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Electrochemically induced ring-closing of photochromic 1,2-dithienylcyclopentenes

Andrea Peters and Neil R. Branda*

Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, Canada V5A 1S6. E-mail: nbranda@sfu.ca

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An unprecedented combination of photochromism and electrochromism is observed for two 1,2-bis(dithienyl)cyclopentene derivatives; the ring-opening reactions are photochemically driven while the ring-closing reactions can be triggered by electrochemical oxidation.

The interest in using photochromic 1,2-dithienylethene derivatives in optical recording and switching applications has arisen primarily because they possess appealing photochromic properties such as thermal stability of both the colorless and colored forms, and fatigue resistance in the photochemical ring-closing and ring-opening processes.[1] We have recently described the important discovery that the ring-opening reaction and decolorization of several photochromic 1,2-dithienylcyclopentene derivatives, such as bis(terthiophene) **1c** (Scheme 1), can also be triggered by electrochemical or chemical oxidation.[2] We can conclude, to date, that this electrochromism[3] is contingent on having non-alkyl groups attached to the carbons involved in forming the new single bond. This preliminary conclusion is based on the fact that when the 2-methyl groups in bis(dithiophene) **2** are replaced by aryl rings (thiophene or benzene, for example) the colored ring-closed forms rapidly re-open when they are oxidized to their thermally unstable radical cations.[2]

The radical cation generated by electrochemically oxidizing the ring-closed form of bis(dithiophene) **2c** appears to be relatively stable and does not undergo oxidative ring-opening as is shown by the reversible redox couple ($E^{1/2}$ = 0.82 V) in the cyclic voltammogram†(Fig. 1, bottom trace). On closer inspection of the redox properties of both the ring-open (**2o**) and ring-closed (**2c**) forms, we noticed that the reduction peak in the voltammogram of the ring-open form appears at the same potential (0.80 V) as that for the radical cation of its corresponding ring-closed isomer suggesting that the ring-closing reaction is also triggered by the oxidation process. Additional support for this suggestion is the appearance of a new oxidation peak at the same potential (0.85 V) where the ring-closed form (**2c**) is oxidized when the sample of the ring-open form (**2o**) is swept through several redox cycles (Fig. 1, inset). This new observation prompted us to reinvestigate the electrochemical behavior of the bis(dithiophene) derivative. We now report the first example of a photochromic 1,2-dithienylalkene derivative that exhibits redox-driven ring-closing.[4]

Two photochromic dithienylalkene derivatives, 1,2-bis(2-methyl-5,2′-dithiophen-3-yl)perfluorocyclopentene **2o** and 1,2-bis(2,5′-dimethyl-5,2′-dithiophen-3-yl)perfluorocyclopentene **3o**, differing only in the groups attached to the external heterocycles were prepared in one step from the known photochromic dichloride **4**[5] *via* the dibromide **5** using the coupling procedure shown in Scheme 2.‡ The methylated version, **3o**, was prepared in order to investigate the electrochemical properties of the ring-open forms of these photochromic 1,2-dithienylethenes at the high potentials needed to generate their radical cations. The absence of these methyl groups has little effect on the photochemical ring-closing and ring-opening reactions but does play a significant role in minimizing the electrochemical polymerization that is characteristic for thiophenes.[6] Selective photophysical and electrochemical properties are summarized in Table 1.

Both photochromic compounds undergo similar photochemical ring-closing and ring-opening reactions. When CH_2Cl_2 or CH_3CN solutions (2×10^{-5} M) of the ring-open forms of the photochromic bis(dithiophenes) **2o** and **3o** are irradiated with ultraviolet light (365 nm)§ they are converted to their deep blue ring-closed forms (**2c** and **3c**), which have strong absorption bands in the visible region of the UV-VIS absorption spectrum (Table 1). After 10 minutes of irradiation, the photostationary states are reached which are composed of greater than 97% of the ring-closed isomers.¶ Subsequent

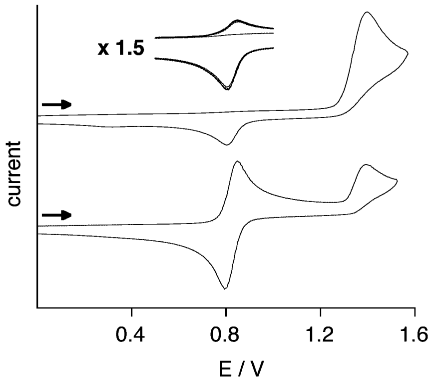
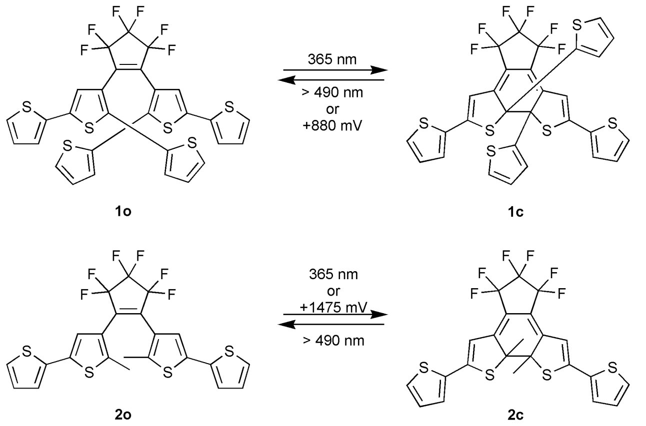
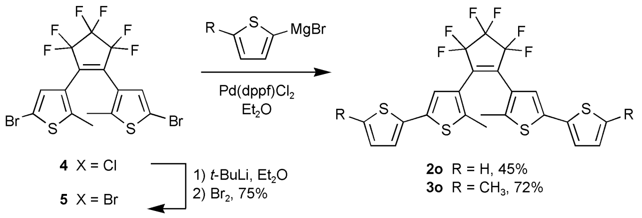


Fig. 1 Cyclic voltammograms of CH_3CN solutions (1×10^{-3} M) of **2o** (top) and **2c** (bottom) at 200 mV s^{-1}. The inset shows multiple sweeps of **2o** (5 cycles).



Scheme 1



Scheme 2

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Table 1 Selective electrochemical and photophysical data for CH_3CN solutions of 1,2-dithienylethenes **2o** and **3o** and their ring-closed forms in the photostationary states

Compound	E_{ox}/V	E_{red}/V	λ_{max}/nm
2o	1.41[a]	0.80[b]	312
2c	0.85	0.80	605
3o	1.26[a]	0.70[b]	320
3c	0.76	0.70	612

[a] Irreversible oxidation. [b] The small peaks observed are assigned to the reduction of the radical cation of the ring-closed form.

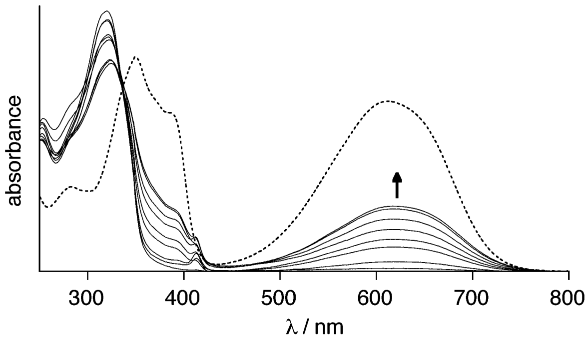

Fig. 2 Changes in the UV-VIS absorption spectra of **3o** upon electrolysis at 1.35 V. Electrolysis periods are every 20 seconds until a 160 second period was reached. The dotted trace shows the spectrum of the photostationary state containing >97% **3c**. The photostationary state was obtained by irradiating a solution of **3o** with 365 nm light until no spectral changes were observed (~60 seconds). The concentrations of all solutions are 2×10^{-5} M.

irradiation of these blue solutions at wavelengths greater than 490 nm[§] for 15 minutes results in complete decoloration of the solutions and the restoration of the absorption spectra to their original traces by regenerating the ring-open isomers quantitatively.

UV-VIS absorption spectroscopy can also be used to monitor the progress of the electrochemical ring-closing reactions. When a colorless CH_3CN solution of the ring-open form of bis(dithiophene) **3o** containing tetrabutylammonium hexafluorophosphate (Fig. 2) is electrolyzed at 1.35 V,[‖] it immediately turns the same deep blue color and generates the same absorption spectrum as is observed for the photochemical ring-closing event. After 160 seconds of electrolysis, the growth in the intensity of the absorption at 600 nm levels off. The resulting absorption profile is the same as that recorded when **3o** is photochemically ring-closed, except that the absorption peak in the visible region is only half as intense. At this point, electrochemical degradation is minimized and the resulting electrochemically generated deep blue solution can be photobleached by exposing it to light of wavelength greater than 490 nm (15 minutes). If the electrolysis is continued beyond this point, the electrochemical degradation becomes more significant as is attested by both the loss of any isobestic points and the inability to regenerate a spectrum that overlaps with that for the ring-open isomer **3o**. We attribute this to electrochemical polymerization at the remaining 3′-position of the terminal thiophene heterocycles, although these polymers have yet to be isolated and characterized.

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Notes and references

† Electrochemical cyclic voltammetry experiments were performed using a platinum disk working electrode, a platinum wire counter electrode, an Ag/AgCl (in a saturated NaCl solution) reference electrode and tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte. All results were referenced against ferrocene (0.40 V *vs.* SCE).

‡ *Preparation of* **5**: A solution of 1,2-bis(5′-chloro-2′-methylthien-3′-yl)perfluorocyclopentene (500 mg, 1.14 mmol) in Et_2O (40 mL) cooled to −78 °C was treated with *tert*-butyllithium (1.34 mL of a 1.7 M solution in pentane) dropwise under argon. After stirring for 15 min, a solution of bromine (0.117 mL, 2.28 mmol) in Et_2O (10 mL) was added dropwise. The reaction was stirred at −78 °C for 20 min, warmed slowly to room temperature and quenched with H_2O. The organic layer was separated, washed with H_2O (2×10 mL), followed by brine (10 mL), dried (Na_2SO_4) and filtered. The solvent was evaporated under reduced pressure and the resulting crude product was purified using column chromatography through silica (hexanes) to afford 0.452 g (75%) of the pure product as a white solid. mp 146–148°C. ^1H NMR (300 MHz, $CDCl_3$) δ/ppm: 6.99 (s, 2H), 1.87 (s, 6H). ^{13}C NMR (100 MHz; $CDCl_3$) δ/ppm: 143.3, 135.6, 129.1, 125.2, 115.8, 110.0, 14.4. Anal. Calcd for $C_{15}H_8Br_2F_6S_2$: C, 34.24, H, 1.53. Found: C, 34.07, H, 1.56%. *Preparation of bis(dithiophene)s* **2o** *and* **3o**: A solution of 2-bromothiophene or 2-bromo-5-methylthiophene (1 mmol) in Et_2O (10 mL) was treated with magnesium turnings (30 mg, 1.2 mmol) and heated at reflux for 45 min. The heating source was removed, the reaction mixture was allowed to cool to room temperature and it was added to a mixture of dibromide **5** (263 mg, 0.5 mmol), a catalytic amount of $Pd(dppf)Cl_2$ (~4 mol%) and Et_2O (10 mL) at 0 °C dropwise *via* a cannula. The reaction was stirred at this temperature for 1 h. It was allowed to come to room temperature, stirred overnight and quenched with 5% HCl (5 mL). The aqueous layer was separated and extracted with Et_2O (3×10 mL). The combined organic layers were washed with H_2O (3×10 mL), followed by brine (10 mL), dried (Na_2SO_4) and filtered. The solvent was removed under reduced pressure and the crude product was purified using column chromatography through silica (hexanes) to afford the pure product as a white solid. Selected data for **2o**: mp 127–128 °C. ^1H NMR (600 MHz; CD_2Cl_2) δ/ppm: 7.28 (dd, J = 5.1, 1.2 Hz, 2H), 7.16 (dd, J = 3.6, 1.2 Hz, 2H), 7.15 (s, 2H), 7.03 (dd, J = 5.1, 3.6 Hz, 2H), 1.97 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm 140.8, 136.2, 135.5, 127.9, 125.5, 124.9, 124.1, 122.8, 14.4. Anal. Calcd for $C_{23}H_{14}F_6S_4$: C, 51.87, H, 2.65. Found: C, 52.05, H, 2.59%. Selected data for **3o**: mp 124–125 °C. ^1H NMR (400 MHz, CD_2Cl_2) δ/ppm 7.04 (s, 2H), 6.94 (d, J = 3.6 Hz, 2H), 6.69 (dq, J = 3.4, 1.0 Hz, 2H), 2.47 (d, J = 0.8 Hz, 6H), 1.94 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 140.2, 139.7, 135.9, 133.9, 126.0, 125.4, 123.9, 122.0, 15.3, 14.4. Anal. Calcd for $C_{25}H_{18}F_6S_4$: C, 53.56; H, 3.24. Found: C, 53.47; H, 3.26%.

§ Standard lamps used for visualizing TLC plates (Spectroline E-series, 470 mW cm^{-2}) were used to carry out the ring-closing reactions of **2o** and **3o**. The ring-opening reactions were carried out using the light of a 150 W tungsten source that was passed through a 490 nm cutoff filter to eliminate higher energy light.

¶ The compositions of all photostationary states were measured using ^1H NMR spectroscopy.

‖ Electrolysis experiments were performed under similar conditions as described for the cyclic voltammetry experiments except the platinum working electrode was replaced by a platinum coil. A potential 15–20 mV more positive than the half-wave potential for **3o** was used for the electrolysis experiment. This typically was in the range 1.35–1.39 V depending on the particular Ag/AgCl reference electrode used. In a typical experiment, a 1×10^{-3} M solution of **3o** in CH_3CN was electrolyzed, 40 μL aliquot amounts were periodically removed and diluted to 2×10^{-5} M with fresh CH_3CN containing 0.1 M NBu_4PF_6 for analysis by UV-VIS absorption spectroscopy.

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