# A multifunctional organometallic switch with carbon-rich ruthenium and diarylethene units†

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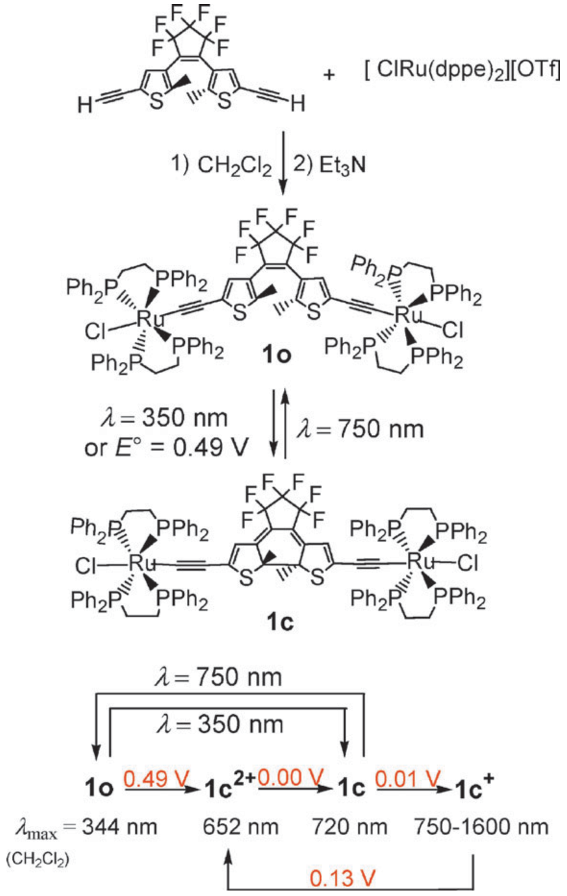
**The perturbation of a dithienylethene system by a ruthenium carbon-rich system, and *vice versa*, was used to reach a unique and sophisticated light- and electro-triggered multifunctional switch featuring multicolor electrochromism, electrocyclization at remarkably low voltage, and photo/electro tuning of electronic communication.**

Much attention has been focused on the switching of physical properties by using appropriate stimuli such as light or electricity, in order to obtain functional materials.[1] For instance, metal systems are good candidates for electrochromism as they give rise to strong optical contrast, high coloration and low switching potential.[2] Photochromic compounds that display a reversible transformation between two chemical forms with different properties by which a key process can be modulated present also a high potential for application in switching devices.[1,3]

In the search of multiple controllable properties into a single component system,[4] it should be possible to obtain a system displaying unique synergetic properties with an accurate combination of a metal complex and a photochromic unit.[5–8] Carbon-rich ruthenium complexes have been involved in the building of original redox active molecular wires,[9] junctions,[10] sensors,[11] NLO materials,[12] owing to their optical properties (charge transfer bands) and the excellent ability of the system to promote a strong electronic coupling between the metal centers and the conjugated organic ligands. On the other hand, dithienylethene (DTE) is an ideal photochromic molecule that undergoes reversible interconversion between a non-conjugated open form and a π-conjugated closed form.[3] The photo- or electro-gating of properties such as magnetic interactions,[13] electron transfer,[7] conductivity[14] or NLO activity,[8] could thus be achieved. In this work, we have taken advantage of the association in the same molecule of the electronic and optical properties of both the DTE unit and the ruthenium fragment $[Cl(dppe)_2Ru]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) to achieve a multifunctional responsive material. As described below, this engineering leads to a molecular switch that for the first time gathers synergetic and efficient properties, all attractive for optoelectronic devices, *i.e.* multicolor electrochromism, electrocyclization at remarkably low voltage, and photo/electro control of electronic communication within a molecular wire. These conclusions were supported by careful parallel experimental and theoretical investigations.

The dinuclear target compound **1o** was readily obtained from the reaction between the diethynyl-substituted dithienylethene and the five-coordinate $[Cl(dppe)_2Ru]^+$ cation (Scheme 1). On the basis of $^1H$ and $^{31}P$ NMR characterizations, only one isomer is formed. Molecular modeling clearly shows that the anti-parallel rotamer is highly favored as the parallel one is sterically unlikely (Fig. S6, ESI†). Isomerization studies in toluene and $CH_2Cl_2$ unambiguously show that the photochromic process upon irradiation of **1o** to the very stable **1c** complex is complete and fully reversible (Fig. 1). For example in toluene, the colorless complex **1o** displays an absorption at $\lambda_{max}$ = 346 nm (ε = 17 900 L $mol^{-1}$ $cm^{-1}$).



**Scheme 1**

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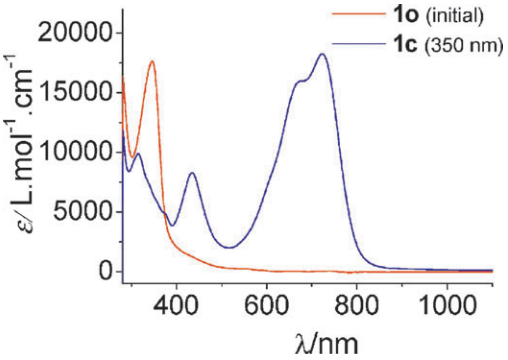

**Fig. 1** UV-Vis absorption spectral changes in toluene upon 350 nm irradiation. The initial spectrum was recovered after bleaching at 750 nm.

TD-DFT calculations performed on the optimized geometry reveal that the orbitals involved in this excitation are π(DTE) and [Cl–Ru–$C_2$] in character and that this excitation leads to a charge transfer to both the π* of the DTE and the (Ru–P)* orbitals (Table S1, ESI†). Upon irradiation with UV light (350 nm), this band vanishes, while a broad absorption assigned to the deep green closed isomer **1c** appears at $\lambda_{max}$ = 722 nm (ε = 18 200 L $mol^{-1}$ $cm^{-1}$). TD-DFT results show that this unusual broad band results from the overlapping absorptions of different rotamers of **1c** with various orientations of the metallic units toward the DTE plane (Table S2, ESI†). This new low energy band corresponds mainly to a HOMO ($M_{d/\pi}$–$C_2DTE_{\pi}$) → LUMO ([$M_{d/\pi}$–$C_2DTE_{\pi*}$]*) allowed transition consistent with the new structural arrangement since both ruthenium atoms and the conjugated path are now in the same plane. This solution can be further bleached to the colorless solution under visible light (750 nm), with quantitative recovering of the initial spectra. Complete conversions were also confirmed with $^{31}$P and $^{1}$H NMR studies, namely with the characteristic upfield and downfield shifts of the thiophene and methyl group protons, respectively (Fig. S3, ESI†).

Typical cyclic voltammograms (CV) of **1o** are shown on Fig. 2. At scan rates above 50 V $s^{-1}$, a broad reversible wave is observed at *ca.* 0.49 V *vs.* SCE.[15] A closer inspection reveals that this broad wave is the result of two close one-electron systems attributed to the two non-communicating ruthenium carbon-rich centers (*vide infra*). In contrast, at low scan rates (0.2 V $s^{-1}$), this wave becomes irreversible, and during the reverse cathodic scan, two new waves appear at less positive potentials. These two new well-separated redox systems are reversible and located at $E^{\circ}_{c1}$ = 0.009 and $E^{\circ}_{c2}$ = 0.130 V, respectively, as seen on the second consecutive scan. They are ascribed to the $\mathbf{1c}^{+}$/**1c** and $\mathbf{1c}^{2+}$/$\mathbf{1c}^{+}$ processes involving some closed isomer electrochemically generated. Indeed, identical systems are obtained after photolysis (350 nm) of **1o**, in addition to the vanishing of the broad reversible wave at *ca.* 0.49 V (Fig. 2). Moreover, controlled-potential electrolysis performed on **1o** at 0.50 V also leads to a CV displaying only the two redox systems at $E^{\circ}_{c1}$ = 0.009 and $E^{\circ}_{c2}$ = 0.130 V after a two-electrons/mol oxidation. Further two-electron reduction of the resulting anolyte, followed by NMR and UV analysis of the reduced solution confirmed the efficiency of the electrocyclisation process leading to complete conversion of **1o** to **1c**.

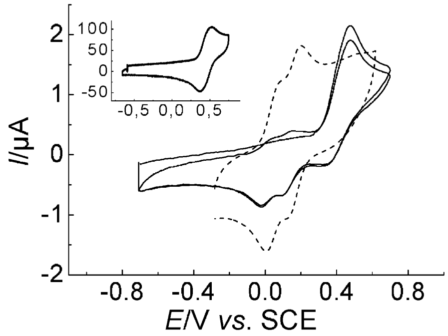

**Fig. 2** CV of **1o** at 0.2 V $s^{-1}$ (0.2 M $Bu_4NPF_6$ $CH_2Cl_2$) with two consecutive scans (solid line), and scan of **1c** obtained after irradiation of **1o** at 350 nm (dotted line). The inset shows scan of **1o** at 50 V $s^{-1}$.

The optical properties of **1o** were investigated by means of UV/Vis/NIR spectroelectrochemistry in $CH_2Cl_2$ (Fig. 3). Upon two-electron oxidation of **1o**, the intense absorption band at $\lambda_{max}$ = 344 nm (ε = 28 800 L $mol^{-1}$ $cm^{-1}$) vanishes and two new bands attributed to the closed isomer $\mathbf{1c}^{2+}$ (*vide infra*) concomitantly show up at $\lambda_{max}$ = 452 nm (ε = 13 200 L $mol^{-1}$ $cm^{-1}$) and 652 nm (ε = 20 200 L $mol^{-1}$ $cm^{-1}$). Further electrochemical reduction of $\mathbf{1c}^{2+}$ leads to the clean spectrum of **1c** ($\lambda_{max}$ = 720 nm, ε = 225 00 L $mol^{-1}$ cm). The reduction proceeds *via* $\mathbf{1c}^{+}$ that displays a remarkably broad absorption band in the NIR region from 750 nm to 1600 nm with $\lambda_{max}$ = 1100 nm (ε = 13 000 L $mol^{-1}$ $cm^{-1}$) assigned to metal perturbed π → π* transitions of the extended conjugated system. Further two-electron oxidation of the **1c** solution to $\mathbf{1c}^{2+}$ leads to a spectrum identical to that obtained upon the first two-electron oxidation of **1o**, confirming the initial fast ring closure on the experiment timescale.

On the basis of numerical simulation, the broad oxidation wave observed for **1o** virtually corresponds to two separated one-electron oxidation processes with $E^{\circ}o_1$ = 0.405, $E^{\circ}o_2$ = 0.490 V, and $\Delta E^{\circ}$ = 85 mV. Also, simulations considering a closing mechanism involving $\mathbf{1o}^{2+}$ match the experimental CVs whereas a mechanism involving $\mathbf{1o}^{+}$ failed (Fig. S5, ESI†). If **1o** is submitted to a 10 s pre-electrolysis at 0.40 V, the resulting forward scan does not exhibit the redox waves corresponding to the ring-closed isomer, while the CV obtained after treatment at 0.45 V does. Thus, these observations strongly suggest that the ring closure occurs in the $\mathbf{1o}^{2+}$ state.

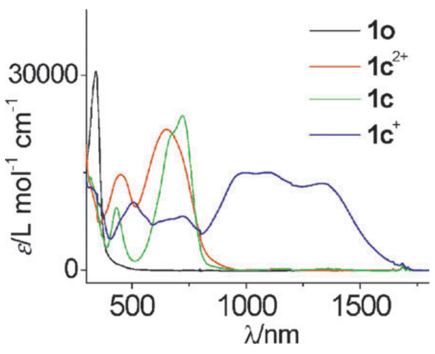

**Fig. 3** UV-Vis-NIR absorption spectra obtained upon spectroelectrochemical experiment (0.2 M $Bu_4NPF_6$ $CH_2Cl_2$).

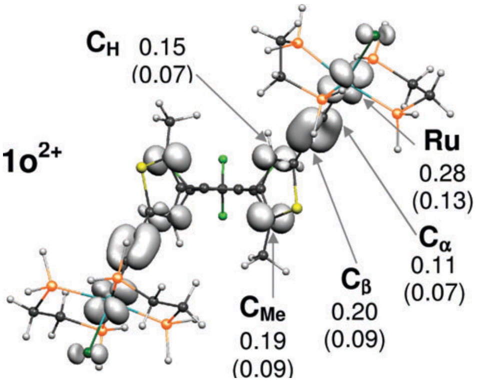

**Fig. 4** Top view of calculated isosurface (0.0045 e bohr$^{-3}$), and atomic spin densities of the modeled **1o**$^{2+}$ compared with those of **1o**$^{+}$ (in parentheses).

A rate constant of 15 s$^{-1}$ was obtained for this step, indicating a possible kinetic control. It is also worth noting that the positive shift of the two waves of **1c** as compared to those of **1o** together with the 120 mV peak-separation are consistent with the switching of electronic communication upon closure (π-system extension). They are also in line with DFT calculations which show that (i) the first ionization potential of **1c** is 0.46 eV less energetic than that of **1o**, and (ii) **1c**$^{+}$ and **1c**$^{2+}$ are more stable that their open analogues by 0.39 and 0.71 eV.

This efficient closing event is unprecedented and contrasts to that of the similar iron compound which leads to slow electro-opening.[7a] In particular, the cyclization occurs at an exceptionally low potential, far below pure DTE processes that generally occur around 1 V.[16] This is the result of the unique electronic structure of such ruthenium complexes that leads, in radical species, to electron delocalization on the carbon-rich ligand, including the thiophene rings in the present case as illustrated by the spin density maps (Fig. 4). The **1o**$^{2+}$ form has a triplet ground state, and the spin density on the carbon atoms linked to the methyl groups is sufficient to drive a radical coupling to form the more stable **1c**$^{2+}$ isomer. This mechanism is in sharp contrast with those reported in previous studies in which the DTE closing event always occurs in the first oxidation state, as elegantly demonstrated by Launay,[16b] *via* charge stabilization on the central DTE cycle that is highly unfavorable with fluorinated DTE.

In summary, the perturbation of the DTE system by the ruthenium system and *vice versa* was sophisticatedly used to reach a unique light and electro-triggered multifunctional switch. The originality of this system containing two metals lies in the gathering of several properties: (i) an efficient reversible photochromic activity along with an efficient low potential metal-promoted electrocyclisation, in contrast with all other metallic systems, (ii) a photochemically gated multicolor-electrochromism with high contrast, and (iii) a significant light/electro-triggered electronic communication also relevant for electrical conductivity switching. Therefore this is a multi-addressable system with memory for charge storage, and optical memories. Non-destructive read out is possible *via* inactive wavelength (450 nm) and/or *via* high speed oxidation/reduction cycles. Besides, further functionalization on the metal atoms offer an increased potential to this system by introduction of substituents with tunable electronic properties and/or with anchoring moieties for future integration in molecular devices such as optical, conductive or NLO switches.

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