Synthesis and Characterization of Triphenylene Derivatives Containing Two Terminal Functional Groups at the Periphery

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*Three novel series of triphenylene-based derivatives possessing functional group (ester, carboxylic acid, or hydroxy) at the ends of two aliphatic chains on the opposite position of triphenylene core have been synthesized and studied on mesomorphic properties. Their chemical structures were characterized by FT-IR, ¹H-NMR, ¹³C-NMR, MS, and the thermotropic liquid crystalline properties were also investigated by polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction. It is found that the triphenylene derivatives containing terminal carboxylic acid or hydroxyl chains in the series of **9** or **10** show themortropic columnar mesophase, while the corresponding derivatives possessing terminal esters don't show any mesomorphism.*

INTRODUCTION

Discotic liquid crystals are usually composed of disk-shaped molecules with aliphatic tails. A variety of mesophase, such as discotic nematic phase, ordered hexagonal phases, tilted columnar phases, rectangular disordered columnar phases, plastic columnar phases, and highly ordered helical phases have been observed in discotic liquid crystals [1]. Such columnar structures are characteristic for rapid one-dimensional transport of excitons or charge carriers, which makes discotic liquid crystal materials potentially applicable in the areas of one-dimensional conductors, light-emitting diodes, phototconductors, information storage, field effect transistors, and high-resolution

xerography, photovoltaic solar cells *etc.* [2–6]. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than that in the perpendicular direction [7].

Triphenylene derivatives are one of the best and longest studied families of discotic liquid crystals, due to their high tendency to form the required columnar phases and the presence of large conjugated aromatic molecular core with a large delocalized π-electron system [8–10]. Triphenylene-based discotic liquid crystals have also been extensively studied for various physical properties, such as one-dimensional charge and energy migration, electroluminescence, ferroelectric switching, alignment, and self-assembling behavior on surfaces and other properties [11–13].

But many of those potential applications require thin films of polymeric discotic liquid crystals. The prerequisite to study the properties of polymers is to synthesize asymmetrically-substituted discotic monomers as precursor molecules for polymeric discotics [14,15]. So far, the asymmetrical functionalization of triphenylene can be achieved either by sophisticated synthetic routes or by statistical methods involving partial alkylation of the hexaacetoxy-triphenylene or partial ether cleavage of hexaalkoxytriphenylene [16,17]. These methods would definitely result in a mixture of inseparable isomers of ill-defined structure. However, an efficient way to the synthesis of unsymmetrically substituted ethers of triphenylene derivatives has been developed and reported by Boden [18,19], to obtain highly-pure functionalized triphenylene derivatives using the iron (III) chloride mediated coupling of a dialkyloxybene to a tetraalkoxybiphenyl, followed by a reductive work-up.

In our previous work, triphenylene derivatives containing terminal ester or carboxylic acid groups at neighboring position on triphenylene core have been reported [20,21], which shows that the mesomorphic phase can be stabilized by strong intermolecular hydrogen-bonding interaction. Here, Boden's strategy for the synthesis of unsymmetrically substituted triphenylene derivatives was adopted in this work. Novel triphenylene derivatives possessing opposite terminal functional chains are designed and synthesized with an improved synthetic process of the required dialkoxy-biphenyl. Application of tosylate group, not acetate group, in the synthesis of biphenyl in this work results in large-scale and a convenient process for preparation of alkoxybiphenyl and pure functional triphenylene derivative, which overcame the difficulties of poor yield, limited scale and a mixture of inseparable isomers of ill-defined structure.

EXPERIMENTAL PROCEDURES

The synthetic route to the triphenylene derivatives **9** containing unsymmetrically substituted carboxylic acid chains and **10** containing hydroxyl group is outlined in Scheme I. Compound **1** was prepared by tosylation of anisole, instead of acetylation [21], which shows high orienting effect on the iodation at the metaposition of tosylate. Thus, satisfactory yield and convenient purification process of compound **3** were obtained by iodination and hydrolysis of **1**. An unsymmetrical
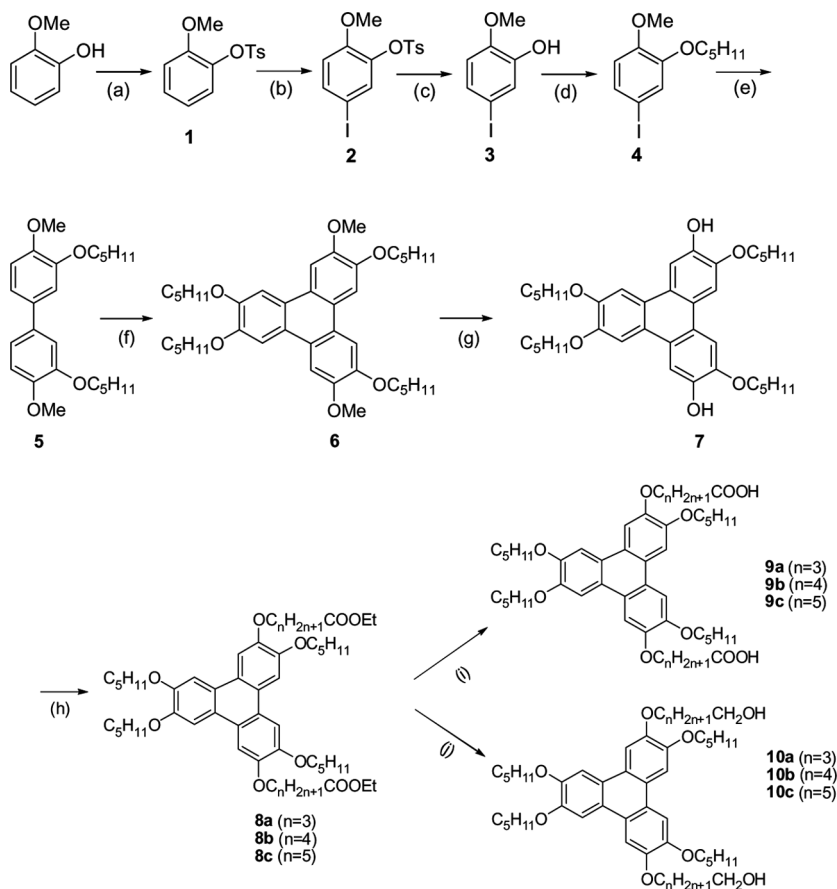
SCHEME I (a). TosCl, Et$_3$N, 15°C, 6 h, 96%; (b) ICl, HAc, ZnCl$_2$, 92%; (c) KOH, Ethanol reflux, 87%; (d) C$_5$H$_{11}$Br, K$_2$CO$_3$, Ethanol, reflux, 86%; (e) Cu powder, 270°C, 54%; (f) FeCl$_3$, 74%; (g) Ph$_2$PH, n-BuLi, THF, 77%; (h) Br (CH$_2$)$_n$COOEt, K$_2$CO$_3$, EtOH, reflux; (i) KOH, EtOH; (j) LiAlH$_4$, THF.

triphenylene derivative **6** was synthesized using an iron (III) chloride mediated oxidative coupling of 4,4′-dimethoxy-3,3′-bis (pentyloxy)-biphenyl and 1,2-dipentyloxy benzene, followed by a reductive methanol work-up procedure. Subsequent demethylation with lithium diphenylphosphide gave the diphenol. Thus, hydrolysis or reduction of **8** containing ester chain gave **9** and **10**, respectively.

General Information

^{1}H-NMR, ^{13}C-NMR spectra were recorded in CDCl$_3$ on a Bruker AV-500 spectrometer. Chemical shifts for ^{1}H-NMR spectra are reported in ppm downfield from TMS (Trimethyl Chlorosilane), chemical shifts for ^{13}C-NMR spectra are reported in ppm relative to internal chloroform (δ 77.0 ppm for ^{13}C). Low-resolution mass spectra (MS) were recorded on a HP5989 mass spectrometer. Infrared (IR) spectra were recorded on AVATAR 370 FT-IR spectrometer. The transition temperatures and thermal behavior were determined by differential scanning calorimetry (DSC) (Net2stch STA409PC, Germany) operated at a scanning rate of 5°C/min. The mesophases were identified according to the textures observed under an Orthlux-II POLBK polarizing microscope. X-ray diffraction (XRD) studies were conducted with XRD (Rigaku D/max 2550, CuKα) with a custom-built hot stage, performed over angular ranges of $2\theta = 4$–$30°$, scanned at a speed of $0.01°$/s and a step of $0.01°$.

2-Methoxyphenyl 4-Methylbenzenesulfonate (1)

4-Methylbenzene-1-sulfonyl chloride was added dropwise to the mixture of anisole (37.4 g, 0.34 mol) and triethylamine (300 ml) with stirring over 1 hr and the mixture stirred for a further 5 hrs maintaining the reaction temperature under 15°C. The solid was filtered and washed by triethylamine and water, afforded **1** (78.3 g, 94%), mp 84.0–85.4°C. IR (KBr), ν_{max} cm^{-1}: 1597, 1499 s (C=C, in plane, str), 1185s (C−O, str), 781,758 (Ar−H, w). ^{1}H-NMR (CDCl$_3$) δ/ppm: 7.52 (dd, 4H, Ar−<u>H</u>), 7.17 (m, 2H, Ar−<u>H</u>), 6.88 (m, 2H, Ar−<u>H</u>), 3.55 (s, 3H, O<u>CH</u>$_3$), 2.44 (s, 3H, Ar−<u>CH</u>$_3$).

2-(Methyloxy)-5-iodophenol (3)

Compound **1** (33 g, 0.12 mol) and anhydrous zinc chloride were dissolved in acetic acid (150 mL) and cooled to 10°C. Iodine monochloride (25 g, 0.154 mol) in acetic acid (50 mL) was added dropwise, maintaining the reaction temperature between 8 to 13°C. The mixture was

stirred at room temperature overnight and washed with sodium meta-bisulfite until the iodine color disappeared, and then washed with water. The white solid was filtrated *in vacuo* to give white solid 5-iodo-2-methoxyphenyl-4-methylbenzenesulfonate **2** (42.5 g, 90%), mp 147.5°C. IR (KBr), ν_{max} cm^{-1}: 1595, 1493s (C=C, in plane, str), 1184 s (C−O, str), 781,758 (Ar−H, w). ^{1}H-NMR (CDCl$_3$) δ/ppm: 7.62 (d, 2H, Ar−$\underline{H}$), 7.32 (d, 2H, Ar−$\underline{H}$), 7.45 (d, 1H, Ar−$\underline{H}$), 7.41 (s, 1H, Ar−$\underline{H}$), 6.60 (d, 1H, Ar−$\underline{H}$), 3.55 (s, 3H, O$\underline{CH_3}$), 2.46 (s, 3H, Ar−$\underline{CH_3}$).

The white solid **2** (30 g) was further dissolved in ethanol (100 mL) and a solution of sodium hydroxide (20 g) in ethanol (50 mL) and water (50 mL) was added. The solution was refluxed for 24 h, allowed to cool, and carefully acidified with 40% sulfuric acid. The mixture was extracted with dichloromethane and the organic solutions were dried (MgSO$_4$). Removal of solvent *in vacuo* followed by recrystallization of the residue from ethanol gave a white crystal **3** (15.8 g, 87%), mp 87.3°C. IR (KBr), ν_{max} cm^{-1}: 3471, 857, 798 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ/ppm: 7.23 (s, lH, Ar−$\underline{H}$), 7.15 (d, lH, $J = 8$ Hz, Ar−$\underline{H}$), 6.59 (d, lH, $J = 8$ Hz, Ar−$\underline{H}$), 5.58 (s, lH, O−$\underline{H}$), 3.85 (s, 3H, O$\underline{CH_3}$).

2-(Pentyloxy)-5-iodoanisole (4)

Compound **3** (15.1 g, 0.06 mol) and potassium carbonate (50 g) were stirred in ethanol (100 mL) for 10 min. *n*-Bromopentane (10 g, 0.066 mol) was added and the solution was stirred at room temperature for 3 days. The mixture was acidified with dilute sulfuric acid and extracted with dichloromethane. The solvents were removed *in vacuo* and the residue was recrystallized from ethanol to give white solid **4** (14.6 g, 76%), mp 59.4°C. IR (KBr), ν_{max} cm^{-1}: 1604, 1502 (C=C, in plane, str), 1251s (C−O, str), 857, 796, 747 (Ar−H, w). ^{1}H-NMR (CDCl$_3$) δ/ppm: 7.09 (d, lH, Ar−$\underline{H}$), 7.04 (s, lH, Ar−$\underline{H}$), 6.43 (d, lH, Ar−$\underline{H}$) 3.94 (t, 2H, Ar−$\underline{H}$), 3.83 (s, 3H, O$\underline{CH_3}$), 1.71 (m, 2H, OCH$_2$$\underline{CH_2}$), 1.31 (m, 4H, CH$_2$$\underline{CH_2}$), 0.90 (t, 3H, $\underline{CH_3}$).

4,4′-Dimethoxy-3,3′-bis(pentyloxy)biphenyl (5)

Compound **4** (12 g, 37.5 mmol) was mixed intimately with copper powder (24 g). The mixture was heated rapidly to 250°C and carefully to 270°C, where an exothermic reaction took place causing the temperature to rise to 320°C. After cooling the mixture was extracted repeatedly with dichloromethane (350 mL). The solvent was removed *in vacuo* and the residue was recrystallized from methanol to give **5** (3.9 g, 54%), mp 69.8°C. IR (KBr), ν_{max} cm^{-1}: 1610, 1509s (C=C, in plane, str), 1256s (C−O, str), 841, 798 (Ar−H, w). ^{1}H-NMR (CDCl$_3$)

δ/ppm: 7.08 (m, 4H, Ar$-$<u>H</u>), 6.90 (d, 2H, Ar$-$<u>H</u>), 4.07 (t, 4H, O<u>CH$_2$</u>), 3.90 (s, 6H, O<u>CH$_3$</u>), 1.85 (m, 4H, OCH$_2$<u>CH$_2$</u>), 1.45 (m, 8H, CH$_2$<u>CH$_2$</u>), 0.92 (t, 6H, <u>CH$_3$</u>).

2,7-Dimethoxy-3,6,10,11-tetra-pentyloxy)triphenylene (6)

Compound **5** (3 g, 7.77 mmol) and 1,2-bis(pentyloxy)benzene (5.83 g, 23.3 mmol) were stirred in dichloromethane (50 mL) and iron (II1) chloride (18.9 g) was added. After stirring for 1 h, the mixture was poured onto methanol (100 mL) and the resulting solid immediately filtered off and dried in a desiccator. Purification by column chromatography (silica gel, petroleum:dichloromethane 4:l) afforded **6** (3.6 g, 73%), mp 102.4°C. MS (ESI, m/z): M$^+$ 632.7. IR (KBr), ν_{max} cm^{-1}: 1619, 1518s (C=C, in plane, str), 1263s (C$-$O, str), 840 (Ar$-$H, w). ^{1}H-NMR (CDCl$_3$) δ/ppm: 7.91 (t, 6H, Ar$-$<u>H</u>), 4.21 (dd, 8H, O<u>CH$_2$</u>), 4.1 (s, 6H, O<u>CH$_3$</u>), 1.95 (m, 8H, OCH$_2$<u>CH$_2$</u>), 1.55 (m, 16H, CH$_2$<u>CH$_2$</u>), 1.0 (t, 12H, <u>CH$_3$</u>).

2,7-Dihydroxy-3,6,10,11-tetra(pentyloxy)triphenylene (7)

Diphenylphosphine (2 mL, 11.8 mmol), was dissolved in dry THF (Tetrahydrofuran) (20 mL) and cooled in an ice bath under argon. Butyllithium (1.6 M in hexanes, 12 mL, 30.7 mmol) was added over 10 min. Compound **6** (3.0 g, 4.75 mmol) was added and the solution magnetically stirred at 50–60°C for 4 h and at room temperature overnight. The mixture was poured onto dilute sulfuric acid and extracted with ethyl acetate. The solvent was removed *in vacuo* and the residue precipitated from dichloromethane with methanol. The precipitate was filtered off, dried, and purified by column chromatography (silica gel, petroleum: dichloromethane 1:2) to give **7** (2.2 g, 77%), mp 105.0°C. MS (ESI, m/z): M$^+$ 604.8. IR (KBr), ν_{max} cm^{-1}: 3529, 3393 (O$-$H, str), 1615, 1512s (C=C, in plane, str), 1266s (C$-$O, str), 849 (Ar$-$H, w). ^{1}H-NMR (CDCl$_3$) δ/ppm: 7.95 (s, 2H, Ar$-$<u>H</u>), 7.8 (s, 2H, Ar$-$<u>H</u>), 7.7 (s, 2H, Ar$-$<u>H</u>), 5.9 (s, 2H, O$-$<u>H</u>), 4.3 (t, 4H, O<u>CH$_2$</u>), 4.2 (t, 4H, O<u>CH$_2$</u>), 1.95 (m, 8H, O<u>CH$_2$</u>CH$_2$), 1.55 (m, 16H, CH$_2$<u>CH$_2$</u>), 1.0 (m, 12H, <u>CH$_3$</u>).

Representative Procedure for the Synthesis of Diethyl-5,5′-(3,6,10,11-Tetrakis(pentyloxy)triphenylene-2,7-diyl)bis(oxy)-dipentanoate (8b)

Compound **7** (0.5 g, 0.83 mmol) was dissolved in ethanol (20 mL), potassium carbonate (0.165 g, 1.2 mmol) was added and ethyl

5-bromopentanoate (0.21 g, 1.0 mmol) was added in drops. The solution was magnetically stirred at 78°C for 2 days. The mixture was poured into dilute sulfuric acid and extracted with ethyl acetate. The solvent was removed *in vacuo* and the precipitate was purified by column chromatography (silica, dichloromethane) to give **8** (0.6 g, 74%), mp 63.7°C. MS (ESI, m/z): M^+ 860.5. IR (KBr), ν_{max} cm^{-1}: 1734 (C=O, str), 1616, 1514s (C=C, in plane, str), 1262s (C−O, str), 837 (Ar−H, w). ^{1}H-NMR (500 MHz, CDCl$_3$) δ/ppm): 7.83 (s, 6H, Ar−H), 4.28 (m, 12H, $J = 6$ Hz, OCH$_2$), 4.13 (q, 4H, OCH$_2$), 2.49 (t, 4H, CH$_2$CO), 2.00–1.93 (m, 16H, OCH$_2$CH$_2$), 1.60–1.53 (m, 8H, CH$_2$), 1.50–1.41 (m, 8H, CH$_2$), 1.24 (t, 6H, $J = 6$ Hz, CH$_2$CH$_3$), 0.98 (t, 12H, CH$_2$CH$_3$). ^{13}C-NMR (126 MHz, CDCl$_3$, δ/ppm): 174.1, 149.2, 149.1, 148.9, 123.7, 107.5, 107.4, 107.3, 51.7, 33.9, 29.3, 29.2, 29.0, 28.6, 28.5, 22.8, 22.7, 21.9, 14.3, 14.2.

Analytical Data for Diethyl-5,5′-(3,6,10,11-Tetrakis (pentyloxy)triphenylene-2,7-diyl)bis(oxy)-dibutanoate (8a)

Mp 63.7°C. MS (ESI, m/z): $M^{+\cdot}$ 832.9. IR (KBr), ν_{max} cm^{-1}: 1734s (C=O, str), 1616, 1514s (C=C, in plane, str), 1262, 1174 (C−O, str), 837 (Ar−H, w). ^{1}H-NMR (500 MHz, CDCl$_3$, δ/ppm): 7.90 (s, 2H, ArH), 7.88 (s, 2H, ArH), 7.85 (s, 2H, ArH), 4.32 (t, 4H, $J = 6$ Hz, OCH$_2$), 4.29–4.24 (m, 8H, $J = 6.5$ Hz, OCH$_2$), 4.19 (q, 4H, $J = 7$ Hz, OCH$_2$), 2.67 (t, 4H, $J = 7$ Hz, COCH$_2$), 2.28 (m, 4H, OCH$_2$CH$_2$), 2.00–1.95 (m, 8H, OCH$_2$CH$_2$), 1.62–1.46 (m, 8H, CH$_2$), 1.30 (t, 6H, $J = 7$ Hz, CH$_3$), 1.02–0.99 (m, 12H, CH$_3$).^{13}C-NMR (126 MHz, CDCl$_3$, δ/ppm): 173.4, 149.1, 148.9, 148.7, 123.7, 123.6, 107.5, 107.4, 107.2, 60.4, 30.7, 29.2, 29.1, 28.5, 28.4, 24.7, 22.6, 22.5, 14.3, 14.1.

Analytical Data for Diethyl-5,5′-(3,6,10,11-Tetrakis (pentyloxy)triphenylene-2,7-diyl)bis(oxy)-dihexanoate (8c)

Liquid 81%. IR (KBr), ν_{max} cm^{-1}: 1736 s (C=O, str), 1616, 1519s (C=C, in plane, str), 1262, 1172 (C−O, str), 840 (Ar−H, w). ^{1}H-NMR (500 MHz, CDCl$_3$, δ/ppm): 7.83 (s, 6H, ArH), 4.23 (m, 12H, OCH$_2$), 4.13 (q, 4H, $J = 7$ Hz, OCH$_2$), 2.38 (t, 4H, $J = 7$ Hz, COCH$_2$), 2.28 (m, 4H, OCH$_2$CH$_2$), 1.90 (m, 16H, CH$_2$), 1.62–1.46 (m, 20H, CH$_2$), 1.30 (t, 6H, $J = 7$ Hz, OCH$_2$CH$_3$), 0.98 (t, 12H, $J = 7$ Hz, CH$_3$). ^{13}C-NMR (126 MHz, CDCl$_3$, δ/ppm): 173.6, 149.0, 148.9, 148.8, 123.7, 123.6, 123.5, 107.4, 107.3, 107.2, 60.3, 34.3, 32.2, 29.2, 28.4, 26.4, 24.8, 22.6, 14.3, 14.1.

Representative Procedure for the Synthesis of 5,5′-(3,6,10,11-Tetrakis(pentyloxy)triphenylene-2,7-diyl)bis(oxy)-dipentanoic acid (9b)

Compound **8b** (1.5 g, 1.74 mmol) was dissolved in ethanol (20 mL) and a solution of potassium hydroxide (1.5 g, 26.8 mmol) in ethanol (20 mL) and water (10 mL) was added. The solution was refluxed for 24 h, allowed to cool, and carefully acidified with 20% sulfuric acid. The mixture was extracted with dichloromethane and the organic solutions were dried (MgSO$_4$). The solvent was removed *in vacuo* and the precipitate was further purified by column chromatography (silica gel, petroleum:ethyl acetate 5:2) to give **9b** (1.0 g, 71%). MS (ESI, m/z): M$^+$ 804.7. IR (KBr), $\nu_{\max}$ cm^{-1}: 3448–2500 (COOH, str), 1706 (C=O, str), 1619, 1517s (C=C, in plane, str), 1262s (C−O, str), 836 (Ar−H, w). ^{1}H-NMR (500 MHz, CDCl$_3$, δ/ppm): 11.45 (s, 2H, COO$\underline{H}$), 7.82 (s, 6H, Ar−$\underline{H}$), 4.26–4.21 (m, 12H, OC$\underline{H}_2$), 2.53 (t, 4H, $\underline{CH}_2$CO), 2.02–1.92 (m, 16H, OCH$_2$C$\underline{H}_2$), 1.60–1.53 (m, 8H, CH$_2$C$\underline{H}_2$), 1.59–1.41 (m, 8H, C$\underline{H}_2$), 1.00 (t, 12H, C$\underline{H}_3$). ^{13}C-NMR (126 MHz, CDCl$_3$, δ/ppm): 179.4, 149.0, 148.9, 148.7, 123.7, 123.6, 123.5, 107.3, 107.2, 107.0, 33.8, 29.2, 29.1, 28.7, 28.4, 22.6, 22.5, 21.7, 14.1.

Analytical Data for 5,5′-(3,6,10,11-Tetrakis(pentyloxy) triphenylene-2,7-diyl)bis(oxy)-dibutaonic acid (9a)

Yield 65%. MS (ESI, m/z): M$^{+\cdot}$ 776 IR (KBr), $\nu_{\max}$ cm^{-1}: 3442–2500br (COO−H, str), 1708 (C=O, str), 1618, 1517s (ArC=C, in plane, str), 1173 (C−O), 837 (ArC−H, w). ^{1}H-NMR (500 MHz, CDCl$_3$, δ/ppm): 10.53 (s, 2H, COO$\underline{H}$), 7.93 (s, 2H, Ar$\underline{H}$), 7.90 (s, 2H, Ar$\underline{H}$), 7.87 (s, 2H, Ar$\underline{H}$), 4.17 (t, 4H, OC$\underline{H}_2$), 4.11 (t, 4H, OC$\underline{H}_2$CH$_2$), 2.52 (t, 4H, C$\underline{H}_2$CO), 2.06–2.01 (m, 4H, OCH$_2$C$\underline{H}_2$), 1.79–1.72 (m, 8H, C$\underline{H}_2$), 1.47–1.29 (m, 16H, CH$_2$), 0.85–0.82 (m, 12H, C$\underline{H}_3$). ^{13}C-NMR (126 MHz, CDCl$_3$, δ/ppm): 173.7, 149.2, 149.1, 148.9, 123.7, 123.6, 123.5, 107.4, 107.1, 107.0, 29.8, 28.4, 24.8, 22.4, 13.6, 13.5.

Analytical Data for 5,5′-(3,6,10,11-Tetrakis(pentyloxy)-triphenylene-2,7-diyl)bis(oxy)-dihexanoic acid (9c)

Yield 69%. MS (ESI, m/z): M$^{+\cdot}$ 832. IR (KBr), $\nu_{\max}$ cm^{-1}: 3450–2500br (COOH, str), 1707 (C=O, str), 1617, 1518s (ArC=C, in plane, str), 1261, 1172s (C−O, str), 837 (Ar−H, w). ^{1}H-NMR (500 MHz, CDCl$_3$, δ/ppm): ^{1}H-NMR (500 MHz, CDCl$_3$, δ/ppm): 7.81 (s, 6H, Ar$\underline{H}$), 4.21 (m, 12H, OC$\underline{H}_2$), 2.43 (t, 4H, COC$\underline{H}_2$), 1.97–1.90 (m, 12H, OCH$_2$C$\underline{H}_2$), 1.78 (m, 4H, C$\underline{H}_2$), 1.64 (m, 4H, C$\underline{H}_2$), 1.54 (m, 4H,

C$\underline{H}_2$), 1.46 (m, 4H, C$\underline{H}_2$), 0.97 (t, 12H, C$\underline{H}_3$). ^{13}C-NMR (126 MHz, CDCl$_3$, δ/ppm): 177.8, 149.3, 149.2, 149.0, 123.9, 123.8, 123.7, 107.8, 107.7, 107.5, 33.8, 33.1, 29.3, 29.2, 28.5, 25.9, 24.7, 22.7, 22.6, 14.3.

Representative Procedure for the Synthesis of 5,5′-(3,6,10,11-Tetrakis(pentyloxy)triphenylene-2,7-diyl)bis(oxy)dipentan-1-ol (10b)

A solution of compound **8b** (1.5 g, 1.74 mmol) in dry THF (10 mL) was added dropwisely to a mixture of LiAlH$_4$ (0.5 g, 0.85 mmol) and THF (10 mL) under ice bath. After refluxed for 2 hrs, Na$_2$SO$_4 \cdot 10$H$_2$O (10 g, 32 mmol) was added to the mixture. The crude product was obtained by extracted by CHCl$_3$ and further purified by column chromatography (silica gel, CHCl$_3$:EtOAc 1:1) to give **10b** (0.8 g, 59%). MS (ESI, m/z): M$^{+\cdot}$ 776. IR (KBr), $\nu_{\max}$ cm^{-1}: IR (KBr, cm^{-1}) $\nu_{\max}$: 3421 (O−H), 2952, 2929, 2859 (C−H), 1618, 1517 (C=C, in plane, str), 1262, 1173 (C−O), 836 (w, Ar−H, out of plane). ^{1}H-NMR (500 MHz, CDCl$_3$, δ/ppm): 7. 82 (s, 6H, Ar$\underline{H}$), 4.26–4.22 (m, 12H, OC$\underline{H}_2$), 3.72 (t, 4H, $J = 6$ Hz, OC$\underline{H}_2$), 2.00–1.96 (t, 12H, OCH$_2$C$\underline{H}_2$), 1.74–1.66 (m, 10H, C$\underline{H}_2$), 1.60–1.42 (m, 8H, C$\underline{H}_2$), 0.98 (t, 12H, $J = 8.5$ Hz, CH$_3$). ^{13}C-NMR (126 MHz, CDCl$_3$, δ/ppm): 149.0, 148.7, 148.8, 123.7, 123.5, 107.3, 107.2, 107.1, 69.7, 69.4, 69.5, 62.8, 32.5, 29.2, 29.1, 28.4, 28.3, 22.6, 22.5, 14.2.

Analytical Data for 4,4′-(3,6,10,11-Tetrakis(pentyloxytriphenylene-2,7-diyl)bis(oxy)dibutan-1-ol (10a)

Yield 59%. MS (ESI, m/z): M$^+$ 748. IR (KBr), $\nu_{\max}$ cm^{-1}: 3445 (O−H), 2952, 2928, 2862 (C−H), 1618, 1517 (C=C, in plane, str), 1262 (C−O), 836 (w, Ar−H, out of plane). ^{1}H-NMR (500 MHz, CDCl$_3$, δ/ppm): ■7.83 (s, 2H, Ar$\underline{H}$), 7.82 (s, 2H, Ar$\underline{H}$), 7.80 (s, 2H, Ar$\underline{H}$), 4.29 (t, 4H, $J = 6$ Hz, OC$\underline{H}_2$), 4.23 (t, 8H, $J = 6.5$ Hz, OC$\underline{H}_2$), 3.80 (t, 4H, $J = 6$ Hz, Hz, OC$\underline{H}_2$), 2.10–2.06 (m, 4H, OCH$_2$C$\underline{H}_2$), 1.99–1.85 (m, 12H, C$\underline{H}_2$), 1.60–1.42 (m, 16H, C$\underline{H}_2$), 0.98 (t, 12H, $J = 8.5$ Hz, C$\underline{H}_3$). ^{13}C-NMR (126 MHz, CDCl$_3$, δ/ppm): 149.1, 148.7, 148.4, 123.6, 123.5, 123.4, 107.3, 106.6, 106.4, 69.7, 69.4, 69.3, 62.4, 30.1, 29.2, 29.0, 28.4, 25.9, 22.6, 22.5, 14.2, 14.1.

Analytical Data for 6,6′-(3,6,10,11-Tetrakis(pentyloxy)triphenylene-2,7-diyl)bis(oxy)dihexan-1-ol (10c)

Yield 64%. MS (ESI, m/z): M$^+$ 804.9. IR (KBr), $\nu_{\max}$ cm^{-1}: 3510 (O−H), 2955, 2934, 2860 (C−H), 1614, 1511 (C=C, in plane, str),

1264, 1170 (C−O), 837 (w, Ar−H, out of plane). ^{1}H-NMR (500 MHz, CDCl$_3$, δ/ppm): 7.83 (s, 6H, Ar$\underline{H}$), 4.24–4.22 (m, 12H, OC$\underline{H}_2$), 3.69 (t, 4H, $J = 6.5$ Hz, OC$\underline{H}_2$), 1.98–1.92 (m, 12H, OCH$_2$C$\underline{H}_2$), 1.66–1.42 (m, 28H, C$\underline{H}_2$), 0.98 (t, 12H, $J = 8.5$ Hz, C$\underline{H}_3$). ^{13}C-NMR (126 MHz, CDCl$_3$, δ/ppm): 149.0, 148.9, 148.4, 123.7, 123.6, 107.4, 107.3, 69.7, 69.5, 69.4, 62.9, 32.8, 29.4, 29.2, 29.1, 28.4, 28.3, 26.0, 25.6, 22.6, 22.5, 14.2.

RESULTS AND DISCUSSION

Thermal behaviors of three triphenylene-based series of **8a–c**, **9a–c**, and **10a–c** were studied by DSC and the phase texture is investigated under crossed polarizing optical microscope (POM) with custom hot-stage. Results show that none of **8a**, **8b**, **8c**, which contain two terminal ester chains at periphery, can exhibit thermotropic liquid crystalline behavior on heating and cooling run. However, columnar mesophase was observed in the series of **9a**, **9b**, **9c**, in which terminal carboxylic acid chains substitute terminal ester chains in the corresponding series of **8a**, **8b**, **8c**. It is found that mesophase can't be observed in compounds **9a** and **9c** on heating under polarizing microscopy, which was also confirmed by DSC measurements that only one endothermic peak was found on heating process. However, fine fan-shape texture for **9a** and **9c** was seen under POM on cooling from isotropic phase. And also, it is found that this monotropic columnar phase was so unstable that crystallization behaviors began while the columnar mesophase appeared on slow cooling from isotropic phase. The columnar texture for **9c** taken under POM at 104°C was given in Figure 1. Crystallization behavior could be clearly observed from Figure 1 while the fan-shape domains appeared on cooling from isotropic phase.

As for compound **9b**, the DSC measurements show two endothermic peaks at around 107.3°C and 116.3°C, respectively, on first heating run. On cooling, only one exothermic peak was observed at 113.6°C (Fig. 2).

The study of liquid crystalline properties on **9b** was further determined by POM. It is found that compound **9b** exhibits two phase transitions of solid state-mesophase and mesophase-isotropic phase on heating, which correspond to the result of DSC at 107.3°C and 116.3°C, respectively. On cooling the isotropic phase at around 100°C, a well-defined texture of columnar mesophase appeared (Fig. 3), which corresponds to the exothermic peak at 113.6°C by DSC. No crystallization peak down to room temperature was found in DSC, which was also confirmed by the observation of the stable mesomorphic texture at room temperature for a few hours on cooling.
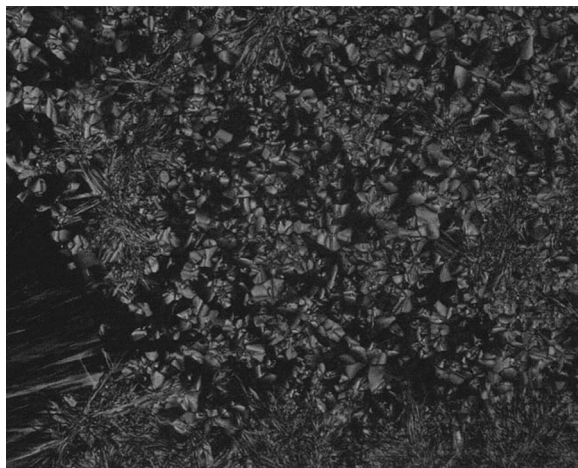
FIGURE 1 Texture of **9c** obtained with a polarizing microscope on cooling at 104°C (×200).

The exact nature for the columnar mesophase was deduced by detailed powder XRD studies for **9b**. Figure 4 shows XRD patterns for **9b** at 90°C. It is typical for a hexagonal columnar (Col$_h$) mesophase, which is often obtained for the untreated low molecular mass discotic liquid crystals in the Col$_h$ mesophase [22,23], and this pattern for **9b** is comparable with those. The lattice constant α_{hex} for **9b** was calculated
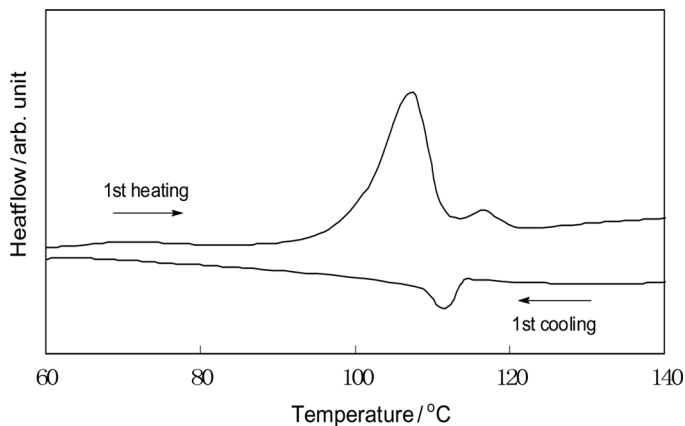

FIGURE 2 The DSC traces of **9b** on heating and cooling (scan rate 5°C min^{-1}).

FIGURE 3 Texture of **9b** obtained with a polarizing microscope on cooling at 100°C (×200)

to be 20.4 Å, which is much smaller than the estimated diameter of a fully extended **9b** (28.5 Å). Two additional reflections were also observed at c.4.4 Å (broad halo) and c.3.6 Å (weak peak), which are assigned to the average distance of the molten alkyl chains and the intracolumnar order, respectively. These results strongly indicate the existence of an ordered hexagonal columnar mesophase (Col$_{ho}$) of compound **9b**.

Meanwhile, TG (Thermogravimetry analysis) results showed that the synthesized compound **9b** had a high thermal stability until 340°C.
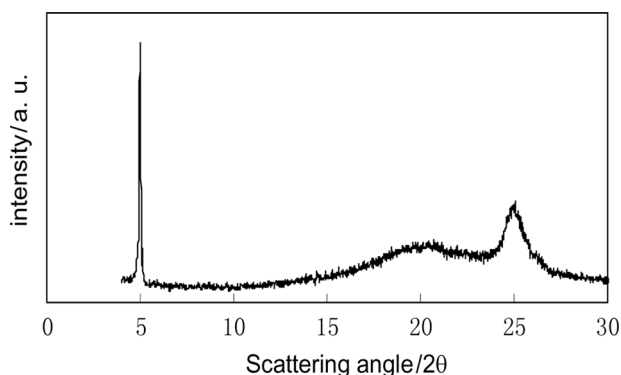
FIGURE 4 X-RD of **9b** at 90°C on cooling.

For the series **10a–c**, which possessing two terminal hydroxy chains at the periphery of the triphenylene core, only monotropic columnar mesophases could be observed for the compounds **10a** and **10c**. Typical fan-shape texture was observed under polarizing microscopy. However, **10b** didn't show any mesomorphism by studying its DSC curve and observation under POM.

The phase transition and enthalpy of the three series of **8**, **9**, and **10** are summarized in Table 1.

As only the two series of **9** and **10** show thermotropic columnar mesophase, it can be inferred from Table 1 that the strong intermolecular hydrogen bonding interaction of functional group of carboxylic acids, or the intermolecular hydrogen bonding interaction between hydroxyl groups, which are at the end of the aliphatic chain of the triphenylene core, would contribute to the formation of columnar mesophase. As the hydroxyl bonding interaction between carboxylic acids is stronger than that between hydroxyl group, thus, the series **9**, which have terminal carboxylic acid chains, exhibit more stable meosphase than the series **10**, which contain terminal hydroxyl chains. The effect of hydrogen bonding interaction on the mesomorphism is under study.

In conclusion, we have synthesized a new kind of triphenylene derivatives containing two terminal ester, carboxylic acid and hydroxyl chains on the opposite position of discotic triphenylene core. None of the compounds **8a**, **8b**, **8c**, possessing ester chains, shows

TABLE 1 Transition Temperatures and Enthalpies of **8**, **9** and **10**

Compounds	Phase transition	Temperatures (°C)	$\Delta H / kJ \cdot mol^{-1}$
8a	Cr—Iso	63.1	48.93
8b	Cr—Iso	70.0	40.33
8c	—[a]	—	—
9a	Cr—Iso	147.7	43.15
	(Col$_h$-Iso)	135.5	3.05
9b	Cr—Col$_h$	107.3	53.06
	Col$_h$—Iso	116.3	2.28
9c	Cr—Iso	115.5	60.73
	(Col$_h$-Iso)	107.8	2.84
10a	Cr—Iso	100.4	41.25
	(Col-Iso)	95.0	3.42
10b	Cr—Iso	91.7	37.99
10c	Cr—Iso	80.3	45.62
	(Col-Iso)	75.5	2.89

[a]Liquid at room temperature.

mesomorphism, while most of the corresponding triphenylene deriva-tives containing carboxylic acid chains or hydroxyl chains exhibit col-umnar mesophase. In addition, the suitable length of carboxylic acid chain on the triphenylene core, for example **9b**, is found to show stable Col$_{ho}$ mesophase and exhibits high thermal stability. The three series of **8**, **9**, and **10** are also good monomer candidates for the synthesis of discotic liquid crystals polymers.

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