New functionalized and soluble bis-tetrathiafulvalene derivatives as building blocks in the construction of fullerene-derived electroactive triads

José L. Segura, Eva Mª Priego and Nazario Martín*

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040, Madrid, Spain

Received 27 July 2000; accepted 1 August 2000

Abstract

Novel functionalized bis-tetrathiafulvalene (TTF) derivatives are built on the 1,3,5-benzene core. Long alkyl chains have been incorporated on peripheral positions of the TTF moieties in order to increase the solubility of the final products. After appropriate functionalization of the bis-TTF it has been covalently attached to the C_{60} core yielding the first C_{60}–TTF_2 triad. Electrochemical and spectroscopic studies of the target compounds suggest that there are no significant interactions between the TTF units and the C_{60} moiety in the ground state. © 2000 Elsevier Science Ltd. All rights reserved.

Many efforts have been devoted in recent years to the development of new systems containing two or more tetrathiafulvalene (TTF) units.[1–3] Because of the intramolecular through-bond or through-space interactions between the TTF units, this kind of system may display multi-stage redox behavior which might provide the possibility of controlling the stoichiometry, band filling and molecular assembly in desired conductive complexes. On the other hand, extensive efforts have been dedicated to the development of new C_{60}-based donor–acceptor systems endowed with various electron donors which present light-induced intramolecular charge-separation (CS).[4] Among them, we have paid special attention to the development of a strategy probing organic donor molecules (e.g. TTF derivative **1** and π-extended TTF derivatives **2** and **3**, Fig. 1) linked to the fullerene core that gain rather than lose aromaticity on charge separation.[5]

---

* Corresponding author. Tel: +34-91-3944227; fax: +34-91-3944103; e-mail: nazmar@eucmax.sim.ucm.es
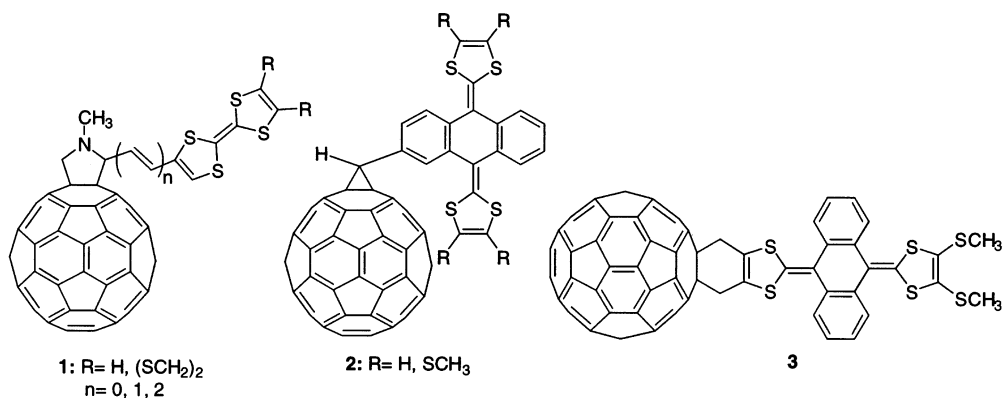
Figure 1.

Different strategies have been proposed as efficient ways of decreasing charge recombination rates, thus increasing lifetimes of charge-separated states. One way of achieving this is to increase the interchromophore separation. However, this cannot easily be done using simple bichromophoric systems without compromising the efficiency of formation of the CS state. This problem can be circumvented, (i) by stabilizing the radical cation species of the donor fragment by gaining of aromaticity upon oxidation as in the TTF derivatives and (ii) by using polychromophoric systems, i.e. triads, tetrads, pentads, etc.[6] The synthesis of appropriately functionalized bis-tetrathiafulvalene (TTF) derivatives built on the 1,3,5-benzene core allows two conjugated electroactive TTF units to be covalently attached to the C_{60} core yielding the first C_{60}–TTF_2 triad.

Upon treatment of a refluxing solution of 3,5-dimethylbenzoate (**4**)[7] in carbon tetrachloride with NBS and AIBN under argon atmosphere, the corresponding dibromomethyl derivative **5** was obtained in a 31% yield. Subsequent treatment of **5** with triphenylphosphine in refluxing *N,N*-dimethylformamide (DMF) gives the bis(triphenylphosphonium) salt derivative **6** in a 60% yield. Lithium ethoxide catalyzed Wittig reaction of the bis(triphenylphosphonium methyl)benzene bromide **6** with bis(dodecylthio)substituted formyltetrathiafulvalene **7**[8] was carried out in chloroform:ethanol (3:5) at 50°C, leading to a mixture of *cis/trans* isomers. Attempts at isomerization to the all-*trans* stereoisomer by using the usual iodine-catalyzed conditions were not successful due to the rapid formation of a charge-transfer salt between the TTF donor fragments and iodine. However, the major isomer (tlc) formed was finally isolated by careful chromatography in a 37% yield. Spectroscopic analyses confirmed that the isolated isomer corresponds to the more stable all-*trans* configuration, the coupling constants measured in the ^{1}H NMR spectrum for the vinyl protons being 15.7 Hz. Reduction of the ester group with DIBAL-H in dry methylene dichloride yielded the hydroxymethyl derivative **9**, which is an interesting building block given that it will allow the incorporation of this bis-TTF into more complex molecular or macromolecular systems by using simple reactions for the synthesis of esters or ethers. Thus, reaction of **9** with a fullerene derivative endowed with a solubilizing polyether chain and a carboxylic group (**10**) in chloroform in the presence of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) afforded the triad **11** as the main reaction product in a 30% yield (Scheme 1). Interestingly, despite the general lack of solubility of rigid TTF dimers and fullerene derivatives, the presence of long alkyl chains on the TTF
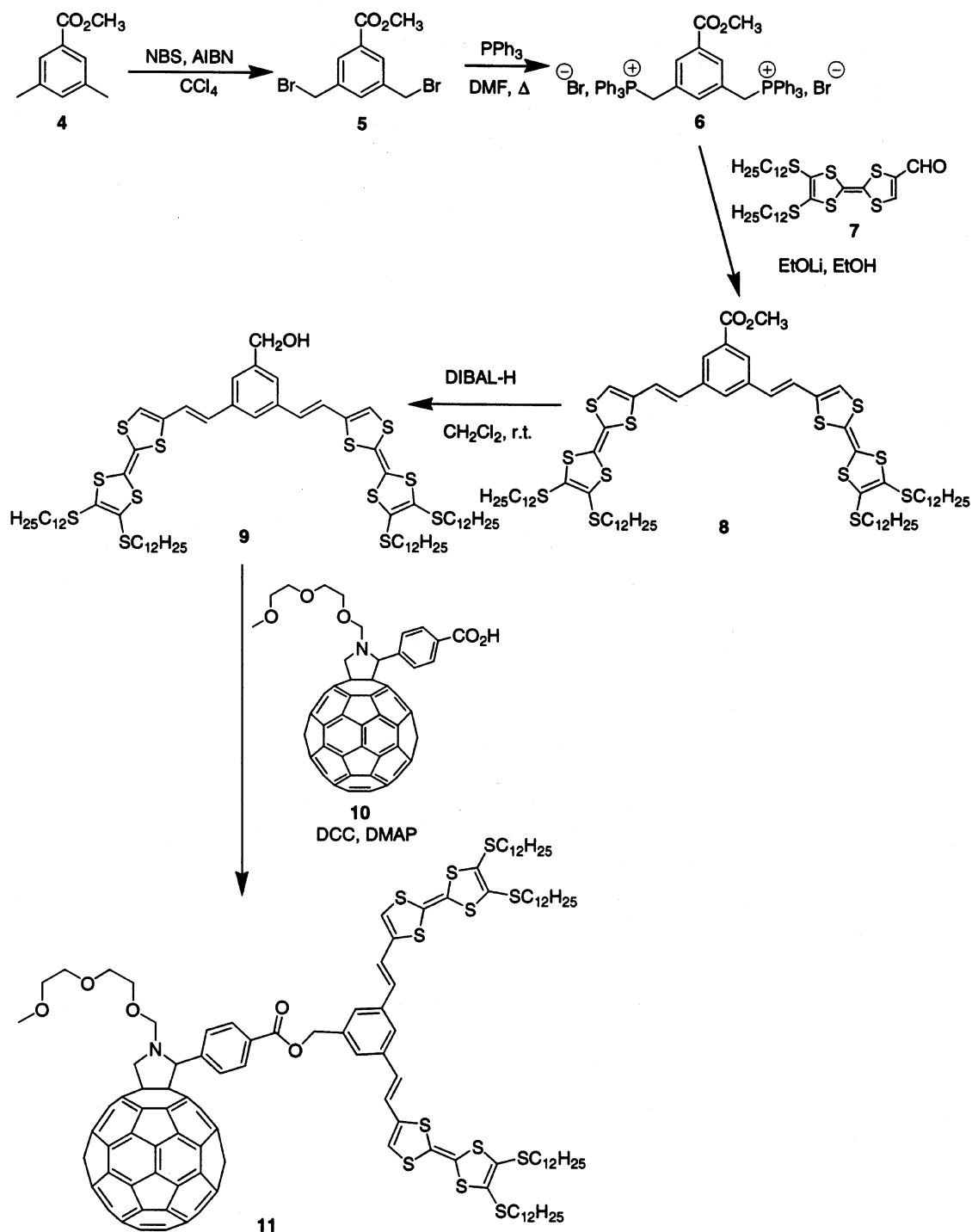
Scheme 1.

moieties as well as the polyether chain on the fullerene system provide enhanced solubility to **11**, thus allowing full spectroscopic and electrochemical characterization of the system.[†]

Although systems containing two TTF units should be oxidizable up to the tetracation because each TTF unit can release two electrons, the number of electrochemical oxidation processes observed by using cyclic voltammetry measurements in different TTF dimers reported in the literature is strongly variable depending upon the electronic interaction between the two electroactive units. Only two electrochemical processes corresponding to oxidation to the bis(radical cation) and tetracation are observed for those systems in which the TTF units are not interacting.[9] Thus, two quasireversible redox waves are observed in the cyclic voltammetry measurements performed for the functionalized bis-TTFs **8** and **9** (measurements performed in dichloromethane, reference electrode: SCE; working electrode: glassy carbon; supporting electrolite: $Bu_4N^+ClO^-_4$, at 200 mV/s). Anodic peaks of $E^1_{ox} = 0.50$ V and $E^2_{ox} = 0.91$ V were measured for dimer **9**. Cyclic voltammetry of triad **11** shows an amphoteric redox-active behaviour. In particular, it shows, together with two quasireversible oxidation waves ($E^1_{ox} = 0.51$ V and $E^2_{ox} = 0.92$ V) corresponding to the bis-TTF system, three quasireversible waves ($E^1_{red} = -0.75$ V, $E^2_{red} = -1.15$ V and $E^3_{red} = -1.67$ V), which can be assigned to the fulleropyrrolidine core.

The absorption spectrum of triad **11** in dichloromethane solution discloses superimposed features of the C_{60} and the bis-TTF unit, respectively. Taking the electrochemical data and the absorption features into consideration, we reached the conclusion that no significant interactions arise between the two redox-active moieties in the ground state of the combined units, which is in agreement with that observed for previously reported TTF–C_{60} dyads.[5]

In conclusion, we have reported the synthesis of soluble functionalized bis-TTF derivatives which are appealing building blocks for the preparation of more complex molecular and macromolecular systems containing this multiple electroactive unit. As a practical application, we have prepared the C_{60}–TTF_2 triad by formation of an ester linkage between the hydroxymethyl substituted TTF-dimer and a C_{60} derivative endowed with a carboxylic acid functionality. Given the good lifetimes found for the charge separated (CS) states observed for previous examples of TTF–C_{60} dyads,[5] work is in progress in order to explore the photoinduced electron transfer properties of **11** to compare the lifetime of the CS state with that of analogous systems containing only one TTF unit.

Acknowledgements

[†] Compounds **8**, **9** and **11** gave satisfactory analytical and spectroscopic data. Selected spectroscopic data for **11**: ^{1}H NMR (C_6D_6, 200 MHz): δ (ppm): 7.85 (d, 2H, $J = 8.5$ Hz), 7.57 (d, 2H, $J = 8.5$ Hz), 7.40 (s, 2H), 7.37 (s, 1H), 6.91 (d, 2H, $J = 15.7$ Hz), 6.36 (d, 2H, $J = 15.7$ Hz), 6.30 (s, 2H), 5.30 (s, 2H), 5.20 (s, 2H), 4.7 (d, 1H, $J = 9.5$ Hz), 4.3 (d, (d, 1H, $J = 9.5$ Hz), 3.8–3.5 (m, 11H), 2.77 (t, 8H), 1.19 (m, 80H), 0.81 (t, 12H). IR (KBr): 2926, 2853, 1700, 1626, 1110, 527 cm^{-1}. UV–Vis (CH_2Cl_2): 260, 318, 374, 420, 436 nm.

References

1. For a review on bis-TTF derivatives, see: Otsubo, T.; Aso, Y.; Takimiya, K. *Adv. Mater*. **1996**, *8*, 203.

2. For reviews on TTF oligomers, see: (a) Adam, M.; Müllen, K. *Adv. Mater*. **1994**, *6*, 439. (b) Becher, J.; Lau, J.; Mørk, P. In *Electronic Materials: The Oligomer Approach*; Müllen, K.; Wegner, G., Eds.; Wiley-VCH: New York, 1998, pp. 198–233.

3. For reviews on macromolecular TTF chemistry, see: (a) Bryce, M. R.; Davenport, W.; Goldenberg, L. M.; Wang, C. *Chem. Commun*. **1998**, 945. (b) Simonsen, K. B.; Becher, J. *Synlett* **1997**, 1211.

4. (a) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev*. **1998**, *98*, 2527. (b) Imahori, H.; Sakata, Y. *Adv. Mater*. **1997**, *9*, 537. (c) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem*. **1999**, 2445. (d) Guldi, D. M. *Chem. Commun*. **2000**, 321.

5. (a) Martín, N.; Sánchez, L.; Seoane, C.; Andreu, R.; Garín, J.; Orduna, J. *Tetrahedron Lett*. **1996**, *37*, 5979. (b) Martín, N.; Sánchez, L.; Pérez, I.; Seoane, C. *J. Org. Chem*. **1997**, *62*, 5690. (c) Herranz, M. A.; Martín, N. *Org. Lett*. **1999**, *1*, 2005. (d) Martín, N.; Sánchez, L.; Guldi, D. M. *Chem. Commun*. **2000**, 113. (e) Guldi, D. M.; González, S.; Martín, N.; Antón, A.; Garín, J.; Orduna, J. *J. Org. Chem*. **2000**, *65*, 1979. (f) Martín, N.; Sánchez, L.; Herrnaz, M. A.; Guldi, D. M. *J. Phys. Chem. A* **2000**, *104*, 4648.

6. Jolliffe, K. A.; Langford, S. J.; Ranasinghe, M. G.; Shephard, M. J.; Paddon-Row, M. N. *J. Org. Chem*. **1999**, *64*, 1238.

7. (a) Kurz, K.; Göbel, M. W. *Helv. Chim. Acta* **1996**, *79*, 1967. (b) Löwik, D. W. P. M.; Weingarten, M. D.; Brockema, M.; Brouwer, A. J.; Still, W. C.; Liskamp, R. M. J. *Angew. Chem., Int. Ed*. **1998**, *37*, 1846.

8. González, A.; Segura, J. L.; Martín, N. *Tetrahedron Lett*. **2000**, *41*, 3083.

9. (a) Formigué, M.; Batail, P. *J. Chem. Soc., Chem. Commun*. **1991**, 1370. (b) Yunoki, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *Tetrahedron Lett*. **1997**, *38*, 3017. (c) Lau, J.; Becher, S. *Synthesis* **1997**, 1015. (d) Blanchard, P.; Svenstrup, N.; Becher, J. *J. Chem. Soc., Chem. Commun*. **1996**, 615. (e) Balchard, P.; Svenstrup, N.; Rault-Berthelot, J.; Riou, A.; Becher, J. *Eur. J. Org. Chem*. **1998**, 1743.