ORGANIC
LETTERS

2006
Vol. 8, No. 6
1173−1176

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

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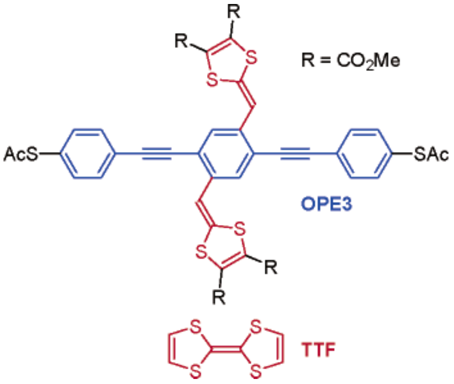
Received January 11, 2006

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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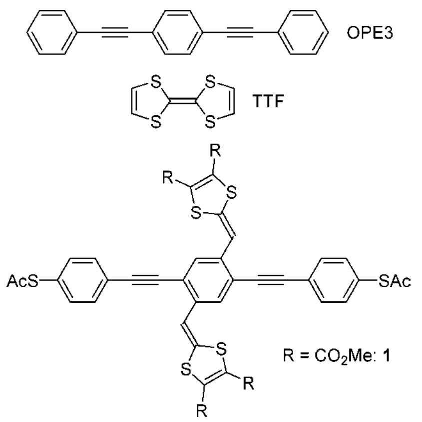


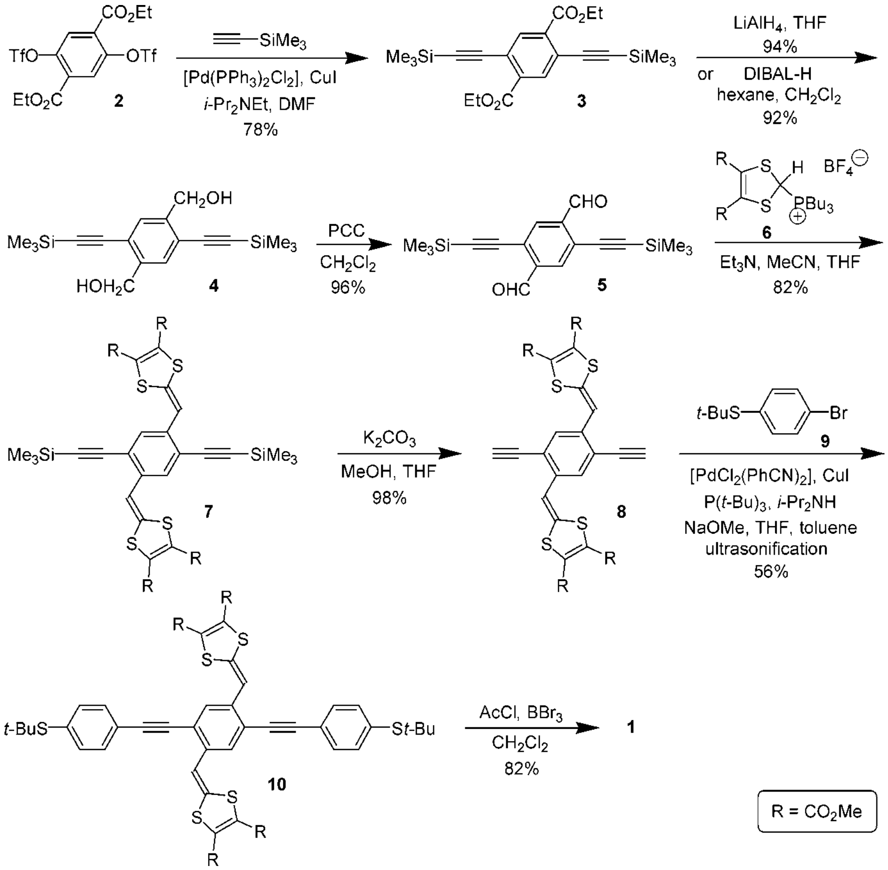
Figure 1. Target molecule **1** derived from OPE3 and TTF.

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]

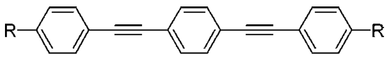
The cruciform target molecule **1** contains an OPE3 functionalized with two dithiafulvene donor groups at the lateral positions and acetyl-protected thiol end-groups. The thiol group is commonly employed as the anchoring group for adhesion onto gold electrodes. The single molecule conductivity is expected 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-Bu)$_2$AlH (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$_2$CO$_3$ 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.

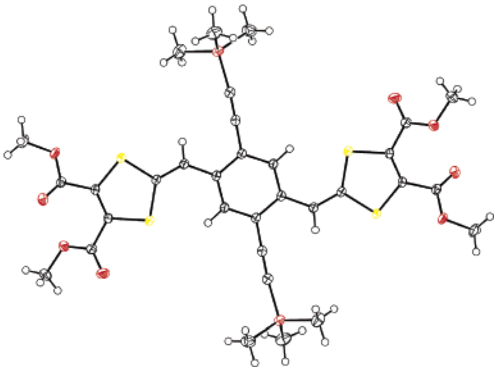


Figure 3. X-ray crystal structure of **7** (CCDC 294502). Drawing made by ORTEP-II.[18]

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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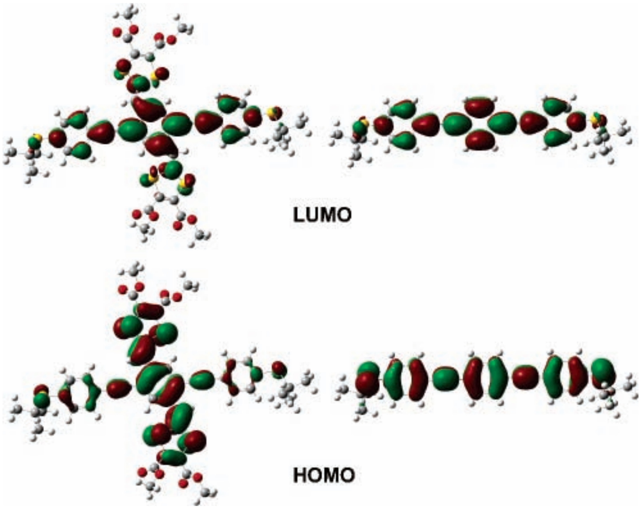

Figure 4. Calculated HOMO and LUMO orbitals (B3LYP/6-31+g(d,p)) for the compounds **10** (left) and **11** (right).

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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