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# Tetrathiafulvalene-based podands bearing one or two thiol functions: immobilization as self-assembled monolayers or polymer films, and recognition properties

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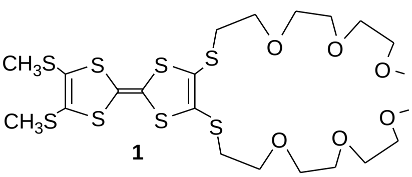
**Abstract**—The synthesis of various thiol and dithiol derivatives of a tetrathiafulvalene-based receptor is presented, as well as their immobilization on gold as self-assembled monolayers (SAMs). The formation of films incorporating TTF units is also shown by electrooxidation of TTF–dithiol derivatives. The ability of the monolayers to electrochemically recognize $Pb^{2+}$ is demonstrated.

## 1. Introduction

Self-assembled monolayers (SAMs) incorporating electroactive probes are subject to intensive works, in particular for sensing applications.[1]

On this basis, several groups have described in the last decade, the preparation of SAMs involving the tetrathiafulvalene framework.[2] This electroactive unit is known for its well-established redox properties, involving three stable redox states (neutral, cation-radical, dication) reached upon two successive reversible one-electron redox processes.[3] The continuous synthetic efforts led around this species,[4] have allowed to introduce a great variety of functionalities on its periphery, including thiol or disulfide functions for the preparation of SAMs.[2] In addition to anchoring –SH or –S–S– groups, binding units for metal cation recognition have also been introduced onto TTF, in order to generate SAMs able to electrochemically respond upon complexation of a guest cation.[2b–e,5]

We have recently communicated the redox-switchable binding properties of a TTF–podand assembly **1** for Pb(II).[6] In particular, this system, once immobilized into a conducting film, binds or expulses $Pb^{2+}$ just by tuning the TTF redox state (Scheme 1).



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**Scheme 1.**

Whereas modification of electrodes by formation of SAMs with adsorbates bearing one sulfur-based grafting site (thiol or disulfide group) is well-known,[1] much less attention has been given to systems bearing two or more thiol groups. In that case, it was demonstrated that a tetrathiol–TTF derivative can be deposited either as SAMs or as polymer films.[2f]

In this paper, we present our results concerning the synthesis of various thiol and dithiol derivatives of ligand **1** as well as their immobilization on gold as SAMs. The formation of polymer films incorporating TTF units is also shown by electrooxidation of TTF–dithiol derivatives. Finally, the ability of the SAMs to electrochemically recognize $Pb^{2+}$ is demonstrated.

## 2. Results and discussion

The synthetic strategy involves the thiolate protection/deprotection methodology previously developed in the TTF series by Becher et al.[7] The starting five-member heterocycles **2a** and **2b** were synthesized according to the

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*Keywords*: SAMs; Tetrathiafulvalene; Cyclic voltammetry; Polydisulfides.

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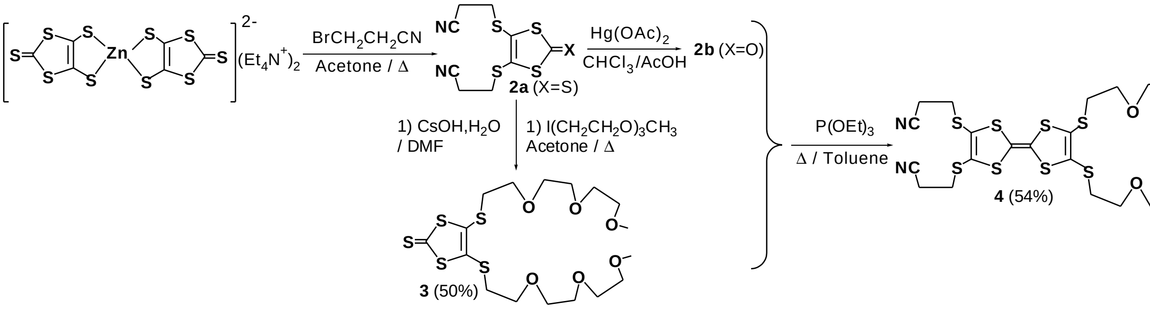


Scheme 2.

literature,[7] from the bis(2-thioxo-1,3-dithiole-4,5-dithio)-zincate salt (Scheme 2).[8] The counter part **3** to reach a TTF skeleton, was obtained from **2a** and ω-iodo triethyleneglycol monomethyl ether[9] as the electrophile. Cross coupling of **2b** and **3** in presence of triethylphosphite afforded the key dissymetrical TTF intermediate **4** in 54% yield.

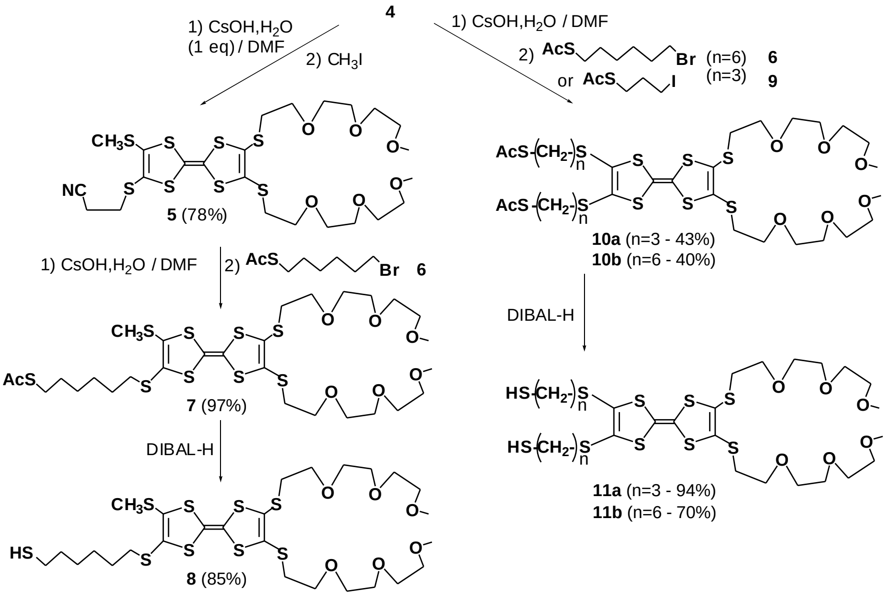
Compound **4** bearing two protected thiolate functionalities, allows introduction of one or two grafting sites on the periphery of the TTF skeleton (Scheme 3).

One equivalent of cesium hydroxide was added to **4**, and the TTF–thiolate intermediate was treated by iodomethane to produce the monomethylated derivative **5** in 78% yields. Subsequent deprotection of the residual thiolate of **5** under basic conditions followed by a nucleophilic substitution onto thioester **6**, allowed introduction of the lateral hexamethylene chain of **7** in quantitative yields. The brominated derivative **6**[5] was prepared by a Mitsunobu reaction with 6-bromohexanol in presence of thioacetic acid.

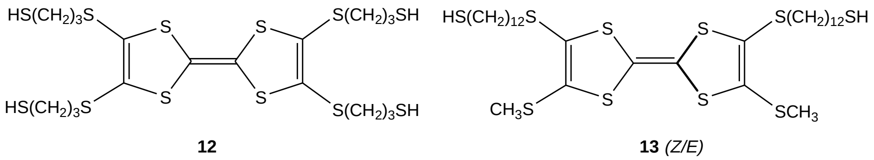
Similarly, two lateral chains incorporating either six or three methylene fragments were introduced by reaction of the dithiolate derivatives generated from **4** with CsOH, $H_2O$, and thioesters **6** or **9**, respectively. The iodinated precursor **9** was prepared by halogen exchange (NaI, acetone), from the corresponding commercially available chlorinated analogue.

Finally, the target mono- and dithiol derivatives could be obtained in good yields by reduction with DIBAL-H. These compounds have been fully characterized and their $^1$H NMR spectra exhibit in particular, a triplet located at 1.34–1.38 ppm corresponding to the SH signal. It should be noted that this signal tends to disappear within a few hours, which is assigned to the self-oxidation of these thiols to the corresponding disulfides. Similar observations have already been made recently with other TTF-substituted thiols, and are attributed to an electron-transfer process involving catalytic amounts of $TTF^{\cdot+}$.[2g,5]

The electrochemical behaviour of TTF–thiols derivatives **8**, **11a** and **11b** was studied by cyclic voltammetry under homogeneous conditions with a Pt working electrode. The three compounds behave similarly, and show the expected two successive one electron redox systems of the TTF framework at $E^1_{ox}=0.55$–$0.57$ V and $E^2_{ox}=0.86$–$0.90$ V versus Ag, AgCl. In the cases of the dithiol derivatives **11a**,**b**, we could observe a third wave, irreversible, located at a higher oxidation potential ($E^3_{ox}=1.25$ V) and attributed to the oxidation of the thiol functionalities into a disulfide.



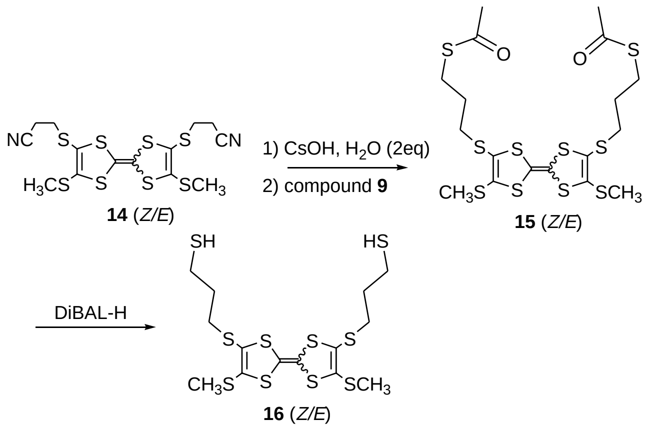
Scheme 3.



**Scheme 4.**

Considering this observation, as well as the presence of two thiol functions per TTF unit in **11a**,**b**, we checked the possibility to electrodepose these compounds as poly(disulfides) via an intermolecular reaction. A polymerization, carried out on glassy carbon electrodes, was already described by Fujihara et al. from TTF–tetrathiol derivatives **12** (Scheme 4) under potentiodynamic conditions.[2f] Nevertheless, no film growing could be observed with our TTF–dithiol derivatives **11a**,**b** by scanning the potentials between 0.10 and 1.60 V Ag, AgCl on a Pt, Au or a glassy carbon electrode.

In order to check the effect of the localization of the thiol linkers on the film formation ability of TTF–polythiols, we therefore synthesize TTF–dithiol **16** for which both functions are located on the 2,7-positions of the TTF framework. According to a similar synthetic methodology as for compounds **8** or **11**, and starting from the dicyano TTF derivative **14**,[10] we could isolate the model compound **16** in two steps (Scheme 5), as a mixture of *Z*/*E* isomers. TTF–dithiol derivatives with longer thiol linkage ($C_{12}$) (compound **13**), were also recently prepared by Hellberg et al. according to a different synthetic strategy.[2h]



**Scheme 5.**

CV experiments led on **16** with a gold electrode are particularly significant. Recurrent scanning of the potentials between 0 and 1.20 V, allowed a very regular film deposition on the surface (Fig. 1a), denoted by a progressive increase of both peaks intensity. In particular, the shape of the two redox waves becomes thinner upon increasing, as expected from a change from diffusion-controlled to surface-confined redox processes. The modified electrode was then thoroughly rinsed with methylene chloride and dipped in a monomer-free electrolytic solution (Fig. 1b). Two well-defined reversible oxidation peaks are observed, whose shape is characteristic of surface confined redox couples.[11] In addition, the anodic–cathodic peaks separation for both redox steps is very closed to 0 V confirming that the redox processes of the TTF system are not limited by charge and/or mass transport within the film.

As expected, and in contrast with conducting polypyrroles or polythiophenes bearing pendant TTF units that we described recently,[6,12] for which the conducting polymer backbone can be characterized on the CV besides the two redox waves belonging to TTF, no additional electrochemical signature is observed besides the TTF signals in the case of poly(**16**). Finally, no alteration of the CV was observed upon recurrent potentials cycling, illustrating the stability of the films obtained.

It appears therefore that compound **16** presents a similar ability as the TTF–tetrathiol **12**[2f] to polymerize. Conversely, using the same conditions as for **16** (recurrent scanning of the potentials between 0 and 1.20 V), we could not observe any film formation from TTF–dithiol **11**. On this basis, we can extrapolate that two thiol linkages are enough to promote electropolymerization (compare **16** vs **12**), but providing that both of them are located on the 2,7-positions of TTF (**16** vs **11**) and that the chains are not too long (**16** vs **13**).[13] Such observations can be rationalized by the analysis of the parameters favouring intra- versus inter-molecular disulfide bonds formation. With short linkages located on the 2,7 positions (**12** and **16**), the intramolecular disulfide bond is unlikely to arise because of the important strain, which would be generated in the resulting macrocycle fused to the rigid TTF skeleton. On the contrary, intra-molecular disulfides are likely to occur when thiol functions can be spatially closed, as it is the case with **11** for which the pendant thiol functions occupy vicinal positions on the TTF, or for **13** for which the chains can mutually arrange spatially more easily because of their length, which is also confirmed by the isolation of the intra-molecular disulfide product.[2h]

The ability of the receptor molecules **8** and **11** to form self-assembled monolayers (SAMs), was then explored. SAMs of **8** and **11** were prepared in a glovebox under Ar atmosphere. Gold (111) bead electrodes[14,15] were immersed in a dichloromethane solution of **8**, **11a** or **11b** ($1\times10^{-3}$ M) for 24–48 h, and the resulting modified electrodes were thoroughly rinsed with dichloromethane, and introduced in a freshly prepared electrolytic acetonitrile solution ($Bu_4NPF_6$, 0.1 M). The efficiency in SAMs formation was evaluated by cyclic voltammetry.

The CV response of the SAMs obtained from **8** or **11** shows the expected two one-electron oxidation processes corresponding to the successive reversible oxidation of neutral TTF ($TTF^{\circ}$) to the radical-cation ($TTF^{\cdot+}$) and to dication ($TTF^{2+}$) (Fig. 2). Upon sequential scanning from 0.3 to 1.1 V (200 cycles in acetonitrile, ($Bu_4NPF_6$, 0.1 M)), the SAMs derived from **8** and **11** demonstrate a good stability,

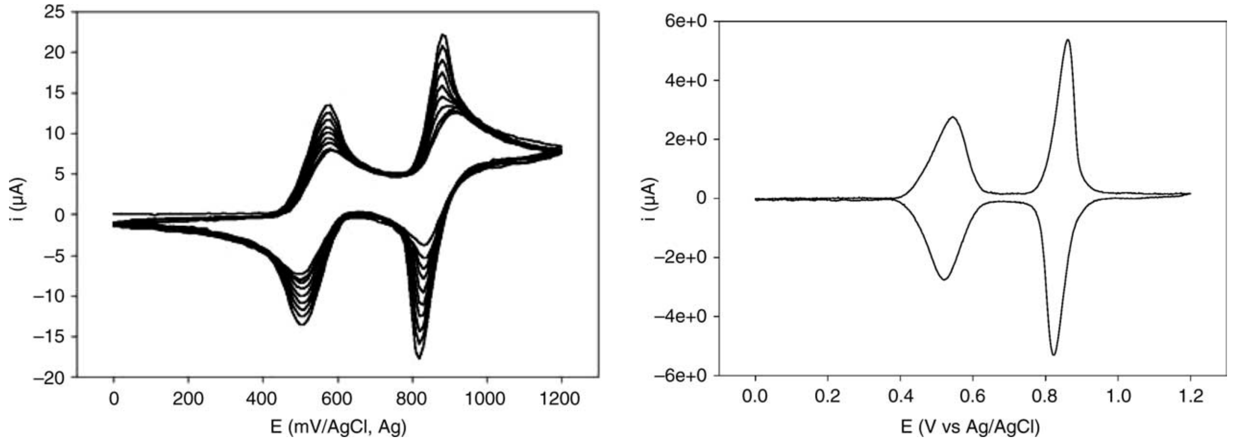


**Figure 1.** (a) Growing of the film from **16** (1 mM), in 0.10 M $Bu_4NPF_6/CH_2Cl_2$, 10 cycles at 100 mV $s^{-1}$, Au; (b) CV response of the film ($\Gamma = 1.1 \times 10^{-9}$ mol TTF $cm^{-2}$), in 0.10 M $Bu_4NPF_6/CH_2Cl_2$, Au.

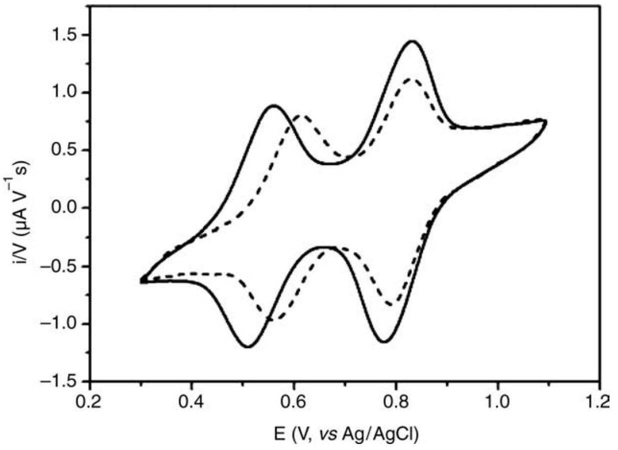


**Figure 2.** Cyclic voltammogram for self-assembled monolayers of compound **8** without (solid line) and in the presence (dashed) of $1.2 \times 10^{-2}$ mM $Pb(ClO_4)_2$, Au electrode; $\Gamma = 1 \times 10^{-10}$ mol $cm^{-2}$, $CH_3CN$, $Bu_4NPF_6$ (0.1 mol $L^{-1}$) versus Ag/AgCl.

as shown by the constant peaks intensity. It is surprising that we could not observe any significant difference in the stability of these monolayers depending on the number of anchoring sites or on the length of the linker. The electrochemical response of these SAMs is consistent with a redox system confined at the electrode surface, as shown by the linearity of both oxidative peak currents with the scan rate $\nu$ ($\nu = 1$–30 V $s^{-1}$), by the constant values of the anodic ($E^i_{ox}$) and cathodic ($E^i_{red}$) peaks and of $\Delta E$ ($= E^i_{ox} - E^i_{red}$) on varying $\nu$. The surface coverage ($\Gamma$)[15] reaches a value of $\Gamma = 1 \times 10^{-10}$ mol $cm^{-2}$ for **8**, in the expected range for a monolayer. The coverage is significantly larger for the TTF–dithiol analogues **11**, since we observed $\Gamma = 1.4 \times 10^{-10}$ mol TTF $cm^{-2}$ for **11b** and $8 \times 10^{-10}$ mol TTF $cm^{-2}$ for **11a**. Possible formation of small quantities of TTF oligomers by formation of intermolecular TTF–disulfide bonds, in addition to the SAM formation, may explain these values.

Addition of $Pb^{2+}$ ($C = 1.2 \times 10^{-2}$ mM) to the electrolytic solution containing the SAMs modified electrodes, led to a positive shift of $E^1_{ox}$ (+60 mV), whereas $E^2_{ox}$ remains constant (Fig. 2). Such high level of electrochemical recognition is consistent—though of lower degree—with observations made with the parent TTF–ligand (without any thiol linkage) in homogeneous solution ($\Delta E^1_{ox} = +120$ mV), or once immobilized on a surface via a conducting polymer ($\Delta E^1_{ox} = +100$ mV),[6] and results from the electrostatic interactions occurring between the metal cation and the positively charged oxidized species of TTF. A possible explanation to justify the lower degree of the $E^1_{ox}$ positive shifting in the case of SAMs of **8** compared to the corresponding polythiophene film,[6] can be found in the difference of density in TTF–podands between the two cases. The nature of the grafting sites (–SH vs ethylene (dioxy)thiophene) leads to a more compact arrangement for the SAMs, where the ligands are therefore spatially closer, which may alter their ability to bind a given cation. Finally, no significant differences in the recognition properties were observed between the SAMs obtained from **8** and **11b**[16] (see Supplementary data).

## 3. Conclusion

To conclude, we have synthesized a series of TTF–mono and –dithiol derivatives **8**, **11a** and **11b** incorporating polyether chains for the recognition of Pb(II). Dithiol derivatives **11** could not be electropolymerized, presumably because of the vicinal positions of the thiol-linkages on the periphery of the TTF core, which favour intra- rather than inter-molecular disulfide bonds formation. This was rationalized by the synthesis of a corresponding TTF–dithiol substituted on the 2,7-positions **16**, which exhibits a very good ability to electropolymerize. SAMs formation could be achieved with the three podand TTF–dithiol **8**, **11a** and **11b**. The monolayers obtained, present in the three cases a good stability and demonstrate a very good ability to electrochemically recognize Pb(II).

## 4. Experimental

### 4.1. Instrumentation

NMR spectra were recorded on a Bruker Advance DRX500 spectrometer operating at 500 and 125.7 MHz for $^1H$ and $^{13}C$, respectively, $\delta$ values are given in ppm (relative to TMS). Electrochemical experiments were carried out with a PAR273 Potentiostat-Galvanostat. Characteristics of the gold electrodes are given in Refs. 14 and 15. Solvents used were of electrochemical grade, and electrochemical studies were carried out in glovebox under Ar atmosphere.

## 4.2. Synthesis

**4.2.1. 4,5-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl]-1,3-dithiole-2-thione (3).** Cesium hydroxide monohydrate (6.9 g, 2.5 equiv, $4.11\times10^{-2}$ mol) in dry methanol (10 mL) was added to thione **2a** (5 g, $1.64\times10^{-2}$ mol) dissolved in dry and degassed DMF (200 mL). The reaction mixture was stirred during 10 min. Then, 1-(2-iodoethoxy)-2-(2-methoxyethoxy)ethane ($3.77\times10^{-2}$ mol, 2.3 equiv) in dry and degassed DMF (20 mL) was added in one portion. The reaction mixture was stirred for one night. The solvent was removed in vacuo, the residue was dissolved in dichloromethane (150 mL), washed with three times with water and dried over magnesium sulfate. The mixture was concentrated in vacuo and the orange residue was purified by chromatography on a silica gel column (eluent: petroleum ether/ethyl acetate: 1:1). Yield 50%; red oil; $C_{17}H_{30}O_6S_5$; $^1$H NMR ($CDCl_3$): 3.72 (t, 4H, $CH_2OMe$), 3.65 (m, 12H, $CH_2O$), 3.55 (m, 4H, $SCH_2CH_2O$), 3.38 (s, 6H, $CH_3O$), 3.05 (t, 4H, $CH_2S$); $^{13}$C NMR ($CDCl_3$): 211.0 (C=S), 136.6 (C=C), 72.0, 70.7, 70.6, 70.65, 69.9 ($CH_2O$), 59.0 ($OCH_3$), 36.2 ($SCH_2CH_2O$); HRMS (EI), $(M)^+$ Theo.: 490.0646, found: 490.0643.

**4.2.2. 6,7-Bis(2-cyanoethylsulfanyl)-2,3-bis[2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl]tetrathiafulvalene (4).** 1,3-Dithiole-2-one **2b** (0.6 g, $2.08\times10^{-3}$ mol) and thione **3** (1.0 g, $2.04\times10^{-3}$) were introduced in toluene (25 mL) and 10 mL of triethylphosphite was then added. The mixture was refluxed for 3 h, and then cooled down to rt. Solvents are evaporated in vacuo. The resulting residue was dissolved in 150 mL de $CH_2Cl_2$, washed three times with water and then dried over $MgSO_4$. After evaporation of the solvent, the product was obtained as red oil (0.82 g, 54% yield) after a silicagel column chromatography (dichloromethane 7/ethyl acetate 3). Yield 54%; red oil; $C_{26}H_{38}O_6N_2S_8$; $^1$H NMR (acetone-$d_6$): 3.69 (t, 4H, $CH_2OMe$), 3.57 (m, 12H, $CH_2O$), 3.46 (t, 4H, $SCH_2CH_2O$), 3.29 (s, 6H, $CH_3O$), 3.24 (t, 4H, $SCH_2CH_2CN$), 3.07 (t, 4H, $CH_2S$), 2.94 (t, 4H, $CH_2CN$); $^{13}$C NMR ($CDCl_3$): 128.1, 128.0 (lateral C=C), 117.4 (CN), 114.1, 107.7 (central C=C), 71.9, 70.6, 70.5, 70.4, 70.0 ($CH_2O$), 59.0, 58.9 ($OCH_3$); 35.5 ($SCH_2CH_2O$); 31.3 ($SCH_2CH_2CN$); 18.9 ($CH_2CN$); HRMS (ESI+): $(M+Na)^+$ Theo.: 753.0496, found: 753.0440.

**4.2.3. 2,3-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl]-6-(2-cyanoethylsulfanyl)-7-(methylsulfanyl)tetrathiafulvalene (5).** Cesium hydroxide monohydrate (0.154 g, $9.2\times10^{-4}$ mol) in dry methanol (10 mL) was added to tetrathiafulvalene dicyano derivative **4** (0.61 g, $8.36.10^{-4}$ mol) dissolved in dry and degassed DMF (50 mL). The reaction mixture was stirred during 10 min, the colour becoming dark red. Then, an excess of iodomethane (2 mL) was added in one portion. The colour of the reaction mixture turned back to orange, and the reaction mixture was stirred at rt for 1 h. The solvent was removed in vacuo, the residue was dissolved in dichloromethane (100 mL), washed three times with water and dried over magnesium sulfate. The mixture was concentrated in vacuo and the residue was purified by chromatography on a silica gel column (eluent: ethyl acetate). Compound **5** was obtained in 78% yield (0.45 g) as a red oil. Yield 78%; red oil; $C_{24}H_{37}O_6NS_8$; $^1$H NMR ($CD_3CN$): 3.62 (t, 4H, $CH_2OMe$), 3.53 (m, 12H, $CH_2O$), 3.45 (t, 4H, $SCH_2CH_2O$), 3.28 (s, 6H, $CH_3O$), 3.01 (m, 6H, $4\times CH_2S+2\times SCH_2CH_2CN$), 2.71 (t, 2H, $CH_2CN$), 2.45 (s, 3H, $SCH_3$); $^{13}$C NMR ($CDCl_3$): 135.1, 128.2, 127.8, 120.3 (lateral C=C), 117.5 (CN), 112.2, 109.4 (central C=C), 72.0, 70.6, 70.6, 70.1, 70.1 ($CH_2O$), 59.0 ($OCH_3$), 35.5 ($SCH_2CH_2O$), 31.3 ($SCH_2CH_2CN$), 19.1 ($SCH_3$), 18.8 ($CH_2CN$); HRMS (ESI+): $(M^+)$ Theo.: 691.0387, found: 691.0400; microanalysis: % Calcd: C, 41.65; H, 5.39; N, 2.02; O, 13.87, %. Found: C, 42.41; H, 5.35; N, 1.91; O, 13.95.

**4.2.4. 2,3-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl]-6-(6-acetylsulfanylhexyl-1-sulfanyl)-7-(methylsulfanyl)tetrathiafulvalene (7).** Cesium hydroxide monohydrate (0.092 g, $5.46\times10^{-4}$ mol) in dry methanol (5 mL) was added to tetrathiafulvalene derivative **5** (0.27 g, $3.9\times10^{-4}$ mol) dissolved in dry and degassed DMF (30 mL). The reaction mixture was stirred during 10 min, the colour becoming dark red. Then, thioacetyl derivative **6** (0.186 g, $7.8\times10^{-4}$ mol), was added in one portion. The colour of the reaction mixture turned back to orange, and the reaction mixture was stirred at rt for 2 h. The solvent was removed in vacuo, the residue was dissolved in dichloromethane (100 mL), washed three times with water and dried over magnesium sulfate. The mixture was concentrated in vacuo and the residue was purified by chromatography on a silica gel column (eluent: ethyl acetate). Compound **7** was obtained in 97% yield (0.30 g) as an orange oil. Yield: 97%; orange oil; $C_{29}H_{48}O_7S_9$; $^1$H NMR ($CDCl_3$): 3.60–3.73 (m, 16H, $CH_2O$), 3.55 (m, 4H, $SCH_2CH_2O$), 3.39 (s, 6H, $OCH_3$), 3.02 (t, 4H, $SCH_2CH_2O$), 2.92 (2t, 4H, $CH_2$), 2.43 (s, 3H, $SCH_3$), 2.32 (s, 3H, $COCH_3$), 1.52–1.75 (m, 4H, $CH_2$), 1.30–1.50 (m, 4H, $CH_2$); $^{13}$C NMR ($CDCl_3$): 195.9 (C=O); 129.5, 127.8, 127.7, 125.6 (lateral C=C), 110.94, 109.95 (central C=C), 71.9, 70.6, 70.5, 70.5, 70.0 ($CH_2O$), 59.0 ($OCH_3$), 36.1, 35.4, 30.6, 29.4, 29.3, 28.9, 28.2, 27.8 ($SCH_2$, $SCOCH_3$, $CH_2$), 19.2 ($SCH_3$); HRMS (ESI+): $(M+Na)^+$ Theo.: 819.0784, found: 819.0780.

**4.2.5. 2,3-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl]-6-(6-mercaptohexyl-1-sulfanyl)-7-(methylsulfanyl)-tetrathiafulvalene (8).** Thioacetyl derivative **7** (0.150 g, $1.88\times10^{-4}$ mol) was dissolved in 50 mL of dry dichloromethane. A solution of DIBAL-H (1 M in toluene, $9.42\times10^{-4}$ mol) was added dropwise to **7** cooled at −78 °C, in 15 min under nitrogen. After 45 min stirring at −78 °C, the reaction mixture was treated with a chlorhydric acid solution (3 M) in methanol. At rt, 80 mL of dichloromethane were added. The organic phase was washed with water and dried over $MgSO_4$. Evaporation of the solvent, and silicagel chromatography (ethyl acetate), afforded **8** (120 mg) as an orange oil. Yield: 85%; orange oil; $C_{27}H_{46}O_6S_9$; $^1$H NMR ($CDCl_3$): 3.64–3.68 (m, 16H, $CH_2O$), 3.55 (m, 4H, $SCH_2CH_2O$), 3.38 (s, 6H, $OCH_3$), 3.01 (t, 4H, $SCH_2CH_2O$), 2.82 (t, 2H, $SCH_2$), 2.53 (dd, 2H, $CH_2SH$), 2.43 (s, 3H, $SCH_3$), 1.60–1.65 (m, 4H, $CH_2$), 1.41–1.44 (m, 4H, $CH_2$), 1.34 (t, 1H, SH); $^{13}$C NMR ($CDCl_3$):

129.6, 127.8, 127.8, 125.6 (lateral C=C), 110.9, 110.0 (central C=C), 71.9, 70.6, 70.6, 70.5, 70.0 ($CH_2O$), 59.0 ($OCH_3$), 36.1, 35.4, 33.8, 29.5, 27.8, 27.7 ($CH_2$, $SCH_2$), 24.5 ($CH_2SH$), 19.2 ($SCH_3$); HRMS (ESI+): $(M+Na)^+$ Theo.: 777.0679, found: 777.0662.

**4.2.6. 1-Iodo-3-thioacetyl propane (9).** A solution of the commercially available 3-chloropropyl thioacetate (12 g, 0.049 mol) and sodium iodide (36 g) in 300 mL of acetone, was refluxed for 12 h. The solvent was evaporated and the resulting mixture was dissolved in dichloromethane (200 mL), washed with water, and dried over magnesium sulfate. The iodinated product was isolated from a silicagel chromatography (dichloromethane/petroleum ether 1:1), as a yellow oil (2.9 g, 90%). Yield 90%; yellow oil; $C_5H_9OSI$; $^1H$ NMR ($CDCl_3$): 3.20 (t, 2H, $CH_2I$), 2.95 (t, 2H, $SCH_2$), 2.33 (s, 3H, $SCOCH_3$), 2.07 (q, 2H, $CH_2CH_2CH_2$).

### 4.3. Bis(thioacetyl)–TTF derivatives (10a) and (10b)

Compounds **10a** and **10b** were prepared according a similar procedure as for monothioacetyl–TTF derivative **7**, starting from the dicyano–TTF derivative **4** and using 2.5 equiv of cesium hydroxide monohydrate. Compounds **10a** and **10b** were purified by silicagel column chromatography (ethyl acetate).

**4.3.1. 2,3-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl]-6,7-bis(3-acetylsulfanylpropyl-1-sulfanyl)tetrathiafulvalene (10a).** Yield 43%; orange oil; $C_{30}H_{48}O_8S_{10}$; $^1H$ NMR ($CDCl_3$): 363–3.70 (m, 16H, $CH_2O$), 3.56 (m, 4H, $SCH_2CH_2O$), 3.38 (s, 6H, $OCH_3$), 3.01 (m, 8H, $CH_2$), 2.87 (t, 4H, $CH_2$), 2.34 (s, 6H, $SCOCH_3$), 1.91 (c, 4H, $CH_2$); $^{13}C$ NMR ($CDCl_3$): 195.3 (COMe), 128.0, 127.90 (lateral C=C), 110.4, 110.3 (central C=C), 72.0, 70.6, 70.5, 70.1 ($CH_2O$), 59.0 ($OCH_3$), 35.5, 34.9, 30.6, 29.5, 27.7 ($SCH_2$, $CH_2$, $SCOCH_3$); HRMS (ESI+): $(M+Na)^+$ Theo.: 879.0454, found: 879.0417.

**4.3.2. 2,3-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl]-6,7-bis(6-acetylsulfanylhexyl-1-sulfanyl)tetrathiafulvalene (10b).** Yield 40%; orange oil; $C_{36}H_{60}O_8S_{10}$; $^1H$ NMR ($CDCl_3$): 3.59–3.75 (m, 16H, $CH_2O$), 3.55 (m, 4H, $SCH_2CH_2O$), 3.37 (s, 6H, $OCH_3$), 3.01 (t, 4H, $SCH_2CH_2O$), 2.76–2.87 (2t, 8H, $CH_2$), 2.31 (s, 6H, $COCH_3$), 1.52–1.79 (m, 8H, $CH_2$), 1.34–1.50 (m, 8H, $CH_2$); $^{13}C$ NMR ($CDCl_3$): 195.8 (COMe), 127.9, 127.79 (lateral C=C), 110.9, 109.5 (central C=C), 72.0, 70.6, 70.6, 70.1 ($CH_2O$), 59.0 ($OCH_3$), 36.2, 35.5, 30.6, 29.4, 29.3, 29.0, 28.3, 28.1 ($SCH_2$, $CH_2$, $SCOCH_3$); HRMS (ESI+): $(M+Na)^+$ Theo.: 963.1393, found: 963.1412.

### 4.4. TTF–dithiol derivatives (11a) and (11b)

Compounds **11a** and **11b** were prepared according a similar procedure as for monothiol–TTF derivative **8**, starting from the bis(thioacetyl)–TTF derivative **10a** and **10b**, respectively. They were purified by silicagel column chromatography (ethyl acetate).

**4.4.1. 2,3-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl]-6,7-bis(3-mercaptopropyl-1-sulfanyl)tetrathiafulvalene (11a).** $C_{26}H_{44}O_6S_{10}$; orange oil; Yield: 94%; $^1H$ NMR ($CDCl_3$): 3.64–3.69 (m, 16H, $CH_2O$), 3.55 (m, 4H, $SCH_2CH_2O$); 3.38 (s, 6H, $OCH_3$), 3.00 (t, 4H, $SCH_2CH_2O$), 2.95 (t, 4H, $SCH_2$), 2.68 (dd, 4H, $CH_2SH$), 1.93 (c, 4H, $CH_2$), 1.38 (t, 2H, SH); $^{13}C$ NMR ($CDCl_3$): 128.0 (lateral C=C), 110.7 (central C=C), 72.0, 70.7, 70.6, 70.1 ($CH_2O$), 59.0 ($OCH_3$), 35.5, 34.5, 33.4, ($SCH_2$, $CH_2$), 23.0 ($CH_2SH$); HRMS (ESI+): $(M+Na)^+$) Theo.: 793.0264, found: 793.0063.

**4.4.2. 2,3-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl]-6,7-bis(6-mercaptohexyl-1-sulfanyl)tetrathiafulvalene (11b).** Yield 70%; orange oil; $C_{32}H_{56}O_6S_{10}$; $^1H$ NMR ($CDCl_3$): 3.64–3.69 (m, 16H, $CH_2O$), 3.56 (m, 4H, $SCH_2CH_2O$), 3.38 (s, 6H, $OCH_3$), 3.00 (t, 4H, $SCH_2CH_2O$), 2.82 (t, 4H, $SCH_2$), 2.52 (dd, 4H, $CH_2SH$), 1.60–1.66 (m, 8H, $CH_2$), 1.41–1.43 (m, 8H, $CH_2$), 1.35 (t, 2H, SH); HRMS (ESI+): $(M+Na^+)$ Theo.: 877.1030, found: 877.1025.

**4.4.3. 2,6(7)-Bis(methylsulfanyl)-3,7(6)-bis(3-acetylsulfanylpropyl-1-sulfanyl)tetrathiafulvalene (15).** Compounds **15** was prepared according a similar procedure as for monothioacetyl–TTF derivative **7**, starting from the dicyano–TTF derivative **14**[10] and using 2.6 equiv of cesium hydroxide monohydrate. Compound **15** was purified by silicagel column chromatography (petroleum ether/dichloromethane: 9:1) and was obtained as a mixture of *Z*/*E* isomers. Yield 97%; Orange solid; $C_{18}H_{24}O_2S_{10}$; $^1H$ NMR ($CDCl_3$): 3.01 (t, $J=7.1$ Hz, 4H, $CH_2SCOCH_3$), 2.86 (t, $J=7.1$ Hz, 4H, $CH_2S$), 2.43, 2.44 (two s, 6H, $CH_3S$), 2.34 (s, 6H, $CH_3CO$), 1.91 (quint., $J=7.1$ Hz, 4H, $CH_2CH_2S$); $^{13}C$ NMR ($CDCl_3$): 195.3 (CO, 31.0 and 131.1 (lateral C=C), 124.6, 124.4, 110.6 (central C=C), 34.9 ($SCH_2$), 30.6 ($SCOCH_3$), 29.4, 29.7 ($CH_2CH_2S$), 27.6 ($CH_2SCO$), 19.2 ($SCH_3$); MS (FAB): 591.8 ($M^+$); HRMS (FAB): ($M^+$) Theo.: 591.8983, found: 591.8994.

**4.4.4. 2,6(7)-Bis(methylsulfanyl)-3,7(6)-bis(3-mercaptopropyl-1-sulfanyl)tetrathiafulvalene (16).** Compounds **16** was prepared according a similar procedure as for monothiol–TTF derivative **8**, starting from the bis(thioacetyl)–TTF derivative **15**. The final product **16**, obtained as a *Z*/*E* mixture, was purified by silicagel column chromatography (petroleum ether/dichloromethane: 9:1). Yield 92%; Orange oil; $C_{14}H_{20}S_{10}$; $^1H$ NMR ($CDCl_3$): 2.94 (t, $J=6.8$ Hz, 4H, $CH_2S$), 2.69 (dd, $J=7.0$, 7.7 Hz, 4H, $CH_2SH$), 2.44 (s, 6H, $CH_3S$), 1.93 (m, 4H, $CH_2CH_2S$), 1.38 (t, $J=8.1$ Hz, 2H, SH); $^{13}C$ NMR ($CDCl_3$): 130.9, 131.1 (lateral C=C); 124.6, 124.5, 110.6 and 110.7 (central C=C), 33.3, 34.4 ($CH_2S$ and $CH_2CH_2SH$), 23.0 ($CH_2SH$), 19.2 ($SCH_3$); MS (FAB): 507.9 ($M^+$); HRMS (FAB): ($M^+$) Theo.: 507.8772, found: 507.8754.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2006.02.054. Electrochemical (CV) titration study for self-assembled monolayers of compound **11b** with $Pb(ClO_4)_2$.

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16. As pointed by one referee that we acknowledge, the previous hypothesis—a higher TTF density leads to a lower electrochemical recognition—may be supported by the fact that a slight decrease of $\Delta E^1_{ox}$ (= +50 mV) is observed with SAMs from **11b** ($\Gamma = 1.4 \times 10^{-10}$ mol TTF $cm^{-2}$) compared to SAMs from **8** (same alkyl chain length) ($\Gamma = 1.0 \times 10^{-10}$ mol TTF $cm^{-2}$ for **8**).