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Synthesis of an End-Capped Sexithiophene Bearing Fused Tetrathiafulvalene (TTF) Units

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ABSTRACT

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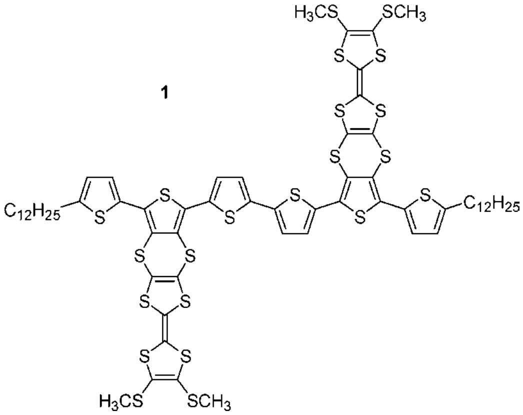

We report the synthesis of a novel end-capped sexithiophene derivative bearing two pendent, fused tetrathiafulvalene (TTF) units linked to the main chain through 1,4-dithiin heterocycles. Cyclic voltammetry and absorption spectroscopy are used to investigate the electronic properties of this hybrid electroactive material. The oligomer has a band gap of 2.1 eV, and the material can be oxidized through the sexithiophene and TTF units simultaneously.

Tetrathiafulvalene (TTF) derivatives and oligothiophenes are two of the most well-known series of electron-donor materials in the field of organic conductors. Whereas TTF systems are classically recognized as components in metallic or superconducting charge-transfer salts,[1−5] oligothiophenes are studied more for their semiconducting properties.[6] Nevertheless, the application of these materials should not be stereotypical: TTFs have been applied in semiconductor devices such as field-effect transistors,[7−9] and metallic charge-transfer salts of end-capped oligothiophenes have

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been reported.[10−12] There has been fervent interest in the properties of hybrid TTF−polythiophenes,[13−21] mainly to investigate how two highly electroactive components behave when they are forced into close proximity through covalent attachments. Recent work in our group has shown that fusing the TTF skeleton to the [3,4-*b*] position of a thiophene unit within PT (polythiophene) or PTV (polythienylenevinylene)[13,14] turns off the electroactivity of the polymer backbone and directs oxidation processes exclusively within the TTF units. However, the materials' semiconducting properties remain intact and a PTV variant has been shown to function otherwise normally in an organic solar cell device.

Once the TTF unit is moved away from the polythiophene backbone (by incorporating covalent spacers), truly hybrid electroactivity is observed, but the properties of doped intermediates are complex. In relation to this, end-capped oligothiophenes are attractive materials to study by electrochemical methods because they usually give well-defined redox signatures and stable charged intermediates. To elucidate the complex electrochemical behavior of TTF−polythiophenes, we embarked on the synthesis of a model system, comprising an end-capped sexithiophene (6T) bearing two TTFs linked via fused 1,4-dithiin heterocycles. Notably, there is only one (very recent) example of oligothiophenes linked to TTFs.[22] Herein, we report the multistep synthesis and electrochemical characterization of a new dodecyl end-capped TTF−6T diad (**1**).

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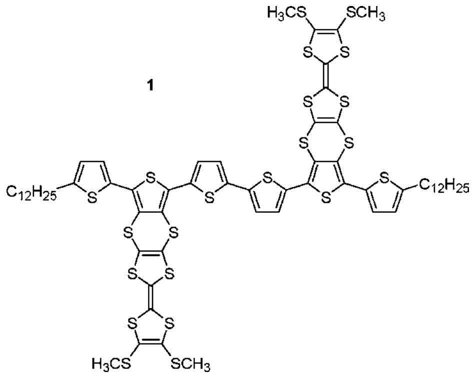

Our synthetic scheme begins with the construction of a 1,3-dithiole-2-thione unit appended to a dodecyl end-blocked terthiophene. The strategy, which is depicted in Scheme 1, follows a similar procedure for an H-terminated symmetrical analogue.[23] Bromination of compound **2** gave the bromoacetyl **3** which in turn formed adduct **5** upon addition of aminoacetyl derivative **4**. Rearrangement of **5** resulted in the isolation of butene-1,4-dione **7**, and the cycloaddition of this compound with oligomer **6**[24] gave compound **8** in good yield. The transchalcogenation (**8** to **9**) and cyclization steps proceeded smoothly to give the terthiophene **10** in an overall yield of 22% from compound **2**.

The phosphite-mediated cross-coupling reaction between the 1,3-dithioles **10** and **11**[25] proceeded in good yield (**12**, 71%). Deprotection of the cyanoethylene groups with sodium methoxide, followed by methylation with CH_3I, gave the TTF derivative **13** in 97% yield.

The preparation of sexithiophene **1** was achieved by four different routes. The cleanest method involved electrochemical oxidation of **13** and was achieved by potentiostatic deposition of the product on the working electrode (ITO glass or a glassy carbon disc), from a 2:1 dichloromethane/hexane solution, containing tetrabutylammonium hexafluorophosphate as the supporting electrolyte (0.1 M). The procedure is limited in its scale, but chemical oxidation with ferric chloride was employed as an alternative method for larger quantities of starting material. In the case of $FeCl_3$ (carried out in nitrobenzene at room temperature), the product was isolated by precipitation with methanol, followed by purification by column chromatography.

Iodination of compound **13** with LDA and perfluorohexyl iodide gave **14** in 74% yield; isolation of this material enabled us to explore the Ullmann and Yamamoto routes to sexithiophene **1**. Under the various chemical coupling conditions, the consumption of the iodo derivative was quantitative, apart from the Ni(0)-mediated dimerization from which we were able to recover unreacted compound **14** (10%). Deiodination occurred in the case of the Ullmann reaction, and compound **13** was obtained as a side product in 16% yield. Complications arose with metal impurities forming complexes with the 6T system. As in the case of the sexithiophenes **15**[26] and **16**,[27] prepared by ferric chloride oxidative coupling, compound **1** can be purified to give well-resolved aromatic peaks in the ^{1}H NMR spectrum (see

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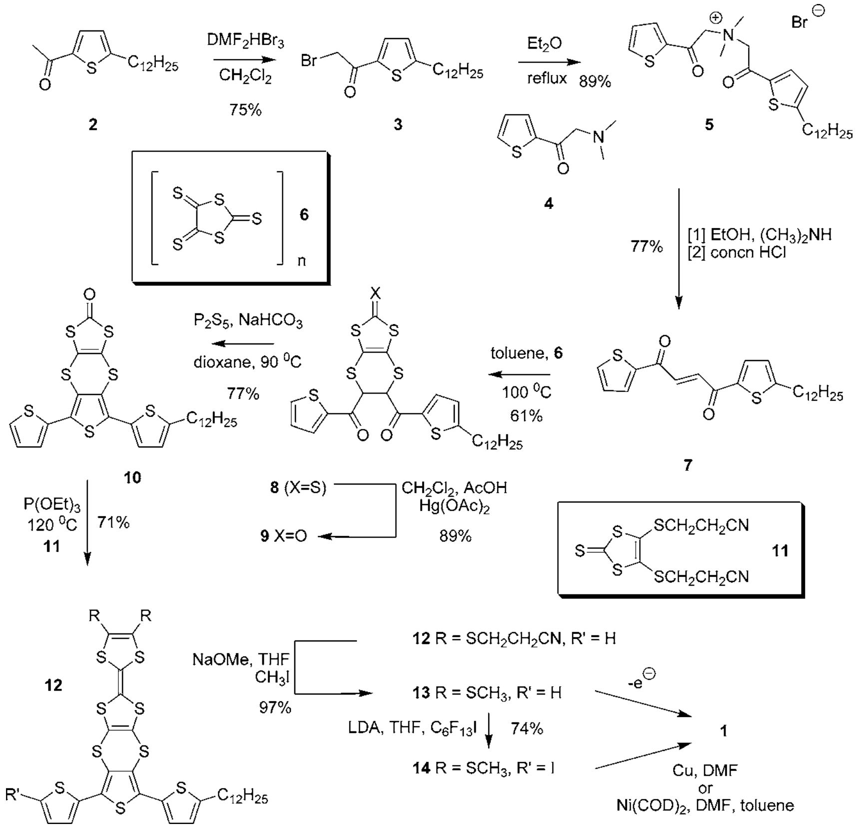
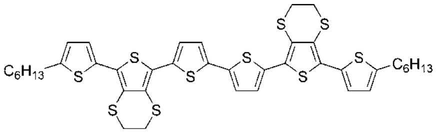
Scheme 1. Synthesis of the Dodecyl End-Capped Sexithiophene **1**



Supporting Information for purification procedures and the corresponding spectrum). In summary, the yields for the three coupling methods employed were as follows: FeCl$_3$, 24%; Ullmann, 43%; Yamamoto, 10%.



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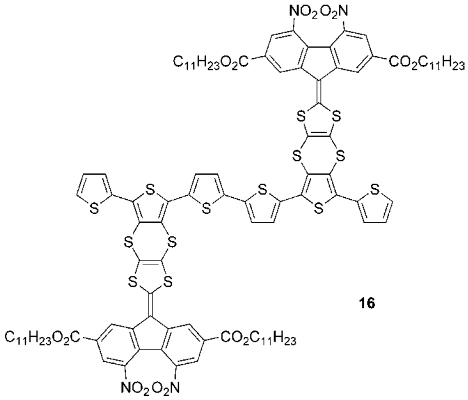

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Cyclic voltammetry experiments were conducted on compounds **1**, **13**, and **14**. The terthiophenes give very similar redox potentials and characteristics with two sequential, reversible waves due to the electroactivity of the TTF units (**13**, $E_{1ox}^{1/2}$ = +0.02 V; $E_{2ox}^{1/2}$ = +0.43 V; **14**, $E_{1ox}^{1/2}$ = +0.09 V; $E_{2ox}^{1/2}$ = +0.45 V; values are vs ferrocene in dichloromethane) and one irreversible oxidation of the terthiophene component at higher potentials (**13**, E_{3ox} = +0.88 V; **14**, E_{3ox} = +1.06 V). In the latter case, the difference of 180 mV between the oxidation peaks is due to the substituent effect of the iodine atom in **14**. Upon cycling the voltammogram of **13** over the range −0.45 to +0.95 V (vs ferrocene), we observed the growth of the "TTF" peaks with the concomitant deposition of the 6T system (**1**), but the second oxidation appears to grow at a faster rate (see Supporting Information Figure S1). Potentiostatic growth of the material on ITO glass (+1.0 V, vs ferrocene) allowed us to investigate the electrochemistry of the dimer product in monomer-free solution as well as the corresponding absorption spectra (Figure 1).

The absorption spectra for compounds **13** and **14** show peak maxima at 310 and 341 nm, together with a shoulder at 369 nm for **13** and at 378 nm for **14** (see Supporting Information, Figure S3). The discrepancy in the latter indicates that the shoulders arise from the $\pi-\pi^*$ transition of the terthiophene units (difference due to the effect of the iodine substituent). After electrochemical dimerization of **13** to produce **1**, the $\pi-\pi^*$ absorption band (Figure 1) shifts to the red (449 nm), and the broad peak centered around 735 nm indicates that the material is deposited in its doped state. Figure 1 also shows the absorption spectrum of oligomer **1** obtained from the Ullmann reaction. The longest-wavelength

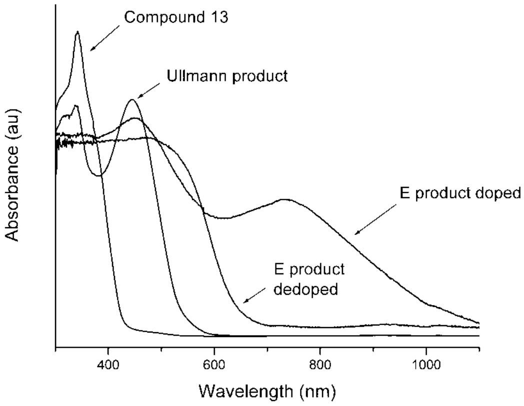

Figure 1. Absorption spectra of compounds **13** and **1** in dichloromethane.

absorption peak matches that of the electrodimerized product at 449 nm, but the absence of any lower-energy bands shows that the chemically prepared material has been isolated in the neutral state. Interestingly, the peak maximum of electrochemically dedoped **1** is red-shifted with respect to the Ullmann product and is likely due to the morphology of the film after "electrochemical annealing". The optical band gap of **1** was found to be 2.1 eV, which is slightly smaller than that of **15** in the same solvent. Oxidation of **15** to the dication under spectroelectrochemical conditions gives peaks at 631 and >1100 nm.[26] The peak at 735 nm for doped **1** indicates that the electrochemically as-made dimer has the signature of a radical cation centered within the TTF unit.[13]

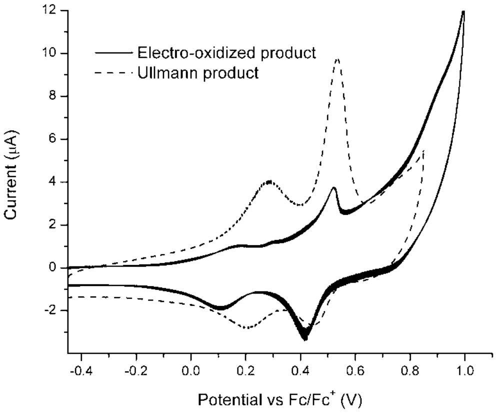

Figure 2. Cyclic voltammograms of 6T derivative **1** in 1:1 dichloromethane/hexane in solution (Ullmann product, Pt electrode) and in the solid state (electrochemically dimerized system, glassy carbon electrode). Pt wire counter electrode, Ag wire pseudoreference, $TBAPF_6$ (0.1 M).

The electrochemistry of **1** is depicted in Figure 2, which shows that only small changes are observed between solution and solid-state samples. Under the same solvent conditions (CH_2Cl_2/hexane, 1:1), there are negligible differences between the TTF-based oxidation potentials of **1** ($E_{1ox}{}^{1/2}$ = +0.24 V, $E_{2ox}{}^{1/2}$ = +0.50 V) and terthiophene **13** (see Supporting Information, Figure S4). The main feature in the electrochemistry of **1** is that the second oxidation peak of the TTF coalesces with the oxidation of the end-capped 6T system; this is responsible for the increase in the peak current for E_{2ox}. Our assumption that the oxidation potentials of these two redox sites (TTF and 6T) coincide is based on the fact that compound **15** is also oxidized at ca. +0.3 to +0.5 V, vs ferrocene.

In conclusion, we have presented the synthesis of a complex, end-capped 6T system bearing two fused TTF units. A more detailed spectroelectrochemical study will be reported elsewhere, and we look forward to the possibility of generating charge-transfer materials by electrocrystallization.

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Supporting Information Available: Full experimental data for compounds **10**, **12**−**14**, and **1**; deposition of **1** by cyclic voltammetry and peak current dependence upon scan rate; CV of **13**; and absorption spectra of **13** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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