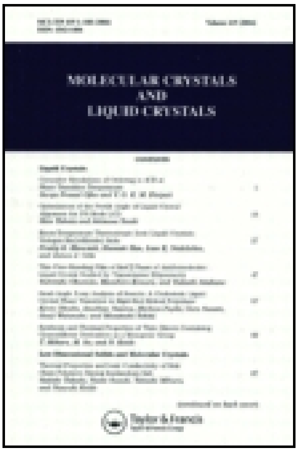

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Synthesis and Mesomorphism of Novel Chiral Triphenylene-Based Discotic Liquid Crystals

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Synthesis and Mesomorphism of Novel Chiral Triphenylene-Based Discotic Liquid Crystals

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A series of new chiral triphenylene-based discotic liquid crystals with one or three chiral soft chains were synthesized through Mitsunobu reactions. Yields of the chiral discotic liquid crystals were achieved up to 84%. Chemical structures were confirmed by ^1H *NMR; and mesomorphism was studied by polarized optical microscopy as well as by differential scanning calorimetry. The mesomorphic studies have shown that 1) the chiral discogens have either hexagonal columnar or plastic columnar mesophases; and 2) the introduction of chirality to triphenylene-based discotic liquid crystals could widen mesophase range by lowering melting points. In addition, an unexpected odd-even effect of mesomorphism was observed.*

Keywords Discotic liquid crystals; hexagonal columnar mesophase; Mitsunobu reactions; odd-even effect; plastic phase; triphenylene

1. Introduction

In recent years, triphenylene-based discotic liquid crystals (TPDLCs) have attracted great attentions. This is because TPDLCs normally have high charge carrier mobility [1,2], and therefore could be applied as organic photovoltaic [3–5] and other electronic materials [6,7].

The formation of ordered hexagonal columnar mesophases ($\mathrm{Col_h}$) is responsible for TPDLCs' electronic properties. As a result, in order to improve TPDLCs' electronic properties, current research has been focused on the stabilization of $\mathrm{Col_h}$ mesophases and the manipulation of molecular symmetry [8–10]. Traditionally, anchoring $\mathrm{Col_h}$ mesophases, through the introduction of hydrogen bonds [11,12], more aromatic rings [13,14], or fluoroalkyl groups [15,16], has been a useful way to increase charge carrier mobility of TPDLCs.

Another possible yet unreported way to make TPDLCs as better candidates for electronic materials is to introduce chiral segments. This is because chiral moieties would decrease the molecular symmetry, and therefore lower TPDLCs' melting points. In addition, the introduction of proper chiral fragments would not affect much TPDLCs' clearing points. Consequently, hexagonal mesomorphic temperature ranges along with liquid crystal properties would be improved.

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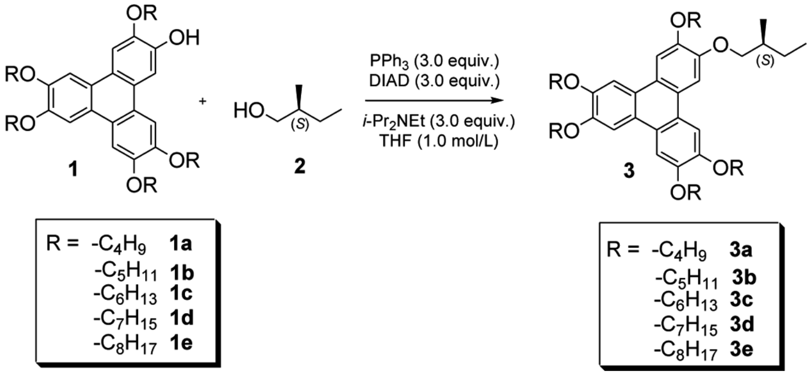
Table 1. The synthesis of chiral triphenylenes[a]



Entry	Substrate	Time (d)	Yield%[b]
1	**1a**	3	34
2	**1b**	3	76
3	**1c**	3	84
4	**1d**	5	59
5	**1e**	5	34

[a] All reactions were carried out using 1.0 equiv. **1**, 3.0 equiv. **2**, DIAD, PPh_3 and i-Pr_2NEt in 0.1 mol/L THF at room temperature for 3d.

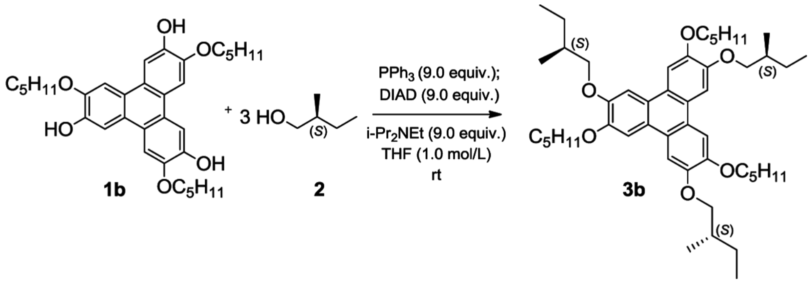
[b] Yields of isolated, purified products.

Herein, we report the first synthesis and mesomorphic studies of several novel chiral triphenylene-based discotic liquid crystals (CTPDLCs) installed with one or three chiral soft chains. The synthetic schemes for the CTPDLCs were shown in Table 1 and Scheme 1.

2. Experimental Methods

2.1. *General Methods*

^1H NMR experiments were carried out on a Bruker-Advance-600 instrument. $CDCl_3$ was used as the solvent, TMS was used as the internal standard. Phase transitions



Scheme 1. The synthesis of the tri-chiral fragment substituted triphenylene **3f**.

and enthalpy changes were measured on a TA-DSC instrument with heating and cooling rates of 10°C/min under N_2 atmosphere. Liquid crystal textures were observed on a XP-201 polarizing optical microscope (POM) installed with an XPR-201 heating plate.

Tetrahydrofuran (THF) was distilled with sodium metal before uses. Triphenylene derivatives (**1a-1e**) were prepared according to literature procedures [17]. Unless otherwise noted, all other chemicals were commercially available and were directly used without further purifications.

2.2. *Synthesis and Characterizations*

General Procedures for the Synthesis of Mono-Chiral Substituted Products (**3a-3e**). To a mixture of 2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylene (**1a-1e**) (1.0 equiv.), (*S*)-2-methylbutanol (3.0 equiv.), PPh_3 (3.0 equiv.), *i*-Pr_2NEt (3.0 equiv.) in THF (1.0 mol/L) under ice-water bath (0°C) was added dropwise with diisopropyl azadicarboxylate (DIAD, 3.0 equiv.) under N_2 atmosphere. After the addition, the reaction was stirred for an additional 10 minutes when the ice-water bath was removed and the reaction was allowed to slowly warm up to the ambient temperature. The reaction was monitored by thin-layer chromatography. Upon completion [18], the reaction was quenched with 5% HCl (w/w) aqueous solution, and was extracted with CH_2Cl_2 (3×). The combined organic layers were dried through $MgSO_4$, concentrated on a rotary evaporator under reduced pressure, and was purified by column chromatography. Then it was further recrystallized in ethanol to give the desired product **3a-3e**.

(S)-2-(2-Methylbutyloxy)-3,6,7,10,11-penta(butyloxy)triphenylene (**3a**). White solid, 34% isolated yield. **^{1}H NMR** ($CDCl_3$, 600 MHz): 1.01–1.07 (m, 18H); 1.12 (d, $J = 7.2$ Hz, 3H); 1.34–1.41 (m, 1H); 1.57–1.64 (m, 10H); 1.65–1.73 (m, 1H); 1.90–1.96 (m, 10H); 2.01–2.07 (m, 1H); 4.02 (dd, $J = 8.4$ Hz, 15 Hz, 1H); 4.11 (dd, $J = 6.6$ Hz, 15 Hz, 1H); 4.24 (t, $J = 5.7$ Hz, 10H); 7.81–7.88 (m, 6H). **IR** (KBr) v: 3099, 2923, 2853, 2746, 1618, 1516, 1466, 1437, 1386, 1263, 1173, 1066, 1048, 1034, 836, 800, 722, 607 cm^{-1}. **EA** calcd. for $C_{43}H_{62}O_6$: C 76.52, H 9.26. Found: C 76.32, H 9.35.

(S)-2-(2-Methylbutyloxy)-3,6,7,10,11-penta(pentyloxy)triphenylene (**3b**). White solid, 76% isolated yield. **^{1}H NMR** ($CDCl_3$, 600 MHz): 0.98 (t, $J = 7.2$ Hz, 15H); 1.03 (t, $J = 7.2$ Hz, 3H); 1.13 (d, $J = 6.0$ Hz, 3H); 1.35–1.52 (m, 11H); 1.53–1.63 (m, 10H); 1.66–1.75 (m, 1H); 1.89–2.00 (m, 10H); 2.01–2.09 (m, 1H); 4.01 (dd, $J = 8.4$ Hz, 15 Hz, 1H); 4.10 (dd, $J = 6.6$ Hz, 15 Hz, 1H); 4.23 (t, $J = 6$ Hz, 10H); 7.82–7.83 (m, 6H). **IR** (KBr) ν: 3103, 2954, 2925, 2854, 2746, 1618, 1519, 1465, 1437, 1387, 1263, 1172, 1048, 834, 725, 620 cm^{-1}. **EA** calcd. for $C_{48}H_{72}O_6$: C 77.38, H 9.74. Found: C 77.28, H 9.87.

(S)-2-(2-Methylbutyloxy)-3,6,7,10,11-penta(hexyloxy)triphenylene (**3c**). White solid, 84% isolated yield. **^{1}H NMR** ($CDCl_3$, 600 MHz): 0.93 (t, $J = 7.2$ Hz, 15H); 1.02 (t, $J = 7.2$ Hz, 3H); 1.13 (d, $J = 6.6$ Hz, 3H); 1.35–1.44 (m, 11H); 1.54–1.62 (m, 10H); 1.66–1.74 (m, 1H); 1.90–1.97 (m, 10H); 2.01–2.08 (m, 1H); 4.00 (dd, $J = 6.6$ Hz, 9.0 Hz, 1H); 4.10 (dd, $J = 6.0$ Hz, 8.4 Hz, 1H); 4.17–4.28 (m, 10H); 7.82–7.84 (m, 6H). **IR** (KBr) v: 3099, 2954, 2927, 2856, 2746, 1617, 1516, 1466, 1437, 1386, 1261, 1173, 1049, 837, 799, 726, 602 cm^{-1}. **EA** calcd. for $C_{53}H_{82}O_6$: C 78.08, H 10.06. Found: C 78.08, H 9.94.

(S)-2-(2-Methylbutyloxy)-3,6,7,10,11-penta(heptyloxy)triphenylene (**3d**). White solid, 58%. ^{1}**H NMR** ($CDCl_3$, 600 MHz): 0.91 (t, $J=6.6$ Hz, 15H); 1.03 (t, $J=7.2$ Hz, Hz, 3H); 1.13 (d, $J=6.6$ Hz, 3H); 1.24–1.27 (m, 1H); 1.31–1.47 (m, 30H); 1.52–1.61 (m, 10H); 1.66–1.74 (m, 1H); 1.90–2.01 (m, 10H); 2.02–2.07 (m, 1H); 4.01 (dd, $J=6.6$ Hz, 9.0 Hz, 1H); 4.08 (dd, $J=7.2$ Hz, 15 Hz, 1H); 4.20–4.26 (m, 10H); 7.81–7.85 (m, 6H). **IR** (KBr) v: 3103, 2958, 2932, 2862, 2748, 1618, 1517, 1466, 1438, 1388, 1263, 1170, 1052, 828, 774, 733, 621, 601 cm^{-1}. **EA** calcd. for $C_{58}H_{92}O_6$: C 78.68 H 10.47. Found: C 78.48 H 10.57.

(S)-2-(2-Methylbutyloxy)-3,6,7,10,11-penta(octyloxy)triphenylene (**3e**). White solid, 33% isolated yield. ^{1}**H NMR** ($CDCl_3$, 600 MHz): 0.90 (t, $J=6.6$ Hz, 15H); 1.03 (t, $J=7.2$ Hz, 3H); 1.13 (d, $J=6.6$ Hz, 3H, $3\times CHC\mathbf{H}_3$); 1.27–1.45 (m, 41H); 1.53–1.60 (m, 10H); 1.64–1.74 (m, 1H); 1.90–1.97 (m, 10H); 2.00–2.09 (m, 1H); 4.01 (dd, $J=6.6$ Hz, 9.0 Hz, 1H); 4.10 (dd, $J=6$ Hz, 9.0 Hz, 1H); 4.18–4.27 (m, 10H); 7.82–7.83 (m, 6H). **IR** (KBr) v: 3103, 2960, 2932, 2868, 2748, 1617, 1516, 1465, 1437, 1387, 1263, 1173, 1101, 1072, 1032, 866, 801, 700, 620 cm^{-1}. **EA** calcd. for $C_{63}H_{102}O_6$: C 79.19 H 10.76. Found: C 78.96 H 10.64.

The Synthetic Procedure for Synthesis of the Tri-Chiral Fragments Substituted Product (**3f**). To a mixture of 2,6,10-trihydroxy-3,7,11-tri(pentyloxy)triphenylene (**1f**) (101 mg, 0.185 mmol), (*S*)-2-methylbutanol (148 mg, 1.66 mmol), PPh_3(437 mg, 1.66 mmol), *i*-Pr_2NEt (218 mg, 1.66 mmol) in THF (0.5 mL) under ice-water bath (0°C) was added dropwise DIAD (356 mg, 1.66 mmol) under N_2 atmosphere. After the addition, the reaction was stirred for an additional 10 minutes when the ice-water bath was removed and the reaction was allowed to slowly warm up to the ambient temperature. The reaction was monitored by thin-layer chromatography. Upon completion, the reaction was quenched with 5% HCl (w/w) aqueous solution, and was extracted with CH_2Cl_2 (3×). The combined organic layers were dried through $MgSO_4$, concentrated on a rotary evaporator under reduced pressure, and was purified by column chromatography. Then it was recrystallized in ethanol to yield **3f** as a white solid (77% yield).

sym-(S)-2,6,10-tris(2-methylbutyloxy)-3,7,11-tri(pentyloxy)triphenylene (**3f**). White solid, 77% isolated yield. ^{1}**H NMR** ($CDCl_3$, 600 MHz): 0.97 (t, $J=6.9$ Hz, 9H); 1.03 (t, $J=7.5$ Hz, 9H); 1.13 (d, $J=6.6$ Hz, 9H); 1.33–1.41 (m, 3H); 1.42–1.49 (m, 6H); 1.53–1.60 (m, 6H); 1.67–1.74 (m, 3H); 1.91–1.97 (m, 6H); 2.01–2.08 (m, 3H); 3.99–4.03 (dd, $J=9$ Hz, 15 Hz, 3H); 4.08–4.12 (dd, $J=6$ Hz, 15 Hz, 3H); 4.21–4.24 (t, $J=6.6$ Hz, 6H); 7.821–7.839 (m, 6H). **IR** (KBr) v: 3248, 3076, 2954, 2924, 2873, 1634, 1577, 1552, 1498, 1466, 1377, 1315, 1284, 1151, 891, 838, 741, 704, 629 cm^{-1}. **EA** calcd. for $C_{48}H_{72}O_6$: C 77.38 H 9.74. Found: C 77.30 H 9.80.

3. Results and Discussions

3.1. *Reaction Optimizations for the Mitsunobu Reaction*

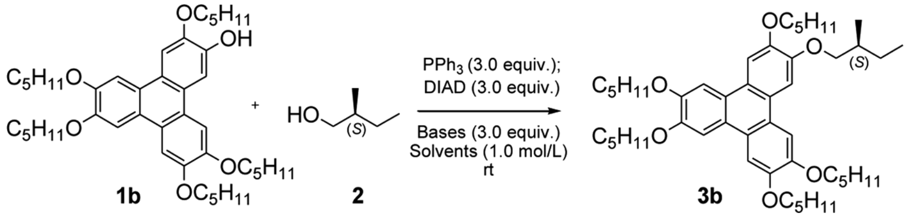
We selected triethylamine (Et_3N) as the base and THF as the solvent for the initial trial of our Mitsunobu [19–21] synthesis of **3b** (entry 1, Table 2). Though the reaction was successful, the transformation left with a large amount of starting material not reacted and offered only a 20% isolated yield. Inspired by Arunachalam [19], who importantly pointed out the great influence of bases on the yields of Mitsunobu reactions, diisopropylethylamine (DIPEA), a sterically more hindered and stronger base was then used (Table 2). In sharp contrast, the yield of **3b** was dramatically raised to 73% in 3 days (entry 3). In addition, dichloromethane was also used as the solvent, though the yield of **3b** was further improved to 76%, the reaction required 4 days to complete (entry 4). Taking both the reaction efficiency and yields into considerations, we decided to adopt entry 3 as our optimized reaction condition for the synthesis of other CTPDLCs (**3a**, **3c-3e** in Table 1 and **3f** in Scheme 1).

3.2. *Mesomorphism*

We then studied the mesomorphic properties of the CTPDLCs. Transition temperatures and enthalpy changes of **3a**~**3f** were recorded on a DSC; and their mesomorphic textures were observed under a POM. The types of mesophases were confirmed by miscibility test with 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene which shows $\mathrm{Col_h}$ phase, and 2,3,6,7,10,11-hexakis(butyloxy)triphenylene which shows $\mathrm{Col_p}$ phase. The DSC results were summarized in Table 3 and Figure 1; and several selected POM photographs were showed in Figure 2.

Except for compound **3a** and **3f**, all other CTPDLCs exhibited hexagonal columnar mesophases ($\mathrm{Col_h}$, Table 3, Figs. 1 and 2). However, **3a** and **3f** showed typical plastic columnar mesophases ($\mathrm{Col_p}$, Table 3, Figs. 1 and 2). Compound **3a**'s $\mathrm{Col_p}$ mesophase might be due to its excessive molecular rigidity, which was brought by its short peripheral soft alkyl chains. In addition, the reduced level of intermolecular π-π stackings resulted from the three chiral side chains could explain the formation of $\mathrm{Col_p}$ instead of $\mathrm{Col_h}$ mesophase of **3f**. The phenomenon (introducing too many chiral fragments to mesogens would lead to the disappearance of hexagonal columnar mesophases) has also been observed by Laschat [22].

Table 2. Optimizations of the Mitsunobu reaction[a]



Entry	Bases	Solvents	Yield(%)[e]
1	Et_3N	THF	20
2	i-Pr_2NEt	THF	42[b]
3	i-Pr_2NEt	THF	73[c]
4	i-Pr_2NEt	CH_2Cl_2	76[d]

[a] Unless otherwise noted, all reactions were carried out using 0.148 mmol of **1b** and 0.444 mmol of **2** for 3d.

[b] The reaction was carried out for only 1d.

[c] The reaction was carried out for 3d.

[d] The reaction was carried out for 4d.

[e] Yields of pure, isolated **3b**.

Table 3. Mesomorphic properties of the chiral triphenylene[a] (**3a-3e**).

	Transition temperature, enthalpy changes and mesophases	
Compd.	Second heating/°C(ΔH, J/g)	First cooling/°C (ΔH, J/g)
3a	Cry 70 (3.2) $\mathrm{Col_p}$ 139 (22.0) Iso	Iso 137 (21.1) $\mathrm{Col_p}$ 67 (1.7) Cry
3b	Cry 46 (29.2) $\mathrm{Col_h}$ 114 (14.2) Iso	Iso 112 (15.6) $\mathrm{Col_h}$ 7 (25.9) Cry
3c	Cry 53 (44.0) $\mathrm{Col_h}$ 90 (7.0) Iso	Iso 88 (7.1) $\mathrm{Col_h}$ 27 (44.1) Cry
3d	Cry 37 (37.5) $\mathrm{Col_h}$ 78 (3.1) Iso	Iso 74 (3.7) $\mathrm{Col_h}$ 7 (35.3) Cry
3e	$\mathrm{Cry_1}$ 39 (5.1) $\mathrm{Cry_2}$ 48 (49.9) $\mathrm{Col_h}$ 70 (4.5) Iso	Iso 68 (4.4) $\mathrm{Col_h}$ 19 (45.1) Cry
3f	Cry 56 (1.9) $\mathrm{Col_p}$ 99 (21.2) Iso	Iso 95 (21.8) $\mathrm{Col_p}$

[a] Cry, crystal state. $\mathrm{Col_h}$, hexagonal column phase. $\mathrm{Col_p}$, plastic column phase Iso, isotropic liquid.

As for the liquid crystal textures shown in Figure 2, mesogens **3b**, **3c** and **3e** (Fig. 2a, c, d) showed unique fan-shaped textures of $\mathrm{Col_h}$ mesophases; and exhibited excellent homeotropic alignments. Besides, compound **3f** (Fig. 2b) showed slice-shaped textures of $\mathrm{Col_p}$ mesophases.

More insights were then given to the mesomorphism of CTPDLCs **3b-3e** (Fig. 1). Very importantly, most of our CTPDLCs were room-temperature liquid crystals. More interestingly, a not-well-known odd-even trend of melting points was observed. With the lengthening of the CTPDLCs' peripheral alkyl chains (Figs. 1, 3), melting points were first increased, then decreased, followed by another increase; while the mesomorphic ranges showed an inversed odd-even effect: they were first

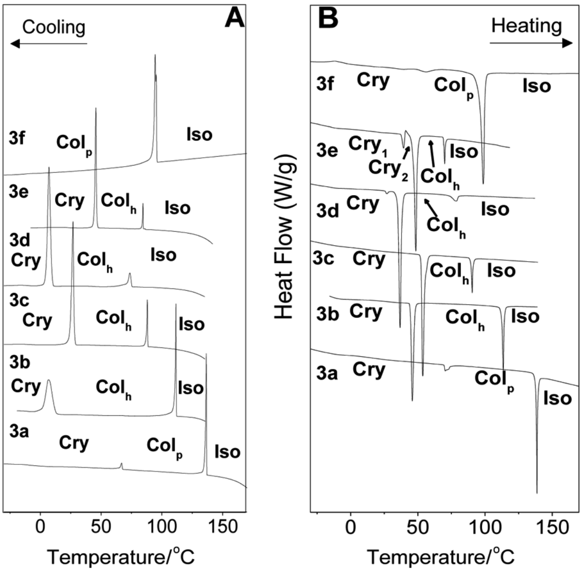
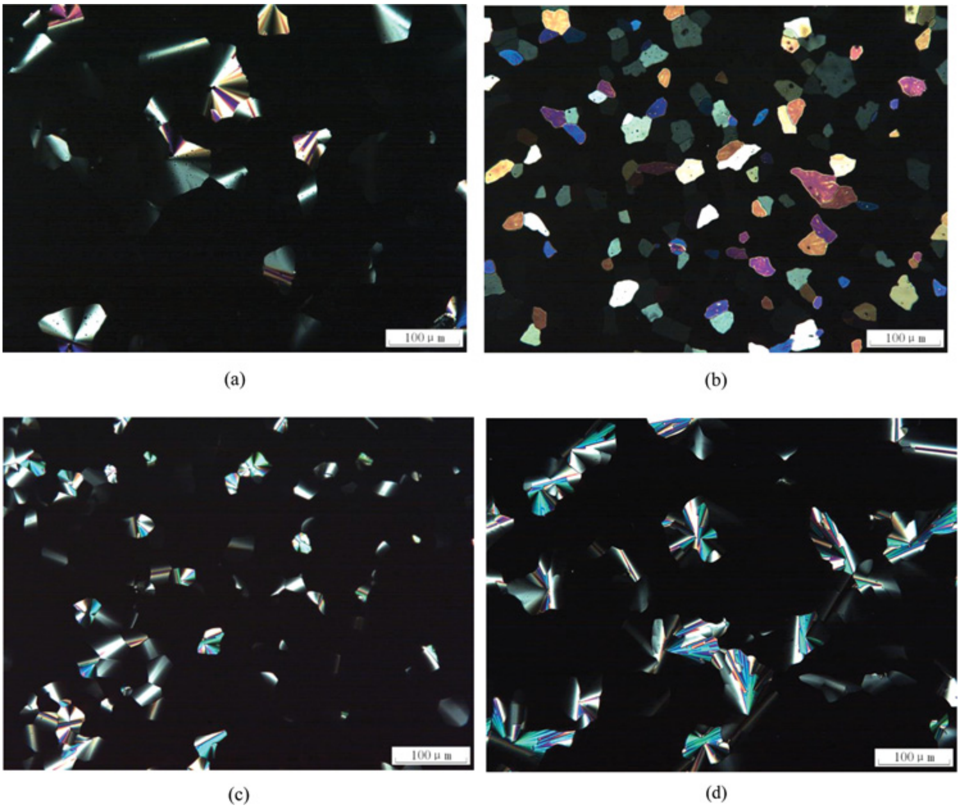


Figure 1. DSC curves of chiral triphenylenes (with heating and cooling rate of 10°C/min).



(a) (b)

(c) (d)

Figure 2. Polarising photomicrographs of chiral triphenylene discogens. a) Col_h, compound **3e**, cooling to 60°C from isotropic liquid; b) Col_p, compound **3f**, cooling to 82°C from isotropic liquid; c) Col_h, compound **3c**, cooling to 77°C from isotropic liquid; d) Col_h, compound **3b**, cooling to 80°C. (Figure appears in color online.)

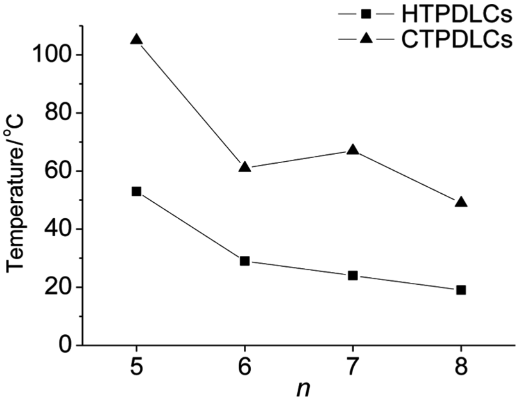


Figure 3. Comparisons of mesomorphic temperature ranges between the CTPDLCs $[TP(OC_nH_{2n+1})_5(OR^*)]$ (**3b**-**3e**) and HTPDLCs $[TP(OC_nH_{2n+1})_6]$.

decreased, then increased, followed by another decrease. This odd-even effect has been very rarely observed; and no explanations could be provided at this stage.

Very noteworthy, our CTPDLCs exhibited much lower melting points but drastically wider mesomorphic ranges, compared with the corresponding hexaalkoxytriphenylene discotic liquid crystal (HTPDLCs) (Fig. 3) [23]. This is because the introduction of chirality would result larger distances among molecules and less intermolecular interactions. Hence, the CTPDLCs have lower melting points. Given that the clearing points of our CTDPLCs were similar to those of their HTPDLCs partners, our CTPDLCs exhibited much wider mesomorphic temperature ranges (Fig. 3). Thus, the introduction of chirality into triphenylene-based discotic liquid crystals is proven to be a novel and effective way to lower the melting points and widen $\mathrm{Col_h}$ mesophases.

4. Conclusions and Perspectives

In summary, a series of novel chiral triphenylene-based discotic liquid crystals were synthesized through Mitsunobu reactions with moderate to high yields. Reaction conditions of the Mitsunobu process were optimized, which has re-clarified the importance of proper selection of bases for the transformation. Besides, we have proved that the introduction of chirality to triphenylene discotic liquid crystals could broaden hexagonal columnar mesophases. Furthermore, mesomorphic studies of the new liquid crystals have unexpectedly disclosed a not-well-studied odd-even effect. Future work will be focused on the mesomorphic properties and “sergeants and soldiers” effect after mixing the new CTPDLCs and their HTPDLC partners; as well as a rationalization of the odd-even effect.

Acknowledgment

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[18] The reaction was quenched when starting materials showed no further consumptions. In all cases, unreacted starting materials were observed.

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