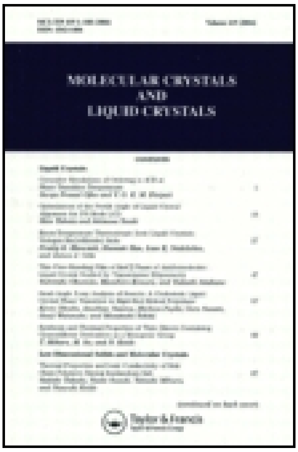

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Synthesis and Mesomorphism of Asymmetric Triphenylene Discotic Liquid Crystals Bearing with Mono-Amido-Based Alkyl Soft Chains

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Synthesis and Mesomorphism of Asymmetric Triphenylene Discotic Liquid Crystals Bearing with Mono-Amido-Based Alkyl Soft Chains

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A series of triphenylene discotic liquid crystals with amido-based alkyl chains in different lengths were synthesized and characterized. The liquid crystal properties were studied with differential scanning calorimetry and polarizing optical microscopy. The influences of amide alkyl chain lengths on the mesomorphism were discussed. Based on the results, we concluded that the triphenylene discogens with an amido-based alkyl chain could form intermolecular hydrogen bonds inside their columnar stacks, and hence, exhibit higher melting and clearing points, and wider mesophase ranges.

Keywords Columnar phase; discotic liquid crystal; intermolecular hydrogen bonds; mesophase anchoring; supramolecular; triphenylene

1. Introduction

A discotic liquid crystal (DLC) molecule is normally composed of a polycyclic aromatic core, which is a big conjugated π-electron system, and six to eight peripheral soft alkyl chains [1]. Triphenylene discotic liquid crystal (TPDLC) is one of the most widely investigated DLCs [2,3].

TPDLCs, through the π-π interactions among triphenylene cores, can spontaneously assemble to highly ordered helical phase and hexagonal columnar mesophase, and therefore, demonstrate high charge carrier mobility [4–6]. These properties have attracted much attentions on TPDLCs, especially on their great potential applications as molecular conducting wires, organic light emitting diodes (OLED), solar cells, high-speed copy machines, scanner's photo-conducting toners, and so on [1,4,6].

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The fast charged carrier mobility of TPDLCs' has been proved to be associated with their highly ordered columnar phases [7–9]. As a result, most research on TPDLCs, up to date, is focused on stabilizing their columnar phases or the molecules' ordered stackings by means of molecular designs. Introducing intermolecular hydrogen bonds in TPDLCs for controlling the ordered columnar stacks and molecular dynamics is one of those very effective methods.

Intermolecular hydrogen-bonds are dynamically reversible and are responsive to external stimulations. The utilization of intermolecular hydrogen bonds to build dynamically functionalized, environmentally friendly, low cost and processing materials is an attractive direction of material research [10–13]. In addition, liquid crystals with hydrogen bond interactions are featured with a variety of properties, such as charge conductivity, information storage, molecular sensing and dynamic behaviors. These liquid crystals are also able to respond to external stimulations and change their self-assembled structures through hydrogen-bonding associations and dissociations. Stabilizing columnar phases through intermolecular hydrogen bonds among amido-groups has been studied by several research groups [14–17] and shown improved semi-conducting properties [7–9,18–22].

Besides, we [23–25] synthesized various triphenylene discogens $C_{18}H_6(OR)_{6-n}$-$(OCH_2CONHC_4H_9)_n$ (n = 1, 2, 3). Our experimental results, combined with semi-quantitative calculation studies [26,27], showed that the intermolecular hydrogen

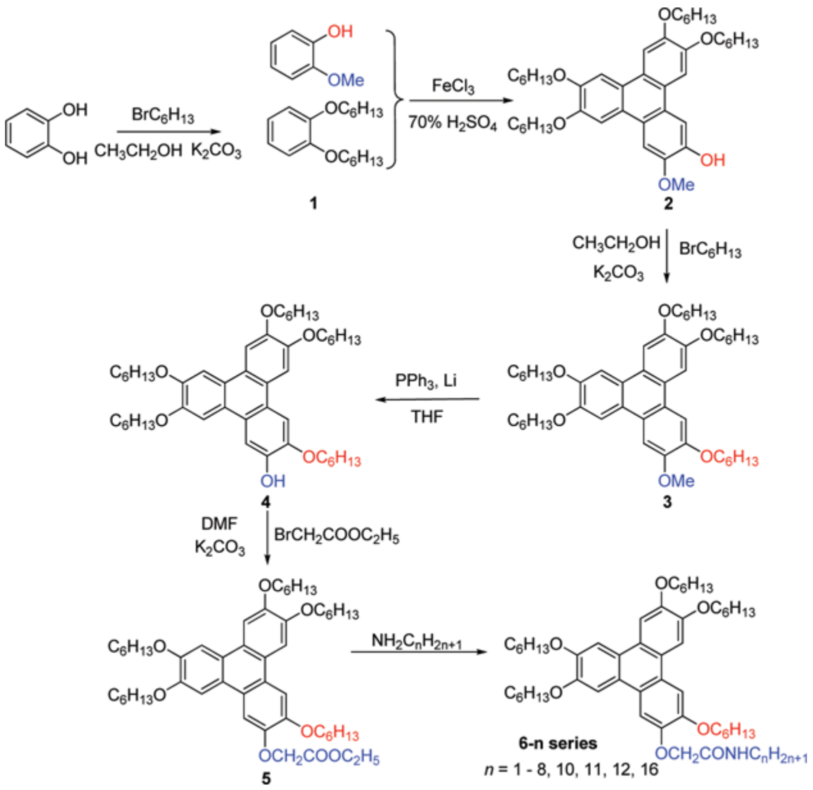

Figure 1. Synthesis of mono-amido-triphenylene discotic liquid crystals. (Figure appears in color online.)

bondings could cooperatively contribute to the stability of the hexagonal columnar phases (Col_h).

In this article, we are focusing on the mesomorphism of TPDLCs. The mesomorphism, as we expected, could be affected by both intermolecular hydrogen bondings and the molecular symmetry of discogens; and the latter is associated with the length of amide alkyl soft chains. As a result of this, we designed, synthesized and studied a series of triphenylene discotic compounds $C_{18}H_6(OC_6H_{13})_5$-$(OCH_2CONHC_nH_{2n+1})$, n = 1–8, 10, 11, 12, 16, in which five peripheral hexyloxy chains remain unchanged, only one amide-based alkyl chain was varied in its length. We also compared our TPDLCs with the previously reported hexaalkoxytriphenylene discogens $C_{18}H_6(OC_6H_{13})_5(OC_mH_{2m+1})$ [28]; and found that the amide group could improve the mesomorphism of discogens.

Our target TPDLCs were synthesized as described in Figure 1.

2. Experimental

Instruments and Methods

NMR was recorded on a Bruker-Advance-600 MHz instrument using TMS as the internal standard, $CDCl_3$ as the solvent. Mesomorphic textures were observed and recorded using XP-201 Polarized Optical Microscope (POM) installed with a XP-201 hotplate and a XPR-201 temperature controller. Phase transition temperatures and enthalpies of discogens were investigated using a TA-DSC Q100 instrument under N_2 atmosphere with heating and cooling rates as 10°C/min. Unless otherwise noted, the reagents and solvents were commercially available and used without further purifications. The commercial unavailable primary amines were prepared according to the Gabriel synthesis method [29].

2-Hydroxyl-3-methoxy-6,7,10,11-tetra(hexyloxy)triphenylene **(2)**. It was synthesized according to a reported method [30].

2-Methoxy-3,6,7,10,11-penta(hexyloxy)triphenylene **(3)**. A mixture of **2** (4.7 g, 6.97 mmol), $C_6H_{13}Br$ (1.73 g, 10.46 mmol) and K_2CO_3 (3.85 g, 27.88 mmol) in EtOH (100 ml) was heated refluxed. The reaction was monitored by TLC (40% chloroform in petroleum ether). After 24 hours, the reaction was poured into hydrochloride acid (3% as an aqueous solution), extracted with CH_2Cl_2 (3 × 50 ml). The combined organic layers were dried through $MgSO_4$, concentrated. Resulting blue solid was purified by column chromatography (28% chloroform in petroleum ether). Recrystallization from ethanol followed by drying under high vacuum give a light blue crystal as the title compound **3** (5.14 g, 97% yield.)

2-Hydroxyl-3,6,7,10,11-penta(hexyloxy)triphenylene **(4)**. Li (0.23 g, 32.55 mmol) was added to a solution of Ph_3P (3.56 g, 13.56 mmol) in freshly distilled THF (30 mL). The reaction was carried out under N_2 atmosphere. After refluxing for 3 hours, *t*-BuCl (1.25 g, 13.56 mmol) was added and the reaction was refluxed for additional 1 hour when **3** (5.14 g, 6.78 mmol) was added. The reaction was then monitored by TLC (33% CH_2Cl_2 in petroleum ether). After refluxing for another 5 hours, the reaction was cooled to room temperature, and was poured into hydrochloride acid (3% as an aqueous solution), extracted with CH_2Cl_2 (3 × 50 ml). The combined organic layers were dried through $MgSO_4$, concentrated under reduced pressure. The resulting white solid was purified by column chromatography (17% CH_2Cl_2 in petroleum ether). Recrystallization from ethanol followed by drying under high vacuum give a white crystal as the title compound **3** (4.04 g, 80% yield.)

2-(Ethoxycarbonylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene, $C_{18}H_6(OC_6H_{13})_5(OCH_2COOC_2H_5)$, 5. The reaction of **4** (1.5 g, 2 mmol), $BrCH_2COOC_2H_5$ (0.41 g, 2.5 mmol) and K_2CO_3 (1.10 g, 8 mmol) in DMF (15 ml) was carried out under room temperature. The reaction was monitored by thin-layer chromatography (75% CH_2Cl_2 in petroleum ether). After 24 hours, the reaction was poured into hydrochloride acid (3% as an aqueous solution), extracted with CH_2Cl_2 (3×50 ml). The combined organic layers were dried through $MgSO_4$, concentrated under reduced pressure. The resulting white solid was purified by column chromatogarphy (67% CH_2Cl_2 in petroleum ether). Recrystallization from ethanol followed by drying under high vacuum gave a white crystal as the title compound **3** (1.54 g, 92% yield.)

General procedure for the synthesis of TPDLCs **6-n**. The mixture of $C_{18}H_6(OC_6H_{13})_5(OCH_2COOC_2H_5)$ (**5**) (1.0 equiv.) and a primary amine (3 mL) was heated to reflux under 80°C. The reaction was monitored by thin-layer chromatography. After completion, the reaction was concentrated under reduced pressure, and purified by column chromatography. TPDLCs **6-n** were then recrystallized from ethanol, and dried under high vacuum.

6–1: *2-(Methylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–1** was synthesized by the reaction of **5** (150 mg, 0.18 mmol) with methylamine (3 mL, 21 mmol) following the general procedure, afforded the compound as a white solid in yield 98%. ^1H NMR ($CDCl_3$, TMS, 600 MHz) δ: 0.92–0.96 (m, 15H), 1.37–1.45 (m, 20H), 1.55–1.60 (m, 10H), 1.91–1.97 (m, 10H), 2.97 (d, $J = 2.7$ Hz), 4.22–4.27 (m, 10H), 4.76 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.85 (b, 5H). IR (KBr) ν: 3422, 1691, 1659, 1618 cm^{-1}. Anal. calcd for $C_{51}H_{77}NO_7$: C 75.05, H 9.51, N 1.72; found C 74.68, H 9.53, N 1.62.

6–2: *2-(Ethylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–2** was synthesized by the reaction of **5** (120 mg, 0.15 mmol) with ethylamine (3 mL, 36 mmol) following the general procedure, afforded the compound as a white solid in yield 89%. ^1H NMR ($CDCl_3$, TMS, 600 MHz) δ: 0.93–0.96 (m, 15H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.38–1.42 (m, 20H), 1.54–1.61 (m, 10H), 1.93–1.97 (m, 10H), 3.42–3.46 (m, 2H), 4.22–4.27 (m, 10H), 4.74 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) ν: 3408, 1688, 1618 cm^{-1}. Anal. calcd for $C_{52}H_{79}NO_7$: C 75.23, H 9.59, N 1.69; found C 75.30, H 9.46, N 1.65.

6–3: *2-(Propylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–3** was synthesized by the reaction of **5** (120 mg, 0.15 mmol) with *n*-propylamine (3 mL, 36.5 mmol) following the general procedure, afforded the compound as a white solid in yield 91.5%. ^1H NMR ($CDCl_3$, TMS, 600 MHz) δ: 0.95–0.99 (m, 18H), 1.37–1.44 (m, 20H), 1.55–1.64 (m, 12H), 1.91–1.97 (m, 10H), 3.35–3.39 (m, 2H), 4.22–4.27 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) ν: 3416, 1690, 1618 cm^{-1}. Anal. calcd for $C_{53}H_{81}NO_7$: C 75.40, H 9.67, N 1.66; found C 75.40, H 9.52, N 1.64.

6–4: *2-(Butylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–4** was synthesized by reaction of **5** (120 mg, 0.15 mmol) with *n*-butylamine

(3 mL, 30.4 mmol) in yield 93.2%. ^{1}H NMR (CDCl$_3$, TMS, 600 MHz) δ: 0.93–0.96 (m, 18H), 1.36–1.44 (m, 22H), 1.56–1.62 (m, 12H), 1.91–1.98 (m, 10H), 3.35–3.39 (m, 2H), 4.21–4.26 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) ν: 3416, 1689, 1618 cm^{-1}. Anal. calcd for $C_{54}H_{83}NO_7$: C 75.57, H 9.75, N 1.63; found C 75.57, H 9.53, N 1.60.

6–5: *2-(Pentylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–5** was synthesized in yield 80.5%. ^{1}H NMR (CDCl$_3$, TMS, 600 MHz) δ: 0.88–0.90 (m, 3H), 0.92–0.96 (m, 15H), 1.33–1.44 (m, 24H), 1.55–1.60 (m, 12H), 1.91–1.98 (m, 10H), 3.37–3.41 (m, 2H), 4.22–4.27 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) ν: 3414, 1689, 1619 cm^{-1}. Anal. calcd for $C_{55}H_{85}NO_7$: C 75.73, H 9.82, N 1.61; found C 75.64, H 9.70, N 1.58.

6–6: *2-(Hexylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–6** was synthesized in yield 88%. ^{1}H NMR (CDCl$_3$, TMS, 600 MHz) δ: 0.86 (t, $J = 6.9$ Hz, 3H), 0.92–0.96 (m, 15H), 1.28–1.30 (m, 4H), 1.36–1.44 (m, 22H), 1.56–1.60 (m, 12H), 1.93–1.97 (m, 10H), 3.39 (d, $J = 3.3$ Hz, 2H), 4.22–4.27 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) ν: 3414, 1689, 1619 cm^{-1}. Anal. calcd for $C_{56}H_{87}NO_7$: C 75.89, H 9.89, N 1.58; found C 75.96, H 9.85, N 1.58.

6–7: *2-(Heptylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–7** was synthesized in yield 78%. ^{1}H NMR (CDCl$_3$, TMS, 600 MHz) δ: 0.86 (t, $J = 6.9$ Hz, 3H), 0.92–0.96 (m, 15H), 1.23–1.30 (m, 6H), 1.36–1.44 (m, 22H), 1.55–1.60 (m, 12H), 1.93–1.97 (m, 10H), 3.39 (d, $J = 3.3$ Hz), 4.22–4.27 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) ν: 3412, 1689, 1619 cm^{-1}. Anal. calcd for $C_{57}H_{89}NO_7$: C 76.04, H 9.96, N 1.56; found C 75.77, H 9.91, N 1.51.

6–8: *2-(Octylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–8** was synthesized in yield 86%. ^{1}H NMR (CDCl$_3$, TMS, 600 MHz) δ: 0.86 (t, $J = 6.9$ Hz, 3H), 0.92–0.96 (m, 15H), 1.23–1.29 (m, 8H), 1.33–1.44 (m, 22H), 1.55–1.61 (m, 12H), 1.93–1.97 (m, 10H), 3.38 (d, $J = 3.3$ Hz, 2H), 4.22–4.27 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) ν: 3407, 1688, 1619 cm^{-1}. Anal. calcd for $C_{58}H_{91}NO_7$: C 76.19, H 10.03, N 1.53; found C 75.92, H 10.09, N 1.54.

6–10: *2-(Decylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–10** was synthesized in yield 88%. ^{1}H NMR (CDCl$_3$, TMS, 600 MHz) δ: 0.87 (t, $J = 6.9$ Hz, 3H), 0.92–0.96 (m, 15H), 1.23–1.29 (m, 12H), 1.33–1.44 (m, 22H), 1.55–1.60 (m, 12H), 1.93–1.97 (m, 10H), 3.38 (d, $J = 3.3$ Hz, 2H), 4.22–4.27 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) ν: 3411, 1690, 1618 cm^{-1}. Anal. calcd for $C_{60}H_{95}NO_7$: C 76.47, H 10.16, N 1.49; found C 76.38, H 10.27, N 1.49.

6–11: *2-(Undecylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–11** was synthesized in yield 84%. ^{1}H NMR (CDCl$_3$, TMS, 600 MHz) δ: 0.87 (t, $J = 6.9$ Hz, 3H), 0.92–0.96 (m, 15H), 1.23–1.29 (m, 14H), 1.33–1.44 (m, 22H), 1.55–1.61 (m, 12H), 1.93–1.97 (m, 10H), 3.38 (d, $J = 3.3$ Hz, 2H), 4.22–4.27 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) ν: 3417, 1689, 1619 cm^{-1}. Anal. calcd for $C_{61}H_{97}NO_7$: C 76.60, H 10.22, N 1.46; found C 76.67, H 10.15, N 1.47.

6–12: *2-(Dodecylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–12** was synthesized in yield 87%. ^{1}H NMR (CDCl$_3$, TMS, 600 MHz) δ: 0.88 (s, 3H), 0.92–0.96 (m, 15H), 1.23–1.33 (m, 16H), 1.38–1.43 (m, 22H), 1.56–1.60 (m, 12H), 1.93–1.97 (m, 10H), 3.37–3.4 (m, 2H), 4.22–4.27 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) v: 3415, 1689, 1619 cm^{-1}. Anal. calcd for $C_{62}H_{99}NO_7$: C 76.73, H 10.28, N 1.44; found C 76.46, H 10.32, N 1.43.

6–16: *2-(Hexadecylcarbamoylmethoxy)-3,6,7,10,11-penta(hexyloxy)triphenylene.* TPDLC **6–16** was synthesized in yield 88%. ^{1}H NMR (CDCl$_3$, TMS, 600 MHz) δ: 0.93–0.96 (m, 18H), 1.23–1.33 (m, 24H), 1.37–1.44 (m, 22H), 1.54–1.60 (m, 12H), 1.93–1.97 (m, 10H), 3.37–3.40 (m, 2H), 4.22–4.27 (m, 10H), 4.75 (s, 2H), 7.26 (s, 1H), 7.77 (s, 1H), 7.84 (b, 5H). IR(KBr) v: 3412, 1689, 1618 cm^{-1}. Anal. calcd for $C_{66}H_{107}NO_7$: C 77.22, H 10.51, N 1.36; found C 76.76, H 10.35, N 1.34.

3. Results and Discussion

3.1. *Synthesis and Characterizations*

Hydroxytriphenylenes are key intermediates for the synthesis of functional or polymeric TPDLCs [30–37], and 2-Hydroxyl-3,6,7,10,11-pentahexyloxytriphenylene **4** is an important intermediate for the synthesis of mono-amido-functionalized TPDLCs. It has been prepared by reacting FeCl$_3$ with 1,2-dihexyloxybenzene **1** and 2-methoxyphenol. After the reaction, 2-hydroxyl-3-methoxy-6,7,10,11-tetrahexyloxytriphenylene **2** [34] and the by-product 2,3,6,7,10,11-hexahexyloxytriphenylene were obtained, which were then easily separated using flash chromatography **2** was then treated with 1-bromohexane to form 2-methoxy-3,6,7,10,11-pentahexyloxytriphenylene **3**, followed by demethylation with Ph$_2$Li to obtain 2-hydroxy-3,6,7,10,11-pentahexyloxy triphenylene **4** [35].

Comparing with other reported synthetic methods for hydroxytriphenylenes, this route has the advantage of readily available starting materials, less synthetic steps, easy experimental operations, isomer separations and product purifications. Besides, this route also provides moderate yields, and can be easily scaled up to multi-grams synthesis.

The alkylation of hydroxytriphenylene **4** with ethyl bromoacetate produced **5**, it further reacted with alkylamine yielding the target compounds **6-n**. In addition, several primary amines we used in the last step were prepared via Gabriel synthesis [29].

3.2. *Mesomorphism of Compounds* 6-n

We then studied the liquid crystal properties of compounds **6-n** using POM installed with a hot plate as well as using DSC. Except for **6–16** (no mesophase was observed), all other **6-n** compounds were found to possess one columnar mesophase. The phase transition temperatures and the corresponding enthalpy changes were included in Table 1. Besides, these TPDLCs were found to have fan-shaped textures (Fig. 2) that are typically shown by columnar mesophases. The DSC traces of heating and cooling runs were shown in Figure 3.

Furthermore, most compounds among **6-n** only exhibited transition peaks corresponding to changes from crystal to liquid crystal then to liquid phases in the DSC curves. However, interestingly, compounds **6–1, 6–11** and **6–12** showed an extra transition peak representing a change from crystal to crystal phase during the second

Table 1. Thermotropic properties of triphenylene discogens, $TP(OC_6H_{13})_5(OCH_2CONHC_nH_{2n+1})$, [n = 1–8, 10, 11, 12, 16]

	Mesophases, transition temperature and enthalpy changes	
Compd.	Second heating/°C (ΔH, KJ/mol)	First cooling/°C (ΔH, KJ/mol)
n = 1	$Cry_2$71 (3.94) Cry_1 79 (38.70) Col_h 133 (5.12) I	I 133 (5.49) Col_h 46 (34.78) Cry
n = 2	Cry 69 (39.45) Col_h 138 (6.57) I	I 138 (6.33) Col_h 51 (39.00) Cry
n = 3	Cry 74 (34.63) Col_h 141 (6.48) I	I 140 (6.41) Col_h 57 (36.23) Cry
n = 4	Cry 69 (39.97) Col_h 143 (7.32) I	I 142 (7.14) Col_h 52 (6.85) Cry_1 47 (1.02) Cry_2
n = 5	Cry 65 (36.28) Col_h 138 (7.05) I	I 138 (6.93) Col_h 51 (36.22) Cry
n = 6	Cry 57 (35.78) Col_h 135 (7.24) I	I 134 (6.67) Col_h 39 (34.59) Cry
n = 7	Cry 65 (40.85) Col_h 127 (6.13) I	I 127 (6.26) Col_h 42 (37.67) Cry
n = 8	Cry 64 (44.87) Col_h 117 (5.37) I	I 118 (5.49) Col_h 41 (39.94) Cry
n = 10	Cry 64 (59.19) Col_h 96 (3.99) I	I 98 (4.51) Col_h 36 (48.38) Cry
n = 11	Cry_2 62 (26.15) Cry_1 67 (10.11) Col_h 88 (3.85) I	I 88 (3.67) Col_h 39 (45.09) Cry
n = 12	Cry_2 54 (2.82) Cry_1 58 (21.56) Col_h 77 (2.76) I	I 75 (2.69) Col_h 37 (34.15) Cry
n = 16	Cry 55 (41.35) I	I 40 (38.23) Cry

heating run; and **6–4** also gave an extra transition peak indicating a crystal to crystal phase change during a second cooling run.

Phase diagrams of compounds **6-n** were shown in Figure 4. From the pictures, the clearing points of compounds **6-n** were increasing and arrived at the highest when n = 4. Then the clearing points started to decrease with the alkyl chain lengthening. Importantly, the compound **6–12** still demonstrated liquid crystal properties.

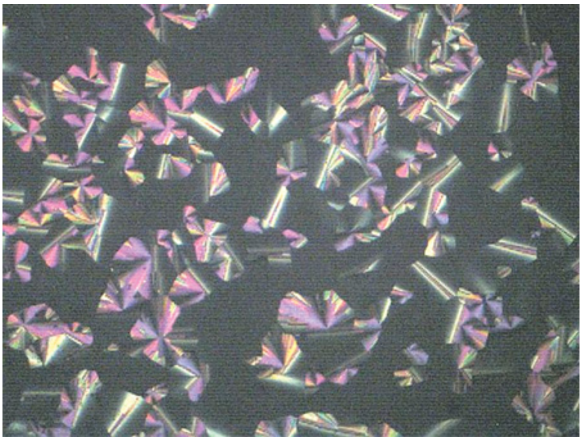

Figure 2. Polarising optical photomicrograph of triphenylene discogen. (Figure appears in color online.)

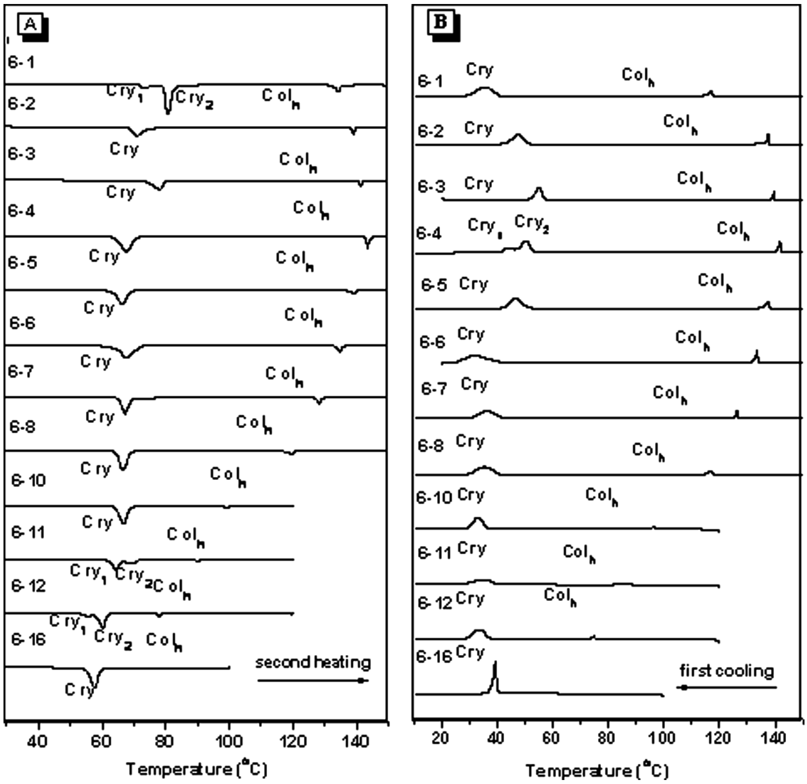

Figure 3. DSC traces of triphenylene derivatives, $C_{18}H_6(OC_6H_{13})_5(OCH_2CONHC_nH_{2n+1})$ (n = 1 ~ 8, 10, 11, 12, 16): (A) is obtained at 2nd heating, and (B) at 1st cooling, with heating and cooling rate of 10°C/min.

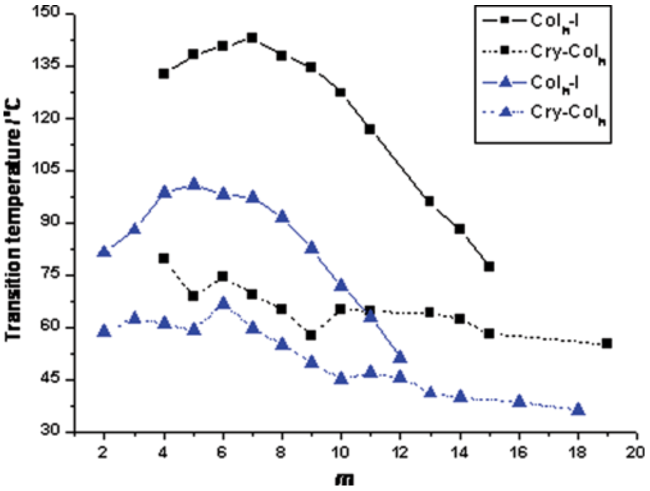

Figure 4. Phase diagram of triphenylene discogens, (■) $C_{18}H_6(OC_6H_{13})_5(OCH_2CONHC_nH_{2n+1})$ (m = n + 3); (▲), $C_{18}H_6(OC_6H_{13})_5(OC_mH_{2m+1})$ [28]. (Figure appears in color online.)

Besides, compound **6–1** had the highest melting point, and compound **6–3**, which possesses the highest molecular symmetry, had the second highest melting point.

Through the formation of intermolecular hydrogen bonds and the lengths variations of the amide alkyl chains, molecular dipoles of TPDLCs **6-n** could be changed. The mesomorphic ranges of compounds **6–1** to **6–6** tended to change in an odd-even fashion; and compound **6–6** showed the widest mesomorphic scope, which could be explained as a result of the equilibrium among intermolecular forces and the molecular symmetry. Such equilibrium could also be mirrored when an excessive alkyl chain length was given. When alkyl chains were too long, though molecular flexibility was increased, its rigidity was dropping down and molecular symmetry was lowered. This could lower down intermolecular forces and disturb the columnar ordered stackings of discotic molecules. Hence, mesomorphic ranges got narrowed.

By comparing **6-n** with previously reported six-alkyl-chain TPDLCs $C_{18}H_6(OC_6H_{13})_5(OC_mH_{2m+1})$, $m = 2 \sim 14$, 16, 18 [28] that bear the same length of periphery, though both serieses have similar trends of phase transition temperature changes, but clearing points and melting points of **6-n** are around 30°C, and 5~10°C higher than those of the six-alkyl-chain TPDLCs, respectively. Furthermore, **6-n** exhibited wider mesomorphic temperature ranges, which are important for the measurements of charge carrier mobilities and practical applications of materials as organic semiconductors.

Besides, **6–12** still possesses liquid crystal property (K 58°C $\mathrm{Col_h}$ 77°C Iso), but the six-alkyl-chain triphenylene $C_{18}H_6(OC_6H_{13})_5(OR)$, as previously reported, began to lose the mesomorphism from tridecyloxy (C_{13}) [28]. This difference might be explained by that the amido-TPDLCs, through the formation of intermolecular hydrogen bonds, had high tendency to form columnar mesophase and can tolerate with low molecular symmetry caused by lengthening of one peripheral chain. In more details, in addition to intermolecular π-π interactions and van der Waals forces, introducing amido functionalities into the alkyl soft chains of triphenylene molecules could increase dipole interactions and intermolecular hydrogen bonds. These effects would improve the columnar stackings of discotic molecules, and consequently, the stability of columnar phases. As a result, it is true that length changes of one alkyl chains on the triphenylene core could affect the molecular symmetry, which has adverse effects on mesomorphism; but intermolecular hydrogen bondings could counteract such adverse effect and stabilize the columnar phases of discogens.

4. Conclusions

In summary, we have synthesized a series of asymmetric TPDLCs bearing amido functional groups $C_{18}H_6(OC_6H_{13})_5(OCH_2CONHC_nH_{2n+1})$ and have investigated their thermotropic liquid crystal properties. We also found that with the increase of the amido alkyl chain length, clearing points of our TPDLCs were first increased and then decreased till the loss of mesomorphism when $n = 16$. By comparing our TPDLCs with previously reported six-alkoxy-chain TPDLCs $[C_{18}H_6(OC_6H_{13})_5(OC_mH_{2m+1})]$, the introduction of amido group has made our TPDLCs with higher clearing points and wider mesomorphic temperature ranges. As a result, the one amido-alkyl-chain TPDLCs, through π-π interaction and van der Waals interaction, as well as intermolecular hydrogen bonds, could anchor columnar phases and counteract the adverse effects on discotic mesomorphism brought by the low molecular symmetry.

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