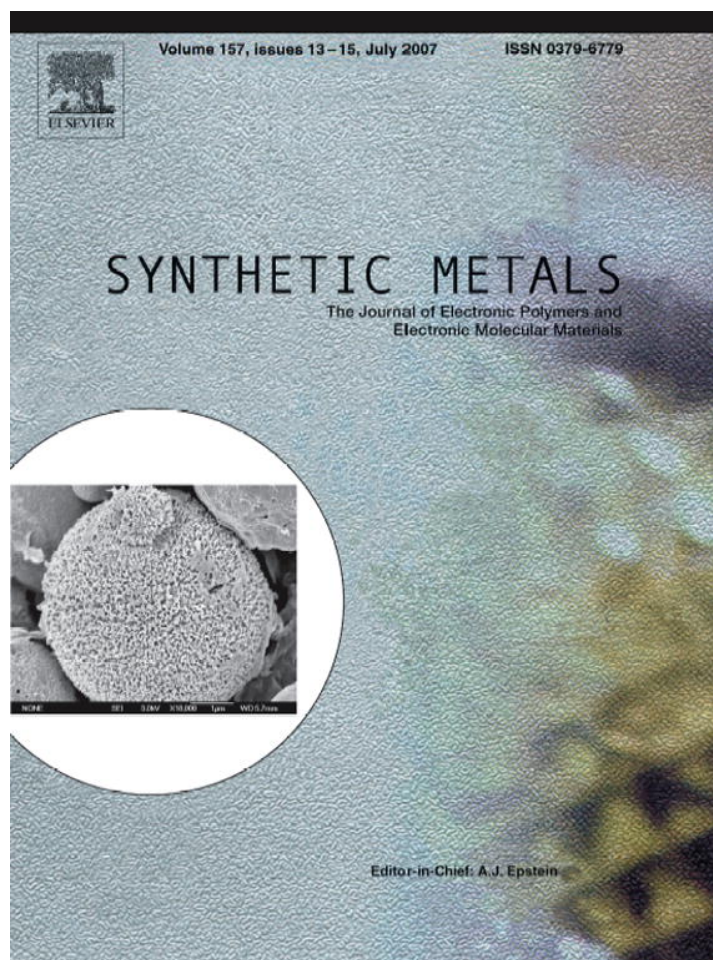


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article was published in an Elsevier journal. The attached copy is furnished to the author for non-commercial research and education use, including for instruction at the author's institution, sharing with colleagues and providing to institution administration.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



New TTF and bis-TTF containing thiophene units: Electrical properties of the resulting salts

Tahar Abbaz^{a,b}, Abdel-K. Gouasmia^{a,b}, Hideki Fujiwara^c, Takashi Hiraoka^c,
Toyonari Sugimoto^c, Marc Taillefer^{a,*}, Jean-M. Fabre^{a,*}

^a Institut Charles Gerhardt, UMR CNRS 5253, AM₂N, ENSCM, 8 rue de l'école normale, 34296 Montpellier Cedex 5, France

^b Laboratoire de Chimie des Matériaux Organiques, Centre Universitaire de Tébessa, route de Constantine, Tébessa, Algeria

^c Department of Chemistry, Graduate School of Science, Osaka Prefecture University, 1-2 Gakuen-cho, Sakai 599-8570, Japan

Received 8 March 2007; accepted 7 May 2007

Available online 13 July 2007

Abstract

Series of new TTF and bis-TTF containing a thiophene ring as a substituent or as a spacer group were prepared by using a palladium-catalyzed cross-coupling reaction from tributylstannyl–trimethyltetrathiafulvalene (tMeTTF–SnBu₃) and different halogeno and dihalogenothiophene derivatives. The reducing power of each new precursor was determined by cyclic voltammetry. Radical cations salts and charge transfer complexes of the donors with TCNQ were prepared and characterized. The electrical conductivity of these materials was measured and discussed in terms of (electronic) structure.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Tetrathiafulvalene; Thiophene; Radical cation; Conductivity; Electrochemistry

1. Introduction

For 35 years, the tetrathiafulvalene (TTF) and its derivatives have been intensely studied because of their abilities to form organic metals and superconducting solids [1,2] together with, to date, many other materials exhibiting a great variety of physical properties [3]. During the last decade, a particular attention has been devoted to the design of TTF donors involving a π -extended system [2,4] known to stabilize the metallic state of the resulting conducting salts by reducing on-site Coulombic repulsion and increasing dimensionality [2,5]. TTF derivatives incorporating aromatic substituents [6,7] and dimeric TTFs linked by different aromatic conjugated spacers [8,9] were successfully used to form highly conducting salts [10,11].

Thus, in order to develop new series of donors for two-dimensional metals in particular, we have synthesized several original TTF and bis-TTF containing thiophene units as substituent or as conjugated spacer. 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.

2. Results and discussion

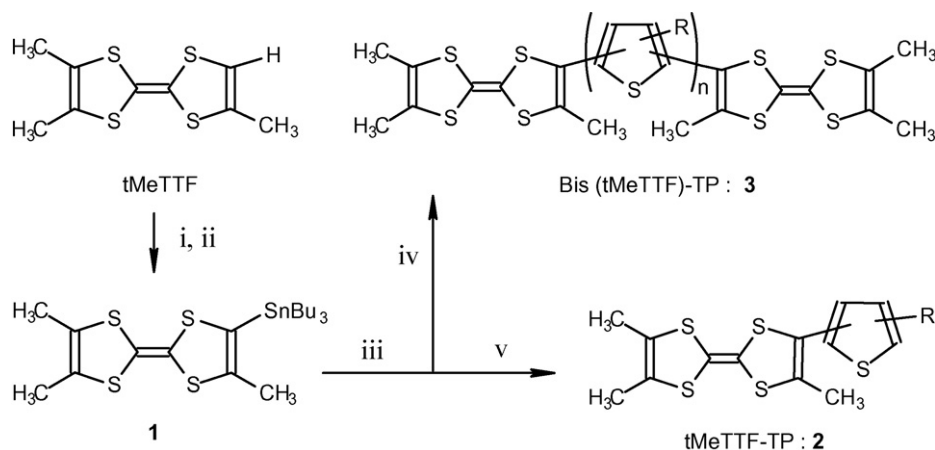
2.1. Synthesis

The synthesis of the electron donors of TTF **2** and bis-TTF **3** types (Scheme 1) was carried out using a palladium-catalyzed cross-coupling reaction involving various bromo or dibromothiophene and the tributylstannyl–trimethyltetrathiafulvalene **1** (tMeTTF–SnBu₃). The latter was previously synthesized in 79% yield [6] by using lithiation of trimethyltetrathiafulvalene (tMeTTF) [12] followed by treatment with tributyltinchloride.

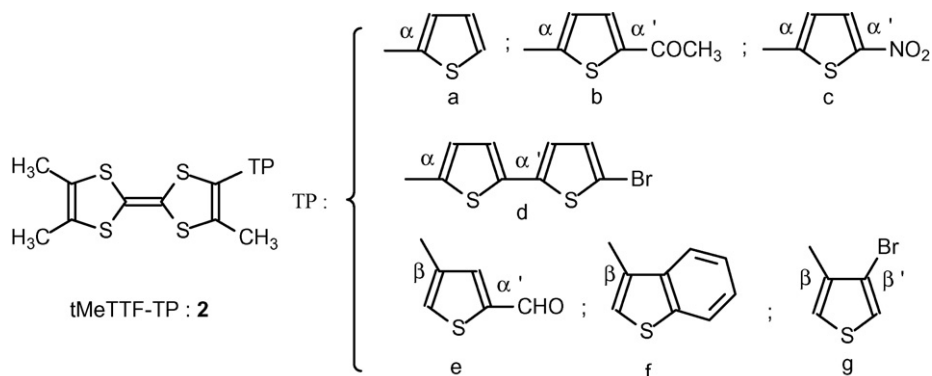
Following the above general procedure a series of new trimethyltetrathiafulvalenylthiophene (tMeTTF-TP) **2a–g** was prepared and characterized (Scheme 2). All the compounds show a direct covalent bond between the tMeTTF unit and the α position (**2a–d**) or the β one (**2e–g**) of the thiophene moiety.

* Corresponding authors. Tel.: +33 467144352; fax: +33 467144319.

E-mail addresses: marc.taillefer@enscm.fr (M. Taillefer),
jean-marc.fabre@enscm.fr (J.-M. Fabre).



Scheme 1. Syntheses of several new TTF 2 and bis-TTF 3, (i) LDA/THF (-78°C), (ii) ClSnBu_3 (-78 to 25°C), (iii) $\text{Pd(PPh}_3)_4$, (iv) dibromothiophenes, (v) bromothiophenes.

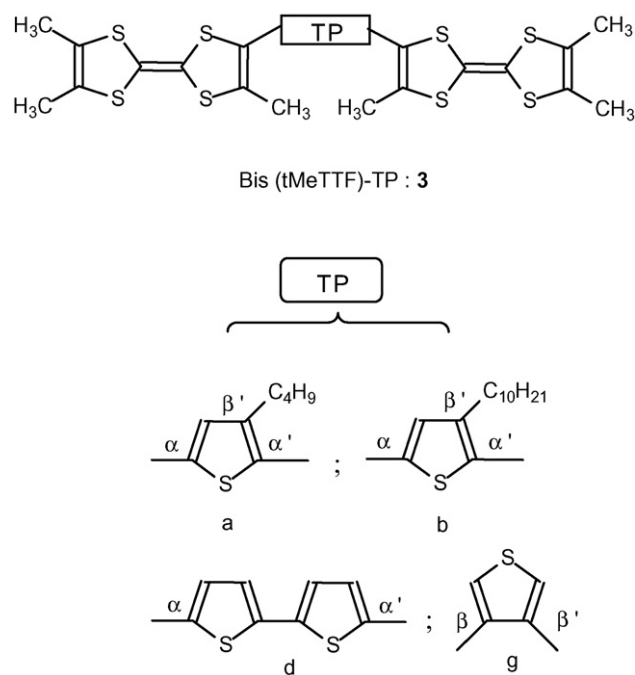


Scheme 2. New TTF 2 obtained.

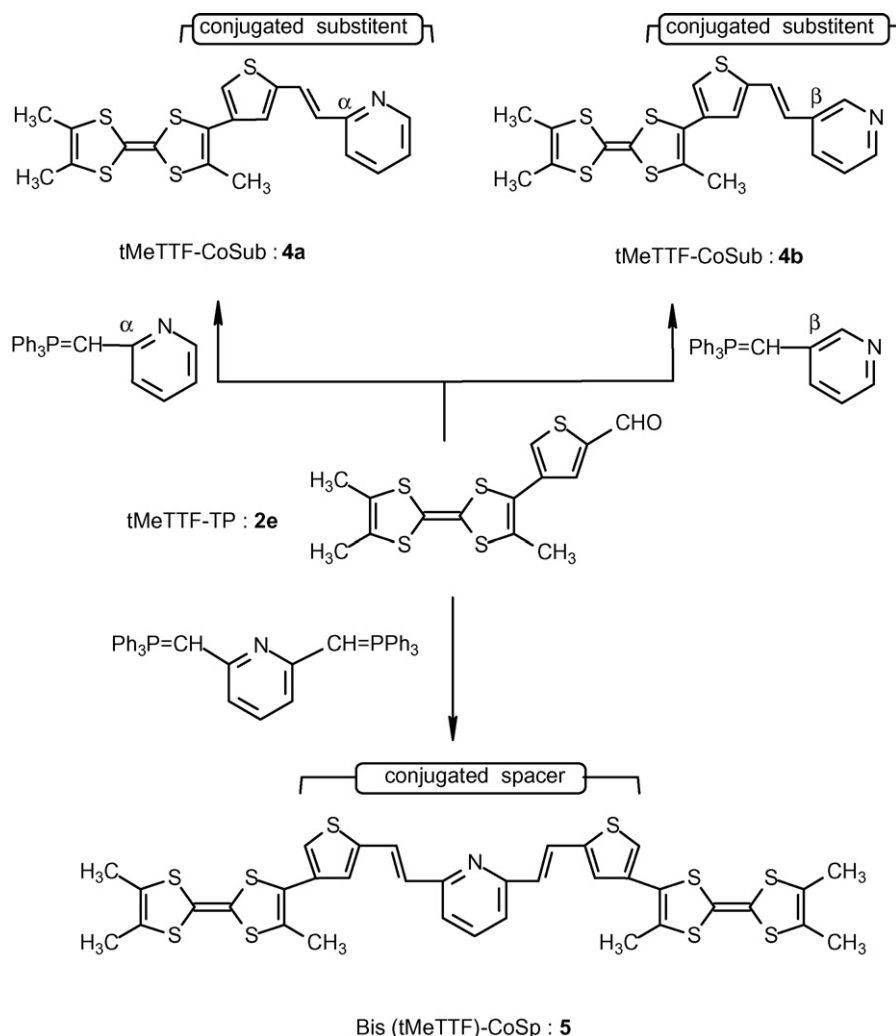
It is worth noting that, in this series, the mono-brominated compounds **2d** (16%) and **2g** (23%) were isolated in low yields because they were obtained as a by-product from reactions leading to the corresponding bis-TTF **3d** and **3g** (Scheme 3). Their formation resulted in fact in an incomplete cross-coupling reaction (single condensation) between the stannylated TTF **1** and, respectively, the 5,5'-dibromo-2,2'-bithiophene and the 3,4-dibromothiophene.

Of course, the main product (or often the exclusive compound) obtained from such palladium-catalyzed double cross-coupling reactions of **1** (2 equiv) with various dibromothiophene and bithiophene (1 equiv) were the corresponding bis-TTFs **3a**, **3b**, **3d**, and **3g** (Scheme 3).

Contrary to insoluble compounds **3d** and **3g** which precipitated in the reaction mixture and were isolated by filtration in 55 and 61% yield, respectively, compounds **3a** and **3b** were found soluble due to the butyl or decyl chain incorporated on the thiophene unit. These compounds were extracted by using dichloromethane and finally purified by column chromatography (SiO_2 , hexane/ CH_2Cl_2 3:1) to give **3a** (42%) and **3b** (24%). In the latter case, the steric hindrance of the long decyl chain can explain the low yield (24%) obtained and can induce a rotation between the rings of the thiophene spacer and those of the tMeTTF units leading to a non-planar molecule **3b**.



Scheme 3. New TTF 3 obtained.

Scheme 4. Syntheses of TTF **4** and **5**.

In order to produce precursors of types **2** and **3** exhibiting an extended π system [13,14] a pyridine ring was incorporated into the tMe-TTF-Thiophene molecule [15,16], either as substituent or as spacer. The corresponding compounds **4a**, **4b** and **5** were synthesized by using a Wittig type condensation [5,8] involving the tMeTTF-thiophenecarboxaldehyde **2e** and an appropriate phosphonium ylide (Scheme 4). The later was generated in situ in refluxing acetonitrile in presence of an excess of triethylamine and of the corresponding phosphonium salt, respectively: the triphenyl(2-pyridylmethyl) phosphonium chloride (one equivalent for **4a**), the triphenyl(3-pyridylmethyl) phosphonium chloride (1 equiv for **4b**) and the triphenyl(2,6-pyridylmethyl)phosphonium dichloride (0.5 equiv for **5**) (Scheme 4).

According to the NMR coupling constant value found for the vinyl group ($J=15.75$ Hz) (see below), a trans configuration can be attributed to the isolated compounds **4** and **5**. This configuration is not surprising because it corresponds to a Wittig reaction performed from an ylide of stabilized type.

3. Electrochemical characterization

The redox properties (half-wave potentials $E_{1/2}$) of tMe-TTF and of isolated compounds **2–5** measured by cyclic voltammetry (CV) are shown in Table 1.

As already mentioned in the literature about TTF [17a–d], the introduction on the TTF core of a thiophene ring, through its 2 position, increases slightly the first redox potential of the resulting donor. This is also shown in Table 1 ($\delta E = +38$ mV) by comparing the $E_{1/2}^1$ values of **2a** ($E_{1/2}^1 = 0.365$ V) with that of tMeTTF ($E_{1/2}^1 = 0.327$ V).

Moreover, as expected, higher $E_{1/2}^1$ values versus $E_{1/2}^1(\text{tMeTTF})$ were found when a more and more electron-withdrawing substituent is attached on the five position of the thiophene unit of compounds **2**. This stronger effect is clearly shown (Table 1) in **2d** ($\delta E = +44$ mV), **2b** ($\delta E = +81$ mV) and **2c** ($\delta E = +134$ mV) compounds, which respectively, contain a bromothiophene, an acetyl or a nitro group as an attracting substituent grafted on the thiophene ring. However, as illustrated

Table 1
Half-wave potentials of tMeTTF and of compounds **2–5**^a

Compound	$E_{1/2}^1(V)$	$E_{1/2}^2(V)$	$\Delta E(V) = E_{1/2}^2 - E_{1/2}^1$	$\delta E(mV) = E_{1/2}^1(2-5) - E_{1/2}^1(\text{tMeTTF})$
tMeTTF	0.327	0.780	0.453	–
2a	0.365	0.792	0.427	(365 – 327) = 38
2b	0.408	0.800	0.392	(408 – 327) = 81
2c	0.461	0.841	0.380	(461 – 327) = 134
2d	0.371	0.784	0.413	(371 – 327) = 44
2e	0.374	0.773	0.399	(374 – 327) = 47
2f	0.355	0.805	0.450	(355 – 327) = 28
2g	0.352	0.797	0.445	(352 – 327) = 25
3a	0.373	0.790	0.417	(373 – 327) = 46
3b	0.383	0.752	0.369	(383 – 327) = 56
3d	0.394	0.753	0.359	(394 – 327) = 67
3g	0.400	0.740	0.340	(400 – 327) = 73
4a	0.332	0.750	0.418	(332 – 327) = 5
4b	0.329	0.720	0.391	(329 – 327) = 2
5a	0.334	0.730	0.396	(334 – 327) = 7

^a Recorded in TBAP/CH₂Cl₂ (0.1 M) solution on Pt electrodes vs. SCE; scan rate 0.1 V s⁻¹.

by derivatives **2e–g** (Table 1), these effects were found less effective when the tMeTTF is connected to the thiophene ring through the three positions. This is in particular shown in (**2e**) and (**2g**) donors in which the attracting 5-formyl and 4-bromo groups induce a weak shift of the first oxidation potential versus $E_{1/2}^1(\text{tMeTTF})$, to slightly higher values ($\delta E = +47$ mV: **2e** and $\delta E = +25$ mV: **2g**).

In addition to these effects, the difference between the first and second oxidation potentials ($\Delta E = E_{1/2}^1 - E_{1/2}^2$) of derivatives **2** (Table 1) are found reduced compared with that of tMeTTF ($\Delta E = 0.453$ V). This is ascribed to a decrease in intramolecular Coulombic repulsion between the positive charges created in the oxidised forms of donors **2** (radical cation **2**⁺ and dication **2**²⁺) which would indicate an extended π -conjugation [4] in these molecules and in the TTF and bis-TTF derivatives **3–5**.

However, as exemplified by compound **2b** (Fig. 1a), the voltammograms of the whole donors **2–5** exhibit two reversible oxidation waves as suggested by the two oxidation peaks of equal area observed on the square wave (SQW) diagram of **2b** (Fig. 1b). This despite a broad, but not split, first oxidation peak was observed in compounds **5**.

In the case of bis-TTFs **3** and **5** this simple two-step oxidation pattern reflected a weak interaction between the two TTF parts of the molecule. This suggest that each TTF moiety acts as an isolated donor unit [18] leading at first to a bis-(radical-cation): (TTF^{•+}-spacer-TTF^{•+}) at $E_{1/2}^1$ and then to a bis-(dication): (TTF²⁺-spacer-TTF²⁺) at $E_{1/2}^2$. Similar results indicating a weak effective conjugation of the two TTF moieties into bis-TTFs containing unsaturated spacers were often observed in the literature [5,8].

It must also be mentioned that, in spite of the expected oxidation peak that was observed at 1.24 V on the voltammogram of the 2-bromothiophene taken as a reference, no such oxidation peak due to the incorporated thiophene unit was observed on the voltammograms of compounds **2–5**. This is valid even when the measurements under identical conditions, were performed, as shown in the case of

2b, from 0 to 2 V (Fig. 1 c) instead of from 0 to 1.5 V (Fig. 1 a).

Finally, all the isolated donors **2–5** present the first oxidation potentials close to that of TTF ($E_{1/2}^1 = 0.376$ V) which, in principle, make them able to be converted into conducting salts [1].

3.1. Synthesis, crystal structure and electrical properties of complexes and salts derived from donors 2–5: preliminary results

Except in the case of **2c** which was obtained in a too small amount and the failure observed with the bis-TTF **3g** poorly soluble into the different solvents used (acetonitrile and toluene), most of the compounds **2–5** formed charge transfer complexes with TCNQ (tetracyano-*p*-quinodimethane) used as an electron acceptor (A) [1,4]. All the solids were isolated as black powders of variable D–A stoichiometry (calculated from elemental analyses data: Table 2) after cooling the hot acetonitrile solution obtained by mixing equimolar amounts of the donor (D) and of TCNQ (A).

Several radical cation salts involving either a tetrahedral (perchlorate) or an octahedral (hexafluorophosphate) anion were also prepared by using the standard galvanostatic electrocrystallization method [19]. Platinum electrodes, a constant current of 3 μ A and appropriate tetrabutylammonium salts in THF were used as an electrolyte. In the case of the FeCl₄ salt of **3d**, an electrochemical oxidation was performed in a chlorobenzene/ethanol (9/1, v/v) solution of **3d** and tetraethylammonium salt of FeCl₄ at 20 °C under a constant current of 0.3 μ A. Compounds **2a**, **2d–e**, **3a** and **5a** lead so far to microcrystalline black salts unfortunately not suitable for a structural study by X-ray diffraction except in the case of **3d** (FeCl₄)₂(ethanol) isolated as single crystals.

Crystal structure analysis of the FeCl₄⁻ salt of donor **3d** was performed on a tiny single crystal using a Rigaku AFC-8 Mercury CCD diffractometer with a confocal X-ray mirror system. In the unit cell, there are one crystallographically independent donor molecule, two kinds of the FeCl₄⁻ ions and

Table 2
m.p. (°C), stoichiometry: D–A (from elemental analysis), electrical conductivity: σ_{RT} ($S\text{ cm}^{-1}$) of charge transfer complexes donor-TCNQ (D–A) and radical cation salts donor-perchlorate (or FeCl_4) and donor-hexafluorophosphate (D–A) obtained from donors **2–5**^a

Donor	Donor-TCNQ			Donor-ClO ₄ or FeCl ₄ *			Donor-PF ₆		
	m.p.	D–A	(σ_{RT})	m.p.	D–A	(σ_{RT})	m.p.	D–A	(σ_{RT})
2a	212	1–1	5.0×10^{-3}	–	–	–	–	–	–
2c	–	–	–	–	–	–	–	–	–
2b	217	3–2	7.3×10^{-2}	203	3–2	2.5×10^{-5}	214	–	2.0×10^{-4}
2d	200	2–1	8.5×10^{-3}	198	–	5.2×10^{-6}	205	–	4.0×10^{-6}
2e	226	3–2	9.1×10^{-3}	197	3–2	2.2×10^{-5}	209	–	7.6×10^{-6}
2f	197	1–1	3.6×10^{-2}	–	–	–	–	–	–
2g	194	1–1	7.8×10^{-3}	–	–	–	–	–	–
3a	213	1–1	2.2×10^{-3}	201	–	8.8×10^{-6}	210	–	5.6×10^{-6}
3b	230	1–2	3.1×10^{-3}	–	–	–	–	–	–
3d	283	3–2	8.1×10^{-3}	–	–	–	–	–	–
3d*	–	–	–	>300	1–2 ^b	6×10^{-3}	–	–	–
3g	–	–	–	–	–	–	–	–	–
4a	207	2–1	2.0×10^{-2}	–	–	–	–	–	–
4b	204	2–1	2.0×10^{-3}	–	–	–	–	–	–
5a	229	3–2	8.1×10^{-3}	207	1–2	1.6×10^{-6}	213	–	3.3×10^{-6}

^a Electrical conductivity measured on compressed pellets by a two-probe technique.

^b Stoichiometry of **3d**(FeCl_4)₂(ethanol) salt determined from the crystal structure data.

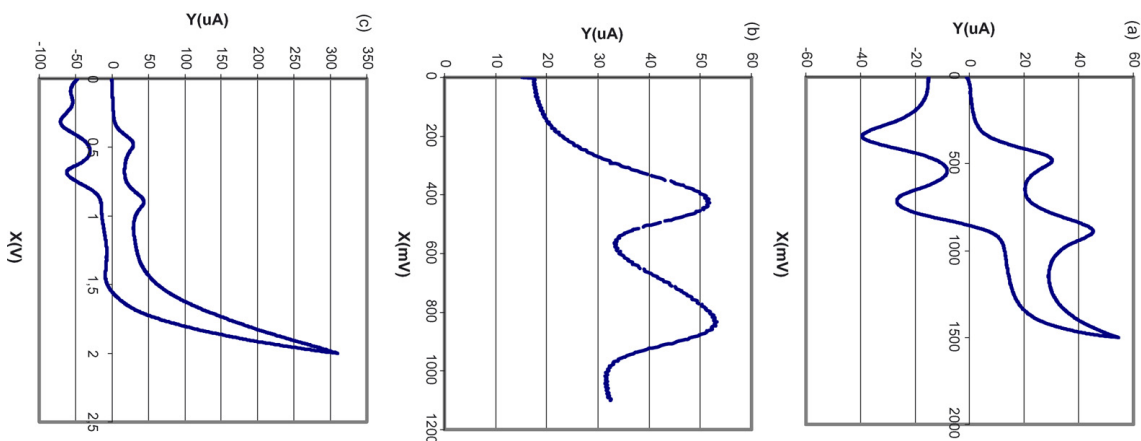


Fig. 1. (a) Voltammogram of **2b**, (b) square wave diagram of **2b**, and (c) voltammogram of **2b** (0–2 V).

one ethanol molecule as an interstitial solvent (Fig. 2a). From this D: A stoichiometry, each of two TTF parts has +1 valence state. As Fig. 2b illustrates, two TTF parts of donor **3d** are almost parallel to each other with small dihedral angle between the TTF planes (<2°), but connect to the bis-thiophene unit with large twisted angles of 24.2° and 16.7°, respectively. The donor

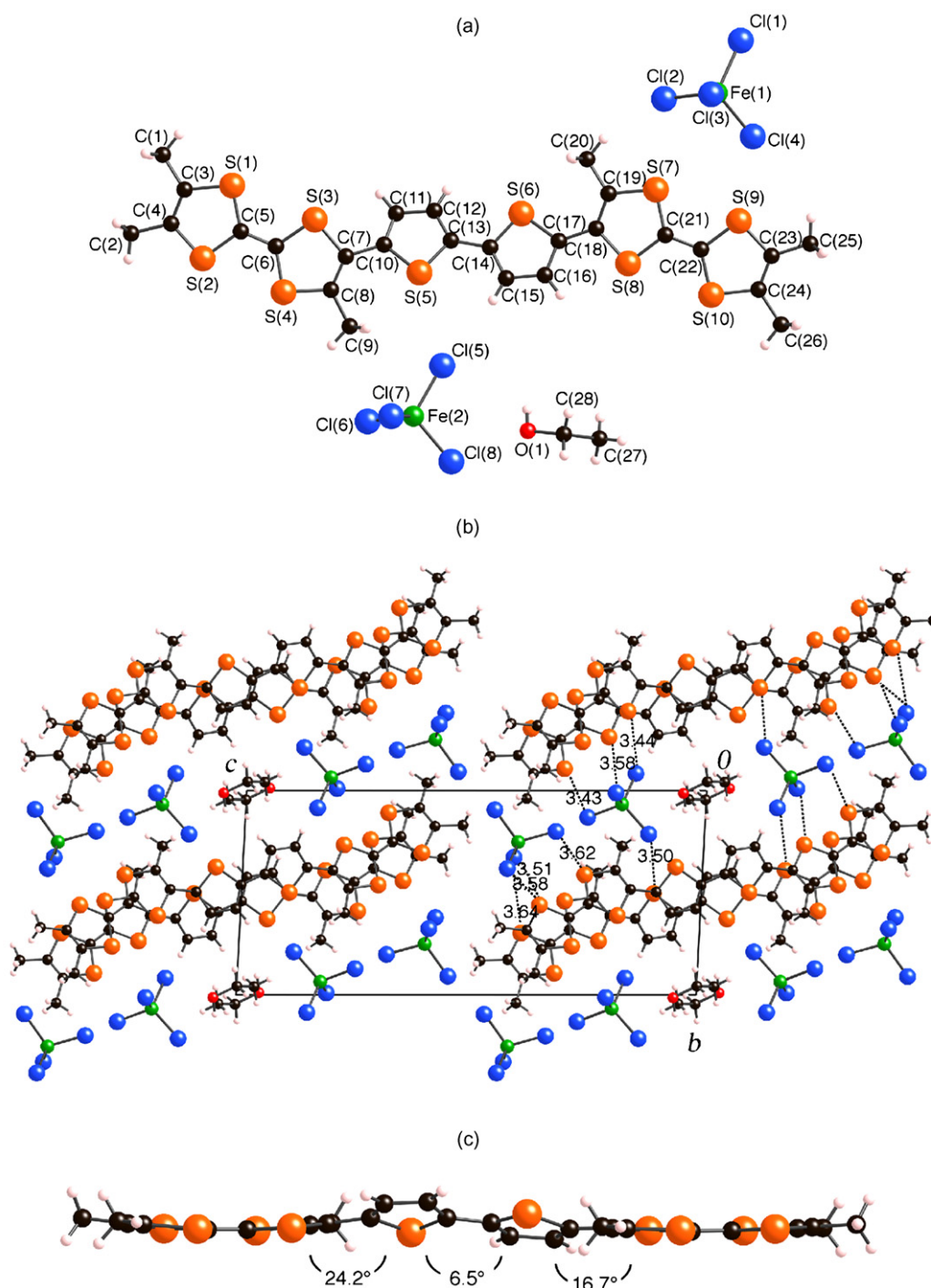


Fig. 2. (a) Crystallographically independent unit in the $3\mathbf{d}(\text{FeCl}_4)_2(\text{ethanol})$ salt, (b) crystal structure of the $3\mathbf{d}(\text{FeCl}_4)_2(\text{ethanol})$ salt projected to the bc plane, and (c) side view of the donor molecule $3\mathbf{d}$.

molecules form a dimer with a ring-over-ring type eclipsed overlapping mode and construct a one-dimensional stacking structure along the a -axis (see Fig. 2c). The FeCl_4^- ions are located between the columns of donor molecules $3\mathbf{d}$ and there are several $\text{S}\cdots\text{Cl}$ contacts shorter than the sum of the van der Waals radii of S and Cl atoms (3.65 Å) as shown by the dotted lines in the Fig. 2c, suggesting a strong π - d interaction between the donor molecules and the FeCl_4^- ions in this salt.

The room temperature conductivity of these solids was measured by using a two-probe technique on compressed pellets and on a single crystal in the case of $3\mathbf{d}(\text{FeCl}_4)_2(\text{ethanol})$. The results obtained are summarized in Table 2.

It is worth noting that, despite a different stoichiometry encountered in $(3\mathbf{d})_3-(\text{TCNQ})_2$ and $(5\mathbf{a})_3-(\text{TCNQ})_2$ on one hand, and $3\mathbf{b}-(\text{TCNQ})_2$ on the other hand (Table 2), the electrical conductivity of these complexes is quite similar and found

to be around $10^{-3} \text{ S cm}^{-1}$ suggesting similar electronic structure. On the other hand, owing to the two-electron oxidation processes encountered in bis-TTF [8] **3** and **5** (Table 1), the lower value ($\sigma_{\text{RT}}: 1.6 \times 10^{-6} \text{ S cm}^{-1}$) observed in **5a**-(ClO₄)₂ can be explained by the fully oxidized character of the bis-TTF donor into a bis-(radical-cation) **5a**²⁺.

Despite its one-dimensional stacking structure and a strong π - π interaction between the donor molecules and the FeCl₄⁻ ions, the salt **3d**-(FeCl₄)₂(ethanol) exhibits a low value of conductivity ($\sigma_{\text{RT}}: 6.0 \times 10^{-3} \text{ S cm}^{-1}$) and a semiconducting behaviour with an activation energy of 0.28 eV. This result can also be due to the 1:2 stoichiometry of this salt and consequently to the +1 valence state of the two TTF units of the donor (**3d**).

In comparison with these complexes involving bis-TTF, the electrical conductivity of salts obtained from mono-TTF **2** and **4** which present two one-electron oxidation processes [20] (Table 1), is also found in the range of 10^{-2} to $10^{-3} \text{ S cm}^{-1}$. A result which may account for a mixed valence structure in D₂-TCNQ (with D = **2d**, **4a**, **b**) and D₃-(TCNQ)₂ (with D = **2e**, **b**) complexes in particular. In contrast, the decrease of conductivity ($\sigma_{\text{RT}}: 10^{-5}$ to $10^{-6} \text{ S cm}^{-1}$) found in salts D₃-(ClO₄)₂ (with D = **2e**, **b**) and in other isolated salts (Table 2), could indicate a structural disorder in the solid leading to a less effective overlap of the organic cations [1,17a–c].

4. Conclusions

We have developed, as new precursors of organic materials, the synthesis of series of TTF (**2**, **4**) and bis-TTF (**3**, **5**) containing a thiophene ring attached through the 2 or 3 positions to the TTF unit and substituted by different groups. All the precursors can be quite easily oxidized and can lead to charge transfer complexes with TCNQ and radical cations salts exhibiting various stoichiometries. Part of the solids present a fairly high conductivity which can be related to a mixed valence state whatever the conjugation degree of the donor (2 and 3 or 4 and 5), the link position between the TTF and the thiophene moieties or the nature of the thiophene substituents. In the other hand, although they still present a favourable mixed valence state, some other salts and complexes exhibit a much lower conductivity ($\sigma_{\text{RT}}: >10^{-5} \text{ S cm}^{-1}$) which can be explained in terms of irregular arrangements of the TTF units in the solid. In order to confirm such an assessment other experiments under different conditions (current intensity, solvent, donor concentration etc.) are in progress to obtain single crystals of such solids and then to correlate their electrical properties with their crystal structure.

5. Experimental section

5.1. Synthesis of compounds **2** and **3**: general organometallic procedure

5.1.1. Compounds **2**: *tMeTTF-TP*

To a stirred solution of 4,4',5-trimethyl-5'-tributylstannyltetrathiafulvalene **1** (700 mg, 1.30 mmol: 1 equiv) in dry

toluene (30 ml) was added dropwise the bromothiophene derivative (1.30 mmol: 1 equiv) and then tetrakis-triphenylphosphine palladium [Pd(PPh₃)₄] (75 mg, 0.065 mmol: 0.05 equiv). The reaction mixture was refluxed for 60 h under nitrogen and then concentrated in vacuo. The residue was chromatographed on a silica column eluting with hexane-dichloromethane (2:1) to afford the expected compound as a solid.

2a: red powder (33% yield); m.p.: 100 °C; ¹H NMR (CDCl₃): δ 1.97 (6H, s, CH₃); 2.20 (3H, s, CH₃); 7.04 (1H_{thioph.}, d, $J=3.60$ Hz); 7.07 (1H_{thioph.}, t, $J=4.45$ Hz); 7.32 (1H_{thioph.}, d, $J=4.45$ Hz); MS (FAB⁺): 328 (M⁺).

2b: brown-red powder (75% yield); m.p.: 185 °C; ¹H NMR (CDCl₃): δ 1.94 (6H, s, CH₃); 2.16 (3H, s, CH₃); 2.23 (3H, s, COCH₃); 6.99 (1H_{thioph.}, d, $J=4.05$ Hz); 7.57 (1H_{thioph.}, d, $J=4.05$ Hz); MS (FAB⁺): 370 (M⁺).

2c: dark green powder (85% yield); m.p.: 205 °C; ¹H NMR (CDCl₃): δ 1.98 (6H, s, CH₃); 2.29 (3H, s, CH₃); 6.95 (1H_{thioph.}, d, $J=4.32$ Hz); 7.87 (1H_{thioph.}, d, $J=4.32$ Hz); MS (FAB⁺): 373 (M⁺).

2d: red powder (16% yield); m.p.: 175 °C; ¹H NMR (CDCl₃): δ 1.98 (6H, s, CH₃); 2.23 (3H, s, CH₃); 6.92 (1H_{thioph.}, d, $J=3.85$ Hz); 6.95 (1H_{thioph.}, d, $J=3.85$ Hz); 6.99 (1H_{thioph.}, d, $J=3.85$ Hz); 7.03 (1H_{thioph.}, d, $J=3.85$ Hz); MS (FAB⁺): 489 (M⁺).

2e: red powder (62% yield); m.p.: 153 °C; ¹H NMR (CDCl₃): δ 1.96 (6H, s, CH₃); 2.22 (3H, s, CH₃); 7.69 (1H_{thioph.}, s); 7.80 (1H_{thioph.}, s); 9.94 (1H, s: CHO); MS (FAB⁺): 356 (M⁺).

2f: yellow-orange powder (68% yield); m.p.: 135 °C; ¹H NMR (CDCl₃): δ 1.99 (6H, s, CH₃); 2.20 (3H, s, CH₃); 7.41 (1H_{arom.}, t, $J=2.75$ Hz); 7.44 (1H, t, $J=1.90$ Hz); 7.48 (1H_{thioph.}, s); 7.86 (1H_{arom.}, d, $J=9.10$ Hz); 7.90 (1H_{arom.}, d, $J=9.10$ Hz); MS (FAB⁺): 378 (M⁺).

2g: yellow-orange powder (23% yield); m.p.: 144 °C; ¹H NMR (CDCl₃): δ 1.93 (6H, s, CH₃); 1.97 (3H, s, CH₃); 7.33 (1H_{thioph.}, s); 7.36 (1H_{thioph.}, s); MS (FAB⁺): 407 (M⁺).

5.1.2. Compounds **3**: *bis(tMeTTF)-TP*

Same experimental procedure as **2** with addition of a dibromothiophene derivative (0.65 mmol: 0.5 equiv).

3a: orange powder (42% yield); m.p.: 190 °C; ¹H NMR (CDCl₃): δ 0.94 (3H, t, $J=7.55$ Hz, CH₃); 1.34 (2H, m, $J=7.55$ Hz, CH₂); 1.57 (2H, m, $J=7.55$ Hz, CH₂); 1.95 (12H, s, CH₃); 2.22 (6H, s, CH₃); 2.51 (2H, t, $J=7.55$ Hz, CH₂); 6.86 (1H_{thioph.}, s). MS (FAB⁺): 628 (M⁺).

3b: red powder (24% yield); m.p.: 110 °C; ¹H NMR (CDCl₃): δ 0.86 (3H, t, $J=7.45$ Hz, CH₃); 1.24 (16H, m, CH₂); 1.94 (12H, s, CH₃); 2.17 (6H, s, CH₃); 2.46 (2H, t, $J=7.45$ Hz, CH₂); 6.79 (1H_{thioph.}, s). MS (FAB⁺): 712 (M⁺).

3d: brown powder (55% yield); m.p.: 280 °C; ¹H NMR (CDCl₃): δ 1.96 (12H, s, CH₃); 2.23 (6H, s, CH₃); 6.89 (2H_{thioph.}, d, $J=4.00$ Hz); 7.04 (2H_{thioph.}, d, $J=4.00$ Hz). MS (FAB⁺): 654 (M⁺).

3g: orange powder (61% yield); m.p.: 287 °C; ¹H NMR (CDCl₃): δ 1.94 (12H, s, CH₃); 2.00 (6H, s, CH₃); 7.35 (2H_{thioph.}, s). MS (FAB⁺): 572 (M⁺).

5.2. Synthesis of compounds 4 and 5: general Wittig type procedure [5,8]

5.2.1. Compounds 4: *tMeTTF-CoSub*

To a stirred solution of trimethylthiophenecarboxaldehyde-tetrathiafulvalene 2e (200 mg, 0.56 mmol: 1 equiv) and triphenylheteroarylmethylphosphonium chloride (0.62 mmol: 1.1 equiv) in dry acetonitrile (30 mL) was added excess triethylamine (0.79 mL, 5.61 mmol: 10 equiv). The reaction mixture was refluxed for 4h under nitrogen. After cooling, the precipitate was filtered, washed with acetonitrile (2 × 30 mL) and dried to afford the expected solid compound.

4a: red-brown powder (64% yield); m.p.: 154 °C; ^1H NMR (CDCl_3): δ 1.94 (6H, s, CH_3); 2.10 (3H, s, CH_3); 6.95 ($1\text{H}_{\text{ethylenic}}$, d, $J=15.75$ Hz); 7.13 (1H_{arom} , t, $J=5.95$ Hz); 7.30 (1H_{arom} , d, $J=7.80$ Hz); 7.60 ($1\text{H}_{\text{thioph}}$, s); 7.64 (1H_{arom} , t, $J=7.80$ Hz); 7.64 ($1\text{H}_{\text{thioph}}$, s); 7.66 ($1\text{H}_{\text{ethylenic}}$, d, $J=15.75$ Hz); 8.57 (1H_{arom} , d, $J=4.60$ Hz). MS (FAB^+): 431 (M^+).

4b: orange powder (36% yield); m.p.: 160 °C; ^1H NMR (CDCl_3): δ 1.94 (6H, s, CH_3); 2.10 (3H, s, CH_3); 6.95 ($1\text{H}_{\text{ethylenic}}$, d, $J=15.75$ Hz); 7.32 (1H_{arom} , d, $J=8.05$ Hz); 7.60 ($1\text{H}_{\text{thioph}}$, s); 7.64 ($1\text{H}_{\text{thioph}}$, s); 7.66 ($1\text{H}_{\text{ethylenic}}$, d, $J=15.75$ Hz); 7.81 (1H_{arom} , t, $J=8.05$ Hz); 8.52 (1H_{arom} , d, $J=4.85$ Hz); 8.70 (1H_{arom} , d, $J=2.10$ Hz). MS (FAB^+): 431 (M^+).

5.2.2. Compounds 5: *bis(tMeTTF)-CoSp*

Same experimental process as 2 with addition of triphenyl(2,6-pyridylmethyl)phosphonium chloride (196 mg, 0.280 mmol: 0.5 equiv).

5a: light-brown powder (73% yield); m.p.: 190 °C; ^1H NMR (CDCl_3): δ 1.94 (12H, s, CH_3); 2.10 (6H, s, CH_3); 6.96 ($2\text{H}_{\text{ethylenic}}$, d, $J=15.75$ Hz); 7.16 (2H_{arom} , d, $J=7.70$ Hz); 7.58 (1H_{arom} , t, $J=7.70$ Hz); 7.60 ($2\text{H}_{\text{thioph}}$, s); 7.64 ($2\text{H}_{\text{thioph}}$, s); 7.80 ($2\text{H}_{\text{ethylenic}}$, d, $J=15.75$ Hz); MS (FAB^+): 783 (M^+).

5.3. X-Ray data collection, structure solution and refinement for $3d(\text{FeCl}_4)_2(\text{ethanol})$

The X-ray diffraction data were collected at 293 K for a black plate-like single crystal of $3d(\text{FeCl}_4)_2(\text{ethanol})$ (Crystal dimension: 0.08 mm × 4 mm × 1 mm) on a Rigaku AFC-8 Mercury CCD diffractometer equipped with a confocal X-ray mirror system (Mo $\text{K}\alpha$ radiation: $\lambda=0.71070$ Å). Crystal Data: $\text{C}_{28}\text{H}_{22}\text{Cl}_8\text{Fe}_2\text{OS}_{10}$, $M=1090.40$, triclinic, $P-1$, $a=7.758(4)$, $b=11.203(5)$, $c=25.120(12)$ Å, $\alpha=86.577(10)$, $\beta=85.200(10)$, $\gamma=84.534(10)^\circ$, $V=2163(2)$ Å³, $Z=2$, $\rho_{\text{calcd}}=1.674$ g cm⁻³, $\mu(\text{Mo K}\alpha)=16.71$ cm⁻¹. Intensity data were collected to a maximum 2θ value of 55.1°. Of the 48,064 collected reflections, 9771 were unique. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.56 to 1.00. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR92 [21]), and expanded (DIRDIF-99 [22]). The non-hydrogen atoms except for those of ethanol molecule included in the crystal were anisotropically refined. The isotropic temperature factors

were used for the atoms of ethanol molecule. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement on F was based on 3165 observed reflections [$I>2.50\sigma(I)$] and 456 variable parameters. The final R and R_w were 0.099 and 0.073, respectively. All the calculations were performed using the crystal structure crystallographic software package of the Molecular Structure Corporation [23]. The structure for the crystal of $3d(\text{FeCl}_4)_2(\text{ethanol})$ has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 634212.

Acknowledgments

This work was achieved in the framework of a ‘‘Franco-Algerian Inter-University Cooperation Programme’’ (PROFAS) with the support of the CMEP, the Algerian Ministry of Education and the French Ministry of Foreign Affairs that we thank warmly. We thank Prof. H. Kobayashi (Institute for Molecular Science, Japan) for the use of a Rigaku AFC-8 Mercury CCD diffractometer.

References

- [1] J.M. Williams, J.R. Ferraro, R.J. Thorn, K.D. Carlson, U. Geiser, H.H. Wang, A.M. Kini, M.-H. Whangbo, Organic Superconductors, Prentice-Hall, Englewood Cliffs, New Jersey, 1992.
- [2] J.M. Fabre, J. Solid State Chem. 168 (2002) 367, and references cited therein.
- [3] J.L. Segura, N. Martin, Angew. Chem., Int. Ed. 40 (2001) 1372.
- [4] P. Frère, P. Skabara, J. Chem. Soc. Rev. 34 (2005) 69.
- [5] A. Bitoh, Y. Kohchi, T. Otsubo, F. Ogura, K. Ikeda, Synth. Met. 70 (1995) 1123.
- [6] S. Bouguessa, A.K. Gouasmia, S. Golhen, L. Ouahab, J.M. Fabre, Tetrahedron Lett. 44 (2003) 9275.
- [7] R. Andreu, I. Malfant, P.G. Lacroix, P. Cassoux, Eur. J. Org. Chem. (2000) 737.
- [8] S. Gonzalez, N. Martin, J.L. Segura, C. Seoane, Tetrahedron Lett. 39 (1998) 3051.
- [9] (a) M. Iyoda, M. Hasagawa, Y. Kuwatani, H. Nishikawa, K. Fukami, S. Nagase, G. Yamamoto, Chem. Lett. (2001) 1146; (b) M. Iyoda, M. Hasegawa, J. Takano, K. Hara, Y. Kuwatani, Chem. Lett. (2002) 590.
- [10] (a) M. Mizutani, K. Tanaka, K. Ikeda, K. Kawabata, Synth. Met. 46 (1992) 201; (b) K. Ikeda, K. Kawabata, K. Tanaka, M. Mizutani, Synth. Met. 1993 (2007) 55–77.
- [11] K. Kawabata, K. Tanaka, M. Mizutani, N. Mori, Synth. Met. 70 (1995) 1141.
- [12] A.J. Moore, M.R. Bryce, A.S. Batsanov, J.C. Cole, A.K. Howard, Synthesis (1995) 675.
- [13] F. Iwahori, S. Golhen, L. Ouahab, R. Carlier, J.P. Sutter, Inorg. Chem. 40 (2001) 6541.
- [14] J. Nakazaki, M.M. Matsushita, A. Izuoka, T. Sugawara, Tetrahedron Lett. 40 (1999) 5027.
- [15] T. Sugimoto, S. Yamaga, M. Nakai, M. Tsujii, H. Nakatsuji, N. Hosoiito, Chem. Lett. 1993 (1817).
- [16] S. Bouguessa, K. Hervé, S. Golhen, L. Ouahab, J.M. Fabre, N. J. Chem. 27 (2003) 560.
- [17] (a) M. Iyoda, Y. Kuwatani, N. Ueno, M. Oda, J. Chem. Soc. Chem. Commun. (1992) 158; (b) M. Iyoda, M. Fukuda, S. Sasaki, M. Yoshida, Synth. Met. 70 (1995) 1171;

- (c) U. Kux, M. Iyoda, *Synth. Met.* 70 (1995) 1173;
(d) R. Gomper, J. Hock, *Synth. Met.* 84 (1997) 339.
- [18] L. Zou, W. Xu, X. Shao, D. Zhang, Q. Wang, D. Zhu, *Org. Biomol. Chem.* 1 (2003) 2157.
- [19] K. Bechgaard, K. Carneiro, F.B. Rasmussen, M. Olsen, *J. Am. Chem. Soc.* 103 (1981) 2440.
- [20] I. Pérez, S.-G. Liu, N. Martin, L.J. Echegoyen, *Org. Chem.* 65 (2000) 3796.
- [21] A. Altomare, M.C. Burla, M. Gamalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidre, *J. Appl. Crystallogr.* 27 (1994) 435, The SIR92 program.
- [22] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, D. de Gelder, R. Israel, J.M.M. Smith, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999, The DIRDIF-99 program.
- [23] Crystal Structure, Single Crystal Structure Analysis Software. Version 3.5.1. Molecular Structure Corporation: The Woodlands, TX, 2003.