Effects of thiophene-based mesogen terminated with branched alkoxy group on the temperature range and electro-optical performances of liquid crystalline blue phases

Weikai Zhang, WanLi He, Chenchen Di, Xin Wang, Zhou Yang, Dong Wang, Hui Cao, Dengke Yang, and Huai Yang

Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, P.R. China; Chemical Physics Interdisciplinary Program, Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA; Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing, P.R. China

ABSTRACT
A series of symmetrically thiophene-based bent-shaped molecules with branched terminal was synthesised and characterised. Then, their effects as dopants on the blue phase (BP) range of the chiral nematic liquid crystal (N*LC) host were investigated. It was found that the bent-shaped dopants with branched terminal had better miscibility in LC host than the bent-shaped dopants with straight terminal, and contributed to induce BP and enhance the BP temperature range, with the maximum BP temperature range about 20.4°C. Besides, the electro-optical (E-O) performances of the blue phase liquid crystal doped with Th-BC6 (a bent-shaped dopant with the widest induced BP range in N*LC) were also explored. It was found that the drive voltage reduced first and then increased with the doping amount of Th-BC6 increasing. When the doping amount of Th-BC6 was about 15 wt%, the hysteresis could be strikingly reduced.

ARTICLE HISTORY
Received 16 August 2015
Accepted 22 November 2015

KEYWORDS
Blue phase; bent-shaped molecules; liquid crystal; branched terminal; electro-optical performances

CONTACT Wan Li He hewanli@mater.ustb.edu.cn; Huai Yang Yanghuai@pku.edu.cn
Supplemental data for this article can be accessed here.

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1. Introduction

Liquid crystalline blue phases (BPs) which appear between the isotropic and chiral nematic states have sparked enormous interest in recent decades.[1–6] BPs are built from double-twist cylinders which are self-assembled and form three-dimensional cubic lattices. [7,8] Such an arrangement endows BPs possess unique optical properties and great potential applications as fast-response display and tunable photonic crystals. [9,10] However, some bottleneck problems of the BPs block its applications. The serious one is the narrow temperature range, usually less than a few Kelvins. To resolve this problem, some attempts were carried out, including stabilising the BPs with a polymer network, [11] hydrogen bond [12] or nanoparticles [13,14] and using low-weight molecules [15] such as T-shaped molecules [16] and bent-core molecules.[17]

Among these methods, bent-shaped molecules stabilised BPs are considered as one promising route that had attracted much interest. It has already been theoretically predicted that biaxiality,[18] flexo-electricity [19] and elasticity [20] of LC materials play an important role in stabilising BPs. Fortunately, bent-shaped molecules possess all of these characteristics.[21] To obtain wide blue phase (BP) range in the systems possessing molecular biaxiality, many bent-shaped compounds with the moieties have been investigated by either blending them with the high twisted power chiral dopants or doping them into the chiral nematic liquid crystal (N*LC). Among these liquid crystal mixtures, the BPs were reported over a temperature range of 20–30°C. [22–30] Recently, thiophene-based bent-shaped mesogens were used as dopants in blue phase liquid crystal (BPLC), extending the BPs temperature range to about 25.9°C.[17] However, most liquid crystalline composites have the disadvantages of high viscosity, poor compatibility, complicated synthesis and high phase-transition temperature.

In order to solve these problems, the structure of bent-shaped molecules was developed in our study. As mentioned earlier, the incorporation of thiophene as a core fragment in the mesogen contributes to an increase of optical anisotropy, a decrease of the melting point, a promotion of a negative dielectric anisotropy, a reduction in viscosity and fast switching times.[31,32] Herein, we design the materials with a 2,5-substituted thiophene moiety as a central element of the mesogen and synthesised a series of symmetrically thiophene-based bent-shaped molecules with branched terminal which was expected to reduce the viscosity, lower the melting point and improve the miscibility with liquid crystal. It was found in this study that thiophene-based bent-shaped dopants could effectively induce and enhance BP in the host N*LC as well as improve the electro-optical (E-O) performances of BPLC. The thermotropic liquid-crystalline behaviours of all the bent-shaped compounds, their effects on the BP range of the LC host and the E-O performances are presented in detail later.

2. Experimental

2.1. Materials

The liquid crystal material was a mixture comprising the following materials: SLC7011-100 (92.0 wt%, Yongsheng Huatsing Liquid Crystal Co., Ltd., Δε = 16.1 at 298 K, cleaning point = 68.2°C) and Iso-(8OBA)2 (8.0 wt%, synthesised in our laboratory). 2,5-dibromothiophen and 3,7-dimethyl-1-octanol were purchased from J&K Technology Co., Ltd. 4-methylphenylboronic acid was purchased from Energy Chemical. 2-ethylhexyl bromide was purchased from Alfa Aesar (Tianjin) Chemical Co., Ltd. S-(-)-octanol was purchased from Sdano Fine Chemical Co., Ltd. 4-toluene sulphonyl chloride was purchased from Beijing Chemical Reagent Company. 4-hydroxy-cinnamic acid was purchased from Aladdin. 4-[(2-ethylhexyl)oxy] benzoic acid was synthesised in our laboratory. Other solvents and medicines were purchased from Beijing Lan Yi Chemical Products Co., Ltd.

2.2. Synthesis

The synthesis of thiophene-based bent-shaped molecules with different branched terminals was carried out according to Scheme 1. And the chemical structures of the bent-shaped molecules and chiral dopant were shown in Figure 1.

2.2.1. Synthesis of 2,5-bis(4-methoxyphenyl) thiophene

A 500 mL round-bottomed flask was charged with 4-methylphenylboronic acid (17.59 g, 115 mmol), CTMAB (1.56 g, 5 wt%) and PdCl2(PPh3)2 (0.52 g, 0.5 mol%). Then, saturated K2CO3 solution (60 mL), THF (80 mL) and 2,5-dibromothiophen (10.14 g, 42 mmol) were added dropwise to the mixture under nitrogen atmosphere. The mixture was refluxed at 70°C for 15 h. After reaction, the mixture was cooled to room temperature. The crude product was extracted with dichloromethane and dried over anhydrous MgSO4. After evaporation of the solvent, the crude product was purified by silica column chromatography eluting with petroleum ether/dichloromethane (V:V = 3:1) as
Scheme 1. Synthetic routes of the intermediate and the final compounds. Reagents and conditions: (a) 4-methylphenylboronic acid, PdCl$_2$(PPh$_3$)$_2$/CTMAB, saturated K$_2$CO$_3$ solution/THF, reflux, 15 h; (b) pyridine hydrochloride, 150°C, 25 min; (c, d, e, f) K$_2$CO$_3$ (Kl), DMF (acetone), reflux, 40 h; (g, h) DCC/DMAP, R.T., 48 h; (i, II) (CH$_3$)$_3$ N-HCl, Et$_3$ N/CH$_2$Cl$_2$, 0°C, 5 h; (iii) KOH/KI, C$_2$H$_5$OH, reflux, 40 h.

Figure 1. Chemical structures of the thiophene-based bent-shaped molecules with different branched terminals and chiral dopant.
eluent to afford compound 2,5-bis(4-methoxyphenyl) thiophene; yield: 70%. FT-IR (KBr, cm\(^{-1}\)): 2958, 2838 (-CH\(_2\) stretching), 1605 (C=C shaking of benzene ring), 1501, 1279, 1250 (C–O–Ar stretching), 1180, 1030, 832, 796, 501. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.51–7.53 (d, \(J = 8.0\) Hz, 4H, ArH), 7.12 (s, 2H, ThH), 6.89–6.91 (d, \(J = 8.0\) Hz, 4H, ArH), 3.82 (s, 6H, Ar–O–CH\(_3\)).

### 2.2.2. Synthesis of 2,5-bis(4-hydroxyphenyl) thiophene

The procedure was modified as following.[33] A mixture of 2,5-bis(4-methoxyphenyl)thiophene (1.40 g, 4.7 mmol) and pyridine hydrochloride (6.00 g, 52 mmol) was placed in a stopped round-bottomed flask and subjected to microwave irradiation at 150°C for 25 min under nitrogen atmosphere. After complete conversion, pure water was added, and the product was filtered; yield: 95%. FT-IR (KBr, cm\(^{-1}\)): 3282 (–OH stretching), 1604 (C=C shaking of benzene ring), 1498, 1250, 1170, 1030, 828, 801, 493. \(^1\)H NMR (400 MHz, DMSO, \(\delta\)): 9.64 (s, 2H, Ar-OH), 7.44–7.46 (d, \(J = 8.0\) Hz, 4H, ArH), 7.24 (s, 2H, ThH), 6.78–6.80 (d, \(J = 8.0\) Hz, 4H, ArH).

### 2.2.3. Synthesis of 2,5-bis(4-(hexyloxy)phenyl) thiophene (Th-BC1)

A mixture of 2,5-bis(4-hydroxyphenyl)thiophene (1.12 g, 4.2 mmol), bromohexane (2.00 g, 12.1 mmol), K\(_2\)CO\(_3\) (2.00 g, 14.5 mmol), KI (0.26 g) and acetone (200 mL) was placed in a 500 mL round-bottomed flask, and the mixture was refluxed at 60°C for 40 h. After reaction, the mixture was evaporated to remove the solvent. Then, the crude product was extracted with dichloromethane (500 mL) and washed with water, dried over anhydrous MgSO\(_4\) and finally evaporated. The resulting residue was purified via column chromatography eluting with petroleum ether/dichloromethane (V:V = 3:1) to afford compound 2,5-bis(4-(hexyloxy)phenyl)thiophene; yield: 60%. FT-IR (KBr, cm\(^{-1}\)): 2931, 2857 (–CH\(_2\)–, –CH\(_3\) stretching), 1606 (C=C shaking of benzene ring), 1498, 1276, 1246 (C–O–Ar stretching), 1178, 1119, 943, 833, 798. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.49–7.51 (d, \(J = 8.0\) Hz, 4H, ArH), 7.11 (s, 2H, ThH), 6.86–6.88 (d, \(J = 8.0\) Hz, 4H, ArH), 4.33–4.38 (d, \(J = 20.0\) Hz, 4H, Ar–O–CH\(_2\)–), 1.29–1.74 (m, 26H, –CH(CH\(_3\))\(_2\)–(CH\(_2\))\(_2\)–), 0.85–0.88 (m, 6H, –CH\(_3\)).

### 2.2.4. Synthesis of 2,5-bis(4-(octan-2-ylxylo)phenyl) thiophene (Th-BC2)

To synthesise the intermediate product(I), a mixture of S-(+)-octanol (5.00 g, 39 mmol), triethylamine (7.90 g, 78 mmol), trimethylamine hydrochloride (3.72 g, 39 mmol) and dichloromethane (100 mL) was placed in a 500 mL round-bottomed flask and transferred to ice-water bath. Then, 4-toluene sulphonyl chloride (8.98 g, 47 mmol) was dissolved in dichloromethane (100 mL) and slowly added via pressure-equalised dropping funnel to the mixture. The reaction mixture was stirred for 5 h. After reaction, the white precipitate was filtered off, and the filtrate was washed by water, dried over anhydrous MgSO\(_4\) and finally evaporated to give the product (I) S(+)-2-methyl-octyl-4-methyl-benzene-sulphonate; yield: 80%.

A 500 mL round-bottomed flask was charged with 2,5-bis(4-hydroxyphenyl)thiophene (1.14 g, 4.2 mmol), S(+)-2-methyl-octyl-4-methyl-benzene-sulphonate (5.07 g, 17.9 mmol), K\(_2\)CO\(_3\) (2.50 g, 18.1 mmol) and acetone (200 mL). The mixture was refluxed at 80°C for 40 h. After reaction, the mixture was evaporated to remove the solvent. Then, the crude product was extracted with dichloromethane (500 mL) and washed by water, dried over anhydrous MgSO\(_4\) and finally evaporated. The resulting residue was purified via column chromatography eluting with petroleum ether/dichloromethane (V:V = 3:1) to afford compound 2,5-bis(4-(octan-2-ylxylo)phenyl)thiophene; yield: 56%. FT-IR (KBr, cm\(^{-1}\)): 2935, 2861 (C=C stretching), 1606 (C=C shaking of benzene ring), 1501, 1279, 1250 (C–O–Ar stretching), 1180, 1030, 828, 801, 493. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.49–7.52 (d, \(J = 12.0\) Hz, 4H, ArH), 7.12 (s, 2H, ThH), 6.89–6.91 (d, \(J = 8.0\) Hz, 4H, ArH), 3.98 (t, \(J = 12.0\) Hz, 4H, ArH), 1.29–1.74 (m, 26H, –CH(CH\(_3\))\(_2\)–(CH\(_2\))\(_2\)–), 0.88–0.91 (m, 6H, –CH\(_3\)).
To synthesise the final product, a mixture of 2,5-bis (4-hydroxyphenyl)thiophene (1.21 g, 4.5 mmol), 4-((2-ethylhexyl)oxy)cinnamic acid (2.86 g, 10.4 mmol), DCC (2.14 g, 10.4 mmol), DMAP (0.68 g) and dichloromethane (200 mL) was placed in a 500 mL round-bottomed flask. The mixture was stirred at room temperature for 48 h. After reaction, the crude product was filtered and evaporated to remove the solvent. The resulting residue was purified via column chromatography eluting with petroleum ether/dichloromethane (V:V = 1:4) to give the product; yield: 51%. FT-IR (KBr, cm⁻¹): 2958, 2920, 2872 (–CH₂–, –CH₃ stretching), 1611 (C=O stretching), 1630 (C=C stretching), 1603 (C=C shaking of benzene ring), 1512, 1288, 1250 (C=O–Ar stretching), 1163, 1143, 827, 520.¹H NMR (400 MHz, CDCl₃, δ): 7.81–7.85 (d, J = 16.0 Hz, 2H, Ar–CH=CH–), 7.62–7.64 (d, J = 8.0 Hz, 4H, ArH), 7.51–7.53 (d, J = 8.0 Hz, 4H, ArH), 7.24 (s, 2H, ThH), 7.18–7.20 (d, J = 8.0 Hz, 4H, ArH), 6.91–6.93 (d, J = 8.0 Hz, 4H, ArH), 6.46–6.50 (d, J = 16.0 Hz, 2H, Ar–CH=CH–), 3.87–3.88 (d, J = 4.0 Hz, 4H, Ar–OCH₂–), 1.70–1.74 (m, 2H, Ar–OCH₂CH (CH₂CH₃)–), 1.29–1.50 (m, 16H, –CH(CH₂CH₃)–(CH₃)₃), 0.87–0.92 (m, 12H, –CH₃).

2.2.8. Synthesis of 2,5-bis(4-((2-ethylhexyl)oxy)benzoate)phenyl)thiophene (Th-BC6)
To synthesise 2,5-bis(4-((2-ethylhexyl)oxy)benzoate)phenyl)thiophene, 2,5-bis(4-hydroxyphenyl)thiophene (0.76 g, 2.8 mmol) and 4-((2-ethylhexyl)oxy)benzoic acid (1.73 g, 6.9 mmol) were used. The crude product was purified via column chromatography eluting with petroleum ether/dichloromethane (V:V = 1:1) to afford the product; yield: 38%. FT-IR (KBr, cm⁻¹): 2958, 2928, 2860 (–CH₂–, –CH₃ stretching), 1725 (C=O stretching), 1604 (C=C shaking of benzene ring), 1509, 1255 (C=O–Ar stretching), 1210, 1163, 1070, 840, 792, 692.¹H NMR (400 MHz, CDCl₃, δ): 8.07–8.09 (d, J = 8.0 Hz, 4H, ArH), 7.59–7.62 (d, J = 12.0 Hz, 4H, ArH), 7.20–7.21 (d, J = 4.0 Hz, 4H, ArH), 7.19 (s, 2H, ThH), 7.16–7.17 (d, J = 4.0 Hz, 4H, ArH), 3.86–3.87 (d, J = 4.0 Hz, 4H, Ar–OCH₂–), 1.69–1.73 (m, 2H, Ar–OCH₂CH (CH₂CH₃)–), 1.20–1.47 (m, 16H, –CH(CH₂CH₃)–(CH₃)₃), 0.87–0.92 (m, 12H, –CH₃).

2.3. Measurements
The chemical structures of the synthesised compounds were identified by the ¹H NMR (Bruker DMX-300) and FT-IR spectrometer (Nicolet 510P).
The phase assignments and corresponding transition temperatures for the final compounds were determined by using the thermal optical microscopy with a polarising microscope (Olympus BX-51) equipped with a hot stage calibrated to an accuracy of ±0.1°C (Linkam LK-600PM). The temperatures and enthalpies of the transition were investigated using differential scanning calorimetry (DSC, Mettler DSC822e) at a heating rate of 10.0°C/min under a dry nitrogen purge. Electro-optic performances were investigated using Tektronics AFG3011 C with the applied voltage changed by 5 V each time during the voltage-rising process and the decaying process. The voltage–transmittance (VT) curve was measured by placing the in-plane switching (IPS) cell between two crossed polarisers. The electrode direction of the cell was oriented at ±45° to the polariser’s transmittance axis to reach maximum transmittance. The testing wavelength was 633 nm. The cell was driven by a square-wave signal with a frequency of 1 kHz. The rise time was defined as the time for the transmittance to change from 10% to 90% of the maximum transmittance, and the decay time was the time that the transmittance changes from 90% to 10% of the maximum transmittance.

3. Results and discussion

3.1. Mesomorphic properties of the thiophene-based bent-shaped compounds

Table 1 shows the thermotropic liquid crystalline behaviours of the thiophene-based bent-shaped compounds. It could be found that the compounds Th-BC2, Th-BC3 and Th-BC4 show no mesogenic properties, while the compounds Th-BC1, Th-BC4 and Th-BC5 exhibited polymorphism. Moreover, increasing the length and the number of side chains linked to the terminal alkoxy chain decreased the melting temperature. Besides, the more rigid groups in the bent-core compounds, the higher phase-transition temperature and melting temperature the compounds had.

| Compounds | Phase transition (°C) and enthalpy (J/g) heating/cooling |
|-----------|---------------------------------------------------------|
| Th-BC1    | Cr 161.6 (52.6) N 176.7 (2.6) Iso/Iso 174.8 (3.4) N 154.9 (47.7); Cr |
| Th-BC2    | Cr 37.1 (28.2) Iso/Iso 8.7 (14.9); Cr |
| Th-BC3    | Cr 50.7 (55.6) Iso/Iso 29.9 (52.5); Cr |
| Th-BC4    | Cr 109.3 (49.0) Iso/Iso 100.1 (50.1); Cr |
| Th-BC5    | Cr 124.9 (39.4) SmA 250.8 (0.5) Iso/Iso 246.6 (0.4) SmA 88.7 (32.6); Cr |
| Th-BC6    | Cr 116.7 (32.7) SmC 125.8 (0.9) N 177.4 (0.2) Iso/Iso 174.6 (0.2) N 123.0 (0.5) SmC 91.6 (34.3); Cr |

Note: Cr, crystalline; Sm, smectic phase; N, nematic phase; Iso, isotropic liquid.

Compound Th-BC1 formed a nematic phase. However, compounds Th-BC2, Th-BC3 and Th-BC4 had lower melting point and were not easy to form the liquid crystalline phase which may result from the fact that the introducing branched terminal would distract the conjugation of benzene ring and had a negative impact on the rigidity of the molecules.[34] The L/D ratio of these compounds could not reach the requirements of forming the liquid crystalline phase, which maybe another reason. When lengthening the rigid cores by introducing the cinamate group or benzoate group, compound Th-BC5 formed a SmA phase and compound Th-BC6 formed a SmC phase and a nematic phase, which means that the introduction of rigid cores and extending the length of the rigid groups would make it more favourable for the formation of a mesophase.

3.2. Effect of the chiral dopant on thiophene-based bent-shaped compounds

As is known BP only occurs in a chiral system. Introducing the chirality in LC systems is a key point to induce the BP. Herein, the transition behaviour of binary mixtures of thiophene-based bent-shaped compounds and a chiral compound Iso-(8OBA)_2 was investigated. For the three bent-shaped thermotropic mesogens (compounds Th-BC1, Th-BC5 and Th-BC6), when doped with Iso-(8OBA)_2, the mixture of compound Th-BC1 and chiral compound could not form BP.

However, when doped with a small percentage (5.0–10.0 wt%) of Iso-(8OBA)_2, compounds Th-BC5 and Th-BC6 could form BP. As shown in Figure 2(a), the BP range in the mixtures of Th-BC5 and Iso-(8OBA)_2 appeared to expand with the concentration of the chiral dopant increased. In the case of the mixture blended with 10.0 wt% chiral dopants, the temperature range of BP was extended to 8.0°C and the POM texture of blue phase I (BPI) in the systems was as shown in Figure 3(a). In comparison, as shown in Figure 2(b), the BP range in the mixtures of Th-BC6 and Iso-(8OBA)_2 was wider than the mixtures of Th-BC5 and Iso-(8OBA)_2 with the same chiral dopant, and the widest BP range was extended to 18.2°C when the mixture blended with 10.0 wt% chiral dopants. Besides, as shown in Figure 3(b), the typical colourful platelets were also observed in the systems with a high concentration of the chiral dopant, which indicated a typical BP. The reason of stabilising and extending BPs could be explained due to the Landau theory,[35–37] increasing the chiral parameter allowed BPs to exist. With the increase of the concentration of the chiral dopant, the double-twisted arrangement of BPLCs was further enhanced.
3.3. Effect of thiophene-based bent-shaped compounds on the BP range of N*LC

As presented in Table 2, the effects of these thiophene-based bent-shaped compounds on the BP range and the solubility of the liquid crystal system and thiophene-based bent-shaped compounds were investigated in detail. Here, the N*LC host formed no BP which contains 92 wt% SLC7011-100 and 8 wt% Iso-(8OBA)$_2$, and the transition temperature from isotropic to nematic was 56.1°C. From Table 2, it was found that the samples containing compound Th-BC1 or Th-BC2 could not induce BPs. This could be explained due to the fact that the bent angle was too small to stabilise the BPs. However, to our surprise, as shown in Table 2 and Figure 4(a), when doped with compounds Th-BC3, Th-BC4, Th-BC5 and Th-BC6, the BPs could be induced and stabilised. The systems doped with non-mesogenic compound Th-BC3 or Th-BC4 could extend the BP range to 7.6°C and 7.8°C. In comparison, when doped with mesogenic compound Th-BC5 or Th-BC6, the mixtures show the widest BP range of 11.5°C and 20.4°C. Figure 3(c) shows the typical POM texture of BPI in N*LC doped with 10 wt% Th-BC3, while Figure 3(d) shows the typical colourful platelets of the N*LC doped with 10 wt% Th-BC4. Besides, as shown in Figure 4(b), with 15 wt% of doping compounds, Th-BC4, Th-BC5 and Th-BC6 induced wider

Figure 2. (colour online) Blue phase range for mixtures of thiophene-based molecules and Iso-(8OBA)$_2$ on cooling: (a) Th-BC5; (b) Th-BC6.

Figure 3. (colour online) POM photos of the natural textures of BPs in the mixtures. (a) Compound Th-BC5 blended with 10 wt% Iso-(8OBA)$_2$; (b) compound Th-BC6 blended with 9 wt% Iso-(8OBA)$_2$; (c) BPI in N*LC doped with 10 wt% Th-BC3; (d) BPI in N*LC doped with 10 wt% Th-BC6.
BPs compared with chiral compound R811, which means that these compounds could effectively replace R811.

Comparing all the results, it was not difficult to find that there is a great difference in the BP range and the miscibility among the samples containing the thiophene-based bent-shaped molecules with different rigid cores and branched terminal. First of all, the BPLC doped with the bent-shaped molecules with grafted less rigid cores were easier to form phase separation. When the bent-shaped molecules had more ester-connecting rigid cores and formed mesophase, the miscibility with the N*LC host could be improved, and the maximum doping amount was about 50 wt%. Second, the molecules grafted with branched terminal used as dopants in N*LC were more likely to induce and enhance BP. Besides, when doping the same amount of bent-shaped compounds, Th-BC5 and Th-BC6 induced wider BPs compared with Th-BC3 and Th-BC4. This could be due to the fact that Th-BC5 and Th-BC6 formed mesophase and possessed better miscibility with the N*LC host, and the miscibility and the shape or conformation of the bent-shaped molecules significantly contributed to the stabilization of BPs. Improving their miscibility enhances the ability of chiral transfer between a chiral dopant and a guest material, and extending the rigid body of bent-shaped molecules increases their biaxiality and dipole moment, which are vital aspects for inducing and enhancing BP.

### 3.4. Electro-optical performances

In this experiment, the E-O performances in the BPI of Th-BC6 doping composites were investigated due to its better effect on inducing and enhancing the stability of BPs as well as BP temperature range. The mixtures were injected into the IPS cells with electrode width 5.0 µm, cell gap 10.0 µm and electrode gap 5.0 µm. The samples in IPS...
cells were placed at an inclination angle of 45° with respect to incident light, and the temperature was controlled with a hot stage. Then, the E-O performances were investigated using Tektronics AFG3011 C with the applied voltage changed by 5 V each time during the voltage-rising process and the decaying process.

Figure 5 shows the voltage–transmittance (V-T) curve for BPI in the N*LC doped with Th-BC6: (a) 5.0 wt%; (b) 10.0 wt%; (c) 15.0 wt%; (d) 20.0 wt%; (e) 25.0 wt%; (f) 30.0 wt%.

Figure 5. (colour online) Normalised voltage–transmittance curves of BPI in the N*LC doped with Th-BC6: (a) 5.0 wt%; (b) 10.0 wt%; (c) 15.0 wt%; (d) 20.0 wt%; (e) 25.0 wt%; (f) 30.0 wt%.

Interestingly, when doped with 15 wt% Th-BC6, the drive voltage was just 12.0 V and the saturation voltage was 26.9 V, which was lower than the other samples. When the doping amount of Th-BC6 was more than 20 wt%, the drive voltage was amplified, which may result from the fact that the cubic structures of BPI would be disordered when doping the excessive amount of the Th-BC6. Besides, BPI of sample F5 and F6 could never reverse again after being switched with the electric field when the applied voltage was too high, which may be caused by the electric field–induced phase transition. The drive voltage ($V_{\text{on}}$), saturation voltage ($V_{\text{sat}}$), rise time and decay time are shown in Table 3. As presented in Table 3, the rise time and decay time of all the four samples were less than 1 ms. Interestingly, when doped with 15 wt% Th-BC6, the drive voltage was just 12.0 V and the saturation voltage was 26.9 V, which was lower than the other samples. When the doping amount of Th-BC6 was less than 20 wt%, the increase of viscosity of the mixture was small and acceptable. However, the viscosity of the mixture became larger and caused an irreversible phase transition in an external electric field, when the amount of Th-BC6 was added more than 20 wt%, which indicated that a small doping
amount of Th-BC6 was beneficial to improve optical performance. Figure 6 shows Kerr constants for the BPI of samples F1–F4. It was found that Kerr constant increases at first and then decreases with the doping amount of Th-BC6 increases. As is known, the Kerr constant can be approximated by the following equation \[ K = \frac{\Delta n_{\text{induced}}}{\lambda E^2} \approx \Delta n \Delta \varepsilon \frac{\varepsilon_0 P^2}{k\lambda(2\pi)^2} \] (1) where \( \Delta n_{\text{induced}} \) is the induced birefringence; \( \Delta n, \Delta \varepsilon \) and \( k \) are the intrinsic birefringence, dielectric anisotropy and elastic constant of the host LC materials, respectively; and \( P \) is the pitch length. The incorporation of a thiophene moiety as a core fragment in the mesogen is known to contribute to a promotion of the negative dielectric anisotropy,\[32\] therefore, as the doping amount of Th-BC6 increases, \( \Delta \varepsilon \) of the liquid crystalline composites may increase first and then decrease, and \( \Delta \varepsilon \) may be one of the reasons for the change of Kerr constant.

4. Conclusions

In summary, a series of symmetrically thiophene-based bent-shaped molecules with branched terminal was synthesised. Due to the grafting of branched alkoxy group, the molecules with five rings were much easier to form mesophase than those with three rings. It was found that these compounds had better miscibility with LC host, and the maximum doping amount was about 50 wt%. When these compounds were used as dopants, BP could be induced in N*LC without BP before doping, and extended with maximum BP temperature range of about 20.4°C. In addition, it was found that the BPLC doped with Th-BC6 had a faster response speed, and the drive voltage reduced first and then increased with the increase of doping amount of Th-BC6. It was calculated that the Kerr constant increased first and then decreased. Besides, the hysteresis could be substantially reduced when the doping amount of Th-BC6 was 15 wt%. These observations could provide a new promising approach for designing of BPLC materials and stabilising BP.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Major Project of International Cooperation of the Ministry of Science and Technology [grant number 2013DFB50340], the National Natural Science Foundation of China [grant numbers 61370048, 51333001, 51173017, 51203011, 51103010]; the Fundamental Research Funds for the Central Universities [grant number FRF-TP-14-013A2].

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Table 3. Drive voltage \( (V_{\text{on}}) \), saturation voltage \( (V_{\text{sat}}) \), rise time and decay time of F1–F4.

| Samples | \( V_{\text{on}} \) (V) | \( V_{\text{sat}} \) (V) | Rise time (ms) | Decay time (ms) |
|---------|----------------|----------------|----------------|----------------|
| F1      | 15.1           | 36.1           | 0.71           | 0.52           |
| F2      | 14.8           | 34.0           | 0.55           | 0.53           |
| F3      | 12.0           | 26.9           | 0.73           | 0.53           |
| F4      | 15.6           | 36.8           | 0.57           | 0.63           |

Figure 6. (colour online) Kerr constants for the BPI of samples F1–F4.
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