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Synthesis and Characterization of Functionalized Ethylenediselenotetrathiafulvalenes: a Comparative Study with their All-Sulfur Analogues

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Abstract: The synthesis of the first monofunctionalized and some new difunctionalized ethylenediseleno-TTF (EDS-TTF) derivatives is described, including systems with alcohol, ester and aldehyde substituents. The mass spectrometric behaviour of these compounds has been studied for the first time and a comparative electrochemical study with their all-sulfur analogues has been carried out.

INTRODUCTION

The chemistry of tetrathiafulvalene (TTF) and its derivatives [1] has been at the forefront of research in the field of organic conductors for the last twenty five years.[2] Most of the organic superconductors reported to date are radical-cation salts derived from bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), and the study of structure-property relationships in these salts has established, among many other subtle factors, the important role played by the sulfur atoms at the periphery of the TTF core.[2,3] Thus, it is not surprising that interest in the synthesis of new multichalcogen π-electron donors remains unabated. One of the structural modifications carried out in this respect involves the substitution of the outer S atoms of BEDT-TTF by larger, more polarizable, Se atoms, with a view to enhancing the dimensionality in the transport properties of derived charge-transfer salts.[4] In this context, (BEDS-TTF)$_2$X [5] and, more recently, (EDS-TTF)$_2$X [6] salts have been prepared and studied. [BEDS-TTF: bis(ethylenediseleno)tetrathiafulvalene; EDS-TTF: ethylenediselenotetrathiafulvalene].

In this work we focus on the synthesis and characterization of the first monofunctionalized, and new difunctionalized, EDS-TTF derivatives. These compounds are interesting because: a) unsymmetrical π-donors are now known to afford superconducting radical-cation salts [2a] and b) the presence of functional groups in their structures allows incorporation into other supramolecular assemblies, such as Langmuir-Blodgett films.[7] Compounds **7** and **11** are especially noteworthy in that they possess hydroxymethyl groups which can engage in hydrogen-bonding, a factor whose importance in the field of organic conductors has recently been reviewed.[1a] Moreover, the all-sulfur analogue of **7** has given rise to charge-transfer salts with κ-phase structures.[8]

Besides the preparation of new functionalized derivatives **6**, **7**, **10**, **11** and **12**, we report improved syntheses of thione **3** and diester **5**, and an alternative route to EDS-TTF (**9**), together with the first mass spectral study of EDS-TTF derivatives. The electrochemical properties of the new π-donors have been studied by cyclic voltammetry and their redox potentials are compared with those of the corresponding EDT-TTF analogues. The gas phase π-donor abilities of both series of compounds have also been evaluated by *ab initio* calculations. Preliminary results concerning a charge-transfer complex of alcohol **7** with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) are also reported.

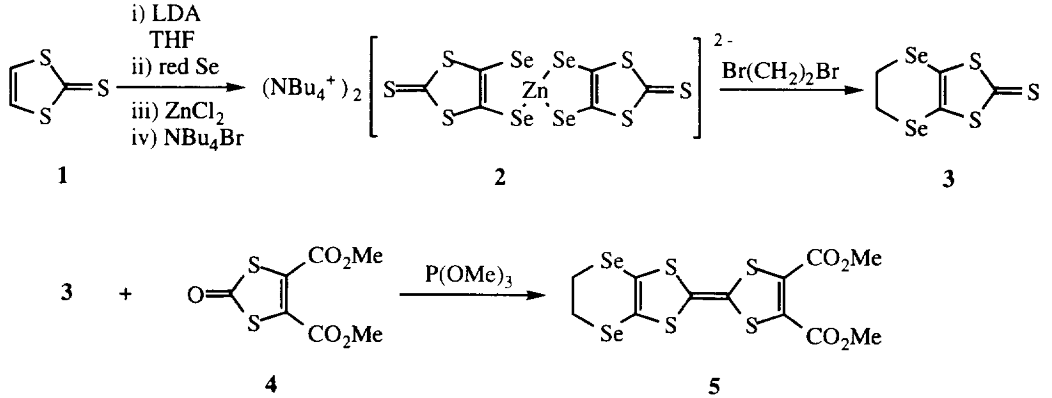
RESULTS AND DISCUSSION

Synthesis

The starting material in our synthesis of functionalized EDS-TTF derivatives was 4,5-ethylenediseleno-1,3-dithiole-2-thione **3**. The obvious entry to 4,5-bis(alkylseleno)-1,3-dithiole-2-thiones involves the lithiation of vinylene trithiocarbonate **1**, followed by insertion of elemental selenium, to generate the corresponding 4,5-bis(lithioseleno) derivative. Unfortunately, the alkylation of this intermediate is moderately successful only when alkyl halides,[9] but not alkylene dihalides, are used.[5] The main reasons for this drawback seem to be competing intermolecular alkylation reactions and formation of Se-Se bonds, both leading to polymeric by-products. Similar difficulties have been noted in the treatment of tetrakis(lithioseleno)TTF with 1,2-dibromoethane [10,11] and only extensive modification of the reaction conditions [4] or the use of blocking groups [10] have led to successful syntheses of BEDS-TTF.

Keeping these precedents in mind, we turned our attention to compounds of the type $(NBu_4)_2$ [M(dsit)$_2$] (dsit = 1,3-dithiole-2-thione-4,5-diselenolate), which are shelf-stable equivalents of the desired lithium diselenolates. Although $(NBu_4)_2$ [Ni(dsit)$_2$] was the first salt of this series to be prepared, [12-16] we found that the corresponding zincate salt **2** [17-19] was a convenient starting material and we prepared it according to the method of Olk *et al.* [17] using red selenium. Contrary to a previous report, [19] we advocate the use of the red form of selenium[16] instead of the grey one, since in our hands, the former results in higher yields, no doubt because of its higher reactivity.

Treatment of **2** with excess 1,2-dibromoethane in refluxing acetonitrile led to compound **3** in 78% yield (Scheme 1). This procedure compares favourably with other related methods for preparing **3** in that: i) no prior treatment of the dsit derivative with LiBr is necessary, [13,14] and ii) it gives the highest overall yield reported to date [18,19] for the conversion of **1** to **3** (55%).

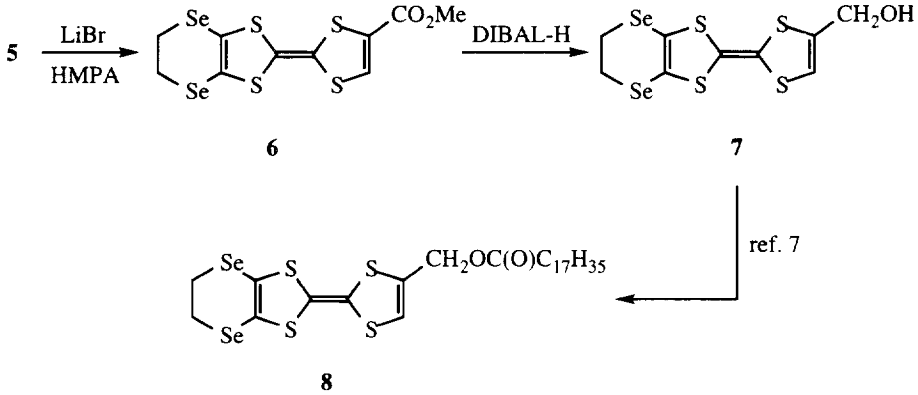


Scheme 1

The unsymmetrical compound **5** [18] looked promising for the preparation of the desired functionalized EDS-TTF derivatives, and it was synthesized by coupling of **3** and **4** [20] in the presence of trimethyl phosphite in 41% yield (Scheme 1) after separation from the corresponding symmetrical products.

It is worth noting that this is the first time that thione **3** has been used to prepare an EDS-TTF derivative (including BEDS-TTF), since all previous examples of phosphite-mediated coupling in this series have been carried out with the corresponding 2-oxone [5,6a,13,14]. Moreover, the use of **3** in the preparation of **5** is advantageous, since cross-coupling of 4,5-ethylenediseleno-1,3-dithiol-2-one and 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione affords the desired compound in 20% yield only. [18]

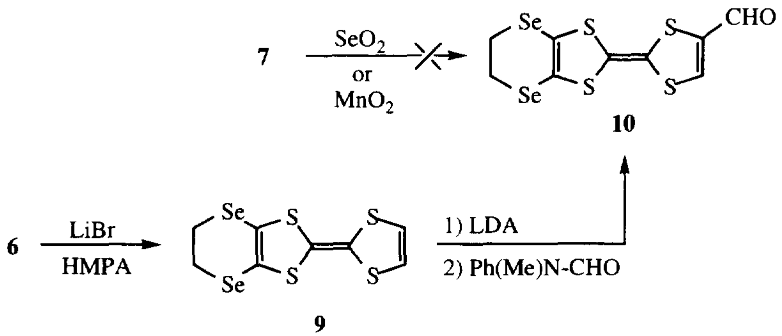
Selective monodecarbomethoxylation of **5** with LiBr in HMPA gave the first monofunctionalized EDS-TTF derivative (**6**) [18] in very good yield (87%) (Scheme 2). Careful control of the reaction conditions in this step was essential for obtaining pure compound **6** (see experimental).



Scheme 2

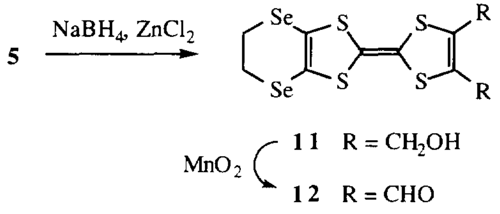
In turn, the reduction of **6** with DIBAL-H afforded alcohol **7** (64%), which is a good candidate for forming charge-transfer salts (*vide infra*). Esterification of **7** with octadecanoyl chloride gave the first amphiphilic EDS-TTF **8** (56% yield), Langmuir-Blodgett films of which have been assembled onto solid substrates and studied.[7]

Starting from **7** we tried to synthesize formyl derivative **10** *via* oxidation with MnO_2 [20b] or SeO_2, a method which, in our hands, has proved successful in the preparation of a number of tetrathiafulvalenecarbaldehydes. [21-23] However, this approach was unsuccessful, and a different route, taking advantage of our experience in the synthesis of other formyl-TTF derivatives *via* lithiation/formylation, [21,23,24] was applied (Scheme 3). We first prepared the parent compound, EDS-TTF (**9**). Its synthesis was carried out starting from ester **6** since, in our hands, this method gave better results, concerning isolation and purification of the final product, than the one-pot double decarbomethoxylation of **5**. [18] This approach constitutes a useful alternative to the previously reported one-pot synthesis of EDS-TTF from TTF itself, which gives compound **9** albeit in low yield (18%). [25] Attempted lithiation of **9** was hindered by its low solubility in both ether and THF. However, using the conditions reported previously for lithiation of EDT-TTF, [22b,26] (LDA in THF at -80°C) followed by addition of *N*-methylformanilide, we obtained formyl derivative **10** in 30% yield.



Scheme 3

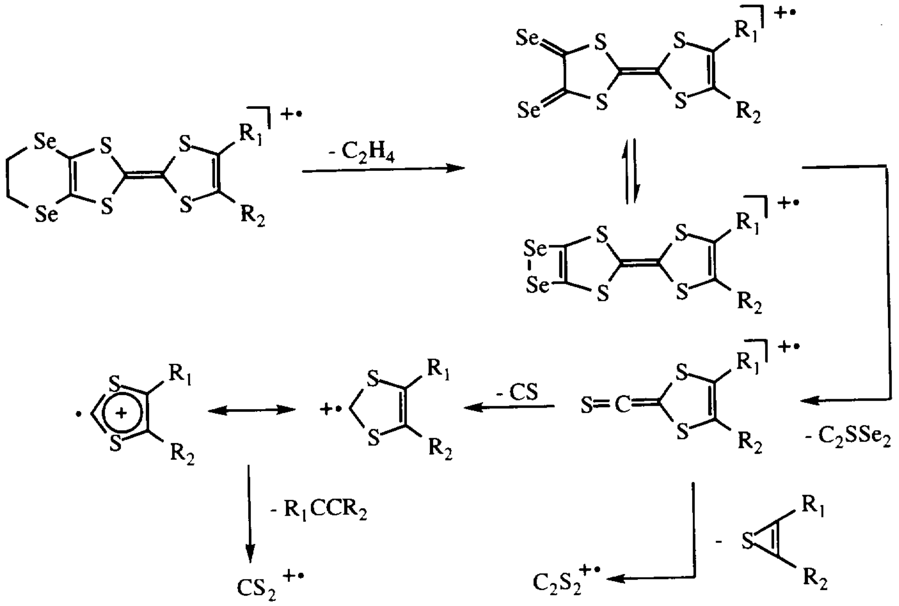
New difunctionalized EDS-TTF derivatives [27] **11** and **12** were prepared according to Scheme 4. The ester groups of compound **5** were smoothly reduced by reaction with sodium borohydride in the presence of zinc chloride to afford dialcohol **11** (92%), which, in turn, gave the dialdehyde **12** (39%) upon treatment with manganese dioxide.



Scheme 4

Mass Spectrometry

The synthesis of the new tetrathiafulvalenes herein reported offers the opportunity of studying the mass spectrometric behaviour of EDS-TTF derivatives for the first time. Their mass spectra show common features to those of other tetrathiafulvalenes.[28] Furthermore, the fragmentation pathways depicted in Scheme 5 are nearly identical to those reported for similar EDT-TTF derivatives.[29] Ethylene extrusion *via* a retro-Diels-Alder reaction constitutes the main fragmentation channel of molecular ions, and successive losses of C_2SSe_2 and CS give rise to stable dithiolium radical-ions, which are characteristic fragments of the TTF moiety. The ease of elimination of selenium, compared with that of sulfur in analogous compounds, [30] is responsible for the high abundance of $Se_2^{+\cdot}$ radical-ions, that has no parallel in the EDT-TTF series.[29]



Scheme 5

Cyclic Voltammetry

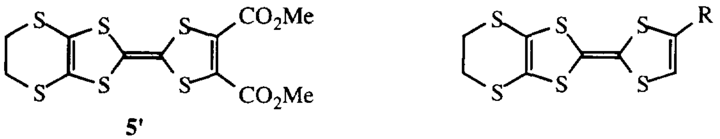
The solution redox properties of some of the newly prepared EDS-TTF derivatives have been studied by cyclic voltammetry in acetonitrile solution. The data are collected in Table 1, where BEDS-TTF and BEDT-TTF have been included for comparison (see also Figure 1). All the compounds studied show two, separate, reversible, one-electron oxidation waves. As expected, the half-wave potentials of these donors are higher than those of TTF itself ($E_1^{1/2}$ = 0.35 V; $E_2^{1/2}$ = 0.74 V) measured under the same conditions.

Table 1. Cyclic Voltammetric Data [a]

Compound	$E_1^{1/2}$	$E_2^{1/2}$	Compound	$E_1^{1/2}$	$E_2^{1/2}$
9	0.41	0.74	**9'**	0.43	0.75
7	0.41	0.73	**7'**	0.43	0.74
6	---[b]	---[b]	**6'**	0.56	0.87
10[c]	0.55	0.85	**10'**	0.59	0.91
5	0.62	0.94	**5'**	0.64	0.95
BEDS-TTF	0.48	0.77	**BEDT-TTF**	0.52	0.78

[a] In volts. 0.1 M TBA PF_6 / MeCN *vs*. Ag/AgCl, scan rate 200 mV s^{-1}. Working electrode: glassy carbon. Counter electrode: Pt. [b] Insoluble in MeCN, CH_2Cl_2 and DMF. [c] Data obtained in MeCN / $CHCl_3$ (5:1 v/v).

It is worth noting that, although the redox potentials of BEDS-TTF have been reported, [10,11,13,14] the cyclic voltammetry of EDS-TTF and its derivatives have not been described previously. Thus, it was of interest to carry out a comparative study with the corresponding EDT-TTF derivatives to explore the effect of: a) the substitution of Se for S and b) the substituents on the TTF moiety. To that end, EDT-TTF (**9'**) [20b] and its derivatives **5'**,[31] **6'**,[32] **7'**,[32] and **10'** [22] were prepared (Fig. 1). (For a detailed procedure for the synthesis of **10'** see the experimental section).

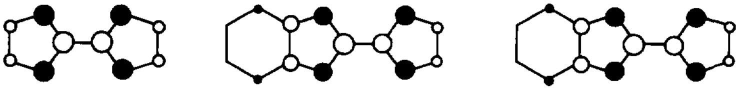


5'

R	H	CH_2OH	CO_2Me	CHO
Compound	**9'**	**7'**	**6'**	**10'**

Figure 1

From Table 1 it can be seen that substituting S with Se has very little influence on the $E_1^{1/2}$ values in each case. To support these observations we performed theoretical calculations at the *ab initio* 6-31G* level, and the results are displayed in Figure 2. It can be seen that the energies of the HOMO of EDT-TTF and of EDS-TTF are nearly identical and that the small contribution of the Se atoms to the HOMO of **9** is comparable to that of the corresponding peripheral sulfur atoms of **9'**. These results are in good agreement with previous studies and indicate a poor mixing of the TTF HOMO and the $4p_\pi$ Se [6a] and the $3p_\pi$ S orbitals [33], respectively. Table 1 also shows that $E_1^{1/2}$ values of the EDS-TTF derivatives are slightly lower than those of their corresponding all-sulfur analogues. The same effect has been observed when comparing the redox potentials of BEDT-TTF and BEDS-TTF [10] and other pairs of analogous compounds. [34] This trend is observed in solution and, therefore, cannot be directly correlated with the E_{HOMO} values (calculated in the gas phase) of the corresponding π-donors. In fact, a comparison of the photoelectron and electrochemical data of TTF, BEDT-TTF, and BEDO-TTF reveals the important role played by solvation effects.[35]



TTF E_{HOMO} = -6.59 eV

EDT-TTF (**9'**) E_{HOMO} = -6.61 eV

EDS-TTF (**9**) E_{HOMO} = -6.59 eV

Figure 2. HOMO of TTF, EDT-TTF and EDS-TTF

As expected, the presence of electron-withdrawing groups on the TTF core raises the oxidation potentials. Good correlations between E^{ox} peak potentials and substituent constants have been obtained in the past for a number of substituted tetrathiafulvalenes, [33] but no selenium-containing substituents were studied. As some of these compounds were now in hand, together with their sulfur analogues, we plotted their $E_1{}^{1/2}$ potentials *vs.* $\Sigma\sigma_m$, where σ_m is the Hammett σ_{meta} constant [36] of each substituent on the TTF core. Figure 3 reveals a good correlation between these variables and also stresses the fact that the mesomeric effect of the substituents is small.

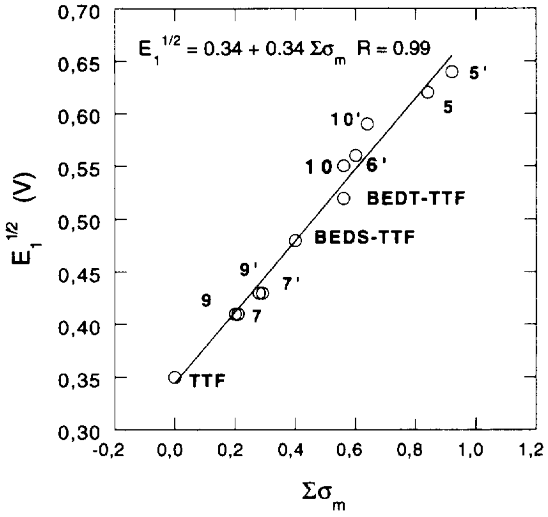


Figure 3. Correlation between $E_1{}^{1/2}$ and $\Sigma\sigma_m$

Compound **7** is noteworthy since it bears an -OH group which, through hydrogen-bonding, can give rise to interesting structural and electronic properties in its derived materials. [1a] In fact, κ-phase radical-cation salts of its analogue **7'** have been described, [8] whereas the related donor Me_3TTF-CH(OH)-Me forms a 1:1 complex with TCNQ which shows unique structural and magnetic properties. [37]

Alcohol **7** also formed a 1:1 charge-transfer complex with TCNQ, the room temperature conductivity value of which is $\sigma_{rt} = 0.1$ S.cm^{-1} (two probe, compressed pellet data). This implies that there is segregated stacking and partial charge-transfer from donor to acceptor. The degree of charge-transfer has often been estimated by the infrared stretching frequency of the nitrile group of TCNQ. [38] However, this method is not useful in this case, [39] since for complex **7**·TCNQ, ν_{max} is 2151 cm^{-1}, which lies outside the range TCNQ^0-TCNQ^{-1} (2227-2183 cm^{-1}). Efforts to grow single crystals of this complex and related cation-radical salts are underway.

In conclusion, we have synthesized the first monofunctionalized and some new difunctionalized EDS-TTF derivatives bearing methoxycarbonyl, formyl and hydroxymethyl groups. The mass spectrometric and electrochemical behaviour of these new donors has been studied and compared with that of their corresponding EDT-TTF analogues. Preliminary data concerning the formation of a conducting charge transfer complex of 4-(hydroxymethyl)-EDS-TTF and TCNQ are also reported.

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EXPERIMENTAL

General. All new compounds gave satisfactory microanalyses. Melting points were measured on a Büchi 510 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were measured with a Varian Unity-300 or a Bruker ARX-300 spectrometer. IR spectra (Nujol mulls) were recorded on a Perkin-Elmer FTIR 1600 spectrophotometer. Mass spectra were obtained on a VG Autospec mass spectrometer. Selenium-containing mass peaks are reported for the ^{80}Se isotope. Cyclic voltammograms were measured using a μ-Autolab (Eco-Chemie) potentiostat. Molecular orbital calculations were performed on a Pentium® PC-compatible computer. The geometries of TTF, EDT-TTF, and EDS-TTF were optimized at the semiempirical PM3 level as implemented in Hyperchem 4.5 (HyperCube Inc., Waterloo, Ontario, Canada). *Ab initio* calculations were carried out using the Gaussian 94 program.[40]

4,5-Ethylenediseleno-1,3-dithiole-2-thione (**3**). A solution of $(NBu_4)_2$ $[Zn(dsit)_2]$ (**2**)[17] (5 g, 4.42 mmol) in acetonitrile (200 mL) was refluxed for 1 h under N_2. 1,2-dibromoethane (36 g, 190 mmol) was added dropwise and the mixture was refluxed for 17 h and then allowed to cool to room temperature. The precipitate thus obtained was filtered and washed three times with Et_2O. A second crop was obtained by column chromatography of the filtrate (silica gel 70-230 mesh, CH_2Cl_2/hexane (1:1 v/v)). Recrystallization from EtOH gave pure compound **3** (2.2 g, 78%); mp 156-157°C (lit.[14] mp 157-158°C). ^1H-NMR ($CDCl_3$) δ: 3.47 (s). MS(EI): *m/z* = 320 ($M^{+\cdot}$, 100%), 292 (41), 216 (54), 168 (41), 136 (47), 88 (31), 76 (41).

4,5-Bis(methoxycarbonyl)ethylenediselenotetrathiafulvalene (**5**). A solution of **3** (940 mg, 2.9 mmol) and **4**[20] (687 mg, 2.9 mmol) in freshly distilled trimethyl phosphite (5 mL) was refluxed for 2 h under N_2 and then allowed to cool to room temperature. The mixture was filtered to separate the precipitated BEDS-TTF (98 mg, 11%) and trimethyl phosphite was eliminated from the filtrate by distillation under vacuum. The crude product was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane (2:1 v/v)) to give compound **5** as a violet solid (610 mg, 41%); mp 120°C (lit.[18] mp 113°C). IR ν (cm^{-1}): 1735, 1713. ^1H-NMR ($CDCl_3$) δ: 3.33 (s, 4H), 3.82 (s, 6H). ^{13}C-NMR ($CDCl_3$) δ: 26.72, 53.37, 112.74, 114.42, 131.92, 159.92. MS(EI): *m/z* = 506 ($M^{+\cdot}$, 20%), 478 (28), 262 (100), 218 (26), 160 (58), 88 (36), 76 (41). HR-MS: 505.7773, calculated for $C_{12}H_{10}O_4S_4Se_2$: 505.7792.

4-(Methoxycarbonyl)ethylenediselenotetrathiafulvalene (**6**). To a solution of **5** (622 mg, 1.23 mmol) in HMPA (20 mL), LiBr (1.2 g, 13.5 mmol) and a drop of water were added. The mixture was heated at 80°C for 1 h, during which time gas evolution (CH_3Br) was observed. After cooling to room temperature, a saturated aqueous solution of NaCl was added and the product was extracted with EtOAc. The organic layer was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The resulting orange oil was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane (2:1 v/v)), giving **6** as an orange solid (481 mg, 87%); mp 220°C (dec.; darkening from 200°C) (lit.[18] mp 150°C). IR ν (cm^{-1}): 1718. ^1H-NMR ($CDCl_3$) δ: 3.33 (s, 4H), 3.79 (s, 3H), 7.33 (s, 1H). MS(EI): *m/z* = 448 ($M^{+\cdot}$, 32%), 420 (38), 204 (100), 160 (36), 88 (49), 76 (38). HR-MS: 447.7776, calculated for $C_{10}H_8O_2S_4Se_2$: 447.7737.

4-(Hydroxymethyl)ethylenediselenotetrathiafulvalene (7). To a solution of **6** (636 mg, 1.42 mmol) in dry CH_2Cl_2 (40 mL), cooled at -78°C and under a N_2 atmosphere, DIBAL-H (1 M in CH_2Cl_2, 7mL, 7 mmol) was added dropwise. After 2 h, the mixture was treated at -78°C with a 1:1 mixture of 6 M aqueous HCl and MeOH (12 mL) and then allowed to reach room temperature. Dichloromethane (200 mL) was added and the organic layer was washed with 1 M aqueous HCl (200 mL), then with water, dried ($MgSO_4$), and concentrated under vacuum. The remaining yellow oil was purified by column chromatography (silica gel 70-230 mesh, initial eluent CH_2Cl_2, then increasing the polarity until CH_2Cl_2/MeOH (9:1 v/v) was used) to give **7** as an orange solid (384 mg, 64%) which can be recrystallized from CH_2Cl_2/pentane; mp 126°C. ^{1}H-NMR ($CDCl_3$) δ: 1.77 (t, J = 6.3 Hz, 1H), 3.34 (s, 4H), 4.39 (dd, J = 6.3 Hz, J' = 1.0 Hz, 2H), 6.24 (t, J = 1.0 Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ: 26.76, 27.16, 59.25, 105.89, 111.14, 111.22, 114.33, 117.65, 138.40. MS(EI): m/z = 420 ($M^{+\cdot}$, 38%), 392 (47), 176 (100), 160 (70), 132 (48), 88 (55), 76 (67). HR-MS: 419.7782, calculated for $C_9H_8OS_4Se_2$: 419.7788.

Ethylenediselenotetrathiafulvalene (9). To a solution of **6** (197 mg, 0.44 mmol) in HMPA (20 mL), LiBr (0.42 g, 4.9 mmol) and a drop of water were added. The mixture was heated at 150°C for 0.5 h and, after cooling to room temperature, a saturated aqueous solution of NaCl was added and the product was extracted with EtOAc. The organic layer was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The resulting oil was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane (1:1 v/v)), to give pure compound **9** (52 mg, 30%), identical in all respect to an independently prepared sample.[25]

4-(Formyl)ethylenediselenotetrathiafulvalene (10). A solution of LDA, generated at 0°C from diisopropylamine (0.08 mL, 0.6 mmol), *n*-BuLi (1.6 M in hexane, 0.35 mL, 0.6 mmol) in anhydrous THF (5 mL) was added dropwise to a suspension of **9** (195 mg, 0.5 mmol) in anhydrous THF (5 mL) at -78°C under argon. After stirring at -78°C for 2 h, a solution of *N*-methylformanilide (67 mg, 0.5 mmol) in anhydrous THF (2 mL) was syringed into the mixture and stirring continued at -78°C for 1 h, then the mixture was allowed to warm to 20°C. Water (15 mL) was added and the mixture was acidified with 2 M HCl. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2; the combined extracts were washed with water, dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Chromatography of the residue (silica gel 70-230 mesh, CH_2Cl_2/hexane (1:1 v/v)) afforded unreacted **9** (65 mg, 33%) followed by compound **10** as a violet solid (70 mg, 30%); mp 159-163°C. ^{1}H-NMR ($CDCl_3$) δ: 3.33 (s, 4H), 7.41 (s, 1H), 9.47 (s, 1H). HR-MS: 417.7629, calculated for $C_9H_6OS_4Se_2$: 417.7632.

4-(Formyl)ethylenedithiotetrathiafulvalene (10'). To a solution of **7'** [32] (972 mg, 3 mmol) in dry dioxane (30 mL), SeO_2 (366 mg, 3.3 mmol) was added. The mixture was refluxed for 3 h under N_2 and then allowed to cool to room temperature. The resulting black precipitate (elemental selenium) was filtered off and washed with dioxane several times. The filtrate was concentrated under reduced pressure and the remaining red solid was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane (1:1 v/v)), to give compound **10'** as a violet solid (610 mg, 61%); mp 152-153°C, (lit. [22b] 153°C). ^{1}H-NMR ($CDCl_3$) δ: 3.28 (s, 4H), 7.41 (s, 1H), 9.46 (s, 1H). ^{13}C-NMR ($CDCl_3$) δ: 30.12, 110.86, 113.08, 113.52, 114.34, 139.31, 141.23, 179.64. MS(EI): m/z = 322 ($M^{+\cdot}$, 100%), 294 (87), 218 (25), 206 (20), 174 (94), 130 (43), 88 (85), 76 (51).

4,5-Di(hydroxymethyl)ethylenediselenotetrathiafulvalene (11). A mixture of **5** (320 mg, 0.6 mmol), zinc chloride (100 mg, 0.72 mmol) and sodium borohydride (100 mg, 2.64 mmol) in dry dichloromethane (30 mL) was refluxed under N_2 for 5 h. The resulting orange solution was cooled to 0°C and a saturated aqueous solution of NH_4Cl (*ca.* 20 mL) was added dropwise, followed by EtOAc (100 mL). The organic layer was separated, and the aqueous layer extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with NH_4Cl solution (50 mL), separated, dried ($MgSO_4$) and the solvent evaporated *in vacuo* to yield compound **11** as an orange solid (260 mg, 92%) after recrystallization from $CHCl_3$; mp 165°C (decomp.). ^1H-NMR (dmso-d6) δ: 3.43 (s, 4H), 4.23 (d, J = 6 .0 Hz, 4H), 5.53 (t, J = 6.0 Hz, 2H). HR-MS: 449.7878, calculated for $C_{10}H_{10}O_2S_4Se_2$: 449.7894.

4,5-Di(formyl)ethylenediselenotetrathiafulvalene (**12**). A suspension of compound **11** (250 mg, 0.53 mmol) and MnO_2 (1.85 g, 21.2 mmol) in CH_2Cl_2 (200 mL) was stirred at 20°C for 3 h, then the precipitate was removed by filtration, and the filtrate evaporated to dryness, and the resultant solid was purified by column chromatography (silica gel 70-230 mesh, eluent CH_2Cl_2) to afford **12** as a dark blue solid (80 mg, 39%) mp 167-170°C. ^1H-NMR ($CDCl_3$) δ: 3.36 (s, 4H), 10.21 (s, 2H). HR-MS: 445.7590, calculated for $C_{10}H_6O_2S_4Se_2$: 445.7581.

Complexation of 7 and TCNQ. Equimolar amounts of **7** (42 mg, 0.1 mmol) and TCNQ (20.4 mg, 0.1 mmol) were separately dissolved in boiling acetonitrile, and the solutions were mixed while hot. Immediate darkening occurred and, after slow cooling to room temperature, the resulting black microcrystalline precipitate was filtered off, washed with Et_2O and dried under a nitrogen stream. 30 mg (48% yield) of this complex were isolated. Elemental analysis revealed a 1:1 stoichiometry.

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