Semiconducting Oligo-(Aryleneethynylene)s with Coplanarity of Main Chain and Tetrathiafulvalene (TTF) Side Chains: Synthesis, Self-Assembly, and Conductive Properties

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Full Paper

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Two oligo-(aryleneethynylene)s, with coplanarity of main chain and tetrathiafulvalene (TTF) side chains, have been prepared and characterized. The X-ray diffractions (XRDs) show that their \( \pi \)-extended coplanar backbones can form continuous \( \pi \)-stacking. For the two oligomers, one stacks in the inter-digitation packing mode; another stacks in the end-to-end packing mode. Cyclic voltammetries reveal that the two oligomers have almost the same reversible electroactive properties. The TTF units of the two oligomers can be oxidized to TTF\(^{1+} \) by Fe(bpy)\(_3\)(PF\(_6\))\(_3\) (bpy = 2,2'-bipyridine). The band gaps, deduced from UV-Vis absorption spectra, are 1.92 and 2.03 eV, respectively. The conductivities of the two oligomers are \( 1 \times 10^{-5} \) and \( 6 \times 10^{-8} \) S \( \cdot \) cm\(^{-1} \) at room temperature. The charge transfer (CT) complexes of the oligomers and tetracyanoquinodimethane (TCNQ) exhibit higher conductivity up to 0.2 S \( \cdot \) cm\(^{-1} \).

**Introduction**

Since the discovery of high conductivity in doped polyacetylene samples three decades ago,\(^{[1]} \) \( \pi \)-conjugated polymers have attracted great interest for their unique electronic properties.\(^{[2,3]} \) Because the electronic properties of conjugated polymers sensitively depend on their molecular structures, a lot of conjugated polymers with different main chains and various substituents have been synthesized for different applications.\(^{[4,5]} \) In addition, tetrathiafulvalene (TTF) and its derivatives are well-known for their unique electron-donating property and reversible electroactivity.
They were often used in the metallic charge transfer (CT) complexes as the donors.\cite{6-8} So the concept of combining TTF with linear \(\pi\)-conjugated polymers offers exciting potentialities to develop original organic conducting materials.\cite{9} From the viewpoint of polymer physical properties, polymers are well known for their good film-forming property. The association of TTF units with linear \(\pi\)-conjugated polymers could overcome the brittle and unprocessable properties of the CT complexes.\cite{10-12} Moreover, for the conjugated polymers with TTF units, a charge conducting path can be formed not only along the main chains of the polymers via \(\pi\)-conjugation, the self-assembly regular stacking of TTF units might also form another conducting pathway via inter-molecular \(\pi\)-orbital overlap.\cite{9-13} Furthermore, the TTF polymer constitutes a highly polarizable species due to the large number of sulfur atoms in the structure. Thus, the extended conjugation could decrease the intra-molecular Coulomb repulsive energy between the donor units, and enhance intra-molecular and inter-stack interactions and further enhance conductivity of these materials.\cite{10,14}

There are many reports about preparing the conjugated polymers with TTF units either in the main chains or in the side chains.\cite{10,15} For some TTF polymers, the strong propensity of TTFs to self-assemble into regular \(\pi\)-stacking is an interesting approach for indirectly controlling the long-range order of the conjugated chains. However, for most of the reported TTF polymers, the TTF units and the polymer skeletons can give rise to a lot of possible conformations. Especially, for the polymers with TTF side chains, it is difficult to achieve the coplanarity of main chains and TTF side chains, so the whole molecules couldn’t form continuous stacking.\cite{15} Recently, we preliminary report a novel oligo-(p-aryleneethynylene) with coplanarity of main chain and TTF side chains, in which the \(\pi\)-conjugated TTF units attach to the planar main chain by the conjugated phenazine rings.\cite{16} As expected, the \(\pi\)-extended coplanar backbones of the oligomer could form continuous stacking in the solid state. If tetracyanoquinodimethane (TCNQ) is added to the TTF polymers, the CT between the TTF units and TCNQ will make the conducting pathway of the TTF units’ stacking become completely through, and the conductivity of the polymer will increase a lot. As a part of the continuous work, two oligomers were synthesized. The CT complexes of the two oligomers and TCNQ were also obtained. Herein we describe the preparation, self-assembly, and electroactive characterization of the two oligomers. The conductive properties of the oligomers and the complexes are also discussed.

### Experimental Part

#### Measurements

\(^1\)H NMR spectra were recorded on a Bruker AC-300 Spectrometer. Mass spectra (MS) were recorded using a Thermofinnigan LCQ Advantage mass spectrometer. Elemental analyses were performed on a Thermo Electron FLASH/EA 1112 instrument. Gel permeation chromatography (GPC) analysis was conducted on Polymer Lab PL-220 using polystyrene as standard. FT-IR spectra were recorded on Bruck Vector-22 spectrometer. Thermogravimetric analysis (TGA) measurements were performed on a TA instrument SDT-TG Q600 under nitrogen atmosphere at a heating rate of \(10^\circ\text{C} \cdot \text{min}^{-1}\). Differential scanning calorimetry (DSC) measurements were recorded on a TA instrument DSC-2910 under an atmosphere of \(N_2\) at a heating rate of \(10^\circ\text{C} \cdot \text{min}^{-1}\). X-ray diffraction (XRD) were performed with a Rigaku X-ray diffractometer (D/max-2500). UV-Vis spectra were recorded on a JASCO-V570 spectrometer. Cyclic voltammetry (CV) measurements were performed on a LK98B II Microcomputer-based Electrochemical Analyze at room temperature with a three-electrode cell in a solution of \(Bu_4\)NPF\(_6\) (0.1 M) in acetonitrile at a scanning rate of 100 mV \cdot s\(^{-1}\). A platinum wire was used as a counter electrode, and an Ag/AgNO\(_3\) electrode was used as a reference electrode. After measurement the reference electrode was calibrated with ferrocene (Fc) and the potential axis was corrected to Fc/Fc\(^+\).

The conductivities of the oligomers were conducted on a computer controlled Keithley 2400 source measure unit. Electron paramagnetic resonance (EPR) studies were performed with a Bruker EMX-6/1 spectrometer.

#### Materials

Unless stated otherwise, all chemicals and reagents were purchased reagent-grade and used without further purification. Air and/or water-sensitive reactions were conducted under nitrogen using dry, freshly distilled solvents. The synthesis of 5,6-diamino-2-[4,5-bis(alkylthio)-1,3-dithiole-2-ylidene]benzo[d]-1,3-dithiolates (3\(_a\), 3\(_b\)), 2,7-diiodophenantherene-9,10-dione (4), 1,4-diethylibenzene (6), 1,4-bis[dodecylxoylo]-2,5-diethylibenzene (7) and Fe(bpy)\(_3\)(PF\(_6\))\(_3\) (bpy = 2,2’-bipyridine) were prepared according to the literature procedures.\cite{16-21}

#### Monomer Synthesis

4',5'-Bis(dodecylthio)tetra(thiaphenalenyl)2,7-diiodenedibenzo[a,c]phenazine (5\(_a\))

The mixture of compound 3\(_a\) (0.343 g, 0.5 mmol) and 4 (0.23 g, 0.5 mmol) in 60 mL ethanol was refluxed for 3 h under \(N_2\) and protected from light. After filtration, the precipitate was collected. By following similar procedure above, 4 and 3\(_b\) were used to give 5\(_b\) as a deep blue solid (yield 70%). \(^1\)H NMR (300 MHz, \(\text{CDCl}_3\)) \(\delta = 9.30\)
Polymer Synthesis

Oligomer P1-tetrathiafulvalene (P1-TTF)

Disopropylamine (2 mL) was added to a mixture of compound 5a (0.111 g, 0.1 mmol), Pd(PPh3)4 (0.012 g, 0.01 mmol) and CuI (0.002 g, 0.01 mmol) in 30 mL THF under an argon atmosphere. The mixture was refluxed for 48 h. After being cooled to room temperature, the solid was collected by filtration and washed with a lot of methanol, and dried under vacuum (yield: 88%).

Chemical Oxidization of P1-tetrathiafulvalene and P2-tetrathiafulvalene

Excess of solid Fe(bpy)3(PF6)3 was added to the solutions of P1-TTF, P2-TTF in o-dichlorobenzene under N2, respectively. The mixtures were stirred at room temperature under dark for 1 h. After filtration, the P1-TTF<sup>1+</sup> and P2-TTF<sup>1+</sup> solutions were obtained, which were immediately used in the EPR and UV-Vis spectra measurements.

Results and Discussion

Synthesis and Characterizations

The synthetic pathway for the monomers 5<sub>a</sub>, 5<sub>b</sub> is outlined in Scheme 1. The starting materials 1, 2<sub>a</sub>, 2<sub>b</sub>, 4, and monomers 6, 7 were synthesized according to the literatures. All compounds were purified by chromatographic separation and have been fully characterized.

The oligomers P1-TTF, P2-TTF were synthesized through Pd-Cu-catalyzed Sonogashira coupling reactions (Scheme 2). After purification and drying, deep-blue P1-TTF and brown P2-TTF were obtained. P2-TTF is insoluble in tetrahydrofuran (THF) and CHCl<sub>3</sub>, but it could be dissolved in o-dichlorobenzene and has a relatively good solubility in 1,2,4-trichlorobenzene. P2-TTF has a very good solubility in common solvents (such as THF, CHCl<sub>3</sub>, o-dichlorobenzene, 1,2,4-trichlorobenzene, etc.). Very interestingly, we found that after the P2-TTF THF solution was kept in the dark for...
five days, there was a solid appearing in the solution. Confirmed by the $^1$H NMR spectrum, the precipitated solid was still P$_2$-TTF, and it could be re-dissolved in THF by ultrasonification. Since the main chain and TTF side chains are coplanar, we suspect that the molecules of P$_2$-TTF realigned slowly in the solution, and the coplanar $\pi$-extended backbone of P$_2$-TTF formed the good $\pi$-$\pi$ stacking, which result in the precipitation. This was confirmed by XRD patterns of P$_2$-TTF (see below). The average molecular weights of P$_1$-TTF and P$_2$-TTF were estimated by GPC with polystyrene as calibration standard. Because of the poor solubility of P$_1$-TTF in THF, 1,2,4-trichlorobenzene was chose as the eluent for P$_1$-TTF. Data from GPC and the yields are presented in Table 1.

The thermal stabilities of the two oligomers were investigated by TGA under inert nitrogen atmosphere. The TGA analysis revealed that the onset temperatures of the weight loss of P$_1$-TTF, P$_2$-TTF were all about 230 °C. It is obvious that both oligomers exhibit good thermal stability. DSC measurements of the oligomers were also conducted in the inert nitrogen atmosphere. There is no thermal transition observed below 230 °C for the two oligomers, indicating that their molecules are so rigid that the $T_g$ may be higher than the decomposition temperature.

**Electroactive Properties**

The electroactive properties of the two oligomers were investigated by CV. Figure 1 shows the cyclic voltammograms of their thin-films on a Pt electrode in a 0.1 M Bu$_4$NPF$_6$ acetonitrile solution. The results of the electrochemical measurements are summarized in Table 2. Obviously, the two oligomers have almost the same redox behavior. The two quasi-reversible single-electron oxidation waves at about 0.5 and 0.77 V are the typical redox peaks of the TTF unit, corresponding to its $E_{\text{ox1}}$ and $E_{\text{ox2}}$.[22–24] The first oxidation is attributed to the bis(thioether)-substituted half-unit of TTF, whilst the second arises from the phenazinedithiol TTF moiety. This assignment is justified by the electron withdrawing effect of the TTF-fused phenazine.[23] Moreover, the two oligomers have a quasi-reversible reduction process at about $-1.76$ V, which could be assigned to the reduction of the electron-withdrawing phenazine moieties and $\equiv C\equiv$ groups.[24–26] The redox
properties of P1-TTF and P2-TTF are similar to that of other similar TTF-fused donor-acceptor (D-A) ensembles. For all the redox processes, their anodic/cathodic peak separation (ΔE_p) should ideally be zero for a surface reaction. However, the measured ΔE_p values are about 160 mV. Roncali and coworkers[27] suggested the reason was that the redox processes were partially limited by charge and/or mass transformation in the polymer film.

Chemical oxidations of P1-TTF and P2-TTF were performed by Fe(bpy)_3(PF_6)_3. After addition of Fe(bpy)_3(PF_6)_3 to the solutions of two oligomers, a sharp signal with g = 2.005 showed up in the EPR spectra (Figure 2). They are in line with the characteristic EPR signal of the cation radical TTF/C_15^-1. Thus we believe that the oxidation of P1-TTF and P2-TTF generated the radical cations, P1-TTF/C_15^-1_R, and P2-TTF/C_15^-1_R, as outlined in Figure 2. At the same time, these also indicate that the first oxidation wave of P1-TTF and that of P2-TTF in their CVs happen on the TTF units of the two oligomers.

Table 2. Electrochemical characteristics of P1-TTF and P2-TTF.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>n-doping</th>
<th>p-doping (first process)</th>
<th>p-doping (second process)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1-TTF</td>
<td>-1.76</td>
<td>0.50</td>
<td>0.77</td>
</tr>
<tr>
<td>P2-TTF</td>
<td>-1.76</td>
<td>0.50</td>
<td>0.77</td>
</tr>
</tbody>
</table>

a) E_ox and E_red values are the peak values.

Optical Properties

The UV-Vis absorption spectra of P1-TTF, P2-TTF solutions in o-dichlorobenzene and those of their films on quartz plate are shown in Figure 3. In the visible region, P1-TTF has one absorption peak at 530 nm and a shoulder peak at ≈380 nm, and P2-TTF has two absorption peaks, which are located at 520 and 400 nm, respectively. The absorptions in the visible region corresponds to the π-π* transition of the conjugated backbone.[29,30] In comparison with the absorption spectra of the oligomers solutions, those of their films in the visible region become bathochromically shifted by about 20 nm. This long wavelength band shift indicates the formation of J-aggregates. There exists the offset stacking between the polymer backbones in the films,[31] which is consistent with the XRD results (see below). The optical band-gaps (E^opt_g) of P1-TTF, P2-TTF are 1.92 and 2.03 eV, estimated from their absorption edges.

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X-Ray Diffraction

X-ray diffraction (XRD) patterns of P1-TTF and P2-TTF are shown in Figure 4. Note that the XRD for P2-TTF before and
length of the rigid portion of the side chain is about 15 Å. Adding the short butyl chains, the total length of the side chain is about 19 Å, which also approves that P_2-TTF take the end-to-end packing mode.

Since the effective cross-section of the alkyl chains is about S = 20 Å², their hexagon-like aggregation give about d = 4.2 Å. This value is in agreement with what we observed for the peak at d_3 from the oligomers, as shown in Figure 4. The value of d_4 is very close to the π-stacking distances of reported TTF-fused D-A organic compounds, which were observed from their single crystal structures. So d_4 is considered to be the offset stacking

![Figure 5. Schematic representation of an inter-digitation packing mode of P_2-TTF in solid state.](image)

Figure 5.
distance between the coplanar backbones. Obviously, the two oligomers formed ordered structures in the solid state due to the stacking of the π-extended coplanar backbones and the crystallinity of the long alkyl chains.

Moreover, since the peaks of P1-TTF are much sharper than that of P2-TTF, P1-TTF molecules are believed to pack in a better ordered structure in the solid state. The long alkoxy chains on the main chain of P2-TTF might inhibit more the π-stacking of the backbones. But for P2-TTF, by slowly realigning in THF solution, the amorphous phase diminished a lot, as observed from the enhanced XRD peaks in Figure 4.

Conductivity Measurements

Because of the good continuous stacking of P1-TTF and P2-TTF, we expect that the two oligomers have good electronic properties. So the conductivity measurements by four-probe methods were performed on compress pellets of the two oligomers at room temperature. The conductivities of the powders of P1-TTF and P2-TTF are 1 × 10^{-8} and 6 × 10^{-8} S · cm^{-1}. Obviously, P2-TTF has poorer conductivity than P1-TTF. However, by slowly re-precipitating from its THF solution, the conductivity of P2-TTF increases to 4 × 10^{-8} S · cm^{-1}. P2-TTF has better ordered-structure after realigning in the solution, which results in the improvement of the conductivity.

The two oligomers reacted with electron acceptor TCNQ in 1,2,4-trichlorobenzene solutions to give CT adducts. Among these adducts, the CT complex of P1-TTF/TCNQ (1:2 molar ratio of TTF units/TCNQ) shows the maximum conductivity of 0.2 S · cm^{-1} as measured on the compressed pellet of the complex. The conductivity of P2-TTF/TCNQ (1:2 molar ratio of TTF units/TCNQ) is 0.07 S · cm^{-1}. The interesting results should come from the increase in dimensionality of the conduction process. For the neutral TTF-fused oligomers, charge conduction is only along the conjugated backbone. However, when TTF units form the CT complex with TCNQ, the π-orbital overlap stacking of TTF units also become the conducting pathway.

Conclusion

To summarize, we have prepared two novel TTF-fused oligo(aryleneethynylene)s with coplanarity of main chain and TTF side chains. They reveal good reversible electroactivity. The coplanarity of the main chain and the donor TTF side chains ensure that the oligomers can form continuous π-stacking in the solid state and show semiconductivity. So when the oligomers formed the CT complexes with TCNQ, the π-orbital overlap stacking of TTF units also become the conducting pathway. The continuous stacking and reversible electroactive properties indicate that this kind of TTF-fused oligomers may become a promising active material for organic electronic applications.

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