Synthesis of symmetrical and asymmetrical singly bridged bis-TTFs containing sulfur and selenium atoms. A study of some of their radical cation salts

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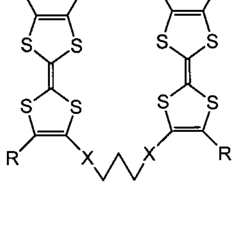
By using a chalcogenolate (thiolate or selenolate) protection–deprotection strategy, a series of singly bridged bis-TTFs, **3a**–**c**, **4a**, have been prepared in high yield (84–96%) through two different routes. Route 2, involving the reaction between a monochalcogenolate TTF derivative with a previously prepared monoiodinated TTF species, appears to be a very useful and general strategy to selectively prepare bis-TTFs in high yields (84–90%). The bis-TTFs, **3a**–**c**, **4a**, are easily converted into the corresponding dimethylated derivatives **3a′**–**c′**, **4a′** in a basic (2 equiv.) IMe medium. The electron-donating ability of this series of bis-TTFs has been determined by cyclic voltammetry. Several salts, mainly perchlorates, of the donors **3a**, **4a**, **3a′**–**c′** have been obtained as black powders by galvanic electrosynthesis. Their room temperature electrical conductivity as compressed powder pellets has been measured, together with the temperature dependence of the ESR signal.

In the past decade, dimeric and oligomeric tetrathiafulvalenes (TTFs)[1–5] have received much attention for applications as conducting materials. This type of extended π-donor in particular seems to allow for control of the stoichiometry, band filling and molecular assembly in the resulting conducting salts.[5] They also seem to be able to induce a stabilised metallic state down to low temperature by adopting 2D and even 3D arrangements.[6] In this work we describe a series of dimeric TTFs in which the TTF units are linked by one saturated spacer (–$SCH_2CH_2CH_2S$– or –$SeCH_2CH_2CH_2Se$–), leading to flexible bis-TTF donors potentially able to lead to two dimensional salts.[5,7] Furthermore, as shown in Scheme 1, each TTF unit contains on one end of the TTF heterocycle, either an ethylene dichalcogeno (S, Se) group or methyl groups, as found in BEDT-TTF, BEDS-TTF (BEST) and TMTTF, respectively known to give highly conducting salts.[8]

Bis-TTFs very often have been prepared by the common trialkylphosphite-promoted dimeric coupling of a bis-1,3-dithiole-2-chalcogenone[9] or from its bis-triphenylphosphonium salt derivative (or the corresponding phosphonate) in a Wittig-like (or Wittig–Horner) condensation.[10] However, this method can not be applied to the selective synthesis of asymmetric bis-TTFs in which substituents R_1 and R_2 (see Scheme 1) are different. In order to obtain such bis-TTFs, we have adapted the selective thiolate protection–deprotection strategy developed by Becher and coworkers,[11,12] and we have extended it to the corresponding selenium derivatives. This strategy involves the functional key intermediate **1** or **2** (see Scheme 2) in which the cyanoethyl protecting group can be easily removed in a basic medium to be converted into the very useful monodeprotected thiolate **1′**[13,14] or selenolate **2′**.



R = XCH_2CH_2CN, XCH_3
R_1–R_1, R_2–R_2 = XCH_2CH_2X, CH_3
X = S, Se

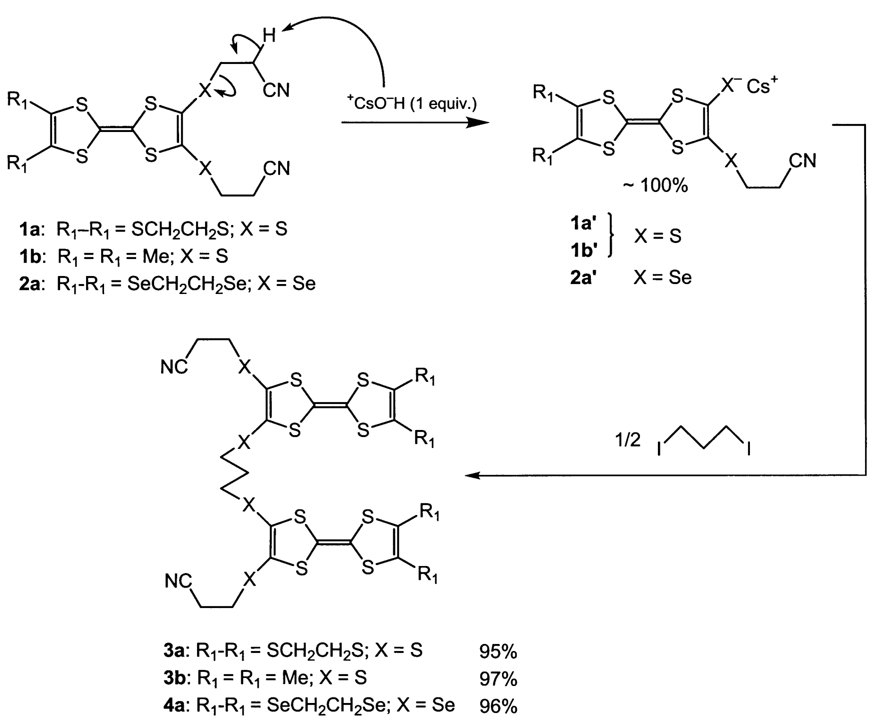
Scheme 1

Results and discussion

Synthesis of singly bridged bis-TTFs

Two different routes were used to independently prepare the symmetric and asymmetric bis-TTFs. The very useful methodology of Route 1 (Scheme 2) allows one to easily obtain the symmetric bis-TTFs **3a** and **3b** and the selenium derivative **4a**, but is of no relevance for the synthesis of the asymmetric species **3c** because an undesirable mixture of the three **3** species is expected in this case. However, the asymmetric bis-TTF **3c** can be specifically prepared through the reliable Route 2 method (Scheme 3), which is in fact a general procedure to prepare both symmetric and asymmetric bis-TTFs. Moreover, the latter method is extendable to the synthesis of various asymmetric oligo-TTFs.

Synthesis of symmetric bis-TTFs 3a, 3b and 4a (Route 1). These three compounds have been obtained in high yield (**3a**: 95%; **3b**: 97%; **4a**: 96%) from the appropriate key precursors **1a**, **1b**[14] and **2a**, respectively. As outlined in Scheme 2, compound **1** or **2** in anhydrous DMF is first selectively monodeprotected[12] by slow addition of 1 equiv. of $CsOH \cdot H_2O$ in a methanolic solution. Then the air-sensitive



Scheme 2

monothiolate **1′** or monoselenolate **2′** is alkylated by addition of 0.5 equiv. of diiodopropane. The expected TTF **3** or **4**, dissolved in dichloromethane, is precipitated by addition of cold hexane and is then isolated. It is worth noting that compounds **3a** and **3b** have also been obtained in 86% and 84% yield, respectively, by using Route 2 (Scheme 3).

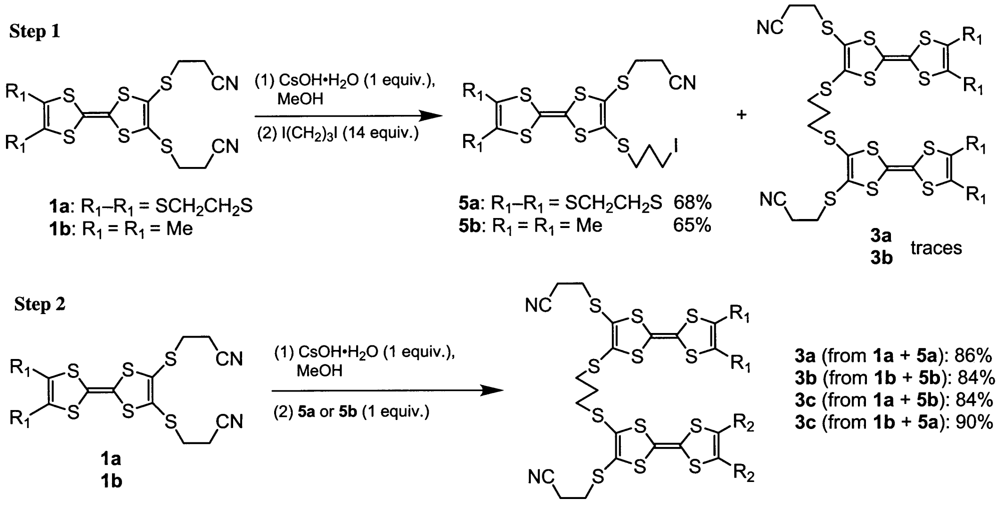
Synthesis of asymmetric bis-TTF 3c (Route 2). Compound **3c** was selectively prepared by making use of the two-step synthesis of Route 2 detailed in Scheme 3. In the first step, the monodeprotection of the appropriate intermediate **1a** or **1b** occurred as described above. After the addition of a large excess of 1,3-diiodopropane (14 equiv.) to the corresponding monothiolates **1′** obtained, the expected monohalogenated derivative **5a** or **5b** was isolated by column chromatography (SiO_2, CH_2Cl_2–hexane 7 : 3) in 68 and 65% yield, respectively. In the second step, after the monodeprotection of **1** into **1′**, condensation of the monothiolate **1′** with an equimolar amount of the monoiodinated compound **5** led to the bis-TTF **3c**, obtained as a precipitate by slow addition of cold hexane. The reaction yield was found to be very similar whatever the starting compounds used: 84% from **1a** + **5b** and 90% from **1b** + **5a**.

Methylation of the bis-TTFs 3a–c and 4a. As shown in Scheme 4, the target series of bis-TTFs **3a′**, **3b′**, **3c′** and **4a′** were obtained, in high yield (90, 85, 92 and 83%, respectively), by dropwise addition of 2.2 equiv. of caesium hydroxide in methanol to a dry DMF solution of **3** (or **4**) and subsequent addition of a large excess of methyl iodide.

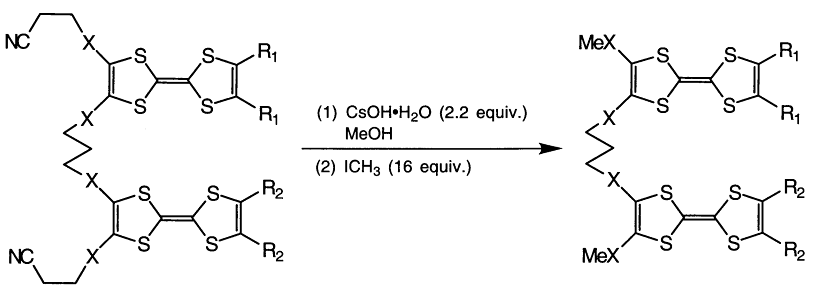
Cyclic voltammetry

Electrochemical solutions of all the new donors have been studied by cyclic voltammetry (CV) and square wave voltammetry (SQW) to determine their oxidation potentials (E^{ox}). SQW is able to distinguish two waves when conventional CV shows only one broad wave. For example, in compound **3a′**, SQW displays two waves at 477 and 563 mV, whereas CV displays only one wave at 563 mV (Fig. 1a and b). The E^{ox} potentials listed in Table 1 were obtained by using SQW.

Compounds **1a**,**b**, **2a** and **5a**,**b** display two single-electron redox waves typical of the TTF system. For compounds **3c**, **4a**, **4a′** and **3a′**–**c′**, three waves have been observed: the first two are more or less separated depending on the nature of the substituents. It also appears that substituting Se for the S atoms does not affect the values of the oxidation potentials



Scheme 3



3a: R_1–R_1 = R_2–R_2 = SCH_2CH_2S; X = S
3b: R_1 = R_2 = Me; X = S
3c: R_1–R_1 = SCH_2CH_2S; R_2 = Me; X = S
4a: R_1–R_1 = R_2–R_2 = $SeCH_2CH_2Se$; X = Se

3a': 90%
3b': 85%
3c': 92%
4a': 83%

Scheme 4

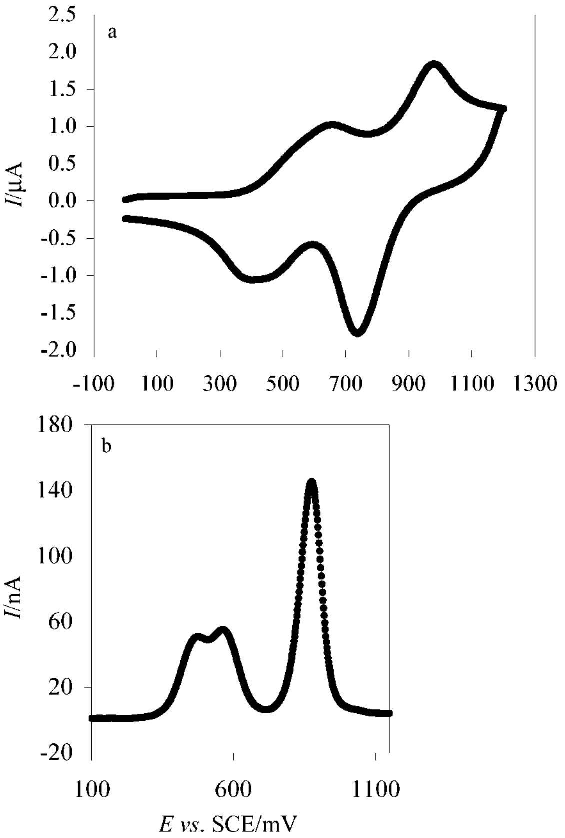


Fig. 1 (a) CV of compound **3a′** on Pt in a CH_2Cl_2 solution using a scan rate of 100 V s^{-1}. (b) SQW of compound **3a′** on Pt in a CH_2Cl_2 solution.

(**3a**,**a′**, **4a**,**a′**). Methylation of the bis-TTF (**3b**,**c**) leads to a positive inductive effect, slightly decreasing the three values of E^{ox} (**3b′**,**c′**). Similar values of oxidation potentials have been reported for another family of bis-TTFs in which the TTF units are linked to each other by a single bond.[15] For the bis-TTFs of type **3**, it is worth noting that the symmetric species (**3a**, **3b**) display a single two-electron wave, whereas **3c**, which contains two different TTF units, gives two one-electron waves. Furthermore the difference in potential $E_2^{ox} - E_1^{ox}$ is larger in the symmetrical bis-TTFs (**3c**, **c′**) than in the symmetrical species (**3a′**, **b′**, **4a**, **a′**).

Radical ion salts: preliminary results

The radical cation salts were prepared by galvanostatic electrochemical oxidation on a platinum electrode in a 15 ml H-type cell from a solution of n-Bu_4NX (0.5 M, typically in tetrahydrofuran) containing a bis-TTF (10^{-3} M), **3a**, **3a′**–**c′** or **4a**. The results of these electrocrystallisations for different bis-TTFs and those of the electrical conductivity measurements are listed in Table 2.

The electrical conductivity was measured on compressed powders by the 2-contacts method. For each salt, the conductivity was found to be very low ($\approx 10^{-4}$–10^{-6} S cm^{-1}). The poor crystalline quality of these salts did not allow for their X-ray crystal structure analysis. However, the magnetic properties of the perchlorate and hexafluorophosphate salts of **3a′** have been studied.

The ESR spectra have been measured on powder samples between 300 and 4 K. Only a single resonance signal has been detected at all temperatures. Its integration gives the relative spin susceptibility, which increases upon cooling. Standard plots such as χ^{-1} *vs.* T did not reveal a simple behaviour of

Table 1 E_{ox} values (±5 mV) of mono-TTFs **1**, **2**, **5** and bis-TTFs **3**, **4**, **3′**, **4′** measured by square wave voltammetry[a]

	Compound	E_1^{ox}/mV	E_2^{ox}/mV	E_3^{ox}/mV	$E_2^{ox} - E_1^{ox}$
Mono-TTF	**1a**	587(1e)[b]	952(1e)		365
	1b	464(1e)	906(1e)		442
	2a	594(1e)	989(1e)		395
	5a	570(1e)	942(1e)		348
	5b	510(1e)	980(1e)		470
Bis-TTF	**3a**	562(2e)		886(2e)	—
	3b	446(2e)		870(2e)	—
	3c	424(1e)	576(1e)	890(2e)	152
	4a	512	570	880	58
	3a′	477(1e)	563(1e)	880(2e)	86
	3b′	392	434	840	42
	3c′	370	545	850	175
	4a′	482	574	891	92

[a] All oxidation potentials (E^{ox}) were determined in CH_2Cl_2 containing 0.1 M Bu_4NPF_6, with SCE as the reference electrode and platinum as working and counter electrodes. [b] (1e) and (2e) represent, respectively, one- and two-electron redox processes evaluated by coulometry.

Table 2 Electrocrystallisation conditions, crystal aspect and electrical conductivity of radical cation salts of bis-TTFs **3a**, **4a** and **3a′**–**c′**

Compound	Counter anion X	Intensity[a]/ μA	Crystal aspect	Electrical conductivity /S cm^{-1}
3a	AsF_6^-	3.0	Black spheres	4.1×10^{-4}
	PF_6^-	0.5	No salt	—
	ClO_4^-	0.5	Black blocks	$1.5–39 \times 10^{-6}$
	ReO_4^-	0.5	Fine powder	2.5×10^{-5}
	BF_4^-	0.5	Black platelets	—
	$FeCl_4^-$	0.5[b]	Small spheres	5.5×10^{-6}
4a	ClO_4^-	0.5	Powder	3.7×10^{-6}
3a′	AsF_6^-	3.0	Black spheres	1.3×10^{-5}
	PF_6^-	2.0	Black spheres	6×10^{-5}
	ClO_4^-	2.0	Powder	5×10^{-6}
3b′	ClO_4^-	2.0	Powder	5×10^{-6}
3c	ClO_4^-	2.0	Powder	1.4×10^{-6}

[a] In tetrahydrofuran (THF) unless otherwise noted. [b] In a 1 : 1 mixture of THF–TCE (1,1,2-trichloroethane).

the samples. On the other hand, a log–log plot such as given in Fig. 2 leads to the same straight line for both salts. This means that the spin susceptibility follows a power law dependence $\chi(T) = CT^{-\alpha}$ with $\alpha \approx 0.8$. This result is reminiscent of that obtained for disordered materials.[16] However, the crystal structure would be necessary to deepen this discussion.

ESR also gives the g factor and the linewidth. As we used a powder sample, we have obtained averaged values. Both quantities are almost temperature independent. We have obtained $g \approx 2.0074$ in both cases. A slight increase has been found at low temperature for the ClO_4^- salt (for which $g \approx 2.0074$ at 4 K), meanwhile the linewidth (slightly larger for this salt) also increases (see Fig. 3). The main conclusion remains the absence of a noticeable temperature dependence of the ESR linewidth, which suggests the absence of collective effects in the relaxation process.

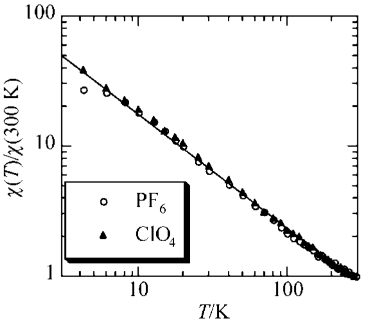


Fig. 2 ESR normalised susceptibility as a function of temperature on a log–log plot.

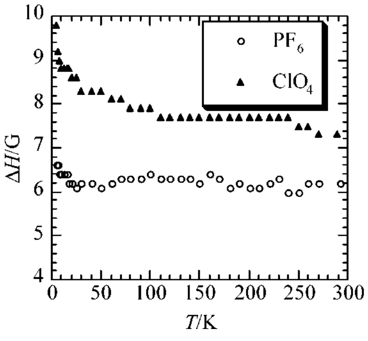


Fig. 3 Temperature dependence of the ESR linewidth.

Conclusion

A series of singly bridged bis-TTFs was obtained in high yield by using two different routes involving a chalcogenolate protection–deprotection strategy.[11,12] This method was successfully extended to the synthesis of a bis-TTF (**4**) containing selenium atoms. Route 2 was found to be particularly efficient in the synthesis of both symmetric and asymmetric bis-TTFs (**3**, **4**). These new compounds were easily converted into their dimethylated derivatives (**3′**, **4′**). The study of these bis-TTFs by cyclic voltammetry showed a donor ability similar to that found for similar compounds[15] and consistent with the inductive effects exerted by the substituents of the TTF core. Moreover, in several cases a three-wave voltammogram was observed. From these donors, radical cation salts were obtained as powder or crystals of poor quality. The electrical conductivity, measured on compressed powder pellets, showed values lower than 4×10^{-4} S cm^{-1}, indicating a semiconducting character for these salts. Finally, the study of the magnetic properties of two salts (PF_6^-, ClO_4^-) of the donor **3a′** showed the absence of a noticeable temperature dependence of the ESR linewidth, which suggests the absence of collective effects in the relaxation process. It was also observed that the spin susceptibility followed a power law dependence, which could be associated with a disordered material.[15] Doubly bridged bis-TTFs could probably be, by inducing less disorder, better candidates to produce the expected 2D conducting salts.

Experimental

All reactions involving generation of chalcogenates were carried out under dry N_2. All solvents were dried by standard methods and all commercial reagents used without purification. NMR spectra were recorded on a Brucker AC 200 instrument. FAB mass spectra were recorded on a JEOL JMS-DX 300 spectrometer. Melting points were measured on a Buchi apparatus. Cyclic voltammetry measurements were carried out on a home-made potentiostat interfaced with a PC computer using $TBAPF_6$ as the supporting electrolyte (dried by melting and pumping under vacuum immediately before use) in a 0.1 mol L^{-1} CH_2Cl_2 solution. A gold working microelectrode (125 μm), a Pt wire as auxiliary electrode and a SCE as reference electrode were used. Square wave voltammetry data were recorded on a PAR-273 potentiostat/galvanostat. ESR measurements (between 300 and 4 K) were performed on an X-band Brucker ESP 300E spectrometer equipped with an ESR 900 Oxford Instruments cryostat.

Syntheses

Compounds **1a** and **1b** were obtained as described in the literature.[14]

1,3-Bis(2-cyanoethylthio)-6,7-ethylenedithiotetrathiafulvalene (1a). Yellow powder. Yield 60%; mp 142 °C, ^{1}H NMR ($CDCl_3$): δ 2.75 (4H, t, $J = 6.7$ Hz, SCH_2); 3.10 (4H, t, $J = 6.7$ Hz, CH_2CN); 3.29 (4H, s, SCH_2CH_2S); MS (EI) *m/z*: 464 $[M]^+$. Anal. calc. for $C_{14}H_{12}N_2S_8$: C 36.2, H 2.6, N 6.0%.

1,3-Bis(2-cyanoethylthio)-6,7-dimethyltetrathiafulvalene (1b). Orange powder. Yield 70%; mp 121–122 °C. ^{1}H NMR ($CDCl_3$): δ 1.92 (6H, *t*, $J = 7.0$ Hz, CH_3); 2.68 (4H, t, $J = 7.0$ Hz, SCH_2); 3.03 (4H, t, $J = 7.0$ Hz, CH_2CN); MS (EI) *m/z*: 402 $[M]^+$. Anal. calc. for $C_{14}H_{14}N_2S_6$: C 41.8, H 3.5, N 7.0%.

1,3-Bis(2-cyanoethylseleno)-6,7-ethylenediselenotetrathiafulvalene (2a). 4,5-Bis(2-cyanoethylseleno)-1,3-dithiole-2-one[14] (400 mg, 1.05 mmol) and 4,5-(ethylenediseleno)-1,3-dithiole-2-thione[14] (333 mg, 1.05 mmol) were suspended in freshly distilled $P(OEt)_3$ (8 ml) 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, dried *in vacuo* and chromatographed (SiO_2, CH_2Cl_2). Isolation of the middle fraction gave the product **2a** as a yellow powder. Yield 117 mg (17%); mp 113 °C. ^{1}H NMR ($CDCl_3$): δ 2.86 (4H, t, $J = 6.8$ Hz, CH_2CN); 3.08 (4H, t, $J = 6.9$ Hz, CH_2Se); 3.36 (4H, s, $SeCH_2CH_2Se$). MS (FAB) *m/z*: 653 $[M]^+$. Anal. calc. for $C_{14}H_{12}N_2S_4Se_4$: C 25.77, H 1.84; Found C 25.99, H 1.90%.

1,3-Bis[3(2-cyanoethylthio)-6,7-ethylenedithiotetrathiafulvalene-2-ylthio]propane (3a). *Route 1:* To a solution of **1a**[14] (497 mg, 1.07 mmol) in DMF (27 ml) was added dropwise, under inert atmosphere, a solution of $CsOH \cdot H_2O$ (188 mg, 1.12 mmol) in MeOH (2.7 ml). The mixture was stirred 15 min before adding 1,3-diiodopropane (62 µl, 0.54 mmol). After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH_2Cl_2 and washed with water several times. After drying ($MgSO_4$) and evaporation of the solvent, precipitation of the red oil obtained by addition of cold hexane gave **3a** as a pink powder. Yield 446.4 mg (95%); mp 129–130 °C.

Route 2: To a solution of **1a**[14] (100 mg, 0.215 mmol) in DMF (10 ml) was added dropwise, under inert atmosphere, a solution of $CsOH \cdot H_2O$ (39 mg, 0.23 mmol) in MeOH (1 ml). The mixture was stirred 15 min before adding **5a** (124.6 mg, 0.215 mmol). After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH_2Cl_2 and washed with water several times. After drying ($MgSO_4$) and evaporation of the solvent, precipitation of the red oil obtained by addition of cold hexane gave **3a**. Yield 160 mg (86%). ^{1}H NMR ($CDCl_3$): δ 1.98 (2H, q, $J = 6.9$ Hz, $SCH_2CH_2CH_2S$); 2.71 (4H, t, $J = 6.9$ Hz, CH_2CN); 3.03 (8H, m, CH_2S); 3.31 (8H, s, SCH_2CH_2S). ^{13}C NMR ($CDCl_3$): δ 18.86, 29.55, 30.24, 31.51, 34.65, 112.02, 113.96, 117.56, 124.73, 131.46. MS (FAB) *m/z*: 862 $[M]^+$. Anal. calc. for $C_{25}H_{22}N_2S_{16}$: C 34.80, H 2.55; found C 34.96, H 2.59%.

1,3-Bis[3(2-cyanoethylthio)-6,7-bis(methyl)tetrathiafulvalene-2-ylthio]propane (3b). *Route 1:* To a solution of **1b**[14] (48 mg, 0.012 mmol) in DMF (7 ml) was added dropwise, under inert atmosphere, a solution of $CsOH \cdot H_2O$ (20.3 mg, 0.012 mmol) in MeOH (1 ml). The mixture was stirred 15 min before 1,3-diiodopropane (7 µl, 0.006 mmol) was added. After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH_2Cl_2 and washed with water several times. After drying ($MgSO_4$) and evaporation of the solvent, the precipitation of the oil obtained by addition of cold hexane gave **3b** as a yellow powder. Yield 43 mg (97%); mp 137 °C (dec).

Route 2: To a solution of **1b**[14] (39 mg, 0.097 mmol) in DMF (7 ml) was added dropwise, under inert atmosphere, a solution of $CsOH \cdot H_2O$ (17 mg, 0.1 mmol) in MeOH (1 ml). The mixture was stirred 15 min before **5b** (50 mg, 0.097 mmol) was added. After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH_2Cl_2 and washed with water several times. After drying ($MgSO_4$) and evaporation of the solvent, precipitation of the red oil obtained by addition of cold hexane gave **3b**. Yield 60 mg (84%). ^{1}H NMR ($CDCl_3$): δ 1.95 (14H, s + q, Me + $SCH_2CH_2CH_2S$); 2.7 (4H, t, $J = 6.8$ Hz, CH_2CN); 2.98 (4H, t, $J = 6.9$ Hz, CH_2S); 3.03 (4H, t, $J = 7.1$ Hz, CH_2S). ^{13}C NMR ($CDCl_3$): δ 13.89, 18.94, 29.57, 31.5, 34.69, 117.75, 122.97, 131.74 (some signals of quaternary carbons are not visible). MS (FAB) *m/z*: 737 $[M]^+$. Anal. calc. for $C_{25}H_{26}N_2S_{12}$: C 40.65, H 3.52; found C 40.70, H 3.48%.

1,3-Bis[3(2-cyanoethylseleno)-6,7-ethylenediselenotetrathiafulvalene-2-ylseleno]propane (4a). To a solution of **2a** (61.1 mg, 0.094 mmol) in DMF (10 ml) was added dropwise, under inert atmosphere, a solution of $CsOH \cdot H_2O$ (16.9 mg, 0.094 mmol) in MeOH (2 ml). The mixture was stirred 15 min before 1,3-diiodopropane (5.4 µl, 0.047 mmol) was added. After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH_2Cl_2 and washed with water several times. After drying ($MgSO_4$) and evaporation of the solvent, precipitation of the oil obtained by addition of cold hexane gave **4a** as a brown powder. Yield 55.3 mg (96%); mp 86–89 °C. ^{1}H NMR ($CDCl_3$): δ 2.18 (2H, q, $SeCH_2CH_2CH_2Se$); 2.84 (4H, t, $J = 6.7$ Hz, CH_2CN); 3.03 (8H, m, CH_2Se); 3.37 (8H, s, $SeCH_2CH_2Se$). MS (FAB) *m/z*: 1239 $[M]^+$. Anal. calc. for $C_{25}H_{22}N_2S_8Se_8$: C 24.23, H 1.77; found C 24.46, H 1.82%.

Asymmetric bis-TTF (3c). *Route 2, step 1:* To a solution of **1a** (43.7 mg, 0.093 mmol) in DMF (5 ml) was added dropwise, under inert atmosphere, a solution of $CsOH \cdot H_2O$ (17.4 mg, 0.1 mmol) in MeOH (1 ml). The mixture was stirred 15 min before **5b** (48 mg, 0.093 mmol) was added. After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH_2Cl_2 and washed with water several times. After drying ($MgSO_4$) and evaporation of the solvent, the precipitation of the red oil obtained by addition of cold hexane gave **3c** as an orange-pink powder. Yield 62 mg (84%); mp 124.5–125.5 °C.

Step 2: To a solution of **1b** (55 mg, 0.137 mmol) in DMF (5 ml) was added dropwise, under inert atmosphere, a solution of $CsOH \cdot H_2O$ (25 mg, 0.148 mmol) in MeOH (1 ml). The mixture was stirred 15 min before **5a** (79 mg, 0.137 mmol) was added. After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH_2Cl_2 and washed with water several times. After drying ($MgSO_4$) and evaporation of the solvent, the precipitation of the red oil obtained by addition of cold hexane gave **3c**. Yield 98.6 mg (90%). ^{1}H NMR ($CDCl_3$): δ 1.95 (8H, s + q, Me + $SCH_2CH_2CH_2S$); 2.7 (4H, t, $J = 7.1$ Hz, CH_2CN); 3.01 (8H, m, CH_2S); 3.30 (4H, s, SCH_2CH_2S). ^{13}C NMR ($CDCl_3$): δ 13.91, 18.95, 29.6, 30.31, 31.48, 31.61, 34.62, 34.79, 103.07, 113.97, 116.43, 117.75, 122.99, 124.75, 131.61. MS (FAB) *m/z*: 800 $[M]^+$. Anal. calc. for $C_{25}H_{24}N_2S_{14}$: C 37.46, H 3.02; found C 37.20, H 3.09%.

Methylated bis-TTF (3a′). To a solution of **3a** (217 mg, 0.25 mmol) in DMF (15 ml) was added dropwise, under inert atmosphere, a solution of $CsOH \cdot H_2O$ (90 mg, 0.54 mmol) in MeOH (1.3 ml). The mixture was stirred 15 min before iodomethane (0.25 ml, 4 mmol) was added. After a few minutes a yellow compound started to precipitate. After stirring for 2 h, the precipitate was filtered off, dissolved in CH_2Cl_2 and washed several times with water. After drying ($MgSO_4$), filtration on SiO_2 and evaporation of the solvent, product **3a′**

was obtained as a yellow powder: Yield 176 mg (90%); mp 170 °C. ^{1}H NMR (CDCl$_3$): δ 1.95 (2H, q, $J = 6.9$ Hz, SCH$_2$C*H*$_2$CH$_2$S); 2.44 (6H, s, SMe); 2.95 (4H, t, $J = 6.9$ Hz, SCH$_2$); 3.31 (8H, s, SCH$_2$CH$_2$S). MS (FAB) *m*/*z*: 784 [M]$^+$. Anal. calc. for $C_{21}H_{20}S_{16}$: C 32.11, H 2.56; found C 31.78, H 2.51%.

Methylated bis-TTF (3b′). To a solution of **3b** (44 mg, 0.06 mmol) in DMF (12 ml) was added dropwise, under inert atmosphere, a solution of CsOH · H$_2$O (21 mg, 0.125 mmol) in MeOH (1 ml). The mixture was stirred 15 min before iodomethane (0.05 ml, 0.95 mmol) was added. After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH$_2$Cl$_2$ and washed with water several times. After drying (MgSO$_4$), filtration on SiO$_2$ and evaporation of the solvent, product **3b**′ was obtained as a yellow powder. Yield 33.3 mg (85%); mp 173 °C (decomp.). ^{1}H NMR (CDCl$_3$): δ 1.95 (14H, q + s, SCH$_2$C*H*$_2$CH$_2$S + Me); 2.42 (6H, s, SMe); 2.94 (4H, t, $J = 6.9$ Hz, SCH$_2$). MS (FAB) *m*/*z*: 662 [M]$^+$. Anal. calc. for $C_{21}H_{24}S_{12}$: C 38.18, H 3.64; found C 38.36, H 3.65%.

Methylated bis-TTF (3c′). To a solution of **3c** (119 mg, 0.149 mmol) in DMF (10 ml) was added dropwise, under inert atmosphere, a solution of CsOH · H$_2$O (54 mg, 0.32 mmol) in MeOH (1 ml). The mixture was stirred 15 min before iodomethyl (0.15 ml, 2.38 mmol) was added. After a few minutes a yellow compound started to precipitate. After stirring for 2 h, the precipitate was filtered off, dissolved in CH$_2$Cl$_2$ and washed several times with water. After drying (MgSO$_4$), filtration on SiO$_2$ and evaporation of the solvent, product **3c**′ was obtained as a yellow powder. Yield 98.7 mg (92%); mp 171.5–172.5 °C. ^{1}H NMR (CDCl$_3$): δ 1.94 (8H, s + q, Me + SCH$_2$C*H*$_2$CH$_2$S); 2.43 (6H, s, SMe); 2.95 (4H, t, $J = 6.8$ Hz, SCH$_2$); 3.29 (4H, s, SCH$_2$CH$_2$S). MS (FAB) *m*/*z*: 722 [M]$^+$. Anal. calc. for $C_{21}H_{22}S_{14}$: C 34.87, H 3.06; found C 34.45, H 3.15%.

Methylated bis-TTF (4a′). To a solution of **4a** (61 mg, 0.049 mmol) in DMF (20 ml) was added dropwise, under inert atmosphere, a solution of CsOH · H$_2$O (18.6 mg, 0.110 mmol) in MeOH (2 ml). The mixture was stirred 15 min before iodomethyl (0.06 ml, 1.14 mmol) was added. After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH$_2$Cl$_2$ and washed with water several times. After drying (MgSO$_4$), filtration on SiO$_2$ and evaporation of the solvent, product **4a**′ was obtained as a yellow powder. Yield 47.4 mg (83%); mp 121 °C (decomp.). ^{1}H NMR (CDCl$_3$): δ 2.13 (2H, q, SeCH$_2$C*H*$_2$CH$_2$Se); 2.34 (6H, s, SMe); 2.99 (4H, t, $J = 6.8$ Hz, SeCH$_2$); 3.34 (8H, s, SeCH$_2$CH$_2$Se). MS (FAB) *m*/*z*: 1161 [M]$^+$. Anal. calc. for $C_{21}H_{20}S_8Se_8$: C 21.72, H 1.72; found C 21.96, H 1.80%.

2-(2-Cyanoethylthio)-3-(3-iodopropylthio)-6,7-(ethylenedithio)tetrathiafulvalene (5a). To a solution of **1a** (200 mg, 0.43 mmol) in DMF (9 ml) was added dropwise, under inert atmosphere, a solution of CsOH · H$_2$O (77 mg, 0.45 mmol) in MeOH (1 ml). The mixture was stirred 15 min before iodomethane (495 μl, 4.3 mmol) was added. After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH$_2$Cl$_2$ and washed with water several times. After drying (MgSO$_4$) and evaporation of the solvent, the oil obtained was subjected to column chromatography (SiO$_2$, CH$_2$Cl$_2$–hexane: 2 : 1.5). Collection of the orange band afforded **5a** as a bright orange powder. Yield 168 mg (68%); mp 101.5–102.5 °C. ^{1}H NMR (CDCl$_3$): δ 2.11 (2H, q, $J = 6.7$ Hz, SCH$_2$C*H*$_2$CH$_2$I); 2.70 (2H, t, $J = 7.1$ Hz, CH$_2$CN); 3.01 (4H, m, CH$_2$S); 3.31 (6H, s + t, SCH$_2$CH$_2$S + CH$_2$I). MS (FAB) *m*/*z*: 579 [M]$^+$. Anal. calc. for $C_{14}H_{14}INS_8$: C 29.00, H 2.43; Found C 29.22, H 2.49%.

2-(2-Cyanoethylthio)-3-(3-iodopropylthio)-6,7-bis(methyl)-tetrathiafulvalene (5b). To a solution of **1b** (118 mg, 0.29 mmol) in DMF (6 ml) was added dropwise, under inert atmosphere, a solution of CsOH · H$_2$O (52 mg, 0.3 mmol) in MeOH (1 ml). The mixture was stirred 15 min before iodomethane (337 μl, 2.9 mmol) was added. After stirring for 2 h under inert atmosphere, the mixture was dissolved in CH$_2$Cl$_2$ and washed with water several times. After drying (MgSO$_4$) and evaporation of the solvent, the oil obtained was subjected to column chromatography (SiO$_2$, CH$_2$Cl$_2$–hexane 2 : 1.5). Collection of the orange band afforded **5b** as an bright orange powder. Yield 97 mg (65%); mp 95 °C. ^{1}H NMR (CDCl$_3$): δ 1.96 (6H, s, CH$_3$); 2.11 (2H, q, $J = 6.7$ Hz, SCH$_2$C*H*$_2$CH$_2$I); 2.69 (2H, t, $J = 7.2$ Hz, H$_2$CH$_2$CN); 2.95 (2H, t, $J = 6.8$ Hz, CH$_2$S); 3.01 (2H, t, $J = 7$ Hz, CH$_2$S); 3.31 (2H, t, $J = 6.7$ Hz, CH$_2$I). MS (FAB) *m*/*z*: 516 [M]$^+$. Anal. calc. for $C_{14}H_{16}INS_8$: C 32.49, H 3.09; found C 32.64, H 3.11%.

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