

# Syntheses and Characterization of Columnar Discotic Liquid Crystals Based on TTF Core for Organic Electronic Materials

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## Abstract

We report the first TTF compounds having columnar LC phase at room temperature. Based on the thermal, structural, and morphological observations, it was concluded that TTF derivative with long alkyl chains has highly ordered oblique columnar LC at room temperature. The new TTF derivatives have excellent oxidative stability which is desirable for a p-type (hole transport) materials.

## 1. Introduction

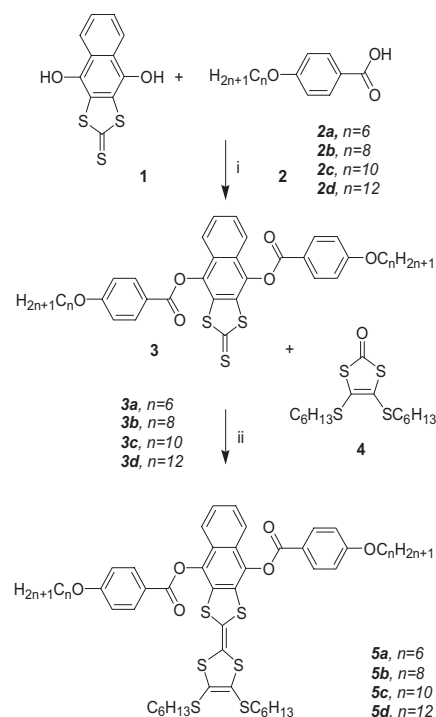
Among the various candidates of organic materials for optoelectronic applications,<sup>1-6</sup> tetrathiafulvalene (TTF) is one of the best candidates due to its excellent electron-donating properties. However, most researches about TTF and its derivatives have been focused on their crystalline phases. In order to enhance their electron mobility, it is necessary to control their structures and morphologies to get rid of grain boundaries between the domains and to obtain the macroscopically oriented single domain. One of the possible way to obtain a defect-free single crystal-like TTF domain is the columnar LC phase. Surprisingly, based on our best knowledge, there are only a few reports for the LC compounds based on TTF, and none of them shows LC phase at room temperature.<sup>7</sup> Additionally, because of the strong electron-donating property of TTF, its derivatives are usually sensitive to air and light, which is one of the main drawbacks of TTF for the practical applications. In order to overcome this barrier, electron-withdrawing groups can be introduced as to decrease its HOMO energy level, which results in the improved air/light stability.<sup>8</sup>

In this presentation, we report a new type of TTF derivatives **5a-5d** possessing columnar LC phases at room temperature, which are for the first time to our knowledge. In order to create TTF-based mesomorphic states, a series of 4-alkyloxybenzoic acid (**2**) with various alkyl chain lengths were

introduced to either side of TTF core. The electron withdrawing ester linkage was adopted to increase the air/light stability by decreasing HOMO levels of TTF derivatives.

## 2. Experiments

**Instruments:** The 1D WAXD experiments were conducted in the reflection mode of a Rigaku 12 kW rotating-anode X-ray (Cu K $\alpha$  radiation) generator coupled to a diffractometer. The cyclic voltammetry measurements were performed by Versa STAT3 of Princeton Applied Research in a solution of Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) in water-free dichloromethane with a scan rate of 50 mV/s at room temperature. A glass carbon



i: DCC, DMAP, p-TsOH, rt, CH<sub>2</sub>Cl<sub>2</sub>; ii: P(OEt)<sub>3</sub>, 120°C

Scheme 1. Synthetic route of TTF

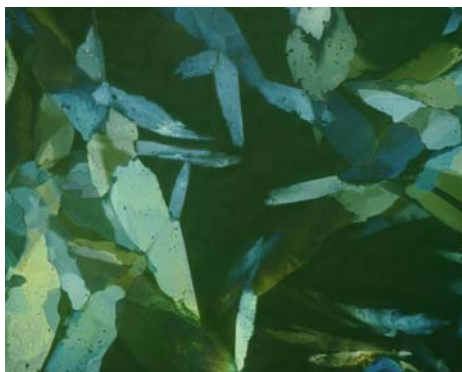


Fig. 1. POM image of **5d** at 95 °C.

electrode, a Ag/AgCl electrode and a platinum wire were used as a working electrode, a reference electrode and a counter electrode, respectively.

**Synthesis of compound 3:** Starting materials **1** and **2a-2d** were prepared according to the literatures.<sup>9,10</sup>

The mixture of compound **1** (1.33 g, 5.0 mmol), 4-alkoxy-benzoic acid (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 dried CH<sub>2</sub>Cl<sub>2</sub> (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 **3** was obtained as yellow solid (1.60 g, 47.4%).

### 3. Results and discussion

The syntheses of these liquid crystalline compounds were accomplished by 2-step reactions: an esterification reaction followed by a phosphate-induced cross-coupling reaction. The detailed synthetic procedures are shown in Scheme 1. The cross-coupling reaction of **3** with excess of **4** in P(OEt)<sub>3</sub> at 120 °C for 4 h yielded an asymmetric mesogenic core structure. Their chemical structures and purities were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, Fourier-transform infrared spectroscopy, elemental analyses and high-resolution mass spectrometry.

The phase structural evolutions of TTF derivatives from **5a** to **5d** were investigated by the combined techniques including differential scanning calorimetry (DSC), cross-polarized optical microscopy (POM) and 1D wide angle X-ray diffraction (WAXD). The DSC results are summarized in Table 1. The listed temperatures are the onset temperatures of the first cooling. Compounds **5a** and **5b** do not show any mesomorphic LC states, whereas the compounds **5c** and **5d** having longer chain lengths show LC phases below the isotropic temperature (*T<sub>i</sub>*). Especially, **5d**

**Table 1. Phase-transition temperature (°C) and enthalpies (kJ/mol) of TTF derivatives 5a-d determined by POM and DSC in the first cooling scan (cooling rate: 5 °C/min)**

Compound	Phase transition temperatures (onset) [°C] / transition enthalpies [kJ/mol]
<b>5a</b>	Cr 120/25.8 I
<b>5b</b>	Cr 93/43.1 I
<b>5c</b>	Cr 57/5.1 Col 96/39.1 I
<b>5d</b>	Cr 9/13.2 Col 96/25.7 I

Cr = Crystal, Col = Columnar phase, I = Isotropic phase, T = Temperature, E = Enthalpies

having the longest alkyl chain (*n* = 12) exhibited a LC phase in a wide temperature window between 9 and 96 °C, even below the room temperature. In the POM image (Fig. 1), a mosaic texture typical in columnar LC phase was observed. Based on the experimental results of POM observation and 1D WAXD measurement of **5d** at 95°C, it was identified that the phase is a highly ordered discotic columnar LC phase. The three Bragg reflections in the low angle region of 1D WAXD at  $2\theta = 2.57^\circ$ ,  $3.80^\circ$  and  $5.30^\circ$  allowed us to build a 2D *a\*b\** lattice based on the triangulation method. The highly ordered columnar phase perpendicular to the columnar long axis is considered to be oblique, which is common in LC compounds with asymmetric discotic mesogens.

Compound **5d** was mechanically sheared at 95°C, and the deformed morphology was observed under the POM. A macroscopically oriented single domain was obtained due to the alignment of LC molecules (Fig. 2). Furthermore, the onset temperature of *T<sub>i</sub>* and its heat of transition for **5c** and **5d** did not change

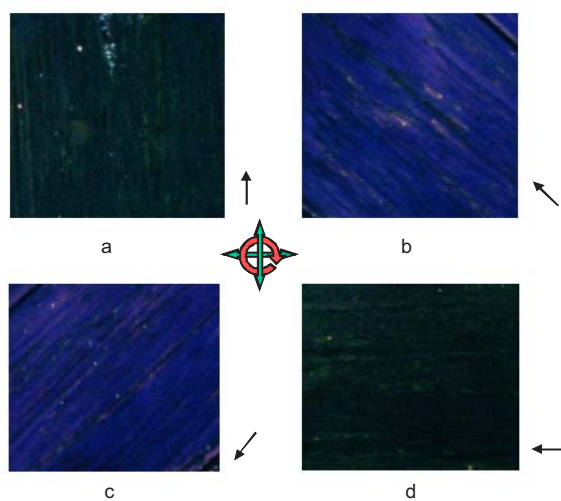


Fig. 2. Cross-polarized optical microscopic image of sample **5d** sheared at 95 °C observed at different angle to polarizer.

**Table 2 . Optical, electrochemical potentials and energy levels of compounds 5a-d.**

	$E_1^a$ (V)	$E_2^a$ (V)	UV (nm)	$E_g^b$ (eV)	HOMO <sup>c</sup> (eV)
<b>TTF</b>	0.34 <sup>d</sup>	0.73 <sup>d</sup>	-	-	-
<b>5a</b>	1.07	1.34	376	2.77	-5.39
<b>5b</b>	1.06	1.39	391	2.74	-5.39
<b>5c</b>	1.04	1.37	388	2.74	-5.37

<sup>a</sup> $E_1$  and  $E_2$  mean the half wave oxidation potentials. <sup>b</sup> $E_g = hc/\lambda_{0.1max}$ .  $E_g$  means the optical band gap energy,  $\lambda_{0.1max}$  means wavelength at which the absorption coefficient drops to 10% of the peak value. <sup>c</sup> $E_{HOMO} = -(E_{onset}^{ox} + 4.4 \text{ eV})$ , where  $E_{onset}^{ox}$  are the onset potentials for the oxidation. <sup>d</sup>from Ref. 13.

significantly with respect to the cooling and heating rates in DSC, which is often observed in the transition of  $I \leftrightarrow LC$ .<sup>11</sup>

All the TTF derivatives from **5a** to **5d** are soluble in common organic solvents, such as dichloromethane, chloroform, toluene and THF, which can allow us to fabricate thin films by a solution-processing. In order to investigate optical property, UV absorption was measured in chloroform and the data were listed in Table 2. Absorption maxima of **5a-5d** in chloroform were found at ~390 nm. The optical band gaps were calculated to be 2.72-2.77 eV, significantly higher than that of pentacene (2.2 eV), indicating a better air stability.<sup>12</sup>

The cyclic voltammetry (CV) measurements were performed in a dry dichloromethane solution of  $Bu_4NBF_4$  (0.1 M) (Table 2). TTF derivatives from **5a** to **5d** showed two reversible single-electron oxidation peaks at ~1.06 and 1.37 V, corresponding to the formation of radical cations and dication, respectively. Both oxidation potentials of **5a-5d** are higher than those of TTF probably due to the existence of electron-withdrawing ester linkages. Their HOMO levels were estimated from the onset of oxidation potentials to be between -5.17 and -5.39 eV. HOMO levels of good *p*-type organic semiconductor are known typically to be in the range of 4.9 and 5.5 eV. Low HOMO levels and large energy gaps, in addition to the highly ordered liquid crystalline property, suggest that **5c** and **5d** are promising hole transporting organic materials.

#### 4. Summary

A series of new liquid crystalline TTF derivatives were synthesized. Based on the thermal, structural, and morphological observations, compounds with longer alkyl chains exhibited highly ordered oblique

columnar LC phases in a wide temperature range including room temperature. The new series of TTF derivatives has good oxidative stability which is desirable for a *p*-type (hole transport) materials.

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