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Binary Liquid Crystal Mixtures Based on Schiff Base Derivatives with Oriented Lateral Substituents

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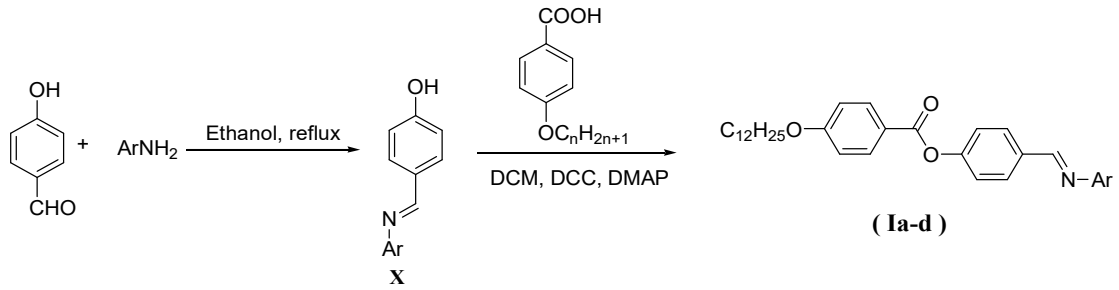
1. Experimental

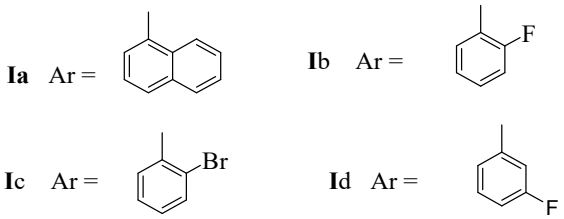
1.1. Materials

4-Dodecyloxybenzoic acid, 4-hydroxybenzaldehyde, 3-fluoroaniline, 2-fluoroaniline, 2-bromoaniline and 2-aminonaphthalene were purchased from Sigma Aldrich (Germany). dichloromethane, *N,N'*- dicyclohexylcarbodiimide (DCC), ethanol and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich (Wisconsin, USA).

1.2. Synthesis

Compounds **Ia-d**, were prepared according to the following scheme:





Scheme 1: Synthesis of 4-((2' or 3'-arylimino)methyl)phenyl-4''-alkoxy benzoates, Ia-d.

Synthesis of 4-((2' or 3'-arylimino)methyl)phenyl 4''-dodecyloxybenzoates, (**Ia-d**)

Molar equivalents of 4-((2'-or 3'-arylimino)methyl)phenol (**X)** or 4-dodecyloxybenzoic acid (0.01 mol) were dissolved in dry methylene chloride (DCM) (25 ml). 0.02 molar of *N, N'*-dicyclohexylcarbodiimide (DCC) and trace amount of 4-dimethylaminopyridine (DMAP) were added to the reaction mixture. The reaction left under stirring at room temperature for 72 H. The

separated byproduct, dicyclohexylurea (DCU), was filtered off, and the filtrate then evaporated and the solid crystallized from ethanol.

4. -Naphthyliminomethyl)phenyl 4"-dodecyloxybenzoate Ia

Yield: 96 %; mp 99 ˚C, FTIR (ύ, cm^{-1}): 2917, 2852 (CH_2 stretching), 1724 (C=O), 1621 (C=N), 1600 (C=C), 1458 (C-O Asym), 1246 (C-O Sym).^{1}HNMR (500 MHz, $CDCl_3$):δ = 0.87 (t, 3H, $CH_3(CH_2)_9CH_2CH_2$, *J* = 7.5 Hz), 1.27-1.56 (m, 14H, $CH_3(CH_2)_9CH_2CH_2$), 1.82 (q, 2H, *J* = 8.5 Hz, *J* = 7.0 Hz, $CH_3(CH_2)_7CH_2CH_2$), 4.06 (t, 2H, $CH_3(CH_2)_9CH_2CH_2$, *J* = 7.0 Hz), 6.97 (dd, 2H, *J* = 6.5, *J* = 2.5, Hz, Ar-H), 7.05 (d, 1H, *J* = 7.0 Hz, Ar-H), 7.36 (d, 2H, *J* = 7.0 Hz, Ar-H), 7.45 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.48-7.52 (m, 4H, Ar-H), 7.71 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.85 (dd, 1H, *J* = 6.5, *J* = 2.5, Hz, Ar-H), 8.07 (d, 2H, *J* = 9.0 Hz, Ar-H), 8.15 (dd, 2H, *J* = 8.0, *J* = 3.0, Hz, Ar-H), 8.33 (dd, 1H, *J* = 7.0, *J* = 3.0, Hz, Ar-H), 8.55 (s, 1H, CH=N). ^{13}C NMR (125 MHz, $CDCl_3$) δ:ppm:14.10, 22.67, 25.97, 29.07, 29.29, 29.34, 29.53, 31.88, 68.35, 112.68, 114.37, 121.18, 122.34, 123.94, 125.76, 125.85, 126.03, 126.42, 127.62, 128.78, 130.18 132.38, 133.92, 133.99, 149.20, 153.58, 159.23, 163.72, 164.64.

4. -((2'-Florophenylimino)methyloxy)phenyl 4"-dodecyloxybenzoate Ib

Yield: 92 %; mp 103 ˚C, FTIR (ύ, cm^{-1}): 2920, 2857 (CH_2 stretching), 1723 (C=O), 1625 (C=N), 1602 (C=C), 1471 (C-O Asym), 1254 (O-CH_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm: 0.85 (t, 3H, $CH_3(CH_2)_9CH_2CH_2$, *J* = 7.0 Hz), 1.27-1.73 (m, 12H, $CH_3(CH_2)_{10}CH_2$), 4.02 (t, 2H, $CH_3(CH_2)_9CH_2CH_2$, *J* = 6.4 Hz), 6.94 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.13-7.14 (m, 4H, Ar-H), 7.31 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.96 (d, 2H, *J* = 8.5 Hz, Ar-H), 8.11 (d, 2H, *J* = 8.5 Hz, Ar-H), 8.51 (s, 1H, CH=N). ^{13}C NMR (125 MHz, CDCl3) δ:ppm: 14.04, 22.60, 25.93, 29.03, 29.16, 29.27, 30.87, 31.75, 68.33, 114.33, 116.13, 116.28, 121.09, 121.97, 122.25, 124.44, 126.66, 126.73, 130.16, 132.32, 133.48, 153.76, 156.13, 161.72, 163.68, 164.52, 207.02.

4. -((2'-Bromophenylimino)methyloxy)phenyl 4"-decyloxybenzoate Ic

Yield: 94 %; mp 93 ˚C, FTIR (ύ, cm^{-1}): 2921, 2852 (CH_2 stretching), 1720 (C=O), 1618 (C=N), 1599 (C=C), 1465 (C-O Asym), 1246 (O-CH_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm: 0.86 (t, 3H, $CH_3(CH_2)_9CH_2CH_2$, *J* = 7.0 Hz), 1.27-1.55 (m, 14H, $CH_3(CH_2)_9CH_2CH_2$), 1.82 (q, 2H, *J* = 7.5, *J* = 6.5 Hz, $CH_3(CH_2)_9CH_2CH_2$), 4.05 (t, 2H, *J* = 6.5 Hz, $CH_3(CH_2)_9CH_2CH_2$,), 6.96-7.08 (m, 5H, Ar-H), 7.31-7.35 (m, 1H, Ar-H), 7.62 (d, 2H, *J* = 7.5 Hz, Ar-H), 8.00 (d, 2H, *J* = 9.0 Hz, Ar-H), 8.14 (dd, 2H, *J* = 8.5, *J* = 3.0 Hz, Ar-H), 8.35 (s, 1H, CH=N). ^{13}C NMR (125 MHz, $CDCl_3$) δ:ppm:14.10, 22.67, 25.97, 29.07,29.30, 29.34, 29.53, 31.88, 68.36, 76.74, 112.68, 114.37, 121.18, 122.33, 123.93, 125.76, 125.84, 126.02, 126.41, 127.62, 128.78, 130.17, 132.38, 133.91, 133.98, 149.19, 153.58, 159.23, 163.72, 164.63,

4. -((3'-Fluorophenylimino)methyloxy)phenyl 4"-decyloxybenzoate, Id

Yield: 95.0 %; mp 89 ˚C, FTIR (ύ, cm^{-1}): 2916 2854 (CH_2 stretching), 1728 (C=O), 1593 (C=N), 161589 (C=C), 1472 (C-O Asym), 1243 (O-CH_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm: 0.91 (t, 3H, $CH_3(CH_2)_7CH_2CH_2$, *J* = 7.2 Hz), 1.27-1.40 (m, 14H, $CH_3(CH_2)_7CH_2CH_2$), 1.48-1.53 (m, 2H, $CH_3(CH_2)_7CH_2CH_2$), 4.07 (t, 2H, $CH_3(CH_2)_7CH_2CH_2$, *J* = 8.0 Hz), 6.39-6.48 (m, 1H, Ar-H), 7.36 (d, 2H, Ar-H, *J* = 12 Hz), 7.98-8.00 (m, 3H, Ar-H), 8.15-8.17 (m, 3H, Ar-H), 8.47 (m, 3H, Ar-H), 10.04 (s, 1H, CH=N). ^{13}C NMR (125 MHz, CDCl3) δ:ppm: 191.09, 156.11, 142.21, 133.89, 132.43, 131.28, 130.26, 122.65, 122.40, 120.66, 114.44, 68.41, 31.56, 29.05, 28.94, 25.67, 25.58, 22.61, 22.44, 22.43, 14.07.

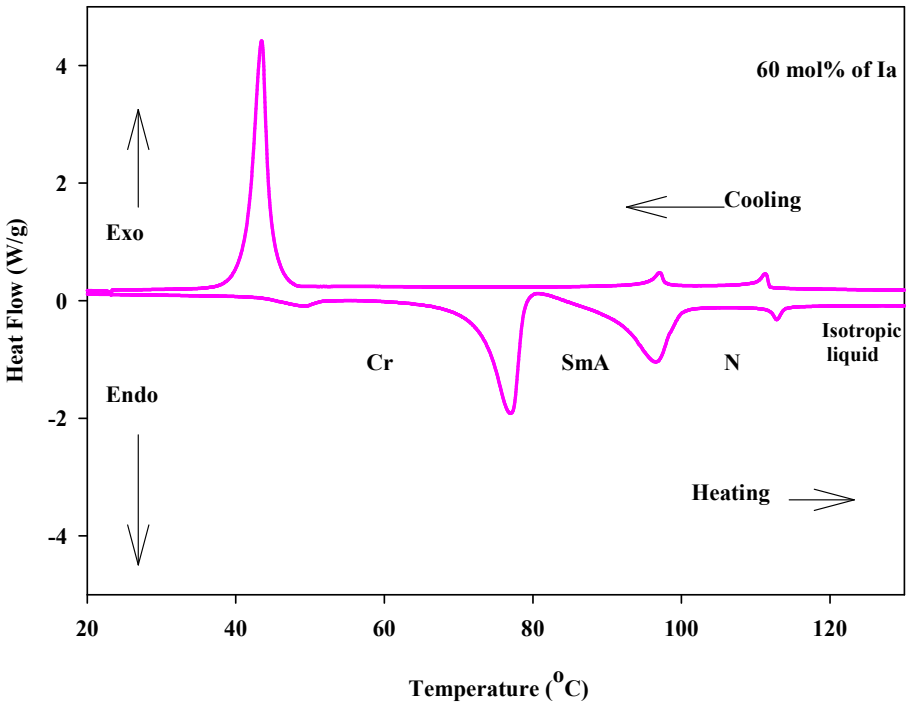


Figure S1. DSC thermograms of binary mixture 60 mol% **Ia** for system **Ia/Ib** upon heating/cooling cycles with rate 10 °C /min.

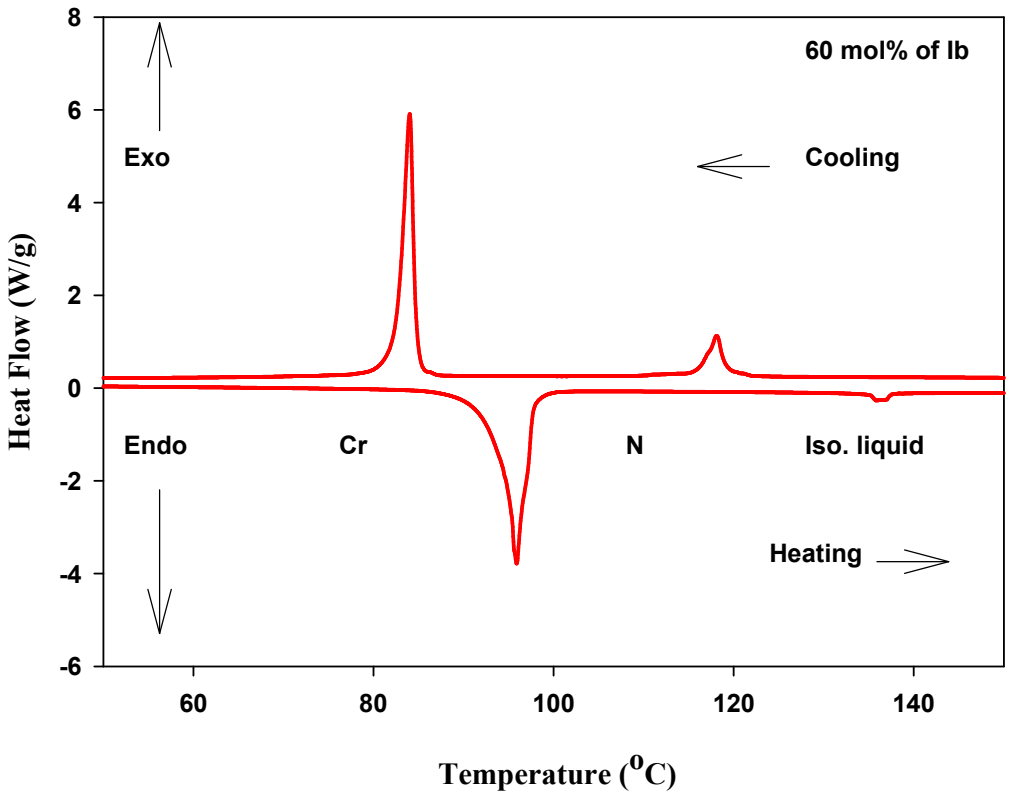


Figure S2. DSC thermograms of binary mixture 60 mol% **Ib** for system **Ib/Id** upon second heating/cooling cycles with rate 10 °C /min.

It is clearly shown that upon heating, the binary mixture 60 mol% **Ib** for system **Ib/Id** (**FigureS2**) showed two endotherms characteristic of the crystal–N and N–isotropic transitions. While, during the cooling cycle, it exhibit only nematic phase but its transition is shifted to lower temperatures compared with these observed through heating cycle. The POM measurements revealed textures which confirmed purely N mesophase. This indicated that this binary mixture possessed enantiotropic monotropic properties. That shift occurs also in our previously reported work [1].

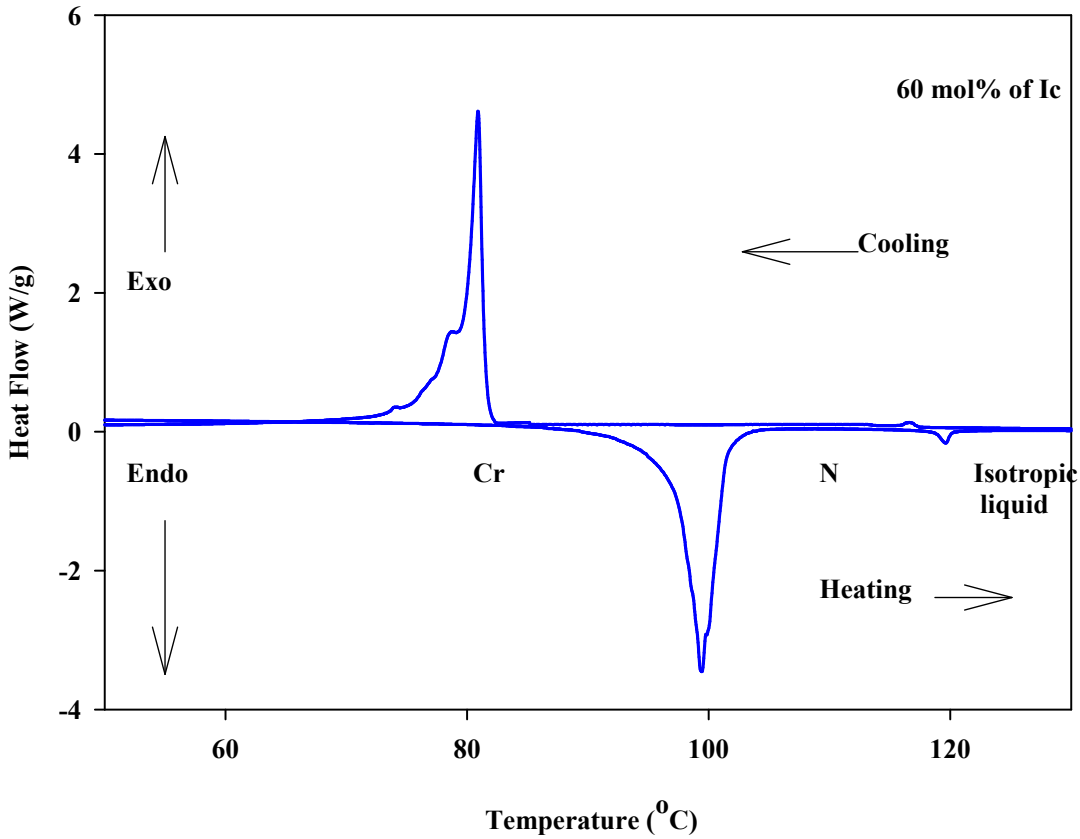


Figure S3. DSC thermograms of binary mixture 60 mol% **Ic** for system **Ic/Id** upon second heating/cooling cycles with rate 10 °C /min.

Figure S4. POM textures of binary mixtures upon heating (a) N phase of 60 mol% **Ia** for system **Ic/Id** at 112 °C; (b) SmA phase of 60 mol% **Ia** for system **Ia/Ib** at 84 °C ;(c) N phase of 60 mol% **Ia** for system **Ia/Ib** at 101 °C.

References

[1] Nagwa H. S. Ahmed, Gamal R. Saad, Hoda. A. Ahmed and Mohamed Hagar. New wide-stability four-ring azo/ester/Schiff base liquid crystals: synthesis, mesomorphic, photophysical, and DFT approaches. RSC *Advances*, **2020**; *10*, 9643.