9th International Electronic Conference on Synthetic Organic Chemistry. ECSOC-9
1-30 November 2005. http://www.usc.es/congresos/ecsoc/9/ECSOC9.HTM & http://www.mdpi.net/ecsoc/

[A003]

Synthesis and Mesomorphism of Novel Triphenylene-based Discotic Liquid Crystals with Chiral Peripheral Chains[1]

YUAN Fu-Jing, WANG, Bi-Qin, HU Ping, ZHAO Ke-Qing*
College of Chemistry and Material Science, Sichuan Normal University,
Chengdu, 610066, Sichuan, China

Email: zhaokeqing@yahoo.com.cn; Tel./fax: 028-84764743

Abstract:

Symmetrical and asymmetrical triphenylene-based discotic liquid crystals with mixed ether-ester peripheral chains, the ester ones with a chiral carbon [abbreviated as *sym*-$TP(OC_nH_{2n+1})_3(OOCC^*HClCH_2CHMe_2)_3$ and *asym*-$TP(OC_nH_{2n+1})_3(OOCC^*HClCH_2CHMe_2)_3$, n = 4 ~ 8， 11] were synthesized. The phase transition temperature and the liquid crystal states were determined with polarized optical microscopy (POM) and differential scanning calorimetry (DSC). It was found that the symmetrical isomers have lower clearing points. Some of the discogens show as many as three kinds of columnar mesophases.

Keywords: Triphenylene, discotic liquid crystal, columnar mesophase, chirality, polymesomorphism

Introduction

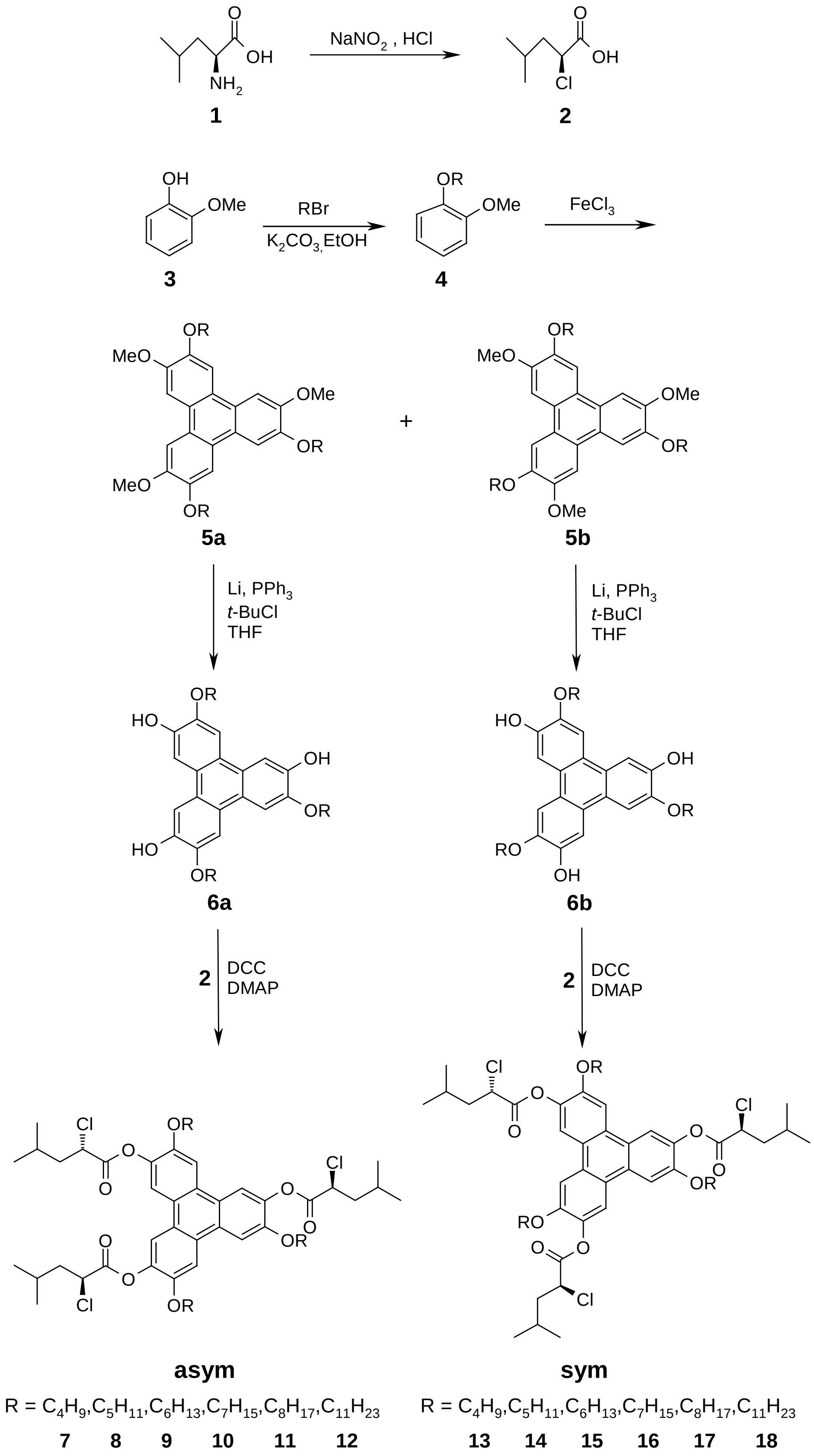
Discotic liquid crystalline materials based on polyaromatic molecules have attracted increasing attention because of their one-dimensional charge and energy transport capabilities in the highly ordered columnar mesophase.[1, 2] Triphenylene-based discogens are among the most intensively studied discotic liquid crystalline materials, as their synthetic methodologies have been well developed and high purity compounds can be prepared through column chromatography and

---

[1] Supported by National Nature Science Foundation of China (No.50473062) and Youth Foundation of Sichuan Province (04ZQ026-044).

recrystallization.[3] They can self-assembly to homeotropic mono domain and have been used as active components for organic electronics and optoelectronic devises.[4,5] Triphenylene-containing discotic nematic optical compensation film for liquid crystal display has been developed in Fuji Company and this is the first commercial application of discotic liquid crystalline materials since its discovery in 1977.[3,6]

Recent years ferroelectric discotic liquid crystals have been investigated for device application. Most efforts in this field have concentrated on the creation of chiral discogens and relied on the relatively weak chirality imparted by the introduction of a chiral center into the highly disordered side chains or by adding chiral dopants.[7-9] Some ferroelectric discotic liquid crystals exhibited quite surprising mesophases, such as discotic nematic phase (N_D).[6,10] Although nematic phase for rod-shaped lquid crystals are common, it occurring for disc-shaped mesogen is rare. Heppke reported a triphenylene derivative of the chiral alkoxy chain substituted hexabenzoates exhibit a discotic blue phase in 2000.[11] The introduction of chirality into discotic liquid crystals is an interesting and important subject in the material science.[12,13] We are interested in this topic and attempt to prepare chiral discotic liquid crystals based on triphenylene cores. Here we report the synthesis of a series of triphenylene discogens with three alkoxy chains and three alkanoyloxy chains containing the optically active group, as well as their thermotropic liquid crystal properties. The synthesis of target triphenylene derivatives, see Scheme 1.



Scheme 1 Synthetic route of the triphenylene discogens

Experimental

Instruments and chemical reagents

^{1}H NMR spectra were recorded on a Brucker ACE-600 Spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. Mettler Toledo 822e DSC series differential scanning carlorimeter was used for thermal analysis, with heating and cooling rate 10℃/min. YM-130 polarized optical microscopy with hot-stage was used for the melting point and clearing point measurement, as well as liquid crystal phases and textures characterization.

The analytical grade chemicals and solvents were commercial products and used without further purification.

Synthesis of (*S*)-(+)-2-chloro-4methylpentanoic acid (2)[14]

L-Leucine (10g, 0.076 mol) was dissolved in 64 ml 5 N HCl by stirring and cooling to –5℃-0℃ at which temperature of Sodium nitrite (5.5 g , 0.08 mol) in 15 ml water was added in drops. The mixture was stirred for 1 h below 0 ℃, and 5 h at 10℃-15℃. Saturated aqueous potassium carbonate was added to the mixture until pH to 2. The resulting mixture was extracted with ethyl acetate (3×30 ml). The organic layers were combined, washed with brine and dried with $MgSO_4$. The dry agent was filtered off and the filtrate concentrated by rotary evaporation. The residue was distilled at 135℃-140℃ (10mmHg), afforded **2** (5.3 g, 46%) as yellowish oil.

Synthesis of 1-alkyloxy-2-methylbenzene (4)

To the mixture of guaiacol (112 g, 0.9 mol) and K_2CO_3 (250 g, 1.8 mol) in 500 ml of EtOH, 1-bromoalkane (0.9 mol) was added under protection of N_2 and refluxed for 24 h. After the reaction finished, water was added to the mixture and extracted with CH_2Cl_2. The organic layer was washed with aqueous K_2CO_3 and dried with $MgSO_4$. The solvent was distilled out and the residue distilled in vacuum to get products, yields 91%-96%.

Synthesis of 2,6,11-trialkoxy-3,7,10-trimethoxytriphenylene, 5a and

2,6,10-trialkoxy-3,7,11-trimethoxytriphenylene, 5b

To the ice-cooled mixture of 2-alkoxy-1-methoxybezene (0.5 mol) in 300 ml dry CH_2Cl_2 and two drops of concentrated H_2SO_4, $FeCl_3$ (151 g, 1.5 mol) was added for eight parts under N_2. The mixture was further stirred at room temperature for 1 h, and 300 ml cold methanol added. Water was added to the mixture, separated the organic layer, and the aqueous phase was extracted with 400ml CH_2Cl_2. The organic layers were combined, washed with water and dried with $MgSO_4$. The solvent was removed by rotary evaporation, the residue separated by column chromatography (SiO_2, CH_2Cl_2-light petroleum) to give two isomers of **5a** and **5b** in the yield of 44%.

Synthesis of 6a and 6b

To the mixture of PPh_3 (26.2g, 0.1 mol) in 100 ml dry THF under Argon, Lithium (1.4 g, 0.2 mol) was added with stirring. The reaction mixture was further stirred at room temperature for 2 h. Cooling the mixture to 0℃, *t*-BuCl (9.5 g, 0.1 mol) in 20 ml THF was added and refluxed for 1 h. Then 0.02 mol of **5a** was added to the mixture and refluxed for other 2 h. To the resulting mixture dilute hydrochloric acid was added with stirring until the aqueous phase was acidic. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3×50 ml). The organic layers were combined, washed with brine and dried with $MgSO_4$. The solvent was removed by rotary evaporation and residue was recrystallized from ethanol to give **6a** as a white solid in yield of 91%.

Compound **6b** was synthesized by the same procedure.

General synthetic procedure of 7-18

To a stirred solution of **2** (75 mg, 0.5 mmol), **6a** or **6b** (0.18 mmol) in dry dichloromethane (15 ml) at room temperature were added DCC (112 mg, 0.54 mmol) and DMAP as a catalyst. The resulting solution was stirred for 24 h, filtered and concentrated by rotary evaporation to give a crude mixture. Column chromatography (SiO_2, dichloromethane-light petroleum) offered **7-18** as white solid in the yield of 51%-86%.

2,6,11-tripentoxy-3,7,10-tri[(*S*)-2-chloro-4-meyhylpentanoyloxy]triphenylene (**8**) ^{1}H NMR($CDCl_3$, 600 MHz) δ：8.06(s, 1H, Ar**H**), 7.88(s, 1H, Ar**H**), 7.86(s, 1H, Ar**H**), 7.77(s, 1H, Ar**H**), 7.76(s, 1H, Ar**H**), 7.68(s, 1H, Ar**H**), 4.64-4.73 (m, 3H, -OCOC**H**Cl-), 4.12-4.24(m, 6H, -OC$\mathbf{H}_2$-), 2.02-2.16(m, 9H, -CHClC$\mathbf{H}_2$C**H**Me_2), 1.82-1.92 (m, 6H, -OCH_2C$\mathbf{H}_2$-), 1.47-1.53(m, 6H, -OC_2H_4C$\mathbf{H}_2$-), 1.38-1.46(m, 6H, -OC_3H_6C$\mathbf{H}_2$-), 1.02-1.12 [m, 18H, -CH(C$\mathbf{H}_3$)$_2$], 0.94-1.00(m, 9H, -OC_4H_8C$\mathbf{H}_3$)

2,6,10-tripentoxy-3,7,11-tri[(*S*)-2-chloro-4-meyhylpentanoyloxy]triphenylene (**14**) ^{1}H NMR($CDCl_3$, 600 MHz) δ：7.86(s, 3H, Ar**H**), 7.41(s, 3H, Ar**H**), 4.80 (s, 3H, -OCOC**H**Cl-), 4.07-4.22(m, 3H, -OC$\mathbf{H}_2$-), 3.93-4.06(m, 3H, -OC$\mathbf{H}_2$-), 2.17-2.28[m, 3H, -C**H**(CH_3)$_2$], 2.04-2.16(m, 6H, -CHClC$\mathbf{H}_2$-), 1.73-1.91(m, 6H, -OCH_2C$\mathbf{H}_2$-), 1.38-1.55(m, 12H, -$OC_2H_4C_2$$\mathbf{H}_4$-), 1.03-1.15[dd, *J* = 6.3 Hz, 18H, -CH(C$\mathbf{H}_3$)$_2$], 0.96-1.02(t, *J* = 6.9 Hz, 9H, -OC_4H_8C$\mathbf{H}_3$)

The spectra data of other analogous compounds are similar to compounds **8** and **14**.

Results and discussion

The structural characterization of prepared compounds was carried out on ^{1}H NMR. From the ^{1}H NMR spectra, the symmetrical compounds showed two single peaks with chemical shifts (δ) at 7.4 and 7.8, and triphenylene core with two kinds of H. While the asymmetrical compounds displayed six single peaks with δ from 7.6 to 8.1. The H of alkoxy chain linkage (-OCH_2-) is influenced by electric-effect of strong negative Cl atom of neighboring ester chain, resulting in a multiple peak with δ about 4 for symmetrical compounds and two multiple peaks for asymmetrical compounds. In addition, the H on chiral carbon appears a single peak with δ from 4.6 - 4.7 for symmetrical compounds and a multiple peak with δ about 4.8 for symmetrical compounds.

All the target compounds possess discotic liquid crystal phases. The phase transition temperature and thermal analytical data of compounds **7-18** are summarized in table 1. It can be seen from table 1 that all the compounds are room temperature discogens (blow 30℃). The low melting points of these compounds would be caused by the stereo-effect of α - chlorine in the ester chain.[15] The transition enthalpies of Col→Iso are comparatively bigger than hexaalkoxytriphenylene, indicating highly ordered columnar mesophases.

Table 1. Phase transition temperature and enthalpies for the synthesized discogen TP(OR)3($OCOCHClCH_2CHMe_2$)$_3$ [a]

Compd.	**R**	**T / °C (ΔH, kJ mol^{-1})**	
		Heating [b]	**cooling**
7	C_4H_9 (asym)	Col 259(21.6) I [c]	I 252(-11.8) Col [d]
8	C_5H_{11} (asym)	Col 244(39.4) I	I 245(-26.9) Col
9	C_6H_{13} (asym)	Col 220(26.6) I	I 223(-25.3) Col
10	C_7H_{15} (asym)	Col 216(28.2) I	I 217(-27.4) Col
11	C_8H_{17} (asym)	Col 203(22.0) I	I 203(-22.3) Col
12	$C_{11}H_{23}$ (asym)	Col 159(12.3) I	I 165(-11.8) Col
13	C_4H_9 (sym)	Col 229(21.6) I	I 252(-11.8) Col
14	C_5H_{11} (sym)	Col_1 99(1.0) Col_2 151(4.8) Col_3 205(11.2) I	I 234(-5.7) Col_3 154(-0.6) Col_2
15	C_6H_{13} (sym)	Col 197(12.0) I	I 207(-12.7) Col
16	C_7H_{15} (sym)	Col_1 187(5.9) Col_2 112(10.2) Col_3 203(12.5) I	I 205(-12.7) Col
17	C_8H_{17} (sym)	Col_1 107(12.2) Col_2 175(9.8) I	I 197(-9.4) Col_2 84(-5.7) Col_1
18	$C_{11}H_{23}$ (sym)	Col_1 82(3.2) Col_2 108(1.1) Col_3 132(5.9) I	I 133(-5.7) Col_3 108(-1.2) Col_2 75(-1.9) Col_1

*Col = Discotic columnar mesophase, Col_1, Col_2, Col_3, three columnar phases to be identified, I, isotropic liquid.
[a] Transition temperature (℃) and enthalpies (kJ · mol^{-1}) were determined by DSC (at a rate of 10 ℃/min). [b] First heating starts from 30℃. [c] Transition observed only under microscope. [d] This phase supercools until 40℃.

Comparing the symmmetrical and asymmetrical isomers of the compounds, it is apparent that the "sym" isomers exhibited more complicated mesophase behavior. The "asym" isomer compounds **7-12** exhibit only one mesophase transition during both the first heating and cooling cycle. For the "sym" isomers there is an "odd-even effect" in the mesophase transition. The "even" (the number of carbon atoms and oxygen in the alkyloxy chain is even) symmetric isomers **14** (R = C_5H_{11}) **16** (R = C_7H_{15}) and **18** (R = $C_{11}H_{23}$) exhibit three mesophases in the first heating run, and during cooling run, two mesophases for **14**, one for **16**, and three for **18** were observed. In “odd” symmetric isomers, only one mesophase when alkyl chain R is short (**13**, R = C_4H_9 and **15**, R = C_6H_{13}) but two mesophases when alkyl chain R long enough (**17**, R = C_8H_{17}) were observed (see Figure 1).

Under the polaring optical microscopy (POM), all compounds display the fan-shape texture typical for columnar mosophases (see Figure 2). Compounds **14, 16, 17** and **18** exhibited more than one kinds of columnar mesophases. These mesophases should be further characterized in detail with X-ray diffraction. So far no evidence showed the chiral center in molecules influence mesogenic behavior of the compounds.

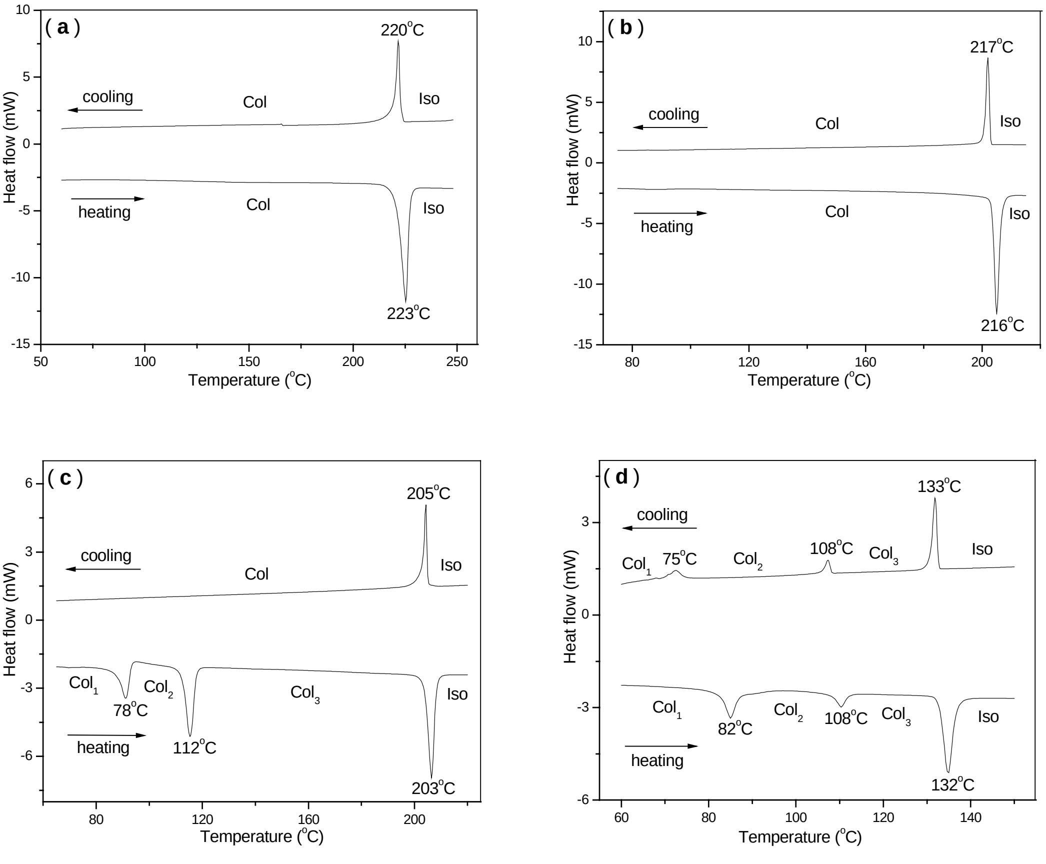


Figure 1 DSC traces of first heating and cooling run. (a) **9** (R = C_6H_{13}, *asym.*), (b) **10** (R = C_7H_{15}, *asym.*), (c) **17** (R = C_8H_{17}, *sym.*) and (d) **18** (R = $C_{11}H_{23}$, *sym.*).

Another difference between the “sym” and “asym” isomers is that the “sym” isomers had lower clearing points, which imply the molecular symmetry has influence on the phase transition temperature (Col→I). Figure 3 shows the clearing point difference of the “sym” and “asym” isomers. It is interesting to note that when R =

C_7H_{15}, the difference in clearing point between the “sym” and “asym” isomers is smallest. The feature of asymmetrical isomers possessing higher clearing points indicates that stronger intermolecular interaction exists in the column of asymmetrical isomers that that of symmetrical isomers.

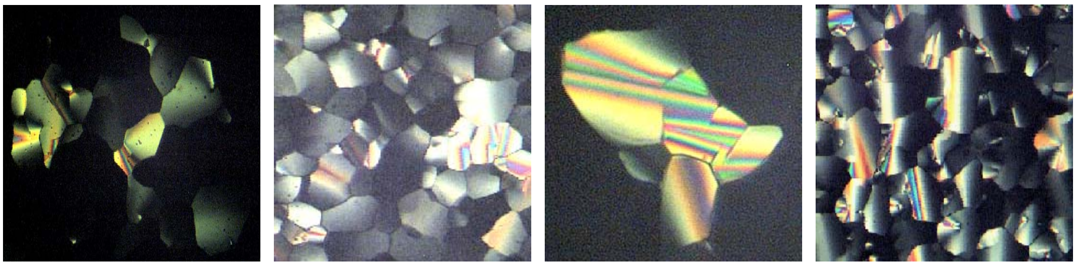

(a) (b) (c) (d)

Figure 2 Optical texture of (a) **11**(R = C_8H_{17}-asym) at 160℃, (b) **12**(R = $C_{11}H_{23}$-asym) at 125℃, (c) **15**(R = C_6H_{13}-sym) at 177℃ and (d) **18**(R = $C_{11}H_{23}$-sym) at 130℃ on cooling cycle.

One possible explanation would be that in the ‘asym’ isomer compounds, the molecules are arranged in such a way that the ester chain containing α – chlorine neighboring ones are staggered with respect to each other, leading to a better packing and therefore a stronger interaction.[16,17]

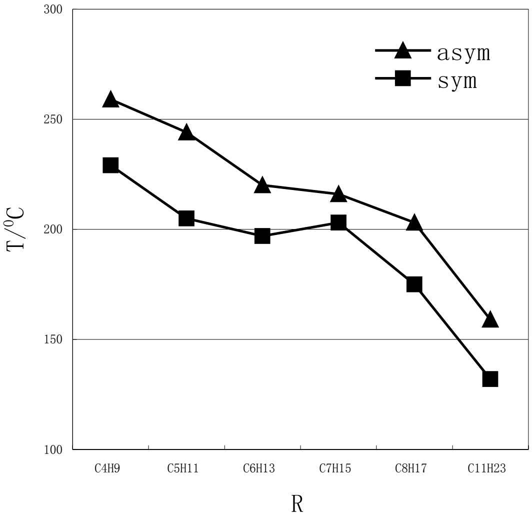


Figure 3 Clearing points (Col→Iso) of the symmetrical and asymmetrical discogens.

Figure 3 also illustrated the decrease in clearing point as alkyl chain R increase from C_4H_9 to $C_{11}H_{23}$. This decrease in phase transition temperature is similar to other triphenylene-containing liquid crystals.[8,18] It is because the short side chain leads to a highly ordered molecular packing in the column, resulting in higher clearing point. Therefore the clearing points with long side chains are lower than those of short side chains.

Conclusion

Symmetrical and asymmetrical triphenylene discotic liquid crystals with two different side chains and one with a chiral center have been prepared. The symmetrical compounds showed lower clearing points. The clearing points of all compounds decrease as the alkyl chain R increasing. The influence of chirality in molecules on mesogenic behavior was not observed. The symmetrical compounds displayed complicated mesomorphic behavior and possessed more than one columnar mesophases, which should be further investigated with XRD in detail.

Reference

1 Bushby, R. J.; Lozman, O. R. Discotic liquid crystals 25 years on. *Curr. Opin. Coll. Interf. Sci.* **2002**, *7*, 343-354.

2 Boden, N.; Bushby, R. J.; Cammidge, A. N. Triphenylene-based discotic liquid crystalline Polymers: a universal rational synthesis. *J. Am. Chem. Soc.* **1995**, *117*, 924-927.

3 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.

4 Destrade, C.; Tinh, N. H.; Gasparoux, H. Disc-like Mesogens: A Classification. *Mol. Cryst. Liq. Cryst.* **1981**, *71*, 111-135.

5 Handbook of liquid crystal research. Collings, P. J. Datel, J. Oxford Uni. Press. (USA), **1997**, 40.

6 Kumar, S. Recent developments in the chemistry of triphenylene-based discotic liquid crystals. *Liq. Cryst.* **2004**, *31*(8), 1037-1059.

7 Hirst, D.; Diete, S. Laschat, S.; Nimtz, M. Combination of chiral and achiral triphenylene units in a novel unsymmetrical columnar twin. *Helv. Chim. Acta* **2001**, *84*, 1190-1196.

8 Schultz, A.; Laschat, S.; Morr, M.; Diele, S.; Dreyer, M.; Bringmann, G. Highly branched alkanoic acids from the preen-gland wax of the domestic goose as building blacks for chiral triphenylenes. *Helv. Chim. Acta* **2002**, *85*, 3909-3918.

9 Boden, N.; Bushby, R. J.; Cammidge, A. N.; Duckworth, S.; Headdock, G. α-halogenation of triphenylene-based discotic liquid crystals: towards a chiral nucleus. *J. Mater. Chem.* **1997**, *7*(94), 601-605.

10 Malthete, J.; Jacques; Tinh, N. H.; Destrade, C. Macroscopic evidence of molecular chirality in columnar mesophases. *Nature* **1982**, *298*(1), 46-48

11 Heppke, G.; Kruerke, D.; Lohning, C.; Lotzsch, D.; Moro, D.; Muller, M.; Sawade, H. *Liq. Cryst.* **2000**, *27*, 643.

12 Allen, M. T.; Diele, S.; Harris, K. D. M.; Hegmann, T.; Kariuki, M.; Lose, D.; Preece, J. A.; Tscherske, C. Intermolecular organization of triphenylene-based discotic mesogens by interdigitation of alkyl chains. *J. Mater. Chem.* **2001**, *11*, 302-311.

13 Gestel, J. V.; Palmans, A. R. A.; Titulaer, B.; Vekemans, J. A. J. M.; Meijer, E. W. “Majority-rules” operative in chiral columnar stacks of C_3-symmetrical molecules. *J. Am. Chem. Soc.* **2005**, *127*, 5490-5494.

14 Xi, G. G.; Xiao, F. H.; Zhao, M.; Sun, J. Synthesis and study of the chiral ferroelectric liquid crystals with large spontaneous polarization. *Chin. J. Liq. Cryst. Disp.* **1997**, *12*(2), 79-83. (in Chinese)

15 Zhang, Z. Y.; Mo, X. M.; Lu, W. F.; Shi, Y. Z. Synthesis and property of liquid crystal compounds: α – methyl biphenyl esters. *Chin. J. Appl. Chem.* **2003**, *21*(1), 57-64. (in Chinese)

16 Paul, P. H. J.; Jager, W. F.; Mijs, W. J.; Picken, S. J. Specific interactions in discotic liquid crystals. *J. Mater. Chem.* **2003**, *13*, 458-469.

17 Motoyanagi, J.; Fuhushima, T.; Aida, T. Discotic liquid crystals stabilized by interionic interactions: imidazolium ion-anchored paraffinic triphenylene. *Chem. Commun.* **2005**, 101-103.

18 Manickam, M.; Kumar, S. New mixed tail triphenylene discotic liquid crystals. *Mol. Cryst. Liq. Cryst.* **1998**, *326*, 165-176.