Synthesis and Characterization of a Novel TTF Derivative

Lei Wang, Myong-Hoon Lee*
Department of Polymer Science and Technology, Chonbuk National University,
664-1 Dukjin, Chonju, Chonbuk 561-756, Korea
TEL: 82-63-270-2337, E-mail: mhlee2@chonbuk.ac.kr

Keywords : TTF, liquid crystals, semiconductor

Abstract

We report the syntheses and characterizations of a novel TTF derivative. To extend the mesogenic core, alkoxy naphthalenic group and short alkyl chains were introduced on either side of TTF unit, which results in asymmetric planar structure. TTF molecule is expected to show many interesting properties.

1. Introduction

Discotic liquid crystals (LCs) materials have attracted considerable attention as promising charge-transfer candidates. On one hand, the intermolecular p-orbital overlap within ordered one-dimensional columnar stacks of discotic of LCs can increase the carrier mobilites. On the other hand, some discotic and smectic liquid crystals can avoid "grain boundaris" effect, which orginates from molecular alignment in crystalline materials. Charge transport LCs materials can act as a new type of semiconductor used for field-effect transistors, organic light-emitting devices.

Since the first synthesis of tetrathiafulvalene (TTF) and the discovery of metallic conductivity of an organic charge transfer complex based on TTF and 7,7,8,8- tetracyanoquinodimethane, in particular the finding of the first organic supreconductor, studies of TTF derivatives and their analogues have received great attention. Various TTF derivatives were designed and synthesized for studies of organic conductors, and even organic superconductors, as well as for the preparation of a range of molecular materials. The p-p stacting and S··S interaction can shows high carrier mobilities. TTF based discotic liquid crystals are promising CT materials, however, until now, there are not many TTF based LCs were reported, and only one TTF based LCs used as semiconductor for OFET. Crystallization often happened in TTF systems because of strong intermolecular interactions between TTF cores, so an asymmetric TTF molecule is suitable for showing LC phase at lower temperature and wider range. We designed and synthesized a new TTF derivative.

2. Experimental

Compound 1:

i: Powdered K_2S (16.75 g,152 mmol) and CS_2 (7.5 mL, 125 mmol) were added to 40 mL DMF, respectively. After the mixture was stirred for 2 h at room temperature, the mixture was dark yellow. 2,3-dichloronaphthoquinone (14.2 g, 62.5 mmol) was added, and the mixture became dark red. After stirring for 30 min, a large amount of water was added to the reaction mixture, and then extraction with CH_2Cl_2. Combine CH_2Cl_2 solution, dried with Na_2SO_4 and partially evaporated. The product was precipitated by addition of methanol, and 11.2 g of red crystals was obtained by filtration. (Yield = 68%)

Compound 2:

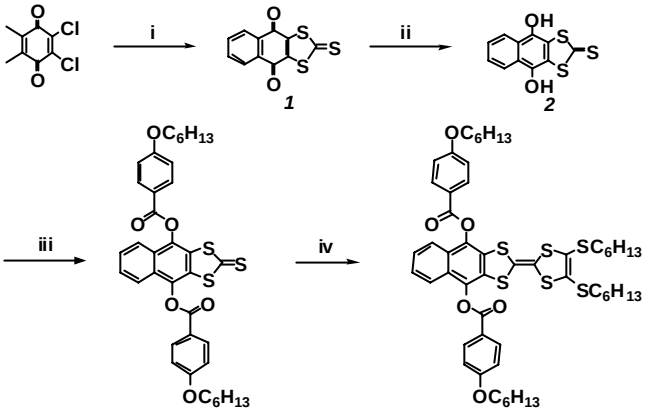
ii: Mixture of a organic solution of compound 1 (10 g, 37.8 mmol) and an aqueous solution of $Na_2S_2O_4$ (4% w/w, 400ml) was stirred for 30 min. The initial red solution became yellow, and the organic layer was washed with water for three times, dried with Na_2SO_4. The yellow powder (8.6 g) was obtained by rotating evaporation. (Yield = 84%)

Compound 3:

iii: The mixture of compound 2 (1.33 g, 5.0 mmol), 4-dodecyloxy-benzoic acid (3.2 g, 10.5 mmol), DMAP (1.2 g 10.0 mmol), p-toluenesulfonic acid (0.19 g, 5.0 mmol), and DCC (2.38 g, 11.5 mmol) and dry CH_2Cl_2 (50 mL) were stirred at room temperature for 12 h. The initial red mixture became orange. Filtration, and then the solvent was removed by rotating evaporation. The yellow solid (2.06 g) was obtained by column chromatography with PE: MC = 4:1 as the eluant. (Yield = 49%)

Compound 4:

iv: Compound 3d (0.50 g, 0.59 mmol) and 4,5-bis-hexylsulfanyl-[1,3]dithiolan-2-one (0.50 g, 1.42 mmol) were dissolved in 25 mL triethyl phosphate, the mixture was heated to 120 ºC for 4 h. After the solution was cooled down to the room temperature, The yellow precipitation came out, filtration, then column chromatography with PE: MC = 5:1 as the eluant was used for purification. The orange solid, 0.4 g was obtained. (Yield: 67%)



i: K_2S, CS_2, DMF. ii: $Na_2S_2O_4$. iii: DCC, DMAP, p-TsOH, 4-alkyloxy- benzoic acid. iv: 4,5-Bis-hexylsulfanyl-[1,3]dithiol-2-one, $P(OEt)_3$.

Scheme 1. synthesis route of TTF derivative.

3. Results and discussion

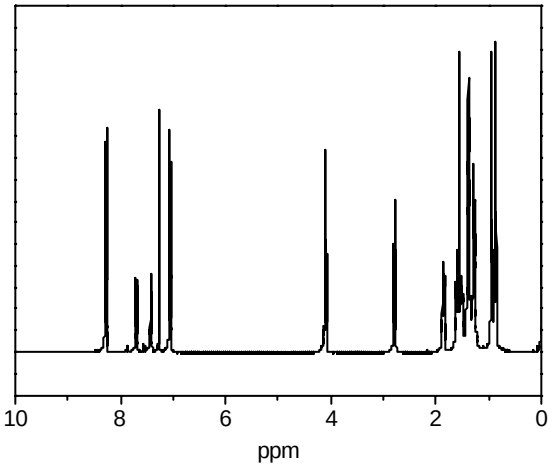


Figure 1: H1-NMR spectrum of compound 4, $CDCl_3$ as solvent.

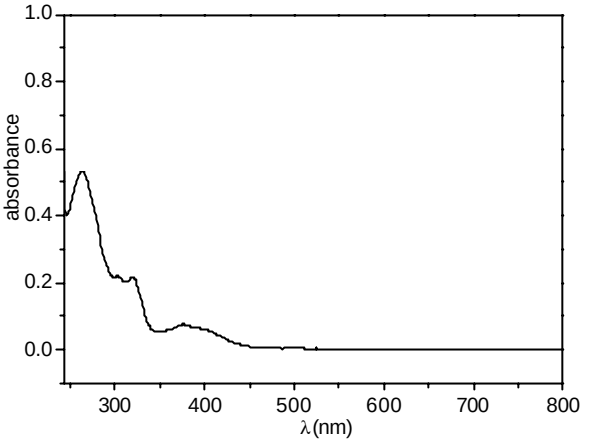


Figure 2: UV spectrum of compound 4, $CHCl_3$ as solvent.

The resulting TTF derivative was determined by 1H NMR, UV, FT-IR and DSC measurement. Figure 1 shows the NMR spectrum of 4: NMR ($CDCl_3$) d: 8.28 (m, 4H), 7.69 (m, 2H), 7.42 (m, 2H), 7.05 (m, 4H), 4.09 (t, 4H), 2.78 (t, 4H), 1.85 (m, 4H), 1.69-1.18 (m, 28H), 1.02-0.79 (m, 12H).

UV spectrum of the TTF derivative was studied in $CHCl_3$ solution, which was shown in Figure 2. there is a strong peak at around 263nm, and two peaks at 303nm, 319nm, respectively. At 376nm, there is a brand and weak absorbance.

Figure 3 is the IR spectrum of compound 4, which was measured by KBr pellet method: (KBr, cm^{-1}) 3446(m), 3064(w), 2920(s), 2857(s), 1731(s), 1607(s), 1576(s), 1509(s), 1466(s), 1414(w), 1393(w), 1365(w), 1311(w), 1247(s), 1152(s), 1078(s), 1046(s), 1003(s), 844(m), 759(s). The strong peak at 1731cm^{-1} proves that the C = O bond exists in the final compound 4. The four peaks 1607(s), 1576(s), 1509(s), 1466(s) are specific peaks of aromaticity, which can be further confirmed by 3064(w) peak (Ar - H).

The DSC was taken at N_2 atmosphere, and 10 ºC/min of heating and cooling rate. Figure 4 shows DSC diagram, there is only one melting point and one crystallizing point. Unfortunately, it is a crystal, not a liquid crystal we want. On the first heating, the compound 4 melted at 144 ºC, and it crystallized at 106 ºC on cooling.

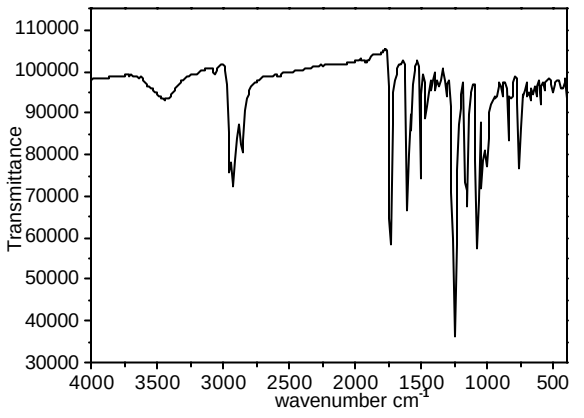


Figure 3: IR spectrum of compound 4, KBr(cm-1).

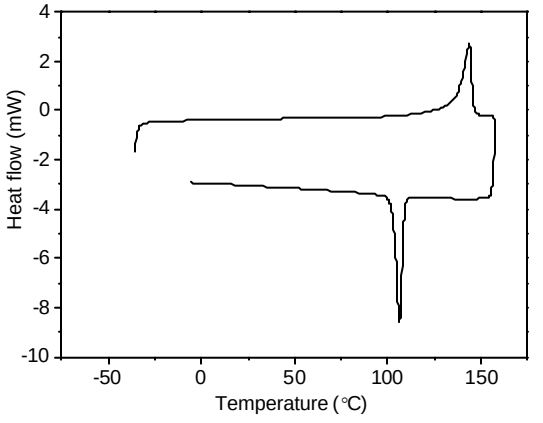


Figure 4: DSC diagram of compound 4. 10 ℃/min, N_2 atmosphere.

4. Summary

A new TTF derivative was designed and synthesized for liquid crystal candidate material. The characterization of the resulting compound 4 was performed by 1H-NMR, IR, UV, DSC. The DSC data indicate that compound 4 does not show any liquid crystal phases. Syntheses of TTF derivatives to search liquid crystals involving longer alkyl chains are on progress. Polymerizable functional groups will be introduced to this system for OTFT and TFT-LCD application. The arcrylate functional groups will be attached for further polymerization at the end of alkyl peripheral chains, which can make possible to fix the liquid crystal molecules in nematic or smectic states.

4. Acknowledgement.

This work was supported by grant No. R01-2004-000-10014-0 from the Basic Research program of the Korea Science & Engineering Foundation.

5. References

1. Y. Xu, S. Leng, C. Xue, R. Sun, J, Pan, J. Ford, and S. Jin, Angew. Chem. Int. Ed. 46, 1-5(2007).
2. H. Pninzbach, H. Berger, A. Luttringhaus, Angew. Chem. Int. Ed. Engl., 4, 436(1965).
3. J. Ferraris, D. O. Cowan, V. J.Walatka, H. J. Perlstein, J. Am. Chem. Soc. 95, 948(1973).
4. F. Dumur, N. Gautier, N. Gallego-Planas, Y. Sahin, E. Levillain, N. Mercier, and Pietrick Hudhomme, J. Org. Chem, 69, 2164-2177(2004).
5. R. Andreu, J. Garin, J. Orduna, J. Barbera, J. Serrano, T. Sierra, M. Salle and A. Gorgues Tetrahedron 54, 3895-3912(1998).