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Oxidative Electrochemical Switching in Dithienylcyclopentenes, Part 1: Effect of Electronic Perturbation on the Efficiency and Direction of Molecular Switching**

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Abstract: The electro- and spectroelectrochemical properties of dithienylhexahydro- and dithienyhexafluorocyclopentenes are reported. The large effect of variation in the central cyclopentene moieties on the redox properties of the dithienylcyclopentenes is in striking contrast to the minor effect on their photochemical properties. The electronic properties of the oxidised compounds in the +1 and +2 oxidation state are reported, and the possibility of electrochemical cyclisation and cycloreversion were explored by UV/Vis spectroelectrochemistry. The efficiency of electrochemical switching is found to be dependent both on the central cyclopentene unit and on the nature of the substituents at C5 of the thienyl rings. For the hexahydrocyclopentene-based compounds oxidative ring closure of the ring-open form is observed, while for the hexafluorocyclopentene-based compounds oxidative ring opening of the ring-closed form is observed. However, the introduction of electroactive groups such as methoxyphenyl allows oxidative ring closure to occur in the hexafluoro compounds. The effect of electrolyte, solvent and temperature on the spectroelectrochemical properties were examined, and the switching process was found to be sensitive to the donor properties of the solvent/electrolyte system employed. In addition, thermally activated reversible isomerisation of the dicationic closed form was observed. The driving force for electrochemical ring opening and closure appears to be dependent on the relative stabilisation of the dicationic ring-open and ring-closed states. This study provides insight into the factors which determine the direction of cyclisation.

Keywords: cyclization · electrochemistry · photochromism · redox chemistry · UV/Vis spectroscopy

Introduction

Molecules capable of reversible change via external stimuli, preferably in a unidirectional multistate cycle, are receiving continuing attention in the development of molecular devices and as molecular memory materials.[1] A key prerequisite for effective development of such materials is, however, addressability, that is, the ability to detect each state independently of the switching process. Photo- and electrochromic compounds and materials offer distinct advantages in this regard, not only due to the wide range of spectroscopic and electrochemical techniques available to address (read out) these systems, but also in the close relationship between photophysical and redox processes.[2]

Photochromic materials based on diarylethenes and spiropyrans have received considerable attention over the last few years with regard to their rich photochemical behaviour. In addition, the use of external stimuli such as pH change and binding of transition metal ions to control the photoreactivity of both diarylethene and indophenylethenes has been demonstrated.[3] Many of these studies have utilised the inherent difference in conformational flexibility and dependence on excitation wavelength of the photoreactivity with considerable success;[4] for example, their photochromism has been adapted to drive changes in bulk material

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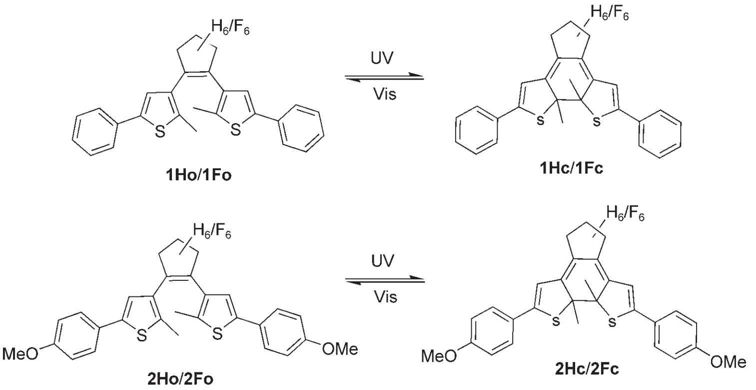
properties (e.g., gelation properties,[5] liquid-crystal phase changes[6]). The photochromic process is quite robust with regard to the environment, and indeed several studies have demonstrated the application of dithienylethene-[7] and spiropyran-based[8] compounds in modified electrode devices. Recently, we demonstrated one-way optoelectronic switching of dithienylethenes on gold using breakjunction techniques.[9] The use of redox-active groups covalently attached to the dithienylethenes has been examined in an effort to marry the electronic and redox properties in multicomponent systems,[10,11] but only in a few examples have the electrochemical properties been explored.[12] Only recently, the redox chemistry of dithienylethenes has received attention in reports of electrochemical ring opening and closing.[2,11b,13]

To date, relatively few studies dealing with specific examples of electrochemically driven ring-opening and ring-closing reactions have been reported.[11b,13] Earlier, we reported the synthesis and characterisation of a series of (dithienyl)cyclopentenes in which the well-known hexafluorocyclopentene moiety is replaced by hexahydrocyclopentene,[14] with only a modest effect on the photochemical properties of the switches. In the present contribution, both the hexafluoro (**F**) and the recently developed hexahydro switches (**H**) are employed to investigate the potential for manipulation of electronic, photochemical and redox properties of this distinct class of photochromic materials (i.e., the dithienylcyclopentenes). The bridging cyclopentene groups are themselves redox-inactive, but they represent extremes: the hexafluorocyclopentene group is electron-withdrawing and thereby decreases the electron density on the central alkene group, while the electron-donating hexahydrocyclopentene increases the electron density on the same group. Phenyl groups are employed at the C5 position of the thienyl (i.e., **1H** and **1F**) rings to minimise interference by reactions other than ring-opening and -closure, such as cationic polymerisation.[15] Both **1H** and **1F** exhibit excellent photochemically driven switching properties that allow reversible formation of a closed (bis(*trans*-butadiene) structure, **1Hc**/**1Fc**) and open (1,2-bis(thiophene)ethene structure, **1Ho**/**1Fo**) forms by UV and visible light, respectively. The methoxy groups in the *para* positions of the phenyl rings in **2H** and **2F** add an extra dimension of complexity to the electrochemical properties[16] through both their inherent redox activity and their electron-donating properties. Hence, they are employed to explore the role of peripheral redox groups in the electrochemical processes of the dithienylethene switches, and to counter the electron-withdrawing properties of the hexafluorocyclopentene group. A detailed examination of the influence of solvent, electrolyte and temperature on the electrochemical reactivity is presented to gain a better mechanistic understanding of these processes. Ultimately, by unravelling the fundamental processes which govern electrochemical switching, rational design of photo- and electroactive compounds may be achieved for application in the emerging field of photonic devices.

Results and Discussion

Compounds **1H, 2H, 1F** and **2F** (Scheme 1) were prepared according to procedures reported earlier.[14] The electronic and photochemical behaviour of the four compounds in their open and closed forms are discussed briefly in the context of the relationship between structure and electronic properties. The redox properties of **1H**/**2H** and **1F**/**2F** are explored in detail to elucidate the parameters which determine their electrochemical behaviour. The properties of **1F** and **2F** are compared to those of **1H** and **2H**, and the factors responsible for the contrasting behaviour of these compounds towards oxidative ring opening/closing are discussed.



Scheme 1. Dithienylcyclopentene switches examined in the present report: suffix **o** denotes open form, **c** denotes closed form; **H** and **F** denote hexahydrocyclopentene and hexafluorocyclopentene, respectively.

Electronic properties: The electronic properties of the four compounds in their open (o) and closed (c) states are presented in Table 1. Comparison of the electron-rich hexahydrocyclopentene-based compounds (**1Ho**/**1Hc** and **2Ho**/**2Hc**) with the electron-deficient hexafluorocyclopentene-based compounds (**1Fo**/**1Fc** and **2Fo**/**2Fc**) shows a bathochromic shift in the lowest energy absorption bands in both the open and closed forms (Figure 1). The changes in energy observed for higher energy absorption bands of the closed forms are equally pronounced. The methoxyphenyl-substituted compounds **2H** and **2F** (Scheme 1) show, in the closed state, an additional intense absorption at 303 (**2Hc**) and 344 nm (**2Fc**) (and 284 nm in **2Ho**), which is assigned tentatively to the methoxyphenyl group. The large bathochromic shift in this band observed in the closed form (**2Hc** versus **2Fc**) is not as pronounced in the open form (**2Ho** versus

Table 1. Electronic and redox properties of **1H**/**1F** and **2H**/**2F** in open and closed forms.[a]

	Abs. λ_{max} [nm] (ε [10^3 cm^{-1}M^{-1}])	$E_{p,a}$ [V] vs SCE ($E_{p,a}$ where irr)	ΔE [mV] (c/c$^+$/c^{2+})
	Open form		
1Ho	278 (18), 303 (sh)	1.16 (irr), −2.53 (irr)	
1Fo	285 (33)	1.59 (irr), −1.75 (irr)	
2Ho	284 (28), 308 (sh)	0.99 (irr)	
2Fo	296 (38)	1.2 (irr), −1.7 (irr)	
	Closed form		
1Hc	267 (15), 349 (5.2), 360 (6.4) 527 (8.8)	0.67, 0.43, −1.74 (irr), −2.03 (irr)	240
1Fc	308 (22), 366 (8.8), 380 (9.1) 588 (12)	0.85 (qr), −1.13 (qr)	<50
2Hc	237 (14), 303 (24), 345 (9.5) 519 (13)	0.45, 0.32, −1.84 (irr), −2.16 (irr)	130
2Fc	344 (25), 376 (sh) 593 (18)	0.67, −1.16 (qr), −1.46 (irr)	<20

[a] sh = shoulder, irr = irreversible, qr = quasireversible (see ref. [18] for definitions used in present work); ΔE = separation of the first and second oxidation processes in closed state (c/c$^+$/c^{2+}). Electronic spectra were recorded in CH_3CN. Redox measurements were carried out in 0.1 M TBAP/CH_3CN.

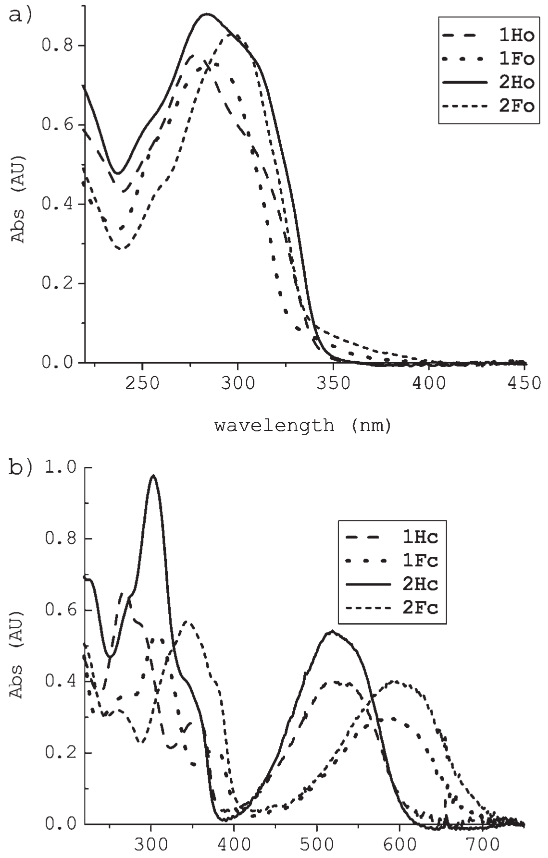


Figure 1. UV/Vis absorption spectra of **1H**, **1F**, **2H** and **2F** (a: open form, b: closed form) in CH_3CN.

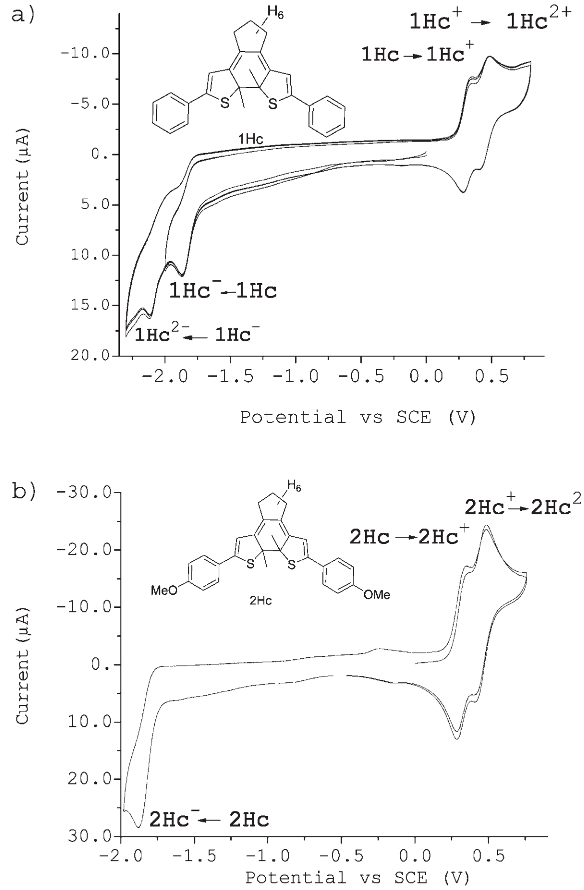


Figure 2. Cyclic voltammetry of **1Hc** (a) and **2Hc** (b) in CH_3CN (0.1 M TBAP) at 0.1 V s^{-1}. (For **2Hc** only the first reduction is shown due to pacification of the electrode on the second reduction).

2Fo), and this suggests that the influence of the hexafluorinated group on the methoxyphenyl moiety is minor in the open form. This difference is rationalised on the basis of loss of conjugation of the thienyl ring with the bridging cyclopentene in the more flexible open state,[17] while the minor bathochromic shift (**2Ho** versus **2Fo**) is attributed to inductive effects.

Redox properties: Electrochemical data for **1H**/**2H** (Figure 2) and **1F**/**2F** (Figure 3), in open and closed states, are presented in Table 1.[18] The hexahydro- and hexafluorocyclopentene units represent extreme limits in terms of the electronic properties of the bridging cyclopentene unit, and hence significant differences in the redox properties of the two sets of dithienylethene compounds are expected. For the phenyl-substituted compounds **1H**/**1F** very large anodic shifts in both the oxidation (ca. 420–430 mV) and reduction (ca. 670–780 mV) processes are observed (**1F** vs **1H**, see Table 1); this indicates that the hexafluoro substitution stabilises the LUMO (i.e., the first reduction process) to a greater extent than the HOMO (i.e., the first oxidation process). The smaller HOMO–LUMO gap measured elec-

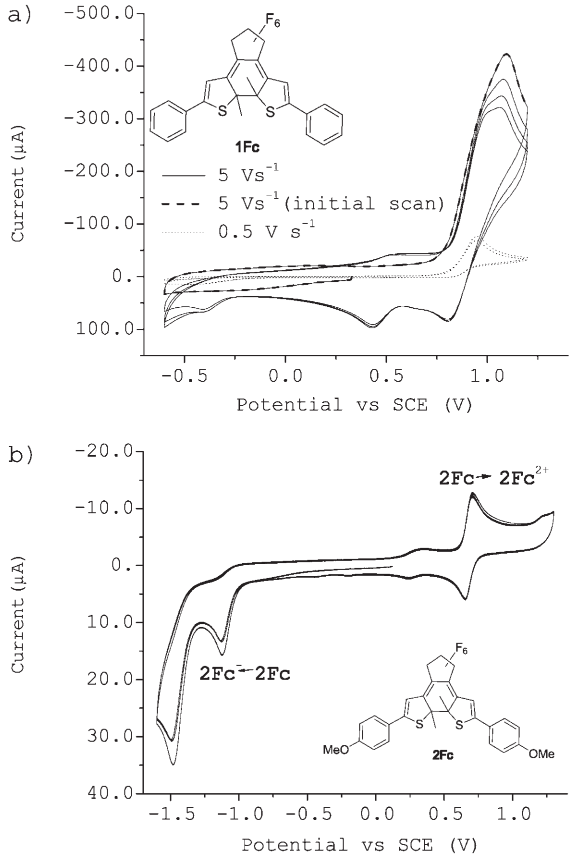


Figure 3. Cyclic voltammetry of **1Fc** (a) at 0.5 and 5 $V s^{-1}$ and **2Fc** at 0.1 $V s^{-1}$ (b) in CH_3CN (0.1 м TBAP).

trochemically suggests that overall a reduction in the HOMO–LUMO gap should be observed for **1F** compared with **1H**. In the electronic spectra this is seen as a bathochromic shift in the lowest absorption band (vide supra). For the closed methoxyphenyl-based compounds **2Hc**/**2Fc** an almost identical situation is observed, but in the open forms, **2Ho**/**2Fo**, a more complex electrochemical behaviour is present (vide infra), due to the non-innocent nature of the methoxyphenyl group. In the first instance it is apparent that the electron-withdrawing properties of the hexafluorocyclopentene unit are effectively compensated by the introduction of the methoxyphenyl moiety. However, the absence of such a compensatory effect of the methoxyphenyl group in the closed form suggests that more complex electrochemical behaviour is present. Overall, however, it is clear that the redox properties (in terms of redox potentials) are very sensitive to, and hence tuneable by, modification of both the bridging cyclopentene unit and substitution at the C5 position.

Electrochemical properties in the closed state: The closed states were prepared readily by UV irradiation at $\lambda = 313$ nm to yield a photostationary state (PSS) containing the closed forms in greater than 98% purity (determined by ^1H NMR spectroscopy). Overall, in the closed state, the dithienylethenes show destabilisation of the HOMO, and hence less anodic redox potentials, than in the open state. For **1Hc** and **2Hc** two fully reversible oxidation processes are observed between 0.0 and 1.0 V (vs SCE), assigned to two one-electron oxidation steps (Figure 2). Similarly, two irreversible reduction steps are observed between −1.5 and −2.2 V (vs SCE). The separation between the first and second oxidation processes indicates that the monocationic species is stable both chemically[19] and with regard to disproportionation ($1/K_c$, vide infra).[20]

For **1Fc**, a quasireversible oxidation is observed at 0.85 V (Figure 3) and a quasireversible reduction at −1.13 V. At high scan rates (>2 $V s^{-1}$), two oxidation processes are partially resolved ($30 < \Delta E < 50$ mV) and two reduction waves are observed on the return cycle. The scan-rate dependence of the reversibility suggests that the oxidation processes are electrochemically reversible and that the irreversibility observed at low scan rates is due to a moderately slow (10^{-3} to 10^{-2} s^{-1}) subsequent chemical reaction (an EC mechanism).[21] This is in agreement with results obtained from spectroelectrochemistry (vide infra). For **2Fc** the reversibility of the oxidation is considerably improved, and the observation of two quasireversible reductions also indicates a more complex electrochemical behaviour than for **1Fc**. The separation of the first and second oxidation processes (ΔE) is less than the resolution limit for both cyclic and differential pulse voltammetry (<30 mV). The reduction in ΔE from **1Fc** to **2Fc** is in agreement with that observed for **1Hc** to **2Hc**. Together with the reduction in ΔE observed between **1Hc** and **1Fc**, this indicates that the two thienyl units (or more specifically the two *trans*-butadiene units) do not form an extended conjugated system over the entire dithienylethene but are predominantly localised on each thienyl ring (vide infra). For both **2Hc** and **2Fc**, however, the similarity of the redox properties and potentials with those of the phenyl-substituted compounds **1Hc** and **1Fc**, provide strong evidence that the electrochemical processes observed are governed primarily by the dithienylethene core and not the methoxyphenyl substituents. The first reduction process for **2Fc** is assigned to reduction of the dithienylethene core on the basis of its similarity to that observed for **1Fc**, whilst the second is assigned tentatively to a reduction process involving the methoxyphenyl units.

Overall, it is apparent that the stability and reversibility of the oxidised compounds can be affected quite profoundly by C5 substitution, even though substitution in the C5 position of the thienyl ring results in relatively minor changes in the redox potentials of the closed dithienylcyclopentenes in comparison to substitution of the hexahydrocyclopentene group (**H**) for the hexafluorocyclopentene group (**F**).

Electrochemical properties in the open state: As has been reported previously for related compounds,[2,10,12,13] in the open state all of the compounds examined exhibit an irreversible oxidation process at more anodic potentials than in the closed state. As with the dithienylhexahydrocyclopen-

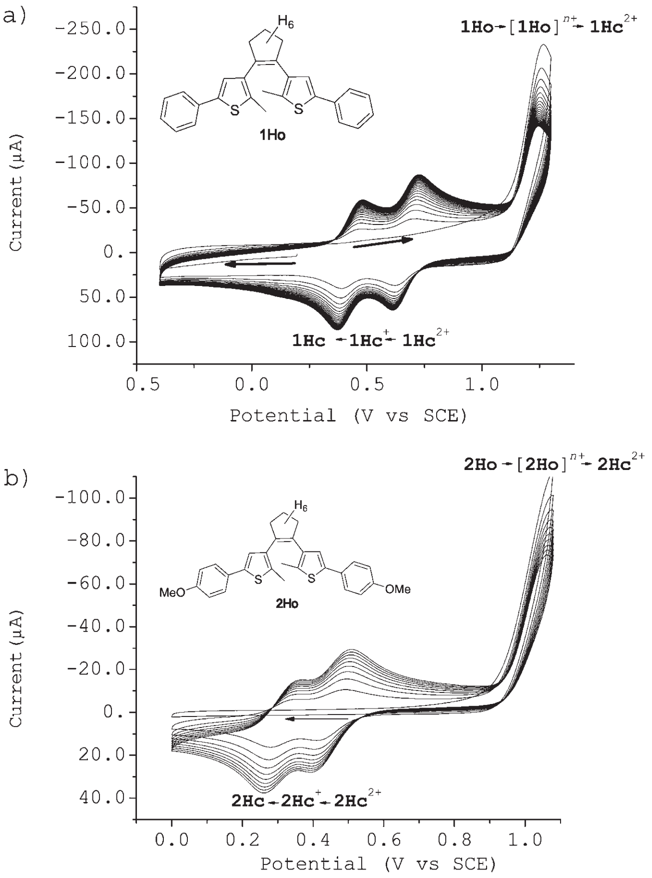


Figure 4. Oxidative conversion of **1Ho** to **1Hc** (50 cycles, a), and **2Ho** to **2Hc** (b), by repetitive cyclic voltammetry at 0.5 Vs^{-1} in 0.1 M TBAP/CH_3CN. Initial scan direction is cathodic and starting point is 0 V versus SCE.

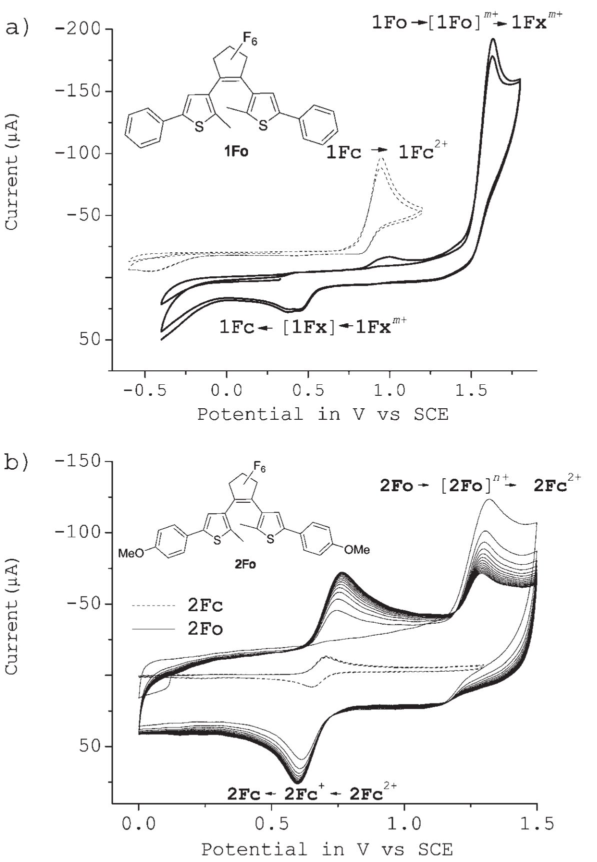


Figure 5. Cyclic voltammetry of **1Fc/1Fo** (a) and **2Fc/2Fo** (b) at 0.5 Vs^{-1} (0.01 M TBAP in CH_3CN). Initial scan direction is cathodic and starting point is 0.0 V versus SCE.

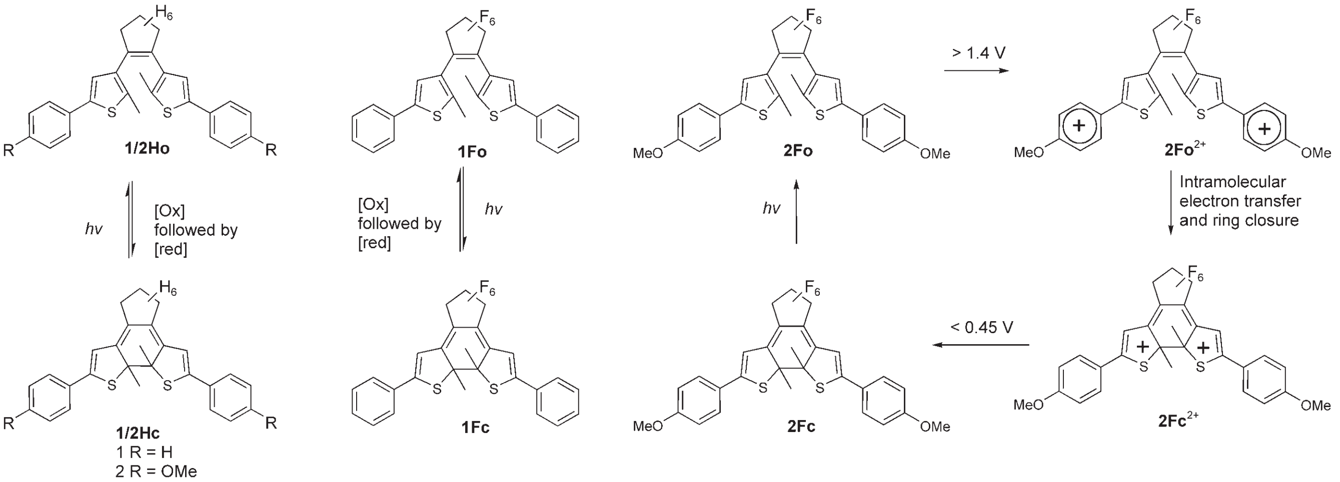
tenes in the closed state (i.e., **1Hc** and **2Hc**), in the open state a cathodic shift (150 mV) is observed on introduction of the methoxyl group, which reflects its electron-donating properties. In contrast to the closed forms, the open form shows a single irreversible two-electron[22] redox process at anodic potentials, typical of thiophene oxidation chemistry.[18,23] For both **1Ho** and **2Ho** oxidation is completely irreversible.[26] Indeed with a Pt microelectrode (10 µm), no reversibility in the oxidation of the open form **1Ho** was observed at scan rates up to 1000 Vs^{-1}, which places the rate of the ring-closure reaction at greater than 10^4 s^{-1}. However, in the return cycle two new reduction processes are observed at potentials coincident with those of the closed forms. Repetitive cycling at higher scan rates results in a significant buildup of the closed form (**1Ho**→**1Hc** and **2Ho**→**2Hc**) in the diffusion layer of the electrode (Figure 4).[24,2,13]

For **1Fo** and **2Fo** a more complex situation is observed. In contrast to **1Ho**, repetitive cycling of **1Fo** leads to a new irreversible reduction process at 0.3 V (assigned to **1Fx**, vide infra), which itself results in a new oxidation process at about 0.9 V (coincident with the oxidation process observed for **1Fc**). The difference in reduction potential between **1Fx** (Figure 5) and **1Hx** (see Figure 7b) of about 500 mV is in agreement with the difference in potential observed between **1Fo** and **1Ho** (ca. 430 mV).

For **2Fo** an irreversible oxidation process at 1.2 V is observed, but in contrast to **1Fo**, for **2Fo** direct ring closure is observed on oxidation of the open state (Figure 5). As in the case of **2Fc**, replacement of the phenyl rings by methoxyphenyl groups results in a cathodic shift (ca. 400 mV, **1Fo** to **2Fo**) in the first oxidation process, but the first reduction process (at −1.75 V) is virtually unaffected (compared to **1Fo**). This remarkable difference in electrochemical behaviour between **1Fo** and **2Fo**, together with the large difference in oxidation potential (400 mV), suggests that in contrast to **2Ho**, for **2Fo** the oxidation process involves the methoxyphenyl unit and not the dithienylethene unit (vide supra).

Overall, it may be concluded that whereas the hexahydrocyclopentene-based compounds **1H**/**2H** undergo ring closure on oxidation of the ring-open form, the hexafluorocyclopentene-based compound **1F** is unreactive towards ring closure. In contrast, ring opening on oxidation of the ring-closed form **1Fc** is observed (see Figure 5 and below). Thus, the driving force for electrochemical ring opening and closure appears to be controllable.

To exploit this "tunability" in the direction of the reaction, the underlying driving force for ring opening and closing must first be understood. Assuming that the two thienyl rings of the open form (and by analogy the two *trans*-butadiene systems of the closed form) behave as independent redox units, then it is possible that the most important factor is the relative stabilisation of the cation located on the thiophene heterocycle (i.e., in the open form) compared with the cation located on the extended *trans*-butadiene (i.e., in the closed form). To a first approximation the cyclic cation would be expected to be the most stable state, and hence the natural direction of electrochemical switching is from the closed to the open form. However, in the hexahydrocyclopentene-based compounds, sufficient delocalisation of the positive charge of the cation over the entire dithienylethene group occurs, renders the closed cation the most stable state and hence allows ring closure. A further consideration is the role of substituents at C5 of the thienyl rings. The reversal of reactivity towards ring closure observed in **1Ho** (compared with **1Fo**) is achieved also by introduction of electroactive groups such as the methoxyphenyl unit (**2F**).[2] Although the role the peripheral redox groups play in ring closure is not certain at this stage, it is possible that ring closure occurs by an intramolecular electron-transfer process subsequent to oxidation of **2Fo** (Scheme 2).



Scheme 2. Tuning of direction of electro- and photochemical ring-opening/closing. For **1H/2H** oxidative (followed by reduction) ring-closure is observed, whereas for **1F**, oxidative (followed by reduction) ring-opening is observed. Proposed mechanism for ring-closure during the oxidation of **2Fo**.

To investigate the mechanism and driving forces behind electrochemical switching in dithienylethene-based systems, a better understanding of the species formed on oxidation and their relative stabilities is required. In addition, application of this class of compound in molecular devices and functional materials requires that the role of environment in their electrochemical behaviour also be understood. In the following sections, the role of solvent, electrolyte and temperature in controlling the cyclisation/cycloreversion of the dithienylcyclopentenes are explored in an effort to answer some of the questions raised above.

Solvent and electrolyte dependence of the electronic and redox properties of 1Ho/1Hc: The effect of solvent and the nature of the electrolyte on reaction rates, in particular in systems exhibiting chemical reactions subsequent to electrochemical processes, is well established.[25] The solvent dependence of the electronic and redox chemistry of **1H** was examined in detail to explore the role solvent and other environmental factors play in determining the chemical processes which the oxidised open and closed states undergo. The influence of solvent on the absorption spectra of **1Ho** and **1Hc**, although modest, is apparent (see Supporting Information, Figure S2). For **1Hc**, a distinct perturbation of the band shape with changing polarity of the solvent and a bathochromic shift in the bands both at $\lambda_{max} \approx 350$ nm and at $\lambda_{max} \approx 525$ nm (10 nm, 450 cm^{-1}) is observed with decreasing solvent polarity. The absence of a pronounced solvatochromic behaviour suggests the lowest energy absorption in **1Hc** is predominantly $\pi\pi^*$ in nature and has little, if any, charge-transfer character.

The solvent dependence of the redox properties of **1Ho** and **1Hc** is presented in Table 2. Although the first oxidation process of both **1Ho** and **1Hc** is predominantly solvent-independent (**1Ho** 1.12 ± 0.06 V, **1Hc** 0.41 ± 0.07 V),[26] the separation ΔE between the first and second oxidation steps of **1Hc** is very sensitive to both solvent and electrolyte. The relationship between ΔE for the closed forms and solvent acceptor number and dielectric constant (or polarity) was explored, but no clear relationship was observed (see Supporting Information, Table S1).[27] In contrast a relatively good correlation ($R^2 = 0.92$) was observed between ΔE and the Guttmann solvent donor number (Figure 6); ΔE decreases with increasing solvent donor strength.[27] The relationship between solvent donor number and ΔE indicates that a significant degree of stabilisation of the monocation $\mathbf{1Hc}^+$ is achieved through solvation. As the solvent donor strength decreases, the electron density on the closed form

Table 2. Solvent dependence of electrochemical properties of **1H**.

Solvent[a]	Open form $E_{p,a}$ [V] vs SCE (all processes are irr)	Closed form $E_{1/2}$ [V] vs SCE ($E_{p,a}$ where irr)		ΔE [mV]	DN[b] (solvent)
CH_3OH[c]	1.09	0.51 (irr)	0.38	70	19
C_2H_5OH[c]	1.09	0.56 (irr)	0.45 (irr)	110	20
$(CH_3)_2SO$	1.14	0.63 (irr)	0.515 (irr)	115	29.8
DMF	1.15	0.62 (irr)	0.46 (irr)	160	26.6
THF	1.33	0.82 (irr)	0.61	170	20
$(CH_3)_2CO$	1.13	0.69 (irr)	0.47	190	17.0
CH_3CN	1.16	0.67	0.43	240	14.1
$CHCl_3$	1.18	0.73 (irr)	0.46 (qr)	200	<10
$PhNO_2$	1.11	0.68 (qr)	0.34 (qr)	305	4.4
CH_3NO_2	1.08	0.58	0.31	270	2.7
CH_2Cl_2	1.10	0.68	0.34	360	0
Et_2O[d]	1.18	0.86 (irr)	0.345	490	19.2
THF[d]	[e]	0.86 (irr)	0.50	320	20

[a] Unless stated otherwise, measured at 298 K, 0.1 M TBAP supporting electrode, scan rate 100 mV s^{-1}. [b] Guttman donor numbers (DN) are for pure solvents. The effect of the high concentrations (0.1 M) of electrolyte, although nonnegligible, is assumed to be constant throughout the series of solvents. [c] 0.1 M $NaClO_4$ supporting electrolyte. [d] 0.1 M NaBArF, [e] not measured.

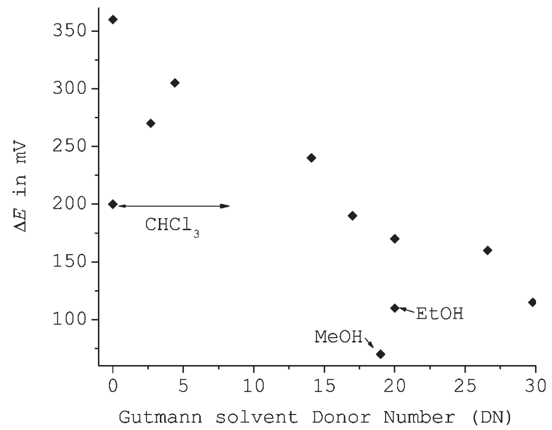


Figure 6. Solvent dependence of ΔE for **1Hc** [$E_{1/2}$(**1Hc**$^+$/**1Hc**$^{2+}$)$-E_{1/2}$(**1Hc**/**1Hc**$^+$)] in 0.1 M TBAP/solvent at 0.1 V s^{-1}. For MeOH and EtOH 0.1 M $NaClO_4$ was employed as supporting electrolyte. For $CHCl_3$ the DN is estimated as <10, but trace impurities may raise the DN of the solvent and hence bring the value of ΔE into alignment. See Table 2 for data.

of the dithienylethene increases, which renders the second oxidation step more difficult and moves it to more anodic potentials.

The value of ΔE obtained in diethyl ether solution is significantly higher than expected (i.e., by comparison with THF, Table 2). This, initially surprising, result is due to the use of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBArF) in place of Bu_4NPF_6 (TBAP) as supporting electrolyte.[28] Although anions such as PF_6^- are generally accepted as being innocent with regard to their coordination properties, they are nevertheless stronger electron donors than the solvents employed. The larger $BArF^-$ anion is a much weaker electron donor than more compact anions (e.g., PF_6^-), and hence its ability to stabilise the monocation (**1Hc**$^+$) would be expected to be much lower, so that an increase in ΔE results.[29] To test this hypothesis the effect of NaBArF (instead of TBAP) was examined. Indeed, in THF the dependence of ΔE on the electrolyte is striking ($\Delta(\Delta E) = 47\,\%$).[29] Correction of the value obtained in diethyl ether[30] ($\Delta E = 490$ mV) for the electrostatic contribution of the electrolyte results in a value of $\Delta E = 260$ mV, which is consistent with data obtained with TBAP. The increased values obtained with $BArF^-$ reflect its poorer donor properties compared with PF_6^-. The importance of the electrolyte is demonstrated further by the fact that in protic solvents (i.e., MeOH and EtOH), values for ΔE lower than expected are obtained. Again the use of $NaClO_4$ as supporting electrolyte is a possible contributing factor to the lower value of ΔE. The effect appears to be restricted to the anionic component of the electrolyte, as in CH_3CN using KPF_6 instead of TBAP has no observable effect on the oxidation chemistry. This sensitivity to the electrolyte indicates that stabilisation by the electrolyte anion (ClO_4^-, PF_6^- or $BArF^-$) through ion pairing is more important than stabilisation through the solvent donor properties. Delocalisation of the SOMO over the entire conjugated system is encouraged by the use of poorer donor environments and leads to an increase in the relative potential of the second oxidation step. Overall the dependence of ΔE on solvent and electrolyte indicates that the first oxidation step (**1Hc** to **1Hc**$^+$) is not delocalised over the entire conjugated system but is localised on a single thienyl ring.

It is clear from Figure 6 that both solvent and electrolyte play a crucial role in stabilisation of the monocation **1Hc**$^+$. In addition, the reversibility of the first and second oxidation processes (i.e., the chemical stability of the mono- and dications **1Hc**$^+$ and **1Hc**$^{2+}$ is very dependent on the solvent employed. The stability of these species is essential if electrochemical ring closure of the open form **1Ho** is to be observed.

Solvent dependence of electrochemical reversibility for switching of 1Ho to 1Hc: The effect of the solvent on the stability of the mono- and dications of the closed forms and the switching processes was examined for **1H**. In strong donor solvents neither process is reversible; the first oxidation step results in rapid decomposition (only the first oxidation process is observable at scan rates <100 mV s^{-1}). In weaker donor solvents such as acetone, the first oxidation process of the closed form becomes fully reversible (vide supra). Nevertheless a pronounced dependence on scan rate of the reversibility of the second redox process (with improved reversibility at higher scan rates) is observed in several weaker donor solvents, and formation of a stabilised cationic species is observed (vide infra). These observations indicate that several factors influence the electrochemical stability of these systems.

Figure 7 shows cyclic voltammograms of **1Hc** (a) and **1Ho** (b) in diethyl ether. As for **1Ho** in acetonitrile, an irreversible oxidation process is observed at about 1.18 V (vs

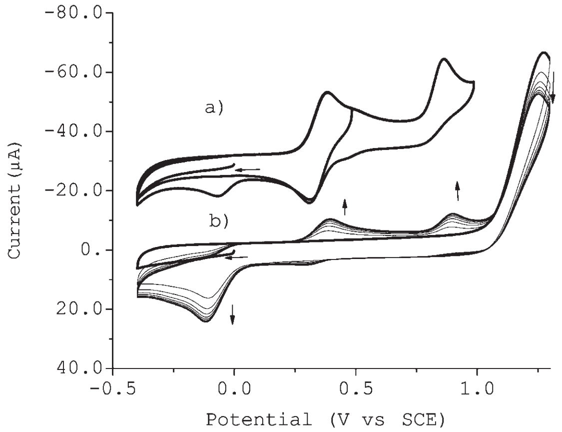


Figure 7. Repetitive cyclic voltammetry of a) **1Hc** and b) **1Ho** in diethyl ether (0.1 M NaBArF) at 298 K and 1 $V s^{-1}$.

SCE). However, only negligible amounts of **1Hc**$^{2+}$ are observed on the return scan. Instead a reduction process at −0.1 V is observed, which is attributed to an additional species (**1Hx**). This new species is cationic and is formed by reversible chemical rearrangement of **1Hc**$^{2+}$ (vide infra). The reduction process observed on the return cycle (at −0.1 V) is itself irreversible and results in two new oxidation processes being observed on the second scan at potentials coincident with those of the closed form (**1Hc**), as for **1Fo** in CH_3CN (see Figure 3).

Similar behaviour was obtained for the closed form **1Hc** (Figure 7). Oxidation processes observed at 0.345 and 0.86 V (vs SCE) are assigned to the formation of the mono- (**1Hc**$^{+}$) and dicationic (**1Hc**$^{2+}$) forms, respectively (vide supra). The first oxidation process is fully reversible, but the second oxidation process is irreversible and yields a reduction process at −0.1 V (as observed for **1Ho**) on the return cycle. Similar behaviour is observed in acetone, THF, dichloromethane and $CHCl_3$, albeit with increasing reversibility of the second oxidation process of the closed form with increasing solvent donor strength. This solvent dependence highlights the role of solvent in the stabilisation of **1Hc**$^{2+}$ and **1Hc**$^{+}$. In every case, at higher scan rates reversibility of the redox chemistry of **1Hc** is improved, and this confirms that the formation of **1Hx** occurs by an electrochemical–chemical (EC) mechanism and that the transformation is not directly coupled to the electron-transfer process itself (Figure 8). Clearly, for **1Hc**, both the first and second oxidation processes are electrochemically reversible, and the formation of the oxidation product (**1Hx**, observed at −0.1 V) is due to a subsequent chemical reaction (presumably a reversible intramolecular reaction given its chemical reversibility), that is, the process has an EC mechanism[21] (vide infra). Hence, overall, the conversion of **1Ho** to **1Hc** may be viewed as an ECEC mechanism in diethyl ether. A broad overview of the mechanisms discussed in this section is presented in Figure 8.

Overview of redox processes: It is clear from cyclic voltammetry (vide supra) that **1Ho** yields the dication **1Hc**$^{2+}$ and/or **1Hx** on oxidation, with a clear solvent dependence for the formation of either species. Both **1Hc**$^{2+}$ and **1Hx** are also formed by oxidation of the closed form above the second oxidation process (e.g., > 0.7 V). For **1Hc** an intermediate species (monocation **1Hc**$^{+}$) is formed between the first and second oxidation processes (ca. 0.4 to ca. 0.6 V, see Table 1). For **1Fc**, although the first oxidation process is electrochemically reversible, the irreversibility of the second oxidation process (which occurs at almost the same potential) renders the oxidation irreversible overall (Figure 3). In contrast, for **2Fc** fully reversible oxidation processes were observed, and **2Fo** undergoes electrochemical ring closure to form **2Fc**. To gain deeper insight into the electrochemical processes observed by cyclic voltammetry, the spectroscopic properties of the various oxidation products were investigated by spectroelectrochemistry.

Spectroelectrochemistry: Spectroelectrochemistry is a powerful tool in the elucidation of redox processes and the identification of oxidation products.[31] It is surprising then that this technique has not been applied to dithienylcyclopentene-based electrochromic compounds, with the exception of one isolated example.[13d] It is clear from cyclic voltammetry that oxidation of **1Ho**, **2Ho** or **2Fo** leads to ring closure to form **1Hc**$^{2+}$, **2Hc**$^{2+}$ or **2Fc**$^{2+}$. However, for **1Fo** ring closure is not observed, presumably due to the irreversible nature of the oxidation of **1Fc** to **1Fc**$^{2+}$. To establish the ultimate products of these oxidation processes spectroelectrochemical characterisation of all four compounds in both open and closed states was carried out.

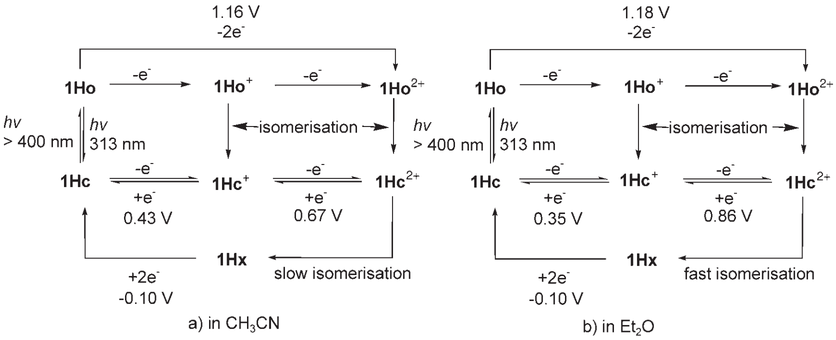


Figure 8. Schematic diagram of electrochemical processes observed for **1Ho**/**1Hc** in a) CH_3CN (0.1 M TBAP) and b) diethyl ether (0.1 M NaBArF). Arrows indicate chemical reversibility only. The rate of isomerisation is relative to electrochemical scanning rate (0.1 $V s^{-1}$). The point of ring closure (i.e., via **1Ho**$^{+}$ or **1Ho**$^{2+}$) is discussed further in the text (vide infra).

Table 3. Electronic properties of **1Hc**$^{m+}$/**o** and **2Hc**$^{m+}$/**o** (m = 0, 1, 2, from Figures 9 and 10) and **1Hx** (from Figure 10) in CH_3CN (0.1 M TBAP).[a]

	Abs. λ_{max} [nm]		Abs. λ_{max} [nm] (ε)
1Ho	278, 303 (sh)	**2Ho**	284, 308 (sh)
1Hc	267, 287 (sh), 349, 360, 527	**2Hc**	237, 273 (sh), 303, 345, 519
1Hc$^+$	387, 447, 753, 838(sh), >1100	**2Hc**$^+$	392, 444, 528, 757, 846, 1043
1Hc^{2+}	390, 537	**2Hc**$^{2+}$	387, 435, 546, 582
1Hx	406 (sh), 427, 674		

[a] sh = shoulder.

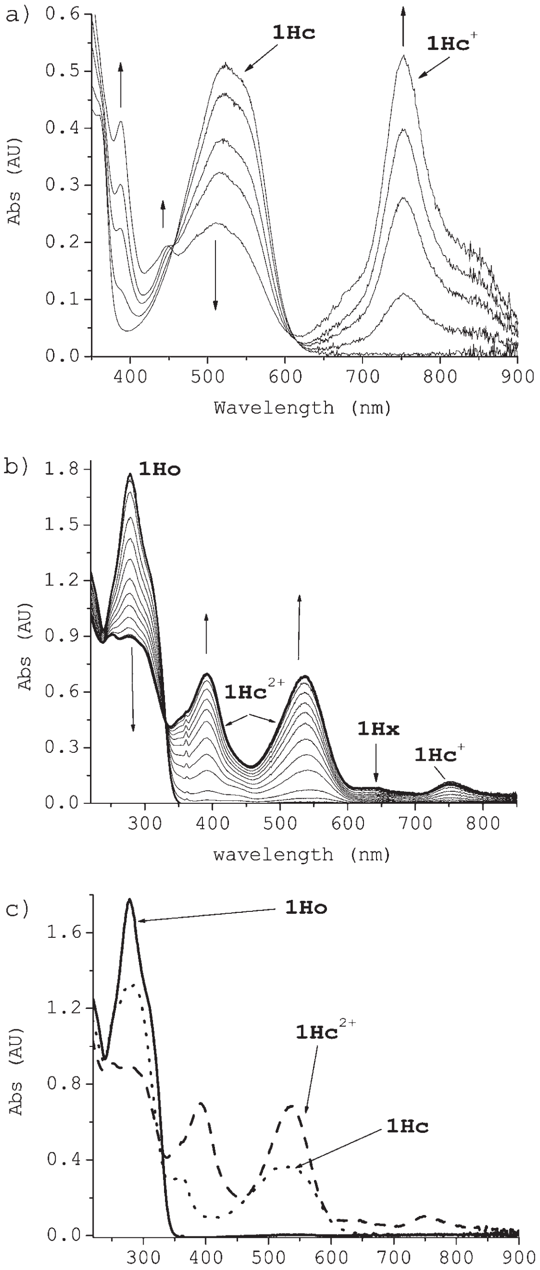


Figure 9. a) Oxidation of **1Hc** to **1Hc**$^+$ at 0.55 V, b) oxidation of **1Ho** to **1Hc**$^{2+}$ at 1.3 V and c) subsequent reduction to **1Hc** at 0 V and 273 K in 0.1 M TBAP/CH_3CN.

Spectroelectrochemical properties of 1Ho/1Hc: For **1Hc** the large separation between the first and second oxidation steps allows generation of both the monocationic (**1Hc**$^+$) and dicationic (**1Hc**$^{2+}$) species (see Table 3). Oxidation at 0.55 V (i.e., at a potential intermediate between the first and second oxidation processes of **1Hc**) results in depletion of the absorption of **1Hc** (at ca. 530 nm) with a concomitant formation of strong absorption bands at about 750 nm and >1100 nm and sharp transitions at 387 and 447 nm (possibly formally spin forbidden transitions, as indicated by their narrow peak shape). Complete recovery of the original spectrum of **1Hc** is observed on subsequent reduction at 0.0 V. The low-energy absorption bands and the narrow transitions at higher energy support the assignment of the spectrum as that of the monocation **1Hc**$^+$.[32] Oxidation of **1Hc** (or **1Hc**$^+$) at 0.9 V resulted in the formation of **1Hc**$^{2+}$ (λ_{max} = 390, 537 nm) at 273 K. At higher temperatures, (e.g., 298 K) **1Hc**$^{2+}$ was unstable, and the absorptions at 390 and 537 nm decreased, while new bands appeared at 685, 425 and 403 nm (**1Hx**). The species formed is cationic[33] and can be reduced to the closed form **1Hc** at −0.2 V versus SCE. The species is assigned as the same species **1Hx** observed by cyclic voltammetry (see Figures 4 and 7).

On oxidation of **1Ho** at 1.3 V (at 273 K), a marked decrease in the absorption intensity around 280 nm is observed, accompanied by the appearance of new bands at 390 and 537 nm (**1Hc**$^{2+}$). In addition, bands assignable to **1Hc**$^+$ and **1Hx** (vide supra) are also present, but reach only very low pseudo-steady-state concentration prior to complete oxidation of **1Ho**. Reduction of the oxidised sample (i.e., **1Ho** electrolysed at 1.3 V) at 0.0 V results in a decrease in the absorption intensity at 554 nm, together with an almost complete loss of the absorption bands at 396 and 428 nm and a transient increase in the absorption at 750 nm (assigned to **1Hc**$^+$). The transient formation of **1Hc**$^+$ during reduction of **1Hc**$^{2+}$ is not unexpected. The reduction of **1Hc**$^{2+}$ to **1Hc** is not a concerted two-electron transfer but occurs in two single-electron reduction steps. Partial recovery of the absorption intensity around 280 nm also occurs, but a strong absorption at about 530 nm remains (Figure 9c). As expected, no change in the absorption at 685 nm (**1Hx**) is observed until reduction at −0.2 V is carried out (**1Hx** is most likely formed via **1Hc**$^{2+}$, vide supra). Reduction at −0.2 V results in depletion of **1Hx** (i.e., bands at 685 and 425 nm), further recovery of the 280 nm absorption and a small increase in the absorption at 530 nm. The absorption spectrum (in the visible region, λ_{max} = 530 nm) is identical to that of **1Hc**, that is, ring closure occurred during the oxidation and subsequent reduction process.

Formation and properties of 1Hx: The formation of **1Hx** directly from **1Hc**$^+$ is improbable, as the rate of conversion is quite modest when oxidation is carried out at 0.55 V. This conclusion is supported by the fact that at lower temperature the formation of **1Hx** is suppressed effectively and also by the fact that in diethyl ether the **1Hc**/**1Hc**$^+$ redox couple is fully reversible (Figure 7). At 298 K, oxidation at 0.9 V results in very rapid formation of **1Hx** and transient formation of **1Hc**$^+$ with no spectral evidence for the formation of **1Hc**$^{2+}$. It is probable then that formation of **1Hc**$^{2+}$ results in reversible rearrangement to the more stable species **1Hx**. Reduction of **1Hx** at −0.2 V results in reformation of the spectrum of **1Hc** (Figure 10). Hence, it can be concluded that the disproportionation of **1Hc**$^+$ [i.e., $2\,\mathbf{Hc}^+ \rightleftharpoons \mathbf{1Hc}^{2+} + \mathbf{1Hc}$, see Eq. (1) below], although thermodynamically unfavourable, is driven by the rapid conversion of **1Hc**$^{2+}$ to **1Hx**. The isosbestic points observed on reduction of **1Hx** to **1Hc** suggests the chemical reaction which follows reduction is rapid with no long-lived intermediates.

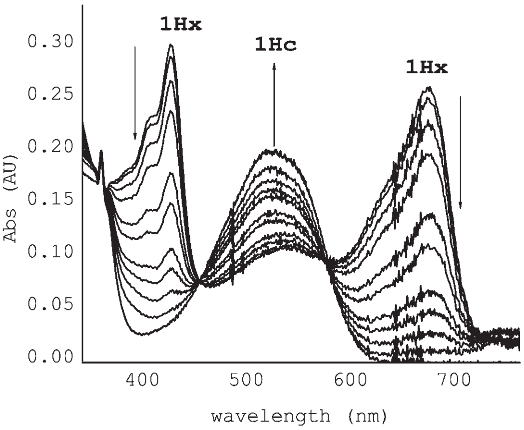


Figure 10. Reduction of **1Hx** (generated by oxidation of **1Hc** at 0.9 V) to **1Hc** at −0.2 V at 298 K in 0.1 M TBAP/CH_3CN.

The rapid conversion of **1Hx** to **1Hc** on reduction indicates that the formation of **1Hx** occurs with retention of structure (i.e., it involves an intramolecular rearrangement). The molecular structure of **1Hx** is, at present, unknown, but its intense visible absorption spectrum, very low oxidation potential and insolubility in hexane confirm that it is a cationic species. In addition, its rapid formation from **1Hc**$^{2+}$ indicates that **1Hx** is a dication. The strong temperature and electrolyte dependence, together with the absence of a concentration or O_2 dependence, of the formation of **1Hx** indicates that the conversion of **1Hc**$^{2+}$ to **1Hx** is an intramolecular process.

Selective oxidation by chemical oxidants has been employed previously to induce electrochemical ring opening.[13] The use of selective oxidants in achieving ring closure was also explored. The monocation **1Hc**$^+$ could be prepared by selective oxidation with ferrocenium hexafluorophosphate (0.39 V vs SCE) in several solvents (see Figure S3 in the Supporting Information).[19] The absorption spectrum of the monocation is largely solvent-independent (752–760 nm), but the lowest energy absorption feature (>1100 nm) is beyond the range of the instrument. Similarly, chemical oxidation with the stronger oxidant Ce^{IV} (ca. 0.9 V vs SCE),[19] at 298 K results in oxidation of **1Ho** and **1Hc** to **1Hx**. Spectral features of both **1Hc**$^+$ and **1Hc**$^{2+}$ could be observed during the oxidation process. It is clear that electrochemical ring closure by chemical oxidation is possible, however it is difficult to control, and the formation of **1Hx**, (which requires subsequent reduction to form **1Hc**, Figure 7 and 10 highlight the complexity of the cyclisation/cycloreversion processes observed for this class of compound (Figure 8).

*Spectroelectrochemical properties of **2Ho**/**2Hc***: The methoxyphenyl-based compounds (**2H**) exhibited electrochemical ring closure of **2Ho** and reversible oxidation of **2Hc** to **2Hc**$^+$ and **2Hc**$^{2+}$. For **2H** similar spectroelectrochemical behaviour to that of **1H** was observed (Figure 9). Bulk oxidation of **2Ho** (at 1.0 V) leads to the formation of intense bands in the visible region, which show more structure than that observed for **1Ho** (Figure 11). Formation of **2Hc**$^+$ (ca. 50%) was also observed during oxidation, with complete disappearance of features assigned to **2Hc**$^+$ towards the end of the oxidation process resulting in **2Hc**$^{2+}$ (Figure 11). No evidence for the formation of a species equivalent to **1Hx** in significant amounts was observed, however. This is possibly due to the stabilising effect of the

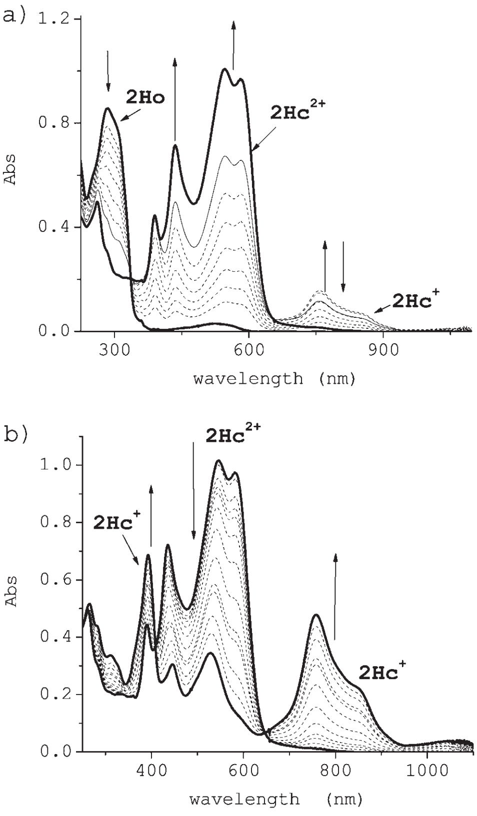


Figure 11. Oxidation of **2Ho** to **2Hc**$^{2+}$(a) at 1.3 V and subsequent reduction to **2Hc**$^+$ at (b) 0.35 V at 273 K in 0.1 M KPF_6/CH_3CN.

methoxyphenyl groups on cation **2Hc**$^+$ and dication **2Hc**$^{2+}$. Reduction of **2Hc**$^{2+}$ did not occur, except below 0.45 V (as expected), and at 0.35 V complete conversion to monocation **2Hc**$^+$ was observed. Subsequent reduction at 0.0 V leads to complete loss of the spectral features assigned to **2Hc**$^+$ and the formation of a spectrum similar[34] to that of **2Hc** generated photochemically from **2Ho** (Figure 12). The differences between the spectrum generated electrochemically and that generated photochemically are attributable to minor (<10%) degradation under electrochemical conditions.

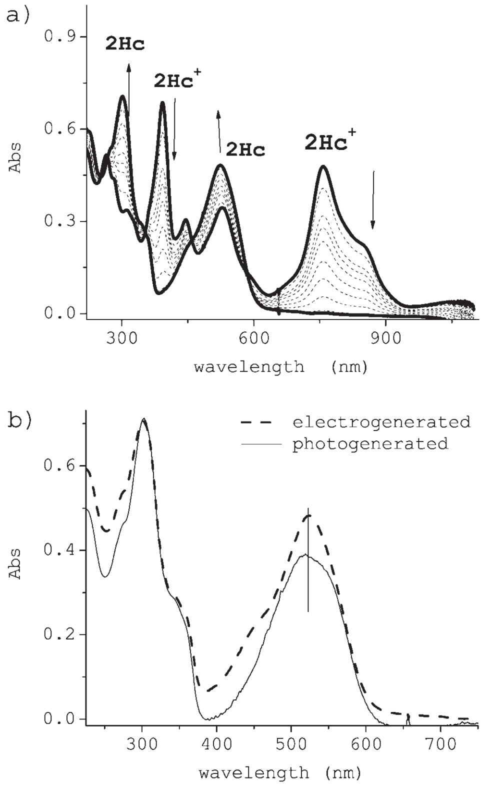


Figure 12. Reduction of **2Hc**$^+$ to **2Hc** (a) at 0 V at 273 K in 0.1 M KPF_6/CH_3CN and overlay of spectra of photochemically generated closed form with electrochemically generated compound (b).

*Spectroelectrochemical properties of **1Fo/1Fc***: In contrast to **1Ho** and **2Ho**, electrochemical ring closure was not observed by cyclic voltammetry for **1Fo**. Moreover, oxidation of **1Fc** resulted in very rapid subsequent chemical reactions, and hence an effectively irreversible oxidation process was observed at slow scan rates. To investigate further the products of both these oxidation processes, spectroelectrochemical studies were carried out on **1Fo** and **1Fc**. For **1F**, efficient and quantitative electrochemical ring opening of **1Fc** to **1Fo** was observed on controlled potential electrolysis at 1.0 V (vs SCE, Figure 13). No evidence for additional bands in the visible region was obtained during the course of the oxidation process, but the conversion of **1Fc** to **1Fo** (via **1Fc**$^{2+}$) is clearly not immediate on oxidation (as evidenced by the slower formation of the open form compared with the rate of loss of the closed form). As expected from cyclic voltammetry, oxidation of **1Fo** resulted in irreversible oxidation with a significant modification of the absorption spectrum in the UV region, that is, degradation. Although oxidation of **1Fo** did not lead to ring closure, regeneration of **1Fc** was possible by UV irradiation ($\lambda = 313$ nm). Subsequent ring opening by oxidation and photochemical ring closure were achieved (at 298 K) with less than 10% degradation per cycle (possibly due to formation of reactive species such as NH_3 during the electrochemical oxidation).[35] Recently, Zhou et al.[13d] showed that electrochemical ring opening of hexafluorocyclopentene-based compounds in which the substituent at C5 of the thienyl ring is H or -$CH(COCH_3)$-(CO_2CH_3)[36] is a general feature of this class of compound. For compounds which incorporate electroactive groups, ring opening was reported to occur.[13d]

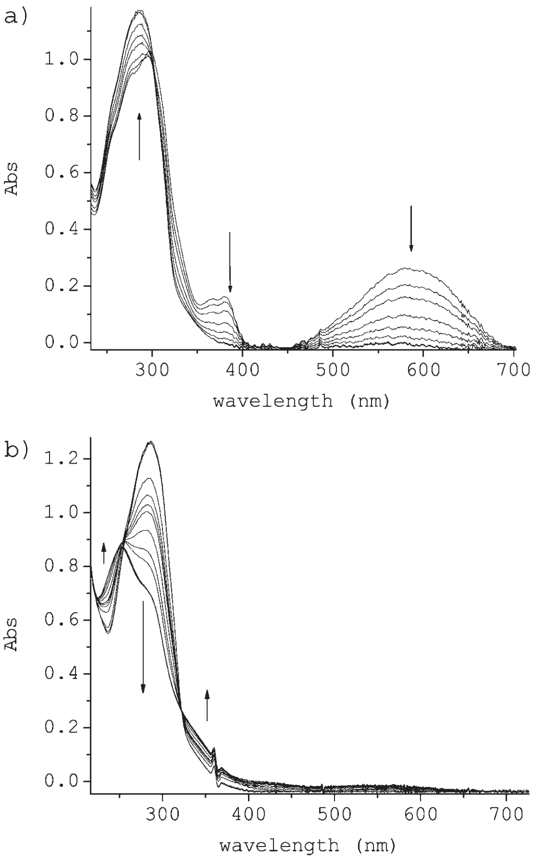


Figure 13. Oxidation of **1Fc** (a) at 1.0 V and **1Fo** (b) at 1.4 V at 273 K in 0.1 M TBAP/CH_3CN.

*Spectroelectrochemistry of **2Fc/2Fo***: Cyclic voltammetry shows that the redox properties of **2F** are in marked contrast to those of **1F**. Clearly, in the closed form the oxidation process is localised on the dithienylcyclopentene unit, but in the open form the low redox potential and clearly opposite redox behaviour to **1Fo** supports assignment of the oxidation process at 1.2 V as being methoxyphenyl-based. In contrast to the hexahydrocyclopentene-based compounds **1H**/**2H**, more complex spectroelectrochemical behaviour (Figures 14 and 15) is observed for methoxyphenyl-based **2F**.

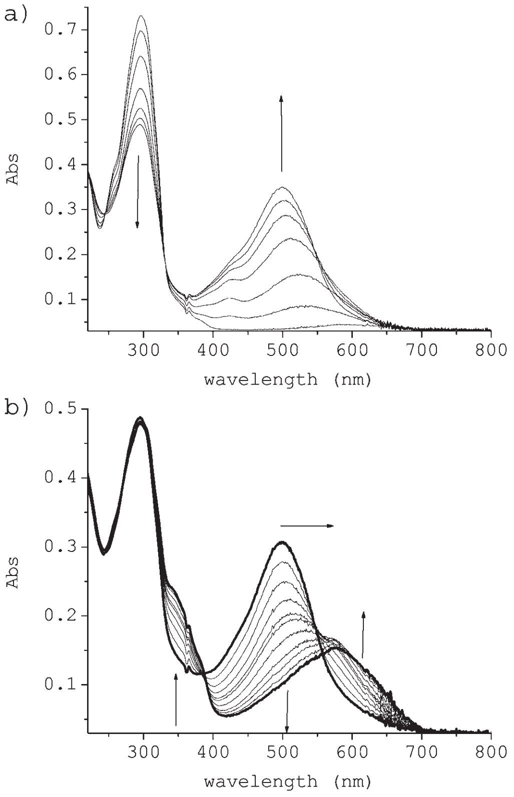


Figure 14. Oxidation of **2Fo** at 1.4 V to **2Fc**$^{2+}$ (a) followed by reduction of the oxidation product at 0 V to **2Fc** (b).

Oxidation of **2Fo** at 1.4 V results in a decrease in absorbance at 295 nm and increase in absorbance in the visible region (Figure 14a). The growing in of the band at 500 nm is preceded by the initial formation of two bands at 422 and 530 nm (the intermediate spectrum resembles that obtained for **2Fc** on oxidation, vide infra). Reduction at 0.0 V resulted in only minor changes at 295 nm, but the absorption maximum at 500 nm undergoes a decrease in intensity and a red shift to 575 nm, and the increase in absorbance at 350 nm is similar to that observed for **2Fc**. The absence of clear isosbestic points indicates that several species are involved in the redox processes.

For the closed form **2Fc**, oxidation at 1.0 V results in the appearance of a weak absorption band at about 750 nm and a blue shift in the visible absorption spectrum, from 595 to 559 initially, followed by a further blue shift to 525 nm and the appearance of a new band at 430 nm. In the near-UV region a collapse in the absorption band of **2Fc** at 350 nm is observed. Formation of the monocation **2Fc**$^+$ is not practical due to the absence of significant separation of the first and second oxidation steps. Nevertheless, previous studies on both organic and inorganic systems have shown that it is possible to form the monocation in appreciable amounts.[37]

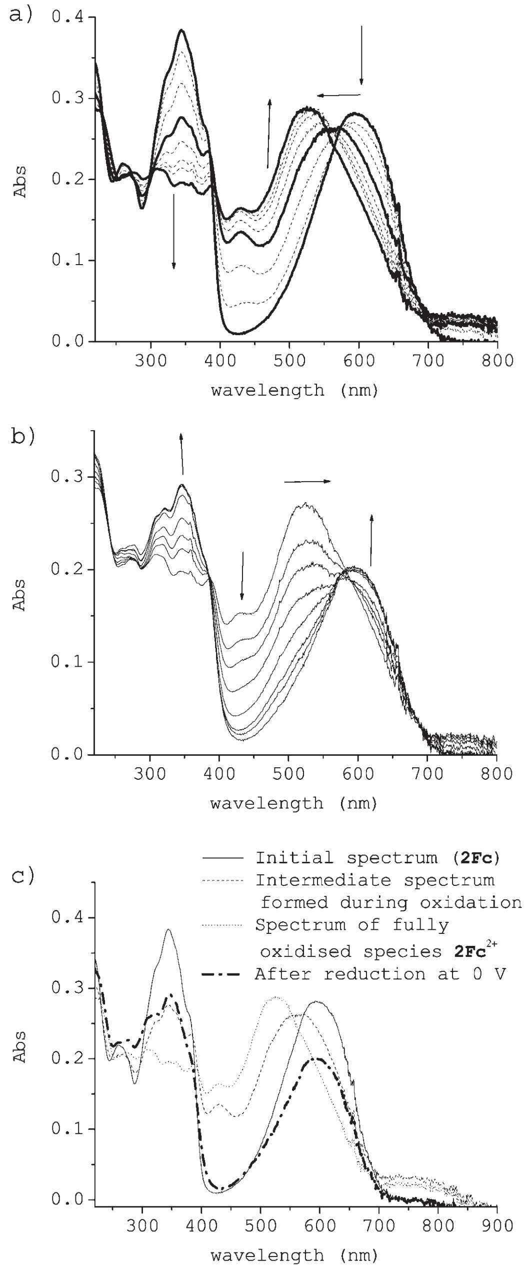


Figure 15. Oxidation of **2Fc** at 1.0 V to **2Fc**$^{2+}$ (a) followed by reduction of the oxidation product at 0 V to **2Fc** (b). Overlay of initial, oxidised and final spectra and spectra observed during oxidation (c).

Subsequent reduction at 0.0 V resulted in partial reformation of the spectrum of **2Fc** (60 %) and a small increase in absorption at 305 nm. The lack of evidence for increased absorption at 285 nm suggests ring opening does not occur. It is possible that during the oxidation process "deprotection" of the methoxyl groups occurs, but this is unlikely given that the absorption features are distinctly different to those reported by Lehn et al. for the demethylated compound.[2] Possibly, the lack of a clear isosbestic point at any stage during the oxidation and subsequent reduction of **2Fc** is due to formation of the monocation.[37]

Localisation of the HOMO: methoxyphenyl versus thienyl, and the driving force for ring closure: The driving force for ring opening/closing in the dithienylcyclopentene compounds may be rationalised (at least to a first approximation) by consideration of the relative frontier orbital energies and the effect of varying the bridgehead (the cyclopentene unit) and the C5 substituents.[38] The oxidation potential for the methoxyphenyl unit is typically about 1.2–1.5 V versus SCE,[39] and hence for **2H** the low redox potentials (Table 1) of both the open and closed forms and the close similarity in behaviour of **2H** and **1H** suggest that the redox chemistry does not involve oxidation of the methoxyphenyl unit. It is clear from both electrochemical and spectroelectrochemical studies that for **1H** and **2H** the redox properties are dominated by the dithienylethene unit. In the case of **2H** the effect of the methoxyphenyl unit is predominantly that of an electrochemically innocent electron-donating group. The differences observed in the electrochemical properties of **1H** and **2H** (i.e., the lower value of ΔE and species **2Hx** is not observed) can be rationalised on the basis of increased stabilisation of the mono- and dications by the methoxyphenyl group. Similarly, for **2Fc**, the first oxidation process is sufficiently cathodic relative to the expected methoxyphenyl oxidation that the oxidation process at 0.67 V can be assigned with confidence to the dithienylethene unit itself. In the case of **2Fo**, however, assignment of the first oxidation process is more difficult. The oxidation potential of 1.2 V for **2Fo** is shifted considerably less anodically from that observed for **2Ho** (200 mV) than would be expected by comparison with **1Ho**/**1Fo** (420 mV).

The similar spectroelectrochemical behaviour of **1H** and **2H** in both open and closed forms and the marked dissimilarity in behaviour of **1F** and **2F** suggests that the electrochemical properties of hexahydrocyclopentene compound **2H** are largely due to the dithienylethene unit, whereas in the hexafluorocyclopentene-based **2F** the electrochemical properties involve extensive mixing between the dithienylethene unit and the peripheral methoxyphenyl groups.

Comproportionation constant, ΔE and charge localisation in the monocationic form $\mathbf{1Hc}^+$: The comproportionation constant K_c[20] is a measure of the stability of the monocation $\mathbf{1Hc}^+$ with respect to disproportionation into neutral species **1Hc** and dication $\mathbf{1Hc}^{2+}$ [Eqs. (1)–(3), Sw_c = dithienylcyclopentene].[20] The parameter of interest is the separation ΔE between the two thienyl-based oxidation processes. This separation is related to the stability of the monocation.[20]

$$Sw_c + Sw_c^{2+} \rightleftharpoons 2\,Sw_c^{+} \tag{1}$$

$$K_c = [Sw_c^{+}]^2/[Sw_c][Sw_c^{2+}] \tag{2}$$

$$K_c = \exp(\Delta E/25.69) \tag{3}$$

The value of K_c and the separation between the first and second redox process for the closed dithienylethene raises a central issue: what is the nature of the redox chemistry of the switches. In the open form, two thienyl units are present and they are undoubtedly not coplanar to any significant extent. In the absence of any effective orbital overlap mediated by the alkene orbitals of the cyclopentene ring, each thienyl ring can be treated as a separate electrochemical entity. Hence, the oxidation and reduction of each ring may potentially occur as two independent electron-transfer processes. For the closed switch a different situation arises due to the change in the nature of the thienyl rings, the two *trans*-butadiene components of the closed form and the coplanarity of the three rings. In contrast to the open form, the question arises whether the closed form can be treated as a single redox entity or remains as two independent units. To answer this question two issues must be considered. Firstly, what is the extent of delocalisation of the HOMO and LUMO in the closed form. Secondly, if the closed form is composed of two "independent" redox-active units, to what proportion do electrostatic interactions contribute to the comproportionation constant K_c.

The electrostatic interaction between the redox units can potentially be estimated by examination of the open forms of the dithienylethene compounds. The absence of separation between the first and second redox processes in the open form suggests that electrostatic contributions are minimal. However, the absence of separation can be rationalised also by considering the possibility that ring closure occurs after the first oxidation process of **1Ho**. If the first oxidation step (**1Ho** to $\mathbf{1Ho}^+$) leads instantaneously to the closed monocation $\mathbf{1Hc}^+$, then the monocation will immediately be oxidised to the dication $\mathbf{1Hc}^{2+}$ (Figure 4). That this occurs is supported, to some extent, by the observation of significant amounts of the monocations $\mathbf{1Hc}^+$ and $\mathbf{2Hc}^+$ prior to observation of the dications $\mathbf{1Hc}^{2+}$ and $\mathbf{2Hc}^{2+}$ in spectroelectrochemical studies on the open forms (Figures 9 and 11). The very small separation between the first and second oxidation processes of **1Fc** and **2Fc** indicate that in the present systems the electrostatic contribution to K_c is at most very small (<30 mV).

The decrease in K_c on going from **1Hc** to **1Fc** (and similarly from **2Hc** to **2Fc**) and the reduction observed on introduction of the electron-donating methoxyl substituent support the assignment of the oxidation of the closed form as involving two weakly coupled redox active units (Type II in the classification of Robin and Day[40]), each centered on a thienyl ring (or more specifically on a thio-*trans*-butadiene system, the localised model, see Figure 16). If this is indeed the case then the decrease in K_c by the introduction of the perfluorocyclopentene group (and also the electron-donating methoxyphenyl groups) suggests that the mechanism for interaction between the thio-*trans*-butadiene units is a HOMO-mediated superexchange process (see Scheme 3).

Electrochemical ring-opening versus ring-closing: The driving force for electrochemical ring opening and closing observed in **1H**, **1F**, **2H** and **2F** can be rationalised on the basis of the nature of the oxidation process. In the oxidised forms either a cyclic thiophene-based monocation or an acy-

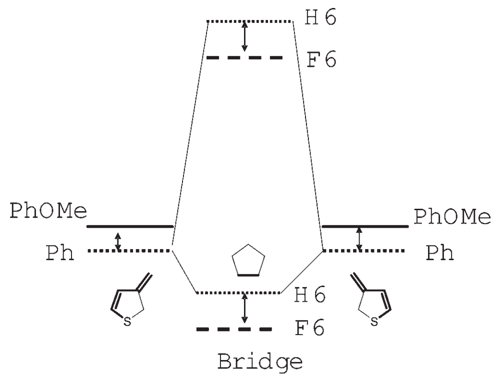


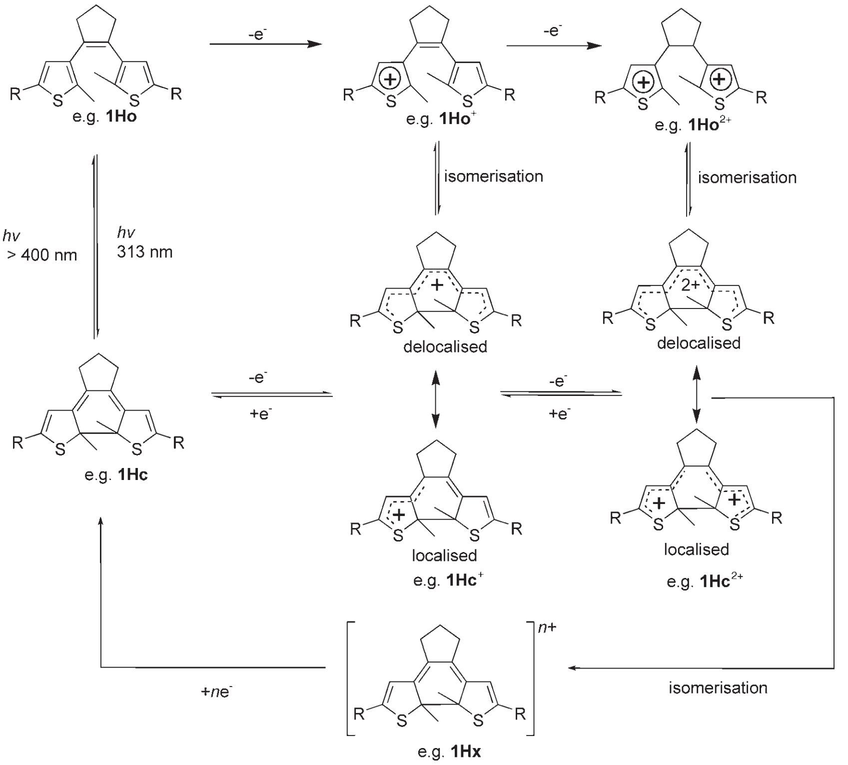
Figure 16. Schematic diagram illustrating effect of cyclopentene unit and C5 substitution on relative frontier orbital energies. The double arrows indicate relative stabilisation/destabilisation of the molecular orbitals.

clic *trans*-butadiene moiety can form. The driving force behind the ring opening/closing reactions can be considered in terms of the extent of delocalisation of the positive charge in the oxidised forms. For **1Fc** oxidation results in ring-opening to **1Fo**. The hexafluorocyclopentene ring would be expected to be very poor in facilitating delocalisation of charge over both rings or facilitating rapid electron transfer between the thiophene moieties, so that ring opening with localisation of the charge on the thiophene rings results. For **1H** the reverse situation is apparent. The hexahydrocyclopentene unit is better at facilitating communication between the two thiophene units, and hence stabilisation of the mono- and dications of the closed form would be expected. The observation of **1Hc**$^+$, albeit at a low concentration, is significant and suggests ring closure occurs through formation of **1Ho**$^+$ leading to **1Hc**$^+$, which is oxidised to **1Hc**$^{2+}$.

Conclusion

A key feature of both the dithienylhexafluoro- and dithienylhexahydrocyclopentenes is their propensity to undergo ring-closure and ring-opening photochemically. Electrochemically driven ring-opening and ring-closing has received much less mechanistic attention. In contrast to the photochemical (excited state) processes, the mechanism and factors that influence oxidative ring-opening/closing of the dithienylcyclopentene systems had not been investigated in detail. In the present study, it has been established that the efficiency of electrochemically driven processes and the direction of the oxidatively driven switching is dependent on the nature of the cyclopentene unit and the solvent employed. The driving force for ring closure appears to be the stabilisation achieved by the mono- and/or dication of the open form in converting to the ring-closed form. Spectroelectrochemistry of **1Ho** reveals that both the open and closed switches form the same oxidation product, and this indicates that ring closure on oxidation is quite fast (i.e., faster than the electrochemical timescale). In the case of **2Fo**, the involvement of the methoxyphenyl group in electrochemical ring closure is apparent from cyclic voltammetry, but from spectroelectrochemistry it is clear that the process is not direct and involves initial oxidation of the methoxyphenyl groups followed by an intramolecular process. This opens the exciting possibility of using intramolecular electron transfer to achieve switching in directions other than would be preferred by the central dithienylethene core (e.g., the different directions of switching between **1F** and **2F**).

We have presented a detailed examination of various aspects of the electronic and redox properties of dithienylethene-based switches. The effect of solvent, temperature and bridging cyclopentene unit on both the electronic and redox properties was explored. Important-



Scheme 3. General scheme for electrochemical processes observed in dithienylethene based systems (the structure shown for **1Hx** is for illustrative purposes only).

ly, from the results presented, it is clear that the mechanism of electrochemical ring opening and ring closure is not simple and involves the balancing of both the medium and molecular structure. The information obtained here provides a solid basis to understand the intrinsic properties of the dithienylethene cores. This insight is essential for enabling rational design of more complex electrochemically responsive systems and predicting their behaviour in various environments (e.g., solvent, electrolyte, etc.). In a further report, the effects of substitution of the phenyl moiety and the introduction of asymmetry will be explored.

Experimental Section

For all spectroscopic measurements Uvasol-grade solvents (Merck) were employed. All reagents employed in synthetic procedures were of reagent grade or better and used as received unless otherwise stated. Compounds **1H**, **2H**, **1F** and **2F**[14] and ferrocenium hexafluorophosphate[19] were prepared by previously reported procedures. UV/Vis absorption spectra (accuracy ±2 nm) were recorded on a Hewlett-Packard UV/Vis 8453 spectrometer. Electrochemical measurements were carried out on a Model 630B Electrochemical Workstation (CHInstruments). Analyte concentrations were typically 0.5–1 mM in anhydrous acetonitrile containing 0.1 M TBAP or 0.1 M NaBArF[41] (except where stated otherwise in the text). Unless otherwise stated, a Teflon-shrouded glassy carbon working electrode or 10 μm diameter platinum microelectrode (CHInstruments), a Pt wire auxiliary electrode and SCE or nonaqueous Ag/Ag^+ ion reference electrode were employed. Reference electrodes were calibrated with 0.1 mM solutions of ferrocene (0.38 V versus SCE in 0.1 M TBAP/CH_3CN). Solutions for reduction measurements were deoxygenated by purging with dry N_2 gas (presaturated with solvent) prior to the measurement. Cyclic voltammograms were obtained at sweep rates of between $10\,mV\,s^{-1}$ and $50\,V\,s^{-1}$; differential pulse voltammetry (DPV) experiments were performed with a scan rate of $20\,mV\,s^{-1}$, a pulse height of 75 mV and a duration of 40 ms. For reversible processes the half-wave potential values are reported; identical values were obtained from DPV and CV measurements. Redox potentials are ±10 mV. Spectroelectrochemistry was carried out with a custom-made OTTLE setup comprising a platinum gauze mesh working electrode (52 mesh, 0.1 mm wire diameter, Aldrich) a custom-made quartz cuvette with 2 mm path length (Chandos Intercontinental, UK) equipped with a solvent reservoir holding the reference electrode and a platinum gauze counterelectrode (separated from the main solution by a ceramic frit) or in a SPECAC OTTLE cell (0.5 mm path length). Measurements were made at 0 °C with a Quantum Northwest Peltier-cooled cell holder, modified for the UV/Vis spectrometer.

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[35] The formation of NH_4^+ under bulk electrochemical conditions was confirmed by the observation of the 1:1:1 triplet at about 6.5 ppm by ^{1}H NMR spectroscopy.

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