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Polyfluoroalkylsulfanyl-substituted tetrathiafulvalene derivatives: synthesis, electrochemical properties, and derived cation radical salts

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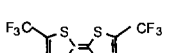
Abstract

Polyfluoroalkylsulfanyl-substituted tetrathiafulvalene derivatives have been synthesised via self- or cross-coupling of suitable 2-(thi)oxo-1,3-dithioles. Key intermediates are 4,5-bis(polyfluoroalkyl-sulfanyl)-2-thioxo-1,3-dithioles, formed from reaction between 2-(F-alkyl)-1-iodoethanes C_nF_{2n+1}–C_2H_4I ($n=6,8$) and bis(tetraethylammonium) bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate, and 4-[2′-(F-hexylethylsulfanyl]-5-methylsulfanyl-2-thioxo-1,3-dithiole. Self- and cross-coupling products are formed in fair to very good yields by using tri-isopropylphosphite, instead of the more usual triethyl or trimethylphosphite. All of these new TTF-derivatives exhibit quasi reversible voltammograms. Cation radical salts have been obtained mainly from one of these derivatives, whose anodic oxidation, in the presence of tetrabutylammonium hexafluorophosphate or perchlorate, allows isolation of very thin 'hair-like' threads. © 1997 Elsevier Science S.A.

Keywords: 2-(F-alkyl)-ethyl derivatives; Tetrathiafulvalene; Synthesis; Cyclic voltammetry; Cation radical salts

1. Introduction

Tetrathiafulvalene (TTF) and related compounds constitute a continuously growing family, due to their ability to generate conducting or superconducting charge transfer and cation radical salts [1,2]. However, to our knowledge, very few fluoro derivatives in this series are reported in the literature: the tetrakis(trifluoromethyl)-substituted compounds **1** [3–5], **2** and **3** [6] and more recently the bis(perfluorobenzo)-TTF **4** [7]. This small number of fluorinated TTFs can be accounted for by the experimental difficulties of their preparation, while their weaker electron donor power compared to TTF itself, due to the strong electronegativity of fluorine, may also have discouraged further work in this field. Nevertheless, the synthesis of long alkyl chain-substituted TTF derivatives has been largely developed in the last decade, because of interest in the formation of conducting Langmuir–Blodgett films from these compounds [8–12]. The good organization of the molecular assemblies in these multilayer LB films is mainly related to Van der Waals interactions between the long alkyl chains. From this point of view, another property of fluorine, namely the well known propensity of perfluoroalkyl groups (C_6 or more) to self-assembly [13], might also be used with benefit from TTFs bearing such long perfluoroalkyl chains. Recently, weakly conducting well ordered LB films have been obtained from compound **5** [14].



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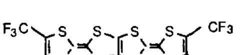

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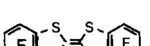

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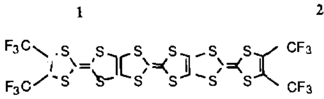

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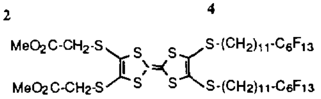

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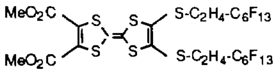
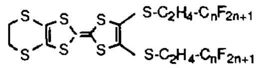
These results have prompted us to develop this family of fluorinated TTFs, and the present paper describes the synthesis and the electrochemical properties of several new polyfluoroalkylsulfanyl-substituted TTF derivatives **12–15**.



12



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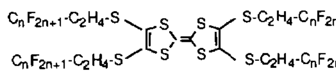
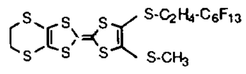
13b n = 8



14a n = 6
14b n = 8



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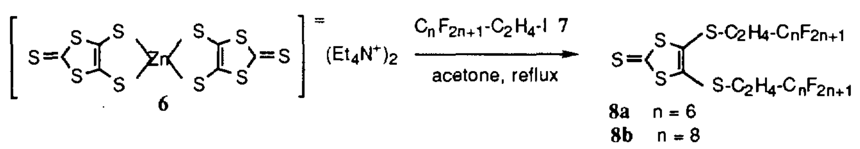


Scheme 1.

2. Results and discussion

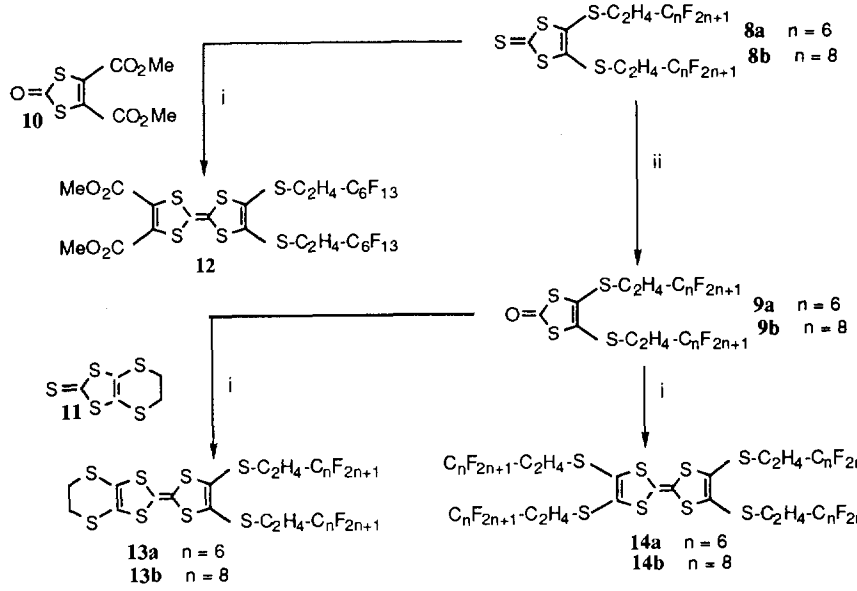
2.1. Synthesis of compounds 12–15

For obtaining the TTF derivatives **12–14** (Scheme 2), the key compounds are the 4,5-bis(polyfluoroalkylsulfanyl)-2-thioxo-1,3-dithioles **8a** and **8b**. These compounds are obtained according to Steimecke [15] by reaction between the zincate salt **6** and 2-(F-alkyl)-1-iodoethanes C_nF_{2n+1}–C_2H_4–I **7a** ($n = 6$) and **7b** ($n = 8$), which are known to easily react as electrophiles towards thiolate anions [16,17] (Scheme 1). In this process, best yields are usually observed by using an excess of iodo derivative; however, since remaining **7b** is not easy to remove from the reaction mixture, it is more convenient in this latter case to use an excess of zincate **6**, despite the lower yield of **8b** compared to **8a**.

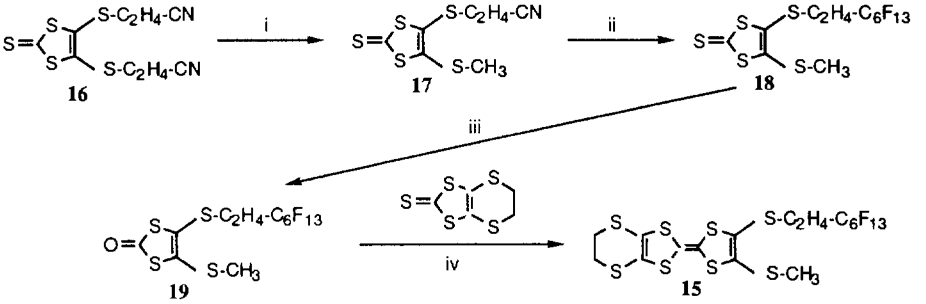
The formation of compounds **12–15** relies on cross- or self-coupling reactions from suitable 4,5-disubstituted-2-(thi)oxo-1,3-dithioles, these reactions being usually induced by trimethyl- or triethylphosphite [18]. For this purpose, we prepared the 4,5-bis(polyfluoroalkylsulfanyl)-2-oxo-1,3-dithioles **9a** and **9b**, which were obtained almost quantitatively from the corresponding 2-thioxo derivatives **8a** and **8b** after reaction with $Hg(OAc)_2$ [19,20]. On the other hand, we observed that using triisopropylphosphite $(i\text{PrO})_3P$ instead of $(MeO)_3P$ or $(EtO)_3P$, both as the reagent and the solvent, may facilitate the coupling reaction. This improvement, apparently associated with the size of the alkyl groups in $(i\text{PrO})_3P$, was also pointed out in other coupling reactions [21]. In our conditions the expected unsymmetrical TTF derivatives **12–13** and symmetrical **14a** are formed with fair to very good yields (27–92%), except **14b** (15%) presumably because of the low solubility of starting compound **9b**. In particular, the cross-coupling reactions were very selective whereas they are often reported to give rise to notable amounts of undesired symmetrical TTF derivatives; the side self-coupling reaction was only observed to a very small extent during the preparation of **12**, tetrakis-(methyloxycarbonyl)-TTF being produced in this case.

The derivatives **14a** and **14b** are polyfluoro analogues of 'molecular fasteners' recently reported to display semiconducting properties as neutral molecules [22,23]. Unfortunately single crystals of the good enough quality required for accurate conductivity measurements could not be obtained, and no conducting character could be detected on a compaction pellet of **14a** (four-probe method [24]).

The same strategy was developed for obtaining the unsymmetrical derivative **15**. One of the precursors is the 2-thioxo-1,3-dithiole **18**, prepared by adapting the methodology recently introduced by Becher's group [25,26]. The starting compound is the 4,5-bis(cyanoethylsulfanyl)-2-thioxo-1,3-dithiole **16** [25] from which each cyano–ethyl group –C_2H_4–CN is successively replaced first by a methyl group, leading to compound **17** [26], then by a –C_2H_4–C_6F_{13} group (Scheme 3). The 2-thioxo-1,3-dithiole **18** is thus formed with a good overall yield (50%), then readily transformed into the corresponding 2-oxo derivative **19** (96%). Finally, the cross-coupling reaction induced by $(i\text{PrO})_3P$



Scheme 2. Reagents and conditions (i) triisoprophyl phosphite, nitrogen, 130°C; (ii) mercuric acetate, acid–chloroform.



Scheme 3. Reagents and conditions (i) cesium hydroxide monohydrate, methanol, then iodomethane; (ii) potassium *t*-butylate then compound 7a, methanol–dimethyl formamide, nitrogen; (iii) mercuric acetate, acetic acid–chloroform; (iv) compound 6, triisopropyl phosphite, nitrogen, 130°C.

Table 1
Cyclic voltammetric data for compounds **12**, **13a–b**, **14a** and **15** in the presence of Bu_4N^+ PF_6^- [a]

Donor	Ep_{a1}	Ep_{c1}	Ep_{a2}	Ep_{c2}	$\Delta Ep = Ep_{a2} - Ep_{a1}$
12	0.82	0.72	1.17	1.07	0.35
13a	0.65	0.55	1.00	0.90	0.35
13b	0.65	0.56	0.99	0.91	0.34
14a[b]	0.75	0.67	1.02	0.94	0.27
15	0.57	0.49	0.94	0.86	0.37

[a] Solvent: CH_2Cl_2, donor: 10^{-3} mol l^{-1}, Bu_4N^- PF_6^- 0.1 mol l^{-1} as supporting electrolyte, scan rate 100 mV s^{-1}, anodic (Ep_a) and cathodic (Ep_c) peak potentials in V vs. SCE, 20°C, PAR electrochemical analyzer).
[b] Saturated solution in CH_2Cl_2 (concentration $< 10^{-3}$ mol l^{-1}).

(Scheme 3) affords the unsymmetrical TTF **15** in a satisfactory yield (47%).

2.2. *Cyclic voltammetry*

The redox properties of compounds **12**, **13a–b**, **14a** and **15** have been studied by cyclic voltammetry, the results being summarized in Table 1. All donors exhibit two well defined reversible one-electron oxidation processes corresponding to the successive formation of a cation radical (Ep_{a1}) then of a dication (Ep_{a2}) (see typical examples in Fig. 1). The fairly good electrochemical reversibility of these two redox processes is clearly shown by the difference $Ep_a - Ep_c = 0.08$–0.1 V between the anodic and cathodic peak potentials, these values being not very far from the 0.06 V theoretical value assigned to a fully reversible system.

Compared to TTF itself ($Ep_{a1} = 0.43$ V and $Ep_{a2} = 0.88$ V, measured under the same conditions), the donor ability of these polyfluoroalkylsulfanyl-substituted TTFs **12–15** appears to be reduced. Thus, Ep_{a1} is 0.75 V for tetrakis[2′-(F-hexyl)-ethylsulfanyl]-TTF **14a**, the highest value being $Ep_{a1} = 0.82$ V for compound **12** in which, by comparison with **14a**, two CO_2Me groups replace two polyfluoroalkylsulfanyl groups $S–C_2H_4–C_6F_{13}$. These latter values also show that the electron-withdrawing effect of a polyfluoroalkylsulfanyl group is slightly smaller than that of the methyloxycarbonyl. On the other hand, the oxidation potential Ep_{a1} from **14a** is 0.22 V more anodic than that provided by $TTF(SCH_3)_4$ in the same conditions ($Ep_{a1} = 0.55$ V/SCE, $Ep_{a2} = 0.83$ V/SCE, Bu_4NPF_6, CH_2Cl_2[1]). This result indicates that the effect of the strong electron-withdrawing character of the C_nF_{2n+1} moiety,[2] although still present, is notably reduced in the $S–C_2H_4–C_nF_{2n+1}$ group, most likely owing to the presence of the C_2H_4 spacer group. Likewise the replacement of only one $–C_2H_4–C_6F_{13}$ group in **13a** by a methyl group in **15** results in a smaller anodic shift of Ep_{a1} (0.08 V instead of 0.22 V). Such an effect of a $(CH_2)_n$ spacer group has already been observed in the case of electro-polymerized 3-[C_6F_{13}–$(CH_2)_n$]-thiophenes whose oxidation potentials ($n = 2$, 1.1 V/SCE; $n = 3$, 0.92 V/SCE) remain very close to that (1.0 V/SCE) of the polymer prepared from 3-octyl-thiophene [28]. Besides, as might be expected, the length of the two

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[1] P. Leriche, unpublished results.

[2] The dramatic electron withdrawing character of a CF_3 group is well evidenced by comparison of Ep_{a1} values from TTF (0.43 V/SCE) and $TTF(CF_3)_4$ (1.23 V/SCE [2b]).

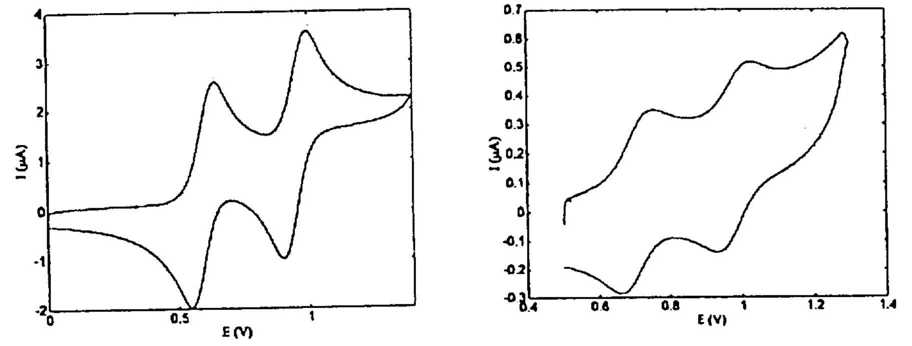

Fig. 1. Cyclic voltammograms of compounds **13a** (left) and **14a** (right). Recording conditions: see Table 2.

Table 2
Cyclic voltammetric data for compounds **13a** and **14a** in the presence of $Bu_4N^+ ClO_4^-$ [a]

Donor	Ep_{a1}	Ep_{c1}	Ep_{a2}	Ep_{c2}	$\Delta Ep = Ep_{a2} - Ep_{a1}$
13a	0.63	0.56	0.89	0.82	0.26
14a	0.74	0.66	0.91	0.83	0.17

[a] Same recording conditions as in Table 1, except $Bu_4N^+ ClO_4^-$ as supporting electrolyte.

different perfluoroalkyl groups C_nF_{2n+1} in **13a** and **13b** exerts no influence on the oxidation potential values.

It is also to be noticed that $\Delta Ep = Ep_{a2} - Ep_{a1}$ (Table 1), which is indicative of the intramolecular coulombic repulsion in the dication redox stage [29,30], is smaller for compound **14a** (0.27 V) than for the other compounds studied (0.34–0.37 V). Furthermore, such a low ΔEp value is still observed for **14a** when the supporting electrolyte is Bu_4N^+ ClO_4^- instead of the PF_6^- salt, other recording conditions of the C.V. data being unchanged (Table 2). In these two sets of data, the gap between the ΔEp values from both **13a** and **14a** remains quasi constant (0.08–0.09 V lower for **14a**).

Although the reason for this gap is not clear, we observe that **14a** is the only compound substituted by four polyfluoroalkylsulfanyl groups. However, if we consider the electronic effects of a polyfluoroalkyl group $-C_2H_4-C_6F_{13}$ (see above), the stabilization of the positive charge of the dication stage is not expected to be better in **14a** (thus lowering the ΔEp value) than in **13a** where two such groups are replaced by the $-(CH_2)_2-$ moiety. In the absence of further structural information, a possible explanation might come from the four external TTF-bonded sulphur atoms if they share to some extent the positive charge of the dication, and in this case this share would be slightly more pronounced in **14a** than in **13a**. By comparison, low ΔEp values are also encountered from tetrakis(methylsulfanyl)-TTF ($Ep_{a1} = 0.55$ V, $Ep_{a2} = 0.77$ V, $\Delta Ep = 0.22$ V, acetonitrile), tetrakis(benzoylsulfanyl)-TTF ($Ep_{a1} = 0.66$ V, $Ep_{a2} = 0.89$ V, $\Delta Ep = 0.23$ V, acetonitrile) [27].

Another feature may be pointed out from the data collected in Tables 1 and 2. The Ep_{a2} values for compounds **13a** and **14a** were strongly reduced (*ca.* 100 mV) when PF_6^- was replaced by ClO_4^-, whereas the Ep_{a1} values remained approximately the same, thus leading to much lower ΔEp values in the latter case. In particular, **14a** provides $\Delta Ep = 0.17$ V which appears, to our knowledge, to be the lowest value reported for a substituted TTF. Since the nature of the anion is the only variable parameter between the two sets of experiments, we may consider that the presence of ClO_4^- anions in the supporting electrolyte greatly favours the decreasing of the ΔEp values, and therefore the associated decreasing of the coulombic repulsion in the corresponding dications. A dication–anion interaction stronger with ClO_4^- than with PF_6^- might account for the observed results, this latter anion having already been reported as more weakly coordinating than ClO_4^- [31,32].

2.3. Preparation of cation radical salts

As shown above (Table 1), the stability of the oxidation states formed from donors **12–15** is good. These compounds may thus be considered as possible precursors of organic metals, and we have studied the formation of corresponding cation radical salts by anodic oxidation under galvanostatic conditions. We were unable to study compounds **14** owing to their too weak solubility.

Crystal growing at the anode was observed from compounds **13a** and **13b**, and most of the studies were carried out with **13a** which was prepared in good yield. We also notice that **13a** and **13b** are new examples of EDT-TTF derivatives, this family having already been reported as a good precursor of organic metals [33,34]. We have reported in a preliminary communication that **13a** gives well organized multilayer LB films on a solid substrate, whose diiodine doping leads to a conducting stable mixed valency state ($\sigma \sim 10^{-2}$ s cm^{-1} at room temperature) [35].

The anodic oxidation of **13a** was performed with a constant current intensity ($i = 1$ μA) in the presence of Bu_4N^+ PF_6^- (or more rarely Bu_4N^+ ClO_4^-) as the supporting electrolyte. The formation of the oxidation product in the anodic compartment was favoured by a saturated solution of the donor in a 1:2 v/v CH_2Cl_2/EtOH mixture, the resultant salt being soluble in methylene chloride and practically insoluble in ethanol. The salt was harvested as dark 'hair-like' very thin threads both on the anode and at the bottom of the cell. In particular we have observed that the formation of the salt during the electrolysis seems to be favoured in the part of the cell which contains undissolved donor **13a**. One may thus assume that the neutral **13a** is involved in the building of the material, and, in this hypothesis, a mixed-valence cation radical salt is likely to be produced. Replacing Bu_4N^+ PF_6^- by Bu_4N^+ ClO_4^- did not change the morphology of the salt as examined by scanning electron microscopy. The polycrystalline character of the material was thus clearly shown, and precluded any X-ray diffraction study. Chemical oxidation of **13a** through diiodine is currently under investigation; depending on the experimental conditions different salts have been obtained whose structure and physical properties are being studied.

3. Conclusion

New polyfluoroalkylsulfanyl-substituted tetrathiafulvalene derivatives have been easily synthesised, thus opening up further developments for 2-[F-alkyl]-1-iodoethanes as starting materials. The electrochemical study of these new electron donors allows the characterization of the electronic effect of $S-C_2H_4-C_nF_{2n+1}$ groups, in which the presence of the C_2H_4 spacer group reduces to some extent the influence of the tail C_nF_{2n+1}. Consequently, as substituents on a TTF core, such polyfluoroalkylsulfanyl groups combine two advantages: owing to their extra-core sulphur atoms, as in

EDT- or BEDT-TTF derivatives, they may increase the possible interactions between TTF cores in the solid state, and due to their fluorophilic character the C_nF_{2n+1} tails may also contribute to the formation of ordered structures of derived cation radical salts. In this respect, the EDT-TTF derivatives **13ab** are the best examples. Furthermore, compound **13a** behaves as a good precursor of new organic materials, as shown in our electrocrystallization experiments and in other studies devoted to the generation of LB films [36,37]. In this latter case, the effect of the perfluoro tail C_nF_{2n+1} appears to be important, since the compound **15** does not lead to as good LB films as does **13a** [37]. These results suggest that other conducting organic materials may be formed from **13a**, and our current work on its chemical oxidation seems to be encouraging.

4. Experimental details

^1H and ^{13}C NMR spectra were recorded on a JEOL 270 instrument operating at 270.05 MHz for protons and 67.8 MHz for carbon nuclei. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) as internal standard. All J values are in Hz. IR spectra were run in KBr discs on a Perkin Elmer 841 spectrophotometer. Mass spectra were recorded on a EBE VG Autospec spectrometer. Zincate salt **6** [15], 4,5-bis(methyloxycarbonyl)-2-oxo-1,3-dithiole **10** [38], 4,5-ethylenedisulfanyl-2-thioxo-1,3-dithiole **11** [15] and 1,3-dithiole derivatives **16** [25] and **17** [26] were prepared as previously described.

*4.1. Preparation of 4,5-bis[2'-(F-hexyl)ethylsulfanyl]-2-thioxo-1,3-dithiole **8a***

Zincate salt **6** (5 g, 6.96 mmol) and C_6F_{13}–C_2H_4–I **7a** (19.8 g, 41.76 mmol) were dissolved in acetone (100 ml), and this solution was refluxed under nitrogen for 4 h. After the solvent was evaporated, the remaining crude solid was purified by column chromatography (SiO_2, eluent CH_2Cl_2), thus providing pure **8a** (8 g, 65%) which was recrystallised from hexane as yellow–green needles. Mp 81°C. δ_H ($CDCl_3$) 2.46–2.49 (m, 4H), 3.1–3.13 (m, 4H); δ_C ($CDCl_3$) 27.43 (t, S–CH_2, $^3J_{CF}$ 4.15), 31.88 (t, CH_2, $^2J_{CF}$ 22.35), 106.1–123.5 (C_6F_{13}), 135.66 (C=C), 209.45 (C=S); ν_{max} (KBr)/cm^{-1} 1062 (C=S), 1100–1300 (C–F). Found: C, 25.66; H, 0.89; F, 55.76; S, 17.81. $C_{19}H_8S_5F_{26}$ requires: C, 25.63; H, 0.91; F, 55.47; S, 18.00%.

*4.2. Preparation of 4,5-bis[2'-(F-octyl)ethylsulfanyl]-2-thioxo-1,3-dithiole **8b***

Preparation of **8b** was analogous to **8a** (see above), in the following conditions: zincate salt **6** (5 g, 6.96 mmol), C_8F_{17}–C_2H_4–I **7b** (12 g, 20.92 mmol), 100 ml acetone, reflux for 9 h. After recrystallisation from hexane, **8b** (0.75 g, 7%) was obtained as a light brown powder. Mp 69°C. δ_H ($CDCl_3$) 2.3–2.5 (m, 4H, CH_2), 3.11–3.18 (m, 4H, CH_2) · ν_{max} (KBr)/cm^{-1} 1063 (C=S), 1147–1201 (C–F). Found $[M+H]^+$, 1090.8792; $C_{23}H_9F_{34}S_5$ requires 1090.8765.

*4.3. Preparation of 4,5-bis[2'-(F-hexyl)ethylsulfanyl]-2-oxo-1,3-dithiole **9a***

A suspension of mercuric acetate (1.8 g, 5.6 mmol) in 15 ml acetic acid was added to a solution of **8a** (2 g, 2.25 mmol) in chloroform (30 ml). The reaction mixture was stirred for 1 h at room temperature, then the non-soluble mercuric salts were filtered off, washed with diethyl ether and discarded. The ethereal solution was washed successively with water, then with a saturated aqueous $NaHCO_3$ solution, and finally with water until neutrality. After drying over anhydrous Na_2SO_4 and evaporation, the crude solid residue was chromatographed (silica column, eluting dichloromethane). Compound **9a** (1.94 g, 99%) was obtained as a light yellow powder. Mp 47°C. δ_H ($CDCl_3$) 2.38–2.57 (m, 4H, CH_2), 3.05–3.13 (m, 4H, CH_2) · ν_{max} (KBr)/cm^{-1} 1142–1210 (C–F), 1671 (C=O). Found M^+ · 873.90474; $C_{19}H_8F_{26}OS_4$ requires 873.90429.

*4.4. Preparation of 4,5-bis[2'-(F-octyl)ethylsulfanyl]-2-oxo-1,3-dithiole **9b***

Compound **9b** (0.7 g, 95%) was obtained as a light yellow powder in the same conditions as used above, from mercuric acetate (0.6 g, 1.6 mmol) in acetic acid (5 ml) and compound **8b** (0.75 g, 0.76 mmol) in chloroform (10 ml). Mp 52°C. δ_H ($CDCl_3$) 2.38–2.56 (m, 4H, CH_2), 3.0–3.13 (m, 4H, CH_2) · ν_{max} (KBr)/cm^{-1} 1147–1201 (C–F), 1673 (C=O). Found M^+ · 1073.8849; $C_{23}H_8F_{34}OS_4$ requires 1073.8915.

*4.5. Preparation of 2,3-bis(methyloxycarbonyl)-6,7-bis[2'-(F-hexyl)ethylsulfanyl]-TTF **12***

A solution of 4,5-bis(methyloxycarbonyl)-2-oxo-1,3-dithiole **10** (0.48 g, 2.05 mmol) and compound **8a** (0.92 g, 1.03 mmol) in triisopropylphosphite (10 ml) was heated under nitrogen for 1.5 h, the temperature being gradually increased from 80°C to 130°C during this period. After cooling to −25°C, the obtained solid was filtered off, washed with hexane and purified by chromatography (silica column, eluting dichloromethane). Thus was isolated compound **12** (0.3 g, 27%) as a red orange powder, along with a small amount of tetrakis(methyloxycarbonyl)-TTF (0.04 g). Mp 87–88°C. δ_H ($CDCl_3$) 2.37–2.53 (m, 4H, CH_2), 3.03–3.09 (m, 4H, CH_2), 3.86 (s, 6H, CH_3); δ_C ($CDCl_3$) 26.98 (S–CH_2), 31.97 (t, CH_2, $^2J_{CF}$ 22.35), 53.42 (CH_3), 109.78 and 111.3 (C=C center), 104–124 (C_6F_{13}), 128.23 and 131.93 (C=C ext), 159.76 (CO_2Me). Found M^+ · 1075.8819; $C_{26}H_{14}F_{26}O_4S_6$ requires 1075.8801.

*4.6. Preparation of 2,3-bis[2'-(F-hexyl)ethylsulfanyl]-6,7-ethylenedisulfanyl-TTF **13a***

A mixture of compound **9a** (1 g, 1.14 mmol) and 4,5-ethylenedisulfanyl-2-thioxo-1,3-dithiole **11** (0.51 g, 2.27 mmol) in triisopropylphosphite (20 ml) was heated at 130°C under nitrogen for 2.5 h. The reaction mixture was cooled to −25°C (freezer), and the orange solid was collected by filtration and washed with dichloromethane. The filtrate was concentrated under vacuum in order to eliminate dichloromethane and excess triisopropylphosphite, then the residue was purified by column chromatography (SiO_2, eluent CH_2Cl_2). Compound **13a** thus obtained was recrystallised from dichloromethane, giving orange needles (0.83 g, 69%). Mp 110–112°C. δ_H ($CDCl_3$) 2.40–2.46 (m, 4H, CH_2), 3.02–3.08 (m, 4H, CH_2), 3.3 (s, 4H, C_2H_4). Found: C, 27.29; H, 1.07; F, 47.07; S, 24.53. $C_{24}H_{12}F_{26}S_8$ requires: C, 27.43; H, 1.15; F, 47.01; S, 24.41%.

*4.7. Preparation of 2,3-bis[2'-(F-octyl)ethylthio]-6,7-ethylenedisulfanyl-TTF **13b***

Preparation of compound **13b** was analogous to **13a**, in the following conditions: 4,5-ethylenedisulfanyl-2-thioxo-1,3-dithiole **11** (0.18 g, 0.82 mmol) and compound **9b** (0.4 g, 0.41 mmol) in triisopropylphosphite (7 ml), this mixture being heated for 1.5 h under nitrogen. Compound **13b** was isolated as **13a**, as an orange powder (0.17 g, 35.5%). Mp 125°C. δ_H ($CDCl_3$) 2.40–2.49 (m, 4H, CH_2), 3.02–3.08 (m, 4H, CH_2), 3.31 (s, 4H, C_2H_4).

*4.8. Preparation of tetrakis-[2'-(F-hexyl)ethylsulfanyl]-TTF **14a***

A mixture of compound **9a** (0.95 g, 1.09 mmol) and triisopropylphosphite (10 ml) was heated at 130°C for 2 h under nitrogen. After cooling to −25°C, the crystals being formed were filtered off and washed with hexane, thus providing pure compound **14a** (0.84 g, 92%) as orange needles. Mp 118°C. Found: C, 26.63; H, 0.92; F, 57.51; S, 14.80. $C_{38}H_{16}F_{52}S_8$ requires: C, 26.58; H, 0.94; F, 57.54; S, 14.94%.

*4.9. Preparation of tetrakis-[2'-(F-octyl)ethylsulfanyl]-TTF **14b***

Compound **14b** was prepared as **14a**, by self-coupling of compound **9b** (0.1 g, 0.1 mmol) in triisopropylphosphite (2 ml), and was obtained as a yellow orange powder (0.015 g, 15%). Mp 145°C. Found: C, 26.02; H, 0.78; F, 60.97. $C_{46}H_{16}S_8F_{68}$ requires: C, 26.1; H, 0.76; F, 61.02%. Note: compounds **14a** and **14b** are not soluble enough in usual solvents to be analyzed by n.m.r.

*4.10. Preparation of 2,3-ethylenedisulfanyl-6-methylthio-7-[2'-(F-hexyl)ethylthio]-TTF **15***

4,5-Ethylenedisulfanyl-2-thioxo-1,3-dithiole **11** (0.58 g, 2.58 mmol) and compound **19** (0.7 g, 1.29 mmol) are dissolved into triisopropylphosphite (20 ml). This reaction mixture was heated at 130°C for 1 h under nitrogen. After cooling to room temperature, this mixture is chromatographed (silica column): heptane was first used as eluent for eliminating most of triisopropylphosphite, then eluting with dichloromethane gave the expected compound **15** which was further washed with petroleum ether and recrystallised from methanol (0.44 g, 72%, orange solid). Mp 76°C. δ_H ($CDCl_3$) 2.35–2.6 (m, CH_2), 2.46 (s, CH_3), 3–3.04 (m, CH_2), 3.31 (s, C_2H_4). Found: C, 28.34; H, 1.46; F, 33.93; S, 36.02. $C_{17}H_{11}F_{13}S_8$ requires: C, 28.29; H, 1.53; F, 34.37; S, 35.7%.

*4.11. Preparation of 4-[2'-(F-hexyl)ethylsulfanyl]-5-methylsulfanyl-2-thioxo-1,3-dithiole **18***

A solution of potassium tertbutylate (0.28 g, 2.49 mmol) in dry methanol (1.5 ml) was added to compound **17** (0.6 g, 2.26 mmol) dissolved in a minimum of dimethyl–formamide (3 ml), under nitrogen at 0°C. This reaction mixture was stirred for 1 h, leading to a dark red solution. Then C_6F_{13}–C_2H_4–I **7a** (1.29 g, 2.72 mmol) was added, and the resulting solution was heated at 30–40°C for 2 h under nitrogen. After cooling to room temperature, water (40 ml) was poured into this reaction mixture which was extracted with diethyl ether(4×30 ml). After usual work-up, a crude brown compound was isolated, and purified by column chromatography (SiO_2, eluent CH_2Cl_2), leading to compound **18** (0.88 g, 70%); a further recrystallisation from petroleum ether gave yellow–orange crystals. Mp 42°C. δ_H ($CDCl_3$) 2.37–2.6 (m, CH_2), 2.54 (s, CH_3), 3.05–3.11 (m, CH_2) · ν_{max} (KBr)/cm^{-1} 1055 (C=S), 1150–1270 (C–F).

*4.12. Preparation of 4-[2'-(F-hexyl)ethylsulfanyl]-5-methylsulfanyl-2-oxo-1,3-dithiole **19***

A mixture of compound **18** (0.28 g, 0.5 mmol) and mercuric acetate (0.48 g, 1.5 mmol) in chloroform (7.5 ml) and acetic acid (2.5 ml) was stirred for 1.5 h at room temperature. After usual work-up (see the preparation of compound **9a**), compound **19** (0.27 g, 98%) was obtained; recrystallisation from petroleum ether afforded yellow crystals. Mp 34°C. δ_H ($CDCl_3$) 2.37–2.60 (m, CH_2), 2.51 (s, CH_3), 3.03–3.09 (m, CH_2) · ν_{max} (KBr)/cm^{-1}: 1100–1270 (C–F), 1673 (C=O).

4.13. Cyclic voltammetry

Cyclic voltammetric experiments were performed in a one compartment cell with platinum working and counter electrodes and saturated calomel electrode as the reference. Measurements were made with a PAR 273 electrochemical analyzer. The cell contained a solution of donor (ca. 10^{-3}

mol l^{-1}) with commercial tetrabutylammonium hexafluorophosphate or perchlorate (ca. 10^{-1} mol l^{-1}) as supporting electrolyte in dry dichloromethane. All solutions were purged with nitrogen and retained under an inert atmosphere while the cyclic voltammograms were recorded.

4.14. Anodic oxidations (electrocrystallisation)

Anodic oxidation experiments were performed in a two compartment cell with platinum working and counter electrodes under galvanostatic conditions. The donor (ca. 5–10 mg) was partially dissolved in the anodic compartment which contained a 10^{-1} mol l^{-1} solution of Bu_4N^+ PF_6^- or ClO_4^- in a CH_2Cl_2/EtOH (1/2 v/v ratio) medium. A constant current (1 μA) was applied and the precipitated material was collected after a few days.

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