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Journal of Organometallic Chemistry 599 (2000) 232–237

Synthesis and physical properties of α,ω-bis[$Co_2(CO)_6\{\mu$-$\eta^2{:}\eta^2$-C(R)≡C$\}$]oligothiophenes

Taeg Sung Jung [a], Joo Hwan Kim [b], Eun Kyung Jang [a], Dong Hyun Kim [a],
Yoon-Bo Shim [b], Bongjin Park [c], Sung Chul Shin [a,*]

[a] *Department of Chemistry and Division of Applied Life Science, Gyeongsang National University, Chinju 660-701, South Korea*
[b] *Department of Chemistry, Pusan National University, Pusan 609-735, South Korea*
[c] *Department of Chemistry, Sunmoon University, Tangjung Myun Kalsanli 100, Asan, Choongnam 336-840, South Korea*

Received 9 November 1999; received in revised form 21 December 1999; accepted 24 December 1999

Abstract

α,ω-Bis[$Co_2(CO)_6\{\mu$-$\eta^2{:}\eta^2$-C(R)≡C$\}$]oligothiophene derivatives (**6**–**10**), in which two dicobalt hexacarbonyl acetylides are π-conjugated onto both terminals of the oligothiophene, were prepared by the reaction of the α,ω-bis(alkynyl)oligothiophenes (**1**–**5**) with $Co_2(CO)_8$. The molecular structures of new compounds were identified by spectroscopic methods and elemental analysis. In cyclic voltammetry of the clusters **6**–**10**, two oligothiophene-based oxidation processes (one for **7**) occur between -0.2 and 1.5 V, and the one reductive process of the metal cluster moieties occurs between 0.0 and -1.6 V, which is not present for the oligothiophenes (**1**–**5**). The silence of the expected electronic communication of the clusters **6**–**10** may be attributed to the reduction process followed by fast chemical reactions at ambient temperature. The clusters **6**–**10** commonly exhibit three characteristic bands: a moderately intense, high-energy band, strong medium-energy band and weak-low energy band. The high-energy bands are attributed to the a π–π^* localized excitation. The medium- and low-energy bands may be ascribed to the metal-to-ligand (d_{Co}–π^*_{ligand}) charge-transfer transitions of the cluster moiety.

Keywords: Cyclic voltammetry; Conducting polymers; Cluster; Oligothiophenes

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1. Introduction

There is currently a widespread interest in thiophene-based conducting polymers because of their interesting physicochemical properties and potential applications to molecular devices [1,2]. Many properties of the polythiophenes have been studied extensively via oligothiophenes because they exhibit similar electrochemical behaviors, and their well-defined molecular structure can be related directly to the observed properties of the corresponding polythiophenes [3,4]. A variety of substituents have been grafted into the oligothiophenes to tune their physical properties [3,4]. π-Conjugation of organo-transition-metal moieties into the oligothiophene should provide interesting models that possess unique properties, being impossible via classical organic functionalities. Specific properties of such molecular systems will result primarily from the ability for the synergistic interaction of the transition-metal d-orbital with the conjugated π-orbital of the oligothiophene [5–9]. Limited examples of the oligothiophene-based organo-transition metals have been reported [3,10–12]. In order to investigate how the organocobalt cluster unit can modulate the physical properties of the oligothiophenes, we have prepared a series of α,ω-bis[$Co_2(CO)_6\{\mu$-$\eta^2{:}\eta^2$-C(R)≡C$\}$]oligothiophene derivatives, in which two dicobalt hexacarbonyl acetylides are π-conjugated onto both terminals of the oligothiophene, and studied their spectroscopic and electrochemical behavior.

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[*] Corresponding author. Fax: +82-591-7616022.
E-mail address: scshin@nongae.gsnu.ac.kr (S.C. Shin)

0022-328X/00/$ - see front matter
PII: S0022-328X(00)00003-6

2. Experimental

2.1. Materials

Reagent grade tetrahydrofuran (THF) was dried and distilled under nitrogen from sodium benzophenone ketyl, and diisopropylamine was degassed prior to use. All other chemicals were purchased from the Aldrich Chemical Co. and were used as received. Column chromatography was performed on Kiesel gel 60 (230–400 mesh). 2,5-Dibromothiophene, 2,5′-dibromobithiophene, and 2,5″-dibromoterthiophene were prepared according to the known procedures [13].

2.2. Measurements

Melting points was uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ were recorded on a Brucker DRX 500 spectrometer using $SiMe_4$ as an internal standard. Infrared spectra were taken on a Hitachi 270-50 spectrometer with KBr disc and UV–vis absorption spectra on a Gilford RESPONSETM spectrophotometer. Mass spectra and elemental analyses were performed at the Analytical Center of Gyeongsang National University. The electrochemical 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 the alkynylated oligothiophene and the acetylide clusters was 1.5 mM. Cyclic voltammetry was performed with a Pine Instruments Bipotentiostat, model AFRDE4. A platinum disc (2 mm outside diameter) was used as a working electrode, a platinum wire as a counter, and an Ag|AgCl wire as a reference electrodes; this was internally calibrated versus the chemical redox couple of ferrocene|ferrocenium [14].

2.3. Preparations

2.3.1. 2,5-Bis(1-hexynyl)thiophene (**1**)

To a mixture of 2,5-dibromothiophene (4.80 g, 20 mmol), $Pd(dppf)Cl_2$ (0.33 g, 2 mol%), and CuI (114 mg, 3 mol%) in degassed diisopropylamine (300 ml) was added 1-hexyne (4.93 g, 60 mmol). The reaction mixture was refluxed with stirring for 12 h under N_2 atmosphere. Water was poured onto the reaction mixture 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 silica gel column using *n*-hexane to give 3.0 g (61% yield) of **1** as a yellow oil. ^{1}H-NMR: δ 0.93 (t, $J = 7.3$ Hz, 6H, $-CH_3$), 1.43–1.60 (m, 8H, $-CH_2-$), 2.41 (t, $J = 7.1$ Hz, 4H, $\equiv C-CH_2-$), 6.90 (s, 2H, thienyl). ^{13}C-NMR: δ 14.0, 19.8, 22.4, 31.0, 73.9, 95.3, 124.7, 131.0. IR: 2228 cm^{-1}. MS: *m*/*z* 244 [M$^+$]. HRMS: *m*/*z* Anal. Calc. for $C_{16}H_{20}S$, 244.1286; Found, 244.1279%.

2.3.2. 2,5-Bis(phenylethynyl)thiophene (**2**)

The same procedure used with **1** was performed from 2,5-dibromothiophene (2.4 g, 1.2 mmol) and phenylacetylene (2.2 g, 2.3 mmol), affording 1.9 g (67%) of **2** as yellow solids. m.p.: 83–83.5°C. ^{1}H-NMR: δ 7.14 (s, 2H, thienyl), 7.32–7.52 (m, 10H, phenyl). ^{13}C-NMR: δ 82.9, 94.6, 123.2, 125.2, 129.0, 129.2, 132.0, 132.4. IR: 2197 cm^{-1}. MS: *m*/*z* 284 [M$^+$]. HRMS: *m*/*z* Anal. Calc. for $C_{20}H_{12}S$, 284.0660; Found, 284.0661%.

2.3.3. 2,5′-Bis(1-hexynyl)bithiophene (**3**)

The same procedure used with **1** was performed from 2,5′-dibromobithiophene (6.48 g, 20 mmol) and 1-hexyne (6.57 g, 80 mmol), affording 4.2 g (64%) of **3** as yellow solids. m.p.: 33–33.5°C. ^{1}H-NMR: δ 0.94 (t, $J = 7.3$ Hz, 6H, $-CH_3$), 1.44–1.60 (m, 8H, $-CH_2-$), 2.43 (t, $J = 7.1$ Hz, 4H, $\equiv C-CH_2-$), 6.96 (dd, $J = 3.8$, 4.0 Hz, 4H, thienyl). ^{13}C-NMR: δ 13.6 19.5, 22.0, 30.6, 73.6, 96.0, 97.7, 123.4, 131.7, 136.9. IR: 2220 cm^{-1}. MS: *m*/*z* 326 [M$^+$]. HRMS: *m*/*z* Anal. Calc. for $C_{20}H_{22}S_2$, 326.1163; Found, 326.1158%.

2.3.4. 2,5′-Bis(phenylethynyl)bithiophene (**4**)

The same procedure used with **1** was performed from 2,5′-dibromobithiophene (2.0 g, 6.2 mmol) and phenylacetylene (1.3 g, 12.4 mmol), affording 1.7 g (62%) of **4** as yellow solids. m.p.: 164–164.5°C. ^{1}H-NMR: δ 7.13 (dd, $J = 3.8$, 4.0 Hz, 4H, thienyl), 7.34–7.52 (m, 10H, phenyl). ^{13}C-NMR: δ 82.5, 94.6, 122.7, 122.8, 124.0, 128.4, 128.6, 131.4, 132.8, 138.1 IR: 2194 cm^{-1}. MS: *m*/*z* 366 [M$^+$]. HRMS: *m*/*z* Anal. Calc. for $C_{24}H_{14}S_2$, 366.0540; Found, 366.0545%.

2.3.5. 2,5″-Bis(1-hexynyl)terthiophene (**5**)

The same procedure used with **1** was performed from 2,5″-dibromoterthiophene (2.0 g, 5 mmol) and 1-hexyne (0.93 g, 11 mmol), affording 1.5 g (73%) of **5** as yellow solids. m.p.: 93–93.5°C. ^{1}H-NMR: δ 0.95 (t, $J = 7.3$ Hz, 6H, $-CH_3$), 1.45–1.61 (m, 8H, $-CH_2-$), 2.44 (t, $J = 7.1$ Hz, 4H, $\equiv C-CH_2-$), 6.97–7.02 (m, 6H, thienyl). ^{13}C-NMR: δ 13.6 19.5, 22.1, 30.6, 73.6, 96.1, 123.2, 123.3, 124.5, 131.8, 136.0, 137.0. IR: 2228 cm^{-1}. MS: *m*/*z* 408 [M$^+$]. HRMS: *m*/*z* Anal. Calc. for $C_{24}H_{24}S_3$, 408.1040; Found, 408.1035%.

2.3.6. 2,5-Bis[$Co_2(CO)_6\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(C_4H_9)\equiv C\}$]thiophene (**6**)

To a THF solution (20 ml) of $Co_2(CO)_8$ (4.2 mmol) was added 2,5-bis(1-hexynyl)thiophene (**1**) (0.49 g, 2.0 mmol) at room temperature (r.t.) under N_2 atmosphere, and after confirmation of the disappearance of the starting **1** by TLC (in most case within 1 h), the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column using *n*-hexane to give 1.57 g (96% yield) of **6** as dark-red solids. m.p.: 46–47°C. ^{1}H-NMR: δ 1.01 (br, t, 6H, $-CH_3$), 1.55–1.75 (br, m, 8H, $-CH_2-$), 2.98 (br, t, 4H, $-CH_2-$), 7.12 (br, s, 2H, thienyl). ^{13}C-NMR: δ 13.9, 22.8, 33.7, 34.0, 81.3, 101.2, 129.9, 142.7, 199.3. IR: 2088, 2050, 2026, 2005 cm^{-1}. MS: m/z 816 [M$^+$], 815 [M − 1], 787 [M − CO], 759 [M − 2CO], 731 [M − 3CO], 703 [M − 4CO], 677 [M − 5CO], 647 [M − 6CO], 619 [M − 7CO], 591 [M − 8CO], 563 [M − 9CO], 535 [M − 10CO], 507 [M − 11CO], 479 [M − 12CO]. Anal. Calc. for $C_{20}H_{20}Co_4O_{12}S$: C, 41.20; H, 2.47; S, 3.93. Found: C, 40.94; H, 2.22; S, 3.81%.

2.3.7. 2,5-Bis[$Co_2(CO)_6\{\mu$-η^2:η^2-C(Ph)≡C$\}$]thiophene (*7*)

The same procedure as that used for **6** was performed with 2,5-bis(phenylethynyl)thiophene (**2**) (0.5 g, 1.76 mmol), affording 1.4 g (96%) of **7** as dark-red solids. m.p.: 97–98°C. ^{1}H-NMR: δ 7.26 (br, s, 2H, thiophene), 7.38 (br. m, 10H, phenyl). ^{13}C-NMR: δ 81.3, 92.2, 128.2, 129.0, 129.3, 129.9, 137.9, 143.3, 198.8. IR: 2084, 2054, 2030, 1998 cm^{-1}. MS: m/z 856 [M$^+$], 828 [M − CO], 800 [M − 2CO], 772 [M − 3CO], 744 [M − 4CO], 715 [M − 5CO], 687 [M − 6CO], 659 [M − 7CO], 632 [M − 8CO], 604 [M − 9CO], 547 [M − 10CO], 519 [M − 11CO]. Anal. Calc. for $C_{32}H_{12}Co_4O_{12}S$: C, 44.90; H, 1.41; S, 3.75. Found: C, 45.03; H, 1.33; S, 3.94%.

2.3.8. 2,5′-Bis[$Co_2(CO)_6\{\mu$-η^2:η^2-C(C_4H_9)≡C$\}$]-bithiophene (*8*)

The same procedure as that used for **6** was performed with 2,5′-bis(1-hexynyl)bithiophene (**3**) (0.5 g, 1.53 mmol), affording 1.3 g (94%) of **8** as dark-red solids. m.p.: 101–102°C. ^{1}H-NMR: δ 1.02 (br. t, 6H, $-CH_3$), 1.56–1.75 (br. m, 8H, $-CH_2-$), 2.99 (br. t, 4H, $-CH_2$), 7.09–7.13 (br, dd, 4H, $-CH_2-$). ^{13}C-NMR: δ 13.5, 22.5, 33.4, 33.6, 80.8, 100.7, 124.4, 129.2, 137.5, 140.9, 198.9. IR: 2087, 2052, 2003, 2019 cm^{-1}. MS: m/z 898 [M$^+$], 870 [M − CO], 842 [M − 2CO], 814 [M − 3CO], 786 [M − 4CO], 730 [M − 6CO], 702 [M − 7CO], 674 [M − 8CO], 646 [M − 9CO], 619 [M − 10CO], 590 [M − 11CO], 562 [M − 12CO]. Anal. Calc. for $C_{32}H_{22}Co_4O_{12}S_2$: C, 42.78; H, 2.47; S, 7.14. Found: C, 43.04; H, 2.26; S, 7.24%.

2.3.9. 2,5′-Bis[$Co_2(CO)_6\{\mu$-η^2:η^2-C(Ph)≡C$\}$]bithiophene (*9*)

The same procedure as that used for **6** was performed with 2,5′-bis(phenylethynyl)bithiophene (**4**) (0.5 g, 1.36 mmol), affording 1.1g (%) of **9** as dark-red solids. m.p. (dec.): 178°C. ^{1}H-NMR: δ 7.13–7.69 (br. m, 14H, thienyl + phenyl). ^{13}C-NMR: δ 81.9, 92.7, 125.4, 128.8, 129.5, 129.6, 130.2, 138.3, 138.5, 142.0, 199.2. IR: 2087, 2052, 2023, 2004 cm^{-1}. MS: m/z 938 [M$^+$], 937 [M − 1], 909 [M − CO], 853 [M − 3CO], 825 [M − 4CO], 797 [M − 5CO], 769 [M − 6CO], 741 [M − 7CO], 713 [M − 8CO], 657 [M − 10CO], 629 [M − 11CO]. Anal. Calc. for $C_{36}H_{14}Co_4O_{12}S_2$: C, 46.08; H, 1.50; S, 6.83. Found: C, 45.81; H, 1.81; S, 7.09%.

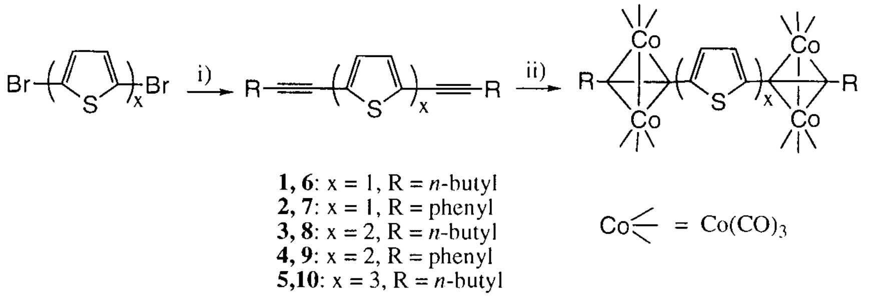
2.3.10. 2,5″-Bis[$Co_2(CO)_6\{\mu$-η^2:η^2-C(C_4H_9)≡C$\}$]-terthiophene (*10*)

The same procedure as that used for **6** was performed with 2,5″-bis(1-hexynyl)terthiophene (**5**) (0.6 g, 1.50 mmol), affording 1.3 g (88%) of **10** as dark-red solids. m.p.: 86–87°C. ^{1}H-NMR: δ 1.03 (br. t, 6H, $-CH_3$), 1.56–1.75 (br. m, 8H, $-CH_2-$), 3.00 (br. t, 4H, $-CH_2$), 7.08–7.14 (br. m, 6H, thienyl). ^{13}C-NMR: δ 14.3, 23.3, 34.2, 34.4, 81.6, 101.6, 123.8, 125.0, 129.9, 136.7, 138.3, 141.5, 199.7. IR: 2085, 2046, 2026, 2009 cm^{-1}. MS: m/z 980 [M$^+$]. Anal. Calc. for $C_{36}H_{24}Co_4O_{12}S_3$: C, 44.10; H, 2.47; S, 9.81. Found: C, 43.92; H, 2.30; S, 10.14%.

3. Results and discussion

3.1. Synthesis

The acetylide clusters (**6**–**10**) were synthesized in a two-step procedure involving the preparation of the alkynylated oligothiophenes (**1**–**5**) using the Heck-type coupling [15] followed by organocobaltization as shown in Scheme 1. Thus, the oligothiophenes **1**–**5** were ob-



1, 6: x = 1, R = *n*-butyl
2, 7: x = 1, R = phenyl
3, 8: x = 2, R = *n*-butyl
4, 9: x = 2, R = phenyl
5,10: x = 3, R = *n*-butyl

Scheme 1. Reaction conditions: (i) R–C≡CH, Pd(dppf)Cl_2, CuI, diisopropylamine, reflux; (ii) $Co_2(CO)_8$, THF, r.t.

Table 1
Cyclic voltammetry data in CH_2Cl_2 for α,ω-bis(1-alkynyl)oligothiophenes (**1**–**5**) and α,ω-bis[$Co_2(CO)_6${μ-η^2:η^2-C(R)≡C}]oligothiophenes (**6**–**10**) [a]

	$E^1_{p.a}$ (V) [b]	$E^2_{p.a}$ (V) [b]	$E_{p.c}$ (V) [c]
1 [d]	1.67		
2 [d]	1.56		
3 [d]	1.30		
4 [d]	1.31	1.44	
5 [d]	1.14		
6	0.74	1.16	−1.06
7	0.87		−0.97
8	0.89	1.15	−1.08
9	0.78	0.96	−1.07
10	0.72	1.28	−0.96

[a] Measured at room temperature with a scan rate of 100 mV s^{-1} in 0.1 M TBAP at a Pt electrode.

[b] Anodic peak potentials for these irreversible processes.

[c] Cathodic peak potentials for these irreversible processes.

[d] No reduction processes were observed this compound between 0 and −1.6 V.

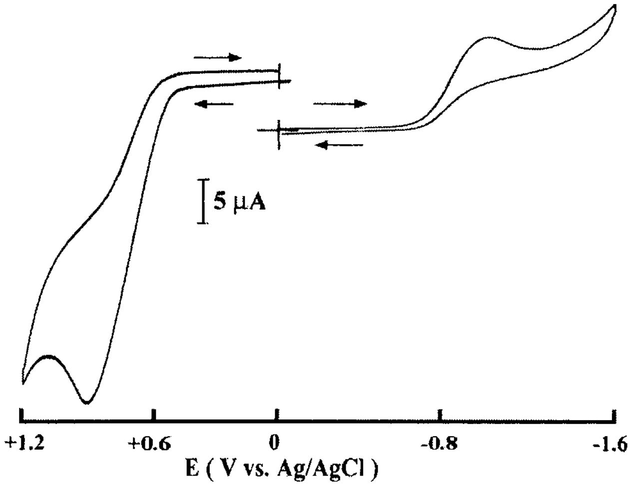


Fig. 1. Cyclic voltammograms of the cluster **7** in CH_2Cl_2, 0.1 M TBAP, at 100 mV s^{-1} at a Pt electrode.

tained in 61–73% yields by coupling of α,ω-dibromooligothiophenes with 1-alkynes in the presence of [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II)] [Pd(dppf)Cl_2] and CuI in diisopropylamine, respectively. The oligothiophenes **1**–**5** were treated with two equivalents of $Co_2(CO)_8$ at r.t. in THF within 1 h to give the clusters **6**–**10** in nearly quantitative yields, respectively. In all cases the reactions were monitored by TLC, showing the disappearance of the starting oligothiophene. All the clusters **6**–**10**, as dark-red solids, were purified by chromatography. They are stable in air as solids, highly soluble in nonpolar organic solvents and slightly soluble in polar solvents.

3.2. Spectroscopy

The IR spectra of the clusters **6**–**10** exhibit four characteristic bands (five bands for **6**) in the terminal carbonyl stretching region, as reported previously for similar acetylide clusters [16]. The C≡C stretching band of the oligothiophenes is merged into the strong carbonyl peaks of the acetylide clusters. The ^{1}H-NMR spectra of the clusters **6**–**10** show line-broadening of all the peaks due to the quadrupolar relaxation of the ^{59}Co-nuclei [17]. All ring protons of the clusters **6**–**10** are shifted downfield slightly from those of the corresponding alkynylated oligothiophenes, due to the strong electron-withdrawing effect of the cobalt carbonyl moieties. The shift amount of the alkyl resonances of the clusters **6**, **8** and **10** decreases gradually as they get farther from the cluster moiety. The ^{13}C-NMR spectra of the clusters **6**–**10** also show downfield shift of the resonances and one unique, broad signal due to the carbonyl groups bound directly to cobalt metal around 200 ppm, respectively. As generally observed for metal carbonyl complexes, the mass spectra of the clusters **6**–**10** exhibit in addition to the molecular ion, successive CO losses (except for **10**) and a peak consistent with the loss of one hydrogen atom [18–20].

3.3. Electrochemical studies

The cyclic voltammetric (CV) data of the oligothiophenes **1**–**5** and clusters **6**–**10** are given in Table 1, and as a typical CV of **7** are presented in Fig. 1. The CVs of the oligothiophenes **1**–**3** and **5** in dichloromethane solution exhibit one highly irreversible oxidation process (two for **4**), respectively. In comparison with previous reports for other α-capped oligothiophenes, the oxidations are consistent with processes that result in radical cation for **1**–**3** and **5**, and sequential formation of radical cation and dication for **4** [11,21–23]. The oxidation potential for the formation of radical cation decreases gradually on going from **1** to **3** to **5** in the hexynyl substituted oligothiophenes and from **2** to **4** in the phenethynyl substituted those, indicating the decrease of the π-conjugation length in serial order.

The clusters **6**–**10** exhibit two oligothiophene-based oxidation processes (one for **7**) between −0.2 and 1.5 V, and the one reductive process of the metal cluster moieties between 0.0 and −1.6 V that is not present for the oligothiophenes **1**–**5**. The systems in which two transition-metal redox centers are covalently spanned by π-conjugated organic spacer often undergo an extensive electronic mixing between the metal d-orbitals and the spacer π-orbitals. Those systems generally produce two well-resolved waves in their CVs as the result of the electronic communication between the metal centers [24–27]. Since the present clusters **6**–**10** undergo only a single irreversible reduction process, the redox centers of clusters appear not to see each other. The silence of the electronic communication may be attributed to the reduction process followed by fast chemical reactions: i.e. an EC mechanism. This is compared with $\Delta E°$ for the closely related systems [R–C≡C–(R)–C≡C–R]-$[Co_2(CO)_6]_2$ (R = Ph, ferrocenyl, (R) = naphthyl etc.) [12], whose competing EC reactions involving the primary radical anions are quenched below −80°C and two distinct reversible couples (electronic communication between the two equivalent $Co_2(CO)_6$ centers) can be discerned. The result of Ref. [12] suggests that there might be a possibility to suppress the EC reactions of the present clusters and observe their electronic communications at very low temperature. However, the low temperature experiment could not be carried out because of our facility limitation.

3.4. UV–vis absorption studies

The electronic spectral data for the energy maxima and the absorption coefficients of the oligothiophenes **1**–**5** and the clusters **6**–**10** in dichloromethane are listed in Table 2, together with those of the corresponding oligothiophene for comparison. Absorption coefficients were obtained from Beer's law studies and determined from at least four dilution points. They basically exhibit a moderately intense high-energy transition and a very intense lower-energy transition. These two bands are generally observed for oligothiophenes; the high-energy bands are attributed to a π–π* localized excitation of the heteronucleus while the broader, lower-energy band is attributed to π–π* transition of the conjugated π-system [28]. They exhibit many fine structures whose numbers are decreased gradually on going from **1** to **3** to **5** in alkynylated oligothiophenes and from **2** to **4** in phenethynyl substituted those. The λ_{max} values of the lower-energy bands are significantly red-shifted on going from **1** to **3** to **5** and from **2** to **4** while the high-energy bands nearly unshifted. The clusters **6**–**10** commonly exhibit three characteristic bands; a moderately intense high-energy band, strong medium-energy band and weak low-energy band. The high-energy bands are attributed to the a π–π* localized excitation. The medium- and low-energy bands may be ascribed to the metal-to-ligand (d_{Co}–π^*_{ligand}) charge transfer transitions of the cluster moiety. The possibility that the medium-energy bands come from the π–π* transition is excluded because their energies are lower than those of the corresponding oligothiophenes **1**–**5**. Since orthogonal incorporation of the cluster to the C≡C triple bond vector partially breaks the π-conjugation, their λ_{max} should blue-shift from those of the alkynylated oligothiophenes. The π–π* transitions of the cluster conjugated systems cannot be identified due to their merging into the strong transitions of d_{Co}–π^*_{ligand}.

Table 2
UV–vis data for α,ω-bis(1-alkynyl)oligothiophenes (**1**–**5**) and α,ω-bis[$Co_2(CO)_6\{\mu$-η^2:η^2-C(R)≡C\}]oligothiophenes (**6**–**10**)

Compounds	λ_{max} (nm)	ε (10^3 M^{-1} cm^{-1}) [a]	CH_2Cl_2 solutions
Thiophene	243		
Bithiophene	243 (11)	302 (12)	
Terthiophene	245 (13)	355 (25)	
1	305 (19)		
2	252 (18)	364 (11)	
3	257 (3)	357 (13)	
4	253 (7)	385 (16)	
5	254 (10)	386 (28)	
6	260 (13) [b]	377 (4) [b]	582 (1)
7	265 (22) [b]	368 (11)	583 (2)
8	254 (11) [b]	403 (8)	576 (2)
9	274 (18) [b]	403 (14)	582 (2)
10	260 (14) [b]	423 (14)	565 (3)

[a] Reported values of ε are not corrected for overlap with other absorption bands.

[b] Shoulder.

Acknowledgements

This work was supported by the Basic Science Research Institute program, Ministry of Education, Korea, 1995 (Project no. BSRI-96-3441), and KOSEF, Korea, 1999 (Grant no. 1999-2-122-001-3).

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