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RESEARCH ARTICLE

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Synthesis and mesomorphism of mixed ether-ester tail triphenylene discotic liquid crystals with long alkyloxy peripheral chains

Abstract Symmetrical and asymmetrical triphenylene discotic liquid crystals with two kinds of different peripheral chains, *sym*-TP$(OC_{11}H_{23})_3(O_2CR)_3$ and *asym*-TP$(OC_{11}H_{23})_3(O_2CR)_3$, ($R = CH_2OC_2H_5, CH_2OC_3H_7, CH_2OC_4H_9, CH_2OC_5H_{11}, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}$) were synthesized. Their thermotropic liquid crystalline properties were studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The results showed that the asymmetrical compounds had higher melting and clearing points than that of their corresponding symmetrical compounds. For the same series of compounds, TP$(OC_{11}H_{23})_3(O_2CR)_3$, their melting points decrease and clearing points increase gradually with the lengthening of ester chains. Most of the β-oxygen containing esters of triphenylene derivatives, TP$(OC_{11}H_{23})_3(O_2CR)_3$, ($R = CH_2OC_2H_5$, $CH_2OC_3H_7$, $CH_2OC_4H_9$, $CH_2OC_5H_{11}$), symmetrically or asymmetrically attached on triphenylene cores, have higher melting and clearing points than those of triphenylene derivatives, TP$(OC_{11}H_{23})_3(O_2CR)_3$, ($R = C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}$), with the same length of peripheral chains. The triphenylene derivatives with longer peripheral chains have shown mesophase at room temperature.

Keywords triphenylene, discotic liquid crystal, columnar mesophase, ether-ester mixed tail, beta-oxygen effect, molecular symmetry

Discotic liquid crystal, which was first discovered by Chandrasekhar in 1977 [1], is different from conventional rod-like thermotropic liquid crystals in molecular geometry, phase behavior, and optic-electric property, and show huge potential application as organic semiconductors. Therefore, it has attracted increasing attention since its discovery [2–11]. Generally, the discotic liquid crystal molecule consists of a flat-like polycyclic rigid aromatic core and six or more peripheral flexible alkyl chains [6–12]. So there are two different methods for the synthesis of new discotic liquid crystals: change aromatic cores with different size and shape or modify the peripheral chains. On one hand, the aromatic core can be modified by introducing hetero-atoms instead of carbon atoms, such as triphenylene and hexaazotriphenylene, and aromatic core size with different number of carbon atoms, for example, triphenylene and hexabenzocoronene. On the other hand, peripheral chains can be modified by variation of chain length, or introducing hydrophilic, hydrophobic, hydrogen bonding, perfluorinated chains, metal-containing chains, and polymerisable functional groups [13–16]. Mesomorphism and charged carrier mobility behaviors of discotic liquid crystals depend both on the aromatic cores and peripheral chains. After the rigid core of the discotic liquid crystal is selected, the properties can be changed by peripheral chain modification. The discotic mesogens, triphenylene derivatives have played an important role because of their chemical stability, structure variation, well developed synthetic methods, availability of high purity samples, and high charged carrier mobility as organic semiconductors [17] reported in the literature. In order to investigate the influence of soft chain on mesomorphism of triphenylenes, many research groups have prepared triphenylenes with different functional groups [18–22]. For example, we have prepared symmetrical and asymmetrical triphenylenes with ether functional group and studied the influence of ether chain length on mesomorphism [23,24]. Kumar [25] has reported symmetrical and asymmetrical hexa-substituted ether-ester mixed tail triphenylenes and the correlation of chemical structure and physical property. Up to now, most of the reported studies are concentrated on short chain triphenylenes, such as

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pentyl, or hexyl. There are very few reports on longer chain triphenylene derivatives, maybe due to their disadvantage of having lower synthetic yields, low melting points and difficulty for purification through recrystallization from organic solvents. On the other hand, longer chain triphenylenes possess the advantage of being liquid crystal states at room temperature. The applicable liquid crystals in fields of optoelectrical display and organic semiconductors should be in liquid crystal state with broad temperature ranges, such as −50 to 70°C, and have high thermo-, photo- and chemical stability. Therefore, synthesis and development of discotic liquid crystals with longer chain are of importance in both the point of views of academic and industry application. Then, in order to know the structure-property correlation of long chain triphenylene derivatives, based on previous reported results [23–25], we designed and synthesized two series of symmetric and asymmetric triphenylene derivatives with ether-ester mixed tails, and investigated the molecular symmetry, ester chain length, and beta-oxygen-atom effects on mesomorphism. We hope the information accumulation on the structure-property relationship can contribute to the practical applications of triphenylene derivatives. Scheme 1 describes the synthesis routes of target triphenylene derivatives.

1 Experimental

1.1 Instruments and characterization methods

^{1}H NMR of triphenylene derivatives were recorded with Bruker-Avance-600 spectrometer, Me_4Si as the internal standard. Elemental analysis was measured with Carlo Erba 110b micro elementary analysis instrument. The optical textures of discotic liquid crystals were observed with XP-201 polarized optical microscope, with XP-201 heating plate, and XPR-201 temperature controller. The photomicrograph was recorded after the sample in two untreated glasses slowly cooled from isotropic liquid. Phase transition temperature and enthalpies were measured with differential scanning calorimetry (TA-DSC Q100), with heating and cooling rate at 10°C/min under N_2 atmosphere. The thermal stability of samples was measured by thermal gravimetry analysis (TGA) with a TA-TGA Q500 instrument.

1.2 Chemical reagents and organic solvents

Chemical reagents and organic solvents are commercial products and used without purification unless otherwise indicated. Butanoyl chloride, C_3H_7COCl, was prepared by the reaction of butanoic acid with benzoyl chloride, by controlling the refluxing and distillation rate. Other acid chlorides were synthesized directly from the reaction of acids between $SOCl_2$ under refluxing and distillation.

2-alkoxyacetic chloride, $ROCH_2COCl$ were prepared as follows [26]. ROH was carefully reacted with sodium, and then 2-chloroacetic acid was added for further reaction. Through acidic aqueous work-up, the product was purified by vacuum distillation. The prepared β-alkoxy-acetic acid reacted with excess $SOCl_2$, refluxed for 6 h with two drops of DMF as catalyst. After the excess $SOCl_2$ was distilled out, the acid chloride was collected by vacuum distillation. Product yield was in the range of 72%–83%.

1.3 Intermediates synthesis

1.3.1 Synthesis of **2**, $C_6H_4(OMe)(OC_{11}H_{23})$,2-methoxy-1-undecyloxybenzene

$C_6H_4(OMe)(OH)$, $C_{11}H_{23}Br$, anhydrous K_2CO_3 were added to dry ethanol, catalytic amount of KI added and refluxed 12 h with thorough stirring. After workup, the product **2** was collected as yellow oil, with a yield of 98%.

1.3.2 Synthesis of **s-3** and **a-3**, 2,6,10-tri(methoxy)-3,7,11-tri(undecyloxy)triphenylene and 2,6,11-tri(methoxy)-3,7,10-tri(undecyloxy)triphenylene

s-3 and **a-3** were prepared as reported in Ref. [27]. To the mixture of **2** and dichloromethane, 3 drops of concentrated sulfuric acid were added as catalyst, and anhydrous $FeCl_3$ was added carefully in three portions. After workup with cold methanol, the triphenylene derivatives f **s-3** and **a-3** were isolated as a mixture. After separation of the mixture by silica column chromatograph, **s-3** and **a-3** were isolated as pure form with a yield of 31% and 50%, and with a melting point of 74°C and 45°C, respectively.

1.3.3 Synthesis of **s-4** and **a-4**, 2,6,10-trihydroxy-3,7,11-tri(undecyloxy)triphenylene, 2,6,11-trihydroxy-3,7,10-tri(undecyloxy)-triphenylene

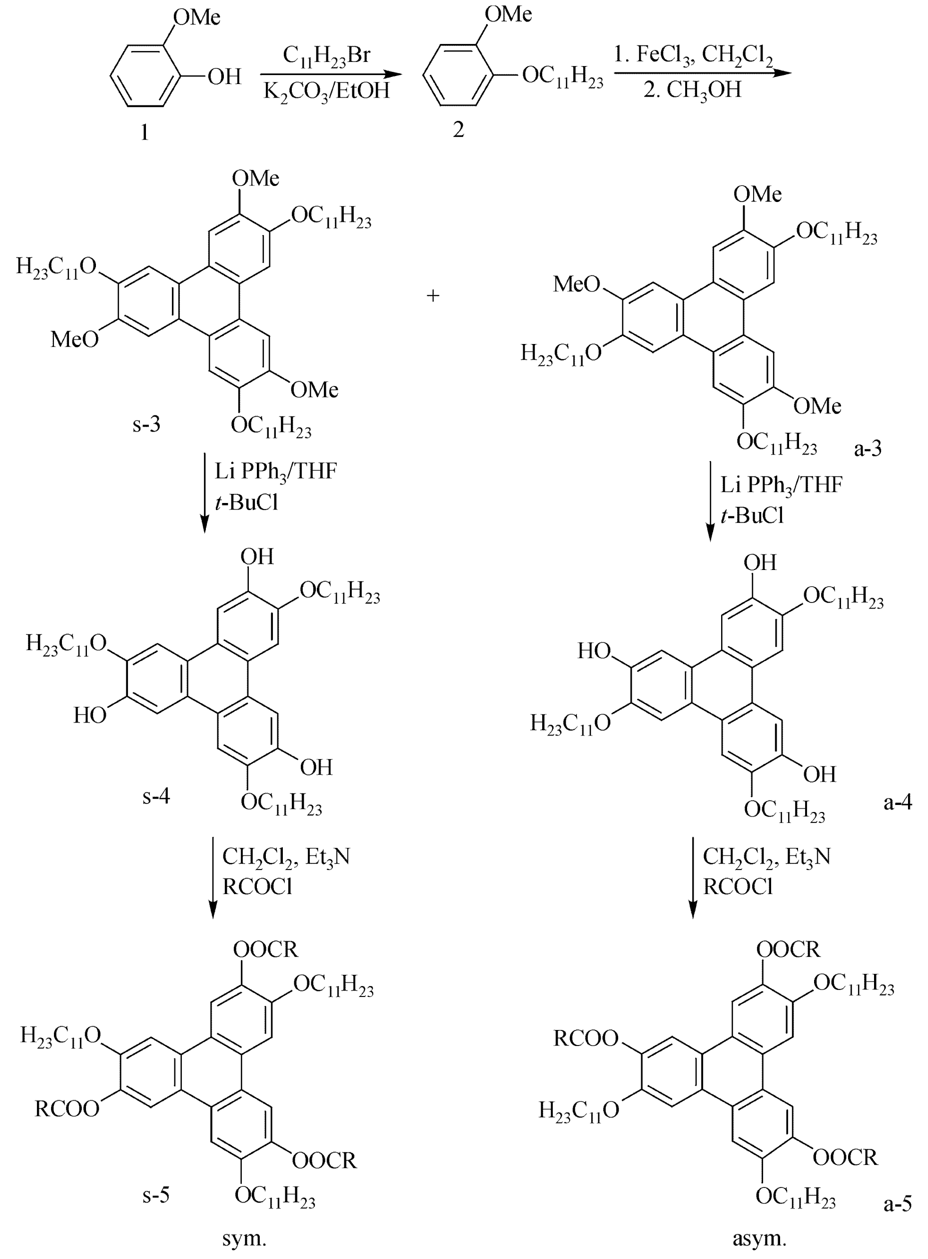
s-4 and **a-4** were synthesized as reported [28,29]. First, the reaction of PPh_3 and metal Li in dry THF produced Ph_2PLi and PhLi, and then dry tert-butyl chloride was added carefully for reaction with PhLi. After that, pure **s-4** or **a-4** was added and further refluxed 6 h with stirring under N_2 for the demethylation reaction. After acidic aqueous workup, **s-4** or **a-4** was further purified with silica gel column chromatograph and collected with a yield of 87% or 88%, and a melting point of 76°C and 134°C, respectively.

Compound **s-4**, *sym*-$TP(OH)_3(OC_{11}H_{23})_3$

^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 0.88 (t, J = 6.84 Hz, 9H), 1.15–1.38 (m, 30H), 1.39–1.47 (m, 6H), 1.48–1.68 (m, 12H), 1.86–2.00 (m, 6H), 4.25 (t, J = 6.57 Hz, 6H), 5.92 (s, 3H), 7.78 (s, 3H), 7.91 (s, 3H).

Compound **a-4**, *asym*-$TP(OH)_3(OC_{11}H_{23})_3$

^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 0.88 (t, J =



R = $CH_2OC_2H_5$,	$CH_2OC_3H_7$,	$CH_2OC_4H_9$	$CH_2OC_5H_{11}$
s-5a	s-5b	s-5c	s-5d
a-5a	a-5b	a-5c	a-5d

R = C_3H_7,	C_4H_9,	C_5H_{11},	C_6H_{13},	C_7H_{15}
s-5e	s-5f	s-5g	s-5h	s-5i
a-5e	a-5f	a-5g	a-5h	a-5i

6.81 Hz, 9H), 1.16–1.38 (m, 26H), 1.39–1.46 (m, 6H), 1.47–1.71 (m,16H), 1.86–2.01 (m, 6H), 4.26 (t, J = 7.29 Hz, 6H), 5.88 (s, 3H), 7.72 (s, 2H), 7.78 (s, 1H), 7.92 (s, 1H), 7.94 (s, 2H).

1.4 The synthesis of target molecules **s-5** and **a-5**

The *sym*-TP($OC_{11}H_{23}$)$_3$(O_2CR)$_3$ and *asym*-TP ($OC_{11}H_{23}$)$_3$(O_2CR)$_3$ were synthesized by the reaction of trihydroxy-tri(undecyloxy)triphenylene, **s-4** or **a-4** with the corresponding acid chloride in the presence of weak organic base, such as triethyl amine. After weak acidic aqueous workup, the product was purified through SiO_2 column chromatograph, and collected in white wax form, with a yield of 52%–78%.

Compound **s-5b**, *sym*-TP($OOCCH_2OC_3H_7$)$_3$($OC_{11}H_{23}$)$_3$ ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 0.89 (t, J = 6.99 Hz, 9H), 1.04 (t, J = 7.41 Hz, 9H), 1.19–1.35 (m, 36H), 1.35–1.43 (m, 6H), 1.44–1.53 (m, 6H), 1.73–1.87 (m, 12H), 3.70 (t, J = 6.78 Hz, 6H), 4.08 (t, J = 6.42 Hz, 6H), 4.46 (s, 6H), 7.43 (s, 3H), 7.87 (s, 3H); Anal. calcd for $C_{66}H_{102}O_{12}$: C 72.93, H 9.39; found C 72.97, H 9.43. The spectra data of **s-5a**, **s-5c** and **s-5d** are similar with **s-5b**.

Compound **s-5g**, sym-TP$(OOCC_5H_{11})_3(OC_{11}H_{23})_3$
^1H NMR ($CDCl_3$, TMS, 600 MHz) *δ*: 0.89 (t, *J* = 6.99 Hz, 9H), 0.99 (t, *J* = 7.17 Hz, 9H), 1.22–1.36 (m, 36H), 1.36–1.42 (m, 6H), 1.42–1.47 (m, 6H), 1.47–1.52 (m, 12H), 1.77–1.92 (m, 12H), 2.65 (t, *J* = 7.62 Hz, 6H), 4.12 (t, *J* = 6.60 Hz, 6H), 7.55 (s, 3H), 7.90 (s, 3H); Anal. calcd for $C_{69}H_{108}O_9$: C 76.67, H 10.00; found C 76.57, H 10.05. The spectra data of **s-5e**, **s-5f**, **s-5h**, **s-5i** are similar with **s-5g**.

Compound **a-5b**, *asym*-TP$(OOCCH_2OC_3H_7)_3(OC_{11}H_{23})_3$
^1H NMR ($CDCl_3$, TMS, 600 MHz) *δ*: 0.89 (t, *J* = 6.84 Hz, 9H), 1.03 (t, *J* = 5.94 Hz, 9H), 1.19–1.37 (m, 36H), 1.37–1.46 (m, 6H), 1.46–1.56 (m, 6H), 1.69–1.80 (m, 6H), 1.80–1.93 (m, 6H), 3.69 (t, *J* = 6.72 Hz, 6H), 4.12 (t, *J* = 6.45 Hz, 2H), 4.17 (t, *J* = 6.36 Hz, 2H), 4.20 (t, *J* = 6.27 Hz, 2H), 4.43 (s, 2H), 4.45 (s, 2H), 4.49 (s, 2H), 7.58 (s, 1H), 7.70 (s, 2H), 7.74 (s, 1H), 7.76 (s, 1H), 8.03 (s, 1H); Anal. calcd for $C_{66}H_{102}O_{12}$: C 72.93, H 9.39; found C 72.92, H 9.47. Compound **a-5a**, **a-5c**, **a-5d** showed similar spectra feature with **a-5b**.

Compound **a-5h,** *asym*-TP$(OOCC_6H_{13})_3(OC_{11}H_{23})_3$
^1H NMR ($CDCl_3$, TMS, 600 MHz) *δ*: 0.88 (t, *J* = 6.87 Hz, 9H), 0.95 (t, *J* = 5.73 Hz, 9H), 1.18–1.35 (m, 36H), 1.36–1.44 (m, 18H), 1.45–1.55 (m, 12H), 1.75–1.93 (m, 12H), 2.73–2.57 (t, *J* = 6.00 Hz, 6H), 4.17 (t, *J* = 6.57 Hz, 6H), 7.70 (s, 1H), 7.77 (s, 1H), 7.79 (s, 1H), 7.87 (s, 1H), 7.89 (s, 1H), 8.02 (s, 1H); Anal. calcd for $C_{72}H_{114}O_9$: C 77.01, H 10.16; found C 76.76, H 10.14. Compound **a-5e**, **a-5f**, **a-5g**, and **a-5i** had spectra character of compound **a-5h**.

2 Results and discussion

2.1 Synthesis

We synthesized the key intermediates **s-3** and **a-3**, in statistic mixture (in rate of 1:3) through oxidative cyclic trimerization of 1,2-dialkoxybenzene with anhydrous $FeCl_3$. The triphenylene mixture was separated by SiO_2 column chromatograph, and **s-3** and **a-3** were collected as pure form before the next demethylation reaction step, which resulted in **s-4** and **a-4**. The selective demethylation reagent in this step is $LiPPh_2$, which was reported in-situ preparation through reaction of BuLi with $HPPh_2$ [30]. Because $HPPh_2$ is highly toxic and expensive, here instead we used metal Li reduction of Ph_3P in dry THF for producing Ph_2P-Li and Ph-Li. The by-product PhLi in this step was further decomposed by its reaction with dry tert-butyl chloride [28]. To guarantee the complete demethylation of **3**, excess Ph_2PLi was used, in our case five equivalents of Ph_2PLi was used, and **4** was prepared in high yield.

The target discotic triphenylene derivatives **5** with ether-ester mixed tails were prepared by the reaction of **4** with acid chloride in the presence of weak organic base triethylamine. The β-oxygen containing acid chlorides, $ROCH_2COCl$, was not commercially available and prepared by the nucleophilic substitution reaction of sodium alkoxide with 2-chloroacetic acid, and further reacted with excess thionyl chloride.

2.2 Spectroscopic characterization of synthesized compounds

Triphenylene derivatives were purified with silica column chromatography and recrystallization from organic solvent, such as methanol, ethanol or acetone. The pure compounds were fully characterized by 600 MHz NMR and elemental analysis. In the high resolution NMR spectra, the chemical shift values of Ar–H are in the range of 7–8, and symmetrical compounds showed two single peaks (3H for each peak), while asymmetrical compounds exhibited six peaks (1H for each peak). Compound **s-4** and **a-4** have three hydroxyl groups attached on the triphenylene core, and **s-4** showed a single peak at 5.9 (3H for–OH), while **a-4** had three single peaks separated around 5.9. All triphenylene derivatives showed their aliphatic C–H protons *δ*-values in the range of 0.9–4.0. The methylene of alkoxy-acetyl group ($ROCH_2CO$–) containing triphenylenes (**5a**–**5d**) had its signs at a much lower field, about 4.45: the symmetrical derivative showed a single peak (6H), while the asymmetrical one exhibited three single peaks (2H for each peak).

2.3 Liquid crystalline properties of triphenylenes

Intermediates triphenylenes **3** and **4** did not show a liquid crystalline phase, as they contained very short methoxy or hydroxyl groups on aromatic core. The liquid crystalline properties of target triphenylene **5** (**5a**–**5i**) were investigated by DSC, TGA and POM. Table 1 and Table 2 summarize the liquid crystalline properties of triphenylenes with β-oxygen-containing ester chains (**5a**–**5d**) and with aliphatic ester chains (**5e**–**5i**), respectively. **s-5e** has no mesophase, due to the obvious length difference of the periphery (C11 and C4) [31] and molecular symmetry. **s-5f** is in liquid state at room temperature and DSC measurement did not find its phase transition even cooling to −50°C. All other triphenylenes showed liquid crystalline phases.

2.3.1 Thermal stability and mesophase characteristic features of triphenylenes 5

Figure 1 shows four TGA curves of typical triphenylenes, which demonstrated that these ether-ester mixed chain triphenylene derivatives are thermally stable until 350°C. Because the clearing points of triphenylenes were lower than this decomposing temperature, the DSC measurement and POM observation are investigated in the thermal stable state of **5**.

Table 1 Thermotropic properties of triphenylene-containing discogens, $TP(OC_{11}H_{23})_3(O_2CR)_3$, $R = CH_2OC_nH_{2n+1}$

Compd.	R	Mesophases, transition temperature and enthalpy changes	
		First heating/°C (ΔH, kJ·mol^{-1})	First cooling/°C (ΔH, kJ·mol^{-1})
s-5a	$CH_2OC_2H_5$	Col 54 I^a	I 54 Col
a-5a	$CH_2OC_2H_5$	K 56 (59.1) Col 118 (0.4) I	I 112 (0.6) Col 49 (0.3) K
s-5b	$CH_2OC_3H_7$	K 4 (1.1) Col 113 (1.6) I	I 115 (1.3) Col-12 (1.8) K
a-5b	$CH_2OC_3H_7$	K 0 (2.1) Col 153 (3.7) I	I 154 (3.5) Col-5 (1.6) K
s-5c	$CH_2OC_4H_9$	Col 137 (4.7) I^a	I 138 (4.4) Col
a-5c	$CH_2OC_4H_9$	K-19 (2.5) Col 153 (4.8) I	I 159 (4.0) Col-19 (1.7) K
s-5d	$CH_2OC_5H_{11}$	Col 141 (4.7) I^a	I 142 (4.0) Col
a-5d	$CH_2OC_5H_{11}$	K 4 (2.0) Col 165 (3.9) I	I 166 (5.2) Col-7 (1.9) K

Note: K: crystal state; Col: discotic columnar phase; I: isotropic liquid; ^{a} Melting point is below −50°C.

Table 2 Thermotropic properties of triphenylene-containing discogens, $TP(OC_{11}H_{23})_3(O_2CR)_3$, $R = C_nH_{2n+1}$

Compd.	R	Mesophases, transition temperature and enthalpy changes	
		First heating/°C (ΔH, kJ·mol^{-1})	First cooling/°C (ΔH, kJ·mol^{-1})
s-5e	C_3H_7	K 50 I	I 51 K
a-5e	C_3H_7	K 58 (6.4) Col 70 (19.2) I	I 70 (19.0) Col 10 (13.3) K
s-5f	C_4H_9	—^{a}	—^{a}
a-5f	C_4H_9	K 41 (53.8) Col 117 (3.3) I	I 120 (3.1) Col 7 (20.6) K
s-5g	C_5H_{11}	K_2 -3 (14.7) K_1 33 (13.1) Col 100 (0.5) I	I 100 (0.5) Col 27 (0.3) K_1 -23 (2.1) K_2
a-5g	C_5H_{11}	K_2 17 (1.1) K_1 39 (40.9) Col 142 (5.1) I	I 141 (4.7) Col-7 (20.4) K
s-5h	C_6H_{13}	K 23 (1.1) Col 135 (2.2) I	I 133 (3.0) Col 21 (1.2) K
a-5h	C_6H_{13}	K_2 5 (1.8) K_1 24 (37.6) Col 151 (5.3) I	I 151 (5.2) Col-14 (0.7) K_1 -15 (14.9) K_2
s-5i	C_7H_{15}	K_2 -6 (7.5) K_1 15 (1.3) Col 146 (4.2) I	I 147 (3.9) Col 14 (1.4) K_1 -26 (2.7) K_2
a-5i	C_7H_{15}	K_2 5 (8.8) K_1 18 (26.7) Col 152 (6.2) I	I 156 (5.9) Col-9 (21.3) K

Note: K: crystal state; Col: discotic columnar phase; I: isotropic liquid; ^{a} Clearing point is below room temperature.

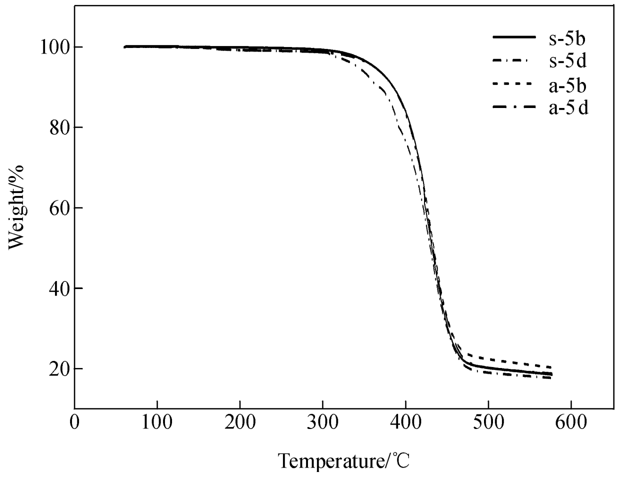


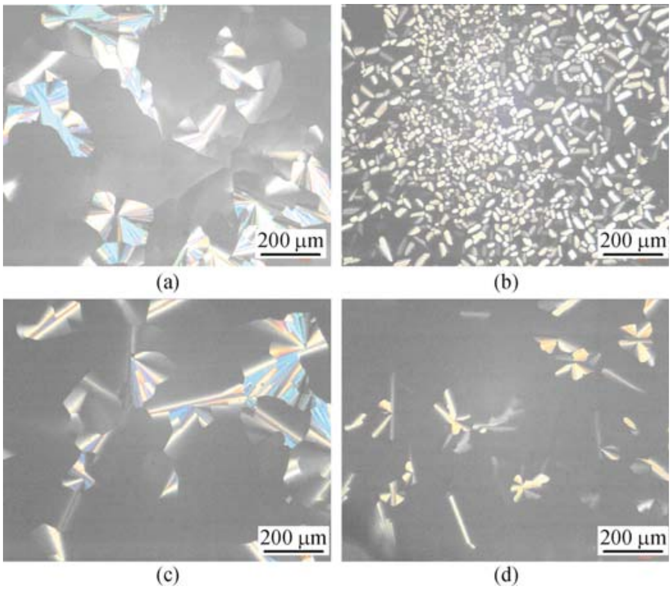
Fig. 1 TGA traces of triphenylene derivatives

The mesophase characteristics of **5** were studied with polarizing optical microscopy, and Fig. 2 shows four typical microphotographs of triphenylenes. The optical textures showed here are fan-shaped, which are common to discotic columnar phase. Figure 2(d) shows the texture structure of **a-5g**, which displayed its homeotropic alignment behavior. The self-assembled discotic columnar molecular stacking benefits in charged carrier mobility along the column axis and must promote the photoconductivity of discogens. Compounds **5a**–**5i** possess high thermal stability and moderate clearing temperature, self organized homeotropic alignment behaviors of discotic liquid crystals which favor physical property measurement and devices fabrication [32].

2.3.2 The influence of molecular symmetry, peripheral chain length and β-oxygen atom on mesomorphism

The thermotropic liquid crystalline properties of all triphenylenes were investigated by DSC with heating and cooling rate of 10°C/min under N_2 atmosphere, and the DSC traces of four triphenylene discogens as shown in Fig. 3. Compound **a-5i** displayed polymorphism, its DSC trace showed three peaks in the heating run: the first peak represents $K_2 \rightarrow K_1$ transition; the second, $K_1 \rightarrow$Col transition; the third, Col→Iso transition. On the cooling run it just showed two peaks: the Iso→Col and Col→K_2 transitions. Analyzing the data summarized in Tables 1 and 2, some other triphenylenes can be found possessing polymorphism, supercooling phenomena and being in liquid crystalline states at room temperature.

Figure 4 and Fig. 5 show the phase diagrams of two series triphenylene derivatives, one with β-oxygen-containing ester chains, the other one with aliphatic ester chains. Analyzing the phase diagrams, one can seen that with the ester chains length n increase, the melting points decrease and clearing points increase, and mesophase ranges broaden. When discotic liquid crystals were heated up to their melting points, the periphery transformed from solid



(a) (b)

(c) (d)

Fig. 2 Polarizing optical photomicrographs of liquid crystal compounds: (**a**) compound **s-5c** cooling to 125°C, (**b**) compound **a-5h** cooling to 80°C, (**c**) compound **a-5c** cooling to 140°C and (**d**) compound **a-5g** cooling to 134°C

crystalline packing to isotropic liquid; further heated to their clearing points, the aromatic discotic cores change from ordered columnar stacking into disordered isotropic liquid. From this point of view that the ester chain length increases, its melting points will be lowered. The ester chain length increased gradually when its length reached $-C_{11}H_{23}$, the six peripheral chains gradually became equal in length, and molecular symmetry is improved, therefore the columnar intermolecular stacking becomes more stable, and clearing point increased. The phase transition temperature trend found here is different from the reported result in literature [33].

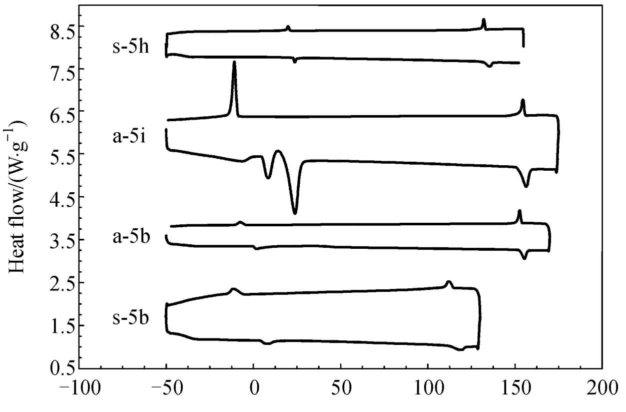


Fig. 3 DSC traces of triphenylene derivatives

Further analysis of Fig. 4 and Fig. 5, the phase diagrams of the mesogens, directly showed that asymmetrical compounds have higher clearing points than that of their symmetrical counterparts. These results are different from Kumar's report [25] about $C_{18}H_6(OC_5H_{11})_3(O_2CR)_3$, in which symmetrical triphenylenes showed higher clearing points than that of the asymmetrical ones. It is worth noting that in Kumar's report, triphenylenes have three short peripheral alkyl chains (C_5H_{11}); the discogens prepared in this report have three long alkyl chains ($C_{11}H_{23}$). The difference in molecular structure would result in the physical property variation.

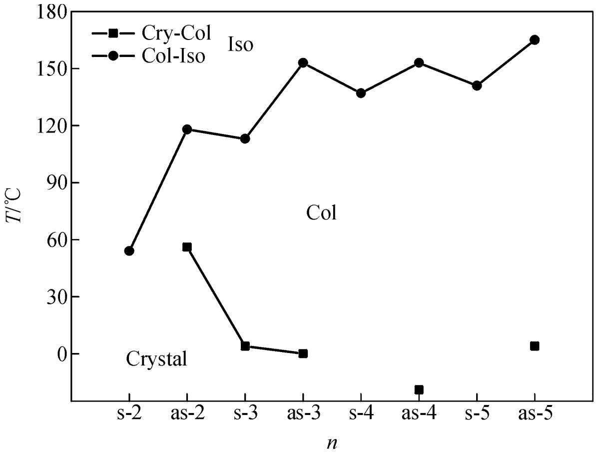


Fig. 4 Phase diagram of mesogens $TP(OC_{11}H_{23})_3(OOC\text{-}CH_2OC_nH_{2n+1})_3$, **5a**–**5d**. s: symmetry; as: asymmetry

Comparing the phase behaviors of the two series, triphenylene discogens with β-oxygen substituted ester chains have higher clearing points than that of their aliphatic ester counterparts. It is also explained by the beta-oxygen substituted peripheral chains that the intermolecular interaction increased compared with the aliphatic acid derivatives [13–16].

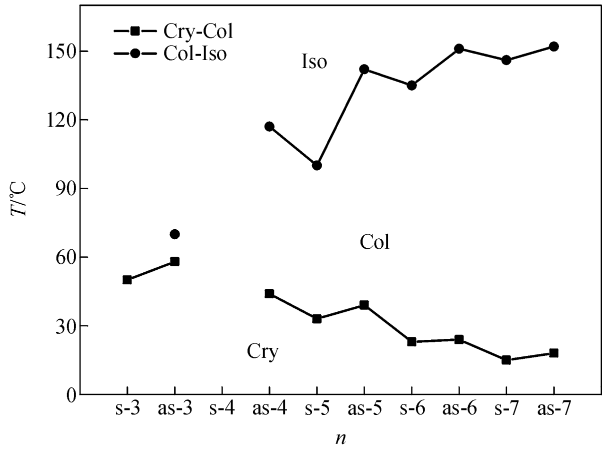


Fig. 5 Phase diagram of mesogens $TP(OC_{11}H_{23})_3(OOCC_nH_{2n+1})_3$, **5e**–**5i**. s: symmetry; as: asymmetry

Figure 6 and Fig. 7 describe the molecular stacking model of two symmetrical and asymmetrical triphenylenes of each other on top. Compared to all ether tail triphenylene systems, $TP(OR)_6$, with just the aromatic π-π interactions promoted the columnar molecular self assembly. However, in the system of triphenylenes connecting ester groups, they have both aromatic π-π interactions and dipole-dipole interaction of the ester groups, and make the intermolecular columnar stacking more stable. The asymmetrical isomers may have stronger intracolumnar intermolecular interaction, such as the dipole interaction, and therefore could cause their clearing points to be higher. The β-oxygen containing ester derivatives showing higher clearing points than that of the aliphatic ester derivatives can be explained by the same reason [13–16]. However, the oxygen atom in the other place of soft chain (not the beta position) would have opposite effect [34].

3 Conclusion

In this paper, we have reported the synthesis of symmetrical and asymmetrical ether-ester mixed-tail triphenylene derivatives with long ether chains (C11). The asymmetrical discogens have exhibited higher melting points and clearing points than their symmetrical counterparts. With the ester chain lengthening, the homologous discogens have shown decreased melting points, increased clearing points, and broadened columnar mesophase ranges. The triphenylene derivatives with β-oxygen ester chains have displayed higher clearing points and more stable Col phases. Because these triphenylene discogens contain long

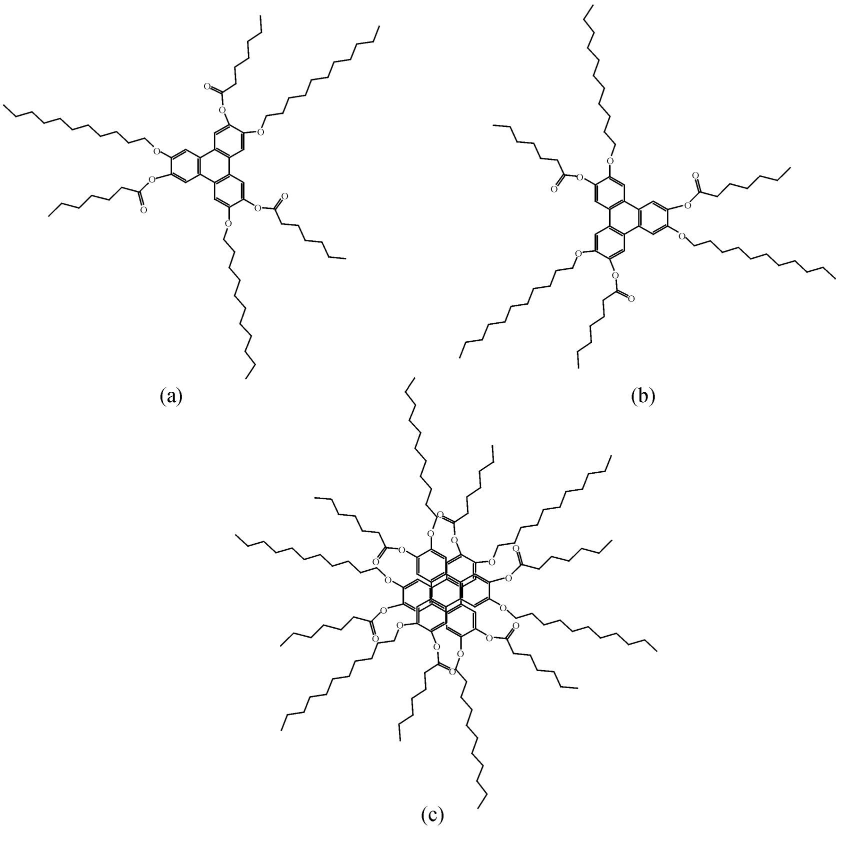


Fig. 6 Molecular packing of symmetrically substituted triphenylene discogen **s-5h**. (**a**) molecular structure of symmetrical discogen; (**b**) structure a was rotated by 180°C, structure (**b**) was stacked over structure (**a**).

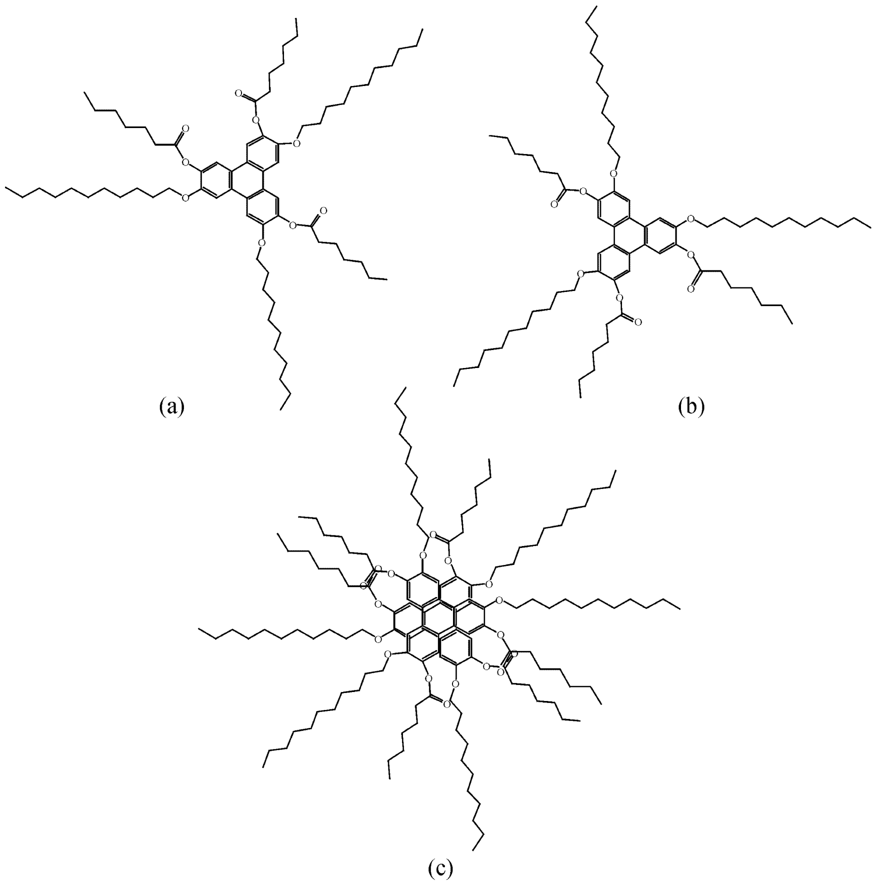


Fig. 7 molecular packing of asymmetrically substituted triphenylene discogen **a-5h**. (**a**) molecular structure of asymmetrical discogen; (**b**) structure a was rotated by 180°C, structure (**b**) was stacked over structure (**a**).

alkyloxy chains, most of them are in columnar mesophase at room temperature, which is in favor of the charge carrier mobility and electronic devices fabrication.

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References

1. Chandrasekhar S, Sadashiva B K, Suresh K A. Liquid crystals of disc-like molecules. Pramana, 1977, 7: 471–480
2. Tian Y, Zhao Y, Tang X. Brief introduction of discotic liquid crystals. Chin J Liquid Crystals and Displays, 1997, 12(1): 38–48
3. Perez D, Guitian E. Selected strategies for the synthesis of triphenylenes. Chem Soc Rev, 2004, 33: 274–283
4. Mao H, He Z, Zhang C. Advances in the synthesis of triphenylene derivatives with flexible side chains. Chin J Org Chem, 2006, 26(4): 413–418 (in Chinese)
5. Boden N, Borner R C, Bushby R J, Clements J. First observation of a n-doped quasi-one-dimensional electronically-conducting discotic liquid crystal. J Am Chem Soc, 1994, 116: 10807–10808
6. Kumar S. Recent developments in the chemistry of triphenylene-based discotic liquid crystals. Liq Cryst, 2004, 31: 1037–1059
7. Kumar S. Triphenylene-based discotic liquid crystal dimers, oligomers and polymers. Liq Cryst, 2005, 32(9): 1089–1113
8. Bushby R J, Lozman O R. Photoconducting liquid crystals. Current Opinion in Solid State and Materials Science, 2002, 6: 569–578
9. Bushby R J, Lozman O R. Discotic liquid crystals 25 years on. Current Opinion in Colloid and Interface Science, 2002, 7: 343–354
10. Shimizu Y, Oikawa K, Nakayama K, Guillon D. Mesophase semiconductors in field effect transistors. J Mater Chem, 2007, 17: 4223–4229
11. Laschats S, Baro A, Steinke N, Giesselmann F, Hagele C, Scalia D, Judele R, Kapatsina E, Sauer S, Schreivogel A, Tosoni M. Discotic liquid crystals: from tailor-made synthesis to plastic electronics. Angew Chem Int Ed, 2007, 46: 4832–4887
12. Kumar S, Manickam M, Balagurusamy V K. Electrophilic aromatic substitution in triphenylene discotics: synthesis of alkoxynitrotriphenylenes. Liq Cryst, 1999, 26: 1455–1466
13. Zhao K Q, Hu P, Wang B Q, Yu W H, Chen H M, Wang X L, Shimizu Y. Synthesis of mixed tail triphenylene discotic liquid crystals: molecular symmetry and oxygen-atom effect on the stabilization of columnar mesophases. Chin J Chem, 2007, 25: 375–381

14. Tabushi I, YamamuraK, Okada Y. Liquid crystals. 1. β-oxygen effect on stabilization of haxakis(acryloxy)benzene mesophase. J Org Chem, 1987, 52: 2502–2505
15. Collard D M, Lillya C P. Control of thermal phase behavior of disklike molecules by modification of side-chain structure. J Am Chem Soc, 1989, 111: 1829–1830
16. Collard D M, Lillya C P. Effect of heteroatoms in the side chains of disklike molecules on the formation of discotic liquid crystalline phases. J Org Chem, 1991, 56: 6064–6066
17. Kumar S, Manickam M. First examples of functionalized triphenylene discotic dimers: molecular engineering of advanced materials. Liq Cryst, 1999, 26: 1567–1571
18. Kreuder W, Ringsdore H. Liquid crystalline polymers with disc-like mesogens. Makromol Chem Rapid Commun, 1983, 4: 807–815
19. Kreuder W, Ringsdore H, Tschirner P. Liquid crystalline polymers with disc-like mesogens in the main chain. Makromol Chem Rapid Commun, 1985, 6: 367–373
20. Boden N, Bushby R J, Cammidg A N. Triphenylene-based discotic-liquid-crystalline polymers: a universal, rational synthesis. J Am Chem Soc, 1995, 117: 924–927
21. Boden N, Bushby R J, Cooke G, Lozman O R, Lu Z. CPI: a recipe for improving applicable properties of discotic liquid crystals. J Am Chem Soc, 2001, 123: 7915–7916
22. Schonherr H, Manickam M, Kumar S. Surface morphology and molecular ordering in thin films of polymerizable triphenylene discotic liquid crystals on HOPG revealed by atomic force microscopy. Langmuir, 2002, 18: 7082–7085
23. Zhao K Q, Wang B Q, Hu P, Li Q, Zhang L F. Synthesis of new triphenylene-containing discotic liquid crystals and the influence of fluorophilic effect and molecular symmetry on mesomorphism. Chin J Chem, 2005, 23: 767–774
24. Zhao K, Gao C, Hu P, Wang B, Li Q. Synthesis of triphenylene discotic liquid crystals substituted with ester or amide functional groups and the effect of hydrogen bonding on mesogenic behaviors. Acta Chimica Sinica, 2006, 64(10): 1051–1062 (in Chinese)
25. Manickam M, Kumar S. New mixed tail triphenylene discotic liquid crystals. Mol Cryst Liq Cryst, 1999, 326: 165–176
26. Fan N. Dictionary of Organic Synthesis. Beijing: Beijing Institute of Technology Press, 1992: 249–250 (in Chinese)
27. Chapuzet J M, Simonet J. The anodic trimerization of aromatic orthodiethers: new developments. Tetrahedron, 1991, 47: 791–798
28. Zhou H, Lu Y, LuS, Zhen Y, Fu H. Synthesis of tetra(diphenylphosphino)-neopentane and studies on the catalysis of its cobalt complexes for olefin hydroformylation. Journal of Molecular Catalysis (China), 1994, 8(2): 99–104 (in Chinese)
29. Boden N, Bushby R J, Lu Z B. A rational synthesis of polyacrylates with discogenic side groups. Liq Cryst, 1998, 25: 47–58
30. Boden N, Bushby R J, Cammidge A N, Martin P. Glass-forming discotic liquid-crystalline oligomers. J Mater Chem, 1995, 5: 1857–1860
31. Cross S G, Goodby G W, Hall A W, Hird M, Kelly S M, Toyne K J, Wu C. Unsymmetrical alkoxy-substituted triphenylenes: the dependence of mesomorphism on molecular shape. Liq Cryst, 1998, 25: 1–11
32. Hatsusaka K, Ohta K, Yamamoto I, Shirai H. Discotic liquid crystals of transition metal complexes, Part 30: spontaneous uniform homeotropic alignment of octakis(dialkoxyphenoxy)-phthalocyaninatocopper(II) complexes. J Mater Chem, 2001, 11: 423–433
33. Destrade C, Tinh N H, Gasparoux H, Malthete J, Levelut A M. Disc-like mesogens: a classification. Mol Cryst Liq Cryst, 1981, 71: 111–135
34. Okazaki M, Kawata K, Nishikawa H, Negoro M. Polymerizable discoticnematic triphenylene derivatives and their application to an optically anisotropic film. Polym Adv Technol, 2000, 11: 398–403