Novel unsymmetrically *p*-acetoxyphenyl and *p*-hydroxyphenyl tetrathiafulvalenes: Synthesis, electrochemical properties and electrical conductivity of their charge transfer complexes

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Organic molecules such as tetrathiafulvalene (TTF) and its derivatives are important precursors in the design of new conducting, optical and magnetic materials. A new series of unsymmetrically tetrathiafulvalenes have been synthesised. The synthesis of *p*-acetoxyphenyl tetrathiafulvalenes **5a-d** has been carried out by Wittig reaction and their deprotection leads to *p*-hydroxyphenyl tetrathiafulvalenes **6a-d**. The structures have been assigned by ^{1}H NMR spectroscopy and mass spectra. The reducing power of each new precursor has been determined by cyclic voltammetry. Charge transfer complexes of the donors with Tetracyanoquinodimethane (TCNQ) have been prepared and characterized. The electrical conductivity of these materials have been measured and discussed.

Keywords: Tetrathiafulvalenes, organic materials, redox potentials, conductivity

Tetrathiafulvalene (TTF)[1-3] and its derivatives have attracted intense interests in various areas of chemistry and materials science due to their versatile behaviours, such as reversible redox properties and strong electron donating capabilities for preparing charge-transfer (CT) salts[4], donneurs-accepters (D-A) systems and other fields[5-7]. Since the discovery of the first metallic charge transfer salts based on tetrathiafulvalene (TTF)[8], a great number of TTF derivatives have been synthesized and investigated, such as tetrathiafulvalenylallene[9], TTF oligomers[10,11], and π-extended TTF derivatives[12]. They have been extensively studied for various applications, such as sensors, receptors, switches, conductors[13-19] and in the field of conducting organic materials involving intermolecular charge-transfer interactions with various π-accepting molecules[20,21].

In previous work[22-27] we have described the synthesis of various functional tetrathiafulvalenes. In continuation of our efforts to design and synthesize new electron donors precursors for conducting charge-transfer complexes, we have extended our studies to a series of new asymmetrical donors containing acetoxyphenyl and hydroxyphenyl groups, synthesized *via* cross-coupling and deprotection methods. The redox behaviour of such precursors has been studied by cyclic voltammetry and finally the electrical conductivity of charge transfer complexes was measured.

Results and Discussion

The synthesis of 2-Methylseleno-4-(*p*-acetoxy-phenyl)-1,3-dithioliumtrifluoro-methane sulfonate **3** was achieved according to multistep synthesis by adjusting literature procedures[28] (**Scheme I**).

The treatment of 4-*p*-acetoxyphenyl-1,3-dithiole-2-ylidenepiperidinium hexafluoro-phosphate **1** with sodium hydrogen selenide, prepared *in situ* from selenium and sodium borohydride in ethanol at low temperature, followed by an aqueous work up, afford after filtration and purification over silica gel chromato-graphy the desired product **2** in 83% yield. The alkylation of 4-(*p*-Acetoxyphenyl)-1,3-dithiole-2-selenone **2** with triflate in methylene chloride led the corres-ponding 2-Methylseleno-4-(*p*-acetoxyphenyl)-1,3 dithiolium trifluoromethane sulfonate **3** in 85% yield.

Scheme II exhibits the synthetic routes for the preparation of compounds **5a-d** and **6a-d**. The
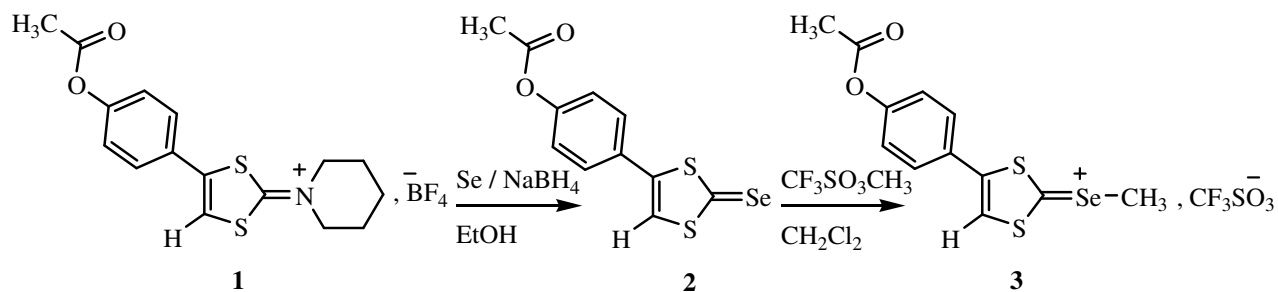
Scheme I — Synthetic route of 1,3 dithiolium trifluoromethane sulfonate **3**

a R = R = CH$_3$
b R = R = (CH$_2$)$_3$
c R = R = (CH$_2$)$_4$
d R = R = (CH=CH)$_2$
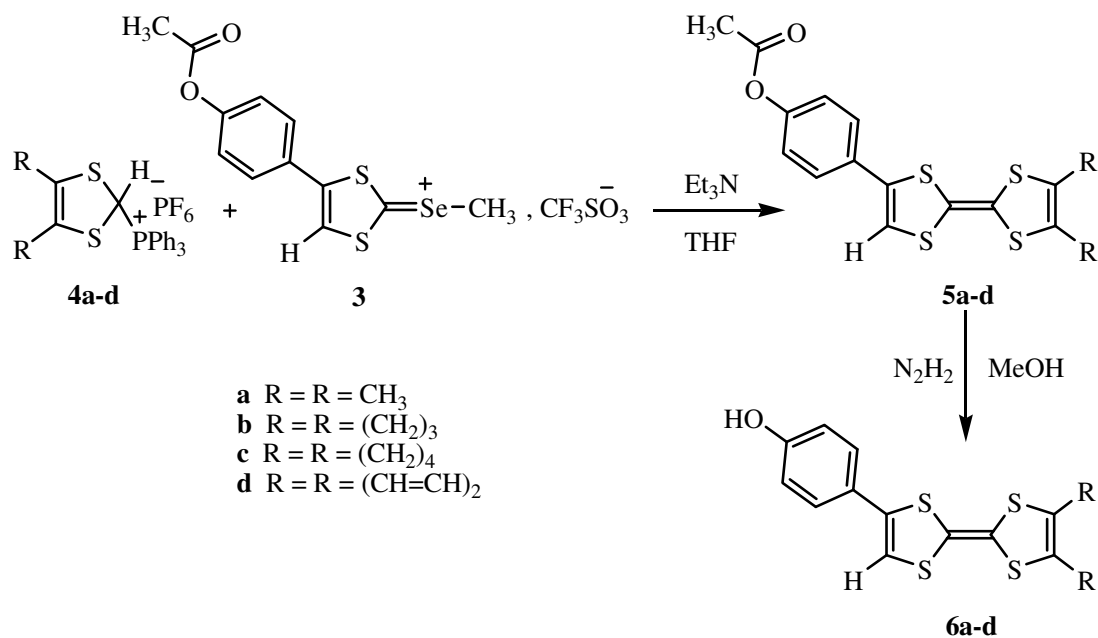
Scheme II — Synthetic route of *p*-acetoxyphenyl **5a-d** and *p*-hydroxyphenyl tetrathiafulvalenes **6a-d**

condensation *via* Wittig-type reaction of the phosphonium salts **4a-d** (Ref 28) with the selenoxonium salt **3**, in the presence of triethylamine at R T under nitrogen, leads to the formation of the desired 2-(4-acetoxy-phenyl)-6,7-dialkyl tetrathiaful-valenes **5a-d** in moderate yields (15-24%) after column chromatography. Treatment of these *p*-acetoxyphenyl-tetrathiafulvalenes **5a-d** with hydrazine in methanol followed by hydrolysis gave the unsymmetrically *p*-hydroxyphenyl-tetrathiaful-valenes **6a-d** in good to excellent yields (89-95%).

In the ^{1}H NMR spectra of compounds **5a-d**, methyl acetoxy group proton showed a singlet at δ 2.60, but compounds **6a-d** revealed the absence of the methyl acetoxy group proton signals and the presence of hydroxy group proton signals as singlet around δ 9.59-10.13. In addition, the ^{1}H NMR spectra of compounds **5a-d** and **6a-d** showed aromatic group protons as two doublets around δ 7.60-7.68 and δ 7.87-7.94, thus vinyl protons (CH=C) exhibit a singlet around δ 7.34-7.50. On the other hand, the spectrum of **5a** and **6a** exhibited a singlets for CH$_3$ groups at δ 2.05 and δ 2.22, respectively. Compound **5b** showed a multiplet at δ 2.43 for CH$_2$C**H$_2$**CH$_2$ and a triplet at δ 2.56 for C=CC**H$_2$**, the same multiplet and triplet were observed for the same protons at δ 2.45 and 2.60 respectively for compound **6b**. Compound **5c** revealed the presence of two multiplets at δ 1.70 for CH$_2$C**H$_2$** and at δ 2.20 for C=CC**H$_2$**, the same multiplets were observed for the same protons at δ 1.80 and δ 2.60 respectively for compound **6c.** Finally, compounds **5d** and **6d** showed the presence of a multiplets around δ 7.37-7.55 and δ 7.20-7.40 respectively, for aromatic protons.

Mass spectrometry analysis validated the structure of the examined derivatives. In all compounds, fragmentation peaks confirmed the structure of the analyzed molecules.

Electrochemical Properties

The redox properties of these new TTF derivatives were investigated 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 tetrabutyl-ammonium perchlorate (*n*-Bu$_4$NClO$_4$, 0.1 M) in dry acetonitrile, as supporting electrolyte. A scan rate of 100 mVs^{-1} was used. The results are reported in **Table I**. Each of the TTFs exhibits two reversible monoelectronic waves **(Figure 1)**, as usually observed for TTF derivatives. It may be noted that the electron-donating capabilities of these new compounds are slightly influenced by the presence of the *p*-acetoxy-phenyl and *p*-hydroxyphenyl groups linked to the donor core.

The three compounds **5a-c** reported here have similar structures. Compared to **5a**, compound **5c** has a lower redox potential (about 0.36 V) because the weak donor property of the methyl group enriches the electron density of the donor. Apparently, compound **5d** shows the lowest redox potential among all donors, indicating that the introduction of a phenyl group on the TTF molecule framework extends the

Table I — Data from cyclic voltammetry of compounds **5a-d** and **6a-d** in acetonitrile

Donor	E$^1_{1/2}$ (V)	E$^2_{1/2}$ (V)	ΔE$_{1/2}$ (V)
5a	0.36	0.76	0.40
5b	0.34	0.72	0.38
5c	0.31	0.67	0.36
5d	0.28	0.66	0.38
6a	0.38	0.80	0.42
6b	0.33	0.71	0.38
6c	0.31	0.69	0.38
6d	0.29	0.65	0.36
TTF	0.32	0.69	0.37
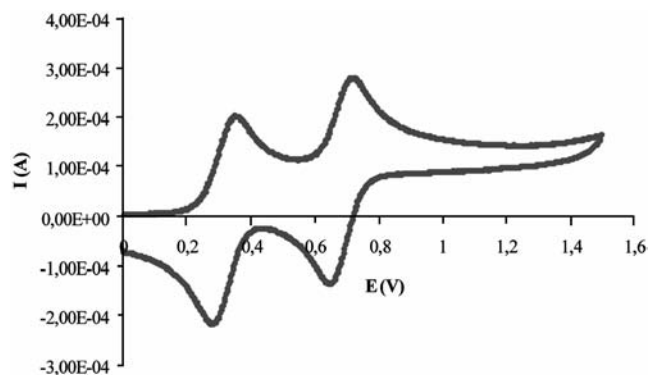
Figure 1 — Voltammogram of TTF **6b**

conjugated system and improves the electron density. Similar remarks were observed about the other series of TTFs **6a-d**.

Preparation and Electrical Conductivity of Charge Transfer Complexes

A research group led by Cowan and Ferraris observed that crystals of the 1:1 salt TTF$^+$ TCNQ$^-$ exhibited metallic-like conductivities of about 500 Scm^{-1} at RT (Ref. 8). This compares with the conductivity of copper, known to be *ca*. 10^6 Scm^{-1} at RT. Furthermore, the conductivity of TTF$^+$ TCNQ$^-$ increases as temperature decreases[8], which is characteristic of metallic behaviour[29], a maximum conductivity of 10^4 Scm^{-1} being reached at 59 K. At lower temperatures, the conductivity decreases as temperature decreases, a characteristic feature of semiconductors[29].

Further breakthroughs in the search for new organic metals came, when tetraselenafulvalene (TSF)-TCNQ was reported[30] to have a conductivity of 700 Scm^{-1}. Since then, great interest has been devoted to this type of material, and a great number of new organic donors and acceptors have been synthesized as well as their charge-transfer salts.

Therefore, all compounds **5a-6d** formed charge transfer complexes with TCNQ (tetracyano-*p*-quino-dimethane) used as an electron acceptor (A)[31-33]. The solids were isolated of variable D-A stoichiometry (calculated from elemental analyses data: **Table II**) after cooling the hot acetonitrile solution obtained by mixing equimolar amounts of the donor (D) and of TCNQ (A). Most of the materials were obtained as powders with various colours except compounds **5c** and **6a** were collected as green urchins and green needles, respectively.

The room temperature conductivity of these solids was measured by using a two probe technique on compressed pellets. The results obtained are summarized in **Table II**.

Table II — Aspect, melting points, stoichiometry and electrical conductivity of charge transfer complexes

Complex	Aspect	m.p. (°C)	D-A	σ$_{RT}$ (S cm^{-1})
5a-TCNQ	black powder	186	3-2	5,27 10^{-3}
5b-TCNQ	green powder	192	1-2	2.18 10^{-3}
5c-TCNQ	green urchins	180	1-2	2.85 10^{-3}
5d-TCNQ	yellow powder	196	3-2	8.56 10^{-3}
6a-TCNQ	green needles	182	2-1	3.64 10^{-1}
6b-TCNQ	green powder	210	2-1	4.47 10^{-1}
6c-TCNQ	green powder	175	2-1	4.28 10^{-1}
6d-TCNQ	black powder	172	1-1	3.32

It is worth noting that, despite a different stoichiometry encountered in **(5a)₃-(TCNQ)₂** and **(5d)₃-(TCNQ)₂** on one hand, and **5b-(TCNQ)₂, 5c-(TCNQ)₂** on the other hand **(Table II)**, the electrical conductivity of these complexes is quite similar and found to be around 10^{-3} Scm^{-1} suggesting similar electronic structure. On the other hand, a *p*-hydroxy-phenyl group attached to a TTF framework seems to increase the conductivity, compared with the corresponding *p*-acetoxyphenyl group.

CTC resulting from *p*-acetoxyphenyl-TTF can be classified in the category of semi-conductors materials. In fact, they have conductivity around 10^{-3} Scm^{-1}. This can be due to a structural disorder. Other, CTC resulting from *p*-hydroxyphenyl-TTF can be classified in the area of conductors, with a conductivities measured on powder compressed pellets from 3.64 10^{-1} to 3.32 Scm^{-1}, that allows a conductivity ten times greater on single crystal.

Experimental Section

NMR spectra were recorded on a Brucker AC 250 instrument. FAB mass spectra were recorded on a JOEL JMS-DX 300 spectrometer. Uncorrected melting points were measured on a 510 Buchi apparatus. Cyclic voltammetry measurements were carried out on a PAR-273 potentiostat/galvanostat. All solvents were dried by standard methods and all commercial reagents used without purification. All reactions were performed under an inert atmosphere of nitrogen.

4-(*p*-Acetoxyphenyl)-1,3-dithiole-2-selenone, 2. Black powdered selenium (1.4 g, 17.68 mmol) was added in one portion with magnetic stirring at 0°C under nitrogen to a solution of sodium borohydride (3.8 g, 35.37 mmol) in ethanol (30 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 (1 mL, 17.68 mmol) and 4-*p*-acetoxyphenyl-1,3-dithiole-2-ylidenepiperidinium hexafluorophosphate **1** (7.2 g, 17.68 mmol) were added and the reaction mixture was allowed to stand at RT for *ca*. 2 hr. 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** (4.6 g, 83% yield) as red orange crystals; m.p. 141°C; TLC: R$_f$ = 0.65 (CHCl₃); ¹H NMR (CDCl₃): δ 2.33 (s, 3H, CH₃); 7.16 (d, 2H$_{arom}$, *J* = 8.60 Hz); 7.55 (d, 2H$_{arom}$, *J* = 8.60 Hz); 7.12 (s, 1H) ; MS (NOBA, FAB > 0): 316 [M + H]$^+$; M = 315; Anal. Calcd for : C, 41.90; H, 2.56; S, 20.34. Found: C, 42.13; H, 2.76; S, 20.15%.

2-Methylseleno-4-(*p*-acetoxyphenyl)-1, 3-dithioliumtrifluoromethane sulfonate, 3. A suspension of 4-(*p*-acetoxyphenyl)-1,3-dithiole-2-selenone (3.52 g, 11.20 mmol) in dry methylene chloride (30 mL) was treated with methyl triflate (1.6 mL, 12.8 mmol). The mixture was stirred under nitrogen for 4 hr. A layer of dry ether (100 mL) was added. The deep reddish-orange salt **3** was filtered after 24 hr, washed with more dry ether, and dried. Yield: 4.56 g (85%); m.p. 151°C; ¹H NMR (CDCl₃): δ 2.07 (s, 3H, Se-CH₃); 2.52 (s, 3H, CH₃); 6.96 (d, 2H$_{arom}$, *J* = 8.63 Hz); 7.64 (d, 2H$_{arom}$, *J* = 8.63 Hz); 8.93 (s, 1H) ; M S (NOBA, FAB > 0): 480 [M + H]$^+$; M = 479; Anal. Calcd: C, 32.57; H, 2.31; S, 20.06. Found: C, 32.76; H, 2.46; S, 21.96%.

2-(4-Acetoxyphenyl)-6,7-dialkyl tetrathiafulvalenes, 5a-d. A solution of 2-methylseleno-4-(*p*-acetoxyphenyl)-1,3-dithiolium trifluoromethane sulfonate (2 g, 4.17 mmol) and 4,5-dialkyl-1,3-dithiole-2-triphenylphosphonium (4.17 mmol) in tetrahydrofuran (50 mL) was treated with triethylamine (15 mL) at R T under nitrogen. After the reaction mixture was stirred for 4hr, 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-Acetoxyphenyldimethyltetrathiafulvalene, 5a. Yield: 19%; m.p. 130°C; TLC: R$_f$ = 0.90 (benzene); ¹H NMR (DMSO *d₆*): δ 2.05 (s, 6H); 2.60 (s, 3H); 7.50 (s, 1H); 7.65 (d, 2H$_{arom}$, *J* = 8.45 Hz); 7.5 (s, 1H); 7.88 (d, 2H$_{arom}$, J = 8.45 Hz) ; MS (NOBA, FAB > 0): 367 [M + H]$^+$; M = 366 Anal. Calcd: C, 52.42; H, 3.84; S, 34.99. Found: C, 52.59; H, 3.98; S, 34.84%.

2-(4-Acetoxyphenyl)-6,7-(propane-1,3-diyl)tetrathiafulvalene, 5b. Yield: 15%; m.p. 153°C; TLC: R$_f$ = 0.86 (benzene); ¹H NMR (DMSO*d₆*): δ 2.43(q, 2H, *J* = 6.90 Hz); 2.56 (t, 4H, *J* = 6.90 Hz); 2.60 (s, 3H); 7.43 (s, 1H); 7.64 (d, 2H$_{arom}$, *J* = 8.45 Hz); 7.87 (d, 2H$_{arom}$, *J* = 8.45 Hz) ; MS (NOBA, FAB > 0): 379 [M + H]$^+$; M = 378 Anal. Calcd: C, 53.93; H, 3.72; S, 33.88. Found: C, 54.20; H, 3.92; S, 33.59%.

2-(4-Acetoxyphenyl)-6, 7-(butane-1,4-diyl)tetrathiafulvalene, 5c. Yield: 24%; m.p. 134°C; TLC: R$_f$ = 0.82 (benzene); ¹H NMR (DMSO*d₆*): δ 1.70 (m, 4H); 2.20 (m, 4H); 2.60 (s, 3H); 7.37 (s, 1H); 7.66 (d, 2H$_{arom}$, *J* = 8.45 Hz); 7.89 (d, 2H$_{arom}$, *J* = 8.45 Hz); MS (NOBA, FAB > 0): 393 [M + H]$^+$; M = 392 Anal. Calcd : C, 55.07; H, 4.10; S, 32.67. Found: C, 55.27; H, 4.26; S, 32.44%.

2-(4-Acetoxyphenyl)-6, 7-(buta-1,3-dien-1,4-diyl)-tetrathiafulvalene, 5d. Yield: 18%; m.p. 162°C; TLC: R_f = 0.80 (benzene); ^{1}H NMR (DMSOd_6): δ 2.60 (s, 3H); 7.34 (s, 1H); 7.68 (d, 2H$_{arom}$, J = 8.45 Hz); 7.90 (d, 2H$_{arom}$, J = 8.45 Hz); 7.37 – 7.55 (m, 4H$_{arom}$) ; MS (NOBA, FAB > 0): 389 [M + H]$^+$; M = 388 Anal. Calcd: C, 55.64; H, 3.11; S, 33.01. Found: C, 55.94; H, 3.38; S, 32.70%.

2-(4-Hydroxyphenyl-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 R T. After the reaction mixture was stirred for 4 hr, water was added. The precipitate was collected by filtration and washed with water. The solid was collected and column chromatographed on silica gel with dichlomethane as eluent to afford **6a-d**.

***p*-Hydroxyphenyldimethyltetrathiafulvalene, 6a**. Yield: 93%; m.p. 161°C; TLC: R_f = 0.84 (CH$_2$Cl$_2$); ^{1}H NMR (DMSOd_6): δ 2.22 (s, 6H); 7.41 (s, 1H); 7.60 (d, 2H$_{arom}$, J = 8.65 Hz); 7.92 (d, 2H$_{arom}$, J = 8.65 Hz); 9.95 (s, 1H, OH) ; MS (NOBA, FAB > 0): 325 [M + H]$^+$; M = 324 Anal. Calcd: C, 51.81; H, 3.72; S, 39.52. Found: C, 51.99; H, 3.87; S, 39.32%.

2-(4-Hydroxyphenyl-6,7-(propane-1,3-diyl)tetra-thiafulvalene, 6b. Yield: 89%; m.p. 170°C; TLC: R_f = 0.80 (CH$_2$Cl$_2$); ^{1}H NMR (DMSOd_6): δ 2.45 (q, 2H, J = 6.93 Hz); 2.60 (t, 4H, J = 6.93 Hz); 7.43 (s, 1H); 7.59 (d, 2H$_{arom}$, J = 8.65 Hz); 7.91 (d, 2H$_{arom}$, J = 8.65 Hz); 10.00 (s, 1H, OH) ; MS: (NOBA, FAB > 0): 337 [M + H]$^+$; M = 336 Anal. Calcd: C, 53.53; H, 3.59; S, 38.11. Found: C, 52.33; H, 3.69; S, 38.28%.

2-(4-Hydroxyphenyl)-6, 7-(butane-1,4-diyl)tetra-thiafulvalene, 6c. Yield: 95%; m.p. 120°C; TLC: R_f = 0.77 (CH$_2$Cl$_2$); ^{1}H NMR (DMSOd_6): δ 1.80 (m, 4H); 2.60 (m, 4H); 7.42 (s, 1H); 7.61 (d, 2H$_{arom}$, J = 8.65 Hz); 7.93 (d, 2H$_{arom}$, J = 8.65 Hz); 10.05 (s, 1H, OH); MS: (NOBA, FAB > 0): 351 [M + H]$^+$; M = 350 Anal. Calcd: C, 54.82; H, 4.02; S, 36.59. Found: C, 54.97; H, 4.12; S, 36.39%.

2-(4-Hydroxyphenyl)-6,7-(buta-1,3-dien-1,4-diyl)-tetrathiafulvalene, 6d. Yield: 92%; m.p. 155°C; TLC: R_f = 0.74 (CH$_2$Cl$_2$); ^{1}H NMR (DMSOd_6): δ 7.20- 7.40 (m, 4H$_{arom}$); 7.45 (s, 1H); 7.63 (d, 2H$_{arom}$, J = 8.65 Hz); 7.94 (d, 2H$_{arom}$, J = 8.65 Hz); 10.13 (s, 1H, OH); M.S: (NOBA, FAB > 0): 347 [M + H]$^+$; M = 346 Anal. Calcd: C, 55.46; H, 2.91; S, 37.01. Found: C, 55.71; H, 3.11; S, 36.73%.

Conclusions

In conclusion, we present a two-step synthesis of new functionalized tetrathiafulvalene derivatives starting from selenoxonium and phosphonium salt through Wittig-type reaction. Eight new asymmetric TTFs derivatives containing *p*-acetoxyphenyl and *p*-hydroxyphenyl groups have been synthesized and characterized during the course of this work. The oxidation potentials were determined by cyclic voltammetry. Charge transfer complexes of the donors with TCNQ were prepared and the electrical conductivity of these materials was measured, some CTC are conductive.

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