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# Synthesis and Mesogenic Properties of Novel Terthiophene Derivatives

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# Synthesis and Mesogenic Properties of Novel Terthiophene Derivatives

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**Abstract:** To develop novel oligothiophene-based liquid crystals involving hydrogen bonding, new terthiophene derivatives containing a stearylamide group, N,N'-distearyl-5,5"-dicyano-2,2':5',2"-terthiophene-4,4"-dicarboxamide (DNC<sub>18</sub>DCN 3T) and N,N'-distearyl-5,5'-dipropyl-2,2':5',2'-terthiophene-4,4"-dicarboxamide (DNC<sub>18</sub>DP3T), were designed and synthesized, and their thermal behavior examined. Although DNC<sub>18</sub>DP3T did not exhibit liquid crystallinity, DNC<sub>18</sub>DCN3T was found to form smectic A phase.

Keywords: Liquid crystal, terthiophene derivatives

#### 1. INTRODUCTION

Oligothiophenes with well-defined structures have recently received a great deal of attention not only as model compounds for electrically conducting polythiophenes but also as a new class of functional  $\pi$ -electron systems. A variety of oligothiophenes have been synthesized,<sup>[1]</sup> and their molecular and crystal structures, <sup>[2,3]</sup> self-ordering,<sup>[4,5]</sup> electrochemical,<sup>[6,7]</sup> photophysical,<sup>[8]</sup> optical,<sup>[9,10]</sup> and electrical properties<sup>[11,12]</sup> have been studied. In addition their

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potential applications for field-effect transistors, photovoltaic devices,<sup>[13]</sup> and organic electroluminescent devices<sup>[14]</sup> have been investigated.

Oligothiophenes are crystalline in nature because of their planar molecular structures. Vacuum-evaporated and spin-coated films of oligothiophenes have been reported to be polycrystalline. Because the properties and functionality of a material are greatly affected by its morphology, it is of both fundamental and technological interest to exert control over morphology of oligothiophenes in the design of novel functional organic materials.

Recently, several reports on the liquid crystalline properties of oligothiophene derivatives have appeared.<sup>[15–17]</sup> It has been reported that terthiophenes substituted with long alkyl or alkanoyl groups at the terminal  $\alpha$ - and  $\alpha''$ positions, for example, 5-alkyloxycarbonyl-5''-alkyl-2,2' : 5',2''-terthiophenes and 5, 5''-dialkyl-2,2' : 5',2''-terthiophenes, exhibit a smectic liquid crystalline phase. 5-Substituted and 5'''-disubstituted quarterthiophenes have also been reported to exhibit a smectic and nematic liquid crystalline phase. However, examples of oligothiophene-based liquid crystals are still scarce.

This article reports on the synthesis of new compounds containing a terthiophene moiety, N,N'-distearyl-5,5"-dicyano-2,2' : 5',2"-terthiophene-4,4"-dicarboxamide (DN C<sub>18</sub>DCN3T) and N,N'-distearyl-5,5"-dipropyl-2,2' : 5',2"-terthiophene-4,4"-dicarboxamide (DNC<sub>18</sub>DP3T). The relationship between molecular structure and liquid crystalline behavior is discussed (Scheme 1).

## 2. RESULTS AND DISCUSSION

Novel families of terthiophene derivatives containing an stearylamide group at the  $\beta$ - and  $\beta'$ -position of 2,2':5',2"-terthiophene, DNC<sub>18</sub>DCN3T and DNC<sub>18</sub>DP3T, were synthesized according to the procedures shown in Scheme 2. All compounds were characterized by IR and <sup>1</sup>H NMR spectroscopy, mass spectrometry, and elemental analysis.

Differential scanning calorimetry (DSC) and polarized light microscopy performed on DNC<sub>18</sub>DCN3T revealed that the compound, containing two stearylamide groups at the  $\beta$ - and  $\beta'$ -positions of 3T, formed a smectic A (SmA) phase. Figure 1 shows the polarizing micrograph of the DNC<sub>18</sub>DCN3T SmA phase formed from the isotropic liquid in the cooling process. A focal-conic fan texture typical of the SmA phase was clearly observed.



Scheme 1.





The formation of a SmA phase by DNC<sub>18</sub>DCN3T was also evidenced by DSC. Figure 2 shows the DSC curves for DNC<sub>18</sub>DCN3T. When the crystalline sample of DNC<sub>18</sub>DCN3T was heated, an endothermic peak was observed at 94°C to give a SmA phase. Upon further heating, the onset of the transition from the SmA phase into the isotropic liquid was observed at 138°C. When the isotropic liquid was cooled, the onset of the transition into the SmA phase was observed at around 139°C. The SmA phase crystallized at 99°C. The trace was reproducible.

In our previous study, we found that N,N'-distearyl-5,5"-dibromo-2,2':5',2"-terthiophene-4,4"-dicarboxamide (DNC<sub>18</sub>DBr3T) forms a smectic A phase, but 4,4"-bis(stearyloxycarbonyl)-5,5"-dibromo-2,2':5',2"-terthiophene (DOC<sub>18</sub>DBr3T) did not exhibit liquid crystallinity. The absence of liquid crystallinity for DOC<sub>18</sub>DBr3T and changes in the IR spectra suggest that intermolecular hydrogen bonding through the stearylamide group is involved in liquid-crystal-phase formation.<sup>[18]</sup>

It is noteworthy that DNC<sub>18</sub>DP3T did not form a liquid crystal phase; it showed only the phase transition between the crystal and the isotropic liquid. The reason why DNC<sub>18</sub>DP3T did not form liquid crystal phase is thought to be that the propyl group at the  $\alpha$ - and  $\alpha'$ -positions of 3T can



*Figure 1.* Photomicrograph of the texture of the SmA phase of  $DNC_{18}DCN3T$  obtained upon cooling the melt (magnification  $\times$  200).



*Figure 2.* DSC curves for DNC<sub>18</sub>DCN3T.

make the liquid crystalline phase unstable, and it thus favors direct crystallization from the isotropic liquid. However, the cyano group at the  $\alpha$ - and  $\alpha'$ positions of 3T can make the liquid crystalline phase stable.

Table 1 summarizes the transition temperatures of DNC<sub>18</sub>DCN3T and DNC<sub>18</sub>DBr3T together with the enthalpy changes ( $\Delta$ H) associated with the phase transitions.

When the isotropic liquid was cooled, the onset of the transition into the SmA phase for  $DNC_{18}DCN3T$  was higher than the  $DNC_{18}DBr3T$ . When the SmA phase was cooled, the the onset of the transition into the crystalline phase for  $DNC_{18}DCN3T$  was lower than that for the  $DNC_{18}DBr3T$ . The temperature range of liquid crystalline phase for  $DNC_{18}DBr3T$  and  $DNC_{18}DCN3T$  is 16°C

*Table 1.* Transition temperatures and enthalpy changes of  $DNC_{18}DBr3T$  and  $DNC_{18}DCN3T$ 

Compound	Transition temperature/°C; enthalpy change (in parentheses)/kJ mol <sup><math>-1</math></sup>				
DNC <sub>18</sub> DBr3T <sup>[18]a</sup>	K	107 (56)	SmA	123 (3.7)	I
DNC <sub>18</sub> DCN3T <sup>a</sup>	K	99 (43)	SmA	139 (66)	I

Note: K: crystal, SmA: smectic A liquid crystal, I: isotropic liquid.

<sup>a</sup>Transition temperatures and enthalpy changes were determined by DSC on cooling.

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and 40°C, respectively. These results indicate that the cyano group is better than the bromo group for making the liquid crystalline phase stable.

### 3. CONCLUSION

A novel terthiophene derivatives containing a stearylamide group,  $DNC_{18}DCN3T$  and  $DNC_{18}DP3T$ , were designed and synthesized.  $DNC_{18}DCN3T$  was found to form a SmA phase, so constituting new oligothiophene-based liquid crystals.  $DNC_{18}DP3T$  did not exhibit liquid crystallinity.

#### 4. EXPERIMENTAL

#### 4.1 Synthesis

2-Bromothiophene, 2,5-dibromothiophene, [1,3-bis-(diphenyphosphino)propane] nickel(II) chloride [NiCl<sub>2</sub>-(dppp)], magnesium, diisopropylamine, butyllithium (hexane solution), thionyl chloride, triethylamine, and monostearylamines (C<sub>18</sub>H<sub>37</sub>NH<sub>2</sub>) were commercially available and used without further purification. 2,2': 5',2"-Terthiophene (3T) was prepared by Grignard coupling reaction of 2,5-dibromothiophene with 2-bromomagnesiumthiophene in ether at a refluxing temperature. Synthetic procedures are illustrated in Scheme 2.

4.1.1. Synthesis of *N*,*N*'-Distearyl-5,5"-dicyano-2,2':5',2"-terthiophene-4,4"-dicarboxamide (DNC<sub>18</sub>DCN3T)

5,5''-Dicyano-2,2':5',2''-terthiophene (DCN3T) was prepared by the reaction of 3T (10.0 g, 12.1 mmol) with *N*-chlorosulfonyl isocyanate (CSI) (99.28 mL, 160.8 mmol) in methylene chloride (100 mL) at room temperature for 4 h, and then DMF (348 mL) was added. The mixture was stirred again for 15 h and then hydrolyed with water (100 mL). The product was purified by silica-gel column chromatography using toluene as eluent, yielding a yellow solid (5.15 g, 43%).

A hexane solution of butyllithium was added to a THF solution of diisopropylamine at  $-78^{\circ}$ C under a nitrogen atmosphere to give lithium diisopropylamine (LDA). DCN3T (3.0 g, 10.05 mmol) was added to a THF solution (50 mL) of LDA (40.20 mmol) at  $-78^{\circ}$ C and the solution stirred for 1 h. Excess dry ice was added to the solution, and the resulting mixture was stirred for 2 h. The solution was allowed to warm to room temperature, and aqueous hydrochloric acid was added. After stirring for 5 h, the resulting solid was collected and washed with hot acetonitrile to give 5,5"-dicyano-2,2': 5',2"-terthiophene-4,4"-dicarboxylic acid (yield 58% based on DCN3T).

A dichloromethane solution (100 mL) of 5,5''-dicyano-2,2':5',2''-terthiophene-4,4"-dicarboxylic acid (2.0 g, 5.17 mmol), and SOCl<sub>2</sub> (1.23 g, 5.17 mmol)10.34 mmol) was heated at reflux for 8 h. After the solvent was removed under reduced pressure, the resulting solid was added to a THF solution (100 mL) of stearylamine (2.79 g, 10.34 mmol) in the presence of triethylamine (2.5 mL) at 0°C, and the solution was stirred for 5 h at 0°C. The solvent was removed under reduced pressure to give DNC<sub>18</sub>DCN3T. The product was purified by silica-gel column chromatography using chloroform as the eluent (yield 60% based on 5,5"-dicyano-2,2':5',2"-terthiophene-4,4"-dicarboxylic acid). <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>):  $\delta$  (ppm) = 7.32 (s, 2H, ArH), 7.28 (t, 2H, NH), 7.25 (s, 2H, ArH), 3.33 (dt, 4H, stearyl α-CH<sub>2</sub>), 1.58 (tt, 4H, stearl β-CH<sub>2</sub>), 1.45-1.21 (m, 60H, stearyl CH<sub>2</sub>), 0.88 (t, 6H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 3303 ( $\nu_{N-H}$ ), 2957, 2923, 2857 ( $\nu_{C-H}$ ), 1625  $(\nu_{C=0})$ . MS(EI): m/z 889(M<sup>+</sup>). Elemental analysis: found C, 69.95; H, 9.33; N, 6.22; S, 10.86%; calcd. for  $C_{52}H_{80}N_4S_3O_2$  C, 70.22; H, 9.07; N, 6.30; S, 10.81%.

4.1.2. Synthesis of N,N'-Distearyl-5,5"-dipropyl -2,2' : 5',2"-terthiophene-4,4"-dicarboxamide (DNC<sub>18</sub>DP3T)

5,5''-Dipropyl-2,2':5',2''-terthiophene (DP3T) was prepared by a Grignard coupling reaction of DBr3T with bromomagnesiumpropyl in ether at refluxing temperature (yield 75%).

DP3T (3.0 g, 9.02 mmol) was added to a THF solution (50 mL) of LDA (36.08 mmol) at  $-78^{\circ}$ C, and the solution was stirred for 1 h. Excess dry ice was added to the solution, and the resulting mixture was stirred for 2 h. The solution was allowed to warm to room temperature, and aqueous hydrochloric acid was added. After stirring for 5 h, the resulting solid was collected and washed with hot acetonitrile to give 5,5"-dipropyl-2,2':5',2"-terthiophene-4,4"-dicarboxylic acid (yield 73% based on DP3T).

A dichloromethane solution (100 mL) of 5,5"-dipropyl-2,2' : 5',2"-terthiophene-4,4"-dicarboxylic acid (2.0 g, 4.76 mmol) and SOCl<sub>2</sub> (1.13 g, 9.52 mmol) was heated at reflux for 8 h. After the solvent was removed under reduced pressure, the resulting solid was added to a THF solution (100 mL) of stearylamine (2.56 g, 9.52 mmol) in the presence of triethylamine (2.5 mL) at 0°C, and the solution was stirred for 5 h at 0°C. The solvent was removed under reduced pressure to give DNC<sub>18</sub>DP3T. The product was purified by silica-gel column chromatography using chloroform as the eluent (yield 65% based on 5,5"-dipropyl-2,2' : 5',2"-terthiophene-4,4"-dicarboxylic acid). <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>):  $\delta$  (ppm) = 7.41 (t, 2H, NH), 7.36 (s, 2H, ArH), 7.27 (s, 2H, ArH), 3.36 (dt, 4H, stearyl  $\alpha$ -CH<sub>2</sub>), 2.80 (t, 4H, propyl  $\alpha$ -CH<sub>2</sub>), 1.63 (tt, 4H, stearyl  $\beta$ -CH<sub>2</sub>), 1.55 (tt, 4H, propyl  $\beta$ -CH<sub>2</sub>), 1.43–1.21 (m, 60H, stearyl CH<sub>2</sub>), 0.88 (t, 12H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 3311 ( $\nu$ <sub>N-H</sub>), 2958, 2913, 2853 ( $\nu$ <sub>C-H</sub>), 1619 ( $\nu$ <sub>C=O</sub>). MS(EI): m/z 923

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 $(M^+)$ . Elemental analysis: found C, 72.98; H, 10.45; N, 2.85; S, 10.35%; calc. for  $C_{56}H_{94}N_2S_3O_2$  C, 72.83; H, 10.26; N, 3.03; S, 10.41%.

#### 4.2. Characterization

Differential scanning calorimetry (DSC) was performed using a SSC/5200 (SEIKO I&E) calorimeter. Polarizing microscopy was carried out with an OPTI-PHOT X2 (Nikon) microscope, fitted with a TH-600PM hot stage (Linkam) and crossed polarizers.

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### REFERENCES

- Bäuerle, P.; Fischer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. Oligothiophenes— Yet longer synthesis, characterization, and scanning tunneling microscopy images of homologous, isomerically pure oligo(alkylthiophene)s. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 303–307.
- 2. Yassar, A.; Garnier, F.; Deloffre, F.; Holowitz, G.; Ricard, L. Crystal structure of  $\alpha$ ,  $\omega$ -bis(triisopropylsilyl)-sexithiophene: Unusual conjugated chain distortion induced by interchain steric effects. *Adv. Mater.* **1994**, *6*, 660–663.
- Fichou, D.; Bachet, B.; Demanze, F.; Billy, I.; Horowitz, G.; Garnier, F. Growth and structural characterization of the quasi-2D single crystal of α-octithiophene. *Adv. Mater.* **1996**, 8, 500–504.
- Soukopp, A.; Glöckler, K.; Bäuerle, P.; Sokolowski, M.; Umbach, E. High order and submolecular imaging of end-capped quinquethiophene on Ag(111). *Adv. Mater.* 1996, 8, 902–906.
- Azumi, R.; Götz, G.; Bäuerle, P. Self-assembly of alkylsubstituted oligothiophenes. Synth. Met. 1999, 101, 569–572.
- Bäuerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. Electronic structure of monoand dimeric cation radicals in end-capped oligothiophenes. *J. Am. Chem. Soc.* 1993, 115, 10217–12223.
- Bäuerle, P.; Segelbacher, U.; Gauda, K. U.; Huttenlocher, D.; Mehring, M. Didodecylsexithiophene—A model compound for the formation and characterization of charge carriers in conjugated chains. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76–78.
- Bennati, M.; Grupp, A.; Mehring, N.; Nemeth, K.; Surjan, P. R. Zero-field splitting of the lowest excited triplet state in thiophene oligomers. An experimental and theoretical investigation.. *Synth. Met.* **1997**, *84*, 607–608.

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- Tour, J. M.; Wu, R. Synthesis and UV-visible properties of soluble α-thiophene oligomers. Monomer to octamer. *Macromolecules* 1992, 25, 1901–1907.
- Fichou, D.; Dumarcher, V.; Nunzi, J. M. One and two-photon stimulated emission in oligothiophenes single crystals. *Synth. Met.* **1999**, *101*, 610–613.
- 11. Horowitz, G.; Garnier, F.; Yassar, A.; Hajlaoui, R.; Kouki, F. Field-effect transistor made with a sexithiophene single crystal. *Adv. Mater.* **1996**, *8*, 52–54.
- Nakanishi, H.; Sumi, N.; Aso, Y.; Otsubo, T. Synthesis and properties of the longest oligothiophenes: the icosamer and heptacosamer. J. Org. Chem. 1998, 63, 8632–8633.
- Videlot, C.; Fichou, D. Influence of molecular orientation on the photovoltaic properties of octithiophene. Synth. Met. 1999, 102, 885–886.
- Geiger, F.; Stoldt, M.; Schweizer, H.; Bäuerle, P.; Umbach, E. Electroluminescence from oligothiophene-based light-emitting devices. *Adv. Mater.* 1993, *5*, 922–925.
- Azumi, R.; Götz, G.; Bäuerle, P. Thermal behavior of α-alkylated oligothiophenes. Synth. Met. 1999, 101, 544–545.
- Yamada, T.; Azumi, R.; Tachibana, H.; Sakai, H.; Abe, M.; Bäuerle, P.; Matsumoto, M. Liquid crystalline behavior of α-substituted oligothiophenes. *Chem. Lett.* 2001, 10, 1022–1023.
- Ponomarenko, S.; Kirchmeyer, S. Synthesis and thermal behaviour of α, α'-didecyloligothiophenes. J. Mater. Chem. 2003, 13, 197–202.
- Liu, P.; Zhang, Y. M.; Feng, G. J.; Hu, J. H.; Zhou, X. P.; Zhao, Q. Z.; Xu, Y. H.; Tong, Z.; Deng, W. J. Synthesis and liquid crystal properties of a novel family of oligothiophene derivatives. *Tetrahedron* 2004, *60*, 5259–5264.

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