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The *bis*-Linking of Tetrathiafulvalene (TTF) to C_{60} : Towards the Control of Electron Transfer between π-donors and C_{60}

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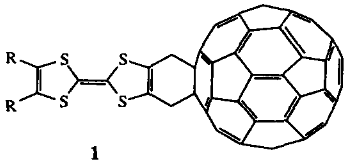
Abstract : The *bis*-linking of a tetrathiafulvalene (TTF) to C_{60} is carried out by [4+2] Diels-Alder cycloaddition of C_{60} to the 2,3-dimethylene-TTF **2**, this transient diene being generated by KI-[18]crown-6 mediated dibromine reductive elimination of the 2,3-*bis*(bromomethyl)TTF **3**. The C_{60}-TTF target cycloadduct **1a** is characterized by spectroscopy and electrochemical study.

Despite many attempts, electron transfer (ET) between organic π-donors and C_{60} as the acceptor still remains a challenging problem.[1] To date, in the best cases, weak spontaneous intermolecular interactions are exhibited in the solid state network.[2] Concerning intramolecular ET, after few convincing arguments,[3] evidence of a photoinduced process has been only recently demonstrated.[4] In order to force the ET to occur, main trend currently developed consists in the covalent binding of both antagonistic redox counterparts close together,[1c] for example that of tetrathiafulvalene (TTF) as the donor and of C_{60} as the acceptor.[5] On these grounds, we have designed the new donor-acceptor (D-A) molecular assemblies **1** and **1'**.[6]



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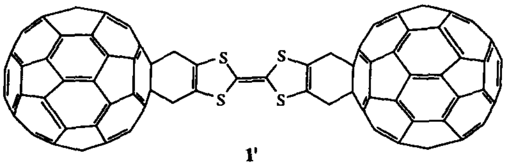
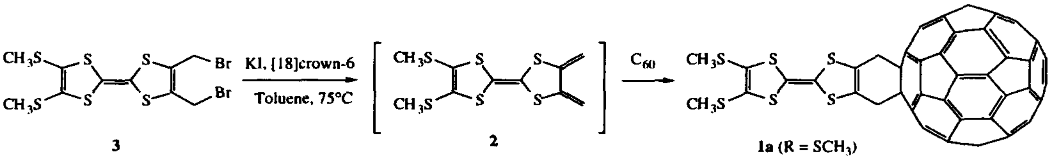


1'

Following our preliminary approach to the latter compounds,[7] we have just succeeded in preparing **1a** and we report here its straightforward synthesis and characterization. Since our first strategy involving the [4+2] Diels-Alder cycloaddition of C_{60} and 2-(thi)oxo-4,5-bis(methylene)-1,3-dithiole was hindered in the final coupling reaction, we have decided to apply a similar methodology but with prior introduction of the TTF core, *i.e.* by Diels-Alder reaction of the transient 2,3-dimethylene-TTF **2** with C_{60} (scheme 1).



Scheme 1

First, to get the conjugated diene **2**, we decided to use a route starting from **3**, an unprecedented TTF bearing two vicinal bromomethyl groups. This latter could be conveniently prepared upon treatment of the corresponding 2,3-bis(hydroxymethyl)-6,7-bis(methylsulfanyl)-TTF[8] with phosphorus tribromide (70% yield after SiO_2 column chromatography).[9] According to the methodology developed by Müllen *et al.*,[10] the [4+2] cycloaddition of **2** to C_{60} could readily be achieved by treatment of **3** with potassium iodide in the presence of [18]crown-6.[11]

Best confirmation of structure for **1a** is supported by its FAB(+) mass spectrum (2-nitrophenyl octyl ether as matrix). This exhibited the molecular ion peak at *m/z* 1042, the isotopic distribution being in agreement with the calculated pattern, and the base peak at *m/z* 720 corresponding to C_{60}. The ^1H nmr spectrum (*o*-dichlorobenzene-d_4) revealed the presence of both expected singlets at δ 2.37 (SCH_3) and 4.24 (CH_2). Furthermore, the UV-Vis spectrum (toluene solution) shows that the addition of diene **2** to C_{60} has occurred at the reactive 6,6-ring junction : peaks at 434 and 701 nm are also typical of a C_{60} mono-adduct.[7] In the cyclovoltammogram, both donor (TTF) and acceptor (C_{60}) moieties are clearly evidenced (see table and figure).

compound	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4	E_{ox}^1	E_{ox}^2
C_{60}	- 0.72	- 1.12	- 1.56	- 2.19		
1a	- 0.76	- 1.15	- 1.65	- 1.92	+ 0.60	+ 1.04

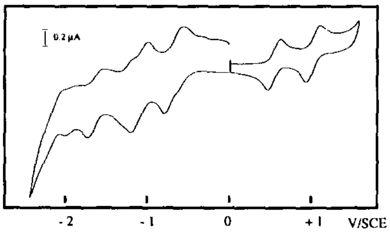


Table and figure : [1a]<10^{-3} M in *o*-dichlorobenzene-*n*-Bu_4NPF_6 0.1 M, Pt electrode, v = 100 mVs^{-1}, E_{red} and E_{ox} in V/SCE

Of course, the cyclovoltammetric data seem to preclude any possibility of electron transfer (ET), which is confirmed by the absence of CT band in the UV-Vis spectrum. However, since electronic spins are cleanly shown in the EPR spectrum,[12] further studies will be necessary to understand these surprising results.

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11 A mixture of compound **3** (130 mg, 0.27 mmol), C_{60} (299 mg, 0.41 mmol), [18]crown-6 (571 mg, 2.16 mmol) and dry potassium iodide (99 mg, 0.6 mmol) in dry toluene (90 mL) was stirred under a nitrogen atmosphere for 3 h at 75°C. After work up and silica gel column chromatography (CS_2), cycloadduct **1a** was isolated in 32% yield as black crystals (calculated from **3**, 160 mg of C_{60} being recovered), which slowly decompose in solution with formation of a new solid under investigation.
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