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Synthesis and characterization of TTF-type precursors for the construction of conducting and magnetic molecular materials

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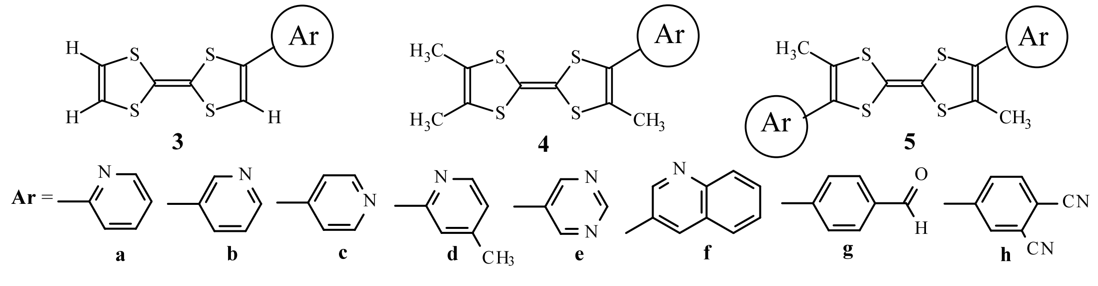
Abstract—New TTF precursors for the construction of conducting and magnetic materials have been synthesized by using the palladium-catalyzed cross-coupling reaction between a mono- or a bis(trialkylstannyl)tetrathiafulvalene and a series of heteroaryl halides. The redox potential and some crystallographic data of these new building blocks are presented and discussed.

One of the current objectives in the field of conducting molecular materials derived from tetrathiafulvalene (TTF) is to try to correlate within the same solid two distinct physical properties[1] such as magnetic and conducting properties,[2] seeking to establish in this case a magnetic coupling between the conduction electrons and the spins.[3] These materials could be obtained starting from precursors containing both a TTF unit as source of conducting electrons and a pyridine-type heterocycle as a ligand of a transition metal carrying a localized spin. The work achieved until now in this area is sparse.[4,5] We present here the synthesis, the redox properties and some crystallographic data of a series of conjugated and compact precursors of type **3**, **4** and **5** which could give access to salts manifesting the required spin-electron correlations.

1. Synthesis

Although the 4,5-dimethylthio-4′-(4-pyridyl)tetrathiafulvalene was recently prepared by a cross-coupling reaction of the corresponding 1,3-dithiole-2-thiones,[6] the poor yield obtained (15%) suggests the use of the organometallic strategy described by Iyoda and coworkers[7,8] because it recently led to the 4,4′,5-trimethyl-5′-(pyridyl)tetrathiafulvalene in 63% yield.[9] We thus chose to develop this strategy to prepare compounds of type **3** and **4** from several heterocyclic halides containing nitrogen atom(s) and to extend it to the synthesis of disubstituted TTF derivatives of type **5** by using, as a new intermediate, a bis-trialkylstannyl-TTF derivative (**2c**) (Scheme 1).

In the first step of the process, the mono and bis-tributylstannyl-TTF derivatives **2a**–**c**, were respectively prepared by the successive treatment of TTFs **1a**–**c** with LDA and tributyltin chloride at −78°C in dry THF. According to the degree of substitution of the starting TTF **1a**–**c**, 1.2, 1.5 and 3 equiv. of these reagents were used respectively to lead, after column chromatography purification (SiO_2, pentane–CH_2Cl_2 9.5:0.5), to the expected compounds **2a** (70%), **2b** (79%) and **2c** (76%).



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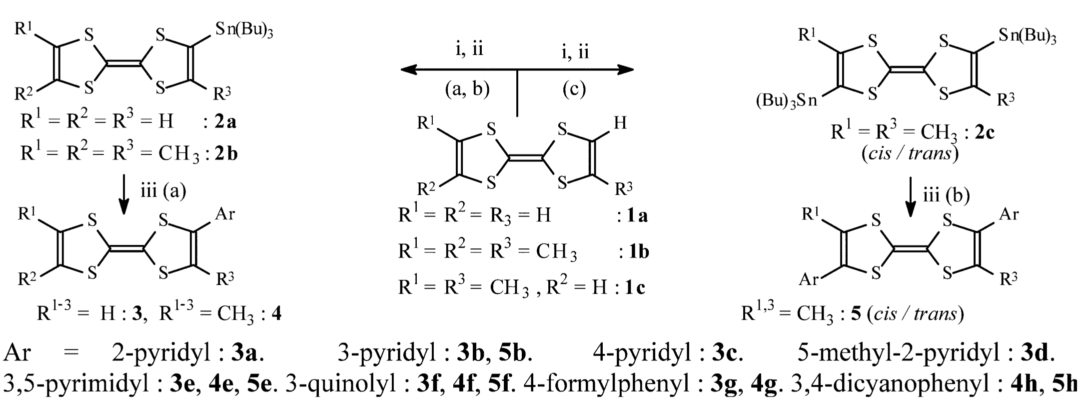
To prevent the observed decomposition of these tributylstannyl-TTFs on the SiO_2, the silica was first basified with triethylamine. Despite the excess of reagent (1.2 equiv. of LDA and of $ClSnBu_3$) used in the synthesis of **2a**, 20% of unreacted TTF was recovered whereas only traces of starting materials were recovered from the syntheses of **2b** and **2c**.

The second step of the synthesis consisted in the Stille palladium-catalyzed condensation (using $Pd(PPh_3)_4$) between the organostannyltetrathiafulvalene **2** and a heterocyclic aromatic halide **6**–**13**, in refluxing dry toluene. The results obtained are reported in Table 1.

Although better reactivity was generally observed with aryl iodides in this type of reaction,[7] compound **3b** was obtained in 74% yield using **2a** and 3-bromopyridine. A 60% yield was obtained with 3-iodopyridine and no reaction was observed with 3-chloropyridine. Thus aryl bromides were used except in the case of 4-iodophthalonitrile **13**, a commercially available compound from Aldrich.

It is also worth noting that the result of the reaction is closely related to the nature of the organometallic compound **2**. Thus the reactivity appeared better with the parent product **2a** than with its trimethylated derivative **2b**, whereas the bis-stannylated derivative **2c** led surprisingly to quite high yields in spite of the similar hindrance to that of **2b**. This was illustrated by the results obtained in the reactions between **2a**, **2b** and **2c** with 5-bromopyrimidine **10** and 3-bromoquinoline **11**, which afforded **3e** (70%), **4e** (45%) and **5e** (77%) (entries 5, 11 and 16) and **3f** (67%), **4f** (26%) and **5f** (47%) (entries 6, 12 and 17), respectively.



Scheme 1. *Reagents and conditions*: (i) LDA (THF), −78°C (1.5 h); (ii) $ClSnBu_3$, −78°C (1 h, then rt, (a) 1.2, (b) 1.5, (c) 3 equiv.; (iii) refluxing toluene (48 h), (a) $Pd(PPh_3)_4$ (5%), ArX (1 equiv.), (b) $Pd(PPh_3)_4$ (10%), ArX (2 equiv.)

Table 1. Yields and electrochemical data[a] for compounds of type **3**, **4** and **5**

Entry	Synthesis			Product	Electrochemical data (mV)		
	$TTFSnR_3$	Ar–X	Yield (%)		E_{ox}^1	E_{ox}^2	ΔE
1	**2a**	**6**	41	**3a**	542	1094	552
2	**2a**	**7** (Br, I, Cl)	74, 60, 0	**3b** (from ArBr)	580	1076	496
3	**2a**	**8**	36	**3c**			
4	**2a**	**9**	34	**3d**	508	1066	558
5	**2a**	**10**	70	**3e**	660	1118	458
6	**2a**	**11**	67	**3f**	610	1132	522
7	**2a**	**12**	73	**3g**	578	1096	518
8	**2a**	**13**	87	**3h**	650	1128	428
9	**2b**	**7** (Br)	<5	**4b**			
10	**2b**	**9**	0	**4d**			
11	**2b**	**10**	45	**4e**	546	1036	490
12	**2b**	**11**	26	**4f**	470	976	506
13	**2b**	**12**	41	**4g**	468	968	500
14	**2b**	**13**	21	**4h**	534	1004	470
15	**2c**	**7** (Br)	59	**5b**	552	1024	472
16	**2c**	**10**	77	**5e**	650	1076	426
17	**2c**	**11**	47	**5f**	554	1020	466

6: 2-bromopyridine; **7**: 3-halopyridine; **8**: 4-bromopyridine hydrochloride; **9**: 2-bromo-4-methylpyridine; **10**: 5-bromopyrimidine; **11**: 3-bromoquinoline; **12**: 4-bromobenzaldehyde; **13**: 4-iodophthalonitrile.

[a] All measurements were performed by cyclic voltammetry (CV) in CH_2Cl_2 containing 0.1 M Bu_4PF_6, with SCE (reference electrode), platinum (working and counter electrodes), scan rate 0.1 V s^{-1}.

2. Redox properties

The cyclic voltammograms of all the compounds **3**, **4** and **5** display the two reversible one-electron oxidation waves expected to convert successively the TTF unit into the radical cation and then into the dication. The corresponding E_{ox}^1 and E_{ox}^2 values are reported in Table 1. By comparison with the E_{ox}^1 values of TTF **1a** (586 mV) and of its methylated derivatives **1b** (450 mV) and **1c** (480 mV) also measured as reference, a pyridine-type substituent did not seem to induce a significant effect on the E_{ox}^1 value (entry 2) as has already been reported in the literature.[6,9] However, a positive shift of about 20–100 mV was observed for compounds **3e**, **3f**, and **3h**, (entries 5–7), **4e–h** (entries 11–14) and **5e–f** (entries 16–18) and in the case of **5b** (double effect due to a double substitution) which indicates the electron withdrawing effect exerted, in particular, by the pyrimidine and the phthalonitrile substituents (entries 5, 11, 16 and 8, 14, 18, respectively). Surprisingly a low E_{ox}^1 value was observed (entry 7) for **3g** despite the presence of an aldehyde function on the phenyl substituent of this TTF. All the E_{ox}^1 values measured for compounds **3**, **4** and **5**, were found to be lower than 666 mV, the oxidation potential (E_{ox}^1) of BEDT-TTF. These results showed the good π-donor ability of this new series of TTF derivatives which consequently should lead, in a similar manner to BEDT-TTF, to conducting materials.

3. Structural data

The ORTEP drawings and crystal structures of compounds **3g** and **4f** are presented in Figures 1 and 2, respectively.[10] Molecule **3g** reveals an angle of 8.8(2)° between the TTF unit and the 4-formylphenyl plane. The molecular packing (Fig. 1c) shows several short intermolecular contacts (the shortest being S1···O1 = 3.214 Å) and a potential hydrogen bonding O1···H8 = 2.547 Å. Molecules are stacked along the *a* axis; in one column the shortest distance between two TTF planes is around 3.60 Å. Along the *b* direction, the TTF units belonging to two adjacent columns form an angle of 46.95(7)° while an angle of 51.36(2)° is observed between TTF units of two stacks along the *c* axis.

Molecule **4f** reveals an angle of 46.95(7)° between the TTF unit and the 3-quinolyl group. The molecular packing is shown in Figure 2b. It can be seen that two molecules are packed together through the 3-quinolyl fragment (3.5 Å), however, the distance between two TTF units is too large to allow overlapping.

In conclusion, as shown by these structural data, once oxidized these molecules seem to be good candidates for multiproperty materials, due to the possibility of TTF packing for conductivity and the presence of coordination sites for paramagnetic metals able to induce magnetic properties to the corresponding salts. The synthesis of such materials is now in progress.

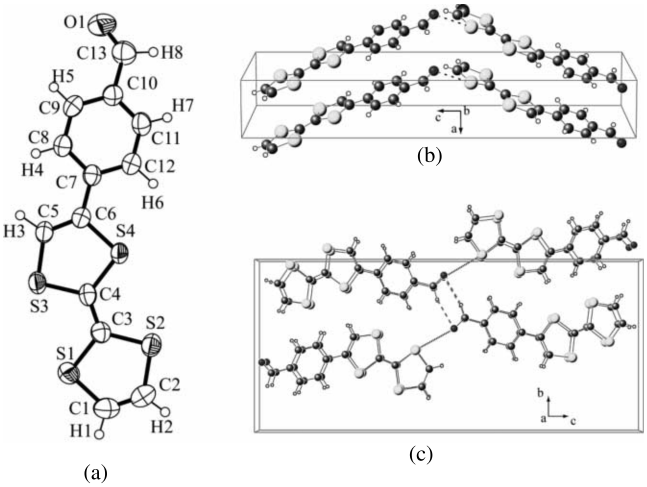


Figure 1. (a) ORTEP drawing of **3g**. (b) Packing of **3g** along the *a* direction. (c) Shortest S···O and O···H intermolecular interactions.

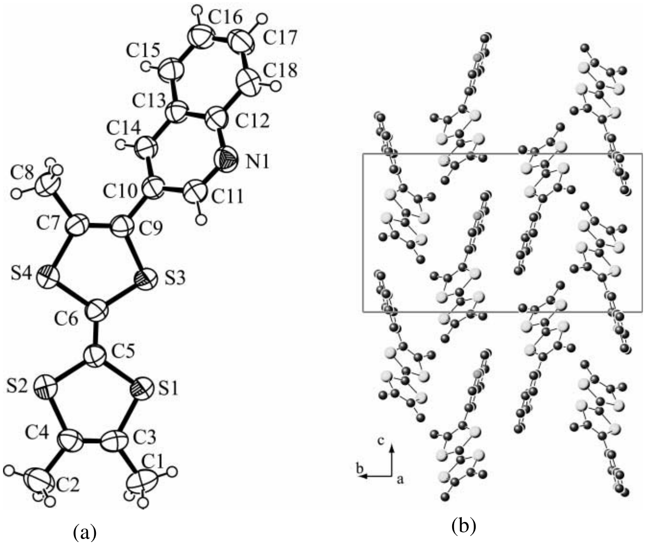


Figure 2. (a) ORTEP drawing of **4f**. (b) Unit cell of **4f** in the *bc* plane.

Acknowledgements

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10. Data for X-ray structure analysis were collected at room temperature on a Nonius Kappa CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Structures were solved by direct methods and refined against F^2 with the full-matrix, least-squares methods using SHELXS-97 and SHELXL-97, respectively. Crystal data for **3g**: C_{13} H_8 O S_4, $Mw = 308.43$, orthorhombic, space group $P2_12_12_1$, $a = 4.0040(1)$, $b = 11.9920(3)$, $c = 26.9750(6)$ Å, $V = 1295.23(5)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.582$ g cm^{-3}, $R_1 = 0.0448$, $wR_2 = 0.1164$ for 2955 observed reflections with $I > 2\sigma(I)$. Crystal data for **4f**: $C_{18}H_{15}NS_4$, $Mw = 373.55$, monoclinic, space group $P2_1/n$, $a = 8.0910(3)$, $b = 19.4730(7)$, $c = 11.3960(4)$ Å, $\beta = 104.215(2)°$, $V = 1740.53(5)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.426$ g cm^{-3}, $R_1 = 0.0553$, $wR_2 = 0.1817$ for 2246 observed reflections with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for these structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-216267 and CCDC-216268. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44-(0)1223-336033, or e-mail: deposit @ccdc.cam.ac.uk).