Supporting information for

Stereoisomer effect on ferroelectric nematics: stabilization and phase behavior diversification

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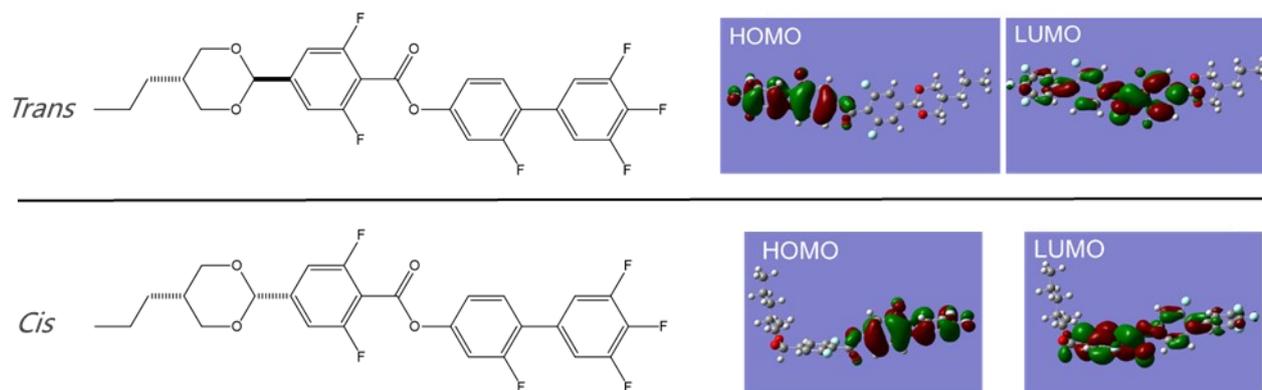Supplementary Discussion 1-3

Supporting figures

Figure S1. The optimized molecular structures of the straight and bent conformer of DIO optimized by the density functional theory calculation.
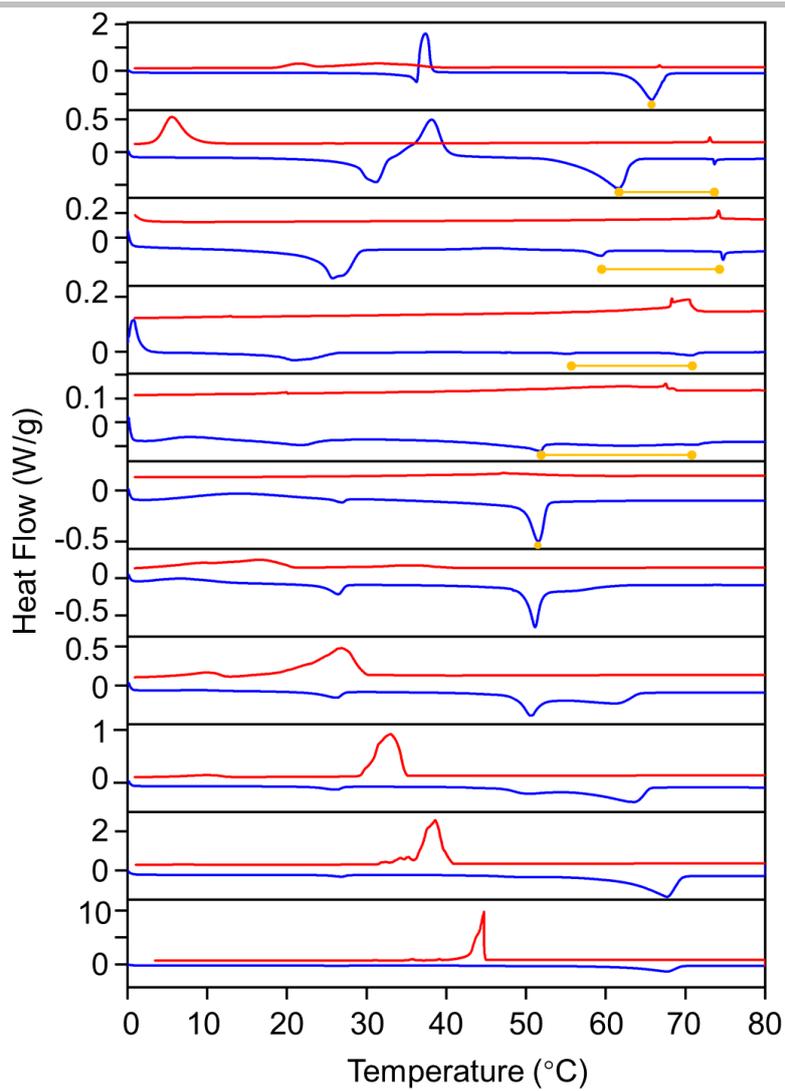
Figure S2. *c*-dependent DSC profiles for c=0-100 wt% by a 10 wt% step in an ascending order. The orange lines are the stable (enantiotropic) temperature range of the N_F phase.
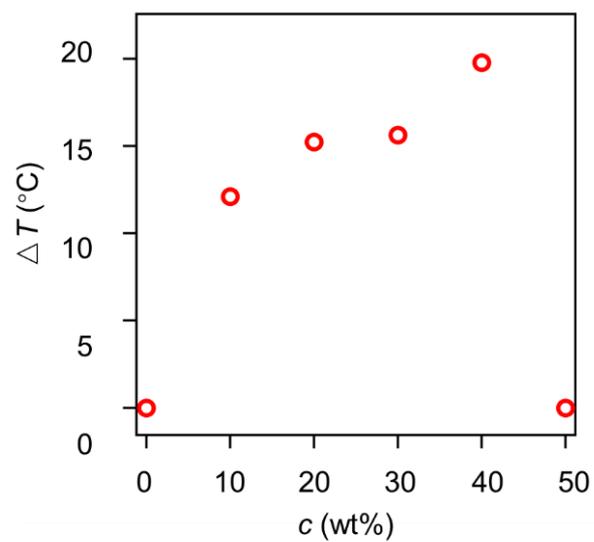
Figure S3. The plot of c-dependent stable (enantiotropic) temperature window of the N_F phase deduced from DSC profiles.
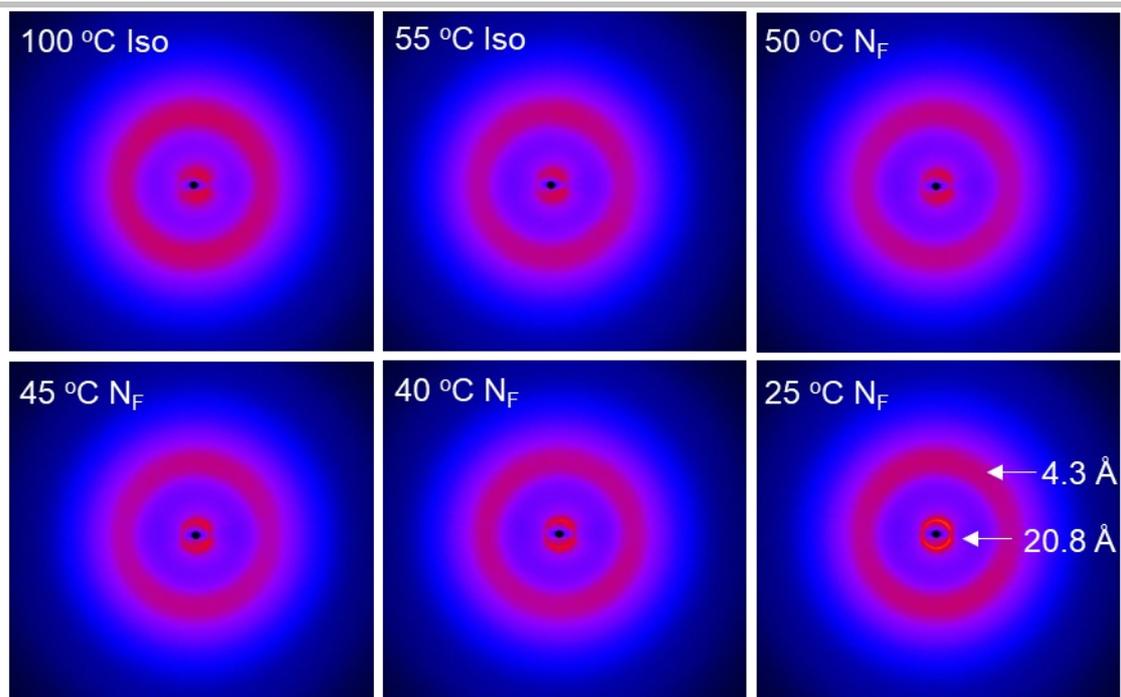
Figure S4. X-ray diffraction data for c=50% mixture. The small-angle diffraction peak remains diffused but increases its intensity with decreasing temperature.
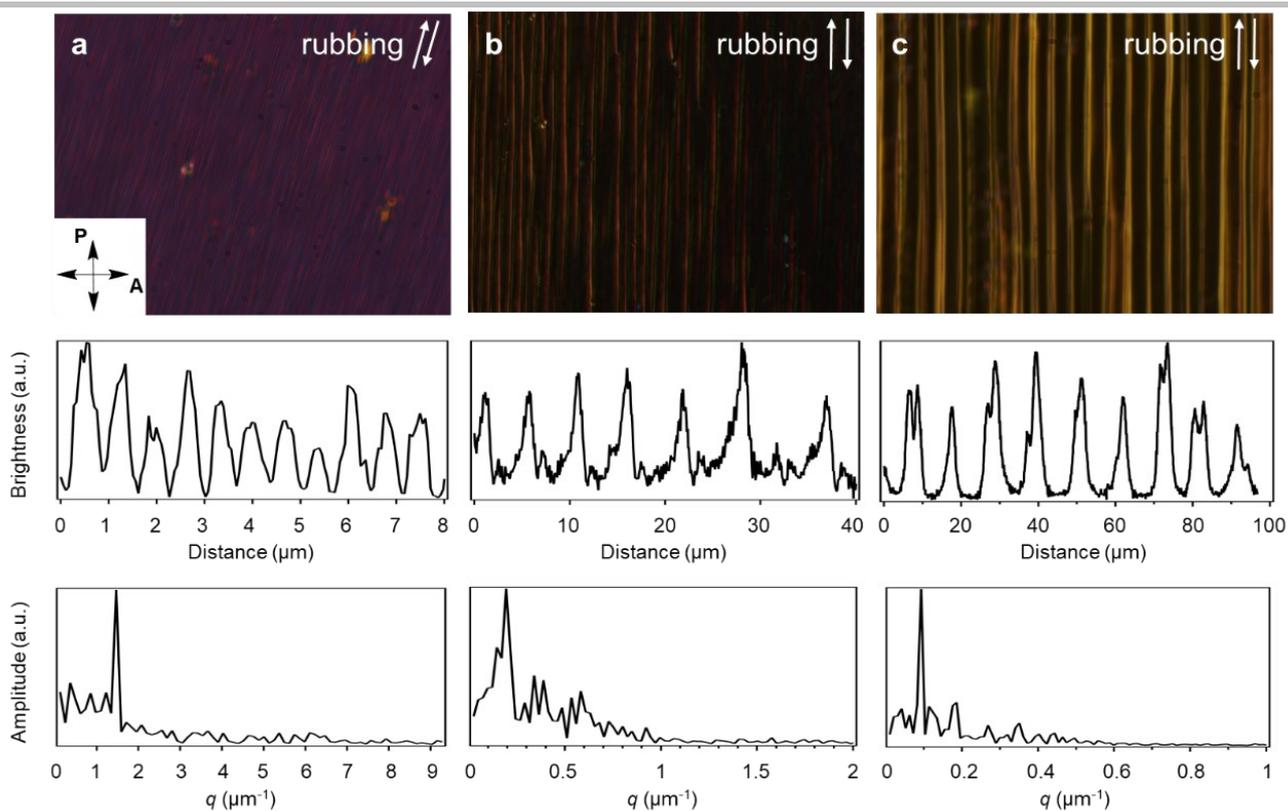
Figure S5. The evolution of stripe pattern for the mixture with c=30 wt% in the N_x phase: (a) 74 °C, (b) 73 °C and (c) 72 °C. The plots of the brightness along the wavevector direction the stripes and the corresponding FFT analyses are shown below the textures. The periodicity is (a) 0.7, (b) 5.2 and (c) 10.8 um, respectively.
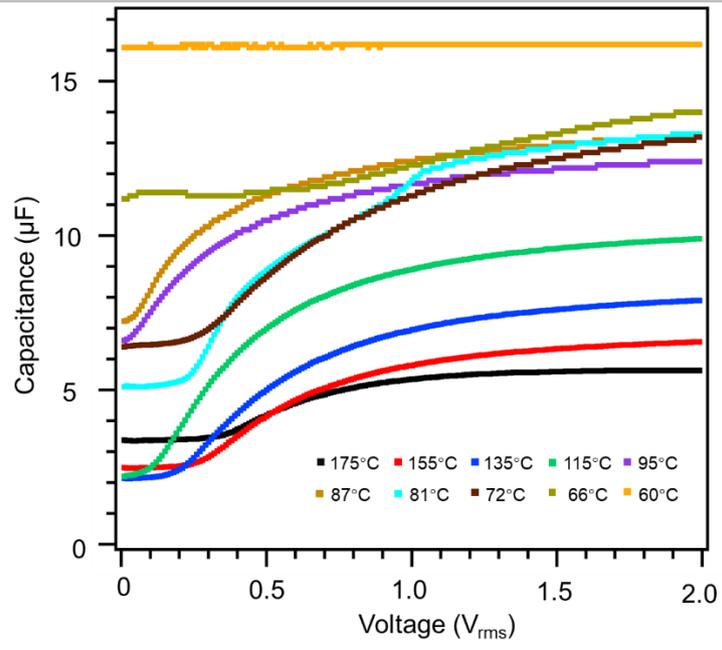
Figure S6. Voltage dependence of capacitance of *c*=0 wt% at different temperatures measured at 1 kHz by using planar cells.
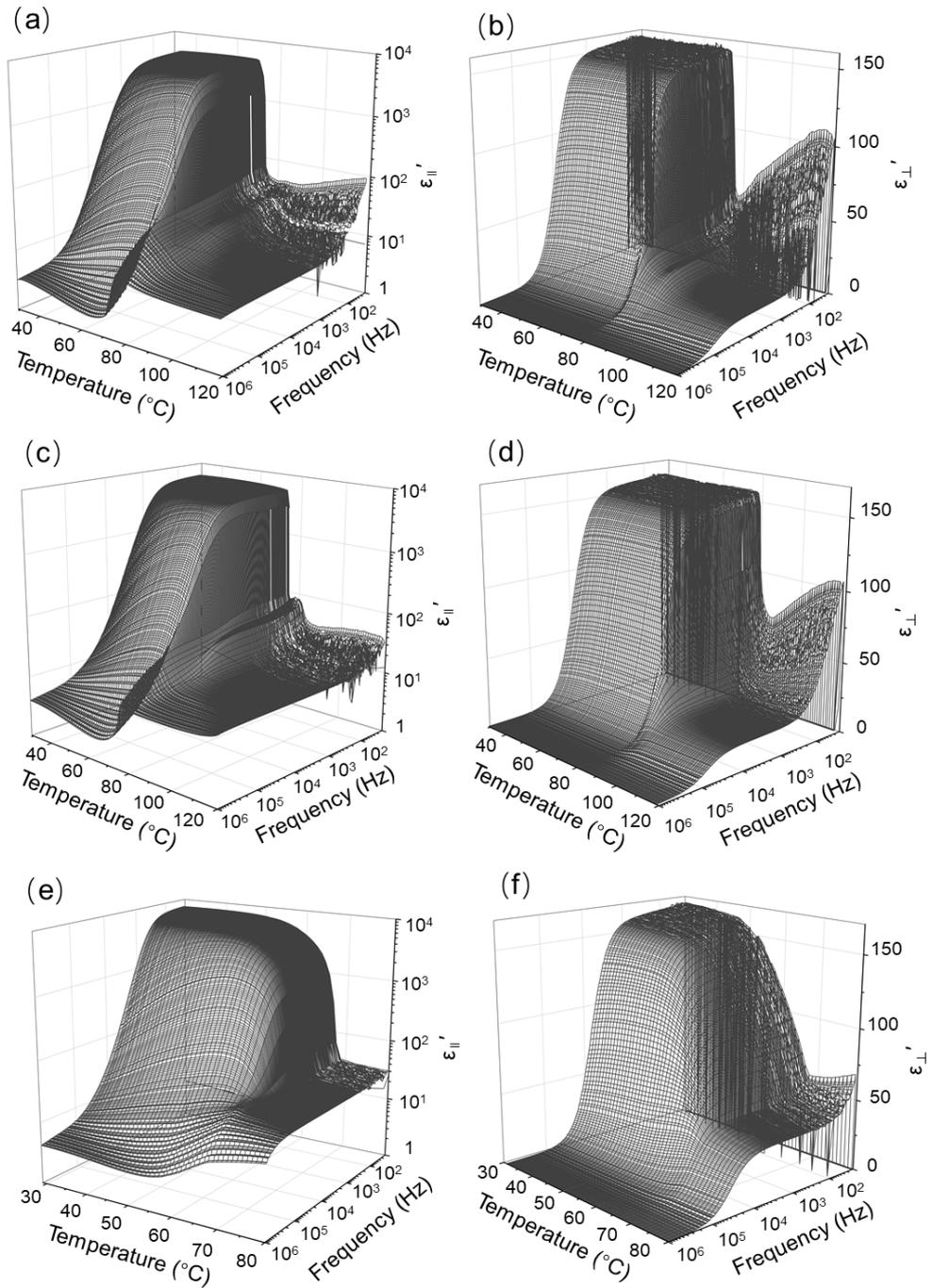
Figure S7. Temperature and frequency dependences of the real part of $\varepsilon_{//\,(effectvie)}$ and $\varepsilon_{\perp}$ for mixtures of c=10 wt % (a,b), c=20 wt% (c,d) and c=40 wt% (e,f). The measurements were made at 50 mV$_{pp}$.
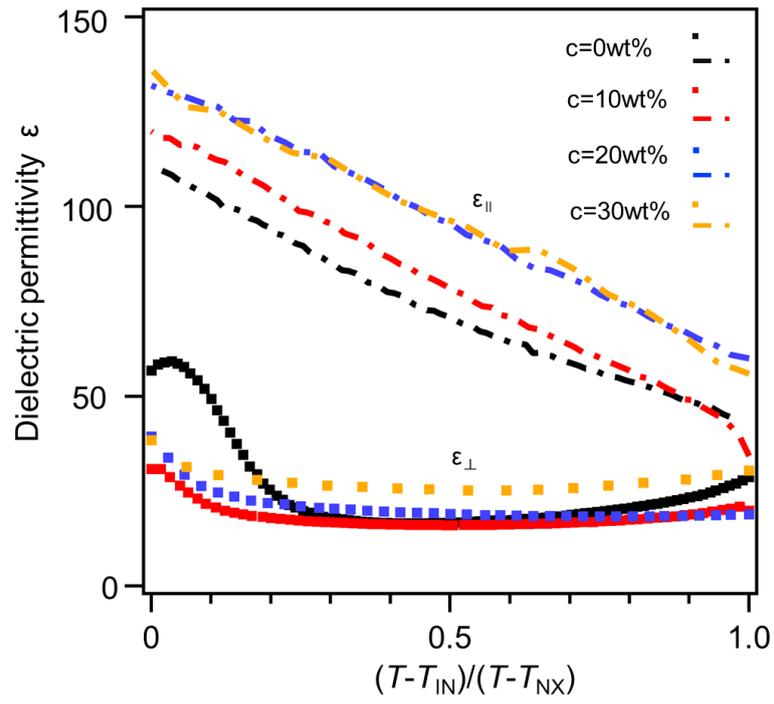
Figure S8. Temperature dependencies of dielectric permittivity (dielectric permittivity perpendicular the director $\varepsilon_\perp$ and along the director of $\varepsilon_{//}$) in the N phase for the mixtures of c=0-30 wt%. The data were measured at 1 kHz.
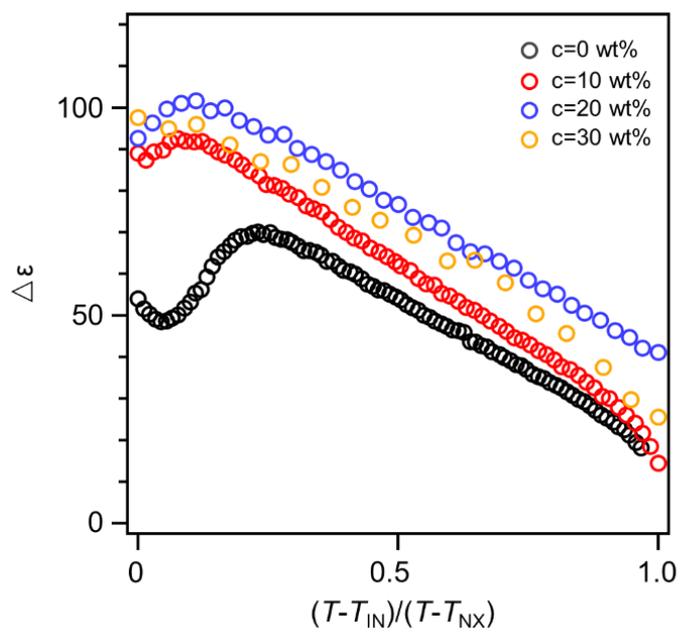
Figure S9. Temperature dependence of the dielectric anisotropy in the N phase for the mixtures with c=0-30 wt% measured at 1 kHz.
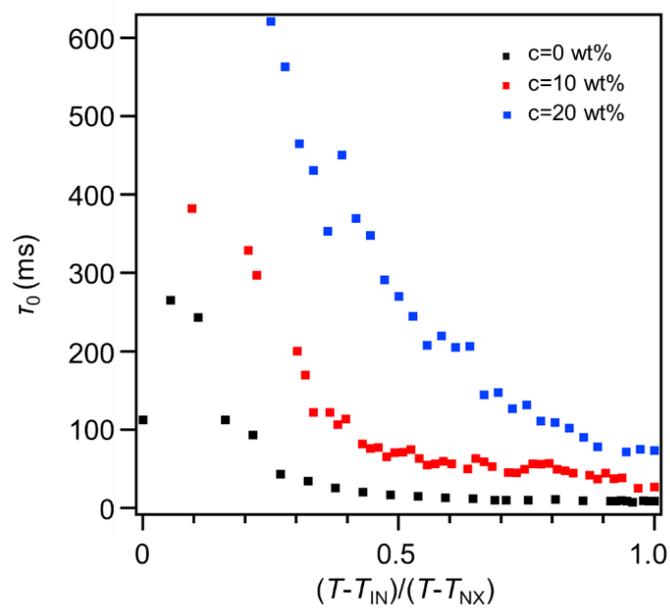
Figure S10. Temperature dependence of off-switching time (τ_0) in the N phase for the mixtures with c=0-20 wt%.

Figure S11. Temperature dependence of rotational viscosity (γ_1) in the N phase for the mixtures with c=0-20 wt%.

Supplementary Discussion 1: Fréedericksz transition measurement

To measure the splay constant K_{11} in the N phase, we employed the Fréedericksz transition method by using planar cells. The electric field was applied normal to the substrates. The dielectric constant as a function of the voltage was recorded by using an LCR meter (4284a, Agilent). The splay constant K_{11} was deduced from the threshold of the 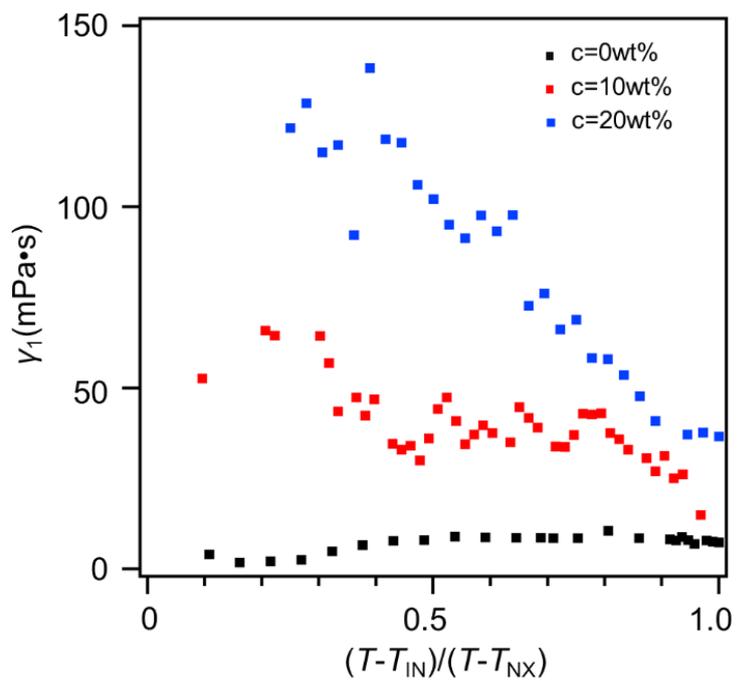capacitance curve (Figs. 3, S6 and S8) and temperature dependence of anisotropy of the dielectric constant was then calculated (Fig. S8) following the equation below:

$$V_{\text{th}} = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta \varepsilon}}.$$

The bend elastic K_{33} in the N phase was further calculated through the formulation of the relationship between the voltage and capacitance by the following equation:

$$\frac{C - C_\perp}{C_\perp} = \gamma - \frac{2\gamma}{\pi}(1 + \gamma \sin^2 \phi_m)^{\frac{1}{2}} \frac{V_{th}}{V} \times \int_0^{\sin \phi m} \left[\frac{(1 + kx^2)(1 - x^2)}{(1 + \gamma x^2)(\sin^2 \phi_m - x^2)} \right]^{\frac{1}{2}} dx \ .$$

Where the parameter γ and k correspond to the reduced quantities $\gamma = \frac{\varepsilon_{\parallel}}{\varepsilon_\perp} - 1$ and $k = \frac{K_{33}}{K_{11}} - 1$.

Supplementary Discussion 2: phase-decay-time measurement

To measure the viscosity coefficient (γ_1), we employed the phase-decay-time method where the time decay of optical phase was measured. A small voltage was applied to a liquid crystal cell to deform the nematic director field by a small variation. On removal of the field at time $t = 0$, the director restores back to the initial condition with a characteristic relaxation time τ_0:
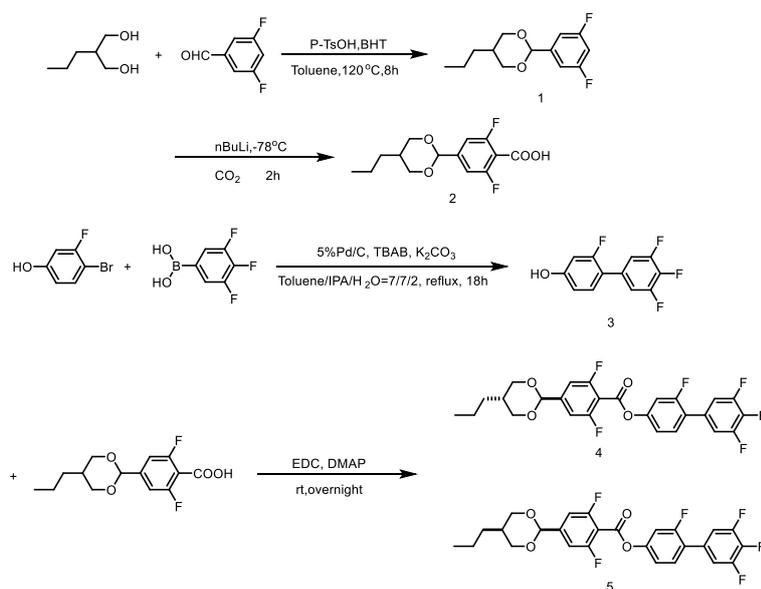
$$\tau_0 = \frac{\gamma_1 d^2}{k_{11} \pi^2}.$$

The decay time is expressed as:

$$\delta(t) = \delta_0 exp(-2t/\tau_0).$$

The slope of this linear plot is $2/\tau_0$. The accompanying phase change $\delta(t)$ is calculated from the time-dependent intensity I(t) from the following equation:

$$I(t) = I_0 \sin^2\{[\Delta_{total} - \delta(t)] / 2\}.$$

Supplementary Discussion 3: Synthetical protocals

OH + OHC — P-TsOH,BHT / Toluene,120 °C,8h → 1

nBuLi,-78 °C / CO₂ 2h → 2 — COOH

HO— —Br + HO–B(OH)₂ — 5%Pd/C, TBAB, K₂CO₃ / Toluene/IPA/H₂O=7/7/2, reflux, 18h → HO— 3

+ — COOH — EDC, DMAP / rt,overnight → 4

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2-phenyl-5-propyl-1,3-dioxane (1): 2-propylpropane-1,3-diol (5.0 g, 42.3 mmol), 3,5-difluorobenzoic acid (5.57 g, 35.3 mmol), BHT (0.116 g, 0.53 mmol), p-TsOH (0.30 g, 1.76 mmol) were added to 150 mL toluene in a 250 mL flask and reflux at 125℃ over 8h. Then the mixture was cooled to room temperature, extracted by DCM, washed with brine, dried over anhydrous Na_2SO_4. The organic phase was concentrated under vacuum, purified by flash chromatograph and recrystallized from EtOH as the pale-yellow compound 1 (mixture of isomers with molar ratio of 1/5, 6.41 g, 75%). 1H NMR (400 MHz, Chloroform-d) δ 7.02 (d, J = 6.1 Hz, 2H), 6.81 – 6.71 (m, 1H), 5.35 (s, 1H), 4.22 (dd, J = 11.8, 4.6 Hz, 2H), 3.51 (t, J = 11.5 Hz, 2H), 2.19 – 2.05 (m, 1H), 1.37 – 1.28 (m, 2H), 1.13 – 1.03 (m, 2H), 0.95 (d, J = 4.2 Hz, 3H). 13C NMR (101 MHz, Chloroform-d) δ 162.84(162.92), 142.28(142.47), 109.28, 103.97, 99.65(99.99), 72.56(70.64), 33.93(34.03), 30.29(31.62), 19.55(20.57), 14.19(14.08).

4-(5-propyl-1,3-dioxan-2-yl)benzoic acid (2): A 50 mL three-neck flask was loaded with compound 1(1.0 g, 4.13 mmol) and dry THF 25 mL, then the mixture was flashed with N_2 for 5 minutes. The solution was cooled to -78 ℃, n-BuLi (2.5 M hexane solution, 1.98 mL, 4.95 mmol) was injected to the mixture over 10 min. After stirring 1 h, excess amount of dried ice was input into the solution under N_2 atmosphere and stirred for 1h. After that the reaction mixture was quenched by 1M HCl aq. THF solvent was removed. The residue was dissolved in EA, washed with water, dried by $MgSO_4$. Then the solvent was removed and the crude product was recrystallized from EtOH as white solid (mixture of isomers with molar ratio of 1/5, 1.05 g, 86%). ¹H NMR (500 MHz, DMSO-d6) δ 13.97 (s, 1H), 7.18 (d, J = 8.7 Hz), 5.49 (s, 1H), 4.15 (d, J = 16.3 Hz, 2H), 3.52 (t, J = 11.4 Hz, 2H), 1.97 (t, J = 11.3 Hz, 1H), 1.31 – 1.23 (m, 2H), 1.09 – 0.99 (m, 2H), 0.91 – 0.83 (m, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 166.51, 161.15(161.20), 145.30(145.50), 110.26, 109.45, 98.86(99.13), 72.55(70.62), 33.86(33.92), 30.19(31.50), 14.16(14.07).

2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-ol (3): In a 50 ml flask, (3,4,5-trifluorophenyl)boronic acid (1.0 g, 5.69 mmol), 4-bromo-3-fluorophenol (0.98 g, 5.17 mmol), TBAB (0.426 g, 1.29 mmol), K2CO3 (1.43 g, 10.34 mmol), and palladium on carbon (10 wt%, 0.20 g) were added, then the mixed solvent of volume ratio 7/7/2 (toluene/isopropanol/H₂O) was added to the bottle. After refluxed for 6 h, the system was cooled to room temperature and poured into water, followed by extracting with toluene, washing with saturated brine (50 mL× 2), drying over anhydrous $MgSO_4$. Then the solvent was vacuum removed. The crude was purified by silica gel chromatography and the colorless solids were obtained (70.6%). ¹H NMR (400 MHz, Chloroform-d) δ 8.68 (s, 1H), 7.76 (s, 1H), 3.76 (d, J = 7.1 Hz, 2H), 1.26 (s, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 160.12, 157.59, 151.08, 138.91, 131.77, 130.86, 118.50, 112.89, 112.04, 104.07.

***Trans*-DIO (4) and *cis*-DIO (5):** The compound 2(1 g, 3.49 mmol), compound 3(0.829 g, 3.42 mmol), EDC (0.812 g, 5.24 mmol) and DMAP (0.021 g, 0.0175 mmol) were combined into a dried flask with 20 mL DCM added. The suspension was vigorously stirred until the formation of the ester was complete (14 – 18h). The solution was

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stripped of solvent by rotary evaporation, and dry-loaded onto a silica gel column for purification using EA/hexane=3:97 as eluent. Compound 4 (64%) and compound 5 (16%) were obtained as white powders. The NMR information of compounds 4 and 5 will be presented in detail in the following sections.

Compound 4 (*trans*-DIO): ^{1}H NMR (500 MHz, Chloroform-d) δ 7.47 – 7.37 (m, 1H), 7.21 – 7.11 (m, 6H), 5.39 (s, 1H), 4.31 – 4.18 (m, 2H), 3.59 – 3.47 (m, 2H), 2.13 (ttt, J = 11.4, 7.0, 4.6 Hz, 1H), 1.39 – 1.29 (m, 2H), 1.16 – 1.03 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 161.01 (dd, J = 258.2, 5.7 Hz), 159.44 (d, J = 251.2 Hz), 159.39, 151.26 (ddd, J = 249.6, 9.9, 4.2 Hz), 151.04 (d, J = 11.1 Hz), 145.72 (t, J = 10.0 Hz), 139.62 (d, J = 252.9 Hz), 131.16 – 130.74 (m), 130.74, 124.39 (d, J = 13.1 Hz), 118.23 (d, J = 3.7 Hz), 113.31 (dt, J = 16.7, 3.4 Hz), 110.74 (d, J = 26.0 Hz), 110.39 (dd, J = 24.0, 3.1 Hz), 109.50, 98.87, 72.67, 33.97, 30.30, 19.61, 14.27. MS: M+Na$^+$, 533.11 (calculated 533.12). FTIR (KBr, cm^{-1}): 3461(w), 3100(w), 2964(w), 2929(w), 2854(w), 1743(s),1641(w), 1619(m), 1580(w), 1537(m), 1500(s), 1434(m), 1409(w), 1392(w), 1366(w), 1328(w), 1248(s), 1199(w), 1148(s), 1119(s), 1086(s), 1047(s), 1027(s), 1005(w), 986(w), 961(w), 914(w), 885(w), 864(m), 818(w), 784(w), 763(w), 704(w), 655(w), 640(w), 594(w), 524(w), 488(w).

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Compound 5 (*cis*-DIO): ^1H NMR (500 MHz, Chloroform-d) δ 7.43 (t, J = 8.6 Hz, 1H), 7.22 – 7.13 (m, 6H), 5.50 (s, 1H), 4.14 – 4.02 (m, 4H), 1.77 – 1.70 (m, 2H), 1.49 (tq, J = 7.2, 2.2 Hz, 1H), 1.46 – 1.39 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 161.05 (dd, J = 258.3, 5.6 Hz), 159.44 (d, J = 251.2 Hz), 159.38, 151.26 (ddd, J = 249.8, 10.2, 4.2 Hz), 151.05 (d, J = 10.9 Hz), 145.93 (t, J = 9.8 Hz), 141.03 – 137.94 (m), 131.07 – 130.76 (m), 130.74 (d, J = 3.8 Hz), 124.38 (d, J = 13.0 Hz), 118.23 (d, J = 3.6 Hz), 113.30 (dt, J = 17.1, 3.8 Hz), 110.73 (d, J = 26.1 Hz), 110.35 (dd, J = 23.7, 3.4 Hz), 109.50 (t, J = 17.1 Hz), 99.17, 70.77, 34.02, 31.62, 20.62, 14.16. MS: M+Na$^+$, 533.11 (calculated 533.12). FTIR (KBr, cm^{-1}): 3465(w), 3084(w), 2963(w), 2934(w), 2862(w), 1752(s), 1644(w), 1619(m), 1588, 1538(m), 1501(s), 1432(m), 1406(w), 1394(w), 1380(w), 1364(w), 1323(w), 1245(s), 1196(w), 1166(w), 1144(s), 1116(s), 1074(s), 1047(s), 1021(s), 984(w), 962(w), 860(m), 813(w), 763(w), 705(w), 655(w), 639(w), 594(w), 525(w), 505(w), 469(w).