Sequential Functionalisation of Bis-Protected Tetrathiafulvalene-dithiolates

Klaus B. Simonsen, Niels Svenstrup, Jesper Lau, Ole Simonsen, Pernille Mørk, Gitte J. Kristensen, Jan Becher*
Department of Chemistry, Odense University, Campusvej 55, DK-5230 Odense M, Denmark

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The utilisation of the 2-cyanoethyl group as a versatile protecting group for 2-thioxo-1,3-dithiole-4,5-dithiolates and tetrathiafulvalene-thiolates is reported. Mono deprotection of bis-protected 2-thioxo-1,3-dithiole-4,5-dithiolate and of bis-protected tetrathiafulvalene-2,3-dithiolates [obtained by cross coupling of 4,5-bis(2-cyanoethylthio)-1,3-dithio-2-one **5** and the 1,3-dithiole-2-thiones **2b–h** and **2j** in triethyl phosphite] was achieved in very high yields. The monothiolates were generated from the bis-protected starting materials by selective mono deprotection in dimethylformamide solution using one equivalent of caesium hydroxide monohydrate in methanol. Subsequent quenching with iodomethane gave the resulting methylthio-substituted 1,3-dithiole-2-thione **2i** and tetrathiafulvalenes **8** in near quantitative yield. The X-ray crystal structure of the air-stable caesium tetrathiafulvalene-thiolate **10** is reported. This is the first single crystal X-ray structure determination of a tetrathiafulvalene-thiolate.

The search for new tetrathiafulvalene-based organic metals[1] has stimulated the development of new synthetic methodologies for the preparation of functionalised tetrathiafulvalenes over the last two decades.[2] Furthermore, there has recently been an increasing interest in incorporating the tetrathiafulvalenes into macrocyclic and supramolecular compounds,[3] although the lack of easily functionalisable tetrathiafulvalene derivatives has severely restricted the speed of progress in this area.

A more intricate problem concerning the functionalisation of tetrathiafulvalene and its incorporation into macrocyclic structures arises from the fact, that tetrathiafulvalene is D_{2h} symmetrical and possesses four identical potential attachment sites (a) (Figure 1), while most building blocks for supramolecular assemblies (including hydroquinone and 4,4′-bipyridine) are D_{2h} symmetrical with two potential attachment sites. Thus, an arbitrary difunctionalisation of tetrathiafulvalene can, therefore, in principle give rise to a symmetrical disubstituted tetrathiafulvalene (b) and a pseudo-symmetrical disubstituted tetrathiafulvalene (c), both with inherent *cis/trans* problems due to facile isomerisation around the central double bond,[4] or one asymmetrical disubstituted tetrathiafulvalene (d).[5] Our present approach eliminates these problems by making (d) by a completely selective synthetic strategy.

Until recently, the synthesis of structurally modified tetrathiafulvalenes has been accomplished using two different synthetic strategies: (i) lithiation of a preformed tetrathiafulvalene and subsequent treatment with an electrophile;[6] or (ii) dimerisation (coupling) of the corresponding 1,3-dithiole derivatives forming the central double bond of the tetrathiafulvalene in the last step.[2] Although successful for many purposes, these strategies have limited utility in the synthesis of larger molecular assemblies for the following reasons: strategy (i) employs somewhat expensive starting materials, and difunctionalisation gives rise to a mixture of isomers (b), (c) and (d),[7] and its use is therefore limited to the synthesis of monofunctionalised tetrathiafulvalenes, although monolithiation reactions can be complicated by the facile disproportionation of monolithiated tetrathiafulvalene. This complication can be circumvented by the use of blocking groups, as demonstrated previously.[8] Strategy (ii) is limited to substitutents that are stable under the conditions of the dimerisation reaction, and a number of synthetic steps are needed, because this strategy lacks a late common intermediate. Despite these facts, this method has been used succesfully for the preparation of macrocyclic tetrathiafulvalenes, for example in the work of Staab et al.[9]

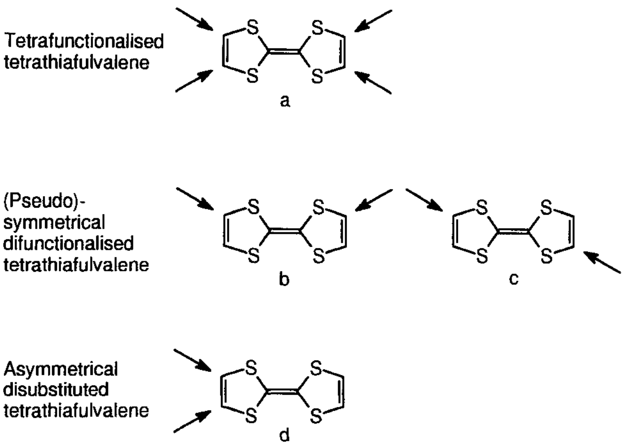
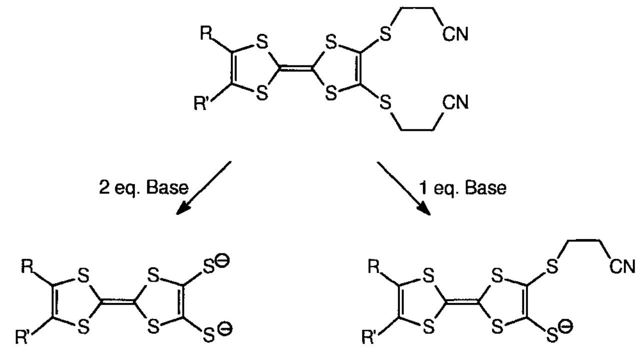


Figure 1. Symmetry properties of substituted tetrathiafulvalenes.[5]

We report here the synthesis of a series of bis-functionalised tetrathiafulvalenes of type (d), having the two thiolate groups in the 2- and 3-positions protected with 2-cyanoethyl groups.[10] Since selective sequential deprotection and alkylation of a preformed tetrathiafulvalene is possible, this combines the advantages of the two strategies (i) and (ii) (regiospecific difunctionalisation of a late common intermediate, readily available from inexpensive starting materials), hence making the incorporation of tetrathiafulvalenes into macromolecular assemblies possible on a synthetically useful scale by deprotection and subsequent alkylation of a preformed tetrathiafulvalene. The 6,7-bis(alkylthio)-2,3-bis(2-cyanoethylthio)tetrathiafulvalenes **6** can be selectively mono- and/or bis-deprotected under mild conditions, using one or two equivalents of base respectively (Scheme 1) and re-alkylated with a variety of electrophiles.

In the present work, the highly selective monodeprotection of 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione and 6,7-bis(alkylthio)-2,3-bis(2-cyanoethylthio)tetrathiafulvalenes **6** is described. The generated thiolate was trapped by subsequent quenching with iodomethane,



Scheme 1

yielding the corresponding methylated compounds. The use of iodomethane as the electrophile was chosen to show the consistency of the mono deprotection, but this strategy can be used with a variety of electrophiles.

The corresponding bisdeprotection and re-alkylation with an appropriate electrophile, follows the preparation of tetrathiafulvalene-tetrathiolate from the tetrakis-protected tetrathiafulvalene tetrakis(2-cyanoethylthio)tetrathiafulvalene described previously.[11]

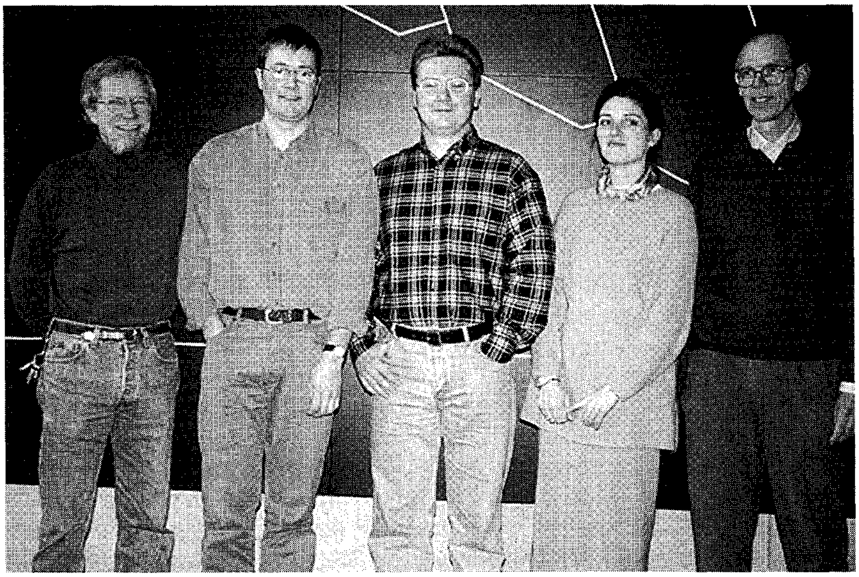
The tetrathiafulvalenes with one or two available thiolate groups serve as excellent building blocks for the incorporation of tetrathiafulvalenes into larger assemblies and, hence, makes the synthesis of supramolecular tetrathiafulvalenes possible by simple alkylation of the generated thiolate.[16]

The syntheses of larger assemblies including tetrathiafulvalenes, such as bistetrathiafulvalenes,[12] macrocyclic tetrathiafulvalenes,[9,13] tetrathiafulvalene-dithiolate metal complexes[14] and oligomeric tetrathiafulvalenes[15] have all been reported previously using different methods.

Preparation of 4,5-Bis(alkylthio)-1,3-dithiole-2-thiones

The starting 4,5-bis(alkylthio)-1,3-dithiole-2-thiones **2a–e** were prepared using a modified version of the classical procedure developed by Steinmecke et al.[17] Saito et al. described the preparation of 4,5-bis(alkylthio)-1,3-dithiole-2-thiones and the phosphite coupling to the corresponding tetrakis(alkylthio)tetrathiafulvalenes from methylthio to octadecylthio substituents,[18] but unfortunately these 1,3-dithiole-2-thiones were reported in a very general form, and no experimental or spectroscopical data were published.

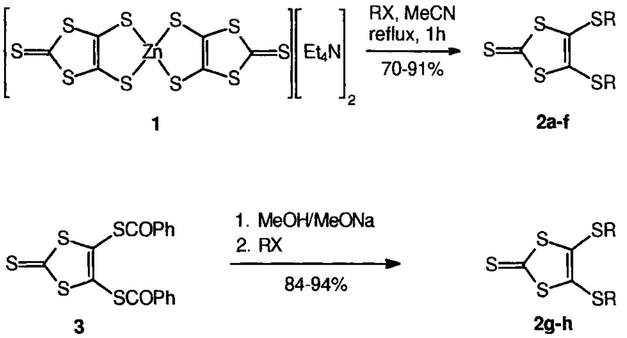
Biographical Sketches



From left to right: J. Becher, J. Lau, N. Svenstrup, P. Mørk and O. Simonsen

Jan Becher (1939) graduated in 1966 from Professor Ole Buchardt's group (University of Copenhagen), gained his Dr. scient. in 1986 and docent (professorship) in 1989, Odense University. **Ole Simonsen** (1937) graduated in 1966 from Professor K. A. Jensen's group (University of Copenhagen) and is presently a lecturer at Odense University. **Klaus B. Simonsen** (M. Sc. 1994) is a Ph. D. student with Jan Becher working on the incorporation of the tetrathiafulvalene group into supramolecular assemblies together with other electroactive groups; he is presently a guest Ph. D. student with Professor Michael P. Cava (University of Alabama). **Niels Svenstrup** (M. Sc. 1994) is presently a Ph. D. student with Professor Becher working on a project aimed at exploring tetrathiafulvalenes as building blocks in the synthesis of supramolecular assemblies. From September 1993, he spent six months as a visiting postgraduate student in the laboratories of Professor Fraser Stoddardt in Birmingham, UK. **Jesper Lau** (M. Sc. 1995) joined Professor Becher's group in 1992, where he is currently working on his Ph. D. project on oligomeric and macrocyclic tetrathiafulvalenes. In 1993 he spent six months in Professor Michael P. Cava's group. **Pernille Mørk** (M. Sc 1995) and **Gitte J. Kristensen** (M. Sc.) both did their graduate work for Professor Becher working on macrocyclic tetrathiafulvalenes.

In the present publication, six 1,3-dithiole-2-thiones differing by the substituents in the 4- and/or 5-position were prepared in high yield according to the procedure outlined in Scheme 2, by treatment of bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate (**1**, DMIT) with primary alkyl halides in refluxing acetonitrile. The amphiphilic dithioles **2g** and **2h** were prepared from 4,5-bis(benzoylthio)-1,3-dithiole-2-thione **3** and the resulting bromo compounds in methanol (Scheme 2).[19] The eight compounds **2a**–**2h** are outlined in Table 1.



Scheme 2

Table 1. Preparation of starting 1,3-dithiole-2-thiones **2**.

RX	Product	R	Yield (%)	Mp (°C)[a]
$NCCH_2CH_2Br$	**2a**	$NCCH_2CH_2$	87	83
MeI	**2b**	Me	79	100–101
EtBr	**2c**	Et	82	oil
$BrCH_2CH_2Br$	**2d**	CH_2CH_2	80	120–121
$PhCH_2CH_2Br$	**2e**	$PhCH_2CH_2$	70	oil
$C_5H_{11}Br$	**2f**	C_5H_{11}	91	oil
$C_{10}H_{21}Br$	**2g**	$C_{10}H_{21}$	84	40
$C_{18}H_{37}Br$	**2h**	$C_{18}H_{37}$	94	77–78

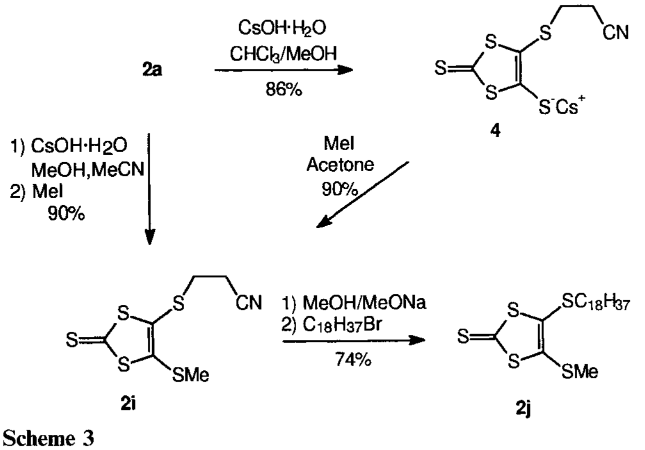
[a] For the recrystallisation solvent, see Experimental Section.

Deprotection of the Bis-Protected 2-Thioxo-1,3-dithiole-4,5-dithiolate

Olk et al. have reported the monodeprotection of 4,5-bis(benzoylthio)-1,3-dithiole-2-thione using 1 equivalent of caesium hydroxide monohydrate in a mixture of methanol and chloroform.[20] This relatively stable monocaesium salt precipitates in quantitative yield. We have adopted this strategy for monodeprotection of the corresponding 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione (**2a**);[10] thus treatment of a chloroform solution of 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione (**2a**) with one equivalent of caesium hydroxide monohydrate in methanol selectively generates the monocaesium salt **4**, which precipitates from the reaction mixture in excellent yield (Scheme 3). The caesium thiolate **4** is stable, can be stored for several months, and provides a useful precursor to asymmetrically substituted 1,3-dithiole-2-thiones.

The caesium salt **4** underwent smooth alkylation in acetone with iodomethane to give the corresponding asymmetric 1,3-dithiole-2-thione **2i**. Compound **2i** could also be prepared by in situ mono deprotection in acetonitrile by the slow addition of one equivalent of base dissolved in methanol, followed by quenching with iodomethane giving **2i** in quantitative yields. Treatment of **2i** with sodium methoxide in methanol and subsequent re-alkylation with octadecyl bromide gave the asymmetrically bis-alkylated 1,3-dithiole-2-thione **2j** in good yield.

In conclusion, this strategy enables us to control the selective stepwise incorporation of two different alkylthio substituents in the 4- and 5-positions of 1,3-dithiole-2-thione in three subsequent high yielding reactions starting from the readily available zincate salt **1**.

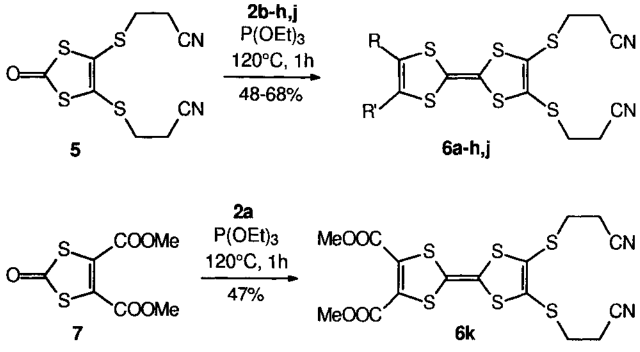


Scheme 3

Asymmetrically Bis-Protected Tetrathiafulvalene-2,3-dithiolates

Since the first reported synthesis of an asymmetrical tetrathiafulvalene by phosphite coupling of a mixture of two different 1,3-dithiole-2-thiones and the subsequent discovery of metallic conductivity and superconductivity in asymmetrical tetrathiafulvalene derivatives,[21] a variety of synthetic strategies have been employed for preparing such analogues, for example, the reaction of 1,3-dithiole-2-ylidene-λ^5-phosphanes with 1,3-dithiolium salts[12] or 2-alkylseleno-1,3-dithiolium salts,[22] or dimerisation of two 1,3-dithiolium salts.[23]

Recently it has been reported that coupling of an equimolar amount of a 1,3-dithiole-2-thione and a 1,3-dithiol-2-one in neat triethyl phosphite gave much higher yields (up to 60%) of the asymmetrical tetrathiafulvalene.[24] This methodology has been successfully employed in the present work in the preparation of the bis-cyanoethyl protected tetrathiafulvalenes **6** (Scheme 4, Table 2).



Scheme 4

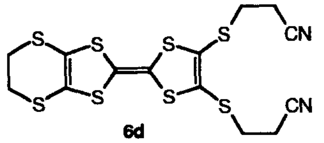
Table 2. Preparation of Cross-Coupled Tetrathiafulvalenes **6**.

6	R	R′	Yield[c] (%)	Mp[a] (°C)	CV[b]	
					$E_1^{1/2}$	$E_2^{1/2}$
a[c]	SCH_2CH_2CN	SCH_2CH_2CN	72	209–210	0.75	1.06
b	SMe	SMe	68	113–114	0.59	0.92
c	SEt	SEt	48	89–90	0.63	0.98
d	SCH_2CH_2S	SCH_2CH_2S	48	141–142	0.60	0.98
e	SCH_2CH_2Ph	SCH_2CH_2Ph	64	134	0.57	0.91
f[d]	SC_5H_{11}	SC_5H_{11}	64	93–94	0.57	0.91
g[d]	$SC_{10}H_{21}$	$SC_{10}H_{21}$	48	110–111	0.62	1.00
h	$SC_{18}H_{37}$	$SC_{18}H_{37}$	49	107	0.62	0.98
j	SMe	$SC_{18}H_{37}$	51	104–105	0.59	0.98
k	COOMe	COOMe	47	103–104	0.75	1.06

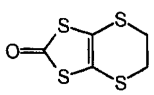
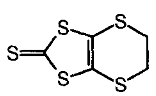
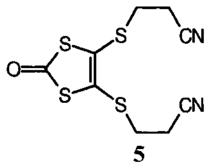
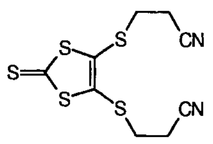
[a] For the recrystallisation solvent, see Experimental Section.
[b] Redox potentials are reported relative to Ag/AgCl in CH_2Cl_2.
[c] Standard coupling of **5** in toluene/$P(OEt)_3$.
[d] Cross coupling performed in a mixture of toluene/$P(OEt)_3$.

Reaction of an equimolar mixture of the thiones **2b–h** and **2j** and 4,5-bis(cyanoethylthio)-1,3-dithiol-2-one **5**[11] in neat triethyl phosphite at 120 °C gave the asymmetrical tetrathiafulvalenes in satisfying yields (48–68 %) after chromatographic separation. It is important to note that due to the polarity of the cyanoethyl groups compared to the normal alkylthio groups, good chromatographic separation of the reaction mixture could be achieved, and the separation could easily be scaled up to an amount of more than 6 g of the asymmetrical tetrathiafulvalene. The symmetrical byproducts tetrakis(2-cyanoethylthio)tetrathiafulvalene and tetrakis(alkylthio)tetrathiafulvalene have R_f values close to 0 and 1 respectively, whereas all the asymmetric tetrathiafulvalenes **6b–j** and **6k** have R_f values between 0.4 and 0.6 in the solvent systems employed (usually dichloromethane).

Table 3. Isolated Yields of the Asymmetrical Tetrathiafulvalene **6d** by Different Cross Coupling Reactions



6d

	 **5a**	 **2d**
 **5**	20 %	48 %
 **2a**	22 %	–

In order to optimise the important cross-coupling reaction, other combinations of reagents were tested. The inverse coupling, using the thione **2a** and the 4,5-ethylenedithio-1,3-dithiol-2-one **5a**, only afforded **6d** in very low yield (22 %). Likewise, we also performed the coupling between to different 1,3-dithiol-2-ones, starting from the 1,3-dithiol-2-one **5** and **5a**, which also gave the cross-coupled product **6d** in 20 % yield (Table 3). The mixed coupling between **5** and an appropriate 4,5-bis(alkylthio)-1,3-dithiole-2-thione gave consistently high yield in all reactions (Table 2).

The attempted preparation of **6k** following the conditions described above afforded only the symmetric tetrathiafulvalene **6a**, most likely a result of the electron-withdrawing effects of the ester groups of 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione.[24] The synthesis of the tetrathiafulvalene **6k** by the phosphite coupling of 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-one (**7**) and the corresponding thione **2a** was carried out, **6k** being isolated from the reaction mixture in moderate yield.

Monodeprotection of 2,3-Bis(2-cyanoethylthio)tetrathiafulvalene

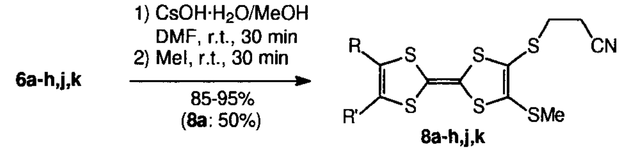
Next, the selective monodeprotection was extended to the tetrathiafulvalene series. The corresponding 2,3-bisprotected tetrathiafulvalenes **6a–h** and **6j–k** could be mono or bisdeprotected using one or two equivalents of base respectively. Subsequent alkylation with a range of electrophiles yielded the corresponding mono- or bis-substituted tetrathiafulvalenes in high yields.

The selective monodeprotection of **6a–h** and **6j–k**, outlined in Scheme 5, shows the generality of this strategy. When a dimethylformamide solution of the appropriate tetrathiafulvalene **6** was treated dropwise with a methanol solution of caesium hydroxide monohydrate (one equivalent), the tetrathiafulvalene-monothiolate was generated selectively. Subsequent quenching of the thiolate with iodomethane gave the corresponding methylthio-substituted tetrathiafulvalenes **8** in near quantitative yield (Table 4).

Table 4. Monodeprotection of bis-protected tetrathiafulvalenes.

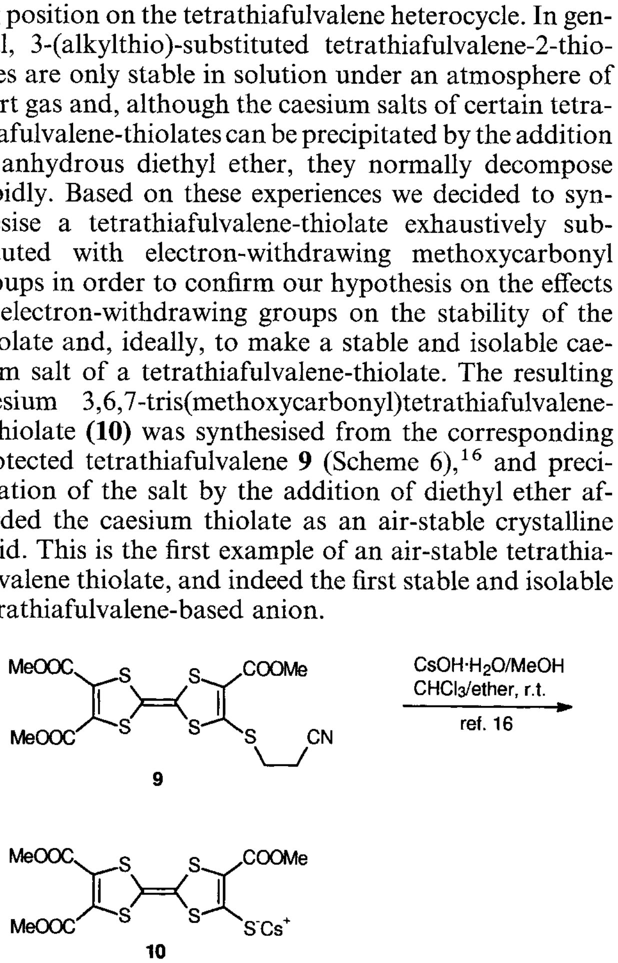
8	R	R′	Yield (%)	Mp[a] (°C)	CV[b]	
					$E_1^{1/2}$	$E_2^{1/2}$
a	SCH_2CH_2CN	SCH_2CH_2CN	50	146–148	0.58	0.89
b	SMe	SMe	94	102–104	0.57	0.92
c	SEt	SEt	95	81–82	0.56	0.91
d	SCH_2CH_2S	SCH_2CH_2S	93	109–110	0.57	0.92
e	SCH_2CH_2Ph	SCH_2CH_2Ph	95	129–129.5	0.55	0.87
f	SC_5H_{11}	SC_5H_{11}	85	84	0.55	0.89
g	$SC_{10}H_{21}$	$SC_{10}H_{21}$	95	92	0.55	0.89
h	$SC_{18}H_{37}$	$SC_{18}H_{37}$	86	95–96	0.58	0.88
j	SMe	$SC_{18}H_{37}$	89	89–90	0.54	0.89
k	COOMe	COOMe	89	78–79	0.70	1.01

[a] For the recrystallisation solvent, see Experimental Section.
[b] Redox potentials are reported relative to Ag/AgCl in CH_2Cl_2.



Scheme 5

The high selectivity in the monodeprotections of the bis-protected tetrathiafulvalene-dithiolates and the bis-protected 2-thioxo-1,3-dithiole-4,5-dithiolates probably arises from an electrostatic repulsion from the monothiolate making the second deprotection less favourable. Furthermore, the stability of a tetrathiafulvalene-thiolate is greatly influenced by the substituent in the neighbouring position on the tetrathiafulvalene heterocycle. In general, 3-(alkylthio)-substituted tetrathiafulvalene-2-thiolates are only stable in solution under an atmosphere of inert gas and, although the caesium salts of certain tetrathiafulvalene-thiolates can be precipitated by the addition of anhydrous diethyl ether, they normally decompose rapidly. Based on these experiences we decided to synthesise a tetrathiafulvalene-thiolate exhaustively substituted with electron-withdrawing methoxycarbonyl groups in order to confirm our hypothesis on the effects of electron-withdrawing groups on the stability of the thiolate and, ideally, to make a stable and isolable caesium salt of a tetrathiafulvalene-thiolate. The resulting caesium 3,6,7-tris(methoxycarbonyl)tetrathiafulvalene-2-thiolate (**10**) was synthesised from the corresponding protected tetrathiafulvalene **9** (Scheme 6),[16] and precipitation of the salt by the addition of diethyl ether afforded the caesium thiolate as an air-stable crystalline solid. This is the first example of an air-stable tetrathiafulvalene thiolate, and indeed the first stable and isolable tetrathiafulvalene-based anion.



Scheme 6

The X-ray crystal structure of **10** was solved with the aim of increasing our understanding of the properties leading to stability of the caesium tetrathiafulvalene-thiolate.

The crystal structure of **10** is disordered concerning the caesium ion and the methoxycarbonyl group [C12, O13, O14, (C15)] closest to the thiolate function (Figure 2). Two symmetry-independent caesium ion positions were located and associated with the population parameters 0.64(1) and 0.19(1), respectively. It was impossible to locate the methyl carbon atom (C15) in the ester group [C12, O13, O14, (C15)], probably caused by the caesium ion disorder which also gave unrealistic bond distances for C4-C12: 1.63(8) Å, C12-O13: 1.66(7) Å and C4-S3: 1.95(5) Å.

However, some structural characteristics are trustworthy: the angle between the least squares planes defined by the two five-membered rings is 1.0(9)°. The tetrathiafulvalene moiety is therefore planar. The ester groups (C16, O18, O17, C19) and (C20, O21, O22, C23) are twisted 25(5)° and 12(2)° respectively out of the plane defined by the five-membered ring to which they are attached. The shortest Cs...O contact distance [2.95(4) Å] involves O22, the carbonyl oxygen atom in the less twisted ester group. This probably reflects some π-electron delocalisation from S8 to O22. A similar delocalisation was observed for caesium 5-methoxycarbonyl-2-thioxo-1,3-dithiol-4-thiolate[16] and mentioned as an important factor for the ionisation potential of 4-(6-bromohexanoyl)tetrathiafulvalene.[25] The thiolate sulfur atom and all the carbonyl oxygen atoms are involved in coordination to the caesium ion in such a way that caesium is surrounded by two thiolate sulfur atoms and four carbonyl oxygen atoms (Figure 3). The contact distances are [Cs...S: 3.62(2), 3.71(2) Å; Cs...O: 2.95(4)-3.34(4) Å]. Similar distances were found in the crystal structure of caesium 5-methoxycarbonyl-2-thioxo-3-dithiol-4-thiolate [Cs...S: 3.636(3), 3.700(4) Å; Cs...O: 3.089(9) Å][16] and caesium dimethylcarbamate [Cs...O: 3.12(2)-3.34(2) Å].[26]

The crystal structure of **10** is characterised by two kinds of infinite channels parallel to the c axis (Figure 3). One kind is occupied by caesium ions around which the anions are grouped. This stacking creates an other type of rather large, probably empty, channels. A content of solvent molecules (water) in these channels could not be definitely confirmed by X-ray diffraction or microanalysis. Crystal structures with channels are not unusual, for example many zeolites have such structures. Some cyanides with hexagonal channels of large cross section have been described.[27,28]

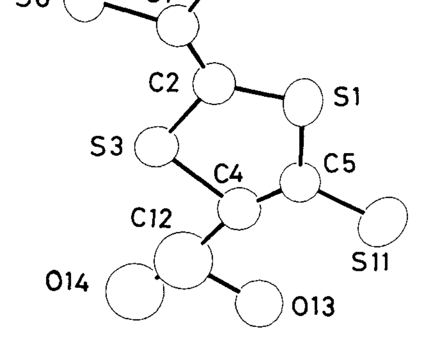


Figure 2. Plot of **10** with displacement ellipsoids and displacement spheres. Ellipsoids and spheres are drawn at the 50% probability level.

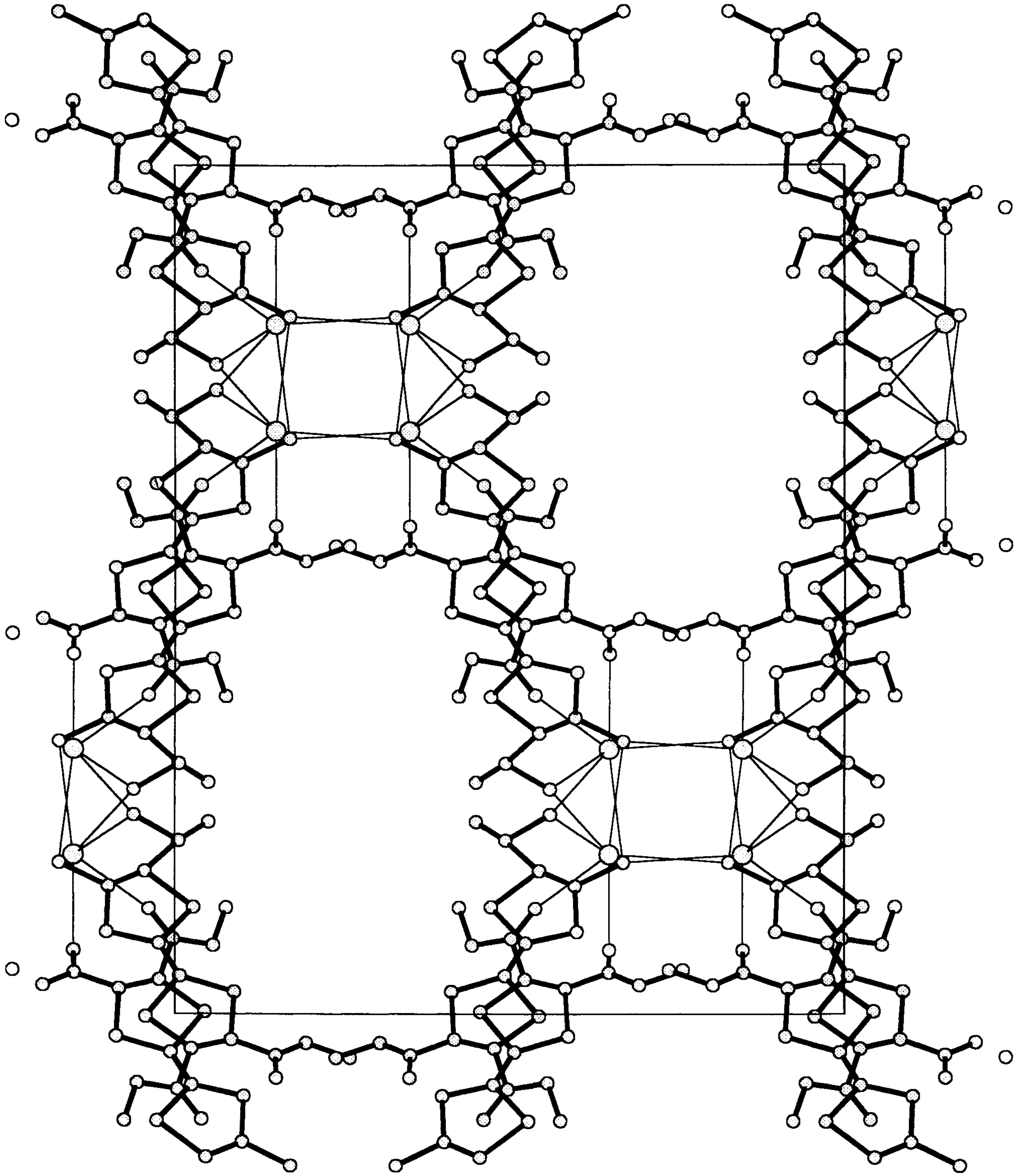
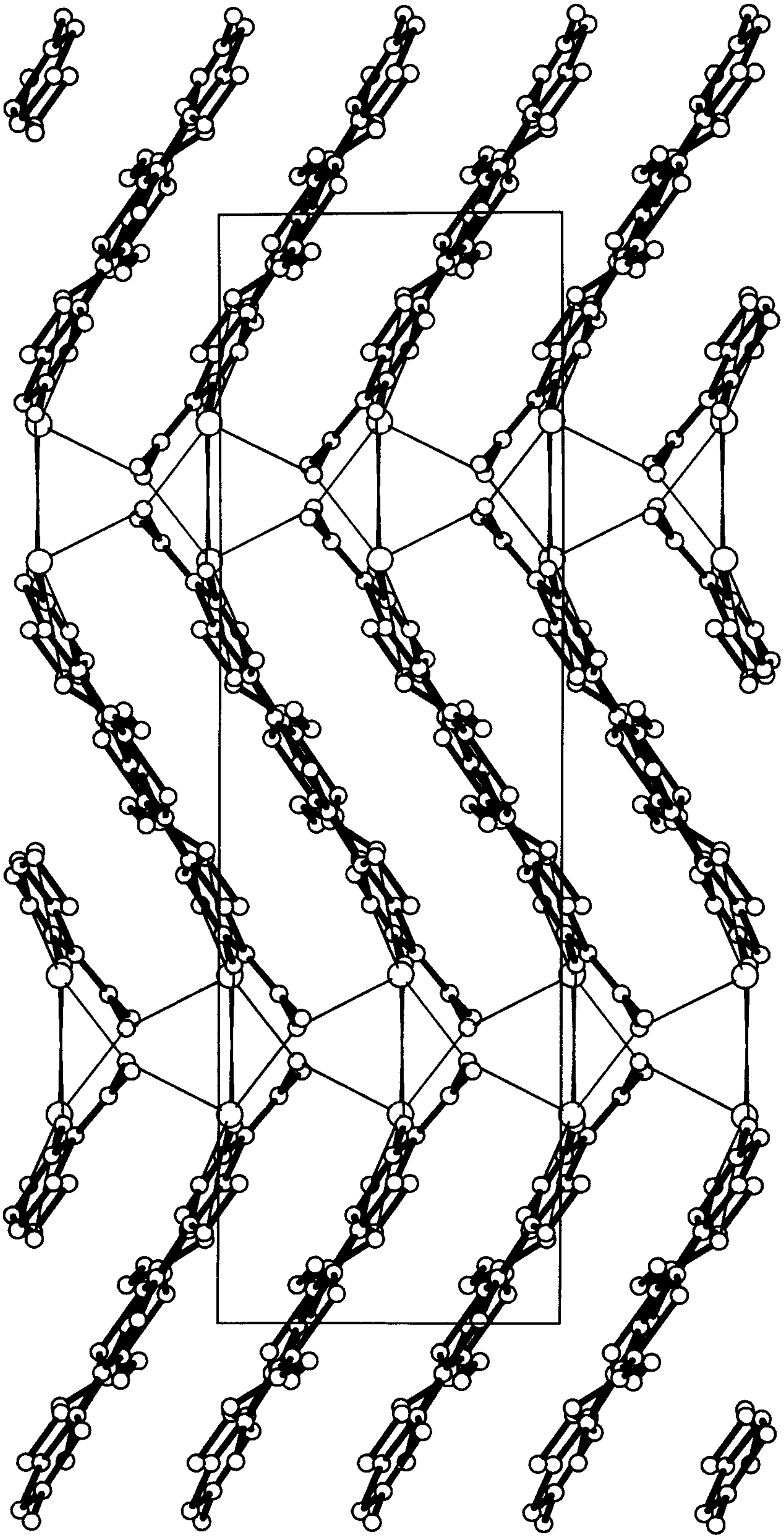
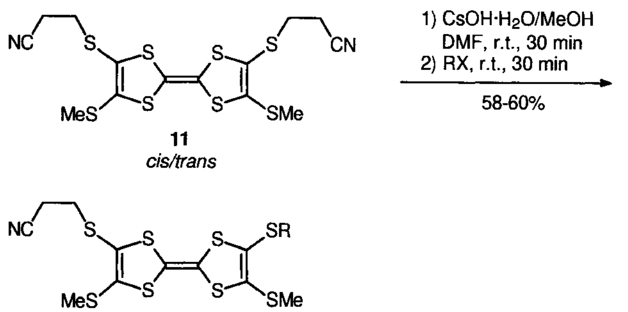


Figure 3. The coordination environment of the caesium ion.



An attempt was made to monodeprotect the pseudosymmetrical 2,6-bis(2-cyanoethylthio)-3,7-bis(methylthio)tetrathiafulvalene (**11**) (Scheme 7).[10] Despite much effort, we were only able to isolate the corresponding alkylated tetrathiafulvalenes 2-(2-cyanoethylthio)-3,6,7-tris(methylthio)tetrathiafulvalene (**8b**) and 2-(2-cyanoethylthio)-3,6(7)-bis(methylthio)-7(6)-(2-phenylethylthio)tetrathiafulvalene (**12**) in moderate yields after quenching with iodomethane and 2-phenylethyl bromide, respectively. The reason for the lack of selectivity in this system is that there are considerably less pronounced electrostatic effects between the two potential thiolate functions. The deprotection of this bis-protected tetrathiafulvalene dithiolate is therefore closer to the statistical distribution. This is consistent with the result obtained in the deprotection of **6a**.



8b, R = CH_3, X = I (60%)
12, R = CH_2CH_2Ph, X = Br (58%, *cis/trans*)

Scheme 7

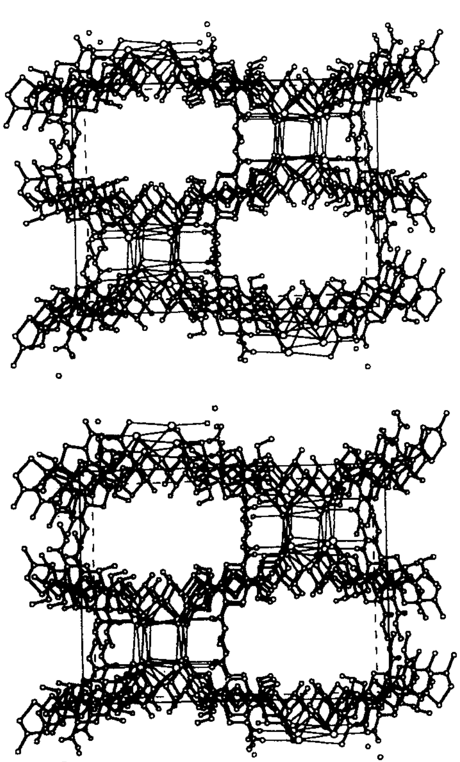


Figure 4. Stereo drawing of the unit cell of **10**. The thin lines represent contact distances between Cs^+ and (S_2).

The bis-protected tetrathiafulvalenes **6** serve as excellent building blocks in the syntheses of macrocyclic and oligomeric tetrathiafulvalenes.[10,16] The tetrathiafulvalenes **6** are ideal starting materials being the readily available and shelf-stable late intermediates that have been pursued by tetrathiafulvalene chemists for a long time. As the synthetic operations involved are very simple and give consistently high yields, we hope that chemists specialised outside the field of tetrathiafulvalene chemistry will begin to utilise the tetrathiafulvalene moiety as a general electron donor, for example in supramolecular assemblies.

All reactions involving tetrathiafulvalenes were carried out under an atmosphere of dry N_2. THF was distilled from Na/benzophenone immediately prior to use, MeCN was distilled from CaH_2 and MeOH from Mg. DMF was allowed to stand over molecular sieves (4Å) for at least 3d before use. All reagents were standard grade and used as received unless otherwise stated. Analytical TLC was performed on Merck DC-Alufolien Kieselgel 60 F_{254} 0.2 mm thickness. Column chromatography was performed with Merck Kieselgel (0.040–0.063 mm, 230–400 mesh ASTM) on a 400 mm × 60 mm Ø column using a volume of 400 mL silica gel. Mps were determined on a Büchi melting point apparatus and are uncorrected. Microanalyses were performed at the Microanalytical Laboratory, University of Copenhagen, or at the Microanalytical Laboratory, Leo Pharmaceuticals, Copenhagen. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC250 instrument at r.t. using TMS as internal standard. EI-MS spectra were recorded on a Varian MAT 311A instrument, while FAB-MS were recorded an a Kratos MS 50 TC using 3-nitrobenzyl alcohol as a matrix. IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer. Cyclic Voltammetry (CV) was carried out using CH_2Cl_2 as the solvent employing Et_4NPF_6 as supporting electrolyte, with a sweep rate of 100 mV · s^{-1}. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl.

4,5-Bis(2-cyanoethylthio)-1,3-dithiole-2-thione (2a); Typical Procedure for 2a–2f:

To a solution of bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate (**1**, 14.37 g, 0.02 mol) in MeCN (250 mL) was added 3-bromopropionitrile (13.40 g, 0.1 mol) and the mixture was refluxed for 1 h. The resulting solution was cooled to r.t. and the precipitated salt was filtered. The brown-yellow filtrate was concentrated in vacuo, the resulting product was redissolved in CH_2Cl_2 (250 mL) and washed with H_2O (4 × 200 mL), dried ($MgSO_4$) and the solvent removed in vacuo. Recrystallisation from toluene/petroleum ether (bp 100–140 °C) gave **2a** as long yellow needles; yield: 10.59 g (87 %); mp 83 °C.

^1H NMR ($CDCl_3$/TMS): $\delta = 3.16$ (t, $J = 6.8$ Hz, 4H), 2.80 (t, $J = 6.8$ Hz, 4H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 206.54, 133.25, 114.49, 29.26, 16.45$.

IR (KBr): $\nu = 2249$ (CN), 1072 cm^{-1} (C=S).

MS (EI): m/z (%) = 304 (M^+, 99).

Anal. $C_9H_8N_2S_5$ (304.5): calc. C 35.50, H 2.65, N 9.20; found C 35.54, H 2.63, N 9.12.

4,5-Bis(methylthio)-1,3-dithiole-2-thione (**2b**); recrystallisation from CH_2Cl_2/petroleum ether (bp 100–140 °C) gave **2b** as yellow needles; yield: 79 %; mp 100–101 °C (Lit.[17] 100–101 °C).

4,5-Bis(ethylthio)-1,3-dithiole-2-thione (**2c**); chromatographic purification (silica gel, CH_2Cl_2) through a short column gave **2c** as a dark yellow oil; yield: 4.07 g (82 %).

^1H NMR ($CDCl_3$/TMS): $\delta = 2.93$ (q, $J = 7.3$ Hz, 4H), 1.36 (t, $J = 7.3$ Hz, 6H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 211.25, 136.23, 30.88, 14.84$.

IR (KBr): $\nu = 1070$ cm^{-1} (C=S).

MS (EI): m/z (%) = 254 (M^+, 100).

Anal. $C_7H_{10}S_5$ (254.5): calc. C 33.04, H 3.96; found C 33.30, H 4.12.

4,5-(Ethylenedithio)-1,3-dithiole-2-thione (**2d**); recrystallisation from $CHCl_3$/EtOH gave **2d** as yellow needles; yield: 80%; mp 120–121 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.41$ (s, 4 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 208.07, 123.05, 29.85$.

MS (EI) m/z (%) = 224 (M^+, 100).

Anal. $C_5H_4S_5$ (224.4): calc. C 26.76, H 1.80; found C 26.79, H 1.88.

4,5-Bis(2-phenylethylthio)-1,3-dithiole-2-thione (**2e**); chromatographic purification (silica gel, CH_2Cl_2 cyclohexane 1:1) through a short column gave **2e** as a red oil; yield: 8.00 g (70%).

^{1}H NMR ($CDCl_3$/TMS): $\delta = 7.27$–7.14 (m, 10 H), 3.07 (m, 4 H), 2.94 (m, 4 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 210.61, 138.62, 135.87, 128.45, 127.89, 126.65, 37.57, 36.00$.

IR (KBr): $\nu = 1066\ cm^{-1}$ (C=S).

MS (EI): m/z (%) = 406 (M^+, 100).

Anal. $C_{19}H_{18}S_5$ (406.65): calc. C 56.12, H 4.46; found C 56.22, H 4.43.

4,5-Bis-(pentylthio)-1,3-dithiole-2-thione (**2f**); chromatographic purification (silica gel, CH_2Cl_2-cyclohexane 2:1) through a short column gave **2f** as a dark red oil; yield: 12.93 g (91%).

^{1}H NMR ($CDCl_3$/TMS): $\delta = 2.87$ (t, $J = 7.2$ Hz, 4 H), 1.67 (q, $J = 7.2$ Hz, 4 H), 1.5–1.3 (m, 8 H), 0.91 (t, $J = 6.9$ Hz, 6 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 211.32, 136.26, 36.69, 30.56, 29.28, 22.08, 13.83$.

IR (KBr): $\nu = 1068\ cm^{-1}$ (C=S).

MS (EI): m/z (%) = 338 (M^+, 100).

Anal. $C_{13}H_{22}S_5$ (338.6): calc. C 46.13, H 6.55; found C 46.32, H 6.53.

4,5-Bis(decylthio)-1,3-dithiole-2-thione (2g); Typical Procedure:
To a solution of 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (**3**, 7.52 g, 0.018 mol) in MeOH (100 mL) was slowly added a solution of sodium (1.08 g, 0.047 mol) in MeOH (50 mL), whereupon the solution turned dark red. The reaction mixture was stirred for an additional 30 min and 1-bromodecane (10.15 g, 0.046 mol) was added. The mixture was left overnight and the resulting yellow crystals were filtered and washed with H_2O (2 × 50 mL) and MeOH (2 × 10 mL); yield: 7.40 g (84%); mp 40 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 2.86$ (t, $J = 7.3$ Hz, 4 H), 1.66 (q, $J = 7.3$ Hz, 4 H), 1.5–1.2 (m, 28 H), 0.88 (t, $J = 6.8$ Hz, 6 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 211.30, 136.21, 36.64, 31.76, 29.53, 29.39, 29.36, 29.17, 28.95, 28.38, 22.55, 13.99$.

IR (KBr): $\nu = 1061\ cm^{-1}$ (C=S).

MS (EI): m/z (%) = 478 (M^+, 100).

Anal. $C_{23}H_{42}S_5$ (478.9): calc. C 57.69, H 8.84, S 33.47; found C 57.87, H 9.02, S 33.34.

4,5-Bis(octadecylthio)-1,3-dithiole-2-thione (**2h**); Prepared like **2g** with **3** (6.48 g, 0.016 mol) and 1-bromooctadecane (10.15 g, 0.046 mol). Recrystallisation from EtOAc gave **2h** as yellow crystals; yield: 10.54 g (94%); mp 77–78 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 2.86$ (t, $J = 7.2$ Hz, 4 H), 1.63 (q, $J = 7.3$ Hz, 4 H), 1.5–1.2 (m, 60 H), 0.88 (t, $J = 6.9$ Hz, 6 H).

IR (KBr): $\nu = 1061\ cm^{-1}$ (C=S).

MS (EI): m/z (%) = 702 (M^+, 100).

Anal. $C_{39}H_{74}S_5$ (703.3): calc. C 66.60, H 10.61; found C 66.39, H 10.61.

4-(2-Cyanoethylthio)-5-methylthio-1,3-dithiole-2-thione (2i):
Method A: To a solution of **4** (5.00 g, 0.013 mol) in degassed acetone (50 mL) was added MeI (7.5 g, 0.052 mol), and the dark red solution immediately changed colour to light yellow. The reaction mixture was stirred for 30 min and then purged with N_2 for 30 min (to evaporate the excess of MeI). The mixture was poured into H_2O (150 mL) and the resulting yellow powder was filtered off and washed with H_2O (50 mL) and Et_2O (20 mL). Recrystallisation from MeOH gave **2i** as long yellow needles; yield: 3.10 g (90%); mp 90–91 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.09$ (t, $J = 7.1$ Hz, 2 H), 2.76 (t, $J = 7.1$ Hz, 2 H), 2.56 (s, 3 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 209.96, 142.80, 117.08, 31.83, 18.92, 18.79$.

IR (KBr): $\nu = 2248$ (CN), $1055\ cm^{-1}$ (C=S).

MS (EI): m/z (%) = 265 (M^+, 100).

Anal. $C_7H_7NS_5$ (265.4): calc. C 31.67, H 2.66, N 5.28; found C 32.00, H 2.34, N 5.28.

Method B: To a solution of **2a** (1.21 g, 4 mmol) in degassed MeCN (60 mL) was added a solution of $CsOH \cdot H_2O$ (0.71 g, 4.2 mmol) in MeOH (6 mL) over a period of 30 min, whereupon the solution turned dark red. The mixture was stirred for an additional 30 min whereupon MeI (5.68 g, 40 mmol) was added. The reaction was stirred for 30 min, followed by purging with N_2 for 10 min. The yellow solution was concentrated in vacuo and the resulting solid was redissolved in CH_2Cl_2 (50 mL), washed with H_2O (3 × 50 mL), dried ($MgSO_4$) and the solvent removed in vacuo. Chromatographic separation (silica gel, CH_2Cl_2) gave **2i**; yield: 0.96 g (90%). The analytical data were identical with those above.

4-Methylthio-5-octadecylthio-1,3-dithiole-2-thione (2j):
To a solution of **2i** (1.00 g, 3.8 mmol) in MeOH (30 mL) was slowly added a solution of sodium (0.10 g, 4.3 mmol) in MeOH (10 mL), whereupon the solution turned dark red. The reaction mixture was stirred for an additional 30 min and a solution of 1-bromooctadecane (1.50 g, 4.4 mmol) in $CHCl_3$ (5 mL) was added. The mixture was left overnight and the resulting crystals were filtered and washed with H_2O (2 × 20 mL) and MeOH (2 × 10 mL) to give a yellow powder of analytically pure **2j**; yield: 1.30 g (74%); mp 52–53 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 2.86$ (t, $J = 7.2$ Hz, 2 H), 2.49 (s, 3 H), 1.66 (q, $J = 7.1$ Hz, 2 H), 1.5–1.2 (m, 30 H), 0.88 (t, $^3J_{(HH)} = 6.7$ Hz, 3 H).

IR (KBr): $\nu = 1070\ cm^{-1}$ (C=S).

MS (EI): m/z (%) = 464 (M^+, 100).

Anal. $C_{22}H_{40}S_5$ (464.9): calc. C 56.84, H 8.67; found C 56.81, H 8.64.

Caesium 5-(2-Cyanoethylthio)-2-thioxo-1,3-dithiole-4-thiolate (4):
Compound **2a** (1.52 g, 5 mmol) was dissolved in $CHCl_3$ (40 mL) and the mixture was purged for 15 min. To the mixture was added a solution of $CsOH \cdot H_2O$ (0.84 g, 5 mmol) in MeOH (4 mL) during 30 min and the yellow caesium salt soon started to precipitate. The mixture was stirred for an additional 1 h. The salt was filtered and washed with $CHCl_3$ (10 mL) and Et_2O (2 × 40 mL) to give a yellow powder of analytically pure **4**; yield: 1.65 g (86%); mp 136–138 °C.

^{1}H NMR (CD_3OD): $\delta = 3.22$ (t, $J = 6.9$ Hz, 2 H), 2.93 (t, $J_{(H,H)} = 6.9$ Hz, 2 H).

^{13}C NMR (CD_3OD): $\delta = 215.18, 168.64, 120.28, 115.79, 31.95, 19.31$.

IR (KBr): $\nu = 2245$ (CN), $1059\ cm^{-1}$ (C=S).

Anal. $C_6H_4CsNS_5$ (383.3): calc. C 18.80, H 1.05, N 3.65; found C 19.09, H 1.25, N 3.61.

2,3-Bis(2-cyanoethylthio)-6,7-bis(methylthio)tetrathiafulvalene (6b); Typical Procedure for 6b–h and 6j:
A suspension of compound **2b** (3.46 g, 0.015 mol) and **5** (3.40 g, 0.015 mol) in freshly distilled $P(OEt)_3$ under an atmosphere of N_2 was heated to 120 °C. After 10–15 min a dark-orange precipitate started to form and the mixture was stirred for an additional 1–1.5 h and then allowed to cool to r.t. MeOH (30 mL) was added, the product was filtered and washed with MeOH (3 × 50 mL) and dried in vacuo. The resulting product was chromatographed (silica gel, CH_2Cl_2) and isolation of the middle fraction ($R_f \sim 0.5$) gave the cross-coupling product.[29] The solvent was removed in vacuo and recrystallisation from CH_2Cl_2/petroleum ether (bp 80–100 °C) or toluene/petroleum ether (bp 80–100 °C) gave **6b** as orange needles; yield: 3.76 g (68%); mp 113–114 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.09$ (t, $J = 7.1$ Hz, 4 H), 2.74 (t, $J = 7.1$ Hz, 4 H), 2.44 (s, 6 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 127.93$, 127.49, 117.33, 114.25, 107.63, 31.23, 19.11, 18.81.

IR (KBr): $\nu = 2251$ cm^{-1} (CN).

MS (EI): m/z (%) = 466 (M^+, 100).

Anal. $C_{14}H_{14}N_2S_8$ (466.8): calc. C 36.02, H 3.02, N 6.00; found C 36.05, H 2.93, N 5.99.

2,3-Bis(2-cyanoethylthio)-6,7-bis(ethylthio)tetrathiafulvalene (**6c**); chromatography (silica gel, CH_2Cl_2) and recrystallization from toluene/petroleum ether (bp 80–100 °C) gave coupling in toluene/ $P(OEt)_3$ **6c**; yield: 48 %; mp 89–90 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.09$ (t, $J = 7.1$ Hz, 4 H), 2.86 (q, $J = 7.4$ Hz, 4 H), 2.74 (t, $J = 7.1$ Hz, 4 H), 1.33 (t, $J = 7.3$ Hz, 6 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 128.00$, 127.92, 114.74, 106.66, 117.38, 31.27, 30.56, 18.90, 15.05.

IR (KBr): $\nu = 2250$ cm^{-1} (CN).

MS (EI): m/z (%) = 494 (M^+, 80).

Anal. $C_{16}H_{18}N_2S_8$ (494.8): calc. C 38.84, H 3.67, N 5.66; found C 38.79, H 3.67, N 5.59.

2,3-Bis(2-cyanoethylthio)-6,7-(ethylenedithio)tetrathiafulvalene (**6d**); chromatography (silica gel, CH_2Cl_2) and recrystallisation from toluene/petroleum ether (bp 80–100 °C) gave **6d**; yield: 48 %; mp 141–142 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.30$ (s, 4 H), 3.08 (t, $J = 7.1$ Hz, 4 H), 2.74 (t, $J = 7.1$ Hz, 4 H).

^{13}C NMR (DMSO-d_6): $\delta = 127.51$, 118.63, 112.89, 112.25, 108.37, 30.82, 29.48, 18.08.

IR (KBr): $\nu = 2247$ cm^{-1} (CN).

MS (EI): m/z (%) = 464 (M^+, 16).

Anal. $C_{14}H_{12}N_2S_8$ (464.7): calc. C 36.18, H 2.60, N 6.03; found C 36.30, H 2.57, N 6.13.

2,3-Bis(2-cyanoethylthio)-6,7-bis(2-phenylethylthio)tetrathiafulvalene (**6e**); chromatography (silica gel, CH_2Cl_2) and recrystallisation from CH_2Cl_2/petroleum ether (bp 80–100 °C) gave **6e**; yield: 64 %; mp 134 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 7.23$ (m, 10 H), 3.09 (t, $J = 6.8$ Hz, 4 H), 3.06 (m, 4 H), 2.94 (m, 4 H), 2.74 (t, $J = 6.8$ Hz, 4 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 139.29$, 128.48, 128.43, 127.92, 127.69, 126.57, 117.26, 114.23, 107.86, 37.30, 36.14, 31.18, 18.81.

IR (KBr): $\nu = 2251$ cm^{-1} (CN).

MS (EI): m/z (%) = 646 (M^+, 10).

Anal. $C_{28}H_{26}N_2S_8$ (647.0): calc. C 51.98, H 4.05, N 4.33, S 39.64; found C 52.30, H 3.78, N 4.18, S 39.75.

2,3-Bis(2-cyanoethylthio)-6,7-bis(pentylthio)tetrathiafulvalene (**6f**); chromatography (silica gel, CH_2Cl_2/cyclohexane 2:1) gave analytically pure **6f**; yield: 64 %; mp 93–94 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.09$ (t, $J = 7.1$ Hz, 4 H), 2.82 (t, $J = 7.2$ Hz, 4 H), 2.74 (t, $J = 7.1$ Hz, 4 H), 1.66 (q, $J = 7.0$ Hz, 4 H), 1.5–1.2 (m, 8 H), 0.91 (t, $J = 6.8$ Hz, 6 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 127.81$, 127.65, 117.30, 114.52, 106.34, 36.17, 31.09, 30.47, 29.21, 22.02, 18.75, 13.81.

IR (KBr): $\nu = 2251$ cm^{-1} (CN).

MS (EI): m/z (%) = 578 (M^+, 44).

Anal. $C_{22}H_{30}N_2S_8$ (579.0): calc. C 46.79, H 5.31, N 4.96; found C 46.39, H 5.24, N 4.77.

2,3-Bis(2-cyanoethylthio)-6,7-bis(decylthio)tetrathiafulvalene (**6g**); chromatography (silica gel, CH_2Cl_2) and recrystallisation from toluene/petroleum ether (bp 80–100 °C) coupling in toluene/$P(OEt)_3$ gave **6g**; yield: 48 %; mp 110–111 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.08$ (t, $J = 7.2$ Hz, 4 H), 2.82 (t, $J = 7.2$ Hz, 4 H), 2.73 (t, $J = 7.2$ Hz, 4 H), 1.63 (q, $J = 7.3$ Hz, 4 H), 1.5–1.2 (m, 28 H), 0.88 (t, $J = 6.8$ Hz, 6 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 128.01$, 127.89, 122.31, 117.36, 106.50, 36.38, 31.88, 31.26, 29.70, 29.52, 29.50, 29.29, 29.11, 28.50, 22.66, 18.90, 14.08.

IR (KBr): $\nu = 2251$ cm^{-1} (CN).

MS (FAB): m/z (%): 718 (M^+, 100).

Anal. $C_{32}H_{50}N_2S_8$ (719.2): calc. C 53.44, H 7.01, N 2.89, S 35.66; found C 53.36, H 7.05, N 3.99, S 35.52.

2,3-Bis(2-cyanoethylthio)-6,7-bis(octadecylthio)tetrathiafulvalene (**6h**); chromatography (silica gel, $CHCl_3$) and recrystallisation from toluene/petroleum ether (bp 80–100 °C) gave **6h**; yield: 49 %; mp 107 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.08$ (t, $J = 7.2$ Hz, 4 H), 2.82 (t, $J = 7.2$ Hz, 4 H), 2.78 (t, $J = 7.2$ Hz), 4 H), 1.63 (q, $J = 7.3$ Hz, 4 H), 1.5–1.2 (m, 60 H), 0.88 (t, $J = 6.8$ Hz, 6 H).

IR (KBr): $\nu = 2253$ cm^{-1} (CN).

MS (FAB): m/z (%) = 940 (M^+, 100).

Anal. $C_{48}H_{82}N_2S_8$ (943.7): calc. C 61.09, H 8.76, N 2.97; found C 60.96, H 8.66, N 3.11.

2,3-Bis(2-cyanoethylthio)-6-methylthio-7-(octadecylthio)tetrathiafulvalene (**6j**); chromatography (silica gel, CH_2Cl_2) and recrystallisation from EtOH gave **6j**; yield: 51 %; mp 104–105 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.08$ (t, $J = 7.0$ Hz, 4 H), 2.82 (t, $J = 7.2$ Hz, 2 H), 2.73 (t, $J = 7.0$ Hz, 4 H), 2.43 (s, 3 H), 1.6–1.2 (m, 32 H), 0.88 (t, $J = 6.7$ Hz, 3 H).

IR (KBr): $\nu = 2251$ cm^{-1} (CN).

MS (EI): m/z (%) = 704 (M^+, 10).

Anal. $C_{31}H_{48}N_2S_8$ (705.2): calc. C 52.80, H 6.86, N 3.97, S 36.37; found C 52.79, H 6.62, N 3.98, S 36.42.

2,3-Bis(2-cyanothylthio)-6,7-bis(methoxycarbonyl)tetrathiafulvalene (6k):

A mixture 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-one (**7**) and 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione (**2a**) was subjected to cross coupling as described above. Chromatography (silica gel, CH_2Cl_2/EtOAc 19:1) and recrystallisation from MeOH gave **6k**; yield: 47 %; mp 103–104 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.85$ (s, 6 H), 3.10 (t, $J = 6.9$ Hz, 4 H), 2.75 (t, $J = 6.9$ Hz, 4 H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 159.59$, 131.81, 128.19, 117.30, 112.10, 109.45, 53.39, 31.33, 18.84.

IR (KBr): $\nu = 2251$ cm^{-1} (CN).

MS (EI): m/z (%) = 490 (M^+, 100).

Anal. $C_{16}H_{14}N_2O_4S_6$ (490.7): calc. C 39.17, H 2.88, N 5.71; found C 39.39, H 2.92, N 5.74.

Monodeprotection and Re-alkylation to 8a–h, 8j and 8k:

The appropriate tetrathiafulvalene (1 mmol) was dissolved in dry DMF (40 mL) and degassed with N_2 for 30 min. A solution of $CsOH \cdot H_2O$ (0.168 g, 1.05 mmol) in dry MeOH (5 mL) was added dropwise to the mixture over a period of 30 min. During the addition the solution turned to a slightly darker orange colour. After stirring for an additional 30 min, MeI (1 mL ~ 2.28 g, 16 mmol) was added in one portion. The reaction mixture was stirred for 30 min and then degassed with N_2 for 30 min to evaporate the excess of MeI. The solvent was removed in vacuo and the resulting orange compound was purified by column chromatography (silica gel, CH_2Cl_2) to give the methylthio-substituted tetrathiafulvalene as an analytically pure compound.

2,3,6-Tris(2-cyanoethylthio)-7-methylthiotetrathiafulvalene (**8a**); yield: 50 %; mp 146–148 °C [CH_2Cl_2/petroleum ether (bp 80–100 °C)].

^{1}H NMR (DMSO-d_6): $\delta = 3.15$ (m, 6 H), 2.88 (m, 6 H), 2.48 (s, 3 H).

^{13}C NMR (DMSO-d_6): $\delta = 127.18$, 118.74, 109.03, 30.82, 18.45, 18.15.

IR (KBr): $\nu = 2251$ cm^{-1} (CN).

MS (EI): m/z (%) = 505 (M^+, 100).

Anal. $C_{16}H_{15}N_3S_8$ (505.8): calc. C 37.99, H 2.99, N 8.31; found C 38.05, H 3.05, N 8.25.

2-(2-Cyanoethylthio)-3,6,7-tris(methylthio)tetrathiafulvalene (**8b**); yield: 94%; mp 102–104 °C (toluene/cyclohexane).

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.02$ (t, $J = 7.2$ Hz, 2H), 2.70 (t, $J = 7.2$ Hz, 2H), 2.47 (s, 3H), 2.43 (s, 6H).

IR (KBr): $\nu = 2248$ cm^{-1} (CN).

MS (EI): m/z (%) = 427 (M$^+$, 100).

Anal. $C_{12}H_{13}NS_8$ (427.7): calc. C 33.70, H 3.06, N 3.27; found C 33.89, H 3.13, N 3.29.

2-(2-Cyanoethylthio)-6,7-bis(ethylthio)-3-methylthiotetrathiafulvalene (**8c**); yield: 95%; mp 81–82 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.02$ (t, $J = 7.2$ Hz, 3H), 2.86 (q, $J = 7.4$ Hz, 4H), 2.74 (t, $J = 7.1$ Hz, 2H), 2.47 (s, 3H), 1.33 (t, $J = 7.4$ Hz, 6H).

IR (KBr): $\nu = 2250$ cm^{-1} (CN).

MS (FAB): m/z (%) = 455 (M$^+$, 100).

Anal. $C_{14}H_{17}NS_8$ (455.8): calc. C 36.89, H 3.76, N 3.07; found C 37.20, H 3.86, N 3.04.

2-(2-Cyanoethylthio)-6,7-(ethylenedithio)-3-methylthiotetrathiafulvalene (**8d**); yield: 93%; mp 109–110 °C [CH_2Cl_2/petroleum ether (bp 80–100 °C)].

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.30$ (s, 4H), 3.02 (t, $J = 7.1$ Hz, 3H), 2.69 (t, $J = 7.1$ Hz, 2H), 2.47 (s, 3H).

IR (KBr): $\nu = 2247$ cm^{-1} (CN).

MS (EI): m/z (%) = 425 (M$^+$, 100).

Anal. $C_{12}H_{11}NS_8$ (425.7): calc. C 33.86, H 2.60, N 3.29; found C 33.86, H 2.67, N 3.37.

2-(2-Cyanoethylthio)-3-methylthio-6,7-bis(2-phenylethylthio)tetrathiafulvalene (**8e**); yield: 95%; mp 129–129.5 °C [CH_2Cl_2/petroleum ether (bp 80–100 °C)].

^{1}H NMR ($CDCl_3$/TMS): $\delta = 7.25$ (m, 10H), 3.05 (m, 6H), 2.94 (m, 4H), 2.70 (t, $J = 7.1$ Hz, 2H), 2.48 (s, 3H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 139.45$, 135.14, 128.56, 127.88, 127.66, 126.66, 120.13, 117.49, 37.40, 36.29, 31.22, 19.09, 18.75.

IR (KBr): $\nu = 2250$ cm^{-1} (CN).

MS (EI): m/z (%) = 607 (M$^+$, 18).

Anal. $C_{26}H_{25}N_1S_8$ (608.0): calc. C 51.37, H 4.14, N 2.30; found C 51.31, H 4.24, N 2.36.

2-(2-Cyanoethylthio)-3-methylthio-6,7-bis(pentylthio)tetrathiafulvalene (**8f**); chromatography [silica gel, CH_2Cl_2/petroleum ether (bp 60–80 °C) 2:1]; yield: 85%; mp 84 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.02$ (t, $J = 7.3$ Hz, 2H), 2.82 (t, $J = 7.2$ Hz, 4H), 2.70 (t, $J = 7.2$ Hz, 2H), 2.48 (s, 3H), 1.66 (q, $J = 7.1$ Hz, 4H), 1.5–1.2 (m, 8H), 0.91 (t, $J = 6.9$ Hz, 6H).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 135.07$, 127.94, 127.65, 120.07, 117.50, 112.86, 108.15, 36.29, 31.18, 30.62, 29.38, 22.15, 19.04, 18.71, 13.91.

IR (KBr): $\nu = 2250$ cm^{-1} (CN).

MS (EI): m/z (%) = 539 (M$^+$, 100).

Anal. $C_{20}H_{29}NS_8$ (540.0); calc. C 44.51, H 5.37, N 2.59; found C 44.74, H 5.47, N 2.53.

2-(2-Cyanoethylthio)-6,7-bis(decylthio)-3-methylthiotetrathiafulvalene (**8g**); deprotection was carried out in a mixture of DMF (40 mL) and THF (10 mL); yield: 95%; mp 92 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.08$ (t, $J = 7.2$ Hz, 2H), 2.82 (t, $J = 7.2$ Hz, 4H), 2.73 (t, $J = 7.2$ Hz, 2H), 2.46 (s, 3H), 1.63 (q, $J = 7.3$ Hz, 4H), 1.5–1.2 (m, 28H), 0.88 (t, $J = 6.8$ Hz, 6H).

IR (KBr): $\nu = 2249$ cm^{-1} (CN).

MS (FAB): m/z (%) = 679 (M$^+$, 100).

Anal. $C_{30}H_{49}NS_8$ (680.2): calc. C 52.97, H 7.26, N 2.06; found C 52.99, H 7.29, N 2.06.

2-(2-Cyanoethylthio)-3-methylthio-6,7-bis(octadecylthio)tetrathiafulvalene (**8h**); deprotection was carried out in THF (60 mL) and the residue was chromatographed (silica gel, $CHCl_3$); yield: 86%; mp 95–96 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.02$ (t, $J = 7.2$ Hz, 2H), 2.82 (t, $J = 7.2$ Hz, 4H), 2.73 (t, $J = 7.2$ Hz, 2H), 2.46 (s, 3H), 1.63 (q, $J = 7.3$ Hz, 4H), 1.5–1.2 (m, 60H), 0.88 (t, $J = 6.8$ Hz, 6H).

IR (KBr): $\nu = 2251$ cm^{-1} (CN).

MS (FAB): m/z (%) = 903 (M$^+$, 100).

Anal. $C_{46}H_{81}NS_8$ (904.6): calc. C 61.07, H 9.02, N 1.55; found C 61.44, H 9.11, N 1.55.

2-(2-Cyanoethylthio)-3,7(6)-bis(methylthio)-6(7)-(octadecylthio)tetrathiafulvalene (**8j**); deprotection was carried out in a mixture of DMF (40 mL) and THF (20 mL) and chromatographed [silica gel, CH_2Cl_2/petroleum ether (bp 60–80 °C) 3:1]; yield: 89%; mp 89–90 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.02$ (t, $J = 7.0$ Hz, 2H), 2.81 (t, $J = 7.1$ Hz, 2H), 2.70 (t, $J = 7.2$ Hz, 2H), 2.46 (2 s, 3H, *c/t* SMe), 2.42 (2 s, 3H, *c/t* SMe), 1.6–1.2 (m, 32H), 0.88 (t, $J = 6.7$ Hz, 6H).

IR (KBr): $\nu = 2249$ cm^{-1} (CN).

MS (FAB): m/z (%) = 665 (M$^+$, 100).

Anal. $C_{29}H_{47}NS_8$ (666.2): calc. C 52.29, H 7.11, N 2.10; found C 52.60, H 7.21, N 2.13.

2-(2-Cyanoethylthio)-6,7-bis(methoxycarbonyl)-3-methylthiotetrathiafulvalene (**8k**); yield: 89%; mp 78–79 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.85$ (s, 6H), 3.02 (t, $J = 7.1$ Hz, 2H), 2.70 (t, $J = 7.1$ Hz, 2H), 2.47 (s, 3H).

IR (KBr): $\nu = 2250$ cm^{-1} (CN).

MS (EI): m/z (%) = 451 (M$^+$, 100).

Anal. $C_{14}H_{13}NO_4S_6$ (451.6): calc. C 37.23, H 2.90, N 3.10; found C 37.22, H 2.90, N 3.06.

Monodeprotection of the Pseudo-Symmetrical Bis-Protected Tetrathiafulvalene 11 and Re-Alkylation to 8b and 12:
The general procedure for monodeprotection described above was used.

2-(2-Cyanoethylthio)-3,6,7-tris(methylthio)tetrathiafulvalene (**8b**); yield: 60%. The analytical data were identical with those reported above.

2-(2-Cyanoethylthio)-3,6(7)-bis(methylthio)-7(6)-(2-phenylethylthio)tetrathiafulvalene (**10**); recrystallisation from $CHCl_3$/petroleum ether (bp 60–80 °C); yield: 58%; mp 96.5–97 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 7.3$–7.1 (m, 5H), 3.1–2.9 (m, 6H), 2.70 (t, $J = 7.2$ Hz, 2H), 2.47 (s, 3H), 2.43 (s, 3H).

IR (KBr): $\nu = 2251$ cm^{-1} (CN).

MS (EI): m/z (%) = 517 (M$^+$, 100).

Anal. $C_{19}H_{19}NS_8$ (517.8): calc. C 44.07, H 3.70, N 2.70; found C 44.08, H 3.65, N 2.55.

Crystal data for compound **10**: Cs^+, $C_{12}H_9O_6S_5^-$, M = 542.46, orthorhombic, space group Pccn (from Weissenberg films), a = 20.677(3), b = 26.797(3), c = 8.149(3) Å, V = 4545(3) Å^3, Z = 8, $D_c = 1.585$ g · cm^{-3}. Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 20.8$ cm^{-1}, F(000) = 2112. The crystals are black needles. A crystal fragment (cut) with dimensions 0.03 × 0.13 × 0.33 mm was used for X-ray data collection at 296 K on a Enraf-Nonius CAD4F diffractometer, using Mo radiation and a graphite monochromator. The cell parameters were obtained from setting angles from 25 reflections in the range $8.27° < \theta < 13.24°$. A total of 2270 independent reflections were measured in the range of $2.0° < \theta < 25.0°$, 1078 were considered as observed [$I > 2.5\sigma(I)$]. The data were corrected for Lorentz and polarization effects and decay. Absorption correction was applied. The transmission factor varied between 0.761 and 0.934. The structure was solved by direct methods using the programme SHELXS86.[30] Full-matrix least squares refinements and geometric calculations were performed with the Xtal3.2 program system.[31] The final R indices are R = 0.127 and $R_w = 0.121$. The atoms O13,O14 were refined isotropically, the other atoms anisotropically. Two independent caesium ion positions could be refined with a reasonable result and were associated with the population parameters 0.64(1) and 0.19(1), respectively. No H-atoms were localized. The maximum final shift/e.s.d. was 2.46, the average final shift/e.s.d. was 0.151. Min, max values in final difference electron density maps were -1.40 eÅ^{3} and 1.83 eÅ^{3}. Atomic scattering factors were taken from ref.[32]

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