Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(3): 311-315

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis and electrical conductivity of new organic materials bearing a tetrathiafulvalene unit

Rachida Khammar[1], Amel Bendjeddou[1], Tahar Abbaz[1,2,*], Merzoug Benahmed[3], Abdelkrim Gouasmia[2], Rabah Rehamnia[4], Mebrouka Dekhici[5] and Didier Villemin[5]

[1]Laboratory of Aquatic and Terrestrial Ecosystems, University of Souk Ahras, Algeria
[2]Laboratory of Organic Materials and Heterochemistry, University of Tebessa, Algeria
[3]Laboratory of Bioactive Molecules and Applications, University of Tebessa, Algeria
[4]Laboratory of Nanomaterials-Corrosion and Surface Treatment, University of Annaba, Algeria
[5]Laboratory of Molecular and Thio-Organic Chemistry, UMR CNRS 6507, INC3M, FR 3038, Labex EMC3, ENSICAEN & University of Caen, Caen 14050, France

---

ABSTRACT

New bisymmetric tetrathiafulvalenes (TTFs) containing conjugated substituents (thiophene-π-pyridine) ***4-6*** *were synthesized by the condensation of TTF-thiophenecarboxaldehyde derivatives* ***1-3*** *with aromatic amines. Electrochemical studies based on cyclic voltammetry demonstrated, for all these new molecules, electrochemical characteristics favoring the formation of charge transfer complexes (CTCs). Measurements of electrical conductivity at room temperature were carried out on compacted powder, for all the materials obtained. All the CTCs synthesized were found to be semiconductors.*

Keywords: Tetrathiafulvalenes, Electrochemistry, Organic materials, Conductivity

---

INTRODUCTION

One of the key axes of research in modern organic synthesis is the design of molecules for the development of materials destined for use in particular, precisely defined fields [1]. The optimization of materials with multiple properties [2-5] requires careful consideration of the choice of molecules and of synthesis strategies to be used.

The tremendous utility of highly conductive organic materials [6,7] justifies the intense research in this domain. Charge transfer complexes (CTCs) or radical ion salts (RISs) obtained from tetrathiafulvalene (TTF) or its analogs and various electron acceptors, such as tetracyanoquinodimethane (TCNQ), are considered good models for the development of organic conductors [8-10].

Building on the previous work of our group [11-17], we developed an approach to the synthesis of large electron donors with a conjugated bond. These molecules were synthesized by a condensation reaction between aromatic amines and TTF-thiophenecarboxaldehyde derivatives. We were able to obtain a large number of compounds, generally in high yields, and the donor characteristics of each of these molecules were studied by cyclic voltammetry.

Different types of CTCs were obtained by formation of complexes with TCNQ. However, we were unable to determine the structure of these CTCs, because mono-crystals were not obtained. Electrical conductivity was measured on compacted powder and indicated that our organic materials were semiconductors.

EXPERIMENTAL SECTION

General

NMR spectra were recorded on an RMN 400 WP apparatus (Bruker BioSpin GmbH, Silberstreifen 4, 76287 Rheinstetten, Germany). FAB-MS spectra were recorded on a JOEL JMS-DX 300 spectrophotometer (JEOL Europe, Planet II, Gebouw B., Leuvensestreenweg 542, B-1930 Zaventem, Belgium). Uncorrected points of fusion were assessed with a Buchi 510 apparatus (BÜCHI Labortechnik AG, Meierseggstrasse 40, 9230 Flawil, Switzerland). Cyclic voltammetry was carried out on a PAR-273 potentiostat/galvanostat (Alltest Instruments, Inc. 500 Central Ave. Farmingdale, NJ, USA). All computations were performed with the Gaussian 09 program package (Gaussian, Inc. 340 Quinnipiac St Bldg 40 Wallingford, CT, USA) using the 6-31G(d,p) basis set. Density functional theory (DFT) calculations were carried out using a B3LYP method (public field method). All the solvents were dried by standard procedures and commercial reagents were used without further purification. All reactions were carried out under an inert nitrogen atmosphere.

General procedure for the synthesis of compounds 4-6

TTF-thiophene carboxaldehyde and an equivalent amount of aromatic amine were dissolved in anhydrous dichloromethane. Molecular sieves (4Å) were then added. The mixture was heated under reflux for 24 h, under a nitrogen atmosphere. The solvent was evaporated off under vacuum and the residue was purified by chromatography on a silica gel column (CH_2Cl_2 / CH_3OH).

N-((4-TTFthiophen-2-yl)methylene)pyridine-2-amine 4a: Yield = 57%; Rf = 0.79 (CH_2Cl_2 / CH_3OH); red-orange powder; Mp = 129°C; PNMR ($CDCl_3$) δ ppm: 6.58(s, 2H, H_{TTF}); 7.24(s, 1H, H_{TTF}); 7.35(m, 2H, H_{py}); 7.49(S, 1H, H_{thio}); 7.60(s, 1H, H_{thio}); 7.92(t, 1H, H_{py}); 8.51(d, 1H, H_{py}); 9.13(s, 1H, CH=N); MS (FAB^+) = 390 (M^+); EA : calculated : C, 49.20; H, 2.58; S, 41.05; found: C, 49.19; H, 2.45; S, 41.29.

N-((4-TTFthiophen-2-yl)methylene)pyridine-3-amine 4b: Yield = 63%; Rf = 0.76 (CH_2Cl_2 / CH_3OH); red-orange powder; Mp = 135°C; PNMR ($CDCl_3$) δ ppm: 6.56(s,, 2H, H_{TTF}); 7.37(m, 1H, H_{py}); 7.43(s, 1H, H_{TTF}); 7.54(s, 1H, H_{thio}); 7.66(s, 1H, H_{thio}); 7.71(m, 1H, H_{py}); 8.41(m, 2H, H_{py}); 8.66(s,, 1H, CH=N); MS (FAB^+) = 390 (M^+); EA : calculated: C, 49.20; H, 2.58; S, 41.05; found: C, 48.90; H, 2.43; S, 41.28.

N-((4-TTFthiophen-2-yl)methylene)pyridine-4-amine 4c: Yield = 33%; Rf = 0.74 (CH_2Cl_2 / CH_3OH); red-orange powder; Mp = 143°C; PNMR ($CDCl_3$) δ ppm: 6.57(s, 2H, H_{TTF}); 7.15(d, 2H, H_{py}); 7.49(s, 1H, H_{TTF}); 7.57(s, 1H, H_{thio}); 7.68(s, 1H, H_{thio}); 8.53(d, 2H, H_{py}); 8.59(s, 1H, CH=N); MS (FAB^+) = 390 (M^+); EA : calculated: C, 49.20; H, 2.58; S, 41.05; found: C, 49.15; H, 2.45; S, 41.36.

N-((4-trimethylTTFthiophen-2-yl)methylene)pyridine-2-amine 5a: Yield = 67%; Rf = 0.83 (CH_2Cl_2 / CH_3OH); pink powder; Mp = 229°C; PNMR ($CDCl_3$) δ ppm: 1.97(s, 6H, H_{TTF}); 2.21(S, 3H, H_{TTF}); 7.31(m, 2H, H_{py}); 7.44(s, 1H, H_{thio}); 7.57(s, 1H, H_{thio}); 7.89(t, 1H, H_{py}); 8.47(d, 1H, H_{py}); 9.06(s, 1H, CH=N); MS (FAB^+) = 432 (M^+); EA : calculated: C, 52.74; H, 3.73; S, 37.06; found: C, 52.51; H, 3.62; S, 37.23.

N-((4-trimethylTTFthiophen-2-yl)methylene)pyridine-3-amine 5b: Yield = 74%; Rf = 0.80 (CH_2Cl_2 / CH_3OH);); pink powder; Mp = 236°C; PNMR ($CDCl_3$) δ ppm: 1.95(s, 6H, H_{TTF}); 2.26(S, 3H, H_{TTF}); 7.34(m, 1H, H_{py}); 7.51(s, 1H, H_{thio}); 7.64(s, 1H, H_{thio}); 7.68(m, 1H, H_{py}); 8.39(m, 2H, H_{py}); 8.63(s, 1H, CH=N); MS (FAB^+) = 432 (M^+); EA : calculated: C, 52.74; H, 3.73; S, 37.06; found: C, 52.61; H, 3.57; S, 37.31.

N-((4-trimethylTTFthiophen-2-yl)methylene)pyridine-4-amine 5c: Yield = 42%; Rf = 0.78 (CH_2Cl_2 / CH_3OH);); pink powder; Mp = 241°C; PNMR ($CDCl_3$) δ ppm: 1.96(S, 6H, H_{TTF}); 2.34(s, 3H, H_{TTF}); 7.11(d, 2H, H_{py}); 7.54(s, 1H, H_{thio}); 7.63(s, 1H, H_{thio}); 8.49(d, 2H, H_{py}); 8.56(s, 1H, CH=N); MS (FAB^+) = 432 (M^+); EA : calculated: C, 52.74; H, 3.73; S, 37.06; found: C, 52.65; H, 3.52; S, 37.37.

N-((4-trimethylthioTTFthiophen-2-yl)methylene)pyridine-2-amine 6a: Yield = 78%; Rf = 0.87 (CH_2Cl_2 / CH_3OH);); purple powder; Mp = 163°C; PNMR ($CDCl_3$) δ ppm: 2.43(s, 6H, H_{TTF}); 2.48(s, 3H, H_{TTF}); 7.28(m, 2H, H_{py}); 7.39(s, 1H, H_{thio}); 7.54(S, 1H, H_{thio}); 7.85(t, 1H, H_{py}); 8.42(d, 1H, H_{py}); 8.94(s, 1H, CH=N); MS (FAB^+) = 528 (M^+); EA : calculated: C, 43.15; H, 3.05; S, 48.50; found: C, 43.01; H, 2.92; S, 48.69.

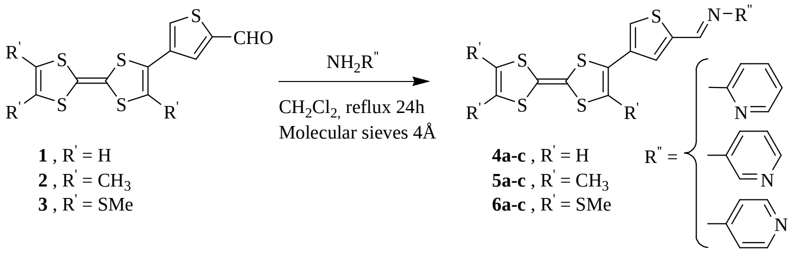
N-((4-trimethylthioTTFthiophen-2-yl)methylene)pyridine-3-amine 6b: Yield = 84%; Rf = 0.85 (CH_2Cl_2 / CH_3OH); purple powder; Mp = 177°C; PNMR ($CDCl_3$) δ ppm: 2.41(s, 6H, H_{TTF}); 2.56(S, 3H, H_{TTF}); 7.31(m, 1H, H_{py}); 7.47(s, 1H, H_{thio}); 7.58(S, 1H, H_{thio}); 7.64(m, 1H, H_{py}); 8.36(m, 2H, H_{py}); 8.57(s, 1H, CH=N); MS (FAB^+) = 528 (M^+); EA : calculated: C, 43.15; H, 3.05; S, 48.50; found: C, 42.92; H, 2.94; S, 48.71.

N-((4-trimethylthioTTFthiophen-2-yl)methylene)pyridine-4-amine 6c: Yield = 45%; Rf = 0.84 (CH_2Cl_2 / CH_3OH); purple powder; Mp = 186°C; PNMR ($CDCl_3$) δ ppm: 2.40(s, 6H, H_{TTF}); 2.58(s, 3H, H_{TTF}); 7.08(d, 2H, H_{py}); 7.49(s, 1H, H_{thio}); 7.59(s, 1H, H_{thio}); 8.47(d, 2H, H_{py}); 8.52(S, 1H, CH=N); MS (FAB^+) = 528 (M^+); EA : calculated: C, 43.15; H, 3.05; S, 48.50; found: C, 43.09; H, 2.93; S, 48.83.

RESULTS AND DISCUSSION

Compounds **4-6** were synthesized according to the chemical synthesis pathway shown in schema **1.** TTF-thiophenecarboxaldehyde derivatives **1-3** [11, 16, 18] were condensed with aromatic amines in refluxing dichloromethane in the presence of a 4Å inert molecular sieve, to generate the corresponding derivatives of TTF-thiophene-π-pyridine **4-6**, with moderate yields.

Scheme 1. Synthesis pathway for compounds 4-6



Electrochemical study

Cyclic voltammetry involves a linear sweep towards anodic potentials and then towards cathodic potentials (in the case of TTFs), for the range of potentials in which the product is oxidized and reduced. Peaks are observed, corresponding to the various stages of oxido-reduction [19, 20]. If the species formed at the electrode remains stable over the time period of the analysis, allowing a passage backwards and forwards under tension, then the system is reversible.

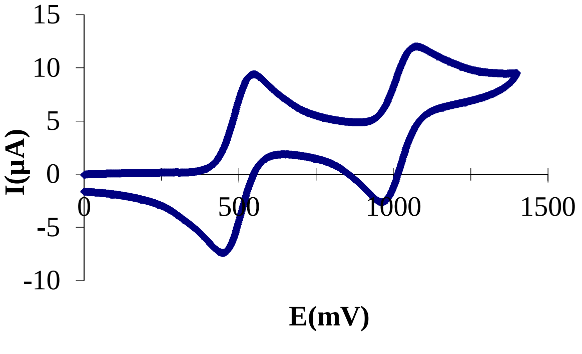
We evaluated the reducing power of the new donors in solution by cyclic voltammetry to test whether they could readily be oxidized to generate new potentially conductive materials. This also allowed the stability of the oxidation states obtained (reversibility of redox systems and determination of oxidation potentials, as appropriate) to be tested.

Table 1. First and second oxidation potentials for compounds 4-6

Compound	E^1_{ox} (mV)	E^2_{ox} (mV)
BEDT-TTF	666	1080
4a	525	1048
4b	536	1137
4c	534	1028
5a	418	918
5b	427	984
5c	424	932
6a	632	1129
6b	648	1245
6c	646	1132

Figure 1. Voltammogram for compound 4a

Solvent: *CH_2Cl_2;* ***Electrolyte support:*** *nBu_4NClO_4 (0.1M);* ***Working electrode and counterelectrode:*** *platinum;* ***Reference electrode:*** *saturated calomel electrode (SCE);* ***Scan speed:*** *100 mV/s.*



All the compounds isolated (**4-6**) displayed the expected two reversible waves of oxidation (figure 1); the values obtained were similar to those for bis-ethylenedithiotetrathiafulvalene (BEDT-TTF), which was used here as a reference and has been used to produce a large number of superconductors (table 1).

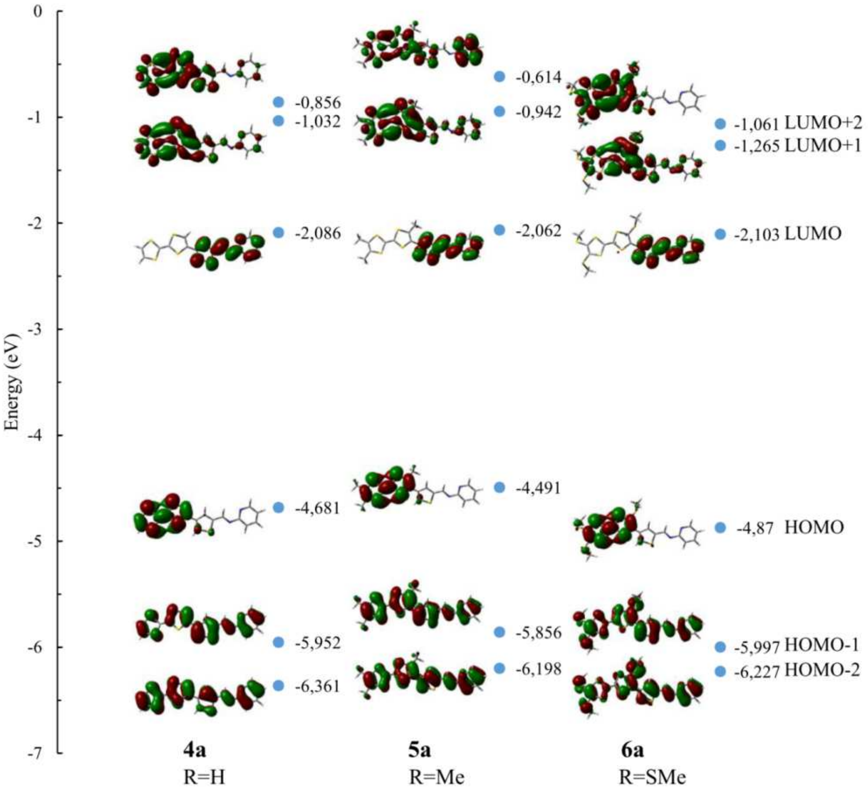
Theoretical calculation

The energy of the frontier orbitals of the various products (**4-6**) was calculated according to density functional theory (DFT; base 6-31G, method B3LYP Figure 2). Based on the energy levels of the highest occupied molecular orbital (HOMO), compounds **5a-c** were identified as the best donor molecules for the formation of TTF-TCNQ CTCs.

Table 2. Energy level (eV) of the molecular orbitals for products 4a–6c

Compound	LUMO+2	LUMO+1	LUMO	HOMO	HOMO-1	HOMO-2
4a	-0.856	-1.032	-2.086	-4.681	-5.952	-6.361
4b	-0.936	-1.096	-2.087	-4.757	-6.086	-6.428
4c	-0.997	-1.159	-2.211	-4.802	-6.194	-6.634
5a	-0.614	-0.942	-2.062	-4.491	-5.856	-6.198
5b	-0.650	-0.995	-2.064	-4.562	-5.969	-6.297
5c	-0.704	-1.054	-2.189	-4.607	-6.041	-6.513
6a	-1.061	-1.265	-2.103	-4.870	-5.997	-6.227
6b	-1.134	-1.321	-2.102	-4.937	-6.101	-6.315
6c	-1.181	-1.385	-2.220	-4.978	-6.169	-6.521

Figure 2. Molecular orbitals (HOMO and LUMO) for compounds 4a, 5a and 6a



Preparation of the materials

We used the direct synthesis method based on oxido-reduction in solution [1, 2, 21] to prepare the CTCs. The two components (the electron donor and acceptor) were dissolved separately in boiling acetonitrile and the two hot solutions were then mixed. The mixture was allowed to cool slowly and some of the solvent was allowed to evaporate, and we thereby isolated a solid with the characteristics of the expected complex.

The conductivity of materials is best measured with mono-crystal samples. In this situation, conductivity is dependent on the direction of the electric field with respect to the axes of the crystal. In general, the growth axis of the crystal, which corresponds to the axis along which the molecules are stacked, is the most conductive. However, in the absence of such mono-crystals, bars of compressed powder can be used for these measurements. This approach provides a mean value for the conductivity of the material. It should be noted, however, that bars of compacted powder are generally about an order of magnitude less conductive than single crystals.

Table 3. Fusion temperature and electrical conductivity of charge transfer complexes

Material	T_f °C	Conductivity σ ($\Omega^{-1}.cm^{-1}$)
4a-TCNQ	228	7.14×10^{-4}
4b-TCNQ	235	4.58×10^{-4}
4c-TCNQ	244	3.65×10^{-4}
5a-TCNQ	216	4.84×10^{-4}
5b-TCNQ	231	2.23×10^{-4}
5c-TCNQ	224	1.47×10^{-4}
6a-TCNQ	195	8.35×10^{-3}
6b-TCNQ	207	5.49×10^{-3}
6c-TCNQ	192	4.63×10^{-3}

All the materials synthesized were classified as semiconductors (table 3). The conductivity measured for a bar of compacted powder was 10^{-4} to 10^{-3} $S.cm^{-1}$ for these materials. Values of conductivity 10 times higher could be anticipated for single crystals.

CONCLUSION

During the course of this work, we developed new precursors of organic materials. A series of π-donors containing thiophene-π-pyridine units was synthesized by condensing TTF-thiophenecarboxaldehyde derivatives with aromatic amines. All the donors synthesized were characterized by routine spectroscopy techniques and their oxidation potentials were determined by cylic voltammetry. The charge transfer complexes of the donors synthesized with TCNQ were prepared and the electrical conductivity of these materials was measured. All the complexes prepared were classified as semiconductors.

Acknowledgments

This work received funding from the Directorate General for Scientific Research and Technological Development, DGRSDT.

REFERENCES

[1] JL Segura; N Martin,*Angew. Chem. Int. Ed.*,**2001**, 40, 1372–1409.
[2] JM Fabre, *J. Solid State Chem.*,**2002**, 168, 367–383.
[3] H Nishikawa; A Machida; T Morimoto; K Kikuchi; T Kodama; I Ikemoto; JI Yamada; H Yoshino; K Murata, *Chem. Commun.*,**2003**, 494–495.
[4] E Coronado; JR Galan-Mascaros; C Gimenez-Saiz; CJ Gomez-Garcia; C Ruis-Perez,*Eur. J. Inorg. Chem.*,**2003**, 2290–2298.
[5] M Otero; MA Herranz; C Seoane; N Martin; J Garin; J Orduna; R Alcala; B Villacampa,*Tetrahedron*,**2002**, 58, 7463–7475.
[6] D Canevet;M Sallé; G Zhang; D Zhang; D Zhu, *Chem. Commun.*,**2009**, 17, 2245–2269.
[7] J Singleton, *J. Solid State Chem.*,**2002**, 168, 675–689.
[8] T Devic; M Evain; Y Moelo; E Canadell; P Auban-Senzier; M Fourmigué; P Batail, *J. Am. Chem. Soc.*,**2003**, 125, 3295–3301.
[9] W Suzuki; E Fujiwara; A Kobayashi; Y Fujishiro; E Nishibori; M Takata; M Sakata; H Fujiwara; H Kobayashi, *J. Am. Chem. Soc.*,**2003**, 125, 1486–1487.
[10]JI Yamada; T Toita; H Akutsu; S Nakatsuji; H Nishikawa; I Ikemoto; K Kikuchi; ES Choi; D Graf; JS Brooks, *Chem. Commun.*,**2003**, 2230–2231.
[11]T Abbaz; A Bendjeddou; Ak Gouasmia; D Villemin; T Shirahata, *Int. J. Mol. Sci.*,**2014**, 15, 4550-4564.
[12]T Abbaz; A Bendjeddou; Ak Gouasmia; D Bouchouk; C Boualleg; N kaouachi; N Inguimbert; D Villemin, *Lett. Org. Chem.*,**2014**, 11, 59-63.
[13]T Abbaz; A Bendjeddou; A.k Gouasmia; D Villemin, *J. Chem. Pharm. Res.*,**2013**, 5, 262-266.
[14]T Abbaz; A Bendjeddou; Ak Gouasmia; Z Regainia; D Villemin, *Int. J. Mol. Sci.*,**2012**, 13, 7872-7885.
[15]T Abbaz; A Bendjeddou; Ak Gouasmia; Z Regainia; D Villemin, *Der Chemica Sinica*,**2012**, 3, 717-721.
[16]T Abbaz;AK Gouasmia; H Fujiwara; T Hiraoka; T Sugimoto; M Taillefer; JM Fabre, *Synth. Met.*,**2007**, 157, 508-516.
[17]T Abbaz; A Bendjeddou; N Nait Said; R Khammar; D Bouchouk; S Bouacherine; N Sedira; S Maache; Ak Gouasmia; R Rehamnia; M Dekhici; D Villemin, *J. Chem. Pharm. Res.*, **2014**, 6, 1385-1389.
[18]J Nakazaki; MM Matsushita; A Izuoka; T Sugawara, *Tetrahedron Letters*,**1999**, 40, 5027-5030.
[19]M Iyoda; Y Kuwatani; N Ueno; M Oda,*J. Chem. Soc., Chem. Commun.*,**1992**, 158-159.
[20]R Gomper; J Hock, *Synth. Met.*,**1997**, 84, 339-340.
[21]P Frère; P Skabara,*J.Chem. Soc. Rev.*,**2005**, 34, 69-68.