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Synthesis and liquid crystal properties of a novel family of oligothiophene derivatives

Ping Liu,[a,*] Yamin Zhang,[a] Guiju Feng,[a] Jianhua Hu,[a] Xiaoping Zhou,[a] Qizhong Zhao,[a] Yunhua Xu,[b] Zhen Tong[a] and Wenji Deng[b]

[a]*Polymer Structure and Modification, Research Institute of Materials Science, South China University of Technology, Guangzhou 510640, China*
[b]*Department of Applied Physics, South China University of Technology, Guangzhou 510640, China*

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Abstract—In order to develop novel oligothiophene-based liquid crystals capable of hydrogen bonding, new terthiophene derivatives containing an alkylamide group, *N*,*N*′-dialkyl-5,5″-dichloro-2,2′:5′,2″-terthiophene-4,4″-dicarboxamide (DNC$_n$DCl3T, n=8, 18), *N*,*N*′-dialkyl-5,5″-dibromo-2,2′:5′,2″-terthiophene-4,4″-dicarboxamide (DNC$_n$DBr3T, n=5, 8, 16, 18), or *N*,*N*′-dialkyl-5,5″-diiodo-2,2′:5′,2″-terthiophene-4,4″-dica-rboxamide (DNC$_n$DI3T, n=8, 18), were designed and synthesized, and their thermal behaviour was examined. It was found that DNC$_{18}$DCl3T, DNC$_{18}$DI3T and DNC$_n$DBr3T (n=8, 16, 18) form a smectic A phase and that the alkyl chain length greatly affects liquid crystal phase formation. The absence of liquid crystallinity in the corresponding ester derivatives suggests that intermolecular hydrogen bonding also plays a role in the formation of a liquid crystal phases in the DNC$_n$DBr3T system.

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1. Introduction

Oligothiophenes with well defined structures have recently received a great deal of attention not only as model compounds for conducting polythiophenes, but also as a new class of functional π-electron systems. A variety of oligothiophenes have been synthesized[1] and their molecular and crystal structures,[2,3] self ordering,[4,5] electrochemical,[6,7] photophysical,[8,9] optical,[10,11] and electrical properties,[12,13] have all been studied. In addition, their potential application in field-effect transistors,[14] photovoltaic devices,[15] and organic electroluminescent devices[16] has been investigated.

Oligothiophenes are crystalline compounds because of their planar molecular structures and both vacuum-evaporated and spin-coated films of oligothiophenes have been reported to be polycrystalline. Since 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 the morphology of oligothiophenes in the design of novel functional organic materials.

Recently, several reports regarding the liquid crystalline properties of oligothiophene derivatives have appeared.[17–20] It has been reported that terthiophenes substituted with long alkyl or alkanoyl groups at the terminal α- and α″-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. Both 5-substituted and 5‴-disubstituted quarterthiophenes have also been reported to exhibit smectic and nematic liquid crystalline phases. However, examples of oligothiophene-based liquid crystals are still scarce.

This paper reports on the synthesis of new compounds containing a terthiophene moiety, *N*,*N*′-dialkyl-5,5″-dichloro-2,2′:5′,2″-terthiophene-4,4″-dicarboxamide (DNC$_n$DCl3T, n=8, 18), *N*,*N*′-dialkyl-5,5″-dibromo-2,2′:5′,2″-terthiophene-4,4″-dicarboxamide (DNC$_n$DBr3T, n=5, 8, 16, 18), or *N*,*N*′-dialkyl-5,5″-diiodo-2,2′:5′,2″-terthiophene-4,4″-dicarboxamide (DNC$_n$DI3T, n=8, 18) (Scheme 1), and their liquid crystal properties. The relationship between molecular structure and liquid crystalline behaviour is discussed.

2. Results and discussion

Novel families of oligothiophene derivatives containing an alkylamide group at the β- and β′-position of 2,2′:5′,2″-terthiophene, DNC$_n$DCl3T (n=8, 18), DNC$_n$DBr3T (n=5, 8, 16, 18) and DNC$_n$DI3T (n=8, 18), were synthesized according to the procedures shown in the Scheme 2. All

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Keywords: Oligothiophene derivatives; Liquid crystal; Intermolecular hydrogen bonding.

* Corresponding author. Tel.: +86-20-87111686;
e-mail address: mcpliu@scut.edu.cn

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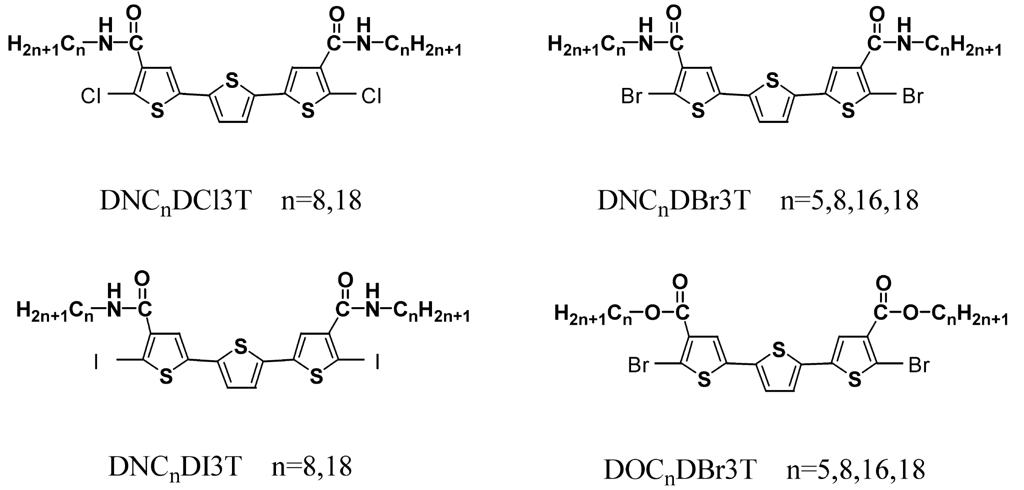
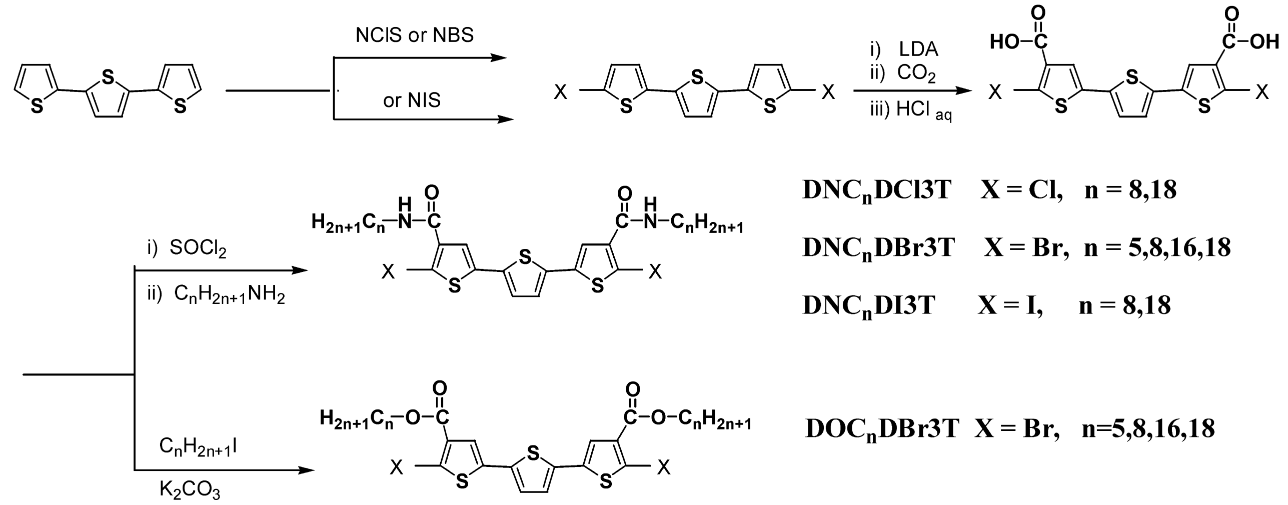


Scheme 1.



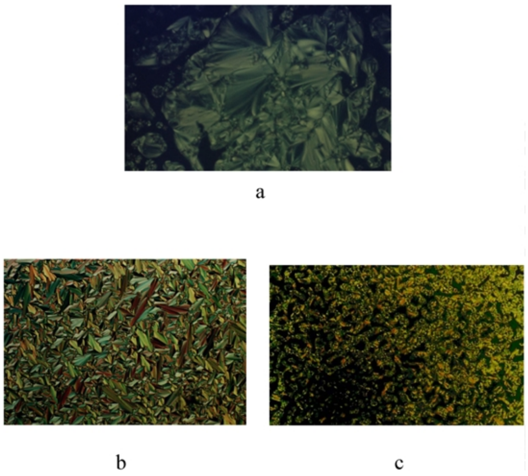
Scheme 2.

compounds were characterized by IR and ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis.

DSC and polarized light microscopy performed on DNC$_{18}$DCl3T, DNC$_n$DBr3T (n=8, 16, 18) and DNC$_{18}$DI3T revealed that these compounds, containing two alkylamide groups at the β- and β′-position of 3T, formed a smectic A (SmA) phase. Figure 1 shows the polarizing micrograph of the DNC$_{18}$DCl3T, DNC$_{18}$DBr3T and DNC$_{18}$DI3T SmA phase formed from the isotropic liquid in the cooling process. A focal-conic fan texture typical of a SmA phase was clearly observed.

The formation of a SmA phase by DNC$_{18}$DCl3T, DNC$_{18}$DBr3T and DNC$_{18}$DI3T was also evidenced by DSC. Figure 2 shows the DSC curves for DNC$_{18}$DBr3T. When the crystalline sample of DNC$_{18}$DBr3T was heated, an endothermic peak was observed at 110 °C to give a smectic A phase. Upon further heating, the onset of the transition from a SmA phase into the isotropic liquid was observed at 121 °C. When the isotropic liquid was cooled, the onset of the transition into a SmA phase was observed at approximately 123 °C. The SmA phase crystallized at 107 °C. The trace was reproducible.

The effects of the alkyl chain length in the alkylamido group on liquid crystalline behaviour were investigated. Like DNC$_{18}$DBr3T, DNC$_{16}$DBr3T was found to form a SmA phase. In addition, DNC$_{16}$DBr3T exhibited crystal


a

b c

Figure 1. Photomicrograph of the texture of the SmA phase of DNC$_{18}$DCl3T, DNC$_{18}$DBr3T and DNC$_{18}$DI3T obtained on cooling the melt. (a): DNC$_{18}$DCl3T; (b): DNC$_{18}$DBr3T; (c): DNC$_{18}$DI3T (magnification×200).

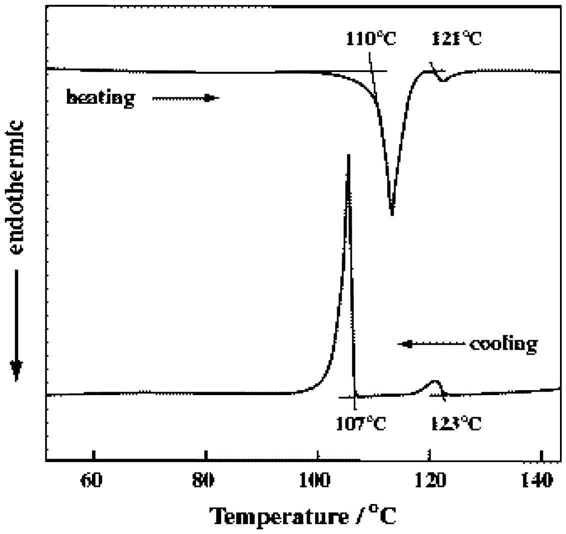


Figure 2. DSC curves for $DNC_{18}DBr3T$.

polymorphism, showing two different crystal forms. In contrast, with DNC_8DBr3T, the formation of a liquid crystalline phase did not occur on heating. However, a SmA phase appeared on cooling in the temperature range from about 126–109 °C, as observed by polarized light microscopy.

It is noteworthy that DNC_8DCl3T DNC_5DBr3T, and DNC_8DI3T did not form liquid crystal phase, and showed only the phase transition between the crystal and the isotropic liquid, as revealed by DSC and polarized light microscopy. The absence of a liquid crystalline phase for DNC_8DCl3T, DNC_5DBr3T and DNC_8DI3T is thought to be because there are strong hydrogen bonding interactions in these molecules, and they thus favor direct crystallization from the isotropic liquid.

In order to gain information on the importance of the amide group in the formation of liquid crystal phases, the thermal behavior of the corresponding ester compounds, DOC_n-DBr3T (n=5, 8, 16, 18) were examined. It was found that DOC_nDBr3T (n=5, 8, 16, 18) did not exhibit a liquid crystalline phase, showing only melting and crystallization behavior upon heating and cooling. These results indicate that the alkylamide groups in the β- and β′-position of 3T play an important role in the formation of liquid crystal phases in the DNC_nDBr3T system. Table 1 summarizes the transition temperatures of $DNC_{18}DCl3T$, DNC_nDBr3T (n=8, 16, 18) and $DNC_{18}DI3T$, together with the enthalpy changes (ΔH) associated with the phase transitions.

Table 1. Transition temperatures and enthalpy changes of $DNC_{18}DCl3T$, DNC_nDBr3T (n=8, 16, 18) and $DNC_{18}DI3T$

Compound	Transition temperature (°C); enthalpy change (in parentheses) (kJ mol^{-1})				
$DNC_{18}DCl3T$[a]	K	114(43)	SmA	121(3.3)	I
DNC_8DBr3T[b]	K	109(—)	SmA	126(—)	I
$DNC_{16}DBr3T$[c]	K	110(46)	SmA	127(3.6)	I
$DNC_{18}DBr3T$[a]	K	107(56)	SmA	123(3.7)	I
$DNC_{18}DI3T$[a]	K	130(62)	SmA	143(4.3)	I

K: crystal, S_A: smectic A liquid crystal, I: isotropic liquid.

[a] Transition temperatures and enthalpy changes were determined by DSC upon cooling.

[b] Transition temperatures and enthalpy changes were determined by polarized light microscopy.

[c] Transition temperatures and enthalpy changes were determined by DSC upon heating.

It is suggested that intermolecular hydrogen bonding between the amido groups is involved in liquid crystal phase formation. The presence of intermolecular hydrogen bonding was evidence by infrared (IR) absorption spectroscopy. Figure 3 shows the IR absorption spectra of $DNC_{18}DBr3T$ in its crystalline and liquid crystalline phases in the wavelength region of the N–H stretching vibration mode. The crystalline sample showed only a broad absorption at around 3300 cm^{-1}, which is attributable to the stretching vibration of hydrogen-bonded N–H groups. The liquid crystalline sample showed both the hydrogen bonded absorption band and a sharp absorption peak at 3419 cm^{-1} that is attributable to the free N–H groups. The spectrum of the isotropic liquid was almost identical to that of the liquid crystal. The changes in the IR absorption spectra between the crystal and the liquid crystal phases during both heating and cooling were reproducible. This indicates that the molecules in the SmA phase only partly forms intermolecular hydrogen bonds, whereas in the crystal phase all the molecules are fixed tightly by the intermolecular hydrogen bonding. Partial intermolecular hydrogen bonding interactions may play a role in the formation of liquid crystal phases in the DNC_nDBr3T system.

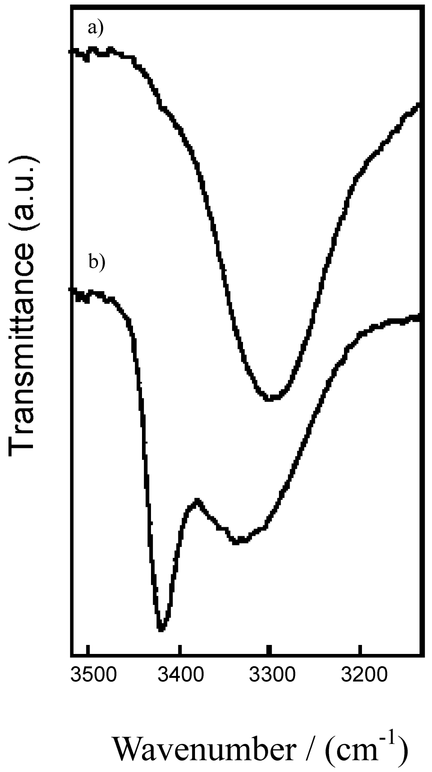


Figure 3. Infrared absorption spectra of $DNC_{18}DBr3T$; (a) crystal at 100 °C; (b) SmA phase at 120 °C formed on heating the crystal.

3. Conclusion

A novel family of terthiophene derivatives containing an alkylamide group, DNC$_n$DCl3T, (n=8, 18), DNC$_n$DBr3T, (n=5, 8, 16, 18) or DNC$_n$DI3T, (n=8, 18), were designed and synthesized. DNC$_{18}$DCl3T, DNC$_n$DBr3T, (n=8, 16, 18) and DNC$_{18}$DI3T, were found to form a SmA phase, thereby constituting a new class of oligothiophene-based liquid crystals. It was shown that the alkyl chain length greatly affected liquid crystal phase formation. The absence of liquid crystallinity for DOC$_n$DBr3T and changes in the IR spectra suggest that the alkylamide group is involved in liquid crystal phase formation in the DNC$_n$DBr3T.

4. Experimental

4.1. Synthesis

2-Bromothiophene,2,5-dibromothiophene,[1,3-bis-(diphenyphosphino) propane] nickel(II) chloride (NiCl$_2$-(dppp), magnesium, diisopropylamine, butyllithium (hexane solution), thionyl chloride, triethylamine, monoalkylamines (C$_n$H$_{2n+1}$NH$_2$, n=5, 8, 16, 18), and 1-iodoalkanes (C$_n$H$_{2n+1}$I, n=5, 8, 16, 18) were commercially available and used without further purification. 2,2′:5′,2″-Terthiophene (3T) was prepared by the Grignard coupling reaction of 2,5-dibromothiophene with 2-bromomagnesiumthiophene in ether at refluxing. Synthetic procedures are illustrated in the Scheme 2.

4.1.1. Synthesis of *N*,*N*′-dialkyl-5,5″-dichloro-2,2′:5′,2″-terthiophene-4,4″-dicarboxamide (DNC$_n$DCl3T, n=8, 18). 5,5″-Dichloro-2,2′:5′,2″-terthiophene (DCl3T) was prepared by the reaction of 3T (3.0 g, 12.1 mmol) with *N*-chlorosuccinimide (3.2 g, 24.2 mmol) in chloroform (200 mL) at room temperature for 5 h and purified by silica gel column chromatography using chloroform as eluent, followed by recrystallization from a benzene/hexane mixture (1:2 v/v).

A hexane solution of butyllithium was added to a THF solution of diisopropylamine at −78 °C under a nitrogen atmosphere to give lithium diisopropylamine (LDA). DCl3T (3.0 g, 9.46 mmol), was added to a THF solution (50 mL) of LDA (37.84 mmol) at −78 °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″-dichloro-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid (yield 65% based on DCl3T).

A dichloromethane solution (100 mL) of 5,5″-dichloro-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid (1.0 g, 2.47 mmol) and SOCl$_2$ (0.59 g, 4.94 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 octylamine (0.64 g, 4.94 mmol) in the presence of triethylamine (2.5 mL) at 0 °C and the solution stirred for 5 h at 0 °C. The solvent was removed under reduced pressure to give DNC$_8$DCl3T. The product was purified by silica gel column chromatography using chloroform as the eluent (yield 62% based on 5,5″-dichloro-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid). ^{1}H NMR (400 MHz, THF-d_8): δ (ppm)=7.34 (s, 2H, ArH), 7.30 (t, 2H, NH), 7.29 (s, 2H, ArH), 3.36 (dt, 4H, octyl α-CH$_2$), 1.60 (tt, 4H, octyl β-CH$_2$), 1.47–1.22 (m, 20H, octyl CH$_2$), 0.88 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 3301 ($\nu_{\mathrm{N-H}}$), 2956, 2922, 2855 ($\nu_{\mathrm{C-H}}$), 1623 ($\nu_{\mathrm{C=O}}$). MS(EI): *m*/*z* 628 (M$^+$). Elemental analysis: found C 57.49, H 6.40, N 4.38%. Calcd for $C_{30}H_{40}N_2S_3O_2Cl_2$ C 57.40, H 6.42, N 4.47%.

The DNC$_{18}$DCl3T was synthesized using analogous procedures with stearylamine (yield 55%). ^{1}H NMR (400 MHz, THF-d_8): δ (ppm)=7.33 (s, 2H, ArH), 7.32 (t, 2H, NH), 7.26 (s, 2H, ArH), 3.39 (dt, 4H, stearyl α-CH$_2$), 1.61 (tt, 4H, stearyl β-CH$_2$), 1.45–1.23 (m, 60H, stearyl CH$_2$), 0.88 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 3311 ($\nu_{\mathrm{N-H}}$), 2958, 2919, 2847 ($\nu_{\mathrm{C-H}}$), 1618 ($\nu_{\mathrm{C=O}}$). MS(EI): *m*/*z* 908 (M$^+$). Elemental analysis: found C 66.03, H 9.01, N 3.15%. Calcd for $C_{50}H_{80}N_2S_3O_2Cl_2$ C 66.12, H 8.88, N 3.08%.

4.1.2. Synthesis of *N*,*N*′-dialkyl-5,5″-dibromo-2,2′:5′,2″-terthiophene-4,4″-dicarboxamide (DNC$_n$DBr3T, n=5, 8, 16, 18). 5,5″-Dibromo-2,2′:5′,2″-terthiophene (DBr3T) was prepared by the reaction of 3T (3.5 g, 14.1 mmol) with *N*-bromosuccinimide (5.0 g, 28.2 mmol) in chloroform (200 mL) at room temperature for 5 h and purified by silica gel column chromatography using chloroform as eluent, followed by recrystallization from a benzene/hexane mixture (1:2 v/v).

DBr3T (2.8 g, 6.89 mmol), was added to a THF solution (50 mL) of LDA (27.44 mmol) at −78 °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″-dibromo-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid (yield 65% based on DBr3T).

A dichloromethane solution (100 mL) of 5,5″-dibromo-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid (1.0 g, 2.0 mmol) and SOCl$_2$ (0.48 g, 4.0 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 amylamine (0.35 g, 4.0 mmol) in the presence of triethylamine (2.3 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$_5$DBr3T. The product was purified by silica gel column chromatography using chloroform as the eluent (yield 71% based on 5,5″-dibromo-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid). ^{1}H NMR (600 MHz, THF-d_8): δ (ppm)=7.35 (s, 2H, ArH), 7.32 (t, 2H, NH), 7.28 (s, 2H, ArH), 3.36 (dt, 4H, pentyl α-CH$_2$), 1.60 (tt, 4H, pentyl β-CH$_2$), 1.45–1.33 (m, 8H, pentyl CH$_2$), 0.88 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 3388 ($\nu_{\mathrm{N-H}}$), 2958, 2927, 2859 ($\nu_{\mathrm{C-H}}$), 1625 ($\nu_{\mathrm{C=O}}$). MS(EI): *m*/*z* 632 (M$^+$). Elemental analysis: found C 45.65, H 4.44, N 4.47%. Calcd for $C_{24}H_{28}N_2S_3O_2Br_2$ C 45.58, H 4.46, N 4.43%.

The DNC$_8$DBr3T, DNC$_{16}$DBr3T and DNC$_{18}$DBr3T were synthesized using analogous procedures with octylamine, 1-hexadecylamine, or stearylamine (yields 55–63%).

DNC$_8$DBr3T: ^{1}H NMR (600 MHz, THF-d_8): δ (ppm)=7.36 (s, 2H, ArH), 7.31 (t, 2H, NH), 7.28 (s, 2H, ArH), 3.38 (dt, 4H, octyl α-CH$_2$), 1.61 (tt, 4H, octyl β-CH$_2$), 1.46–1.23 (m, 20H, octyl CH$_2$), 0.88 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 3302 (ν_{N-H}), 2958, 2923, 2853 (ν_{C-H}), 1625 ($\nu_{C=O}$). MS(EI): *m/z* 716 (M$^+$). Elemental analysis: found C 50.38, H 5.60, N 3.96%. Calcd for $C_{30}H_{40}N_2S_3O_2Br_2$ C 50.28, H 5.63, N 3.91%.

DNC$_{16}$DBr3T: ^{1}H NMR (600 MHz, THF-d_8): δ (ppm)=7.35 (s, 2H, ArH), 7.32 (t, 2H, NH), 7.29 (s, 2H, ArH), 3.34 (dt, 4H, cetyl α-CH$_2$), 1.58 (tt, 4H, cetyl β-CH$_2$), 1.48–1.15 (m, 52H, cetyl CH$_2$), 0.88 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 3328 (ν_{N-H}), 2948, 2921, 2850 (ν_{C-H}), 1619 ($\nu_{C=O}$). MS(EI): *m/z* 941 (M$^+$). Elemental analysis: found C 58.74, H 7.64, N 3.01%. Calcd for $C_{46}H_{72}N_2S_3O_2Br_2$ C 58.71, H 7.71, N 2.98%.

DNC$_{18}$DBr3T: ^{1}H NMR (600 MHz, THF-d_8): δ (ppm)=7.35 (s, 2H, ArH), 7.31 (t, 2H, NH), 7.28 (s, 2H, ArH), 3.38 (dt, 4H, stearyl α-CH$_2$), 1.60 (tt, 4H, stearyl β-CH$_2$), 1.45–1.22 (m, 60H, stearyl CH$_2$), 0.88 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 3312 (ν_{N-H}), 2956, 2918, 2849 (ν_{C-H}), 1619 ($\nu_{C=O}$). MS(EI): *m/z* 997 (M$^+$). Elemental analysis: found C 60.36, H 8.00, N 2.79%. Calcd for $C_{50}H_{80}N_2S_3O_2Br_2$ C 60.22, H 8.09, N 2.81%.

4.1.3. Synthesis of *N*,*N*′-dialkyl-5,5″-diiodo-2,2′:5′,2″-terthiophene-4,4″-dicarboxamide (DNC*$_n$*DI3T, *n*=8, 18). 5,5″-Diiodo-2,2′:5′,2″-terthiophene (DI3T) was prepared by the reaction of 3T (3.0 g, 12.1 mmol) with *N*-iodosuccinimide (5.4 g, 24.2 mmol) in chloroform (200 mL) at room temperature for 5 h and purified by silica gel column chromatography using chloroform as eluent, followed by recrystallization from a benzene/hexane mixture (1:2 v/v).

DI3T (2.8 g, 5.60 mmol), was added to a THF solution (50 mL) of LDA (22.4 mmol) at −78 °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″-diiodo-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid (yield 75% based on DI3T).

A dichloromethane solution (100 mL) of 5,5″-diiodo-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid (1.0 g, 1.7 mmol) and SOCl$_2$ (0.40 g, 3.4 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 octylamine (0.43 g, 3.4 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$_8$DI3T. The product was purified by silica gel column chromatography using chloroform as the eluent (yield 75% based on 5,5″-diiodo-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid). ^{1}H NMR (400 MHz, THF-d_8): δ (ppm)=7.37 (s, 2H, ArH), 7.33 (t, 2H, NH), 7.27 (s, 2H, ArH), 3.38 (dt, 4H, octyl α-CH$_2$), 1.62 (tt, 4H, octyl β-CH$_2$), 1.47–1.24(m, 20H, octyl CH$_2$), 0.88 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 3303 (ν_{N-H}), 2957, 2922, 2854 (ν_{C-H}), 1624 ($\nu_{C=O}$). MS(EI): *m/z* 810 (M$^+$). Elemental analysis: found C 44.18, H 5.05, N 3.43%. Calcd for $C_{30}H_{40}N_2S_3O_2I_2$ C 44.45, H 4.97, N 3.46%.

The DNC$_{18}$DI3T was synthesized using analogous procedures with stearylamine (yield 72%). ^{1}H NMR (400 MHz, THF-d_8): δ (ppm)=7.32 (s, 2H, ArH), 7.30 (t, 2H, NH), 7.27 (s, 2H, ArH), 3.36 (dt, 4H, stearyl α-CH$_2$), 1.60 (tt, 4H, stearyl β-CH$_2$), 1.43–1.21 (m, 60H, stearyl CH$_2$), 0.88 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 3313 (ν_{N-H}), 2957, 2916, 2850 (ν_{C-H}), 1617 ($\nu_{C=O}$). MS(EI): *m/z* 1091 (M$^+$). Elemental analysis: found C 54.98, H 7.45, N 2.54%. Calcd for $C_{50}H_{80}N_2S_3O_2I_2$ C 55.04, H 7.39, N 2.57%.

4.1.4. Synthesis of 4,4″-bis-(alkyloxycarbonyl)-5,5″-dibromo-2,2′:5′,2″-terthiophene (DOC*$_n$*DBr3T, *n*=5, 8, 16, 18). 5,5″-Dibromo-2,2′:5′,2″-terthiophene-4,4″-dicarboxylic acid (0.5 g, 1.0 mmol) was reacted with 1-iodopentane (0.40 g, 2.0 mmol) in the presence of potassium carbonate (0.20 g, 1.5 mmol) in hexamethylphosphorotriamide (20 mL) at room temperature for 24 h under a nitrogen atmosphere. The resulting solid was collected to give DOC$_5$DBr3T. The product was purified by silica gel column chromatography using chloroform as the eluent (yield 91%). ^{1}H NMR (400 MHz, THF-d_8): δ (ppm)=7.45 (s, 2H, ArH), 7.40 (s, 2H, ArH), 4.29 (t, 4H, pentyl α-CH$_2$), 1.64–1.27 (m, 12H, pentyl CH$_2$), 0.93 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 2953, 2935, 2862 (ν_{C-H}), 1683 ($\nu_{C=O}$). MS (EI): *m/z* 634 (M$^+$). Elemental analysis: found C 45.44, H 4.00%. Calcd for $C_{24}H_{26}S_3O_4Br_2$ C 45.43, H 4.13%.

The DOC$_8$DBr3T, DOC$_{16}$DBr3T and DOC$_{18}$DBr3T were synthesized using analogous procedures with 1-iodooctane, 1-iodohexadecane, or 1-iodooctadcane (yields 91–93%).

DOC$_8$DBr3T: ^{1}H NMR (400 MHz, THF-d_8): δ (ppm)=7.45 (s, 2H, ArH), 7.40 (s, 2H, ArH), 4.28 (t, 4H, octyl α-CH$_2$), 1.59–1.13 (m, 24H, octyl CH$_2$), 0.89 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 2958, 2924, 2852 (ν_{C-H}), 1707 ($\nu_{C=O}$). MS(EI): *m/z* 718 (M$^+$). Elemental analysis: found C 50.19, H 5.32%. Calcd for $C_{30}H_{38}S_3O_4Br_2$ C 50.14, H 5.33%.

DOC$_{16}$DBr3T: ^{1}H NMR (400 MHz, THF-d_8): δ (ppm)=7.45 (s, 2H, ArH), 7.39 (s, 2H, ArH), 4.20 (t, 4H, cetyl α-CH$_2$), 1.55–1.05 (m, 56H, cetyl CH$_2$), 0.86 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 2955, 2917, 2848 (ν_{C-H}), 1688 ($\nu_{C=O}$). MS (EI): *m/z* 943 (M$^+$). Elemental analysis: found C 58.82, H 7.47%. Calcd for $C_{46}H_{70}S_3O_4Br_2$ C 58.59, H, 7.48%.

DOC$_{18}$DBr3T: ^{1}H NMR (400 MHz, THF-d_8): δ (ppm)=7.45 (s, 2H, ArH), 7.39 (s, 2H, ArH), 4.28 (t, 4H, stearyl α-CH$_2$), 1.57–0.99 (m, 64H, stearyl CH$_2$), 0.88 (t, 6H, CH$_3$). IR (KBr, cm^{-1}): 2956, 2918, 2849 (ν_{C-H}), 1689 ($\nu_{C=O}$). MS(EI): *m/z* 999 (M$^+$). Elemental analysis: found C 60.82, H 8.06%. Calcd for $C_{50}H_{78}S_3O_4Br_2$ C 60.11, H 7.87%.

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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