ORGANIC
LETTERS

2006
Vol. 8, No. 6
1173−1176

Synthesis of Oligo(phenyleneethynylene)-Tetrathiafulvalene Cruciforms for Molecular Electronics

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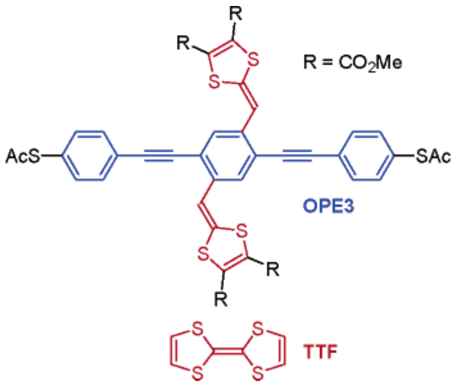
Received January 11, 2006

ABSTRACT



Novel oligo(phenyleneethynylene) (OPE)-tetrathiafulvalene (TTF) cruciform molecules containing thiol end-groups have been prepared and characterized. These redox-active molecules are interesting for future applications as molecular wires/transistors for molecular electronics.

The rational design and synthesis of molecular wires, rectifiers, switches, and transistors for molecular electronics has attracted immense interest in recent years.[1] Much work has focused on thiol-terminated conjugated π-systems, such as oligo(phenylenevinylene)s (OPVs),[2] oligo(phenyleneethynylene)s (OPEs),[3] and oligothiophenes.[4] The electronic conduction through a molecular wire may be controlled by attachment of suitable functional groups along its backbone. Thus, Reed, Tour, and co-workers[5] have demonstrated conductance on−off switching in devices based on wires functionalized with NH_2 and NO_2 groups.[6]

Nuckolls and co-workers[7] recently introduced a new class of molecules consisting of two perpendicularly disposed π-systems, bis-phenyloxazole and terphenyl, for molecular

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(1) (a) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791−804. (b) Carroll, R. L.; Gorman, C. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 4378−4400. (c) Robertson, N.; McGowan, C. A. *Chem. Soc. Rev.* **2003**, *32*, 96−103. (d) Flood, A. H.; Stoddart, J. F.; Steuerman, D. W.; Heath, J. R. *Science* **2004**, *306*, 2055−2056. (e) Nørgaard, K.; Bjørnholm, T. *Chem. Commun.* **2005**, 1812−1823. (f) Elbing, M.; Ochs, R.; Koentopp, M.; Fischer, M.; von Hänisch, C.; Weigend, F.; Evers, F.; Weber, H. B.; Mayor, M. *Proc. Nat. Acad. Sci. U.S.A.* **2005**, *102*, 8815−8820.

(2) (a) Stuhr-Hansen, N.; Christensen, J. B.; Harrit, N.; Bjørnholm, T. *J. Org. Chem.* **2003**, *68*, 1275−1282. (b) Kubatkin, S.; Danilov, A.; Hjort, M.; Cornil, J.; Brédas, J.-L.; Stuhr-Hansen, N.; Hedegård, P.; Bjørnholm, T. *Nature* **2003**, *425*, 698−701.

(3) (a) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W., Jr.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303−2307. (b) Chanteau, S. H.; Tour, J. M. *J. Org. Chem.* **2003**, *68*, 8750−8766. (c) Stuhr-Hansen, N.; Sørensen, J. K.; Moth-Poulsen, K.; Christensen, J. B.; Bjørnholm, T.; Nielsen, M. B. *Tetrahedron* **2005**, *61*, 12288−12295. (d) Wang, C.; Batsanov, A. S.; Bryce, M. R. *J. Org. Chem.* **2006**, *71*, 108−116.

(4) (a) Purcell, S. T.; Garcia, N.; Binh, V. T.; Jones, L., II; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11985−11989. (b) Hicks, R. G.; Nodwell, M. B. *J. Am. Chem. Soc.* **2000**, *122*, 6746−6753.

(5) (a) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550−1552. (b) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W.; Campbell, I. *Chem. Eur. J.* **2001**, *7*, 5118−5134.

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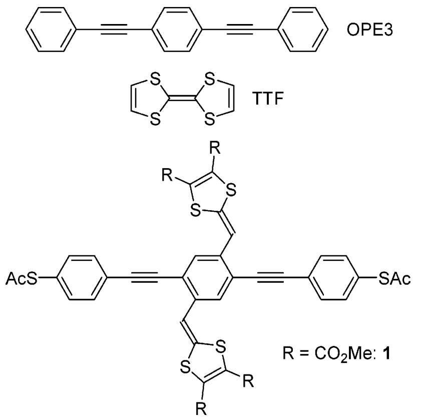


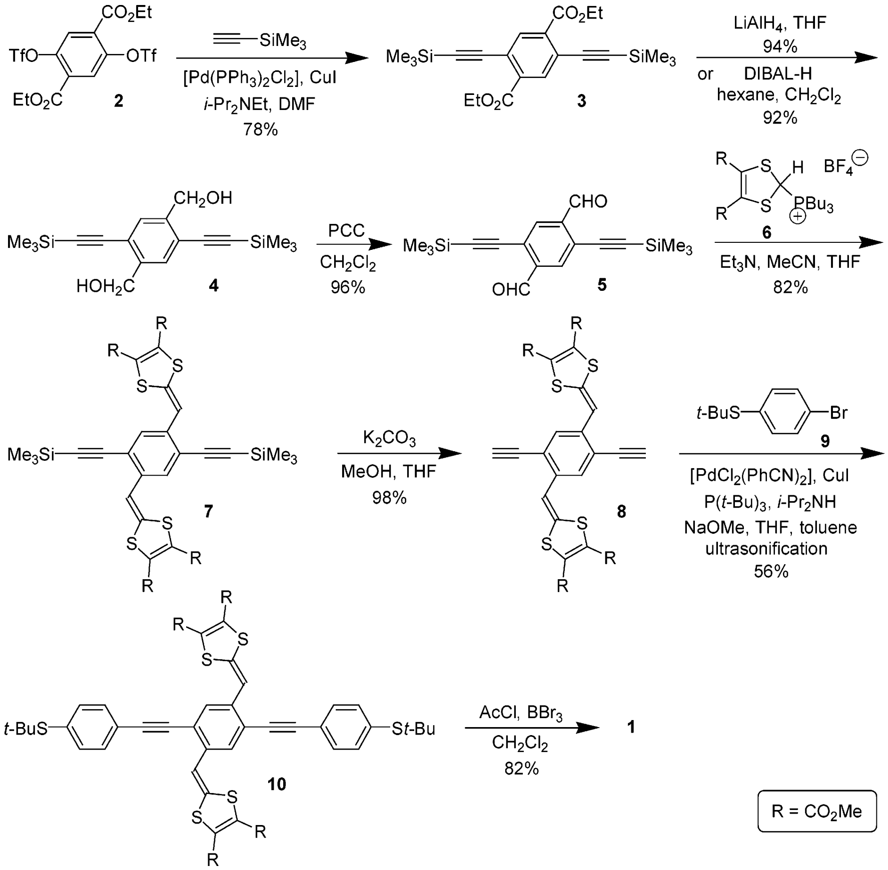
Figure 1. Target molecule **1** derived from OPE3 and TTF.

electronics applications. Other examples of such cruciform molecules were prepared by Bunz and co-workers,[8] who reported a whole class of OPE3s with orthogonally oriented arylvinylenes. We became interested in exploiting the redox-active tetrathiafulvene (TTF) donor together with an OPE3 wire in new cruciforms for molecular electronics (Figure 1), which is a continuation of our work on acetylenic scaffolds of benzene-extended TTFs.[9,10] TTF exhibits two reversible one-electron oxidations steps and has for this reason found wide applications in both materials and supramolecular chemistry.[6a,11]

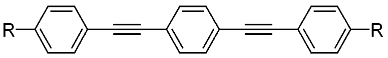
The cruciform target molecule **1** contains an OPE3 functionalized with two dithiafulvene donor groups at the lateral positions and acetyl-protected thiol end-groups. The thiol group is commonly employed as the anchoring group for adhesion onto gold electrodes. The single molecule conductivity is expected to depend on the redox-state of the orthogonal extended TTF moiety (0, +1, +2). Simply put, two-electron oxidation is expected to change the π-electron delocalization along the OPE backbone from linearly conjugated to cross-conjugated (i.e., quinodal structure in the central ring).

The synthesis of the wire **1** proceeds according to Scheme 1. First, the triflate **2**[12] was subjected to a palladium-catalyzed Sonogashira cross-coupling[13] with trimethylsilylacetylene to provide compound **3**.[14] The ester groups were then reduced with $LiAlH_4$ (or alternatively with $(i\text{-}Bu)_2AlH$ (DIBAL-H)), which gave the diol **4** in almost quantitative yield. Oxidation with pyridinium chlorochromate (PCC) furnished the dialdehyde **5** that was subsequently treated with the readily available phosphonium salt **6**[15] and diethylamine to afford the extended TTF **7** in a 2-fold Wittig reaction. Desilylation upon treatment with K_2CO_3 in MeOH/THF gave the product **8** precipitating from the reaction mixture. This compound exhibits a remarkable stability and can be stored at room temperature for several weeks without apparent decomposi-

Scheme 1. Synthesis of OPE3-TTF Cruciform



tion in sharp contrast to previously reported TTFs containing terminal alkyne functionalities.[9,16] Compound **8** was then subjected to a 2-fold palladium-catalyzed cross-coupling with the bromide **9**,[2a] employing slightly modified reaction conditions of Hundertmark et al.,[17] which provided the OPE3-TTF cruciform **10**. We have recently employed similar conditions for synthesizing the parent OPE3 (**11**, Figure 2) with *t*-Bu-protected thiol end-groups.[3c] Addition of NaOMe (1 equiv) increased the yield of **10** from 26% to 56%. Moreover, we applied ultrasonification as we have previously demonstrated its ability to promote the Sonogashira cross-coupling.[16b]



11 (R = S*t*-Bu)

Figure 2. Thiol-terminated OPE3.

One advantage of using *t*-Bu as protecting group is the resistance of *t*-Bu-S-Ar to both strongly basic and acidic conditions.[2a] Furthermore, the OPE3-TTF **10** presents a target molecule in itself for fundamental conductivity studies, as Kubatkin et al.[2b] have demonstrated that *t*-BuS-functionalized wires can be physisorbed onto electrodes by a weak van der Waals contact between the single molecule and the device. However, in a final synthetic step, the *t*-BuS group can be converted into the AcS moiety by means of AcCl/BBr_3. Thus, subjecting **10** to these conditions gave the compound **1**. The Ac groups of **1** can be removed upon treatment with $HNEt_2$/$CHCl_3$ (1:1).

Single crystals of **7** were subjected to an X-ray crystallographic analysis. The structure (Figure 3) reveals planarity of the complete π-system.

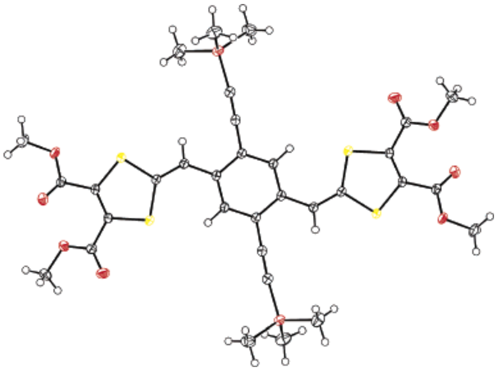


Figure 3. X-ray crystal structure of **7** (CCDC 294502). Drawing made by ORTEP-II.[18]

UV−vis absorption spectra show that the presence of donor groups in **10** results in a significant decrease in the HOMO−LUMO gap relative to that of **11**. The lowest energy absorpton maxima occur at 411 nm (very broad, 3.0 eV) and 320 nm (fine-structured, 3.9 eV) for **10** and **11**, respectively.

Cyclic voltammetry of **10** in CH_2Cl_2 reveals a single irreversible oxidation (scan rate 0.1 V s^{-1}). According to differential pulse voltammetry, the oxidation occurs at 0.47 V vs Fc^+/Fc and is likely a two-electron process. No oxidation peaks are observed for **11** under similar conditions. The irreversible oxidation observed in bulk solution for **10** should not be directly linked to its applicability in single-molecule electronics where the molecule is isolated between gold electrodes.

A computational study was performed to elucidate the frontier orbitals of the OPE3-TTF cruciforms. Compounds **10** and **11** were geometry-optimized at the semiempirical PM3 calculational level using the Gaussian program package.[19] Frontier orbitals (Figure 4) were obtained by density functional theory (DFT) single-point calculations at the B3LYP/6-31+g(d,p) level. Whereas the HOMO is situated along the wire for **11**, this orbital has the strongest coefficients at atoms vertically to the wire in **10**, i.e., at the extended TTF donor moiety. This observation substantiates the rationale behind the molecular design. In contrast, the LUMO of **10** resides mainly along the wire and resembles to a large extent that of **11**. Single-point energy calculations on **10**, $\mathbf{10}^{\bullet+}$, and $\mathbf{10}^{2+}$ (all in the neutral conformation) provide first and second vertical ionization energies (IE) of

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[6] For other examples of conductance switching by oxidation/reduction, see: (a) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433−444. (b) McCreery, R.; Dieringer, J.; Solak, A. O.; Snyder, B.; Nowak, A. M.; McGovern, W. R.; DuVall, S. *J. Am. Chem. Soc.* **2003**, *125*, 10748−10758. (c) Dinglasan, J. A. M.; Bailey, M.; Park, J. B.; Dhirani, A.-A. *J. Am. Chem. Soc.* **2004**, *126*, 6491−6497. (e) Reference 2b.

[7] Klare, J. E.; Tulevski, G. S.; Sugo, K.; de Picciotto, A.; White, K. A.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 6030−6031.

[8] (a) Wilson, J. N.; Josowicz, M.; Wang, Y.; Bunz, U. H. F. *Chem. Commun.* **2003**, 2962−2963. (b) Wilson, J. N.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2005**, *127*, 4124−4125.

[9] (a) Nielsen, M. B. *Synlett* **2003**, 1423−1426. (b) Nielsen, M. B.; Petersen, J. C.; Thorup, N.; Jessing, M.; Andersson, A. S.; Jepsen, A. S.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *J. Mater. Chem.* **2005**, *15*, 2599−2605.

[10] For synthesis and characterization of the parent benzene-extended TTF, see: Salle, M.; Belyasmine, A.; Gorgues, A.; Jubault, M.; Soyer, N. *Tetrahedron Lett.* **1991**, *32*, 2897−2900.

[11] (a) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11−23. (b) Nielsen, M. B.; Lomholt, C.; Becher, J. *Chem. Soc. Rev.* **2000**, *29*, 153−164. (c) Bryce, M. R. *J. Mater. Chem.* **2000**, *10*, 589−598. (d) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372−1409.

[12] Zhang, Q.; Shi, C.; Zhang, H.-R.; Wang, K. K. *J. Org. Chem.* **2000**, *65*, 7977−7983.

[13] Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467−4470.

[14] For a crystal structure of the *i*-Pr_3Si derivative, see: Nicolaisen, B.; Bond, A. D.; Nielsen, M. B. *Acta Crystallogr.* **2004**, *E60*, o784−o785.

[15] Sato, M.; Gonnella, N. C.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 930−934.

[16] (a) Nielsen. M. B.; Gisselbrecht, J.-P.; Thorup, N.; Piotto, S. P.; Boudon, C.; Gross, M. *Tetrahedron Lett.* **2003**, *44*, 6721−6723. (b) Andersson, A. S.; Qvortrup, K.; Torbensen, E. R.; Mayer, J.-P.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M.; Kadziola, A.; Kilså, K.; Nielsen, M. B. *Eur. J. Org. Chem.* **2005**, 3660−3671.

[17] Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729−1731.

[18] ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program. Report ORNL-5138. Johnson, C. K. Oak Ridge National Laboratory, Oak Ridge, TN 1976.

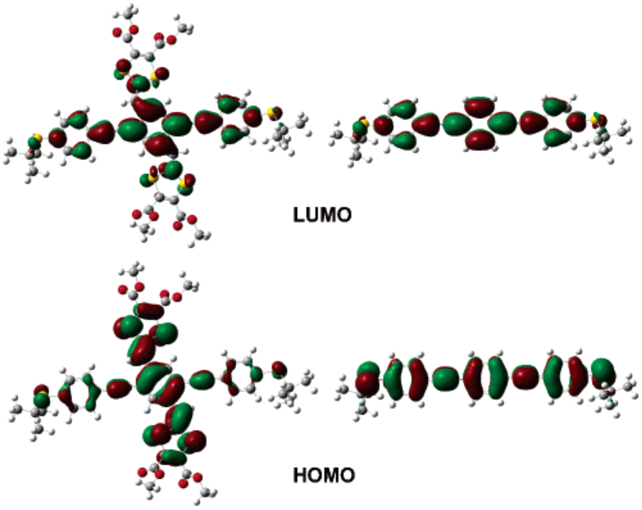

Figure 4. Calculated HOMO and LUMO orbitals (B3LYP/6-31+g(d,p)) for the compounds **10** (left) and **11** (right).

6.07 and 8.60 eV, respectively. The vertical IEs of the parent TTF (devoid of the CO_2Me substituents) were previously calculated to be 6.49 and 11.10 eV, respectively.[20] Hence, compound **10** is a better electron donor (gas phase) than TTF despite the electron-withdrawing CO_2Me groups. For comparison, a vertical IE of 6.46 eV is obtained for **11**.

In conclusion, stable OPE3-TTF cruciform wires with thiol end-caps have been prepared from a sequence of high-yielding steps. Exploitation of both **1** and **10** as redox-controlled switches for molecular electronics is currently under investigation.

Acknowledgment. The Danish Research Agency is acknowledged for financial support (Nos. 2111-04-0018 and 21-04-0084).

Supporting Information Available: Experimental procedures, NMR and UV−vis spectra, and X-ray crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Gaussian 03, Revision B.03: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 2003.

(20) Nielsen, S. B.; Nielsen, M. B.; Jensen, H. J. Aa. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1376−1380.