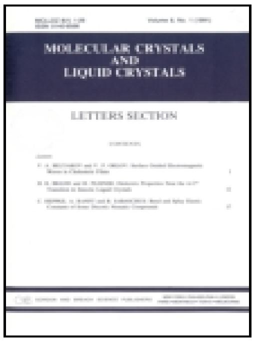

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Photochromic and Electrochromic Properties of Dithienylethene-Based Ruthenium Alkynyl Complexes

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Two new binuclear ruthenium alkynyl complexes with dithienylethene unit $[\{(MePh\text{-}tpy)(PPh_3)_2RuCl\}_2(C{\equiv}C{-}DTE{-}C{\equiv}C)](ClO_4)_2$ (***II-1***) *and* $[Cp^*Ru(dppe)]_2(C{\equiv}C{-}DTE{-}C{\equiv}C)$ (***II-2***) *(*$Cp^* =$ *pentamethylcyclopentadienyl); (DTE = 1,2-bis(2-methylthiophen-3-yl)cyclopentene) were synthesized. Their structures were well confirmed by nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. Their photochromic behaviors and redox properties have also been investigated. The results indicated that the binuclear ruthenium alkynyl complexes* ***II*** *possessed photochromic activity similar to organic DTE derivatives. Electrochemical studies showed that the open-ring isomers of the metal complexes could be triggered by electricity to convert to their closed forms. These investigations clearly suggested that two complexes can be considered as a class of light- and electro-triggered multifunctional molecule switches.*

Keywords Dithienylethene; electrochromism; photochromism; ruthenium alkynyl complexes

Introduction

Due to their potential application in the field of molecular electronics and information storage, photochromic compounds have received increasing attention to perform a molecular switchable function [1]. Among them dithienylethene (DTE) derivatives are the most promising compounds for the application due to their excellent thermal stability, fatigue resistance, and high photochemical quantum yields [2–4]. The representative example is the hexafluoro or hexahydro cyclopentene-based DTE (Scheme 1) [5]. Over the past decades, plenty of dithienylperfluorocyclopentene derivatives have been reported, and some of them have shown good photochromic properties [6–9].

In recent years, searching for the multifunctional switches of the dithienylethene compounds becomes a new goal in this area, an effective method is to modify the structure by attaching the functional groups to the chromic unit, and various attempts have been

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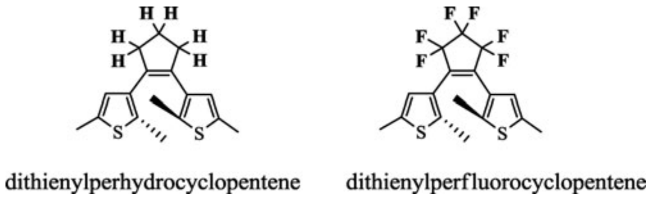
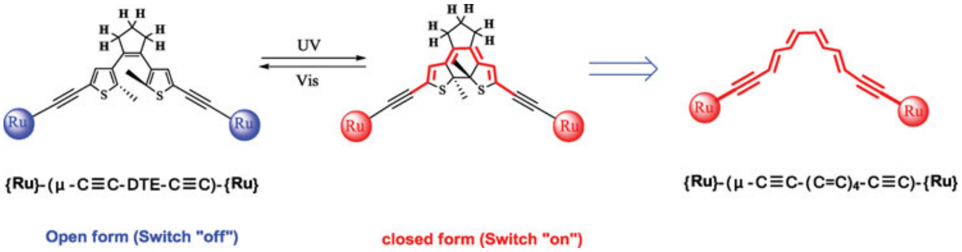


Scheme 1. Two representative examples of DTE photochromic switches.

employed to promote the function of molecules [10–12]. For example, metal complexes system can be potentially applied for the photochromic activity ascribing to their unique properties. Therefore, incorporating the metal to the dithienylethene moiety has drawn much more attention [13–20]. Carbon-rich ruthenium complexes have been involved in the building of original redox active molecular wires, owning to their excellent ability of the system to promote a strong electronic coupling between the metal centers and the conjugated organic ligands [21]. From this viewpoint, we combined the electronic properties of ruthenium fragment and optical properties of DTE (dithienylperhydrocyclopentene) unit in one molecule to achieve multifunctional responsive material. Herein, we described the synthesis and photochromic behavior of two new binuclear ruthenium alkynyl complexes bearing different metal termini (Scheme 2). It has been found that these ruthenium alkynyl complexes exhibited their switchable behavior triggered either by photo- or electrochemical stimuli, providing a means to construct "dual-mode" hybrid optical and electric material.



Scheme 2. Photochromic reactions of ruthenium alkynyl complexes with dithienylethene unit.

Experimental

General

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. Solvents were pre-dried, distilled, and degassed prior to use, except those for spectroscopic measurements, which were of spectroscopic grade. Hexane was distilled under nitrogen from calcium hydride. Methanol was freshly distilled over magnesium-iodine. Triethylamine was freshly distilled over KOH pellets. The starting materials 1,2-bis(5-ethynyl-2-methylthiophen-3-yl)cyclopentene (**I**) [15], {(MePh-tpy)$(PPh_3)_2RuCl$}(ClO_4) [22], and Cp*Ru(dppe)Cl [23] were prepared according to the previously reported methods. Elemental analyses (C, H, and N) were performed by the Microanalytical Services, College of Chemistry, CCNU. ^1H, ^{13}C, and ^{31}P NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to Me_4Si, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

Synthesis of Complex II-1

To a microwave vial (30 mL) were added $\{(MePh\text{-}tpy)(PPh_3)_2RuCl\}(ClO_4)$ (0.48 g, 0.44 mmol) and 1,2-bis(5-ethynyl-2-methylthiophen-3-yl)cyclopentene (0.72 g, 0.20 mmol) under argon atmosphere. The vessel was charged with triethylamine (NEt_3) (1 mL) and methanol (15 mL), and sealed quickly with a microwave tube cap. Under microwave radiation, the mixture was heated on 110 °C for 30 min. Upon cooling to room temperature, the reaction mixture was poured into another flask and evaporated in vacuo. The product was purified by column chromatograph on a silica gel using dichloromethane-acetone (10:1) as eluent to collect deep red band, giving deep red solid product. Yield: 0.12 g, 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (s, 6H, thiophene-Me), 2.06–2.09 (m, 2H, CH_2), 2.45 (s, 6H, ph-Me), 2.84 (t, $J = 7.0$ Hz, 4H, CH_2), 6.60 (s, 2H, thiophene-H), 6.82–7.77 (m, 88H, ph, tpy), 7.96 (d, $J = 8.0$ Hz, 4H, tpy), 8.75 (d, $J = 5.2$ Hz, 4H, tpy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.52, 15.24, 21.32, 38.76, 115.88, 119.93, 122.89, 125.96, 126.42, 126.77, 127.16, 128.12, 129.47, 130.42, 130.70, 130.90, 132.13, 132.84, 133.74, 134.27, 135.35, 136.40, 140.19, 146.96, 154.82, 156.55, 157.82. ^{31}P NMR (160 MHz, $CDCl_3$): δ 26.55 (s). IR (KBr, cm^{-1}): ν 1979m (C≡C), 1090s (ClO_4). Anal. Calcd. for $C_{138}H_{116}Cl_2N_6O_8P_4Ru_2S_2$: C, 67.72; H, 4.78. Found: C, 67.56; H, 5.03.

Synthesis of Complex II-2

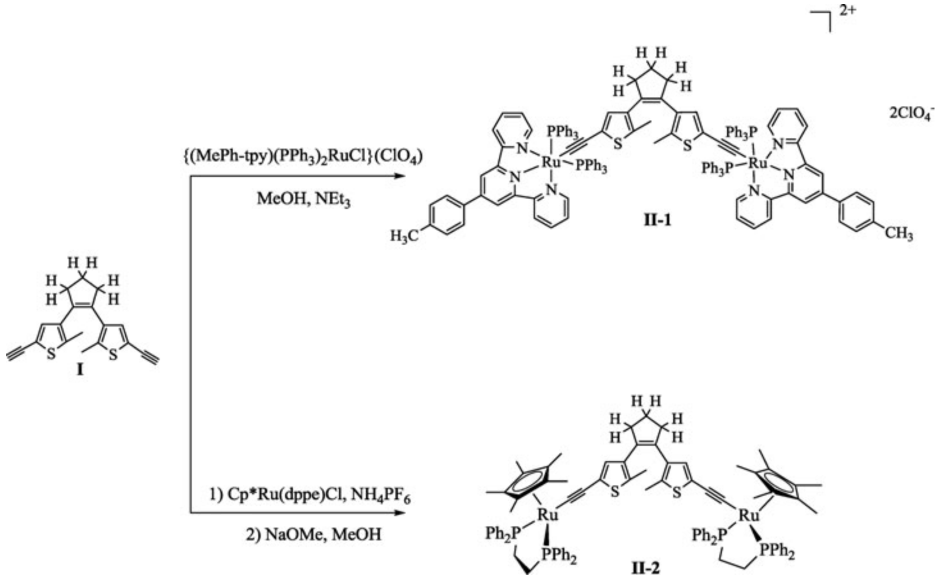
A solution of RuCl(dppe)Cp* (0.20 g, 0.30 mmol) and NH_4PF_6 (0.075 g, 0.45 mmol) in 15 mL of methanol was refluxed for 1 hr under Ar_2. After cooling to room temperature, 1,2-bis(5-ethynyl-2-methylthiophen-3-yl)cyclopentene (0.046 g, 0.15 mmol) was added, and the mixture was stirred for another 8 hr. The resulting suspension was filtered and the filtrate was transferred to another two-neck bottle under an argon atmosphere, then MeONa (1 mL, 0.1 mol/L) was added to generate a large number of precipitation immediately, which was collected by filtration, washed with hexane, and dried under vacuum to give a light green solid (0.14 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (s, 30H, Cp*), 1.78 (s, 6H, CH_3), 1.82–1.88 (m, 2H, CH_2), 1.94–1.97 (m, 4H, CH_2), 2.46–2.52 (m, 4H, CH_2), 2.66–2.70 (m, 4H, CH_2), 6.02 (s, 2H, thiophene-H), 7.18–7.70 (m, 40H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.51(C_5Me_5), 14.62, 22.32, 31.21(dppe), 38.16, 92.7, 114.52, 118.23, 122.03, 122.98, 124.56, 125.34, 126.54, 126.89, 128.34, 134.13, 135.14, 136.56, 137.74, 138.16. ^{31}P NMR (160 MHz, $CDCl_3$): δ 78.44 (s). IR (KBr/cm^{-1}): ν (C≡C) 2056 w. Anal. Calcd. for $C_{93}H_{98}P_4Ru_2S_2$: C, 69.55; H, 6.15. Found: C, 69.32; H, 6.29.

Results and Discussion

Synthesis and Characterization

The binuclear ruthenium alkynyl complex linked by DTE unit **II-1** was successfully synthesized by the reaction of terminal acetylene precursor 1,2-bis(5-ethynyl-2-methylthiophen-3-yl)cyclopentene with two equivalents of $\{(MePh\text{-}tpy)(PPh_3)_2RuCl\}^+$ in a one-pot process under microwave irradiation. Metallic complexes **II-2** was obtained from diacetylene by reaction with RuCl(dppe)Cp* and in situ deprotonation of the resulting vinylidene complex

(Scheme 3). Both of the target complexes **II** were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and elemental analysis.



Scheme 3. Synthetic routes of complexes **II**.

Photochromic Behaviors

The photochromic behaviors of the binuclear ruthenium alkynyl complexes (**II-1** and **II-2**) were examined by means of UV/vis spectrophotometry, and compared with the metal-free DTE molecule **I**. Both of the synthesized metallic complexes underwent reversible photochromic reactions in dichloromethane upon irradiation with UV light (302 nm) and visible light ($\lambda > 420$ nm) using cutoff filters.

Figure 1 shows the spectral changes of complexes dissolved in dichloromethane solution (2.0×10^{-5} mol·dm^{-3}). For complex **II-1**, the original absorption maximum was appeared at 269, 313, and 496 nm as a result of a π–π^* transition and $d\pi(\text{Ru})\rightarrow\pi^*$ (Phtpy) metal-to-ligand charge transfer (MLCT) transitions. Upon irradiation with light of wavelength 302 nm for 40 min, the system reached a photostationary state (PSS) and the red solution of the open-ring isomer turned green, showing a new broad band in the visible region at 420–680 nm due to the formation of the closed isomer. This green color was returned to red by subsequent irradiation with visible light, owing to the complex reverting to its original open-ring state. This suggested that complex **II-2** undergoes reversible photochromic reactions. Similar spectral changes have also been observed for another dithienylethene complex **II-2**. There is a main peak located at 323 nm before irradiation. Upon illumination at a wavelength of 302 nm, the peak in UV region decreased as well as a new broad band in the visible region increased, whereby the pale yellow solutions of the open-ring isomers turned green. Subsequent irradiation of the colored solution with visible light ($\lambda > 420$ nm) caused a reverse color change to regenerate solutions of the original colors, indicating that the ruthenium alkynyl complex [Cp*Ru(dppe)]$_2$(C≡C−DTE−C≡C) (**II-2**) underwent the same photoisomerization as the

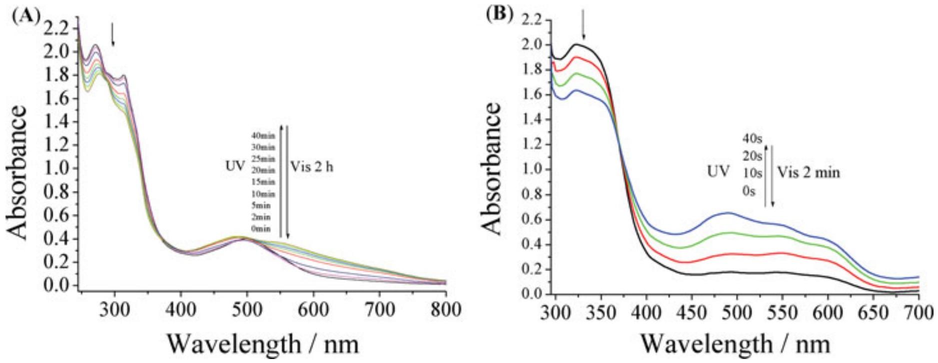


Figure 1. Absorption spectral changes of diarylethene compound by photoirradiation in dichloromethane (2.0×10^{-5} mol·dm^{-3}) at room temperature. (A) **II-1**, (B) **II-2**.

analog [{(MePh-tpy)(PPh$_3$)$_2$RuCl}$_2$(C≡C−DTE−C≡C)](ClO$_4$)$_2$ (**II-1**). However, the reactive rate of the complex **II-2** was faster than that of **II-1**. When the photochemical conversion of samples of approximately 2.0×10^{-5} mol·dm^{-3} was followed by UV/vis spectroscopy (Fig. 1), the photostationary state of the complex **II-1** was attained within 40 sec in contrast to the prolonged irradiation (40 min) required for **II-1**, whereas 60 sec for organic dithienylethene **I**. We deduce that may be the result of the bulky Ru-tpy group, which increases the hindrance to ring closure. Moreover, a similar trend was observed for the reverse process (**IIC→IIO**). It took 2 hr for **II-1** to revert to its open-ring isomer, whereas **II-2** required 2 min. This suggests that ligand had a significant impact on the sensitivity of the ring-closed isomers.

The cyclization/cycloreversion cycle number was also examined in CH$_2$Cl$_2$ at room temperature, as shown in Fig. 2. The metallic complex **II-2** was irradiated alternately with 302 nm and visible light ($\lambda > 420$ nm). No apparent deterioration was observed after repeating this process several times.

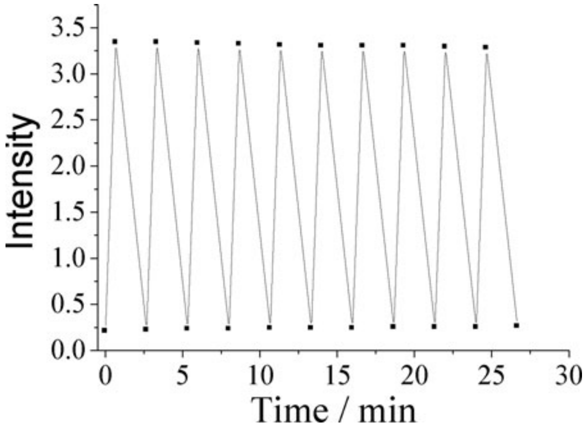


Figure 2. Reversible photochromism of **II-2** monitored by UV-vis spectroscopy ([**II-2**] = 2.0×10^{-5} mol·dm^{-3}; alternating UV (40 s) and visible light (2 min) irradiations) in air atmosphere at room temperature.

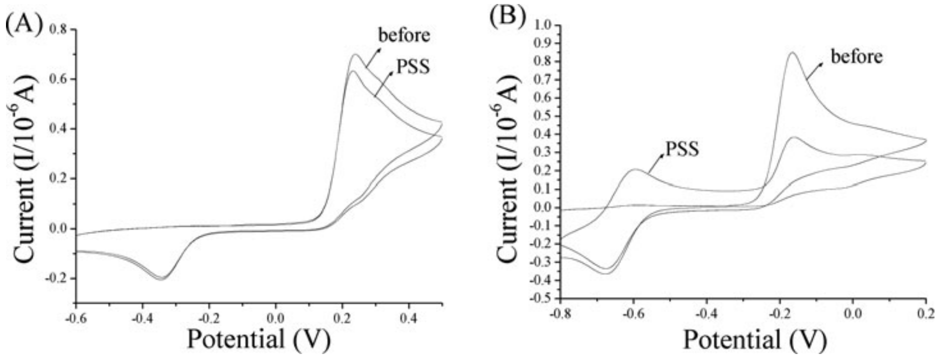


Figure 3. Cyclic voltammograms of complexes **II** in CH_2Cl_2 containing nBu_4NPF_6 (0.1 mol·dm^{-3}), before and after irradiation with 302 nm light at the scan of 100 mV/s. Potentials are given relative to the Ag/Ag$^+$ standard. (A) **II-1**, (B) **II-2**.

Electrochromic Behaviors

The electronic properties and isomerization reaction of the binuclear ruthenium alkynyl complexes (1.0×10^{-3} mol·dm^{-3} in CH_2Cl_2) have been investigated by cyclic voltammetric (CV) techniques using 0.1 mol·dm^{-3} nBu_4NPF_6 as the supporting electrolyte. Typical changes in the cyclic voltammograms of **II-2** before and after irradiation with 302 nm light were shown in Fig. 3. At a scan rate of 0.1 V s^{-1}, an irreversible oxidation wave was observed at −0.16 V, which was attributed to a one-step 2e process of the two non-communicating ruthenium centers in the open isomer. Furthermore, a reduction wave was observed at −0.67 V. Upon irradiation with light of wavelength 302 nm, the system reached PSS. The extent of the interaction between the two metallic termini in the two isomeric forms changed (Scheme 2). Then a new reversible redox wave appeared at less positive potentials ascribing to ruthenium centers in the closed isomer. The redox wave was not well separated as other conjugated bimetallic complexes, maybe because of the long distance between two metallic termini. We noticed that the reduction peak in the ring-open form appeared at the same potential as that for its corresponding ring-closed isomer, suggesting that the cyclization reaction was also triggered by the electrochemical oxidation process. This was in accordance with the findings of Branda's group [24, 25]. The same behavior was observed for complex **II-1** (Fig. 3). Both bis-ruthenium complexes undergo similar electrochemical ring-closing reactions. However, the wave in the ring-closed isomer of **II-1** is irreversible.

Conclusions

Two new binuclear ruthenium alkynyl complexes with dithienylethene unit have been synthesized. We described the photoisomerization reaction of dithienylethene by UV/vis absorption spectra and cyclic voltammograms. The results displayed that these metallic complexes exhibited photochromic activity, and the ligand had a significant impact on the efficiency of the photochromic process. Furthermore, we found that these complexes can also be triggered by electricity to convert to their closed forms. It has clearly been demonstrated that these bis-ruthenium complexes can be used as a class of light- and electrotriggered multifunctional molecule switches.

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