

## Supporting Information to

### Novel Planar Chiral Dopants with High Helical Twisting Power and Structure-Dependent Functions

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## Experimental Section

### Materials

S-BINOL (Suzhou Soochiral chemistry), 4-Hydroxyphenylboronic acid (Suzhou Soochiral chemistry), 6-Bromohexanol (Energy Chemical), Lauryl alcohol (Shanghai Chemical Reagent, Shanghai, China), Tetraethyleneglycol monomethyl ether (J&K), Tetrabutylammonium fluoride (TBAF) solution (Energy Chemical, 1M in THF), Tetrakis (triphenylphosphine)-palladium(0) (97.0%; Sigma-Aldrich), P-Bromophenol (J&K), Diethyl azodicarboxylate (DEAD; Energy Chemical), Sodium azide (NaN<sub>3</sub>; Aldrich; ≥ 99.5 %), (3-Bromoprop-1-yn-1-yl) triisopropylsilane (Bengbu Nako Chemical Co., Ltd), Triphenylphosphine (J&K), Tetramethylethylenediamine (TMEDA; Energy Chemical), Chiral compounds S811 and R811 were purchased from Hecheng Display (China) Co., Ltd. Cuprous iodide (AR; Shanghai Chemical Reagents), Copper (I) bromide (CuBr; chemical pure; Shanghai Chemical Reagent, Shanghai, China) was purified via washing with acetic acid and acetone

and then dried in vacuum. Other reagents mentioned in this article were used directly after purchased without further purification.

### **Characterizations**

Ultraviolet visible (UV-vis) absorption spectra of the samples were recorded on a Shimadzu UV-2600 spectrophotometer at room temperature.

The CD spectra were recorded simultaneously at 25 °C on a JASCO J-815 spectropolarimeter equipped with a Peltier-controlled housing unit using an SQ-grade cuvette, with a path length of 10 mm (with a scanning rate of 100 nm/min, a bandwidth of 2 nm and a response time of 1 s, using a single accumulation).

All  $^1\text{H}$  NMR spectra were collected using a Bruker nuclear magnetic resonance instrument (300 MHz) using tetramethylsilane (TMS) as the internal standard at room temperature. NMR samples were prepared with concentrations of 7-10 mg/mL in  $\text{CDCl}_3$ . The  $^1\text{H}$  NMR spectra were referenced to  $\delta$  7.26 ppm in  $\text{CDCl}_3$ .

The elemental analysis was performed on a Vario EL elemental analysis instrument (Elementar (Donaustraße, Hanau, Germany)).

High-resolution mass spectra (HRMS) were recorded on a Bruker Esquire LC/Ion Trap Mass Spectrometer and JEOL/HX-110.

Powder X-ray diffraction (XRD) was performed on PANalytical X'pert Pro diffractometer using  $\text{Cu K}\alpha$  radiation at a scan speed of 0.1641 °/S.

Textures, reflected colors and disclination line distance changes were observed by polarized optical microscopy (Leika, DM2500P)

The phototuning property of cholesteric LC was examined with an IdeoOptics spectrometer (PG2000) collecting spectra in the dark.

### **Synthesis of TEG-phenylboronate (TEBP)**

The compound TEBP was synthesized according to the method reported in the literature. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford colorless viscous liquid with yield 77.6%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.73 (d, ArH, 2H), 6.93 (d, ArH, 2H), 4.19-4.12 (t, ArOCH<sub>2</sub>-, 2H), 3.90-3.81 (t, ArOCH<sub>2</sub>CH<sub>2</sub>-, 2H), 3.77-3.59 (m, -OCH<sub>2</sub>CH<sub>2</sub>O-, 10H), 3.57-3.50 (m, -CH<sub>2</sub>OCH<sub>3</sub>, 2H), 3.38 (s, -OCH<sub>3</sub>, 3H), 1.33 (s, -CH<sub>3</sub>, 12H).

### **Synthesis of Dodecanyl-phenylboronate (DOBP)**

The compound DOBP was synthesized as follow: 100 mL round bottomed flask was added 4-Hydroxyphenylboronic acid pinacol ester (3.0 g, 13.6 mmol), 1-bromododecane (8.47 g, 34 mmol), K<sub>2</sub>CO<sub>3</sub> (4.7 g, 34 mmol) and DMF 50 mL. The mixture was stirred at 70 °C for 15 h. Then the reaction solution was poured into deionized water and extracted by ethyl acetate. Afterwards, the organic phase was dried by anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated in a reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford colorless viscous liquid with yield 83.9%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.73 (d, ArH, 2H), 6.88 (d, ArH, 2H), 4.02-3.90 (t, ArOCH<sub>2</sub>-, 2H), 1.87-1.65 (m, -OCH<sub>2</sub>CH<sub>2</sub>-, 2H), 1.51-1.13 (m, 30H), 0.88 (t, -CH<sub>2</sub>CH<sub>3</sub>, 3H).

### **Synthesis of C1 and C2**

Compound C1 and C2 were synthesized according to literature procedure.<sup>S1, S2</sup>

## Synthesis of D1

A mixture of C1 (421 mg, 0.45 mmol), TEBP (555 mg, 1.35 mmol), Pd(0)(PPh<sub>3</sub>)<sub>4</sub> (26.3 mg, 0.0225 mmol), THF (7.5 mL) and aqueous 2M K<sub>2</sub>CO<sub>3</sub> (4.5 mL) were added into a 25 mL Schlenk tube. The mixture was degassed by three freeze–pump–thaw cycles, and the test tube was sealed under vacuum. After stirring at 90 °C for 24 h, the aqueous solution was removed and the organic phase was dried by anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated in a reduced pressure. The final crude product was purified by column chromatography (silica gel, THF/petroleum ether = 2/3, v/v) to obtain the compound D1 as red wax (0.31 g, yield: 67.1 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ(TMS, ppm): 8.11-6.98 (m, 34H, ArH), 4.57-4.24 (m, 8H, NaphthylOCH<sub>2</sub>-), 4.19 (t, 4H, ArCH<sub>2</sub>O-), 4.14 (m, 4H, phenyl-CH<sub>2</sub>O-), 3.38 (s, 6H, -OCH<sub>3</sub>). LC-MS m/z: [M]<sup>+</sup> calcd for C<sub>82</sub>H<sub>80</sub>N<sub>4</sub>O<sub>14</sub>Na<sup>+</sup>, 1367.5569; found, 1367.5602. EA: calculated for C<sub>82</sub>H<sub>80</sub>N<sub>4</sub>O<sub>14</sub>: C, 73.20 %; H, 5.99 %; N, 4.16 %. Found: C, 76.49 %; H, 6.13 %; 4.08%.

## Synthesis of D2

A mixture of C2 (400 mg, 0.48 mmol), TEBP (400 mg, 0.96 mmol), Pd(0)(PPh<sub>3</sub>)<sub>4</sub> (28.0 mg, 0.024 mmol), THF (8.0 mL) and aqueous 2 M K<sub>2</sub>CO<sub>3</sub> (4.8 mL) were added into a 25 mL Schlenk tube. The mixture was degassed by three freeze–pump–thaw cycles, and the test tube was sealed under vacuum. After stirring at 90 °C for 24 h, the aqueous solution was removed and the organic phase was dried by anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated in a reduced pressure. The final crude product was purified by column chromatography (silica gel, THF/chloroform = 1/10, v/v) to obtain the compound D2 as orange solid (0.44 g, yield: 89.2 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ(TMS, ppm): 8.29 (s, 1H, triazole), 7.96-6.83 (m, 24H, triazole & ArH), 5.15-5.00 (q, 2H), 4.25-3.52 (m, 24H), 3.73 (s, 3H, -OCH<sub>3</sub>), 1.91-

0.95 (m, 16H). <sup>1</sup>H NMR spectrum was shown in Figure 9. LC-MS m/z: [M]<sup>+</sup> calcd for C<sub>64</sub>H<sub>70</sub>N<sub>8</sub>O<sub>8</sub>H<sup>+</sup>, 1079.5395; found, 1079.5440. EA: calculated for C<sub>64</sub>H<sub>70</sub>N<sub>8</sub>O<sub>8</sub>: C, 71.22 %; H, 6.54 %; N, 10.38 %. Found: C, 71.63 %; H, 6.39 %; N, 10.69 %.

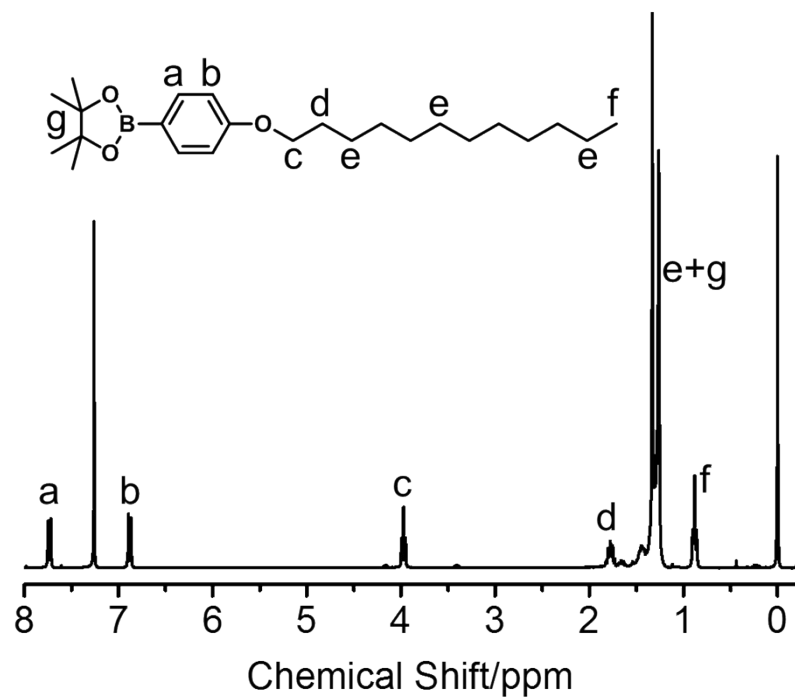
### Synthesis of D3

A mixture of C2 (400 mg, 0.48 mmol), DOBP (370 mg, 0.96 mmol), Pd(0)(PPh<sub>3</sub>)<sub>4</sub> (24.0 mg, 0.02 mmol), THF (6.0 mL) and aqueous 2 M K<sub>2</sub>CO<sub>3</sub> (4.0 mL) were added into a 25 mL Schlenk tube. The mixture was degassed by three freeze–pump–thaw cycles, and the test tube was sealed under vacuum. After stirring at 80 °C for 18 h, the aqueous solution was removed and the organic phase was dried by anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated in a reduced pressure. The final crude product was purified by column chromatography (silica gel, THF/petroleum ether = 1/1, v/v) to obtain the compound D3 as orange solid (0.45 g, yield: 91.8 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ(TMS, ppm): 8.29 (s, 1H, triazole), 7.96-6.83 (m, 24H, triazole & ArH), 5.15-5.00 (q, 2H), 4.23-3.80 (m, 10H), 1.90-0.86 (m, 39H). <sup>1</sup>H NMR spectrum was shown in Figure 10. LC-MS m/z: [M]<sup>+</sup> calcd for C<sub>67</sub>H<sub>77</sub>N<sub>8</sub>O<sub>4</sub>Na<sup>+</sup>, 1079.5887; found, 1079.5385. EA: calculated for C<sub>67</sub>H<sub>77</sub>N<sub>8</sub>O<sub>4</sub>: C, 76.11 %; H, 7.24 %; N, 10.60 %. Found: C, 76.26 %; H, 7.05 %; N, 10.43 %.

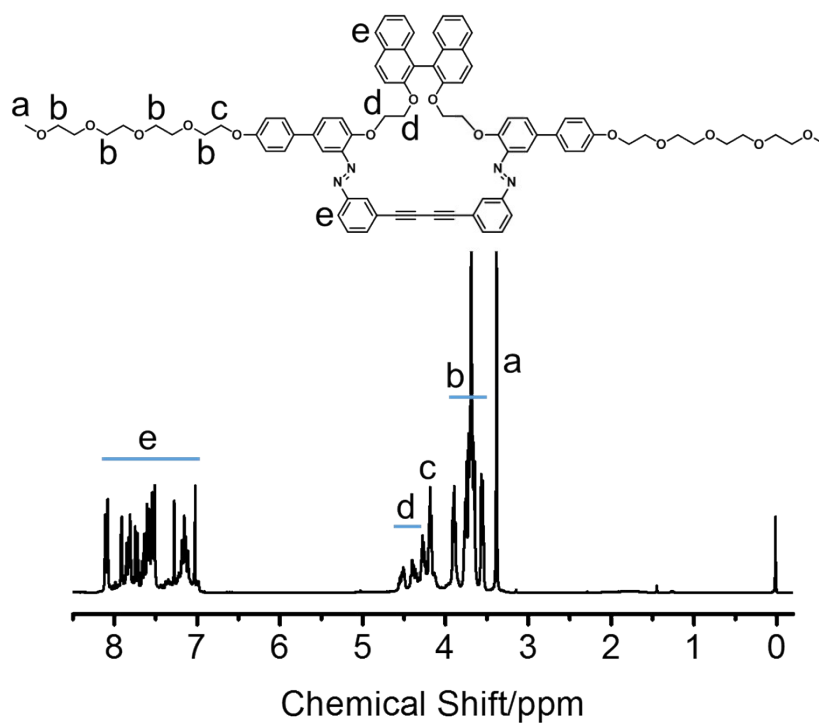
### Miscibility Test

The standard samples S1 and R1 were prepared by doping 10 wt% chiral dopants S811 (HCCH) and R811 (HCCH) into commercially available nematic liquid crystal E7 (HCCH), known to be left-handed and right-handed respectively. And the samples for measurements were prepared by doping 1 wt% chiral dopants (D1, D2, D3) into E7.

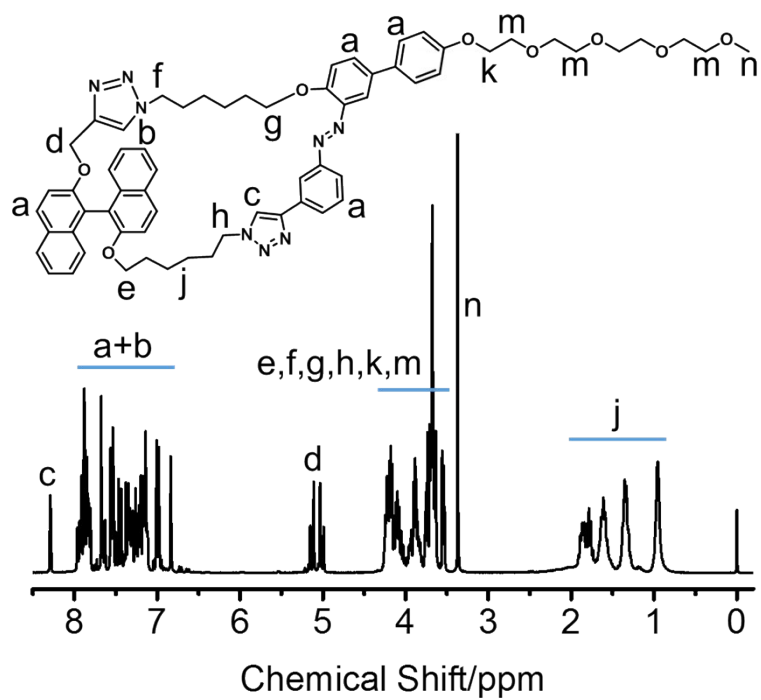




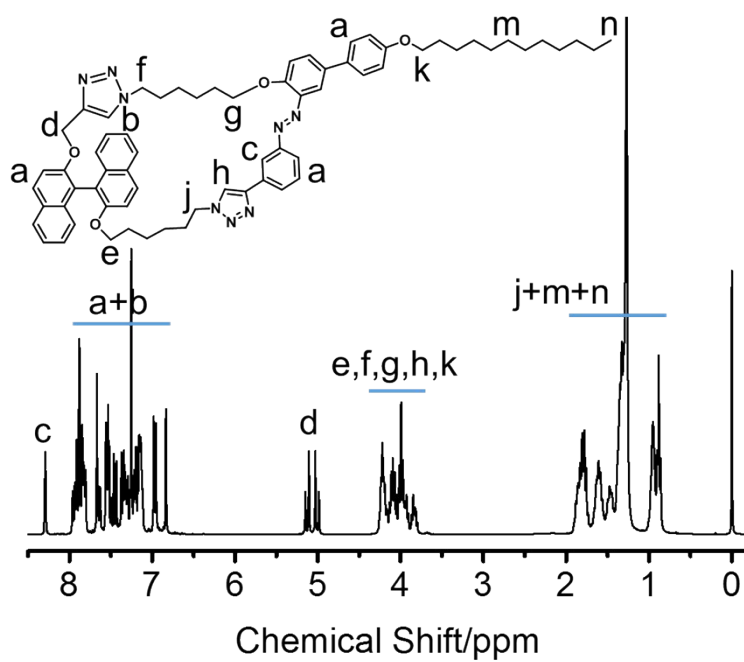
**Figure S2.** <sup>1</sup>H NMR spectrum of DOBP.



**Figure S3.** <sup>1</sup>H NMR spectrum of D1.

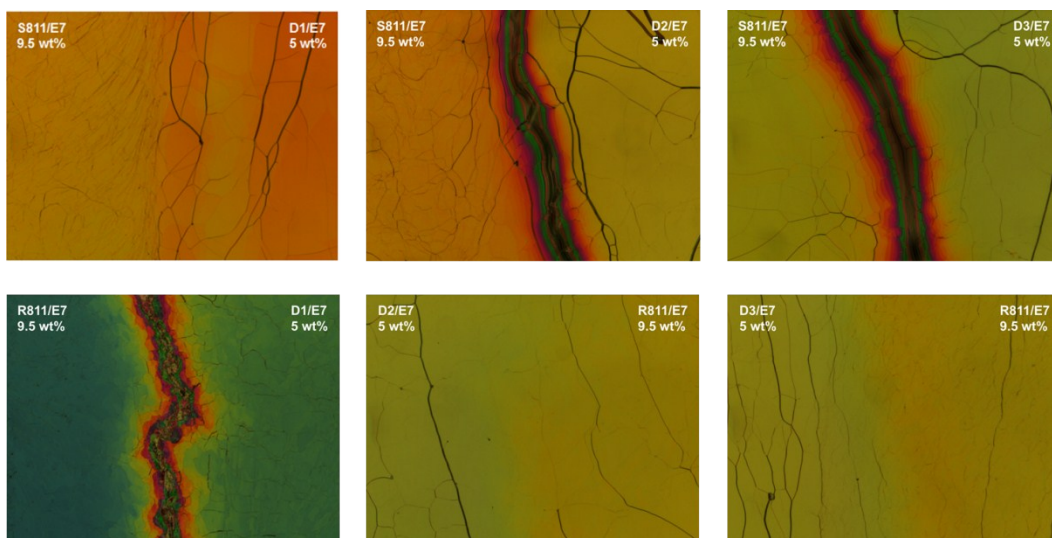


**Figure S4.**  $^1\text{H}$  NMR spectrum of D2.

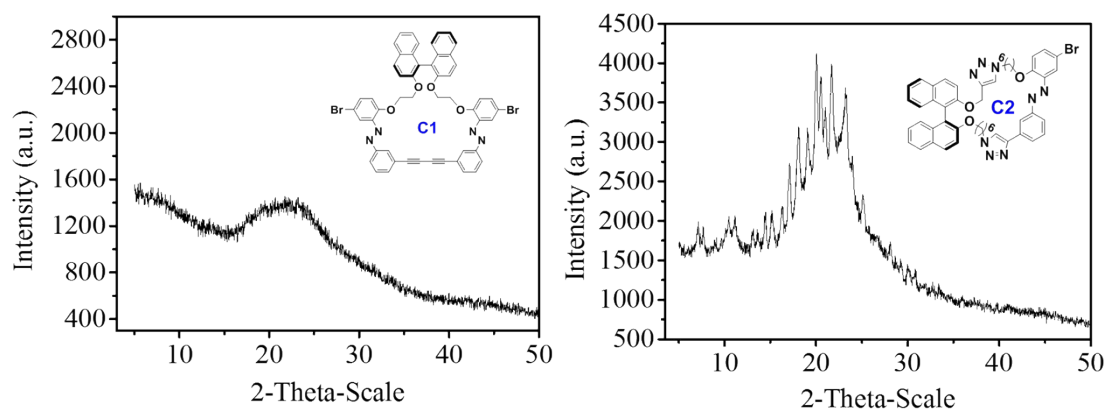


**Figure S5.**  $^1\text{H}$  NMR spectrum of D3.

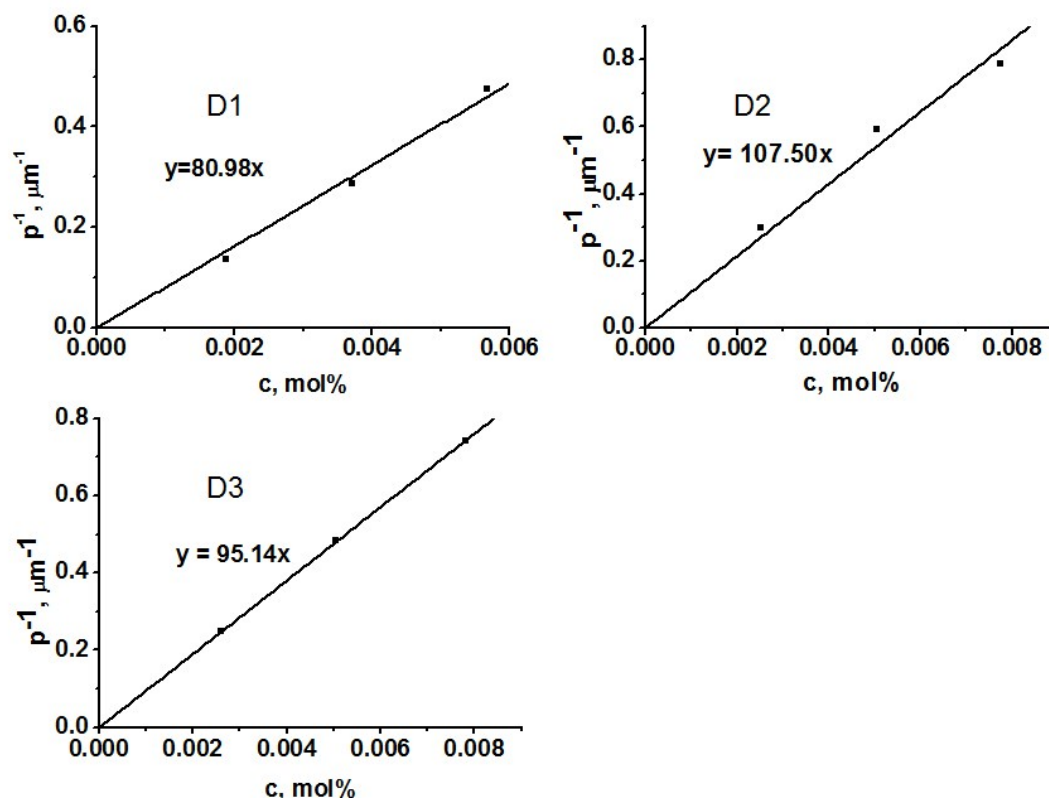




**Figure S6** The optical textures of miscibility test for helical twisting sense between (R1)S1/E7 mixed crystals and chiral nematic liquid crystals induced by D1, D2 and D3, respectively.



**Figure S7.** XRD pattern of (A) C1 and (B) C2.



**Figure S8.** Reciprocal helical pitch as a function of concentration of chiral switch D1, D2 and D3 in LC E7 at initial state.

[S1] J. Lu, A. Xia, N. Zhou, W. Zhang, Z. Zhang, X. Pan, Y. Yang, Y. Wang and X. Zhu, *Chem. Eur. J.*, 2015, **21**, 2324.

[S2] J. Lu, G. Jiang, Z. Zhang, W. Zhang, Y. Yang, Y. Wang, N. Zhou and X. Zhu, *Polym. Chem.*, 2015, **6**, 8144.

[S3] I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH, Weinheim, 2003.