Synthesis, characterization and electrochemical properties of new series of TTF derivatives as useful components for conducting materials

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ABSTRACT

A series of new TTF containing a nitro group were prepared by using a Wittig condensation between a TTF bearing an aldehyde function and an appropriate aromatic phosphonium salt. The reducing power of each new precursor was determined by cyclic voltammetry. Charge transfer complexes of the donors with TCNQ were prepared and characterized. The electrical conductivity of these materials was measured.

Keywords: conductivity, organic materials, redox potentials, tetrathiafulvalenes.

INTRODUCTION

The electroactivity of the tetrathiafulvalene (TTF) has focused a lot of attention as the leading constituent of various molecular materials, displaying a wide range of attractive applications, such as sensors, receptors, switches, and conductors [1-8]. To reach such high versatility, numerous chemical modifications have been realized on the TTF skeleton [1-8]. For example, various coordination functions have been grafted on the TTF core in order to convert the TTF into an electroactive ligand [9] for the elaboration of hybrid multifunctional materials [10-12].

The goal of this work is the synthesis of a series of new molecules of TTF containing either electron-donating or electron-withdrawing aromatic substituents covalently linked to the TTF ring and usable as precursors in materials exhibiting electrical and/or NLO properties [13-16].
Thus, in order to develop new series of donors for two dimensional metals in particular, we have synthesized several original TTF containing nitrophenyl units as substituent. We report here the synthesis, the electrochemical properties of such compounds and finally the electrical conductivity of some of their radical cation salts and charge transfer complexes.

EXPERIMENTAL SECTION

All commercial chemicals and solvents were used as received. Melting points were determined in open tubes on a 510 Büchi apparatus and are uncorrected. Microanalyses were performed in the Microanalytical Laboratory of ENSCM (Montpellier). ¹H Magnetic Resonance spectra were determined on a WP 400-NMR spectrometer. Chemical shifts are recorded in ppm (δ) and coupling constants in Hertz, relative to tetramethylsilane used as internal standard. Multiplicity is indicated as s (singlet), d (doublet), q (quadruplet), m (multiplet) and combinations of these signals. Fast-atom bombardment mass spectra (FAB) were recorded in positive mode with 3-nitrobenzylalcohol (NOBA) as matrix. Cyclic voltammetry measurements were carried out on a PAR-273 potentiostat/galvanostat. All reactions were monitored by Thin Layer Chromatography (TLC) on silica gel Merck 60 F254 precoated aluminium plates. Column chromatography was performed using silica gel 60 (203-400 mesh). All reactions were performed under an inert atmosphere of nitrogen.

General procedure for the preparation of compounds (3-6)

To a stirred solution of aldéhyde-TTF (1 or 2) (1 equiv) obtained in accordance with the methodology shown in the literature [17-18] and nitrobenzyl triphenyl phosphonium bromide (1 equiv) in dry dichlorométhane was added excess of triethylamine (10 equiv). The reaction mixture was allowed to stand at room temperature for 12h under nitrogen and then concentrated in vacuo. acétonitrile was added, after stirring for 15 min, the precipitated obtained was filtered and washed with cold acétonitrile. The filtrate mixture was stirred at -15 °C for 20 min, the medium was filtered and washed with acétonitrile. The filtrate mixture was stirred at -15 °C for 20 min, the precipitated obtained was filtered and washed with cold acétonitrile.

Recrystallization of the first precipitated from acétonitrile/tétrahydrofurane (1:1) gave the isomer Trans (3 or 5) as black-green crystals. The second precipitated was purified by column chromatography on silica gel with dichlorométhane/hexane (2:1) as the eluent. To gave the isomer cis (4 or 6) as green powder.

**Isomere Trans (3):** Yield = 42%; TLC: Rf = 0.65 (dichlorométhane/hexane) (2:1); black-green crystals, mp = 145 °C; ¹H NMR (CDCl₃) δ ppm: 1.96 (s, 6H, CH₃), 2.04 (s, 3H, CH₃), 6.89 (d, 1H, J=15.92Hz, Hₐrøm), 7.10 (s, 1H, Hₐøphiq), 7.15 (s, 1H, H₂Bn), 7.27 (d, 1H, J= 15.92Hz, Hₐøphiq), 7.52 (d, 2H, J=8.56Hz, H₂arøm), 8.14 (2H, J= 8.84Hz, H₂arøm); M.S: (NOBA, FAB > 0): 476 [M + H]+; M = 475; Anal. Calcd for: C, 53.04; H, 3.63; S, 33.67; found: C, 53.04; H, 3.63; S, 33.67.

**Isomere Cis (4):** Yield = 40%; TLC: Rf = 0.92 (dichlorométhane/hexane) (2:1); green powder, mp = 136 °C; ¹H NMR (CDCl₃) δ ppm: 1.96 (s, 6H, CH₃), 2.04 (s, 3H, CH₃), 6.53 (d, 1H, J=12.12Hz, Hₐøphiq), 6.67 (d, 1H, J=12.12Hz, Hₑthylenic), 6.91 (s, 1H, H₂Bn), 7.00 (s, 1H, H₂Bn), 7.45 (d, 2H, J=8.32Hz, H₂arøm), 8.14(d, 2H, J=8.84Hz, H₂arøm); M.S: (NOBA, FAB > 0): 476 [M + H]+; M = 475; Anal. Calcd for: C, 53.02; H, 3.60; S, 33.70; found: C, 53.03; H, 3.63; S, 33.68.

**Isomere Trans (5):** Yield = 43%; TLC: Rf = 0.63 (dichlorométhane/hexane) (2:1); black-green crystals, mp = 167 °C; ¹H NMR (CDCl₃) δ ppm: 1.97 (s, 6H, CH₃), 2.06 (s, 3H, CH₃), 7.39 (d, 2H, J= 8.65Hz, H₂arøm), 7.53 (m, 2H, H₂Bn), 7.55 (d, 1H, J=14.00Hz, Hₑthylenic), 7.60 (d, 1H, J=14.00Hz, Hₑthylenic), 7.67 (m, 2H, H₂Bn), 8.21 (2H, J= 8.67Hz, H₂arøm); M.S: (NOBA, FAB > 0): 458 [M + H]+; M = 457; Anal. Calcd for: C, 57.73; H, 4.18; S, 41.78; found: C, 57.70; H, 4.16; S, 41.78.

**Isomere Cis (6):** Yield = 39%; TLC: Rf = 0.91 (dichlorométhane/hexane) (2:1); green powder, mp = 158 °C; ¹H NMR (CDCl₃) δ ppm: 1.97 (s, 6H, CH₃), 2.06 (s, 3H, CH₃), 6.65 (d, 1H, J=10.40Hz, Hₑthylenic), 7.00 (d, 1H, J=10.40Hz, Hₑthylenic), 7.39 (d, 2H, J= 8.63Hz, H₂arøm), 7.56 (m, 2H, H₂Bn), 7.69 (m, 2H, H₂Bn), 8.22 (2H, J= 8.67 Hz, H₂arøm); M.S: (NOBA, FAB > 0): 458 [M + H]+; M = 457; Anal. Calcd for: C, 57.73; H, 4.18; S, 41.78; found: C, 57.71; H, 4.16; S, 41.78.

RESULTS AND DISCUSSION

The target highly conjugated molecules 3-6 have been prepared by using a Wittig condensation [19,20] between a TTF bearing an aldehyde function and an appropriate aromatic phosphonium salt (scheme I).
The action of triethylamine in dry dichlorométhane at room temperature on nitrobenzyl triphenyl phosphonium bromide salt and aldehyde-TTF to give the target compounds in good yield

In the $^1$H-NMR (CDCl$_3$) spectra of nitrotetrathiafulvalene derivatives 3, 4 the ethylenic protons in compound 3 showed two doublets at 6.89 ppm and 7.27 ppm, with the same coupling constant of 15.92 Hz. While the same protons in compound 4 exhibit two successive doublets at 6.53 ppm and 6.67 ppm, with the same coupling constant of 12.12 Hz. The coupling constant of ethylenic protons of compound 4 is smaller than that of compound 3, this reason we conducted to differentiate between the Trans and Cis isomer (Figure 1, 2).

For compounds 5 and 6 the same reason was used to differentiate between the Trans and Cis isomer.
The redox power of each new compound has been determined through cyclic voltammetry measurements[21, 22]. All the compounds show the expected two reversible oxidation waves with values comparable with those of TTF used as a reference (table 1).

Table 1. Half-wave potentials of TTF and unsymmetrically nitro-tetrathiafulvalenes 3-6.

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_{1/2}^0$(V)</th>
<th>$E_{1/2}^1$(V)</th>
<th>$\Delta E = E_{1/2}^1 - E_{1/2}^0$(V)</th>
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<tbody>
<tr>
<td>TTF</td>
<td>0.45</td>
<td>0.77</td>
<td>0.32</td>
</tr>
<tr>
<td>3</td>
<td>0.46</td>
<td>0.74</td>
<td>0.28</td>
</tr>
<tr>
<td>4</td>
<td>0.46</td>
<td>0.74</td>
<td>0.28</td>
</tr>
<tr>
<td>5</td>
<td>0.46</td>
<td>0.72</td>
<td>0.26</td>
</tr>
<tr>
<td>6</td>
<td>0.46</td>
<td>0.72</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Figure 2. $^1$H NMR spectrum of the isomere Cis 4 in CDCl$_3$

Figure 3. Voltammogram of isomere Trans 3 and isomere Cis 4

Solvent: THF; Electrolyte: nBu$_4$NPF$_6$, 0.1 M; reference electrode: SCE; Working and counter electrodes: platinum; Scan rate: 100mVs$^{-1}$. Figure 3. Voltammogram of isomere Trans 3 and isomere Cis 4
Charge transfer complexes have been obtained by a direct redox reaction, in solution, between a TTF donor 3-6 and TCNQ used as an electron acceptor. The electrical conductivity of the isolated solids have been measured on powder compressed pellets through a two contacts procedure showing, in each case, quite good conductivities (table 2).

<table>
<thead>
<tr>
<th>Complex</th>
<th>mp (°C)</th>
<th>D–A</th>
<th>σ (S cm⁻¹)</th>
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<tbody>
<tr>
<td>3-TCNQ</td>
<td>231</td>
<td>1:2</td>
<td>1.37</td>
</tr>
<tr>
<td>4-TCNQ</td>
<td>180</td>
<td>1:1</td>
<td>0.82</td>
</tr>
<tr>
<td>5-TCNQ</td>
<td>248</td>
<td>1:2</td>
<td>1.12</td>
</tr>
<tr>
<td>6-TCNQ</td>
<td>206</td>
<td>1:1</td>
<td>0.61</td>
</tr>
</tbody>
</table>

CONCLUSION

Some new highly conjugated compounds of the TTF family have been obtained through appropriate synthetic strategies (Wittig condensations).

The redox power of these new donors were determined by cyclic voltammetry and they were then employed to built new series of conducting materials as charge transfer complexes by using TCNQ (tetracyanoquinodimethane). These new molecules which are composed of a donor part (the TTF ring) and an acceptor one (a nitro aromatic unit) will be now analyzed as building blocks able to present NLO properties.

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