Synthesis and Characterization of Tetrathiafulvalene-Based Smectic Liquid Crystals

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Abstract

A series of new symmetric TTF derivatives were designed and synthesized. This facile synthetic method provides an opportunity to prepare TTF-based LC candidates. This series of compounds exhibited smectic A phase based on coplanar TTF core. One of the LC compounds was used as a semiconductor layer to fabricate OTFT.

1. Introduction

π-conjugated liquid crystalline (LC) materials have attracted a lot of attentions as promising charge-transfer organic candidates in optoelectronic devices. First, alkyl chains of LC molecules will increase solubility in common organic solvents, and make them solution-processable, which is technically favorable. In addition, the LC materials almost don't suffer from the boundary effects, which are inevitable drawbacks for the charge transportation in the crystalline materials.

TTF and its derivatives of crystalline materials have been extensively studied, and proved to be a promising molecular building block for organic optoelectronic applications due to special electronic properties and molecular structure. TTF-based LC materials are thought to be more promising semiconductor materials owing to the solution processibility, self-assembling property and possibility of alignment. On the other hand, the study of TTF-based liquid crystal is limited due to the synthetic difficulties as well as less possibility of liquid crystal formation due to the complicated π-π stacking structure.

2. Experimental

Materials:

General method to compound 3:

The mixture of compound 1 (1.33 g, 5.0 mmol), n-alkyl acid (10.5 mmol), DMAP (0.12 g, 1.0 mmol), and DCC (2.38 g, 11.5 mmol) and dried CH_2Cl_2 (50 mL) were stirred at room temperature for 12 h. The solvent was removed by rotating evaporation. The yellow solid was obtained by column chromatography with mixture of PE and MC as the eluant.

Compound **3a**: This compound was prepared according to the general procedure and obtained as yellow solid (0.70g, 27.0 %). 1H-NMR: 7.77 (2H, q), 7.58 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.54-1.25 (16H, m), 0.92 (6H, t). 13C-NMR: 210.49, 170.48, 136.28, 131.38, 127.68, 126.80, 121.24, 33.93, 31.63, 29.14, 28.87, 25.03, 22.60, 14.06. UV: 273.36 nm, 329.47nm, 372.65nm. HRMS calcd for $C_{27}H_{34}O_4S_3$ 518.16, found $(M + H)^+$ 519.15. Anal. Calcd for $C_{27}H_{34}O_4S_3$: C, 62.5; H, 6.6; S, 18.5. Found: 63.4%, 6.7%, 18.8%.

Compound **3b**: This compound was prepared according to the general procedure and obtained as yellow crystals (1.45g, 50.4%). 1H-NMR: 7.77 (2H, q), 7.59 (2H, q), 2.76 (4H, t), 1.87 (4H, f), 1.54-1.22 (24H, m), 0.89 (6H, t). 13C-NMR: 210.45, 170.48, 136.27, 131.38, 127.67, 126.80, 121.24, 33.93, 31.85, 29.40, 29.25, 29.21, 29.19, 25.03, 22.66, 14.10 UV: 272.39nm, 330.44nm, 373.60nm. HRMS calcd for $C_{31}H_{42}O_4S_3$ 574.22, found $(M + H)^+$ 575.24. Anal. Calcd for $C_{31}H_{42}O_4S_3$: C, 64.8; H, 7.4; S, 16.7. Found: 64.9%, 7.4%, 16.8%.

Compound **3c**: This compound was prepared according to the general procedure and obtained as yellow solid (1.75g, 55.4%). 1H-NMR: 7.76 (2H, q), 7.58 (2H, q), 2.75 (4H, t), 1.86 (4H, f), 1.54-1.20 (32H, m), 0.89 (6H, t). 13C-NMR: 210.47, 170.47, 136.27, 131.39, 127.67, 126.78, 121.25, 33.94, 31.91, 29.60, 29.45, 29.33, 29.22, 25.03, 22.69, 14.11. UV:

272.39nm, 329.47nm, 373.60nm. HRMS calcd for $C_{35}H_{50}O_4S_3$ 630.28, found $(M + H)^+$ 631.29. Anal. Calcd for $C_{35}H_{50}O_4S_3$: C, 66.6; H, 8.0; S, 15.2. Found: 66.7%, 8.0%, 15.4%.

Compound **3d**: This compound was prepared according to the general procedure and obtained as yellow solid (2.02g, 58.8%). 1H-NMR: 7.76 (2H, q), 7.57 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.54-1.16 (40H, m), 0.88 (6H, t). 13C-NMR: 210.47, 170.48, 136.27, 131.39, 127.68, 126.81, 121.25, 33.94, 31.93, 29.68, 29.65, 29.60, 29.46, 29.36, 29.22, 29.20, 25.03, 22.69, 14.11. UV: 272.38nm, 329.47nm, 372.65nm. HRMS calcd for $C_{39}H_{58}O_4S_3$ 686.35, found $(M + H)^+$ 687.33. Anal. Calcd for $C_{39}H_{58}O_4S_3$: C, 68.2; H, 8.5; S, 14.0. Found: 68.3%, 8.6%, 14.1%.

*General method to compound **4**:*

Mercury (II) acetate (2.5 eq) was added to a solution of compound **3** in CH_2Cl_2. After stirring at room temperature for 1 h, the mixture became white from orange. The mixture was filtered through a celite, and the filtrate was washed with water (3 x 100 ml), dried with Na_2SO_4, the crude product was obtained after evaporating the solvent, which was purified by column chromatography.

Compound **4a**: This compound was prepared according to the general procedure and obtained as yellow solid (0.42g, 86.7%), 1H-NMR: 7.74 (2H, q), 7.57 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.54-1.25 (16H, m), 0.92 (6H, t). 13C-NMR: 187.50, 170.57, 138.43, 127.46, 126.42, 123.88, 120.99, 33.95, 31.63, 29.14, 28.88, 25.03, 22.59, 14.05. UV: 248.04nm, 303.42nm. HRMS calcd for $C_{27}H_{34}O_5S_2$ 502.18, found $(M + H)^+$ 503.21. Anal. Calcd for $C_{27}H_{34}O_5S_2$: C, 64.5; H, 6.8; S, 12.8. Found: 64.6%, 6.7%, 12.8%.

Compound **4b**: This compound was prepared according to the general procedure and obtained as yellow solid (1.25g, 95.3%), 1H-NMR: 7.74 (2H, q), 7.56 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.53-1.21 (24H, m), 0.89 (6H, t). 13C-NMR: 187.47, 170.55, 138.43, 127.45, 126.42, 123.89, 120.99, 33.95, 31.84, 29.40, 29.25, 29.22, 29.18, 25.03, 22.66, 14.09. UV: 249.01nm, 303.42nm. HRMS calcd for $C_{31}H_{42}O_5S_2$ 558.25, found $(M + H)^+$ 559.30. Anal. Calcd for $C_{31}H_{42}O_5S_2$: C, 66.6; H, 7.6; S, 11.5. Found: 66.7%, 7.6%, 11.6%.

Compound **4c**: This compound was prepared according to the general procedure and obtained as yellow solid (1.60g, 99.5%), 1H-NMR: 7.73 (2H, q), 7.56 (2H, q), 2.75 (4H, t), 1.86 (4H, f), 1.53-1.19 (32H, m), 0.89 (6H, t). 13C-NMR: 187.54, 170.54, 138.45, 127.45, 126.43, 123.90, 121.00, 33.96, 31.91, 29.60, 29.45, 29.33, 29.19, 25.04, 22.68, 14.10. UV: 249.01nm, 303.42nm. HRMS calcd for $C_{35}H_{50}O_5S_2$ 614.31, found $(M + H)^+$ 615.27. Anal. Calcd for $C_{35}H_{50}O_5S_2$: C, 68.4; H, 8.2; S, 10.4. Found: 68.5%, 8.3%, 10.6%.

Compound **4d:** This compound was prepared according to the general procedure and obtained as yellow solid (1.21g, 93.9%), 1H-NMR: 7.74 (2H, q), 7.57 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.54-1.18 (40H, m), 0.88 (6H, t). 13C-NMR: 187.45, 170.54, 138.43, 127.44, 126.42, 123.88, 120.99, 33.95, 31.91, 29.67, 29.64, 29.60, 29.45, 29.34, 29.22, 29.18, 25.03, 22.68, 14.10. UV: 248.04nm, 303.42nm. HRMS calcd for $C_{39}H_{58}O_5S_2$ 670.37, found $(M + H)^+$ 671.35. Anal. Calcd for $C_{39}H_{58}O_5S_2$: C, 69.8; H, 8.7; S, 9.6. Found: 69.6%, 8.8%, 9.8%.

*General method to compound **5**:*

Compound **4** were added to triethyl phosphate, the mixture was heated to 120 ºC for 4 h. After the solution was cooled, the precipitate was filtered, washed with PE and methanol, respectively, and dried. Finally, organe solid was reprecipitated by drop the cholorform solution to PE, filtered and dried.

Compound **5a**: This compound was prepared according to the general procedure and obtained as dark orange solid (0.17g 58.5%). 1H-NMR: 7.60 (4H, q), 7.47 (4H, q), 2.76 (8H, t), 1.89 (8H, f), 1.56-1.26 (32H, m), 0.93 (12H, t). 13C-NMR: 170.47, 137.25, 128.85, 126.89, 126.87, 120.80, 33.98, 31.70, 29.18, 28.92, 25.03, 22.63, 14.10. UV: 247.1nm, 315.0nm, 385.1nm. (1/10: 431.6nm) HRMS calcd for $C_{54}H_{68}O_8S_4$ 972.38, found $(M + H)^+$ 972.38. Anal. Calcd for $C_{54}H_{68}O_8S_4$: C, 66.6; H, 7.0; S, 13.2. Found: 66.6%, 7.1%, 13.2%.

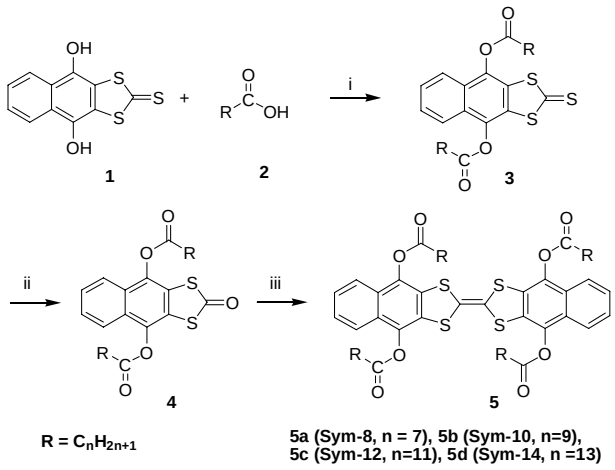
Compound **5b**: This compound was prepared according to the general procedure and obtained as orange solid (1.00g, 89.4%).1H-NMR: 7.59 (4H, q), 7.48 (4H, q), 2.76 (8H, t), 1.90 (8H, f), 1.59-1.23 (48H, m), 0.90 (12H, t). 13C-NMR: 170.46, 137.25, 128.84, 126.89, 126.86, 120.80, 34.00, 31.88, 29.47, 29.30, 29.28, 29.25, 25.05, 22.70, 14.11. UV: 247.1nm, 315.0nm, 383.2nm. (1/10: 432.6nm) HRMS calcd for $C_{62}H_{84}O_8S_4$ 1084.50, found $(M + H)^+$ 1084.59. Anal. Calcd for $C_{62}H_{84}O_8S_4$: C, 68.6; H, 7.8; S, 11.8. Found: 68.8%, 7.8%, 11.7%.

Compound **5c**: This compound was prepared according to the general procedure and obtained as yellow soft solid (1.26g, 85.1%). 1H-NMR: 7.60 (4H, q), 7.46 (4H, q), 2.76 (8H, t), 1.90 (8H, f), 1.60-1.21 (64H, m), 0.88 (12H, t). 13C-NMR: 170.47, 137.25, 128.80, 126.90, 126.86, 120.79, 34.00, 31.93, 29.65, 29.54, 29.37, 29.29, 29.26, 25.06, 22.69, 14.10. UV: 247.1nm, 316.0 nm, 383.7nm. (1/10: 432.6nm)

HRMS calcd for $C_{70}H_{100}O_8S_4$ 1196.63, found (M + H)$^+$ 1196.73. Anal. Calcd for $C_{70}H_{100}O_8S_4$: C, 70.2; H, 8.4; S, 10.7. Found: 70.5%, 8.5%, 10.3%.

Compound **5d**: This compound was prepared according to the general procedure and obtained as soft yellow solid (0.45g, 78.1%). 1H-NMR: 7.62 (4H, q), 7.47 (4Hn q), 2.77 (8H, t), 1.91 (8H, f), 1.54-1.20 (80H, m), 0.89 (12H, t). 13C-NMR: 170.43, 137.25, 128.84, 126.90, 126.86, 120.81, 34.01, 31.93, 29.72, 29.69, 29.66, 29.54, 29.37, 29.30, 29.26, 25.06, 22.68, 14.10. UV: 247.1nm, 315.0nm, 384.5nm. (1/10: 430.6 nm) HRMS calcd for $C_{78}H_{116}O_8S_4$ 1308.76, found (M + H)$^+$ 1309.26. Anal. Calcd for $C_{78}H_{116}O_8S_4$: C, 71.5; H, 8.9; S, 9.8. Found: 71.7%, 9.0%, 9.9%.

TTF-based LC compounds were synthesized via 3-step reactions: 1,3-dicyclohexyl carbodiimide (DCC)/4-dimethylaminopyridine (DMAP) esterification reaction, Hg(OAc)2 oxidation, and a



Scheme 1. Synthesis Route of Symmetric TTF

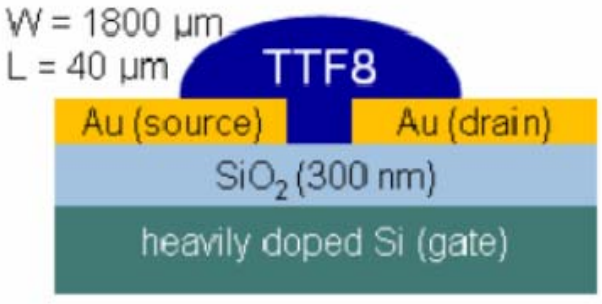
phosphate-induced cross-coupling reaction. The detailed synthetic procedures are shown in Scheme 1. The cross-coupling reaction of 4 at 120 °C for 4 h yields symmetric mesogenic core structure. The yield is 58.5, 89.4, 85.1 and 78.1% for 5a to 5d, respectively.

3. Results and discussion

The phase structural evolutions of TTF derivatives from 5a to 5d were investigated by the combined techniques of differential scanning calorimetry (DSC), polarized optical microscopy (POM) and 1D wide angle X-ray diffraction (WAXD). Compounds 5a-5d show LC phases below the isotropic temperature (Ti). There are three phase transitions for compounds 5a and 5b, while 5c and 5d exhibit two ordered phases: a LC phase and a crystal phase. The melting point decreases from 184 to 165 °C by increasing the number of carbons in the flexible alkyl chains.

The POM images of the compounds 5a-5d display similar texture in their LC phase. These LC phases form macroscopic domains with a single crystal like uniform molecular orientation in contrast to asymmetric TTF series. This can result in more favorable charge carrier mobility as expected. It is interesting that lamellar domains formed at LC phase of 5a during first cooling at the rate of 2 °C/min, the size of lamellar domain is up to millimeter and the uniform birefringence indicates homogeneous molecular alignment. However, the crack formed when the temperature is down to crystalline phase. The generation of cracks could be due to the asymmetric shrinkage during the crystallization process.

To investigate the structure of LC phase and to assign the phase type during the transitions, 1D WAXD experimental results at different temperatures were combined with those of POM. 1D WAXD pattern data of 5a was shown in Figure 1. At 180°C, in the small-angle region of 1D WAXD of 5a, a sharp reflection peak at 2θ = 4.46° was detected, from which a d-spacing of 1.98 nm was estimated. The value corresponds to the spacing between the layers. Its second- and third-order reflections (1.98/n: n = 2 and 3) appeared at 1.00 and 0.67 nm, respectively. These X-ray reflections in the low angle region clearly indicate that 5a generate a layer structure and the diffused scattering halo in the wide-angle region at 22.28° (d-spacing = 0.40 nm) exhibits that the order in the layer is low similar to a liquid isotropic phase. Therefore, it was identified that this phase is SmA LC phase.



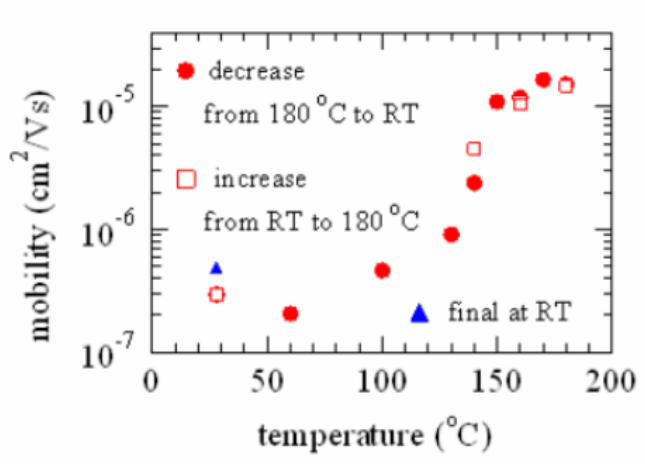


Figure 1. The OTFT structure (up) and the temperature dependent of mobility(down)

The field-effect measurement was carried out using bottom-contact thin film transistor (TFT) geometry. The compound 5a was chosen and allowed to prepare thin film on the prefabricated TFT structure by solution (0.5 wt% solution in chloroform) drop casting due to good solubility. Right after the evaporation of solvent, there is no field-effect transistor characteristics found for compound 5a at room temperature. This happened to polycrystalline film from solution drop casting, where the carrier mobilities are highly limited by domain boundary effect.34 The device was heated to 180 °C, and then cooled down to room temperature at 2 °C/min and measured at every 10 °C. Carrier mobilities were calculated from transfer characteristics following TFT equations in the linear regime.35 It was found that the device in the SmA phase shows that the charge mobility is about 10-5 cm2/Vs. The mobility suddenly decreases to 10-7 cm2/Vs during the phase transition from SmA to Cr2. There is no obvious change during the phase transition between Cr2 to Cr1. These results can be explained by observation of 1D WAXD and POM in different temperatures we mentioned before. In the SmA phase, compound 5a forms an uniform lamellar structure in a macroscopic domain, even bigger than the distance between source and drain. The FET characteristics can be found because of charge transport nature of compound 5a. When compound 5a transformed from SmA to Cr2 during cooling, the structures were shrinked asymmetrically in order to generate a tightly packed crystalline phase. This asymmetric shrinkage generates a mass of cracks during the phase transition, which was confirmed by POM observations. The decrease of mobility should directly relate with these cracks, which block the movement of charges from source to drain. The more cracks formed during the Cr2-Cr1 transition will not affect the mobility because the cracks generated during SmA-Cr2 transition are more than enough to disconnect the organic medium. The field-effect measurement during a subsequent heating process is in agreement with the results measured during a cooling process.

4. Summary

In summary, a series of new symmetric TTF derivatives were designed and synthesized. This facile synthesis method provide an opportunity to prepare TTF LC candidates by introducing various side chains through OH group of naphthalene rings. These symmetric TTF-based compounds exhibited SmA LC phase in addition to crystalline phases at lower temperatures. The morphology of the film can be controlled by thermal treatment or mechanical shearing, which allows us to form continuously well aligned domains. Compound 5a was used as semiconductor layer to fabricate OTFT by solution drop casting, which can be a promising temperature dependent OTFT device. Further study on stabilizing and the alignment of the LC phase is in progress.

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