

# Syntheses of new electron donors with hydroxymethyl groups and studies on their cation-radical salts

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New electron donors 4,5-ethylenedithio-4',5'-(1-hydroxypropane-2,3-diylidithio)tetrathiafulvalene (**1a**), 4,5-bis(methylthio)-4',5'-(1-hydroxypropane-2,3-diylidithio)tetrathiafulvalene (**1b**), 4,5-ethylenedithio-4',5'-(1,4-dihydroxybutane-2,3-diylidithio)tetrathiafulvalene (**1c**) and 4,5-bis(methylthio)-4',5'-(1,4-dihydroxybutane-2,3-diylidithio)tetrathiafulvalene (**1d**) with hydroxymethyl groups were synthesized and characterized spectroscopically. Their redox potentials were determined using cyclic voltammetry. Crystals of cation-radical salts based on these new electron donors, (**1a**)<sub>2</sub>·ClO<sub>4</sub>, (**1c**)<sub>2</sub>·Cl, (**1c**)<sub>2</sub>·I, were obtained by standard electrochemical methods. The crystal structure of (**1c**)<sub>2</sub>·Cl was determined and studied. Electrical measurements of the cation-radical salts indicated that they displayed semiconducting behaviors, however, with good conductivities at room temperature: 0.68 S cm<sup>-1</sup> for (**1a**)<sub>2</sub>·ClO<sub>4</sub> and 0.10 S cm<sup>-1</sup> for (**1c**)<sub>2</sub>·Cl.

## Introduction

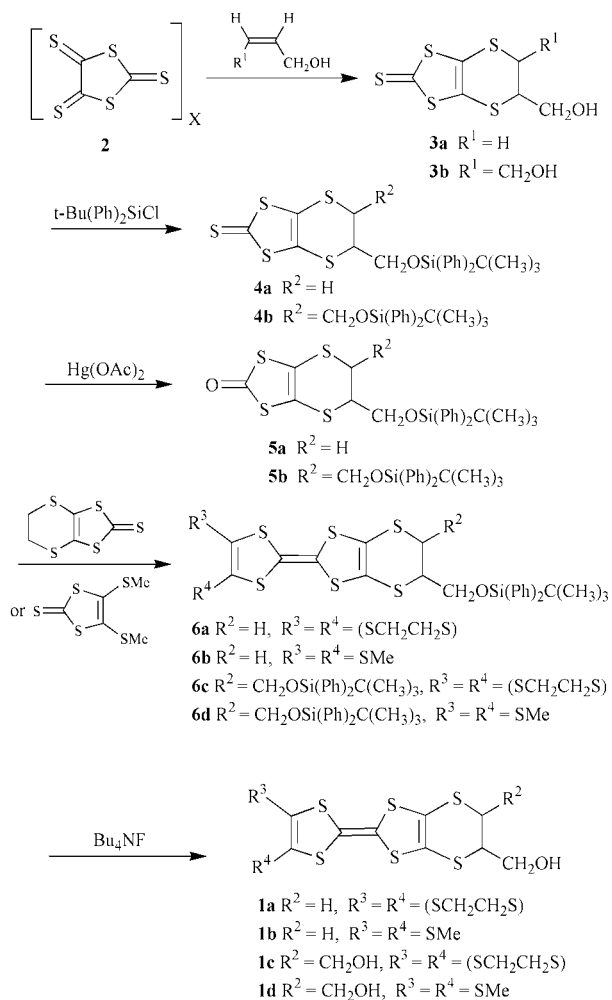
Since the discovery of organic metals in 1973 and superconductors in 1980, great progress has been achieved<sup>1</sup> in the field of organic conductors and superconductors. To date, more than one hundred organic conductors and forty organic superconductors have been discovered.<sup>2</sup> As far as the superconducting transition temperature is concerned, apart from the superconductors derived from C<sub>60</sub>, the organic superconductor based on the cation-radical salt of BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] still holds the record.<sup>2c</sup> Various chemical modifications of BEDT-TTF have been made. These include the substitution of peripheral sulfur atoms with selenium (BETS)<sup>3</sup> [bis(ethylenediseleno)tetrathiafulvalene] and with oxygen (BEDO)<sup>4</sup> [bis(ethylenedioxy)tetrathiafulvalene] atoms as well as extra-substitution with hydroxy, amide, or pyridine groups.<sup>5</sup> In fact, several organic superconductors based on modified BEDT-TTF have been discovered.<sup>6</sup> Recently, we have paid great attention to new electron donors with hydroxy groups since the intermolecular interactions between electron donor and acceptor molecules or counter anions may be enhanced by the formation of intermolecular hydrogen-bonds. We have reported the synthesis of an electron donor with four hydroxy groups and related investigations previously.<sup>7</sup> In this paper, we will describe the synthesis and physical studies on four new electron donors with hydroxy groups and their cation-radical salts.

## Results and discussion

### Synthesis

The synthesis of new electron donors **1a–d** started from trithione oligomer (C<sub>3</sub>S<sub>5</sub>)<sub>x</sub> **2** (see Scheme 1) which was prepared by the oxidation of bis(tetrabutylammonium) bis[2-thioxo-1,3-dithiole-4,5-bis(thiolato)]zincate with iodine.<sup>8</sup> Compounds **3a** and **b** were synthesized by [4 + 2] cycloaddition between allyl alcohol and but-2-ene-1,4-diol, respectively, with trithione oligomer, which decomposed to give the unstable 4,5-dihydro-1,3-dithiole-2,4,5-trithione monomer on heating. A similar strategy was employed for the preparation of alkyl substituted

4,5-ethylenedithio-1,3-dithiole-2-thione.<sup>9</sup> Efforts were also made to synthesize **3a** and **b** by the nucleophilic substitution reaction between 1,3-dithiole-2-thione-4,5-dithiolate (DMIT)



Scheme 1

anion and the corresponding dibromoalkyl alcohols, but there were no target compounds in the reaction mixture as indicated by analysis of thin layer chromatography and the mass spectrum.

The trialkyl phosphite mediated coupling of 1,3-dithiole-2-thiones is standard chemistry in the construction of TTF derivatives. However, direct coupling of compounds **3a–d** failed probably because of the side-reaction between the hydroxy groups and trialkyl phosphite, although triisopropyl phosphite instead of triethyl phosphite was used to hinder such a side-reaction. Thus, **3a** and **b** were converted to **4a** and **b** to protect the hydroxy groups with *tert*-butyldiphenylchlorosilane. Oxidation of **4a** and **b** with  $\text{Hg}(\text{OAc})_2$  gave **5a** and **b** in high yield. The cross coupling reaction between **5a** and **b** and the corresponding 1,3-dithiole-2-thiones afforded compounds **6a–d** in moderate yield. Deprotection of **6a–d**, using tetrabutylammonium fluoride in  $\text{CH}_2\text{Cl}_2$ , afforded target molecules **1a–d** in analytically pure form after isolation by column chromatography on silica gel. Since the target molecules **1a–d** were easily and quickly oxidized in the crude reaction mixture under air, the deprotection step should be performed under a nitrogen atmosphere and tetrabutylammonium fluoride should not be used in large excess. The chemical structures of **1a–d** were confirmed by spectroscopic data ( $^1\text{H-NMR}$ , MS) and elemental analysis.

The crystals of the cation-radical salts based on these new electron donors **1a–d** were grown using standard electrochemical techniques. Crystals of good quality from **1a** with  $\text{Bu}^n_4\text{N}\cdot\text{ClO}_4$ , and from **1c** with  $\text{Bu}^n_4\text{N}\cdot\text{I}_3$  and  $\text{Bu}^n_4\text{N}\cdot\text{GaCl}_4$  were obtained. Their chemical compositions were established with elemental analysis and electron probe microscopy (EPM). The cation-radical salt  $(\mathbf{1c})_2\cdot\text{Cl}^-$ , in which the counter anion was  $\text{Cl}^-$ , not  $\text{GaCl}_4^-$ , was formed by oxidising **1c** under constant current with  $\text{Me}_4\text{N}\cdot\text{GaCl}_4$  as supporting electrolyte in  $\text{CH}_2\text{Cl}_2$ . Similar phenomena with BEDT-TTF as electron donor were described previously.<sup>10</sup> Among them, the crystal structure of  $(\mathbf{1c})_2\cdot\text{Cl}$  was determined.

### Electrochemistry and theoretical calculation

The redox behaviors of compounds **1a–d** were investigated by cyclic voltammetry. They all exhibited two quasi-reversible redox waves. As an example, the cyclic voltammograms of **1c** with  $E_{1/2}^1=0.48\text{ V}$ ,  $E_{1/2}^2=0.88\text{ V}$  was shown in Fig. 1. For comparison, the corresponding redox potentials of BEDT-TTF were also measured under the same conditions ( $E_{1/2}^1=0.48\text{ V}$ ,  $E_{1/2}^2=0.89\text{ V}$ ). The experimental results indicated that compounds **1a–d** show similar electron-donating capabilities to BEDT-TTF. It further indicated that the substituted hydroxy groups of **1a–d** have no significant influence on the electron-donation properties and they all should be good precursors for organic conductors.

The molecular structures of these new electron donors were also theoretically investigated with semi-empirical quantum calculations (PM3 method implemented in MOPAC program<sup>11</sup>). As an example, the energy-minimized conformation of

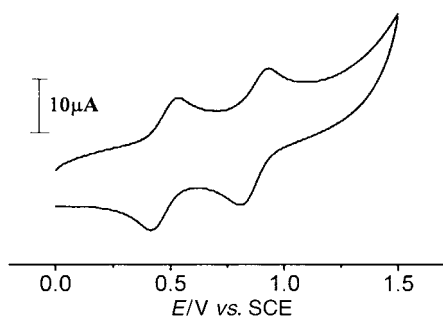


Fig. 1 The cyclic voltammogram of compound **1c**.

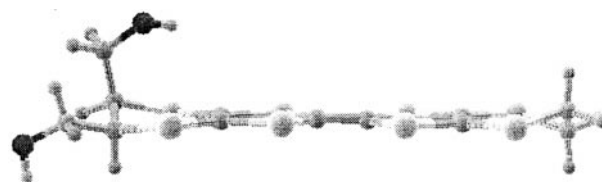


Fig. 2 The energy-minimized conformation of **1c** obtained with semi-empirical quantum calculations: the two hydroxymethyl groups are in a *cis*-configuration.

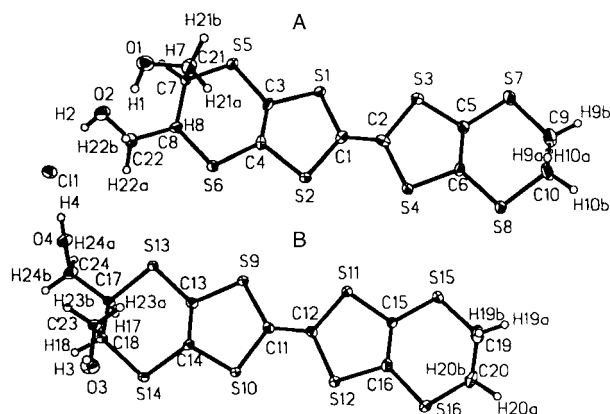


Fig. 3 Asymmetric unit of  $(\mathbf{1c})_2\cdot\text{Cl}$  with atomic numbering scheme.

**1c** is shown in Fig. 2. The two hydroxymethyl groups are in a *cis*-conformation, which is predicted by the Diels–Alder reaction mechanism and corresponds well with the X-ray diffraction analytical results for  $(\mathbf{1c})_2\cdot\text{Cl}$  (see below). Since oxidation implies extraction of one electron from the HOMO, the oxidation potentials of electron donors should be directly related to their HOMO energies. The new donor molecules **1a–d** and BEDT-TTF have similar HOMO energies (*e.g.*  $-8.092\text{ eV}$  for **1c**;  $-8.032\text{ eV}$  for BEDT-TTF), so it can be inferred that **1a–d** should have similar electron-donating abilities as BEDT-TTF, which is fully consistent with the results of cyclic voltammetric measurements as discussed above.

### Crystal structure of $(\mathbf{1c})_2\cdot\text{Cl}^\dagger$

The crystal of  $(\mathbf{1c})_2\cdot\text{Cl}$  (size:  $0.33 \times 0.14 \times 0.02\text{ mm}^3$ ) for structural analysis was obtained by electrochemical methods (for details see Experimental section). The X-ray crystallographic data are as follows. Formula:  $\text{C}_{24}\text{H}_{24}\text{ClO}_4\text{S}_{16}$ . Formula weight: 924.84. Crystal system: triclinic. Space group:  $P\bar{1}$ ;  $a=8.9908(5)\text{ \AA}$ ,  $b=13.2399(5)\text{ \AA}$ ,  $c=15.0602(10)\text{ \AA}$ ,  $\alpha=81.003(4)^\circ$ ,  $\beta=85.747(3)^\circ$ ,  $\gamma=70.911(3)^\circ$ ,  $V=1672.79(16)\text{ \AA}^3$ ,  $Z=2$ ,  $D_c=1.836\text{ g cm}^{-3}$ ;  $F(000)=946$ . Reflections measured 23520; reflections unique 7929 ( $R_{\text{int}}=0.072$ ); reflections  $I > 2\sigma(I)$  6055;  $R=0.0825$ ;  $R_w=0.2000$ .

The asymmetric unit contains two donor molecules A and B as well as the chloride anion (see Fig. 3). Molecules A and B show slight differences with regard to bond lengths and angles, but all of them are still within the normal range as indicated in Table 1 in which representative bond lengths and angles are listed. The differences in bond lengths and angles between molecule A and B indicate that these two molecules may carry different charges. For these two molecules, the central TTF plane plus the peripheral sulfur atoms: S5, S6, S7 and S8 for molecule A; S13, S14, S15 and S16 for molecule B, are almost coplanar. For molecule A, the molecule is folded along the vector of S5–S6 and S7–S8 with angles of  $13.03^\circ$  and  $6.63^\circ$ ,

<sup>†</sup>CCDC reference number 1145/231. See <http://www.rsc.org/suppdata/jm/b0/b003041o> for crystallographic files in .cif format.

**Table 1** Selected bond lengths (Å) and angles (°) of molecules A and B in (1c)<sub>2</sub>·Cl

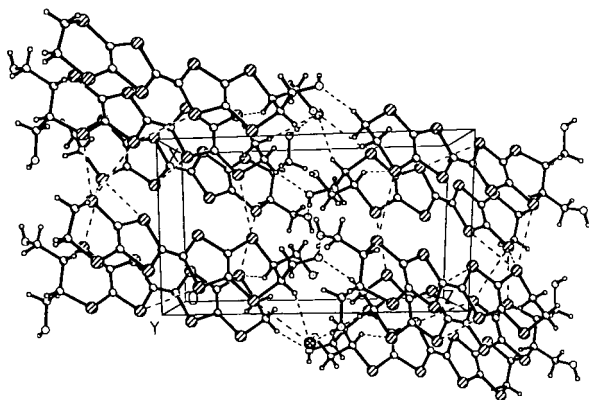
A		B	
S(1)–C(1)	1.745(8)	S(9)–C(11)	1.723(8)
S(1)–C(3)	1.769(8)	S(9)–C(13)	1.768(8)
S(3)–C(5)	1.751(8)	S(11)–C(12)	1.723(8)
S(3)–C(2)	1.752(8)	S(11)–C(15)	1.735(8)
S(5)–C(3)	1.761(8)	S(13)–C(13)	1.738(8)
S(5)–C(7)	1.820(8)	S(13)–C(17)	1.828(8)
S(7)–C(5)	1.745(8)	S(15)–C(15)	1.742(8)
S(7)–C(9)	1.790(10)	S(15)–C(19)	1.802(8)
C(1)–C(2)	1.333(11)	C(11)–C(12)	1.374(10)
C(3)–C(4)	1.337(11)	C(13)–C(14)	1.342(10)
C(5)–C(6)	1.359(11)	C(15)–C(16)	1.384(11)
C(7)–C(8)	1.545(10)	C(17)–C(18)	1.525(10)
C(9)–C(10)	1.479(12)	C(19)–C(20)	1.501(12)
C(1)–S(1)–C(3)	94.9(4)	C(11)–S(9)–C(13)	95.4(4)
C(3)–S(5)–C(7)	100.3(4)	C(13)–S(13)–C(17)	100.2(4)
S(1)–C(1)–S(2)	114.3(4)	S(9)–C(11)–S(10)	115.5(4)
S(5)–C(3)–S(1)	113.5(4)	S(13)–C(13)–S(9)	114.2(4)

respectively. Similarly, for molecule B the central TTF plane forms dihedral angles of 7.39° and 8.48° with the plane of S13, C17, C18 and S14 and that of S15, C19, C20 and S16 respectively. The two hydroxymethyl groups of both molecules A and B are in a *cis*-conformation.

In the crystal, molecules form columns along the *a*-axis (see Fig. 4). Intermolecular interactions in the column are significantly weak because of the larger intermolecular separation (~9 Å). In the *ab* plane, molecules arrange in the sequence of AA'BB'AA'... forming layers (see Fig. 4). Here, molecules A and A' are related by an inversion center. This also holds true for molecules B and B'. Such a molecular arrangement may avoid the direct overlapping of hydroxymethyl groups, and hence reduce the steric hindrance. Neighboring molecular layers are separated by chloride anion columns. In each molecular layer there are several short contacts between sulfur atoms as listed in Table 2. Hydrogen-bonds are not found between the hydroxy groups. Hydroxy groups, however, form hydrogen-bonds with chloride anions as indicated also in Table 2.

### Electrical conductivity of cation-radical salts

The temperature dependence of electrical conductivity of the cation-radical salts (1a)<sub>2</sub>·ClO<sub>4</sub>, (1c)<sub>2</sub>·Cl, (1c)<sub>2</sub>·I, was studied with crystals by the conventional four-probe method.<sup>12</sup> As an example, the variation of resistance ratio ( $R/R_{rt}$ , where  $R_{rt}$  is the resistance at 300 K) of (1c)<sub>2</sub>·Cl with temperature is displayed in Fig. 5. With decreasing temperature, the resistance increases gradually in the temperature range 290–180 K, and below 180 K it increases significantly, being characteristic of a semiconductor. Similarly, the CT salts (1a)<sub>2</sub>·ClO<sub>4</sub> and (1c)<sub>2</sub>·I

**Fig. 4** Molecular packing pattern for (1c)<sub>2</sub>·Cl (*ab* plane).**Table 2** The short atomic contacts for (1c)<sub>2</sub>·Cl in the crystal

S(1)–S(14) <sup>a</sup>	3.454(3)	S(4)–S(15)	3.623(3)
S(5)–S(14) <sup>a</sup>	3.578(3)	S(1)–S(10) <sup>c</sup>	3.571(3)
S(6)–S(16) <sup>b</sup>	3.556(3)	S(8)–S(10) <sup>b</sup>	3.571(3)
S(8)–S(15)	3.544(3)	S(8)–S(14) <sup>b</sup>	3.571(3)
H(2)–Cl(1)	2.306(2)	H(4)–Cl(1)	2.319(9)

Symmetry transformation used to generate equivalent atoms: <sup>a</sup>–1+x, 1+y, z. <sup>b</sup>2–x, 1–y, –z. <sup>c</sup>1–x, 1–y, –z.

also show semiconducting behaviors. The corresponding conductivity at room temperature and activation energies evaluated approximately by the plot of  $\ln(R/R_{rt})$  vs.  $1/T$  (see inset of Fig. 5) are summarized in Table 3.

By now, to the best of our knowledge, most of the cation-radical salts based on electron donors containing hydroxymethyl groups exhibit semiconducting properties,<sup>5b,5e</sup> for which there is still no clear interpretation. We will continue our efforts to prepare CT salts of 1a–d with various experimental conditions, hoping to find new organic conductors.

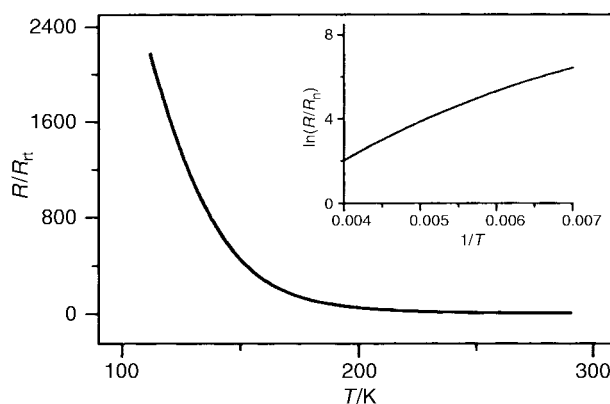
### Summary

Four new electron donors with hydroxy groups were synthesized and characterized. They all show similar electron-donating capabilities as BEDT-TTF. Three cation-radical salts: (1a)<sub>2</sub>·ClO<sub>4</sub>, (1c)<sub>2</sub>·Cl, (1a)<sub>2</sub>·I were obtained. The crystal structure of (1c)<sub>2</sub>·Cl was determined by X-ray diffraction analysis. Conductivity measurements indicated that they all displayed semiconducting behavior. Preparation of other cation-radical salts derived from these new electron donors and corresponding structural and physical investigations are in progress.

### Experimental

#### General

Melting points were measured on an XT<sub>4</sub>-100<sub>X</sub> microscope apparatus and are uncorrected. <sup>1</sup>H-NMR: UNITY 200(Varian). Mass spectra: AEI-MS50 for EI-MS and BEFLEX III for TOF-MS. Elemental analyses: Carlo-Erba-1106 instrument. EPM: ETM810Q instrument. Cyclic voltam-

**Fig. 5** Temperature dependence of electrical resistance for (1c)<sub>2</sub>·Cl.**Table 3** The room temperature conductivity and activation energies of cation-radical salts (1a)<sub>2</sub>·ClO<sub>4</sub>, (1c)<sub>2</sub>·Cl and (1c)<sub>2</sub>·I

	Conductivity (rt)/S cm <sup>-1</sup>	Activating energy/eV
(1c) <sub>2</sub> ·Cl	0.10	0.25
(1c) <sub>2</sub> ·I	0.0071	0.051
(1a) <sub>2</sub> ·ClO <sub>4</sub>	0.68	0.014

metric measurement: EGDG PAR 370 System, TBAPF<sub>6</sub> as electrolyte. Semi-empirical calculations were done with the MOPAC program.

The X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffractometer using graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 120 K. Absorption correction was made for all reflections with  $6.88^\circ < 2\theta < 55.78^\circ$  via the Sortav procedure ( $T_{\min} = 0.864$ ,  $T_{\max} = 0.990$ ). Data reduction was performed with the program HKLScale (Nonius 1995). Unit cell dimensions were refined with the program Denzo (Nonius 1995). The crystal structure was solved by direct methods (SHELXS-97), and refined by full-matrix-least squares method on  $F^2$ . Anisotropic thermal parameters were employed for non-hydrogen atoms. The positions of hydrogen atoms were calculated and refined with isotropic thermal parameters at geometrically restrained positions.

Compounds **3b**, **4b**, **5b** were synthesized according to the reported procedures.<sup>7</sup>

#### 4,5-(1-Hydroxypropane-2,3-diylidithio)-1,3-dithiole-2-thione (3a)

Compound **3a** was prepared, according to the procedure described by Neilands *et al.*<sup>13</sup> by [4+2] cycloaddition of oligo(1,3-dithiole-2,4,5-trithione) **2** (4.8 g) to allyl alcohol (3.0 g, 51.7 mmol) in 1,4-dioxane and the mixture was stirred at 80–85 °C for 4 h. The reaction mixture was filtered and the residue was washed twice with hot ethanol (50 ml). The combined filtrate and washings were decolorized by use of activated charcoal. After removing the solvent, column chromatography of the crude reaction mixture on silica gel with petroleum ether (bp 60–90 °C)–ethyl acetate (4:1) afforded compound **3a** as a yellow powder (2.6 g, 42.0%), mp 88–89 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  3.96 (2H, m), 3.89 (1H, m), 3.40 (2H, m); MS(EI) 254 (M<sup>+</sup>); Anal. Calc. for C<sub>6</sub>H<sub>6</sub>OS<sub>5</sub>: C, 28.33; H, 2.38; S, 63.01; Found C, 28.59; H, 2.25; S, 63.25%.

#### 4,5-(1-tert-Butyldiphenylsilyloxypropane-2,3-diylidithio)-1,3-dithiole-2-thione (4a)

To a solution of compound **3a** (0.25 g, 0.88 mmol) in dry DMF (50 ml) was added sequentially *tert*-butyldiphenylchlorosilane (0.6 g, 2.18 mmol) followed by imidazole (0.5 g, 7.35 mmol) under N<sub>2</sub>, then the mixture was stirred at 20 °C for 16 h. The solvent was removed *in vacuo* and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with water (3  $\times$  20 ml), dried (MgSO<sub>4</sub>) and then the solvent was evaporated. Column chromatography of the residue on silica gel with petroleum ether (bp 60–90 °C)–dichloromethane (3:1) afforded compound **4a** as a yellow powder (0.40 g, 93%), mp 112–114 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.65 (4H, m), 7.42 (6H, m), 3.88 (2H, m), 3.80 (1H, m), 3.39 (2H, m), 1.03 (9H, s); MS(TOF) 492 (M<sup>+</sup>).

#### 4,5-(1-tert-Butyldiphenylsilyloxypropane-2,3-diylidithio)-1,3-dithiol-2-one (5a)

To a solution of compound **4a** (2.0 g, 4.06 mmol) in CH<sub>2</sub>Cl<sub>2</sub>–HOAc (40 ml, 3:1 v/v), mercuric acetate (excess) was added and the mixture was stirred at 20 °C for 5 h. The white precipitate was removed by filtration through Celite and the filtrate was washed with water and dried (MgSO<sub>4</sub>). The solvent was removed to afford compound **5a** as white powder (1.91 g, 99%), mp 61–63 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.59 (4H, m), 7.33 (6H, m), 3.80 (2H, m), 3.68 (1H, m), 3.21 (2H, m), 0.99 (9H, s); MS(EI) 476 (M<sup>+</sup>).

#### 4,5-Ethylenedithio-4',5'-(1-tert-butyldiphenylsilyloxypropane-2,3-diylidithio)tetrathiafulvalene (6a)

4,5-Ethylenedithio-1,3-dithiole-2-thione (0.8 g, 3.57 mmol) was added to a solution of compound **5a** (1.0 g, 2.10 mmol) in neat,

freshly distilled triisopropyl phosphite (8 ml) and the mixture was heated to 140 °C under N<sub>2</sub> and stirred at this temperature for 5 h. After that, the reaction mixture was cooled down to room temperature and distilled *in vacuo* to remove triisopropyl phosphite. Column chromatography of the residue on silica gel with petroleum ether (bp 60–90 °C)–dichloromethane (5:1) yielded compound **6a** as a red oil (0.41 g, 30%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.63 (4H, m), 7.39 (6H, m), 3.85 (2H, m), 3.79 (1H, m), 3.36 (2H, m), 3.20 (4H, t), 1.05 (9H, s); MS(TOF) 652 (M<sup>+</sup>).

Compounds **6b**, **6c**, **6d** were prepared similarly

Compound **6b**: red oil (yield: 32%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.62 (4H, m), 7.38 (6H, m), 3.92 (2H, m), 3.78 (1H, m), 3.21 (2H, m), 2.40 (6H, s), 1.01 (9H, s); MS(TOF) 654 (M<sup>+</sup>).

Compound **6c**: red oil (yield: 40%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.62 (8H, m), 7.38 (12H, m), 3.88 (4H, m), 3.80 (2H, m), 3.25 (4H, t), 0.99 (18H, s); MS(TOF) 920 (M<sup>+</sup>). Anal. Calc. for C<sub>44</sub>H<sub>48</sub>S<sub>8</sub>O<sub>2</sub>Si<sub>2</sub>: C, 57.39; H, 5.20; S, 27.62; Found C, 57.33; H, 5.01; S, 27.62%.

Compound **6d**: red oil (yield: 30%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.60 (8H, m), 7.32 (12H, m), 3.92 (4H, m), 3.79 (2H, m), 2.42 (6H, s), 1.00 (18H, s); MS(TOF) 922 (M<sup>+</sup>).

#### 4,5-Ethylenedithio-4',5'-(1-hydroxypropane-2,3-diylidithio)tetrathiafulvalene (1a)

To a solution of **6a** (1.0 g, 1.53 mmol) in THF (50 ml) was added tetrabutylammonium fluoride trihydrate (0.72 g, 2.28 mmol) and the mixture was stirred at 25 °C for 10 h under N<sub>2</sub>. Then solvent was removed *in vacuo* to afford a viscous oil. Column chromatography of the crude reaction mixture on silica gel with CH<sub>2</sub>Cl<sub>2</sub> yielded **1a** as a dark red powder (0.44 g, 70%), mp 160–161 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  3.84 (2H, m), 3.78 (1H, m), 3.30 (2H, m), 3.28 (4H, t); MS(TOF) 414 (M<sup>+</sup>); Anal. Calc. for C<sub>11</sub>H<sub>10</sub>OS<sub>8</sub>: C, 31.88; H, 2.41; S, 61.84; Found C, 32.18; H, 2.53; S, 61.42%.

Compounds **1b**, **1c** and **1d** were synthesized in a similar manner.

Compound **1b**: red oil (yield: 65%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  3.85 (2H, m), 3.80 (1H, m), 3.27 (2H, m), 2.43 (6H, s). High-resolution MS(EI) for C<sub>11</sub>H<sub>12</sub>OS<sub>8</sub>, Found: 415.8643950; Calc: 415.8648254.

Compound **1c**: red powder (yield: 60%), mp 196–197 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  4.05 (4H, m), 3.93 (2H, m), 3.28 (4H, t); MS(EI) 444 (M<sup>+</sup>). Anal. Calc. for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>S<sub>8</sub>: C, 32.43; H, 2.70; S, 57.65; Found C, 32.33; H, 2.77; S, 57.44%.

Compound **1d**: red powder (yield: 56%), mp 138–139 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  3.95 (4H, m), 3.85 (2H, m), 2.42 (6H, s); MS(TOF) 446 (M<sup>+</sup>). Anal. Calc. for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>S<sub>8</sub>: C, 32.29; H, 3.14; S, 57.40; Found C, 32.29; H, 3.20; S, 57.37%.

#### Preparation of cation-radical salts

Standard electrochemical techniques were employed for the crystal growth of cation-radical salts. For example, (1c)<sub>2</sub>·Cl was prepared as follows: 8.88 mg of compound **1c** and 17.16 mg Me<sub>4</sub>N·GaCl<sub>4</sub> were placed in an H-cell and dissolved in 20 ml of dichloromethane. Constant current (1.0  $\mu$ A) was applied. Black needle single-crystals were obtained after two weeks.

Salts (1a)<sub>2</sub>·ClO<sub>4</sub> and (1c)<sub>2</sub>·I were obtained similarly.

The chemical compositions of (1a)<sub>2</sub>·ClO<sub>4</sub> and (1c)<sub>2</sub>·I were determined by elemental analysis and EPM respectively. EPS data for (1c)<sub>2</sub>·I: element weight of S, 80.2; element number of S, 2.51; element weight of I, 18.5; element number of I, 0.15; estimated composition, (1c)<sub>2</sub>·I; (1a)<sub>2</sub>·ClO<sub>4</sub>: Anal. Calc. for C<sub>22</sub>H<sub>20</sub>S<sub>16</sub>O<sub>6</sub>Cl: C, 28.46; H, 2.16; S, 55.20; Cl, 3.83; Found C, 28.45; H, 2.07; S, 55.27; Cl, 4.18%.

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