



RAPID COMMUNICATION

Synthesis and characterization of tetrathiafulvalene- σ -thiophene dyads

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Abstract. Three Tetrathiafulvalene (TTF)-assembled thiophene molecules were synthesized with the different linkages of σ bridge *via* Steglich esterification and classical SN_2 reaction. The results of UV and CV showed the different substitution effects existed in the new molecules formed by the molecule assembling. Among the new molecules, TTF-Th-2 (TTF-methylene-thiophene), linkage in the shortest σ bridge, exhibited the most obvious substitution effects. Meanwhile, the result of theoretical calculation indicated that TTF-Th-2 exhibited lower bandgap with the evident electron transfer in the LUMO energy level.

Keywords. Tetrathiafulvalene; thiophene; synthesis; substitution effects; theoretical calculation.

1. Introduction

As the most significant classes of conjugated sulfur-rich system, thiophene (Th) derivatives have been extensively applied to organic light-emitting diodes (OLEDs),^{1,2} organic field-effect transistors (OFETs)^{3,4} and electrochemical devices (ECD).^{5,6} Especially for 3-substituted or 3,4-disubstituted thiophene derivatives exhibit not only the lower oxidation potential but also smaller bandgap. The classical Th derivatives like 3-hexylthiophene and 3,4-ethylenedioxythiophene have been reported for extraordinary photoelectric performances due to the modified group effects.^{7,8} Therefore, the donor- π -Th and donor- σ -Th system were synthesized for achieving rapid developments in both theoretical calculation and photoelectric performance.^{9–12}

TTF derivatives, another class of electroactive materials, have been widely used as a functional group with lower oxidation potential and excellent electron donor capability. Ascribing to the unique reversible redox properties, TTF moiety can be combined with other optoelectronic molecules as the application in fluorescent sensors,¹³ dye sensitive solar cells,¹⁴ and

thermoelectric materials.¹⁵ In order to explore the improved performance of TTF moiety, various TTF derivatives were synthesized with the combination of different functional groups.^{16,17}

Thus, the combination of TTF and Th moieties for exploring the novel performances aroused great attention for numbers of researchers.^{18–20} Herein, we report three novel TTF- σ -Th molecules with the different linkage of σ bridge, which synthesized by Steglich esterification and classic SN_2 reaction. The results of UV-Vis spectra and CV exhibited the different substitution effects after the combination of TTF and Th moieties. Also, theoretical calculation showed the distribution of electron cloud in each TTF- σ -Th molecule.

2. Experimental

2.1 General

¹H-NMR and ¹³C-NMR were obtained on a Bruker AVANCE 400 instrument (TMS), EI-MS was recorded on

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an HP-5898 spectrometer (EI); UV-Vis absorption spectra were measured with USB2000+ miniature UV spectrometer (Ocean Optics, USA). Cyclic Voltammetry was carried out with CHI 620E electrochemical workstation (Shanghai Chenhua Instruments Co. Ltd., China). The geometries and electronic structures of TTF- σ -Th were simulated by means of hybrid density functional theory (DFT) method, at the B3LYP/6-311g (d, p) level of theory with basis set performed on Gaussian 09 program package.

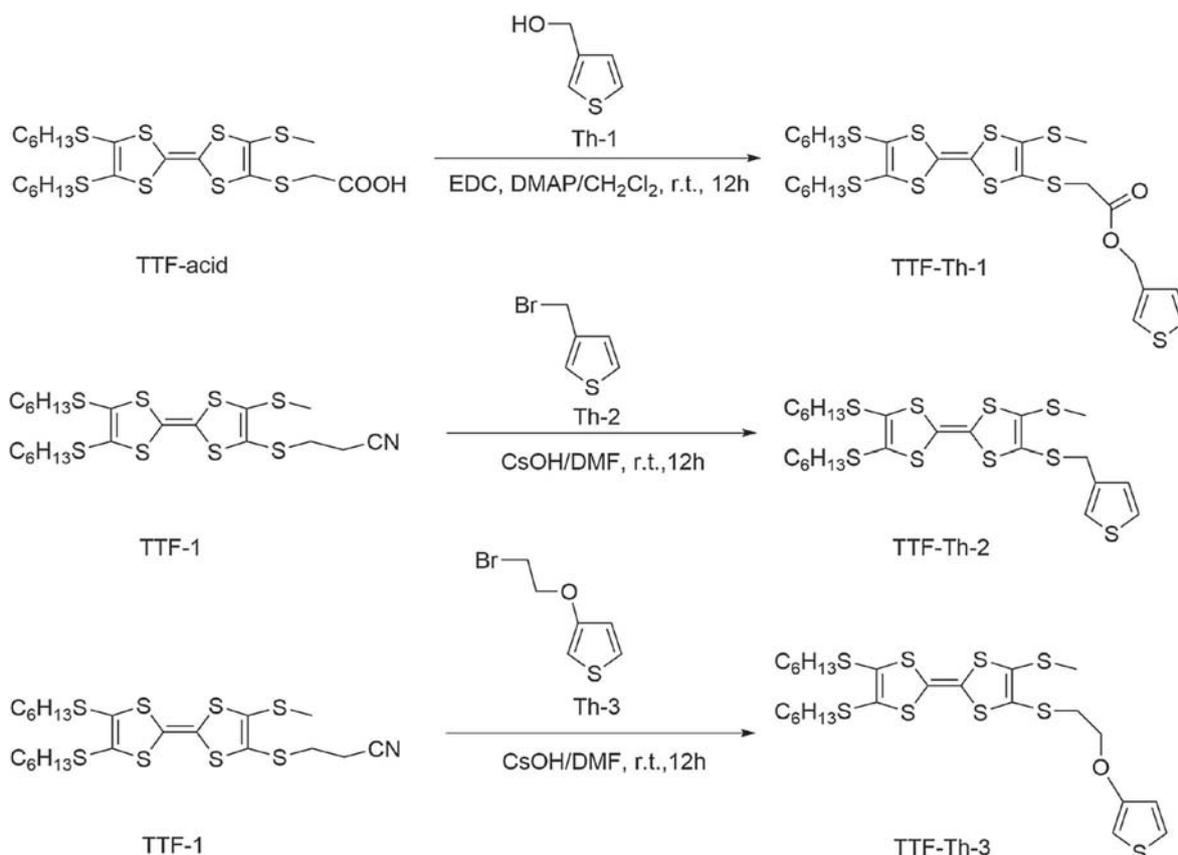
2.2 Synthesis

The synthesis of TTF- σ -Th molecules was outlined in Scheme 1. Applying the processability of cyanoethyl or carboxylic group in each TTF derivatives, TTF-Th-1 was synthesized *via* Steglich esterification, while TTF-Th-2 and TTF-Th-3 were synthesized by the classic SN₂ reaction (Scheme 1).

2.2a Synthesis of TTF-Th-1: TTF-acid (286 mg, 0.5 mmol), DMAP (92 mg, 0.75 mmol), EDC (144 mg, 0.75 mmol), and 3-Thienylmethanol (Th-1) (69 mg, 0.6 mmol) was simultaneously dissolved into the fresh distilled DCM (30 mL). After 12 h stirring in refluxed temperature, the mixture solution changed from dark yellow

to dark red. Washed by 0.1 M HCl (50 mL), water (50 mL) and saturated brine (50 mL) in turn, the mixture was desiccated by anhydrous sodium sulfate overnight. Removing the solvent through the vacuum, the residue was purified by column chromatography on silica gel (PE / DCM = 2:1), the orange oil (252 mg, 73.4%) was collected in the second section.

2.2b Synthesis of TTF-Th-2: After the dissolution of the precursor TTF-1 (284 mg, 0.5 mmol) in desiccative DMF (30 mL), solution of CsOH•H₂O (101 mg, 0.6 mmol) in methanol (5 mL) was slowly added to the mixture. Under 30 min of stirring in room temperature, the mixture solution was gradually changed from bright red to dark red. Subsequently, the solution of 3-thienylbromide (Th-2) (97 mg, 0.55 mmol) in methanol (5 mL) was slowly added to the dark red solution. With the reaction of 12 h at room temperature, the dark red solution changed back to bright red. Quenching through water, the mixture was extracted by ethyl acetate (60 mL). Washed with water (2 × 50 mL) and saturated in brine (50 mL) in turn, the mixture was desiccated by anhydrous sodium sulfate overnight. Removing the solvent through the vacuum, the residue was purified by column chromatography on silica gel (PE), orange oil (268 mg, 87.6%) and was collected in the first section.



Scheme 1. Synthesis of TTF- σ -Th Molecules.

2.2c Synthesis of TTF-Th-3: After the dissolution of the precursor TTF-1 (226 mg, 0.4 mmol) in desiccative DMF (30 mL), solution of CsOH•H₂O (84 mg, 0.5 mmol) in methanol (5 mL) was slowly added to the mixture. Under 30 min of stirring in room temperature, the mixture solution was gradually changed from bright red to dark red. Subsequently, the solution of 3-(2-bromoethoxy) thiophene (Th-3) (124 mg, 0.6 mmol) in methanol (5 mL) was slowly added to the dark red solution. With the reaction of 12 h at room temperature, the dark red solution changed back to bright red. Quenching through water, the mixture was extracted by ethyl acetate (60 mL). Washed by water (2 × 50 mL) and saturated brine (50 mL) in turn, the mixture was desiccated by anhydrous sodium sulfate overnight. Removing the solvent through the vacuum, the residue was purified by column chromatography on silica gel (PE / DCM = 5:1), orange oil (223 mg, 87.4%) was collected in the first section.

3. Results and Discussions

3.1 UV spectra of TTF-σ-Th molecules

The absorption ranges of Th moiety in Th-1, Th-2 and Th-3 were from 230 nm to 260 nm, which was the characteristic absorption of Th ring. All TTF derivatives displayed a B-band absorption from 230 nm to 350 nm, which indicated the π-π* transitions of TTF moiety. The absorption curves of TTF-acid and TTF-Th-1 (Figure 1a) displayed three similar absorption peaks at 263 nm, 311 nm, and 332 nm, respectively, with one new peak at 236 nm ($\epsilon = 1.98 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) for TTF-Th-1, due to the effects of the combination of TTF and Th moieties.

There were obvious changes between TTF-Th-2 and TTF-1 (Figure 1b). Compared to the absorption of TTF-1 with three absorption peaks, TTF-Th-2 showed the distinguished Th moiety absorption peak at 239 nm ($\epsilon = 2.43 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) with the

disappearance of the absorption peak at 262 nm and 311 nm.

TTF-Th-3 and TTF-1 (Figure 1c) exhibited both similar absorption peaks at 311 nm and 332 nm with a slight difference in the absorbance. However, due to the impact from Th moiety, the absorption peak of TTF-Th-3 generated a slight blue shift at 257 nm ($\epsilon = 1.77 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$).

Although slight shifting of absorption peaks were observed in TTF-Th-1 and TTF-Th-3, there is no new significant peak generated. On the contrary, absorption curves of TTF-Th-2 generated obvious absorption changes for showing the absorption peak generated at 239 nm and absorption peaking diminished at 262 nm and 311 nm, ascribing to the shortest σ bridge (methylene) between the TTF and Th moieties. All the absorption curves of TTF-σ-Th molecules exhibited the assembly absorption effects with characteristic peaks of TTF and Th moieties. However, when the TTF and Th moieties were linked with methylene, the substitution effects would be generated to induce the evident absorption peak changes.

3.2 Cyclic voltammetry (CV) of TTF-σ-Th molecules

The CV measurement used a three-electrode system, platinum electrode as the working electrode and counter electrode, Ag/AgCl electrode as the reference electrode, n-Bu₄NPF₆ (10⁻¹ mol / L) as the supporting electrolyte. The initial voltage and ending voltage of each CV process are 0 V and 2 V, at a scan rate of 100 mv/s.

The CV curves of three TTF-σ-Th molecules together with TTF and Th moieties are given in Figure 2. The oxidation potentials of **TTF-acid**, **TTF-1**, **TTF-Th-1**, **TTF-Th-2** and **TTF-Th-3** were listed in Table 1.

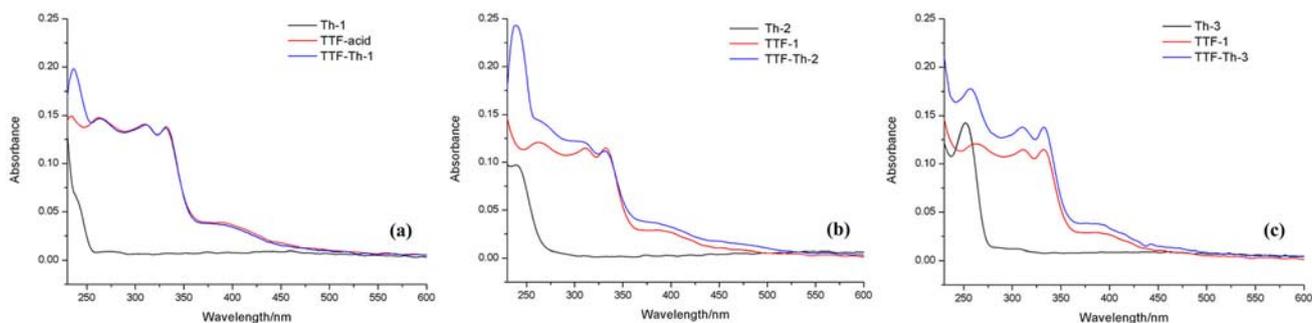


Figure 1. (a) UV absorption spectra of **TTF-Th-1**, **TTF-acid** and **Th-1** (b) UV absorption spectra of **TTF-Th-2**, **TTF-1** and **Th-2** (c) UV absorption spectra of **TTF-Th-3**, **TTF-1** and **Th-3**; 10⁻⁵ M in DCM.

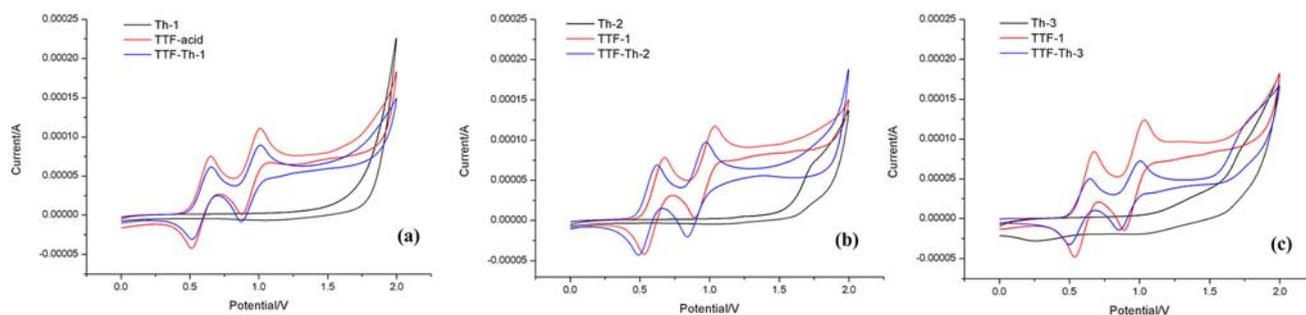


Figure 2. (a) CV curves of **TTF-Th-1**, **TTF-acid**, and **Th-1**; (b) CV curves of **TTF-Th-2**, **TTF-1**, and **Th-2**; (c) CV curves of **TTF-Th-3**, **TTF-1**, and **Th-3**, 10^{-3} M in DCM.

Table 1. Oxidation Potentials of **TTF-acid**, **TTF-1**, **TTF-Th-1**, **TTF-Th-2** and **TTF-Th-3**.

Molecule	$E_{\text{ox1}}^{1/2}$ (V)	$E_{\text{ox2}}^{1/2}$ (V)
TTF-acid	0.650	1.010
TTF-1	0.675	1.030
TTF-Th-1	0.655	1.010
TTF-Th-2	0.620	0.970
TTF-Th-3	0.647	1.002

Table 2. Oxidation Potential Difference of **TTF-Th-1/TTF-acid**, **TTF-Th-2/TTF-1** and **TTF-Th-3/TTF-1**.

Compounds	$\Delta E_{\text{ox1}}^{1/2}$ (mV)	$\Delta E_{\text{ox2}}^{1/2}$ (mV)
TTF-Th-1/TTF-acid	5	0
TTF-Th-2/TTF-1	55	60
TTF-Th-3/TTF-1	28	28

To easily understand the assembly effects between TTF and Th moieties, the oxidation potentials differences of **TTF-Th-1/TTF-acid**, **TTF-Th-2/TTF-1**, **TTF-Th-3/TTF-1** were listed in Table 2 as well.

As shown in Figure 2, TTF-acid, TTF-Th-1, TTF-1, TTF-Th-2, and TTF-Th-3 displayed two reversible peaks, corresponding to the successive oxidation process of TTF moiety from neutral state to radical cation states, i.e., TTF^+ and TTF^{2+} , while Th moiety showed no evident oxidation or reduction process in setting voltage ranges. The oxidation peaks of the TTF moieties in each TTF- σ -Th molecule were moved to the lower potential (Table 1), which indicated the TTF moiety in TTF- σ -Th molecules were easier to be oxidized after linking with Th moiety. Meanwhile, the

data in Table 2 indicated that TTF-Th-2/TTF-1 exhibited the maximum oxidation potential difference ($\Delta E_{\text{ox1}}^{1/2} = 55$ mV, $\Delta E_{\text{ox2}}^{1/2} = 60$ mV) compared to the other TTF derivatives groups.

The phenomenon illustrated the electrochemical process mainly occurred on the TTF moiety rather than Th moiety. The easier oxidation of TTF moiety in TTF- σ -Th indicated the higher electron cloud density on TTF moiety due to the substituent effects of Th with different σ bridge. Methylene σ bridge between the TTF and Th moieties in TTF-Th-2 reduced the electron-withdrawing effect of cyanoethyl group in TTF-1, so that the electron back to TTF moiety. Contrarily, TTF-Th-1, linking with ester bond between TTF and Th moieties, showed no evident oxidation potential decline due to the weaker electron-withdrawing effects of the ester bond.

3.3 Theoretical calculations of TTF- σ -Th molecules

The HOMO and LUMO simulation of TTF- σ -Th molecules were given in the Figures 3–5, where atom colors were exhibited in white, gray, red, and yellow corresponding to H, C, O, and S. The values of calculated energy levels were listed in Table 3.

It is evidently observed that electron clouds are mainly distributed in the TTF moiety at the HOMO energy level, due to the stronger electron donor properties of TTF moiety. However, at the LUMO energy level, TTF- σ -Th molecules showed the extremely different electron distribution when electron clouds activated. Compared to the slight electron density transferring in TTF-Th-1 and TTF-Th-3, the evident transferring of the electron density generated from TTF moiety into Th moiety (TTF-Th-2) in LUMO energy level. Moreover, as shown in Table 3, the results of the calculated energy levels indicated that lower bandgap existed in TTF-Th-2 ($E_g =$

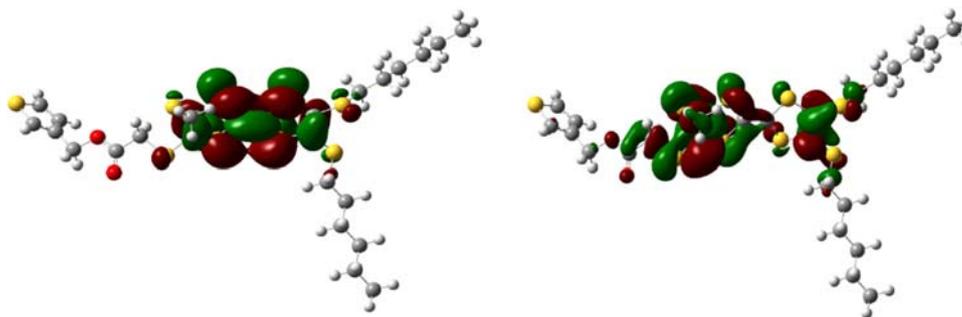


Figure 3. HOMO (left) LUMO (right) simulation of **TTF-Th-1**.

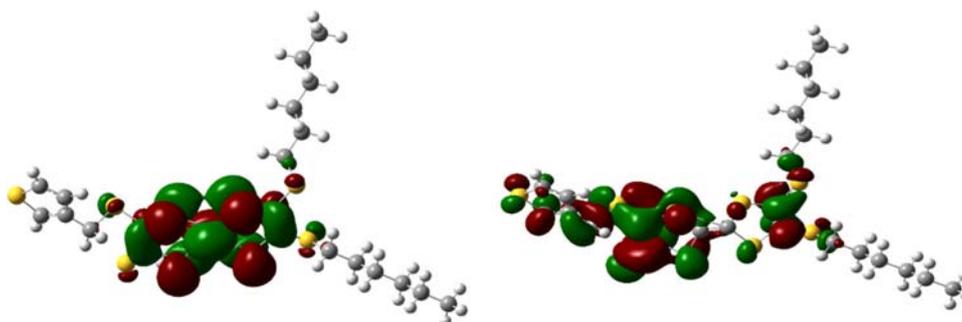


Figure 4. HOMO (left) LUMO (right) simulation of **TTF-Th-2**.

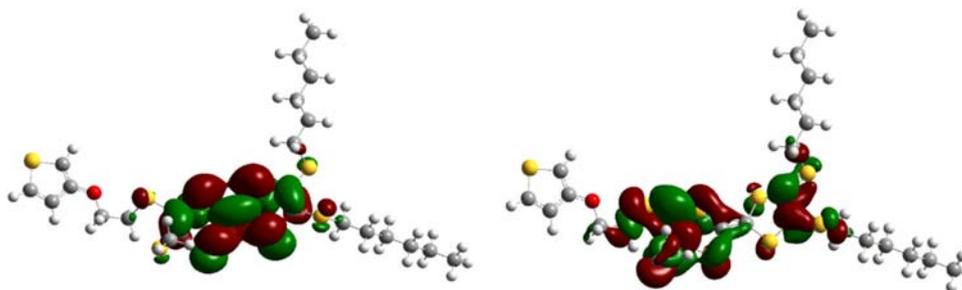


Figure 5. HOMO (left) LUMO (right) simulation of **TTF-Th-3**.

Table 3. Calculated Energy Levels of TTF- σ -Th Molecules by B3LYP/6-311g (d,p).

Molecule	HOMO(eV)	LUMO(eV)	Eg(eV)
TTF-Th-1	-4.9810	-1.3818	3.5992
TTF-Th-2	-4.9688	-1.4106	3.5582
TTF-Th-3	-4.9957	-1.3899	3.6058

3.5582 eV), compared to TTF-Th-1 ($E_g = 3.5992$ eV) and TTF-Th-3 ($E_g = 3.6058$ eV). The lower bandgap implied the lesser energy required for the energy level transition.

4. Conclusions

In summary, the results of $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and EI-MS confirmed that three novel TTF- σ -Th molecules with different σ bridges were successfully prepared by Steglich esterification and classic $\text{S}_{\text{N}}2$ reaction, respectively. The effects of UV and CV indicated that different substitution effects existed in TTF- σ -Th molecules. Also, the theoretical calculation and energy level simulation effects showed the different electron transfer phenomenon and bandgap in TTF- σ -Th molecules. Compared to TTF-Th-1 and TTF-Th-3, TTF-Th-2 exhibited the most evident substitution effects and lower bandgap with the most

evident electron transfer in LUMO energy level, which attributed to the methylene bridge between TTF and Th moieties.

Supplementary Information (SI)

The detailed $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and EI-MS of TTF- σ -Th molecules are outlined in SI (Figures S1–S9). The full CV scanning window of TTF derivatives was provided in the SI (Figure S10–S14). The experimental energy level was provided in the SI (Table S1).

Acknowledgements

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