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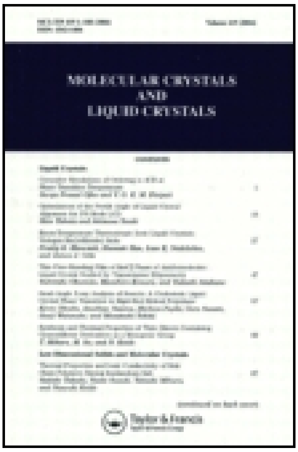

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Synthesis of Triphenylene Discotic Liquid Crystals Possessing Nine Alkyl Chains: Influence of Molecular Symmetry and Chain Length on Mesomorphism

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Synthesis of Triphenylene Discotic Liquid Crystals Possessing Nine Alkyl Chains: Influence of Molecular Symmetry and Chain Length on Mesomorphism

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A series of new triphenylene discotic liquid crystals has been synthesized by a straightway and the influence of molecular symmetry and chain length on the mesomorphism investigated. The symmetrical compounds ***1****, 3,7,11-trimethoxytriphenylene-2,6,10-triyl tris(3,4,5-tris(alkyloxy)benzoate), with alkyl chain lengths of C7, C8, C10, and C12, and the unsymmetrical compounds* ***2*** *were studied by using polarized optical microscopy (POM), differential scanning calorimetry (DSC) and by wide-angle X-ray diffraction (XRD). The results showed that the symmetrical compounds* ***1a*** *(C7) and* ***1b*** *(C8) exhibit a plastic columnar mesophase, whereas the other compounds display a hexagonal columnar mesophase over a wide temperature range. All symmetrical compounds* ***1*** *display higher isotropization temperatures than that of the unsymmetrical* ***2****. The clearing points are lowered as the alkyl chain lengthened.*

Keywords Discotic liquid crystals; hexagonal columnar mesophase; molecular symmetry; triphenylene; plastic columnar phase.

1. Introduction

Liquid crystals (LCs) have emerged as a new kind of organic semiconductor [1–5], which when compared with established inorganic semiconductors show favorable features in terms of cost, solubility, device fabrication, charge carrier mobility, and tunability of physical properties by molecular design.

Discotic LCs (DLCs) self-organize into a columnar mesophase [6], and charged carriers hop favorably along the column axis [7], and the highest charge mobility rate for DLCs has reached 1.5 cm^2/v s [8]. Furthermore, DLCs have been widely investigated as active materials in organic field effect transistors [9,10], organic light-emitting diodes [11], and organic photovoltaic solar cells [12–19].

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Triphenylene derivatives are regarded as one of the most important DLCs [20–25] and have been commercially used as optical compensation films for widening the view angle of LC displays [2]. 2,3,6,7,10,11-Hexakis(alkyloxy)triphenylene displays a hexagonal columnar (Col_h) mesophase with low melting points and clearing points, whereas triphenylene with six ester chains show higher phase transition temperatures; however, both exhibit narrow mesophase ranges for practical applications. Bayer et al. [26] proposed that triphenylene DLCs with ether and ester mixed tails would have improved mesophase and physical properties. It was noted that the subtle balance between the aromatic core size and the peripheral alkyl chains was an important factor in determining the type of mesophase, the phase transition temperature, and also the stability of the mesophase.

Recently, we have reported DLCs as molecular templates [27–31] to construct ordered 2-dimentional frameworks, which host different number of functional molecules, such as porphyrin, phthalocyanine, and fullerene. These molecular frameworks are controlled by the factors of shape of molecule, symmetry of molecules, the size of rigid core, and the length of peripheral flexible chain.

In this report, we have investigated the liquid crystalline properties of the above-mentioned triphenylene DLC template molecules. Compared with hexakis(alkyloxy) triphenylene, these compounds contain a larger rigid core for columnar mesophase stabilization, and nine flexible peripheral chains for lowering the melting point; therefore, wide mesophase temperature ranges would be expected. We highlight the simplified synthesis and separation of the eight new DLC **1** and **2**, and discuss the influence of molecular symmetry and chain length on mesomorphism. Scheme 1 shows the synthesis of the targeted DLCs.

2. Experimental

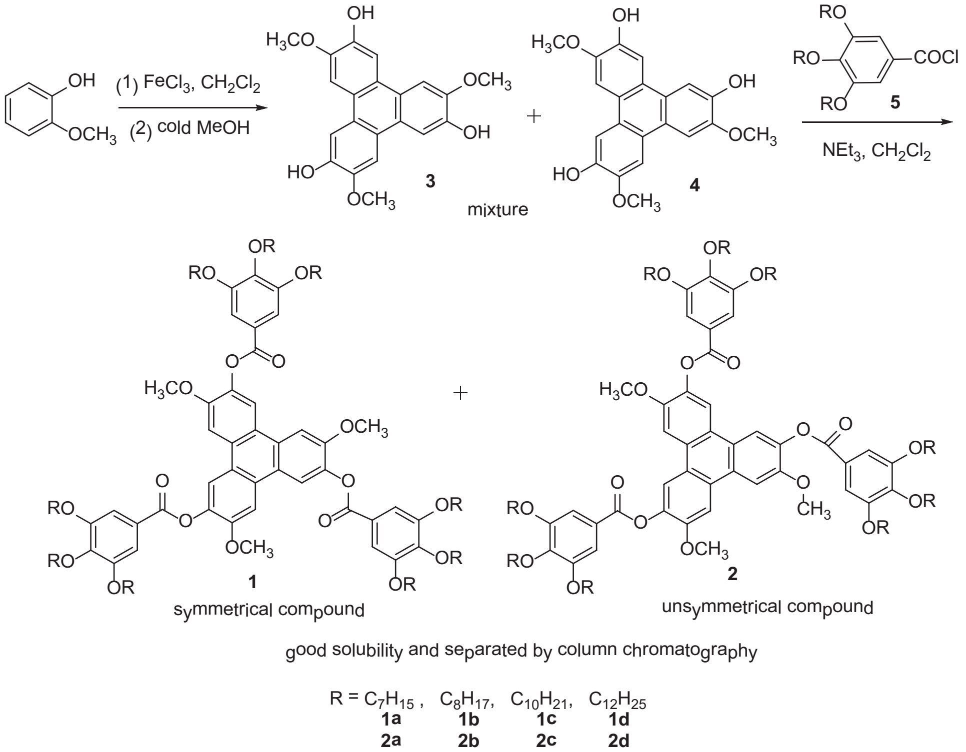
2.1. General

Triphenylene DLCs were characterized using ^{1}H NMR and IR spectroscopy. ^{1}H NMR spectra were recorded using a 400 MHz Varian spectrometer with Me_4Si as an internal standard. IR spectra were obtained with KBr pellets on a BRUKER VERTEX 70 FT-IR spectrometer. The microanalysis was carried out on a Thermal Flash 2000 instrument. The phase transition temperatures and enthalpies were measured by a differential scanning calorimeter (DSC, TA Instrument, 2920MDSC), and the optical textures of the mesophases were observed and recorded on a polarizing optical microscope (POM, Olympus, BH-2), with a hot stage (Mettler, FP80HT) and controller (Mettler, FP80HT). X-ray diffraction (XRD) studies were carried out on a PHILIPS 3 KW X-ray diffractometer.

The reagents and solvents were commercial products and were used without further purification.

2.2. Synthesis

2.2.1. 2,6,10-Trimethoxyltriphenylene-3,7,11-triol, ***3*** *and 2,6,11-Trimethoxyl-3,7,10-trihydroxy-triphenylene,* ***4****.* A mixture of 2-methoxyphenol (5.0 g, 40.3 mmol), concentrated H_2SO_4 (2 drops), $FeCl_3$ (20.0 g, 123.1 mmol), and CH_2Cl_2 (50 mL) was stirred for 45 minutes. Then cold CH_3OH (30 mL) was carefully added and further stirred for 1 hour. The solid precipitate was collected by filtration and washed with cold ethanol and water. The mixture of 2,6,10-trimethoxyltriphenylene-3,7,11-triol, **3** and 2,6,11-trimethoxyl triphenylene-3,7,10-triol, **4** was prepared in a total yield of 40%.



Scheme 1. The synthesis of triphenylene DLCs with nine alkyl chains.

2.2.2. The Synthesis of 3,4,5-Tris(alkoxy)benzoyl Chloride. A mixture of 3,4,5-trihydroxybenzoic acid (50 g, 294.1 mmol), MeOH (200 mL), and H_2SO_4 (5 mL) was refluxed for overnight. Then the cooled mixture was poured into ice water and extracted with CH_2Cl_2. The organic extract was washed with 5% aqueous Na_2CO_3 solution and water, dried, and organic solvent was removed. Crystallization from toluene resulted in methyl 3,4,5-trihydroxybenzoate as a white solid with a yield of 83%.

The mixture of methyl 3,4,5-trihydroxybenzoate (2 g, 11.1 mmol), K_2CO_3, and 1-bromododecane (9.5 g, 38.2 mmol) in ethanol was refluxed for 24 hours. Methyl 3,4,5-tris(dodecyloxy)benzoate was collected from ethanol as a white solid with a yield of 80%.

Methyl 3,4,5-tris(dodecyloxy)benzoate (2 g, 2.9 mmol) was hydrolyzed by using KOH (1 g, 17.9 mmol) in ethanol (95%, 20 mL). 3,4,5-Tris(dodecyloxy)benzoic acid was collected as a white solid after acidification and recrystallization from ethanol with a yield of 90%.

3,4,5-Tris(dodecyloxy)benzoic acid (1.1 g, 1.6 mmol) was refluxed with excess thionyl chloride (5 mL) and N,N-dimethylformamide (1 drop) for 5 hours. After the reaction finished, the excess thionyl chloride was distilled, and 3,4,5-tris(dodecyloxy)benzoyl chloride was ready for use.

2.2.3. 3,7,11-Trimethoxytriphenylene-2,6,10-triyl tris(3,4,5-tris(dodecyloxy)benzoate), ***1d**, and 3,7,10-Trimethoxytriphenylene-2,6,11-triyl tris(3,4,5-tris(dodecyloxy)benzoate),* *2d*. A mixture of 3,7,11-trimethoxyltriphenylene-2,6,10-triol (**3**) and 3,7,10-trimethoxyltriphenylene-2,6,11-triol (**4**) (0.15 g, 0.4 mmol) was dissolved in CH_2Cl_2 (30 mL) and Et_3N (0.3 g, 3.0 mmol) was added, and a solution of 3,4,5-tris(dodecyloxy)benzoyl chloride (1.13 g, 1.6 mmol) in CH_2Cl_2 was added dropwise at 0°C. After stirring for 2 hours, the reaction mixture was refluxed for 5 hours, then poured into aqueous HCl (5%, 20 mL), and extracted with CH_2Cl_2. The organic extract was dried over anhydrous magnesium sulfate and concentrated in vacuum. The residue was separated by column chromatography (SiO_2), eluted with a mixture of solvents (CH_2Cl_2:petroleum ether = 3:1, V/V) followed by crystallization in ethyl acetate resulting in **1d** as a white solid with a yield of 6% and 2**d** as a white solid with a yield of 80%.

The symmetrical compounds **1a**, **1b**, and **1c** and asymmetrical compounds 2**a**, 2**b**, and 2**c** were prepared using the method described above.

***1a**, 3,7,11-Trimethoxytriphenylene-2,6,10-triyl tris-(3,4,5-tris(heptyloxy)benzoate)*: White solid 35 mg, yield 5%, spectral data: ^{1}H NMR ($CDCl_3$, TMS, 400 Hz, δ):8.23 (s, 3H, ArH), 7.71–7.72 (m, 3H, ArH), 7.26–7.32 (m, 6H, ArH), 3.95–4.03 (m, 27H, $ArOCH_2$, $ArOCH_3$), 1.79–1.81 (m, 18H, CH_2), 1.32–1.54 (m, 72H, CH_2), 0.89 (t, J = 6.40 Hz, 27H, CH_3). IR (KBr) ν: 3101, 2956, 2928, 2857, 1723, 1625, 1588, 1500, 1468, 1451, 1430, 1385, 1338, 1269, 1114, 1045, 940, 843, 723 cm^{-1}.

***2a**, 3,7,10-Trimethoxytriphenylene-2,6,11-triyl tris-(3,4,5-tris(heptyloxy)benzoate)*: White solid 584 mg, yield 83%, spectral data: ^{1}H NMR ($CDCl_3$, TMS, 400 Hz, δ):8.27 (s, 1H, ArH), 7.85–7.94 (m, 4H, ArH), 7.70–7.75 (m, 1H, ArH), 7.36–7.47 (m, 6H, ArH), 3.96–4.06 (m, 27H, $ArOCH_2$, $ArOCH_3$), 1.73–1.82 (m, 18H, CH_2), 1.31–1.56 (m, 72H, CH_2), 0.89 (t, J = 2.00 Hz, 27H, CH_3). IR (KBr) ν: 3101, 2955, 2928, 2856, 1728, 1623, 1587, 1517, 1501, 1468, 1430, 1380, 1337, 1268, 1115, 1048, 938, 840, 723 cm^{-1}.

***1b**, 3,7,11-Trimethoxytriphenylene-2,6,10-triyl tris-(3,4,5-tris(octyloxy)benzoate)*: White solid 55 mg, yield 7%, spectral data: ^{1}H NMR ($CDCl_3$, TMS, 400 Hz, δ):8.23 (s, 3H, ArH), 7.65–7.68 (m, 4H, ArH), 7.26–7.31 (m, 5H, ArH), 3.95–4.03 (m, 27H, $ArOCH_2$, $ArOCH_3$), 1.75–1.80 (m, 18H, CH_2), 1.31–1.56 (m, 90H, CH_2), 0.86–0.91 (m, 27H, CH_3). IR(KBr) ν: 3101, 2958, 2926, 2855, 1722, 1625, 1588, 1520, 1500, 1468, 1452, 1430, 1386, 1338, 1267, 1112, 1045, 948, 843, 722 cm^{-1}.

***2b**, 3,7,10-Trimethoxytriphenylene-2,6,11-triyl tris-(3,4,5-tris(octyloxy)benzoate)*: White solid 692 mg, yield 92%, spectral data: ^{1}H NMR ($CDCl_3$, TMS, 400 Hz, δ):8.27 (s, 1H, ArH), 7.67–7.88 (m, 5H, ArH), 7.26–7.47 (m, 6H, ArH), 3.95–4.06 (m, 27H, $ArOCH_2$, $ArOCH_3$), 1.73–1.82(m, 18H, CH_2), 1.30–1.57(m, 90H, CH_2), 0.88(t, J = 4.00 Hz, 27H, CH_3). IR (KBr) ν: 3102, 2955, 2925, 2855, 1727, 1623, 1587, 1518, 1501, 1468, 1430, 1381, 1337, 1269, 1115, 1048, 949, 804, 722 cm^{-1}.

***1c**, 3,7,11-Trimethoxytriphenylene-2,6,10-triyl tris-(3,4,5-tris(decyloxy)benzoate)*: White solid 43 mg, yield 5%, spectral data: ^{1}H NMR ($CDCl_3$, TMS, 400 Hz, δ):8.23(s, 3H, ArH), 7.61–7.64(m, 3H, ArH), 7.26–7.52 (m, 6H, ArH), 3.77–4.02 (m, 27H, $ArOCH_2$, $ArOCH_3$), 1.74–1.79 (m, 18H, CH_2), 1.28–1.57 (m, 126H, CH_2), 0.85–0.91 (m, 27H, CH_3). IR (KBr) ν: 3101, 2955, 2924, 2853, 1722, 1625, 1588, 1521, 1500, 1468, 1452, 1431, 1388, 1338, 1269, 1116, 1045, 948, 843, 721 cm^{-1}.

***2c**, 3,7,10-Trimethoxytriphenylene-2,6,11-triyl tris-(3,4,5-tris(decyloxy)benzoate)*: White solid 593 mg, yield 69%, spectral data: ^{1}H NMR ($CDCl_3$, TMS, 400 Hz, δ):8.27 (s, 1H, ArH), 7.85–7.90 (m, 4H, ArH), 7.68–7.73 (m, 1H, ArH), 7.36–7.42 (m, 6H, ArH), 3.96–4.06 (m, 27H, $ArOCH_2$, $ArOCH_3$), 1.76–1.82 (m, 18H, CH_2), 1.27–1.56 (m, 126H, CH_2), 0.88(d, J = 5.60 Hz, 27H, CH_3). IR (KBr) ν: 2924, 2853, 1722, 1623, 1586, 1518, 1501, 1468, 1430, 1385, 1337, 1268, 1116, 1049, 948, 833, 721 cm^{-1}.

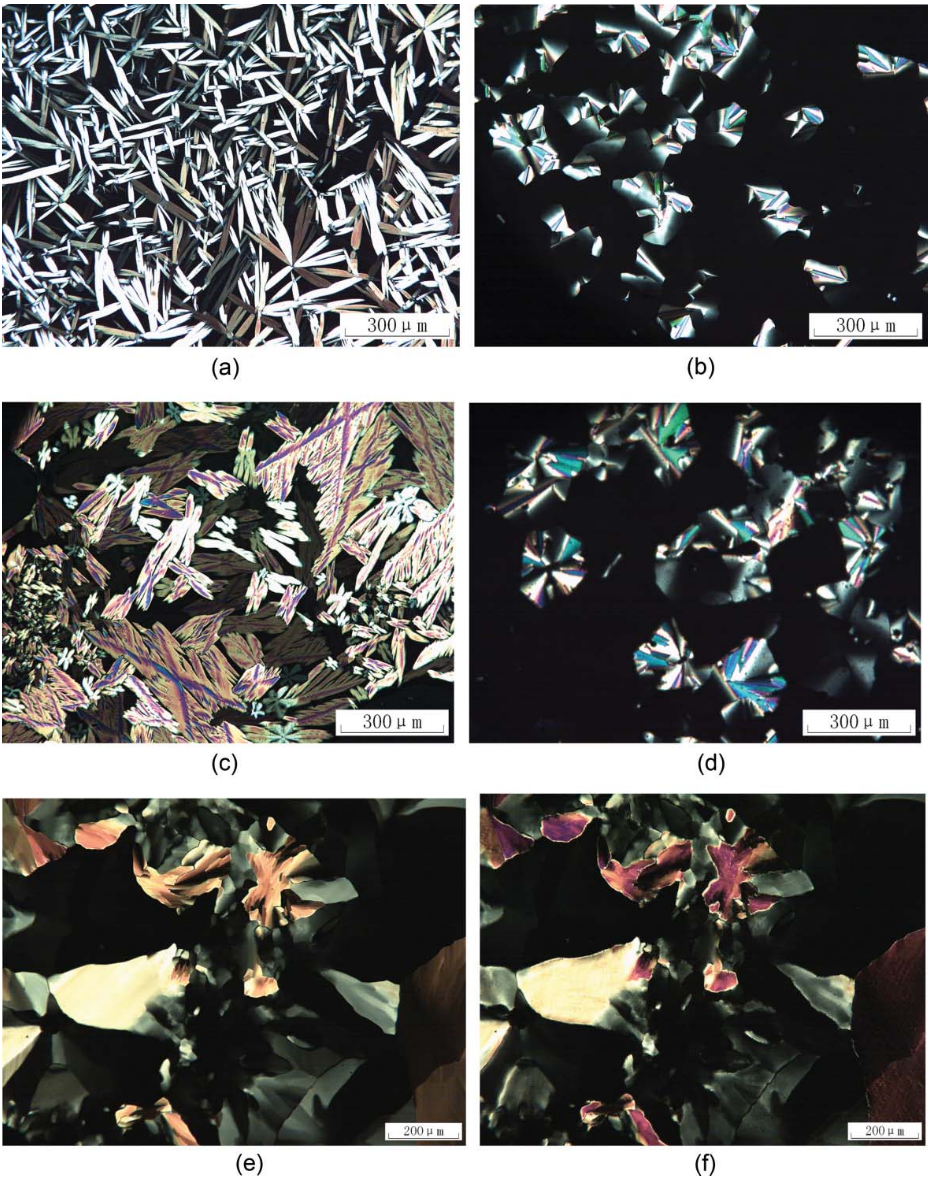


Figure 1. Polarising photomicrographs of triphenylene discogens. (a) **1a**, $\mathrm{Col_p}$, cooling to 270°C from isotropic liquid; (b) **2a**, $\mathrm{Col_h}$, cooling to 200°C from isotropic liquid; (c) **1b**, $\mathrm{Col_p}$, cooling to 200°C from isotropic liquid; (d) **2b**, $\mathrm{Col_h}$, cooling to 180°C from isotropic liquid; (e) **1d,** $\mathrm{Col_{hd}}$, cooling to 190°C from isotropic liquid; (f) **1d,** $\mathrm{Col_{ho}}$, cooling to 153°C from $\mathrm{Col_{hd}}$.

***1d**, 3,7,11-Trimethoxytriphenylene-2,6,10-triyl tris-(3,4,5-tris(dodecyloxy)benzoate)*: White solid 62 mg, yield 6%, spectral data: ^{1}H NMR ($CDCl_3$, TMS, 400 Hz, δ) δ:8.23 (s, 3H, ArH), 7.52–7.61 (m, 3H, ArH), 7.26–7.42 (m, 6H, ArH), 3.93–4.02 (m, 27H, $ArOCH_2$, $ArOCH_3$), 1.77–1.79 (m, 18H, CH_2), 1.25–1.59 (m, 162H, CH_2), 0.86(t, $J = 6.80$Hz, 27H, CH_3). IR (KBr) ν: 2923, 2853, 1723, 1624, 1588, 1520, 1500, 1467, 1431, 1389, 1337,

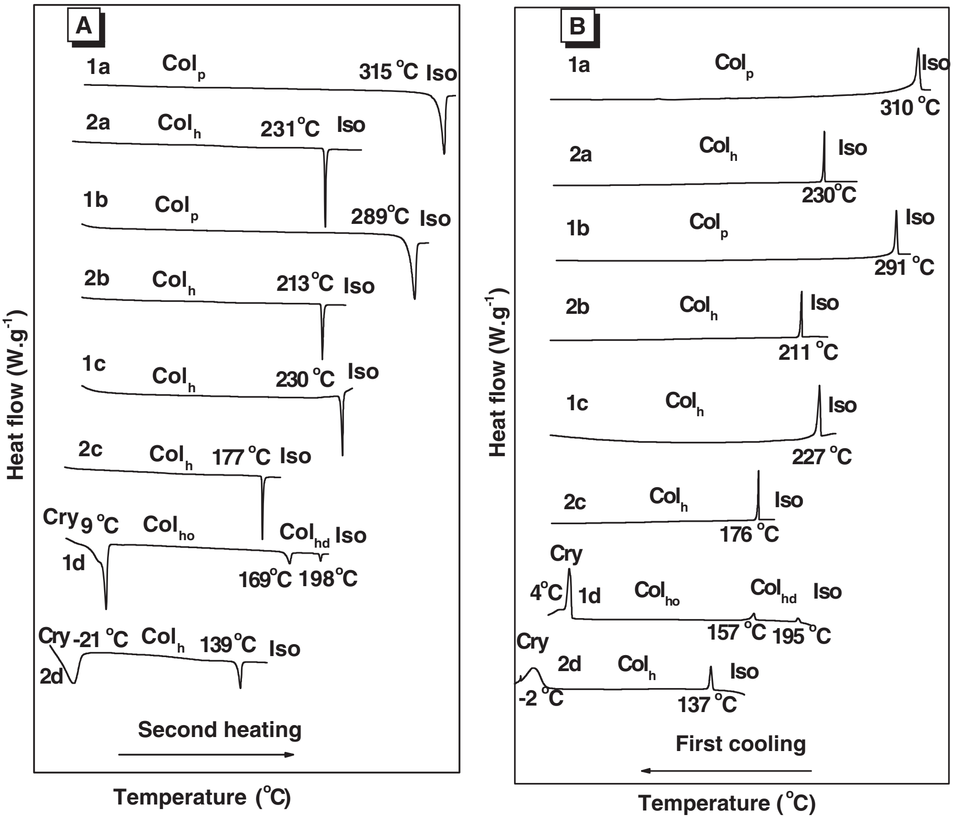


Figure 2. The DSC traces of triphenylene DLCs **1a**–**2d**.

1268, 1118, 1044, 947, 844, 721 cm^{-1}. Anal. Calcd. for $C_{150}H_{246}O_{18}$: C 77.07, H 10.61; found C 78.06, H 10.64.

***2d**, 3,7,10-Trimethoxytriphenylene-2,6,11-triyl tris-(3,4,5-tris(dodecyloxy)benzoate)*: White solid 768 mg, yield 80%, spectral data: ^{1}H NMR ($CDCl_3$, TMS, 400 Hz, δ) δ:8.28 (s, 1H, ArH), 7.87–8.00 (m, 4H, ArH), 7.72–7.73 (m, 1H, ArH), 7.36–7.43 (m, 6H, ArH), 3.96–4.06 (m, 27H, $ArOCH_2$, $ArOCH_3$), 1.74–1.82 (m, 18H, CH_2), 1.25–1.59 (m, 162H, CH_2), 0.85–0.88 (m, 27H, CH_3). IR (KBr) ν: 2923, 2853, 1727, 1624, 1587, 1518, 1501, 1467, 1430, 1385, 1337, 1270, 1116, 1048, 950, 884, 721 cm^{-1}. Anal. Calcd. for $C_{150}H_{246}O_{18}$: C 77.07, H 10.61; found C 78.16, H 10.89.

3. Results and Discussion

3.1. Synthesis and Characterization

The one-pot syntheses of **3**, 2,6,10-trimethoxytriphenylene-3,7,11-triol and **4**, 2,6,11-trimethoxytriphenylene-3,7,10-triol were achieved by the direct oxidation of 2-methoxyphenol with $FeCl_3$ in CH_2Cl_2 followed by treatment with cold MeOH. The mixture of **3** and **4** displayed low solubility in common organic solvents and it was difficult to separate them from each other, and thus they were used directly in the subsequent esterification reaction as a mixture.

Table 1. Thermotropic liquid crystalline properties of triphenylene DLCs **1a–2d**

		Mesophases, transition temperature and enthalpy changes	
Compd	(Cn)	Second heating /°C (ΔH, kJ ·mol^{-1})	First cooling / °C (ΔH, kJ ·mol^{-1})
1a	(C7)	Col$_p$ 315 (68.06) Iso	Iso 310 (43.37) Col$_p$
2a	(C7)	Col$_h$ 231 (22.46) Iso	Iso 230 (20.67) Col$_h$
1b	(C8)	Col$_p$ 289 (37.70) Iso	Iso 291 (40.19) Col$_p$
2b	(C8)	Col$_h$ 213 (20.26) Iso	Iso 211 (17.86) Col$_h$
1c	(C10)	Col$_h$ 230 (17.86) Iso	Iso 227 (19.30) Col$_h$
2c	(C10)	Col$_h$ 177 (13.34) Iso	Iso 176 (13.19) Col$_h$
1d	(C12)	Cry 9 (68.62) Col$_{ho}$169 (9.03) Col$_{hd}$198 (2.96) Iso	Iso195 (3.04) Col$_{hd}$157 (7.54) Col$_{ho}$4 (72.12) Cry
2d	(C12)	Cry −21(57.25) Col$_h$ 139 (8.96) Iso	Iso 137 (8.88) Col$_h$ −2(42.48) Cry

Cry, crystal state; Col, discotic columnar phase; Iso, isotropic liquid.

3,4,5-Tris(alkoxy)benzoyl chloride, **5** was prepared by starting from 3,4,5-trihydroxybenzoic acid through an acid catalyzed esterification in MeOH. Specifically, the Williamson ether synthesis was employed, namely, the reaction of RBr with phenol in the presence of K_2CO_3, hydrolysis of the ester to acid, and finally transformation of the acid to acid chloride by the reaction with $SOCl_2$.

Target compounds **1** and **2** were synthesized by the reaction of **3** and **4** with **5** in the presence of Et_3N. The mixture of **1** and **2** showed good solubility in common organic solvents, and they were separated by column chromatography and collected in the pure form. However, we note that the yields of the symmetrical compounds were much lower than those of the unsymmetrical compounds. **1a**–**2d** were characterized by using 400 MHz ^{1}H NMR and IR spectroscopy, and two compounds were further characterized by using microanalysis.

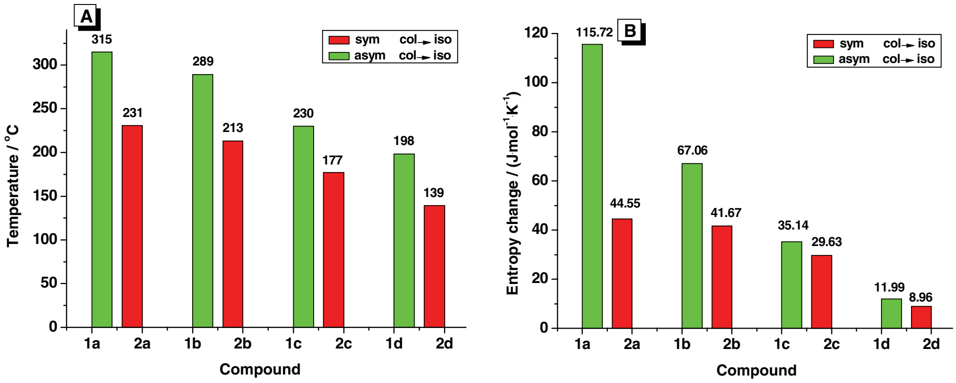


Figure 3. A, Phase diagram of triphenylene discogens **1a**–**2d** from Col phase to Iso. B, Entropy change of triphenylene discogens **1a**–**2d** from Col to Iso. (entropy change $\Delta S = \Delta H/T$).

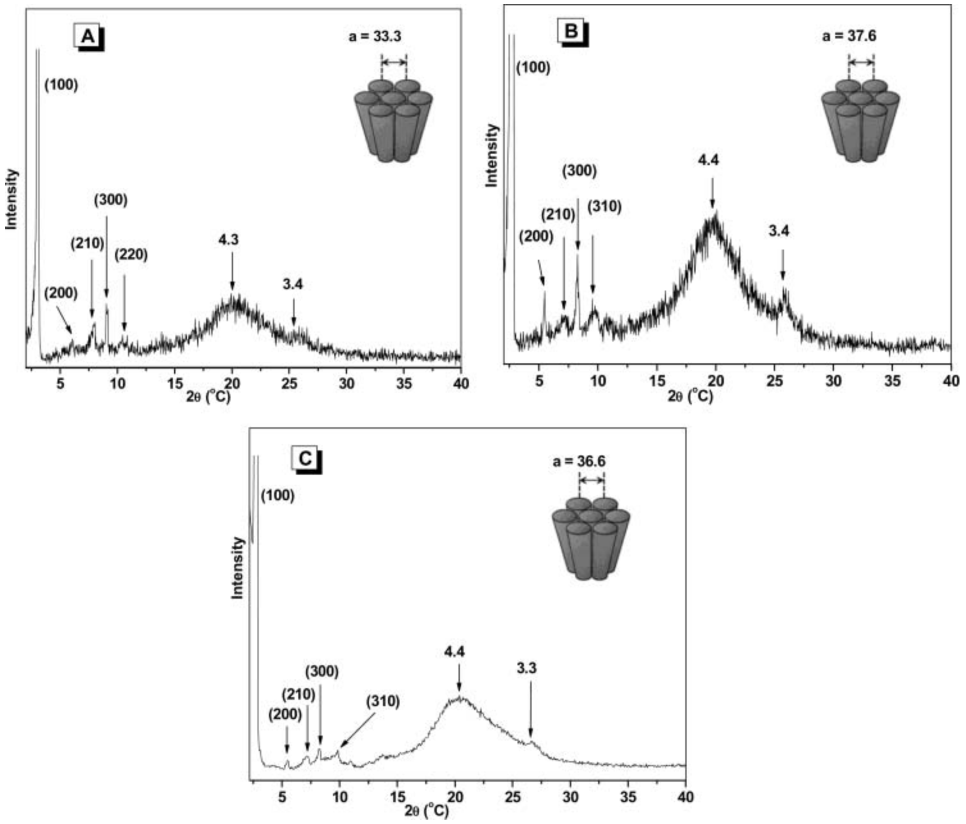


Figure 4. X-ray diffraction patterns of three triphenylene DLCs measured at room temperature. A, **2c** (unsym., C10); B, **2d** (unsym., C12); C, **1d** (sym., C12).

3.2. Mesomorphism

3.2.1. POM Results. Initially, we measured the liquid crystalline properties of the nine-chain triphenylenes by using POM with a heating plate and temperature controller, and part of the photomicrographs is shown in Fig. 1. It was noted that the symmetrical compounds **1a** (sym. C7) and **1b** (sym. C8) with shorter chain length displayed the typical textures of a plastic columnar mesophase (Col_p), whereas all other compounds exhibited textures associated with a discotic columnar mesophase (Col). Interestingly, we found that **1d** (sym. C12) exhibited homeotropic alignment behavior on the untreated glass plate by slowly cooling from its isotropic liquid state. It is known that good homeotropic molecular self-assembly behavior of DLC is a prerequisite for application in organic electronic devices, such as OLEDs and OPVs.

3.2.2. DSC Results. The mesomorphism of the synthesized triphenylene DLCs was further studied by using DSC. The DSC traces of all compounds are displayed in Fig. 2, and the resulting data are summarized in Table 1. It was noted that for the longer chain DLC **1d** (sym. C12) and **2d** (unsym. C12), both melting point and isotropization temperature were tested, whereas for the shorter chain DLCs, only isotropization temperatures were measured. Interestingly, **1d** exhibited two enantiotropic mesophases, which are assigned as the disordered hexagonal columnar mesophase (Col_{hd}) at high temperature zone and the ordered hexagonal columnar mesophase (Col_{ho}) at low temperature; the latter was further confirmed by using XRD at room temperature.

We further summarized the correlation between clearing point temperatures and the alkyl chain length, see Fig. 3(A), and entropy change ($\Delta S_{Col\rightarrow Iso}$) with chain length into Fig. 3(B). Figure 3(A) clearly shows that series **1** (sym.) has higher clearing points than does series **2** (unsym.), whereas Fig. 3(B) reveals that series **1** had higher entropy change values for the phase transition from Col. to Iso. than does series **2**. Based on these results, we conclude that the symmetrical DLCs (series **1**) have more ordered molecular columnar stacking than does the unsymmetrical DLCs (series **2**).

3.2.3. XRD Results. The mesophases of three DLCs, namely, **2c** (unsym. C10), **2d** (unsym. C12), and **1c** (sym. C12) were further investigated by using XRD, and the results are shown in Fig. 4 and Table 2. The XRD diffraction patterns of the three compounds show that they present as Col_{ho} at room temperature. At the small angle region, there is a strong peak correlated to (100) and weak peaks of (200), (210), (300), and (220) or (310). At the wide angle region, the broad halo at 4.3 Å–4.4 Å suggests that the flexible alkyl chains are in a molten state. The small peak at 3.3 Å–3.4 Å demonstrates that the discotic molecules stack on top of each other in a weak ordered form in the columns.

Table 2. Miller indices and lattice parameters for Col_h mesophase of three DLCs

Compound	d_{obs}(Å)[a]	hkl[b]	d_{calcd}(Å)[a]	Lattice parameter
2c (unsym. C10)	28.8	(100)	28.8	a = 33.3 Å
	14.6	(200)	14.4	
	11.0	(210)	10.9	
	9.7	(300)	9.6	
	8.3	(220)	8.3	
	4.3	broad halo		
	3.4	(001)		
2d (unsym. C12)	32.6	(100)	32.6	a = 37.6 Å
	16.1	(210)	16.3	
	12.3	(300)	12.3	
	10.6	(220)	10.8	
	9.1	(310)	9.0	
	4.4	broad halo		
	3.4	(001)		
1d (sym. C12)	31.7	(100)	31.7	a = 36.6 Å
	16.0	(200)	15.8	
	12.3	(210)	12.0	
	10.7	(300)	10.6	
	8.9	(310)	8.8	
	4.4	broad halo		
	3.3	(001)		

[a] d_{obs} and d_{calcd} denote the observed and the calculated diffraction spacing, respectively. [b] hkl are the Miller indices of the 2D hexagonal lattice [7–9].

4. Conclusions

In summary, two series of triphenylene DLCs **1** and **2** have been synthesized and successfully separated by column chromatography. All eight triphenylene derivatives displayed wide plastic or Col mesophase temperature ranges. **1a** (C7) and **1b** (C8) exhibited a plastic columnar phase ($\mathrm{Col_p}$), whereas the other compounds exhibited a $\mathrm{Col_h}$ phase. The symmetrical compounds (series **1**) displayed higher isotropization temperatures and more stable Col phases than did the unsymmetrical compounds (series **2**). **1d** exhibits the two enantiotropic mesophases $\mathrm{Col_{ho}}$ and $\mathrm{Col_{hd}}$. We anticipate that these new DLCs, possessing homeotropic alignment behavior at nanometer to micrometer scale, have potential application in organic solar cells as active additives.

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