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Synthesis and properties of thiophene-functionalized π-extended tetrathiafulvalenes

Min Shao, Yuming Zhao *

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7

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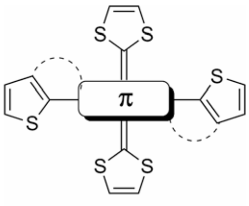
ABSTRACT

Two molecular ensembles composed of an array of thiophene–extended tetrathiafulvalene–thiophene were synthesized using Stille coupling and Horner–Wittig reaction as the key steps. Electrochemical redox and electronic absorption properties were investigated by voltammetric and UV–vis spectroscopic analyses.

Sulfur-rich π-conjugated molecules constitute important building blocks in current research on molecular electronics. Among them, thiophene and tetrathiafulvalene (TTF) are two extraordinary candidates, which show remarkable electronic properties and ample application potentials. Thiophene is the essential repeat unit for a class of well-known conducting polymers (CPs), poly/oligo-thiophenes,[1–3] while TTF and its derivatives are excellent organic electron donors widely applicable in various fields ranging from charge-transfer complexes, nonlinear optical materials, organic transistors, to molecular switches and sensors.[4–7] Remarkable optoelectronic performances have been found with thiophene and TTF-containing organic materials, which has fueled the pursuit for a broad range of thiophene–TTF hybrid materials since the early 1990s.[7–20] In previous reports related to this topic, design motifs were mainly focused on the use of thiophene or oligothiophenes as π-spacers to spatially expand the conjugation of TTF, affording the so-called π-extended TTF derivatives (exTTFs).[16–20] With such modifications, the molecular properties that are advantageous to device fabrications, such as increased dimensionality, improved donor ability, intimated solid-state packing, and enhanced air stability, have become attainable. Another benefit stemming from intermarrying thiophene and TTF lies in the possibility of generating novel electroactive CPs through straightforward electrodeposition means.[8,21–26] Nevertheless, successes in producing TTF-functionalized polythiophenes are still quite limited.[25,26] A major barrier to the electrochemical polymerization of TTF-attached thiophenes comes from the low oxidation potential of TTF, which hampers the formation of suitable thiophene radical cation intermediates for polymerization. Rational molecular design and tailoring based on in-depth understanding of structure–property relationship should offer an effective approach to address the challenges. To this end, synthetic access to various new TTF–thiophene molecular architectures is prerequisite.

Motivated by the issues mentioned above, a type of thiophene-functionalized exTTFs **1** was targeted in our research. The general motif of **1** represents a wide range of thiophene–exTTF–thiophene triads, which are expected to give rise to beneficial features in the context of molecular electronics; for example, tunable redox properties and flexible post-functionalization at the thiophene end groups. In this work, two structures belonging to the family of **1** were explored as shown in Scheme 1. In compound **2,** two thiophene groups were directly attached to an anthraquinoid-type exTTF (namely TTFAQ),[27] while in compound **3** thiophene groups were fused with the conjugated framework of the planar central exTTF core.



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* Corresponding author. Tel.: +1 709 737 8747; fax: +1 709 737 3702.
E-mail address: yuming@mun.ca (Y. Zhao).

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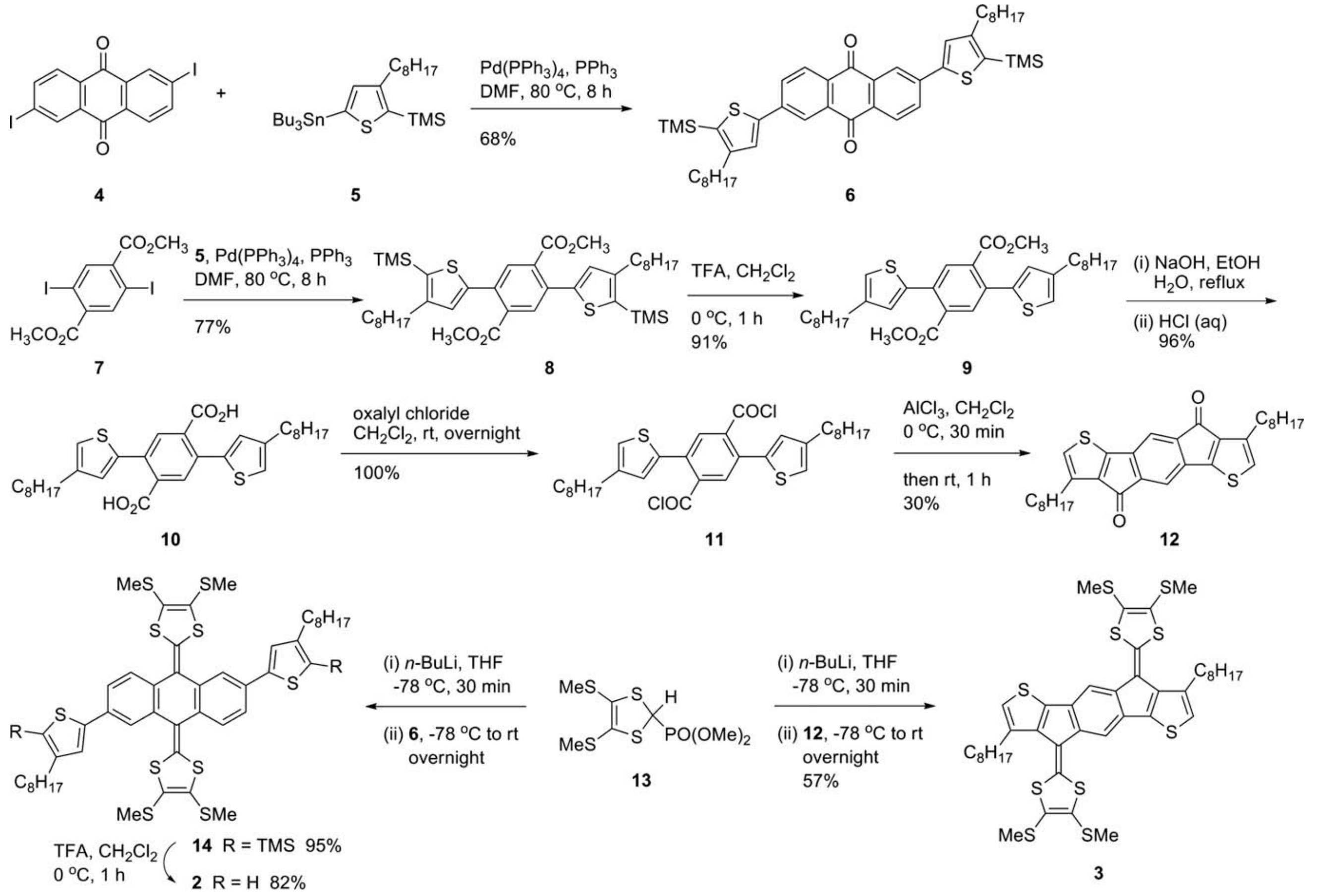

Scheme 1. Synthesis of thiophene–exTTF–thiophene triads **2** and **3**.

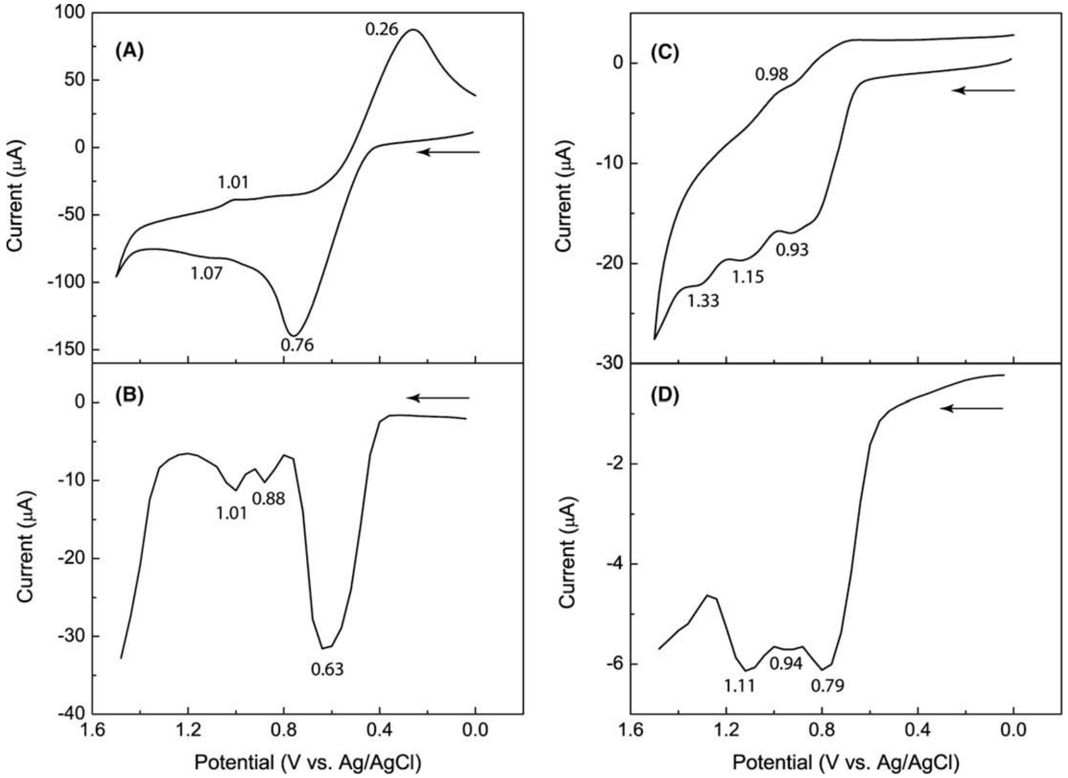

Figure 1. (A) Cyclic voltammogram of **2** (2.1 mM). (B) Differential pulse voltammogram of **2**. (C) Cyclic voltammogram of **3** (2.3 mM). (D) Differential pulse voltammogram of **3**. CV experimental conditions: electrolyte: Bu_4NPF_6 (0.1 M); working: glassy carbon; counter: Pt; reference: Ag/AgCl; scan rate: 100 mV/s. DPV experimental conditions: step: 4 mV; pulse width: 250 mV; period: 200 ms.

The synthesis of exTTF–thiophene triads **2** and **3** is outlined in Scheme 1. 2,6-Diiodoanthraquinone **4**[28] and thienylstannane **5** were subjected to a Stille coupling under the catalysis of Pd(0), affording ketone **6**, which is a key precursor to compound **2**. Upon a Horner–Wittig reaction with the phosphonate ylide generated in situ from compound **13**,[28–30] ketone **6** was converted into exTTF–thiophene **14** in a high yield of 95%. Treatment of **14** with TFA removed the TMS groups, giving the desired product **2**. The presence of *n*-octyl groups on the thiophene units during the synthesis of **2** was essential as they conferred satisfactory solubility to the intermediates and the product.

The synthesis of exTTF–thiophene **3** requires a key precursor, ketone **12**, the preparation of which was implemented following the synthetic route reported by Ng and co-workers.[31,32] It began with a Stille coupling between compound **5** and diiodoarene **7**, which gave compound **8** in 77% yield. Removal of the TMS groups in **8** by TFA yielded compound **9**, which was then subjected to saponification and chlorination to form acyl chloride **11**. Compound **11** underwent a twofold intramolecular Friedel–Crafts cyclization to form the desired ketone precursor **12**. With **12** in hand, a Horner–Wittig reaction was executed to furnish exTTF–thiophene hybrid **3** in 57% yield.

Molecular structures of compounds **2** and **3** were characterized by IR, NMR, and MS analyses,[33] while their electrochemical redox properties were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. Figure 1 illustrates the voltammograms measured in $CHCl_3/CH_3CN$ (4:1, v/v) at room temperature.

In Figure 1A, a prominent pair of redox waves (E^1_{pa} = 0.76 V, E^1_{pc} = 0.26 V) is clearly seen, which can be attributed to a simultaneous two-electron transfer at the central TTFAQ unit, leading to the formation of dication of **2**. The nature of this redox wave pair is quasi-reversible, which is in line with the typical redox behavior of TTFAQ.[34] In addition to this redox couple, two weak current peaks (E^2_{pa} = 1.07 V, E^1_{pc} = 1.01 V) are discernible in the CV of **2**. The DPV of **2** (Fig. 1B) shows the presence of a significant oxidation peak at 0.63 V followed up by two weak peaks at 0.88 and 1.01 V in the course of anodic scan. The two oxidation processes at relatively higher voltages can be explained by that the formed $[\mathbf{2}]^{2+}$ species, to some extent, might have yielded electrochemical byproducts which were subjected to further oxidation.

In the cyclic voltammogram of **3** (Fig. 1C), there are three anodic waves observable at 0.93, 1.15, and 1.33 V, along with a barely noticeable cathodic wave at 0.98 V. The first oxidation presumably leads to the formation of dication of **3**. However, in notable contrast to the CV of **2**, the redox pattern displayed by **3** is completely irreversible. The irreversibility is likely due to an EC mechanism, which results in the decomposition of $[\mathbf{3}]^{2+}$ at high voltage. The DPV of **3** shows three oxidation peaks when scanned anodically from 0 to 1.5 V (see Fig. 1D). This result agrees with its CV data, suggesting the formation of multiple electrochemical products in anodic scan. Compared with compound **2**, compound **3** has higher first oxidation potential, indicating that **3** is a weaker electron donor than **2**. For both compounds **2** and **3**, no indication of the occurrence of electropolymerization was observed from repetitive CV

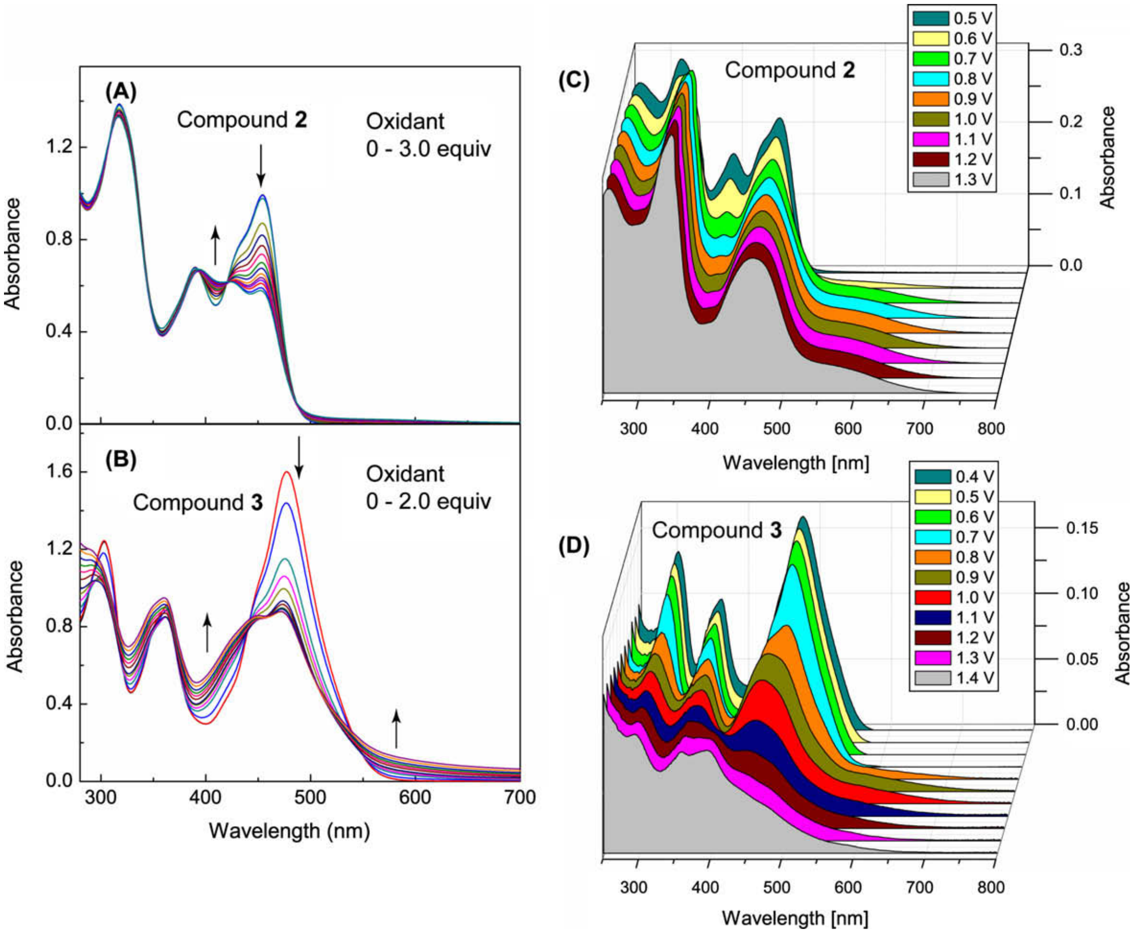

Figure 2. UV–vis spectroscopic changes accompanying: (A) oxidative titration of **2** (3.6 μM). (B) Oxidative titration of **3** (3.3 μM). (C) Controlled-potential oxidation of **2**. (D) Controlled-potential oxidation of **3**. Experimental conditions of spectroelectrochemistry: electrolyte: Bu_4NPF_6 (0.1 M); working: Pt mesh; counter: Pt wire; reference: Ag/AgCl.

scan experiments. In fact, the voltammograms were virtually unchanged after more than 10 cycles of scans. The inability of **2** and **3** to undergo electropolymerization can be rationalized as follows: the exTTF units play a dominating role in oxidation processes, such that the thienyl moieties are not able to form suitable radical cations for electropolymerization.[26]

To investigate the electronic properties of compounds **2** and **3** in neutral and oxidized forms, oxidative UV–vis titration and spectroelectrochemistry measurements were conducted on their $CHCl_3$ solutions (see Fig. 2). In Figure 2A, compound **2** shows three UV–vis absorption bands at 453, 390, and 317 nm in neutral state. Upon titration with an oxidant, $PhI(OAc)_2/CF_3SO_3H$ (note that 1 M equiv of the oxidant theoretically consumes two moles of electrons),[27,29] up to 3.0 M equiv, the absorption peak at 453 nm is observed to steadily decrease in intensity, while the other two peaks show rather insignificant change. An isosbestic point can be clearly seen at 419 nm. Similar UV–vis spectroscopic changes can be observed in Figure 2C, wherein compound **2** is subjected to controlled-potential oxidation in a 1 mm quartz cuvette. These results indicate that a two-species equilibrium, presumably between **2** and $[\mathbf{2}]^{2+}$, is formed during the oxidation.

Compound **3** shows absorption bands at 475, 357, and 301 nm in its UV–vis profile (see Fig. 2B). Upon addition of oxidant up to 2.0 M equiv, the peak at 475 nm decreases considerably. In the meantime, an absorption tail from ca. 550 to 750 nm increases appreciably, the origin of which is assigned to $[\mathbf{3}]^{2+}$. There are two isosbestic points at 538 and 441 nm observed during the titration of oxidant from 0 to 1.0 M equiv, and these two isosbestic points drift slightly when the amount of oxidant is further increased. More significant drift of isosbestic points can be seen in the spectroelectrochemical measurements when the applied voltage is greater than 1.0 V (Fig. 2D). The drift of isosbestic points is also accompanied by decreasing absorption tail from 550 to 750 nm, which substantiates the EC mechanism elicited from voltammetric analysis.

In summary, we have successfully developed synthetic routes to two thiophene–exTTF hybrid systems **2** and **3**. Electrochemical and electronic absorption properties were elucidated by voltammetric techniques in combination with UV–vis spectroscopic analysis. Efforts toward electropolymerization of **2** and **3** have not been successful; however, this barrier is envisaged to be circumvented by incorporation of oligothiophenes to the design motif[26] or through a Ni-catalyzed polymerization[35] of the brominated products of **2** and **3** in our future work. In this vein, further investigations on thiophene–exTTF triads **2** and **3** as well as their analogues are worthwhile and should lead to appealing new electronic materials.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.09.150.

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33. *Characterization data for compound* **2**: IR (neat): 2921, 2851, 1638, 1617, 1558, 1530, 825, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.55 (d, J = 7.99 Hz, 2H), 7.53 (d, J = 8.05 Hz, 2H), 7.21 (s, 2H), 6.90 (s, 2H), 2.64 (t, J = 7.65 Hz, 4H), 2.41 (s, 6H), 2.40 (s, 6H), 1.66 (m, 4H), 1.40–1.25 (m, 20H), 0.89 (t, J = 6.76 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 143.9, 135.5, 133.7, 133.1, 132.0, 126.4, 126.3, 126.2, 125.2, 123.7, 123.6, 122.9, 120.2, 32.3, 31.1, 30.9, 29.9, 29.8, 29.7, 23.1, 19.6, 19.5, 14.6; HR-EIMS (+eV) m/z calcd for $C_{48}H_{56}S_{10}$ 952.1589, found 952.1589 $[M]^+$. *Characterization data for compound* **3**: Mp 158–160 °C; IR (neat) 2941, 2878, 1560, 1507, 1474, 1337 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 2H), 6.84 (s, 2H), 3.08 (t, J = 7.73 Hz, 4H), 2.57 (s, 6H), 2.52 (s, 6H), 1.68 (m, 4H), 1.41 (m, 4H), 1.36–1.24 (m, 20H), 0.88 (t, J = 6.85 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 140.5, 137.4, 137.3, 136.8, 132.1, 129.8, 128.1, 122.5, 121.0, 114.1, 33.0, 32.3, 32.0, 30.0, 29.84, 29.79, 23.1, 19.9, 19.7, 14.5; HR-CIMS (+eV) m/z calcd for $C_{42}H_{50}S_{10}$ 874.1120, found 875.1230 $[M+H]^+$.
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