Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Development of emergent ferroelectric nematic liquid crystals with highly fluorinated and rigid mesogens

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Materials and Methods

Materials

All commercial chemicals and solvents were used as received, unless stated otherwise. p-toluenesulfonic acid (p-TsOH) was obtained from Acros. butylated hydroxytoluene (BHT) was obtained from Bidepharm. Tetrahydrofuran (THF, Energy Chemical), Dichloromethane (DCM, Energy Chemical), Petroleum ether (PE, Energy Chemical), Ethyl acetate (EA, Energy Chemical), Methanol (MeOH, Energy Chemical), Toluene (Energy Chemical), 1,4-dioxane (Energy Chemical), n-Butyllithium (n-BuLi, 1.6mol/l in hexane, Energy Chemical), Iodine (I_2, Energy Chemical), Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, Bidepharm), [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($PdCl_2$(dppf), Bidepharm), Dicyclohexyl(2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphine (SPhos, Bidepharm), Potassium acetate (CH_3COOK, Bidepharm), Potassium phosphate (K_3PO_4, Bidepharm), Magnesium sulfate ($MgSO_4$, Bidepharm), Sodiumthiosulfate ($Na_2S_2O_3$, Bidepharm), 3,5-difluorobenzaldehyde (98%, Bidepharm), 2-propylpropane-1,3-diol (98%, Bidepharm), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (98%, Bidepharm), 4-bromo-2,6-difluorobenzonitrile (98%, Bidepharm), 5-bromo-1,3-difluoro-2-iodobenzene (98%, Bidepharm).

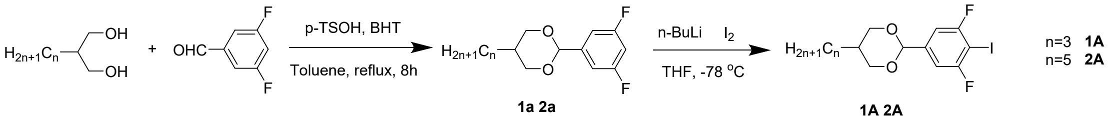
Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H and ^{13}C NMR spectra of the samples were obtained in $CDCl_3$ (Innochem, 99.8 atom % D, with 0.03%(v/v) TMS) solvents utilizing JASTEC JMTC-500/54/JJ 500 MHz NMR spectrometer. ^{1}H NMR spectra were referenced to the residual proton impurities in $CDCl_3$ at δ 7.26 ppm and ^{13}C NMR spectra were referenced to $^{13}CDCl_3$ at δ 77.16 ppm.

Differential Scanning Calorimetry (DSC). Thermal properties of all the samples were characterized utilizing a TA Instruments DSC 2500 with an Intercooler 2P apparatus. The temperature and heat flow scales were calibrated at different heating and cooling rates (5-20 °C/min) using a series of standard materials. For each run of the experiments, the initial mass of the samples used was about 4-5 mg under nitrogen flow.

X-ray diffraction (XRD). XRD was executed by Rigaku Nanopix-SP with an ultrahigh intensity microfocus rotating anode X-ray generator. The wavelength X-ray is 0.154 nm. The samples were melted on a hot stage, then loaded into glass tubes with a diameter of 0.3 mm.

Synthesis



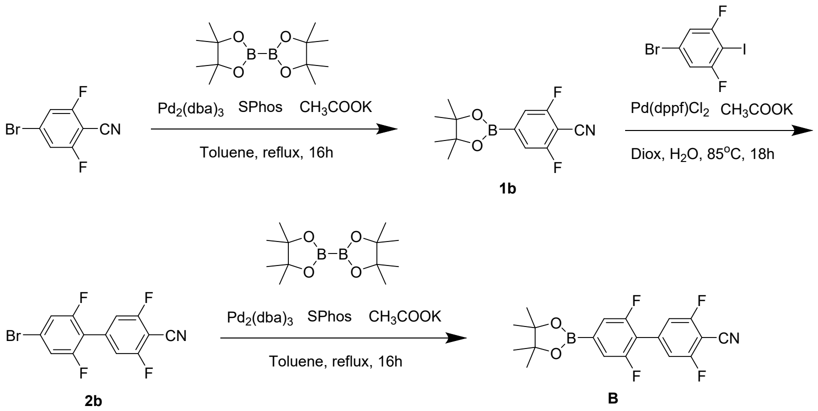
Scheme S1. The synthesis scheme of LC mesogen precursors (A).

2-(3,5-difluorophenyl)-5-propyl-1,3-dioxane (1a): A round bottom flask was charged with 2-propylpropane-1,3-diol (5g, 0.042mol), 3,5-difluorobenzaldehyde (6.31g, 0.044mol), p-TsOH (0.32g, 1.68mmol), BHT (0.09g, 0.42mmol), and 100mL toluene. The solution was degassed by bubbling with nitrogen for 5 min. The solution was heated to reflux, and stirred under nitrogen for 8h. During the reaction, the by-product water was separated. The mixture was cooled to room temperature and extracted with EA. The organic phase was washed with water and brine, then dried with anhydrous $MgSO_4$. The residual after removing solvent by evaporation under reduced pressure was dry-loaded onto a silica gel column for purification using EA/PE as eluent and dried in vacuum oven. Yield: 8.6 g (82.2%) (mixtures of isomers with molar ratio of 4/1); appearance: light yellow oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.05 – 7.00 (m, 2H), 6.76 (tt, J = 8.9, 2.4 Hz, 1H), 5.41 (5.46) (d, J = 49.1 Hz, 1H), 4.26 – 4.20 (4.09 – 4.04) (m, 2H), 3.51 (ddd, J = 11.6, 10.4, 1.6 Hz, 2H), 2.18 – 2.09 (1.47 – 1.44) (m, 1H), 1.37 – 1.31 (1.43 – 1.41) (m, 2H), 1.12 – 1.06 (1.77 – 1.72) (m, 2H), 0.94 (dt, J = 14.6, 7.4 Hz, 3H). ^{19}F NMR (471 MHz, Chloroform-d) δ -109.64 (dt, J = 16.4, 8.3 Hz). ^{13}C NMR (126 MHz, Chloroform-d) δ 164.03 (dd, J = 12.5, 6.1 Hz), 162.06 (dd, J = 12.4, 6.2 Hz), 142.34 (t, J = 9.2 Hz), 109.55 – 109.19 (m), 104.11 (t, J = 25.3 Hz), 99.95 (100.11) (dt, J = 41.9, 2.6 Hz), 71.72 (70.76), 34.04 (34.13), 30.40 (31.72), 19.66 (20.68), 14.31 (14.21).

2-(3,5-difluoro-4-iodophenyl)-5-propyl-1,3-dioxane (1A): A round bottom flask was charged with **1a** (8.4g, 0.035mol) and dry THF 100mL, then the mixture was flashed with N_2 for 5 minutes. The solution was cooled to -78 °C, n-BuLi (23.75mL, 0.038mol, 1.6M in hexane) was injected to the mixture over 30min. After stirring 1h, iodine (9.64g, 0.038mol) was dissolved in 20mL THF, added dropwise and stirred at -78 °C for 1h. Then the solution was restored to room temperature and stirred for 1h. After that the reaction mixture was quenched by 1M HCl aq. and saturated $Na_2S_2O_3$ solution. THF solvent was removed. The residue was dissolved in EA, washed with water, dried by $MgSO_4$. The organic phase was concentrated under vacuum, purified by flash chromatograph using EA/PE as eluent and dried in vacuum oven. Yield: 12.2 g (95.6%) (mixtures of isomers with molar ratio of 4/1); appearance: brown oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.06 – 7.01 (m, 2H), 5.34 (5.45) (d, J = 51.1 Hz, 1H), 4.26 – 4.19 (4.07 – 4.05) (m, 2H), 3.51 (dddd, J = 11.6, 10.4, 4.3, 1.5 Hz, 2H), 2.17 – 2.08 (1.47 – 1.45) (m, 1H), 1.36 – 1.30 (1.44 – 1.39) (m, 2H), 1.11 – 1.06 (1.77 – 1.70) (m, 2H), 0.94 (dt, J = 12.4, 7.3 Hz, 3H). ^{19}F NMR (471 MHz, Chloroform-d) δ -92.08 (dd, J = 21.0, 7.7 Hz). ^{13}C NMR (126 MHz, Chloroform-d) δ 163.61 (d, J = 5.9 Hz), 161.68 (t, J = 5.8 Hz), 142.53 (t, J = 8.8 Hz), 109.44 (dt, J = 26.2, 3.1 Hz), 99.30 (99.59) (m), 72.68 (70.73), 70.89 (d, J = 39.1 Hz), 34.04 (34.08), 30.40 (31.69), 19.65 (20.66), 14.32 (14.21).

2-(3,5-difluorophenyl)-5-pentyl-1,3-dioxane (2a): A round bottom flask was charged with 2-pentylpropane-1,3-diol (5g, 0.034mol), 3,5-difluorobenzaldehyde (5.24g, 0.037mol), p-TsOH (0.24g, 1.41mmol), BHT (0.08g, 0.35mmol), and 100mL toluene. The solution was degassed by bubbling with nitrogen for 5 min. The solution was heated to reflux, and stirred under nitrogen for 8h. During the reaction, the by-product water was separated. The mixture was cooled to room temperature and extracted with EA. The organic phase was washed with water and brine, then dried with anhydrous $MgSO_4$. The residual after removing solvent by evaporation under reduced pressure was dry-loaded onto a silica gel column for purification using EA/PE as eluent and dried in vacuum oven. Yield: 7.9 g (85.5%) (mixtures of isomers with molar ratio of 4/1); appearance: light yellow oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.06 – 7.00 (m, 2H), 6.76 (tt, J = 8.9, 2.4 Hz, 1H), 5.36 (5.45) (d, J = 49.2 Hz, 1H), 4.26 – 4.20 (4.06) (m, 2H), 3.55 – 3.48 (m, 2H), 2.11 (1.44 – 1.40) (ttt, J = 11.4, 6.9, 4.6 Hz, 1H), 1.36 – 1.24 (1.39 – 1.35) (m, 6H), 1.09 (1.78 – 1.73) (dt, J = 8.8, 6.7 Hz, 2H), 0.93 – 0.87 (m, 3H). ^{19}F NMR (471 MHz, Chloroform-d) δ -109.65 (h, J = 6.8, 5.5 Hz). ^{13}C NMR (126 MHz, Chloroform-d) δ 164.03 (dd, J = 12.5, 6.0 Hz), 162.05 (dd, J = 12.3, 6.0 Hz), 142.36 (t, J = 9.2 Hz), 109.55 – 109.21 (m), 104.09 (t, J = 25.3 Hz), 99.78 (100.11) (d, J = 2.9 Hz), 72.70 (70.77), 34.27 (34.43), 32.04 (32.00), 28.20 (29.51), 26.09 (27.31), 22.58 (22.77), 14.11 (14.17).

2-(3,5-difluoro-4-iodophenyl)-5-pentyl-1,3-dioxane (2A): A round bottom flask was charged with **2a** (5.0g, 0.018mol) and dry THF 100mL, then the mixture was flashed with N_2 for 5 minutes. The solution was cooled to -78 °C, n-BuLi (12.7mL, 0.020mol, 1.6M in hexane) was injected to the mixture over 30min. After stirring 1h, iodine (5.15g, 0.020mol) was dissolved in 20mL THF, added dropwise and stirred at -78 °C for 1h. Then the solution was restored to room temperature and stirred for 1h. After that the reaction mixture was quenched by 1M HCl aq. and saturated $Na_2S_2O_3$ solution. THF solvent was removed. The residue was dissolved in EA, washed with water, dried by $MgSO_4$. The organic phase was concentrated under vacuum, purified by flash chromatograph using EA/PE as eluent and dried in vacuum oven. Yield: 7.0 g (95.5%) (mixtures of isomers with molar ratio of 4/1); appearance: brown oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.06 – 7.01 (m, 2H), 5.34 (5.44), 4.25 – 4.19 (4.08 – 4.03) (m, 2H), 3.54 – 3.47 (m, 2H), 2.09 (1.45 – 1.41) (ttt, J = 11.4, 6.9, 4.6 Hz, 1H), 1.34 – 1.25 (1.39 – 1.36) (m, 6H), 1.09 (1.75 – 1.71) (dt, J = 8.7, 6.7 Hz, 2H), 0.89 (td, J = 7.0, 1.7 Hz, 3H). ^{19}F NMR (471 MHz, Chloroform-d) δ -92.02 – -92.17 (m). ^{13}C NMR (126 MHz, Chloroform-d) δ 163.62 (d, J = 6.1 Hz), 161.65 (d, J = 5.7 Hz), 142.52 (t, J = 8.8 Hz), 109.63 – 109.27 (m), 99.33 – 99.29 (99.60) (m), 72.70 (70.76), 71.38 – 70.70 (m), 34.24 (34.38), 31.99 (32.04), 28.18 (29.47), 26.09 (27.29), 22.59 (22.78), 14.14 (14.19).

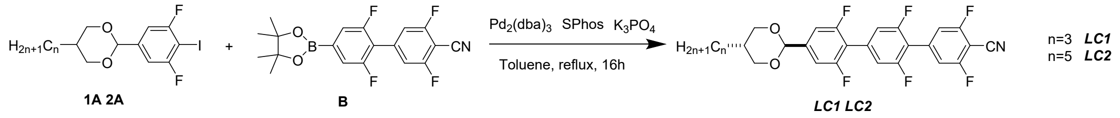


Scheme S2. The synthesis scheme of LC mesogen precursor (B).

2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (1b): A Schlenk flask was charged with 4-bromo-2,6-difluorobenzonitrile (13g, 0.060mol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (22.75g, 0.090mol), CH_3COOK (17.55g, 0.179mol), SPhos (1.95g, 4.74mmol), $Pd(dba)_3$ (2.18g, 2.38mmol), toluene 300mL. Froze the solvent with liquid nitrogen, degassed for 3 times, then refilled nitrogen and heat it to reflux for 16h. The mixture was cooled to room temperature and extracted with EA. The organic phase was washed with water, then dried with anhydrous $MgSO_4$. The residual after removing solvent by evaporation under reduced pressure was dry-loaded onto a silica gel column for purification using EA/PE as eluent and dried in vacuum oven. Yield: 13.2 g (83.4%); appearance: white powder. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.44 – 7.40 (m, 2H), 1.34 (s, 12H). ^{19}F NMR (471 MHz, Chloroform-d) δ -104.67 (d, J = 10.7 Hz). ^{13}C NMR (126 MHz, Chloroform-d) δ 163.83 (d, J = 3.1 Hz), 161.74 (d, J = 3.2 Hz), 117.42 (dd, J = 17.9, 3.7 Hz), 109.47, 94.37, 85.34, 24.95.

4'-bromo-2',3,5,6'-tetrafluoro-[1,1'-biphenyl]-4-carbonitrile (2b): A Schlenk flask was charged with **1b** (8.8g, 0.033mol), 5-bromo-1,3-difluoro-2-iodobenzene (12.67g, 0.040mol), K_2CO_3 (18.35g, 0.133mol), $PdCl_2$(dppf) (0.243g, 0.33mmol), 150mL mixed solvent of 1,4-dioxane/H_2O = 5/2. Froze the solvent with liquid nitrogen, degassed for 3 times, then refilled nitrogen and heat it to 85 ^{o}C for 18h. The mixture was cooled to room temperature and extracted with EA. The organic phase was washed with water, then dried with anhydrous $MgSO_4$. The residual after removing solvent by evaporation under reduced pressure was dry-loaded onto a silica gel column for purification using EA/PE as eluent and dried in vacuum oven. Yield: 5.8 g (52.9%); appearance: white powder. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.29 – 7.24 (m, 2H), 7.18 (dq, J = 9.8, 1.6 Hz, 2H). ^{19}F NMR (471 MHz, Chloroform-d) δ -103.35 (d, J = 8.6 Hz), -111.79 (d, J = 8.4 Hz). ^{13}C NMR (126 MHz, Chloroform-d) δ 164.02 (d, J = 5.2 Hz), 161.94 (d, J = 5.0 Hz), 160.48 (d, J = 6.8 Hz), 158.45 (d, J = 7.1 Hz), 136.47 (t, J = 10.7 Hz), 123.90 (t, J = 12.4 Hz), 116.69 – 116.31 (m), 114.26 (dt, J = 20.8, 3.1 Hz), 108.98, 92.57.

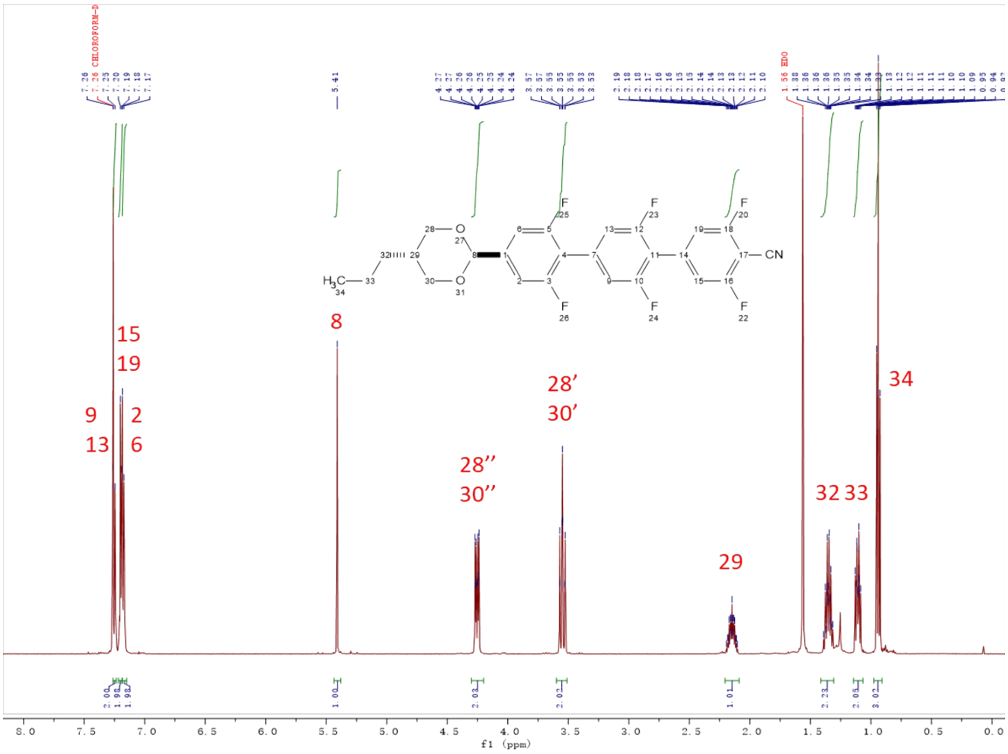
2',3,5,6'-tetrafluoro-4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-carbonitrile (B): A Schlenk flask was charged with **2b** (3g, 9.09mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (3.45g, 0.040mol), CH_3COOK (2.68g, 0.027mol), SPhos (0.30g, 0.73mmol), Pd(dba)$_3$ (0.33g, 0.36mmol), toluene 60mL. Froze the solvent with liquid nitrogen, degassed for 3 times, then refilled nitrogen and heat it to reflux for 16h. The mixture was cooled to room temperature and extracted with EA. The organic phase was washed with water, then dried with anhydrous $MgSO_4$. The residual after removing solvent by evaporation under reduced pressure was dry-loaded onto a silica gel column for purification using EA/PE as eluent and dried in vacuum oven. Yield: 2.9 g (84.6%); appearance: white powder. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.47 – 7.41 (m, 2H), 7.24 – 7.18 (m, 2H), 1.36 (s, 12H). ^{19}F NMR (471 MHz, Chloroform-d) δ -103.89 (d, J = 8.7 Hz), -114.67 (d, J = 9.4 Hz). ^{13}C NMR (126 MHz, Chloroform-d) δ 163.95 (d, J = 5.2 Hz), 161.87 (d, J = 5.1 Hz), 160.16 (d, J = 4.9 Hz), 158.15 (d, J = 5.1 Hz), 137.57 (t, J = 10.6 Hz), 117.99 – 117.67 (m), 117.15, 114.65 – 114.24 (m), 109.15, 92.22, 84.93, 24.97.

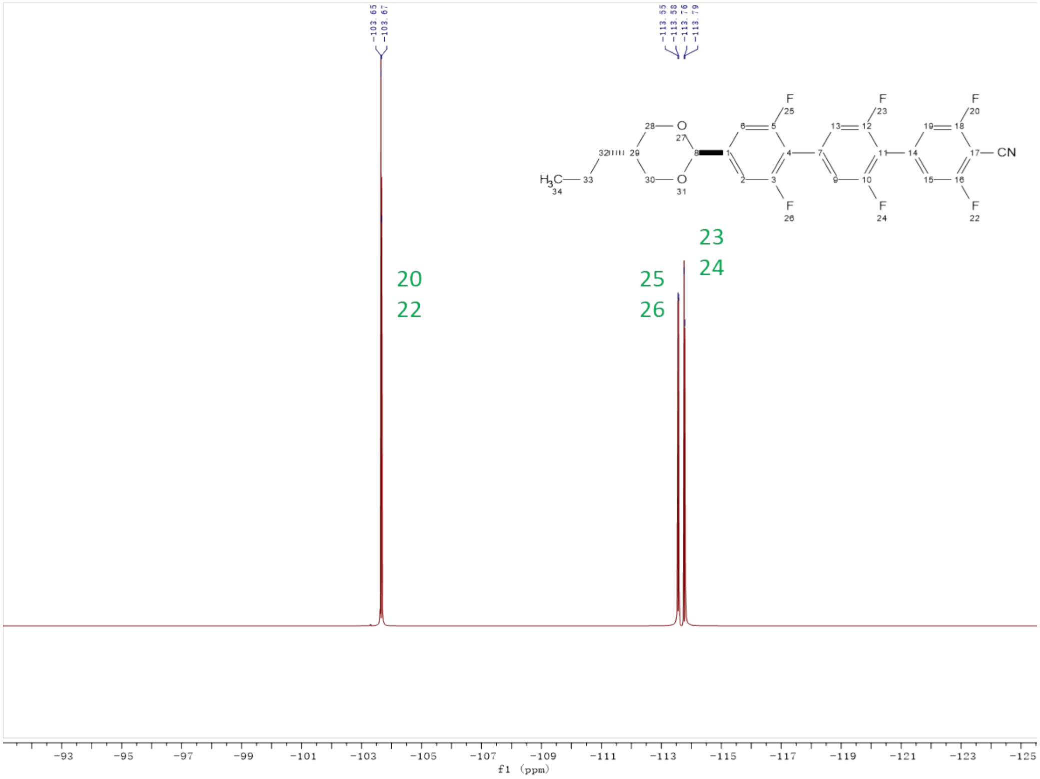


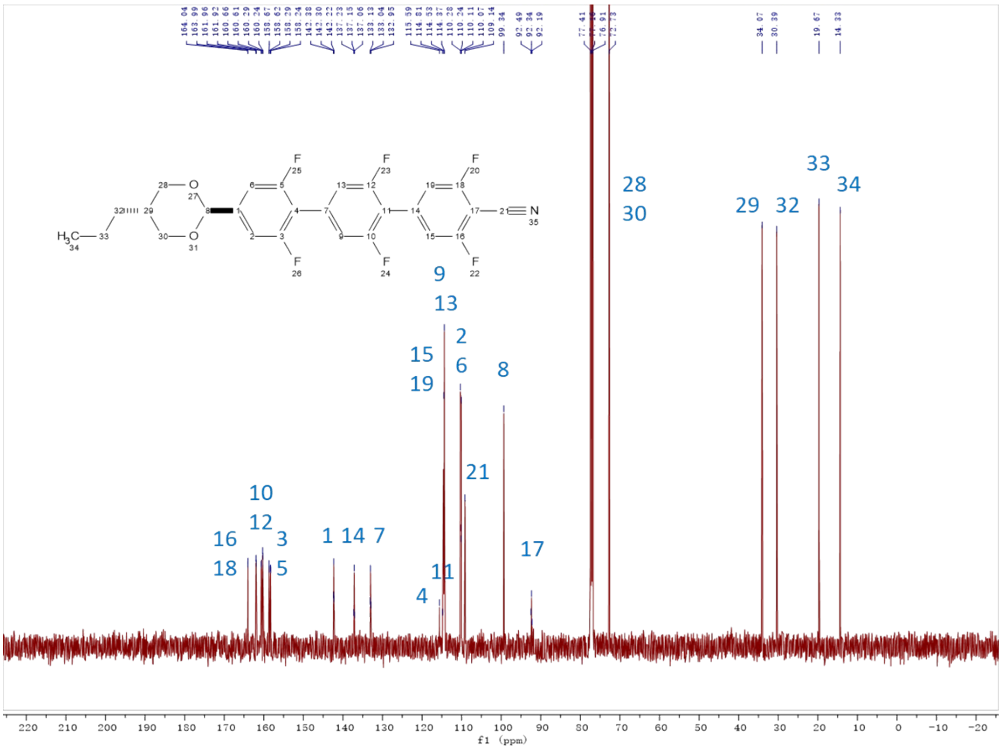
Scheme S3. The synthesis scheme of *LC1* and *LC2*.

2',2'',3,5,6',6''-hexafluoro-4''-((2r,5r)-5-propyl-1,3-dioxan-2-yl)-[1,1':4',1''-terphenyl]-4-carbonitrile (*LC1*): A Schlenk flask was charged with **1A** (2.34g, 7.29mmol), **B** (2.5g, 6.63mmol), K_3PO_4 (4.22g, 0.020mol), SPhos (0.218g, 0.53mmol), Pd(dba)$_3$ (0.243g, 0.27mmol), 50mL mixed solvent of toluene/H_2O = 5/2. Froze the solvent with liquid nitrogen, degassed for 3 times, then refilled nitrogen and heat it to reflux for 16h. The mixture was cooled to room temperature and extracted with EA. The organic phase was washed with water, then dried with anhydrous $MgSO_4$. The residual after removing solvent by evaporation under reduced pressure was dry-loaded onto a silica gel column for purification using THF/PE as eluent and dried in vacuum oven. Yield: 2.1 g (65.4%); appearance: white powder. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.25 (s, 2H), 7.20 (d, J = 5.9 Hz, 2H), 7.18 (d, J = 6.3 Hz, 2H), 5.41 (s, 1H), 4.30 – 4.21 (m, 2H), 3.59 – 3.51 (m, 2H), 2.21 – 2.09 (m, 1H), 1.38 – 1.32 (m, 2H), 1.14 – 1.08 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{19}F NMR (471

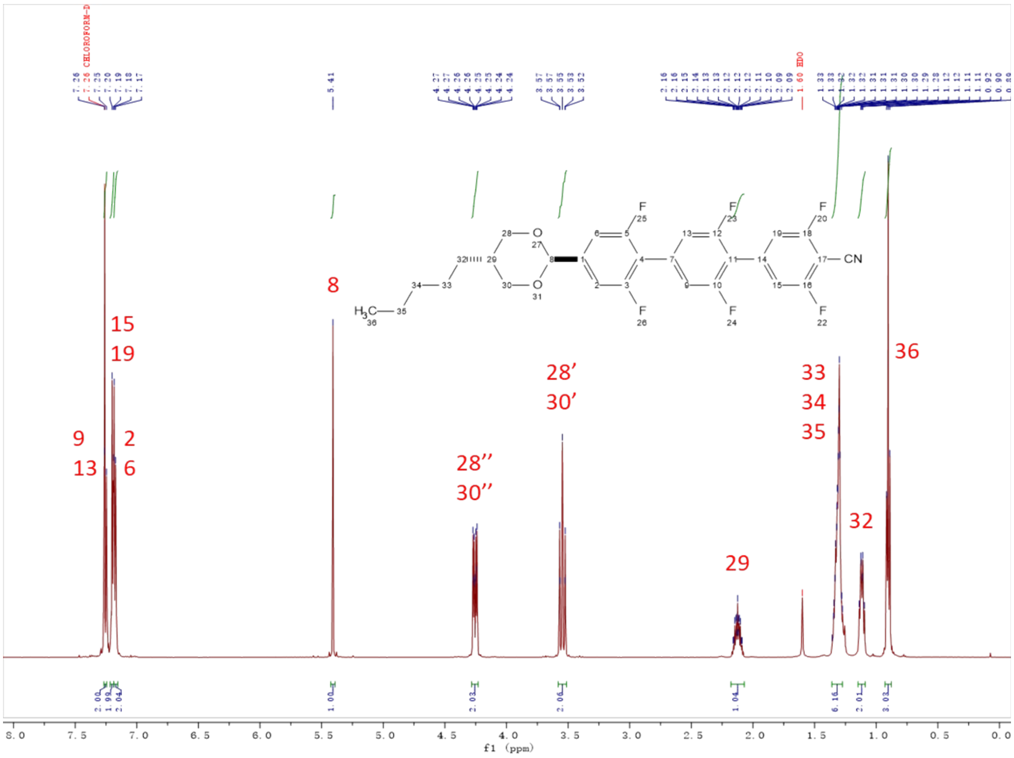
MHz, Chloroform-d) δ -103.66 (d, J = 9.3 Hz), -113.57 (d, J = 10.8 Hz), -113.77 (d, J = 11.0 Hz). ^{13}C NMR (126 MHz, Chloroform-d) δ 164.02 (d, J = 5.4 Hz), 161.94 (d, J = 4.8 Hz), 160.63 (d, J = 6.6 Hz), 160.27 (d, J = 6.9 Hz), 158.64 (d, J = 6.4 Hz), 158.27 (d, J = 6.9 Hz), 142.34 (d, J = 9.6 Hz), 137.15, 133.04, 115.59, 114.53, 114.37, 110.37 – 109.98 (m), 109.14, 99.34, 92.34, 72.73, 34.07, 30.39, 19.67, 14.33.







2',2'',3,5,6',6''-hexafluoro-4''-((2r,5r)-5-pentyl-1,3-dioxan-2-yl)-[1,1':4',1''-terphenyl]-4-carbonitrile (*LC2*): A Schlenk flask was charged with **2A** (0.51g, 1.46mmol), **B** (0.5g, 1.33mmol), K_3PO_4 (0.78g, 3.66mmol), SPhos (0.04g, 0.10mmol), $Pd(dba)_3$ (0.05g, 0.05mmol), 50mL mixed solvent of toluene/H_2O = 5/2. Froze the solvent with liquid nitrogen, degassed for 3 times, then refilled nitrogen and heat it to reflux for 16h. The mixture was cooled to room temperature and extracted with EA. The organic phase was washed with water, then dried with anhydrous $MgSO_4$. The residual after removing solvent by evaporation under reduced pressure was dry-loaded onto a silica gel column for purification using THF/PE as eluent and dried in vacuum oven. Yield: 0.5 g (72.6%); appearance: white powder. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.25 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 5.4 Hz, 2H), 7.18 (d, J = 5.7 Hz, 2H), 5.41 (s, 1H), 4.28 – 4.23 (m, 2H), 3.58 – 3.51 (m, 2H), 2.13 (tddd, J = 11.4, 9.2, 7.0, 4.6 Hz, 1H), 1.36 – 1.26 (m, 6H), 1.12 (dt, J = 8.8, 6.7 Hz, 2H), 0.93 – 0.88 (m, 3H). ^{19}F NMR (471 MHz, Chloroform-d) δ -103.67 (d, J = 11.0 Hz), -113.58 (d, J = 8.9 Hz), -113.78 (d, J = 11.0 Hz). $_{13}$C NMR (126 MHz, Chloroform-d) δ 164.01 (d, J = 5.3 Hz), 161.93 (d, J = 5.2 Hz), 160.63 (d, J = 6.5 Hz), 160.26 (d, J = 6.9 Hz), 158.64 (d, J = 6.6 Hz), 158.26 (d, J = 7.0 Hz), 142.31 (t, J = 9.6 Hz), 137.14 (t, J = 10.5 Hz), 133.04 (t, J = 11.2 Hz), 115.58 (t, J = 17.7 Hz), 114.45 (d, J = 22.1 Hz), 110.38 – 109.97 (m), 109.13, 99.33, 92.34 (t, J = 19.2 Hz), 72.76, 34.30, 32.06, 28.20, 26.10, 22.59, 14.13.



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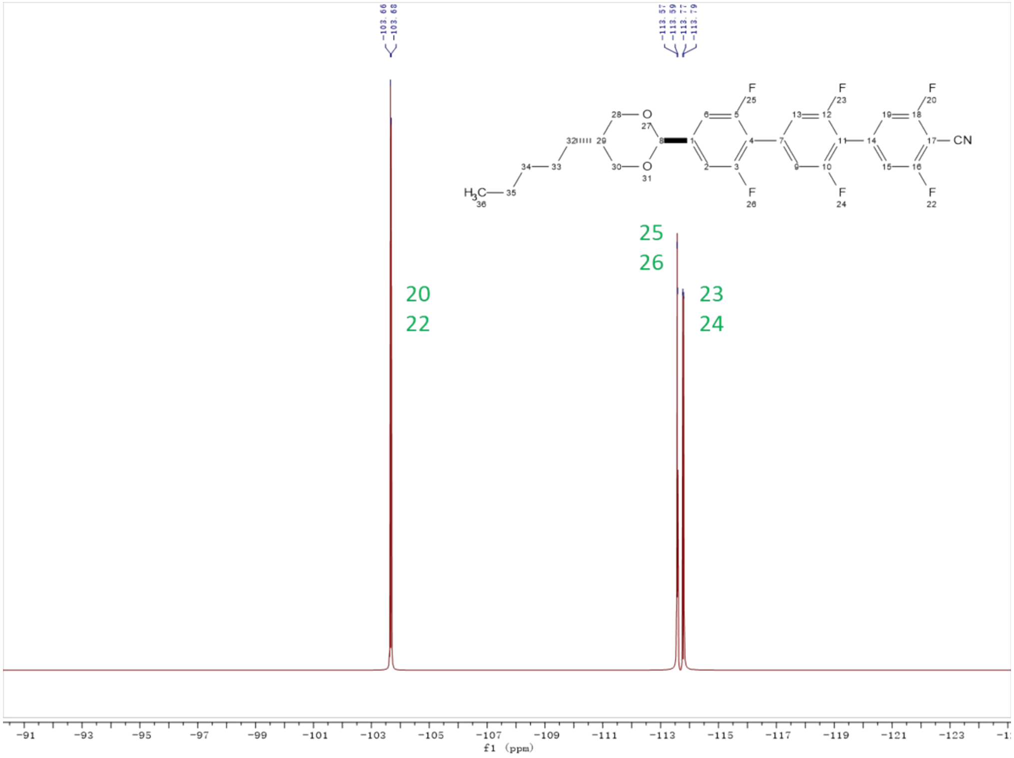

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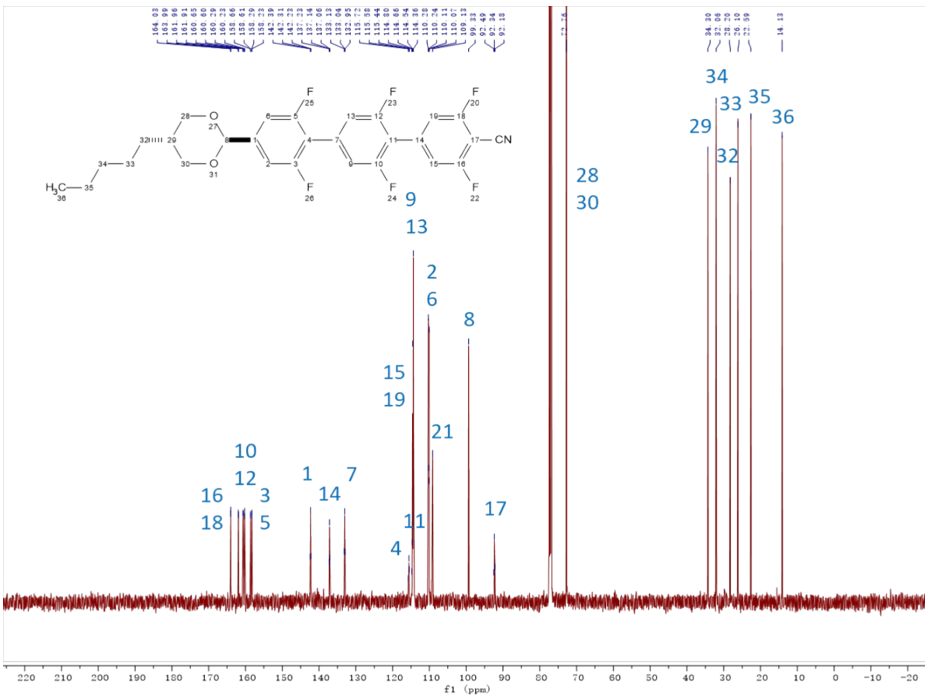
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92.34
92.18
72.76
34.30
32.06
28.20
26.10
22.59
14.13
F
25
F
23
F
20
28
O
27
32
29
8
1
6
5
4
7
13
12
11
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19
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17
CN
30
O
31
2
3
9
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F
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F
24
F
22
34
33
H3C
35
36
34
33
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32
28
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9
13
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21
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12
16
18
3
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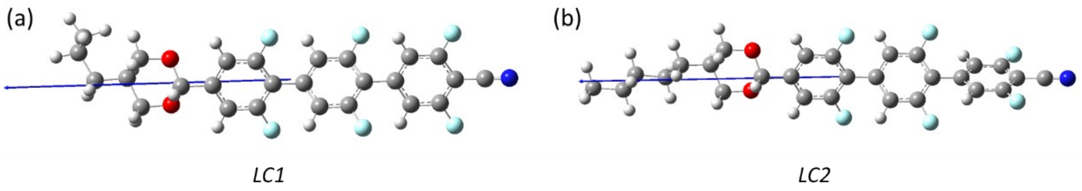
1
14
7
11
4
17
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



LC1

LC2

Figure S1. *The molecular energy-minimized conformations of LC1 (a) and LC2 (b) calculated by the b3lyp/6-311+g(d,p) DFT.*

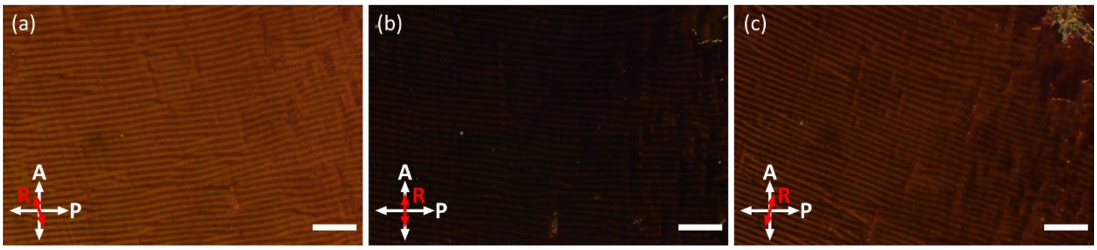


Figure S2. *The PLM textures of LC1 in the* ***X*** *phase under crossed polarizers in LC cells with planar alignment. (a) The LC cell rotated counterclockwise by 10°, (b) The rubbing direction of the LC cell was parallel to the A polarizer, (c) The LC cell rotated clockwise by 10°. Cell thickness: 5 µm. Scale bar: 100 µm. Temperature: 195 °C.*

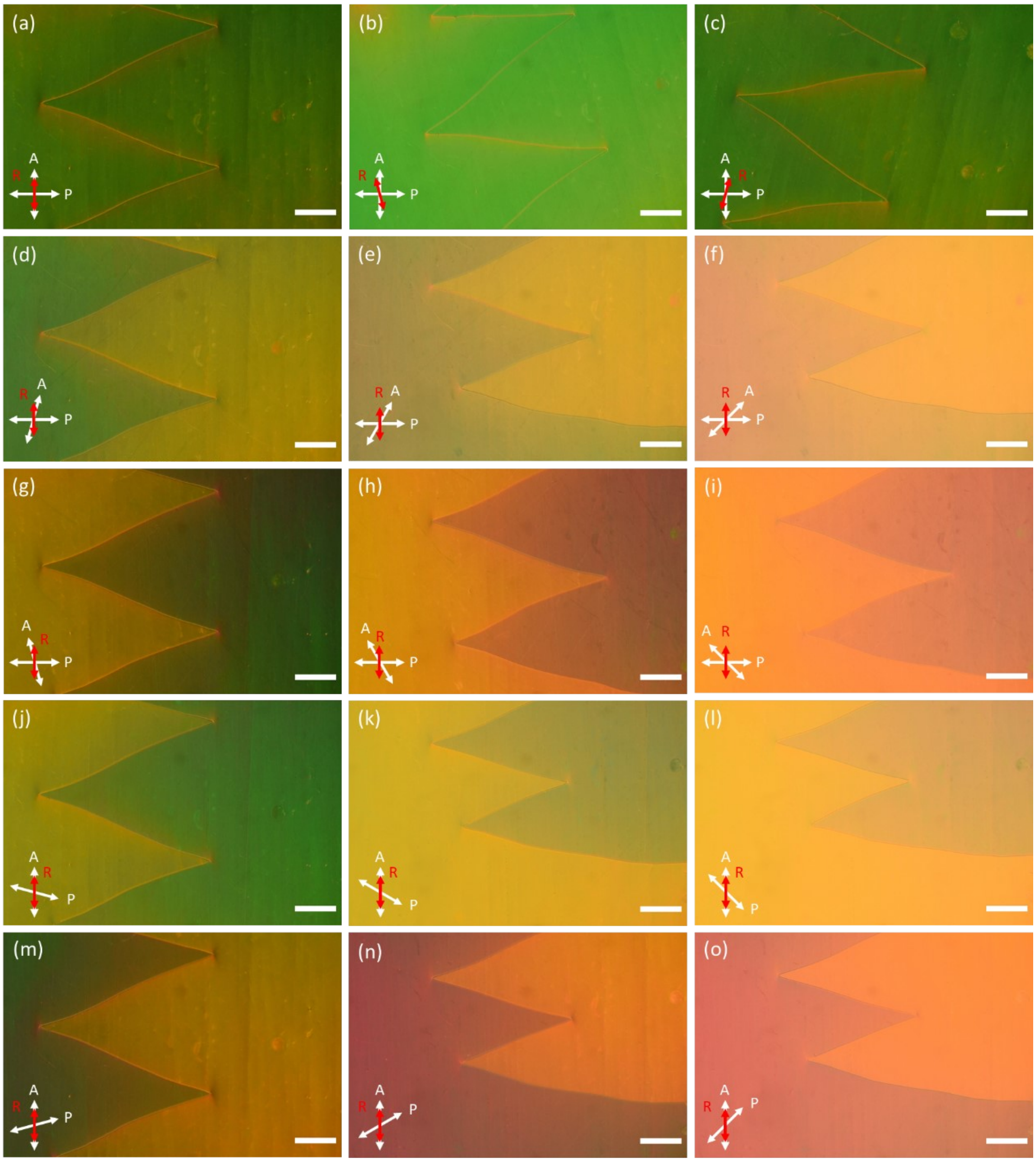


Figure S3. *The PLM observation of the* $\mathbf{N_F}$ *phase of LC1 in an anti-parallel aligned cell. (a) The LC cell was placed parallel to the A polarizer under crossed polarizers, and the LC cell was rotated 15° counterclockwise (b) and clockwise (c). The A polarizer was rotated 15° (d), 30° (e), and 45° (f) clockwise. The A polarizer was rotated 15° (g), 30° (h), and 45° (i) counterclockwise. The P polarizer was rotated 15° (j), 30° (k), and 45° (l) clockwise. The P polarizer was rotated 15° (m), 30° (n), and 45° (o) counterclockwise. Cell thickness: 5μm. Scale bar: 100μm. Temperature: 180* ^{o}*C.*

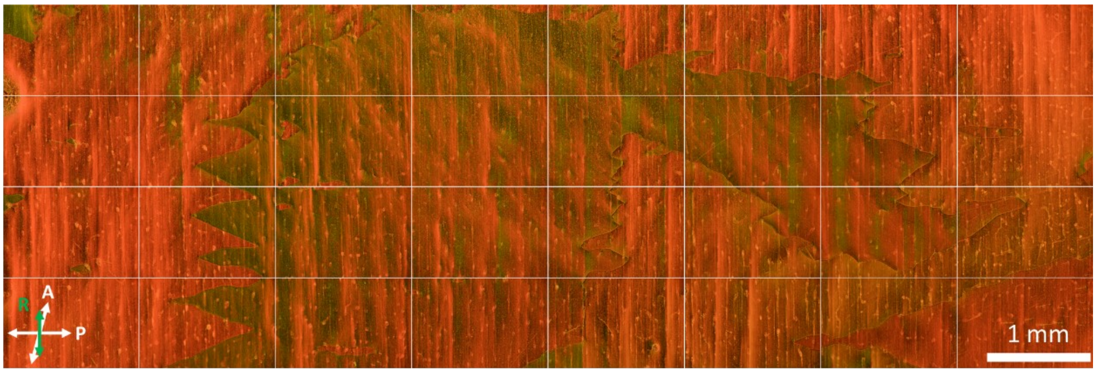


Figure S4. *The combined PLM texture of the* $\mathbf{N_F}$ *phase in the same LC cell under the decrossing analyzer shows the big domain of the 50/50 mixture. Cell thickness: 5 µm. Scale bar: 1 mm. Temperature: 145* ^{o}*C.*

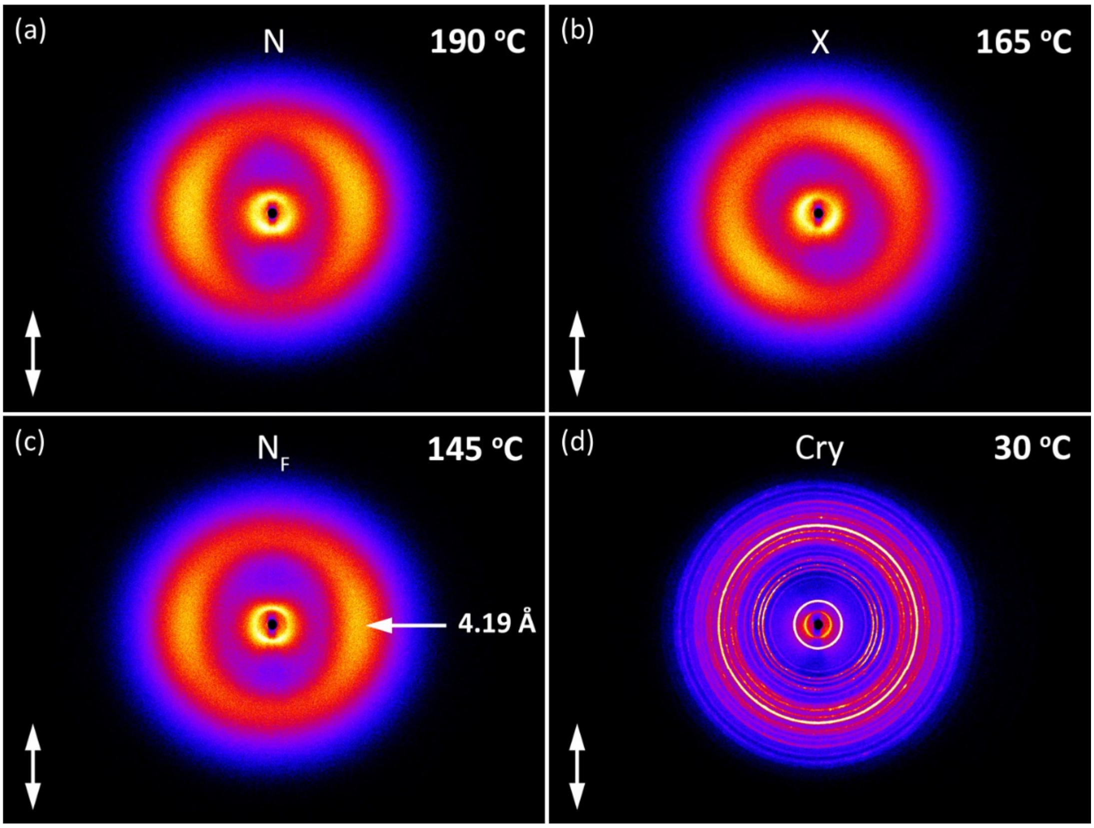


Figure S5. *(2D) XRD patterns of 50/50 mixture during cooling, from* ***N*** *at 190 °C (a) to* ***X*** *at 165 °C (b) and* ***N$_F$*** *at 145 °C (c), and finally to room temperature (****Cry****) (d). The axis at the bottom left indicates the capillary direction in which the sample was melt-loaded. The characteristic peak of* ***N$_F$*** *LC was marked.*

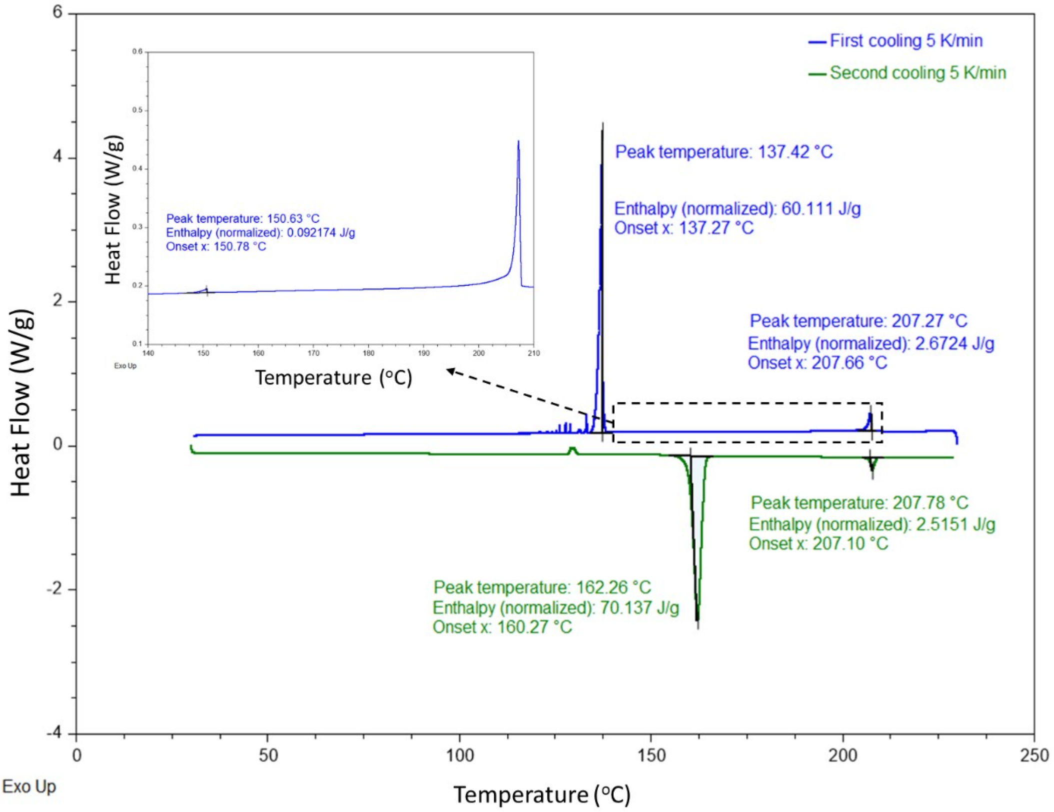


Figure S6. *The DSC profile of LC2. The insert image shows a small exothermal peak at ~150* ^{o}*C, corresponding to the phase transition of **N-X** in the first cooling process. The scanning rate is 5 K/min.*

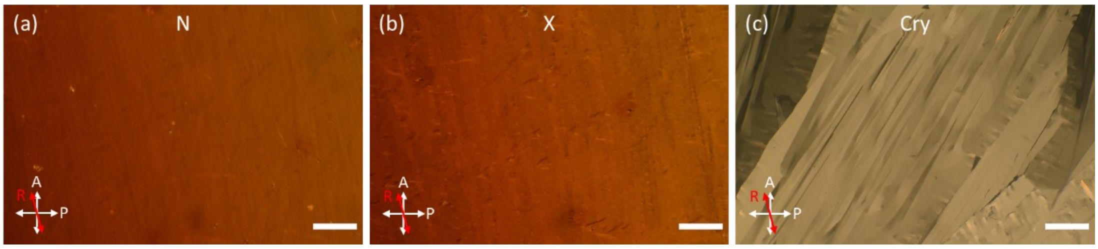


Figure S7. *The representative PLM texture evolution of LC2 under crossed polarizers in an anti-parallel aligned LC cell. (a)* ***N*** *(170 ^{o}C), (b)* ***X*** *(150 ^{o}C) and (c)* ***Cry*** *(135 ^{o}C). Cell thickness: 5μm. Scale bar: 100μm.*

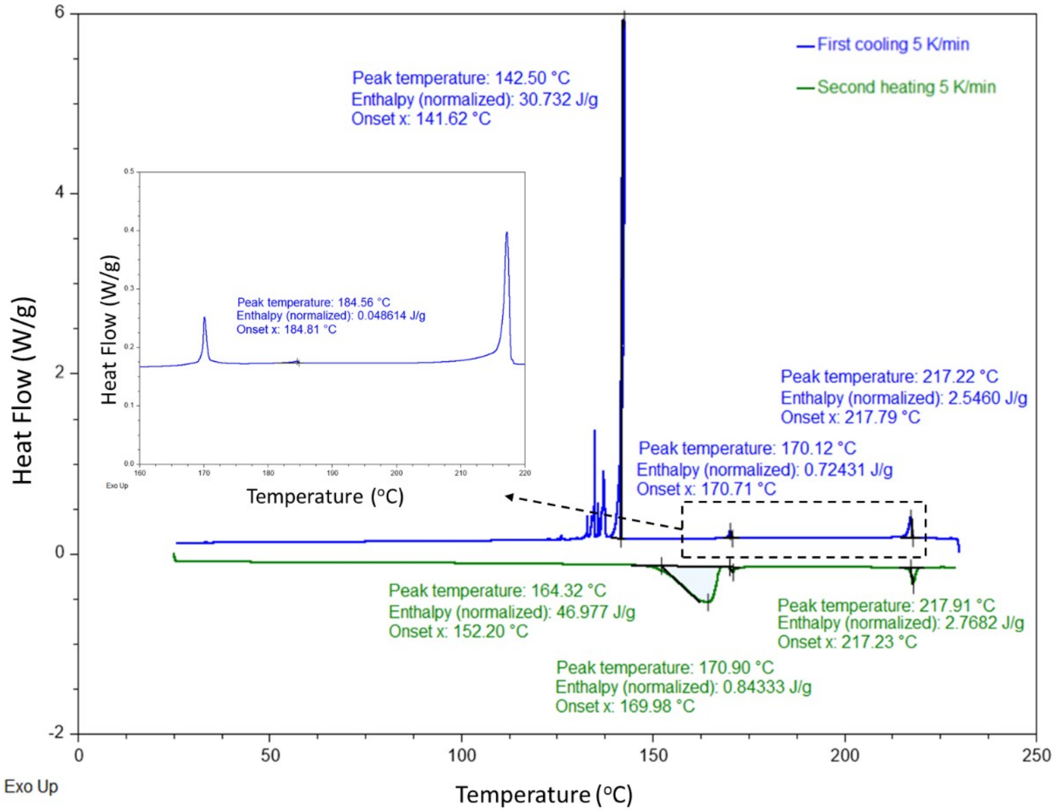


Figure S8. *The DSC profile of 75/25 mixture. The insert image shows a small exothermal peak at ~184 °C, corresponding to the phase transition of* ***N-X*** *in the first cooling process. The scanning rate is 5 K/min.*

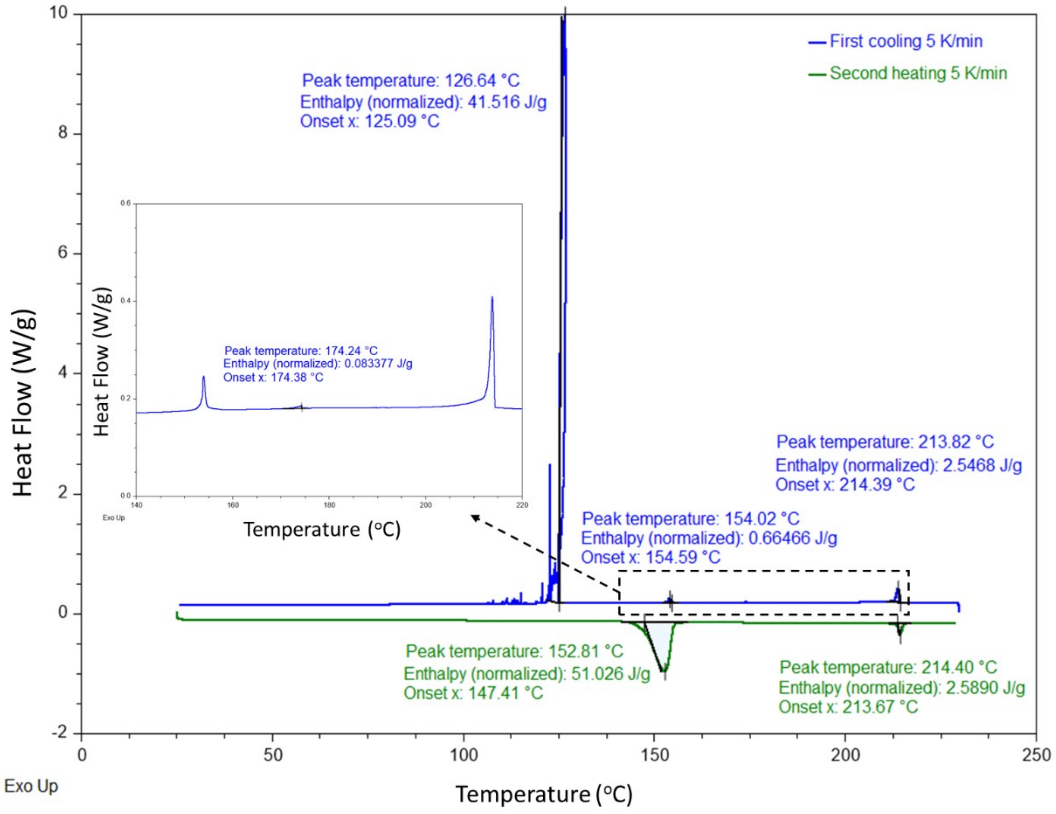


Figure S9. *The DSC profile of 50/50 mixture. The insert image shows a small exothermal peak at ~174 °C, corresponding to the phase transition of **N-X** in the first cooling process. The scanning rate is 5 K/min.*

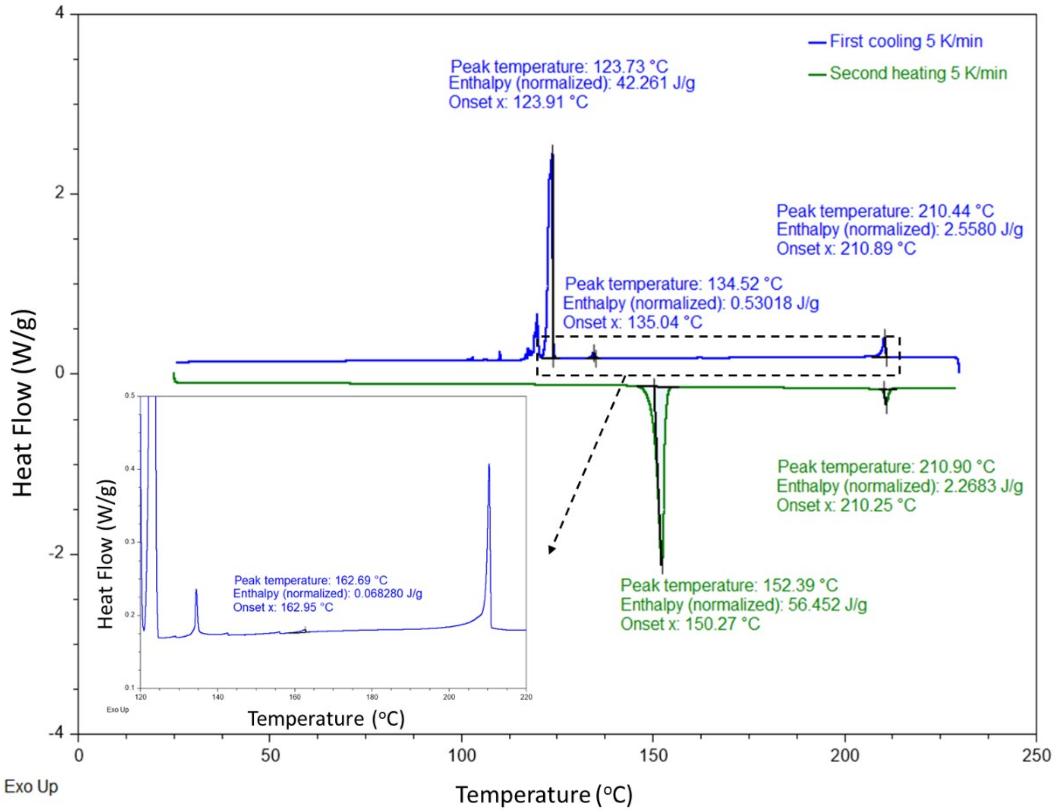


Figure S10. *The DSC profile of 25/75 mixture. The insert image shows a small exothermal peak at ~162 ^{o}C, corresponding to the phase transition of* ***N-X*** *in the first cooling process. The scanning rate is 5 K/min.*

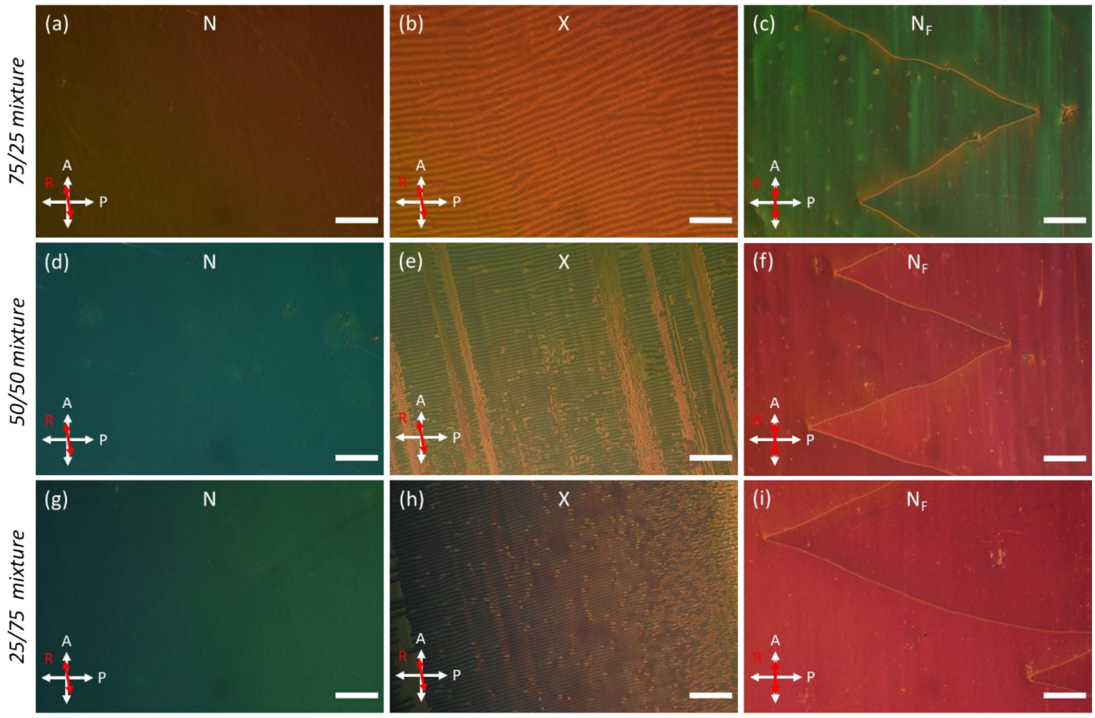


Figure S11. *The representative PLM texture evolution of mixtures with different weight percent under crossed polarizers in anti-parallel aligned LC cells. (a)* ***N*** *(200 °C), (b)* ***X*** *(180 °C) and (c)* $\boldsymbol{N_F}$ *(170 °C) phase of 75/25 mixture. (d)* ***N*** *(200 °C), (e)* ***X*** *(160 °C) and (f)* $\boldsymbol{N_F}$ *(150 °C) phase of 50/50 mixture. (a)* ***N*** *(180 °C), (b)* ***X*** *(1400 °C) and (c)* $\boldsymbol{N_F}$ *(133 °C) phase of 25/75 mixture. Cell thickness: 5μm. Scale bar: 100μm.*

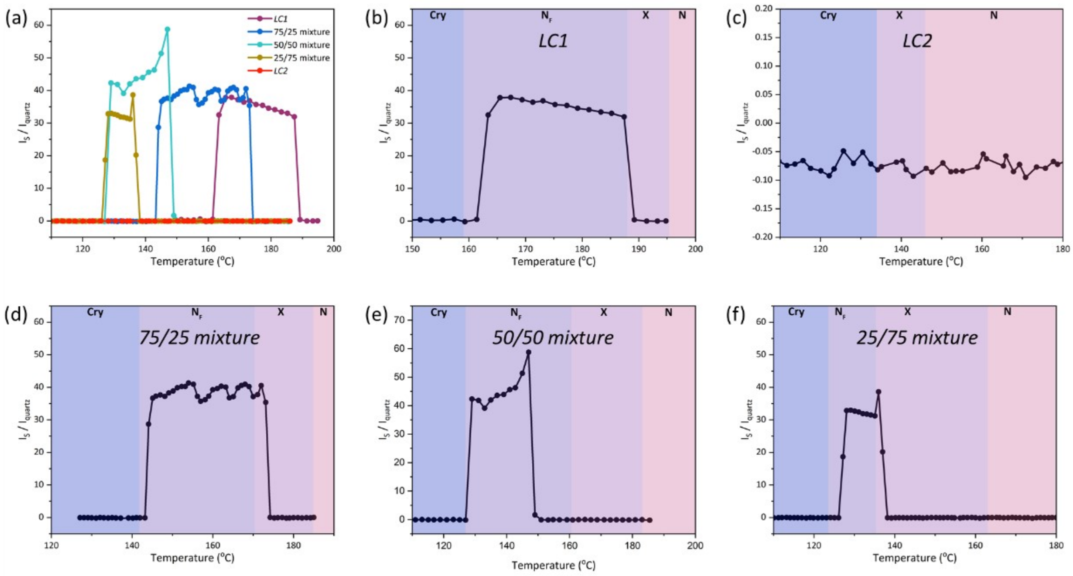


Figure S12. *(a) Temperature dependence of SHG strength of LC1/LC2 mixtures with different weight percent in the same coordinate system. (b-f) Temperature dependence of SHG strength of LC1/LC2 mixtures with different ratios in their respective appropriate coordinate system. A Q-switched pulsed laser beam with a central wavelength of 1064 nm was used as the excitation source. Cell thickness: 5 µm.*

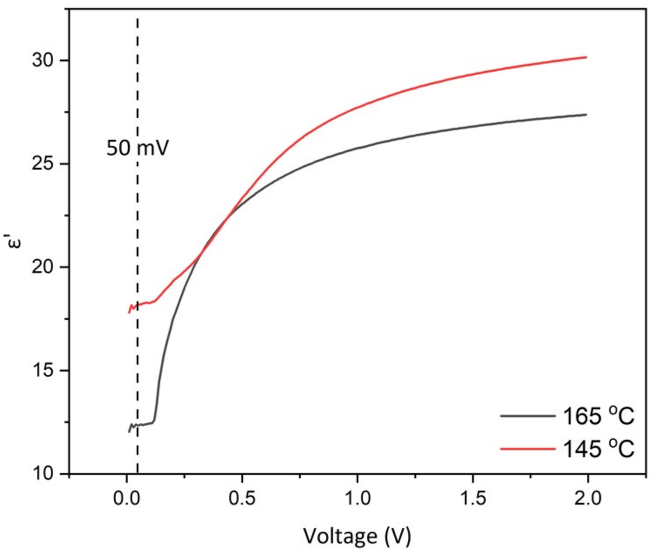
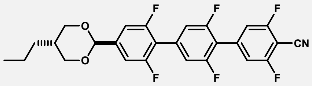
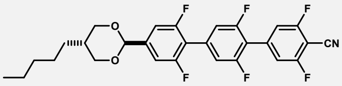


Figure S13. *The dielectric response for 50/50 mixture sample at different applied voltages in the planar aligned ITO cell. Frequency: 1 kHz, Temperature: 165 °C (**X**), 145 °C (**N$_F$**). To demonstrate that the voltage does not induce the Freedericksz transition, we measured the permittivity versus voltage at 1 kHz when the sample (50/50 of LC1 and LC2 mixture) was in the **X** (165 °C) and **N$_F$** (145 °C) phases. When the applied voltage is small, the permittivity does not increase with the increasing voltage, presenting a platform in the low voltage region. When the applied voltage exceeds 110 mV, the curves show obvious inflexion points and the permittivity increase sharply, presumably indicating the start of Freedericksz transition. The dielectric permittivity properties were measured under the voltage of 50 mV, lower than 110 mV. Thus, the applied voltage should not induce the Freedericksz transition and the accompanied permittivity increase.*

Table S1. *The molecular parameters of energy-minimized conformations calculated by the DFT*

Molecule	*LC1*	*LC2*
Molecular structure		
a (Å)	22.52	25.34
b (Å)	5.90	5.69
c (Å)	5.17	4.00
Dipole moment (D)	13.6	13.7
Vector x	13.5	13.6
Vector y	0.7	-0.5
Vector z	1.3	-1.2
Dipole angle (°)	6.3	5.3

Note: $Dipole\ angle = arcsin\left(\frac{\sqrt{y^2+z^2}}{\sqrt{x^2+y^2+z^2}}\right)$.

Table S2. *The phase transitions temperature (T / °C) and the corresponding enthalpy (ΔH / J g^{-1}, in parentheses) are measured by DSC (scanning rate: 5 K/min) during the first cooling process. The star symbol represents the existence of the corresponding phase, while the dash represents the absence.*

Samples	**Iso**	T (ΔH)	**N**	T (ΔH)	**X**	T (ΔH)	**N_F**	T (ΔH)	**Cry**
LC1	*	220 (1.51)	*	196 (0.04)	*	187 (0.49)	*	158 (26.8)	*
75/25 mixture	*	218 (2.55)	*	185 (0.05)	*	171 (0.72)	*	142 (30.7)	*
50/50 mixture	*	214 (2.55)	*	174 (0.08)	*	155 (0.66)	*	125 (41.5)	*
25/75 mixture	*	211 (2.56)	*	163 (0.07)	*	135 (0.53)	*	124 (42.3)	*
LC2	*	208 (2.67)	*	151 (0.09)	*	-	-	137 (60.1)	*