SPECIAL TOPIC — Physical research in liquid crystal

Phase behaviors of binary mixtures composed of electron-rich and electron-poor triphenylene discotic liquid crystals*

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Disk-like liquid crystals (DLCs) can self-assemble to ordered columnar mesophases and are intriguing one-dimensional organic semiconductors with high charge carrier mobility. To improve their applicable property of mesomorphic temperature ranges, we exploit the binary mixtures of electronic donor-acceptor DLC materials. The electron-rich 2,3,6,7,10,11-hexakis(alkoxy)triphenylenes (C4, C6, C8, C10, C12) and an electron-deficient tetrapentyl triphenylene-2,3,6,10-tetracarboxylate have been prepared and their binary mixtures have been investigated. The mesomorphism of the 1:1 (molar ratio) mixtures has been characterized by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and small angel x-ray scattering (SAXS). The self-assembled monolayer structure of a discogen on a solid-liquid interface has been imaged by the high resolution scanning tunneling microscopy (STM). The match of peripheral chain length has important influence on the mesomorphism of the binary mixtures.

Keywords: binary mixtures, discotic liquid crystals, triphenylene, mesomorphism

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1. Introduction

Miscibility of rod-like liquid crystals (LC) has been intensively studied because the blended homologous series of calamitic LC compounds have exhibited wider mesophase temperature ranges and lower melting points, which are very important for their commercial applications in LC displaying industry. Recently, an LC mixture containing a banana-shaped nematogen and a calamitic smectogen has reported to show nematic phase with lowered phase transition temperatures and widened mesophase ranges,[1] and a binary mixture of cross-like molecules exhibited biaxial nematic phase.[2] Discotic LCs are another kind of important mesomorphic materials: they self-assemble into columnar mesophases and have wide applications in display industry, field-effect transistors, organic light emitting diodes, and photovoltaic solar cells.[3–7]

To tune the supramolecular structures and the applicable properties, discotic LCs consisting of both electron-donor discogens and electron-acceptor discogens have been synthesized and investigated by our group.[8,9] However, the synthesis and purification of the discotic oligomers with covalent-bonded different discogens are not highly efficient. Therefore, we are interested in the blends of discotic LCs for applicable property improvement.

In the pioneering research work on discotic LC mixtures, Bushby and co-workers[10] have discovered that the complementary polytopic interaction (CPI) effect between triphenylene derivatives and two larger discotic systems greatly improves the mesomorphism. Park and coworkers[11] have reported electronic donor–acceptor pairs by blend electron-rich hexa(alkoxy)triphenylene with electron-accepting mellitic triimide to obtain much stable columnar mesophases. Mehl and coworkers[12] have reported a case of full miscibility of disk- and rod-shaped mesogens in nematic phase. Geerts and coworkers[13,14] have found that a phthalocyanine discotic mesogen and a perylenediimide lathlike mesogen are full miscible and the composites show a hexagonal columnar mesophase. Grelet and coworkers[15] have reported a case of two discotic columnar liquid crystals of perylene tetracarboxylate and a pyrene tetracarboxylate formed organic donor-acceptor heterojunction, which has potential application in photovoltaic solar cells. Song and coworkers[16] have shown that the miscibility of discotic truxene and truxenone derivatives. However, the investigation of binary mixtures of discotic mesogens is still in its infancy.

In this paper, we will report the phase behaviors of five binary mixtures of electron-rich 2,3,6,7,10,11-hexa(alkoxy)triphenylenes **1 (1a–1e)** with an electron-deficient triphenylene tetraester **6**. Chemical structures and synthetic methods of the studied discogens are depicted in Figs. 1 and 2.[17,18] In **1a–1e**, $R = C_4H_9$, $R = C_6H_{13}$, $R = C_8H_{17}$, $R = C_{10}H_{21}$, and $R = C_{12}H_{25}$, respectively.

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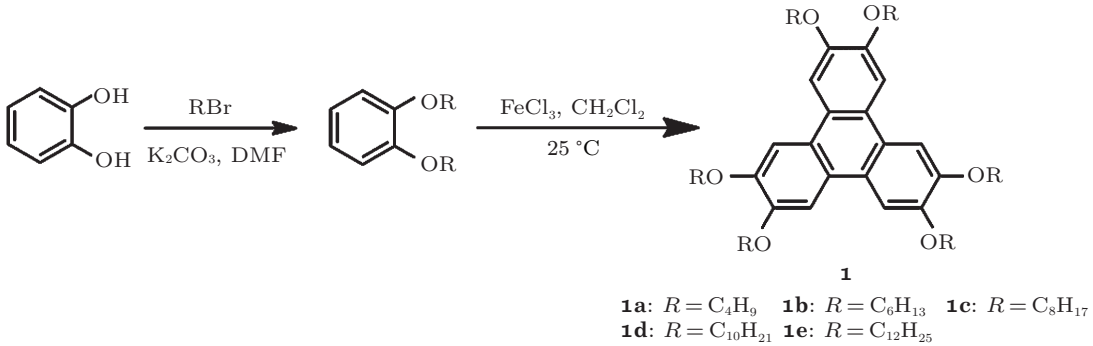


Fig. 1. Synthesis of p-type discotic liquid crystal 2,3,6,7,10,11-hexa(alkoxy)triphenylenes **1.**

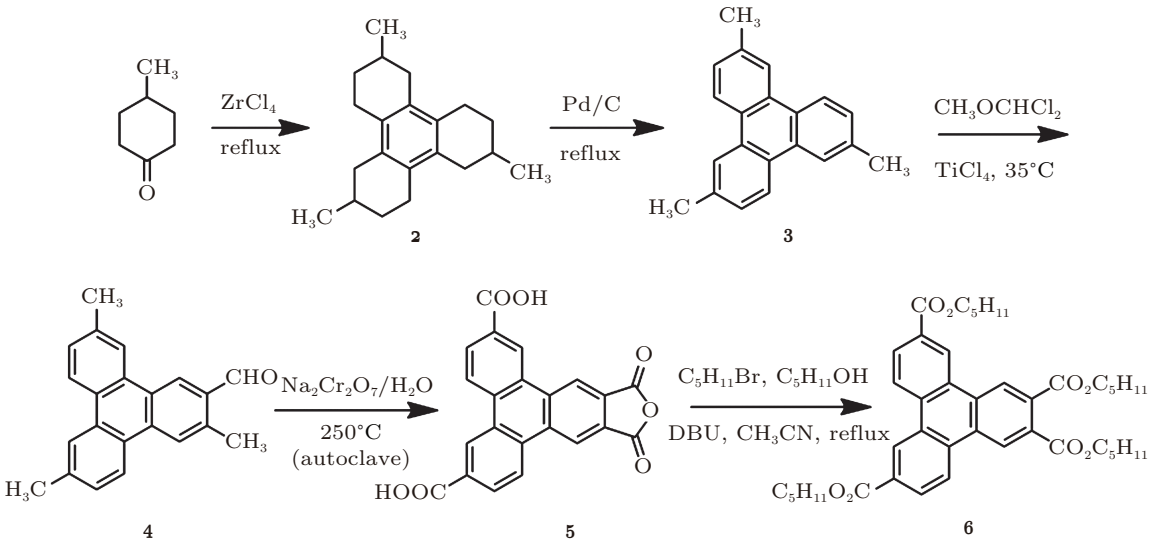


Fig. 2. Synthesis of an n-type discotic liquid crystal tetrapentyl triphenylene-2,3,6,10-tetracarboxylate, **6**.

2. Experimental

2.1. Synthesis of discotic mesogens

2,3,6,7,10,11-Hexa(butyloxy)triphenylene, 1a[17] A mixture of K_2CO_3 (65.5 g, 0.475 mol), 1-bromobutane (45.5 g, 0.332 mol), and pyrocatechol (17.5 g, 0.159 mol) in ethanol (200 mL) was refluxed 24 h with stirring under N_2. After the mixture was cooled, the inorganic was filtered off and the solvent was distilled out under reduced pressure. The residue was distilled under vacuum to get 1,2-dibutoxybenzene (31.83 g, 0.143 mol, 91.0%).

A mixture of $FeCl_3$ (13.01 g, 0.080 mol) in CH_2Cl_2(20 mL) was cooled to 0 °C, 1,2-dibutyloxybenzene (5 g, in 20 mL CH_2Cl_2) was added slowly with stirring. The mixture was stirred 2 h at room temperature. Then, the mixture was cooled and cold methanol (15 mL) was added slowly. The solvent CH_2Cl_2 was distilled out under reduced pressure and the residue poured onto ice–water. The solid was collected by filtration, which was further purified by column chromatography (silica, eluted with CH_2Cl_2/petroleum 1:1) and recrystallization from ethanol to obtain **1a** as a white powder, yield 35%.

2,3,6,7,10,11-Hexakis(hexyloxy)triphenylene, 1b[17] A mixture of K_2CO_3 (32.78 g, 0.24 mol), 1-bromohexane (27.41 g, 0.166 mol), and pyrocatechol (8.71 g, 0.080 mol) in DMF (80 mL) was stirred at 85 °C for 24 h to get 1,2-bis(hexyloxy)benzene (19.77 g, 0.071 mol, 89.7%). Then, $FeCl_3$ (11.436 g, 0.071 mol) oxidation of 1,2-bis(hexyloxy)benzene (5.6 g) in CH_2Cl_2 resulted in **1b**, 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene (3.81 g, 67.4%), as a white powder.

2,3,6,7,10,11-Hexakis(octyloxy)triphenylene, 1c[17] A mixture of K_2CO_3 (18.74 g, 0.14 mol), 1-bromooctane (18.35 g, 0.095 mol), and pyrocaltechol (4.98 g, 0.045 mol) in DMF (50 mL) reacted at 85 °C for 24 h yielding 1,2-bis(octyloxy)benzene (12.91 g, 0.039 mol, 85.4%). The oxidation of 1,2-bis(octyloxy)benzene (1.8 g) with $FeCl_3$ (3.1 g, 19 mmol) in CH_2Cl_2 resulted in **1c** (1.18 g, 65.7%) as a white solid.

2,3,6,7,10,11-Hexakis(decyloxy)triphenylene, 1d[17] The reaction between 1-bromodecane (25.82 g, 0.117 mol) and pyrocaltechol (6.12 g, 0.056 mol) with K_2CO_3 (23.03 g, 0.167 mol) as the base yielded 1,2-bis(decyloxy)benzene (17.94 g, 0.046 mol, 82.7%). The oxidation of 1,2-

bis(decyloxy)benzene (1.5 g) by using $FeCl_3$ (2.184 g, 0.013 mol) in CH_2Cl_2 resulted in **1d** (0.95 g, 63.8%).

2,3,6,7,10,11-Hexakis(dodecyloxy)triphenylene, 1e[17] The reaction of 1-bromododecane (18.30 g, 0.074 mol) with pyrocaltechol (3.85 g, 0.035 mol) in presence of K_2CO_3 (14.49 g, 0.105 mol) in DMF resulted in 1,2-bis(decyloxy)triphenylene (12.57 g, 0.028 mol, 80.5%). The oxidation of 1,2-bis(decyloxy)triphenylene (2.34 g) with $FeCl_3$ (2.979 g, 0.018 mol) in CH_2Cl_2 produced **1e** (1.391 g, 59.7%) as a white solid.

2,6,10-trimethyl-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene, 2[18] The mixture of 4-methylcyclohexanone (48.0 g, 0.25 mol) and $ZrCl_4$ (2.5 g, 0.0105 mol) was stirred with refluxing for 15 h. After cooling, $CHCl_3$ was added to the mixture to dissolve the organics and the inorganic was filtered out. The solid residue after being removed off the solvent was recrystallized from ethanol to get white powder, **2** (15.6 g, 67.1%).

2,6,10-trimethyltriphenylene, 3[18] The mixture of 2,6,10-trimethyl-1,2,3,4,5,6,7,8,9,10,11,12-dodecanhydrotriphenylene (28.2 g, 0.1 mol) and Pd/C (1.4 g, 10%) was carefully heated to 250–310 °C and stirred for 12 h until no hydrogen gas produced. After being cooled, the mixture was added toluene to dissolve the organic solid to separate the Pd/C by filtration. White crystal, **3** (22.6 g, 84%), was collected from the cooled solution of toluene.

Synthesis of 3,7,11-trimethyltriphenylene-2-carbaldehyde, 4[18] To the mixture of **1** (3 g, 11 mmol) in dichloromethane (23 mL) at 0 °C was slowly added $TiCl_4$ (1 M in CH_2Cl_2, 15 mL) with vigorous stirring. Dichloro(methoxy)methane (15 mL, 0.166 mol) was added and stirred at room temperature for overnight, then heated at 40 °C for 90 min. The mixture was poured into water and extracted with CH_2Cl_2 (3×40 mL). The residue after remove off the solvent was purified by column chromatography (silica, CH_2Cl_2/petroleum 2:1) to get white crystal **4** (2.7 g, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.43 (s, 1H, CHO), 8.96 (s, 1H, ArH), 8.48 (d, $J = 8.4$ Hz, 2H, Ar**H**), 8.42 (s, 1H, Ar**H**), 8.35 (d, $J = 10.8$ Hz, 2H, Ar**H**), 7.47 (t, $J = 8.2$ Hz, 2H, Ar**H**), 2.86 (s, 3H, C**H**$_3$), 2.62 (s, 6H, C**H**$_3$).

Synthesis of 10,12-dioxo-10,12-dihydrotriphenyleno[2,3-c]furan-2,6-dicarboxylic acid, 5[18] To a stirred mixture of **4** (7.7 g, 26 mmol) in water (112 mL), $Na_2Cr_2O_7$ (38 g, 128 mmol) was added in small portion. Then transferred the mixture to pump to heat to 250 °C with stirring for overnight (the inner pressure got to 45 bar). After cooling, the mixture was acidified by concentrated hydrochloride acid to get light yellow powder, which was thoroughly washed with water, **5** (9.2 g, 92%).

Tetrapentyl triphenylene-2,3,6,10-tetracarboxylate, 6 A mixture of **5** (0.2 g, 0.52 mmol), 1-bromopentane (1.3 g, 8.32 mmol), 1-pentanol (1.1 g, 11.96 mmol), and DBU (0.83 g, 5.72 mmol) in CH_3CN (11 mL) was heated overnight with stirring. After distilling off the solvent, methanol (39 mL) was added to get solid preciptate, which was further purified by flash chromatography (Silica, CH_2Cl_2/petroleum 1:1) and recrystallization from methanol to get **6** (3.0 g, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.35 (d, $J = 9.6$ Hz, 2H, Ar**H**), 9.03 (d, $J = 4.0$ Hz, 2H, Ar**H**), 8.72 (dd, $J = 29.2$ and 8.8 Hz, 2H, Ar**H**), 8.37 (t, $J = 8.4$ Hz, 2H, Ar**H**), 4.40–4.48 (m, 8H, C**H**$_2$), 1.82–1.91 (m, 8H, C**H**$_2$), 1.40–1.53 (m, 16H, C**H**$_2$), 0.94–1.00 (m, 12H, C**H**$_3$).

2.2. The preparation of the binary mixtures

Equal mole of hexa(alkoxy)triphenylene **1** and the triphenylene ester **6** were dissolved in small amount of CH_2Cl_2, then the solvent was evaporated slowly to get composites **1–6** (**1a–6, 1b–6, 1c–6, 1d–6, and 1e–6**).

3. Results and discussion

The mesomorphism of the 1:1 binary mixtures **1–6** has been investigated by polarizing optic microscopy (POM), differential scanning calorimetry (DSC), and the results compared with the LC properties of composites **1–6**. Triphenylene ester **6** shows "medal-ribbon" texture with featuring of columnar hexagonal mesophase (Col_{hex}) (see Fig. 3). Figure 4 displays the birefringence textures of the hexa(alkyloxy)triphenylene **1** and the mixture of composites **1–6**.

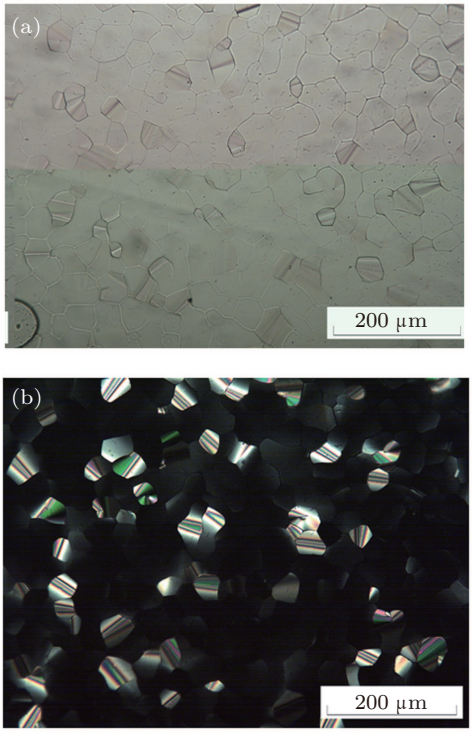


Fig. 3. (color online) Photomicrographs of **6**, $TP(CO_2C_5H_{11})_4$, at 100 °C cooled from isotropic liquid. (a) Non-birefringence between parallel polarizers; (b) birefringent optic texture of ordered columnar hexagonal mesophase under crossed polarizers.

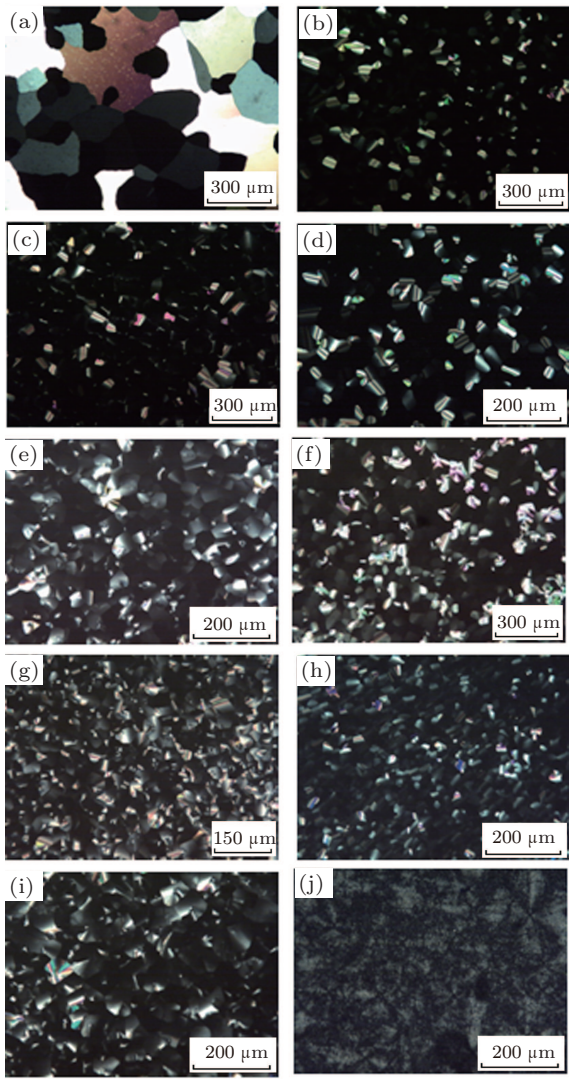


Fig. 4. (color online) Polarizing optical microscopic textures of hexa(alkoxy)triphenylene and their composites measured at cooling runs. (a) and (b) **1a** and **1a–6** at 120 °C; (c) **1b** at 85 °C; (d) **1b–6** at 115 °C; (e) **1c** at 78 °C; (f) **1c–6** at 89 °C; (g) **1d** at 54 °C; (h) **1d–6** at 40 °C; (i) **1e** at 50 °C; (j) **1e–6** at 37 °C.

It is noted that **1a** possesses a monotropic plastic Col_{hp} phase on cooling, but the composite **1a–6** just shows a Col_{hex} phase. The discogen **1e** with the longest peripheral chain of C12 displays narrow Col_{hex} mesophase, while composite **1e–6** does not show any mesomorphism, and directly crystallize when cooled from isotropic liquid (Fig. 4(h)).

The phase transition temperatures have been measured by DSC, and the curves are drawn in Fig. 5, and the data are summaried in Table 2.

The DSC curve of **1a** shows that it has Col_{hex} phase between 87–146 °C on heating, and an monotropic plastic Col_{hex} phase between 77–49 °C on cooling. The blend **1a–6** does not crystallize even cooled to 0 °C, the mesophase range is larger than 130 °C (Fig. 5(a)).

The composite **1b–6** shows a decreased melting point (29 °C) and an increased clearing point (126 °C), so broadened Col_{hex} mesophase compared with its component compounds **1b** and **6** (Fig. 5(b)). The composite **1c–6** exhibits Col_{hex} mesophase between 95 °C and −2 °C on first cooling, with much lowered crystallization temperature. Again, the other composite **1d–6** exhibits Col_{hex} phase in the range of 24–57 °C on the first cooling. The last blend of this series compounds **1e–6** displays melting point of 53 °C on heating and crystallization temperature of 36 °C on cooling, without any mesophase.

The mesophase of the blended composite has been further confirmed by small angel x-ray diffraction (SAXS) (Fig. 6). The SAXS patterns of composite **1c–6** show a π–π stacking peak at 3.5 Å, representing the intracolumnar discotic core-core distance. The halo peak at 4.6 Å shows the molten alkyl chain distance. The strongest peak at low angel region is located at 18.2 Å, the (100) peak of the Col_{hex} mesophase, indicating the lattice parameter a with value of 21.0 Å. At the low temperature of 25 °C and 35 °C, the composite **1c–6** is in a crystalline solid. At 110 °C, the composite is in the isotropic liquid state, and the π–π stacking peak at 3.5 Å disappears.

Table 1. Thermodynamic properties of the discotic LC composites and the components (N_2, heating and cooling rates 10 °C/min).

Compound/composite	Mesophase[a], transition temperature and enthalpy changes[b]	
	Heating/ °C (ΔH, kJ·mol^{-1})	Cooling/ °C (ΔH, kJ·mol^{-1})
6	Cr 50 (13.5) Col_{hex} 121 (2.3) I	I 119 (2.4) Col_{hex} 39 (13.2) Cr
1a	Cr 87 (25.5) Col_P 146 (19.6) I	I 144 (22.2) Col_P 49 (22.0) Cr
1a–6	Cr 76 (5.4) Col_{hex} 34 (6.8) I	I 132 (7.9) Col_{hex}
1b	Cr 68 (40.4) Col_{hex} 99 (5.5) I	I 97 (5.4) Col_{hex} 53 (43.0) Cr
1b–6	Cr 29 (10.7) Col_{hex} 126 (3.5) I	I 123 (3.8) Col_{hex} −20 (13.9) Cr
1c	Cr 59 (48.7) Col_{hex} 81 (4.7) I	I 79 (4.4) Col_{hex} 41 (81.6) Cr
1c–6	Cr 30 (26.8) Col_{hex} 97 (3.9) I	I 95 (2.8) Col_{hex} −2 (35.7) Cr
1d	Cr 59 (88.0) Col_{hex} 72 (3.4) I	I 69 (3.3) Col_{hex} 43 (90.3) Cr
1d–6	Cr 51 (62.2) Col_{hex} 3 (0.9) I	I 57 (1.5) Col_{hex} 24 (61.7) Cr
1e	Cr 58 (64.4) Col_{hex} 62 (16.6) I	I 58 (3.2) Col_{hex} 45 (106.2) Cr
1e–6	Cr 53 (55.2) I	I 36 (58.9) Cr

[a]Cr: crystal state; Col_{hex}: hexagonal columnar mesophase; I: isotropic liquid. [b]enthalpy change value for the composites expressed in J/g.

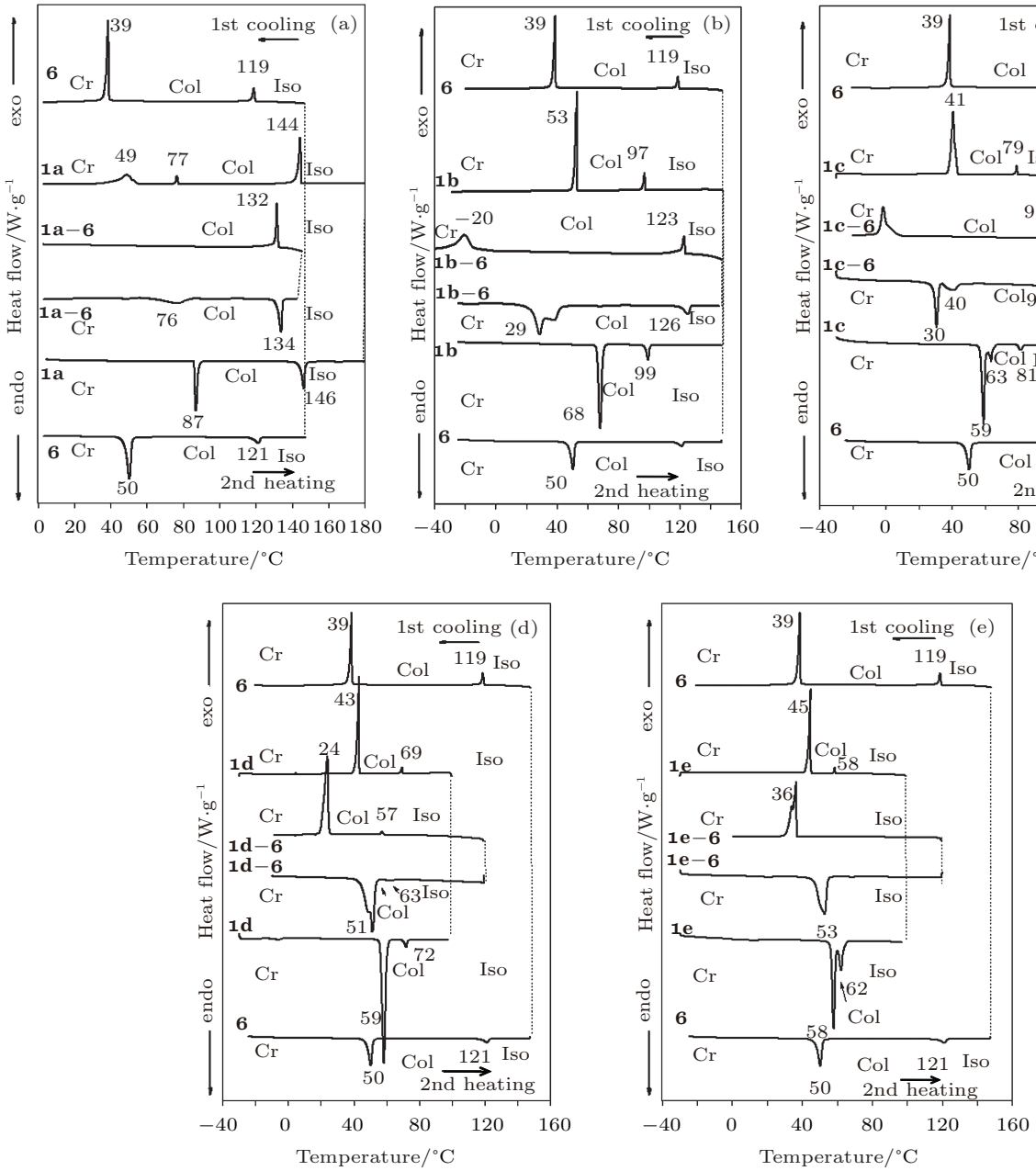


Fig. 5. DSC curves of the binary mixtures: (a) **1a–6**; (b) **1b–6**; (c) **1c–6**; (d) **1d–6**; and (e) **1e–6**.

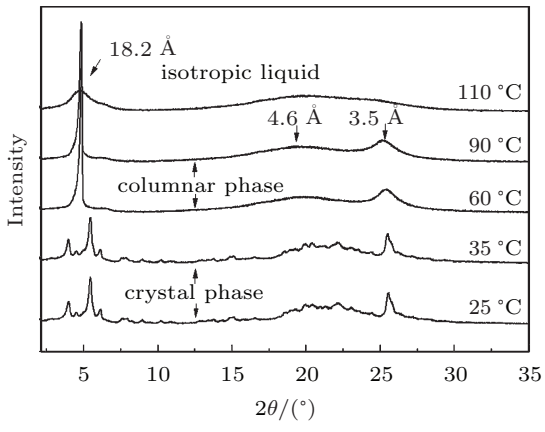


Fig. 6. Small angel x-ray scattering (SAXS) patterns of the 1:1 binary mixture of composite **1c–6** at various temperatures.

The self-assembled monolayer (SAM) structure of **1a** has been investigated by scanning tunneling microscopy (STM), and the images are shown in Fig. 7. On the solid–liquid interface of highly oriented pyrolytic graphite (HOPG) and 1-phenyloctane compound **1a** self-assembles to highly ordered two-dimensional structure (Figs. 7(a) and 7(b)). The bright yellow spots represent the triphenylene aromatic cores, the empty areas are peripheral butyl chains. The STM images of **1a** are well coincident with the 3-dimensional Col_{hex} mesophase and plastic Col_{hex} phase.

The STM images of the blend **1a–6** have not been observed, might be due to the stronger donor–acceptor interactions between **1a** and **6** prevent the monolayer assembly of the

blended composite. The SAM structures of the homologous compounds of **1** with longer chains have been reported and shown different organization patterns upon the flexible chain length.[19]

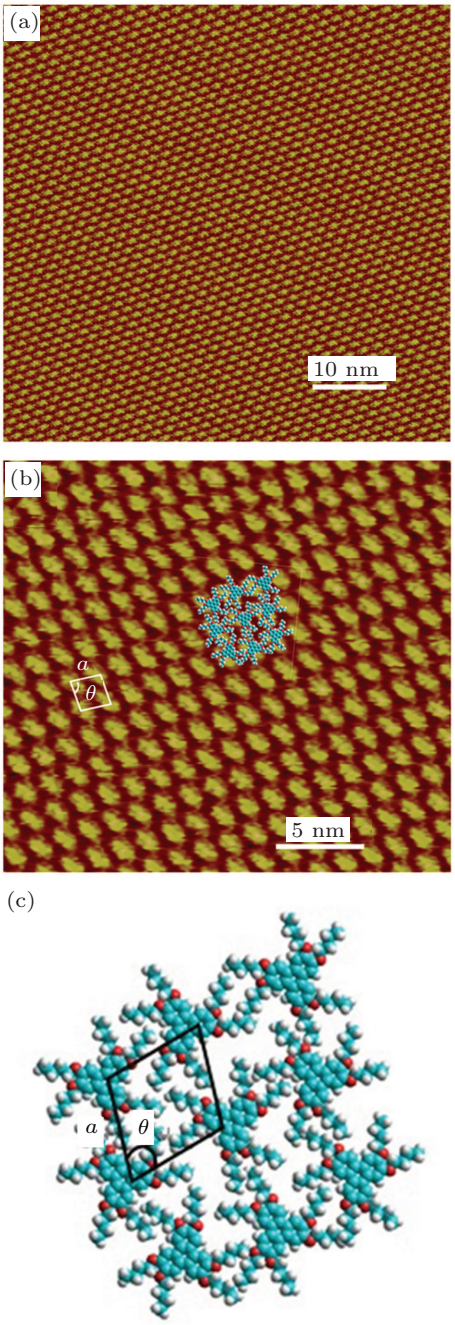


Fig. 7. (color online) STM images of **1a**. The diameter of the bright spots is about 1.0 ± 0.1 nm, which is consistent with the size of the TP core. A unit cell for **1a** structure is outlined with parameters of $a = 3.0 \pm 0.1$ nm, $\theta = 85° \pm 3°$. (a) Large-scale STM image (60 nm×60 nm) of a self-assembled monolayer of **1a** on an HOPG surface. The imaging conditions were $I_{tip} = 299$ pA, $V_{bias} = 650$ mV. (b) High-resolution STM image (25 nm×25 nm) of **1a** self-assembly. The imaging conditions were $I_{tip} = 358$ pA, $V_{bias} = 750$ mV. (c) Structure model for **1a** self-assembly.

4. Conclusion

The binary mixtures of electron-rich organic semiconductors hexa(butoxy)triphenylene (**1a**), hexa(hexyloxy)triphenylene (**1b**), hexa(octyloxy)triphenylene (**1c**), hexa(decyloxy)triphenylene (**1d**), hexa(dodecyloxy)triphenylene (**1e**), with an electron-deficient organic semiconductor pentyl triphenylenyl-2,3,6,10-tetraester (**6**) have been investigated by POM, DSC, and SAXS. They are completely miscible to each other and the blends have not shown any phase separation behaviors. Four mixtures display columnar hexagonal mesophases with decreased crystallization temperatures and broadened mesophase temperature ranges. However, the mixture of the longest chain triphenylene donor **1e** ($C_{12}H_{25}$) with the discotic acceptor **6** (C_5H_{11}) has not shown any mesomorphism due to the mismatch of alkyl chains. The peripheral chain length matches is a key factor to determine the columnar mesophase stability. The charge carrier mobility of the binary mixtures **1–6** will be very interesting and it will be measured by the time-of-flight technique.

References

[1] Cvetinov M, Obadovic D Z, Stojanovic M, Vajda A, Fodor-Csorba K, Eber N and Ristic I 2014 *Chin. Phys. B* **23** 096402
[2] Zhu L and Liu H 2015 *Chin. J. Liq. Cryst. Display* **30** 194
[3] Adam D, Schuhmacher P, Simmerer J, Haussling L, Siemensmeyer K, Etzbach K H, Ringsdorf H and Haarer D 1994 *Nature* **371** 141
[4] Schmidt-Mende L, Fechtenkotter A, Mullen K, Moons E, Friend R H and MacKenzie J D 2001 *Science* **293** 1119
[5] Laschat S, Baro A, Steinke N, Giesselmann F, Hagele C, Scalia G, Judele R, Kapatsina E, Sauer S, Schreivogel A and Tosoni M 2007 *Angew. Chem. Int. Ed.* **46** 4832
[6] Chen J, Du W and Gao C 2014 *Chin. J. Liq. Cryst. Display* **29** 508
[7] Cui X, Wang L, Huang Q, He W, Liu T, Liu Q, Yang Z and Yang H 2011 *Chin. J. Liq. Cryst. Display* **26** 727
[8] Zhao K, Bai X, Xiao B, Gao Y, Hu P, Wang B, Zeng Q, Wang C, Heinrich B and Donnio B 2015 *J. Mater. Chem. C* **3** 11735
[9] Zhao K, An L, Zhang X, Yu W, Hu P, Wang B, Xu J, Zeng Q, Monobe H, Shimizu Y, Heinrich B and Donnio B 2015 *Chem. Eur. J.* **21** 10379
[10] Boden N, Bushby R J, Cooke G, Lozman O R and Lu Z 2001 *J. Am. Chem. Soc.* **123** 7915
[11] Park L Y, Hamilton D G, McGehee E A and McMenimen K A 2003 *J. Am. Chem. Soc.* **125** 10586
[12] Kouwer P H J and Mehl G H 2003 *J. Am. Chem. Soc.* **125** 11172
[13] Zucchi G, Donnio B and Geerts Y H 2005 *Chem. Mater.* **17** 4273
[14] Zucchi G, Viville P, Donnio B, Vlad A, Melinte S, Mondeshki M, Graf R, Spiess H W, Geerts Y H and Lazzaroni R 2009 *J. Phys. Chem. B* **113** 5448
[15] Thiebaut O, Bock H and Grelet E 2010 *J. Am. Chem. Soc.* **132** 6886
[16] Luo J, Chen L, Wang J, Lei T, Li L, Pei J and Song Y 2010 *New J. Chem.* **34** 2530
[17] Boden N, Borner R C, Bushby R J, Cammidge A N and Jesudason M V 1993 *Liq Cryst.* **15** 851
[18] Hassheider T, Benning S A, Kitzerow H, Achard M and Bock H 2001 *Angew. Chem. Int. Ed.* **40** 2060
[19] Wu P, Zeng Q, Xu S, Wang C, Yin S and Bai C 2001 *Chem. Phys. Chem.* **2** 750