Preparation and chemistry of new unsymmetrically substituted tetrachalcogenofulvalenes bearing $CN(CH_2)_2X$ and $HO(CH_2)_2X$ groups (X = S or Se)

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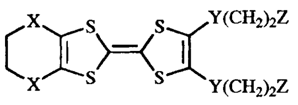
Several unsymmetrically substituted TTFs bearing the $S(CH_2)_2CN$ protecting group have been prepared by standard cross coupling in triethyl phosphite from the key intermediate 4,5-bis(2′-cyanoethylsulfanyl)-1,3-dithiol-2-one 1 and an appropriate 1,3-dichalcogenole-2-chalcogenone, 2–8. TTFs 10, 11 and 12 of type I have been obtained in satisfactory yields (30–60%) and those (13, 14) of type II in low yields (10 and 19%) as a result of differences in the reactivity of the species involved.

Pseudo-Wittig condensations from the key triphenylphosphonium salt 15 have allowed considerable improvement in the synthesis of 13 (70% yield) and 14 (57% yield).

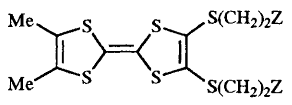
The diselena analogue of 1, 21 has also been obtained. Its derivative 22, a new tetrakis(alkylselena) functionalised TTF, has been isolated in fair yield (69%). Its deprotection in a basic medium followed by a subsequent alkylation has led to BEDSe-TTF 23 (40%). Finally, the same sequence of deprotection–realkylation carried out from unsymmetric species 10 and 12 has successfully been used in a high yield preparation of the corresponding new functionalised TTFs bearing two hydroxyethyl groups.

Since the discovery of a superconducting state in radical cation salts derived from tetrachalcogenofulvalenes[1,2] there has been great interest in the design and preparation of new π-donors of the tetrathiafulvalene (TTF) type.

Currently, research is orientated towards TTF precursors containing functions such as OH, NHR, *etc*. or a large number of chalcogen atoms, particularly selenium, in order to increase the dimensionality in the resulting salts as a result of hydrogen bonds[3,4] and chalcogen contacts,[5] respectively. These interactions are expected to give materials showing either a metallic state stabilized over a larger range of temperature, or superconductivity at temperatures higher than those found so far (*ca*. 12 K) in salts based on the BEDT-TTF molecule.[6,7] In this context, our efforts have been directed towards the synthesis of compounds of type **I** and **II**.



I



II

X = O, S, Se; Y = S, Se; Z = CN, OH

Several strategies can be used to prepare unsymmetric TTFs[8] of this type. The most common is cross-coupling[9] between appropriate chalcogenones leading to a mixture from which the desired species must be separated from the symmetrical by-products. Following a recently reported strategy,[10] this separation becomes easy and allows access to a series of unsymmetrical TTFs of type **I** and **II** (see Scheme 1).

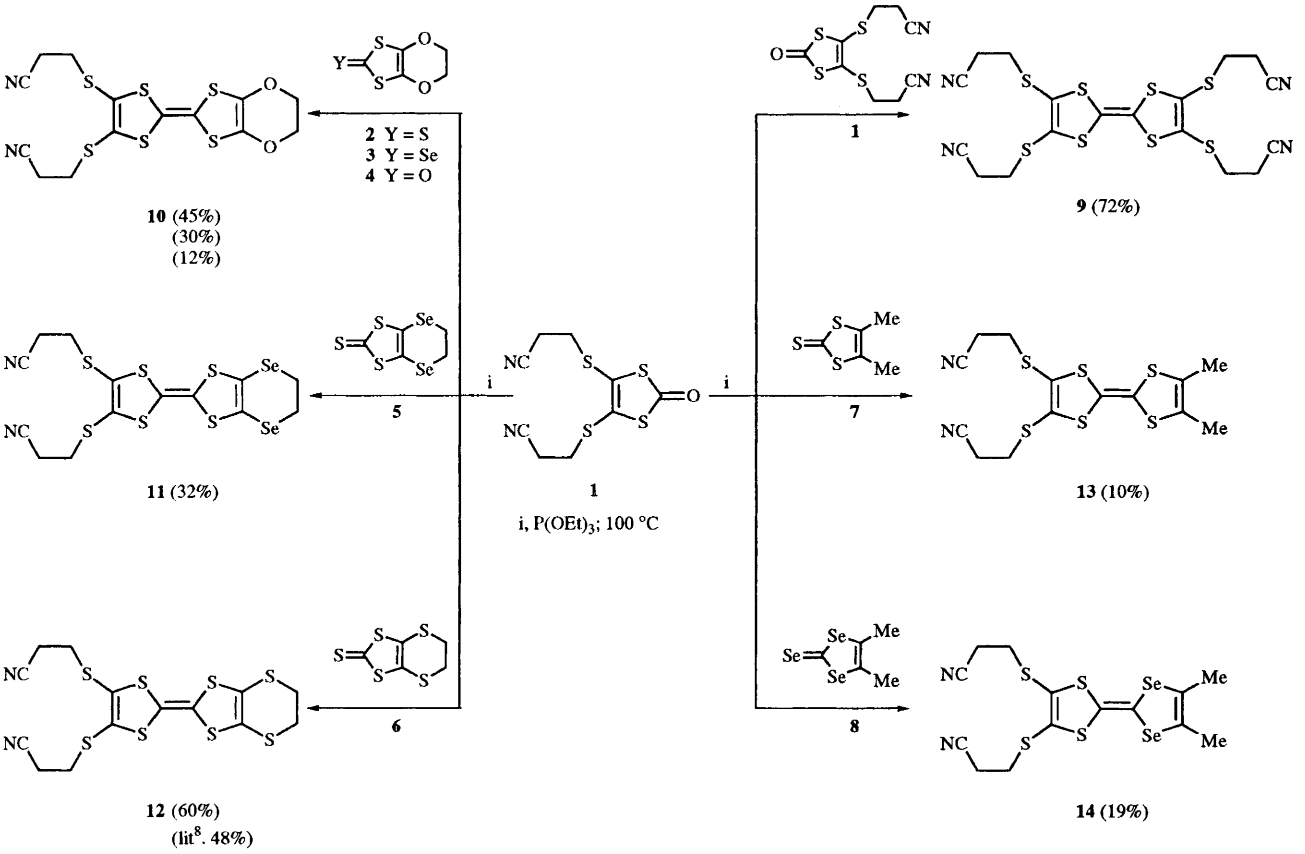
The key compound is the 4,5-bis(2′-cyanoethylsulfanyl)-1,3-dithiol-2-one **1** prepared as described[10] by transchalcogenation of the corresponding thione.

The unsymmetric compounds **10**–**12** (type **I**) and **13**–**14** (type **II**) were prepared under the same conditions as those used to obtain **12**. Treatment of equimolecular amounts of **1** and a required chalcogenone (**2**–**8**) at 100 °C in neat triethyl phosphite gave the expected mixtures of TTFs. Each product was then easily separated by column chromatography (SiO_2, CH_2Cl_2) because of the polarity of the cyanoethyl groups.

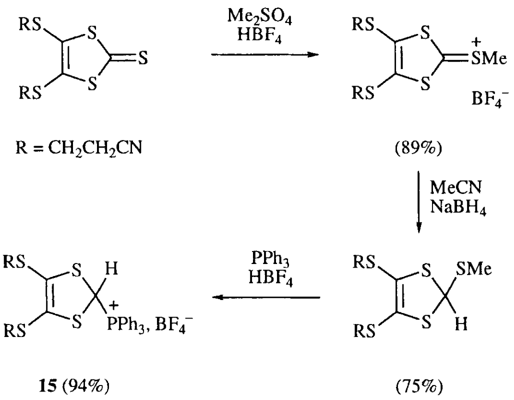
The similar reactivity of the chalcogenones **1** and **2**,[11] **3**,[12] **5**[13] or **6**[14] gave rise to the TTFs **10**, **11** and **12** of type **I** in satisfactory yields (30–60%). It is noteworthy that the cross-coupling between **1** and thione **2** led to a higher yield (45%) than the reactions involving **1** and either the corresponding selenone **3**[12] (30%) or the dithiolone **4**[11] (12%). In contrast, the derivatives **13** and **14** of type **II**, were obtained in low yields (10 and 19%, respectively) probably as a result of the deactivating effect of the electron-releasing methyl groups on the chalcogenones **7**[15] and **8**.[16] This was clearly shown in the reaction between **1** and **7** which gave a mixture containing only 21% of the unsymmetric TTF **13** together with 6% of TMTTF (tetramethyltetrathiafulvalene) and 73% of TTF **9** as a main component. In this case, the deactivating effect seemed to be stronger for the thione **7** reacting with **1**, leading to 10% of **13** as compared to the selenone **8** which gave **14** in 19% yield.

The mechanism proposed in the literature[17,18] for such coupling suggests a thiophilic addition of the phosphite on the chalcogen atom localized on the 2-position of the chalcogenone. A subsequent elimination of a chalcogeno phosphite finally leads to the expected TTF. According to the nature of the substituents in the 4,5-positions of the chalcogenones, the thiophilic addition of the trialkyl phosphite is more or less facilitated. The withdrawing groups (XCH_2CH_2X, X = O, S, Se) in compounds **2**–**6** makes easier the thiophilic addition of the trialkyl phosphite while the releasing methyl groups in **7** and **8** make it more difficult.

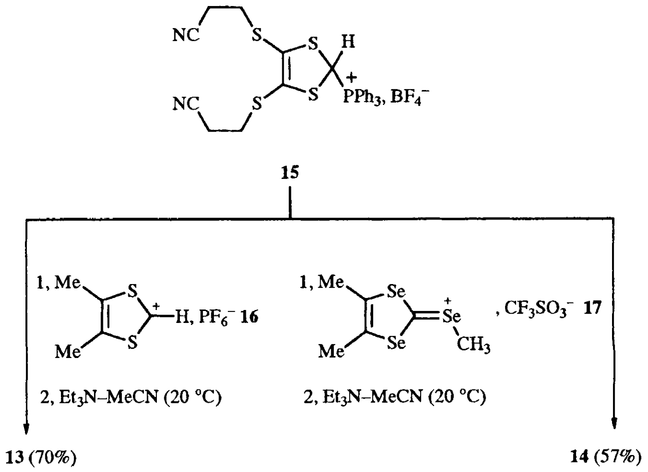
In order to prepare compounds **13** and **14** in higher yield, we turned our attention to the possibility of using a pseudo-Wittig condensation,[19] with the triphenylphosphonium fluoroborate **15** as starting reagent. Compound **15** was obtained in a three-step synthesis from 4,5-bis(2′-cyanoethylsulfanyl)-1,3-dithiole-2-thione[10] in 63% overall yield (Scheme 2).[20] Because the



Scheme 1



Scheme 2



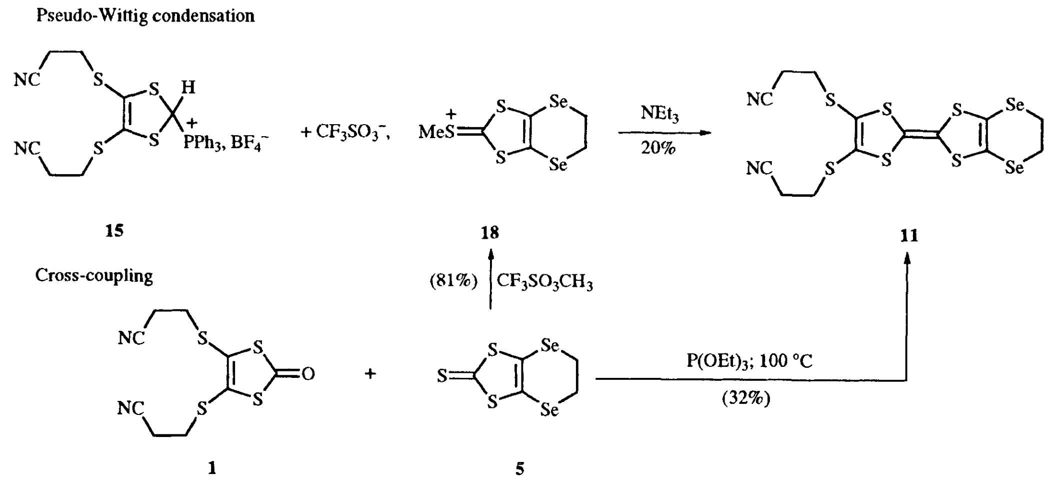
Scheme 3

protective group is stable in triethylamine, both derivatives **13** and **14** were prepared successfully by the pseudo-Wittig reaction (see Scheme 3). Thus, compound **13** was isolated from the reaction of 4,5-dimethyl-1,3-dithiolium hexafluorophosphate **16**[21] and **15** in the presence of triethylamine in acetonitrile at 20 °C in 70% yield. This yield is a significant improvement on that obtained (10%) initially by cross coupling. A similar result was observed (19% to 57%) for compound **14**. In this case, the intermediate **17** was obtained in 87% yield by alkylation of 4,5-dimethyl-1,3-diselenole-2-selenone **8** with methyl triflate in dichloromethane by adaptation of a procedure described in the literature.[22] However, it is noteworthy that in certain cases the Wittig-condensation is not the best way to prepare unsymmetrical TTFs (see Scheme 4). For example, with the trifluoromethanesulfonate **18**[22] which bears electron-withdrawing groups, the Wittig condensation gave a 20% yield of the TTF **11** whereas cross coupling in triethyl phosphite gave **11** in 32% yield.

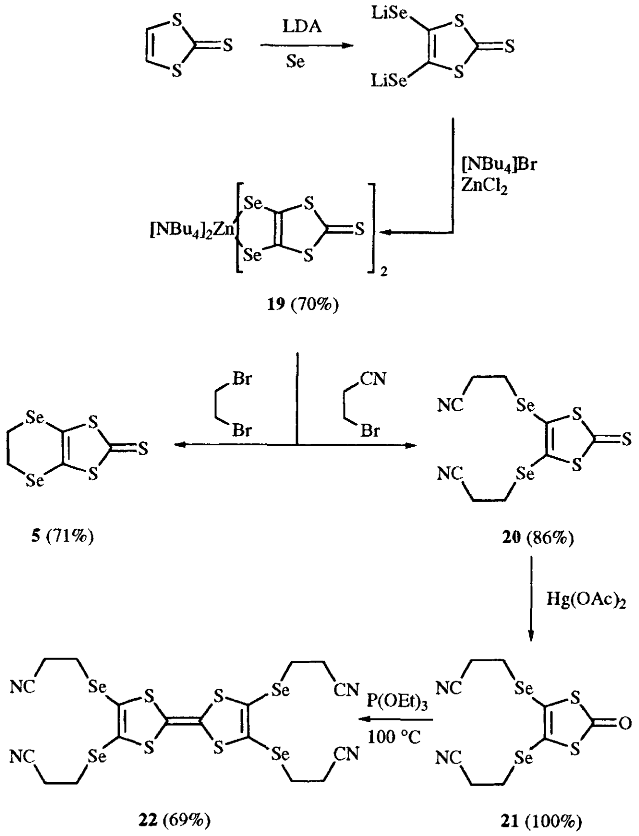
As shown in Scheme 1, compound **1** appeared to be a key precursor for the preparation of a variety of unsymmetrically substituted functionalized TTF derivatives. For that reason, it appeared of interest to prepare the selena analogue **21** and, subsequently, the corresponding tetrathiafulvalene **22** (Scheme 5).

The 1,3-dithiole-2-thione[23] was first lithiated by LDA at −78 °C in dry THF and the resulting salt was converted into the diselenolate by addition of elemental selenium.[13] This air-sensitive dilithium salt was converted into the corresponding stable zincate **19** in a 70% overall yield as previously reported.[24]

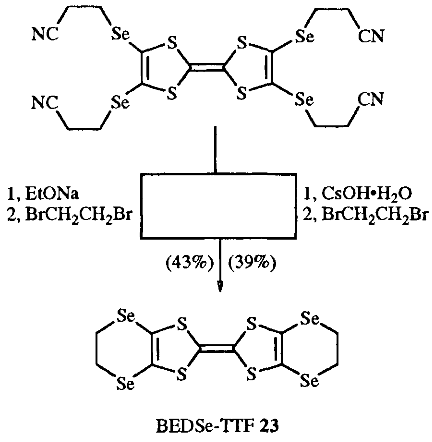
The zincate **19** either gave 4,5-ethylenediseleno-1,3-dithiole-2-thione **5** (71%) or the 4,5-bis(2′-cyanoethylseleno)-1,3-dithiole-2-thione **20** in 86% yield using either dibromoethane or 3-bromopropionitrile. The thione **20** was quantitatively transchalcogenated to the expected dithiolone **21** using mercuric acetate in acetic acid–chloroform.[11] Finally the 2,3,6,7-tetrakis(2′-cyanoethylseleno)tetrathiafulvalene **22** was isolated in 69% yield by self-coupling of **21** in neat triethyl phosphite.[10] As already described[10] for the sulfur analogue **9**, the new 2,3,6,7-tetrakis(2′-cyanoethylseleno)tetrathiafulvalene



Scheme 4



Scheme 5



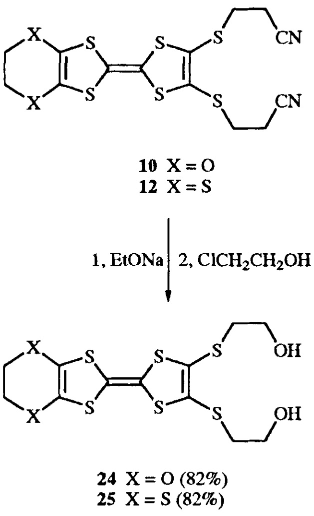
Scheme 6

22 could be used as a precursor of BEDSe-TTF **23**[25,26] (Scheme 6). The conversion proceeded at room temperature in *ca.* 40% yield irrespective of the basic medium used: sodium ethoxide in ethanol (8 equiv.) or caesium hydroxide in THF (8 equiv.) followed by treatment with dibromoethane. A precipitate of elemental selenium was observed in the course of the reaction indicating the partial instability of the sodium and caesium tetrathiafulvalenetetraselenolate intermediates. The instability might explain the lower yield obtained (~40%) as compared with the quantitative yield observed for **9** under the same conditions.

A similar high yield (82%) was observed when the unsymmetric TTFs **10** and **12** were converted into the corresponding diols **24** and **25**, respectively (Scheme 7).

In conclusion, it has been clearly demonstrated that the key dithiolones **1** (sulfur series) and **21** (selenium analogue), can be used to prepare symmetric and unsymmetric TTFs such as **9**, **22** (Schemes 1 and 5) and **10** to **12** (Scheme 1), respectively, by cross-coupling. A pseudo-Wittig reaction is more useful for the unsymmetric TTFs **13** and **14** bearing electron-donating groups (Schemes 3 and 4). In this case, the fluoroborate **15** appears to be the key compound.

Finally, these types of TTF derivative can be deprotected by a basic reagent and, subsequently, by appropriate alkylations, to give a series of new functionalised TTFs (Scheme 7). Extension of this work to related selenium derivatives as well as the synthesis of new materials based on the isolated TTFs of types **I** and **II** is now under way in our laboratory.



Scheme 7

Experimental

General

THF was distilled from Na prior to use and EtOH was stirred over CaH_2 and distilled from Mg. Microanalyses were performed at the Microanalytical Lab., University of Montpellier. NMR spectra were recorded on a Bruker AC 300 and mass spectra on a JEOL JMS-DX 300 spectrophotometer. Melting points (uncorrected) were determined on a Büchi 510 melting point apparatus. The CV experiments were made in CH_2Cl_2 using (0.1 mol dm^{-3} $[NBu_4][PF_6]$) as supporting electrolyte. Counter and working electrodes were Pt, and potentials referenced *versus* SCE. Sweep rate: 100 mV s^{-1}.

Compounds of type I (10, 11, 12) and II (13, 14)

General procedure for cross coupling. 4,5-Bis(2′-cyanoethylsulfanyl)-1,3-dithiol-2-one **1** (0.64 g, 2.2 mmol) and an appropriate 1,3-dichalcogenole-2-chalcogenone **2**–**8** (2.2 mmol) were suspended in freshly distilled $P(OEt)_3$ (15 cm^3) under nitrogen and then stirred and heated at 100 °C for 90 min. The mixture was then cooled to 0 °C and the precipitate filtered off, washed with cold methanol (3 × 15 ml), dried *in vacuo* and chromatographed (SiO_2, CH_2Cl_2). Isolation of the middle fraction gave the mixed coupling product.

Compound 10 (30–45%), an orange powder, mp 154 °C; $\delta_H(CDCl_3\text{–}TMS)$ 2.69 (t, 4 H, CH_2, *J* 7), 3.04 (t, 4 H, CH_2, *J* 7) and 4.23 (s, 4 H, CH_2); *m*/*z* (EI) 432 (M^+) (Found: C, 38.6; H, 3.0; N, 6.3; O, 7.4. Calc. for $C_{14}H_{12}N_2O_2S_6$: C, 38.9; H, 2.8; N, 6.5; O, 7.4%); CV (CH_2Cl_2, 0.1 V s^{-1}, $[NBu_4][PF_6]$, *vs.* SCE): E_1 0.55 V, E_2 0.94 V.

Compound 11 (32%), an orange–yellow powder, mp 148 °C; $\delta_H(CDCl_3\text{–}TMS)$ 2.69 (t, 4 H, CH_2, *J* 7), 3.04 (t, 4 H, CH_2, *J* 7) and 3.32 (s, 4 H, CH_2); *m*/*z* (^{80}Se, EI) 506 (M^+) (Found: C, 30.3; H, 2.1; N, 4.9. Calc. for $C_{14}H_{12}N_2S_6Se_2$: C, 30.1; H, 2.2; N, 5.0%); CV (CH_2Cl_2, 0.1 V s^{-1}, $[NBu_4][PF_6]$, *vs.* SCE): E_1 0.59 V, E_2 0.96 V.

Compound 12 (60%), a yellow powder, mp 142 °C; $\delta_H(CDCl_3\text{–}TMS)$ 2.75 (t, 4 H, *J* 6.7), 3.10 (t, 4 H, *J* 6.7) and 3.29 (s, 4 H); *m*/*z* (EI) 464 (M^+) (Found: C, 36.1; H, 2.6; N, 5.9. Calc. for $C_{14}H_{12}N_2S_8$: C, 36.2; H, 2.6; N, 6.0%) CV (CH_2Cl_2, 0.1 V s^{-1}, $[NBu_4][PF_6]$, *vs.* SCE): E_1 0.60 V, E_2 0.98 V.

Compound 13 (10%) an orange powder, mp 121–122 °C; $\delta_H(CDCl_3\text{–}TMS)$ 1.92 (t, 6 H, CH_3), 2.68 (t, 4 H, CH_2, *J* 7) and 3.03 (t, 4 H, CH_2, *J* 7); *m*/*z* (EI) 402 (M^+) (Found: C, 41.6; H, 3.8; N, 6.8. Calc. for $C_{14}H_{14}N_2S_6$: C, 41.8; H, 3.5; N, 7.0%); CV (CH_2Cl_2, 0.1 V s^{-1}, $[NBu_4][PF_6]$, *vs.* SCE): E_1 0.48 V, E_2 0.92 V.

Compound 14 (19%), a red powder, mp 124–125 °C; $\delta_H(CDCl_3\text{–}TMS)$ 2.1 (s, 6 H, CH_3), 2.68 (t, 4 H, CH_2, *J* 7) and 3.09 (t, 4 H, CH_2, *J* 7); *m*/*z* (^{80}Se, EI) 498 (M^+) (Found: C, 33.7; H, 3.0; N, 5.3. Calc. for $C_{14}H_{14}N_2S_4Se_2$: C, 33.9; H, 2.8; N, 5.6%); CV (CH_2Cl_2, 0.1 V s^{-1}, $[NBu_4][PF_6]$, *vs.* SCE): E_1 0.59 V, E_2 0.96 V.

4,5-Bis(2′-cyanoethylsulfanyl)-2-methylsulfanyl-1,3-dithiolium tetrafluoroborate

A suspension of 4,5-bis(2′-cyanoethylsulfanyl)-1,3-dithiole-2-thione[10] (8.00 g, 26.3 mmol) in dimethyl sulfate (15 cm^3) was stirred at 80 °C for 1 h (until all of the thione had dissolved). The mixture was then cooled to room temperature and diethyl ether (5 cm^3), fluoroboric acid (54% ethereal solution; 6 cm^3) and ether (50 cm^3) were added to it. Decantation and concentration under reduced pressure gave the expected salt as a brown semicrystalline compound, which was recrystallized from acetonitrile–diethyl ether and left in the refrigerator overnight; yield 9.5 g (89%), mp. 94–95 °C; $\delta_H(CDCl_3\text{–}TMS)$ 3.43 (t, 4 H, *J* 6.7, CH_2), 3.18 (s, 3 H, CH_3) and 2.92 (t, 4 H, *J* 6.8, CH_2) (Found: C, 29.5; H, 2.8; N, 6.9. Calc. for $C_{10}H_{11}BF_4S_5$: C, 29.6; H, 2.7; N, 6.9%).

4,5-Bis(2′-cyanoethylsulfanyl)-2-methylsulfanyl-2*H*-1,3-dithiole

A solution of 4,5-bis(2′-cyanoethylsulfanyl)-2-methylsulfanyl-1,3-dithiolium tetrafluoroborate (4.50 g, 11.1 mmol) in acetonitrile (30 cm^3) was slowly added to a suspension of sodium borohydride (0.50 g, 13.2 mmol) in dry isopropyl alcohol (4 cm^3) whereupon the colour changed from brown to light orange. The mixture was stirred for 30 min and then poured onto water (200 cm^3). The precipitated crystals were collected, washed with water (2 × 50 cm^3), dried in a desiccator and recrystallized from toluene–light petroleum (bp 100–140 °C) to give the expected 1,3-dithiole as pale orange crystals (2.65 g, 75%), mp 83–84 °C; $\delta_H(CDCl_3\text{–}TMS)$ 5.72 (s, 1 H, H dithiole), 3.2 (m, 2 H, CH_2), 2.9 (s, 3 H, SCH_2) and 2.8 (m, 4 H, CH_2); *m*/*z* (EI) 320 (M^+) (Found: C, 37.3; H, 4.0. Calc. for $C_{10}H_{12}N_2S_4$: C, 37.5; H, 3.8%).

Triphenyl [4,5-bis(2′-cyanoethylsulfanyl)-1,3-dithiol-2-yl]phosphonium tetrafluoroborate 15

A solution of the preceding 1,3-dithiole (1.00 g, 3.1 mmol) in acetonitrile (40 cm^3) was degassed for 10 min after which it was treated with triphenylphosphine (0.90 g, 3.4 mmol), the mixture then being stirred until all of the phosphine had dissolved. Fluoroboric acid (54% ethereal solution; 0.5 cm^3) was added to the resulting solution which then became light red. After being stirred for an additional 15 min, the mixture was diluted with diethyl ether (150 cm^3) whereupon it turned white; after 5 min white crystals started to precipitate. The crystals were filtered off, washed with diethyl ether, dried and recrystallized from acetonitrile–diethyl ether to give **15** as pale pink crystals (1.79 g, 94%); mp 130–131 °C; $\delta_H(CDCl_3/TMS)$ 8.0–7.8 (m, 15 H, ArH), 7.00 (d, 1 H, *J* 4.1, dithiole H), 2.85 (m, 4 H, CH_2) and 2.60 (m, 4 H, CH_2); *m*/*z* (FAB+) 535 (cation) (Found: C, 51.5; H, 3.9; N, 4.6. Calc. for $C_{27}H_{23}BF_4PS_4$: C, 52.1; H, 3.9; N, 4.5%).

4,5-Dimethyl-2-methylseleno-1,3-diselenolium trifluoromethanesulfonate 17 and 4,5-ethylenediseleno-2-methylsulfanyl-1,3-dithiolium trifluoromethanesulfonate 18

These compounds were prepared by adaptation of a procedure described in the literature.[22]

Compound 17 (87%), a yellow powder, mp 126 °C; $\delta_H(CDCl_3\text{–}TMS)$ 1.98 (s, 6 H, CH_3) and 2.67 (s, 3 H, CH_3); *m*/*z* (^{80}Se, FAB+) 321 (cation).

Compound 18 (83%), a yellow powder, mp 97 °C; $\delta_H(CDCl_3\text{–}TMS)$ 2.61 (s, 3 H, CH_3) and 3.42 (s, 4 H, CH_2), *m*/*z* (^{80}Se, FAB+) 335 (cation).

Pseudo-Wittig condensations

Compounds 11 and 14. The salt **17** or **18** (0.64 mmol) and triethylamine (1 cm^3) were added to a solution of compound **15** (0.40 g, 0.64 mmol) in acetonitrile (20 cm^3) whereupon the solution turned red. The mixture was stirred for 90 min at room temperature after which it was concentrated under reduced pressure and the resulting oil was chromatographed (SiO_2, CH_2Cl_2) to give **11** (20%) and **14** (57%).

Compound 13. Compound **16** (0.18 g, 0.64 mmol) and triethylamine (1 cm^3) were added to a solution of compound **15** (0.40 g, 0.64 mmol) in acetonitrile (20 cm^3) whereupon the solution turned red. The mixture was stirred at room temperature for 45 min after which it was concentrated under reduced pressure. The resulting solid was washed with cold methanol (30 cm^3) and dried to give **13** (0.26 g, 70%).

4,5-Bis(2′-cyanoethylseleno)-1,3-dithiole-2-thione 20

3-Bromopropanenitrile (0.60 g, 4 mmol) was added to a solution of di(tetrabutylammonium) bis(2-thioxo-1,3-dithiole-4,5-diselenolato)zincate[24] **19** (1.0 g, 0.9 mmol) in MeCN (20 cm^3) and the mixture was refluxed for 80 min. It was then cooled to room temperature and filtered to remove the precipitate. The brown filtrate was concentrated under reduced pressure and the resulting oil was redissolved in CH_2Cl_2 (20 cm^3) and the solution washed with water (4 × 10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The resulting solid was chromatographed (SiO_2, CH_2Cl_2) to give **20** as yellow crystals (0.60 g, 86%), mp 91 °C; δ_H($CDCl_3$–TMS) 2.88 (t, 4 H, *J* 6.7) and 3.11 (t, 4 H, *J* 6.7); *m/z* (^{80}Se, EI) 400 (M^+) (Found: C, 27.3; H, 2.0; N, 7.1. Calc. for $C_9H_8N_2S_3Se_2$: C, 27.1; H, 2.0; N, 7.0%).

4,5-Bis(2′-cyanoethylseleno)-1,3-dithiole-2-one 21

A mixture of 4,5-bis(2′-cyanoethylseleno)-1,3-dithiole-2-thione **20** (0.42 g, 1.1 mmol) in $CHCl_3$–AcOH (3:1; 10 cm^3) and $Hg(OAc)_2$ (0.86 g, 2.6 mmol) was stirred under nitrogen at room temperature for 16 h after which it was filtered through Celite to remove the white precipitate. The precipitate was washed with $CHCl_3$ and the combined filtrate and washings were heated under reflux with activated charcoal. The mixture was cooled to room temperature, filtered through Celite, washed with aqueous $NaHCO_3$ (4 mol dm^{-3}; 3 × 10 cm^3) and water (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to afford the title compound as pale yellow crystals (0.40 g, 100%), mp 90 °C; δ_H($CDCl_3$–TMS) 2.85 (t, 4 H, *J* 6.7) and 3.09 (t, 4 H, *J* 6.7); *m/z* (^{80}Se, EI) 384 (M^+) (Found: C, 28.6; H, 2.2; N, 7.5. Calc. for $C_9H_8N_2OS_2Se_2$: C, 28.3; H, 2.1; N, 7.3%).

2,3,6,7-Tetrakis(2′-cyanoethylseleno)tetrathiafulvalene 22

4,5-Bis(2′-cyanoethylseleno)-1,3-dithiole-2-one **21** (0.34 g, 0.9 mmol) was suspended in toluene (12 cm^3) and stirred and heated under reflux while freshly distilled $P(OEt)_3$ (1.2 cm^3) was added to it. After 50 min an orange precipitate started to form. The solution was stirred for a further 2 h under reflux after which it was cooled to room temperature and treated with MeOH (5 cm^3). The product was filtered off, washed with MeOH (3 × 3 cm^3) and dried *in vacuo* to give **22** as yellow powder (0.22 g, 69%), mp 182–183 °C, δ_H($CDCl_3$–TMS) 2.84 (t, 4 H, CH_2, *J* 6.9) and 3.06 (t, 4 H, CH_2, *J* 6.9); *m/z* (^{80}Se, EI) 736 (M^+) (Found: C, 29.0; H, 2.1; N, 7.7. Calc. for $C_{18}H_{16}N_4S_4Se_4$: C, 29.3; H, 2.2; N, 7.7%); CV (CH_2Cl_2, 0.1 V s^{-1}, $[NBu_4][PF_6]$, *vs.* SCE): E_1 0.70 V, E_2 1.01 V.

Bis(ethylenediseleno)tetrathiafulvalene (BEDSe-TTF) 23

Procedure using EtONa–EtOH. 2,3,6,7-Tetrakis(2′-cyanoethylseleno)tetrathiafulvalene **22** (0.45 g, 0.61 mmol) was suspended in anhydrous degassed EtOH (25 cm^3) under N_2 and a solution of Na (0.12 g, 5.2 mmol) in EtOH (12 cm^3) was added to it with a syringe. The mixture was stirred for 3 h after which it was treated with a solution of 1,2-dibromoethane (0.80 g, 4.2 mmol) in EtOH (5 cm^3). The dark red–brown mixture was stirred overnight and then filtered to remove the brown precipitate which was washed with EtOH, water and diethyl ether. The brown solid was chromatographed (SiO_2, CS_2) to give **23** as an orange–brown solid (0.15 g, 43%).

Procedure using CsOH–H_2O–THF. A solution of CsOH·H_2O (0.55 g, 3.3 mmol) in MeOH (5 cm^3) was added with a syringe to a cooled (0 °C) suspension of compound **22** (0.30 g, 0.41 mmol) in anhydrous THF (30 cm^3) under N_2. After the mixture had been stirred for 1 h at 0 °C, a solution of 1,2-dibromoethane (0.63 g, 2.8 mmol) in THF (5 cm^3) was added to it. The brown solution was then stirred for 2 h at 0 °C and then overnight at room temperature. The mixture was then evaporated to afford a brown solid which was washed with EtOH, water and diethyl ether. Chromatography (SiO_2, CS_2) of the brown solid gave compound **23** (0.090 g, 39%); mp 220–225 °C (decomp.) (lit., 220–223 °C;[25] 220–222 °C[26]); δ_H(CS_2) 3.40 (s); *m/z* (^{80}Se, EI) 576 (M^+) (Found: C, 20.8; H, 1.4. Calc. for $C_{10}H_8S_4Se_4$: C, 21.0; H, 1.4%); CV (CH_2Cl_2, 0.1 V s^{-1}, $[NBu_4][PF_6]$, *vs.* SCE): E_1 0.49 V, E_2 0.84 V.

2,3-Bis(2′-hydroxyethylsulfanyl)-6,7-ethylenedichalcogenotetrathiafulvalenes 24 and 25

General procedure. A solution of Na (0.063 g, 2.7 mmol) in EtOH (5 cm^3) was added with a syringe to a suspension of 2,3-bis(2′-cyanoethylsulfanyl)-6,7-ethylenedichalcogenotetrathiafulvalene **10** or **12** (0.65 mmol) in anhydrous degassed EtOH (20 cm^3) under N_2. After being stirred at room temperature for 4 h, the red–brown mixture was treated with 2-chloroethanol (0.83 g, 10 mmol). After a few minutes, the solution turned orange and a precipitate started to form. The mixture was then stirred overnight after which it was treated with water (15 cm^3) and extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$) and concentrated. The resulting solid was chromatographed [SiO_2, CH_2Cl_2–AcOEt (8:2)] to give compound **24** or **25**.

Compound 24 (82%), a red–orange powder, mp 104 °C; δ_H($CDCl_3$–TMS) 2.92 (t, 2 H, OH), 3.05 (t, 4 H, CH_2) 3.78 (m, 4 H, CH_2) and 4.30 (s, 4 H, CH_2); *m/z* (EI) 414 (M^+) (Found: C, 34.9; H, 3.4; O, 15.6. Calc. for $C_{12}H_{14}O_4S_6$: C, 34.8; H, 3.4; O, 15.5%); CV (CH_2Cl_2, 0.1 V s^{-1}, $[NBu_4][PF_6]$ *vs.* SCE): E_1 0.48 V, E_2 0.84 V.

Compound 25 (82%) an orange powder, mp 103–104 °C; δ_H($CDCl_3$–TMS) 2.82 (m, 2 H, OH), 2.95 (t, 4 H, CH_2), 3.25 (s, 4 H, CH_2) and 3.69 (m, 4 H, CH_2); *m/z* (EI) 446 (M^+) (Found: C, 32.5; H, 3.0; O, 7.4. Calc. for $C_{12}H_{14}O_2S_8$: C, 32.3; H, 3.1; O, 7.2%); CV (CH_2Cl_2, 0.1 V s^{-1}, $[NBu_4][PF_6]$, *vs.* SCE): E_1 0.54 V, E_2 0.89 V.

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