few are able to form electroactive polymers by direct anodic electropolymerization.[5] Most involve their copolymerization with unsubstituted pyrrole.

Herein, we report the synthesis and the electrochemical polymerization of [$Mo_2(\eta\text{-}C_5H_5)_2(CO)_4\{\mu^2\text{-}\eta^2:\eta^2\text{-}C(R)\equiv C[C_4HS(C_4H_3S\text{-}2)_2\text{-}2,5]\}$] **1**, in which the $Mo_2(C_5H_5)_2(CO)_4[\mu\text{-}\eta^2:\eta^2\text{-}C(R)\equiv C]$ (R = H or Ph) moiety is appended to the 3′-position of terthiophene, and the optophysical properties of the resulting polymers. The molybdenum binuclear complex moiety bridged by an unsaturated hydrocarbon has been chosen as an organometallic unit since considerable interest has been focused upon such organometallic complexes as models for studying the interaction of organic molecules with metal surfaces during the course of synthetic organic transformations.[6] In present system, two chiral centers are generated at the construction stage of the moiety from [$Mo_2(\eta\text{-}C_5H_5)_2(CO)_4$] and unsymmetric alkynes. Conjugated polymers substituted by chiral groups have potential technological applications as materials for stereoselectivity modified electrodes and/or microwave absorbers.[7] Conducting polymers having catalytic functions are also important in the field of heterogeneous catalysis concerned with electrochemical processes, which has shown rapid development recently.[8] Conducting polymers grafted by chiral organotransition-metal complexes may provide new research models for the heterogeneous chiral catalysts in electrochemical processes. In order to relieve steric hindrance caused by the bulky complex unit in the polymerization process, terthiophene has been chosen as a monomeric unit of polymerization; the distance between the two terminal α-carbon atoms of terthiophene is longer than the size of the $Mo_2(C_5H_5)_2(CO)_4[\mu\text{-}\eta^2:\eta^2\text{-}C(R)\equiv C]$ (R = H or Ph) moiety. To the best of our knowledge, the present report is the first example of electrochemical polymerization of thiophene appended a polynuclear organometallic moiety.

Experimental

Materials

Solvents were distilled under nitrogen, from appropriate drying agents, and degassed prior to use. 3′-Bromoterthiophene[9] and [$Mo_2(\eta\text{-}C_5H_5)_2(CO)_4$][10] were prepared by literature methods. All other chemicals were from commercial suppliers and used without further purification. Column chromatography was performed on Kieselgel 60 (230–400 mesh).

Measurements

Melting points are uncorrected. Proton and ^{13}C NMR spectra in $CDCl_3$ were recorded on a Bruker DRX 500 spectrometer using $SiMe_4$ as an internal standard. Infrared spectra were taken on a Hitachi 270–50 spectrometer with KBr discs, UV/VIS absorption spectra of the monomers on a Gilford RESPONSE™ spectrophotometer. Elemental analyses were performed by the Central Laboratory at Gyeongsang National University. The electrochemical and spectroelectrochemical experiments were performed in CH_2Cl_2 as the solvent, which was purified and dried by distillation from CaH_2 prior to use. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte; it was recrystallized twice from methanol and dried *in vacuo* at 100 °C for several days. The concentration of the solutions of monomers **1a** and **1b** was *ca.* 10^{-4} M. Cyclic voltammetry was performed with a computer-controlled EG&G PAR 273 potentiostat. Platinum discs (1 mm outside diameter) were used as the working electrodes, a platinum wire as the counter electrode, and an Ag–AgCl wire as the reference electrode; this was internally calibrated *vs.* the chemical redox couple ferrocene–ferrocenium. Spectroelectrochemical measurements of the polymer films were carried out in a thin-layer cell incorporating ITO glasses as the optical transparent electrodes, a platinum sheet as the counter electrode, and an Ag–AgCl wire as the reference electrode. The cell was placed in the probe beam of a Perkin-Elmer Lambda 900 spectrophotometer and the applied potential controlled by a EG&G model 264A polarographic analyzer.

Crystallography

All measurements were made on a Rigaku RAXIS-IV imaging-plate area detector. Experimental details are included in Table 1. The structure was solved using TEXSAN crystallographic software[11] by direct methods[12] and expanded using Fourier techniques.[13] Non-hydrogen atoms were refined anisotropically, hydrogen atoms were included but not refined. Neutral atom scattering factors[14] and anomalous dispersion effects[15] were taken from the literature.

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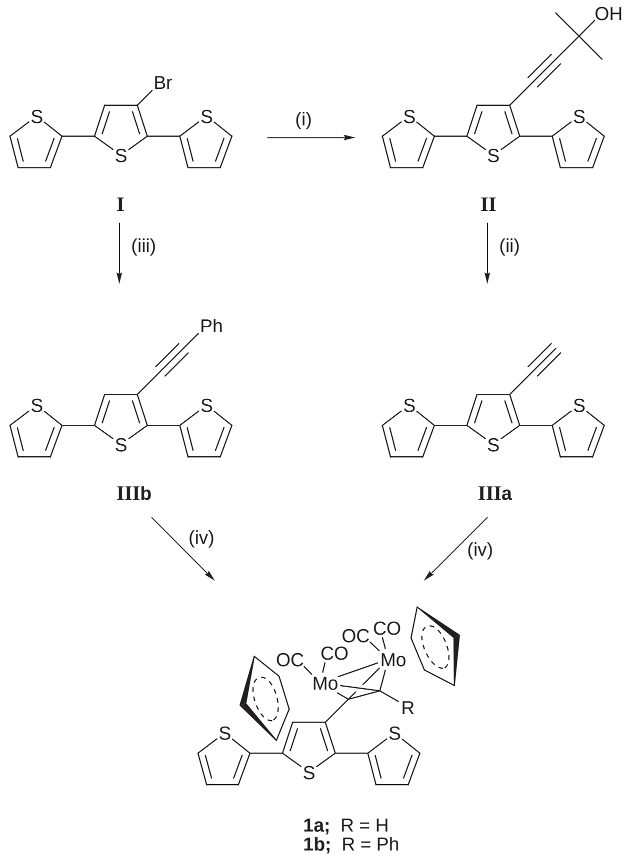
Syntheses

3′-(3-Hydroxy-3-methylbut-1-ynyl)-2,2′:5′,2″-terthiophene II. To a mixture of 3′-bromoterthiophene (2 g, 6.1 mmol), [Pd(dppf)Cl_2] (0.05 g, 1 mol %), and CuI (0.035 g, 3 mol %) in degassed diisopropylamine (30 cm^3) was added 2-methylbut-3-yn-2-ol (0.57 g, 6.8 mmol). The reaction mixture was refluxed with stirring for 24 h under a nitrogen atmosphere. After confirmation of the disappearance of 3′-bromoterthiophene by TLC, the mixture was washed with saturated $NaHCO_3$ and brine, and extracted with CH_2Cl_2. The extract was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column using a mixed eluent of *n*-hexane–ethyl acetate (5:1) to give a pale yellow solid **II** (1.62 g, 80%), m.p. 73–74 °C (Found: C, 61.7; H, 4.30; S, 29.0. $C_{17}H_{14}OS_3$ requires C, 61.8; H, 4.27; S, 29.1%); $\tilde{\nu}_{max}/cm^{-1}$ 2219 and 3454. δ_H 1.70 (s, 6 H, CH_3), 2.20 (s, 1 H, OH), 7.04–7.46 (m, 7 H, aryl). δ_C 31.6, 66.3, 78.2, 98.8, 117.6, 124.6, 125.4, 125.9, 126.0, 127.6, 128.4, 134.5, 136.0, 136.6 and 138.8. EI mass spectrum: *m*/*z* 330 (M^+).

3′-(Ethynyl)-2,2′:5′,2″-terthiophene IIIa. To a solution of compound **II** (2 g, 6.1 mmol) in degassed toluene–methanol (1:1, 50 cm^3) was added KOH (1.7 g, 30 mmol). The mixture was refluxed under a nitrogen atmosphere for 20 h. After confirmation of the disappearance of the starting **II** by TLC, the solvent was evaporated under reduced pressure. Distilled water was poured onto the residue and extracted with CH_2Cl_2. The extract was washed with saturated NH_4Cl and dried over magnesium sulfate, and the solvent removed under reduced pressure. The residue was chromatographed on a silica gel column using *n*-hexane as an eluent to give a yellow solid of **IIIa** (1.2 g, 74%), m.p. 58–59 °C (Found: C, 61.7, H, 2.97; S, 35.2. $C_{14}H_8S_3$ requires C, 61.7; H, 2.96; S, 35.3%); $\tilde{\nu}_{max}/cm^{-1}$ 2047 and 3297. δ_H 3.38 (s, 1 H, ≡CH) and 7.02–7.55 (m, 7 H, aryl). δ_C 77.4, 80.6, 115.0, 122.7, 123.5, 124.2, 124.3, 125.9, 126.0, 126.4, 132.7, 133.7, 134.4 and 137.9. EI mass spectrum: *m*/*z* 272 (M^+).

3′-(Phenylethynyl)-2,2′:5′,2″-terthiophene IIIb. The same procedure used for **II** was performed from 3′-bromothiophene (3.27 g, 10 mmol) and phenylacetylene (1.2 g, 12 mmol), affording a yellow solid of **IIIb** (2.58 g, 74%), m.p. 99–101 °C (Found: C, 68.8; H, 3.49; S, 27.5. $C_{20}H_{12}S_3$ requires C, 68.9; H, 3.47; S, 27.6%); $\tilde{\nu}_{max}/cm^{-1}$ 2172. δ_H 7.03–7.60 (m, 12 H, aryl). δ_C 84.94, 94.06, 117.6, 123.0, 124.0, 124.9, 125.4, 125.6, 126.9, 127.8, 128.3, 131.3, 134.0, 136.1, 136.5 and 138.2. EI mass spectrum: *m*/*z* 348 (M^+).

[Mo_2(η-C_5H_5)$_2$(CO)$_4${μ-η^2:η^2-C(H)≡[$C_4HS(C_4H_3S$-2)$_2$-2,5]}] 1a. To a solution of compound **IIIa** (0.33 g, 1.2 mmol) in toluene (20 cm^3) was added freshly prepared [Mo_2(η-C_5H_5)$_2$(CO)$_4$] (0.43 g, 1 mmol). The mixture was stirred at room temperature under a nitrogen atmosphere for 1 h. After confirmation of the disappearance of the starting **IIIa** by TLC, the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel column using *n*-hexane as an eluent to give a reddish brown solid of **1a** (0.53 g, 75%). X-Ray-quality crystals could be obtained from *n*-hexane–toluene at −20 °C, m.p. 146 °C (decomp.) (Found: C, 47.8; H, 2.55; S, 13.5. $C_{28}H_{18}Mo_2O_4S_3$ requires C, 47.6; H, 2.57; S, 13.6%); $\tilde{\nu}_{max}/cm^{-1}$ 1837, 1905 and 1995. δ_H 4.73 (s, 1 H, ≡CH), 5.26 (s, 10 H, 2C_5H_5) and 7.02–7.39 (m, 7 H, aryl). δ_C 59.0, 73.9, 91.9, 123.7, 124.6, 126.2, 126.7, 127.3, 127.9, 128.5, 128.9, 135.0, 136.5, 136.9, 143.8, 229.4 and 230.9. EI mass spectrum: *m*/*z* 705 (M^+), 622 (M^+ − 3CO) and 594 (M^+ − 4CO).



Scheme 1 (i) 2-Methylbut-3-yn-2-ol, [Pd(dppf)Cl_2], CuI, diisopropylamine, reflux, 24 h; (ii) KOH, toluene–methanol (1:1), reflux, 20 h; (iii) phenylacetylene, [Pd(dppf)Cl_2], CuI, diisopropylamine, reflux, 24 h; (iv) [Mo_2(η-C_5H_5)$_2$(CO)$_4$], toluene, 1 h

[Mo_2(η-C_5H_5)$_2$(CO)$_4${μ-η^2:η^2-C(Ph)≡C[$C_4HS(C_4H_3S$-2)$_2$-2,5]}] 1b. The same procedure as above was performed from compound **IIIb** (0.42 g, 1.2 mmol) and [Mo_2(η-C_5H_5)$_2$(CO)$_4$] (0.43 g, 1 mmol) at 80 °C, affording reddish brown solids of **1b** (0.2 g, 25%), m.p. 143–146 °C (Found: C, 52.1; H, 2.91; S, 12.4. $C_{34}H_{22}Mo_2O_4S_3$ requires C, 52.2; H, 2.83; S, 12.3%); $\tilde{\nu}_{max}/cm^{-1}$ 1845, 1930 and 2000. δ_H 5.08 (s, 10 H, 2C_5H_5) and 6.74–7.22 (m, 12 H, aryl). δ_C 91.3, 95.5, 95.8, 126.0, 126.9, 128.0, 129.4, 129.5, 129.7, 130.3, 130.4, 131.7, 132.0, 132.8, 136.7, 137.2, 139.2, 145.8, 148.3, 232.5 and 233.1. EI mass spectrum: *m*/*z* 726 (M^+ − 2CO) and 671 (M^+ − 4CO).

Results and Discussion

Syntheses

The monomeric complexes **1a** and **1b** have prepared as shown in Scheme 1. 3′-Bromoterthiophene **I** was treated with 2-methylbut-3-yn-2-ol in diisopropylamine in the presence of [Pd(dppf)$_2$-Cl_2] at reflux temperature to give 3′-(3-hydroxy-3-methylbut-1-ynyl)terthiophene **II** in 80% yield. Compound **II** was hydrolysed by KOH in toluene–methanol (1:1) at reflux temperature to afford 3′-(ethynyl)terthiophene **IIIa** in 74% yield. 3′-(Phenylethynyl)terthiophene **IIIb** was obtained in 74% yield from the coupling of **I** with phenylacetylene under the same conditions

Table 1 Crystallographic data for complex **1a**

Empirical formula	$C_{28}H_{18}Mo_2O_4S_3$
M	706.51
Crystal colour, habit	Reddish brown
Crystal dimensions/mm	0.32 × 0.17 × 0.04
Crystal system	Monoclinic
Space group	$C2$ (no. 5)
a/Å	31.815(6)
b/Å	7.640(1)
c/Å	11.483(6)
β/°	104.884(3)
U/Å^3	2697
Z	4
D_c/g cm^{-3}	1.740
$F(000)$	1400
μ(Mo-Kα)/cm^{-1}	11.93
T/K	296
$2\theta_{max}$/°	50.1
No. reflections collected	2431
Observed reflections [$I > 1.00\sigma(I)$]	2419
$R(F_o)$[a]	0.045
$R'(F_o)$[b]	0.056
Maximum, minimum $\Delta\rho$/e Å^{-3}	1.80 and −0.63

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 2 Selected distances (Å), angles (°) and torsion angles (°) of complex **1a**

Mo(1)–Mo(2)	2.986(1)	Mo(1)–C(15)	2.211(9)
Mo(1)–C(16)	2.274(8)	Mo(2)–C(13)	1.99(1)
Mo(2)–C(15)	2.224(10)	Mo(2)–C(16)	2.187(9)
C(15)–C(16)	1.36(1)	C(16)–C(17)	1.49(1)
C(17)–C(18)	1.42(1)	C(18)–C(19)	1.38(1)
C(19)–C(25)	1.51(1)	C(25)–S(3)	1.749(6)
S(3)–C(28)	1.732(6)	C(17)–C(20)	1.40(1)
C(20)–C(21)	1.47(1)	C(21)–S(2)	1.730(6)
S(2)–C(24)	1.729(6)		
Mo(1)–Mo(2)–C(15)	47.5(2)	Mo(1)–Mo(2)–C(16)	49.2(2)
Mo(2)–Mo(1)–C(15)	47.9(3)	Mo(2)–Mo(1)–C(16)	46.8(2)
Mo(1)–C(16)–Mo(2)	84.0(3)	Mo(1)–C(15)–C(16)	74.9(5)
Mo(1)–C(16)–C(15)	69.9(5)	Mo(1)–C(16)–C(17)	131.7(6)
Mo(2)–C(15)–C(16)	70.6(6)	Mo(2)–C(16)–C(15)	73.6(5)
Mo(2)–C(16)–C(17)	131.3(6)	C(15)–C(16)–C(17)	141.8(9)
C(16)–C(17)–C(18)	121.7(8)	C(16)–C(17)–C(20)	127.1(8)

Torsion angles	
Mo(1)–C(15)–C(16)–C(17)	−132(1)
Mo(1)–C(16)–C(17)–C(20)	−135.9(8)
Mo(2)–C(16)–C(17)–C(18)	−79(1)
C(15)–C(16)–C(17)–C(18)	159(1)
S(2)–C(21)–C(20)–C(17)	−25(1)
Mo(1)–C(16)–C(17)–C(18)	46(1)
Mo(2)–C(15)–C(16)–C(17)	1347(1)
Mo(2)–C(16)–C(17)–C(20)	97(1)
C(15)–C(16)–C(17)–C(20)	−23(1)
S(3)–C(25)–C(19)–C(18)	6(1)

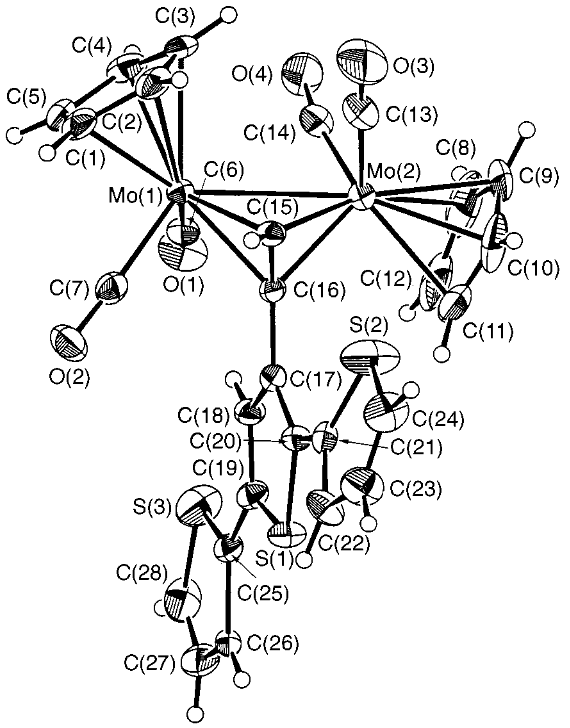


Fig. 1 Crystal structure of complex **1a**. The thermal ellipsoids are drawn at the 30% probability level

used with **II**. The stereogenic reaction of compound **IIIa** with [$Mo_2(\eta-C_5H_5)_2(CO)_4$] in toluene at room temperature furnished the complex *erythro*-**1a** with C_1 symmetry in 75% yield. The complex *erythro*-**1b** was obtained in 25% yield from coupling with 3′-(phenylethynyl)terthiophene **IIIb** at 80 °C. The latter reaction at room temperature gave **1b** in only poor yield (<5%) due to the low reactivity of the phenyl-substituted carbon–carbon triple bond. Generally [$Mo_2(\eta-C_5H_5)_2(CO)_4$] shows low reactivity toward diaryl-substituted acetylenes.[16] Complexes **1a** and **1b** are soluble in $CHCl_3$ and toluene, and moderately soluble in hexane. In the solid state they appear stable on exposure to moisture and air, but in solution are slowly decomposed.

Spectroscopic data for complexes **1a** and **1b** are given in the Experimental section. Their IR spectra exhibit two terminal carbonyl stretching bands (1995, 1905 cm^{-1} for **1a**; 2000, 1930 cm^{-1} for **1b**) and one semibridging carbonyl (1837 cm^{-1} for **1a**, 1845 cm^{-1} for **1b**). In the ^{13}C NMR spectra the carbonyl carbon resonances are centered at δ 229.4 and 230.9 for **1a** and 232.5 and 233.1 for **1b**. These spectral data fall in the ranges of those previously reported for dimolybdenum carbonyl complexes.[16,17] While the parent ion appears in the mass spectrum of **1a**, the spectrum of **1b** shows a strong M − 2CO peak instead of the molecular ion. Both complexes exhibit sequential loss of carbonyls with strong ions corresponding to the loss of four carbonyls (M − 4CO). Such successive CO losses and the bare metal species as strong peaks are often observed for structurally related complexes.[18]

The crystal structure of complex **1a** is depicted in Fig. 1, and the key molecular parameters are given in Table 2. Both of the π bonds, Mo(1)–C(16) and Mo(2)–C(16), on the bimetallic complex unit depart significantly from coplanarity to the middle thiophene ring [torsion angle Mo(1)–C(16)–C(17)–C(18) 46(1), Mo(2)–C(16)–C(17)–C(20) 97(1)°]. Such out-of-coplanarity results from the internal crowding in the molecule, which is commonly observable for the perpendicular bimetallic acetylene complexes.[16] The C(16)–C(17) bond length is 1.49(1) Å, which falls into the range for a single bond. The present structural characteristics with respect to the coplanarity and the bond length indicate that there is no π-type interaction between the terthiophene and the complex unit.

Electrochemistry

A cyclic voltammogram (ν = 100 mV s^{-1}) of complex **1a** in CH_2Cl_2 exhibits three discrete, highly irreversible electrode processes [Fig. 2(a)]. By comparison with the redox properties of terthiophene[19] as a reference compound, the process having E_{pa} = 1.43 V can be assigned to the terthiophene moiety. The cyclic voltammograms of heterol monomers generally show highly irreversible redox waves due to the deposition of electrochemically active polymer films on the electrode surface. Two irreversible processes at more negative potentials, E_{pa} = 0.50 and 0.84 V, are associated with the oxidation of the complex core to the radical cation, $Mo_2^{\bullet +}$ and dication, Mo_2^{2+}, respectively. The cyclic voltammogram of **1b** also exhibits three redox waves [Fig. 2(b)]. The irreversible process at E_{pa} = 1.27 V is

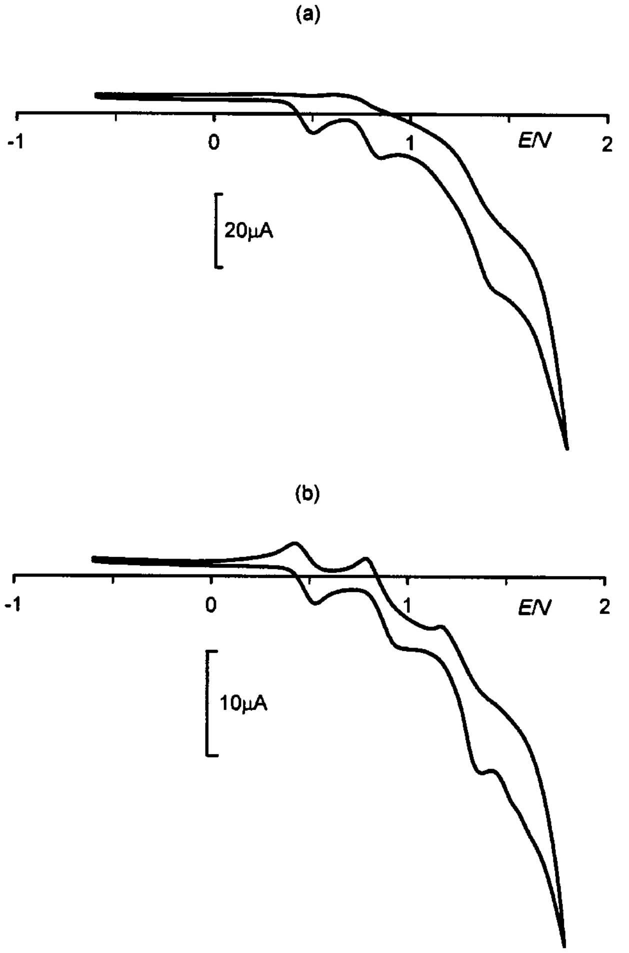


Fig. 2 Single-sweep cyclic voltammograms of (a) complex **1a** and (b) **1b**. Scan rate: 100 mV s^{-1}

assigned to the terthiophene. The redox processes (E_{pa} = 0.47 V for $Mo_2^{\bullet+}$, 0.86 V for Mo_2^{2+}) are electrochemically more reversible than the corresponding electrode processes of **1a**. In contrast to the highly irreversible processes of the complex core of **1a**, the observed more reversible behavior of the core of **1b** is attributed to the higher stability from the dispersion of the extra charge into the incorporated phenyl ring. Although the peak separations for the core-based processes are characteristically larger than the theoretical value, 59 mV, for a reversible process (ΔE_p = 120 mV for $Mo_2^{\bullet+}$, 170 mV for Mo_2^{2+}), the process may be essentially reversible in that a large deviation from the theoretical value is generally observed in cluster electrochemistry[20] and has previously been attributed to uncompensated junction potentials, poisoning of the electrode and/or a slow rate of electron transfer on Pt.[21] Connelly's group[22] investigated the redox properties of some similar bimetallic complexes, $[Mo_2(\eta^5\text{-}L)_2(CO)_4\{\mu\text{-}\eta^2\!:\!\eta^2\text{-}C(R^1)\equiv C(R^2)\}]$ (L = C_5H_5 or C_5Me_5), by cyclic voltammetry. They reported that the peak position and reversibility of the electrode process was variable depending on the substituents. The complexes of the C_5Me_5 system exhibit two reversible redox peaks which are corresponding to the formation of the stable monocation and dication. In the case of C_5H_5-substituted complexes the oxidation process corresponding to the formation of the dication was irreversible. However, in the present study, **1b** having C_5H_5 shows two reversible redox peaks indicating the formation of a stable monocation and dication. To the best of our knowledge, **1b** is the first example of a C_5H_5 complex of this type (as opposed to C_5Me_5) to show two reversible redox chemistry.

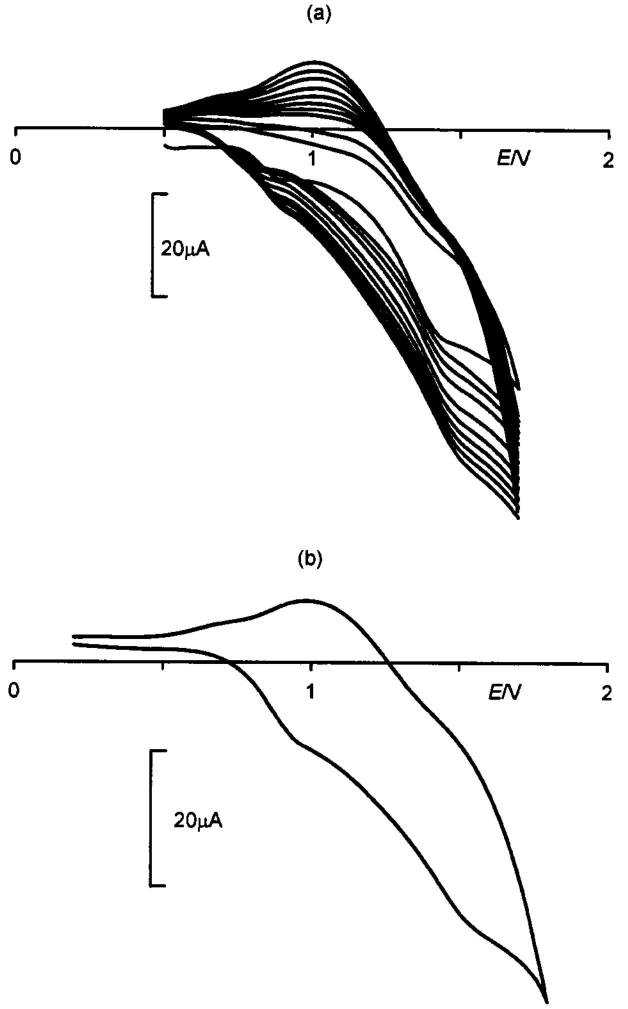


Fig. 3 (a) Electropolymerization of complex **1a** by 20 repeated potential scans and (b) cyclic voltammogram of an electrode modified by the polymer films of **1a**. Scan rate: 100 mV s^{-1}

Electrochemically active, polymer films of complex **1a** could be grown on the platinum electrode surface by repetitive cycling over the potential range from 0.80 to 1.50 V [Fig. 3(a)]. After 20 repetitive scans the modified electrodes were thoroughly rinsed with CH_2Cl_2, dried under vacuum, and studied by cyclic voltammetry. As shown in Fig. 3(b), a single-sweep cyclic voltammogram (ν = 100 mV s^{-1}) of the polymer films exhibits totally irreversible processes due to their high instability. Similarly prepared, polymer films of **1b** reveal significantly more reversible, electrochemical behavior than that of **1a** (Fig. 4). The redox waves of the Mo_2^0–$Mo_2^{\bullet+}$ and $Mo_2^{\bullet+}$–Mo_2^{2+} couples are centered at 0.48 and 0.83 V, respectively. The observed difference between the two films is also attributed to the more effective charge dispersion of the core bound by the phenyl ring compared to the unbound as observed in the cyclic voltammograms of the monomers. In the cyclic voltammograms of the polymer films grown from **1b** the wave positions of the core show no substantial shifts from the corresponding process of the monomers. This indicates that not only the structure of the monomers is essentially kept intact, but also there is no coplanarity of the core with the π-conjugated backbone and thus no π-type electronic interaction between the components. The coplanarity of the core with the backbone must cause a large shift of the redox waves of the core as a result of the extensive charge delocalization over the system.[23] The out-of-planarity of the bimetallic core with the terthiophene backbone is further supported by the X-ray diffraction data.

Absorption spectra

The absorption spectral data of complexes **1a**, **b** and their polymeric films deposited on ITO glass are shown in Fig. 5, together with those of **IIIa** and **IIIb** for comparison. The

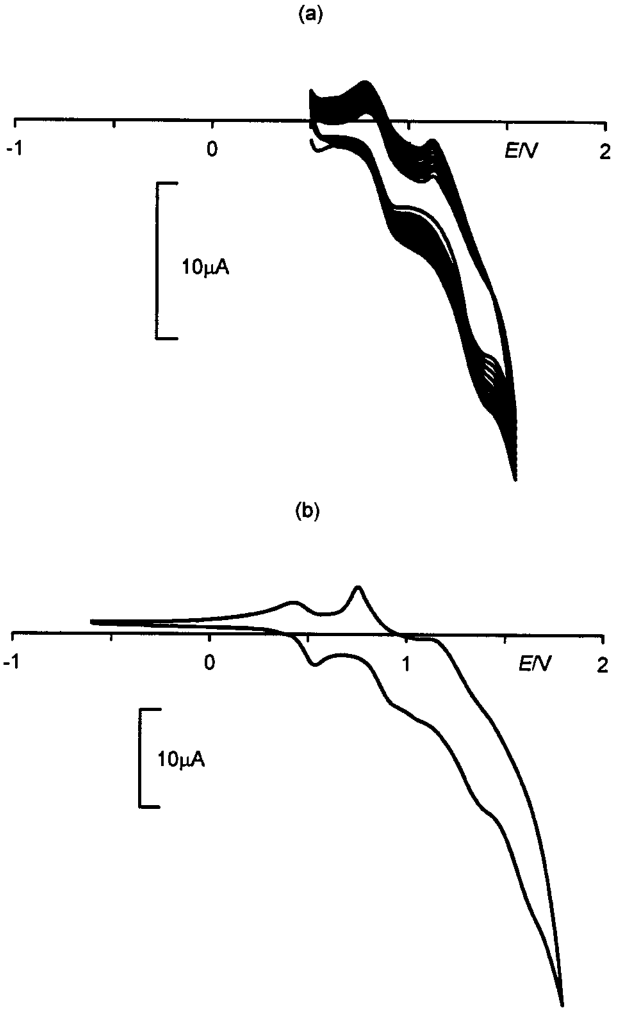


Fig. 4 (a) Electropolymerization of complex **1b** by 20 repeated potential scans and (b) cyclic voltammogram of an electrode modified by the polymer films of **1b**. Scan rate: 100 mV s^{-1}

absorption spectrum of **IIIa** 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 a π–π* localized excitation of the thiophene ring[24] while the lower energy band is attributed to a π–π* transition in the conjugated π system.[25] These two bands are generally observed for oligothiophenes. The absorption spectrum of **IIIb** in CHCl$_3$ also exhibits two bands; an intense, high energy band at 309 nm and a moderately intense low energy band at 376 nm. In the absorption spectrum of **1a** in CHCl$_3$ the π–π* localized excitation of the thiophene ring shifted to the high energy UV region below 250 nm while the π–π* transition of the conjugated π system is blue-shifted by *ca.* 60 nm from that of **IIIa**. This effect is ascribed to the distortion of the terthiophene π system caused by steric hindrance between the bulky complex unit at the 3′ position of the central thiophene and sulfur atoms of the adjacent two thiophenes in their *anti* conformation. A new band at 345 and a lower energy, weak band at 538 nm have been previously assigned to the $\sigma \longrightarrow \sigma^*$ transition for the molybdenum–acetylenic carbon bond and the $d_\pi \longrightarrow d_{\pi^*}$ transition for the Mo–Mo bond, respectively.[6a,26] Binding the complex unit to **IIIb** results in the aspects similar to **1a** in the absorption spectrum. The π–π* localized excitation of the thiophene ring shifts to the higher energy UV region below 250 nm while the π–π* transition of the conjugated π system is blue-shifted by *ca.* 70 nm from that of **IIIb**. The $\sigma \longrightarrow \sigma^*$ transition is buried in the low energy tail of the π–π* transition of the terthiophene π system and the $d_\pi \longrightarrow d_{\pi^*}$ transition is centered at 538 nm. In each optimized absorption spectrum of the polymer films electrochemically deposited on ITO glass from **1a** and **1b** the π–π* transition of the conjugated π system is red-shifted *ca.* 30 nm from those of the monomers as a result of the elongation of the conjugation by the polymerization. The new broad, strong intensity band (ranging from 350 to 600 nm for the polymer from **1a**, from 400 to 600 nm for that from **1b**) cannot be clearly assigned at present. One plausible origin may be intermolecular charge-transfer transitions in the closely contacted state of the polymer molecules but a clear-cut identification must await further research.

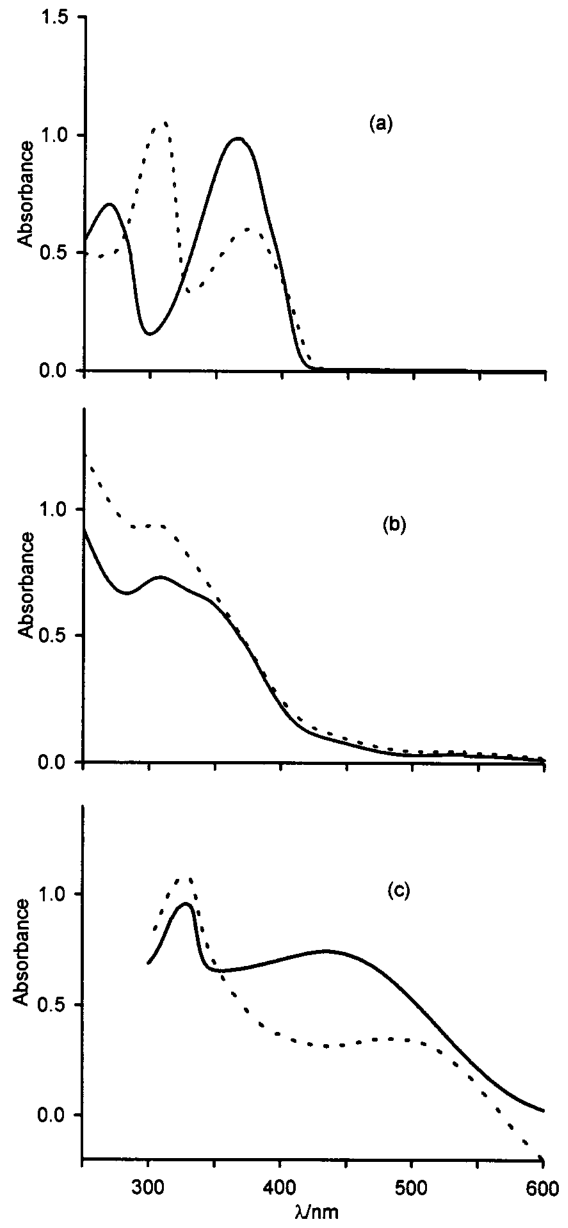


Fig. 5 Absorption spectra of 3.0 × 10^{-5} M solutions of (a) compounds **IIIa** (——) and **IIIb** (······), (b) **1a** (——) and **1b** (······) in CHCl$_3$, and (c) polymer films of **1a** (——) and **1b** (······) on ITO glasses

Conclusion

Terthiophenes bearing pendant organotransition metal complexes, *erythro*-[Mo$_2$(η-C$_5$H$_5$)$_2$(CO)$_4${μ-η^2:η^2-C(R)≡C[C$_4$HS-(C$_4$H$_3$S-2)$_2$-2,5]}] (R = H, **1a** or Ph **1b**) were prepared by a reaction of [Mo$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$] with 3′-alkynylterthiophenes. The Mo–C$_{\text{acetylenic}}$ π bonds of the complex unit in **1a** significantly depart from coplanarity to the middle thiophene ring as a result of the internal crowding in the molecule. Electrochemically active, polymer films of **1a** could be grown on a platinum electrode surface by repetitive cycling over the potential range from 0.80 to 1.50 V. While **1a** shows a totally irreversible electrode process, **1b** reveals a more reversible process which is attributed to the higher stability arising from the dispersion of the extra charge of the complex core into the incorporated phenyl ring. A similar trend is also observed in their polymer films. The absorption spectra of **1a** and **1b** exhibit the $\sigma \longrightarrow \sigma^*$ transition of the molybdenum–acetylenic carbon bond and the $d_\pi \longrightarrow d_{\pi^*}$ transition of the Mo–Mo bond, respectively. The absorption spectra of the corresponding polymer films reveal a $\pi \longrightarrow \pi^*$ transition of the polymer backbone and a new broad, strong intensity band, respectively.

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