Supplementary Information (SI) for Soft Matter.

Supplemental Information

Low Field Electrocaloric Effect at Isotropic - Ferroelectric Nematic Liquid Transition

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I. Material synthesis

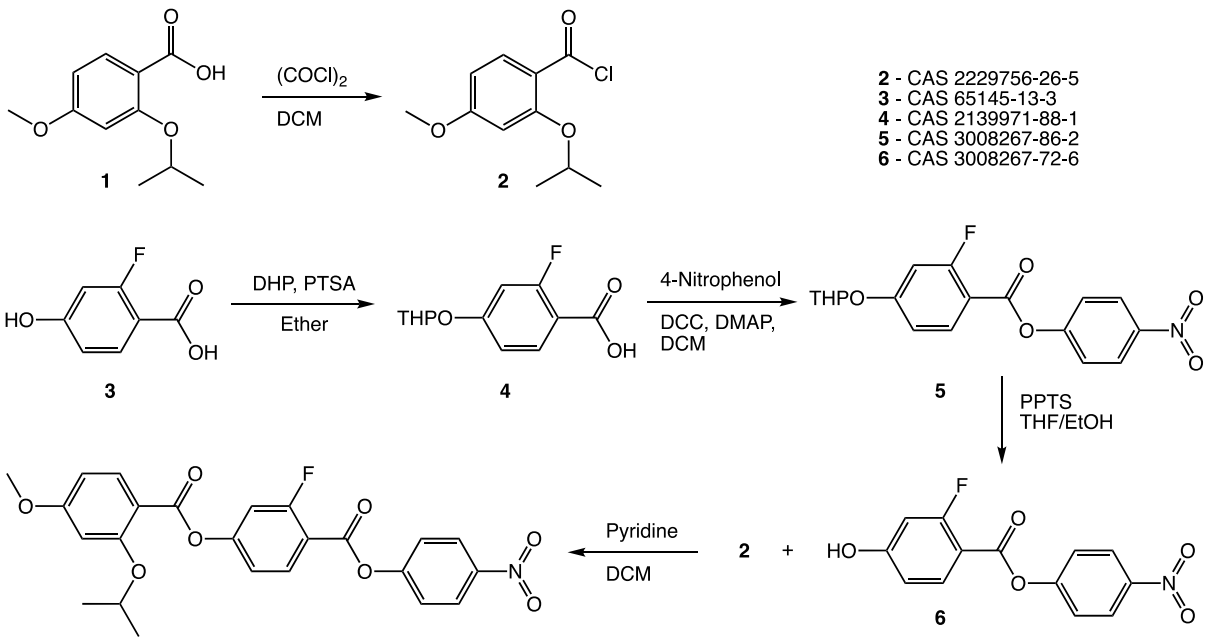
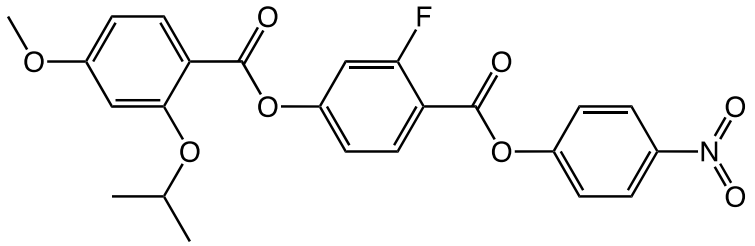


Figure S1*: Reaction Scheme for Preparation of PN03155.*

All the intermediates used in this reaction scheme are known and are found in the literature.

Intermediates **5**, **6** and **7** were prepared in a similar way as described in [1]:

3-fluoro-4-[(4-nitrophenoxy) carbonyl] phenyl 4-methoxy-2-(1-methylethoxy) benzoate



In a 300 ml round bottom flask with stir bar was placed 4-nitrophenyl-2-fluoro-4-hydroxybenzoate (1.386 g, 5.0 mmol) and pyridine (20 ml). The mixture was placed in an ice bath and 2-isopropoxy-4-methoxybenzoyl chloride (1.143 g, 5.0 mmol, dissolved in 3 ml DCM) was added dropwise. The resulting mixture was slowly warmed to room temperature and stirred overnight. After this time, TLC indicated complete consumption of the starting materials to give a single less polar product. The reaction was quenched by addition of cold water (100 ml) and then kept under house vacuum for ten minutes with stirring to remove the DCM. The flask was chilled in an ice bath and the solid precipitate obtained was isolated by suction filtration, washed with water, air dried and finally recrystallized from 1-PrOH (1.961 g, 83%).

^{1}HNMR (DMSO-d_6, 400 MHz) δ 8.38 (d, J = 9.2 Hz, 2H), 8.21-8.25 (t, J = 8.5 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 9.1 Hz, 2H), 7.49 (dd, J = 2.1, 11.7 Hz, 1H), 7.34 (dd, J = 2.3, 8.6 Hz, 1H), 6.67-6.74 (m, 2H), 4.79 (sept, J = 6.0 Hz, 1H), 3.87 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H).

^{19}FNMR (DMSO-d_6, 376 MHz) δ -106.15 (dd, J = 11.8, 8.4 Hz).

^{13}CNMR (DMSO-d_6, 400 MHz) δ165.4, 163.8, 162.6, 161.2, 161.1, 160.8, 156.9, 156.8, 155.6, 145.8, 134.6, 134.0, 125.8, 123.9, 119.3, 114.6, 114.5, 112.3, 112.0, 111.0, 106.6, 101.7, 71.5, 56.2, 22.2.

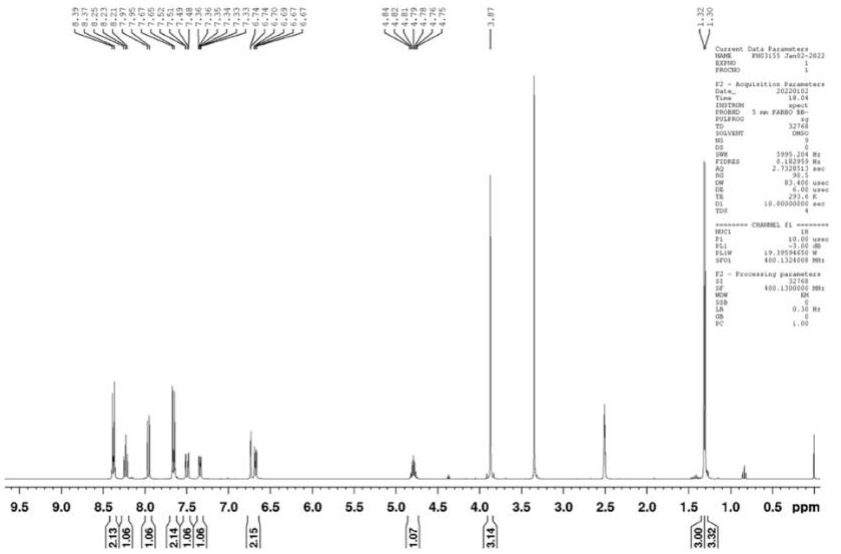


Figure S2: *^{1}H-NMR of PN03155.*

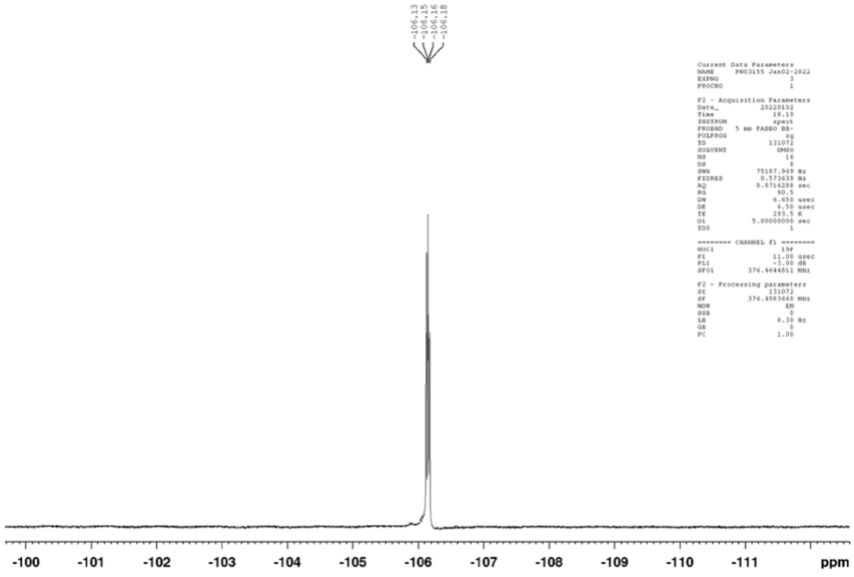


Figure S3: *^{19}F-NMR of PN03155.*

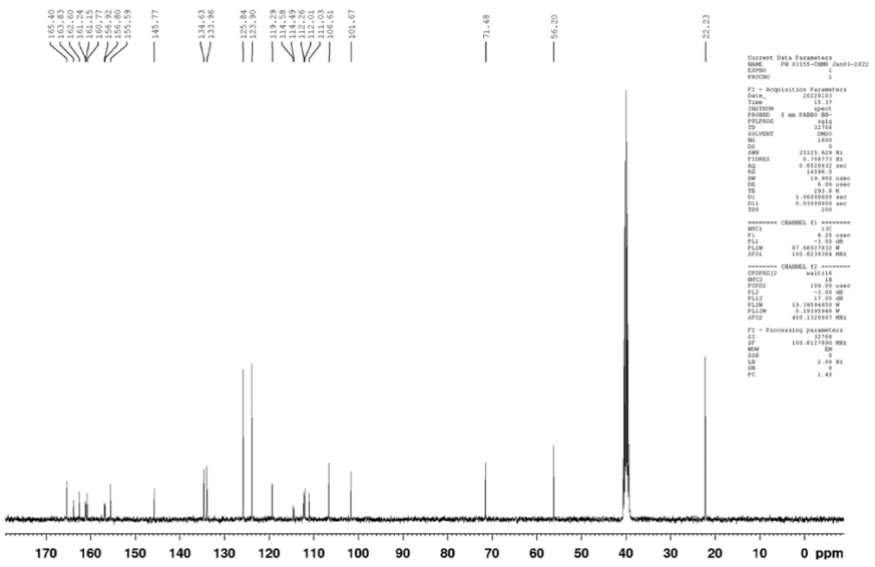


Figure S4: *^{13}C-NMR of PN03155.*

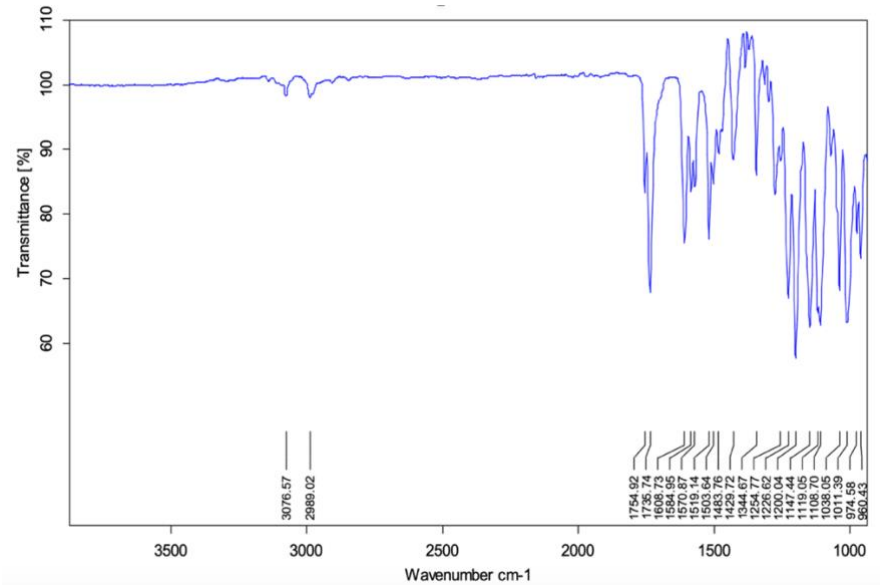


Figure S5: *FTIR spectrum of PN03155.*

II. Methods

For studying the electrocaloric effect a $\approx 10.3\mu m$ thick sandwich cells with area of $8.5\,mm \times 9\,mm$ and anti-parallel rubbing was used. For data collection, a KEYSIGHT InfiniiVision MSO-X 3024A Mixed Signal 200MHz 4GSa/s Oscilloscope and HP 34401A Multimeter were used. See experimental set-up is shown in Figure S6.

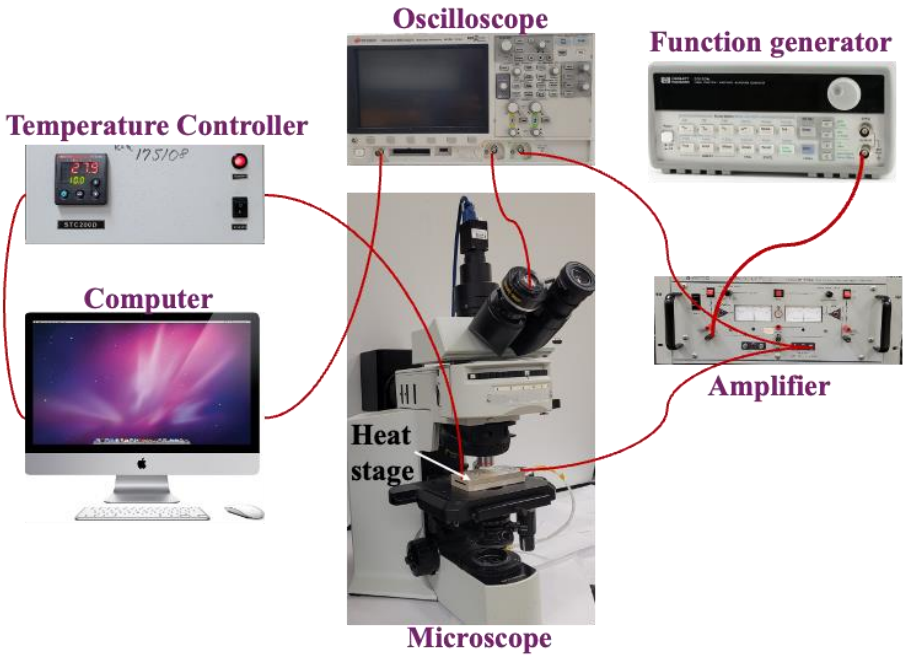


Figure S6*: Experimental Set-up used for electrocaloric measurements.*

The liquid crystal cell is placed inside an Instec HS200 heat stage equipped with a STC200D controller and heated to the desired temperature. AC voltage is applied using an HP33120A 15MHz function/arbitrary waveform generator amplified by a Model BOP 500M 50X Kepco Bipola Operational amplifier. For applying DC voltage, we used HP Harrison 6110A DC power supply.

For temperature dependent textural observations an Olympus BX60 Polarized Optical Microscope (POM) was used. The material PN03155 was filled by capillary action into empty cells bounded by glass substrates coated with parallel rubbed PI2555 polyimide that aligns the director parallel to the rubbing direction. Two types of cells were used: (i) sandwich cells with ITO coating between the glass and the PI2555 on both substrates; (ii) in-plane electrode cells films where the bottom substrates have two $3mm$ wide indium tin oxide (ITO) electrodes separated by $0.5mm$ gap while the top substrate has no ITO. The cells were assembled using NOA68 glue mixed with $10\mu m$ spacers to attain uniform thickness. A computer serves as an interface with the needed software to control the heat stage and take the POM images as connected.

Ferroelectric polarization was measured using the conventional current reversal method [2]. On cells containing PN03155, we apply 80Hz triangular waveform with voltages between the in-

plane electrodes in the range 60V – 500V. To measure the polarization current $I_P = \dot{Q}_P$, a Princeton Applied Research Model 181 current preamplifier with sensitivity $\frac{I}{V} = 10^{-4}$ was used. The ferroelectric polarization P value was calculated from the area $Q_P = \int \dot{Q}_P dt$. P$= Q_P/A$, where $A = d$ x l is the cross-sectional area normal to the polarization vector with d as the film thickness and l as the length of the ITO strips. For this experiment $A = 10.3\mu m$ x $8.5mm = 8.755$ x $10^{-8} m^2$.

III. Material Characterization

The heat capacity was measured following standard procedure using differential scanning calorimetry (DSC). Results of DSC scans are shown in Figure S7.

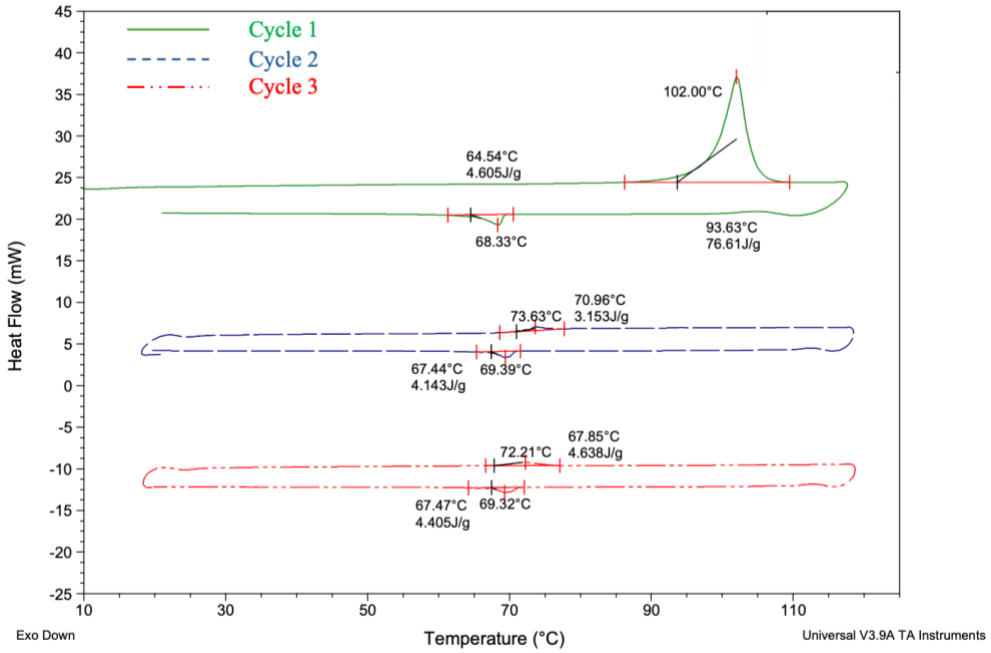


Figure S7: *Sequential DSC scans of PN03155 in 1st, 2nd and 3rd cycles under 1°C/min heating/cooling rate.*

The POM images of a $10.3\mu m$ thick film with parallel rubbed planar alignment coating are shown in the isotropic phase, at the isotropic – ferroelectric nematic two-phase region, and in the ferroelectric nematic phases in **Error! Reference source not found.**(a), (b) and (c, d), respectively.

In the isotropic - ferroelectric nematic phase the N_F droplets coexist in the isotropic phase, while in the N_F phases there are defect lines with different birefringence colors. The droplets formation in the two-phase region is due to the direct isotropic to N_F phase of the material. The defect lines parallel to the rubbing direction in the N_F phase separate regions with alternating direction of the ferroelectric polarization. Change in colors due to the temperature variation of the birefringence.

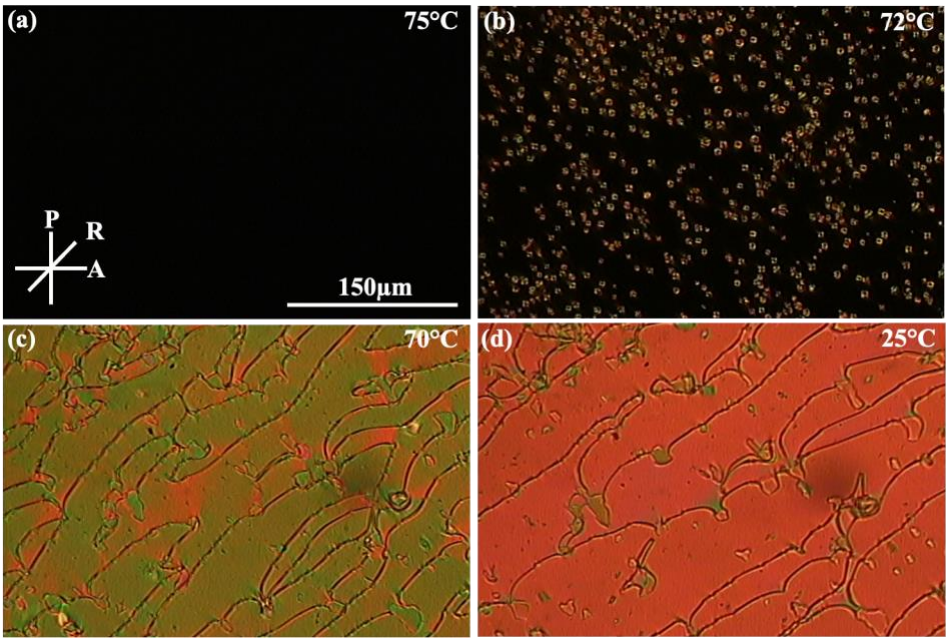


Figure S8*: Polarizing optical microscopy (POM) images at different temperatures of PN03155 during cooling at 2°C/min rate. (a) Isotropic (I) phase; (b) Nematic droplets formation in the I-N_F two-phase region; (c-d) N_F phase after transition from isotropic and at room temperature.*

References:

[1] Stepanafas G, Cruickshank E, Brown S, et al. Ferroelectric nematogens containing a methylthio group. Mater Adv. 2023;5:525–538.

[2] Neeraj, Kumar P, Raina KK. Changes in the electro-optical behaviour of ferroelectric liquid crystal mixture via silica nanoparticles doping. Opt Mater (Amst). 2012;34:1878–1884.