

Photochromic and electrochromic properties of oxo-centred triruthenium compounds with a dithienylethene bis(phosphine) ligand†

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The reaction of 1,2-bis(5-(diphenylphosphino)-2-methylthien-3-yl) cyclopentene (PPh₂-DTE-PPh₂) with the triruthenium cluster precursor [Ru₃O(OAc)₆(py)₂(CH₃OH)](PF₆) (**1**) gave monomeric or dimeric derivatives [Ru₃O(OAc)₆(py)₂{PPh₂-DTE-PPh₂}] (PF₆) (**[2]PF₆**) and [{Ru₃O(OAc)₆(py)₂}-μ-PPh₂-DTE-PPh₂}] (PF₆)₂ (**[3]PF₆**). Reduction of **[2]⁺** and **[3]²⁺** afforded one- or two-electron-reduced neutral products Ru₃O(OAc)₆(py)₂{PPh₂-DTE-PPh₂} (**2**) and {Ru₃O(OAc)₆(py)₂}₂{μ-PPh₂-DTE-PPh₂} (**3**), respectively. These triruthenium complexes show remarkable photochromism through photochemical ring-closing (UV light irradiation) and ring-opening (Vis light irradiation) processes as well as electrochromic properties through oxidation/reduction in the triruthenium cluster. Both the photochromic and electrochromic properties of **2** and **3** are highly reversible.

Introduction

There has been continued interest in the design and synthesis of multifunctional materials for applications in molecular devices and memory media. Much attention has been focused on introducing molecular switch functions into the transition-metal complexes that exhibit multiple physicochemical properties and colour changes in response to UV-Vis irradiation, electricity, or heating, *etc.*^{1–6} A number of mono- and dinuclear metal-terpyridine complexes with dithienylcyclopentene derivatives were synthesized and characterized by Abruña and co-workers.⁷ The studies on the photochromic and electrochromic properties of these transition-metal derivatives showed that their photophysical and electrochemical properties could be tuned by changing the metal centres, the arrangement of metal-terpyridine and dithienylcyclopentenes, and the terminal substituents. Liu and co-workers described diethynyl-substituted dithienylethene bridged carbon-rich dinuclear ruthenium complexes, where the diruthenium complex exhibited multifunctional switching behavior triggered by photo- and/or electrochemical stimuli.⁸

Compared with mono- or dinuclear transition-metal complexes,^{1–8} polynuclear metal cluster moieties are less utilized for the design of molecular photo- and/or electro-switches. Oxo-centred trinuclear ruthenium-carboxylate cluster complexes with the general formula [Ru₃O(OAc)₆(L)(L')(L'')] (*L*, *L'* and *L''* = axial ligand, *n* = 0, 1, 2) are attractive candidates for the design of both photo- and electrochemical driven molecule switches because they exhibit highly delocalised electronic states, multiple redox behavior, intriguing mixed-valence chemistry.^{9–13} The axial ligands are comparatively labile and readily substituted, thus affording an excellent means to control the chemical and electronic properties. This also provides a feasible approach to

use the triruthenium clusters as potential building blocks for constructing molecular-scale electronic and photonic devices.

A judicious selection of the functional switching modules is another important point to modulate the electronic and/or optical properties. The dithienylethene (DTE) derivatives are particularly attractive due to their efficient photochromism and reversibility, thermal stability of both isomers and good fatigue resistance.^{14–20} Furthermore, the DTE derivatives can be used as bridging or pendant ligands for the formation of metal-coordination complexes to produce various multifunctional materials. A number of metal complexes with a bridging or pendant DTE unit have been focused on for investigating photochemical gates, luminescence switches, controlled electron transfers, metal-metal communication, or multicolour-electrochromism.^{7,8,21,22}

Aiming at designing multifunctional molecular switches, we are devoted to the construction of triruthenium clusters derivatives with the DTE unit. In this work, we describe the first example of an oxo-centred trinuclear ruthenium-carboxylate cluster incorporating the DTE-based bis(phosphine) ligand, 1,2-bis(5-(diphenylphosphino)-2-methylthien-3-yl) cyclopentene (PPh₂-DTE-PPh₂). The monomeric Ru₃^{III,III,III} complex [Ru₃O(OAc)₆(py)₂{PPh₂-DTE-PPh₂}] (PF₆) (**[2]PF₆**) and dimeric Ru₃^{III,III,III} complex [{Ru₃O(OAc)₆(py)₂}₂{μ-PPh₂-DTE-PPh₂}] (PF₆)₂ (**[3]PF₆**) as well as the corresponding reduced Ru₃^{III,III,II} complexes Ru₃O(OAc)₆(py)₂{PPh₂-DTE-PPh₂} (**2**) and {Ru₃O(OAc)₆(py)₂}₂{μ-PPh₂-DTE-PPh₂} (**3**) have been isolated and well characterized. The spectroscopic characterization, redox properties, and photochromic and electrochromic behavior are described herein.

Experimental

Synthesis

All manipulations were performed under a dry argon atmosphere using Schlenk techniques. Solvents were dried by standard methods and distilled prior to use except for those of spectroscopic grade for spectroscopic measurements.

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† Electronic supplementary information (ESI) available: ¹H NMR spectral data (Table S1); ¹H NMR spectra (Figs. S1–S4); plots of CV and DPV (Figs. S5); and UV-Vis spectra (Figs. S6–S10). See DOI: 10.1039/b913239b

1,2-bis(5-(diphenylphosphino)-2-methylthien-3-yl)cyclopentene (PPh₂-DTE-PPh₂)²³ and [Ru₃O(OAc)₆(py)₂(CH₃OH)](PF₆) (**1**)²⁴ were prepared according to literature procedures. Other chemicals were commercially available (Alfa Aesar, Acros and Aldrich Chemicals) and used as received.

[Ru₃O(OAc)₆(py)₂{PPh₂-DTE-PPh₂}] (PF₆) (**2**[PF₆]). To a dichloromethane (15 mL) solution of **1** (202.0 mg, 0.20 mmol) was added a dichloromethane (25 mL) solution of PPh₂-DTE-PPh₂ (150.8 mg, 0.24 mmol) with stirring at room temperature for two days. The product was purified by chromatography on a neutral alumina column. The first blue band was collected using dichloromethane–methanol (v/v = 100:1) as eluent. The collected solution was reduced to a minimum volume to give a blue product by diffusion with diethyl ether. Yield: 80% (256.8 mg). Anal. Calcd. for C₆₁H₆₂F₆N₂O₁₃P₃Ru₃S₂: C, 45.64; H, 3.89; N, 1.74. Found: C, 45.40; H, 3.95; N, 1.79. ES-MS: *m/z* (%) 1460 (100) [M – PF₆]⁺.

[Ru₃O(OAc)₆(py)₂{PPh₂-DTE-PPh₂}] (**2**). To a dichloromethane–methanol (v/v 1:15, 16 mL) solution containing **2**[PF₆] (160.5 mg, 0.10 mmol) was added dropwise a 50% aqueous solution of hydrazine (7.5 mL, 0.15 mol), producing a green precipitate. After stirring for 30 min, the precipitate was collected, washed with water and dried *in vacuo*. The product was recrystallized from dichloromethane–petroleum ether. Yield: 90% (131.4 mg). Anal. Calcd. for C₆₁H₆₂N₂O₁₃P₃Ru₃S₂: C, 50.17; H, 4.28; N, 1.92. Found: C, 50.25; H, 4.21; N, 1.85. ES-MS: *m/z* (%) 1461 (100) [M + 1]⁺.

{[Ru₃O(OAc)₆(py)₂]{PPh₂-DTE-PPh₂}] (PF₆)₂ (**3**[PF₆]). To a dichloromethane (10 mL) solution of **1** (222.0 mg, 0.22 mmol) was added a dichloromethane (15 mL) solution of PPh₂-DTE-PPh₂ (62.8 mg, 0.10 mmol) with stirring at room temperature for two days. The product was purified by chromatography on a neutral alumina column. The second blue band was collected using dichloromethane–methanol (v/v 100:1) as eluent. The solution was reduced to a minimum volume to give a blue product by diffusion of diethyl ether. Yield: 82% (211.7 mg). Anal. Calcd. for C₈₃H₉₀F₁₂N₄O₂₆P₄Ru₆S₂: C, 38.61; H, 3.51; N, 2.17. Found: C, 38.52; H, 3.60; N, 2.12. ES-MS: *m/z* (%) 1146 (100) [M – 2PF₆]²⁺.

{[Ru₃O(OAc)₆(py)₂]{PPh₂-DTE-PPh₂}] (**3**). Complex **3** was prepared by the same synthetic procedure as that for **2** except that complex **3**[PF₆] was used in place of **2**[PF₆]. Yield: 92%. Calcd. for C₈₃H₉₀N₄O₂₆P₄Ru₆S₂: C, 43.49; H, 3.96; N, 2.44. Found: C, 43.40; H, 3.91; N, 2.49. ES-MS: *m/z* (%) 2293 (100) [M + 1]⁺.

Physical measurements

Elemental analyses (C, H, N) were carried out on a Perkin-Elmer model 240C automatic instrument. Electrospray mass spectra (ES-MS) were recorded on a Finnigan DECAX-30000 LCQ mass spectrometer using dichloromethane–methanol as mobile phase. ¹H NMR spectra were performed on a Bruker Avance III-400 spectrometer with SiMe₄ as the internal reference.

Spectroscopic measurements

The UV-Vis-NIR absorption spectra were measured on a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer at room temperature with a conventional 1.0 cm quartz cell. The UV irradiations were performed with a standard lamp used for visualizing TLC

plates. The visible irradiations were carried out using the light of a 200-W tungsten source that was passed through the appropriate cutoff filter to eliminate higher energy light.

Electrochemical measurements

The cyclic voltammogram (CV) and differential pulse voltammogram (DPV) were made with a Princeton Applied Research Potentiostat/Galvanostat Model 263A in acetonitrile solutions containing 0.1 M (Bu₄N)PF₆ as supporting electrolyte. CV was performed at a scan rate of 100 mV s^{−1}. DPV was measured at a rate of 20 mV s^{−1} with a pulse height of 40 mV. Platinum wire and glassy graphite were used as counter and working electrodes, respectively, and the potentials were measured against an Ag/AgCl reference electrode. The potential measured was always referenced to the half-wave potentials of the ferrocenium/ferrocene (*E*_{1/2} = 0) couple. Controlled-potential electrolyses were performed in a two-compartment electrochemical cell with a glass frit junction of fine porosity under an argon atmosphere. The working and the counter electrodes were platinum mesh, and the potential was referenced to an Ag/AgCl reference electrode. All the reactions and handling of the compound were carried out with exclusion of light.

Results and discussion

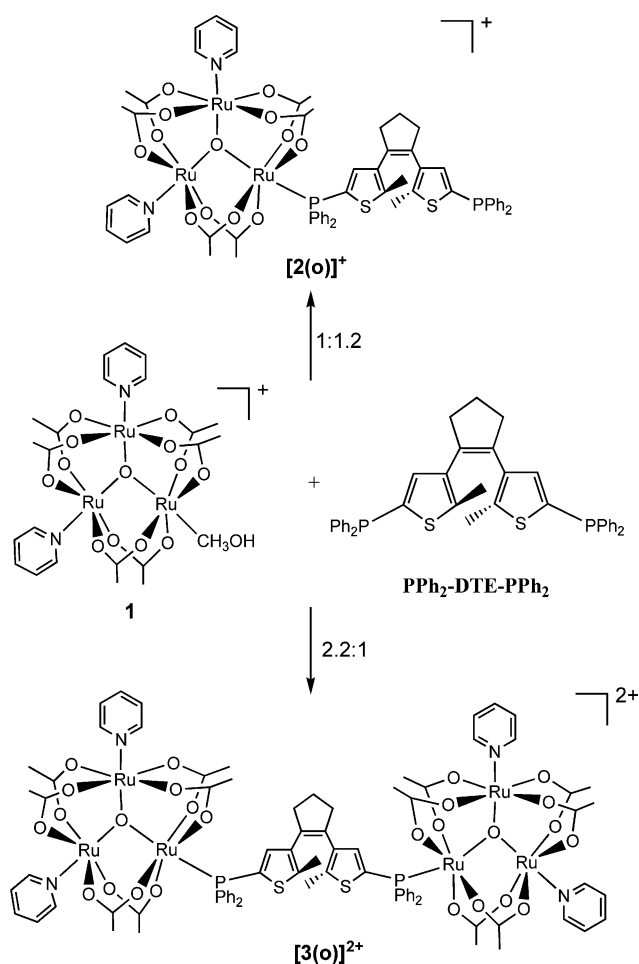
Synthesis and characterization

As shown in Scheme 1, the monomeric triruthenium complex **2(o)**⁺ was readily obtained by reaction of bis(phosphine)-substituted dithienylethene (PPh₂-DTE-PPh₂) with 0.8 equiv of the solvent-coordinated triruthenium clusters [Ru₃O(OAc)₆(py)₂(CH₃OH)](PF₆) (**1**). When the molar ratio of **1** and PPh₂-DTE-PPh₂ was 2.2:1, the main product was the PPh₂-DTE-PPh₂-linked dimeric complex **3(o)**²⁺. The products were readily purified by alumina column chromatography. Reduction of the monomeric and dimeric complexes **2(o)**⁺ and **3(o)**²⁺ using hydrazine gave one- and two-electron-reduced neutral compounds **2(o)** and **3(o)**, respectively.

These complexes were characterized by elemental analyses, ES-MS spectrometry, UV-Vis-NIR, ¹H NMR spectroscopy, and cyclic and differential pulse voltammetry. Elemental analyses (C, H, N) coincide well with the calculated values for all the compounds. Positive ion ES-MS of **2(o)**⁺ and **3(o)**²⁺ showed the corresponding molecular ion fragments [M – PF₆]⁺ or [M – 2PF₆]²⁺ as the principal peaks, respectively, whereas the molecular ion peak [M]⁺ was detected as the base peak for the neutral complex **2(o)** or **3(o)**.

¹H NMR spectra. The ¹H NMR spectral data of paramagnetic 1+ complex **2(o)**⁺, 2+ species **3(o)**²⁺, and reduced neutral products **2(o)** and **3(o)** together with the tentative assignments are collected in Table S1 (ESI†) for the purposes of comparison. ¹H NMR spectral of these complexes are presented as Figs. S1–S4 (ESI†).

Because of the influence of unpaired electron, obvious paramagnetic shifts were detected in the ¹H NMR spectra of 1+ or 2+ compounds compared with those in the corresponding neutral reduced products with diamagnetism. The acetate methyl protons can readily be recognized by comparison of their peak intensity relative to that of the pyridine protons. Acetate methyl protons in



Scheme 1 Synthetic routes to **2** and **3**.

paramagnetic species $[2(o)]^+$ and $[3(o)]^{2+}$ occur in the range 0.898–9.658 ppm, contrasting strikingly with those in the diamagnetic neutral compounds **2(o)** and **3(o)** (1.296–2.133 ppm). Compared with those observed in $[Ru_3O(OAc)_6(py)_3]^+$,^{9,10,24,25} the proton peaks of pyridine in these complexes are tentatively assigned. The proton peaks of pyridine in $[2(o)]^+$ exhibit two set of the *meta* protons, while the *ortho* and *para* proton peaks are overlapped. $[3(o)]^{2+}$ shows three set of separate peaks for the *meta* protons, two set of separate peaks for the *ortho* and *para* protons and one overlapped peaks for the remaining *ortho* and *para* protons. This is likely due to the spatially non-equivalence of the two $Ru_3O(OAc)_6(py)_2$ moieties in $[3(o)]^{2+}$. In contrast, the two axially bonded pyridine ligands in the $Ru_3O(OAc)_6(py)_2$ units of **2(o)** and **3(o)** are spatially equivalent to afford one set of *ortho*, *meta* and *para* protons.

The methyl proton signal of the DTE unit is a singlet at 2.278 ppm for $[2(o)]^+$, 2.351 ppm for $[3(o)]^{2+}$, 2.075 ppm for **2(o)**, and 2.049 ppm for **3(o)**, respectively. For $[2(o)]^+$, the methylene protons displayed three sets of separate triplet peaks at 2.233, 2.847 and 3.005 ppm, respectively. Compounds $[3(o)]^{2+}$, **2(o)** and **3(o)** showed two sets of separate triplet peaks for the methylene protons of the DTE units at 2.370 and 3.099 ppm for $[3(o)]^{2+}$, 0.886 and 2.739 ppm for **2(o)**, and 1.298 and 2.714 ppm for **3(o)**. It is noteworthy that the methyl and methylene protons of the neutral reduced complexes **2(o)** and **3(o)** showed a slight upfield

shift compared with those of 1+ or 2+ compounds $[2(o)]^+$ or $[3(o)]^{2+}$. The thienyl-H resonances of $[2(o)]^+$, $[3(o)]^{2+}$ and **2(o)** were observed at 6.324–7.323 ppm as two sets of peaks, respectively, while that of compound **3(o)** was detected at 7.449 ppm as a doublet. Consequently, the 1H NMR data indicated a symmetrical structure for neutral reduced **3(o)**, but an unsymmetrical structure for the corresponding 2+ complex $[3(o)]^{2+}$.

Upon irradiation with a UV light at 254 nm, the resonance signals of the ring-opening DTE unit of $[2(o)]^+$ were attenuated with the appearance of new signals due to the ring closed form $[2(c)]^+$ as indicated in Fig. 1. After the irradiated system reached the photostationary state, the composition of $[2(c)]^+:[2(o)]^+$ is 0.4:1 deduced from 1H NMR spectral variations. Similarly, the ratio of the ring-closed and ring-open forms of $[3]^{2+}$ was estimated as 0.3:1. As a result, the ratios between the ring-closed and ring-open forms for $[2]^+$ (0.4:1) and $[3]^{2+}$ (0.3:1) are slightly lower than that of the free ligand PPh_2 -DTE- PPh_2 (0.42:1).²³

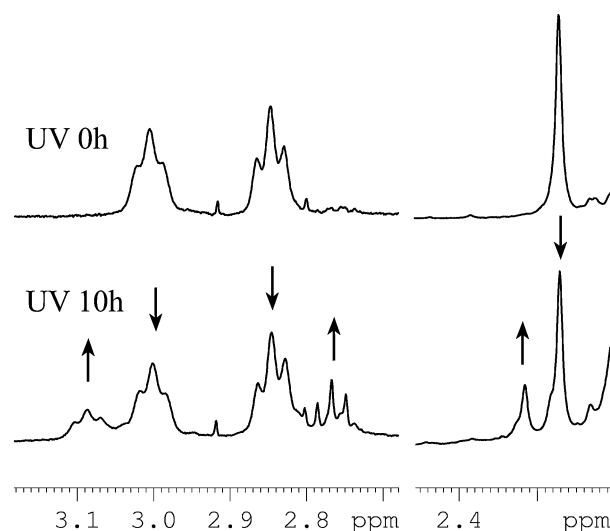


Fig. 1 1H NMR spectra of $[2]^+$ in CD_3CN before and after UV irradiation at 254 nm to the photostationary state.

Redox and electrochromic properties. Redox properties of $[2(o)]^+$ and $[3(o)]^{2+}$ were measured by cyclic and differential pulse voltammetry in acetonitrile solution containing 0.1 M $(Bu_4N)(PF_6)$. Electrochromic behavior was investigated through controlled-potential electrolyses in a two-compartment electrochemical cell with a glass frit junction of fine porosity under an argon atmosphere.

As shown in Fig. 2, the monomeric triruthenium complex $[2(o)]^+$ exhibits three reversible redox waves at +0.66, −0.50 and −1.78 V, ascribable to successive one-electron redox processes $[Ru_3^{IV,III,III}]^{2+}/[Ru_3^{III,III,III}]^+$, $[Ru_3^{III,III,III}]^+/[Ru_3^{III,III,III}]^0$ and $[Ru_3^{III,III,III}]^0/[Ru_3^{III,II,II}]^-$, respectively. For the dimeric complex $[3(o)]^{2+}$ containing two identical $Ru_3O(OAc)_6(py)_2$ moieties linked by PPh_2 -DTE- PPh_2 , three reversible redox waves were detected at similar potentials as those for the monomeric compound $[2(o)]^+$. The peak current, however, is nearly doubled in the dimeric species $[3(o)]^{2+}$ compared with that of the monomeric compound $[2(o)]^+$. This suggests that redox splitting due to cluster–cluster electronic interaction between two identical triruthenium moieties

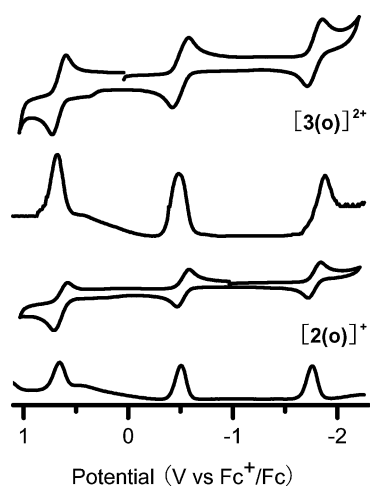


Fig. 2 Plots of cyclic and differential pulse voltammograms for compounds $[2(o)]^+$ and $[3(o)]^{2+}$ in 0.1M acetonitrile solution of $(Bu_4N)(PF_6)$. The scan rates are 100 mV s^{-1} for CV and 20 mV s^{-1} for DPV.

across a bridging PPh_2 -DTE- PPh_2 in $[3(o)]^{2+}$ was inappreciable and irresolvable by CV and DPV measurements.

Upon electrolysis of an acetonitrile solution of the complex $[2(c)]^+$ or $[3(o)]^{2+}$ at -0.70 V (vs Fc^+/Fc), the solution colour changed from dark cyan to green yellow with a 60–250 nm red-shift (Table 1) of low-energy absorption bands in the corresponding UV-vis spectra (Fig. 3). One- or two-electron reduction of the 1+ complex $[2(c)]^+$ or the 2+ species $[3(o)]^{2+}$ to neutral $2(o)$ or $3(o)$ led to an obvious colour change and a distinct spectral response (Fig. 3).

Upon UV light irradiation of $[2(o)]^+$ or $[3(o)]^{2+}$, the ring-open DTE unit is transformed to a ring-closed form to give $[2(c)]^+$ and $[3(c)]^{2+}$, respectively. Significant changes of the redox waves were unobserved in comparison with those of the corresponding ring-open $[2(o)]^+$ or $[3(o)]^{2+}$ (Fig. S5, ESI†). It appears that the ring-closed PPh_2 -DTE- PPh_2 linker is still unfavourable for

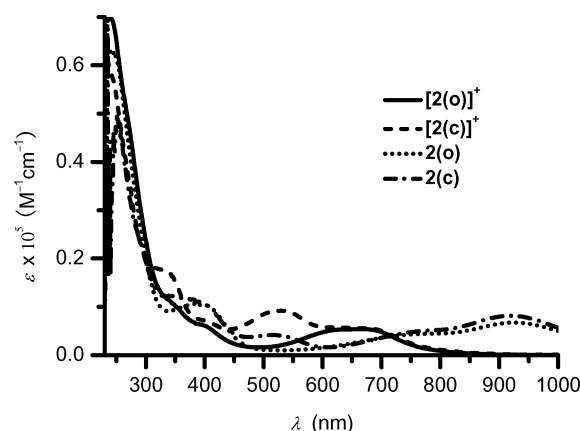


Fig. 3 UV-Vis absorption spectra of $[2(o)]^+$, $2(o)$, $[2(c)]^+$, and $2(c)$ at a concentration of $1.0 \times 10^{-5}\text{ M}$ in dichloromethane.

cluster-cluster interactions between two oxo-centred triruthenium moieties.

Controlled-potential electrolysis performed on $[2(c)]^+$ or $[3(c)]^{2+}$ led to the formation of one- or two-electron-reduced ring-closed $2(c)$ or $3(c)$ with a colour change from purplish blue to sienna. Electrochemical interconversion between $[2(c)]^+$ and $2(c)$, and between $[3(c)]^{2+}$ and $3(c)$ are highly reversible (Scheme 2) with a significant spectral response (Fig. 3) and vivid colour changes (Fig. 4).

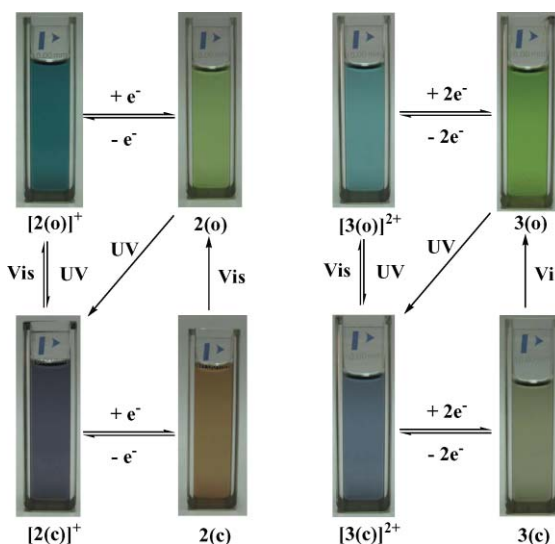


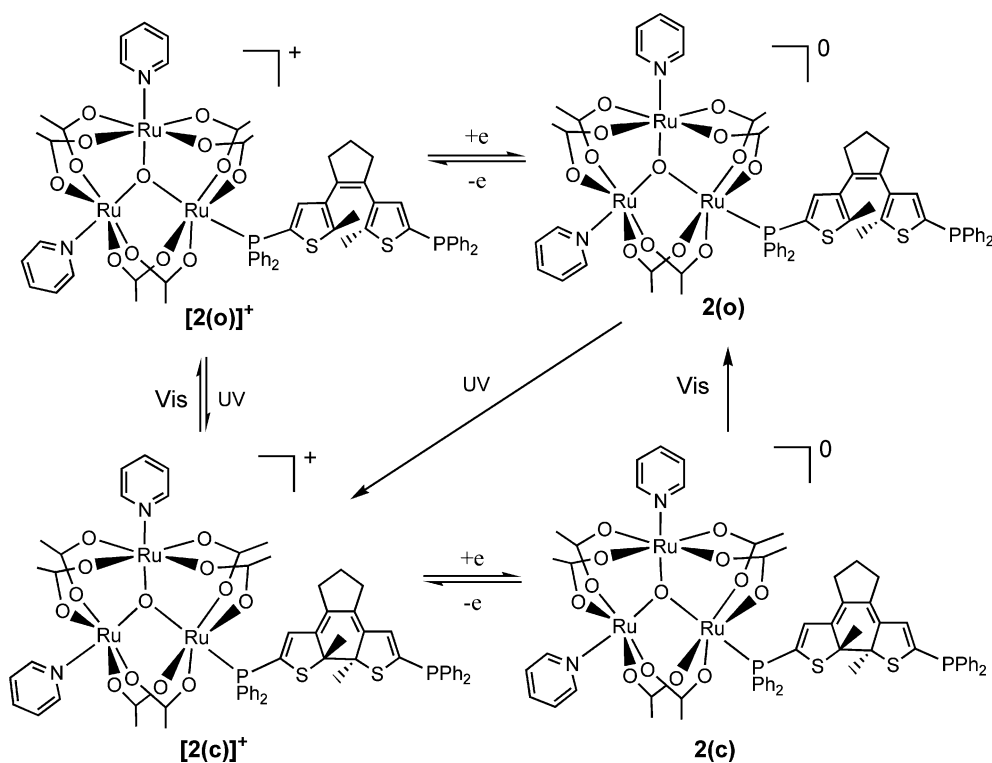
Fig. 4 Photograph of the colour changes of **2** and **3** by the photo- and electrochemical interconversions.

Table 1 UV-Vis absorption spectral data in dichloromethane

| | $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) | | |
|---------------|--|-------------------|--------------------------|
| | DTE-based transitions | CLCT ^a | IC ^b |
| $[2(o)]^+$ | 230 (70200) | 400 (6100) | 669 (5400) |
| $[2(c)]^+$ | 230 (67400) 335 (17400) 530 (9200) | 398 (7120) | 669 (5600) |
| $2(o)$ | 241 (63100) | 396 (10400) | 767 (4400) 920 (6700) |
| $2(c)$ | 251 (49400) 349 (12300) 514 (4100) | 390 (11000) | 770 (5000) 920 (8100) |
| $[3(o)]^{2+}$ | 230 (71800) | 401 (7900) | 673 (6400) |
| $[3(c)]^{2+}$ | 230 (70600) 338 (16200) 540 (5200) ^c | 398 (7600) | 629 (7100) |
| $3(o)$ | 230 (76800) | 402 (13600) | 731 (5900) 921 (8600) |
| $3(c)$ | 230 (73300) 339 (15400) 534 (4800) | 397 (13700) | 733 (5800) 921 (8200) |

^a CLCT is cluster-to-ligand charge transfer transition. ^b IC is an intracuster transition.

Absorption and photochromic properties. The UV-Vis absorption spectra of $[2(o)]^+$, $2(o)$, $[2(c)]^+$, and $2(c)$ are depicted in Fig. 3. The photochromic behaviour was examined through the changes in the absorption spectra upon irradiation with a specific wavelength of light in a 1 cm cell. All these complexes underwent reversible photochromic reactions in dichloromethane by alternating irradiation with UV light at 254 nm and visible light at $>500\text{ nm}$ with cutoff filters. Table 1 presents the electronic absorption spectral data of the open- and closed-ring DTE compounds in dichloromethane. Photochemical and electrochemical



Scheme 2 Photochemical and electrochemical interconversion processes of **2**.

interconversion processes for **2** are depicted in Scheme 2. The photographs of the colour changes of **2** and **3** by the photo- and electrochemical reactions are presented in Fig. 4.

Complex **[2(o)]⁺** showed three absorption bands centred at 230, 400 and 669 nm (Fig. 3). The intense band in the UV region corresponds to the $S_0 \rightarrow S_1$ transition localized on the DTE unit.⁷ The low-energy broad absorption band centred at 669 nm can be assigned to the transition from occupied nonbonding orbitals to vacant antibonding orbitals arising from intracluster charge transfer (IC) transitions.⁹ The shoulder at 400 nm probably arises from cluster-to-ligand charge transfer (CLCT) transitions from the occupied d_π orbitals of the triruthenium cluster to the lowest unoccupied π^* orbitals of the DTE unit.⁹

Upon irradiation with a UV light at 254 nm for 15 min, the system reached a photostationary state and the dark cyan solution of the open-ring isomer **[2(o)]⁺** turned to purplish blue, where two new broad bands centred at 335 and 530 nm were detected along with the decrease of the absorption band at 230 nm due to formation of the closed isomer **[2(c)]⁺** as indicated in Fig. 5. The $S_0 \rightarrow S_1$ absorption of the ring-closed isomer of the DTE moiety shifts from 230 to 530 nm due to better conjugation in the closed form than that in the open form.⁷ The band at 335 nm is ascribable to the $S_0 \rightarrow S_2$ transition of the closed form in the DTE unit.⁷ Upon irradiation with a visible light at 500 nm, the purplish blue solution reverted to dark cyan within 30 min, indicating that the closed-ring state transformed to the original open-ring state.

Electrochemical reduction of **[2(o)]⁺** at -0.70 V (vs Fc^+/Fc) gave the one-electron-reduced neutral compound **2(o)** with a colour change from dark cyan to green yellow (Fig. 4). As shown in Fig. 3, the low-energy bands of one-electron-reduced neutral species **2(o)** or **2(c)** are remarkably red-shifted compared with

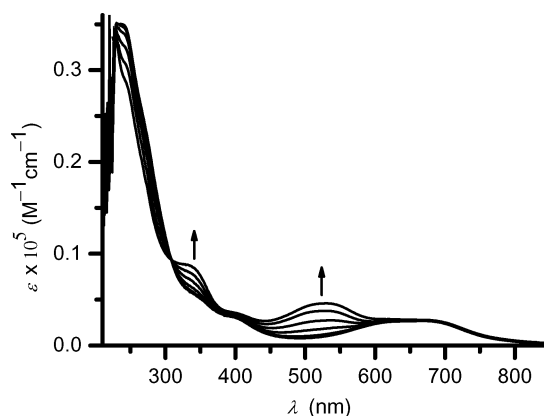


Fig. 5 UV-Vis absorption spectra of **[2]⁺** (2.0×10^{-5} mol L^{-1}) in dichloromethane upon irradiation with UV light (254 nm) at 0, 1, 3, 6, 10, 15 min.

those of the 1+ complex **[2(o)]⁺** or **[2(c)]⁺**. The decrease in energy for these transitions by one-electron reduction reflects a rise of the occupied d_π orbitals level as the number of electrons increases.⁹ Upon irradiation of **2(o)** at 254 nm for 30 min, the green yellow solution turned to purplish blue (Fig. 4), suggesting that the one-electron-reduced species **2(o)** was oxidized to the closed-state 1+ complex **[2(c)]⁺** as indicated by the corresponding spectral changes in Fig. 6. This demonstrates that the one-electron-reduced neutral compound **2(o)** underwent open-to-closed ring conversion as well as the one-electron-oxidized process upon UV irradiation at 254 nm. Thus, the ring-closed form **2(c)** is directly inaccessible from the ring-open form **2(o)** by photocyclization. However, the closed form **2(c)** with a sienna colour could be obtained from

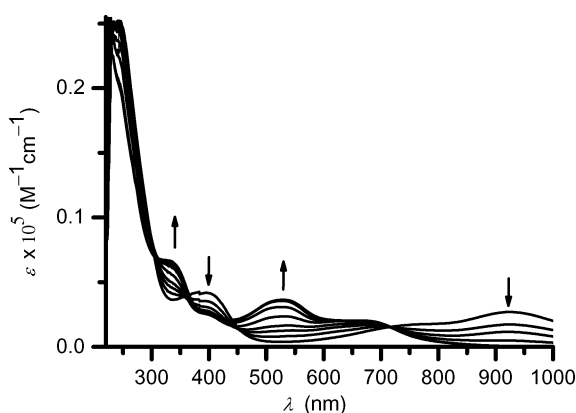


Fig. 6 UV-Vis absorption spectra of **2** (2.0×10^{-5} mol L $^{-1}$) in dichloromethane upon irradiation with UV light (254 nm) at 0, 1, 3, 5, 9, 15, 23, 30 min.

the closed form compound **[2(c)]⁺** by one-electron reduction at -0.70 V (vs Fc $^{+}$ /Fc) (Fig. 4). As shown in Fig. 3, the ring-closed form of the one-electron-reduced neutral compound **2(c)** displayed two new absorption peaks at 349 nm and 514 nm (Fig. 3) in comparison with those of **2(o)**. Upon irradiation with a visible light at $\lambda > 500$ nm, the sienna solution changed to green yellow within 30 min, implying that the closed-ring state was converted to the open-ring state **2(o)**. It is thus concluded that the one-electron-reduced complex **2** did not undergo a reversible photochemical process.

Similar UV-Vis spectral responses and colour changes (Fig. S9 and Fig. S10, ESI $^{+}$) were also detected for the dimeric complexes **[3] $^{2+}$** and **3** induced by both photochemical and electrochemical processes. It took *ca.* 6 min for **[3] $^{2+}$** to reach the photostationary state, whereas the cycloreversion process was completed within 20 min. For the conversion of **3(o)** to the oxidized, closed-state **[3(c)] $^{2+}$** , it took *ca.* 30 min. Furthermore, the cycloreversion process from **3(c)** to **3(o)** was completed within 30 min upon visible light irradiation.

Conclusions

Designed preparations and characterizations of monomeric and dimeric triruthenium cluster derivatives with PPh $_2$ -DTE-PPh $_2$ were carried out. Multiple and reversible colour conversion and spectral responses were detected under UV/visible light irradiation or electrochemical oxidation/reduction. Reduction of the Ru $_3^{III,III,III}$ complexes by chemical or electrochemical methods afforded one- or two-electron-reduced neutral Ru $_3^{III,III,II}$ products with remarkable colour and spectral conversions. The electrochromic properties of PPh $_2$ -DTE-PPh $_2$ containing triruthenium complexes are totally reversible. They show distinct photochromism through photochemical ring closing (by UV irradiation) and opening (by visible light irradiation) processes with dramatic colour changes. For the Ru $_3^{III,III,III}$ species (oxidized form),

the photochromic behaviour is highly reversible and naked-eye perceivable. For the Ru $_3^{III,III,II}$ species (reduced form), however, the ring-opening Ru $_3^{III,III,II}$ species **2(o)** or **3(o)** underwent open-to-closed conversion as well as a one-electron-oxidized process with a transformation to the ring-closing Ru $_3^{III,III,III}$ complex **[2(c)] $^{+}$** or **[3(c)] $^{2+}$** upon irradiation with a UV light. These results indicate that these complexes can be used as potential electro-optical switches and memory devices in molecular electronics.

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