

# Mesomorphic Compounds Containing Chromophoric Mesogens for Opto-electronic Applications

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*Two compounds containing mesogenic cores based on dithiophene and dithienothiophene or fluorene units and hexyl end groups have been synthesized and their thermotropic properties were studied. The mesomorphic behaviour has been analyzed in the thermal stability range, by three complementary methods: polarized light microscopy, differential scanning calorimetry and variable temperature wide angle X ray diffraction. It was established that both compounds form a mesophase at low temperature, whose architecture depends by the mesogen molecular structure. By thermal treatment of the compounds in the mesophase stability range continuous ordered films have been obtained.*

*Keywords: liquid crystal, internal plasticizer, ordered film*

Thermotropic liquid crystals are a well-known class of compounds used in various application fields [1, 2]. Among their applications, opto-electronic devices as field effect transistors (FET), light emitting diodes (LED), light emitting field effect transistors (OLET) are quite new and promising ones [3, 4], increasing the interest for synthesis of new liquid crystals containing chromophoric units [5 - 9]. A short survey of the literature data regarding thermotropic liquid crystals and above mentioned devices shows that both thermotropic liquid crystals and organic compounds used as optoelectronic materials have a common feature - extended conjugation - structural characteristic which facilitates the appearance of mesogenic properties, charge carrier mobility and light emitting, usually together. Some researchers exploited the self-assembling properties into liquid crystalline mesophase to obtain large area monodomain or multi-domain area without grain boundary, with better electric properties, demonstrating the benefits of using mesomorphic properties on charge transport [10, 11]. On the other hand, discotic liquid crystals are well known for their good electrical properties due to their ability to form  $\pi$ -stacks [12]. The processing of organic compounds from mesophase state enables to obtain continuous films, without defects, with a certain degree of molecular order of molecules, leading to improved charge transport [6, 7, 9, 11]. Therefore, it seems reasonable to state that a well understanding of the liquid crystalline properties could allow the choice of the best conditions for materials processing which in turn will conduct to the best device performances.

The aim of this paper is to study thermotropic properties of two oligomers containing dithienothiophene/fluorene (DTF) and dithiophene (DTT) which proved good mobility as charge carriers in FET devices [13, 14] in order to draw a proper method of continuous ordered films preparation. Differential scanning calorimetry, polarized optical microscopy and variable temperature wide angle X-ray diffraction and molecular simulation have been used as complementary methods to study the thermotropic behaviour.

## Experimental part

### Materials and methods

All the solvents used for synthesis and product purifications have been purchased from Aldrich and were used as-received, except tetrahydrofuran which was dried by standard procedure. N-butyllithium in hexane (n-BuLi), 2, 7-dibromofluorene (95 % purity), 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5'-hexyl-2,2'-bithiophene (97% purity), and tetrakis(triphenylphosphine)palladium ((Ph<sub>3</sub>P)<sub>4</sub>Pd) were available from Aldrich. Flash chromatography was carried out using silica gel (200 - 300 mesh ASTM) or LiChroprep RP-18 (Merck). 2, 6-Dibromodithienothiophene has been synthesised according to a literature procedure [15]. The Suzuki reactions with conventional heating were carried out under nitrogen.

Wide Angle X-Ray Diffraction (WAXD) was performed on a Diffractometer Bruker D8 Avance, using the Ni-filtered Cu-K $\alpha$  radiation ( $\lambda = 0.1541$  nm). A MRI-WRTC - temperature chamber (with nitrogen inert atmosphere) and a MRI-TCPU1 - Temperature Control and Power Unit were used. The working conditions were 36 kV and 30 mA. All the diffractograms were investigated in the range of 1.5-40° (2 $\theta$  degrees). Initial samples for X-Ray measurements were crystals as obtained by re-crystallization.

The melting points, thermal transitions and mesomorphic textures were determined by using an Olympus BH-2 polarized light microscope equipped with a THMS 600/HSF9I heating stage. The optical observations were performed by using clean untreated glass slides.

Differential scanning calorimetry (DSC) measurements were carried out by using a Perkin-Elmer Pyris 1 instrument under a nitrogen atmosphere using heating and cooling rates of 20 °C/min.

Thermogravimetric analysis (TGA) was carried out by using a Perkin Elmer TGA-7 apparatus in nitrogen atmosphere, at a heating rate of 10°C/min.

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## Synthesis

The studied compounds have been synthesized by a Suzuki coupling reaction according to the procedure described elsewhere [16], using commercial boronic derivative 97% purity. The products were supplementary purified by refluxing in hexane/ethyl acetate (9/1 v/v), recrystallization from TCE, washing with methanol and drying under vacuum for 12 h. **DTT**: <sup>1</sup>H-NMR(C2D2Cl4, 100°C): δH 7.37(s, 2H), 7.14(d, J = 4.17Hz, 2H), 7.06(d, J = 4.17Hz, 2H), 7.04(d, J = 3.85Hz, 2H), 6.74 (d, J = 3.85Hz, 2H), 2.85(t, J = 8.01Hz, 4H), 1.77-1.72 (m, 4H), 1.47-1.31 (m, 12H), 0.96 (t, J = 6.65 Hz, 6H). M. p. ≈ 320°C. Elemental analysis calc. for C36S7H36: C, 62.39; S, 32.38; H, 5.23. Found: C, 62.31; S, 32.20; H, 5.31.

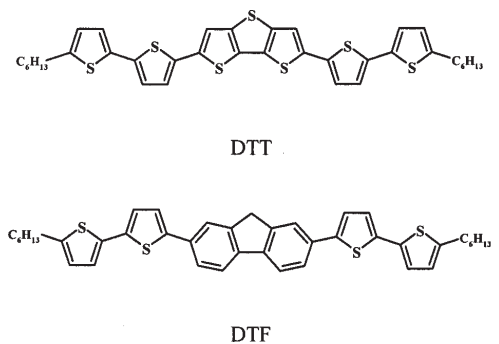
**DTF**: <sup>1</sup>H-NMR(C2D2Cl4, 100°C): δH 7.79(s, 2H), 7.78(d, J = 8.14Hz, 2H), 7.66(d, J = 8.14Hz, 2H), 7.28(d, J = 3.68Hz, 2H), 7.12(d, J = 3.68Hz, 2H), 7.05 (d, J = 3.40Hz, 2H), 6.74 (d, J = 3.40Hz, 2H), 2.85(t, J = 7.50Hz, 4H), 1.78-1.73 (m, 4H), 1.47-1.32 (m, 12H), 0.96 (t, J = 6.75Hz, 6H). M. p. over 300°C. Elemental analysis calc. for C41S4H42: C, 74.28; S, 19.34; H, 6.38. Found: C, 74.07; S, 19.16; H, 6.48.

## Results and discussions

Two liquid crystalline compounds containing chromophoric mesogens have been obtained by Suzuki coupling reaction of dithiophen boronic derivative with fluorene and dithienothiophene dibromide, respectively (scheme 1). The electronic properties of these compounds have been analyzed by UV-Vis and photoluminescence spectroscopy, cyclic voltammetry and finally field effect transistor devices were built [13]. As previously reported [13], from the measurements on FET devices realized by the thermal evaporation in a top contact configuration, good charge carriers mobility (about 10<sup>-2</sup>) and current modulation ratio values resulted, revealing the real potential of these compounds to be used as organic thin films in FET devices [13, 17]. On the other hand, exploring the film surface by AFM [14] it was shown an island morphology of the films with grain boundaries which constitute a diminishing factor of charge transport. Further methods for obtaining continuous films are required for better properties of FET.

## Thermal properties

The transition temperatures and thermal stability of the compounds have been investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC),



Scheme 1. Liquid crystalline compound structures

and thermogravimetric analysis (TGA). The results are enclosed in table 1.

As small amounts of thermally decomposed material drastically affect the thermotropic behaviour of liquid crystals, we evaluated the thermal stability by TGA considering the onset of thermal decomposition i.e. the temperature corresponding to initial 1% of weight loss ( $T_{1\%}$ ) [16]. TGA traces presented in figure 1 show that the fluorene containing derivative is thermally stable in inert atmosphere up to 400°C, while the dithienothiophene containing derivative shows a slow decomposition starting at 115°C. At higher temperatures the compounds show a very fast weight loss. Polarized light microscopy measurements confirm that the weight loss belongs to the thermal decomposition and not to an evaporation of the solvent entrapped in the samples. The derivative thermogravimetry (DTG) curves indicate that the degradation process takes place in a single step. The  $T_{max}$  values, i.e. the temperature corresponding to the maximum rate of weight loss are 480 and 410°C, respectively. As presented in table 1, the characteristic  $T_{1\%}$  value for **DTF** compound is considerably higher than that of the **DTT** sample, with an increase of 285°C. This indicates a less thermal robustness of the dithienothiophene fused ring compared with fluorene one. The degradation process ends around 500°C and 400°C, respectively, and no more weight loss is observed thereafter. The maximum residue yield calculated at 650°C is around 15 wt.% for DTF, whereas the other compound shows heavier residue (ca. 22 wt.%).

The differential scanning calorimetry (DSC) thermograms recorded during a heating-cooling-heating cycle, between room temperature and 350°C, show several transitions for both compounds, suggesting the

Code	DSC T°C (ΔH J/g) <sup>a</sup>	POM	TGA <sup>b</sup> T <sub>1</sub> / T <sub>10</sub>
<b>DTT</b>	<b>1H</b> : Cr 70.9(21.2) M100(1.7) M247.9(52.9) LC <sub>1</sub> 315(1.6) LC <sub>2</sub>	A viscous fluid appear around 75 °C, under shear, and its fluidity increase as temperature increase	100 / 350
	<b>1C</b> : LC <sub>2</sub> 230 LC <sub>1</sub> 225.26 (-23.7) Cr		
	<b>2H</b> : Cr 235.7 (21.3) LC (2H)		
<b>DTF</b>	<b>1H</b> : Cr 92.2(6.4) 130.7(10.4) 151(3.66) LC 326.2(27.8) I	A viscous fluid appear around 100 °C, under shear, and its fluidity increase as temperature increase	300 / 430
	<b>1C</b> : I 323.8 (-27.5) LC frozen		
	<b>2H</b> : LC frozen 327.2(28.54) I		

<sup>a</sup> transition temperatures and corresponding enthalpies, <sup>b</sup> the temperature corresponding to 1% and 10% weight loss, respectively; H: heating; C: cooling

**Table 1**  
THERMAL TRANSITIONS OF THE DTT AND DTF COMPOUNDS

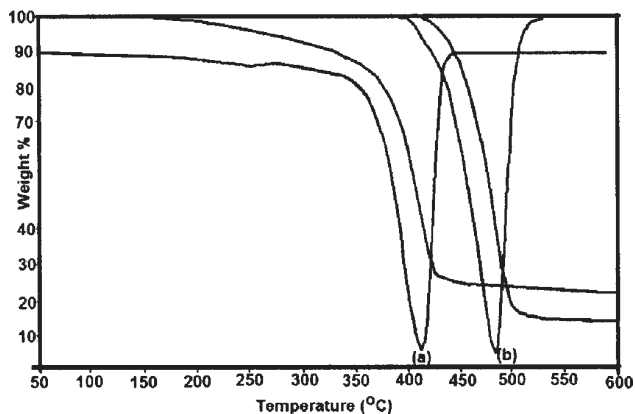


Fig. 1. TGA traces of DTT (a) and DTF (b)

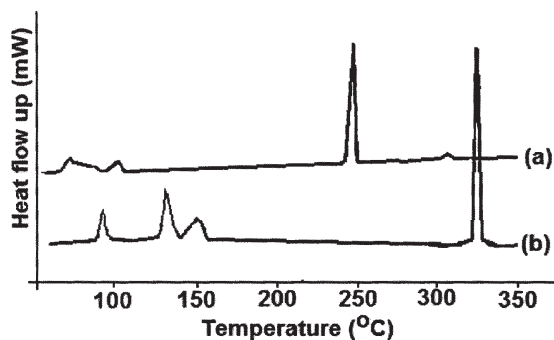


Fig. 2. DSC heating traces of a) DTT and b) DTF

presence of at least one liquid crystalline phase. DSC traces carried out at 20°C/min for both compounds, on the first heating scan, show two kinds of peaks: (i) small and broad endothermic peaks at low temperatures (between 70 – 150°C), involving low enthalpy changes which indicate small morphology modifications; and (ii) a sharp endothermic peak at higher temperature (247 and 326°C, respectively), involving more important enthalpy change, which indicate a transition with drastic morphology modification. Besides, DTT compound shows another weak endothermic peak at much higher temperature (fig. 2). In the first cooling scan no exothermic peaks appears at low temperature, but only an exothermic peak at high temperature for both compounds. Moreover, in the second heating scan only an endothermic peak appears, too. For a proper explanation of this behaviour, polarized light microscopy and X-ray diffraction measurements were carried out in the same temperature conditions.

In polarized light microscopy, corresponding to the endothermic peaks at low temperature, the solid sample becomes a birefringent viscous fluid in the case of both compounds (fig. 3a, b). The viscosity decreased when the temperature increased and the birefringent sample becomes completely fluid around 247°C (DTT) and 326°C (DTF), respectively. The DTT sample transforms slowly in an isotropic liquid around 315°C, and the sample exhibits a strong darkening, indicative of thermal degradation. The isotropization of DTF sample couldn't be catch due to the equipment limitations (working up to 350 p C). In the cooling scan, the isotropic partial decomposed DTT transforms slowly in birefringent liquid which further freezes, while DTF sample freezes in birefringent state. By applying consecutive heating/cooling scans, in the temperature range RT - 110°C (for DTT) and RT - 150°C (for DTF), birefringent continuous films without cracks or pinholes have been obtained (fig. 3c, d).

The variable temperature wide angle diffraction (WXR) patterns of the powder compounds (fig. 4), at room temperature, show reflections in small and wide angle

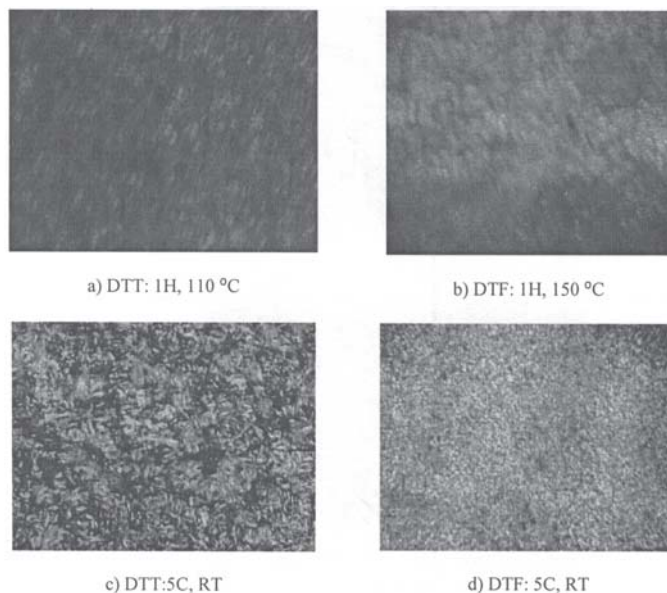


Fig. 3. POM images of DTT and DTF compounds (H: heating; C: cooling, RT: room temperature)

regions suggesting a layered crystalline structure, in which the rigid mesogenic cores come together to form layers, while the terminal alkyl chains form separate regions. This structure is generally met for the compounds containing flexible chains [6-9, 17, 18]. For **DTT** compound, the reflection at small angle (2.25, 2 $\theta$ ) corresponds to the layer spacing value of 39.5 Å, which is close to the molecular length evaluated in the most extended conformation, using Hyper Chem package (fig. 5). The peaks in the wide region indicate an intermolecular distance of 3.89 Å revealing a close packing of the molecules. The WXR pattern recorded in the heating scan, at temperatures corresponding to low thermal transitions in DSC, displays a slight shifting of the peaks to the wider angles and a decrease of their intensities, in both small and wide angle regions. These results indicate the movement and reorganization of the molecules which lead to smaller interplanar and intermolecular distances, and thus more compact packed molecules. An interesting observation is that the WXR pattern obtained after sample cooling is quite similar with the initial one.

DTF compound shows a more complicated WXR pattern, with many reflections in small and medium angle regions indicating a more pronounced polymorphism (fig. 4B). The intermolecular distances calculated for wide angle reflections are slightly smaller than for **DTT**, indicating a denser packing. Noteworthy, by heating the sample at temperatures corresponding in DSC to the low-temperature transitions, the reflections move to smaller angle and decrease progressively in intensity; at 160°C, the peaks in wide angle region almost disappeared, while the peaks in small wide domain transform in two broad halos. These changes are the result of molecules movements leading to their rearrangement in a less dense supramolecular structure with very weak intermolecular correlations and a large polydispersity of interlayer distances. By cooling, the sample freezes in the state gained by heating. The reflection angles, their intensity and the corresponding distances are given in table 2.

Comparing the thermal behaviour of the two samples as reflected by POM, DSC and variable temperature WXR measurements, a special behaviour of each sample is observed. These behaviors are strongly correlated with the molecular structure. Primarily, both samples, by heating

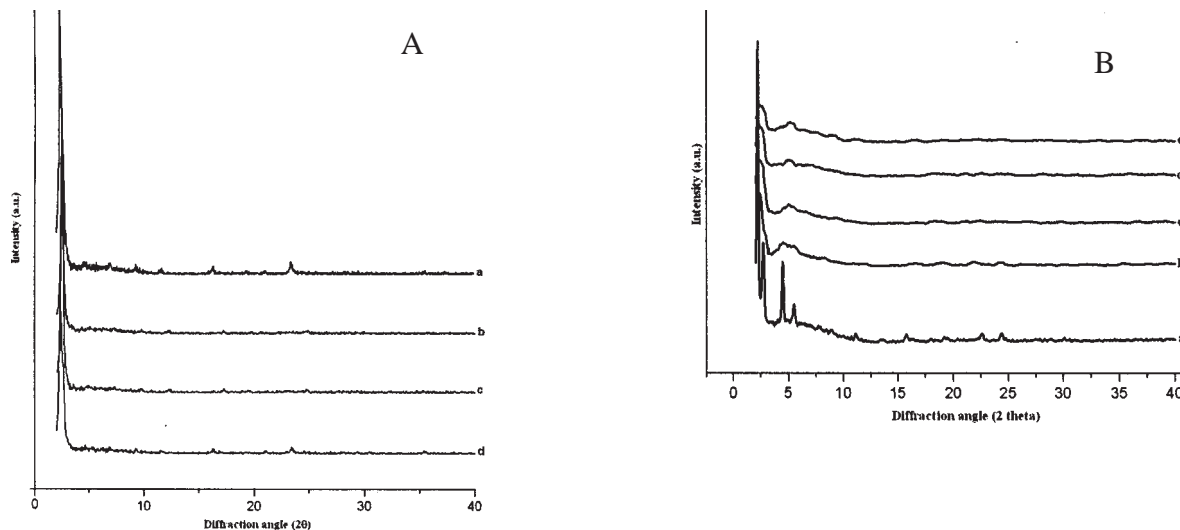


Fig. 4. WXR D patterns of A) DTT in first heating scan: (a) RT, (b) 100°C, (c) 110°C, and in first cooling scan d) RT; B) DTF in first heating scan (a) RT, (b) 100°C, (c) 140°C, d) 160 °C and in first cooling scan e) RT

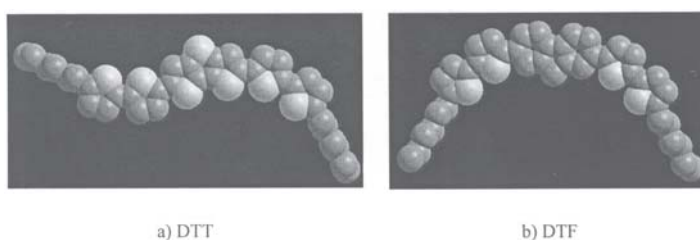


Fig. 5. The molecular models of studied compounds obtained by molecular mechanics (MM+)

**Table 2**  
WXR D PARAMETERS OF DTT AND DTF

<b>DTT</b>	<b>R.T.</b>	2.2(39.5) 782	6.9(12.7)68	9.3(9.5) 71	11.6(7.6) 61	16.2(5.5) 68	23.3(3.89) 75
	<b>100 °C</b>	2.4(36) 625		9.7(9.1) 39	12.2(7.2) 37	17.2(5.2) 35	24.8(3.67) 35
	<b>110 °C</b>	2.4(3.7) 647		9.7(9.1) 45	12.2(7.2) 43.3	17.2(5.2) 46	24.8(3.67) 35
	<b>R.T.</b>	2.3(38.5) 454		9.2(9.6) 27		16.2(5.5) 29	23.4(3.9) 35.6
<b>DTF</b>	<b>R.T.</b>	2.1(40.7) 369	2.7(32.1) 117	4.3(20.1) 111	5.4(16.2) 47	15.7(5.7) 22.6	24.3(3.7) 26
	<b>100 °C</b>	2.1(40.7) 149	2.6(33.2) 80	4.4(19.7) 44.9	5.3(16.6) 33	16.8(5.3) 17	24.2(3.75) 18.4
	<b>140 °C</b>	2.3(37.5) 93	2.6(34.01) 98	4.6(19.2) 22	5.2(17.0) 22		
	<b>160 °C</b>	2.4(35.8)1 07	4.9(17.9) 31				
	<b>R.T.</b>	2.5(35)97	5.1(17.5) 34				

2θ - diffraction angle; d - the corresponding distance calculated using Bragg law; I the intensities of diffraction peaks

around 100 °C, suffer rearrangements of the supramolecular architecture as a result of the rotational motions of the alkyl chains which quickly exchange between trans and gauche conformations [19]. The alkyl chain flexibility increases with the increase of thermal energy, acting as internal plasticizer, and thus the sample became a birefringent viscous fluid (POM). During these transitions, small amounts of thermal energy (DSC) are converted in conformational disorder of the aliphatic terminal chains, but the preformed arrangement of the mesogenic cores in crystalline structure is maintained (WXR D) due to the attractive  $\pi$ -interactions among mesogenic cores. This mesomorphic state is the result of the equilibrium between attractive forces among mesogenic cores and conformational disorder of the aliphatic chains. In the case

of **DTT**, which has a more planar conformation (fig. 5a), indicative of a more extended conjugation and so a significant dipole moment, the attractive forces among rigid cores are dominant and the alkyl chains are thus forced to keep their self assembling, and the supramolecular architecture is kept, even at higher temperature. On the other hand, for **DTF**, which has a less planar conformation (fig. 5b) - indicative of a less extended conjugation and so a weaker dipole moment, the attractive forces among mesogenic cores are weaker and thus, the rotational movements of the alkyl chains disturb the intermolecular correlations, keeping a less pronounced layered structure. Remarkable is the fact, that both compounds have been obtained as continuous ordered films, properties claimed by a good electrical performance.

## Conclusions

Two mesomorphic compounds containing chromophoric mesogens have been obtained and their thermotropic behaviour was studied. The compounds show a mesophase at low temperature which allow the processing of ordered, continuous films. The study indicates that a well knowledge of the mesomorphic properties of organic compounds is a useful tool in processing better quality films as opto electronic materials.

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