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The dumbbell bis Diels–Alder adduct between tetramethylidene[4*H*]tetrathiafulvalene and two C_{60}[†]

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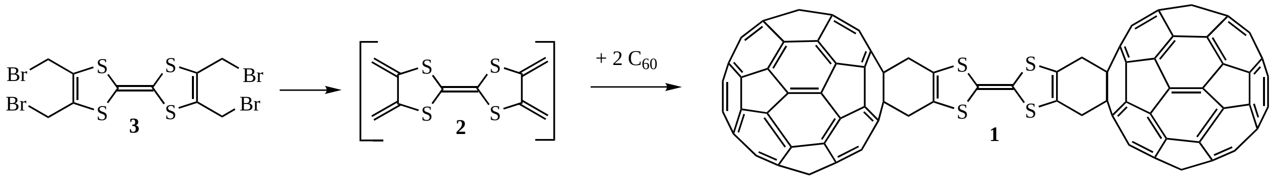
Abstract—Dumbbell C_{60}–TTF–C_{60} was synthesized by a double cycloaddition of C_{60} with the unprecedented tetramethylidene[4*H*]TTF generated in situ from *tetrakis*(bromomethyl)TTF. © 2001 Elsevier Science Ltd. All rights reserved.

The electron-accepting properties of fullerenes[1] combined with their electronic absorption in the visible region[2] and their photophysical properties[3] make them very promising chromophores in photodriven redox processes. Thus, fullerenes could interact with π-donor polymers giving rise to long-lived photoexcited species,[4] which are useful in the conversion of solar energy.[5] Similarly, photoactive fullerene-based donor–acceptor systems have been obtained by linking different π-donors to C_{60}.[6] In this area, the strong π-donor tetrathiafulvalene (TTF) is of particular interest owing to the greater stability of the excited TTF cation radical species. Accordingly, several works have been directed towards the synthesis of polyads assembling TTF and extended analogues to C_{60}[7] and the formation of long-lived charge separated species upon photoexcitation has been demonstrated.[8]

Following our work devoted to TTF-C_{60} dyads,[8a,9] we have been interested in the dumbbell[10] triad **1** which, up to now, resisted many attempts of preparation.[8a,11] We describe here a straightforward synthesis of triad **1** and present some of its spectroscopic and electrochemical properties. Our synthetic strategy involves the generation of transient tetramethylidene[4*H*]TTF **2**, upon naked iodide-induced reduction[12] of *tetrakis*(bromomethyl)TTF **3**,[13] in the presence of C_{60} which cycloadds twice with **2** to give dumbbell **1** (Scheme 1).

The best results were obtained by carrying out the reaction under inert atmosphere, at room temperature, in the dark and in *o*-$C_6H_4Cl_2$ as the solvent. The resulting black precipitate incorporating **1** was filtered off, ground and washed several times, at room temperature as well, consecutively with CS_2 (to remove unreacted C_{60}), an aqueous solution of sodium thiosulfate (to get rid of iodine generated in the reaction), water, acetone, methanol and CH_2Cl_2 in order to eliminate all the impurities formed in the reaction. A second crop of black solid **1** can be recovered by diluting the filtered



Scheme 1. *Reagents and conditions*: dried KI (3 mmol), 18-crown-6 (5 mmol), C_{60} (1 mmol), freshly chromatographed **3** (0.5 mmol), HPLC grade *o*-$C_6H_4Cl_2$ (400 mL), under N_2, rt, vigorous stirring, 36 h (yield of **1**: 50–60%).

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[†] Dedicated to Professor Fred Wudl on the occasion of his 60th birthday.

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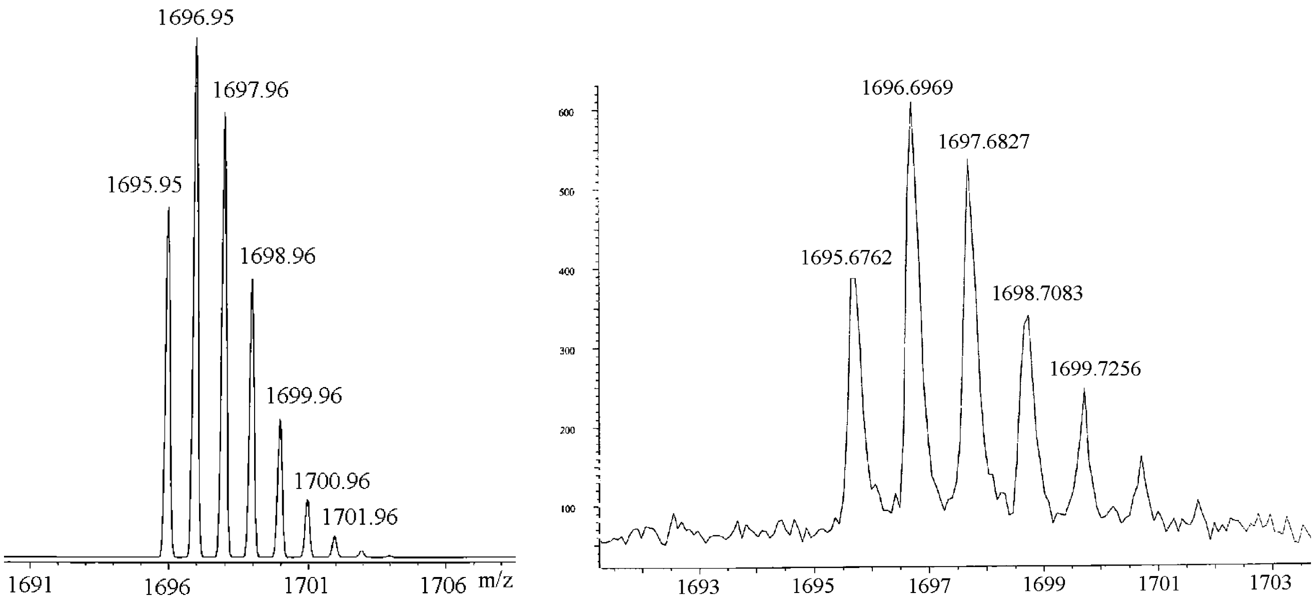

Figure 1. MALDI-TOF spectrum of dumbbell **1**: simulated (left) and experimental (right) isotopic distributions of the molecular peak.

o-$C_6H_4Cl_2$ solution with CH_2Cl_2. Due to its very poor solubility and its thermal instability (e.g. retro Diels–Alder reaction), we were not able to further purify **1** either by recrystallization or Soxhlet extraction or by column chromatography or HPLC. However, the structure of the novel TTF–dibuckyball **1** was undoubtedly supported by spectroscopic and electrochemical data.

The UV–Vis spectrum (*o*-$C_6H_4Cl_2$) was consistent with an adduct of C_{60} at the more reactive 6,6-ring junction, since a broad and weak absorption band around 700 nm and a sharp band at 435 nm are present.[9b,12] However, no intermolecular charge transfer band (mixed valence) could be detected between 710 and 3000 nm. The FT-IR spectrum (KBr pellet) shows the characteristic strong C_{60} band at 527 cm^{-1} together with TTF bands at 767 cm^{-1} (C–S) and 1429 cm^{-1} (central C=C).

In mass spectrometry, using the MALDI-TOF technique (9,10-dimethylanthracene as the matrix), peaks at $m/z=256$ and at $m/z=720$ are observed, which unambiguously agree with the retro Diels–Alder fragmentation of dumbbell **1** into bis-diene **2** and C_{60}, respectively. Moreover, the mass spectrum exhibited another peak at $m/z=847$ (M/2–1) corresponding to the well known symmetrical fragmentation of the TTF central double bond.[14] By using dithranol (1,8-dihydroxy-9[10*H*]-anthracenone) as the matrix, we finally succeeded in showing the molecular peak at $m/z=1696$ with the expected isotopic distribution (Fig. 1), and the peak at $m/z=976$ corresponding to the mono retro Diels–Alder fragmentation.[15]

The cyclic voltammogram of TTF–dibuckyball **1** exhibits in *o*-dichlorobenzene two reversible oxidation peaks, corresponding to the cation radical and dication states of the TTF moiety, at +0.58 and +1.12 V, respectively, and three reversible or quasi-reversible reduction peaks, corresponding to the reduction steps of the fullerene moiety at –0.65, –1.02 and –1.56 V (versus Ag/AgCl) (Fig. 2). The ratio between the intensity of the C_{60} first reduction peak and the intensity of the TTF first oxidation peak was estimated to be 2.0±0.3 from experimental and deconvoluted voltammograms at several scan rates. Since the diffusion coefficient is the same on both these reduction and oxidation waves, this confirms that dumbbell **1** is made up of two C_{60} acceptor moieties and one TTF donor core.

Moreover, ESR spectroscopy provides more detailed and definitive information about the electronic structure of the ion radical species derived from triad **1**. Thus two clear signals corresponding to the cation radical and anion radical were observed upon controlled oxidation and reduction of **1**, respectively (Fig. 3).

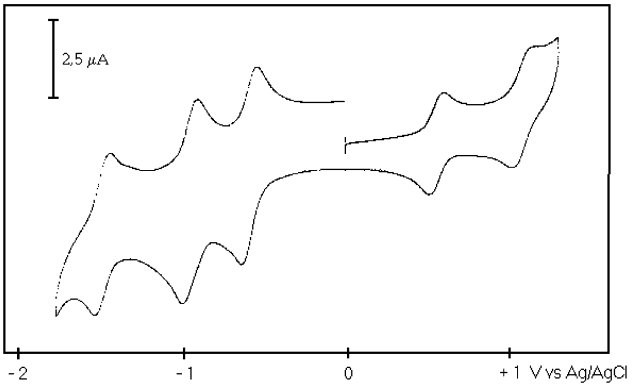

Figure 2. Cyclovoltammogram of dumbbell **1** (saturated in *o*-$C_6H_4Cl_2$–*n*Bu_4NPF_6 0.05 M, Pt electrode, reference: Ag/AgCl, $v=200$ mV s^{-1}). (For C_{60}: –0.61, –1.00 and –1.45 V).

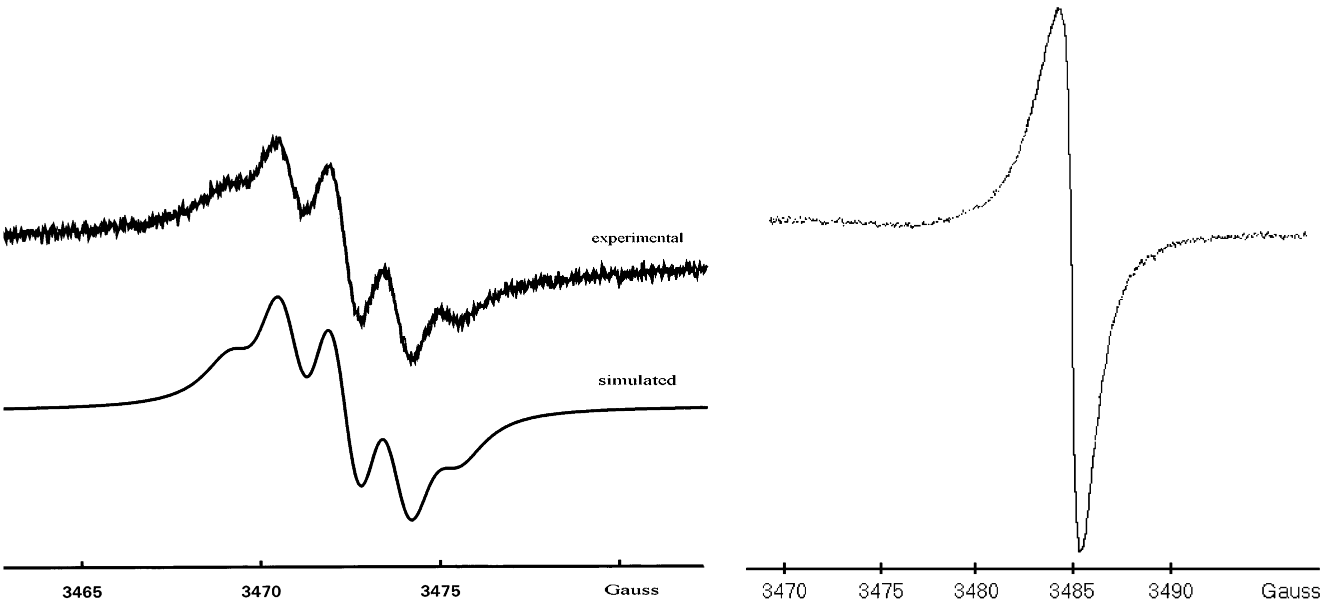

Figure 3. ESR spectrum of **1** in o-$C_6H_4Cl_2$–$n$$Bu_4NPF_6$ 0.05 M, after electrooxidation and electroreduction, respectively.

The anion radical ESR signal of **1**, generated by electroreduction at −0.8 V (versus Ag/AgCl), shows the characteristic line ($\Delta H_{pp} = 1.62$ G, $g = 1.9998$) of fullerides derived from C_{60} cycloadducts.[8a,16] On the other hand, the highly persistent cation radical ESR signal obtained by electrooxidation of **1** at +0.7 V consists of five overlapped lines with the typical pattern of a coupling with four equivalent protons ($g = 2.007258$, $a_H = 1.4$ G and $\Delta H_{pp} = 1.05$ G). Both the g factor and coupling constant with the protons are very similar to those found for the cation radicals derived from related cyclohexene fused C_{60}–TTF dyads.[8a] On these grounds, the four protons can be assigned to the four equivalent axial methylenic protons of the two cyclohexene bridges expected from the structure of triad **1**.

Despite many efforts, in the ^1H NMR spectrum (500 MHz, o-$C_6D_4Cl_2$), the expected singlet at about 4.2 ppm corresponding to the CH_2 bridges has not been evidenced as in other related derivatives.[8a,9b,17] This could be due to: (i) either the very weak solubility of **1** or (ii) the possible bad relaxation of the methylene protons because of their proximity to C_{60} (although this is not the case in the corresponding monoadducts[8a,9]) or (iii) the presence of paramagnetic species in compound **1** giving rise to a contact shift arising at very low concentration and in condition of fast exchange.[18] Note that the ESR spectrum of dumbbell **1**, in solid state, exhibits a weak broad signal, which represents about 1% of radicals in the sample. As happens with pristine C_{60}, this ESR signal shows a reversible oxygen-dependent spin concentration although its intensity is one order of magnitude higher than that of C_{60}.[19]

Accordingly, the synthesis and characterizations of dumbbell **1** previously designed have been achieved. We are now investigating the physical properties of dumbbell **1** and efforts are under way in order to substitute **1** with solubilizing groups.

Acknowledgements

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