

Electronic supplementary information for

Enantiotropic ferroelectric nematic phase in a single compound

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1) Materials and methods

Materials

1-bromo-3,5-difluorobenzene was purchased from Trimen Chemicals (Łódź, Poland) and used as received. Magnesium for Grignard reactions (turnings), oxalyl chloride were purchased from Acros-Organics, (Geel, Belgium) and used as received. Toluene, acetone, hydrochloric acid were purchased from Avantor Performance Materials Poland S.A (Gliwice, Poland) and used as received. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) was purchased from Sigma-Aldrich Sp. z.o.o (Poznan, Poland) and used as received. Pyridine was purchased from Lach-ner (Neratovice, Czech Republic) and used as received. THF was distilled from sodium under nitrogen atmosphere prior to use.

Chemical analysis

Synthesis progress and purity of synthesized compounds were determined using SHIMADZU GCMS-QP2010S (Shimadzu, Kyoto, Japan) series gas chromatograph equipped with quadrupole mass analyser MS(EI), high-performance liquid chromatography HPLC-PDA-MS (APCI-ESI dual source) Shimadzu LCMS 2010 EV (Shimadzu, Kyoto, Japan) equipped with a polychromatic UV-VIS detector (Shimadzu, Kyoto, Japan). and by thin layer chromatography (silica gel on aluminium). Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra in CDCl_3 were collected using a Bruker, model Avance III spectrometer (Bruker, Billerica, MA, USA).

Isomeric purity check

The synthesis of 1,3-dioxane unit results in a mixture of cist/trans isomers. We obtained a compound **(3)** with approximately 50/50 cist/trans isomer ratio. We can clearly determine which peak on the chromatogram corresponds to which isomer, as the trans isomer is known for having the higher retention time. When we obtained the carboxylic acid **(4)**, we performed series of recrystallization processes as we found out that during the recrystallization, the crystal we obtained was constantly enriched with the trans isomer. We performed the recrystallization process until we obtained over 99% isomeric purity. At every stage, we checked both chemical and isomeric purity of **(4)** by GC-MS analysis of the corresponding methyl ester, which we obtained in a quick esterification reaction of **(4)** with methyl iodide and DBU in toluene.

POM observation

Microscopic observations were performed using polarizing optical microscope OLYMPUS BX51(Olympus, Shinjuku, Tokyo, Japan) equipped with a Linkam hot stage THMS-600 (Linkam Scientific Instruments Ltd., Tadworth, United Kingdom) with the sample placed between untreated glass plates.

DSC measurements

DSC measurements were performed using differential scanning calorimeter DSC 204 F1 Phoenix instrument (Netzsch, Selb, Germany) with the scanning rate was 2 Kmin^{-1} on both the heating and cooling cycles with the isothermal time of 5 minutes between cycles.

Dielectric spectroscopy measurements

The complex dielectric permittivity measurements of 3JK sample are measured in planar and homeotropic cells using dielectric analyzers HP- 4192A and HP- 4294. Commercial 5 μ m cells (WAT-3 Poland) are used, coated with 150- 200 nm gold and of low sheet resistance ($R < 0.1 \Omega/\square$).

DFT calculations

DFT calculations were performed in Gaussian 16 (Revision C.01)(1) program package with B3LYP(2, 3) functional and 6-311+G(d,p)(4) basis set on the PLGrid ASK Cyfronet Ares cluster.

2) Synthetic procedures

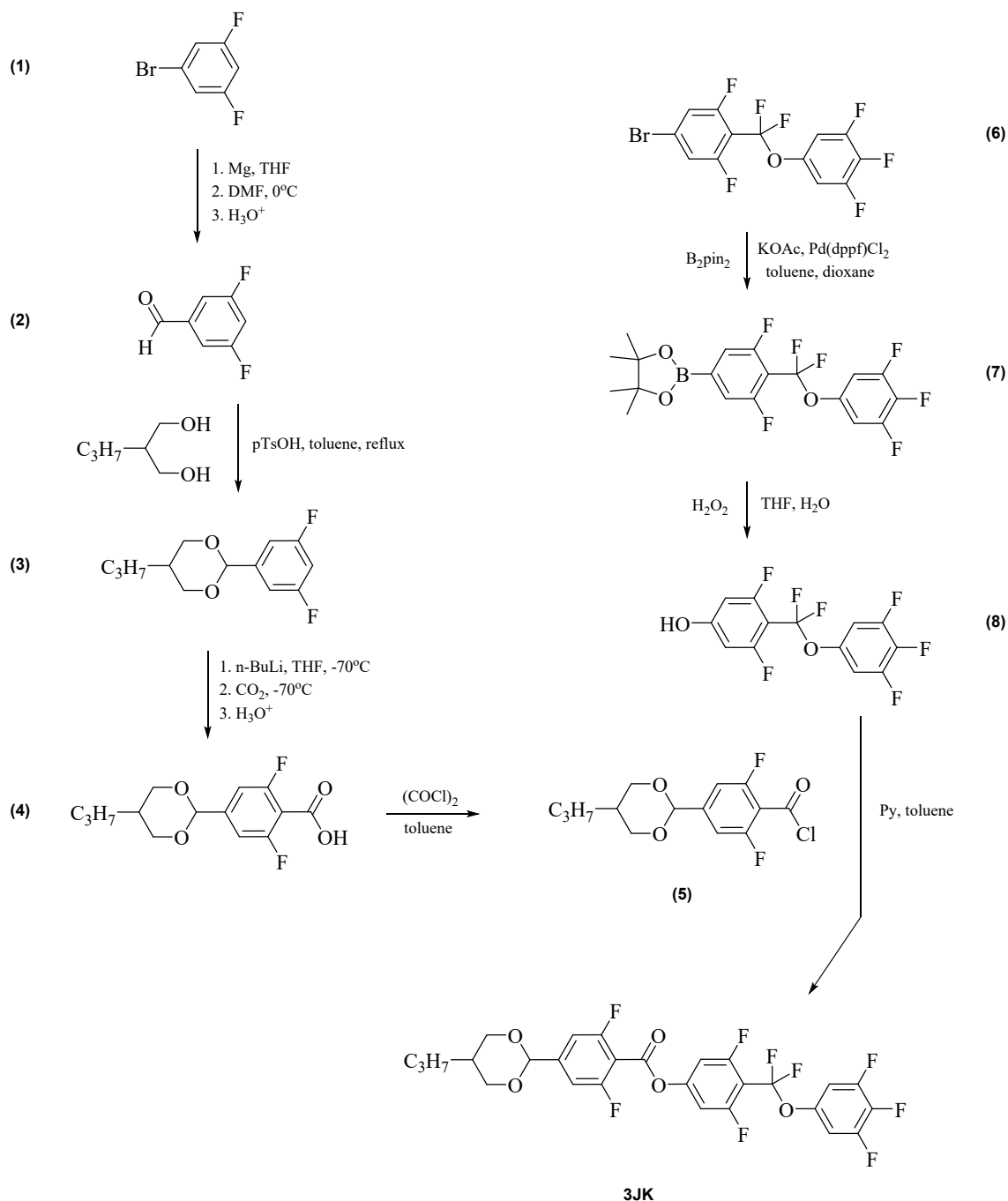


Figure S1. Synthetic route of 3JK.

3,5-difluorobenzaldehyde (2)

Magnesium flakes (12.0g; 0.5mol) and THF (300cm³) were placed in a 2dm³ flask and stirred under nitrogen. Small amount of THF solution of 1-bromo-3,5-difluorobenzene (**1**) (96g; 0.5mol) was added to initialize proper reaction. Then, the rest of solution was added dropwise. Temperature was controlled in a way to not exceed a 70°C limit. After addition, the reaction mixture was stirred for 3 hours. Next, dimethylformamide (60cm³; 0.75mol) was added dropwise to the reaction mixture reaction at 0°C, solution was warmed up to room

temperature. The mixture was poured into 1500 cm³ of water and 100 cm³ of 10% HCl. Crude product was extracted with pentane. Organic layer was washed three times with water, dried over MgSO₄ and solvent was evaporated. Product was purified by distillation under reduced pressure.

Yield 30 g (42%)

Purity 99.78% (GC-MS)

bp=84-86°C (50mmHg)

MS(EI) m/z: 142 (M⁺); 113.

¹H NMR (500 MHz, CDCl₃) δ: 9.95 (t, J=1.7 Hz, 1H, Ar-CHO); 7.41 (m, 2H, Ar-H); 7.09 (tt, J=8.4, 2.4 Hz, 1H, Ar-H)

¹³C NMR (125 MHz, CDCl₃) δ: 189.40 (t, J=2.7 Hz); 163.35 (dd, J=252.5, 11.8 Hz); 139.09 (t, J=7.3 Hz); 112.21 (m); 109.76 (t, J=25.9 Hz)

2-(3,5-difluorophenyl)-5-propyl-1,3-dioxane (3)

A solution 3,5-difluorobenzaldehyde (**2**) (30g; 0.21mol), 2-propylpropane-1,3-diol (28g; 0.23mol), p-toluenesulfonic acid (0.3g; 2mmol) in toluene (200cm³) was refluxed for 4h, while collecting water using Dean-Stark apparatus. After the reaction was completed, mixture was washed three times with water, organic layer was dried over MgSO₄ and concentrated. Product was purified by distillation under reduced pressure.

Yield 45.6 g (90%).

Purity 96,52% (GC-MS)

bp=84-86°C (0.8mmHg)

MS(EI) m/z: 241 (M⁺); 223, 141, 129.

¹H NMR (500 MHz, CDCl₃) δ: 7.05 (m, 2H, Ar-H); 6.79 (tt, J=8.9, 2.4 Hz, 1H, Ar-H); 5.47 (s, 0.5H, Ar-CH); 5.37 (s, 0.5H, Ar-CH); 4.25 (dd, J=11.9, 4.6 Hz, 2H, O-CH₂-CH); 3.53 (t, J=11.4 Hz, 2H, O-CH₂-CH); 2.12 (m, 0.5H, (OCH₂)-CH-CH₂); 1.78 (m, 0.5H, (OCH₂)-CH-CH₂); 1.33 (m, 2H, CH-CH₂-CH₂); 1,12 (m, 2H, CH₂-CH₂-CH₃), 0,93 (t, J=7,0 Hz, 3H, CH₃)

¹³C NMR (125 MHz, CDCl₃) δ: 162.89 (dd, J=248, 12.7 Hz); 142.27 (t, J=9.1 Hz); 109.28 (m); 103.95 (t, J=25.4 Hz); 99,99 (t, J=2.7 Hz); 99.64 (t, J=2.7 Hz); 72.58; 70.65; 34.31; 34.16; 29.74; 29.15; 22.84; 22.78; 14.08; 13.88

2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoic acid (4)

2-(3,5-difluorophenyl)-5-propyl-1,3-dioxane (**3**) (45g; 0.186mol) was mixed with anhydrous THF (300cm³) under nitrogen and cooled to -78°C in an acetone/dry ice bath. Solution of n-butyllithium dissolved in cyclohexane-hexane mixture (0.2mol, 2.5M) was added dropwise, and temperature was kept below -70°C. The reaction mixture was stirred for 2.5h in -78°C. Then the reaction was flushed with gaseous carbon dioxide (not exceeding the -65°C). After the reaction was completed, it was allowed to reach room temperature. 10% solution of H₂SO₄ was added to the mixture. Then the crude product was filtered off, washed with water and hexane. Product was recrystallized three times from hexane-toluene mixture (1:1 v/v).

Yield 28 g (52%).

Purity 99,15% (GC-MS)

mp=126°C

MS(EI) (MS spectra of corresponding methyl ester) m/z: 299 (M⁺); 269, 241, 201, 169, 141, 129

¹H NMR (500 MHz, CDCl₃) δ: 11,61 (s, 1H, COOH); 7,15 (d, J=9,5 Hz, 2H, Ar-H); 5,39 (s, 1H, Ar-CH); 4,25 (dd, J=11,5 Hz, 2H, O-CH₂-CH); 3,54 (t, J=11,5 Hz, 2H, O-CH₂-CH); 2,19-2,09 (m, 2H, (OCH₂)-CH-CH₂); 1,38-1,30 (m, 2H, CH-CH₂-CH₂); 1,12-1,08 (m, 2H, CH₂-CH₂-CH₃), 0,93 (t, J=7,5 Hz, 3H, CH₃)

¹³C NMR (125 MHz, CDCl₃) δ: 166.82, 161.20 (dd, J=258.9, 5.5 Hz), 145.36 (t, J=10 Hz), 110.27 (m), 109.43 (t, J=16.4 Hz), 98.86, 72.56, 33.88, 30.20, 19.52, 14.18

2-(4-(difluoro(3,4,5-trifluorophenoxy)methyl)-3,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)

A solution of 5-bromo-2-(difluoro(3,4,5-trifluorophenoxy)methyl)-1,3-difluorobenzene (**6**) (15g ; 0.038mol), bis(pinacolato)diboron (10g ; 0.038mol), anhydrous potassium acetate (11g ; 0.11mol) in toluene (300cm³) and 1,4-dioxane (300cm³) was flushed with nitrogen at 80°C for 1h. Then the catalyst Pd(dppf)Cl₂ (3mol%) was added and reaction was stirred at 80°C for 5h. Next reaction was cooled to room temperature and poured into 5% HCl solution. Product was extracted with toluene; organic layer was washed three times with water and dried over MgSO₄. Solvent was evaporated under vacuum. Product was recrystallized from ethanol.

Yield 10g (60%),

Purity 99,95% (GC-MS)

mp=94°C.

MS(EI)m/z: 437 (M⁺); 421; 289; 207; 189

¹H NMR (500 MHz, CDCl₃) δ: 7,40 (d, J=10 Hz, 2H, Ar-H), 6,98 (m, 2H, Ar-H); 1,37 (s, 12H, CH₃)

¹³C NMR (125 MHz, CDCl₃) δ: 159.55 (dd, J=261.6, 1.8 Hz); 150.98 (dq, J=250.7, 5.5 Hz); 144.76 (m); 139.43 (t, J=15 Hz); 137.44 (t, J=15.4 Hz); 122.36; 120.24; 118.07 (m); 111.69 (m); 107.43 (m); 84.90; 24.80

4-(difluoro(3,4,5-trifluorophenoxy)methyl)-3,5-difluorophenol (8)

Flask containing 2-(4-(difluoro(3,4,5-trifluorophenoxy)methyl)-3,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7**) (10g; 0.023mol), 30% solution of H₂O₂ (20cm³), tetrahydrofuran 100cm³ and water 100cm³ was mixed at 50°C for 4h. After the reaction was completed THF was evaporated and 5% HCl solution was added. Product was extracted with dichloromethane, organic layer was washed three times with water, dried over MgSO₄ and concentrated. Product was recrystallized twice from hexane.

Yield 3,89 g (52%).

Purity 96,75% (GC-MS)

mp=190°C

MS(EI) m/z: 326 (M⁺); 307; 179

¹H NMR (500 MHz, CDCl₃) δ: 8,19 (s, 1H, OH); 6,96 (m, 2H, Ar-H); 6,47 (d, J=11 Hz, 2H, Ar-H)

^{13}C NMR (125 MHz, CDCl_3) δ : 161.04 (dd, $J=255.2, 8.2$ Hz), 160.59 (t, $J=15.0$ Hz), 151.95 (dd, $J=10.5, 5.0$ Hz), 149.96 (dd, $J=10.5, 5.0$ Hz), 144.94 (m), 139.30 (t, $J=15.0$ Hz), 120.58 (t, $J=264.3$ Hz), 107.33 (m), 101.75 (m), 100.42 (m)

4-(difluoro(3,4,5-trifluorophenoxy)methyl)-3,5-difluorophenyl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoate (3JK)

In the first stage acid chloride ***2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoyl chloride (5)*** was synthesized. In the 250cm³ round-bottom flask ***2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl)benzoic acid (4)*** (1.2g; 4.2 mmol), oxalyl chloride (0.55cm³; 6mmol), 50cm³ toluene and DMF (0.1 cm³) were added and stirred at RT for 5 hours. Then the excess oxalyl chloride was distilled off. In the second stage, the reaction mixture was cooled to room temperature and ***4-(difluoro(3,4,5-trifluorophenoxy)methyl)-3,5-difluorophenol (8)*** (1.5g; 4.6mmol) was added. Then anhydrous pyridine (1cm³; 8.4mmol) was added dropwise at room temperature. The reaction was stirred at RT for 12 hours. Then the reaction mixture was poured into a HCl (10%) solution. The organic layer was washed three times with water, dried over MgSO_4 , and concentrated on a rotary evaporator. Crude product was purified by liquid column chromatography (dichloromethane as a mobile phase) and recrystallized from ethyl alcohol, yielding white crystals.

Yield 1.5g (60%).

Purity 99,45% (GC-MS); 99,48% (LC-MS)

MS (EI) m/z : 593 (M⁺), 447, 347, 269

^1H NMR (500 MHz, CDCl_3) δ : 7,21 (d, $J=9$ Hz, 2H, Ar-H); 7,05-6,97 (m, 4H, Ar-H); 5,42 (s, 1H, Ar-CH); 4,27 (dd, $J=11,5$ Hz, 2H, O- CH_2 -CH); 3,56 (t, $J=11,5$ Hz, 2H, O- CH_2 -CH); 2,19-2,12 (m, 2H, (OCH₂)- CH -CH₂); 1,40-1,33 (m, 2H, CH- CH_2 -CH₂); 1,14-1,10 (m, 2H, CH₂- CH_2 -CH₃), 0,95 (t, $J=7,5$ Hz, 3H, CH₃)

^{13}C NMR (125 MHz, CDCl_3) δ : 161.04 (dd, $J=259.8, 5.5$ Hz); 160.36 (dd, $J=258.9, 7.26$ Hz); 158.32; 153.32 (t, $J=14.08$ Hz); 152.02 (dd, $J=10.90, 5.45$ Hz); 150.02 (dd, $J=10.44, 5.00$ Hz); 146.27 (t, $J=9.99$ Hz); 144.53 (m); 138.51 (dt, $J=250.69, 15.44$ Hz); 119.93 (t, $J=266.58$ Hz); 110.42 (m); 108.31 (m); 107.49 (m); 107.12 (dd, $J=26.79, 4.09$ Hz); 98.69, 72.59, 33.90, 30.21, 19.53, 14.16

^{19}F NMR (470 MHz, CDCl_3) δ : -61.36 (t, $J=26,7$ Hz, 2F); -107.93 (d, $J=9.6$ Hz, 2F); -108.24 (td, $J=26.5, 9.9$ Hz, 2F); -132.37 (dd, $J=20.8, 8.2, 2$ F); -162.97 (tt, $J=20.8, 5.4$ Hz, 1F)

3) Mesomorphic properties

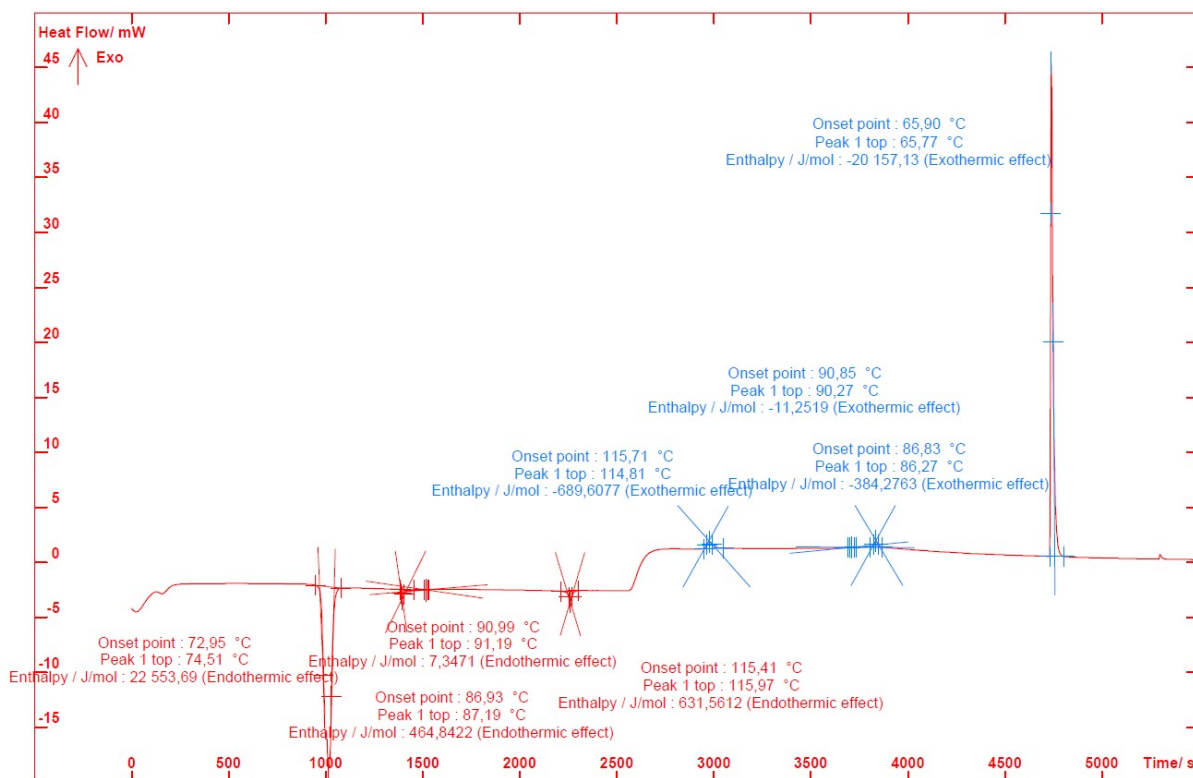


Figure S2. DSC thermogram of 3JK.

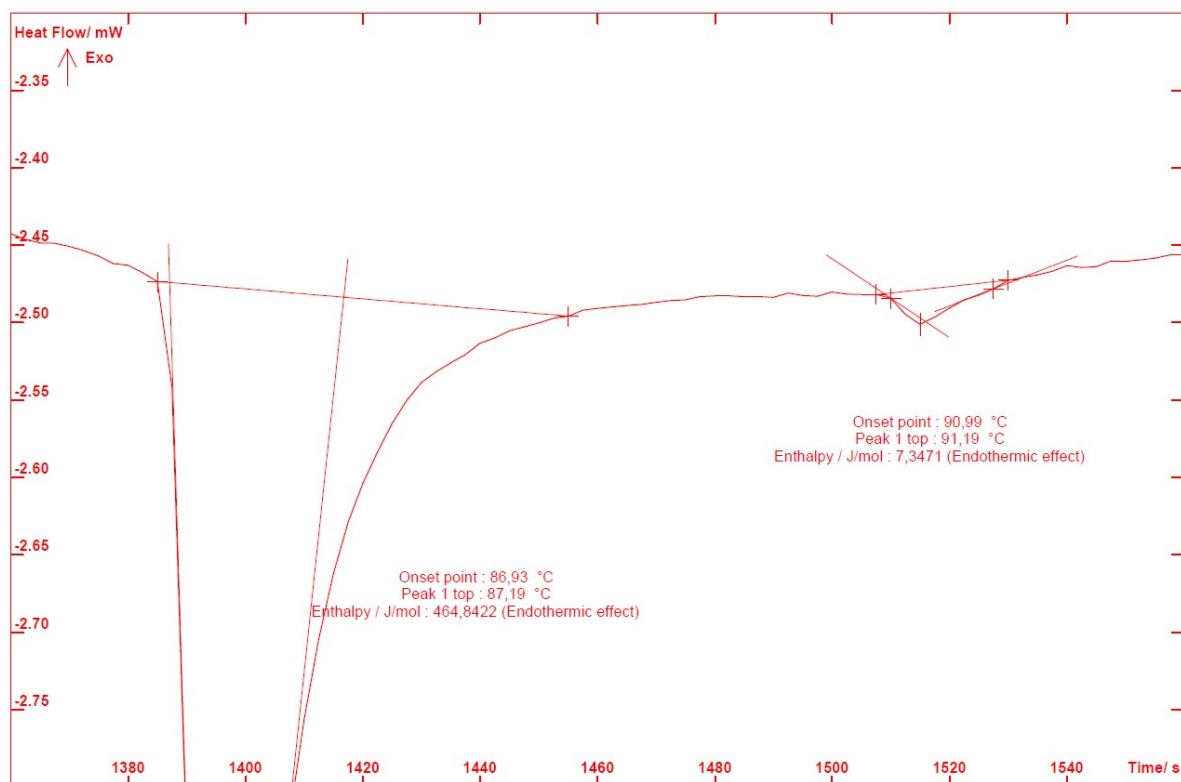


Figure S3. Expanded DSC curve of N_F-N_X-N transition.

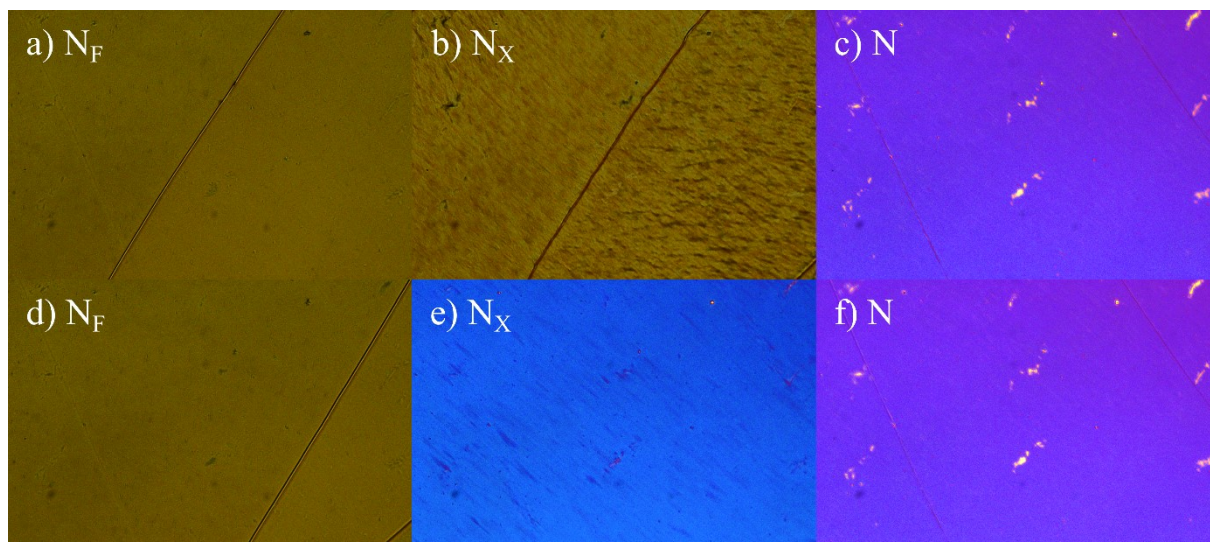


Figure S4. POM textures of N_F , N_X and N phases of 3JK in a $5\mu\text{m}$ -thick planar cell in heating (a-c) and cooling (d-f) cycle.

Table S1. Phase transition temperatures of mixtures of 3JK with RM734 and DIO.

Mixture		Phase transitions temperatures
3JK with RM734		
0.1	heating	Cr 72 N_F 92 N_X 96 N 123 Iso
	cooling	Iso 122.8 N 95.5 N_X 92.3 N_F 68 Cr
0.2	heating	Cr 74 N_F 94.8 N_X 97.4 N 125,8 Iso
	cooling	Iso 124 N 97 N_X 94 N_F 53.3 Cr
0.3	heating	Cr 76 N_F 100 N_X 102.4 N 137 Iso
	cooling	Iso 135 N 106.7 N_X 104.5 N_F 42 Cr
0.4	heating	Cr 77 N_F 102.8 N_X 104.9 N 144.5 Iso
	cooling	Iso 138 N 107 N_X 105,5 N_F 44,5 Cr
0.5	heating	Cr 96 N_F 109,5 N_X 111,5 N 152,5 Iso
	cooling	Iso 152 N 110 N_X 109 N_F 49 Cr
0.6	heating	Cr 130 N 160 Iso
	cooling	Iso 155 N 120,5 N_F 45 Cr
0.8	heating	Cr 134 N 172 Iso
	cooling	Iso 169,6 N 124,5 N_F 62,3 Cr
3JK with DIO		
0.2	heating	Cr 64 N_F 89 N_X 95 N 126 Iso
	cooling	Iso 124.7 N 85.8 N_X 81.2 N_F 47.8 Cr

0.4	heating	Cr 45 N _F 84,8 N _X 93 N 136,5 Iso
	cooling	Iso 135.1 N 92 N _X 84,5 N _F 33.9 Cr
0.5	heating	Cr 56,5 N _F 82,5 N _X 91,5 N 152 Iso
	cooling	Iso 147 N 90.5 N _X 79.5 N _F 16 Cr
0.6	heating	Cr 58 N _F 81,5 N _X 91 N 150 Iso
	cooling	Iso 149 N 90 N _X 79.8 N _F <0 Cr
0.7	heating	Cr 64 N _F 77 N _X 87 N 154 Iso
	cooling	Iso 154 N 88 N _X 76,5 N _F <0 Cr
0.8	heating	Cr 71,5 N 162 Iso
	cooling	Iso 161 N 87.4 N _X 73 N _F <0 Cr

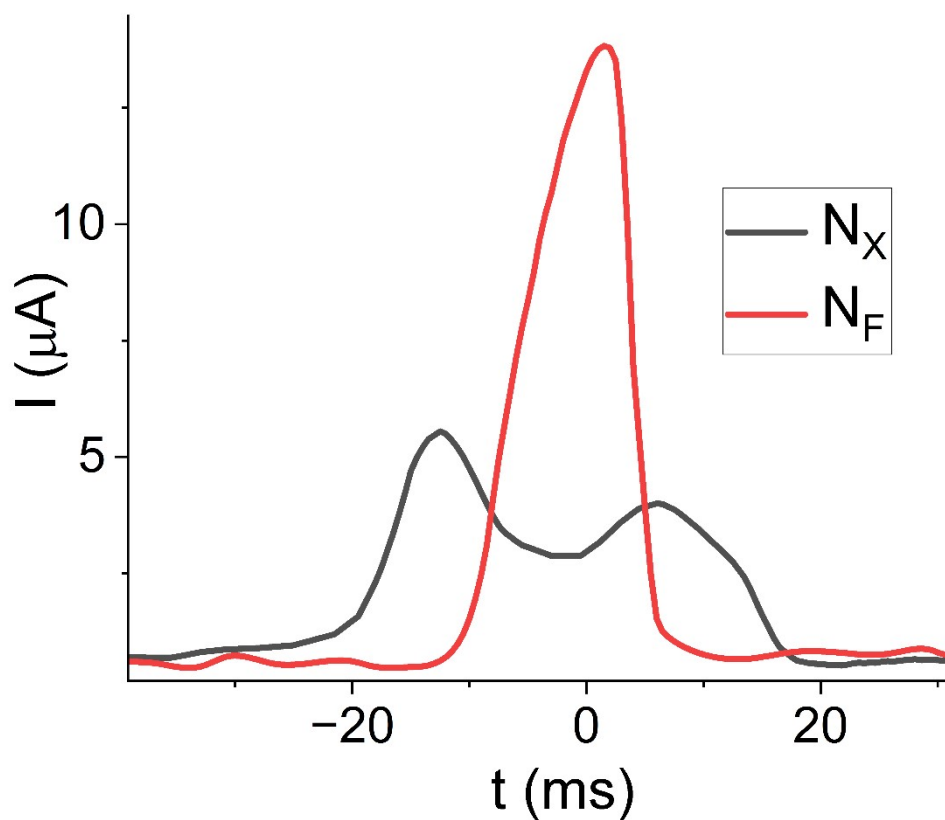


Figure S5. Current response in the N_X (grey line) and N_F (red line) under 9 Hz triangular voltage.

4) References

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