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Acetylacetone substituted tetrathiafulvalenes: towards new redox active ligands

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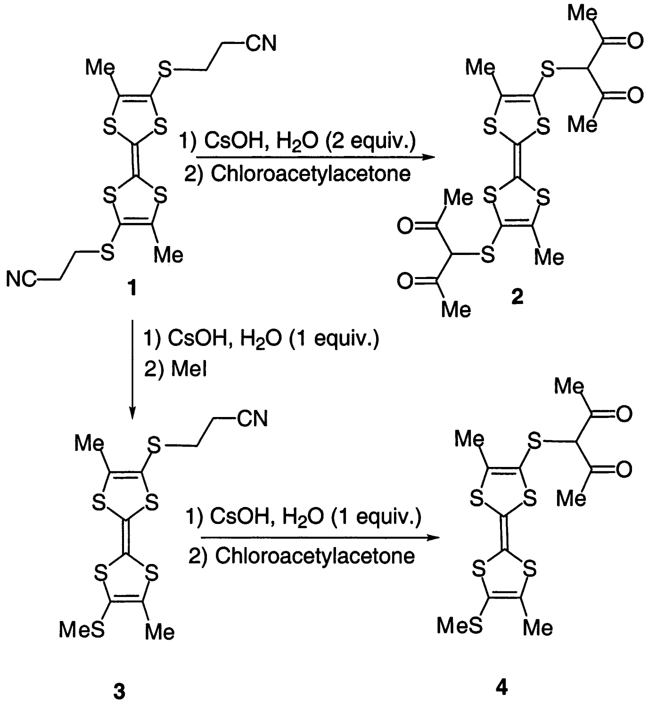
Abstract—A simple synthesis of novel ligands containing tetrathiafulvalenes (TTF) is reported. These compounds have been prepared by introducing an acetylacetone coordination function on the preformed donor core. © 2001 Elsevier Science Ltd. All rights reserved.

Hybrid organic–inorganic materials involving the coordination of transition metal derivatives with organic donors such as tetrathiafulvalene have recently attracted attention due to the various electronic properties expected from this type of materials (conductivity, magnetism, optical...).[1,2] One possibility of forming these hybrid materials consists of functionalizing the organic moiety with appropriate coordination functions and to use these parts as ligands for various metals. For example, TTF substituted by coordination functions such as dithiolene or phosphine ligands have been described with this purpose.[1–5] Dithiolenes and phosphines are not the only ligands presenting a chelating ability towards various transition metal derivatives. Indeed, β-diketones and especially their enolate ions also present powerful chelating properties and form complexes with various transition metals and main group elements.[6] The commonest ligand within this broad class of coordination compounds is the acetylacetonate ion. TTF derivatives substituted with one or two acetylacetone groups are therefore potential ligands which can be involved in the formation of organic–inorganic materials. Depending on the number of acetylacetone substituents introduced on the TTF core, one can expect either polymeric or molecular hybrid materials. In this paper, we report the synthesis of the first examples of TTF substituted by acetylacetone coordination function.

An interesting route for the synthesis of various functionalized TTFs has been developed by Becher and collaborators who demonstrated the efficiency of the cyanoethyl group to protect thiolates.[7] Deprotection is achieved on treatment with a strong base (e.g. alkali metal hydroxide), regenerating the thiolate which can react with various electrophiles. One of our starting materials, bis-cyanoethylthio TTF **1**, was prepared



Scheme 1.

Keywords: tetrathiafulvalene; acetylacetone; ligand.

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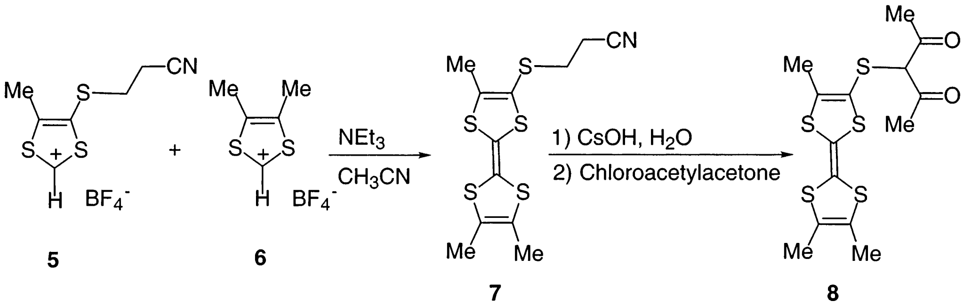

Scheme 2.

Table 1. Cyclic voltammetry data, E in V versus SCE, Pt working electrode with 0.1 M n-Bu_4NPF_6 scanning rate 100 mV/s in CH_2Cl_2

	Epa[1]	Epa[2]	ΔE
TTF **2**	0.51	0.90	0.39
TTF **4**	0.47	0.88	0.44
TTF **8**	0.36	0.81	0.45

according to a known procedure from mesoionic dithiole.[5] The bisthiolate TTF, derived from **1**, was obtained using two equivalents of caesium hydroxide and then trapped by addition of chloroacetylacetone affording TTF **2** in 82% yield (Scheme 1).[8]

In order to prepare the mono acetylacetone TTFs **4** and **8** we used two different strategies. On the one hand, we realized selective monodeprotection of bis-cyanoethylthio TTF **1** by the addition of one equivalent of base. The thiolate was alkylated with iodomethane to give TTF **3** after column chromatography.[5] Deprotection of the second cyanoethylthio group via the same procedure and subsequent quenching with chloroacetylacetone yielded TTF **4** in 88% yield (Scheme 1).[8] Two isomers are observed for all the bis-functionalized TTFs described above (only the trans isomers are represented in Scheme 1).[9]

On the other hand, and with the aim of avoiding the presence of two TTF isomers we prepared the unsymmetrical cyanoethylthiotrimethyl–TTF **7** (Scheme 2). The coupling in basic medium of the two different dithiolium salts, **5** and **6**, afforded two symmetrically substituted TTFs and the unsymmetrical TTF **7**. Separation of those TTFs by column chromatography gave TTF **7** in 25% yield. The protecting group was cleaved with caesium hydroxide and realkylated with chloroacetylacetone leading to TTF **8** in 88% yield.[8]

The redox behavior of these three new building blocks was investigated by cyclic voltammetry and the results are summarized in Table 1. As usually observed for TTFs, these derivatives exhibit two reversible monoelectronic waves. One can see that the presence of two acetylacetone substituents acting as withdrawing groups slightly decreases the donor ability of TTF **2** compared with TTF **4**. Due to the presence of a methyl group instead of a thiomethyl one TTF **8** is therefore easier to oxidize than **4**.

In summary, we have prepared acetylacetone substituted TTFs according to a versatile methodology using preformed TTF derivatives. As ketoenolate anions are powerful chelating species these new compounds will open broad perspectives concerning the elaboration of organic–inorganic materials. We are now investigating routes to form metal β-diketonates complexes.

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8. Selected data; TTF **2**: orange powder; mp 211°C (decomp.); δ_H (200 MHz; $CDCl_3$) 2.22 (s, 6H), 2.52 (s, 12H); δ_C (75 MHz; $CDCl_3$) 15.23, 25.26, 103.24, 109.05, 121.80, 128.05, 197.63; HRMS calcd for $C_{18}H_{20}O_4S_6$ 491.9688. Found 491.9686. TTF **4**: orange powder; mp 146–147°C; δ_H (200 MHz; $CDCl_3$) 2.15 (s, 3H), 2.17 (s,

3H), 2.34 (s, 3H), 2.46 (s, 6H); δ_C (75 MHz; $CDCl_3$) 15.24, 15.56, 19.75, 25.25, 103.25, 108.19, 109.94, 121.22, 121.69, 128.02, 134.22, 197.59; HRMS calcd for $C_{14}H_{16}O_2S_6$ 407.9475, found 407.9469. Anal. calcd for $C_{14}H_{16}O_2S_6$ C, 41.17; H, 3.92; S, 47.15. Found: C, 41.01; H, 3.73; S, 47.57. TTF **8**: orange powder; mp 164–165°C; δ_H (200 MHz; $CDCl_3$) 1.97 (s, 6H), 2.17 (s, 3H), 2.46 (s, 6H); δ_C (50 MHz; $CDCl_3$) 14.24, 15.36, 25.40, 103.44, 121.82, 123.41, 123.48, 128.30, 197.75; HRMS calcd for $C_{14}H_{16}O_2S_5$ 375.9750. Found 375.9754.

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