

## Supplementary Information

### Spiropyran-based liquid crystals: The formation of columnar phases via acid-induced spiro-merocyanine isomerisation

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#### Experimental (General procedure)

All reagents and solvents were purchased from Tokyo Kasei, Aldrich, and Wako. All reagents were used as received without purification except 4-methylbenzene sulfonic acid (**2**), 4-methylbenzoic acid (**4**), and 4-methylphenol (**5**) which were purified by recrystallisation from chloroform. Analytical thin layer chromatography (TLC) was performed on a silica gel plate from E.Merck (silica gel F<sub>254</sub>). Silica gel column chromatography was carried out with silica gel 60 from Kanto Chemical (silica gel 60, spherical 40-50). Recycling preparative GPC was carried out with a Japan Analytical Industry LC-908 chromatograph. Semi preparative HPLC (column: TSKgel ODS-80Ts) was performed on a Jasco LCNetII/ADC liquid chromatograph. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JEOL JNM-LA400 by using CDCl<sub>3</sub>. Chemical shifts of the <sup>1</sup>H and <sup>13</sup>C signals are expressed in parts per million (δ), multiplicity, and coupling constant (Hz) with Me<sub>4</sub>Si as an internal standard. Matrix associated laser desorption ionisation-time of flight mass spectra (MALDI-TOF) was collected on a PerSpective Biosystem voyager DE STR spectrometer. Elemental analysis was performed on a

Yanaco MT-6 CHN autocorder.

Differential scanning calorimetry (DSC) measurements were performed with a NETZSCH DSC204 *Phoenix* at a scanning rate of 10 °C min<sup>-1</sup>. A polarising optical microscope Olympus BX51 equipped with a Mettler FP82 HT hot stage was used for visual observation of the liquid-crystalline phase. Transition temperatures were determined at the onset point of the transition peaks on the second heating and by visual observation under the polarised optical microscope. Wide angle X-ray scattering (WAXD) pattern was obtained using a Rigaku RINT-2500 system with monochromated CuK $\alpha$  irradiation. Two-dimensional small angle X-ray scattering (SAXS) patterns were recorded using an image plate detector (R-AXIS DSC3). Measurements of ionic conductivity were carried out by an alternating current impedance method using a Schlumberger Solartron 1260 impedance analyser (frequency range: 10 Hz-10 MHz, applied voltage: 0.3 V) and a temperature controller. The heating rate of the measurements was fixed at 2 °C min<sup>-1</sup> from 30 to 150 °C. Ionic conductivities were calibrated with an aq. KCl solution (1.00 mmol L<sup>-1</sup>) as the standard conductive solution. Absorption spectra were measured with an Agilent (model 8453) UV-vis spectrophotometer in a 1 cm quartz cell for samples in tetrahydrofuran solvent. For those samples in the bulk state, a sandwiched quartz cell was used for measurements. The density of an equimolar mixture of **1** and **2** was determined by a floatation method in water/methanol.<sup>1</sup>

### Syntheses

1,3,3-trimethyl-6'-hydroxy-spiro-[2H-1-benzopyran-2,2'-indoline] was synthesised by a condensation reaction of 1,3,3-trimethyl-2-methyleneindoline (Fischer's base) with 2,5-dihydroxybenzaldehyde in ethanol.<sup>2</sup> 3,4,5-tris(*n*-octadecyloxy)benzoic acid was

obtained as reported previously.<sup>3</sup>

#### **Synthesis of 1,3,3-Trimethyl-6'-hydroxy-spiro-[2H-1-benzopyran-2,2'-indoline]**

Into a 50 mL round-bottomed flask equipped with a magnetic stirring bar containing 1,3,3-trimethyl-2-methyleneindoline (0.50 g, 2.9 mmol) in a 10 mL ethanol solution, 2,5-dihydroxybenzaldehyde (0.48 g, 3.5 mmol) was added. The mixture was heated to reflux for 6 h under an argon atmosphere and then was cooled to room temperature. The solvent was removed under reduced pressure. Remaining purple solid was subsequently recrystallised from a mixture of hexane/chloroform to give a needle-like light brownish crystal (0.53 g, 62%). NMR:  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ): 7.17 (1H, t,  $J = 7.6$  Hz, aromatic), 7.07 (1H, d,  $J = 7.2$  Hz, aromatic), 6.83 (1H, t,  $J = 7.2$  Hz, aromatic), 6.77 (1H, d,  $J = 10.4$  Hz, vinylic), 6.60-6.50 (4H, m, aromatic), 5.70 (1H, d,  $J = 10.4$  Hz, vinylic), 4.37 (1H, s, OH), 2.72 (3H, s,  $\text{NCH}_3$ ), 1.30 (3H, s,  $\text{CH}_3$ ), 1.16 (3H, s,  $\text{CH}_3$ );  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ): 148.60, 148.55, 148.18, 136.79, 129.0, 127.55, 121.47, 120.42, 119.24, 119.02, 116.34, 115.56, 112.84, 106.75, 103.81, 51.61, 28.94, 25.80, 20.22;  $m/z$  (MALDI-TOF): *calcd* for  $[\text{M}+\text{H}]^+ = 294.14$ , *found* = 294.30.

#### **Synthesis of 2-Bromoethyl-3,4,5-tris(*n*-octadecyloxy)benzoate**

To a mixture of 3,4,5-tris(*n*-octadecyloxy)benzoic acid (4.0 g, 4.3 mmol), 2-bromo ethanol (0.65 g, 5.2 mmol), and 4-(*N,N*-dimethylamino)pyridine (DMAP) (1.60 g, 12.9 mmol) in 20 mL  $\text{CH}_2\text{Cl}_2$  in a round-bottomed flask, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (2.50 g, 12.9 mmol) was added portionwise at room temperature over 5 min. The reaction mixture was stirred overnight under an argon atmosphere. Then, the resulting mixture was poured into a mixture of chloroform and water (300 mL of each). The organic phase was separated and the aqueous phase was extracted three times with chloroform. The combined organic extracts were washed with

water, saturated  $\text{NH}_4\text{Cl}$  and  $\text{NaCl}$  aqueous solutions successively. The washed organic phase was dried over anhydrous  $\text{MgSO}_4$ , filtered through a pad of celite, and concentrated under a reduced pressure. Purification of the residue by flash column chromatography on silica gel (eluent: chloroform,  $R_f = 0.8$ ) and then followed by GPC (eluent: chloroform) gave a white solid (3.6 g, 81 %). NMR:  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ): 7.27 (2H, s, aromatic), 4.59 (2H, t,  $J = 6.0$  Hz,  $\text{OCH}_2\text{CH}_2\text{Br}$ ), 4.01 (6H, t,  $J = 6.4$  Hz,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.63 (2H, t,  $J = 6.0$  Hz,  $\text{OCH}_2\text{CH}_2\text{Br}$ ), 1.71-1.85 (6H, m), 1.16-1.51 (90H, m), 0.88 (9H, t,  $J = 7.0$  Hz,  $\text{CH}_3$ );  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ): 165.89, 152.84, 142.65, 124.01, 108.08, 73.49, 69.14, 64.09, 31.92, 30.31, 29.72, 29.67, 29.63, 29.56, 29.39, 29.37, 29.26, 28.81, 26.08, 26.04, 22.69, 14.12 ; m/z (MALDI-TOF): *calcd* for  $[\text{M}+\text{H}]^+$  = 1033.81, *found* = 1033.90.

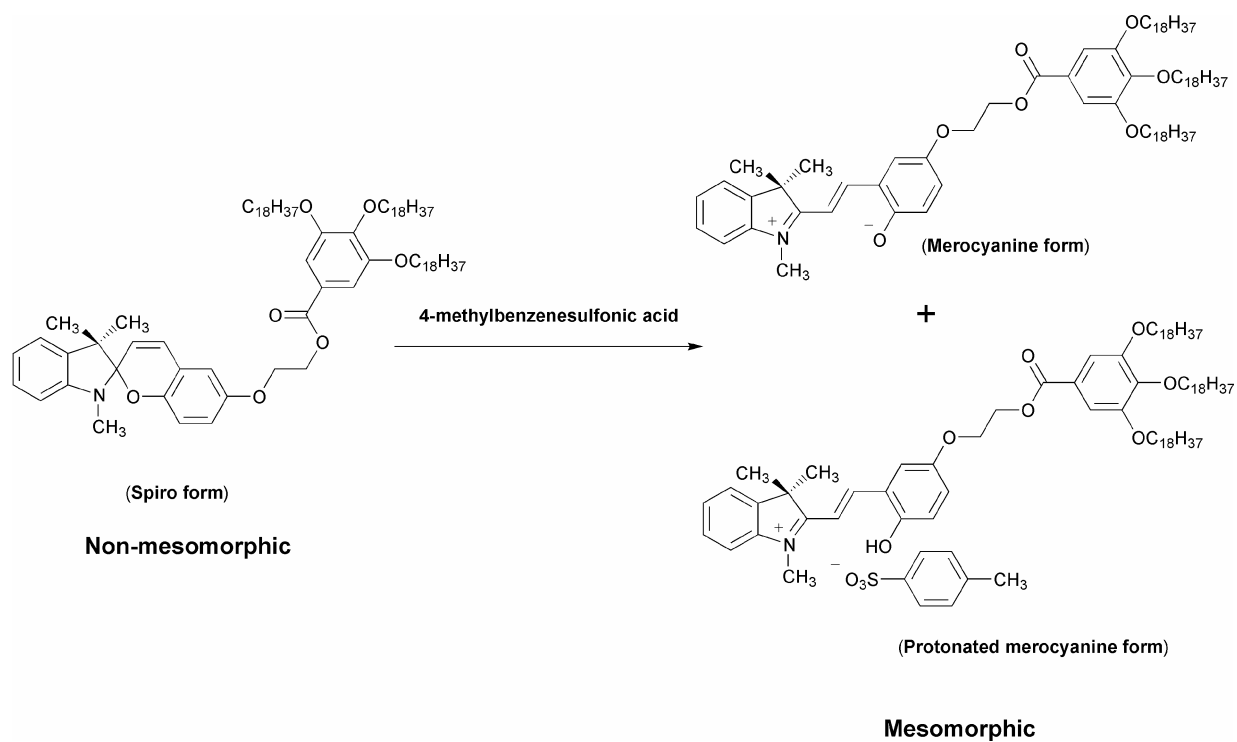
**Synthesis of [1,3,3-Trimethyl-spiro-(2H-1-benzopyran-2,2'-indoline)-6-oxyethyl] (3,4,5- tris(*n*-octadecyloxy)benzoate (1)**

A DMF (10 mL) suspension of 2-bromoethyl-3,4,5-tris(*n*-octadecyloxy)benzoate (0.61 g, 0.59 mmol), 1,3,3-trimethyl-6'-hydroxy-spiro-[2H-1-benzopyran-2,2'-indoline] (0.30 g, 1.0 mmol), and  $\text{K}_2\text{CO}_3$  (0.60 g, 6.0 mmol) in a round-bottomed flask (100 mL) equipped with a magnetic stirring bar was deaerated under reduced pressure and then the flask was back-filled with argon gas. The deaeration procedure was repeated three times to remove oxygen in the flask thoroughly. The mixture was heated at 80 °C for 4 h under vigorous stirring. The resulting mixture was cooled to room temperature and was poured into a mixture of ethyl acetate and water (100 mL of each) The organic phase was separated and the aqueous phase was extracted with ethyl acetate three times. The combined organic extracts were washed with water, saturated  $\text{NH}_4\text{Cl}$  and  $\text{NaCl}$  aqueous solutions successively. The washed organic phase was then dried over anhydrous

MgSO<sub>4</sub>, filtered through a pad of celite, and concentrated under reduced pressure. Next, the obtained light yellowish solid was purified by silica gel column chromatography (eluent: hexane/chloroform-2/1) and then followed by HPLC method (eluent: hexane/chloroform-95/5). The column effluents were monitored at 280 nm. Final compound is a colorless wax-like solid (0.30 g, 41%). NMR:  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.27 (2H, s, aromatic), 7.16 (1H, t,  $J = 7.8$  Hz, aromatic), 7.06 (1H, d,  $J = 7.2$  Hz, aromatic), 6.83 (1H, t,  $J = 7.8$  Hz, aromatic), 6.77 (1H, d,  $J = 10.4$  Hz, vinylic), 6.71-6.63 (3H, m, aromatic), 6.51 (1H, d,  $J = 7.2$  Hz, aromatic), 5.69 (1H, d,  $J = 10.4$  Hz, vinylic), 4.60 (2H, t,  $J = 4.6$  Hz, OCH<sub>2</sub>CH<sub>2</sub>OCO), 4.22 (2H, t,  $J = 4.6$  Hz, OCH<sub>2</sub>CH<sub>2</sub>OCO), 3.99 (6H, t,  $J = 6.6$  Hz, CH<sub>2</sub>CH<sub>2</sub>O), 2.71 (3H, s, NCH<sub>3</sub>), 1.72-1.84 (6H, m), 1.15-1.47 (96H, m), 0.88 (9H, t,  $J = 6.8$  Hz, CH<sub>3</sub>);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>): 166.36, 152.79, 151.99, 148.92, 148.14, 142.49, 136.70, 129.12, 127.53, 124.37, 121.42, 120.36, 119.10, 119.02, 116.16, 115.52, 112.59, 108.08, 106.72, 103.87, 73.44, 69.13, 66.82, 63.37, 51.61, 31.92, 30.31, 29.71, 29.66, 29.63, 29.56, 29.39, 29.36, 29.28, 28.88, 26.08, 26.04, 25.80, 22.68, 20.17, 14.11; m/z (MARDI-TOF): *calcd* for [M+H]<sup>+</sup> = 1247.02, *found* = 1247.50; elemental analysis for C<sub>82</sub>H<sub>135</sub>NO<sub>7</sub>: *calcd* (%): C 78.98, H 10.91, N 1.12; *found*: C 78.82, H 11.03, N 1.17.

### **Representative preparation procedure of the binary mixtures containing 1**

An equimolar mixture of **1** and **2** was prepared by mixing a waxy compound of **1** (10.0 mg,  $8.02 \times 10^{-6}$  mol) with a solution of **2** (1.53 mL,  $5.30 \times 10^{-3}$  M) in a mixture of chloroform and acetone (1:1 by volume). The colorless solution of **2** changed to red immediately upon dissolution of **1**. The mixture solution was dried in the air overnight at room temperature and then was used for characterisation of liquid-crystalline properties. Other binary mixtures of **1** with **2-5** were prepared accordingly.



Scheme S1 Isomerisation process of the compound **1** upon addition of 4-methylbenzenesulfonic acid.

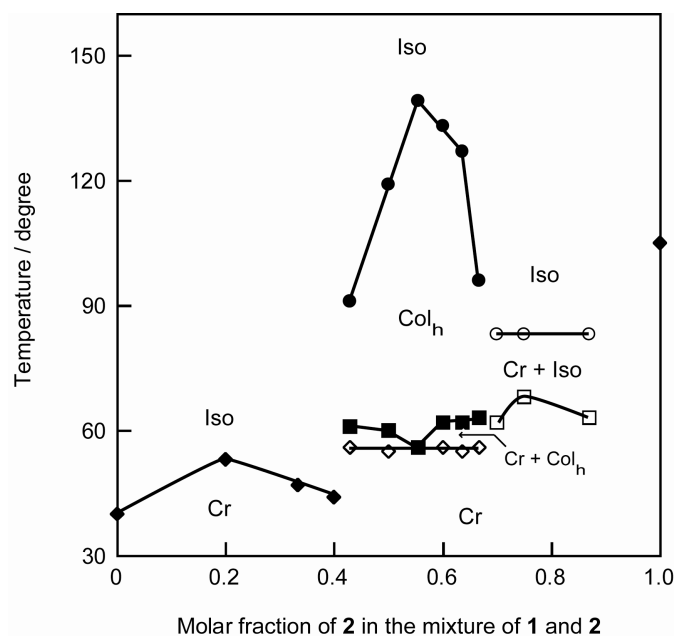


Fig. S1 Phase diagram of the binary mixtures of compounds **1** and **2**. Cr: crystalline; Col<sub>h</sub>: hexagonal columnar; Iso: isotropic.

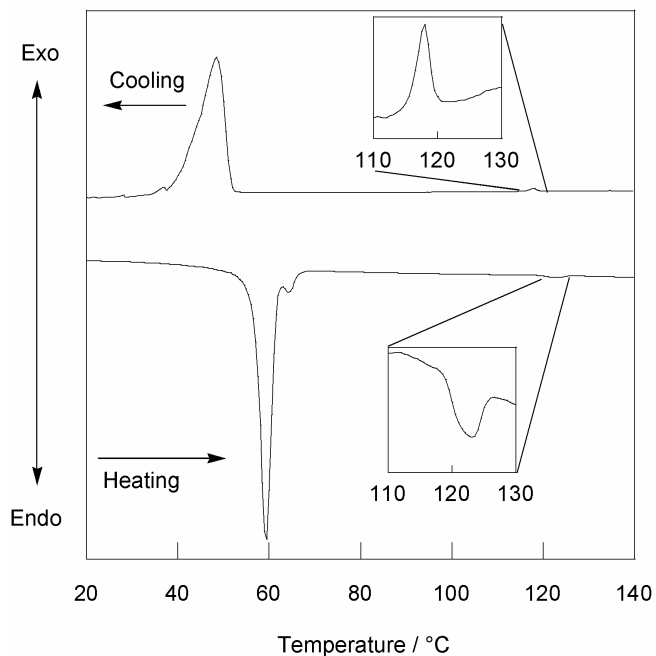


Fig. S2 DSC thermograms of an equimolar mixture of **1** and **2** at a scan rate of 10 °C min<sup>-1</sup>.

Table S1 Thermal properties of equimolar mixtures of **1** with **4** and **5**

Compound	Phase transition behaviour <sup>a</sup> / °C
<b>1</b> and <b>5</b>	Cr 48 Iso (55.7)
<b>1</b> and <b>4</b>	Phase separation

<sup>a</sup> Enthalpy of transition (kJ mol<sup>-1</sup>, in parentheses) determined by DSC (second heating scan, 10 °C min<sup>-1</sup>). Cr: crystalline; Iso: isotropic.

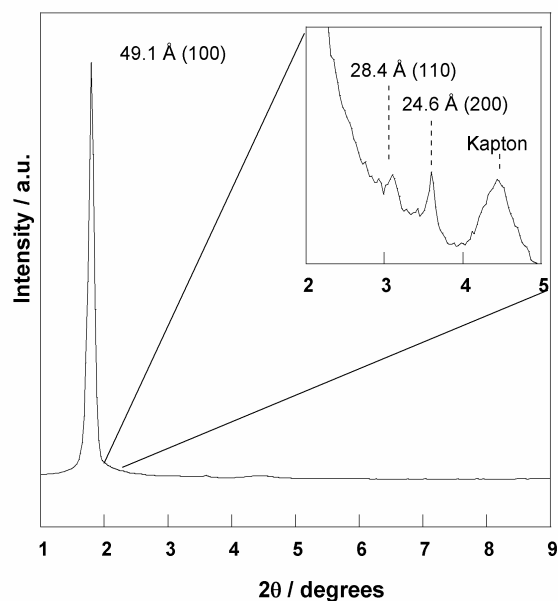
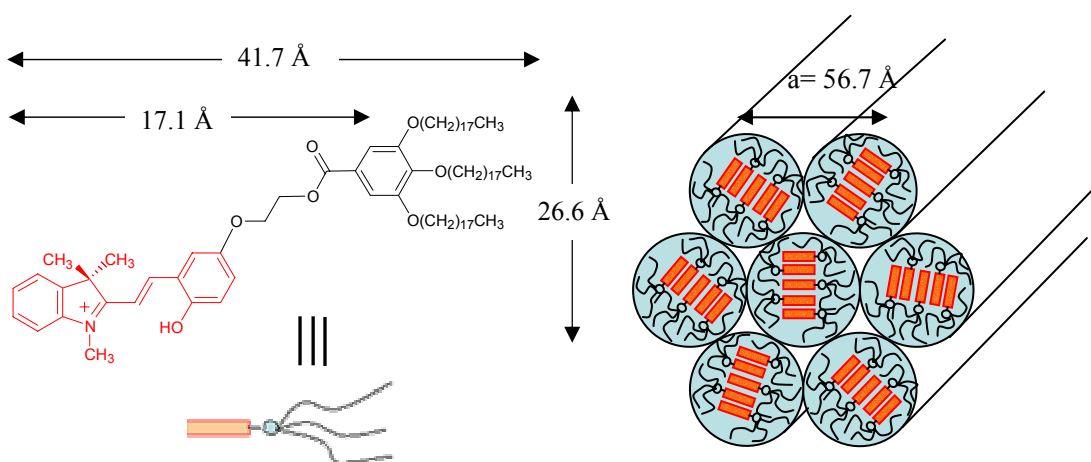


Fig. S3 Small angle X-ray diffraction patterns of an equimolar mixture of **1** and **2** in the hexagonal columnar state at 90 °C. Inset: magnified diffraction pattern.



**Number of molecules per column layer /  $\mu = \sqrt{3}N_A a^2 \rho t / 2M = ca. 5$**

Avogadro's number /  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ , lattice parameter /  $a = 56.7 \text{ \AA}$

Average height of the column layer /  $t = 4.5 \text{ \AA}$

Density of an equimolar mixture of **1** and **2** /  $\rho = 0.98 \text{ g cm}^{-3}$

Molecular weight of an equimolar mixture of **1** and **2** /  $M = 1436.24$

Fig. S4 Schematic illustration of a proposed self-assembled columnar structure of an equimolar mixture of **1** and **2**.



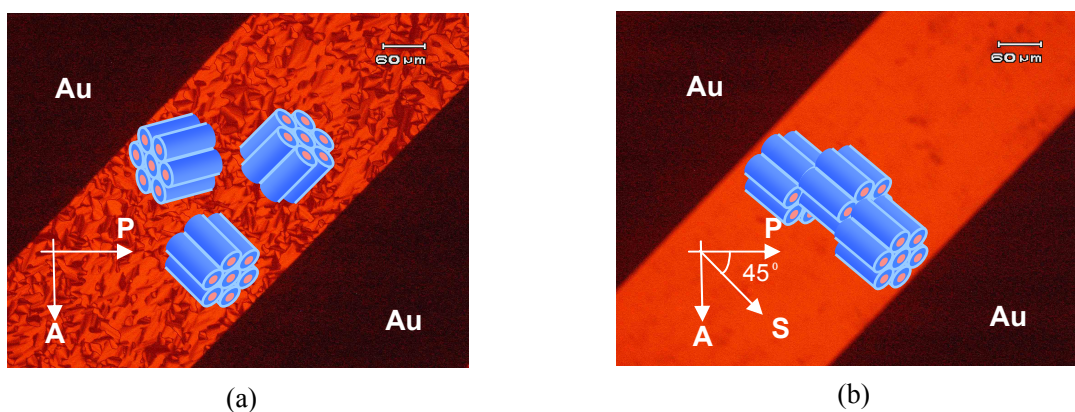


Fig. S5 Polarized optical micrographs of an equimolar mixture of **1** and **2** in the  $Col_h$  state at 90 °C a) before shearing and b) after shearing. Direction of A: analyser, P: polariser, and S: shearing.

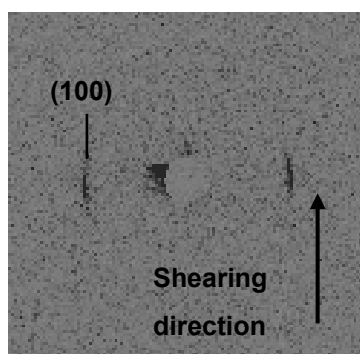


Fig. S6 Two-dimensional small angle X-ray scattering image of the oriented equimolar mixture of **1** and **2** by shearing in the columnar phase at 90 °C.

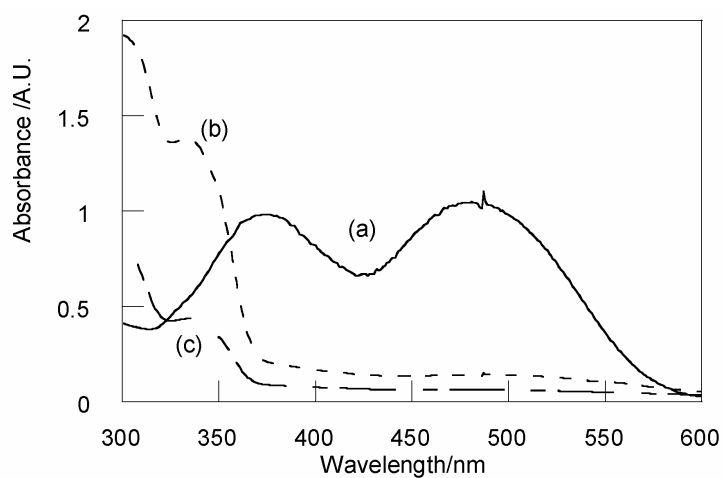


Fig. S7 Absorption spectra of the equimolar mixtures of a) **1** and **3**, b) **1** and **4**, and c) **1** and **5** in the bulk state at 35 °C.

## References

1. G. Ungar, V. Percec, M. N. Holerca, G. Johansson and J. A. Heck, *Chem. Eur. J.*, 2000, **6**, 1258.
2. S. R. Keum, S. H. Lee and S. O. Kang, *Liq. Cryst.*, 2004, **31**, 1569.
3. V. Percec, C. H. Ahn, T. K. Bera, G. Ungar and D. J. P. Yeardley, *Chem. Eur. J.*, 1999, **5**, 1070.