

Full Paper

Synthesis and Properties of Novel Unsymmetrical Donor Molecules Containing *p*-Acetoxy- or *p*-Hydroxyphenyl Units

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Abstract: We report the synthesis and properties of eight new tetrathiafulvalene (TTF) derivatives containing two different functionalities, prepared with the aim of obtaining stable organic materials. The four acetoxyphenyl- and four hydroxyphenyl TTFs were synthesized via Wittig-type condensations. The electrochemical properties of these redox-active molecules were studied by cyclic voltammetry. Charge transfer complexes with tetracyanoquinodimethane (TCNQ) were prepared by chemical redox reactions. The complexes have been proven to give conducting materials. The UV-VIS and IR spectra of the TCNQ salts were recorded and used to characterize and estimate the degree of charge transfer of these complexes.

Keywords: Tetrathiafulvalene, voltammetry, organic materials, conductivity, degree of charge transfer.

Introduction

Because of their exciting electroactive properties, organic tetrathiafulvalene (TTF) compounds are the subject of much interest [1-3]. The most interesting of these systems is the salt formed between TTF and tetracyanoquinodimethane (TCNQ), which displays metallic-like behavior over a wide temperature range and exceptional electrical conductivity ($\sigma_{\max, 58\text{ K}} = 10^4 \text{ S}\cdot\text{cm}^{-1}$) [4-6]. Most of the

prior work, however, has been devoted to the search for new TTF derivatives capable of giving salts with higher electrical conductivity. Consequently, many changes were made to the parent TTF donor leading, for example, to the synthesis of a wide variety of selenium derivatives, asymmetrically substituted compounds, polychalcogenated TTFs, etc. In order to consolidate the asymmetrical character of the donors, several tetrathiafulvalene derivatives containing different groups such as nitronylnitroxide [7], 4,5-diformyl [8], aminomethyl [9] and hydroxymethyl [10] have been described. They were found to be versatile starting new donors for the synthesis of new organic materials.

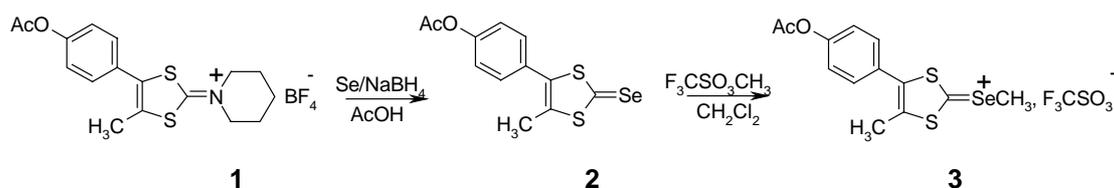
Recently, and proceeding from accessible conducting organic materials, we synthesized a series of TTF derivatives containing peripheral selenium atoms and demonstrated their ability to form charge transfer complexes and radical cation salts [11,12]. Within the framework of our interest in organic materials we now describe in this paper the synthesis and properties of some new asymmetrical donors containing acetoxyphenyl and hydroxyphenyl groups. These compounds have been investigated by means of cyclic voltammetry. The electron donor properties of the various compounds obtained have been found to be lower to those of TTF. Conducting charge transfer complexes are also presented. The degree of charge transfer and molecular stacking were estimated by spectroscopic data.

Results and Discussion

Synthesis

We have synthesized *p*-acetoxyphenyltrimethyltetrathiafulvalene pAcPhTrMeTTF (**5a**) [13] by two different methodologies. The first involved the condensation of 5-(*p*-acetoxyphenyl)-4-methyl-1,3-dithiolium perchlorate with 4,5-dimethyl-1,3-dithiolium hexafluorophosphate in triethylamine to give 2-(4-acetoxyphenyl)-3,6,7-trimethyltetrathiafulvalene in 15% yield. The second route involved the reaction of 2-diethoxyphosphinyl-4,5-dimethyl-1,3-dithiole with 5-(*p*-acetoxyphenyl)-4-methyl-1,3-dithiole-2-ylidenepiperidinium tetrafluoroborate under Wittig-like conditions to form the target TTF **5a** in 20% yield. Despite these poor yields, we nevertheless prepared the other asymmetrical derivatives, that is 2-(4-acetoxyphenyl)-3-methyl-6,7-(propane-1,3-diyl)tetrathiafulvalene (**5b**), 2-(4-acetoxyphenyl)-3-methyl-6,7-(butane-1,4-diyl)tetrathiafulvalene (**5c**) and 2-(4-acetoxyphenyl)-3-methyl-6,7-(buta-1,3-dien-1,4-diyl)tetrathiafulvalene (**5d**) applying the cross-coupling reaction [14] of 1,3-dithiole-2-methyl-selenoxonium salts with 1,3-dithiole-2-triphenylphosphonium salts.

Scheme 1. Synthesis of 2-methylseleno-1,3-dithiolium trifluoromethanesulfonate.

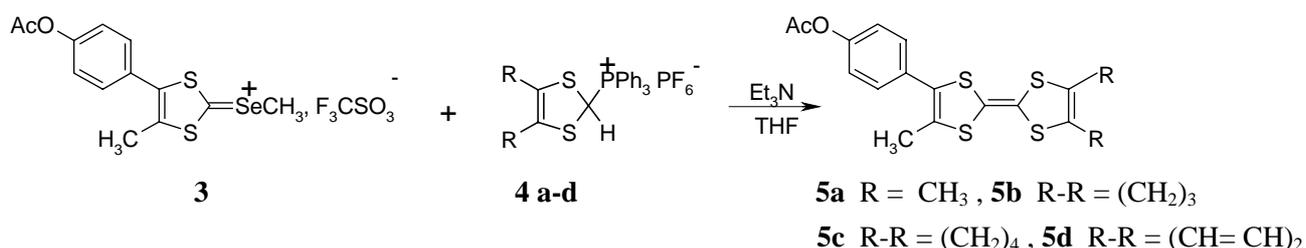


As shown in Scheme 1, treatment of 5-*p*-acetoxyphenyl-4-methyl-1,3-dithiole-2-ylidene-piperidinium tetrafluoroborate (**1**) with sodium hydrogen selenide, prepared *in situ* from selenium and sodium borohydride in ethanol at low temperature, followed by an aqueous work up, led to a good yield (95 %) of the corresponding red 5-(*p*-acetoxyphenyl)-4-methyl-1,3-dithiole-2-selenone (**2**) [15].

2-Methylseleno-5-(*p*-acetoxyphenyl)-4-methyl-1,3-dithiolium trifluoromethanesulfonate (**3**) [16] was obtained in good yield (95 %) by alkylation of **2** with triflate.

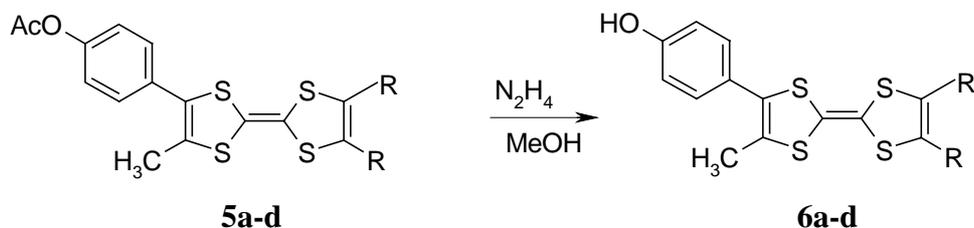
The phosphonium salts **4a-d** [16] were dissolved in dry acetonitrile together with one equivalent of selenoxonium salt **3** (Scheme 2). The mixtures were stirred under nitrogen and an excess of triethylamine was added slowly, followed by a further 3 h of stirring at room temperature. The solvent was evaporated and the crude products were dissolved in chloroform, washed with water and dried. Evaporation of chloroform, followed by purification using chromatography on silica with benzene as eluent and recrystallization from hexane gave *p*AcPhTrMeTTF **5a**, *p*AcPhMeCpTTF **5b**, *p*AcPhMeChTTF **5c** and *p*AcPhMeBzTTF **5d** as red crystals in 15-33 % yields.

Scheme 2. Classic Synthetic Route for the Preparation of *p*AcPhTTF Derivatives



Deacetylation of these asymmetrically *p*-acetoxyphenyltetraathiafulvalenes with hydrazine in methanol (Scheme 3) yielded the desired *p*-hydroxyphenyltetraathiafulvalenes *p*HyPhTrMeTTF **6a**, *p*HyPhMeCpTTF **6b**, *p*HyPhMeChTTF **6c** and *p*HyPhMeBzTTF **6d** as red crystals in 85-90 % yields.

Scheme 3. Efficient Synthetic Route for the Desacetylation of TTF Derivatives



Electrochemical studies

The oxidation potentials of the donor molecules were determined by cyclic voltammetry. Measurements were performed under nitrogen at room temperature using a glassy carbon working electrode, a Pt counter electrode and a standard calomel electrode (SCE) as reference, with tetrabutylammonium perchlorate (n-Bu₄NClO₄, 0.1 M) in dry acetonitrile and 1,2,2-trichloroethane, as supporting electrolyte. A scan rate of 100 mVs⁻¹ was used. The results are reported in Table 1.

All TTFs showed two pairs of reversible waves. These results indicate that the presence of the acetoxy CH₃CO- and hydroxy -OH functions relatively far away from the TTF core on the side C₆H₄-chain, has only a very weak influence on the redox potential values of the compounds **5a-d** and **6a-d**. It is also noteworthy that the benzo -C₆H₄- (buta-1,3-dien-1,4-diyl) grouping exerts withdrawing effects, as indicated by the observed E_{ox1} and E¹_{1/2} values in acetonitrile solution for **5d** (0.48, 0.45 V)

and **6d** (0.46, 0.43 V), respectively. Similar observations can be made about the other series of compounds **5a-c** and **6a-c**.

Table 1. Redox potentials and K_{SEM} data of **5a-d** and **6a-d**.

Donor	Acetonitrile								1,1,2-Trichloroethane					
	E_{ox1}	E_{ox2}	ΔE_{ox}	$E^1_{1/2}$	$E^2_{1/2}$	$\Delta E_{1/2}$	$^a\Delta E_{1/2}$	K_{SEM}	E_{ox1}	E_{ox2}	ΔE_{ox}	$E^1_{1/2}$	$E^2_{1/2}$	$\Delta E_{1/2}$
5a	0.30	0.64	0.34	0.28	0.62	0.34	0.08	$5.8 \cdot 10^5$	0.42	0.86	0.44	0.34	0.78	0.44
5b	0.32	0.80	0.48	0.28	0.67	0.39	0.08	$39 \cdot 10^5$	0.46	0.90	0.44	0.38	0.81	0.43
5c	0.32	0.66	0.34	0.29	0.64	0.35	0.09	$8.5 \cdot 10^5$	0.46	0.92	0.46	0.33	0.79	0.46
5d	0.48	0.82	0.34	0.45	0.77	0.32	0.25	$2.6 \cdot 10^5$	0.62	1.08	0.46	0.53	0.98	0.45
6a	0.30	0.64	0.34	0.26	0.62	0.36	0.06	$13 \cdot 10^5$	0.36	0.82	0.46	0.29	0.73	0.44
6b	0.30	0.64	0.34	0.28	0.61	0.33	0.08	$3.9 \cdot 10^5$	0.38	0.84	0.46	0.32	0.74	0.42
6c	0.34	0.70	0.36	0.31	0.65	0.34	0.11	$5.7 \cdot 10^5$	0.36	0.82	0.46	0.31	0.75	0.44
6d	0.46	0.80	0.34	0.43	0.78	0.35	0.23	$8.5 \cdot 10^5$	0.54	1.00	0.46	0.49	0.92	0.43
TTF	0.37	0.74	0.37	0.32	0.69	0.37	0.12	$1.9 \cdot 10^5$	0.82	1.08	0.26	0.58	1.0	0.42
TMTTF	0.29	0.65	0.36	0.24	0.60	0.36	0.04	$13 \cdot 10^5$	-	-	-	-	-	-

$$^a\Delta E_{1/2} = E^1_{1/2} - E^2_{1/2}; \quad ^*E^1_{1/2} = E^1_{1/2 \text{ red (TCNQ)}} = 0.2 \text{ V}; \quad E^2_{1/2 \text{ red (TCNQ)}} = -0.36 \text{ V}.$$

Due to the well known donating effect exerted by the methyl, propane-1,3-diyl and butane-1,4-diyl substituents these TTF derivatives are better electron donors than the parent TTF taken as a reference. On the other hand, the $\Delta E_{1/2}$ values, in ACN, of the majority of TTFs are smaller than those of the unsubstituted parent compound TTF (0.37 V), which suggests a decrease in the onsite coulombic repulsion in the dication by delocalisation of two positive charges over the whole molecule. In TCE as the solvent, the π -ability of all compounds appears exceptionally strong, since for all of them, the ΔE_{ox} is markedly higher than of the parent TTF (0.28 V). Those complexes have $|E^1_{1/2(D)} - E^1_{1/2(A)}|$ values and favor the partial charge transfer. These results compare well with those of Wheland [17] and Torrance [18].

The thermodynamic stability of radical cations was determined from the difference in potentials of the corresponding radical cation and dication using the equation $\Delta E = E^1_{1/2} - E^2_{1/2} = 0.059 \log K_{SEM}$ (Table 1) where K_{SEM} is the equilibrium constant in equation: $D + D^{2+} \rightleftharpoons 2 D^+$. For electron donor TTF compounds, the thermodynamic stability of the cation radical diminishes in the following order: **5b** > **6a** > **5c** = **6d** > **5a** = **6c** > **6b** > **5d**, due to a decrease in intermolecular coulombic repulsion.

Electrical conductivity and activation energies of charge transfer complexes

Complexation of the donors **5a-d** and **6a-d** with 7,7,8,8-tetracyanoquinodimethane in hot acetonitrile solution gave the corresponding complexes. Most of the solids were isolated in polycrystalline or powder forms. Electrical conductivity was only measured on compressed pellets at room temperature using a two probe technique. The results are reported in Table 2. All TCNQ complexes exhibited a conductivity higher than 0.5 Scm^{-1} ; the **5d**-TCNQ sample displayed semiconducting behavior, with conductivity less than 10^{-6} Scm^{-1} . The **6**-TCNQ salts (0.5 - 5.5 Scm^{-1}) exhibits higher conductivity than that of the other **5**-TCNQ salts ($0.5 - 3.5 \cdot 10^{-6} \text{ Scm}^{-1}$).

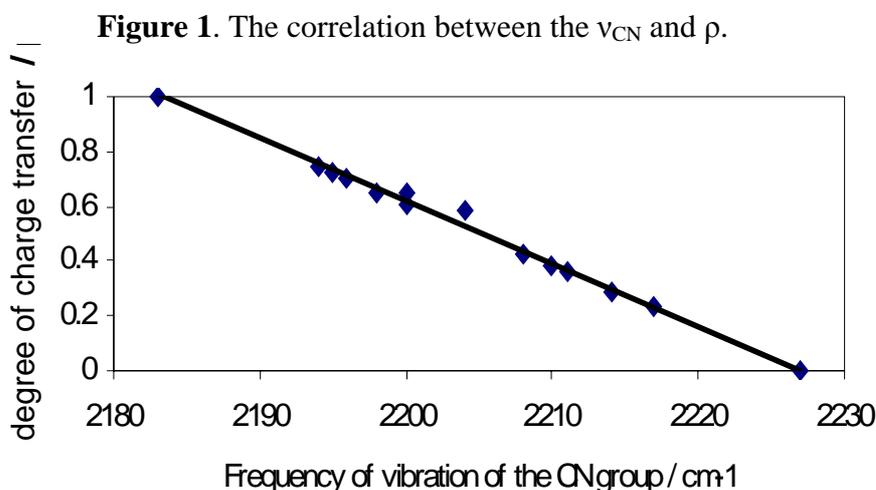
A *p*-hydroxyphenyl group attached to a TTF framework seems to increase the conductivity, compared with the corresponding *p*-acetoxyphenyl group. For the TCNQ complexes with comparatively higher electrical conductivities the E_a values were small (0.09-0.15 eV). On the other hand, an insulating salt such as **5d**-TCNQ had considerably higher activation energy (0.46 eV).

Table 2. Electrical conductivity and activation energies of charge transfer complexes.

Complex	σ_{RT} (S cm^{-1})	E_a (eV)	Complex	σ_{RT} (S cm^{-1})	E_a (eV)
5a -TCNQ	2	0.116	6a -TCNQ	3.5	0.100
5b -TCNQ	0.5	0.152	6b -TCNQ	2.0	0.116
5c -TCNQ	1.5	0.122	6c -TCNQ	5.5	0.090
5d -TCNQ	$3.5 \cdot 10^{-6}$	0.462	6d -TCNQ	0.5	0.152

IR Spectroscopic studies

It is established that the complexes of type TTF-TCNQ have to satisfy two conditions to give a conductor. The first requires the presence of a crystal structure composed of regular segregated stacks ...DDD-AAA... of donors and acceptors [19]; while the second is a partial electron transfer ($0 < \rho < 1$) between these two species. Any of mixed stack "sandwich" structures ...DAD-DAD... of the salt or the absence of a charge transfer (molecular complex) or a complete charge transfer (ionic complex) lead to an insulating material [20, 21].



Due to the lack of monocrystals, various authors were able to estimate the rate of charge transfer of this type of complex from different techniques [22] and in particular from the IR spectra [23, 24]. Based on the relation between the frequency of vibration of the CN group and the degree of charge transfer for reference compounds such as TCNQ⁰ ($\nu_{CN} = 2227 \text{ cm}^{-1}$, $\rho = 0 \text{ e}^-/\text{molecule}$), TCNQ⁻K⁺ (2183 cm^{-1} , 1), TTF-TCNQ (2204 cm^{-1} , 0.59), HMTTF-TCNQ (2195 cm^{-1} , 0.72), TMTTF-TCNQ (2200 cm^{-1} , 0.65), TMTSF-TCNQ (red) (2217 cm^{-1} , 0.23), etc. We were able to draw a $\rho = f(\nu_{CN})$ straight line, which corresponds to the correlation between the vibration frequencies of the CN group and the degree of charge transfer for different TTFs. The curve equation is $y = -0.0228x + 50.71$. The coefficient of determination is $R^2 = 0.9933$ (Figure 1).

We recorded the IR spectra of all complexes prepared in the 2100 and 2250 cm^{-1} range and we obtained the vibration frequency of the CN group for each complex. The ν_{CN} frequency was then used on the calibration $\rho = f(\nu_{\text{CN}})$ curve to determine the approximate value of the degree of charge transfer (ρ). The results are reported in Table 3.

Table 3. Degree of charge transfer of TCNQ complexes.

Complex	$\nu_{\text{CN}} (\text{cm}^{-1})$	$\rho (\text{e}^-/\text{mole})$	Complex	$\nu_{\text{CN}} (\text{cm}^{-1})$	$\rho (\text{e}^-/\text{mole})$
5a -TCNQ	2198	0.69	6a -TCNQ	2211	0.37
5b -TCNQ	2200	0.63	6b -TCNQ	2214	0.30
5c -TCNQ	2196	0.74	6c -TCNQ	2210	0.40
5d -TCNQ	2208	0.45	6d -TCNQ	2194	0.79

It appears that the conducting materials: **5a-c**-TCNQ, and **6a-d**-TCNQ, present a partial degree of charge transfer in the 0.30 to 0.79 $\text{e}^-/\text{molecule}$ range. These values are comparable to those of known conductors, such as Cu(PC)I (0.33), TTF-TCNQ (0.59) and HMTTF-TCNQ (0.72) [24]. Considering these results, it is reasonable to propose that the conducting charge transfer complexes studied here possess a segregated stacking structure.

As for the nonconducting **5d**-TCNQ, the value of the degree of charge transfer is about 0.43 $\text{e}^-/\text{molecule}$. This value is in a range that would favor a metallic behavior for this salt. Since it is semiconducting, we are lead to believe that the requirement regarding the stacking of the molecules is not met. Several explanations for this behavior might be a mixed stack (sandwich) structure, a large separation between stacked donors, the presence of structural disorder [19], etc. When a comparison was made between the $E_{1/2}^1$ values of the hydroxy donors **6a-d** and ρ values of the TCNQ complexes, it was found that the degree of electron transfer from the donor to TCNQ decreases in the TCNQ complex, as the $E_{1/2}^1$ value of the donor becomes smaller.

The electrical results are consistent with those of the electronic spectra of the complexes in KBr pellets. The high conductivity of the conducting complexes was expected from both the black shiny crystals and the broad band observed in the FTIR spectrum at about 2500 cm^{-1} . This band is generally present in all the conducting charge transfer complexes of TTF-TCNQ [19]. The other complex, which is insulator, is slightly colored and the band at 2500 cm^{-1} is not observed in the IR spectrum. The CT band is probably shifted to higher frequencies as it is typical in such semiconducting complexes [19].

Conclusions

Although the Wittig-type synthetic strategy described in this paper affords low overall yields we have prepared two series of new asymmetric TTF derivatives containing *p*-acetoxyphenyl and *p*-hydroxyphenyl groups. The side chains that we introduced preserve the electron donating character of these TTFs, as shown by cyclic voltammetry. Several salts showing comparatively high room temperature conductivity were obtained. We have discussed the origin of the semiconducting behavior of some of the TTF derivatives and indicated that the semiconducting salts exhibited a charge transfer band at higher energy, suggesting stronger coulombic repulsions. The possibility of producing new cation-radical salts in these series and the X-ray structural details [12], are under investigation.

Experimental

General

NMR spectra were recorded on a Bruker AC 250 instrument. FAB mass spectra were recorded on a JOEL JMS-DX 300 spectrometer. IR spectra were recorded at 0.5 cm⁻¹ resolution on an Equinox 55 instrument. Melting points were measured on a Buchi apparatus. Cyclic voltammetry measurements were carried out on a PAR-273 potentiostat/galvanostat. All reagents were of commercial quality and solvents were dried, where necessary, using standard procedures. All reactions were performed under an inert atmosphere of nitrogen. THF was distilled from sodium/benzophenone immediately prior to use in pre-dried glassware.

5-(*p*-Acetoxyphenyl)-4-methyl-1,3-dithiole-2-selenone (**2**)

Black powdered selenium (2.8 g, 35.37 mmol) was added in one portion with magnetic stirring at 0 °C under argon to a solution of sodium borohydride (7.7 g, 70.74 mmol) in ethanol (40 mL). A vigorous reaction with considerable foaming occurred immediately and the selenium was consumed in less than 30 min. The virtually colorless solution of NaHSe which resulted was ready for use without further treatment. After cooling of the solution acetic acid (2 mL, 35.37 mmol) and 5-*p*-acetoxyphenyl-4-methyl-1,3-dithiole-2-ylidenepiperidinium tetrafluoroborate (**1**, 15 g, 35.37 mmol) were added and the reaction mixture was allowed to stand at room temperature for *ca.* 2 h. The ethanol was diluted to 100% with deoxygenated ice water and the red solid filtered, washed with water, dried under vacuum and chromatographed (silica gel, CHCl₃). Recrystallization of the product from heptane gave **2** (11.14 g, 95% yield) as red orange crystals; mp 143-144 °C; ¹H-NMR (CDCl₃) δ 2.28 (s, 3H), 2.33 (s, 3H), 7.28 (m, 4H).

2-Methylseleno-5-(*p*-acetoxyphenyl)-4-methyl-1,3-ditholium trifluoromethane sulfonate (**3**)

A suspension of 5-(*p*-acetoxyphenyl)-4-methyl-1,3-dithiole-2-selenone (11.06 g, 33.62 mmol) in dry methylene chloride (50 mL) was treated with methyl triflate (4.8 mL, 38.4 mmol). The mixture was stirred under nitrogen for 4 h. A layer of dry ether (150 mL) was added. The deep reddish-orange salt **3** was filtered after 24 h, washed with more dry ether, and dried. Yield: 16 g (95 %); mp 148-149 °C; ¹H-NMR (CDCl₃): δ 2.65 (s, 3H), 3.03 (s, 3H), 3.39 (s, 3H), 7.23 (m, 4H).

2-(4-Acetoxyphenyl)-3-methyl-6,7-dialkyl tetrathiafulvalenes **5a-d**

A solution of 2-methylseleno-5-(*p*-acetoxyphenyl)-4-methyl-1,3-ditholium trifluoromethane-sulfonate (**3**, 4g, 8 mmol) and 4,5-dialkyl-1,3-dithiole-2-triphenylphosphonium (8 mmol) in tetrahydro-furan (80 mL) was treated with triethylamine (25 mL) at room temperature under nitrogen. After the reaction mixture was stirred for 4h, the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel with benzene as the eluent. The product was purified by recrystallization from heptane to afford **5a-d**.

p-Acetoxyphenyltrimethyltetrathiafulvalene (**5a**). Yield: 30 %; mp: 220-221 °C; ¹H-NMR (CDCl₃): δ 1.96 (s, 6H), 2.04 (s, 3H), 2.32 (s, 3H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H); ¹³C-NMR (CDCl₃): δ 14.5, 15.7, 21.9, 107.4, 109.8, 122.6, 123.6, 123.7, 126.4, 127.6, 130.9, 151.1, 170.0; IR (KBr, cm⁻¹): 3050, 2900, 1750, 1490, 1430, 1200, 690; MS (FAB) *m/z*: 380 [M]⁺; Anal. Calc. for C₁₇H₁₆O₂S₄: C, 53.68; H, 4.21; S, 33.68. Found: C, 53.76; H, 4.24; S, 33.20.

2-(4-Acetoxyphenyl)-3-methyl-6,7-(propane-1,3-diyl)tetrathiafulvalene (**5b**). Yield: 15 %; mp: 165-166 °C; ¹H-NMR (CDCl₃): δ 2.05 (m, 2H), 2.18 (s, 3H), 2.32 (s, 3H), 2.41 (m, 4H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H); ¹³C-NMR (CDCl₃): δ 14.9, 21.1, 27.6, 30.1, 116.8, 121.8, 125.4, 126.5, 130.2, 133.1, 133.2, 150.4, 169.3; IR (KBr, cm⁻¹): 3030, 2920, 1740, 1500, 1200, 650; MS (FAB) *m/z*: 392 [M]⁺; Anal. Calc. for C₁₈H₁₆O₂S₄: C, 55.10; H, 4.0; S, 32.65. Found: C, 55.23; H, 4.02; S, 32.72.

2-(4-Acetoxyphenyl)-3-methyl-6,7-(butane-1,4-diyl)tetrathiafulvalene (**5c**). Yield: 33 %; mp: 180-181 °C; ¹H-NMR (CDCl₃): δ= 1.79 (m, 4H); 2.04 (m, 4H); 2.32 (s, 6H); 7.13 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H); ¹³C-NMR (CDCl₃): δ 14.9, 21.1, 22.5, 25.7, 107.3, 109.2, 121.8, 125.6, 125.9, 126.0, 126.8, 130.2, 130.3, 150.4, 169.2; IR (KBr, cm⁻¹): 3040, 2900, 2890, 1760, 1430, 1200, 690; MS (FAB) *m/z*: 406 [M]⁺; Anal. Calc. for C₁₉H₁₈O₂S₄: C, 56.15; H, 4.43; S, 31.52. Found: C, 55.85; H, 4.31; S, 31.47.

2-(4-Acetoxyphenyl)-3-methyl-6,7-(buta-1,3-dien-1,4-diyl)tetrathiafulvalene (**5d**). Yield: 31 %; mp: 160-161 °C; ¹H-NMR (CDCl₃): δ 2.07 (s, 3H), 2.33 (s, 3H), 7.13 (m, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.40 (m, 2H); ¹³C-NMR (CDCl₃): δ 14.9, 21.1, 121.8, 121.9, 125.4, 125.8, 130.0, 130.2, 137.0, 137.1, 150.5, 169.2; IR (KBr, cm⁻¹) 3010, 2900, 2890, 1730, 1500, 1200, 690; MS (FAB) *m/z*: 402 [M]⁺; Anal. Calc. for C₁₉H₁₄O₂S₄: C, 56.71; H, 3.48; S, 31.84. Found: C, 56.40; H, 3.36; S, 32.34.

2-(4-hydroxyphenyl)-3-methyl-6,7-dialkyl tetrathiafulvalenes **6a-d**

Hydrazine hydrate (3 mL) was added dropwise to a suspension of **5a-d** (1.4 mmol) in methanol (30 mL) at room temperature. After the reaction mixture was stirred for 4 h, water was added. The precipitate was collected by filtration and washed with water. The solid was collected and column chromatographed on silica gel with dichloromethane as eluent to afford **6a-d**.

p-Hydroxyphenyltrimethyltetrathiafulvalene (**6a**). Yield: 75 %; mp: 158 °C; ¹H-NMR (CDCl₃): δ 2.14 (s, 6H), 2.40 (s, 3H), 7.4 (m, 4H), 9.40 (s, 1H); IR (KBr, cm⁻¹): 3640, 2919, 2850, 1503, 1433, 1168, 693; MS (FAB) *m/z*: 338 [M]⁺.

2-(4-Hydroxyphenyl)-3-methyl-6,7-(propane-1,3-diyl)tetrathiafulvalene (**6b**). Yield: 72 %; mp: 132 °C; ¹H-NMR (CDCl₃): δ 2.5 (m, 6H), 2.46 (s, 3H), 7.35 (m, 4H), 9.85 (s, 1H); IR (KBr, cm⁻¹): 3650, 2917, 2849, 1604, 1439, 1094, 701; MS (FAB) *m/z*: 350 [M]⁺.

2-(4-Hydroxyphenyl)-3-methyl-6,7-(butane-1,4-diyl)tetrathiafulvalene (**6c**). Yield: 78 %; mp: 110 °C; ¹H-NMR (CDCl₃): δ 1.75 (s, 4H), 2.25 (s, 4H), 2.44 (m, 3H), 7.62 (m, 4H), 9.80 (s, 1H); IR (KBr, cm⁻¹): 3649, 3051, 2926, 1604, 1329, 1170, 747; MS (FAB) m/z: 364 [M]⁺.

2-(4-Hydroxyphenyl)-3-methyl-6,7-(buta-1,3-dien-1,4-diyl)tetrathiafulvalene (**6d**). Yield: 80 %; mp: 155 °C; ¹H-NMR (CDCl₃): δ 2.07 (s, 3H), 7.06 (m, 8H), 9.39 (s, 1H); IR (KBr, cm⁻¹): 3417, 3037, 2903, 1358, 1123, 836, 693; MS (FAB) m/z: 360 [M]⁺.

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Sample Availability: Samples of some of the compounds mentioned are available from the authors.

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