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Oxidative Electrochemical Switching in Dithienylcyclopentenes, Part 2: Effect of Substitution and Asymmetry on the Efficiency and Direction of Molecular Switching and Redox Stability**

Wesley R. Browne, Jaap J. D. de Jong, Tibor Kudernac, Martin Walko, Linda N. Lucas, Kingo Uchida, Jan H. van Esch, and Ben L. Feringa*[a]

Abstract: The electrochemical and spectroelectrochemical properties of a series of C5-substituted dithienylhexahydro- and dithienylhexafluorocyclopentenes are reported. The effect of substitution at C5 of the thienyl moiety on the redox properties is quite dramatic, in contrast to the effect on their photochemical properties. The efficiency of electrochemical switching is dependent both on the central cyclopentene unit and on the nature of the substituents, whereby electron-donating moieties favour oxidative electrochemical ring-closure and vice versa. Asymmetrically substituted dithienylcyclopentenes were investigated to explore the ring-closure process in more detail. The results indicate that electrochemically induced ring-closure occurs via the monocation of the open form. In the presence of electroactive groups at C5 of the thienyl ring (e.g., methoxyphenyl) initial oxidation of these groups is followed by intermolecular electron transfer, which drives ring-closure of the open forms.

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

Introduction

In recent years, photo- and electrochromic materials have received considerable attention for potential application in visual-display and molecular information-storage technologies.[1] Systems based on transition metals such as ruthenium(II)[2,3] and organic systems based on spiropyrans[4] and diarylethenes[5] have proven to be especially suitable for such applications. The effectiveness of molecular-based materials requires that their properties can be tuned readily to suit particular functions, a requirement which has prompted many studies on transition metal- and organic-based[2,6] systems. These studies have focussed on understanding the factors which control their photophysical and electrochemical properties. Although the photochromic behaviour of materials based on diarylethenes, fulgides[7] and spiropyrans has been investigated extensively in recent years and has been adapted to drive changes in bulk material properties,[8–13] a detailed understanding of the electrochemical properties of these systems is not yet available, and relatively few studies have been reported in the literature.[14–16]

In Part 1, we examined the electrochemical and spectroelectrochemical properties of two representative sets of dithienylethene switches (**1Ho/1Fo** and **2Ho/2Fo**, Scheme 1) and investigated the mechanism and solvent dependence of the electrochemically driven ring-opening/closing processes.[17] It is clear from our earlier work that electrochemical switching processes are complex and involve interconversion between several cationic species,[16] so assignment of the mechanism involved (e.g., ring-closure via mono- or dicationic species) requires the investigation of asymmetrically substituted systems. Furthermore, although the influence of peripheral substituents (i.e., at C5 of the thienyl ring) on photochemical ring opening/closing has been examined in detail, the influence of these substituents on the electrochemical properties of these compounds has not been established to date. Here we extend our investigations to examine

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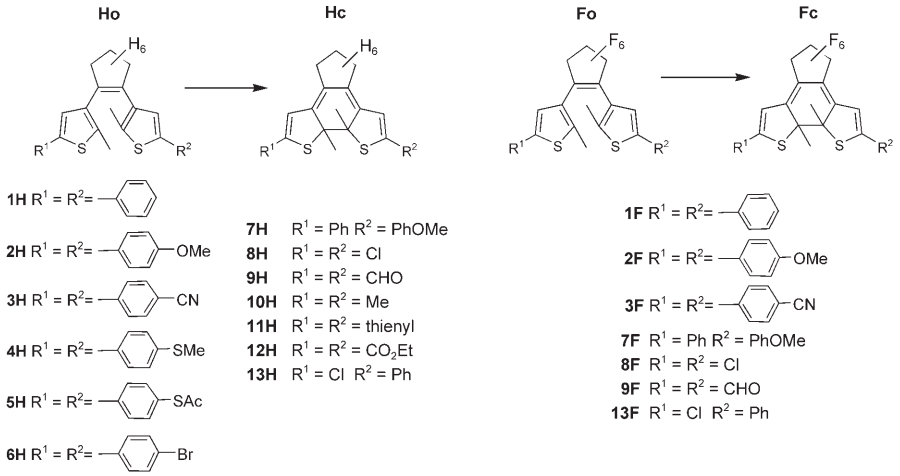
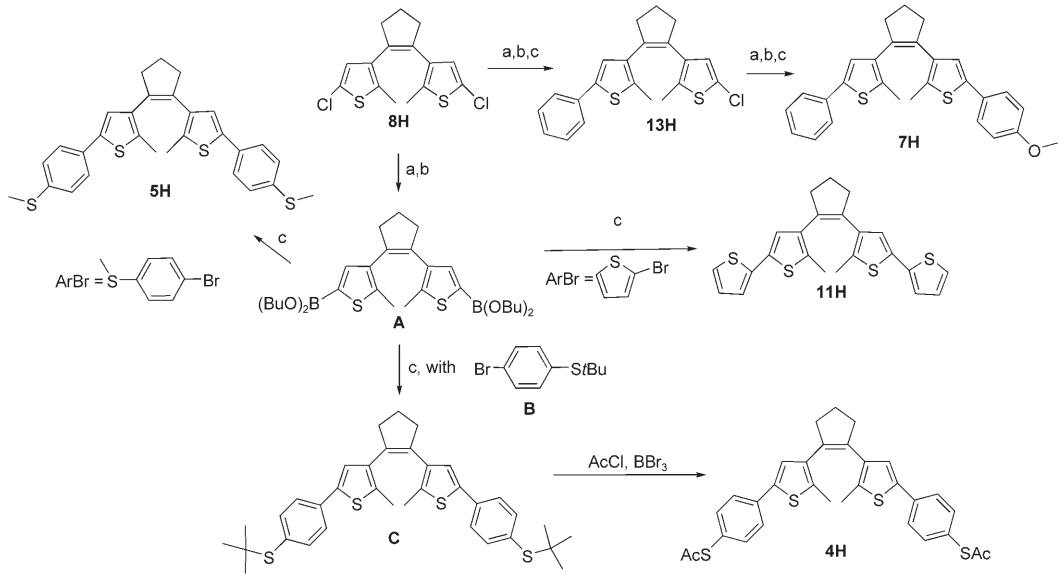


Scheme 1. Dithienylcyclopentene switches described in the text: suffix **o** denotes open form, **c** denotes closed form; **H** and **F** denote hexahydrocyclopentene- and hexafluorocyclopentene-based compounds, respectively.

the effect of substitution of the dithienylethene switches at C5 of the thienyl rings (Scheme 1).[18] Of particular interest is the ability to tune the redox properties of the dithienylethenes independently or at least semi-independently from their electronic and photochemical properties. In addition, asymmetrically substituted dithienylcyclopentenes (i.e., **7H/F** and **13H/F**) are investigated to explore the effect of redox asymmetry on the electrochemical properties of these compounds and to establish the role of peripheral redox groups in the electrochemical processes observed.

Results and Discussion

Synthesis: The symmetric derivatives **1H–3H**, **6H**, **8H–10H**, **1F–3F** and **8F** (Scheme 1) were prepared according to procedures reported previously.[18] Compounds **4H**, **5H**, **7H** and **11H–13H** were prepared from **8H** (see Scheme 2), and **7F**, **9F** and **13F** were prepared from **8F**. Compound **11H** was prepared by Suzuki coupling of the bis(boronic ester) **A**, obtained from **8H**, with 2-bromothiophene (Scheme 2). Similarly, **5H** was prepared, via **A**, from **8H** and 1-bromo-4-methylsulfanylbenzene, but the same reaction failed with either 4-bromobenzenethiol or 4-bromobenzenethioacetate, possibly due to deactivation of palladium catalyst by the free thiol groups. To circumvent this, **4H** was prepared[19] by Suzuki coupling of **A** with 1-bromo-4-*tert*-butylthiobenzene (**B**) to yield **C** (45%). Subsequent substitution of the *t*Bu groups by acetyl groups provided **4H**.[20] The dialdehyde **9F** was obtained by lithiation[18] of **8F**, followed by quenching with DMF. Compound **12H** was obtained by esterification of the corresponding diacid in ethanol with a catalytic amount of 30% aqueous HCl. The asymmetric derivatives **7H** and **13H** were prepared in two steps starting from **8H**. The first Suzuki coupling with bromobenzene was performed under five times more dilute conditions than employed for the symmetric derivatives (to minimise disubstitution) to yield **13H**. After purification of the monosubstituted product **13H**, the second Suzuki coupling was performed under standard conditions to yield **7H** (63%).[21] Similarly, **7F** was prepared from **8F** by an analogous route, but lithiation was performed in di-



Scheme 2. Synthesis of asymmetric 5-aryl-hexahydrothienylcyclopentenes. a) *n*BuLi, THF (or Et_2O for hexafluorocyclopentene-based compounds), 298 K; b) $B(OBu)_3$, THF, 298 K; c) ArBr, $[Pd(PPh_3)_4]$, 2 M aqueous Na_2CO_3, ethylene glycol, THF, reflux. The hexafluorocyclopentene analogues were prepared by similar routes.

ethyl ether to minimise side reactions involving C–F bonds of the hexafluorocyclopentene ring. All compounds were prepared in up to 500 mg scale and were characterised by ^{1}H and ^{13}C NMR spectroscopy and HRMS (see Experimental Section for details).

Electronic properties: In an earlier contribution the electronic properties (in toluene) of several of the compounds were reported.[18] Here a more detailed examination of the electronic spectra in acetonitrile solution is presented. The effect of incorporating a hexahydrocyclopentene group instead of a hexafluorocyclopentene group on the absorption spectra of the dithienylethenes (e.g., **1Ho**: $\lambda_{max}=278$ nm, **1Fo**: $\lambda_{max}=285$) is quite modest, especially considering the very large difference in the redox properties (vide infra) of the hexahydrocyclopentene- (**1Ho–13Ho**) and hexafluorocyclopentene-based (**1Fo–13Fo**) compounds. In contrast, the effect of substitution at C5 of the thiophene ring is much more pronounced: λ_{max} changes by up to 50 nm (ca. 5000 cm^{-1}). The UV absorption spectra of **1Ho–6Ho** are shown in Figure 1a. The data suggest that in the open form the major influence on the HOMO–LUMO energy gap is provided by substitution at C5.

In the closed form (i.e., **1Hc–6Hc**, Figure 1b) the effect of substitution at C5 of the thienyl ring is similar to that observed in the open state. The molar absorptivity shows a marked increase accompanied by a bathochromic shift with increasing electron-donating character of the substituent in the *para* position of the phenyl ring (Table 1).[22] The changes observed in the near-UV region of the spectrum (250–400 nm) on substitution are considerable, and the changes in the band at about 360 nm are similar to those of the band at about 550 nm. The bands at higher energy show a different dependence on substituents than the visible absorption bands. For the non-aryl-substituted compounds (e.g., **8H–10H**, **8F**, **9F**) only the chloro substituted com-

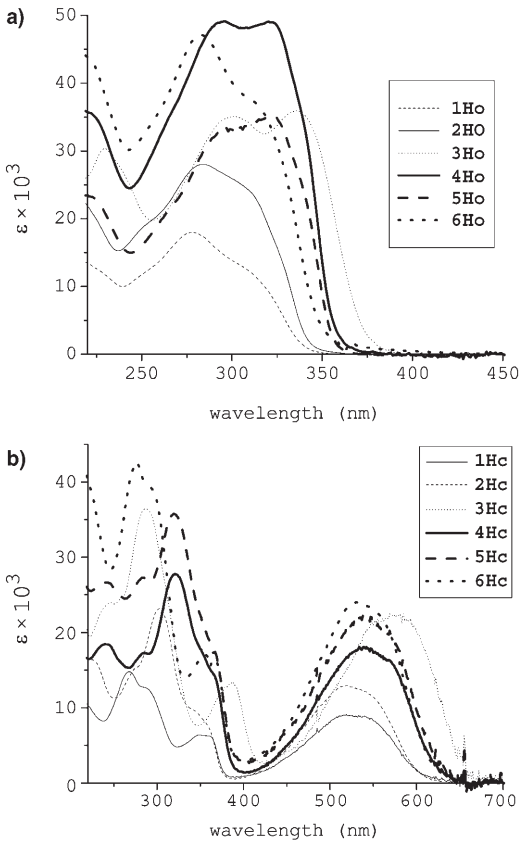


Figure 1. UV/Vis absorption spectra of a) **1Ho–6Ho** and b) **1Hc–6Hc**.

Table 1. Electronic and photochemical properties of open and closed forms in CH_3CN.

	Substituents	PSS[a]	Open form λ_{max}(abs) [nm] (ε [10^3 cm^{-1} M^{-1}])[b]	Closed form λ_{max}(abs) [nm] (ε [10^3 cm^{-1} M^{-1}])[b]	
1H	$R^1=R^2=$Ph	0.99	278 (18), 303 (S)	267 (15), 287 (S), 331 (I, 13), 349 (5.2), 360 (6.4)	527 (8.8)
1F	$R^1=R^2=$Ph	0.92	285 (33)	307 (I, 22), 308 (22), 366 (8.8), 380 (9.1)	588 (12)
2H	$R^1=R^2=$PhOMe	0.99	284 (28), 308 (S)	237 (14), 273 (S), 303 (24), 329 (12), 345 (9.5), 348 (S)	519 (13)
2F	$R^1=R^2=$PhOMe	0.99	296 (38)	321 (I, 21), 344 (25), 376 (S)	593 (18)
3H	$R^1=R^2=$PhCN	0.99	229 (31), 300 (35)	287 (36), 366 (I, 11), 387 (14)	575 (22)
3F	$R^1=R^2=$PhCN	0.99	232 (17), 315 (9.0)	341 (I, 9.4), 374 (5.6), 395 (S)	586 (5.9)
4H	$R^1=R^2=$PhSMe	0.96	295 (S), 320 (35)	344(I, 19), 364 (S)	540 (18)
5H	$R^1=R^2=$PhSAc	–[c]	295 (49), 322 (49)	345 (I), 364 (S)	541
6H	$R^1=R^2=$PhBr	0.99	282 (47), 313 (S)	340 (I, 17), 355 (18), 366 (18)	532 (24)
7H	$R^1=$Ph, $R^2=$PhOMe	0.99	280 (33), 312 (S)	217 (23), 299 (25), 329 (I, 13), 346 (13), 363 (S)	524 (18)
7F	$R^1=$Ph, $R^2=$PhOMe	0.94	256 (S), 292 (36)	273 (15), 313 (21), 317 (I, 20), 338 (20), 362 (S), 379 (S)	591 (18)
8H	$R^1=R^2=$Cl	–[d]	236 (19)		444
8F	$R^1=R^2=$Cl	0.45	242 (22), 305 (4.1)	264 (I, 3.9), 287 (I, 2.0), 305 (I, 2.0), 326 (2.7), 338 (S)	504 (2.1)
9H	$R^1=R^2=$CHO	0.95	269 (25), 315 (8.2)	218 (I, 11), 236 (I, 12), 336 (I, 5.7), 372 (9.3)	577 (8.2)
9F	$R^1=R^2=$CHO	0.95	263 (29), 294 (18)	239 (I, 11), 320 (I, 4.5), 344 (5.1), 395 (6.0)	614 (6.4)
10H	$R^1=R^2=$Me	–[d]	234 (22), 273 (S)		–[e]
11H	$R^1=R^2=$thienyl	0.98	281 (14), 295 (18)	229 (10), 311 (18), 347 (8.5), 356 (9.5), 369 (S)	519 (13)
11F[f]	$R^1=R^2=$thienyl		312		605
12H	$R^1=R^2=CO_2$Et	0.78	258 (27), 297 (S)	316 (I, 21), 354 (21)	540 (21)
13H	$R^1=$Cl $R^2=$Ph	0.75	256 (18), 273 (18), 310 (S)	246 (19), 280 (21), 317 (I, 12), 317 (S)	485 (9.8)
13F	$R^1=$Cl $R^2=$Ph	0.99	255 (22), 285 (19)	240 (15), 298 (I, 17), 298 (17), 348 (7.8), 360 (S)	548 (9.6)

[a] PSS = maximum percentage of closed state formed by photolysis at $\lambda=313$ nm in CH_3CN. [b] I = isosbestic point, S = shoulder. [c] Very low solubility in CH_3CN precluded accurate measurement by ^{1}H NMR spectroscopy. [d] PSS not determined due to overlap of the signals for the open and closed forms in ^{1}H NMR spectrum. [e] Not determined; no clear signal changes occur during irradiation at 313 nm. [f] From reference [16a].

pounds (**8H/F**) display markedly different (hypsochromically shifted) spectroscopic properties compared to the aryl-substituted compounds.

For all C5-substituted derivatives a bathochromic (red) shift of $2200 \pm 250\ cm^{-1}$ is observed on substitution of the hexahydrocyclopentene unit by the hexafluorocyclopentene unit (i.e., **1Hc**→**1Fc**, **3Hc**→**3Fc**, etc.). For the majority of C5-substituted compounds the effect of substitution (i.e., the shift in the lowest absorption band compared with **1Hc** or **1Fc**) is similar and indicates a reduction in the HOMO–LUMO gap. The very modest bathochromic shift of cyanophenyl-substituted hexafluoro compound **3F** compared with **3Hc** suggests that the cyanophenyl group contributes to either the HOMO or LUMO orbital (Table 1).

Photochemistry: Ring-opening (e.g., **1Hc**→**1Ho**) and ring-closing (e.g., **1Ho**→**1Hc**) of all compounds in acetonitrile (by irradiation at $\lambda > 460$ nm and at $\lambda = 313$ nm, respectively) was monitored by UV/Vis spectroscopy. Photostationary states (PSS; Table 1) were characterised by ^{1}H NMR spectroscopy. On irradiation at $\lambda = 313$ nm, absorption bands in the visible region appeared (300–700 nm), and on subsequent irradiation of the closed form (at $\lambda > 460$ nm) complete recovery of the open form was observed. This process could be repeated at least three times with minimal degradation (<5%). However, dependence of the extent of degradation on solvent was observed, whereby solvent purity was an important factor. This suggests that the degradation observed may not, for the most part, be inherent to the dithienylethene systems. With the exception of **5H**, **8H/F, 12H** and **13H**, all compounds show PSS between 90 and 99% on 313 nm irradiation, despite the nonzero overlap in the absorptions of the open and closed forms. The high PSS states achieved indicate that, as in toluene,[18] in acetonitrile the quantum yields for photochemical ring opening are considerably lower than those of ring closure. For **8F**, the very low PSS is most likely due to the weak absorption of **8Fo** and the relatively strong absorption of **8Fc** at the wavelength employed for ring closing ($\lambda = 313$ nm).

Redox properties: In our previous contribution,[17] the electrochemical and spectroelectrochemical properties of **1H/F** and **2H/F** were explored. In particular, the dependence of the direction of oxidative switching was examined and a detailed picture of the various electrochemical processes was developed (see Scheme 3 in reference [17]). Here these studies are extended to examine the effect of substituents on the electrochemical properties of the dithienylethene core and to establish the general applicability of the model developed in our earlier contribution.[17] In addition, asymmetrically substituted dithienylethene switches were examined to answer two key questions: first, does ring closing/opening occur via the mono (e.g., **1Ho$^+$**, **1Fc$^+$**) or dicationic species (e.g., **1Ho^{2+}**, **1Fc^{2+}**) and secondly, does oxidation of peripheral groups (e.g., the methoxyphenyl groups of **2Fo**) lead to immediate ring closure, or is a model involving intramolecular electron transfer more appropriate to rationalise the observations.

Electrochemical data for the hexahydro and hexafluoro compounds in both open and closed forms are presented in Table 2.[23] All redox processes undergo an anodic shift (210–790 mV) on substitution of the hexahydro- by the hexafluorocyclopentene unit.[17] The anodic shift observed for the open forms is similar to that observed for the first oxidation process in the closed forms, with the exception of **2Ho/2Fo**, **3Ho/3Fo** and **7Ho/7Fo**. The smaller anodic shift

Table 2. Redox properties of dithienylcyclopentenes (0.3–1.1 mM in 0.1 M TBAP/CH_3CN).

		Open form [V vs SCE]		Closed form $E_{1/2}$ [V vs SCE]		$c/c^+/c^{2+}$
		$E_{p,a}$	$E_{p,c}$	($E_{p,a}$ where irr)[a]	($E_{p,c}$ where irr)[a]	ΔE [mV][b]
1H	$R^1=R^2=$Ph	1.16 (irr)	−2.53 (irr)	0.67, 0.43	−1.74, −2.03	240
1F	$R^1=R^2=$Ph	1.59 (irr)	−1.75 (irr)	0.85 (qr)	−1.13 (qr)	
2H	$R^1=R^2=$PhOMe	0.99 (irr)		0.45, 0.32	−1.84 (irr), −2.16 (irr)	130
2F	$R^1=R^2=$PhOMe	1.20 (irr)	−1.70 (irr)	0.67	−1.16 (irr), −1.46 (irr)	
3H	$R^1=R^2=$PhCN	1.29 (irr)	−2.06 (irr)	0.78, 0.53	−1.4 (irr)	250
3F	$R^1=R^2=$PhCN	1.46 (irr)		1.05 (irr)	−0.83 (irr)	
4H	$R^1=R^2=$PhSMe	0.89 (irr)		0.44, 0.30		140
5H	$R^1=R^2=$PhSAc	0.97 (irr)		0.50, 0.35	−1.70 (irr)	150
6H	$R^1=R^2=$PhBr	1.15 (irr)		0.69, 0.47		220
7H	$R^1=$Ph $R^2=$PhOMe	1.68 (irr), 1.08 (irr)		0.56, 0.37	−1.81 (irr), −2.11 (irr)	190
7F	$R^1=$Ph $R^2=$PhOMe	1.54 (irr), 1.34 ($E_{1/2}$)	−1.73 (irr)	0.80 (qr)		
8H	$R^1=R^2=$Cl	1.37 (irr)		0.815 (irr), 0.63		125
8F	$R^1=R^2=$Cl	2.03 (irr)	−1.70 (irr)	1.15 (irr)	−1.10 (irr)	
9H	$R^1=R^2=$CHO	1.46 (irr)		1.13 (irr), 0.86 (qr)		240
9F	$R^1=R^2=$CHO	2.25 (irr)	−1.50 (irr)	1.35 (irr)	−0.42 (irr)	
10H	$R^1=R^2=$Me	1.105 (irr)		0.47, 0.37		100
11H	$R^1=R^2=$thienyl	1.06 (irr)		0.53, 0.40	−2.28 (qr)	130
11F[c]	$R^1=R^2=$thienyl	1.41 (irr)		0.82		
12H	$R^1=R^2=CO_2Et$	1.53 (irr), 1.43 (irr)		1.12 (irr), 0.81	−1.22, −1.36	280
13H	$R^1=$Cl, $R^2=$Ph	1.57 (irr), 1.26 (irr)		0.67 (irr), 0.52 (qr)	−1.67 (irr), −1.89 (irr)	
13F	$R^1=$Cl, $R^2=$Ph	1.87 (irr), 1.67 (irr)	-1.62 (irr)	1.03 (irr), 0.92 (irr)	−1.04 (irr), −1.45 (irr)	

[a] irr = irreversible, qr = quasireversible.[23] [b] ΔE = separation between the first and second oxidation processes of the closed form. Where not otherwise stated, $\Delta E < 50$ mV. [c] Values for **11F** are from reference [16a].

of these compounds is due to the non-innocent nature of the substituted aryl groups of the hexafluoro compounds in the open form (vide infra).[17] For the aryl-substituted compounds (**2H**–**6H**) a correlation between the inductive effect of the substituent (σ_I),[24] the redox properties of the open and closed forms (see Supporting Information, Figure S1 and Table 2) and the lack of any correlation with resonance parameters suggest that delocalisation of the HOMO over the aryl ring is not an important feature of these systems. Interestingly, the trend holds both for the neutral compounds and for the monocations, and this suggests that even in the oxidised state delocalisation of the SOMO over the phenyl rings is not significant.[25]

Overall the anodic shift observed on substitution of the hexahydro unit by the hexafluoro unit for the first oxidation process is less than that observed for the first reduction process (vide infra). This implies that a reduction in the HOMO–LUMO gap occurs and is in agreement with the bathochromic shift observed by UV/Vis spectroscopy. For **3Hc**/**3Fc** the anodic shift is comparable for both the first reduction (530 mV) and first oxidation processes (520 mV), which implies a modest (400 cm^{-1}) red shift between **3Hc** and **3Fc**. This is in agreement with the shift observed (330 cm^{-1}) in the UV/Vis spectra (vide supra).

Spectroelectrochemical correlation: Within the present dataset, the potentials of the first oxidation ($E_{c/c+}$), the first reduction ($E_{c/c-}$) process and the lowest energy visible absorption band λ_{max}(abs) for a sizeable group of ring-closed substituted dithienylhexahydro- and dithienylhexafluorocyclopentenes are available (Tables 1 and 2). As has been observed for a wide range of redox-active systems,[26] λ_{max}(abs) varies systematically ($\pm$1000 cm^{-1}) with the HOMO–LUMO energy gap determined electrochemically (Figure 2). In addition, the empirical constant of 2300 cm^{-1} [Eq. (1)] is close to that reported previously for inorganic systems.[27] The difference between the HOMO–LUMO energy gap measured electrochemically and that determined from electronic data is due to the fact that λ_{max} of the absorption band represents the absorption to the Franck–Condon state from the lowest vibronic state. The relationship holds regardless of the nature of the cyclopentene group (i.e., hexahydro vs hexafluoro).

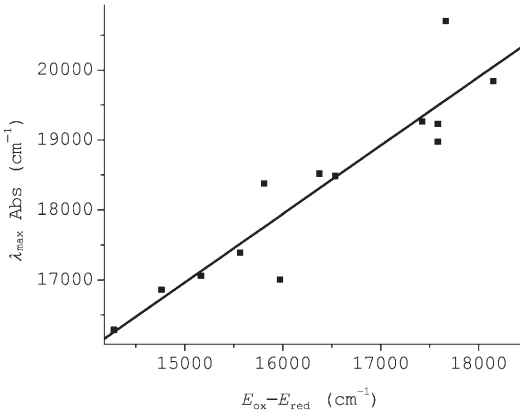


Figure 2. Correlation of the electrochemical and spectroscopic properties of (**1**–**3**, **5**, **7**, **11**–**13**)**Hc** and (**1**–**3**, **8**, **9**, **11**, **13**)**Fc** (R^2 = 0.85, intercept 2300 cm^{-1}).

$$\lambda_{max}(abs)/cm^{-1} = E_{c/c^+}/cm^{-1} - E_{c/c^-}\,cm^{-1} + 2300\,cm^{-1} \quad (1)$$

Substituent dependence of reversibility of redox processes, solvent effects and the comproportionation constant K_c: The effect of substituent on the reversibility of the redox processes is quite striking. In general the reversibility of the first and second oxidation processes improves with increasing electron-donor strength of the substituent. In agreement with the solvent dependence of the redox properties observed for **1Hc**/**1Ho**,[17] the strong dependence of the stability of the various oxidation states and of electrochemical ring closure/opening on the thienyl C5 substituent is related to the electronic stabilisation of the cationic species formed (e.g., $\mathbf{Hc^+}$, $\mathbf{Hc^{2+}}$ etc). Irreversibility was found to be due to chemical instability (thermally related) rather than to intrinsic properties of the electrochemical process itself. The use of strongly electron withdrawing groups resulted in almost complete irreversibility in the oxidation of the closed form. For the hexafluorocyclopentene-based compounds the irreversibility was more pronounced, and only the methoxyphenyl- (**2F**) and phenyl-substituted (**1F**) compounds show significant reversibility.[17] The solvent dependence of the redox properties of **1Ho** and **1Hc** were described earlier.[17]

The effect of donor substituents on the solvent dependence of redox and electronic properties was explored for **5Ho**/**5Hc**. Compound **5H** was chosen due to its redox stability in the closed form and the relatively large effect of the acetylthiophenyl substituent on the oxidation potentials of both the open and closed forms. As for **1Hc**, a correlation was observed between ΔE of **5Hc** and Guttmann solvent donor numbers[28] (see Supporting Information, Figure S2 and Table S2); ΔE decreases with increasing solvent donor strength.

Importantly, however, the magnitude of ΔE for **5Hc** is consistently lower than for **1Hc** and the difference increases with decreasing solvent donor strength, that is, **5Hc** is less sensitive to solvent than **1Hc**. The reduction in ΔE with increasing electron-donating power of the substituent can be rationalised on the basis that the electron-donating properties of the thioacetate group serve to stabilise the positive charge of the monocation and thereby reduce the potential influence of solvent and electrolyte in stabilising the monocation.

For **1Ho** and **1Hc**, temperature, solvent and electrolyte dependence of the formation of **1Hx** (see Scheme 3 in reference [17] for details) was apparent. The formation of **1Hx** from $\mathbf{1Hc^{2+}}$ was found to be a thermally activated process and was inhibited by increasing solvent donor strength. For **5Ho**/**5Hc**, the formation of an equivalent species (**5Hx**) was not as apparent as for **1Ho**/**1Hc**. In acetonitrile, the formation of **5Hx** was not observed at 298 K and, although the

formation of **5Hx** was observed in solvents such as THF and dichloromethane, the rate of formation was at least one order of magnitude lower than for **1Hx**.

The formation of species such as **1Hx** and **5Hx** appears to be a common feature of dithienylethenes. Its formation competes with that of the closed form (e.g., $\mathbf{1Hc^{2+}}$ and $\mathbf{5Hc^{2+}}$), and by choice of solvent, temperature and the nature of the substituents, the formation of this species can be controlled. The very low oxidation potential (e.g., **1Hx** ca. −0.1 V and **1Fx** ca. 0.3 V) indicates that in this state the HOMO of this species is destabilised compared with both the closed and open forms. Hence, whilst in the dicationic form, the high HOMO level leads to stability, it is clear that on reduction it becomes very unstable and undergoes isomerisation to **1Hc**.

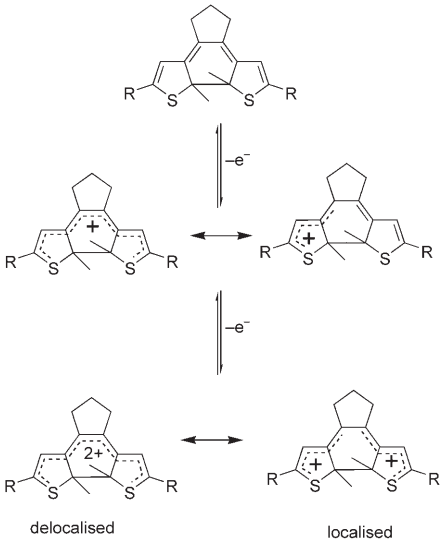
The effect of substituents on the stabilisation of the first oxidation process with respect to disproportionation [$1/K_c$, Eqs. (2)–(4), Sw_c = dithienylcyclopentene] can be determined by examining the separation ΔE (Table 2) between the first and second oxidation processes of the closed form of the dithienylcyclopentenes. Overall, electron-donating groups (**2Hc**, **4Hc**, **5Hc** and **11Hc**) reduce the magnitude of ΔE in comparison to that of **1Hc**, while electron-withdrawing groups increase the magnitude of ΔE (**12Hc**). For **3Hc** and **5Hc** only a modest effect was observed, presumably due to the balance of electron-donating (resonance) and -withdrawing (inductive) effects of the substituents. For **8Hc** (Cl) and **10Hc** (Me), the similarly low values of ΔE (ca. 100 mV) are surprising considering the opposite electronic character of these substituents. This can be rationalised, however, by considering the origin of ΔE (and hence the comproportionation constant K_c). There are two contributing factors to the magnitude of ΔE: the extent to which the initial oxidation step involves the entire dithienylethene system and electrostatic interaction between the oxidised and unoxidised *trans*-butadiene systems (see Scheme 3). From an electrostatic viewpoint, increasing the electron-donating property of the substituents will stabilise the positive charge formed during the first oxidation process and thereby reduce the barrier to the second oxidation process and hence decrease ΔE. Similarly, electron-withdrawing substituents in the C5 position would stabilise the HOMO of the thienyl groups and increase the HOMO-mediated interaction between the two thienyl moieties.

$$Sw_c + Sw_c^{2+} \rightleftharpoons 2\,Sw_c^{+} \quad (2)$$

$$K_c = [Sw_c^{+}]^2/[Sw_c][Sw_c^{2+}] \quad (3)$$

$$K_c = \exp(\Delta E/25.69) \quad (4)$$

Asymmetrically substituted dithienylethenes: To probe further the effect of substituents on the electrochemistry of the dithienylcyclopentenes, the asymmetrically substituted compounds **7H/7F** (R^1 = Ph, R^2 = PhOMe), **13H/13F** (R^1 = Cl, R^2 = Ph) and **12H** (R^1 = Cl, R^2 = Ph) were investigated



Scheme 3. Delocalisation/localisation of the SOMO in the closed state. Depending on the nature of the substituent, the system will favour either of the mesomeric states.

(Scheme 1). For the asymmetric compounds two limiting situations can be envisaged: 1) if the oxidation steps involve independent oxidation of each half of the bis-substituted dithienylcyclopentene and no communication between the two halves occurs, then the properties of the compound will be a superimposition of the properties of the parent molecules (localised model); 2) if the redox processes involve the entire dithienylethene system, the properties of the asymmetric compounds will be an average of those of the two symmetric parent compounds (delocalised model). It would be expected that neither of these limiting cases would be observed, but rather an intermediate situation is present. A further complication are the ring opening/closing processes, for which it is unclear whether the switching processes occur via the mono- or dicationic species. This aspect is potentially addressable by investigating the asymmetrically substituted compounds. Overall, the central question is to what extent delocalisation of charge occurs in the closed and open forms.

Electrochemical properties of 7H/7F: For **7Ho** the first oxidation step at 1.08 V is a one-electron process (Figure 3), while a second oxidation occurs at 1.68 V. The potential of the first process is intermediate between those of the parent symmetric compounds **1Ho** and **2Ho** (1.16 and 0.99 V). For **7Hc** two reversible oxidation process are observed at 0.37 and 0.56 V and, as for **7Ho**, the potential of each process and the separation between the first and second oxidation processes (ΔE = 190) are intermediate between those of the parent compounds **1Hc** (ΔE = 240) and **2Hc** (ΔE = 130). Similarly, the reduction potentials for **7Hc** are intermediate between those of **1Hc** and **2Hc**. The intermediacy of the electrochemical properties of **7H** between those of **1H** and **2H** (−1.81 versus −1.74 and −1.84 V) suggests that the oxidation process is delocalised (at least partially) over the

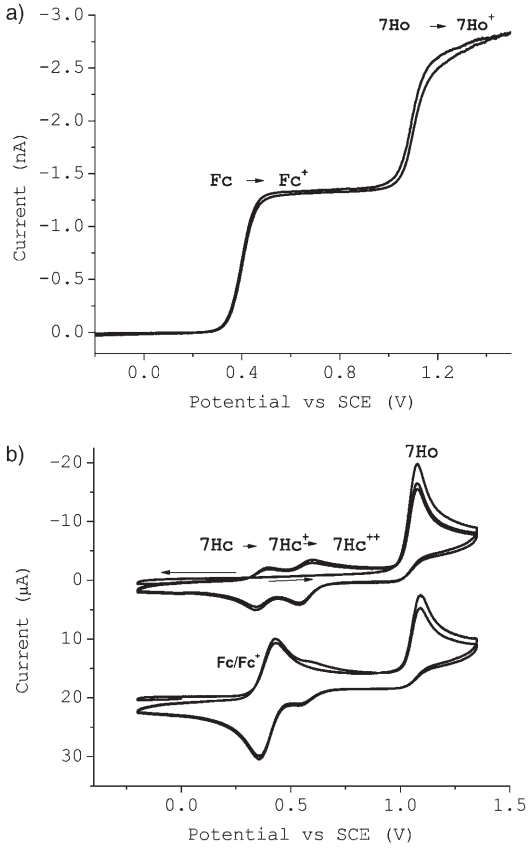


Figure 3. a) Cyclic voltammograms of 1 equiv ferrocene and 1 equiv **7Ho** with a 10 µm Pt microelectrode in 0.1 M TBAP/CH_3CN, 0.01 $V s^{-1}$ showing Fc/Fc^+ redox couple at 0.39 V and first oxidation process of **7Ho** at 1.08 V (a), and at a 2 mm glassy carbon electrode at 0.1 $V s^{-1}$ in the presence (b: bottom) and absence (b: top) of 1 equivalent of ferrocene.

entire molecule and not on individual thienyl units. If the oxidation processes were localised then the first redox process for both **7Ho** and **7Hc** would be expected to be close to those observed for **2Ho** and **2Hc**, respectively.

As with **1Ho** and **2Ho**, electrochemically induced ring closure is observed for **7H**, which indicates that the properties of the asymmetric dithienylhexahydrocyclopentene **7H** are largely those observed for the parent compounds. The one-electron nature of the first redox process observed for **7Ho** suggests that after single-electron oxidation of the open form ring closure occurs, that is, from $\mathbf{7Ho^+}$ to $\mathbf{7Hc^+}$. This is in agreement with the observation of significant amounts of $\mathbf{1Hc^+}$ and $\mathbf{2Hc^+}$ in spectroelectrochemical investigations.[17] As for **2Ho**, the first oxidation process of **7Ho** is assigned to the dithienylcyclopentene unit on the basis of comparison with **1Ho**. The second oxidation process at 1.68 V is assigned tentatively to oxidation of the methoxyphenyl unit.

In contrast to the hexahydro compounds **1H, 2H** and **7H**, which undergo electrochemical ring closure, compounds **1F** and **2F** exhibit very different electrochemical properties.[17] Specifically, **1F** undergoes electrochemical ring opening (**1Fc**→**1Fo**), while **2F** exhibits electrochemical ring closure (**2Fo**→**2Fc**). The difference in the chemical reactivity of the oxidation products of **1F** and **2F** can be ascribed to the involvement of the methoxyphenyl unit in **2F**. For **7F** a more complex electrochemical behaviour is observed than for **7H**.

For **7F** two closely separated oxidation processes are observed at 1.34 and 1.54 V (Figure 4). The first process is electrochemically reversible (at high scan rates, $>5 V s^{-1}$, the subsequent chemical reaction is avoided, Figure 5) whilst the second process at 1.54 V is fully irreversible.

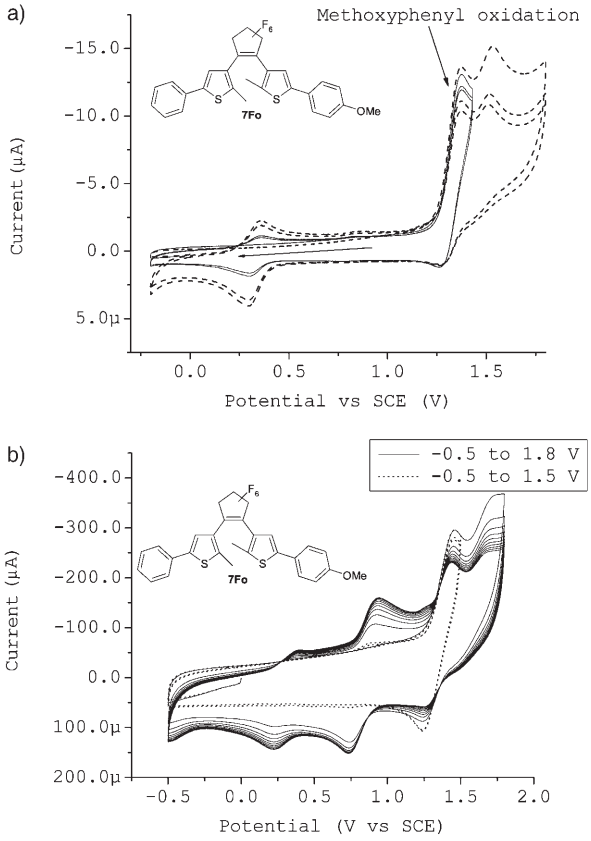


Figure 4. Cyclic voltammogram of **7Fo** at 0.1 $V s^{-1}$ (a) and 10 $V s^{-1}$ (b), −0.2 V to 1.5 V (solid) and −0.2 V to 1.8 V (dashed) in 0.1 M TBAP/CH_3CN.

For **7Fo** at low scan rates (ca. 0.1 $V s^{-1}$), on the return scan after the second oxidation process (1.54 V), a new electrochemically reversible ($E_{p,a}-E_{p,c}=60$ mV) reduction is observed at 0.31 V, and a very minor subsequent oxidation at about 0.80 V, coincident with **7Fc** (Figures 4 and 5). At higher scan rates (ca. 10 $V s^{-1}$) formation of the closed form **7Fc** becomes the dominant electrochemical process following the second oxidation step of **7Fo**.

The redox and photochemical processes for **7F** are summarised in Scheme 4. It is clear from the reversibility at higher scan rates that the first oxidation process (**7Fo**→$\mathbf{7Fo^+}$) is reversible. Based on the potential of the process (compared with **2Fo**), it is assigned to one-electron oxidation of the methoxyphenyl group of **7Fo** (**7Fo-methoxyphenyl**$^+$, Scheme 4). The second irreversible oxidation pro-

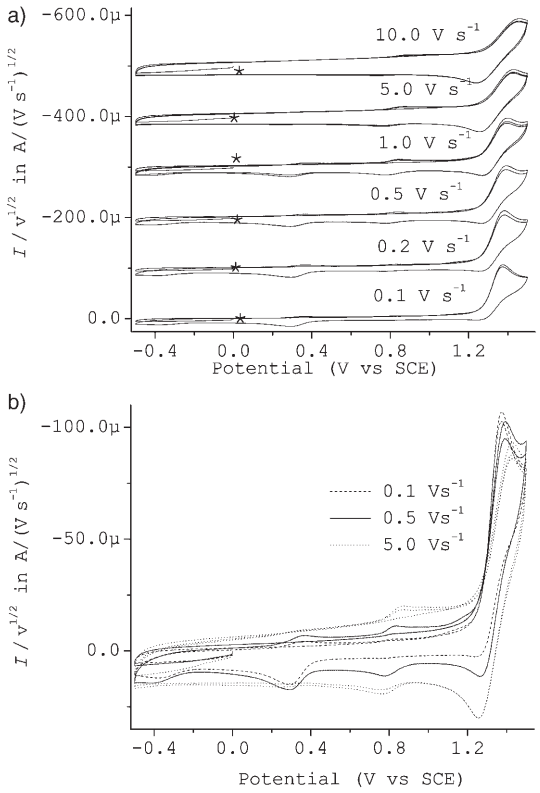
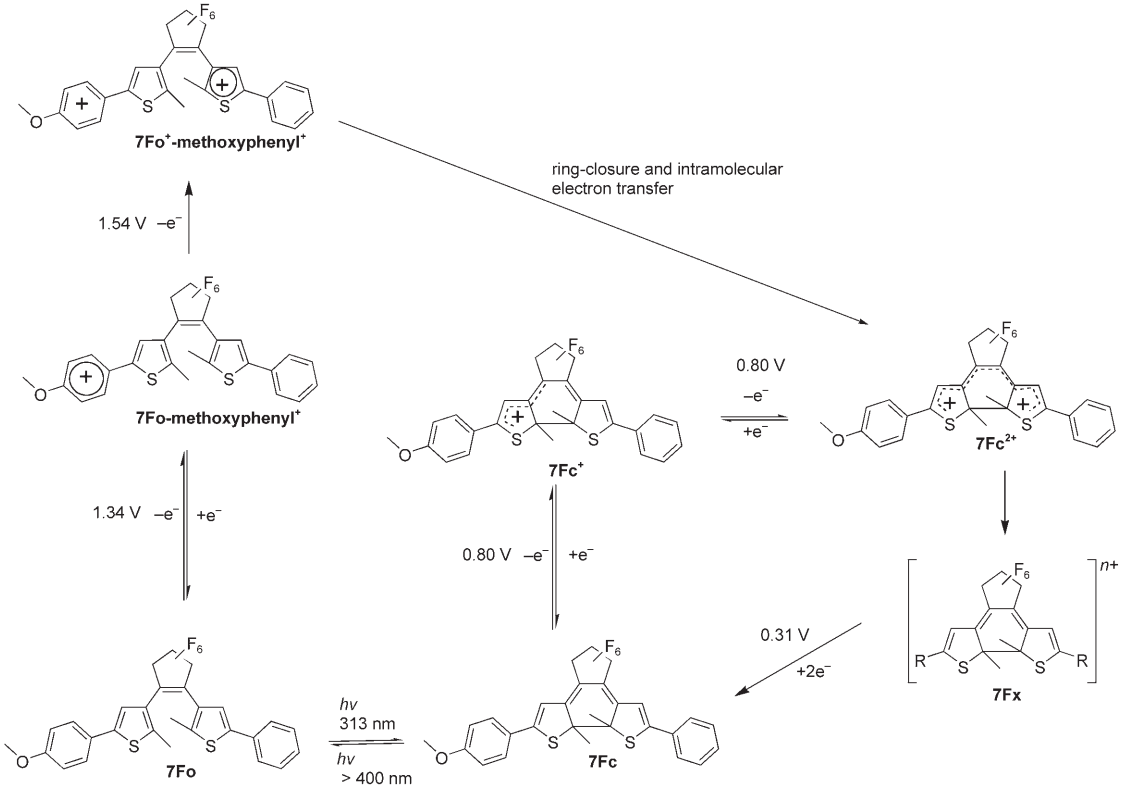


Figure 5. Scan-rate dependence of the oxidation processes of **7Fo** (0.1 $V s^{-1}$ to 10 $V s^{-1}$) in 0.1 M TBAP/CH_3CN. a) Spectra offset for clarity, $I=0$ is indicated for each trace by an asterisk. b) Overlay of 0.1, 05 and 5.0 $V s^{-1}$ traces.

cess at 1.54 V cannot be assigned to a second oxidation of the phenylmethoxy group and is more likely to be an oxidation process localised on the phenyl-substituted thienyl ring (**7Fo$^+$-methoxyphenyl$^+$**, Scheme 4). The oxidation of the thienyl ring is then followed by formation of the closed form, which, due to its lower redox potential (0.8 V), undergoes intramolecular electron transfer from the methoxyphenyl group to form **7Fc^{2+}**. At higher scan rates (>5 $V s^{-1}$) **7Fc^{2+}** is reduced to **7Fc** (via **7Fc$^+$**), but a competitive process (i.e., formation of **7Fx**) occurs at slower scan rates (<5 $V s^{-1}$).

At cathodic potentials **7Fo** undergoes two-electron fully irreversible reduction at -1.73 V, again at a potential intermediate beteween those of **1Fo** and **2Fo**. This suggests that the reduction process involves the entire ring system. For **7Fc** a single electrochemically reversible redox process is observed at -0.80 V, which is very similar to that observed for **1Fo** but with improved chemical stability. As for the hexahydrocylcopentene-based compound the improved stability of this process is attributed to the electron-donating effect of the methoxyphenyl group, which stabilises the mono- and dications (**7Fc$^+$** and **7Fc^{2+}**). The stabilisation is less than that observed for **2Fc**, but this is expected on the basis that **2Fc** has twice the electron donor stabilisation compared with **7Fc**.

For both **7Ho** and **7Fo**, the first oxidation processes can be assigned to one-electron oxidation of the dithienylethene group and methoxyphenyl group, respectively. The difference in the location of the first oxidation process is in agree-



Scheme 4. Redox and photochemical processes observed for **7F**.

ment with the assignments made for **2Ho** and **2Fo**.[17] In contrast to **2Fo**, in which ring closure occurred after the first oxidation process, for **7Fo**, the first oxidation (at 1.34 V) was found to be reversible and localised on the methoxyphenyl moiety. The second oxidation process (1.54 V) then takes place at the dithienylethene moiety and is responsible for ring-closure. It is clear that for **7Fo** the second oxidation process is localised at the dithienylethene core; hence, in agreement with **7Ho**, one-electron oxidation of the dithienylethene appears to be sufficient to allow ring-closure to take place. This has implications for **2Fo**, in that it supports the mechanism whereby double intramolecular electron transfer to the dithienylethene core occurs, together with stabilisation of the dication ($\mathbf{2Fc^{2+}}$) by the electron-donating properties of the two methoxyphenyl groups.

Electrochemical properties of 13H/13F: For **13H** and **13F** ($R^1 = Cl$, $R^2 = Ph$) the first oxidation processes are expected to be located on the phenyl-substituted thienyl ring on the basis of comparison of **1H/F** and **8H/F** (Table 2). For **13Ho** two oxidation processes are observed at 1.26 and 1.57 V. The first oxidation process ($\mathbf{13Ho \rightarrow 13Ho^{+}}$) is close to that of **1Ho**, and the second process ($\mathbf{13Ho^{+} \rightarrow 13Ho^{2+}}$) is considerably more anodic (by 200 mV) than that of **8Ho**, that is, significant communication exists between the two thienyl groups. This implies that the second oxidation step is made more difficult by oxidation of the first thienyl ring. No ring closure is observed even after the second oxidation step of **13Ho** (i.e., above 1.6 V). For **13Hc**, two oxidation processes occur, the second of which is irreversible, at potentials intermediate between those of the parent compounds.

For **13Fo** two oxidation processes are observed at potentials intermediate between those of the parent compounds **1Fo** and **8Fo**. The first process is assigned to oxidation of the phenyl-substituted thienyl group, whilst the second process is assigned to the chloro-substituted thienyl group. The intermediacy of the potential of the oxidation processes of **13Fo** between those of **1Fo** and **8Fo** indicates that some interaction between the thienyl rings occurs. For **13Fc**, two oxidation processes are observed (both fully irreversible), and as for **13Fo** the potentials of the first and second processes lie between those of the parent compounds **1Fc** and **8Fc**. For **13Fc**, two reduction processes are observed at cathodic potentials at -1.04 and -1.45 V. The observation of two processes is unexpected considering that for **1Fc** and **8Fc** a single reduction process at about -1.1 V is observed. This suggests that for the reduced species significant interaction between the thienyl groups is present.

Overall for **7H/F** and **13H/F** it is clear that in both open and closed states the thienyl moieties are not independent of each other and that some interaction (either inductive or by delocalisation) is observed. The effect of asymmetry itself is very much dependent on the substituents employed, and although the redox properties of **7H** and **7F** are broadly intermediate between those of the parent compounds **1H**/**2H** and **1F**/**2F**, the introduction of peripheral redox-active groups (e.g., the methoxyphenyl group) has the additional effect of perturbing the electron density on the thienyl rings, and hence affects the stabilisation of the cationic species, and of introducing separate redox processes, which can bypass the oxidative isomerisation processes of the thienyl core. The introduction of asymmetry though non-redox-active peripheral groups (i.e., the chloro group in **13H/F**) results in only minor perturbation of the redox properties of each thienyl unit. In terms of electrochemical switching the direction of ring switching is very dependent on the substituents chosen. The first oxidation process of **13Ho** is assigned to the phenyl-substituted thienyl ring, but ring closure is not observed (even if it occurs at all) due to the effect of the chloro group, which renders the dication of the closed form ($\mathbf{13Hc^{2+}}$) unstable.

Conclusion

Overall, the results obtained demonstrate that the nature of the redox properties of the dithienylethenes can be tuned towards electrochemical ring-closing or ring-opening by stabilisation and destabilisation of the mono- and dication of the closed state, respectively. Alternatively, redox-active groups may be employed to change the direction of electrochemical switching. Nevertheless, to design molecules which exhibit the desired direction of switching it is important to recognise the mechanism by which these processes occur. Although ring closure occurs immediately after oxidation of the open form, the ring-closed product must subsequently be reduced. The formation of species such as **1Hx** and **5Hx** from $\mathbf{1Hc^{2+}}$ and $\mathbf{5Hc^{2+}}$, respectively, by a thermally activated rearrangement must be inhibited either by environmental control (e.g., solvent and temperature) or by the introduction of electron-donating groups. The latter approach must be taken with caution given that electron-donating groups frequently exhibit redox chemistry themselves (e.g., in **2F**).

The driving force for ring opening and closing appears to lie in the ability of the bridging cyclopentene moiety to allow for stabilisation of the various cationic species. The observation of a reversible methoxyphenyl oxidation process for **7Fo** and the characterisation of the first oxidation process of **7Ho** as being one-electron, taken together with the observation of the monocation in significant quantities during spectroelectrochemistry,[17] provide compelling evidence that ring-closure occurs through the monocation (i.e., $\mathbf{7Ho^{+}}$, in which the positive charge is localised on the thienyl ring system). The driving force for ring-closure is stabilisation of the monocation though (partial) delocalisation of the charge on the second ring. Where the communication between the rings is poor, as is the case in the hexafluoro compounds, the stabilisation achieved does not compensate for the loss of ring stabilisation (aromaticity), and hence ring opening of the monocation/dication of the closed form is favoured.

A key feature of both the dithienylhexafluoro- and dithienylhexahydrocyclopentenes is their propensity to undergo ring closing and opening photochemically and, more recent-

ly, the possibility of using chemical and electrochemical oxidation to achieve similar processes has been highlighted.[16] However, the mechanism and factors which influence the oxidative ring-opening/closing of the switches were unclear and, in particular, an understanding of how substituents drive the direction of switching was lacking, both in terms of the effect of variation in the cyclopentene bridging unit and in terms of the substituent at the C5 position of the thienyl rings. In addition, the mechanism by which redox-active groups attached to the thienyl rings influence the ring-switching process directly had not been investigated. In our previous[17] and present studies these issues were addressed systematically by variation of the bridging cyclopentene group, by variation of substituents at C5 of the thienyl rings and by the introduction of asymmetry in the substitution pattern (e.g., **7H**). The data set now available provides a considerable basis for the further development of this distinct class of photo/electrochromic compounds in functional devices and systems.

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 stated otherwise. The symmetric compounds **1H–3H, 6H, 8H–10H, 1F–3F** and **8F** were prepared by previously reported procedures.[18] The intermediate structures in the syntheses are numbered **A**, **B**, **C** and **D**, with short characterisation for clarity. ^{1}H NMR spectra were recorded at 200, 300, 400 or 500 MHz; ^{13}C NMR spectra at 50.3, 75.4 or 125.7 MHz; and ^{19}F NMR spectra at 188.2 or 470.3 MHz. All spectra were recorded at ambient temperature, with the residual proton signals of the solvent as an internal reference. Chemical shifts are reported relative to TMS.

Mass spectrometry was performed with CI, DEI or EI ionisation procedures. For several of the dithienylethenes, sublimation was difficult and only DEI (desorption electron ionisation) provided mass spectra. Mass spectra were recorded on a Jeol JMS-600 mass spectrometer in the scan range of m/z 50–1000 with an acquisition time between 300 and 900 ms and a potential between 30 and 70 V. Derivatives synthesized starting from compound **8H** are light-sensitive and were therefore handled exclusively in the dark by using brown glassware. Column chromatography (Aldrich silica gel grade 9385, 230–400 mesh) was performed under yellow light. For UV/Vis analyses, each spectrum was recorded by summation of 20 scans. UV/Vis absorption spectra (accuracy ±2 nm) were recorded on a Hewlett-Packard UV/Vis 8453 spectrometer. Electrochemical measurements were carried out as described previously.[17]

1,2-Bis[5′-di-*n*-butoxyboryl-2′-methylthien-3′-yl]cyclopentene (A): Compound **8H** (70 mg, 0.2 mmol) was dissolved in anhydrous THF (8 mL) under a nitrogen atmosphere, and *n*BuLi (0.31 mL, 1.6 M in hexane, 0.5 mmol) was added by syringe. This solution was stirred for 30 min at room temperature, and B(*n*OBu)$_3$ (0.18 mL, 0.6 mmol) was added. The resulting solution was stirred for 1 h at room temperature and used directly in the Suzuki cross coupling-reactions without workup due to hydrolysis of the boronic ester **A** during isolation. Starting from **8F**, the lithiation was carried out in diethyl ether, due to less substitution of the C–F bonds.

1-Bromo-4-*tert*-butylsulfanylbenzene (B): A catalytic amount of $AlCl_3$ was added to a solution of bromothiophenol (2.50 g, 13.3 mmol) and *tert*-butyl chloride (3 g, 2 equiv) in acetonitrile (25 mL).[19] The solution was heated at reflux for 72 h, cooled to room temperature, extracted with water, dried over Na_2SO_4 and concentrated. Chromatography over silica (hexane) produced the desired compound as an oil (2.80 g, 11.5 mmol, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.25$–1.28 (m, 9H), 7.34–7.47 ppm (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 30.9$ (q), 46.1 (s), 123.4 (s), 131.6 (d), 131.8 (s), 138.9 ppm (d).

1,2-Bis[5′-(4″-*tert*-butylsulfanylphenyl)-2′-methylthien-3′-yl]cyclopentene (C): *n*BuLi (6.0 mL, 1.6 M in hexane, 7.0 mmol) was added to a solution of **8H** (1.00 g, 3.05 mmol) in THF (40 mL) under an inert atmosphere. After 1 h, B(OBu)$_3$ (2.50 mL, 6.5 mmol) was added to produce bis(boronic ester) intermediate **A**. A separate flask was charged with 4-bromo-*tert*-butylsulfanylbenzene (1.00 mg, 6.2 mmol), [Pd(PPh$_3$)$_4$] (400 mg, 0.083 mmol), THF (25 mL), aqueous Na_2CO_3 (4 mL, 2 M) and ethylene glycol (5 drops). The mixture was heated to 80 °C and the preformed boronic ester was added slowly by syringe. The reaction mixture was heated at reflux for 3 h, after which it was diluted with diethyl ether (50 mL) and washed with brine (50 mL). The brine solution was washed with additional diethyl ether (50 mL), and the combined organic phases were dried over Na_2SO_4 and concentrated. Chromatography over silica (hexane/diethyl ether 100/1) produced **C** (800 mg, 1.35 mmol, 45%, 95% pure). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.26$–1.29 (m, 18H), 2.00 (s, 6H), 2.06 (m, 2H), 2.82 (t, $J = 7.8$ Hz, 4H), 7.03 (s, 2H), 7.24–7.49 ppm (m, 8H).

1,2-Bis[5′-(4″acetylthio)-2′-methylthien-3′-yl]cyclopentene (4H): BBr_3 (0.08 mL, 1.6 mmol) was added to a solution of **C** (500 mg, 0.80 mmol) and AcCl (0.40 mL) in CH_2Cl_2 (10 mL) under an inert atmosphere.[20] The reaction mixture was stirred overnight and then diluted with diethyl ether (10 mL) and poured over ice (5 g). The phases were separated, the aqueous layer was extracted with additional diethyl ether (20 mL) and the combined organic phases were dried with Na_2SO_4 and concentrated. Chromatography over silica (pentane/diethyl ether 500/1) produced **4H** (130 mg, 0.23 mmol, 29%). M.p. 61–64 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.99$ (s, 6H), 2.08 (m, 2H), 2.41 (s, 6H), 2.83 (t, $J = 7.8$ Hz, 4H), 7.06 (s, 2H), 7.35 (d, $J = 8.1$ Hz, 4H), 7.51 ppm (d, $J = 8.1$ Hz, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 14.4$ (q), 23.0 (t), 30.2 (q), 38.4 (t), 124.8 (d), 125.8 (d), 126.0 (s), 134.7 (s), 134.8 (d), 135.5 (s), 135.6 (s), 136.8 (s), 138.6 (s), 194.2 ppm (s); MS (EI): 560 [M^+]; HRMS calcd for $C_{31}H_{28}O_2S_4$ 560.097, found 560.097.

1,2-Bis[5′-(4″-methylsulfanylphenyl)-2′-methylthien-3′-yl]cyclopentene (5H): *n*BuLi (1.4 mL, 1.6 M in hexane, 2.3 mmol) was added to a solution of **8H** (250 mg, 0.76 mmol) in THF (10 mL) under an inert atmosphere. After 1 h, B(OBu)$_3$ (0.60 mL, 2.3 mmol) was added to produce the bis(boronic ester) intermediate. A separate flask was charged with 2-bromothioanisole (310 mg, 1.5 mmol), [Pd(PPh$_3$)$_4$] (96 mg, 0.083 mmol), THF (5 mL), aqueous Na_2CO_3 (4 mL, 2 M) and ethylene glycol (5 drops). The mixture was heated to 80 °C and the preformed boronic ester was added slowly by syringe. The reaction mixture was heated at reflux for 3 h and then diluted with diethyl ether (50 mL) and washed with brine (50 mL). The brine solution was washed with additional diethyl ether (50 mL) and the combined organic phases were dried over Na_2SO_4 and concentrated. Chromatography over silica (hexane/CH_2Cl_2 10/1) and stirring in hexane (excess)/CH_2Cl_2 produced **5H** (120 mg, 0.26 mmol, 35%). M.p. 162–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.97$ (s, 6H), 2.06 (m, 2H), 2.47 (s, 6H) 2.82 (t, $J = 7.2$ Hz, 4H), 6.97 (s, 2H), 7.20 (d, $J = 8.4$ Hz, 4H), 7.38 ppm (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 14.4$ (q), 16.0 (q), 23.0 (t), 38.4 (t), 123.7 (d), 125.6 (d), 127.0 (d), 131.5 (s), 134.2 (s), 134.6 (s), 136.6 (s), 137.0 (s), 139.1 ppm (s); MS (EI): 504 [M^+]; HRMS calcd. for $C_{29}H_{28}S_4$: 504.108, found: 504.108.

1-[5-(4-Methoxyphenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)cyclopentane (7H): *t*BuLi (0.40 mL, 1.5 M in pentane, 0.593 mmol) was added to a solution of **13H** (200 mg, 0.539 mmol) in THF (7 mL) under an inert atmosphere. After 1 h, B(OBu)$_3$ (0.22 mL, 0.81 mmol) was added and the mixture was stirred for 1 h to produce the bis(boronic ester) intermediate. A separate flask was charged with 4-bromoanisole (0.135 mL, 1.08 mmol), [Pd(PPh$_3$)$_4$] (19 mg, 0.016 mmol), THF (3 mL), aqueous Na_2CO_3 (2 M, 3 mL) and ethylene glycol (3 drops). The mixture was heated to 80 °C and the performed boronic ester was added slowly. The reaction mixture heated at reflux overnight, diluted with diethyl ether (40 mL) and washed with water (40 mL). The aqueous layer was washed with additional diethyl ether (40 mL) and the combined organic phases were dried over Na_2SO_4 and concentrated. Chromatography on

silica gel (hexane) afforded **7H** as a sticky oil (150 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 3H), 2.07 (s, 3H), 2.10–2.16 (m, 2H), 2.88–2.93 (m, 4H), 3.85 (s, 3H), 6.93 (d, J = 8.8 Hz, 2H), 6.99 (s, 1H), 7.12 (s, 1H), 7.20–7.30 (m, 1H), 7.36–7.41 (m, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.57 ppm (d, J = 7.3 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 11.9 (q), 12.0 (q), 20.6 (t), 36.0 (t), 52.9 (q), 111.8 (d), 120.5 (d), 121.6 (d), 122.9 (d), 124.1 (d), 124.5 (d), 125.0 (s), 126.3 (d), 132.0 (s), 132.1 (s), 132.1 (s), 132.3 (s), 134.1 (s), 134.3 (s), 137.1 (s), 156.4 ppm (s); MS (EI): 442 [M^+]; HRMS calcd for $C_{28}H_{26}OS_2$: 442.143, found: 442.141.

1,2-Bis[5′-(thien-2-yl)-2′-methylthien-3′-yl]cyclopentene (11H): 2-Bromothiophene (0.04 mL, 0.4 mmol) was dissolved in THF (5 mL), and after addition of [Pd(PPh$_3$)$_4$] (15 mg, 0.012 mmol), the solution was stirred for 15 min at room temperature Aqueous Na_2CO_3 (1 mL, 2 M) and 6 drops of ethylene glycol were added, and the resulting biphasic system was heated in an oil bath at reflux. The solution of **A** was added dropwise by syringe, after which the reaction mixture was heated at reflux for 2 h, and then allowed to cool to room temperature Diethyl ether (50 mL) and H_2O (50 mL) were added, and the organic layer was collected and dried (Na_2SO_4). After evaporation of the solvent the product was purified by column chromatography (SiO_2, hexane) to gave a purple solid (32 mg, 38%). M.p. 147 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (s, 6H), 2.04 (m, 2H), 2.79 (t, J = 12.5 Hz, 4H), 6.87 (s, 2H), 6.95 (t, J = 6.5 Hz, J = 3.3 Hz, 2H), 7.03 (d, J = 4.5 Hz, 2H), 7.13 ppm (d, J = 8.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.3 (q), 22.9 (t), 38.5 (t), 122.9 (d), 123.7 (d), 124.5 (d), 127.6 (d), 133.0 (s), 134.0 (s), 134.5 (s), 136.3 (s), 137.7 ppm (s); MS (EI): 424 [M^+]; HRMS calcd for $C_{23}H_{20}S_4$: 424.045, found: 424.042.

1,2-Bis[5′-ethoxycarbonyl-2′-methylthien-3′-yl]cyclopentene (12H): Compound **D** (75 mg) was dissolved in EtOH (50 mL) and a catalytic amount of 30% aqueous HCl was added. After the mixture was stirred overnight, the solvent was removed to yield **12H** as a light brown solid in quantitative yield. M.p. 121–122 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, J = 6.9 Hz, 6H), 1.87 (s, 6H), 2.00–2.07 (m, 2H), 2.76 (t, J = 7.5 Hz, 4H), 4.28 (q, J = 6.9 Hz, 4H), 7.49 ppm (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.3 (q), 14.8 (q), 22.8 (t), 38.6 (t), 61.0 (t), 129.6 (s), 134.2 (s), 134.7 (d), 136.5 (s), 142.5 (s), 162.1 ppm (s); MS (EI): 404 [M^+]; HRMS calcd for $C_{21}H_{24}O_4S_2$: 404.112, found: 404.112.

1-(5-Chloro-2-methylthien-3-yl)-2-(2-methyl-5-phenylthien-3-yl)cyclopentene (13H): *n*BuLi (4.70 mL, 1.6 M in hexane, 7.51 mmol) was added to a solution of **8H** (2.25 g, 6.83 mmol) in THF (100 mL) under an inert atmosphere. After 1 h, B(OBu)$_3$ (2.77 mL, 10.3 mmol) was added and the mixture was stirred for a further hour to produce bis(boronic ester) intermediate **A**. A separate flask was charged with bromobenzene (2.86 mL, 27.3 mmol), [Pd(PPh$_3$)$_4$] (0.237 g, 0.21 mmol), THF (23 mL), aqueous Na_2CO_3 (2 M, 18 mL) and ethylene glycol (20 drops). The mixture was heated to 80 °C and the preformed boronic ester was added slowly. The reaction mixture was heated at reflux overnight, cooled to room temperature, diluted with diethyl ether (200 mL) and washed with water (200 mL). The aqueous layer was extracted with additional diethyl ether (200 mL) and the combined organic phases were dried over Na_2SO_4 and concentrated. Subsequent chromatography on silica gel (hexane) afforded **13H** as a sticky oil (1.95 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 2.05 (s, 3H), 2.08–2.16 (m, 2H), 2.78–2.89 (m, 4H), 6.68 (s, 1H), 7.05 (s, 1H), 7.30 (t, J = 7.0 Hz, 1H), 7.37–7.42 (m, 2H), 7.55 ppm (d, J = 7.3 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.1 (q), 14.3 (q), 22.9 (t), 38.4 (t), 38.5 (t), 123.8 (d), 125.0 (s), 125.3 (d), 126.8 (d), 127.0 (d), 128.8 (d), 133.2 (s), 133.7 (s), 134.4 (s), 135.1 (s), 135.3 (s), 136.3 (s), 139.8 ppm (s); MS (EI): 370 [M^+]; HRMS calcd for $C_{21}H_{19}S_2Cl$: 370.062, found: 370.063.

1-[5-(4-Methoxyphenyl)-2-methylthien-3-yl]-2-(2-methyl-5-phenylthien-3-yl)hexafluorocyclopentene (7F): Compound **13F** (0.24 g, 0.5 mmol) was dissolved in anhydrous diethyl ether (5 mL) under nitrogen and *n*BuLi (0.32 mL, 1.6 M in hexane, 0.5 mmol) was added slowly by syringe. This solution was stirred at room temperature for 1 h and B(*n*OBu)$_3$ (0.16 mL, 0.6 mmol) was added in one portion. After the mixture had been stirred for 1 h at room temperature, THF (5 mL), aqueous Na_2CO_3 (1 mL, 2 M), 4-bromoanisole (0.09 mL, 7 mmol) and [Pd(PPh$_3$)$_4$] (6 mg, 0.005 mmol) were added, and the mixture heated at reflux for 16 h. The reaction mixture was cooled to room temperature, H_2O (5 mL) was added, the organic layer separated and the water layer extracted with ethyl acetate (2 × 20 mL). The combined organic layers were dried over Na_2SO_4, and the solvent evaporated. The product was purified by column chromatography (SiO_2, hexane/toluene 9/1) to give **7F** as a white solid (123 mg, 45%). M.p. 127–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 1.97 (s, 3H), 3.84 (s, 3H), 6.91 (d, J = 8.8 Hz, 2H), 7.16 (s, 1H), 7.27–7.33 (m, 2H), 7.39 (t, J = 7.3 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.54 ppm (d, J = 7.3 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.6 (q), 14.7 (q), 55.5 (q), 116.4 (t), 114.5 (d), 118–119 (m), 121.3 (d), 122.5 (d) 125,7 (d), 125.8 (s), 126.0 (s), 126.3 (s), 127.0 (d), 128.0 (d), 129.1 (d), 133.5 (s), 140.4 (s), 141.4 (s), 142.3 (s), 159.6 ppm (s); ^{19}F NMR (188.2 MHz, $CDCl_3$): δ = −111.09 (t, J = 5.6 Hz, 4F), −132.88 ppm (m, 2F); MS (EI): 550 [M^+]; HRMS calcd for $C_{28}H_{20}F_6OS_2$: 550.086, found 550.085.

1,2-Bis(5′-formyl-2′-methylthien-3′-yl)hexafluorocyclopentene (9F): Under the same conditions as described for **11H**, *n*BuLi (1.6 M in hexane, 0.13 mL, 1.8 mmol) was added to a stirred solution of **8F** (30 mg, 0.06 mmol) in anhydrous diethyl ether (5 mL) under nitrogen at room temperature over 30 min, after which the mixture was quenched with anhydrous dimethylformamide (0.05 mL, 0.6 mmol). Trituration from hexane/CH_2Cl_2 afforded the compound as a brown-orange solid (20 mg, 66%). M.p. 182 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.02 (s, 6H), 7.73 (s, 2H), 9.85 ppm (s, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ15.2 (q), 110.1 (t), 115.7 (t), 125.8 (d), 135.3 (s), 136.5 (t) 142.2 (s), 151.3 (s), 181.5 ppm (d); ^{19}F NMR (188.2 MHz, $CDCl_3$): δ = −111.97 (t, J = 4.9 Hz, 4F), −133.55 ppm (quintet, J = 4.9 Hz, 2F); MS (EI): 424 [M^+]; HRMS calcd for $C_{17}H_{10}F_6O_2S_2$ 424.003, found 424.004.

1-(5-Chloro-2-methylthien-3-yl)-2-(2-methyl-5-phenylthien-3-yl)hexafluorocyclopentene (13F): Compound **8F** (2.19 g, 5 mmol) was dissolved in anhydrous diethyl ether (50 mL) under nitrogen and *n*BuLi (3.2 mL, 1.6 M in hexane, 5 mmol) was added slowly by syringe. This solution was stirred at room temperature for 1 h and B(*n*OBu)$_3$ (1.63 mL, 6 mmol) was added in one portion to yield **A**. After the mixture had been stirred for 1 h at room temperature, THF (50 mL), aqueous Na_2CO_3 (10 mL, 2 M), iodobenzene (0.78 mL, 7 mmol) and [Pd(PPh$_3$)$_4$] (58 mg, 0.05 mmol) were added and the mixture was heated at reflux for 16 h. The reaction mixture was cooled to room temperature, H_2O (20 mL) added, the organic layer separated and the aqueous layer extracted with ethyl acetate (2 × 50 mL). The organic layers were combined and dried over Na_2SO_4, evaporated and the crude product purified by column chromatography (SiO_2, hexane) to give a yellowish oil which solidified on standing (1.32 g, 71%). M.p. 80–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, 3H), 1.98 (s, 3H), 6.94 (s, 1H), 7.26 (s, 1H), 7.31 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.3 Hz, 2H), 7.55 ppm (d, J = 7.3 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.5 (q), 14.7 (q), 111.1 (t), 113.8 (t), 116.1 (t), 122.3 (d), 124.5 (s), 125.7 (d), 125.8 (d), 127.9 (s), 128.1 (d), 129.2 (d), 133.3 (s), 140.6 (s), 141.4 (s), 142.6 ppm (s); ^{19}F NMR (188.2 MHz, $CDCl_3$): δ = −111.4 (t, J = 5.1, 4F), −133.0 ppm (m, 2F); MS (EI): 478 [M$^+$]; HRMS calcd for $C_{21}H_{13}F_6S_2Cl$: 478.005, found: 478.001.

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