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Electrochromic tetrathiafulvalene derivatives functionalised with 2,5-diaryl-1,3,4-oxadiazole chromophores†

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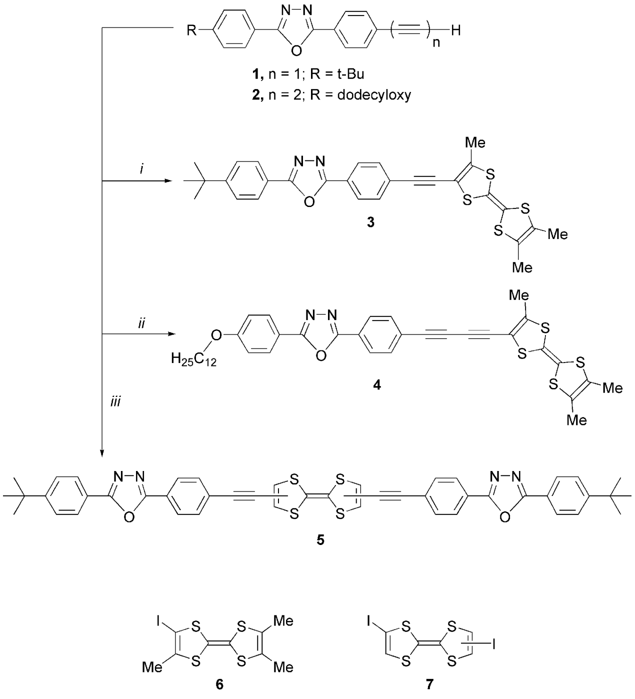
Electrochromism has been demonstrated by three novel electrochemically-reversible compounds 3, 4 and 5, which were synthesised by Pd catalysed cross-coupling of iodotrimethylTTF (6) and 2,6(7)-diiodoTTF (7) with the 2,5-diaryl-1,3,4-oxadiazole derivatives 1 and 2 containing terminal ethyne and butadiyne groups.

Electrochromism is defined as the colour change of a chemical species in the visible region resulting from an electrochemical reaction.[1] This phenomenon is essential for the design of electrochromic car rear-view mirrors (which have been commercialised), smart windows, flat panel displays and other applications.[1] However, for practical use, electrochromic molecules must possess: 1) *reversible* redox properties; 2) *fast* redox response; and 3) *stable* charged species. Molecular systems offer the advantages of narrower absorption bandwidths and more precise redox chemistry and colour tunability compared to polymeric analogues. Tetrathiafulvalene (TTF) derivatives are violene-type systems which possess highly reversible electrochemical oxidations and unusual thermodynamic stability of their cation-radicals and dications.[2] Their low oxidation potentials (TTF, $E^1_{1/2}$ = 0.34 V *vs.* Ag/AgCl) could also mean a low driving voltage and low power consumption for electrochromic devices (ECDs) incorporating TTF derivatives. In this context, we report the synthesis of three new TTF derivatives (**3–5**) bearing diaryl-1,3,4-oxadiazole (OXD) units as chromophores. We demonstrate that the conjugation of TTF and OXD moieties offers great potential as a new class of materials for ECDs.

Compounds **3** and **4** were synthesised by cross-coupling of iodotrimethylTTF (**6**)[3] with 2-(4-*tert*-butylphenyl)-5-(4-ethynylphenyl)-1,3,4-oxadiazole (**1**) and 2-(4-dodecyloxyphenyl)-5-[4-(1,3-butadiynyl)phenyl]-1,3,4-oxadiazole (**2**)[4] under typical Sonogashira conditions. Similarly, compound **5** was obtained by the coupling of **1** with 2,6(7)-diiodoTTF (**7**)[5] (Scheme 1). These compounds were characterised by CNH analysis, ^{1}H and ^{13}C NMR spectroscopy and EI mass spectrometry.‡ The crystal structure of the *trans* isomer of **5** has also been determined by X-ray diffraction (Fig. 1).§

Cyclic voltammograms of **3–5** were recorded in DCM solution containing 0.1 M TBAPF$_6$. All three compounds exhibited reversible TTF-type two-step, one-electron redox couples between 0–1 V (*vs.* Ag/Ag$^+$). Compared with **6**,[3] the half-wave potentials of **3** (0.12 and 0.63 V) and **4** (0.16 and 0.64 V) were anodically shifted by *ca.* 100 mV, due to the electron-withdrawing oxadiazole chromophores. The additional ethynylene spacer in **4** resulted in only a small difference in the electrochemistry between **3** and **4**. Due to the additional OXD chromophore and the absence of the electron-donating methyls, the oxidation potentials of **5** were further anodically shifted: the two redox waves appeared at $E^1_{1/2}$ = 0.31 V and $E^2_{1/2}$ = 0.74 V.

Electrochromism of compounds **3–5** was studied by spectroelectrochemistry and the λ_{max} values of the corresponding neutral and oxidised species are given in Table 1. Fig. 2 shows the UV-Vis absorption profile of **5** in DCM solution containing 0.1 M TBAPF$_6$ as a function of applied voltage (*vs.* Pt wire). Neutral **5** had a single absorption band at λ_{max} = 447 nm in the visible region. The oxidation of **5** gradually led to the formation of cation-radical $\mathbf{5}^{+\cdot}$, resulting in new absorptions at λ_{max} 435 and 722 nm. As the voltage was raised further, these two bands became progressively weaker and a new band at λ_{max} *ca.* 585 nm appeared due to the formation of the dication $\mathbf{5}^{2+}$. Comparing **5** with unsubstituted TTF[2a] reveals a larger red shift in the λ_{max} of the dication (Δ 230 nm) than the cation-radical (Δ 142 nm) suggesting that π-conjugation is especially extended in the dication of **5**. These optoelectrochemical features are typical for all the derivatives **3–5**. Neutral **3** also absorbed at 447 nm, whereas the high-energy band of the cation-radical had two maxima (437 and 468 nm). The low-energy $\mathbf{3}^{+\cdot}$ band appeared at 703 nm and the $\mathbf{3}^{2+}$ species absorbed at 520 nm. The absorption of neutral **4** was red-shifted to 462 nm, consistent with extended π-conjugation of the OXD chromophore.



Scheme 1 *Reagents and conditions*: i) **1** and **6**, Pd[PPh$_3$]$_4$, CuI, THF–triethylamine, r.t. 12 h then 50 °C 1 h, 64%; ii) **2** and **6**, Pd[PPh$_3$]$_2$Cl$_2$, CuI, THF–triethylamine, r.t. 48 h then 50 °C 1 h, 32%; iii) **1** and **7**, Pd[PPh$_3$]$_2$Cl$_2$, CuI, THF–triethylamine, r.t. 2.5 h then reflux 1 h, 82%.

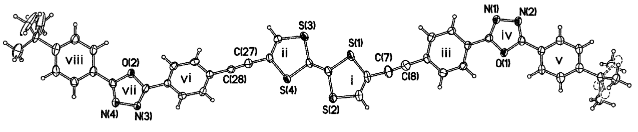


Fig. 1 Molecular structure of *trans*-**5**. One of the *t*-Bu groups is disordered.

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† Electronic Supplementary Information (ESI) available: spectroelectrochemistry of **3** and **4**; ^{1}H-NMR spectra and cyclic voltammograms for **3**, **4** and **5**; crystallographic information for **5**. See http://www.rsc.org/suppdata/cc/b3/b316243p/

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To explore the possibility of using these compounds in ECDs, optical switching has been realised as shown in Fig. 3. While electrical square waves of ±1.03 V (Pt reference was grounded to the pulse generater chassis) were applied across the spectroelectrochemical cell containing a solution of **5** (see Fig. 2 caption), the optical absorption around the $\mathbf{5}^{+\cdot}$ $\lambda_{\max}$ peak was switched leading to a highly-reversible colouring (dark-green)/bleaching (orange) process.

Although TTF derivatives have found uses in many areas of materials chemistry,[6] hitherto their electrochromic properties have been largely ignored.[7,8] We will report electrochromic studies on other TTF derivatives in due course.

Table 1 Visible absorption $\lambda_{\max}$ (nm) of **3–5** and TTF in neutral and their charged states[a]

3	447		
$\mathbf{3}^{+\cdot}$	437, 468		703
$\mathbf{3}^{2+}$		520	
4	462		
$\mathbf{4}^{+\cdot}$	468	596	669, 714
$\mathbf{4}^{2+}$		507	
5	447		
$\mathbf{5}^{+\cdot}$	435		722
$\mathbf{5}^{2+}$		585	
TTF[b]	450		
$\mathbf{TTF}^{+\cdot b}$	438	580	
$\mathbf{TTF}^{2+c}$	*ca.* 350[8]		

[a] DCM solution containing 0.1 M TBAPF$_6$. [b] Also see references 2*a*,8. [c] Under our conditions, $\mathbf{TTF}^{2+}$ precipitated and the spectrum could not be determined clearly.

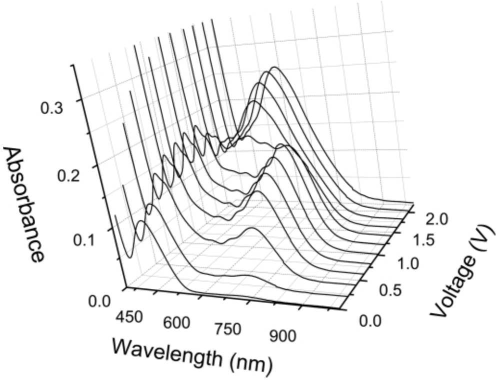

Fig. 2 Absorption spectroelectrochemistry of **5** in DCM solution containing 0.1 M TBAPF$_6$ as the supporting electrolyte. A 1 mm quartz cell with Pt mesh as the anode, Pt wire as both the counter and reference electrodes, was used.

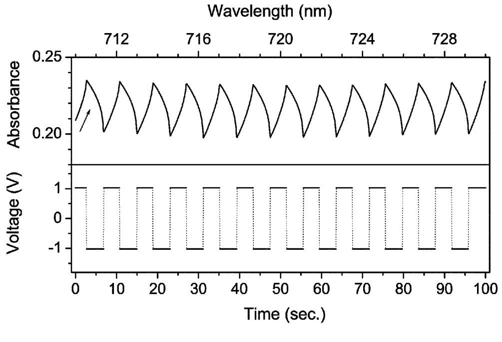

Fig. 3 Demonstration of the optical switching of a DCM solution of **5**, using the spectroelectrochemical cell as described in Fig. 2. While the spectrometer was scanning across the $\lambda_{\max}$ of $\mathbf{5}^{+\cdot}$ from 710 to 730 nm, electrical square waves were applied.

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Notes and references

‡ **3**: Orange crystals, mp 251.8–252.5 °C; ^{1}H NMR (400 MHz, CDCl$_3$, treated with NaOH pellet) δ 1.38 (s, 9H), 1.95 (s, br, 6H), 2.24 (s, br, 3H), 7.56 (d, ^3J = 8.4 Hz, 2H), 7.59 (d, ^3J = 8.4 Hz, 2H), 8.07 (d, ^3J = 8.4 Hz, 2H), 8.11 (d, ^3J = 8.4 Hz, 2H); *m/z* (EI) 546 (M$^+$, 100%). Anal. Calcd for $C_{29}H_{26}N_2OS_4$: C, 63.70; H, 4.79; N, 5.12. Found: C, 63.41; H, 4.72; N, 5.06%. **4**: Red crystals, mp 214.0–215.5 °C; ^{1}H NMR (500 MHz, CDCl$_3$, treated with NaOH pellet) δ 0.88 (t, J = 7.0 Hz, 3H), 1.27 (m, 16 H), 1.47 (m, 2H), 1.82 (m, 2H), 1.94 (s, 3H), 1.95 (s, 3H), 2.20 (s, 3H), 4.03 (t, J = 7.0 Hz, 2H), 7.02 (d, ^3J = 9.0 Hz, 2H), 7.64 (d, ^3J = 9.0 Hz, 2H), 8.05 (d, ^3J = 9.0 Hz, 2H), 8.09 (d, ^3J = 9.0 Hz, 2H); MS (EI) *m/z* 698 (M$^+$, 30%). Anal. Calcd for $C_{39}H_{42}N_2O_2S_4$: C, 67.01; H, 6.06; N, 4.01. Found: C, 66.71; H, 6.05; N, 4.06%. **5**: Dark-red crystals, mp > 310 °C (dec.); ^{1}H NMR (CDCl$_3$) δ 1.38 (s, 18H), 6.66 (s, 2H), 7.56 (d, ^3J = 8.4 Hz, 4H), 7.62 (d, ^3J = 8.4 Hz, 4H), 8.07 (d, ^3J = 8.7 Hz, 4H), 8.13 (d, ^3J = 8.4 Hz, 4H); MS (EI) *m/z* 804 (M$^+$, 0.7%). Anal. Calcd for $C_{46}H_{36}N_4O_2S_4$: C, 68.63; H, 4.51; N, 6.96. Found: C, 68.36; H, 4.46; N, 7.02%. The ^{1}H NMR signals of the methyl groups on the TTF moieties of **3** and **4** were significantly broadened due to the presence of a trace amount of acid in the commercial CDCl$_3$. However, sharp ^{1}H and ^{13}C NMR spectra of **4** were obtained in CDCl$_3$ treated with a pellet of NaOH. Due to the relatively higher oxidation potential of **5**, compared to **3** and **4**, its spectra were less sensitive to the acidity of the NMR solvent and the signals of its TTF-protons were cleanly observable in fresh CDCl$_3$.

§ Data collection: Bruker SMART 3-circle diffractometer with an APEX CCD area detector, 60 W Mo-target microfocus Bede Microsource® X-ray generator with glass polycapillary X-ray optics (Mo-K$_\alpha$ radiation, graphite monochromator, $\bar{\lambda}$ = 0.71073 Å). *Crystal data*: $C_{46}H_{36}N_4O_2S_4$, M = 805.03, T = 120 K, triclinic, space group $P\bar{1}$ (No. 2), a = 6.2187(7), b = 13.8638(17), c = 23.908(3) Å, α = 105.133(6), β = 96.855(6), γ = 96.700(6)°, U = 1951.9(4) Å^3, Z = 2, D_c = 1.370 g cm^{-3}, μ = 0.29 mm^{-1}, 18128 reflections ($2\theta \leq 55°$), 8900 unique, R_{int} = 0.097, R = 0.054 [3381 data with $F^2 \geq \sigma(F^2)$], w$R(F^2)$ = 0.111. CCDC 226866. See http://www.rsc.org/suppdata/cc/b3/b316243p/ for crystallographic data in .cif or other electronic format.

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