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New Versatile Building Block for the Construction of Tetrathiafulvalene-Based Donor–Acceptor Systems

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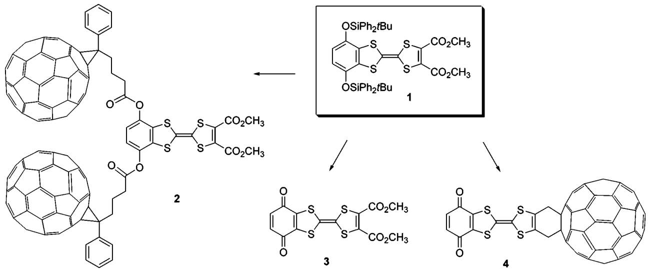
ABSTRACT



A new dissymmetrical tetrathiafulvalene (TTF) derivative 1 was synthesized as a versatile building block to reach TTF-based donor–acceptor assemblies incorporating C_{60} in triad C_{60}–TTF–C_{60} 2 and/or *p*-benzoquinone (Q) in fused dyad Q–TTF 3 and triad Q–TTF–C_{60} 4.

Tetrathiafulvalene (TTF) derivatives are intensively studied because of their unique π-electron donating properties. Discovery of the first metallic charge-transfer TTF-based complex[1] has initiated major research activities in search of new molecular conductors.[2] Efforts are particularly devoted to direct intermolecular interactions in TTF-based crystalline molecular conductors. This concerns specifically TTF molecules functionalized by hydrogen-bonding donor and acceptor groups such as alcohols, carboxylic acids, and amides.[3] Intensive work is also carried out to modify the TTF framework to achieve new original applications using this π-donor.[4] During the past few years, the utility of TTF derivatives as building blocks in supramolecular structures,[5] as well as the incorporation of this donor moiety in donor−acceptor (D−A) systems, has made TTF one of the most extensively studied heterocycles.[6] Particular attention is still given to the construction of TTF-acceptor systems for intramolecular charge-transfer interaction,[7] to photoinduced electron-transfer processes by association with fullerene C_{60},[8] and to reach low HOMO−LUMO gap TTF-based materials as targets for the realization of unimolecular electronic devices.[9]

This work describes the synthesis of novel TTF derivative **1** as an attractive building block to obtain donor−acceptor ensembles that are easily amenable to further functionalization.

The accessibility to the hydroquinone (HQ) template or the quinone (Q) moiety[10] and the possibility of converting

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[1] Ferraris, J.; Cowan, D. O.; Walatka, V. V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948.

[2] Batail, P. Molecular Conductors (Thematic issue). *Chem. Rev.* **2004**, *104*, issue 11.

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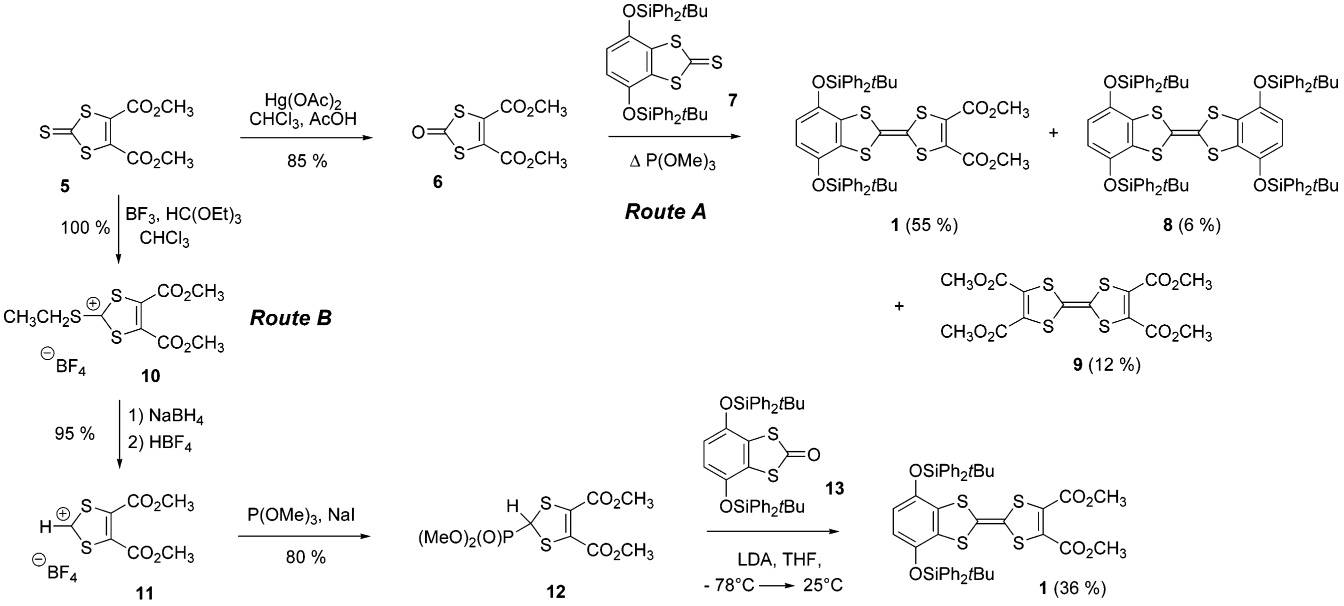
[10] Gautier, N.; Dumur, F.; Lloveras, V.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C.; Hudhomme, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 2765.

10.1021/ol060011i CCC: $33.50

Scheme 1. Two Routes for the Synthesis of TTF Building Block **1**



ester groups into functional intermediates allowing the attachment of C_{60}[11] are utilized to reach A−D−A triad C_{60}−TTF−C_{60} **2**, fused A′−D dyad Q−TTF **3**, and A′−D−A triad Q−TTF−C_{60} **4**.

Two different strategies were considered for the synthesis of target TTF **1** (Scheme 1). Route A employed the straightforward nonselective cross-coupling involving 2-oxo-1,3-dithiole **6**[12] and 2-thioxo-1,3-dithiole **7**.[13] The drawback of this strategy is the formation of both symmetrical species besides the dissymmetrical TTF.[14] Nevertheless, the polarity of the three products was sufficiently different to allow an easy purification of TTF **1** by chromatography on silica gel. Whereas symmetrical TTFs resulting from the self-condensation of 2-thioxo-1,3-dithiole **7** and 2-oxo-1,3-dithiole **6** were isolated in low yields (6 and 12% for TTFs **8** and **9**,[15] respectively), dissymmetrical TTF **1** was isolated in 55% yield.

To suppress the formation of these self-coupling products, we applied the selective Horner−Wadsworth−Emmons (HWE) olefination to create the TTF core (route B).[16] This reaction is based on the nucleophilic addition of the phosphonate anion generated from compound **12** onto 2-oxo-1,3-dithiole derivative **13**.[13] First, tetrafluoroborate dithiolium salt **11** was synthesized from corresponding thione **5** according to a reported three-step procedure[17] including thioalkylation in quantitative yield, reduction of resulting compound **10** with $NaBH_4$, and dethioalkylation with $HBF_4 \cdot Et_2O$ in 95% overall yield. Treatment with trimethyl phosphite in the presence of NaI according to an Arbuzov-type reaction[18] afforded new phosphonate **12** in 80% yield. It should be noted that this compound constitutes a valuable synthetic intermediate for further applications in TTF chemistry. The generation of a carbanion from **12** proceeded smoothly under basic conditions by treatment with the non-nucleophilic reagent LDA, which was preferred to *n*-BuLi in agreement with the presence of ester functionalities. Nevertheless, despite many modifications on the experimental procedure, the yield in compound **1** as the result of this HWE reaction using 2-oxo-1,3-dithiole **13** could not exceed 36%. Consequently, although route A does not lead to a selective synthesis, this still remains the most efficient access to compound **1** at the multigram scale level.

The synthetic scope of building block **1** was investigated. TTF−hydroquinone (HQ−TTF) dyad **14** was isolated in 80% yield after deprotection of silyl groups using Bu_4NF and subsequent acidic hydrolysis using *p*-TsOH·H_2O. To our knowledge, this constitutes the first example of a fused HQ−TTF dyad.[19] The synthetic potential of the hydroquinone functionality was exploited through its transformation into the corresponding triad **2**.[20] Esterification of HQ−TTF **14** with PCBA **15**,[21] prepared by acidic hydrolysis of PCBM,[22] in the presence of DCC as an activating coupling reagent

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[11] Gorgues, A.; Hudhomme, P.; Sallé, M. *Chem. Rev.* **2004**, *104*, 5151.

[12] Parg, R. P.; Kilburn, J. D.; Petty, M. C.; Pearson, C.; Ryan, T. G. *Synthesis* **1994**, 613.

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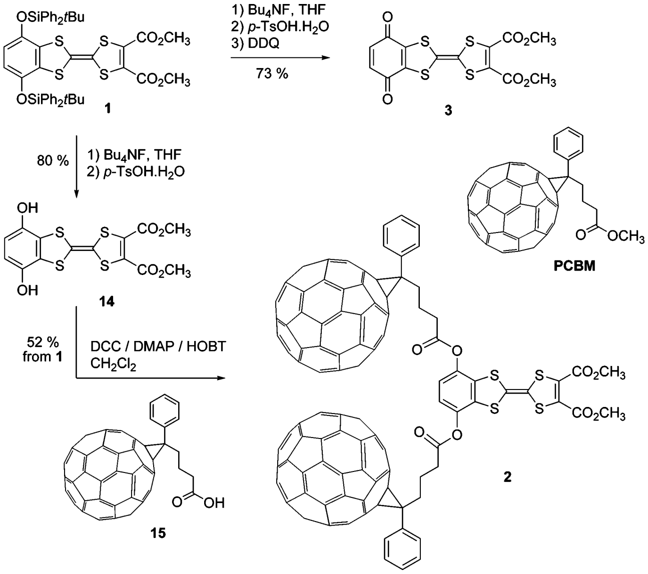
[19] HQ−TTF−HQ and TTF−HQ−TTF triads were reported in, respectively: (a) Watson, W. H.; Eduok, E. E.; Kashyap, R. P.; Krawiec, M. *Tetrahedron* **1993**, *49*, 3035. (b) Frenzel, S.; Müllen, K. *Synth. Met.* **1996**, *80*, 175. A nonfused HQ−TTF dyad was previously described in: Segura, J. L.; Martín, N.; Seoane, C.; Hanack, M. *Tetrahedron Lett.* **1996**, *37*, 2503.

and both DMAP and HOBT afforded C_{60}−TTF−C_{60} triad **2** in 52% yield (calculated from **1**). On the other hand, in situ oxidation of HQ−TTF **14** using DDQ afforded fused Q−TTF **3** which was isolated as blue crystals in 73% yield (Scheme 2).

Scheme 2. Transformations of TTF **1** in Triad C_{60}−TTFC−C_{60} **2** Using the Hydroquinone Template **14** and Fused Dyad Q−TTF **3**



The UV−visible spectrum of **1** presents a maximum absorption band in CS_2 at 452 nm, whereas this band is hypsochromatically shifted to 439 nm in compound **3**. Moreover, a weak charge-transfer band at 810 nm indicates an electronic interaction between TTF and quinone moieties (Figure 1). This charge-transfer absorption has a pronounced negative solvatochromism; the maximum wavelength of Q−TTF **3** decreased while the polarity increased.[23] By comparison with compound **1**, triad **2** exhibits the characteristic weak absorption band of fullerene derivatives at 702 nm.

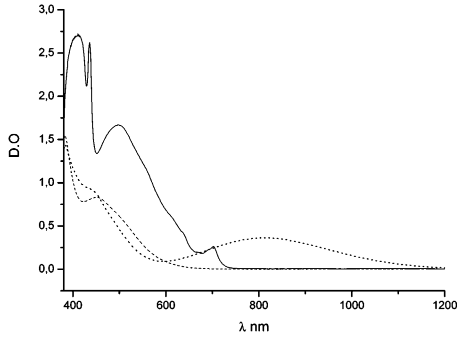
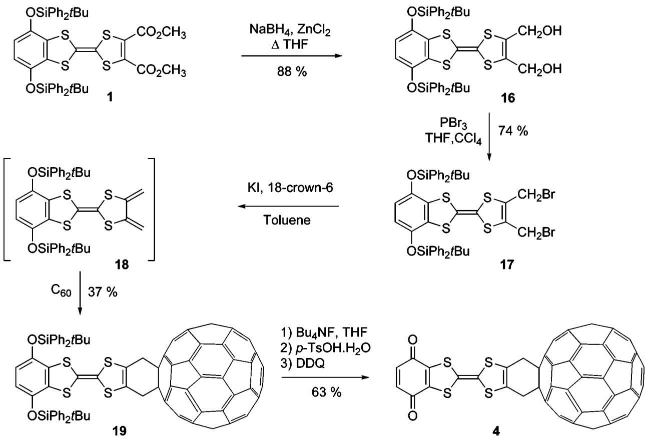


Figure 1. Absorption spectra of **1** (dashed line), **2** (solid line), and **3** (dotted line) in CS_2 ($c = 5 \times 10^{-4}$ M).

Considering the chemical versatility of ester functionalities, we transformed building block **1** into bis(hydroxymethyl)-TTF **16** using $NaBH_4$ associated with $ZnCl_2$ (88% yield).[24] Subsequent TTF derivative **17**[25] was conveniently synthesized in 78% yield upon treatment with PBr_3, referring to a reaction previously applied in the TTF series.[26] Reductive elimination upon treatment of compound **17** with KI in the presence of 18-crown-6 gave rise to transient diene **18** which was trapped by C_{60} according to a Diels−Alder cycloaddition.[27]

Scheme 3. Syntheses of Dyad TTF−C_{60} **19** and Triad Q−TTF−C_{60} **4**



Resulting TTF−C_{60} dyad **19** was easily isolated in 37% yield by column chromatography on silica gel using CS_2 as the eluent (Scheme 3). Deprotection of silyl protecting groups gave the intermediate HQ−TTF−C_{60} as a supramolecular template with the presence of two hydroxy groups. We were able to isolate TTF−C_{60} triad **4** in 63% yield after subsequent oxidation of the hydroquinone group using DDQ. Despite its insolubility, this material was characterized by its infrared spectrum, which showed both the typical band of quinone (1650 cm^{-1}) and the radial vibration of C_{60} (527 cm^{-1}) moieties, and its maldi-tof mass spectrum. The latter exhibits the molecular ion peak at *m*/*z* 1030 with an isotopic

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(20) A C_{60}−TTF−C_{60} triad was previously synthesized by esterification using bis(hydroxymethyl)TTF and PCBA **15**: Ravaine, S.; Delhaès, P.; Leriche, P.; Sallé, M. *Synth. Met.* **1997**, *87*, 93. Or a fulleropyrrolidine carboxylic acid derivative: Segura, J. L.; Priego, E. M.; Martín, N.; Luo, C.; Guldi, D. M. *Org. Lett.* **2000**, *2*, 4021.

(21) [6,6]-phenyl-C_{61}-butyric acid (PCBA) was previously used in esterification reactions: (a) Ravaine, S.; Vicentini, F.; Mauzac, M.; Delhaes, P. *New J. Chem.* **1995**, *19*, 1. (b) Giacalone, F.; Segura, J. L.; Martín, N. *J. Org. Chem.* **2002**, *67*, 3529.

(22) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 532.

(23) λ_{max} (nm) of compound **3** = 810 (CS_2), 793 (CCl_4), 776 (CH_2Cl_2), 768 (toluene), 727 (DMF), 723 (THF), 713 (DMSO), 697 (CH_3CN).

(24) Blanchard, P.; Duguay, G.; Cousseau, J.; Sallé, M.; Jubault, M.; Gorgues, A.; Boubekeur, K.; Batail, P. *Synth. Met.* **1993**, *55*−*57*, 2113.

(25) Its maldi-tof mass spectrum exhibits the molecular ion peak at *m*/*z* 948 and successive fragmentations of each bromine atom corresponding to peaks at *m*/*z* 868 and 788, respectively.

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(27) Kreher, D.; Cariou, M.; Liu, S.-G.; Levillain, E.; Veciana, J.; Rovira, C.; Gorgues, A.; Hudhomme, P. *J. Mater. Chem.* **2002**, *12*, 2137.

Table 1. Cyclic Voltammograms Recorded in Bu_4NPF_6 0.1 M Solution as the Supporting Electrolyte and Platinum Wires as Counter- and Working Electrodes[a]

compd	solvent	$E_{1/2red4}$	$E_{1/2red3}$	$E_{1/2red2}$	$E_{1/2red1}$	$E_{1/2ox1}$	$E_{1/2ox2}$
1	CH_2Cl_2					+0.27	+0.74
1	*o*-$C_6H_4Cl_2$/CH_2Cl_2 (2:1)				−1.93[b]	+0.25	+0.72
2	*o*-$C_6H_4Cl_2$/CH_2Cl_2 (2:1)	−2.13	−1.87[b]	−1.59	−1.20	+0.42	+0.91
PCBM	*o*-$C_6H_4Cl_2$/CH_2Cl_2 (2:1)		−2.10	−1.60	−1.21		
3	CH_2Cl_2		−2.01	−1.33	−0.71	+0.48	+0.85
8	CH_2Cl_2					+0.12	+0.63
19	*o*-$C_6H_4Cl_2$/CH_2Cl_2 (2:1)		−2.05	−1.56	−1.19	+0.32	+0.56

[a] Scan rate: 100 mV/s. V vs Fc^+/Fc. Triad Q−TTF−C_{60} **4** was insoluble in these media to carry out cyclic voltammetry. [b] Irreversible reduction process is attributed to the ester functionality.

distribution in agreement with the calculated pattern and the presence of both peaks at *m*/*z* 720 (C_{60}) and 310 (diene **18**) resulting from the retro Diels−Alder reaction.

Electrochemical properties of these building block and donor−acceptor systems were investigated by cyclic voltammetry to determine the influence of substituents on the redox properties of TTF and the electrochemical HOMO−LUMO difference inside D−A systems. TTF derivatives present two reversible oxidation peaks corresponding to the cation radical $TTF^{+\cdot}$ and dication TTF^{2+} species, respectively. By comparison with oxidation potentials of compound **8** ($E_{1/2ox1}$ = +0.12 V and $E_{1/2ox2}$ = +0.63 V vs Fc^+/Fc), as expected, the electron-withdrawing effect of both methoxycarbonyl groups on the TTF framework in compound **1** resulted in an increase of oxidation potentials ($E_{1/2ox1}$ = +0.27 V and $E_{1/2ox2}$ = +0.74 V) (Table 1). This effect was more importantly evidenced with the subsequent introduction of the quinone moiety in dyad TTF−Q **3** ($E_{1/2ox1}$ = +0.48 V and $E_{1/2ox2}$ = +0.85 V) for $TTF^{+\cdot}$−Q and TTF^{2+}−Q species, respectively.

Two reversible reduction waves at $E_{1/2red1}$ = −0.71 V and $E_{1/2red2}$ = −1.33 V were assigned to the formation of the anion radical TTF−$Q^{\cdot-}$ and dianion TTF−Q^{2-} from the quinone moiety of compound **3**.

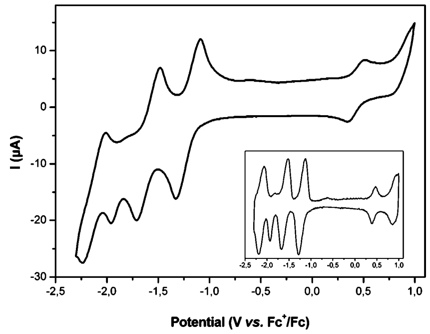

Figure 2. Cyclic voltammogram of triad C_{60}−TTF−C_{60} **2** and its deconvolution in the inset.

Cyclic voltammograms of TTF−C_{60} dyad **19** and TTF−$(C_{60})_2$ triad **2** were compared to those of building block **1** and PCBM. Whereas the dyad **19** showed the expected two reversible oxidation peaks ($E_{1/2ox1}$ = +0.32 V and $E_{1/2ox2}$ = +0.56 V) and three reduction peaks close to those of PCBM, we noted the appearance of an irreversible reduction peak ($E_{1/2red3}$ = −1.87 V) in the case of triad **2** (Figure 2). Being that this irreversible reduction process was also present in reference compound **1**, we unambiguously demonstrated that this phenomenon was resulting in the reduction of the bis(methoxycarbonyl) functionality attached to the TTF moiety.

In summary, we propose an efficient scalable synthetic strategy to elaborate a new building block in the TTF series and exciting TTF-based donor−acceptor systems involving *p*-benzoquinone and/or fullerene C_{60} with the aim of first exploiting the synthetic richness of this platform. We believe that future developments will allow the preparation of promising molecular conductors' architectures governed by hydrogen-bond interactions using the potential of not only the hydroquinone or quinone templates but also the hydroxymethyl, carboxylic acid, or amide functionalities accessible from the ester group.

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Supporting Information Available: Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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