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Synthesis and properties of new metal complexes involving unsymmetrical tetrathiafulvalenes

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ABSTRACT

*A new unsymmetrical tetrathiafulvalenes (TTF) containing nitrophenyl or aminophenyl rings were prepared by using a cross-coupling method of the respective 4,5-dialkyl-1,3-dithiole-2-one **1a-e** with 4-(p-nitrophenyl)-1,3-dithiole-2-thione **2**. The conversion of the nitro moiety **3a-e** to amino groups' **4a-e** used reduction reaction. The reducing power of each new precursor was determined by cyclic voltammetry. Charge transfer complexes of the donors with tetracyanoquino-dimethane (TCNQ) were prepared and characterized. The electrical conductivity of these materials was measured and discussed.*

Keywords: tetrathiafulvalenes; electrochemistry; redox potentials; organic materials; conductivity

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INTRODUCTION

Throughout the last 25 years, a great deal of research has been carried out into the synthesis and study of a relatively new type of organic system, termed organic metals. Organic materials that are capable of conducting electricity in the manner of semiconductors, conductors and superconductors have drawn a huge amount of research interest over the past decade [1, 2].

The sulfur heterocycle tetrathiafulvalene (TTF) has been one of the main materials of interest both in organic metals research and in the wider field of materials science where TTF has found use as a redox active transducer for cation sensors [3], as a π-electron donor for non-linear optical systems [4], it has been incorporated into polymeric [5, 6] and dendritic [7] systems, and exploited as a component for molecular electronic devices.

The synthesis and characterization of new sulfur-based heterocyclic systems have found widespread applications in modern material science and medicinal chemistry [8], the vast majority of these centred on compounds containing derivatives of the basic electron donor TTF.

This paper focuses on the synthesis of novel donor molecules to make charge-transfer complexes, based on the organosulfur donor tetrathiafulvalene (TTF), with particular emphasis on new functionalised derivatives.

As a development of our previous work [9-15] and taking into account the above, we decided to design and realize the synthesis of novel unsymmetrically π-donors containing nitrophenyl or aminophenyl ligand via cross-coupling

and reduction reactions. Finally we also prepared their charge transfer complexes and measured their electrical conductivity.

EXPERIMENTAL SECTION

NMR spectra were recorded on a WP 400-NMR instrument (Bruker BioSpin GmbH, Silberstreifen 4, 76287 Rheinstetten, Germany). FAB mass spectra were recorded on a JOEL JMS-DX 300 spectrometer (JEOL Europe, Planet II, Gebouw B., Leuvensestreenweg 542, B-1930 Zaventem, Belgium). Uncorrected melting points were measured on a 510 Buchi apparatus (BÜCHI Labortechnik AG, Meierseggstrasse 40, 9230 Flawil, Schweiz). Cyclic voltammetry measurements were carried out on a PAR-273 potentiostat/galvanostat (Alltest Instruments, Inc. 500 Central Ave. Farmingdale, NJ, USA). All computations were performed with the Spartan program package using the AM1 (d,p) basis set. All solvents were dried by standard methods and all commercial reagents used without purification. All reactions were performed under an inert atmosphere of nitrogen.

Synthesis and characterization of *p*-nitrophenyl tetrathiafulvalene 3a-e

Under a nitrogen atmosphere, 30 mL of freshly distilled triethyl phosphite was added to the mixture of 4-(*p*-nitrophenyl)-1,3-dithiole-2-thione **2** (1 g, 3.92 mmol) and 4,5-dialkyl-1,3-dithiole-2-one **1a-e** (1 equiv.). The resulting mixture was heated with an oil bath up to 110 °C and stirred for a further 4 h. The solvent was then removed under reduced pressure. Compounds **3a-e** were obtained by column chromatography of the residue (silica gel, eluting with dichloromethane and petroleum ether 2:1).

***p*-Nitrophenyl tetrathiafulvalene (3a)**: Yield = 45%; TLC: Rf = 0.59 (CH_2Cl_2/petroleum ether, 2:1); Lime Green powder, mp = 177 °C; ^{1}H NMR ($CDCl_3$) δ ppm: 2.49(S, 6H, SMe); 6.77(S, 1H, C=C*H*); 7.46(d, *J* = 8.83Hz, 2H, nitrophenyl-*H*); 8.13(d, *J* = 8.83Hz, 2H, nitrophenyl-*H*); M.S: (NOBA, FAB > 0): 418 $[M + H]^+$; M = 417; Anal. Calcd for: C, 40.26; H, 2.65; S, 46.07; found: C, 39.01; H, 2.48; S, 46.37.

***p*-Nitrophenyl tetrathiafulvalene (3b)**: Yield = 30%; TLC: Rf = 0.52 (CH_2Cl_2/petroleum ether, 2:1); Green powder, mp = 183 °C; ^{1}H NMR ($CDCl_3$) δ ppm: 4.42(S, 2H, SCH_2S); 6.86(S, 1H, C=C*H*); 7.49(d, *J* = 8.90Hz, 2H, nitrophenyl-*H*); 8.17(d, *J* = 8.90Hz, 2H, nitrophenyl-*H*); M.S: (NOBA, FAB > 0): 402 $[M + H]^+$; M = 401; Anal. Calcd for: C, 38.88; H, 1.76; S, 47.91; found: C, 38.75; H, 1.67; S, 48.10.

***p*-Nitrophenyl tetrathiafulvalene (3c)**: Yield = 41%; TLC: Rf = 0.56 (CH_2Cl_2/petroleum ether, 2:1); Green powder, mp = 179 °C; ^{1}H NMR ($CDCl_3$) δ ppm: 43.44(S, 4H, SCH_2CH_2S); 6.83(S, 1H, C=C*H*); 7.46(d, *J* = 8.86Hz, 2H, nitrophenyl-*H*); 8.12(d, *J* = 8.86Hz, 2H, nitrophenyl-*H*); M.S: (NOBA, FAB > 0): 416 $[M + H]^+$; M = 415; Anal. Calcd for: C, 40.46; H, 2.18; S, 46.29; found: C, 40.29; H, 2.07; S, 46.60.

***p*-Nitrophenyl tetrathiafulvalene (3d)**: Yield = 38%; TLC: Rf = 0.61 (CH_2Cl_2/petroleum ether, 2:1); Green powder, mp = 168 °C; ^{1}H NMR ($CDCl_3$) δ ppm: 2.60(m, 2H, CH_2); 2.83(t, 4H, SCH_2), 6.78(S, 1H, C=C*H*); 7.44(d, *J* = 8.85Hz, 2H, nitrophenyl-*H*); 8.10(d, *J* = 8.85Hz, 2H, nitrophenyl-*H*); M.S: (NOBA, FAB > 0): 430 $[M + H]^+$; M = 429; Anal. Calcd for: C, 41.93; H, 2.58; S, 44.78; found: C, 41.72; H, 2.45; S, 45.01.

***p*-Nitrophenyl tetrathiafulvalene (3e)**: Yield = 36%; TLC: Rf = 0.70 (CH_2Cl_2/petroleum ether, 2:1); Spring Green, mp = 172 °C; ^{1}H NMR ($CDCl_3$) δ ppm: 4.31(S, 4H, OCH_2CH_2O); 6.88(S, 1H, C=C*H*); 7.50(d, *J* = 8.91Hz, 2H, nitrophenyl-*H*); 8.19(d, *J* = 8.91Hz, 2H, nitrophenyl-*H*); M.S: (NOBA, FAB > 0): 384 $[M + H]^+$; M = 383; Anal. Calcd for: C, 43.85; H, 2.37; S, 33.45; found: C, 43.54; H, 2.25; S, 33.78.

Synthesis and characterization of *p*-aminophenyl tetrathiafulvalene 4a-e

A stirred mixture of 4-*p*-nitrophenyl tetrathiafulvalenes derivatives **3a-e** (4 mmol), tin (0.94 g, 8 mmol), and aqueous solution of HCl (35%) to (1.8 mL, 20 mmol) in ethanol (30 mL) was refluxed for 4 h under nitrogen. During this time the initial black solution turned light yellow. The solution was then concentrated in vacuo and treated with an aqueous solution (100 mL) of sodium hydroxide (0.1 M) and extracted with ether. The organic phase was washed with water, dried ($MgSO_4$), and concentrated in vacuo. The product was subjected to column chromatography on silica gel (CH_2Cl_2), affording the expected compounds **4a-e** as powder.

***p*-Aminophenyl tetrathiafulvalene (4a)**: Yield = 72%; TLC: Rf = 0.54 (CH_2Cl_2); Red Orange powder, mp = 134 °C; ^{1}H NMR ($CDCl_3$) δ ppm: 2.28(S, 6H, SMe); 3.98-4.19(br, 2H, NH_2); 6.75(S, 1H, C=C*H*); 6.43(d, *J* = 8.15Hz, 2H, aminophenyl-*H*); 7.01(d, *J* = 8.15Hz, 2H, aminophenyl-*H*); M.S: (NOBA, FAB > 0): 388 $[M + H]^+$; M = 387; Anal. Calcd for: C, 43.38; H, 3.38; S, 49.63; found: C, 43.57; H, 3.49; S, 49.38.

***p*-Aminophenyl tetrathiafulvalene (4b)**: Yield = 64%; TLC: Rf = 0.45 (CH_2Cl_2); Orange powder, mp = 145°C; ^{1}H NMR ($CDCl_3$) δ ppm: 4.15-4.25(br, 2H, N*H*$_2$); 4.38(S, 2H, SC*H*$_2$S); 6.82(S, 1H, C=C*H*); 6.47(d, *J* = 8.04Hz, 2H, aminophenyl-*H*); 7.11(d, *J* = 8.04Hz, 2H, aminophenyl-*H*); M.S: (NOBA, FAB > 0): 372 $[M + H]^+$; M = 371; Anal. Calcd for: C, 42.02; H, 2.44; S, 51.77; found: C, 41.85; H, 2.25; S, 51.98.

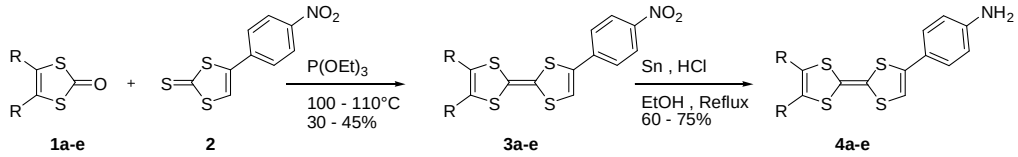
***p*-Aminophenyl tetrathiafulvalene (4c)**: Yield = 75%; TLC: Rf = 0.48 (CH_2Cl_2); Orange powder, mp = 142°C; ^{1}H NMR ($CDCl_3$) δ ppm: 3.72(S, 4H, SC*H*$_2$C*H*$_2$S); 4.03-4.12(br, 2H, N*H*$_2$); 6.74(S, 1H, C=C*H*); 6.43(d, *J* = 8.06Hz, 2H, aminophenyl-*H*); 7.07(d, *J* = 8.06Hz, 2H, aminophenyl-*H*); M.S: (NOBA, FAB > 0): 386 $[M + H]^+$; M = 385; Anal. Calcd for: C, 43.60; H, 2.88; S, 49.89; found: C, 43.71; H, 2.95; S, 49.61.

***p*-Aminophenyl tetrathiafulvalene (4d)**: Yield = 63%; TLC: Rf = 0.52 (CH_2Cl_2); Orange powder, mp = 138°C; ^{1}H NMR ($CDCl_3$) δ ppm: 2.54(m, 2H, C*H*$_2$); 2.72(t, 4H, SC*H*$_2$), 3.82-4.03(br, 2H, N*H*$_2$); 6.40(d, *J* = 8.10Hz, 2H, aminophenyl-*H*); 6.70(S, 1H, C=C*H*); 6.91(d, *J* = 8.10Hz, 2H, aminophenyl-*H*); M.S: (NOBA, FAB > 0): 400 $[M + H]^+$; M = 399; Anal. Calcd for: C, 45.08; H, 3.28; S, 48.14; found: C, 44.91; H, 3.17; S, 48.37.

***p*-Aminophenyl tetrathiafulvalene (4e)**: Yield = 60%; TLC: Rf = 0.63 (CH_2Cl_2); Burnt Orange powder, mp = 146°C; ^{1}H NMR ($CDCl_3$) δ ppm: 4.28(S, 4H, OC*H*$_2$C*H*$_2$O); 4.10-4.23(br, 2H, N*H*$_2$); 6.84(S, 1H, C=C*H*); 6.45(d, *J* = 8.20Hz, 2H, aminophenyl-*H*); 7.18(d, *J* = 8.20Hz, 2H, aminophenyl-*H*); M.S: (NOBA, FAB > 0): 354 $[M + H]^+$; M = 353; Anal. Calcd for: C, 47.57; H, 3.14; S, 36.28; found: C, 47.34; H, 2.99; S, 36.49.

RESULTS AND DISCUSSION

The synthesis of compounds **4a-e** was realized according to the chemical pathway depicted in Scheme 1. The 4-(*p*-nitrophenyl)-1,3-dithiole-2-thione **2** [12] was allowed to react with 4,5-dialkyl-1,3-dithiole-2-one **1a-e** [16] in toluene at reflux in the presence of triethyl phosphite under nitrogen via cross coupling method [17] to obtain the corresponding *p*-nitrophenyl tetrathiafulvalene **3a-e** in moderate yield after column chromatography. In previous work [9, 12, 18] we have described the access to aminophenyl TTFs from nitrophenyl TTFs. the nitro group of *p*-nitrophenyl tetrathiafulvalene **3a-e** was reduced at reflux in the presence of tin and hydrochloric acid into an amino group in ethanol. The *p*-aminophenyl tetrathiafulvalene **4a-e** derivatives were obtained after purification by column chromatography in moderate yields.



a: R = SCH_3 , **b**: 2R = SCH_2S , **c**: 2R = $S(CH_2)_2S$, **d**: 2R = $S(CH_2)_3S$, **e**: 2R = $O(CH_2)_2O$

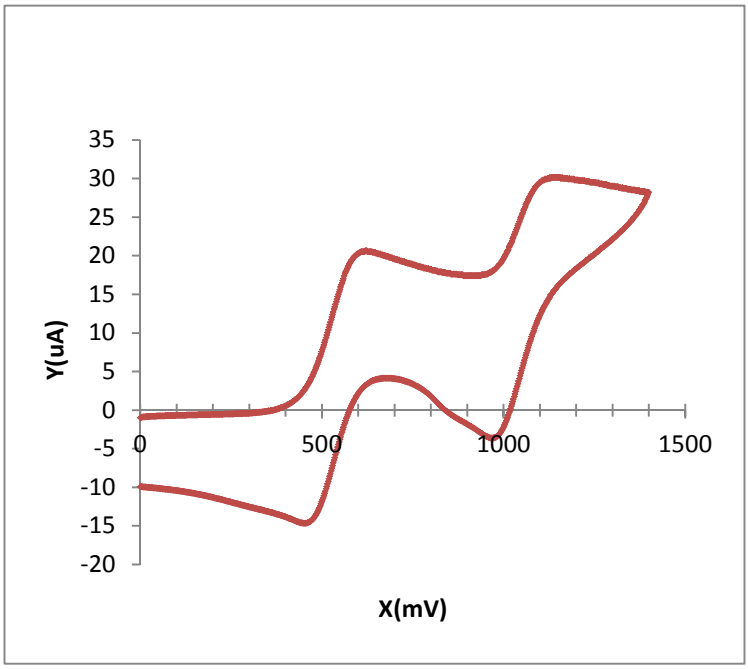
Scheme 1. Synthetic route for the preparation of compounds 3-4

In the ^{1}H NMR spectra the series of *p*-nitrophenyl tetrathiafulvalene **3a-e** exhibited two doublets around 7.44-7.49 and 8.10-8.19 ppm for the nitrophenyl protons. The series of *p*-Aminophenyl tetrathiafulvalene **4a-e** revealed the presence of amino group protons signals as broad band around 3.82-4.25 ppm and the aminophenyl protons showed two doublets around 6.40-6.47 and 6.91-7.18 ppm.

The redox power of each new compound has been determined through cyclic voltammetry measurements [19, 20]. All the compounds show the expected two reversible oxidation waves (Figure **1**) with values comparable with those of bis-ethylenedithio-tetrathiafulvalene (BEDT-TTF) used as a reference which is the origin of many superconductors (table **1**).

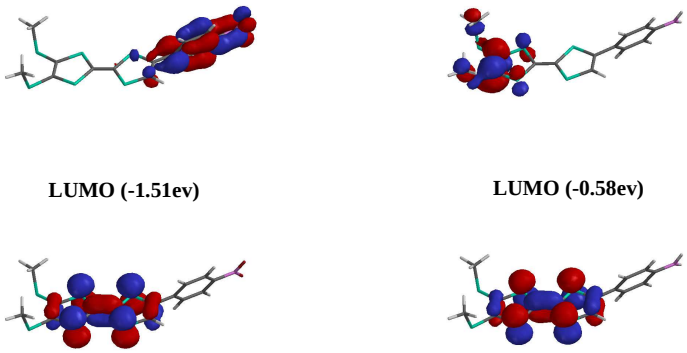
Table 1. Potentials of unsymmetrically tetrathiafulvalenes 3-4

Donor	E^1_{ox}(mV)	E^2_{ox}(mV)
BEDT-TTF	666	1080
3a	452	1027
3b	466	1043
3c	473	1065
3d	480	1076
3e	590	1092
4a	422	973
4b	427	985
4c	431	994
4d	435	1006
4e	446	1024



Solvent: *CH_2Cl_2;* ***Electrolyte:*** *nBu_4NPF_6 0,1 M;* ***reference electrode:*** *SCE;*
Working and counter electrodes: *platinum;* ***Scan rate:*** *$100mVs^{-1}$.*
Figure 1. Voltammogram of donor 3e

The energy of HOMO of different products **3-4** was computed using density functional theory (DFT) calculation (Figure **1**). The levels of HOMO of compound **4a-e** show that these compounds are the better donating molecule for the formation of TTF-TCNQ complexes.



LUMO (-1.51ev) **LUMO (-0.58ev)**

HOMO (-7.74ev) **HOMO (-7.33ev)**

Figure 2. Molecular orbitals of the HOMO and LUMO of compounds 3a and 4a

Charge transfer complexes (CTC) is formed by the interaction of an electron donor (D) and an electron acceptor (A) [21]. The donor and acceptor are bound together by an electrostatic attraction, not a chemical bond. Partial electron transfer between the donor molecule and the acceptor molecule generates this electrostatic attraction.

In our study, all compounds **3-4** formed charge transfer complexes with TCNQ (tetracyano-*p*-quinodimethane) used as an electron acceptor (A) [22-24]. The solids were isolated 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 colors.

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 **2**.

Table 2. Melting points and electrical conductivity of charge transfer complexes

Complex	mp (°C)	σ_{RT} (S cm^{-1})
3a-TCNQ	284	$6{,}89.10^{-4}$
3b-TCNQ	293	$5{,}24.10^{-4}$
3c-TCNQ	284	$5{,}68.10^{-4}$
3d-TCNQ	276	$7{,}29.10^{-4}$
3e-TCNQ	285	$2{,}36.10^{-5}$
4a-TCNQ	247	$7{,}87.10^{-5}$
4b-TCNQ	252	$7{,}12.10^{-5}$
4c-TCNQ	254	$7{,}45.10^{-5}$
4d-TCNQ	246	$8{,}65.10^{-5}$
4e-TCNQ	253	$3{,}58.10^{-6}$

For this family of materials, all charge transfer complexes (CTC) from **3a**-TCNQ to **4e**-TCNQ resulting from *p*-nitrophenyl tetrathiafulvalenes and *p*-aminophenyl tetrathiafulvalenes, can be classified in the area of semi-conductors. In fact, they have a conductivity measured on powder compressed pellets of $3{,}58.10^{-6}$ to $7{,}29.10^{-4}$ S cm^{-1}, which allows conductivity ten times greater on single crystal.

CONCLUSION

In summary, we have developed novel precursors of organic materials, a series of π-donors containing nitrophenyl or aminophenyl ring were synthesized via cross-coupling and reduction synthetic strategies. All donors synthesized during the course of this work have been characterized by cyclic voltammetry and their 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. The complexes have been proven to give semi-conducting materials.

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