

## Supplementary Data

Results of elemental analysis of all the compounds of the synthesized series  $I_{n_{a-e}}$  were found to be satisfactory (S1). Since almost identical infrared and  $^1\text{H}$  NMR spectra were observed for all the members of the five homologous series ( $I_{n_a} - I_{n_e}$ ), FT-IR and  $^1\text{H}$  NMR spectral data of the  $n$ -octyloxy derivatives ( $I_{8_{a-e}}$ ), as examples, are given below:

For  $I_{8_a}$ , FT-IR (KBr,  $\nu_{\text{max}}$ .  $\text{cm}^{-1}$ ): 3067 (C–H aromatic) 2923, 2853 (alkyl group), 1506 (–C=C– aromatic), 1732, 1252 (–COO– group), 1601 (–N=N– group), 839 (p-sub. benzene rings).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 0.89 (t, 3H, –CH<sub>3</sub>), 1.28–1.77 (m, 12H, 6  $\times$  –CH<sub>2</sub>–), 4.08–4.10 (t, 2H, –OCH<sub>2</sub>–), 3.79–3.81 (s, 3H, Ar–OCH<sub>3</sub>), 7.02–7.25, 7.95–8.02, 8.29–8.32 (m, 12 H, p-subst. benzene rings).

For  $I_{8_b}$ , FT-IR (KBr,  $\nu_{\text{max}}$ .  $\text{cm}^{-1}$ ): 3046 (C–H aromatic) 2919, 2851 (alkyl group), 1505 (–C=C– aromatic stre.), 1734, 125160 (–COO– group), 1601 (–N=N– group), 840 (p-sub. benzene rings).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 0.88 (t, 3H, –CH<sub>3</sub>), 1.15–1.77 (m, 12H, 6  $\times$  –CH<sub>2</sub>–), 2.35–2.44 (s, 3H, Ar–CH<sub>3</sub>), 4.11 (t, 2H, –OCH<sub>2</sub>–), 7.17–7.27, 7.94–8.01, 8.32 (m, 12 H, p-sub. benzene rings).

For  $I_{8_c}$ , FT-IR (KBr,  $\nu_{\text{max}}$ .  $\text{cm}^{-1}$ ): 3062(C–H aromatic) 2921, 2853 (alkyl group), 1496 (–C=C– aromatic), 1733, 1259 (–COO– group), 1600 (–N=N– group), 839 (p-sub. benzene rings).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 0.87–0.88 (t, 3H, –CH<sub>3</sub>), 1.28–1.77 (m, 12H, 6  $\times$  –CH<sub>2</sub>–), 4.10–4.14 (t, 2H, –OCH<sub>2</sub>–), 7.14–7.51, 7.90–8.02, 8.3–8.4 (m, 12 H, p-sub. benzene rings).

For  $I_{8_d}$ , FT-IR (KBr,  $\nu_{\text{max}}$ .  $\text{cm}^{-1}$ ): 3063 (C–H aromatic) 2920, 2851 (alkyl group), 1487 (–C=C– aromatic), 1733, 1258 (–COO– group), 1599 (–N=N– group), 1061 (C–Br aromatic), 842 (p-sub. benzene rings).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 0.88 (t, 3H, –CH<sub>3</sub>), 1.30–1.77 (m, 12H, 6  $\times$  –CH<sub>2</sub>–), 4.12 (t, 2H, –OCH<sub>2</sub>–), 7.15–7.36, 7.67, 7.97–8.30 (m, 12 H, p-sub. benzene rings).

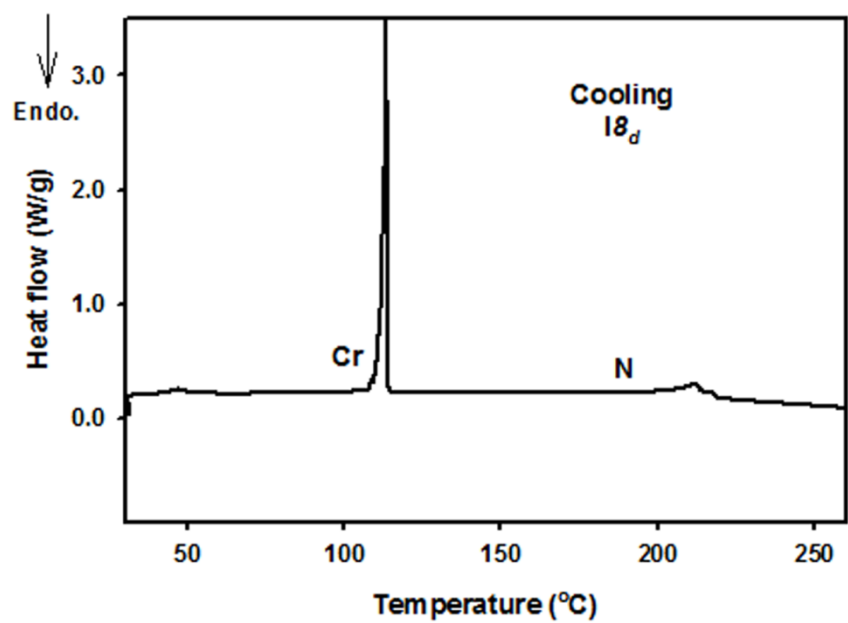
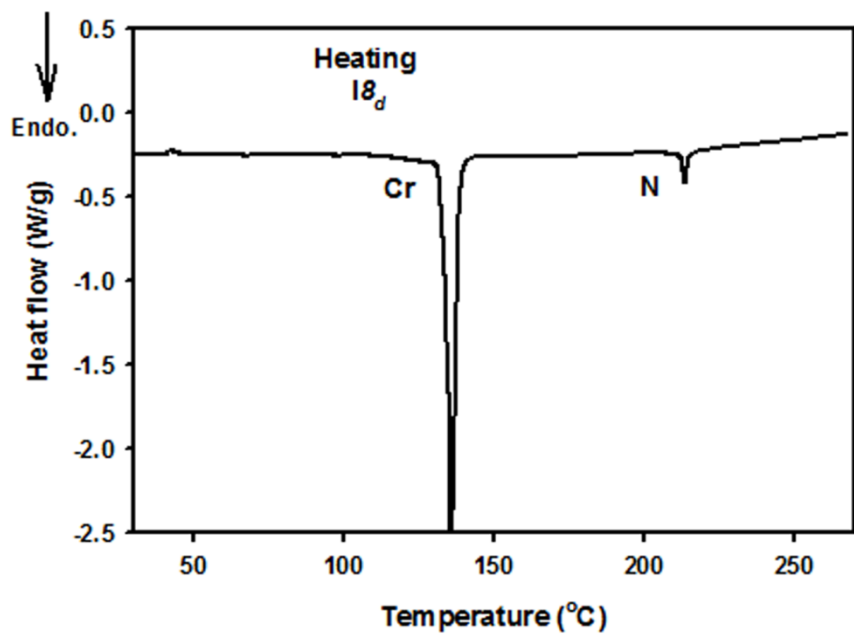
For  $I_{8_e}$ , FT-IR (KBr,  $\nu_{\text{max}}$ .  $\text{cm}^{-1}$ ): 3068 (C–H aromatic) 2923, 2854 (alkyl group), 2238 (–CN), 1501 (–C=C– aromatic), 1732, 1253 (–COO– group), 1601 (–N=N– group), 836 (p-sub. benzene rings).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 0.87 (t, 3H, –CH<sub>3</sub>), 1.28–1.76 (m, 12H, 6  $\times$  –CH<sub>2</sub>–), 4.08–4.10 (t, 2H, –OCH<sub>2</sub>–), 7.14–7.16, 7.58–7.60, 7.97–8.01, 8.31–8.33 (m, 12 H, p-sub. benzene rings).

S1: Elemental analyses of the azo/esters, **I**<sub>n</sub><sub>a-f</sub>.

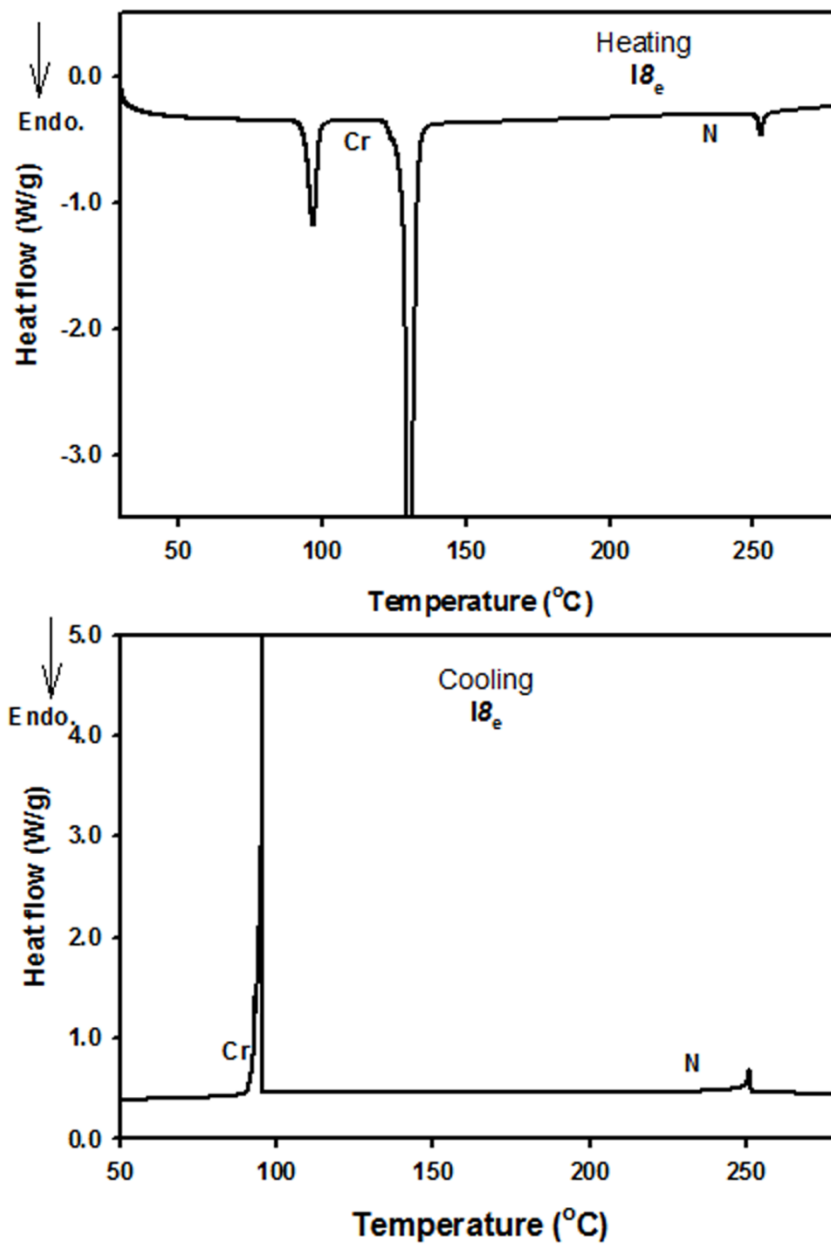


| Comp No.                | N  | X                 | Mol. Wt. | Elemental Analyses Cal. (Found) |             |             |               |
|-------------------------|----|-------------------|----------|---------------------------------|-------------|-------------|---------------|
|                         |    |                   |          | % C                             | % H         | % N         | % Br          |
| <b>I</b> <sub>8a</sub>  | 8  | CH <sub>3</sub> O | 460.58   | 73.02 (73.15)                   | 7.00 (7.21) | 6.08 (5.97) | -             |
| <b>I</b> <sub>8b</sub>  | 8  | CH <sub>3</sub>   | 444.58   | 75.65 (75.74)                   | 7.26 (7.34) | 6.30 (6.13) | -             |
| <b>I</b> <sub>8c</sub>  | 8  | H                 | 430.55   | 75.32 (75.41)                   | 6.97(7.21)  | 6.51 (6,64) | -             |
| <b>I</b> <sub>8d</sub>  | 8  | Br                | 509.45   | 63.37 (63.12)                   | 5.74 (5.83) | 5.50 (5.42) | 15.69(15.81)  |
| <b>I</b> <sub>8e</sub>  | 8  | CN                | 455.56   | 73.82 (74.01)                   | 6.42 (6.28) | 9.22 (9.01) | -             |
| <b>I</b> <sub>10a</sub> | 10 | CH <sub>3</sub> O | 488.80   | 73.72 (73.60)                   | 7.42 (7.45) | 5.73 (5.91) | -             |
| <b>I</b> <sub>10b</sub> | 10 | CH <sub>3</sub>   | 472.63   | 76.24 (76.40)                   | 7.68 (7.45) | 5.93 (5.76) | -             |
| <b>I</b> <sub>10c</sub> | 10 | H                 | 458.60   | 75.95 (75.81)                   | 7.47 (7.35) | 6.11 (5.97) | -             |
| <b>I</b> <sub>10d</sub> | 10 | Br                | 537.50   | 64.48 (64.61)                   | 6.19 (6.34) | 5.21 (5.03) | 14.87 (14.70) |
| <b>I</b> <sub>10e</sub> | 10 | CN                | 483.61   | 74.51(74.38)                    | 6.88 (8.62) | 5.79 (5.63) | -             |
| <b>I</b> <sub>12a</sub> | 12 | CH <sub>3</sub> O | 516.85   | 74.36 (74.24)                   | 7.80 (8.12) | 5.42 (5.24) | -             |
| <b>I</b> <sub>12b</sub> | 12 | CH <sub>3</sub>   | 500.68   | 76.80 (76.63)                   | 8.01(7.96)  | 5.60 (5,45) | -             |
| <b>I</b> <sub>12c</sub> | 12 | H                 | 486.85   | 76.48 (76.32)                   | 7.87(7.69)  | 5.75 (5.68) | -             |
| <b>I</b> <sub>12d</sub> | 12 | Br                | 565.56   | 65.83 (66.12)                   | 6.59 (6.45) | 4.95 (5.21) | 14.13 (14.34) |
| <b>I</b> <sub>12e</sub> | 12 | CN                | 511.67   | 75.12 (74.93)                   | 7.29 (7.36) | 8.21(8.45)  | -             |
| <b>I</b> <sub>14a</sub> | 14 | CH <sub>3</sub> O | 544.87   | 74.94 (75.22)                   | 8.14 (8.25) | 5.14 (5.32) | -             |
| <b>I</b> <sub>14b</sub> | 14 | CH <sub>3</sub>   | 528.74   | 77.24 (77.51)                   | 8.39 (8.48) | 5.30 (5.16) | -             |
| <b>I</b> <sub>14c</sub> | 14 | H                 | 513.91   | 77.13 (77.39)                   | 8.24 (8.11) | 5.45 (5.62) | -             |
| <b>I</b> <sub>14d</sub> | 14 | Br                | 593.61   | 66.77 (77.55)                   | 6.96 (7.16) | 4.72 (4.91) | 13.46 (13.71) |
| <b>I</b> <sub>14e</sub> | 14 | CN                | 539.72   | 75.66 (75.34)                   | 7.66 (7.43) | 7.79 (7.92) | -             |
| <b>I</b> <sub>16a</sub> | 16 | CH <sub>3</sub> O | 572.92   | 75.47 (75.52)                   | 8.27 (8.41) | 4.89 (4.76) | -             |
| <b>I</b> <sub>16b</sub> | 16 | CH <sub>3</sub>   | 556.79   | 77.66 (77.89)                   | 8.51(8.78)  | 5.03 (4.86) | -             |
| <b>I</b> <sub>16c</sub> | 16 | H                 | 541.96   | 77.57 (77.34)                   | 8.37 (8.55) | 5.17 (5.03) | -             |
| <b>I</b> <sub>16d</sub> | 16 | Br                | 621.66   | 67.62 (67.47)                   | 7.13 (7.31) | 4.51 (4.73) | 12.85(13.11)  |
| <b>I</b> <sub>16e</sub> | 16 | CN                | 567.77   | 76.16 (76.41)                   | 7.81(8.03)  | 7.40 (7.24) | -             |

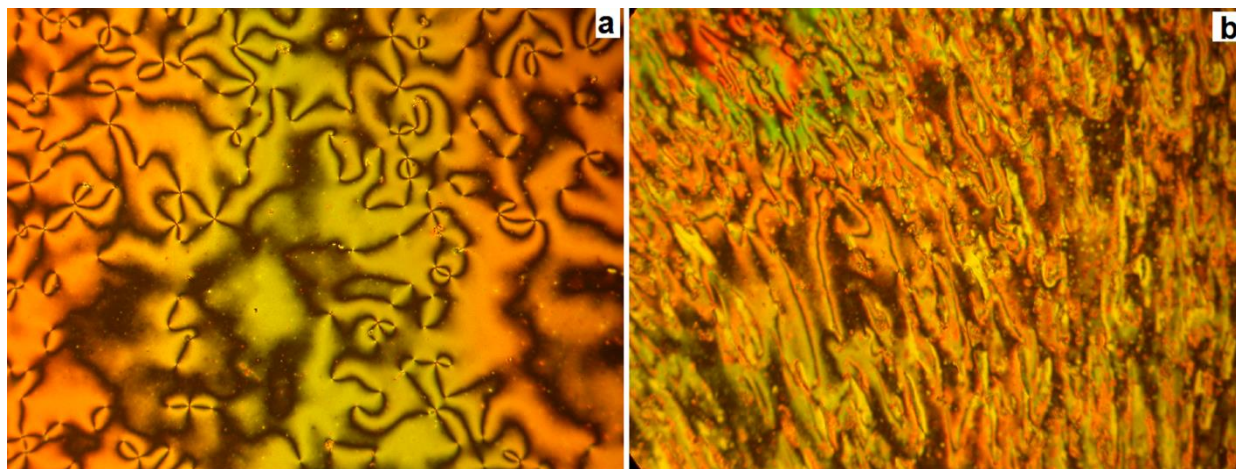
DSC-Curves



Supplementary figure 1. Heating and cooling DSC scans for  $I8_d$ .



Supplementary figure 2. Heating and cooling DSC scans for **I8<sub>e</sub>**.



Supplementary figure 3. Polarized optical micrographs obtained from cooling of isotropic phases of (a) nematic phase of  $I8_d$  at 200°C and (b) of  $I8_e$  at 220°C.