



# Novel [60]fullerene–TTF cyclohexene fused polyadducts: unprecedented tri- and tetra-Diels–Alder adducts of dimethylidene[2*H*]tetrathiafulvalenes with C<sub>60</sub><sup>†</sup>

David Kreher,<sup>a</sup> Sheng-Gao Liu,<sup>a</sup> Michel Cariou,<sup>a</sup> Piétrick Hudhomme,<sup>a,\*</sup> Alain Gorgues,<sup>a,\*</sup> Marta Mas,<sup>b</sup> Jaume Veciana<sup>b</sup> and Concepció Rovira<sup>b</sup>

<sup>a</sup>Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques, UMR CNRS 6501, Université d'Angers, 2 Bd Lavoisier, 49045 Angers Cedex, France

<sup>b</sup>Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, 08193 Bellaterra, Spain

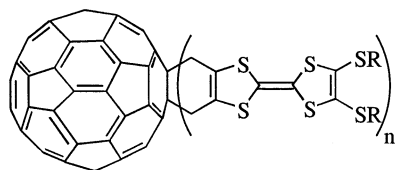
Received 23 March 2001

**Abstract**—The title compounds, which are formed in very low yields by treating 2,3-bis(bromomethyl)tetrathiafulvalenes with naked iodide in the presence of C<sub>60</sub>, can be obtained in much higher yields by successive similar treatments of the major adducts produced at each step. The electrochemical properties of the unprecedented tri- and tetra-TTF/C<sub>60</sub> assemblies are also presented. © 2001 Elsevier Science Ltd. All rights reserved.

In the past few years, the design of dyads or polyads resulting from the covalent linking of  $\pi$ -electron donors (D) to C<sub>60</sub> as the acceptor (A)<sup>1</sup> has emerged as a promising approach in search of intramolecular photo-induced electron transfer useful for the realization of new artificial photosynthetic systems, molecular electronic devices and photovoltaic cells.<sup>2</sup> Among these donors, due to the particular stability of their aromatic cation radicals, tetrathiafulvalenes (TTF) appear as very good candidates since, upon photoexcitation, their assemblies with C<sub>60</sub> may give rise to long-lived charge separated species D<sup>•+</sup> bonded to A<sup>•-</sup>.<sup>3</sup> Thus, strategies are currently being developed for the synthesis of TTF/fullerene based dyads and polyads, through either a

flexible linkage using 1,3-dipolar cycloadditions<sup>4</sup> or a rigid spacer constituted of two methylene groups involving a Diels–Alder reaction of dimethylidene[2*H*]-TTF as diene with C<sub>60</sub> as dienophile.<sup>3a,5,6</sup>

Following our previous work related to C<sub>60</sub>–TTF monoadducts **1** (Scheme 1),<sup>6a,b</sup> we were interested in synthesizing and isolating new diadducts **2** and unprecedented tri- and tetraadducts **3** and **4** to provide access to three-dimensional functionalized fullerenes presenting several electroactive units. Such polyadducts comprised of several isomers resulting from reaction at the different positions on C<sub>60</sub> could also present a great potentiality of applications.<sup>7</sup> Here, we report their straightforward



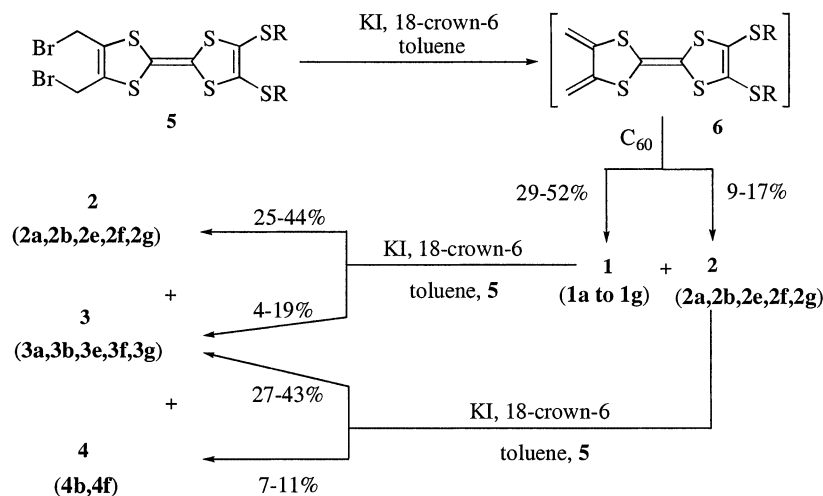
**1** (n=1); **2** (n=2); **3** (n=3); **4** (n=4)

**a** : R = CH<sub>3</sub>                      **e** : R-R = -CH<sub>2</sub>CH<sub>2</sub>-  
**b** : R = (CH<sub>2</sub>)<sub>4</sub>-CH<sub>3</sub>            **f** : R = (CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>  
**c** : R = (CH<sub>2</sub>)<sub>7</sub>-CH<sub>3</sub>            **g** : R = (CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>3</sub>  
**d** : R = (CH<sub>2</sub>)<sub>11</sub>-CH<sub>3</sub>

**Scheme 1.**

\* Corresponding authors. Fax: (33) 2 41 73 54 05; e-mail: piétrick.hudhomme@univ-angers.fr; alain.gorgues@univ-angers.fr

<sup>†</sup> Dedicated to Professor Fred Wudl on the occasion of his 60th birthday.



Scheme 2.

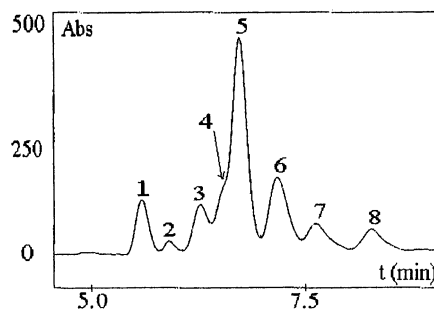
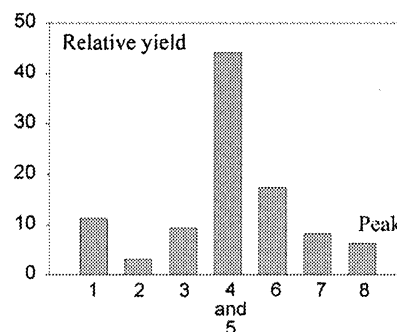
synthesis and present some of their spectroscopic and electrochemical data.

Firstly, our synthetic strategy involves the generation of transient dimethylidene[2H]TTF **6**, by naked iodide-induced reduction<sup>8</sup> of 2,3-bis(bromomethyl)TTF **5**,<sup>9</sup> which cycloadds in the presence of C<sub>60</sub> to afford monoadducts **1**, the subsequent cycloaddition of **1** with diene **6** being responsible for the formation of diadducts **2**. Secondly, applying the same methodology by starting from **1** or **2**, we could reach and isolate the desired triadducts **3** and tetraadducts **4** in acceptable yields (Scheme 2).

Many attempts were carried out in order to optimize the yield of Diels–Alder cycloaddition by modifying parameters of dilution, iodide reagent and stoichiometry of compound **5**.<sup>10</sup> For example, using an excess of diene **6** did not increase the yield of **1**, unreacted C<sub>60</sub> being always recovered in 30–50% yield. All compounds **1–4** were separated by column chromatography, but the isolation of polyadducts appeared to be highly dependent on the chromatographic conditions: firstly, compounds **1–4** appeared not to be stable in chlorinated solvents, except in the case where the TTF core is bearing polyethersulfanyl groups (**1–4f,g**). Secondly, due to the poor solubility of monoadducts **1a**, **1e** and corresponding polyadducts, we used mixture of solvents (CS<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> or toluene) as eluent. Finally, to prevent any protic oxidation<sup>11</sup> and hence the rapid degradation of some adducts (**1c**, **1d**, **1–4f**, and **1–3g**), the eluent was alkalinized by the classical addition of 1% triethylamine. Polyads **2–4** were obtained as a mixture of numerous regioisomers. Whereas the eight isomers of **2b** were analytically separated by HPLC (Figs. 1 and 2),<sup>12</sup> the chromatographic analysis of the high number (around 40 theoretically) of isomers for **3** and **4** has not yet been achieved owing to the complexity of the problem.

The structures of (poly)adducts **1–4** are supported by usual spectroscopic analyses.<sup>13</sup> In particular, adducts **1–4** were characterized by mass spectrometry, especially

MALDI-TOF in positive or negative mode, by changing the nature of solvent and matrix.<sup>14</sup> Indeed, most of these compounds exhibited the molecular ion peak with the expected isotopic distribution. Moreover, the mass

Figure 1. HPLC separation of regioisomers of **2b**.Figure 2. Relative yield of isomers of **2b**.Table 1. Redox potentials  $E_{app}$  of (TTF)<sub>n</sub>C<sub>60</sub><sup>a</sup>

	$E_{red}^1$	$E_{red}^2$	$E_{red}^3$	$E_{red}^4$	$E_{ox}^1$	$E_{ox}^2$
C <sub>60</sub>	-0.61	-1.00	-1.45	-2.08	-	-
<b>1b</b>	-0.72	-1.09	-1.59	-1.84	+0.65	+1.09
<b>2b</b>	-0.82	-1.20	-1.83	-	+0.70	+1.16
<b>3b</b>	-0.98	-1.35	-	-	+0.69	+1.14
<b>4b</b>	-1.16	-	-	-	+0.61	+0.84

<sup>a</sup> [Compound] ~ 10<sup>-3</sup> M in *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>-*n*-Bu<sub>4</sub>NPF<sub>6</sub> (0.05 M), Pt electrode,  $\nu$  = 100 mV s<sup>-1</sup>,  $E_{red}$  and  $E_{ox}$  in V versus Ag/AgCl.

spectrum of these (poly)adducts showed the peaks corresponding to the successive retro Diels–Alder fragmentations and/or the well known fragmentation of the TTF central double bond.<sup>15</sup>

In cyclic voltammetry (Table 1), (poly)adducts **1–4** show two reversible oxidation peaks, corresponding to the cation radical and dication states of the TTF moiety, and one to four quasi-reversible reduction peaks, due to the reduction steps of the fullerene moiety. These reduction potentials are shifted to more negative values when compared to those of pristine C<sub>60</sub>, this corresponding to the classical behavior of fullerene derivatives and the successive saturation of [6,6] double bonds of C<sub>60</sub>. Furthermore, the ratio between the intensities of the first oxidation of peak TTF and the first reduction peak of C<sub>60</sub> was estimated to be  $n \pm 10^{-1} n$  for **1–4**, from experimental and deconvoluted voltammograms (Fig. 3). Since the diffusion coefficient is the same on both these reduction and oxidation waves, this fact confirms that these adducts **1–4** are made up of one C<sub>60</sub> acceptor and  $n$  TTF donors (Fig. 4).

In conclusion, besides some additional examples of mono and diadducts **1** and **2**, we have prepared in significant yields and partially characterized several unprecedented tri and tetraadducts **3** and **4**.

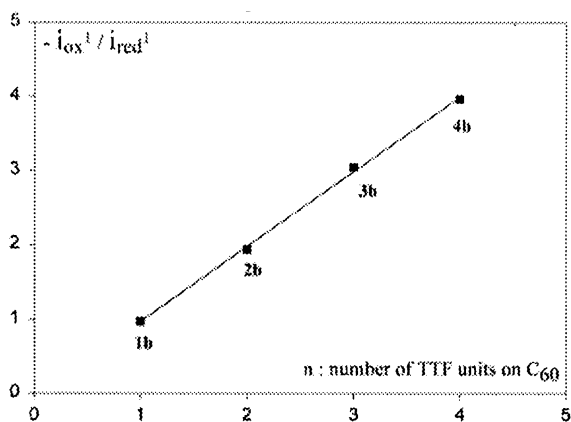


Figure 3.

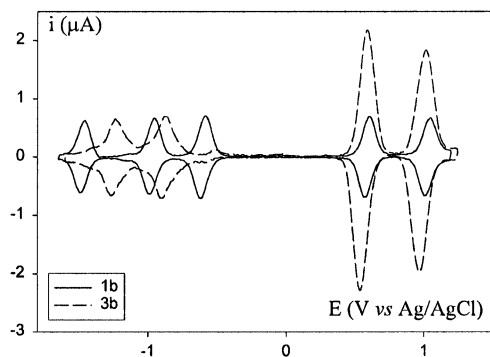


Figure 4. The fourth reduction wave of **1b** is not presented here.

## Acknowledgements

We are grateful to Dr. D. Amabilino (ICMAB) for help in MALDI-TOF mass spectrometry experiments.

## References

- Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527.
- (a) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093; (b) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055; (c) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 445; (d) Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F.; Liu, S.-G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, L.; Krsnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467 and references cited therein.
- (a) Llacay, J.; Veciana, J.; Vidal-Gancedo, J.; Bourdelande, J.-L.; González-Moreno, R.; Rovira, C. *J. Org. Chem.* **1998**, *63*, 5201; (b) Martín, N.; Sánchez, L.; Guldi, D. M. *J. Phys. Chem. A* **2000**, *104*, 4648; (c) Guldi, D. M. *Chem. Commun.* **2000**, 321; (d) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695; (e) Martín, N.; Sánchez, L.; Guldi, D. M. *Chem. Commun.* **2000**, 113.
- (a) Prato, M.; Maggini, M.; Giacometti, C.; Scorrano, G.; Sandona, G.; Farina, G. *Tetrahedron Lett.* **1996**, *52*, 5221; (b) Martín, N.; Sánchez, L.; Seoane, C.; Andreu, R.; Garín, J.; Orduna, J. *Tetrahedron Lett.* **1996**, *37*, 5979; (c) Martín, N.; Pérez, I.; Sánchez, L.; Seoane, C. *J. Org. Chem.* **1997**, *62*, 5690; (d) Simonsen, K. B.; Konovalov, V. V.; Konovalova, T. A.; Kawai, T.; Cava, M. P.; Kispert, L. D.; Metzger, R. M.; Becher, J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 657; (e) Herranz, M. A.; Martín, N.; Sánchez, L.; Seoane, C.; Guldi, D. M. *J. Organomet. Chem.* **2000**, *599*, 2; (f) Guldi, D. M.; González, S.; Martín, N.; Antón, A.; Garín, J.; Orduna, J. *J. Org. Chem.* **2000**, *65*, 1978.
- Llacay, J.; Mas, M.; Molins, E.; Veciana, J.; Powell, D.; Rovira, C. *Chem. Commun.* **1997**, 659.
- (a) Boulle, C.; Rabreau, J.-M.; Hudhomme, P.; Cariou, M.; Jubault, M.; Gorgues, A.; Orduna, J.; Garín, J. *Tetrahedron Lett.* **1997**, *38*, 3909; (b) Hudhomme, P.; Boulle, C.; Rabreau, J.-M.; Cariou, M.; Jubault, M.; Gorgues, A. *Synth. Met.* **1998**, *94*, 73. The latter methodology was fruitfully applied to reach other analogous dyads: (c) Herranz, M. A.; Martín, N. *Org. Lett.* **1999**, *1*, 2005; (d) Liu, S.-G.; Echegoyen, L. *Eur. J. Chem.* **2000**, 1157.
- Hirsch, A. *The Chemistry of the Fullerenes*; Georg Thieme: Stuttgart, 1994.
- (a) Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78; (b) We have applied successfully this methodology in the 2-thioxo-1,3-dithiole series, see: Boulle, C.; Cariou, M.; Bainville, M.; Gorgues, A.; Hudhomme, P.; Orduna, J.; Garín, J. *Tetrahedron Lett.* **1997**, *38*, 81.
- Hudhomme, P.; Liu, S.-G.; Kreher, D.; Cariou, M.; Gorgues, A. *Tetrahedron Lett.* **1999**, *40*, 2927.

10. *Typical procedure for the preparation of 1–4*: To a well-stirred solution of 2,3-bis(bromomethyl)TTF<sup>9</sup> **5** (0.5 mmol) in dry toluene (100 mL), under a nitrogen atmosphere, were successively added C<sub>60</sub> or C<sub>60</sub>-(D)<sub>n-1</sub> (1 equiv.), then potassium iodide (3 equiv.) and 18-crown-6 (10 equiv.). After stirring for 36 h at room temperature, the brown solution was filtered off and the soluble part was poured into water (100 mL). The organic layer was washed consecutively with a saturated aqueous solution of sodium thiosulfate (2×100 mL) and water (2×50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated in vacuo (without heating). The residue was then purified on a silica gel column, using a CS<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> or toluene-based complex eluent.
11. (a) Giffard, M.; Alonso, P.; Garín, J.; Gorgues, A.; Nguyen, T. P.; Richomme, P.; Robert, A.; Roncali, J.; Uriel, S. *Adv. Mater.* **1994**, *6*, 298 and references cited therein; (b) Rathore, R.; Zhu, C.; Lindeman, S. V.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1837.
12. Chromatographic conditions of separation: Shimadzu SCL-10A VP HPLC apparatus; reversed-phase KROMASIL 100 analytical column; toluene/CH<sub>3</sub>CN (40/60) as eluent; flow rate: 0.5 ml min<sup>-1</sup>; UV detection at 254 nm.
13. All new compounds gave satisfactory spectroscopic data. Example for **1f**: dark brown powder; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.07 (t, 2H, S-CH<sub>2</sub>-), 3.39 (s, 3H, CH<sub>2</sub>-OCH<sub>3</sub>), 3.67 (m, 6H, O-CH<sub>2</sub>-), 3.72 (t, 2H, SCH<sub>2</sub>-CH<sub>2</sub>O-), 4.32 (s, 2H, =C-CH<sub>2</sub>-); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 35.66 (2C, SCH<sub>2</sub>), 41.17 (2C, C=C-CH<sub>2</sub>), 59.04 (2C, CO<sub>2</sub>CH<sub>3</sub>), 66.08 (2C, C<sub>sp</sub><sup>3</sup> C<sub>60</sub>), 70.21 (2C, SCH<sub>2</sub>-CH<sub>2</sub>O), 70.68 and 70.70 (12C, CH<sub>2</sub>O), 72.09 (2C, CH<sub>2</sub>-OCH<sub>3</sub>), 108.13 and 113.84 (2C, C=C ylidene), 128.32 and 128.50 (4C, C=C), 135.82–147.84 (C<sub>sp</sub><sup>2</sup> C<sub>60</sub>), 155.30 (2C, C<sub>sp</sub><sup>2</sup>-C<sub>sp</sub><sup>3</sup> C<sub>60</sub>); FT-IR (KBr) ν: 527, 576, 775, 1023, 1037, 1106, 1201, 1487, 1513, 1601; UV (CH<sub>2</sub>Cl<sub>2</sub>) λ: 260, 326, 434 and 701 (C<sub>60</sub> [6,6] junction); MS *m/z* (I%) MALDI-TOF (DTN-CH<sub>2</sub>Cl<sub>2</sub>): 1306 (M<sup>+</sup>), 847, 720, 609, 586 ([M-C<sub>60</sub>]<sup>+</sup>), 556, 459, 294; Cyclic voltammetry (*o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>-*n*-Bu<sub>4</sub>NPF<sub>6</sub>), V versus Ag/AgCl: *E*<sub>pc1</sub> = -0.71, *E*<sub>pc2</sub> = -1.09, *E*<sub>pc3</sub> = -1.61, *E*<sub>pa1</sub> = +0.67, *E*<sub>pa2</sub> = +1.04.
14. Compound **1b**: [M-1]<sup>-</sup> = 1153 and **2b**: M<sup>-</sup> = 1588 (9-nitroanthracene/toluene); **3b**: M<sup>-</sup> = 2022 (9,10-dimethylanthracene/CH<sub>2</sub>Cl<sub>2</sub>); **4b**: M<sup>+</sup> = 2456 (dithranol/CH<sub>2</sub>Cl<sub>2</sub>).
15. (a) Andersen, J. R.; Egsgaard, H.; Larsen, E.; Bechgaard, K.; Engler, E. M. *Org. Mass. Spectrom.* **1978**, *13*, 121; (b) Andreu, R.; Blesa, M. J.; Garín, J.; López, A.; Ordúna, J.; Savirón, M. *J. Org. Chem.* **1997**, *62*, 5642.