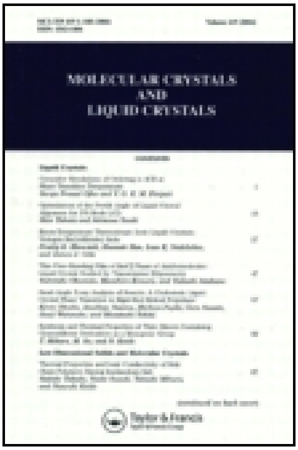


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Tuning Hydrogen-Bonding with Amide Groups for Stable Columnar Mesophases of Triphenylene Discogens

B. Q. Wang [a] , K. Q. Zhao [a] , P. Hu [a] , W. H. Yu [a] , C. Y. Gao [a] & Y. Shimizu [b]

[a] College of Chemistry and Material Science, Sichuan Normal University, Chengdu, China

[b] Mesophase Technology Research Group, Special Division for Human Life Technology, National Institute of Advanced Industrial Science and Technology, AIST-Kansai, Midorigaoka, Ikeda, Osaka, Japan

Version of record first published: 22 Sep 2010

To cite this article: B. Q. Wang, K. Q. Zhao, P. Hu, W. H. Yu, C. Y. Gao & Y. Shimizu (2007): Tuning Hydrogen-Bonding with Amide Groups for Stable Columnar Mesophases of Triphenylene Discogens, Molecular Crystals and Liquid Crystals, 479:1, 135/[1173]-150/[1188]

To link to this article: http://dx.doi.org/10.1080/15421400701680937

Mol. Cryst. Liq. Cryst., Vol. 479, pp. 135/[1173]–150/[1188], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701680937

Tuning Hydrogen-Bonding with Amide Groups for Stable Columnar Mesophases of Triphenylene Discogens

B. Q. Wang
K. Q. Zhao
P. Hu
W. H. Yu
C. Y. Gao
College of Chemistry and Material Science, Sichuan Normal University, Chengdu, China

Y. Shimizu
Mesophase Technology Research Group, Special Division for Human Life Technology, National Institute of Advanced Industrial Science and Technology, AIST-Kansai, Midorigaoka, Ikeda, Osaka, Japan

Tuning hydrogen-bonding of discotic liquid crystal can result in more ordered columnar mesophases and higher charge carrier mobility materials. In this paper, triphenylene derivatives with one, two and three amide groups with structure of $C_{18}H_6(OR)_5(OCH_2CONHBu)$, $C_{18}H_6(OC_5H_{11})_4(OCH_2CONHBu)_2$ *and symmetrical and asymmetrical* $C_{18}H_6(OR)_3(OCH_2CONHBu)_3$ $(R = C_nH_{2n+1}, n = 4\text{–}9)$ *respectively were designed and synthesized. The results showed that each intra-columnar H-bond forming amide (–CONH–) group caused an average increase of 22°C in clearing point from the non-H-bonding ester group (–COO–) triphenylene analogous. This was the first quantitative result of H-bonding on the stabilization of columnar mesophase.*

Keywords: anchorage of columnar phase; columnar mesophase; discotic liquid crystal; intermolecular hydrogen-bonding; supramolecular liquid crystal; Triphenylene

National Natural Science Foundation of China (project Nos. 50473062 and 50673069) supported this work.

Address correspondence to Ke-Qing Zhao, College of Chemistry and Material Science, Sichuan Normal University, 5 Jing-An Road, Chengdu 610066, China. E-mail: kqzhao@sicnu.edu.cn

INTRODUCTION

Discotic liquid crystals (DLCs) consist of an aromatic core and several peripheral flexible alky chains. The π–π interactions of aromatic cores and the van de Waals interactions of alkyl chains enable DLC to self-assemble into highly ordered columns, and charges and energies can transfer along the column due to the aromatic π orbital overlapping. These properties have made DLCs useful candidates as molecular-scale wires in nano-technology.

Present research on discotic liquid crystals showed that charge carrier mobility was related to the size of aromatic core and the order of discotic columnar phase [1–3]. So the molecular designing strategies of new DLCs are concentrated on two aspects [4–7]: one is synthesizing bigger aromatic system, such as hexabenzocoronene derivatives, and the other is modifying peripheral chains by introducing extra intermolecular interaction. The later strategy was widely used in preparation of triphenylene-based discogens. Substitution of one chain with bulky group [8] suppressed intra-columnar molecular dynamic properties and got more ordered Col phase. Using β-oxygen effect [9,10], fluorophobic effect [11,12], hydrophilic-hydrophobic effect [13,14], donor-acceptor interaction [14–16], ionic interaction [17,18] successfully anchored and stabilized columnar mesophases. Hydrogen-bonding [19–24] has been extensively studied in DLC materials and the results showed that H-bonding had improved the order of Col mesophases and higher charge carrier mobility materials were prepared. In this paper, we used one, two and three amide ($-$CONHR) containing chains in place of alkyl chains of 2,3,6,7,10,11-hexaalkoxytriphenylene and hopefully tuned the H-bonding (intra-columnar intermolecular force) and therefore got more stable and higher ordered columnar phase materials.

RESULTS AND DISCUSSION

Molecular Designing and Synthesis

Ivanov [22] reported series of six-fold H-bonding hexaazatriphenylene derivatives which showed the smallest inter-disk distance of 3.18 Å, while most of other measured intra-columnar disk-disk distance value was 3.5 Å. One of the derivatives displayed higher charge mobility of 0.08 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Paraschiv [21] synthesized a discotic liquid crystal with three triphenylene moieties attached on 3-fold H-bonding amide-containing benzene ring through spacer and it exhibited the highest charge mobility of 0.12 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in all triphenylene derivatives.

Shinkai [23] and our results showed that six-fold H-bonding triphenylene $C_{18}H_6(OCH_2CONHR)_6$, $R = C_4H_9$ and $C_{12}H_{25}$ did not possess thermotropic liquid crystal properties. It was obvious that six-fold H-bonding was too strong for triphenylene derivatives to show mesophases. Therefore in this paper's molecular designing, the number of amide groups around triphenylene core decreased. To tune the strength of inter-molecular interaction, mono-, di- and tri-amide containing triphenylene derivatives were designed and prepared. The molecular structures and the columnar hydrogen-bonding diagrams are drawn in Figure 1. Scheme 1 listed the synthetic route of these triphenylene derivatives.

The target molecules of amide-containing triphenylenes were synthesized from key intermediates of hydroxytriphenylene. $C_{18}H_6(OC_nH_{2n+1})_{6-x}(OH)_x$ ($x = 1, 2, 3$) reacted with butyl 2-chloroacetate getting ester, which further reacted with butyl amine on heating leading the amide-containing triphenylenes. 2-Hydroxy-3,6,7,10,11-pentaalkoxytriphenylene [25], 2,7-dihydroxy-3,6,10,11-tetrapentyloxytriphenylene [26], 2,6,10-trihydroxy-3,7,11-trialkoxytriphenylene and 2,6,11-trihydroxy-3,7,10-trialkoxy-triphenylene [27] were prepared according to reported methods.

Mesomorphism

The thermal stability of synthesized compounds was tested with TGA analysis, and the results showed that all these compounds have good thermal stability up to 300°C, which are well above the clearing points of the mesophases.

All prepared triphenylene compounds with ester and amide functional groups were investigated with differential scanning calorimeter (DSC) and polarizing optical microscopy (POM). Figure 2 was the typical microphotograph of these compounds. Judged from DSC analysis results, textures of POM and molecular structural characteristics, the mesophases of these compounds were assigned as discotic columnar (Col) phase and plastic columnar phase (Col_p). These mesophases should be further investigated with X-ray diffraction analysis.

Tables 1–5 listed the phase transition temperatures and transition enthalpies of all these triphenylene compounds. Figures 3, 5, and 6 showed the DSC traces of mono-amide, di-amide, tri-amide triphenylenes. Figures 4 and 7 displayed the phase diagrams of mono-amide series and tri-amide series triphenylene discogens. Figure 8 showed the influence of molecular symmetry of tri-amide triphenylenes on the order of Col phase.

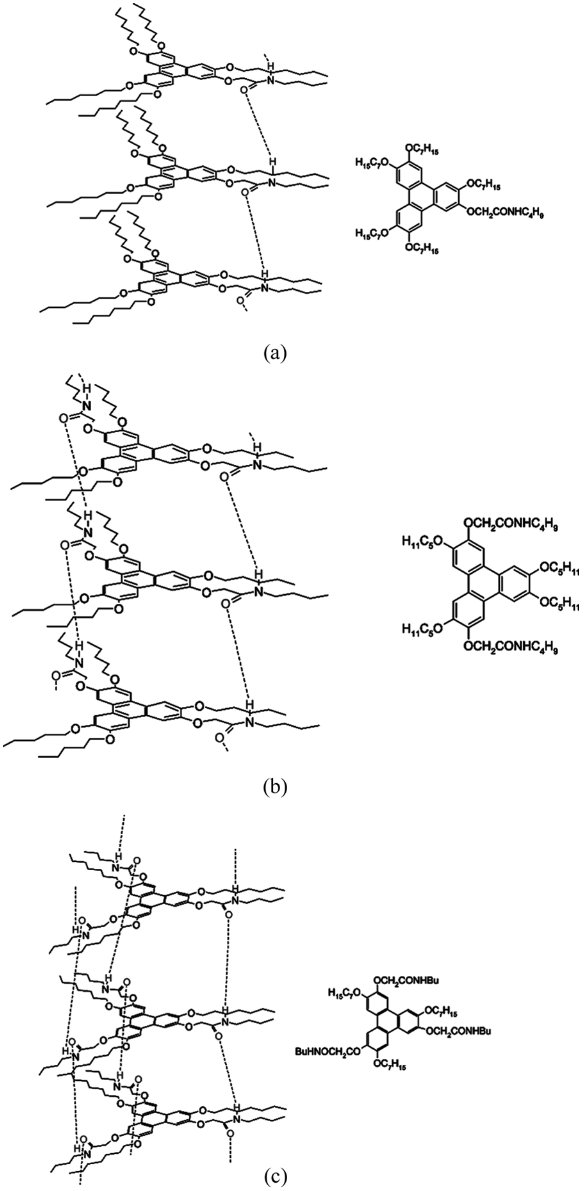
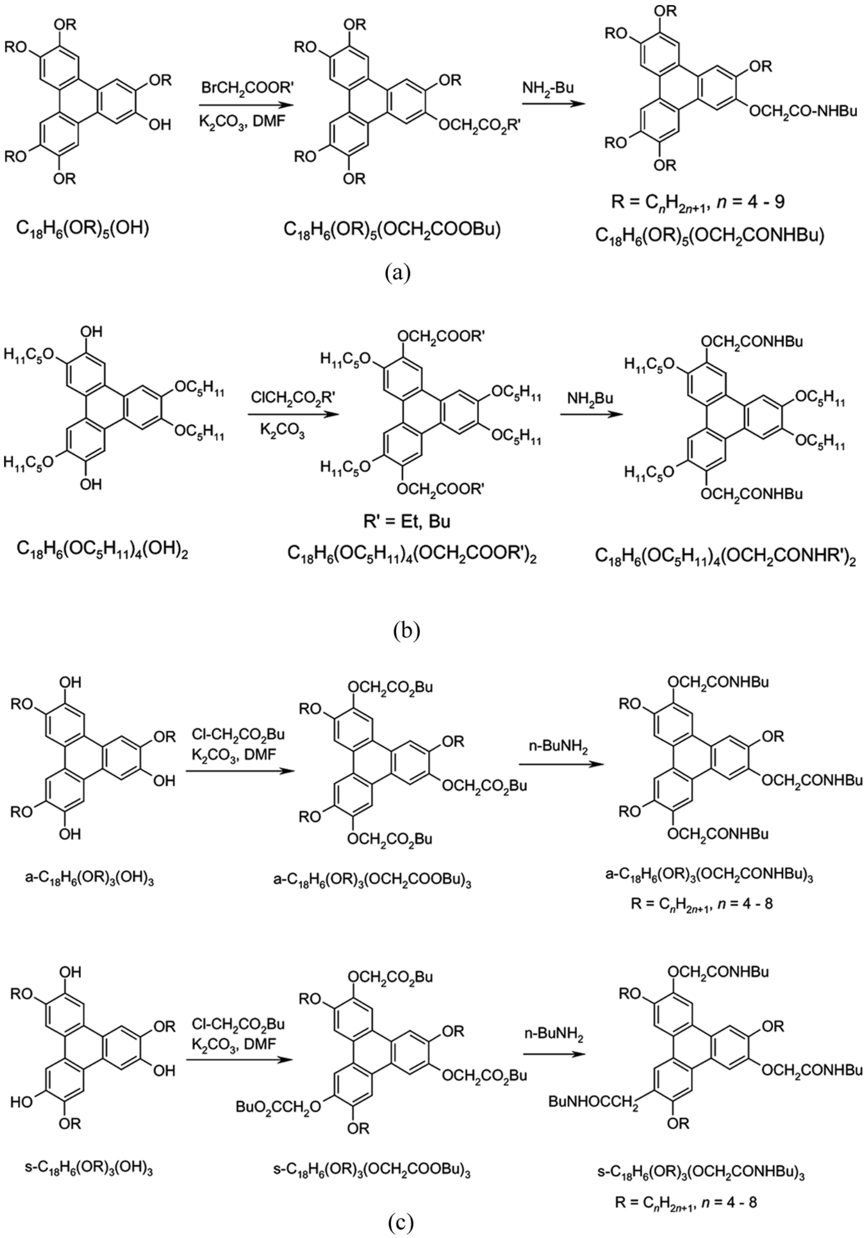


FIGURE 1 Sketches of triphenylene discotic columnar H-bonding and the molecular structures. (a) mono-amide H-bonding stabilized column and the triphenylene molecular structure. (b) di-amide H-bonding stabilized column and the triphenylene molecular structure. (c) symmetrical tri-amide H-bonding stabilized column and the triphenylene molecular structure.



SCHEME 1 (a) Synthesis of mono-amide triphenylenes and their mono-ester analogues. (b) Synthesis of di-amide triphenylene and its di-ester analogues. (c) Synthesis of symmetrical and asymmetrical tri-ester and tri-amide triphenylenes.

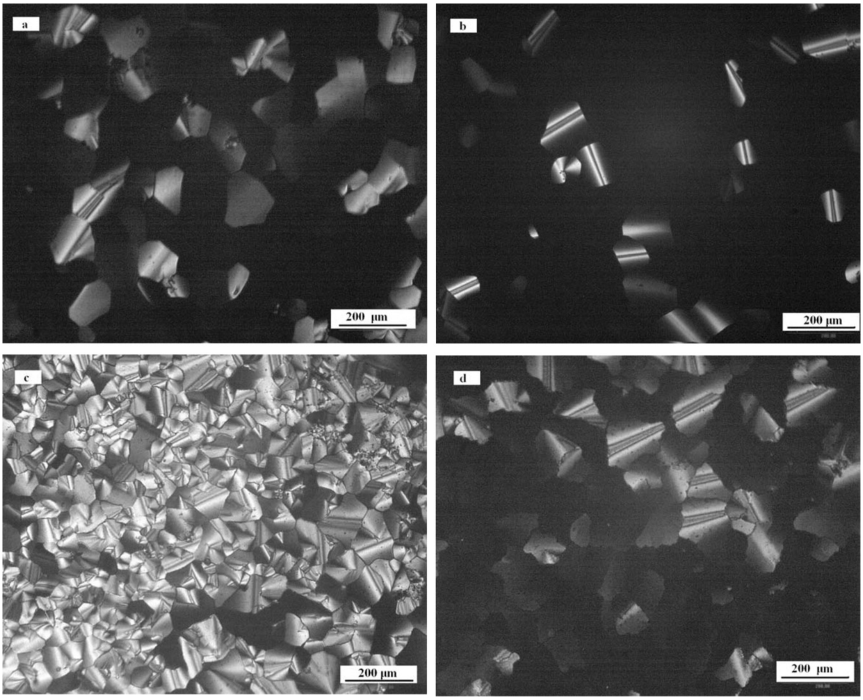


FIGURE 2 Optical textures of amide-containing triphenylenes, indicative of Col phase observed upon cooling from the isotropic state. a: $C_{18}H_6(OC_4H_9)_5(OCH_2CONHBu)$, 100°C. b: $C_{18}H_6(OC_9H_{19})_5(OCH_2CONHBu)$, 100°C. c: s-$C_{18}H_6(OC_4H_9)_3(OCH_2CONHBu)_3$, 160°C. d: a-$C_{18}H_6(OC_4H_9)_3(OCH_2CONHBu)_3$, 148°C.

TABLE 1 Phase Transition Temperatures and Transition Enthalpies of Mono-Ester Triphenylenes $C_{18}H_6(OC_nH_{2n+1})_5(OCH_2COOBu)^a$

n	Heating T/°C (ΔH, kJ/mol, in parenthesis)	Cooling T/°C (ΔH, kJ/mol, in parenthesis)
4	K 70(55.27) Col 132(16.15) Iso	Iso 132(15.88) Col
5	K 52(34.98) Col 132(10.75) Iso	Iso 131(10.68) Col
6	K 24(29.09) Col 119(9.35) Iso	Iso 118(9.33) Col
7	K 28(37.27) Col 114(9.61) Iso	Iso 114(9.37) Col −9(28.16) K
8	K 41(54.42) Col 102(5.68) Iso	Iso 104(6.54) Col 6(44.29) K
9	K 28(46.37) Col 100(7.21) Iso	Iso 101(8.13) Col −1(38.46) K

[a] DSC data measured with heating and cooling rate of 10°C/min under N_2 atmosphere. K, crystal. Col, columnar phase. Iso, isotropic liquid.

TABLE 2 Phase Transition Temperatures and Transition Enthalpies of Mono-Amide Triphenylenes $C_{18}H_6(OC_nH_{2n+1})_5(OCH_2CONHBu)^a$

n	Heating T/°C (ΔH, kJ/mol, in parenthesis)	Cooling T/°C (ΔH, kJ/mol, in parenthesis)
4	K 93(32.40) Col 147(6.66) Iso	Iso 143(6.51) Col 68(29.96) K
5	K 70(31.06) Col 151(7.97) Iso	Iso 151(7.82) Col 45(28.54) K
6	K 69(34.23) Col 142(6.98) Iso	Iso 141(7.05) Col 57(39.46) K
7	K 61(43.63) Col 141(7.51) Iso	Iso 140(7.52) Col 43(39.26) K
8	K 52(47.84) Col 135(7.24) Iso	Iso 134(7.19) Col 38(46.53) K
9	K 47(46.63) Col 128(6.85) Iso	Iso 129(6.78) Col 28(47.05) K

[a] DSC data measured with heating and cooling rate of 10°C/min under N_2 atmosphere. K, crystal. Col, hexagonal columnar phase. Iso, isotropic liquid.

TABLE 3 Phase Transition Temperatures and Transition Enthalpies of Di-Ester and Di-Amide Triphenylenes 2,7-$C_{18}H_6(OC_5H_{11})_4(OR')_2{}^a$

R′	Heating T, °C (ΔH, kJ/mol, in parenthesis)	Cooling T, °C (ΔH, kJ/mol, in parenthesis)
CH_2CO_2Et	K 81.0(43.5) Col 152.4(10.2) Iso	Iso 152.3(9.80) Col
CH_2CO_2Bu	K 40.0(37.4) Col 133.7(10.6) Iso	Iso 133.4(10.4) Col − 38.0(4.2) K
$CH_2CONHBu$	K 167.7(85.7) Col 185.2(12.1) Iso	Iso 185.2(12.2) Col 137.4(82.1) K

[a] DSC data measured with heating and cooling rate of 10°C/min under N_2 atmosphere. K, crystal. Col, columnar phase. Iso, isotropic liquid.

TABLE 4 Transition Temperatures and Enthalpies of Tri-Ester Triphenylenes $C_{18}H_6(OC_nH_{2n+1})_3(OCH_2CO_2Bu)_3{}^a$

n-symmetry	Heating T/°C (ΔH, kJ/mol, in parenthesis)	Cooling T/°C (ΔH, kJ/mol, in parenthesis)
4-s	K 15.5(7.6) Col 138.7(29.9) Iso	Iso 134.6(27.4) Col 12.4(7.7) K
4-a	Col 128.7(11.6) Iso	Iso 128.7(12.0) Col
5-s	K 50(10.4) Col 142(19.5) Iso	Iso 142(19.6) Col
5-a	Col 139(15.6) Iso	Iso 140(15.2) Col
6-s	Col 138(16.9) Iso	Iso 138(16.9) Col
6-a	Col 137(14.6) Iso	Iso 136(14.2) Col
7-s	K −1(0.52) Col 135(16.9) Iso	Iso 135(16.9) Col
7-a	Col 136(14.1) Iso	Iso 136(13.6) Col
8-s	Col 129(14.8) Iso	Iso 129(14.7) Col
8-a	Col 131(13.6) Iso	Iso 131(13.3) Col

[a] DSC data measured with heating and cooling rate of 10°C/min under N_2 atmosphere. K, crystal. Col, columnar phase. Iso, isotropic liquid.

TABLE 5 Phase Transition Temperatures and Enthalpies of Tri-Amide Triphenylenes $C_{18}H_6(OC_nH_{2n+1})_3(OCH_2CONHBu)_3$[a]

	Heating	Cooling
n-symmetry	T/°C (ΔH, kJ/mol, in parenthesis)	T/°C (ΔH, kJ/mol, in parenthesis)
4-s	K 173 (32.5) Iso	Iso 169 (9.2) Col 150 (17.8) K[b]
4-a	K 162 (49.7) Iso	Iso 149 (3.0) Col 144 (36.4) K[b]
5-s	Col$_p$ 162(19.3) Col 195(11.9) Iso	Iso 197 (13.4) Col 144(13.0) Col$_p$
5-a	Col$_p$ 144(35.7) Col 179(7.7) Iso	Iso 181(7.5) Col 139(32.8) Col$_p$
6-s	Col$_p$ 139(11.7) Col 199(12.8) Iso	Iso 200(13.1) Col 128(6.9) Col$_p$
6-a	Col$_p$ 146(39.7) Col 188(7.8) Iso	Iso 189(7.5) Col 138(36.0) Col$_p$
7-s	Col$_p$ 117(20.4) Col 206(14.2) Iso	Iso 206(14.1) Col 111(19.0) Col$_p$
7-a	Col$_p$ 138(35.1) Col 187(8.9) Iso	Iso 191(9.3) Col 136(33.5) Col$_p$
8-s	Col$_p$ 122(23.6) Col 204(13.9) Iso	Iso 204(13.5) Col 114(20.0) K
8-a	Col$_p$ 143(37.7) Col 192(10.2) Iso	Iso 192(10.0) Col 138(35.3) Col$_p$

[a] DSC data measured with heating and cooling rate of 10°C/min under N_2 atmosphere.
[b] monotropic Col phase Col$_p$, plastic columnar phase. Col, columnar phase. Iso, isotropic liquid.

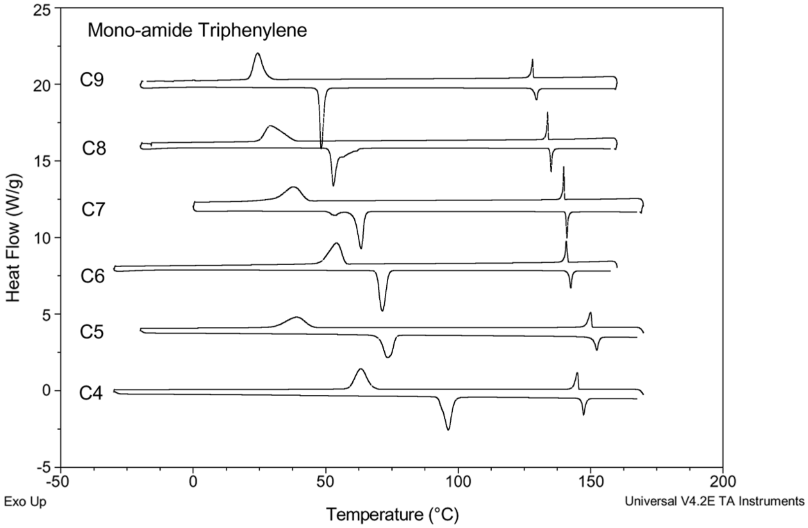


FIGURE 3 DSC traces of mono-amide triphenylenes $C_{18}H_6(OC_nH_{2n+1})_5(OCH_2CONHBu)$, $n = 4$–9 measured with heating and cooling rate of 10°C/min under N_2 atmosphere.

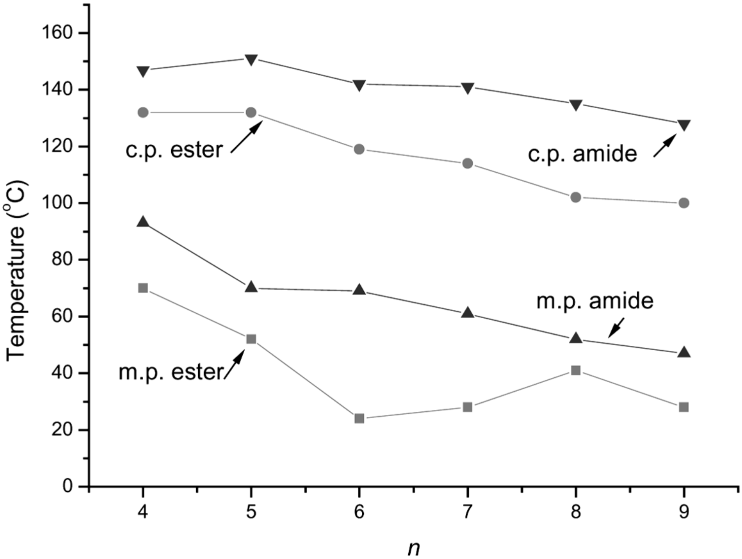


FIGURE 4 Phase diagram of mono-ester and mono-amide triphenylene discotic liquid crystals: $C_{18}H_6(OC_nH_{2n+1})_5(OCH_2COOBu)$ and $C_{18}H_6(OC_nH_{2n+1})_5(OCH_2CONHBu)$, $n = 4–9$.

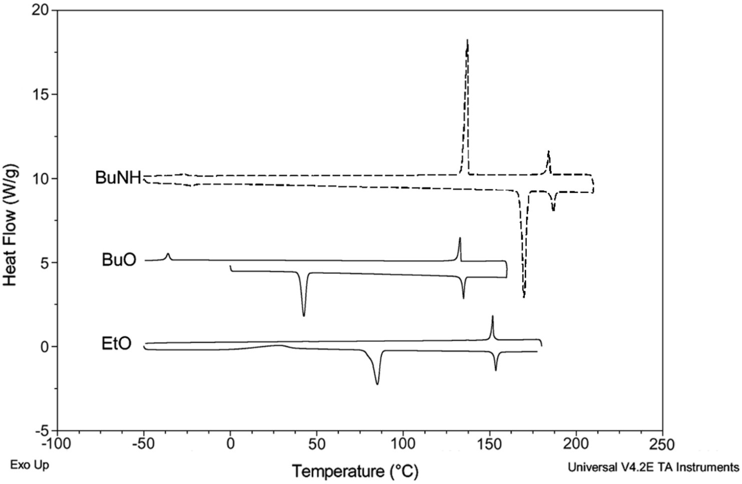


FIGURE 5 DSC traces of di-ester and di-amide triphenylenes: 2,7-$C_{18}H_6(OC_5H_{11})_4(OCH_2COOEt)_2$, 2,7-$C_{18}H_6(OC_5H_{11})_4(OCH_2COOBu)_2$, and 2,7-$C_{18}H_6(OC_5H_{11})_4(OCH_2CONHBu)_2$ measured with heating and cooling rate of 10°C/min under N_2 atmosphere.

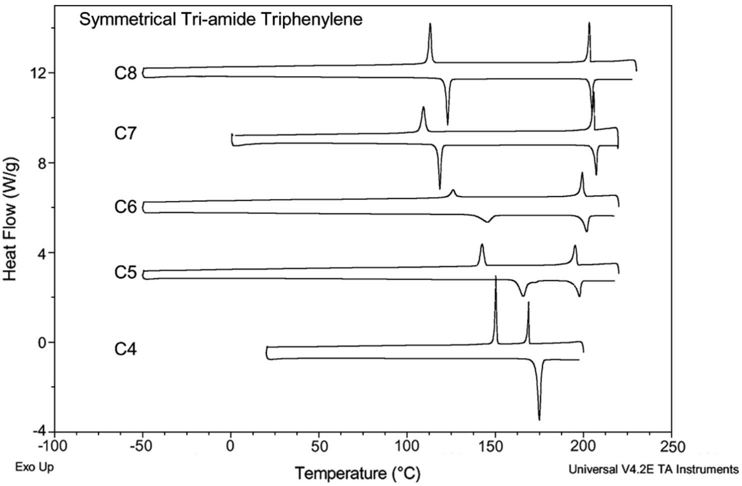


FIGURE 6 DSC traces of symmetrical tri-amide triphenylene discotic liquid crystals s-$C_{18}H_6(OC_nH_{2n+1})_3(OCH_2CONHBu)_3$, $n = 4$–9 measured with heating and cooling rate of 10°C/min under N_2 atmosphere.

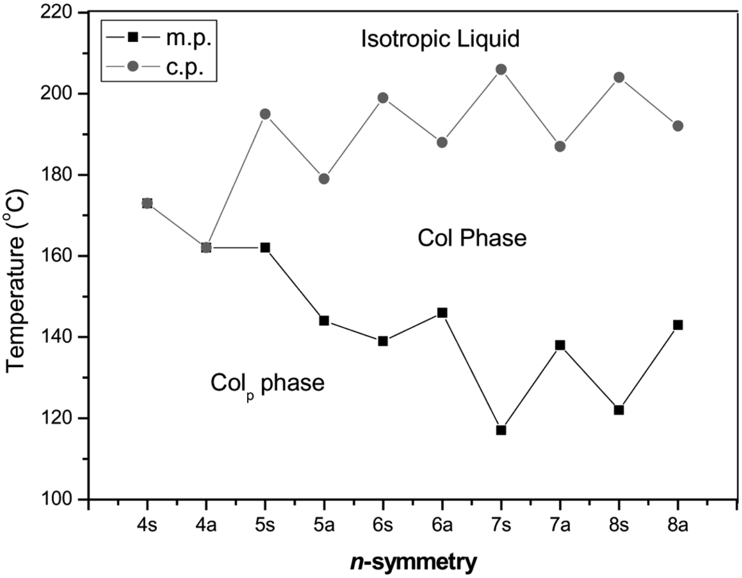


FIGURE 7 Phase diagram of tri-amide triphenylene discotic liquid crystals $C_{18}H_6(OC_nH_{2n+1})_3(OCH_2CONHBu)_3$, $n = 4-8$. s: symmetrical; a: asymmetrical.

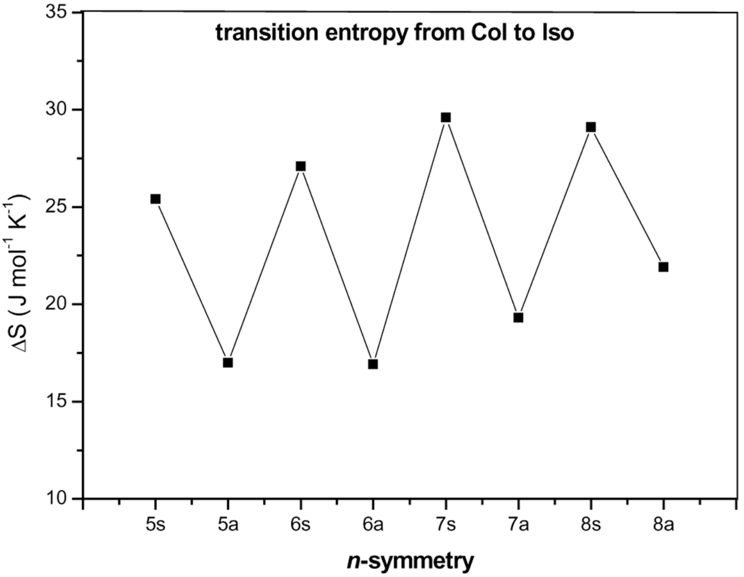


FIGURE 8 Phase transition entropies (from Col to Iso) for tri-amide triphenylenes as a function of *n* and molecular symmetry: $C_{18}H_6(OC_nH_{2n+1})_3(OCH_2CONHBu)_3$, s: symmetry; a: asymmetry.

Mono-amide and Ester Triphenylenes: $C_{18}H_6(OC_nH_{2n+1})_5(OCH_2CONHBu)$ and $C_{18}H_6(OC_nH_{2n+1})_5(OCH_2COOBu)$, $n = 4$–9

All these mono-functionalized triphenylenes showed Col mesophases. Mono-amide triphenylene derivatives possessed higher melting point (m. p.) and clearing point (c. p.) than their counterpart. Figure 3 listed the DSC traces of this series of mono-amide triphenylenes and Figure 4 drew the phase diagram of mono-ester and mono-amide triphenylenes. The mono-amide triphenylenes displayed average c. p. increase of 22°C from its ester analogues. The mono-ester triphenylenes had higher c. p. and broader phase range than its parent compounds 2,3,6,7,10,11-hexaalkoxytriphenylene $C_{18}H_6(OR)_6$ [28]. The stronger dipole–dipole interaction and less rigidity of ester chain caused the increase of clearing point.

2,3,6,7,10,11-hexaheptyloxytriphenylene, $C_{18}H_6(OC_7H_{15})_6$ possessed Col_{ho} phase between 69°C–93°C, while mono-ester triphenylene $C_{18}H_6(OC_7H_{15})_5(OCH_2COOBu)$ displayed Col phase from 28°C to 114°C, therefore, the mono-ester functional group resulted in c. p. increase of 21°C. The asymmterical hexaalkyloxytriphenylene

$C_{18}H_6(OC_6H_{13})_5(OC_7H_{15})$ [29] showed the following phase data: 60°C Col_h 97°C, its mono-ester analogue $C_{18}H_6(OC_6H_{13})_5(OCH_2COOBu)$ had phase transition data: 24°C Col 119°C. Again the mono-ester triphenylene had higher c. p. and broader mesophase range.

Di-Amide and Di-Ester Triphenylene Derivatives: 2,7-$C_{18}H_6(OC_5H_{11})_4(OCH_2COOEt)_2$,2,7-$C_{18}H_6(OC_5H_{11})_4(OCH_2COOBu)_2$, and 2,7-$C_{18}H_6(OC_5H_{11})_4(OCH_2CONHBu)_2$

In this series, one di-amide triphenylene compound, $C_{18}H_6(OC_5H_{11})_4(OCH_2CONHBu)_2$ and two di-ester triphenylenes $C_{18}H_6(OC_5H_{11})_4(OCH_2COOEt)_2$, $C_{18}H_6(OC_5H_{11})_4(OCH_2COOBu)_2$ were prepared and exhibited typical texture of columnar mesophases. Figure 5 drew the DSC traces of three 2,7-di-functional triphenylenes and Table 3 listed their transition temperatures and transition enthalpies. The DSC results showed that the 2,7-substituted di-amide compound had 51°C higher c. p. than its di-ester analogue. Compared with its parent compound hexapentyloxytriphenylene [28] possessing Col_{ho} phase between 69°C–122°C, the di-ester discogen $C_{18}H_6(OC_5H_{11})_4(OCH_2COOEt)_2$ was 31°C higher in c. p.

Symmetrical and Asymmetrical Substituted Tri-Amide and Tri-Ester Triphenylenes: $C_{18}H_6(OR)_3(OCH_2CONHBu)_3$ and $C_{18}H_6(OR)_3(OCH_2COOBu)_3$, R from C_4H_9 to C_8H_{17}

DSC results in Table 5 showed the ten tri-amide triphenylene derivatives, except for the two shortest chain members ($n = 4$) displaying monotropic Col phase, all derivatives showed Col_p phase in low temperature and Col mesophase in high temperatures. Figures 7 and 8 showed that symmetry derivatives possessed higher c. p. and higher ordered Col phase than the asymmetry ones from the clearing transition entropy changes, $\Delta S_{Col \rightarrow Iso}$.

Crystalline forms of tri-amide triphenylenes were collected from ethanol. In the first heating run of DSC measurement, $K \rightarrow Col_p$ transition, $Col_p \rightarrow Col$ transition, and $Col \rightarrow Iso$ transition were observed. In the first cooling run, solid-like Col_p phase did not crystallize even cooled to –50°C. Therefore, tri-amide triphenylenes had very wide ranges of Col_p phase and were suitable for charge carrier mobility measurement.

The molecular symmetry of three-fold H-bonding tri-amide had very important influence on mesomorphism: the symmetrical compounds had C_3 symmetry, and H-bond forming possibility is higher than the asymmetrical ones in the molecular rotation of triphenylenes.

Chain length n increased from 4 to 8, the c. p. gradually increased and then kept stable. The c. p. of symmetrical tri-amide series was higher than tri-ester analogues (average higher 66°C), but the asymmetrical series just had average 51°C c. p. rising than their tri-esters.

The tri-ester triphenylenes $C_{18}H_6(OR)_3(OCH_2COOBu)_3$ showed Col phase, most of them did not crystallize cooled to -50°C from DSC measurement. Unlike the amide series, molecular symmetry of ester series had little influence on their melting point, clearing point, and the order of columnar phase which was judged from the entropy change of clearing transition ($\Delta S_{Col \rightarrow Iso}$). Compared with hexaheptyloxytriphenylene [28], the tri-ester triphenylene $C_{18}H_6(OC_7H_{15})_3(OCH_2COOBu)_3$ had lower c. p. and higher m. p., and wider range of Col mesophase: the symmetrical ester with data of -1°C Col 135°C, asymmetrical ester with c. p. 136°C. Hexaheptyloxytriphenylene $C_{18}H_6(OC_7H_{15})_6$ displayed Col_h phase between 69°C to 93°C [28].

CONCLUSION

1. Series of mono-, di-, tri-amide triphenylene discotic liquid crystals and the their ester analogous were designed and synthesized for fine tuning the intermolecular force, stability of and order of discotic columnar mesophases.
2. The H-bonding mono-amide series ($n = 4$–9) displayed average clearing point increase of 23°C from their ester analogues.
3. The two fold H-bonding di-amide triphenylene showed c. p. raising of 51°C (only one compound with $n = 5$) comparing to its ester analog.
4. The symmetrical three fold H-bonding tri-amide triphenylenes had average c. p. increase of 66°C ($n = 5$–8) and the asymmetrical three fold H-bonding tri-amide displayed c. p. increase of 50°C ($n = 5$–8) from their ester derivatives respectively.
5. H-bonding contribution to stabilization of Col mesophases seems that it can be added: one H-bonding increase 22°C; two fold H-bonding, 51°C and three fold H-bonding, 66°C. So each H-bonding contributed about 22°C clearing point increase from the esters. This was the first quantitative data of H-bonding on stabilization of columnar mesophases.

EXPERIMENTAL

The identification of synthetic products was carried out by ^1H NMR, and by elemental analysis. ^1H NMR spectra were recorded on a Brucker Avance 600 spectrometer using Me_4Si as an internal standard.

The elemental analysis was performed with a Carlo Erba 1106 CH analyzer. The phase transition temperatures and enthalpies were measured with differential scanning calorimetry (DSC) (TA Instrument, DSC Q100) and the textures of the mesophasess were observed with a polarizing optical microscopy (POM) (XP-201) with a hot stage and a controller (XPR-201). 2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylenes [25], 2,7-dihydroxy-3,6,10,11-tetrapentyloxy-triphenylene [26] and 2,6,10-trihydroxy-3,7,11-trialkoxytriphenylenes and 2,6,11-trihydroxy-3,7,10-trialkoxytriphenylenes [27] were synthesized according to reported methods.

Synthesis of Ester-Containing Triphenylenes

To the mixture of $ClCH_2COOC_4H_9$ and K_2CO_3 in dry DMF, hydroxytriphenylene was added and heating at 100°C with stirring for 48 h. After reaction finished, the mixture was poured into ice water and extracted with CH_2Cl_2. The organic phase was dried with $MgSO_4$, and evaporated with rotation evaporator. The residue was purified with column chromatography (SiO_2, CH_2Cl_2 and light petroleum). The crystallization from EtOH resulted in the products in yield of 85%–90%.

Synthesis of Amide-Containing Triphenylenes

The mixture of ester-containing triphenylene and 1-aminobutane was heating at 120°C with stirring for 24 h. After the reaction finished which was monitored with TLC, the product was purified with column chromatography (SiO_2, CH_2Cl_2 and light petroleum). The crystallization from EtOH resulted in the products in yield of 90%–95%. The ^{1}H NMR data of di-ester and di-amide triphenylenes was listed below.

2,7-$C_{18}H_6(OC_5H_{11})_4(OCH_2COOEt)_2$

^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.86(s, 2H), 7.83(s, 2H), 7.82(s, 2H), 4.85(s, 4H), 4.29–4.35(m, 4H), 4.21–4.28(m, 8H), 1.91–2.00(m, 8H), 1.52–1.60(m, 8H), 1.42–1.50(m, 8H), 1.33(t, $J = 7.08$ Hz, 6H), 0.98(t, $J = 7.38$ Hz, 12H).

2,7-$C_{18}H_6(OC_5H_{11})_4(OCH_2COOBu)_2$

^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.92(s, 2H), 7.84(s, 2H), 7.76(s, 2H), 4.87(s, 4H), 4.19–4.28(m, 12H), 1.91–2.00(m, 8H), 1.62–1.69(m, 4H), 1.53–1.60(m, 8H), 1.42–1.50(m, 8H), 1.32–1.40(m, 4H), 0.95–1.01(m, 12H), 0.88(t, J = 7.38 Hz, 6H).

2,7-$C_{18}H_6(OC_5H_{11})_4(OCH_2CONHBu)_2$

^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.84(s, 2H), 7.83(s, 2H), 7.82(s, 2H), 7.11(s, 2H), 4.73(s, 4H), 4.21–4.28(m, 8H), 3.38–3.44(m, 4H), 1.92–2.00(m, 8H), 1.52–1.63(m, 12H), 1.44–1.52(m, 8H), 1.37–1.44(m, 4H), 0.92–1.02(m, 18H).

REFERENCES

[1] van de Craats, A. M. & Warman, J. M. (2001). *Adv. Mater.*, *13*, 130.

[2] van de Craats, A. M., Warman, J. M., de Haase, M. P., Adam, D., Simmerer, J., Haarer, D., & Schuhmacher, P. (1996). *Adv. Mater.*, *8*, 823.

[3] Warman, J. M., de Haase, M. P., Dicker, G., Grozema, F. C., Piris, J., & Debije, M. G. (2004). *Chem. Mater.*, *16*, 4600.

[4] Bushby, R. J. & Lozman, O. R. (2002). *Curr. Opin. Solid State Mater. Sci.*, *6*, 569.

[5] Kumar, S. (2004). *Liq. Cryst.*, *31*, 1037.

[6] Kumar, S. (2005). *Liq. Cryst.*, *32*, 1089.

[7] Eichhorn, H. (2000). *J. Porphyrins Phthalocycnines*, *4*, 88.

[8] Kettner, A. & Wendorff, J. H. (1999). *Liq. Cryst.*, *26*, 483.

[9] Tabushi, I., Yamamura, K., & Okada, Y. (1987). *J. Org. Chem.*, *52*, 2502.

[10] Collard, D. M. & Lillya, C. P. (1991). *J. Org. Chem.*, *56*, 6064.

[11] Terasawa, N., Monobe, H., Kiyohara, K., & Shimizu, Y. (2003). *Chem. Commun.*, 1678.

[12] Terasawa, N., Monobe, H., Kiyohara, K., & Shimizu, Y. (2003). *Chem. Lett.*, *32*, 214.

[13] Barbera, J., Garces, A. C., Jayaraman, M., Omenat, A., Serrano, J. L., & Stoddart, J. F. (2001). *Adv. Mater.*, *13*, 175.

[14] Boden, N., Bushby, R. J., Lu, Z., & Lozman, O. R. (2001). *Liq. Cryst.*, *28*, 657.

[15] Boden, N., Bushby, R. J., Cooke, G., Lozman, O. R., & Lu, Z. (2001). *J. Am. Chem. Soc.*, *123*, 7915.

[16] Weck, M., Dunn, A. R., Matsumoto, K., Coates, G. W., Lobkovshy, E. B., & Grubbs, R. H. (1999). *Angew. Chem. Int. Ed.*, *38*, 2741.

[17] Motoyanagi, J., Fukushima, T., & Aida, T. (2005). *Chem. Commun.*, 101.

[18] Kumar, S. & Pal, S. K. (2005). *Tetrahedron Lett.*, *46*, 4127.

[19] Kato, T., Mizoshita, N., & Kishimoto, K. (2006). *Angew. Chem. Int. Ed.*, *45*, 38; Kato, T. (2000). *Struct. Bonding*, *96*, 95; Paleos, C. M. & Tsiourvas, D. (2001). *Liq. Cryst.*, *28*, 1127; Zhao, K. Q., Gao, C. Y., Hu, P., Wang, B. Q., & Li, Q. (2006). *Acta Chim. Sinica*, *64*, 1051; Harada, Y., Matsunaga, Y., Miyajima, N., & Sakamoto, S. (1995). *J. Mater. Chem.*, *5*, 2305.

[20] Bushey, M. L., Hwang, A., Stephens, P. W., & Nuckolls, C. (2001). *J. Am. Chem. Soc.*, *123*, 8157; Bushey, M. L., Nguyen, T., & Nuckolls, C. (2003). *J. Am. Chem. Soc.*, *125*, 8264; Bushey, M. L., Nguyen, T., Zhang, W., Horoszewski, D., & Nuckolls, C. (2004). *Angew. Chem. Int. Ed.*, *43*, 5446.

[21] Paraschiv, I., Giesbers, M., van Lagen, B., Grozema, F. C., Abellon, R. D., Siebbeles, L. D. A., Marcelis, A. T. M., Zuilhof, H., & Sudhölter, E. J. R. (2006). *Chem. Mater.*, *18*, 968.

[22] Gearba, R. I., Lehmann, M., Levin, J., Ivanov, D. A., Koch, M. H. J., Barbera, J., Debije, M. G., Piris, J., & Geerts, Y. H. (2003). *Adv. Mater.*, *15*, 1614.

[23] Ikeda, M., Takeuchi, M., & Shinkai, S. (2003). *Chem. Commun.*, 1354.

[24] Masuda, M., Jonkheijm, P., Sijbesma, R. P., & Meijer, E. W. (2003). *J. Am. Chem. Soc.*, *125*, 15935.

[25] Schulte, J. L., Laschat, S., Vill, V., Nishikawa, E., Finkelmann, H., & Nimtz, M. (1998). *Euro. J. Org. Chem.*, 2499.

[26] Boden, N., Bushby, R. J., & Cammidge, A. N. (1995). *J. Am. Chem. Soc.*, *117*, 924.

[27] Boden, N., Bushby, R. J., & Martin, P. S. (1999). *Langmuir*, *15*, 3790; Zhao, K. Q., Wang, B. Q., Hu, P., Gao, C. Y., Yuan, F. J., & Li, H. R. (2006). *Chin. J. Chem.*, *24*, 210; Zhao, K. Q., Wang, B. Q., Hu, P., Li, Q., & Zhang, L. F. (2005). *Chin. J. Chem.*, *23*, 767.

[28] Cammidge, A. N. & Bushby, R. J. (1998). In: *Hand Book of Liquid Crystals*, Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., & Vill, V. (Eds.), Chapter VII, Vol. 2B, Wiley-VCH.

[29] Paraschiv, I., Delforterie, P., Giesbers, M., Posthumus, M. A., Marcelis, A. T. M., Zuilhof, H., & Sudhölter, E. J. R. (2005). *Liq. Cryst.*, *32*, 977.