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Self-assembly of liquid crystalline triphenylene–oligo(ethylene oxide)–triphenylene molecules and their complexes with lithium triflate

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Mesomorphic dimeric molecules consisting of discotic triphenylene rigid units and flexible ethylene oxide spacers have been prepared. The liquid crystalline behaviour is greatly dependent on the length of the ethylene oxide chains. The miscibility and phase behaviour have been examined for mixtures of the materials with lithium triflate.

1. Introduction

Columnar liquid crystals can be used for anisotropic materials transporting charge (electron and hole), ions and energy due to their one-dimensional nanostructures [1–7]. Discotic columnar phases are formed by π-conjugated discotic molecules such as triphenylene, hexa-*peri*-hexabenzocoronene and phthalocyanine derivatives based on π-stacking of the molecules [8–16]. These molecules can function as one-dimensional electron/hole transporting materials in their liquid crystalline (LC) assemblies. These LC π-conjugated molecules can be used in, for example organic light-emitting diodes, organic field-effect transistors and photovoltaic solar cells. Among these π-conjugated discotic molecules, triphenylene-based liquid crystals including monomers, dimers, oligomers and polymers have been intensively studied [17, 18].

Moreover, oligo(ethylene oxide) chains have been used as flexible components for LC main chain [19] and side chain polymers [20–23], supramolecular liquid crystals [24–26] and rod–coil block molecules in which the oligo(ethylene oxide) moieties function as coil blocks [27–36]. In addition, they can also function as molecular parts involved in ion–dipolar interactions, which results in the preparation of ion-conductive materials [23, 31–36]. Recently we have reported that self-assembly of LC rod–coil–rod block molecules, figure 1 (*a*), leads to the formation of two-dimensional ion conductors [31–36].

The LC properties of dimeric molecules have been extensively examined [37, 38], while to our knowledge few studies have been reported for disc–oligo(ethylene oxide)–disc molecules, figure 1 (*b*). Our approach is to design LC discotic molecules having triphenylene and oligo(ethylene oxide) moieties, although several dimeric triphenylene derivatives have been reported [39–44]. It is of interest to examine the effects of oligo(ethylene oxide) moieties on the LC properties of disc dimeric molecules. In this paper, we report on the LC properties of triphenylene-based discotic dimers **1a**–**e** containing flexible oligo(ethylene oxide) linkers (n=3, 4, 5, 6, 8) (figure 2). The effects of the addition of ionic species on the self-assembled behaviour of these molecules have also been studied.

2. Experimental

2.1. *General*

^{1}H NMR and ^{13}C NMR spectra were obtained using a JEOL JNM-LA400. Mass spectra (MALDI-TOF-MS) were recorded on a Biosystems BioSpectrometry Workstation model Voyager-DE STR spectrometer using dithranol as the matrix. Elemental analyses were carried out on a Perkin-Elmer CHNS/O 2400II apparatus. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 30 (scanning rate: 5°C min^{-1}). Transition temperatures were assigned to be the transition peak maxima. Polarizing microscopic observations were conducted with an Olympus BX51 microscope equipped with a Mettler FP82HT hot stage. X-ray diffraction (XRD) measurements were

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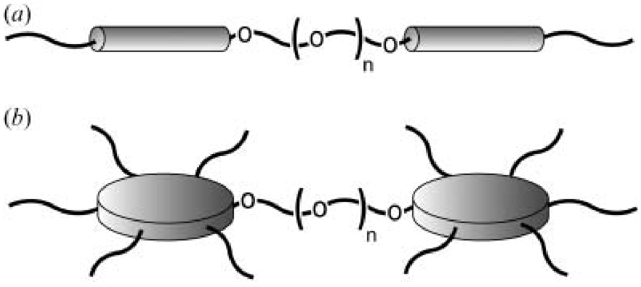


Figure 1. Schematic illustrations of liquid crystalline dimers containing oligo(ethylene oxide) chains: (*a*) a rod dimer (a rod–coil–rod molecule) and (*b*) a disc dimer (a disc–coil–disc molecule).

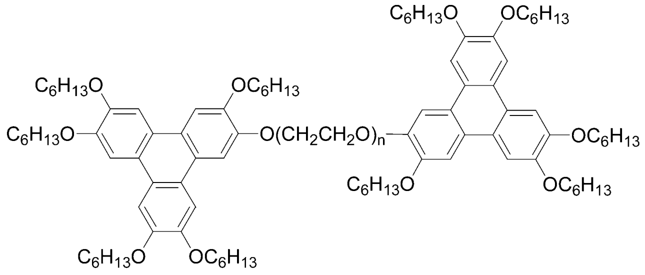
carried out on a Rigaku RINT 2500 diffractometer with a heating stage and with use of Ni-filtered CuK$_\alpha$ radiation.

2.2. *Materials*

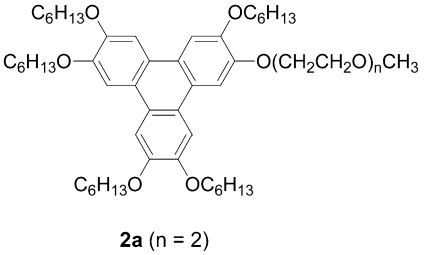
All chemical reagents and solvents were obtained from commercial sources and used without further purification.

2.2.1. 1,8-Bis[3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yloxy]-3,6-dioxaoctane (1a).

3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-ol (300 mg, 4.0×10^{-4} mol), triethylene glycol ditosylate (84 mg, 1.8×10^{-4} mol) and anhydrous potassium carbonate (100 mg, 7.2×10^{-4} mol) were dissolved in *N*,*N*-dimethylformamide (20 ml) and stirred at 75°C for 10 h under an argon atmosphere. The reaction mixture was poured into water and extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous NH_4Cl and NaCl, dried over $MgSO_4$ and filtered; the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluant: hexane/ethyl acetate=7/1) to give **1a** as a white solid in 52% yield (152 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80–7.86 (m, 12H), 4.40 (t, *J*=4.8 Hz, 4H), 4.23–4.26 (m, 20H), 4.03 (t, *J*=4.8 Hz, 4H), 3.86–3.95 (m, 4H), 1.88–2.00 (m, 20H), 1.28–1.80 (m, 60H), 0.93 (t, *J*=6.8 Hz, 30H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.01, 148.97, 148.88, 148.80, 148.30, 124.00, 123.67, 123.52, 123.41, 123.36, 108.18, 107.26, 107.07, 106.87, 106.80, 71.05, 69.97, 69.67, 69.64, 69.55, 69.46, 69.36, 69.30, 31.67, 29.40, 25.84, 22.64, 14.03. MS (MALDI): *m*/*z* 1604.46 (M+H$^+$); calcd, 1604.13. Elemental analysis calcd (%) for $C_{102}H_{154}O_{14}$: C 76.36, H 9.68; found: C 76.50, H 9.91.



1a (n = 3)
1b (n = 4)
1c (n = 5)
1d (n = 6)
1e (n = 8)



2a (n = 2)
2b (n = 3)
2c (n = 4)

Figure 2. Triphenylene-based molecules containing oligo(ethylene oxide) chains prepared in the present study.

2.2.2. 1,11-Bis[3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yloxy]-3,6,9-trioxaundecane (1b).

The synthetic procedure was the same as that for **1a** except that tetraethylene glycol ditosylate was used instead of triethylene glycol ditosylate. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81–7.89 (m, 12H), 4.40 (t, *J*=4.8 Hz, 4H), 4.19–4.27 (m, 20H), 4.00 (t, *J*=4.8 Hz, 4H), 3.84 (t, *J*=4.8 Hz, 4H), 3.76 (t, *J*=4.8 Hz, 4H), 1.88–2.00 (m, 20H), 1.50–1.65 (m, 20H), 1.33–1.47 (m, 40H), 0.91–0.99 (m, 30H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.06, 149.03, 148.92, 148.86, 148.36, 124.04, 123.72, 123.56, 123.46, 123.40, 108.25, 107.33, 107.17, 106.96, 106.89, 70.90, 70.72, 69.96, 69.73, 69.70, 69.62, 69.53, 69.43, 69.32, 31.68, 29.42, 25.84, 22.65, 14.06. MS (MALDI): *m*/*z* 1648.44 (M+H$^+$); calcd, 1648.16. Elemental analysis calcd (%) for $C_{104}H_{158}O_{15}$: C 75.78, H 9.66; found: C 74.95, H 9.93.

2.2.3. 1,14-Bis[3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yloxy]-3,6,9,12-tetraoxatetradecane (1c).

The synthetic procedure was the same as that for **1a** except that pentaethylene glycol ditosylate was used. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80–7.88 (m, 12H), 4.39 (t, *J*=5.2 Hz, 4H), 4.22 (t, *J*=6.4 Hz, 20H), 3.98 (t, *J*=5.2 Hz, 4H), 3.80 (t, *J*=5.2 Hz, 4H), 3.65–3.73 (m, 8H), 1.91–1.96 (m, 20H), 1.55–1.62 (m, 20H), 1.30–1.47 (m, 40H), 0.94 (t, *J*=6.8 Hz, 30H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.98, 148.94, 148.85, 148.79, 148.29, 123.96, 123.63, 123.49, 123.39, 123.33, 108.17, 107.25, 107.07, 106.88, 106.80, 70.83, 70.60, 70.51, 69.87, 69.63, 69.60, 69.51, 69.42, 69.34, 69.24, 31.62, 29.36, 25.78, 22.60, 14.00. MS (MALDI): *m*/*z* 1692.47 (M+H$^+$); calcd, 1692.19. Elemental analysis calcd (%) for $C_{106}H_{162}O_{16}$: C 75.23, H 9.65; found: C 75.02, H 9.92.

2.2.4. 1,17-Bis[3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yloxy]-3,6,9,12,15-pentaoxaheptadecane (1d). The synthetic procedure was the same as that for **1a** except that hexaethylene glycol ditosylate was used. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.79–7.86 (m, 12H), 4.38 (t, J=4.8 Hz, 4H), 4.22 (t, J=6.4 Hz, 20H), 3.98 (t, J=4.8 Hz, 4H), 3.80 (t, J=4.8 Hz, 4H), 3.60–3.70 (m, 12H), 1.88–2.00 (m, 20H), 1.25–1.65 (m, 60H), 0.93 (t, J=6.8 Hz, 30H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 149.04, 149.01, 148.92, 148.84, 148.35, 124.01, 123.69, 123.54, 123.45, 123.38, 108.27, 107.31, 107.14, 106.98, 106.86, 70.86, 70.62, 70.53, 70.50, 69.91, 69.69, 69.67, 69.57, 69.49, 69.41, 69.30, 31.65, 29.39, 25.81, 22.62, 14.03. MS (MALDI): *m*/*z* 1735.72 (M+H$^+$); calcd, 1736.21. Elemental analysis calcd (%) for $C_{108}H_{166}O_{17}$: C 74.70, H 9.64; found: C 74.91, H 10.03.

2.2.5. 1,23-Bis[3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yloxy]-3,6,9,12,15,18,21-heptaoxatricosane (1e). The synthetic procedure was the same as that for **1a** except that octaethylene glycol ditosylate was used. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.81–7.89 (m, 12H), 4.39 (t, J=5.2 Hz, 4H), 4.23 (t, J=6.4 Hz, 20H), 3.99 (t, J=5.2 Hz, 4H), 3.80 (t, J=4.8 Hz, 4H), 3.70 (t, J=4.8 Hz, 4H), 3.58–3.67 (m, 16H), 1.88–2.00 (m, 20H), 1.49–1.65 (m, 20H), 1.32–1.47 (m, 40H), 0.93 (t, J=6.8 Hz, 30H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 149.07, 149.04, 148.96, 148.87, 148.38, 124.05, 123.72, 123.56, 123.47, 123.41, 108.32, 107.35, 107.17, 107.01, 106.88, 70.89, 70.65, 70.57, 70.52, 70.50, 69.93, 69.73, 69.71, 69.61, 69.52, 69.46, 69.34, 31.66, 29.40, 25.83, 22.64, 14.04. MS (MALDI): *m*/*z* 1824.62 (M+H$^+$); calcd, 1824.26. Elemental analysis calcd (%) for $C_{112}H_{174}O_{19}$: C 73.73, H 9.61; found: C 73.08, H 10.10.

2.2.6. 1-[3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-yloxy]-3,6-dioxaheptane (2a). The synthetic procedure was the same as that for **1a** except that diethylene glycol monomethyl ether monotosylate was used. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.80–7.90 (m, 6H), 4.42 (t, J=4.8 Hz, 2H), 4.23 (t, J=6.4 Hz, 10H), 4.00 (t, J=4.8 Hz, 2H), 3.82 (t, J=4.8 Hz, 2H), 3.61 (t, J=4.8 Hz, 2H), 3.41 (s, 3H), 1.90–1.97 (m, 10H), 1.50–1.68 (m, 10H), 1.25–1.50 (m, 20H), 0.93 (t, J=6.8 Hz, 15H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 149.08, 149.04, 148.96, 148.85, 148.35, 124.05, 123.73, 123.57, 123.48, 123.40, 108.33, 107.35, 107.16, 107.01, 106.83, 71.99, 70.84, 69.93, 69.73, 69.70, 69.60, 69.50, 69.46, 69.32, 59.07, 31.66, 29.40, 25.83, 22.64, 14.04. MS (MALDI): *m*/*z* 846.54 (M$^+$); calcd, 846.60.

2.2.7. 1-[3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-yloxy]-3,6,9-trioxadecane (2b). The synthetic procedure was the same as that for **1a** except that triethylene glycol monomethyl ether monotosylate was used. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.80–7.90 (m, 6H), 4.41 (t, J=4.8 Hz, 2H), 4.23 (t, J=6.4 Hz, 10H), 4.00 (t, J=4.8 Hz, 2H), 3.83 (t, J=4.8 Hz, 2H), 3.72 (t, J=4.8 Hz, 2H), 3.67 (t, J=4.8 Hz, 2H), 3.53 (t, J=4.8 Hz, 2H), 3.36 (s, 3H), 1.88–2.00 (m, 10H), 1.50–1.67 (m, 10H), 1.30–1.49 (m, 20H), 0.94 (t, J=6.8 Hz, 15H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 149.07, 149.03, 148.96, 148.87, 148.38, 124.05, 123.72, 123.57, 123.48, 123.40, 108.35, 107.34, 107.17, 107.02, 106.87, 71.88, 70.90, 70.70, 70.53, 69.95, 69.73, 69.70, 69.60, 69.52, 69.46, 69.34, 58.99, 31.66, 29.40, 25.82, 22.64, 14.03. MS (MALDI): *m*/*z* 890.63 (M$^+$); calcd, 890.63.

2.2.8. 1-[3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-yloxy]-3,6,9,12-tetraoxatridecane (2c). The synthetic procedure was the same as that for **1a** except that tetraethylene glycol monomethyl ether monotosylate was used. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.80–7.90 (m, 6H), 4.40 (t, J=4.8 Hz, 2H), 4.23 (t, J=6.4 Hz, 10H), 4.00 (t, J=4.8 Hz, 2H), 3.82 (t, J=4.8 Hz, 2H), 3.58–3.74 (m, 8H), 3.53 (t, J=4.8 Hz, 2H), 3.36 (s, 3H), 1.89–2.00 (m, 10H), 1.50–1.68 (m, 10H), 1.30–1.49 (m, 20H), 0.94 (t, J=6.8 Hz, 15H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 149.09, 149.05, 148.97, 148.88, 148.39, 124.06, 123.73, 123.58, 123.49, 123.41, 108.36, 107.37, 107.34, 107.17, 106.90, 71.88, 70.91, 70.68, 70.58, 70.57, 70.48, 69.95, 69.74, 69.73, 69.62, 69.53, 69.47, 69.37, 59.00, 31.67, 29.40, 25.84, 22.65, 14.05. MS (MALDI): *m*/*z* 934.57 (M$^+$); calcd, 934.65.

3. Results and discussion

3.1. *Liquid crystalline properties*

The thermal properties of triphenylene-based triblock molecules **1a**–**e** are given in table 1. The LC behaviour of the discotic dimers is greatly dependent on the length of the ethylene oxide linkers. The discotic dimers having shorter ethylene oxide chains (**1b**,**c**) (n=4, 5) exhibit enantiotropic hexagonal columnar (Col$_h$) phases, whereas **1a** exhibits a monotropic Col$_h$ phase. In contrast, the dimers having longer ethylene oxide chains (**1d**,**e**) (n=6, 8) do not show LC phases. Figure 3(*a*) shows a photomicrograph of the texture of the Col$_h$ phase for **1b** observed on cooling from the isotropic (I)

Table 1. Phase transition behaviour of triphenylene derivatives containing ethylene oxide chains: **1a–e**, **2a–c** and 2,3,6,7,10,11-hexa(hexyloxy)triphenylene (**3**). Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) determined by DSC (5°C min^{-1}) and polarizing optical microscopy. Col$_h$=hexagonal columnar; Cr=crystalline; I=isotropic.

Compound	1st cooling					2nd heating				
1a (n=3)	I	54 (3)	Col$_h$	20 (39)	Cr	Cr	77 (57)			I
1b (n=4)	I	91 (11)	Col$_h$	0 (53)	Cr	Cr	50 (63)	Col$_h$	93 (12)	I
1c (n=5)	I	77 (6)	Col$_h$	17 (52)	Cr	Cr	50 (57)	Col$_h$	83 (6)	I
1d (n=6)	I			17 (52)	Cr	Cr	43 (57)			I
1e (n=8)	I			16 (59)	Cr	Cr	38 (65)			I
2a (n=2)	I	67 (2)	Col$_h$	40 (30)	Cr	Cr	57 (31)	Col$_h$	72 (1)	I
2b (n=3)	I			22 (52)	Cr	Cr	43 (57)			I
2c (n=4)	I			22 (59)	Cr	Cr	38 (65)			I
3[a]	I	98	Col$_h$	54	Cr	Cr	68 (57)	Col$_h$	100	I

[a] Ref. [1].

phase under crossed polarizers. The six-fold symmetry, figure 3 (*b*), observed for **1a–c** on cooling from the isotropic melt suggests the formation of Col$_h$ phases.

To examine the effects of the dimeric block structures, monomeric compounds containing the single ethylene oxide chains **2a–c** were prepared (figure 2). Compound **2a** alone exhibits a Col$_h$ phase, while **2b** and **2c** do not show LC phases (table 1). Compound **2a** has already been reported by Bushby and co-workers [45]. It is of interest that the dimer series of **1** shows wider mesomorphic temperature ranges than the monomer series of **2**. For example, **1b** exhibits a Col$_h$ phase from 91 to 0°C on cooling, while the corresponding monomer **2a** shows the mesophase from 67 to 40°C on cooling. When the length of the ethylene oxide chains of the molecules increases, no LC phases are observed for either series of triphenylene derivatives **1** and **2**. The melting and isotropization temperatures of series **1** and **2** are lower than that of 2,3,6,7,10,11-hexa(hexyloxy)-triphenylene (HAT6) (**3**), which is a basic discogen in the design of **1** and **2**. For example, **1c** exhibits the Col$_h$ phase between 77 and 17°C, and **3** shows the Col$_h$ phase between 98 and 54°C on cooling. The introduction of longer ethylene oxide moieties to the discogen leads to the depression of crystallization behaviour. It should be noted that room temperature Col$_h$ phases are induced for **1b** and **1c** on cooling. The XRD pattern for the Col$_h$ phase of **1c** gives two peaks with *d*-spacings of 18.6 and 3.6 Å, which correspond to the (1 0 0) and (0 0 1) reflections, respectively. The latter one can be ascribed to $\pi-\pi$ interaction between the stacked triphenylene cores. Based on the XRD patterns, the column–column distance of **1c** is estimated to be 21.4 Å, while the distance for **3** is 21.6 Å. The lattice parameters of **1a–c** are almost equal to those of **2a** and **3** irrespective of the length of ethylene oxide chains.

3.2. *The addition of lithium triflate*

The effects of the salt concentration on the phase transition behaviour were examined for the lithium triflate (LiOTf) complexes based on **1b**. The mixtures were prepared by slow evaporation of the tetrahydrofuran solution of the dimeric compound and requisite amounts of LiOTf [31–36]. Figure 4 presents the DSC thermograms of **1b** containing various amounts of

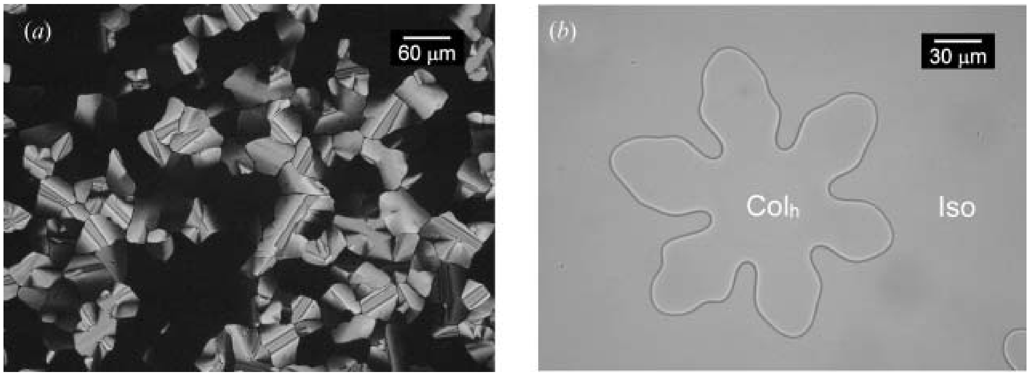


Figure 3. (*a*) Polarizing optical photomicrograph of **1b** in the Col$_h$ phase at 60°C on cooling. (*b*) Optical photomicrograph of **1b** aligned homeotropically in the Col$_h$ phase on cooling from the isotropic melt.

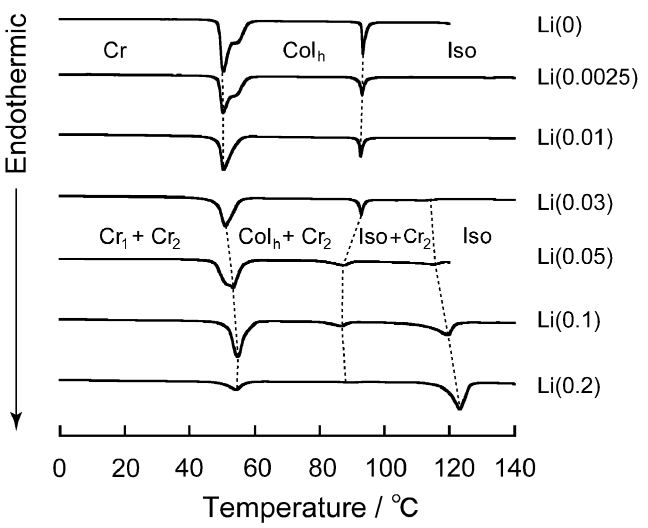


Figure 4. DSC thermograms of mixtures of **1b** and LiOTf on the 2nd heating.

LiOTf (0.0025, 0.01, 0.03, 0.05, 0.1 and 0.2 molar ratio per ethylene oxide unit) on the 2nd heating. Figure 5 shows a phase diagram for the binary mixtures of **1b** and LiOTf.

For mixtures containing a fraction of LiOTf smaller than 0.01, **1b** and LiOTf are miscible and the mixtures show Col$_h$ phases. In contrast, for mixtures containing a fraction of LiOTf larger than 0.03, a crystal phase (Cr$_2$) that is immiscible with the columnar phase is induced, leading to the formation of biphasic structures. The biphasic state composed of the crystal (Cr$_2$) and isotropic phases is also observed above 93°C, while only the isotropic phase is seen for the single component **1b**. When the fraction of LiOTf increases, the enthalpy changes of the melting of the Cr$_2$ phase on heating increase. These results suggest that triphenylene molecule **1b** and LiOTf interact strongly and form a stable crystalline complex. Bushby and co-workers reported that complexes of LC triphenylene and an electron acceptor were immiscible with triphenylene derivatives or electron acceptor alone [46]. The addition of LiOTf to triphenylene-based molecule **1b** might also induce the formation of charge-transfer complexes.

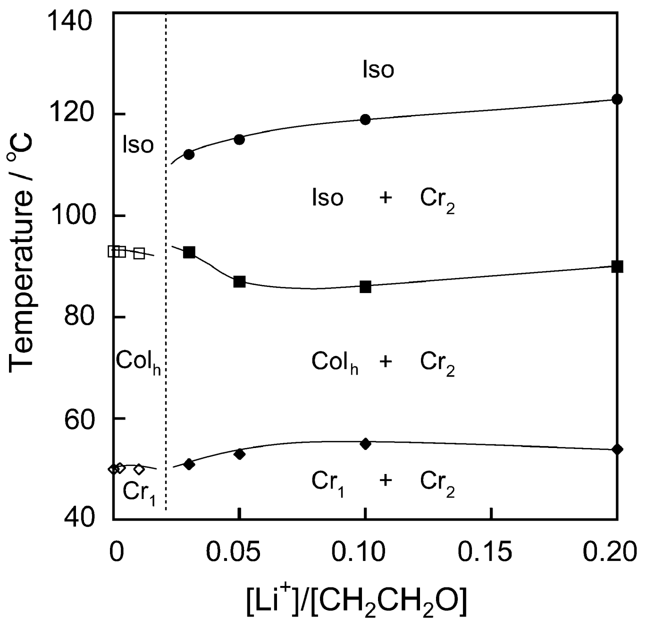


Figure 5. Phase transition behaviour for mixtures of **1b** and LiOTf on the 2nd heating; Iso=isotropic, Cr$_1$=crystalline, Cr$_2$=crystalline, Col$_h$=hexagonal columnar.

4. Conclusions

The introduction of ethylene oxide chains into triphenylene-based molecules lowers the melting and isotropization temperatures of the molecules. For the triphenylene–oligo(ethylene oxide)–triphenylene block molecules, liquid crystallinity is critically dependent on the length of the oligo(ethylene oxide) spacers. The lithium salt complexes of a triphenylene-based triblock compound show a single LC phase at lower concentration. For the disc molecules, the rigid triphenylene parts transport holes, while for the rod–coil–rod molecules studied previously, the rigid part is not conductive. These triphenylene–oligo(ethylene oxide)–triphenylene block molecules can function as anisotropic materials transporting both ions and holes for new types of electronic devices.

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