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Controlling the Stepwise Closing of Identical DTE Photochromic Units with Electrochemical and Optical Stimuli

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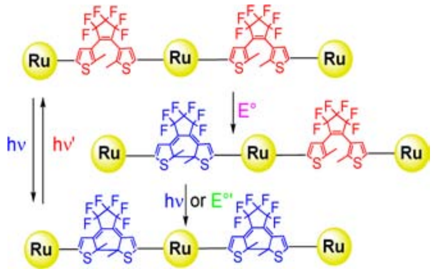
ABSTRACT



The full or stepwise controlled closing of identical photochromic dithienylethene units in the same molecule was addressed with a combination of electrochemical and optical stimuli in a trimetallic carbon-rich ruthenium complex.

The rational design of photochromic molecules operating as molecular switches has attracted a lot of attention.[1,2] Through reversible transformations, these compounds display states with markedly different properties. In that respect, the use of photochromic units as ligand in metal complexes has been advantageously considered.[2] Due to their electronic properties, coordination compounds can lead to isomerization behavior modifications or to isomerization *via* stimulation at the metal center with light or electron transfer. Photochromic units can also be used to affect the metal properties, leading to appealing photochromic and photophysical behaviors. For example, with the use of redox-switchable carbon-rich ruthenium complexes[3,4] allowing different properties modulation,[5−7] we and others reported light- and electro-triggered dithienylethene (DTE) switches of the type [Ru]-DTE-[Ru] with unique features.[8] In particular, such organometallic combinations display an electrochemical DTE cyclization at

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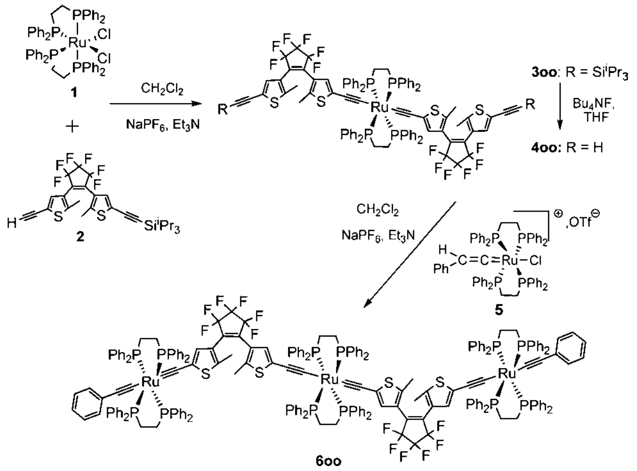
remarkably lower potential than that of organic systems (0.49 vs 1−1.3 V),[9] owing to the unique electronic structure of the ruthenium complexes affording efficient electron delocalization on the carbon-rich ligand, including the thiophene rings.

Associations of several photochromic components in a single molecule were also achieved to obtain multiresponsive materials,[10−12] with many efforts directed toward the most promising DTE units for memory and photoswitching devices. However, with the easiest synthetically accessible compounds displaying two or more identical DTE moieties, the photochemical closing reaction occurs either for all or for a limited number of DTE units, depending on the reactivity of each system. The reasons for partial closing are not fully rationalized,[11−13] and this lack of controllable selectivity in photochromism always leads to two readily isolated states only, thus preventing simple access to challenging multistate switching materials.

Herein, we report for the first time the straightforward stepwise access to all isomers of a system containing two identical DTE units. Specifically, through the design of a unique ruthenium trimetallic complex incorporating two DTE units (**6oo**), and with a judicious use of the orthogonal light and electro-triggered processes, we show that it is possible to control ring closure of one or of two photochromic units.

The precursor **3oo** decorated with two DTE units was prepared in 79% yield from the reaction of *cis*-(dppe)$_2$-RuCl$_2$ (**1**) with the novel ethynyl-substituted DTE compound **2** in the presence of a noncoordinating salt (NaPF$_6$) and a base (Et$_3$N), according to the general procedure to obtain bis(arylacetylide) complexes (Scheme 1).[4d] Under identical experimental conditions and after deprotection of alkyne functions, this precursor was further treated with two equivalents of the vinylidene complex **5**, allowing the formation of the targeted trimetallic adduct **6oo** in 58% yield. These new compounds were characterized by means of ^{31}P, ^{1}H, ^{13}C NMR, IR spectroscopies and mass spectrometry, as well as with elemental analysis (see Supporting Information). For **6oo**, particularly informative are the two sharp singlet signals at δ = 53.3 (central dppe) and 53.8 (remote dppe) ppm in ^{31}P NMR spectroscopy, with a ~1:2 integration ratio. They are characteristic of *trans* bis(σ-arylacetylide) species and reveal the symmetry of the compound with two identical arms. The ^{1}H NMR spectrum displays two singlet resonances at δ = 6.84 and 6.72 ppm corresponding to the inner and outer protons of the thiophene units for the two identical photochromic bridges. Another single sharp signal is typical of the four methyl groups at δ = 2.00 ppm. For steric reasons, as previously established, these signals are attributed to a single isomer with antiparallel conformations for both DTE fragments.[8a] Finally, the IR spectrum reveals a single characteristic $\nu_{(C\equiv C)}$ vibration at 2050 cm^{-1}.

Scheme 1. Synthetic Pathway



Regarding its absorption spectrum, in addition to the strong absorption bands for transitions involving the dppe ligands below 300 nm, **6oo** displays an intense absorption band with a large extinction coefficient at $\lambda_{\max}$ = 352 nm in toluene (Figure 1). This transition should most probably correspond to multiconfigurational MLCT excitations from metal-based MOs toward thiophene-based π^* orbitals, admixed with a strong $\pi \rightarrow \pi^*$ DTE (Intra-Ligand) nature.[8a] As expected, irradiation of the UV−vis cell in this region leads to DTE ring closure(s), and the following isomerization studies show a fully reversible photochromic process. Specifically, upon irradiation with UV light (350 nm), the former band at 352 nm decreases and shifts to $\lambda_{\max}$ = 319 nm. Concomitantly, a broad absorption with a shoulder at 672 nm appears at $\lambda_{\max}$ = 717 nm and progressively shifts to $\lambda_{\max}$ = 736 nm with the same shoulder (Figure 1). This shift may suggest successive closings of the two DTE units within the same molecule to finally afford the deep green closed isomer **6cc**. Note that such broad bands were previously ascribed to the overlapping of metal perturbed DTE ($\pi \rightarrow \pi^*$) absorptions from different rotamers. Eventually, this solution containing the closed form can be further bleached to the open form

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solution under visible light (750 nm), with quantitative recovering of the initial spectrum.

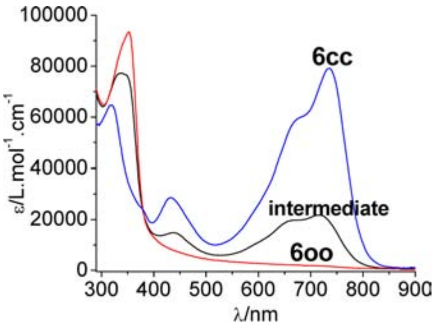


Figure 1. Absorption spectrum of **6oo** and spectral changes upon 350 nm irradiation to **6cc** (toluene, $[c] \approx 5 \times 10^{-5}$ mol L^{-1}).

The highly relevant questions of the number of closed DTE unit(s) per molecule and of the nature of the photostationary state were unambiguously unraveled with NMR studies (Figure S18 and S19). ^{31}P NMR spectroscopy (in C_6D_6) reveals that **6oo** is fully converted to **6cc** with a shift of the two resonances from $\delta = 53.3$ (central dppe) and 53.8 (remote dppe) ppm to $\delta = 52.0$ and 53.0 ppm with the same 1:2 intensity ratio. Upon the experiment, a small transient peak is observed at 52.6 ppm while the two peaks for the two types of remote centers (open and closed) display larger intensities than expected on the basis of the **6oo** and **6cc** central unit signals. Thus, these observations show the transient presence of a third non symmetrical species, illustrating that **6oo** is fully converted to **6cc** through the singly closed intermediate **6oc**. This is further supported by ^{1}H NMR studies, namely with the characteristic upfield and downfield shifts of the thiophene protons from $\delta = 6.84$ and 6.72 ppm (**6oo**) to 5.87 and 5.64 ppm (**6cc**), respectively, and of the methyl group protons from 2.00 to 2.60 and 2.61 ppm. The intermediate **6oc** form is also clearly identified with the thiophene resonances at 6.88 and 6.70 ppm for the open arm, and at 5.82 and 5.65 ppm for the closed arm. The $\nu_{(C\equiv C)}$ vibration at 2050 cm^{-1} for **6oo** also shifts upon closure to lower wavenumbers, that is, 2011 cm^{-1}, for **6cc**. Note that similar isomerization experiments on **3oo** unambiguously show reversible closing of only one DTE unit per molecule to lead to **3oc** (Supporting Information), probably owing to deactivation via energy transfer to a low-lying excited state[11,12] or to unfavorable orbital control rules[13] since subtle modifications of molecules can significantly modify photochromic properties.

Electrochemical properties were analyzed for **3oo** and **6oo** by cyclic voltammetry (CV). Complex **3oo** (Figure S20) displays the expected behavior for a single ruthenium center with a one-electron reversible oxidation at $E° = 0.44$ V vs SCE and an irreversible one at higher potential (E_{pa} = 1.27 V vs SCE) reminiscent of the well-known organic DTE systems.[9] In contrast, **6oo** exhibits a significantly different behavior comparable to that of the bimetallic analogue.[8a] As illustrated in Figure 2a, at low and moderate scan rates (0.1−2 V s^{-1}), the CV of **6oo** shows a broad and partially reversible wave located at c.a. E_{pa} = 0.5 V vs SCE, typical of ruthenium acetylide oxidation. Its shape suggests that it is composed of the three close one-electron oxidations processes for the three electronically independent metal fragments. Consecutively, two new reversible separated redox systems appear at less positive potentials on the return and on the following scans at $E_{c1}° = 0.085$ V and $E_{c2}° = 0.20$ V vs SCE.[8a] They are similar to those observed for the closed bimetallic analogue for two ruthenium centers conjugated through a closed bridge. After a 120 s pre-electrolysis at 0.72 V, these signals increase while the initial broad wave changes into a cleaner simple wave at $E° = 0.43$ V potentially attributable to a remaining non conjugated metal center (Figure S21a). Thus, these first observations suggest that a single ring closure is electrochemically triggered from the oxidation of **6oo** on this time scale of cyclic voltammetry. For scan rates above 2 V s^{-1}, these two well-separated redox systems do not appear while the broad oxidation wave becomes fully reversible, the closing process being too slow on this time scale (Figure S22).

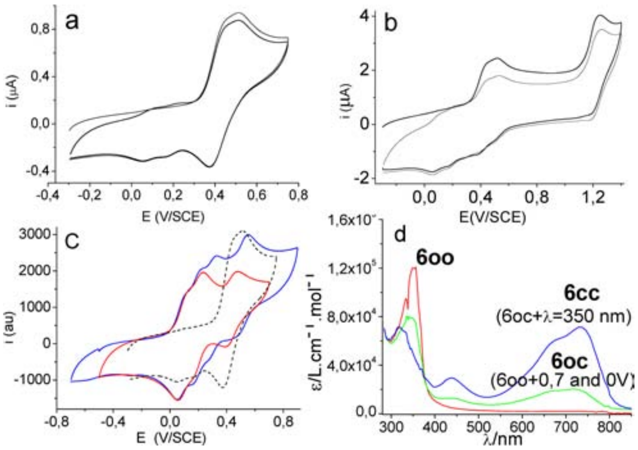


Figure 2. CV of **6oo** in CH_2Cl_2 (0.2 M Bu_4NPF_6) (a) ν = 0.1 V s^{-1}, (b) ν = 0.5 V s^{-1} (c) before (dashed line) and (i) after photoisomerisation at λ = 350 nm leading to **6cc** (blue line) and (ii) after a bulk electrolysis at 0.7 V leading to **6oc** (red line). (d) Absorption spectra obtained upon oxidation of **6oo** and reduction in an OTTLE cell (0.2 M Bu_4NPF_6 in $ClCH_2CH_2Cl$, green line) and further irradiation (350 nm, blue line).

When expanding the potential window, an additional broad anodic peak is observed at E_{pa} = 1.26 V (Figure 2b). This value is close to the usual oxidation potential reported for DTE cores.[9] On the reverse and following scans, new redox systems are observed at lower positive potentials but these signals are much more complex to analyze than the former two reversible separated waves. Actually, pre-electrolysis at 1.30 V reveals four distinct systems at $E°_{cc1}$ = 0.085 V, $E°_{cc2}$ = 0.20 V, $E°_{cc3}$ = 0.30 V, $E°_{cc4}$ = 0.51 V, together with the vanishing of the initial wave (Figure S21b).

After irradiation at 350 nm of an electrochemical cell containing **6oo**, identical electrochemical systems were recorded with **6cc**. They are indeed distinctive of the full closed isomer **6cc** (Figure 2c) for which the first three oxidations are typical of conjugated triruthenium acetylides,[4d] the fourth one being reminiscent of the closed DTE parts.[9] All these features point out the occurrence of a single DTE closure at ca. 0.44 V, whereas the second one is further operated at 1.26 V.

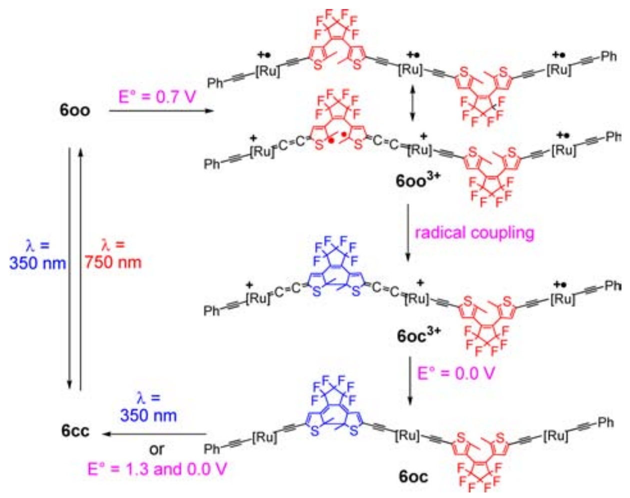
To confirm this stepwise process, a controlled-potential macroelectrolysis was performed on **6oo** at 0.7 V in CH_2Cl_2. After a three-electron per mol oxidation, the broad initial system decreases and the three clean redox systems observed in the 0.72 V pre-electrolysis experiments are clearly identified (Figure 2c). Further reduction of the anolyte, and workup of the solution followed by NMR analysis confirmed the full conversion of **6oo** into its monoclosed forms **6oc**. Indeed, the observation of 3 peaks in ^{31}P NMR at 53.8 (open arm), 53.0 (closed arm) and 52.6 (central core) ppm, along with the related thiophene protons at 5.65 and 5.82 ppm (closed DTE unit), and at 5.65 and 5.82 ppm (open DTE unit) in ^{1}H NMR are characteristic of **6oc** (Figure S24). Further irradiation of this solution (350 nm) led to the two characteristic signals of **6cc** in ^{31}P NMR at 53.1 and 52.0 ppm, showing that the second ring closure can be further achieved by photochemical mean.

The optical properties of **6oo** upon oxidation at 0.75 V were also investigated by means of UV/vis/NIR spectroscopy in an optically transparent thin layer electrochemical (OTTLE) cell in $ClCH_2CH_2Cl$. During the experiment, the initial absorption band at λ_{max} = 348 nm vanishes and three new bands concomitantly appear with a main band at λ_{max} = 783 nm that are attributed to the oxidized closed isomer **6oc**$^{3+}$ (Figure S25). Indeed, further electrochemical reduction leads to a clean spectrum of **6oc** (λ_{max} = 718 nm), with a remaining absorption at 342 nm for the open DTE units (Figure 2d, green line). Worth noting is that an identical spectrum was obtained after the macroelectrolysis cycle described above. The IR spectrum obtained after reduction displays two $\nu_{(C\equiv C)}$ vibrations at 2054 (as in **6oo**) and 2016 (as in **6cc**) cm^{-1} as expected for **6oc**. Note that these spectroscopic features are very similar to those recorded for the bimetallic analogue, also supporting formation of **6oc**. Finally, following the bulk electrolysis experiment, irradiation with UV light of the OTTLE cell containing the electrogenerated **6oc** allows the growing and the shift of the broad band to λ_{max} = 736 nm as expected for the formation of **6cc** in dichloroethane (Figures 2d and S27).

The above results demonstrate that with an accurate choice of the *stimulus*, the three possible forms **6oo**, **6oc**, and **6cc** can be selectively reached (Scheme 2): (i) Irradiation of **6oo** with UV light leads to **6cc** *via* the successive closings of both units, (ii) Oxidation of **6oo** at 0.7 V (and subsequent reduction) leads selectively to **6oc**, (iii) **6oc** can be further converted to **6cc** *via* irradiation with UV light, (iv) oxidation at higher potential (ie. 1.3 V) also affords the double closings from **6oo** or **6oc** to **6cc**, and (iv) reopening of the closed rings occurs *via* irradiation with visible light.

The single electrochemical ring closure can be rationalized on the basis of the behavior of the related bimetallic complex: after oxidation of the ruthenium carbon-rich units offering electron delocalization on the conjugated bridges, ring closure arises from a radical coupling on two suitable C_α positions of thiophene units (EEC mechanism).[8a] Remarkably, the three metal centers present in **6oo** make it possible three oxidations at 0.44 V vs SCE that can provide only one radical coupling, and thus lead to a single ring closure (Scheme 2). Further oxidation at 1.26 V vs SCE leads to a process reminiscent of pure DTE units that allows to the second ring closure, probably *via* the commonly accepted ECE mechanism for those organic compounds.[9]

Scheme 2



In conclusion, the perturbation of a DTE system with a ruthenium carbon-rich system allowed the successful achievement of a unique light and electro-triggered multifunctional switch with an increased degree of sophistication. The judicious choice of the stimulus permits to selectively address single (electrochemical) or double (optical or electrochemical) ring closure(s) with two identical DTE units present in the same molecule. Further functionalization of these systems on the *trans* carbon-rich ligands by introduction of anchoring moieties for future integration in molecular devices is currently under investigation to achieve multistate switching materials.

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Supporting Information Available. Synthetic procedures, spectroscopic and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.