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# Synthesis of Mixed Tail Triphenylene Discotic Liquid Crystals: Molecular Symmetry and Oxygen-atom Effect on the Stabilization of Columnar Mesophases[1]

**[F005]**

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**Abstract**: A series of propyloxyacetyloxy- and alkoxy-containing mixed tail triphenylene based discotic liquid crystals, abbreviated as $TP(OC_nH_{2n+1})_3(OCOCH_2OC_3H_7)_3$, $n = 4 \sim 8$, and hexa(propyloxyacetyloxy)triphenylene, $TP(OCOCH_2OPr)_6$ have been synthesized and their liquid crystalline properties have been investigated through differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). These mixed tail triphenylene derivatives exhibit much more stable hexagonal columnar mesophases ($Col_h$) and much wider mesophase temperature ranges than their hexaalkoxytriphenylene $TP(OR)_6$ and hexaalkanoyloxytriphenylene $TP(OCOR')_6$ analogues. The asymmetrical compounds 2,6,11-trialkoxy-3,7,10-tri(2-propyloxyacetyloxy)triphenylenes with $n = 5 \sim 8$ possess higher clearing points and wider mesophase ranges than their symmetrical isomers 2,6,10-trialkoxy-3,7,11-tri(2-propyloxyacetyloxy)triphenylenes.

**Keywords**: triphenylene, discotic, columnar, β-oxygen-atom effect, molecular symmetry

## Introduction

Discotic liquid crystal materials can self-assemble to be highly ordered hexagonal columnar mesophases ($Col_{ho}$) and have high mobility of charges and energies.[1-4] They are studied as photoconductor,[1-6] charge transport materials of photovoltaic cells,[7] active materials in light emitting diodes,[8] gas sensors materials,[9] ion transport materials,[10] optical materials of display devices,[11,12] and show huge potential applications.

Highly ordered hexagonal columnar mesophase, fine homeotropic alignment behavior and wide mesophase temperature range are the most important parameters in the practical application of

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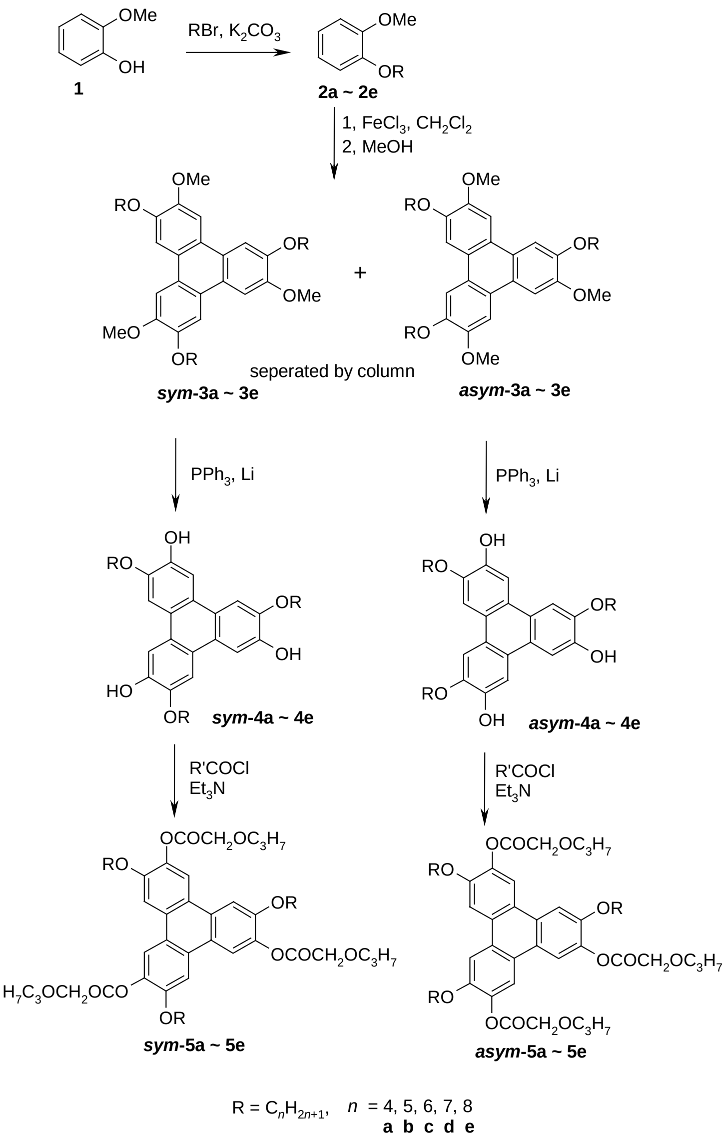
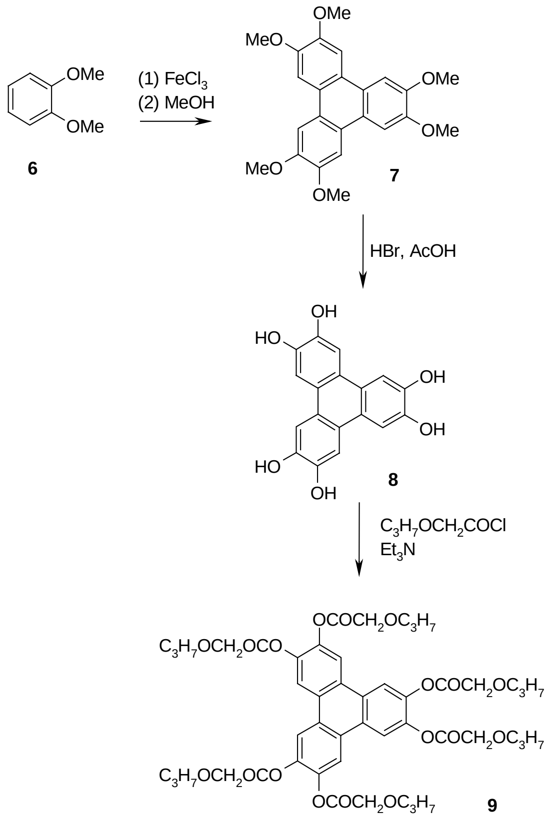
discotic liquid crystal materials. Hexaalkoxytriphenylene discogens TP(OR)$_6$ generally have medium to low clearing points and fine homeotropic alignment behaviors when cooled from isotropic liquid to Col$_h$ phase. Mixed ether-ether or ether-ester tail substituent on the triphenylene core can lower melting points and widen mesophase temperature ranges efficiently.[13-15] The influence of hetero-atom in ester chain on mesophase has been discussed.[16-18] Until now there has been no report on the combination effect of molecular symmetry and oxygen-atom effect to the mesophase behavior of triphenylene discogens. Here we report the synthesis and mesomorphism of novel trialkoxy-tri(2-propyloxyacetyloxy)triphenylenes and hexa(2-propyloxyacetyloxy)triphenylene. The synthetic route see scheme 1 and 2.

Scheme 1



Scheme 2



## Synthesis

The key intermediates for preparation of mixed tail trialkoxy-trialkanoyloxytriphenylene **5a-5e** are trialkoxy-trihydroxytriphenylenes **4a-4e**, which can be synthesized by de-alkylation of hexaalkyloxytriphenylene with 9-bromo-9-borabicyclo[3,3,1]nonane[19,20] or B-bromocatecholborane.[21] These methods yield mixture of symmetrical and asymmetrical trialkyloxy-trihydroxytriphenylenes along with other triphenylene derivatives which need tedious column chromatograph separation. In our experiments, 2-methoxyphenol **1** was used as starting material. Through alkylation and $FeCl_3$ oxidized cyclo-trimerization, statistic mixture of symmetrical and asymmetrical trialkyloxy-trimethoxytriphenylenes **3a-3e** were prepared.[22] The mixture was separated by simple column chromatograph yielding 2,6,10-trialkoxy-3,7,11-trimethoxytriphenylene *sym*-**3a-3e** and 2,6,11-trialkoxy-3,7,10-trimethoxytriphenylene *asym*-**3a-3e**. Selective de-methylation reagent $LiPPh_2$ (prepared from $PPh_3$ and Li) reacted with **3a-3e** yielding key intermediates trialkoxy-trihydroxytriphenylene **4a-4e**.

2-Propyloxyacetic acid was prepared by nucleophilic substitution of 2-chloroacetic acid with PrONa, and it further reacted with $SOCl_2$ yielding 2-propyloxyacetic chloride, wich reacted with trialkoxy-trihydroxytriphenylene **4a-4e** in the presence of organic base $Et_3N$ yielding target compounds trialkoxy-tri(2-propyloxyacetyloxy)triphenylene **5a-5e**. For comparison, Compound **9** $TP(OCOCH_2OPr)_6$ was synthesized from the reaction of hexahydroxytriphenylene $TP(OH)_6$ with the acid chloride.

All the synthesized compounds were characterized with 600MHz $^1H$ NMR and the spectra data are concordant with the chemical structures.

The $^1H$ NMR of *sym*-**5e**, *asym*-**5e** and **9** as follow:

***sym*-$TP(OC_8H_{17})_3(OCOCH_2OC_3H_7)_3$**, $^1H$ NMR($CDCl_3$, 600 MHz) δ: 7.91(s, 3H), 7.48(s, 3H), 4.47(s, 6H), 4.10(t, *J* = 5.67 Hz, 6H), 3.69(t, *J* = 6.75 Hz, 6H), 1.73~1.85(m, 12H), 1.45~1.55(m, 6H), 1.27~1.44(m, 24H), 1.03(t, *J* = 7.35 Hz, 9H), 0.91(t, *J* = 6.75 Hz, 9H).

***asym*-$TP(OC_8H_{17})_3(OCOCH_2OC_3H_7)_3$,** $^1H$ NMR($CDCl_3$, 600 MHz) δ: 8.05(s, 1H), 7.82(s, 1H), 7.77(s, 2H), 7.73(s, 1H), 7.62(s, 1H), 4.48(s, 2H), 4.45(s, 2H), 4.43(s, 2H), 4.21(t, *J* = 6.33 Hz, 2H), 4.17(t, *J* = 6.30 Hz, 2H), 4.13(t, *J* = 6.51 Hz, 2H), 3.65~3.72(m, 6H), 1.81~1.91(m, 6H), 1.70~1.80(m, 6H), 1.47~1.57(m, 6H), 1.27~1.43(m, 24H), 0.98~1.05(m, 9H), 0.85~0.94(m, 9H).

Compound **9**，$TP(OCOCH_2OC_3H_7)_6$, $^1H$ NMR($CDCl_3$, 600 MHz) δ : 7.92(s, 6H), 4.42(s, 12H), 3.65(t, *J* = 6.72Hz, 12H), 1.71-1.77(m, 12H), 1.02(t, *J* = 7.44 Hz, 18H).

# Mesomorphism

The liquid crystalline property of the synthesized triphenylene derivatives were studied with differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The results were summarized in Table 1 and Figure 1. The $C_3$-symmetrical compounds of 2,6,10-trialkoxy-3,7,11-tri(2-propyloxyacetyloxy)triphenylene *sym*-**5a-5e** and asymmetrical compound 2,6,11-trialkoxy-3,7,10-tri(2-propyloxyacetyloxy)triphenylene *asym*-**5a-5e** all exhibit hexagonal columnar phases, and four compounds also possess rectangular columnar mesophase judging from the optical texture and DSC result. All mixed tail discogens display very wide and stable columnar mesophase comparing to their counterpart of hexaalkoxytriphenylene $TP(OR)_6$ and hexaalkanoyloxytriphenylene $TP(OCOR')_6$[23]. For example, hexahexyloxytriphenylene $TP(OC_6H_{13})_6$ [23] exhibits ordered $Col_h$ phase at 69°C to 99°C, and hexahexanoyloxytriphenylene $TP(OCOC_5H_{11})_6$ [23] has melting point at 146°C and does not show mesophase, but *sym*-**5c** displays $Col_h$ mesophase at 70°C to 212°C; *asym*-**5c** shows $Col_h$ mesophase from 62°C to 223°C. Four compounds of *sym*-**5a,** *asym*-**5a**, *asym*-**5b** and *sym*-**5e** possess $Col_r$ and $Col_h$, other homologues just show $Col_h$ mesophases judging from DSC and POM. In the first heating run, the melting point and clearing point were observed on DSC traces, but transition of isotropic liquid to columnar phase was observed in the cooling run and showed very small hysteresis. The transition of columnar to crystal was not observed even at room temperature in DSC. The polarizing optical microscopic photographs of these discogens showed typical polygonal textures of columnar mesophase. See Figure 3.

Figure 1 shows the phase diagram of these triphenylene derivatives. When alkyl chains changed from short to long, the melting point of the compounds kept stable, while clearing point gradually lowered. Except for the lowest homologue *sym*-**5a** and *asym*-**5a**, all asymmetrical compounds have higher clearing points than the symmetrical isomers within the range of 11°C to 14°C. This result is quite different from Kumar's conclusion[13] that symmetrical compounds have higher clearing points than their asymmetrical isomers. The mesophase transition data of tripentyloxy-trihexanoyloxytriphenylene[13] [*sym*- and *asym*-$TP(OC_5H_{11})_3(OCOC_5H_{11})_3$] and trihexyoxy-trihexanoyloxytriphenylene[15] [*sym*- and *asym*-$TP(OC_6H_{13})_3(OCOC_5H_{11})_3$] were listed on table 1. Symmetrical isomer 2,6,10-trihexyoxy-3,7,11-trihexanoyloxytriphenylene (59°C $\mathrm{Col_h}$ 206°C) shows 14°C higher clearing point than the asymmetrical isomer

Table 1 Thermotropic properties of mixed tail triphenylene discogens

| Compound | Abbreviation | Phase transition temperature (°C)[a] and enthalpies (in parenthesis, kJ/mol) | |
|---|---|---|---|
| | | First heating | First cooling |
| ***sym*-5a** | *sym*-$\mathrm{TP(OC_4H_9)_3(OCOCH_2OC_3H_7)_3}$ | K 63(13.98) $\mathrm{Col_r}$ 104(13.90) $\mathrm{Col_h}$ 234(8.17) I | I 228(7.22) $\mathrm{Col_h}$ |
| ***asym*-5a** | *asym*-$\mathrm{TP(OC_4H_9)_3(OCOCH_2OC_3H_7)_3}$ | K 71(21.42) $\mathrm{Col_h}$ 228(9.66) I | I 226(8.42) $\mathrm{Col_h}$ |
| ***sym*-5b** | *sym*-$\mathrm{TP(OC_5H_{11})_3(OCOCH_2OC_3H_7)_3}$ | K 52(6.59) $\mathrm{Col_r}$ 91(27.36) $\mathrm{Col_h}$ 220(2.09) I | I 221(1.43) $\mathrm{Col_h}$ |
| ***asym*-5b** | *asym*-$\mathrm{TP(OC_5H_{11})_3(OCOCH_2OC_3H_7)_3}$ | K 58(3.58) $\mathrm{Col_r}$ 97(24.83) $\mathrm{Col_h}$ 234(10.21) I | I 234(7.52) $\mathrm{Col_h}$ |
| | *sym*-$\mathrm{TP(OC_5H_{11})_3(OCOC_5H_{11})_3}$ | K 110(15.7) $\mathrm{Col_h}$ 218(14.7) I [b] | I 215(12.8) $\mathrm{Col_h}$ |
| | *asym*-$\mathrm{TP(OC_5H_{11})_3(OCOC_5H_{11})_3}$ | K 69(16.6) $\mathrm{Col_h}$ 203(6.5) I [b] | I 201(6.8) $\mathrm{Col_h}$ |
| ***sym*-5c** | *sym*-$\mathrm{TP(OC_6H_{13})_3(OCOCH_2OC_3H_7)_3}$ | K 70 $\mathrm{Col_h}$ 212(8.79) I | I 214(6.39) $\mathrm{Col_h}$ |
| ***asym*-5c** | *asym*-$\mathrm{TP(OC_6H_{13})_3(OCOCH_2OC_3H_7)_3}$ | K 62(29.46) $\mathrm{Col_h}$ 223(8.49) I | I 223(7.92) $\mathrm{Col_h}$ |
| | *sym*-$\mathrm{TP(OC_6H_{13})_3(OCOC_5H_{11})_3}$ | K 59(20.68) $\mathrm{Col_h}$ 206(11.61) I [c] | I 206(10.48) $\mathrm{Col_h}$ 41(8.12) K |
| | *asym*-$\mathrm{TP(OC_6H_{13})_3(OCOC_5H_{11})_3}$ | K 58(27.33) $\mathrm{Col_h}$ 192(5.13) I [c] | I 194(3.51) $\mathrm{Col_h}$ |
| | $\mathrm{TP(OC_6H_{13})_6}$ | K 69 $\mathrm{Col_h}$ 99 I | |
| | $\mathrm{TP(OCOC_5H_{11})_6}$ | K 146 I | |
| **9** | $\mathrm{TP(OCOCH_2OPr)_6}$ | K 79 $\mathrm{Col_h}$ 238 I | |
| ***sym*-5d** | *sym*-$\mathrm{TP(OC_7H_{15})_3(OCOCH_2OC_3H_7)_3}$ | K 71(27.19) $\mathrm{Col_h}$ 202(6.98) I | I 202(4.82) $\mathrm{Col_h}$ |
| ***asym*-5d** | *asym*-$\mathrm{TP(OC_7H_{15})_3(OCOCH_2OC_3H_7)_3}$ | K 45(37.27) $\mathrm{Col_h}$ 216(7.60) I | I 217(7.48) $\mathrm{Col_h}$ |
| ***sym*-5e** | *sym*-$\mathrm{TP(OC_8H_{17})_3(OCOCH_2OC_3H_7)_3}$ | K 54(5.88) $\mathrm{Col_r}$ 66(23.17) $\mathrm{Col_h}$ 188(5.57) I | I 188(5.72) $\mathrm{Col_h}$ |
| ***asym*-5e** | *asym*-$\mathrm{TP(OC_8H_{17})_3(OCOCH_2OC_3H_7)_3}$ | K 67(21.86) $\mathrm{Col_h}$ 204(7.76) I | I 205(7.09) $\mathrm{Col_h}$ |

K, crystal state; $\mathrm{Col_r}$, rectangular columnar mesophase; $\mathrm{Col_h}$, hexagonal columnar mesophase; Iso, Isotropic liquid. [a] onset temperature from DSC. [b] data reported by Kumar.[13] [c] data reported by Zhao.[15]

2,6,11-trihexyoxy-3,7,10-trihexanoyloxytriphenylene (58°C $\mathrm{Col_h}$ 192°C). 2,6,10-tripentyloxy-3,7,11-hexanoyloxytriphenylene(110°C $\mathrm{Col_h}$ 218°C) shows 15°C higher clearing point than 2,6,11-tripentyloxy-3,7,10-trihexanoyloxytriphenylene(69°C $\mathrm{Col_h}$ 203°C).These data show to that of trialkoxy-trialkanoyloxytriphenylene, the symmetrical isomers have higher clearing points. The insertion of oxygen in the ester chain results in that asymmetrical 2-propyloxyacetic acid ester of triphenylene exhibit higher clearing points than the symmetrical isomers. This phenomena could be attributed to the β-oxygen-atom in the ester chains. As oxygen-atom can cause bigger van der Waales interaction than $CH_2$ in the ester chains and therefore 2-propyloxyacetyloxy group $PrOCH_2COO$ has bigger intermolecular interaction than hexanoyloxy group $C_5H_{11}COO$. In columnar mesophase the molecules stagger on each other forming column and the bigger the intermolecular interaction in the column, the higher the clearing point. It is reasonable to deduce that higher interaction exists in asymmetrical propyloxyacetyloxy-containing triphenylenes from figure 3 and figure 4, which are showed the molecular packing of the mixed tail triphenylenes. In the staggered overlap of asymmetrical compounds, the propyloxyacetyloxy moiety from neighbor molecules can exert interaction to each other, while the symmetrical isomers show less opportunity to form this interaction in the staggered overlap. Compound **9** has six peripheral chains of $PrOCH_2COO$- and should possess the strongest interaction. Therefore it is expected that it exhibits highest clearing point of 238°C, the most stable columnar mesophase here.

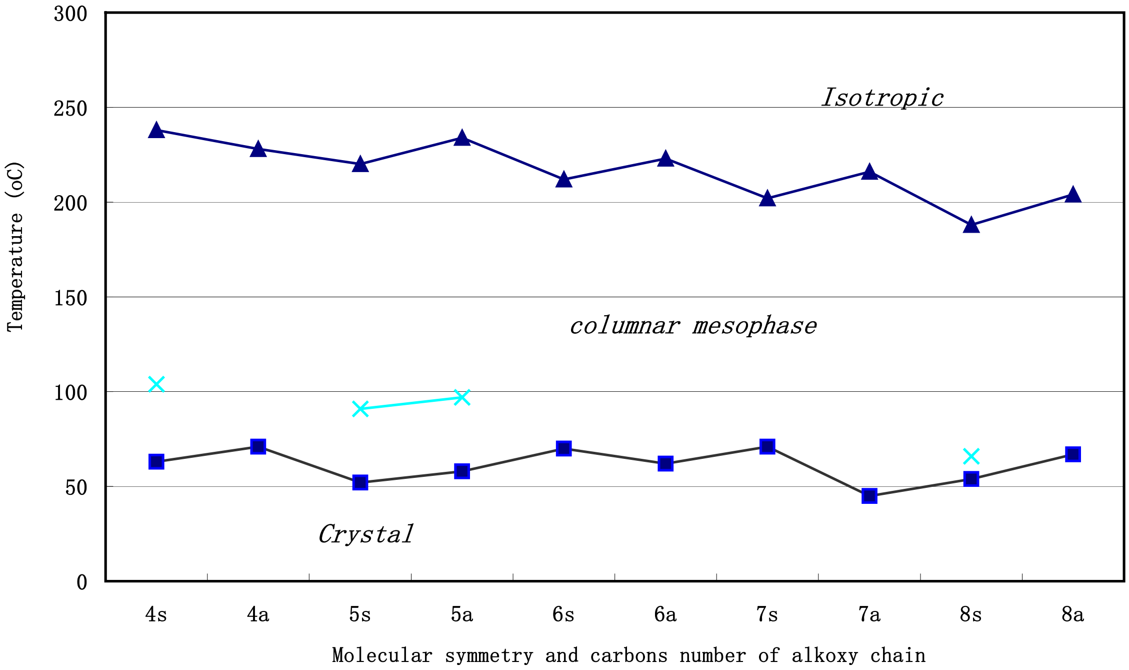
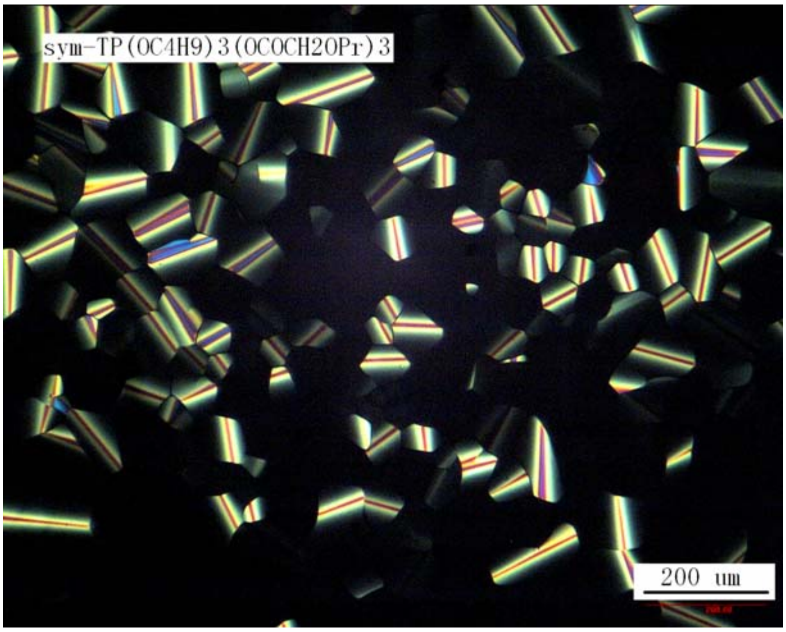


Figure 1, The phase diagram of mixed tail trialkoxy-tri(2-propyloxyacetyloxy)triphenylenes.
The effect of alkoxy chain length and the molecular symmetry on melting points and clearing points.



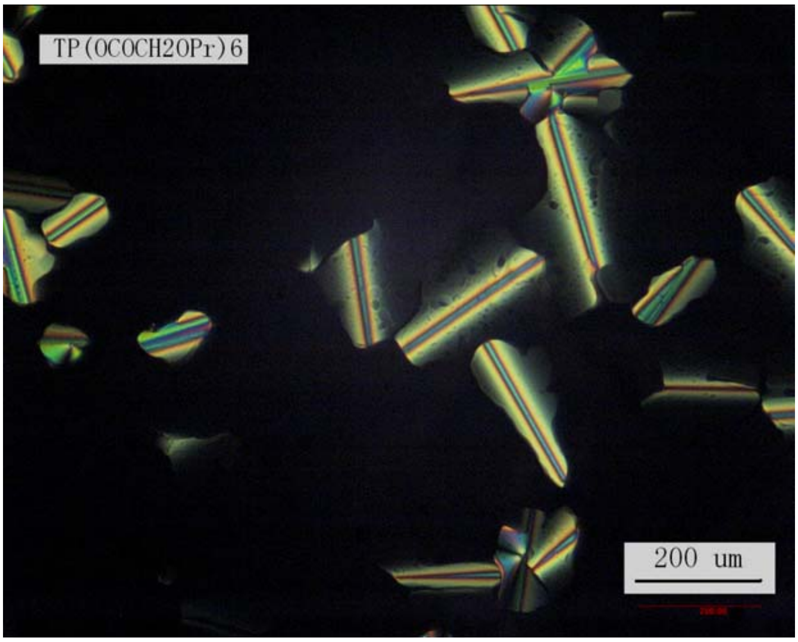


Figure 2, POM photographs of *sym*-**5a** and **9.**

Typical polygonal texture of $Col_h$ mesophase cooled from isotropic liquid.

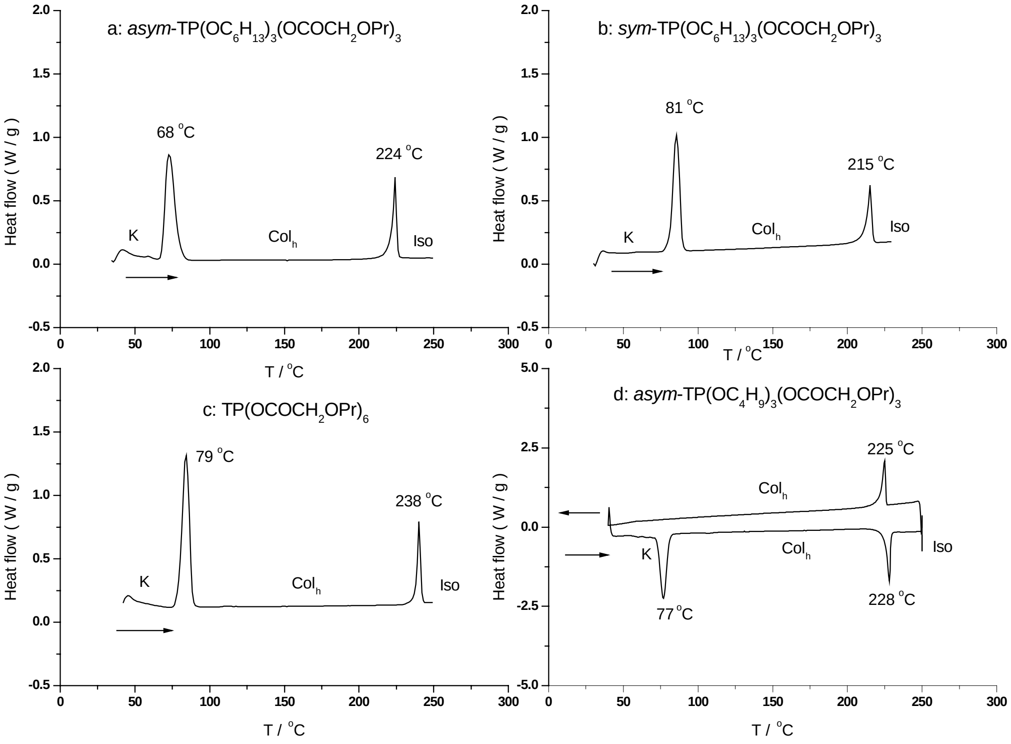


Figure 3a, DSC traces of *asym*-**5c**, *sym*-**5c**, **9**, *asym*-**5a**

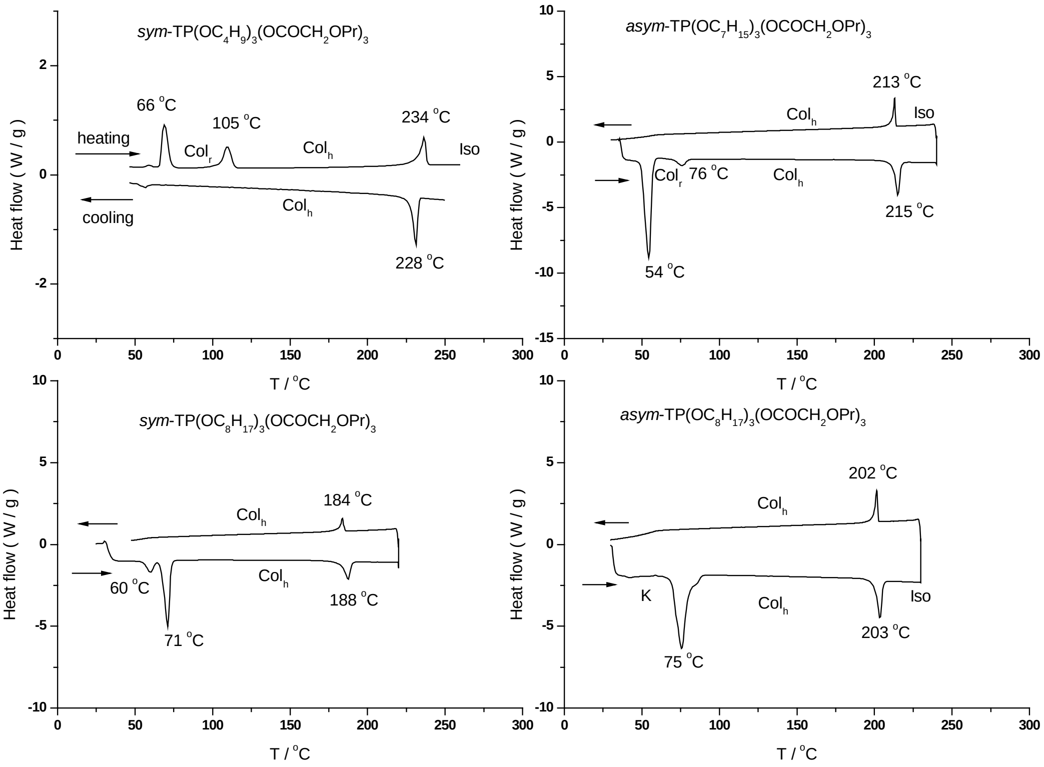


Figure 3b, DSC traces of *sym*-**5a**, *asym*-**5d**, *sym*-**5e** and *asym*-**5e**.

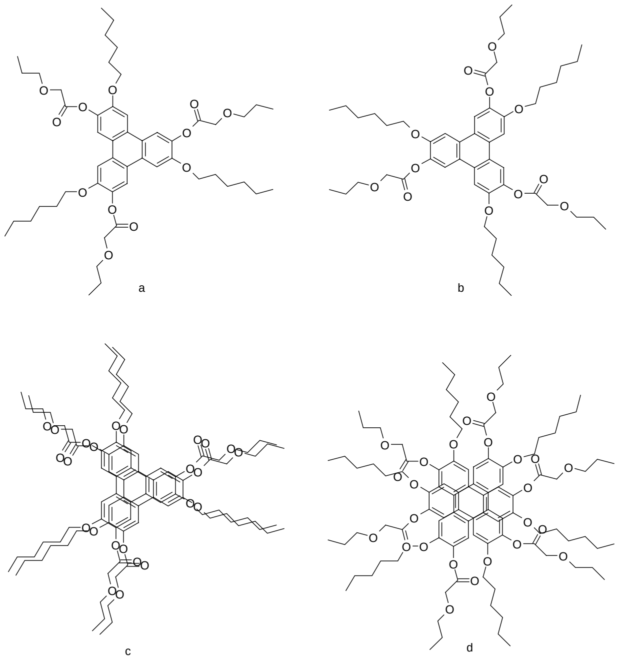


Figure 4a, molecular packing of *sym*-**5c** and β-oxygen effect of ester chain.

a, molecular structure of *sym*-**5c**. b, a rotated $180^{o}$. c, a stacked on another molecule a forming eclipsed overlap. d, b stacked on a forming staggered overlap.

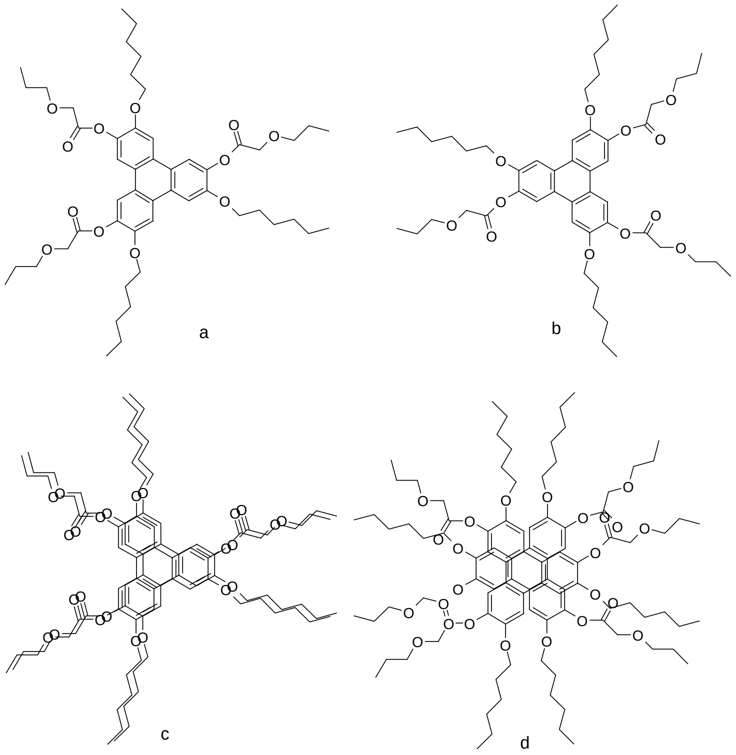


Figure 4b, molecular packing of *asym*-**5c** and β-oxygen effect of ester chain.

a, molecular structure of *asym*-**5c**. b, a rotated $180^o$.

c, a stacked on another molecule a forming eclipsed overlap. d, b stacked on a forming staggered overlap.

## Conclusion

A series of symmetrical and asymmetrical ether-ester mixed tail trialkoxy-tri(2-propyloxyacetyloxy)triphenylenes $TP(OR)_3(OCOCH_2OPr)_3$ and hexa(2-propyloxyacetyloxy)triphenylene $TP(OCOCH_2OPr)_6$ have been prepared. They show very stable $Col_h$ mesophases and wide mesophase temperature ranges. Except for the lowest homologues, the asymmetrical isomers have higher clearing points and wider mesophase temperature ranges than their symmetrical counterparts. 2,3,6,7,10,11-Hexa(2-propyloxyacetyloxy)triphenylene exhibits the highest clearing point and most stable columnar mesophase. It is deduced that the β-oxygen effect of ester chains caused this result.

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