Synthesis of Unsymmetrical Tetrakis(alkylsulfanyl)tetrathiafulvalene Derivatives

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The *p*-acetoxybenzylsulfanyl protecting group is compatible with the triethylphosphite mediated cross-coupling of 4,5-bis(alkylsulfanyl)-1,3-dithiol-2-ones, providing access to bis(protected)-tetrathiafulvalenes, and thus to tetrathiafulvalenedithiolate dianion **10**, which can be alkylated to give unsymmetrical tetrakis(alkylsulfanyl)tetrathiafulvalene derivatives.

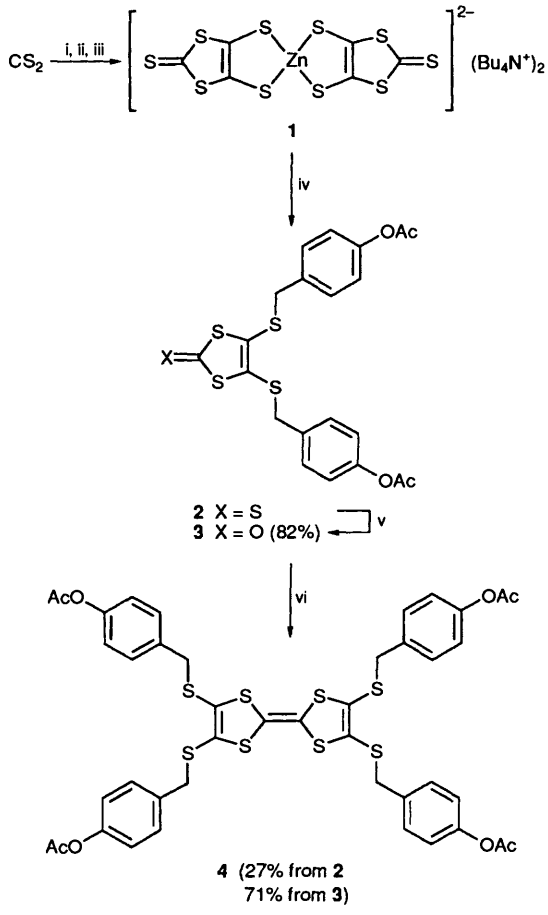
Since the discovery of the metallic and superconducting properties of various salts of tetrathiafulvalene (TTF) derivatives[1] considerable research effort has been applied to the synthesis of more sophisticated derivatives. This work has, until recently, been hampered by the lack of general methodology for selective functionalisation of TTF, and the lack of methods for the synthesis of unsymmetrical TTF derivatives.[2] In the last few years, however, several advances have been made, providing routes to a range of useful functionalised TTF derivatives and which may allow the incorporation of TTF into more sophisticated molecular architectures.[3] In this paper we describe in detail our efforts to develop a route to the TTF dithiolate dianion **10** which would provide a useful entry point for a range of new derivatives.[4]

For the synthesis of a protected TTF dithiolate, we planned to use the well-documented coupling of two 4,5-disulfanyl-1,3-dithiole-2-thione (or oxone) units,[2a] with suitable protecting groups on one of the units. Subsequent deprotection under basic conditions would yield the desired TTF dithiolate anion.[5] One advantage of such a route stems from the ready availability of such thiones (or oxones) on a large scale, from the salt of the $[Zn(dmit)_2]^{2-}$ dianion **1**, prepared by the sodium reduction of carbon disulfide in dimethylformamide (DMF)[6] (Scheme 1). However, the usual thiolate protecting groups, such as benzoyl or acetyl, are incompatible with most of the cross-coupling methods available.[7] We therefore chose to use the *p*-acetoxybenzyl protecting group[8] in the hope that this would be more stable, but could still be removed, under mild and basic conditions, to generate the desired dithiolate.[9]

Thus, *p*-acetoxybenzyl chloride was prepared, according to the method of Taylor *et al.*,[8] and treated directly with the $[Zn(dmit)_2]^{2-}$ dianion salt **1** (Scheme 1). Coupling of this thione, using triethyl phosphite, gave a 27% yield of the symmetrical tetra-protected TTF **4**, but coupling of the corresponding oxone **3**, gave **4** in a much improved yield of 71%, after recrystallisation from toluene–hexane.

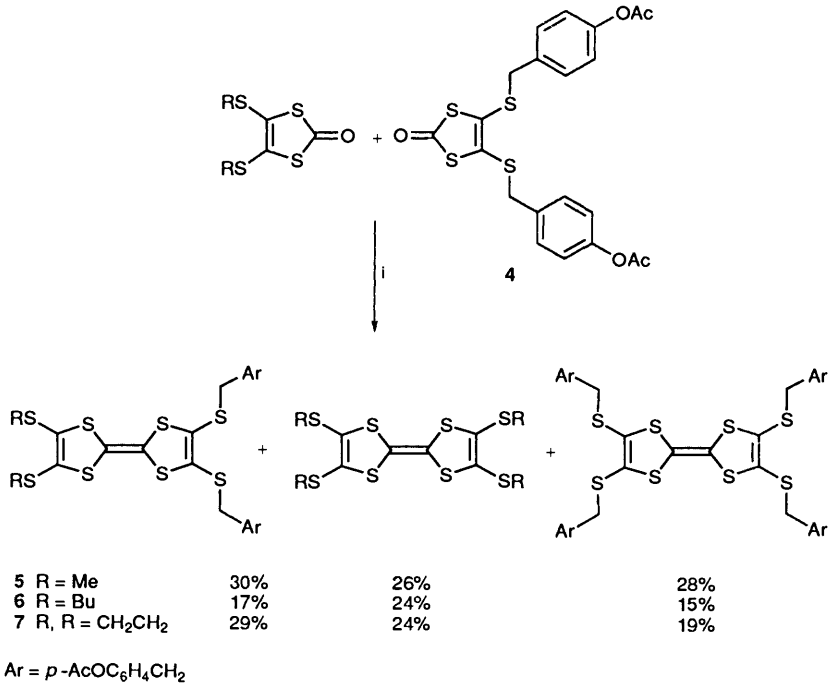
Cross-coupling of oxone **3** with 4,5-bis(methylsulfanyl)-1,3-thiol-2-one gave a mixture of the desired unsymmetrical diprotected TTF derivative **5** in 30% yield along with the two symmetrical TTF derivatives, which could be easily separated using flash column chromatography (Scheme 2). Similar results were found for the cross-coupling of **4** with 4,5-bis(butylsulfanyl)-1,3-thiol-2-one and 4,5-ethylenedisulfanyl-1,3-thiol-2-one, to give the unsymmetrical di-protected TTF derivatives **6** and **7** in 17 and 29% yield, respectively.

Treatment of a suspension of the tetra-protected TTF **4** in ethanol with 4 equiv. of sodium ethoxide, and warming to 50 °C gave a dark red solution of the tetrathiolate anion,[10] which was trapped with methyl iodide, to give tetrakis(methylsulfanyl) TTF **8**[11] in 68% yield, or with 1,2-dibromoethane to yield bis(ethylenedisulfanyl)tetrathiofulvalene (BEDT-TTF) **9**[6b] in 65% (Scheme 3).

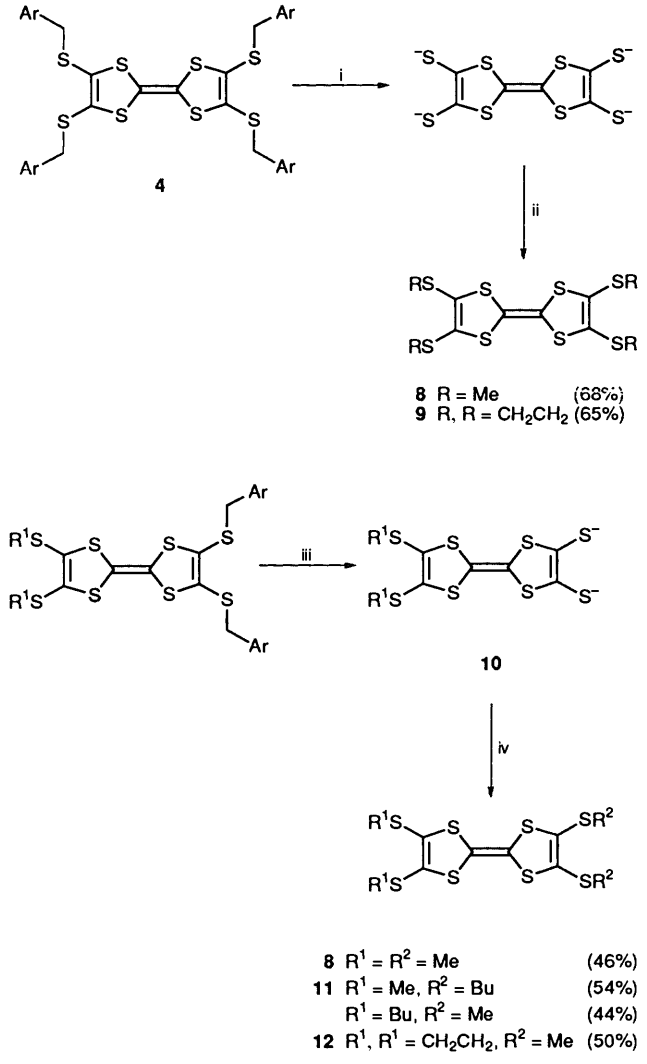


Scheme 1 *Reagents and conditions:* i, Na, DMF; ii, $ZnCl_2$, MeOH; iii, Bu_4NBr; iv, *p*-$AcOC_6H_4CH_2Cl$, acetone; v, $Hg(OAc)_2$, AcOH, $CHCl_3$; vi, $P(OEt)_3$, toluene

Generation of dithiolate anion **10** required different conditions. We first tried treating a suspension of **5** in ethanol with 2 equiv. of sodium ethoxide and warming to 50 °C. The development of a red solution suggested that the desired dithiolate was indeed forming, but addition of methyl iodide or butyl iodide to this solution led to only low yields of the corresponding tetrakis(alkylsulfanyl) TTF derivatives. Addition of sodium ethoxide solution in ethanol, or of sodium 2-



Scheme 2 *Reagents and conditions:* i, $P(OEt)_3$, toluene



Scheme 3 *Reagents and conditions:* i, 4 equiv. NaOEt, EtOH, 50 °C; ii, MeI or $BrCH_2CH_2Br$; iii, 2 equiv. NaOEt, EtOH, THF, −10 °C; iv, MeI, BuI or $BrCH_2CH_2Br$

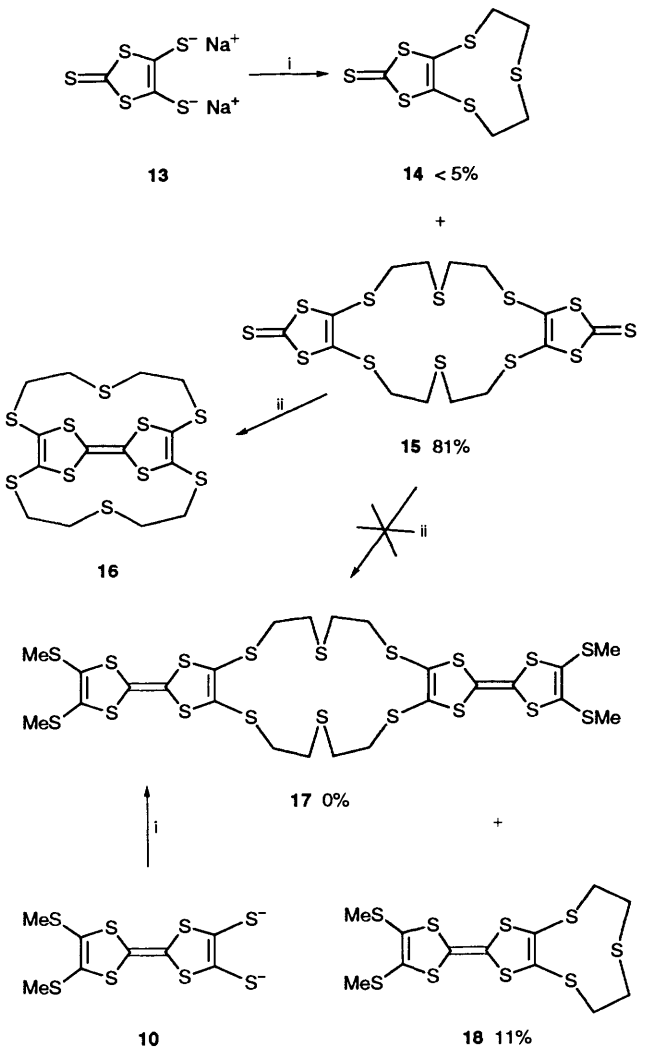
methylpropane-2-thiolate in tetrahydrofuran (THF), to a solution of **5** in tetrahydrofuran, at −10 °C, again gave rise to a deep red solution of the dithiolate anion, which could be alkylated with methyl iodide or butyl iodide to give the desired TTF derivatives **8** and **11** in improved yields of 46 and 54%, respectively. Dithiolate **10** was also successfully trapped with 1,2-dibromoethane to give the known[12] TTF derivative **12** in 50% yield.

The use of the *p*-acetoxybenzyl protecting group therefore provides a convenient route to simple tetrakis(alkylsulfanyl) TTF derivatives, and is superior to the alternative cross-coupling of two 4,5-bis(alkylsulfanyl)-1,3-dithiole-2-thiones (or oxones) where separation of the various products by chromatography can be problematic.

We have previously described in detail the synthesis of a range of macrocycles such as **14** and **15** by the reaction of the sodium dithiolate **13** with suitable biselectrophiles (Scheme 4).[13] Subsequent attempts to convert a range of macrocycles, such as **15**, into bis(TTF)macrocycles, such as **17**, only gave TTF-cage structures, such as **16**, *via* an intramolecular coupling.[13a,b,d,e] One of the aims, in developing a route to TTF dithiolate **10**, was to access the desired macrocyles **17** directly. To this end we looked at the reaction of dithiolate **10** with several bis-electrophiles. Reaction of the dithiolate **10** with 1,5-dibromo-3-thiapentane only gave low yields of the 1:1 adduct **18**, and none of the anticipated 2:2 macrocycle **17**, in contrast to the reaction of **13** which gave the 2:2 adduct **15** in high yield (Scheme 4).[13d]

Similarly, reaction of dithiolate **10** with 2,6-bis(bromomethyl)pyridine gave no identifiable products, while, in earlier work, reaction of the same dibromide with the dithiolate **13** had given the 2:2 macrocyclic produce in high yield.[13a] We reasoned that the low yields could be as a result of problems associated with the *p*-quinonemethide generated in the deprotection and we therefore tried to 'reprotect' the dithiolate with benzoyl chloride or acetyl chloride. From this reaction we were able to isolate the benzoylated product **20** from the reaction, but only trace amounts of the expected product **22** (Scheme 5).

The isolation of **20** suggested that ethanolysis of the acetoxybenzyl protected TTF leads to an equilibrium mixture of the desired dithiolate **10** and the bis-phenoxide **19**. In reaction



Scheme 4 *Reagents and conditions:* i, $BrCH_2CH_2SCH_2CH_2Br$, EtOH; ii, 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione, $P(OEt)_3$, reflux

with alkyl halides such as methyl iodide, the bis-thiolate is eventually trapped out as the desired unsymmetrical tetrakis-(alkylsulfanyl) TTF derivative, in moderate yield. However, with an acylating reagent the phenoxide is preferably trapped out. In an attempt to divert the problematic *p*-quinonemethide by-product, we attempted the deprotection with a range of reagents (NaOMe, CsOH, Cs_2CO_3, $KOBu^t$, $NaSBu^t$, NaOPh, MeLi, BuLi) using at least a two-fold excess of the base, followed by addition of alkyl halide or benzoyl chloride, but this gave no improvement in the overall yields of products. Alternatively, deprotection of **5** or **7** and addition of $ZnCl_2$, followed by tetraethylammonium bromide, gave a precipitate of the crude zinc complex **21**, which could be isolated by filtration, and subsequently treated with benzoyl chloride to give the bis(benzoyl)protected TTF **22** in variable yields of 20–45%.[14] A range of conditions were again investigated for the preparation of the zinc complex, with deprotection using NaOEt in EtOH–THF again giving the best results. The zinc complex **21** could also be alkylated directly, or, alternatively the bis(benzoyl)protected TTF **22** could also be deprotected, using NaOEt in EtOH, and alkylated, to give TTF derivatives **8** and **12**, in yields of greater than 50% (Scheme 5).

In summary, the use of the *p*-acetoxybenzyl protecting group has provided a route to the TTF dithiolate synthon which can be treated with simple alkylating agents, providing a convenient route to unsymmetrical TTF derivatives. Reaction of the dithiolate with more demanding electrophiles, however, is hampered by the difficulty of isolating the dithiolate free from the reactive *p*-quinonemethide generated in the deprotection.[15]

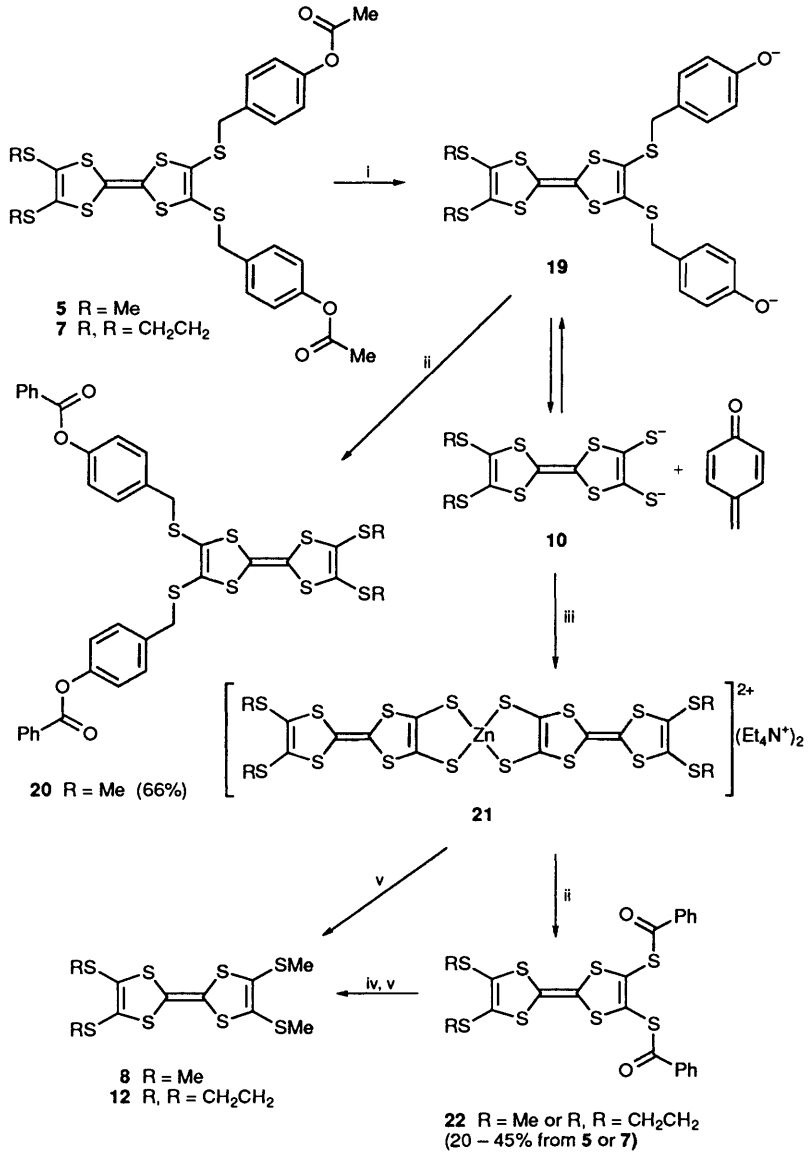
Experimental

All m.p.s were determined in open capillary tubes using a Gallenkamp Electrothermal Melting Point Apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR machine. ^1H NMR spectra at 90 MHz were obtained on a JEOL FX 90 Q spectrometer or at 270 MHz on a JEOL GX 270. Peak positions are quoted against the δ scale relative to the residual chloroform signal (δ 7.27) or to an internal standard of tetramethylsilane (δ 0.00). ^{13}C NMR spectra were recorded at 22.65 MHz on the JEOL FX 90 Q and at 67.94 MHz on the JEOL GX 270. Mass spectra were obtained on a VG analytical 70-250-SE normal geometry double focusing mass spectrometer.

4,5-Bis(p-acetoxybenzylsulfanyl)-1,3-dithiole-2-thione **2**.—A solution of *p*-acetoxybenzyl chloride[8] (24 g, 0.132 mol) in acetone (50 cm^3) was added dropwise to a stirred suspension of zinc complex **1** (19 g, 0.026 mol) in acetone (600 cm^3) and the reaction mixture was refluxed with stirring for 18 h. After cooling, the reaction mixture was filtered under suction and the precipitate was washed with $CHCl_3$ until the filtrate became colourless. The combined filtrates were concentrated under reduced pressure and the resulting solid product was redissolved in $CHCl_3$, and the remaining traces of inorganic solids were removed by filtration. The solution was concentrated under reduced pressure, and the crude product was recrystallised ($EtOH–CH_2Cl_2$) to afford yellow crystals of 4,5-bis(*p*-acetoxybenzylsulfanyl)-1,3-dithiole-2-thione **2** (18.8 g, 68%), m.p. 136–137 °C; $\nu_{max}(CCl_4)/cm^{-1}$ 1768, 1506, 1368 and 1071; $\delta_H(CDCl_3$; 90 MHz) 7.42 (2 H, d, *J* 8, ArH), 7.20 (2 H, d, *J* 8, ArH), 4.10 (2 H, s, CH_2) and 2.50 (3 H, s, CH_3); *m/z* 494 (M^+, 46%) and 107 (C_7H_7O, 100) (Found: C, 50.8; H, 3.6; S, 32.6. $C_{21}H_{18}O_4S_5$ requires C, 51.01; H, 3.64; S, 32.38%).

4,5-Bis(p-acetoxybenzylsulfanyl)-1,3-dithiol-2-one **3**.—This was prepared according to the method of Hartke *et al.*[16] Thus, bis-protected thione **2** (10 g, 0.02 mol) was dissolved in $CHCl_3$ (500 cm^3) and glacial acetic acid (150 cm^3) and the mixture warmed to 60 °C. Mercuric acetate (6.4 g, 0.02 mol) was added portionwise to the stirred solution over 2.5 h. The reaction mixture was heated to reflux and stirred for a further 24 h. After cooling, the mixture was filtered under suction, and the filtrate was washed with aqueous $NaHCO_3$, dried (Na_2SO_4) and then concentrated under reduced pressure. The product was recrystallised (EtOH) to give 4,5-bis(*p*-acetoxybenzylsulfanyl)-1,3-dithiol-2-one **3** as a white crystalline solid (7.9 g, 82%), m.p. 102 °C; $\nu_{max}(CCl_4)/cm^{-1}$ 1768, 1675, 1506, 1368 and 1166; $\delta_H(CDCl_3$; 90 MHz) 7.30 (2 H, d, *J* 8, ArH), 7.05 (2 H, *J* 8, ArH), 3.90 (2 H, s, CH_2) and 2.30 (3 H, s, CH_3); $\delta_C(CDCl_3$; 68 MHz) 189.17 (C=O), 168.84 (C=O), 150.00, 133.44, 129.82, 128.06, 121.57, 39.99 and 20.79; *m/z* 478 (M^+, 8%), 149 ($AcOC_6H_4CH_2$, 28) and 107 (C_7H_7O, 100) (Found: C, 52.5; H, 3.6; S, 26.3. $C_{21}H_{18}O_5S_4$ requires C, 52.71; H, 3.76; S, 26.77%).

4,4′,5,5′-Tetrakis(p-acetoxybenzylsulfanyl)tetrathiafulvalene **4**.—Bis-protected oxone **3** (1.0 g, 2.1 mmol) and triethyl phosphite (1.0 g, 6.0 mmol) in toluene (2 cm^3) were heated at reflux for 20 h, under a nitrogen atmosphere. Upon cooling to room temperature, an orange solid precipitated out of solution. The reaction mixture was filtered under suction, the precipitate collected and recrystallised (toluene–hexane, 5:1 v/v) to give 4,4′,5,5′-tetrakis(*p*-acetoxybenzylsulfanyl)tetrathiafulvalene **4**, as orange crystals (0.69 g, 71%); m.p. 170–173 °C (decomp.); $\nu_{max}(CCl_4)/cm^{-1}$ 1742; $\delta_H(CDCl_3$; 270 MHz) 7.30 (8 H, d, *J* 8,



Scheme 5 *Reagents and conditions:* i, NaOEt, EtOH, THF, −10 °C; ii, PhCOCl; iii, *a*, $ZnCl_2$, MeOH, *b*, Et_4NBr, MeOH; iv, NaOEt, EtOH, room temp.; v, MeI or $BrCH_2CH_2Br$

ArH), 7.05 (8 H, d, *J* 8, ArH), 3.85 (8 H, s, SCH_2) and 2.28 (12 H, s, CH_3); δ_C($CDCl_3$; 68 MHz) 169.42, 150.23, 134.35, 130.24, 129.31, 121.85, 110.63, 40.20 and 21.23; *m*/*z* 924 (M^+, 100%), 775 ($M^+ - C_9H_9O_2$, 27) and 627 ($M^+ - C_{18}H_{17}O_4$, 17) (Found: C, 54.5; H, 3.7; S, 28.0. $C_{42}H_{36}O_8S_8$ requires C, 54.54; H, 3.89; S, 27.70%).

4,5-*Bis*(p-*acetoxybenzylsulfanyl*)-4′,5′-*bis*(*methylsulfanyl*)-*tetrathiafulvalene* **5**.—4,5-Dimethylsulfanyl-1,3-dithiol-2-one (1.1 g, 5.2 mmol) and bis-protected oxone **3** (2.5 g, 5.2 mmol) were dissolved in toluene (5 cm^3). Triethyl phosphite (3.45 g, 20 mmol) was added and the reaction mixture was heated to reflux under a nitrogen atmosphere for 24 h. After cooling, the reaction mixture was filtered and the solvent removed under reduced pressure. The crude product was subjected to flash column chromatography [Merck silica gel 60 (40–63 μm)]. The first fractions from the column (eluting with 5% ethyl acetate in hexane) contained 4,4′,5,5′-tetrakis(methylsulfanyl)tetrathiafulvalene (350 mg, 26%) as a yellow solid. The next fractions (eluting with 10% ethyl acetate in hexane) contained the desired unsymmetrical 4,5-bis(*p*-acetoxybenzylsulfanyl)-4′,5′-bis(methylsulfanyl)tetrathiafulvalene **5** (680 mg, 30%) as an orange–red solid. Finally (eluting with 20% ethyl acetate in hexane) tetra-protected TTF **4** (895 mg, 28%) was obtained as an orange solid.

Compound **5**: m.p. 78–81 °C; ν_{max}(CCl_4)/cm^{-1} 2921, 1766 and 1370; δ_H($CDCl_3$; 270 MHz) 7.30 (4 H, d, *J* 8, ArH), 7.05 (4 H, d, *J* 8, ArH), 3.85 (4 H, s, 2 × SCH_2), 2.42 (6 H, s, 2 × SCH_3) and 2.28 (6 H, s, 2 × CH_3); δ_C($CDCl_3$; 68 MHz) 169.51 (C=O), 150.28, 134.37, 130.30, 127.61, 122.06, 121.91, 115.74, 108.75, 40.30, 21.31 and 19.33; *m*/*z* 656 (M^+, 36%), 507 ($M^+ - C_9H_9O_2$, 10), 359 ($M^+ - C_{18}H_{17}O_4$, 15), 149 ($C_9H_9O_2$, 14) and 107 (C_7H_7O, 100) (Found: C, 47.3; H, 3.7; S, 38.9. $C_{26}H_{24}O_4S_8$ requires C, 47.56; H, 3.65; S, 39.02%).

4,5-*Bis*(p-*acetoxybenzylsulfanyl*)-4′,5′-*bis*(*butylsulfanyl*)-*tetrathiafulvalene* **6**.—Using a procedure identical with that described above for the preparation of the bis-protected TTF derivative **5**, gave 4,5-bis(*p*-acetoxybenzylsulfanyl)-4′,5′-bis(butylsulfanyltetrathiafulvalene **6**, (17%) as a light brown solid, along with the expected symmetrical TTF derivatives (see text).

Compound **6**: m.p. 87–90 °C; ν_{max}(CCl_4)/cm^{-1} 2921, 1767 and 1368; δ_H($CDCl_3$; 270 MHz) 7.28 (4 H, d, *J* 8, ArH), 7.05 (4 H, d, *J* 8, ArH), 3.85 (4 H, s, SCH_2), 2.85 (4 H, t, *J* 7, SCH_2), 2.28 (6 H, s, CH_3CO), 1.40–1.69 (8 H, m, CH_2CH_2) and 0.95

(6 H, t, *J* 8, CH_3); δ_C($CDCl_3$; 68 MHz) 169.48 (C=O), 150.23, 134.36, 130.29, 129.35, 127.87, 121.87, 111.51, 109.42, 40.24 (SCH_2), 36.12 (SCH_2), 31.93 (CH_2), 21.82 (CH_2), 21.32 (CH_3) and 13.77 (CH_3 from Bu group); *m/z* (FAB) 763 ($M^+ + Na^+$, 25%), 740 (M^+, 100), 591 ($M^+ - C_9H_9O_2$, 14) and 443 ($M^+ - C_{18}H_{17}O_4$, 30) (Found: C, 52.1; H, 4.7; S, 34.4. $C_{32}H_{36}O_4S_8$ requires C, 51.86; H, 4.89; S, 34.61%).

4,5-*Bis*(p-*acetoxybenzylsulfanyl*)-4′,5′-*ethylenedisulfanyltetrathiafulvalene* **7**.—Using a procedure identical with that described above for the preparation of the bis-protected TTF derivative **5**, gave 4,5-bis(*p*-acetoxybenzylsulfanyl)-4′,5′-ethylenedisulfanyltetrathiafulvalene **7**, (29%) as an orange–red solid, along with the expected symmetrical TTF derivatives (see text).

Compound **7**: m.p. 99–102 °C; ν_{max}(CCl_4)/cm^{-1} 2930, 1767, 1550 and 1370; δ_H($CDCl_3$; 270 MHz) 7.25 (4 H, d, *J* 8, ArH), 7.05 (4 H, d, *J* 8, ArH), 3.83 (4 H, s, SCH_2), 3.30 (4 H, s, SCH_2CH_2S) and 2.28 (6 H, s, CH_3); δ_C($CDCl_3$; 68 MHz) 169.36 (C=O), 150.17, 134.27, 130.20, 129.35, 121.80, 113.97, 113.28, 109.28, 40.25, 30.29 and 21.12; *m/z* 654 (M^+, 10%), 472 ($M^+ - C_9H_{10}O_2$, 6), 357 ($M^+ - C_{18}H_{17}O_4$, 6), 149 ($C_9H_9O_2$, 25) and 107 (C_7H_7O, 100) (Found: C, 47.8; H, 3.7; S, 38.6. $C_{26}H_{22}O_4S_8$ requires C, 47.68; H, 3.38; S, 39.17%).

Deprotection and Alkylation of 4,4′,5,5′-*Tetrakis*(p-*acetoxybenzylsulfanyl*)*tetrathiafulvalene* **4**.—A solution of sodium ethoxide in ethanol (15 mg Na in 1 cm^3 ethanol) was added to a suspension of tetra-protected TTF **4** (100 mg, 0.11 mmol) in dry ethanol (1.5 cm^3) and the mixture was warmed to 50 °C. After 10 min, dissolution was complete giving a dark red solution of the tetrathiolate tetraanion. Methyl iodide (150 mg, 1.05 mmol) was added and the mixture stirred for 3 h. After cooling, the mixture was concentrated under reduced pressure, dissolved in CH_2Cl_2, and the organic solution was washed with water, dried (Na_2SO_4) and then concentrated under reduced pressure. Flash column chromatography [Merck silica gel 60 (40–63 μm), eluting with 5% CH_2Cl_2 in hexane] gave, in the first few fractions, a yellow solid which could be recrystallised from acetone–CH_2Cl_2 to give the known 4,4′,5,5′-tetrakis(methylsulfanyl)tetrathiafulvalene **8** (29 mg, 68%) as a yellow solid, m.p. 95 °C (lit.,[11] m.p. 94.5–96 °C); δ_H($CDCl_3$; 68 MHz) 2.46 (12 H, s, CH_3); *m/z* 388 (M^+, 100%).

Using an identical procedure, but quenching the tetraanion with dibromethane gave bis(ethylenedisulfanyl)tetrathiafulvalene (BEDT-TTF) (65%) as an orange–brown solid, m.p. 244 °C (lit.,[7b] m.p. 236–240 °C; lit.,[6b] 246–248 °C); δ_H($CDCl_3$; 68 MHz) 3.30 (8 H, s, CH_2).

General Procedure for the Deprotection and Alkylation of 4,5-*Bis*(p-*acetoxybenzylsulfanyl*)-4′,5′-*bis*(*methylsulfanyl*)-*tetrathiafulvalene* **5**.—A solution of sodium ethoxide in ethanol (11 mg Na in 1 cm^3 ethanol) was added to a solution of TTF derivative **5** (90 mg, 1.37 mmol) in dry THF (2 cm^3) at −10 °C, under nitrogen, and the mixture stirred for 30 min, during which time a deep red solution was formed. Methyl iodide (150 mg, 1.05 mmol) in THF (1 cm^3) was added to the solution and the reaction was allowed to warm to room temperature. The mixture was concentrated under reduced pressure, dissolved in CH_2Cl_2, and then the organic solution was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. Flash column chromatography [Merck silica gel 60 (40–63 μm), eluting with 5% CH_2Cl_2 in hexane] gave, in the first few fractions, a yellow solid which could be recrystallised from acetone–CH_2Cl_2 to give 4,4′,5,5′-tetrakis(methylsulfanyl)tetrathiafulvalene **8** (24 mg, 46%) as a yellow solid identical with the sample prepared from tetra-protected TTF **4**.

Cyclic Tetrathiafulvalene **18**.—Following the general procedure above, and using 1,5-dibromo-3-thiapentane as the alkylating reagent, gave the cyclic tetrathiafulvalene derivative **18** as a red–brown oil (11%); R_F 0.64 (ethyl acetate–hexane, 1:2); ν_{max}(CCl_4)/cm^{-1} 2923, 1677 and 1217; δ_H($CDCl_3$; 270 MHz) 3.10 (4 H, m, CH_2), 2.95 (4 H, m, CH_2) and 2.43 (6 H, s, CH_3); *m/z* 446 (M^+, 100%) (isotopic substitution pattern was in accordance with $C_{12}H_{14}S_9$) and 76 (CS_2, 39) (Found: M^+ 445.8571. $C_{12}H_{14}S_9$ requires *M*, 445.8582).

4,5-*Bis*(p-*benzoyloxybenzylsulfanyl*)-4′,5′-*bis*(*methylsulfanyl*)*tetrathiafulvalene* **20**.—Following the general procedure for the deprotection of bis-protected TTF **5**, above, the solution of the dithiolate dianion (from 200 mg of **5**, 0.3 mmol) was treated wth benzoyl chloride (120 mg, 0.7 mmol). Work-up and flash column chromatography [Merck silica gel 60 (40–63 μm), eluting with 5% ethyl acetate in hexane] gave 4,5-bis(p-benzoyloxybenzylsulfanyl)4′,5′-bis(methylsulfanyl)-tetrathiafulvalene **20** as a red solid (160 mg, 66%), R_F 0.70 (ethyl acetate–hexane, 1:2); m.p. 120–122 °C; ν_{max}(CCl_4)/cm^{-1} 1744, 1261 and 1207; δ_H($CDCl_3$; 270 MHz) 8.20 (4 H, d, *J* 7, ArH), 7.63 (2 H, t, *J* 7, ArH), 7.50 (4 H, t, *J* 7, ArH), 7.28 (4 H, d, *J* 7, ArH from C_6H_4 portion), 7.09 (4 H, d, *J* 7, ArH from C_6H_4), 3.95 (4 H, s, CH_2) and 2.45 (6 H, s, CH_3); *m/z* 780 (M^+, 20%), 536 ($M^+ - C_{14}H_{12}O_4$, 46), 388 ($M^+ - C_{26}H_{16}O_4$, 65) and 105 ($PhCO^+$, 100) (Found: C, 55.6; H, 3.5; S, 32.5. $C_{36}H_{28}O_4S_8$ requires C, 55.36; H, 3.61; S, 32.84%) and 4,5-bis(benzoylsulfanyl)-4′,5′-bis(methylsulfanyl)tetrathiafulvalene **22** as a red solid (9 mg, 5%), R_F 0.75 (ethyl acetate–hexane, 1:2); m.p. 165 °C; δ_H($CDCl_3$; 270 MHz), 7.95 (4 H, d, *J* 7, ArH), 7.62 (2 H, t, *J* 7, ArH), 7.49 (4 H, t, *J* 7, ArH) and 2.40 (6 H, s, CH_3); δ_C($CDCl_3$; 68 MHz) 172.42, 139.89, 133.26, 132.74, 130.30, 128.88, 120.92, 114.04, 113.83 and 22.07; *m/z* 568 (M^+, 58%), 463 (M^+ − PhCO, 10) and 105 ($PhCO^+$, 100) (Found: C, 46.8; H, 2.75; S, 44.8. $C_{22}H_{16}O_2S_8$ requires C, 46.45; H, 2.83; S, 45.09%).

4,5-*Bis*(*benzoylsulfanyl*)-4′,5′-*bis*(*methylsulfanyl*)*tetrathiafulvalene* **22** via *the Zinc Complex* **21**.—Following the general procedure for the deprotection of bis-protected TTF **5**, above, the solution of the dithiolate dianion (from 100 mg of **5**, 0.15 mmol) was treated with a solution of zinc chloride (20 mg, 0.15 mmol) in methanol (2 cm^3) dropwise over 10 min. A slight precipitation was observed upon addition of this solution. The mixture was stirred for a further 30 min, then a solution of tetraethylammonium bromide (50 mg, 0.24 mmol) in methanol (1 cm^3) was added dropwise over 10 min. The reaction mixture was stirred at room temperature for 3 h, during which time a precipitate developed. The mixture was filtered under suction and the solid product, which appeared to be air-stable, was washed successively with water, methanol, and diethyl ether. The crude zinc complex, so obtained, was suspended in CH_2Cl_2 at room temperature, and benzoyl chloride (65 mg, 0.45 mmol) was added to it. Work-up and flash column chromatography [Merck silica gel 60 (40–63 μm), eluting with 5% ethyl acetate in hexane] gave 4,5-bis(benzoylsulfanyl)-4′,5′-bis(methylsulfanyltetrathiafulvalene **22** (34 mg, 41%), (based on **5** as starting material) identical with the sample prepared earlier.

By an identical procedure 4,5-bis(benzoylsulfanyl)-4′,5′-ethylenedisulfanyltetrathiafulvalene was prepared from 4,5-bis(*p*-acetoxybenzylsulfanyl)-4′,5′-ethylenedisulfanyltetrathiafulvalene **7**, as a red–brown solid (26%, based on **7** as starting material), m.p. 122 °C; ν_{max}(CCl_4)/cm^{-1} 1737; δ_H($CDCl_3$; 270 MHz) 7.95 (4 H, d, *J* 7, ArH), 7.65 (4 H, t, *J* 7, ArH), 7.48 (2 H, t, *J* 7, ArH) and 3.32 (4 H, s, CH_2); *m/z* 566 (M^+, 49%), 461 (M^+ − PhCO, 12) and 105 ($PhCO^+$, 100) (Found: C, 46.4; H, 2.7; S, 44.9. $C_{22}H_{14}O_2S_8$ requires C, 46.61; H, 2.49; S, 45.25%).

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