Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Large-Δε relaxor-like liquid crystal enables submillisecond switching and millivolt driving

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1. General Information

Materials and Reagents: All commercial chemicals and solvents were used as received, unless stated otherwise. Tetrahydrofuran (THF, Energy Chemical), Dichloromethane (DCM, Energy Chemical), Petroleum ether (PE, Energy Chemical), Ethyl acetate (EA, Energy Chemical), Methanol (MeOH, Energy Chemical), Ethanol (EtOH, Energy Chemical), Toluene (Energy Chemical), 1,4-dioxane (Diox, Energy Chemical), 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).

Nuclear Magnetic Resonance (NMR) Spectroscopy: ^1H, ^{19}F and ^{13}C NMR spectra of the samples were obtained in CDCl3 (Innochem, 99.8 atom % D, with 0.03%(v/v) TMS) solvents utilizing JASTEC JMTC-500/54/JJ 500 MHz NMR spectrometer. ^1H 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): The thermal properties of all the samples were characterized by 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 (10 K min^{-1}) 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.

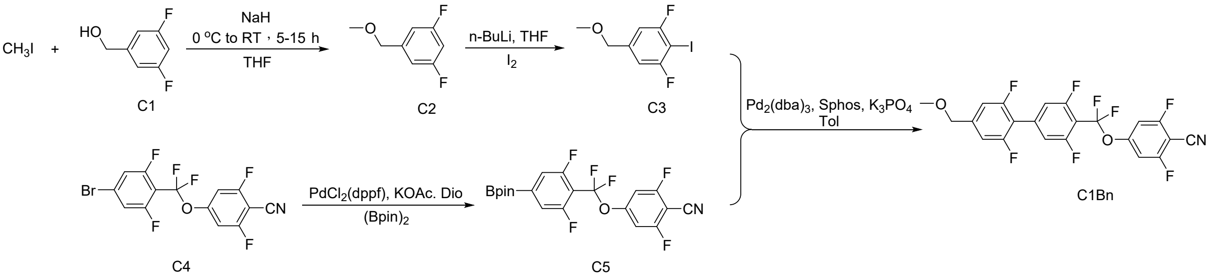
Dielectric spectroscopy: The dielectric spectroscopy was measured in homemade 20-μm-thick ITO-coated LC cells with or without parallel alignment layers, applying an electric field perpendicular to the plane of the ITO glass. The voltage applied to the ITO cell is 50 mV. The dielectric spectroscopy was conducted by using an LCR meter (4284A, Agilent). The collection of the frequency and temperature sweeping data is automated by homemade software written in LabVIEW.

The polarization switching measurement: The polarization switching measurements were conducted using the ferroelectricity measurement system (TOYO FCE10-S, Japan) combined with a waveform generator (Tabor Electronic, WW5064), high-voltage linear amplifier (pendulum, A800), and analyzer (TOYO, Model 6252). Electro-optic observation of polar switching: The polarization switching dynamics under the triangle electric field of the NF and SmAF phase were investigated by POM observation and SHG measurement. The LC cells were assembled with two glass substrates. One of the glass plates has interdigital comb-shaped ITO electrodes. The gap between the adjacent electrodes is 500 μm. The two glass plates were coated with a planar alignment agent (KPI-3000, Shenzhen Haihao Electronic Co. Ltd). The rubbing direction is perpendicular to the interdigital electrode strips, and the rubbing directions of the upper and lower plates are syn-parallel. Photographs of POM (Olympus BH2, Instec mK2000, Nikon D5300) were taken with a green filter (Olympus, IF 550nm) inserted. The relevant equipment parameters of SHG measurement are consistent with those described above. On the basis of SHG, we performed SHG interference measurement to illustrate macroscopic polarization S5 direction information; the reference signal was generated by a fused silica plate. The details are described in the corresponding experimental part.

Sample preparation in LC cell: The samples were introduced to homemade cells with two glass plates, controlled spacers, planar alignment conditions and glue seals. For alignment materials, we used KPI-3000 (Shenzhen Haihao Technology Co. Ltd). Homemade planar cells with syn-parallel or anti-parallel rubbing conditions and cell thickness of 5 μm were used for polarizing optical microscopy (POM, Olympus BX51) observation. The temperature was controlled by the Instec mK2000 hot stage. The photographs of POM were taken with the camera (Nikon D5300). Homemade 5-μm thick cells with planar alignment were used for measuring the birefringence and SH signal as a function of temperature. Homemade 20-μm-thick cells with ITO layer were used for measurements of polarization switching and dielectric properties.

Sample mixing procedure: The mixture materials are prepared by mixing the commercial or homemade apolar nematic LCs (HAE) independently with a ferroelectric nematic LC (C_1Bn) by weight, the steps were as follows: the samples were proportionally weighed and completely dissolved with appropriate chloroform, after 1 min of oscillation, 10 min of ultrasound, the mixtures were put into a blast drying oven and dried at 60 °C. The molecular structures and details are shown in the Experimental Section in Supplementary Information.

1. Experimental Section



Scheme S1. Synthesis scheme of C1Bn

Preparation of C_1Bn

(**C2**) To a stirring suspension of NaH (7.5 mmol, 1.5 equiv.) in THF (0.2 M) was added the alcohol substrates (5 mmol, 1.0 equiv) at 0 °C. After 5 min, MeI (12.5 mmol, 2.5 equiv.) was added in one portion at 0 °C, then the reaction was warmed to room temperature and stirred until completion of the reaction. Upon completion, the mixture was cooled to 0 °C and quenched by the dropwise addition of a saturated aqueous solution of NH_4Cl (caution: H_2 evolution). The aqueous layer was extracted with ethyl acetate (3×20 mL), and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography to give the desired product ethers. The general yield 50%. ^1H NMR (500 MHz, Chloroform-*d*) δ 6.85 (ddq, *J* = 7.0, 2.4, 0.7 Hz, 2H), 6.77 – 6.64 (m, 1H), 4.51 – 4.37 (s, 2H), 3.39 (s, 3H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -109.91

(**C3**) A 50 mL three-neck flask was loaded with C2 (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 °C, n-BuLi (2.5 M hexane solution, 1.98 mL, 4.95 mmol) was injected to the mixture over 10 min. After stirring for 1 h, an excess amount of I_2 was input to the solution under N_2 atmosphere and stirred for 1h. After that, THF solvent was removed. The residue was dissolved in EA, washed with water, and dried with $MgSO_4$. Then the solvent was removed and the crude product was recrystallized from EtOH as a white solid (mixture of isomers with molar ratio of 1/5, 1.05 g, 86%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.96 – 6.79 (m, 1H), 4.41 (d, J = 0.8 Hz, 1H), 3.39 (s, 2H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -92.44.

(**C4**) was synthesized according to the reference[1].

(**C5**) The bromobenzene (1.0 eq.), phenylboronic acid (1.1 eq.), potassium acetate (2.0 eq.), palladium-catalyst ($Pd_2(dba)_3$, 0.02 eq.) were added to a stirred solution of a mixture of dioxane under nitrogen atmosphere at 100 °C. Then the mixture solution was heated under reflux until the complete consumption of the ester (TLC). The reaction was then cooled, water was added to the mixture, and extracted with EA, washed with water and brine. The product was isolated from the crude mixture by column chromatography over silica with ethyl acetate and petroleum ether as the eluent. The general yield 60%[2]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, J = 10.1 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 1.34 (s, 6H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -61.82 (t, J = 26.6 Hz), -101.32, -111.44 – -111.61 (m).

(**C1Bn**) The bromobenzene (1.0 eq.), phenylboronic acid (1.1 eq.), potassium phosphate tribasic (2.0 eq.), dicyclohexyl(2',6'dimethoxy-[1,1'-biphenyl]-2-yl)phosphine (SPhos, 0.04 eq.), palladium-catalyst ($Pd_2(dba)_3$, 0.02 eq.) were added to a stirred solution of a mixture of toluene under nitrogen atmosphere at 100 °C. Then the mixture solution was heated under reflux until the complete consumption of the ester (TLC). The reaction was then cooled, water was added to the mixture, and extracted with EA, washed with water and brine. The product was isolated from the crude mixture by column chromatography over silica with ethyl acetate and petroleum ether as the eluent. The general yield 60%. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.16 (d, J = 10.8 Hz, 1H), 7.02 (dd, J = 8.3, 2.7 Hz, 2H), 4.47 (s, 1H), 3.44 (s, 1H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -61.89, -61.95, -62.00, -101.21 (d, J = 8.6 Hz), -110.68 (td, J = 26.9, 26.3, 11.2 Hz), -113.75 (d, J = 8.6 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.77 (d, J = 6.7 Hz), 162.69 (d, J = 6.5 Hz), 160.67 (d, J = 6.8 Hz), 158.67 (d, J = 6.4 Hz), 155.27 (t, J = 13.5 Hz), 143.23 (t, J = 9.4 Hz), 135.72 (d, J = 11.7 Hz), 122.50, 120.35, 118.21, 115.31 – 114.75 (m), 113.79 (t, J = 17.8 Hz), 112.10 – 109.76 (m), 108.70, 105.87 (d, J = 23.7 Hz), 90.03 (t, J = 19.4 Hz), 73.09, 58.74.

2. Supplementary Figures and Tables

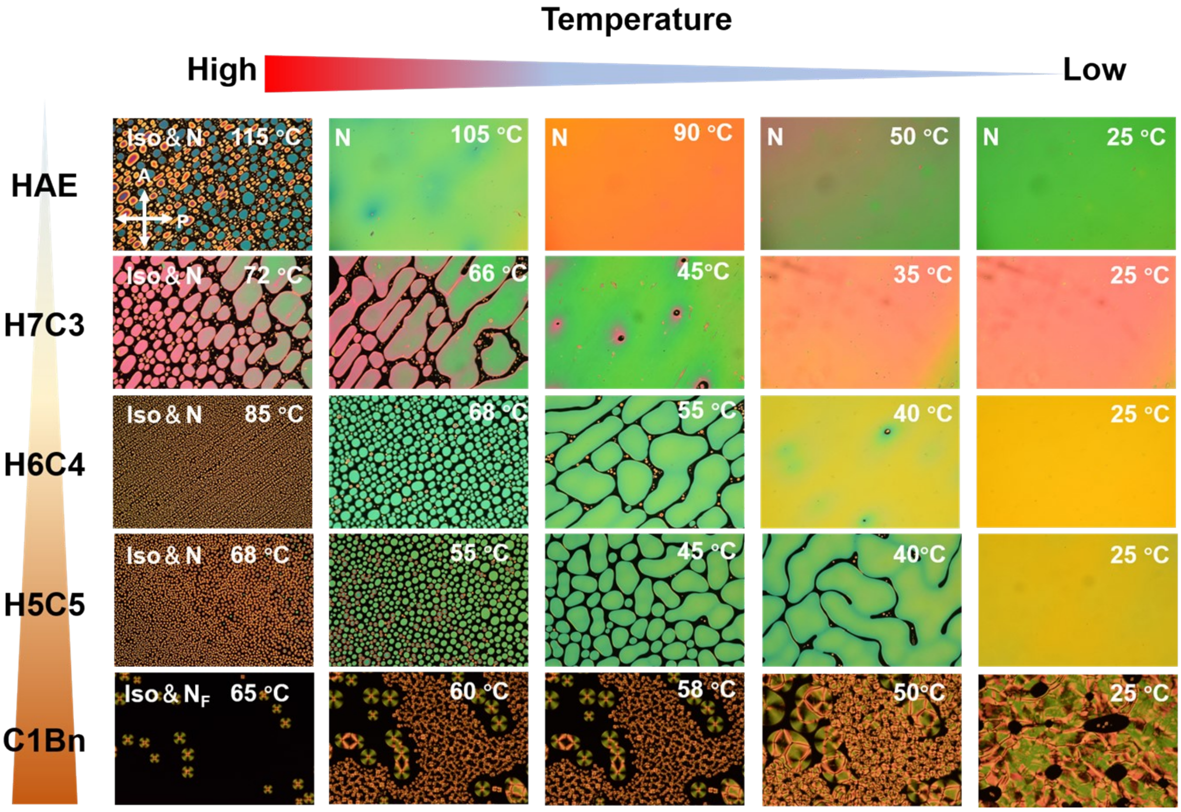


Figure S1. The phase behavior of HAE/C1Bn mixtures. The representative PLM texture evolutions of HAE/C1Bn mixtures (the samples denoted as HxCy, where x and y represent the weight fraction of HAE and C1Bn, respectively) are shown. The thickness of the homemade cell is 5 μm with unoriented.

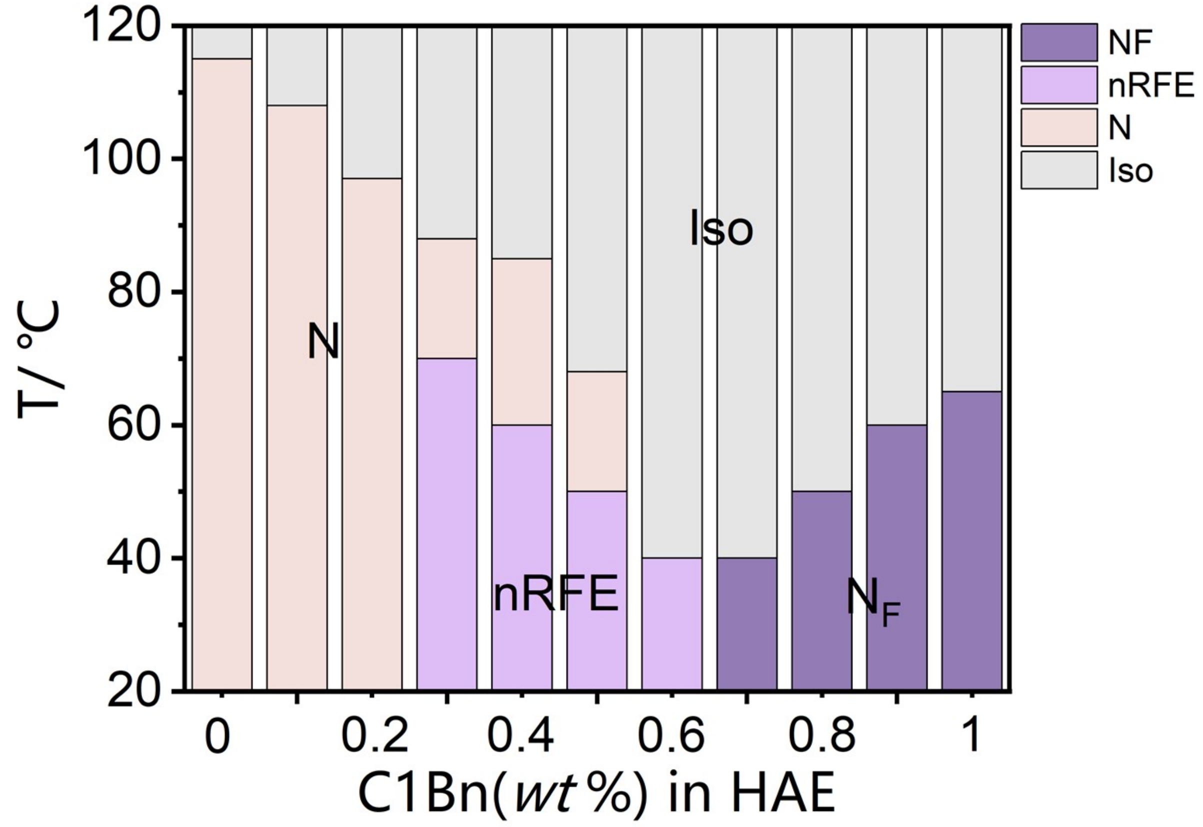


Figure S2. Temperature–composition phase diagram of HAE/C1Bn mixtures with different composition ratios. The difined nRFE transition temperature is fitting by the reciprocal dielectric constant ($1/\varepsilon_{/\!/}$) deviates from the linear Curie-Weiss law, which is taken as the onset of local polarization.

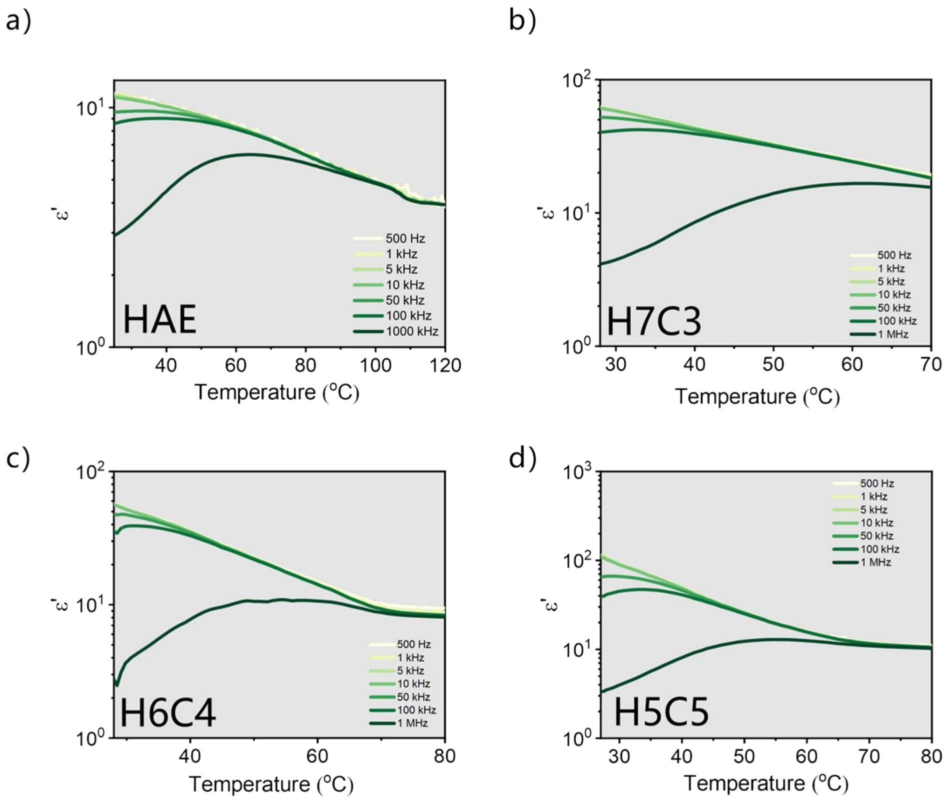


Figure S3. Temperature and frequency dependence of the dielectric permittivity at various frequencies for HmCn mixture. HAE (a), H7C3 (b), H6C4 (c), and H5C5 (d). Different line colors indicate different test electric field temperatures or frequencies. The LC cells were measured with a cell thickness of 20 μm.

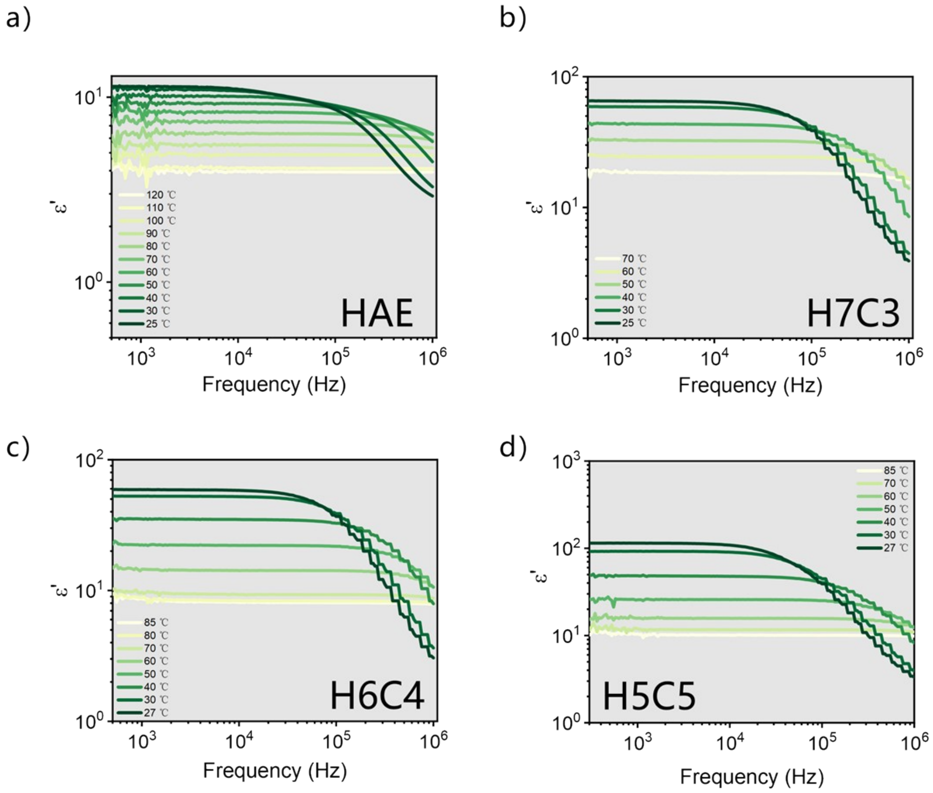


Figure S4. Frequency dependence of the dielectric permittivity at various frequencies for HmCn mixture. HAE (a), H7C3 (b), H6C4 (c), and H5C5 (d). Different line colors indicate different test electric field temperatures or frequencies. The LC cells were measured with a cell thickness of 20 μm.

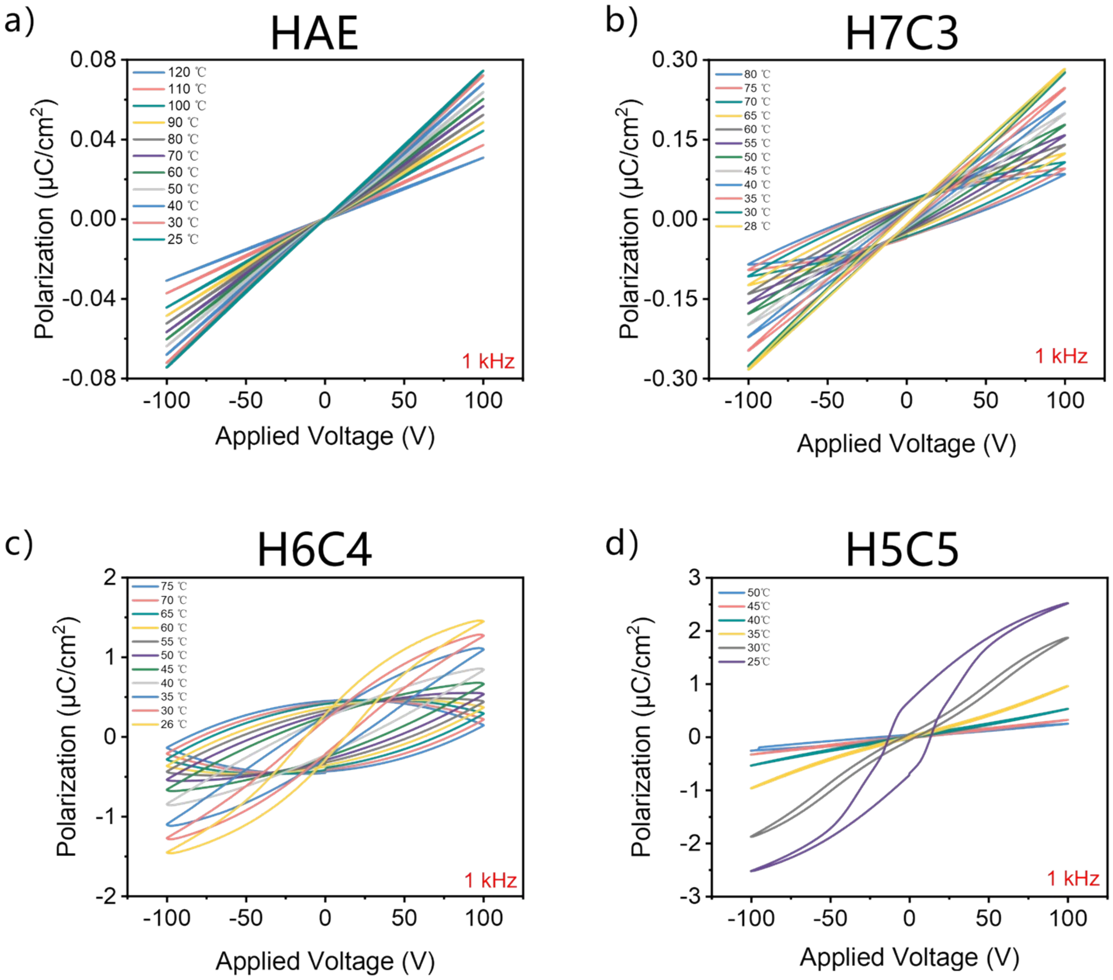


Figure S5. Voltage dependence of the experimental *P*-*E* loop at various temperatures for HAE/C1Bn mixtures: HAE (a), H7C3 (b), H6C4 (c), and H5C5 (d). Different line colors indicate different experimental temperatures. The LC cells were measured with a cell thickness of 20 μm.

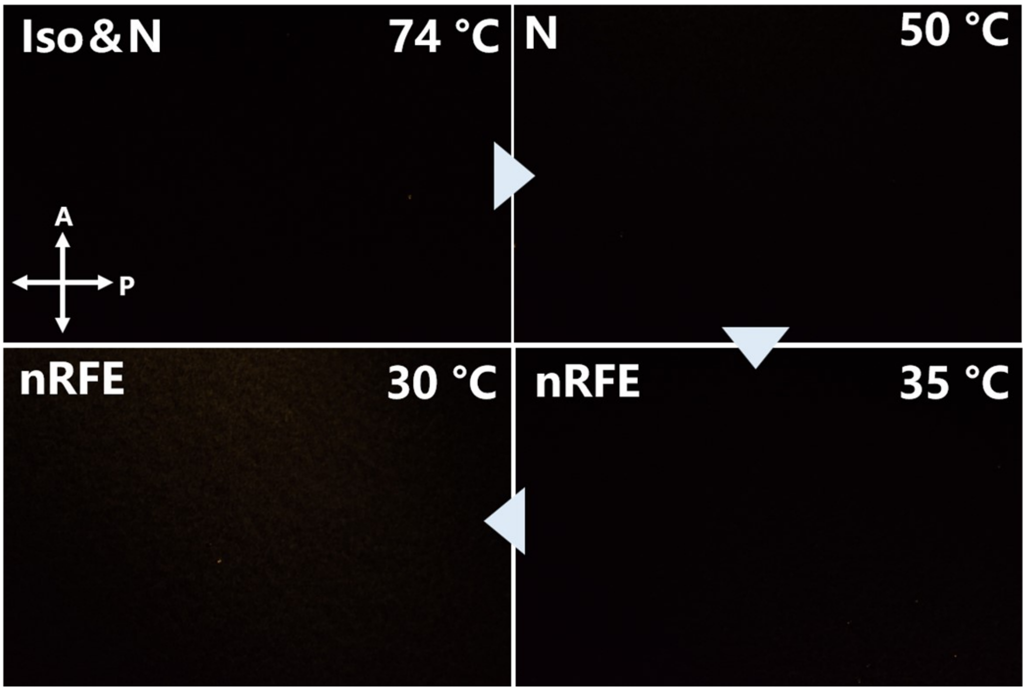


Figure S6. The representative PLM texture evolution of H5C5 mixture under the crossed polarizers. The thickness of the homemade cell is 2 μm under homeotropic alignment conditions.

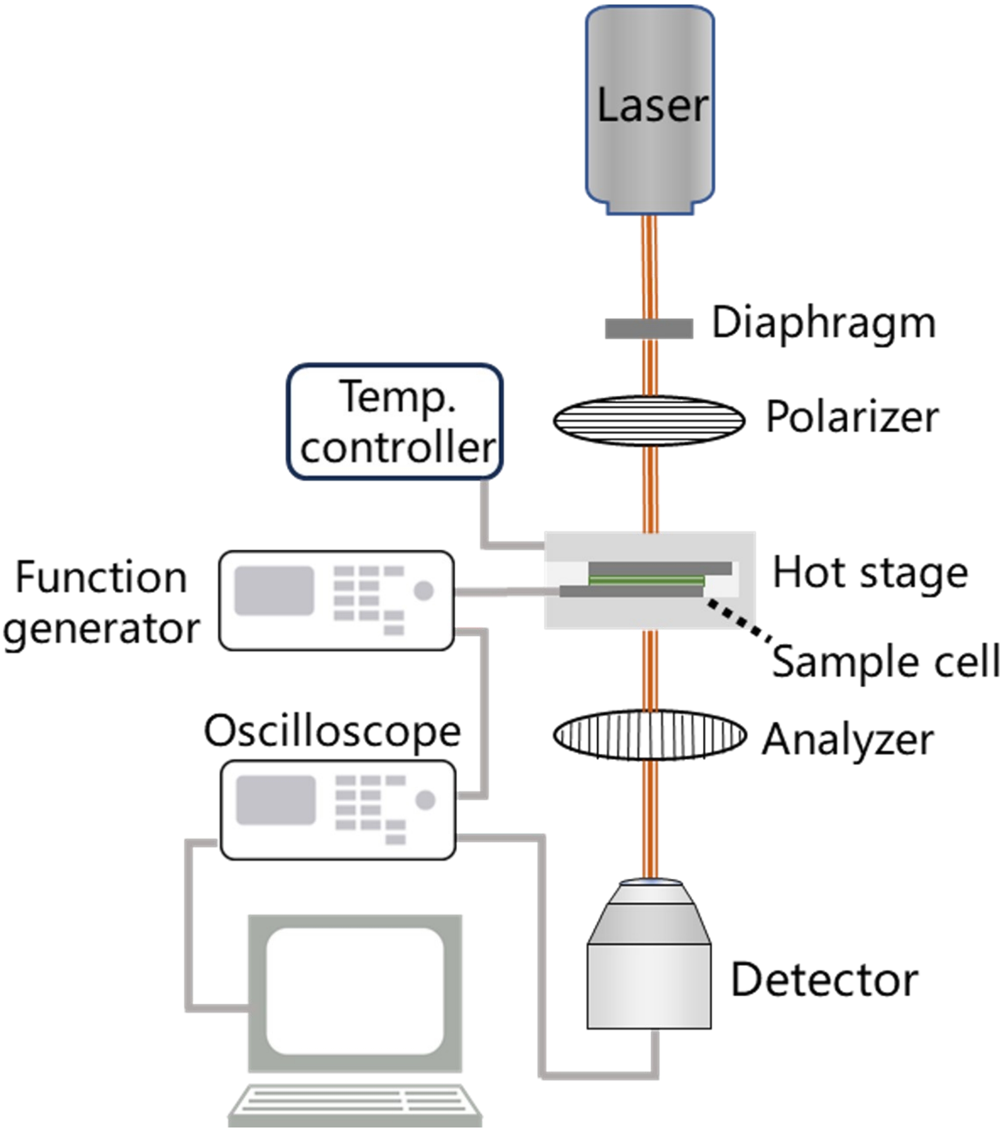


Figure S7. Optical setup for measuring the electro-optic response time under the out-of-plane field switching (OFS) mode.

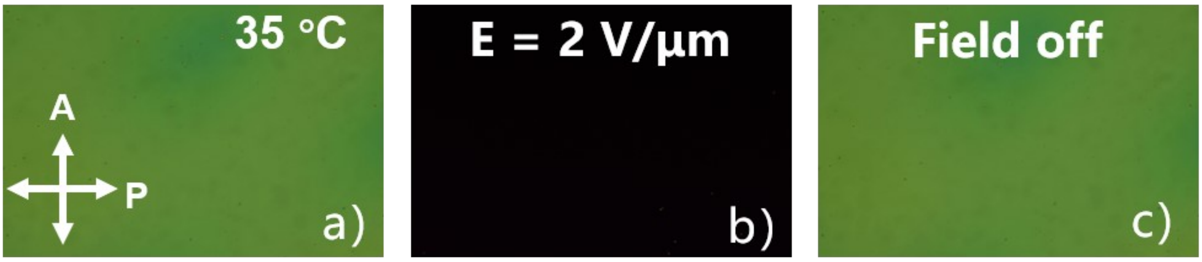


Figure S8. POM of H5C5 during the switching process a) initial state; b) E = 2 V/μm; c) field off.

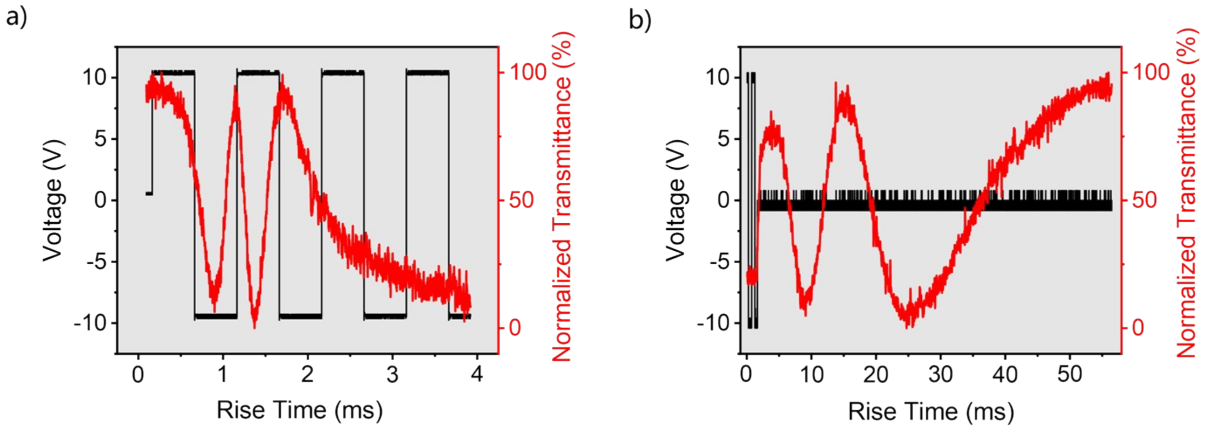


Figure S9. Variation in transmittance during the OFS switching process of HAE under an applied voltage of 10 V for the rising (a) and relaxation (b) process.

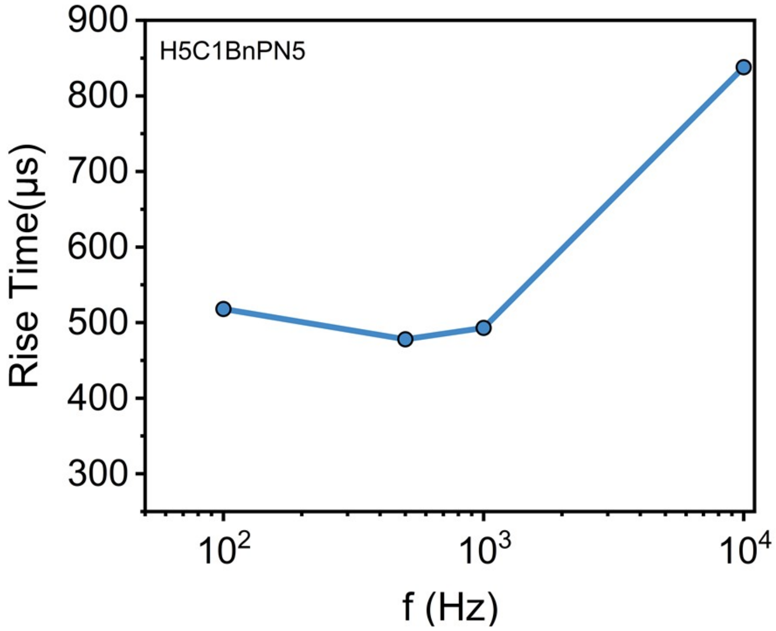


Figure S10. Dependence of electro-optic response time on driving-field frequency

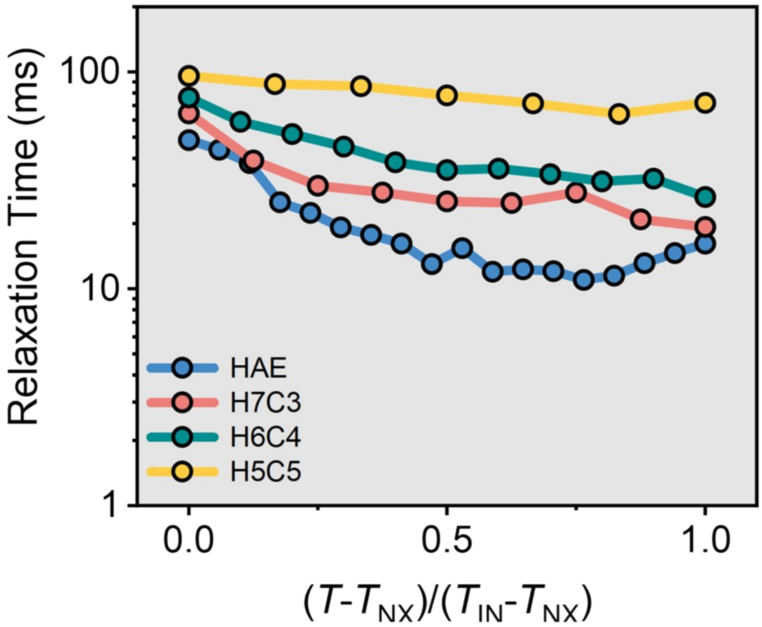


Figure S11. Voltage dependence of the electro-optic response times for different samples under the temperature of 25 °C.

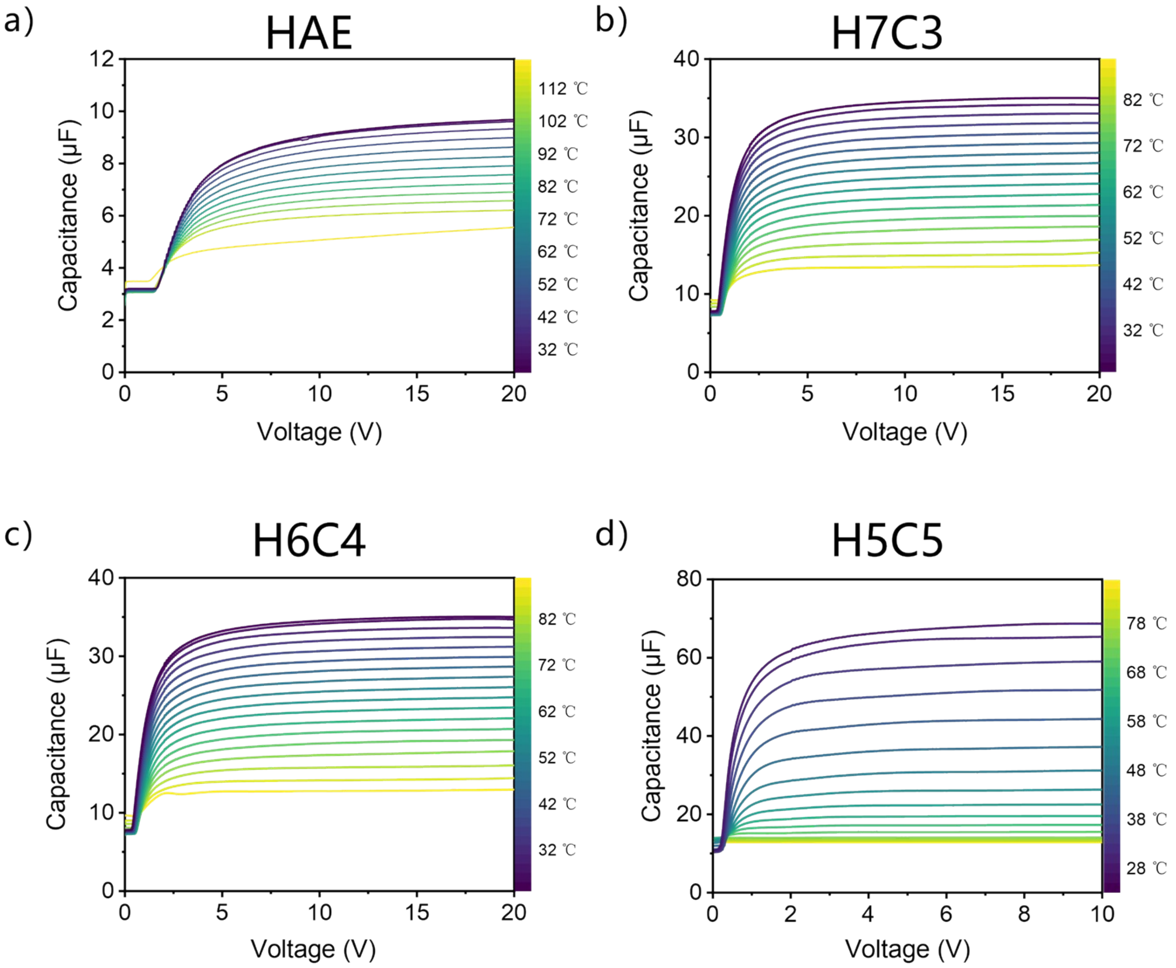


Figure S12. The capacitance versus voltage curves of HAE (a), H7C3 (b), H6C4 (c), and H5C5 (d) under different temperature conditions. The LC cells were measured with a cell thickness of 10 μm at 500 Hz.

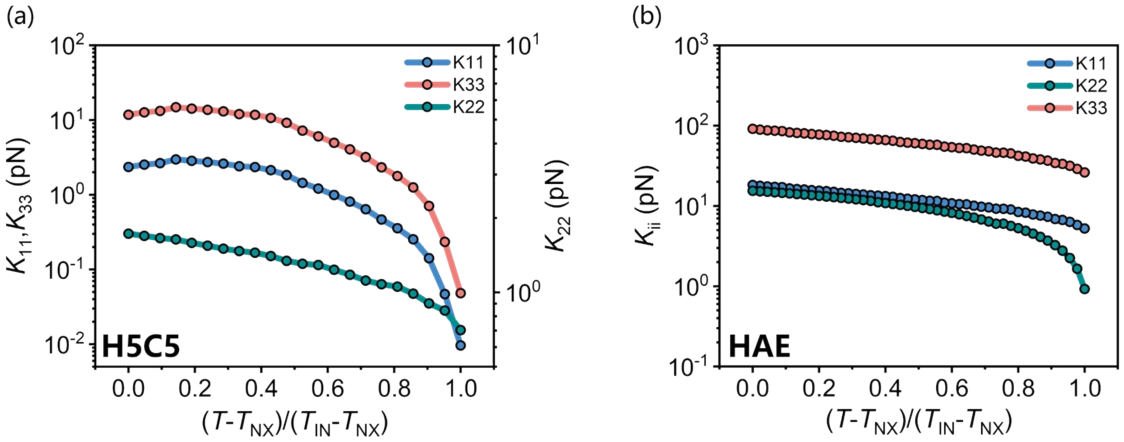


Figure S13. Temperature dependence of the K_{11}, K_{22}, K_{33} for H5C5(a) and HAE(b).

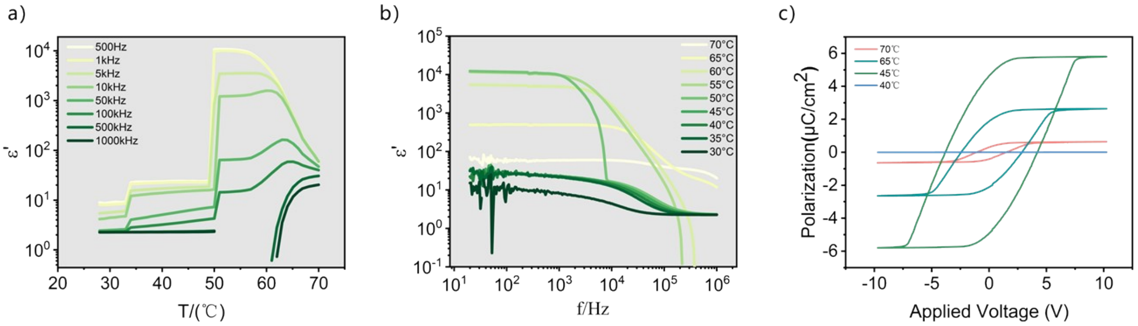


Figure S14. (a) Temperature and frequency dependence of the dielectric permittivity at various frequencies for C1Bn. (b) Frequency dependence of the dielectric permittivity at various frequencies for C1Bn.(c) Voltage dependence of the experimental *P*-*E* loop at various temperatures for C1Bn.

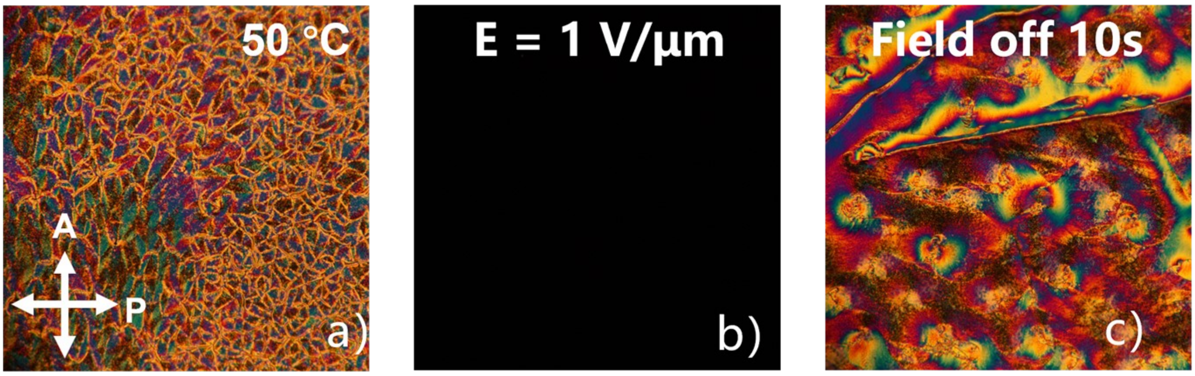


Figure S15. (a) Polarized optical microscopy (POM) images of C1Bn at 50 °C. (b) under an applied electric field of 0.5 V/μm. (c) 10 s after removal of the electric field. Cell thickness: 10 μm.

Supporting references.

1 A. Manabe, M. Bremer and M. Kraska, *Liquid Crystals*, 2021, **48**, 1079–1086.

2 J. Li, H. Nishikawa, J. Kougo, J. Zhou, S. Dai, W. Tang, X. Zhao, Y. Hisai, M. Huang and S. Aya, *Sci. Adv.*, 2021, **7**, eabf5047.