

Supplementary Information

Periodically-modulated unipolar and bipolar orders in nematic fluids: towards miniaturized nonlinear vectorial optics

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Supplementary Information

Supplementary Section 1: Material synthesis flow

Materials

All commercial chemicals and solvents were used as received unless stated otherwise. 2-fluoro-4-methoxybenzoic acid (99%, Adamas), benzyl 4-hydroxy-2-(trifluoromethyl)benzoate (98%, Aladdin), 4-dimethylaminopyridine (DMAP, 99%, TCI), Dicyclohexylcarbodiimide (DCC, 99%, TCI), palladium on carbon (5%, Kaili Catalyst & New Materials Co., Ltd), 4-nitrophenol (99%, Adamas), Tetrahydrofuran (THF, reagent grade, Adamas), Dichloromethane (DCM, reagent grade, Adamas), Ethyl Alcohol (EtOH, reagent grade, Adamas), hydrochloric acid (HCl, reagent grade, Adamas), Magnesium sulfate anhydrous (anhydrous MgSO₄, reagent grade, Adamas), Silica gel (Merck, 230-400 mesh).

Methods

Fig. S1.

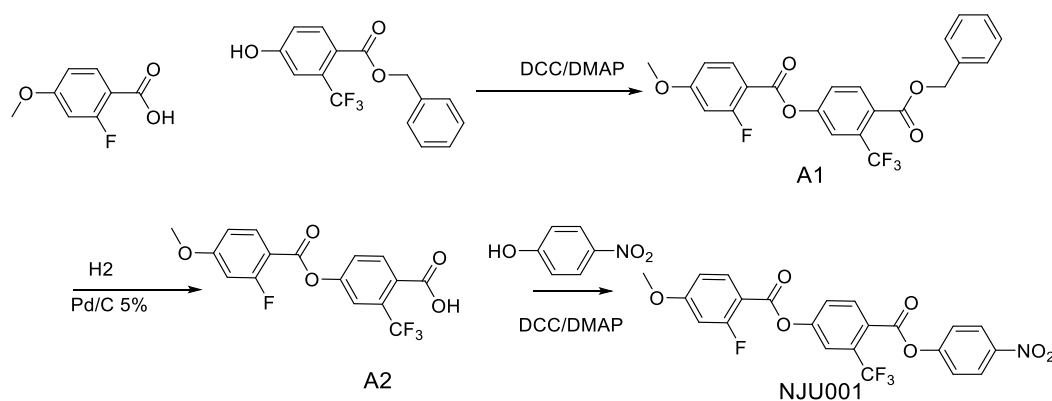


Fig. S1. Chemical synthesis flow of the NJU001 material.

Benzyl 4-((2-fluoro-4-methoxybenzoyl)oxy)-2-(trifluoromethyl)benzoate (A1): A three-necked round bottom flask was charged with 2-fluoro-4-methoxybenzoic acid (8.5 g, 0.05 mol), benzyl 4-hydroxy-2-(trifluoromethyl)benzoate (15 g, 0.05 mol), DMAP (0.2 g), DCM (100 mL), and were cooled to 5 °C with stirring. Then, DCC (12.5 g, 0.06 mol) was added along with 30 mL dichloromethane. The solution was stirred at the temperature range of 5 °C ~ 10 °C for 12 h. The filtrate was collected and washed with 50 mL HCl (1%). Then, the dichloromethane layer was collected, dried by anhydrous MgSO₄, and stripped of the solvent by rotary evaporation. Then, the 50-mL ethyl alcohol was added and recrystallized. Yield: 18.4 g (82.14%).

4-((2-fluoro-4-methoxybenzoyl)oxy)-2-(trifluoromethyl)benzoic acid (A2): A hydrogenating reactor was charged with A1 (15 g, 0.033 mol), THF (50 mL), palladium on carbon (1g, 5%). The reaction was for 12 hours. The filtrate was collected and stripped of the solvent by rotary evaporation. Then, the 50-mL ethyl alcohol was added and recrystallized. Yield: 10.4g (85.11%).

4-((4-nitrophenoxy)carbonyl)-3-(trifluoromethyl)pheny

2-fluoro-4-methoxybenzoate

(NJU001): A three-necked round bottom flask was charged with A2 (8.0 g, 0.022 mol), 4-nitrophenol (3.4 g, 0.0245 mol), DMAP (0.1 g), DCM (100 mL), and were cooled to 5 °C with stirring. Then DCC (5.53 g, 0.0265 mol) was added along with 20-mL dichloromethane. The solution was stirred at the temperature range of 5 °C ~ 10 °C for 12 h. The filtrate was collected and washed with 50 mL HCl (1%). Then, the dichloromethane layer was collected and dried by anhydrous MgSO₄, and the solvent was stripped by rotary evaporation. The solution was dry-loaded onto a silica gel column for purification with petroleum ether/ethyl acetate as eluent. Then, the 50-mL ethyl alcohol was added and recrystallized. Yield: 4.8g (99.3%).

¹H NMR (400 MHz, Chloroform-d) δ 8.39 (d, *J* = 8.8 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.12 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.79 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 12.8 Hz, 1H), 3.96 (s, 3H). ¹³C NMR (400 MHz, Chloroform-d) δ 165.88, 165.09, 163.21, 161.44, 155.08, 153.67, 145.69, 133.98, 132.99, 131.34, 126.25, 125.39, 123.59, 122.30, 121.77, 121.37, 110.79, 108.93, 102.58, 56.01.

Supplementary Section 2: Characterization of the nonlinear optical coefficient d_{33}

The nonlinear optical coefficient d_{33} can be determined using the following equation for second-harmonic generation (SHG):

$$I_2 = \frac{2\omega_2^2 \sin^2(\frac{\Delta k d}{2})}{\epsilon_0 n_2 n_1^2 c^3 (\Delta k)^2} d_{33}^2 I_1^2 = C \frac{\sin^2(\frac{\Delta k d}{2})}{n_2 n_1^2 (\Delta k)^2} d_{33}^2 I_1^2, \quad (S1)$$

where:

$\Delta k = \frac{2\pi\omega_1(n_1-n_2)}{c}$ is the wavevector mismatch;

ϵ_0 is the vacuum permittivity;

ω_1 and ω_2 are the angular frequencies of the fundamental wave (FW) and SH wave;

c is the speed of light;

n_1 and n_2 represent the refractive indices of the FW and SH wave, respectively;

C is a constant related to the measuring system;

d_{33} is the nonlinear optical coefficient,

d is the sample thickness;

I_1 and I_2 represent the intensities of the FW and the SH wave.

Once C is determined, and n_1 and n_2 are measured, we can determine the d_{33} of the NJU001 material by fitting the intensity correlation between FW I_1 and the SH wave I_2 .

(1) Determination of the System Constant C

The constant C was calibrated using a *z*-cut LiNbO₃ crystal ($d=1$ mm in our experiment), where the nonlinear interaction is governed by the d_{22} coefficient under the experimental configuration: optic axis aligned along the *x*-axis, and incident FW polarization along the *y*-axis. Given that $d_{22} = 6.3$ pm/V [*Appl. Phys. Lett.* 5, 234–236 (1964)], the refractive indices $n_1=2.218$ and $n_2=2.279$ at 650 nm and 1300 nm [*Appl. Phys. B.* 91, 343–348 (2008)], and Δk calculated from the dispersion relation, C was determined by fitting the $I_1 - I_2$ intensity correlation.

(2) Measurement of the Refractive Indices in NJU001

The extraordinary (n_e) and ordinary (n_o) refractive indices of NJU001 were measured using an interference method [Science. 383, 1364 (2024)].

Sample Preparation:

A commercial wedge cell (EHC KCRK-05, KERUN EXPERIMENTAL EQUIPMENT CO., LTD) was filled with NJU001 at 145°C via capillary. The rubbing direction was along the thickness gradient.

Interference Fringe Analysis:

Polarized light microscopy with red/near-infrared filters ($\lambda=650/1300$ nm, bandwidth 10 nm).

Dihedral angle α determined from air fringes:

$$\alpha = \frac{\lambda}{2n_{\text{air}}u_{\text{air}}} \quad (\lambda=650 \text{ nm}, n_{\text{air}} = 1). \quad (\text{S2})$$

Refractive indices calculated via:

$$n_{o,e} = \frac{\lambda}{2\alpha u_{LC}}, \quad (\text{S3})$$

where u_{LC} is the fringe spacing in NJU001.

Measurement Protocol:

n_e measured when the director was parallel to the light polarization,

n_o measured when the director was perpendicular.

The temperature-dependent refractive indices at 650 nm and 1300 nm are shown in the following figure.

Fig. S2.

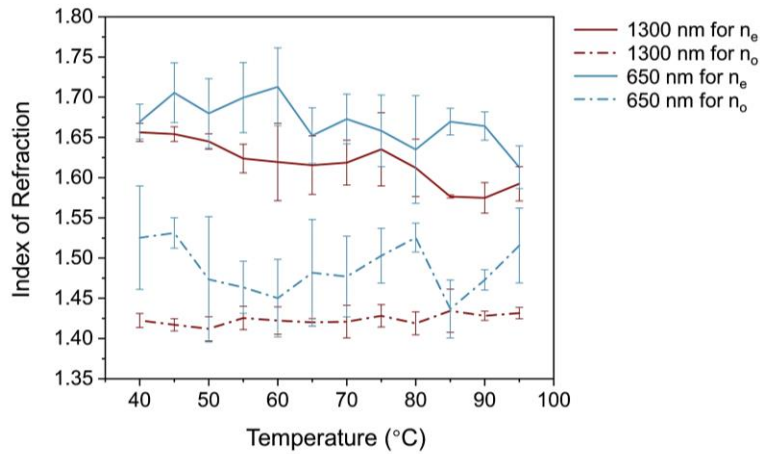


Fig. S2. Temperature-dependent extraordinary and ordinary refractive indices of the NJU001 material at 1300 nm and 650 nm. The refractive indices were determined by analyzing the fringe spacing extracted from interference patterns measured at 5°C intervals. Error bars represent mean $\pm$ standard deviation. Source data are provided as a Source Data file.

After we have obtained the material parameters of n_2 , n_1 , and C , Δk was calculated. Subsequently, the nonlinear optical coefficient d_{33} was extracted by fitting the intensity correlation between FW I_1 and the SH wave I_2 . The temperature-dependent variation of d_{33} is presented in the following figure. As seen from the figure, the laser power/energy meter begins to detect the SHG signal at approximately 64 °C, which shows a slight discrepancy compared to that (~70 °C) in Fig. 1e, which

is derived from the light intensity processed by the CMOS camera in the main text. This difference is attributed to the sensitivity of the detection instruments; specifically, the CMOS camera is capable of detecting weaker SHG signals.

Fig. S3.

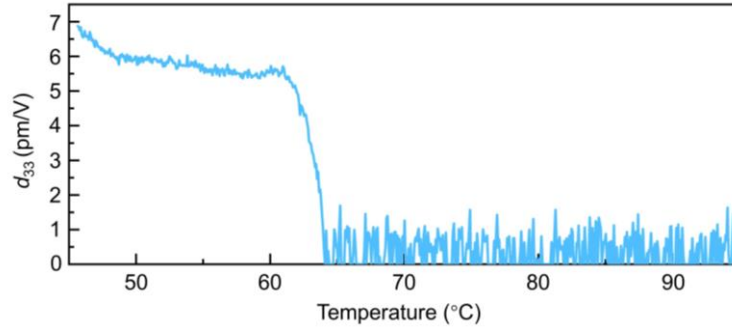


Fig. S3. Temperature-dependent d_{33} . Source data are provided as a Source Data file.

The NJU001 material exhibits $C_{\infty v}$ symmetry and P_S in the direction of the director (i.e., longitudinal ferroelectricity), analogous to the behavior observed in RM734. Usually, the coefficient d_{31} can be measured by illuminating the sample with ordinary light (polarization perpendicular to the director). However, the accurate determination of this coefficient was difficult because of the high d_{33}/d_{31} ratio. As a consequence, the signal remained undetected due to the limited sensitivity of the photodetector (Laser Power and Energy Meter, SKU2256258, Coherent). Thus, we just characterized the d_{33} of the NJU001 material.

Supplementary Section 3: Discussions on possible models for Pathway I and Pathway II

The characteristics of the Ising, Néel, Bloch, and Splay nematic models are described as follows (Fig. S13 and S17).

- (1) The Ising model describes a lattice of discrete anti-polar domains that exist in either of two states [*Nat. Rev. Phys.* 2, 634-648 (2020)]: up (+1) or down (-1). A domain wall forms between domains with opposite polar directions where the polar order parameter diminishes, indicating a lack of alignment.
- (2) The Néel and Bloch models also describe antiferroelectric systems¹, where the transition from one domain to another occurs through a region known as a Néel or Bloch wall. These walls allow for a smooth rotation of dipoles from one domain to the next, maintaining their polar magnitude rather than an abrupt change. For the Néel model, the dipoles rotate around an out-of-plane helical axis. In contrast, for the Bloch model, the helical axis is in-plane, which can provide a more energy-efficient transition compared to the sharp boundaries in the Ising model.
- (3) The Splay nematic model describes alternating anti-polar domains with disclination lines separating them [*Phys. Rev. X* 8, 041025 (2018)] [*Phys. Rev. Lett.* 124, 037801 (2020)]. Unlike the Ising model, the dipoles in the polar domain exhibit a splay deformation due to the dominant flexoelectricity effect.

Pathway I

Considering the unipolar ordered stripes in Pathway I confirmed by the second-harmonic generation interferometry (SHG-I) microscopy (Fig. 2c), we can directly rule out the Ising, Néel, and Bloch models.

Pathway II

The SHG-I imaging confirms the bipolar ordering in the Nx phase in Pathway II (Fig. 2d). Besides Bipolar model, described in the main text, possible models include Ising, Néel, Bloch, and Splay nematic models.

First, we exclude the Néel model because there is no SH signal in the transition regions between bipolar domains upon pumping circularly polarized fundamental wave (FW) (Fig. S11b). In contrast, the in-plane dipoles described by the Néel model will excite SH signals in this condition.

Second, we exclude the Bloch model by the fluorescence confocal polarizing microscopic (FCPM) observation [*Chem. Phys. Lett.* 336, 88-96 (2001)]. As the dipoles in Bloch walls have varied out-of-plane components, the excited fluorescence intensity in these regions will be decreased compared to the in-plane dipoles in polar domains under the excitation of circularly polarized light. While, in our experiment, we observe a uniform fluorescence pattern (Fig. S15b) that was excited by circularly polarized light.

Third, we exclude the Ising and Splay nematic models based on polarized light microscopic (PLM) textures, which show no obvious disclination line in the transition regions (Fig. S17).

Supplementary Section 4: Nonlinear polarization vector field

The second-order nonlinear optical tensor of the liquid-matter ferroelectric material under Kleinman condition in the local (primed) coordinate system (x' , y' , z') is given by [*Liq. Cryst.* 49, 899-906 (2022)]:

$$\mathbf{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{31} & 0 \\ 0 & 0 & 0 & d_{31} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \quad (\text{S4})$$

The z' -axis is along the dipole. Here, the three-index notation of the susceptibility has been contracted to two indices in the usual way. There are only two independent coefficients, d_{33} and d_{31} . The SH signal generated along z' (extraordinary polarization) is driven by the d_{33} coefficient for extraordinary FW and d_{31} for ordinary FW.

For a linear polarization incidence ($\mathbf{E}^\omega = (\mathbf{E}_x^\omega + \mathbf{E}_y^\omega) = A_0(\cos \phi \hat{\mathbf{e}}_x + \sin \phi \hat{\mathbf{e}}_y)$) in the laboratory coordinate (x, y, z)), where A_0 and ω are the amplitude and angular frequency of the FW, ϕ is the polarization angle relative to the x -axis, and $\hat{\mathbf{e}}_x$ ($\hat{\mathbf{e}}_y$) represents the unit vector of the x (y)-axis, we can describe it in the local coordinate system as $\mathbf{E}_{x'} = \mathbf{E}_x^\omega \cdot \cos \alpha + \mathbf{E}_y^\omega \cdot \sin \alpha$, $\mathbf{E}_{y'} = 0$ and $\mathbf{E}_{z'} = \mathbf{E}_x^\omega \cdot \sin \alpha + \mathbf{E}_y^\omega \cdot \cos \alpha$. Then, the second-order nonlinear polarization can be analytically obtained as [*Nonlinear optics*. 3rd edn, (Academic Press, 2008)]

$$\begin{aligned}
\mathbf{P}_\alpha^{2\omega} &= 2\varepsilon_0 \begin{bmatrix} 0 & 0 & 0 & 0 & d_{31} & 0 \\ 0 & 0 & 0 & d_{31} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \mathbf{E}_{x'}^2 \\ \mathbf{E}_{y'}^2 \\ \mathbf{E}_{z'}^2 \\ 2\mathbf{E}_{y'}\mathbf{E}_{z'} \\ 2\mathbf{E}_{x'}\mathbf{E}_{z'} \\ 2\mathbf{E}_{x'}\mathbf{E}_{y'} \end{bmatrix} \\
&= 2A_0^2\varepsilon_0 d_{33} \cos^2(\phi - \alpha) (\cos \alpha \hat{\mathbf{e}}_x + \sin \alpha \hat{\mathbf{e}}_y) \\
&= 2A_0^2\varepsilon_0 d_{33} \cos^2(\phi - \alpha) \hat{\mathbf{e}}_\alpha.
\end{aligned} \tag{S5}$$

ε_0 is the vacuum permittivity, α the orientation of the dipole, and $\hat{\mathbf{e}}_\alpha$ the unit vector along α direction. This expression can also be described by

$$\mathbf{P}_\alpha^{2\omega} = 2A_0^2\varepsilon_0 d_{33} \cos(\phi - \alpha) \begin{pmatrix} \cos^2 \alpha & \cos \alpha \sin \alpha \\ \cos \alpha \sin \alpha & \sin^2 \alpha \end{pmatrix} \begin{pmatrix} \cos \phi \\ \sin \phi \end{pmatrix}. \tag{S6}$$

The intensity of the emitted SH wave is proportional to the quadruplicate magnitude of the electric field of FW $I^{2\omega}(\alpha) \propto A_0^4 \cos^4(\phi - \alpha)$, and the phase of the nonlinear polarization can be expressed as $\varphi_x^{2\omega}(\alpha) = \pi u(\alpha - 0.5\pi) - \pi u(\alpha - 1.5\pi)$ and $\varphi_y^{2\omega}(\alpha) = \pi u(\alpha - \pi)$, where u is a step function. In our case, for $\phi = \frac{1}{2}\pi$, the vector orientation, intensity, and phase of the SH wave are provided in Fig. S19.

Supplementary Section 5: Similarity between light passing through a polarizer and a “nonlinear polar polarizer”

When a linearly-polarized light at an angle ϕ is incident and passes through a polarizer with its transmission axis at θ , the output electric field in the linear optical regime is expressed as:

$$\begin{aligned}
\mathbf{E} &= \begin{pmatrix} E_x \\ E_y \end{pmatrix} = A_0 \begin{pmatrix} \cos^2 \theta & \cos \theta \sin \theta \\ \cos \theta \sin \theta & \sin^2 \theta \end{pmatrix} \begin{pmatrix} \cos \phi \\ \sin \phi \end{pmatrix}, \\
&= A_0 \cos(\phi - \theta) \hat{\mathbf{e}}_\theta
\end{aligned} \tag{S7}$$

where $\hat{\mathbf{e}}_\theta$ represents the unit vector of θ -axis, $\begin{pmatrix} \cos \theta \\ \sin \theta \end{pmatrix}$. The intensity of the output beam is $I = A_0^2 \cos^2(\phi - \theta)$, known as Malus's law. This teaches us that a linear polarizer primarily performs polarization selection (filtering specific polarization states) without active phase modulation, i.e., when the polarizer orientation is set at $\theta = \theta_1$ versus $\theta = \theta_1 + \pi$, the output light exhibits the same polarization direction and identical phase characteristic.

Systems with inversion symmetry breaking exhibit a non-zero second-order nonlinear coefficient, leading to additional even-order nonlinear optical responses like SHG. When an input polarized FW excites a nonlinear medium belonging to the point group $C_{\infty V}$ (e.g., polar LCs composed of orientated dipoles), an SH nonlinear polarization arises as (Supplementary Section 4):

$$\begin{aligned}
\mathbf{P}_\alpha^{2\omega} &= 2A_0^2\varepsilon_0 d_{33} \cos(\phi - \alpha) \begin{pmatrix} \cos^2 \alpha & \cos \alpha \sin \alpha \\ \cos \alpha \sin \alpha & \sin^2 \alpha \end{pmatrix} \begin{pmatrix} \cos \phi \\ \sin \phi \end{pmatrix} \\
&= 2A_0^2\varepsilon_0 d_{33} \cos^2(\phi - \alpha) \hat{\mathbf{e}}_\alpha
\end{aligned} \tag{S8}$$

A_0 is the amplitude of FW, ω the angular frequency, ϕ the polarization angle relative to the x -axis, ε_0 the vacuum permittivity, α the azimuthal angle of the dipole, and $\hat{\mathbf{e}}_\alpha$ the unit vector along the

α direction, $\begin{pmatrix} \cos\alpha \\ \sin\alpha \end{pmatrix}$. The intensity is proportional to the quartic amplitude of the electric field of FW, $I^{2\omega}(\alpha) \propto A_0^4 \cos^4(\phi - \alpha)$, corresponding to an extended nonlinear version of Malus's law.

Fig. S4.

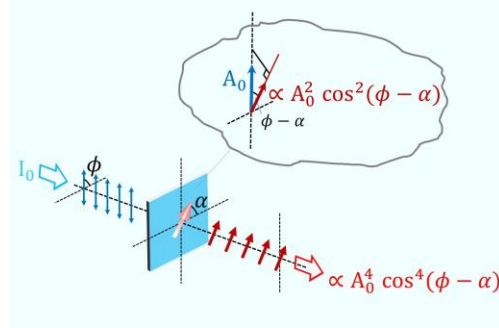


Fig. S4. An extended nonlinear version of Malus's law

Compared with Eq. (S7) that describes linear polarizers filtering specific polarization states without changing the phase, Eq. (S8) describes a new scenario where, for the polar LCs oriented at $\alpha = \alpha_1$ versus $\alpha = \alpha_1 + \pi$, the output SH wave exhibits identical polarization (due to its head-to-tail equivalence), but the electric field vector has an opposite instantaneous direction caused by the π -phase shift (Fig. S5). This means the oriented polar LCs act as a nonlinear polar polarizer with dual capabilities—generating SH wave with its instantaneous nonlinear polarization vector following α within the full angular range $[0, 2\pi]$, enabling on-demand control over both the polarization state and phase of the output SH wave. This immediately generates interest in pixelating polar LCs with spatially varying orientations to develop unprecedented nonlinear vectorial optical devices. However, as a long-standing unsolved problem, the traditional solid-state polar systems barely own the flexibility to realize pixelated dipole orientations. The polar nematics, such as the Nx state, obviously break this limitation, and their designability of polar fields offers us a revolutionary platform.

Fig. S5.

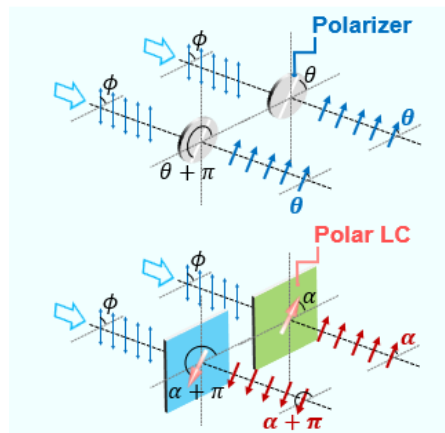


Fig. S5. Comparison of light passing through a polarizer and a “nonlinear polar polarizer”.

Supplementary Section 6: Simulations of linear and nonlinear perfect vector beams

The most charming characteristics of perfect vector beams (PVBs) are their (1) customized distributions of vectors, i.e., linear polarization, on the ring-shaped intensity profile; (2) invariant radii and intensity profiles under changing polarization topological charges [*Opt. Lett.* 40, 597 (2015)] [*Nat. Commun.* 14, 3915 (2023)] [*Phys. Rev. Appl.* 10, 034061 (2018)] [*Photonics Res.* 12, 1036 (2024)] [*Chin. Phys. Lett.* 39, 034201 (2022)] [*J. Phys. Photonics* 5, 032501 (2023)] [*Appl. Phys. Lett.* 119, 011104 (2021)] [*Opt. Lett.* 43, 5981 (2018)]. The optical axis distribution of LCs α is as follows:

$$\alpha = \frac{1}{2}l\varphi + \frac{1}{2}\arg\left[2\sum_{n=1}^{\infty}a_n\sin\left(2\pi\frac{n}{T}r\right)\right]. \quad (\text{S9})$$

where φ and r denote the azimuthal angle and the radial distance in the polar coordinate, a_n represents the Fourier series coefficients, T represents the period of the superstructure in the radial direction, l is the polarization topological charge and $T = 100 \mu\text{m}$ in our experiment.

The generation of linear PVBs can be simulated by employing the Jones matrix calculation [*Fundamentals of liquid crystal devices.* (John Wiley & Sons, 2014)] [*Optics of Liquid Crystal Displays.* (John Wiley & Sons, 1999)] to analyze the diffraction resulting from the light-matter interaction. Considering a half-wave plate with α as its optical axis distribution, the Jones matrix is:

$$\mathbf{J} = \begin{bmatrix} \cos 2\alpha & \sin 2\alpha \\ \sin 2\alpha & -\cos 2\alpha \end{bmatrix}. \quad (\text{S10})$$

For a linear polarization $\mathbf{E}_{\text{in}} = A_0(\cos\phi\hat{\mathbf{e}}_x + \sin\phi\hat{\mathbf{e}}_y)$ incidence, the output light field in the linear optical framework from the device is

$$\mathbf{E}_{\text{out}} = \mathbf{J} \cdot \mathbf{E}_{\text{in}} \quad (\text{S11})$$

Then, the far-field light field can be calculated by $\mathbf{E}_{\text{PVB}} = \mathcal{F}[\mathbf{E}_{\text{out}}]$. The vector distribution of the light field can be characterized by an analyzer:

$$\mathbf{E}_A = \begin{bmatrix} \cos^2\phi_A & \sin\phi_A\cos\phi_A \\ \cos\phi_A\sin\phi_A & \sin^2\phi_A \end{bmatrix} \mathbf{E}_{\text{PVB}}. \quad (\text{S12})$$

where ϕ_A is the angle of the analyzer. Consequently, the linear PVB and its analyzed intensity profiles are calculated in Fig. S23.

One thing should be noted before simulating the nonlinear PVBs: the inherent polar nematic ordering for the topological LC superstructure still cannot be completely determined. According to our SHG-I analysis (Fig. S22), the relative orientations of regional dipoles are deduced from constructive or destructive interference observations. In contrast, the exact dipole orientations (e.g., 0 or π) or relative dipole orientations among different rings are still unknown due to the limited interference area in our experiment. So, two possible structural models (Model 1 and Model 2) are provided in Fig. S24. The difference is the dipole orientations in even concentric rings opposite between Model 1 and Model 2.

Then, we simulate the generated nonlinear PVBs based on the polar ordering in Model 1 and Model 2. The (near-field) nonlinear polarization excited from the topological polar LC superstructure is theoretically calculated according to Eq. (3) in the main text. Numerical simulations of the beam profile of far-field PVBs are performed by calculating the coherent superposition of the local

vectorial light fields in the near field after Fourier transformation. The results are shown in Fig. S24. Obviously, the simulated light fields based on the structural Model 1 agree well with the nonlinear PVB obtained in our experiment and its analyzed intensity profile, while the simulated results from Model 2 deviate from our experimental results (Fig. 5e and Fig. S24). These results suggest that we can design the orientation distribution α of polar LCs based on Eq. (3) and (4) in the manuscript, with comprehensive consideration of the near-field polarization, phase, and intensity distributions, and it can be used to customize vector distribution on the perfect cylindrical beam with invariant radii and intensity profiles. The relationship between the far-field vector orientation and the dipole orientations in even and odd concentric rings in any azimuth direction φ is provided in Fig. S27.

Supplementary Section 7: Electric switching of the miniaturized nonlinear optical LC device

By harnessing the dynamic tunability of liquid-matter ferroelectric medium, we achieve tunable SH PVBs. A triangular electric field ($V_{pp} = 0.12 \text{ V}/\mu\text{m}$ and $f = 0.5 \text{ Hz}$) is applied across the cell. Then, the topological polar LC superstructure undergoes a reversible switch between the initial state and a new formation characterized by emerging stripes against a green background (Fig. 5h,i). This phenomenon is attributed to the field-induced out-of-plane reorientation of dipoles in polar nematic regions; while the apolar nematic regions are unaffected due to the insufficient driving voltage (Fig. 5a, inset), which corroborates our proposed polar ordering of the Nx phase. Consequently, low-field driven, periodic tuning of SH PVB is enabled as shown in Fig. 5j. Besides the above-mentioned SH PVBs, our defect-free tailoring of the dipoles in the Nx phase enables more possibilities in manipulating the nonlinear light fields (Supplementary Section 4 and 6), providing a promising platform for advanced reconfigurable vectorial photonics.

Supplementary Figures

Fig. S6.

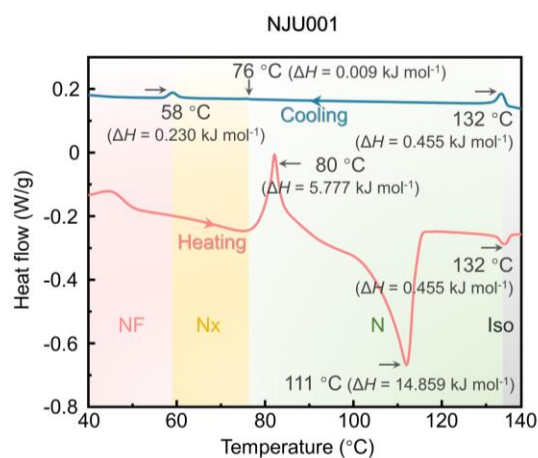


Fig. S6. Differential scanning calorimetry (DSC) traces of the NJU001 material. The heating (red line) and the cooling (blue line) rates are $5 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. This result is obtained by using the differential scanning calorimeter (Mettler-Toledo DSC1, STARe). According to the cooling process, the phase sequence of the NJU001 material follows isotropic (Iso) phase - 132 °C - nematic (N) phase - 76 °C - Nx phase - 58 °C - ferroelectric nematic (NF) phase. Source data are provided as a Source Data file.

Fig. S7.

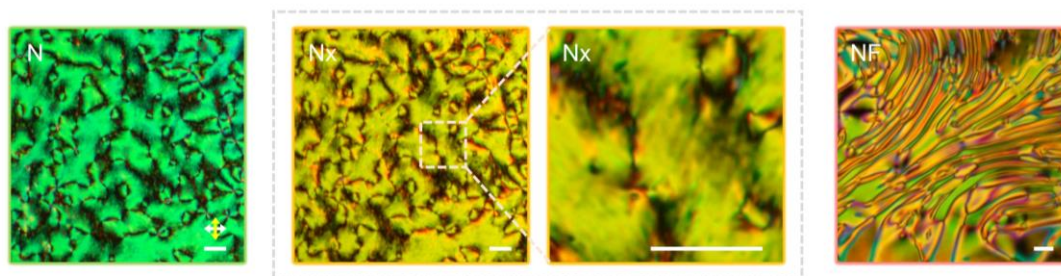


Fig. S7. PLM textures of the randomly aligned NJU001 material in N, Nx, and NF phases. The white and yellow arrows denote crossed polarizers. Scale bar: 25 μm . Source data are provided as a Source Data file.

Fig. S8.

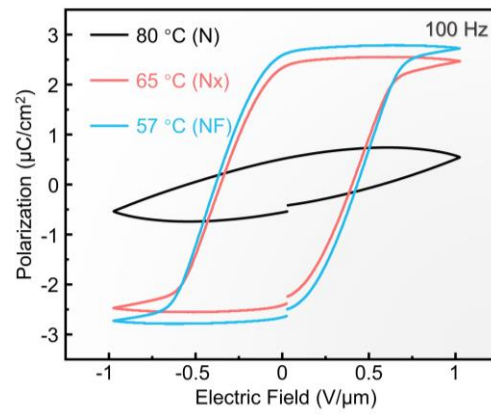


Fig. S8. P-E hysteresis loops of the NJU001 material upon a triangle-wave field application at different temperatures. The applied voltage is 10 V, and the frequency is 100 Hz. Source data are provided as a Source Data file.

Fig. S9.

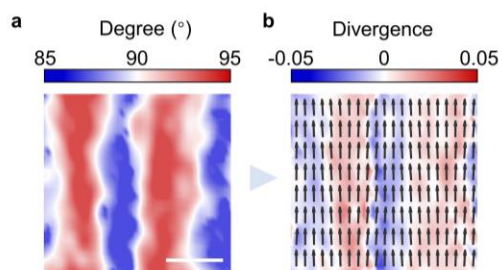


Fig. S9. Characterization of the spatial distribution of LC directors by PolScope. **a**, Colored map of the splay director distribution. **b**, Calculated divergence of the director distribution. Scalar bar: 2 μm . Source data are provided as a Source Data file.

Fig. S10.

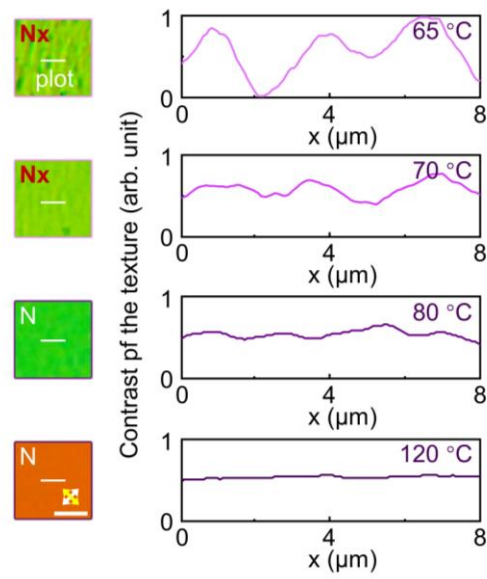


Fig. S10. Contrast of the PLM textures in different phases. The white and yellow arrows denote crossed polarizers. The blue bar represents the alignment direction. The white lines indicate the regions where the contrast profiles are extracted. Scale bar: 10 μm . Source data are provided as a Source Data file.

Fig. S11.

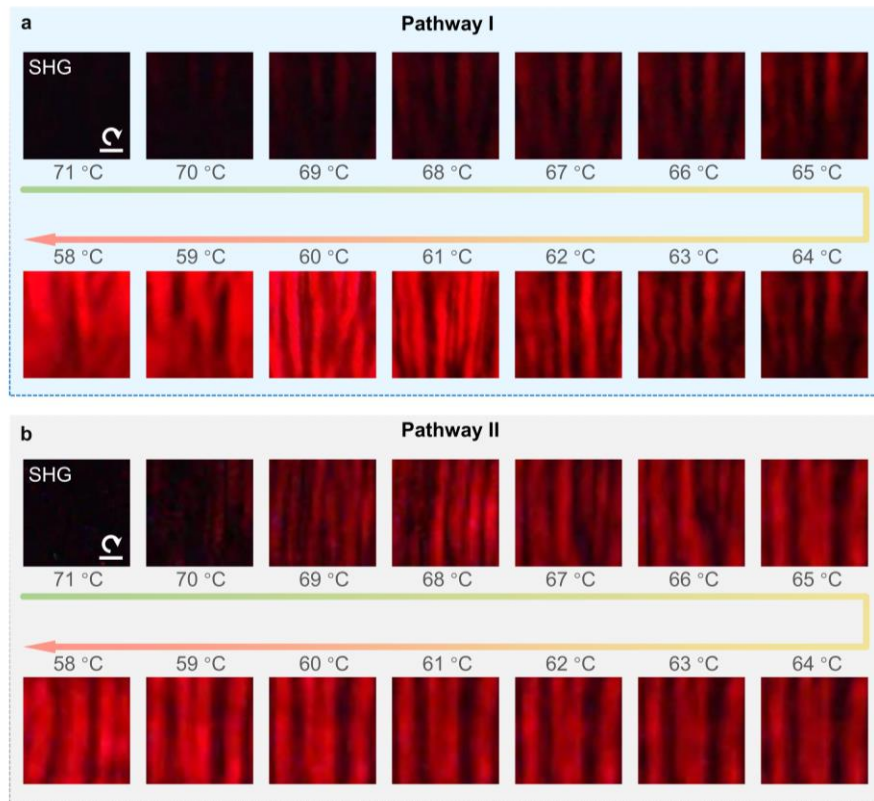


Fig. S11. Spatially-modulated SH signals excited from Nx stripes with circular polarization in Pathway I (a) and Pathway II (b). Scale bar: 5 μm . Source data are provided as a Source Data file.

Fig. S12.

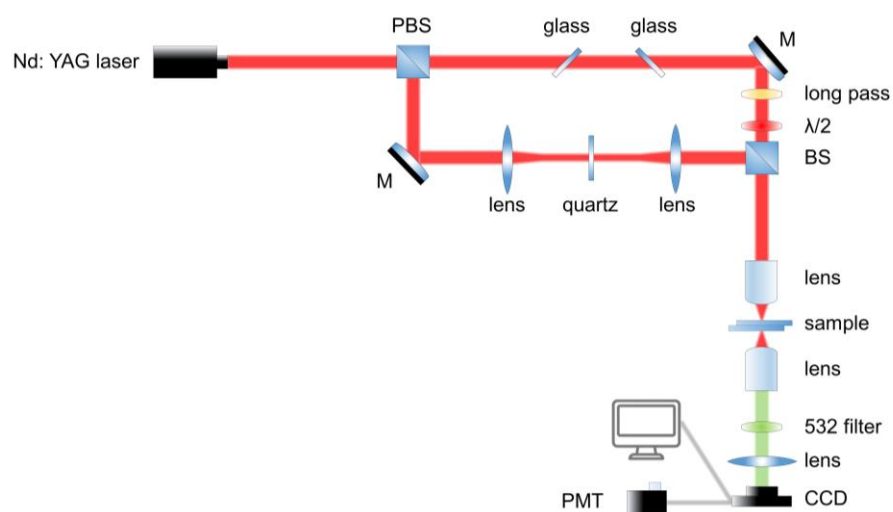


Fig. S12. Schematic of the SHG-I measuring system. M: mirror; PBS: polarization beam splitter; BS: beam splitter; CCD: charge-coupled device; PMT: photomultiplier tube.

Fig. S13.

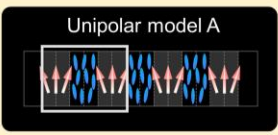
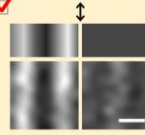
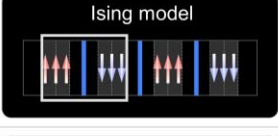
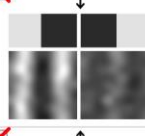
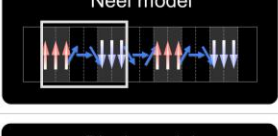
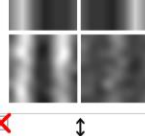
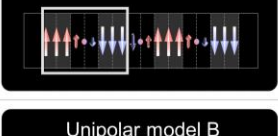
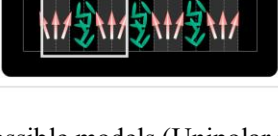
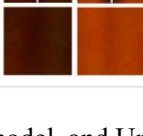
	Model for Pathway I	SHG	SHG-I	FCPM	PLM
1					
2					
3					
4					
5					

Fig. S13. Possible models (Unipolar model A, Ising model, Néel model, Bloch model, and Unipolar model B) for the polar ordering of the Nx phase in Pathway I. We employ SHG, SHG-I, FCPM, and PLM to characterize the polar ordering in the Nx phase in Pathway I. Both the schematics and experimental results are provided in the corresponding cell. The black and red arrows denote crossed polarizers. The experimental results correspond to the schematics of the ordering in white boxes in the second column. Scale bar: 2 μm . Source data are provided as a Source Data file.

Fig. S14.

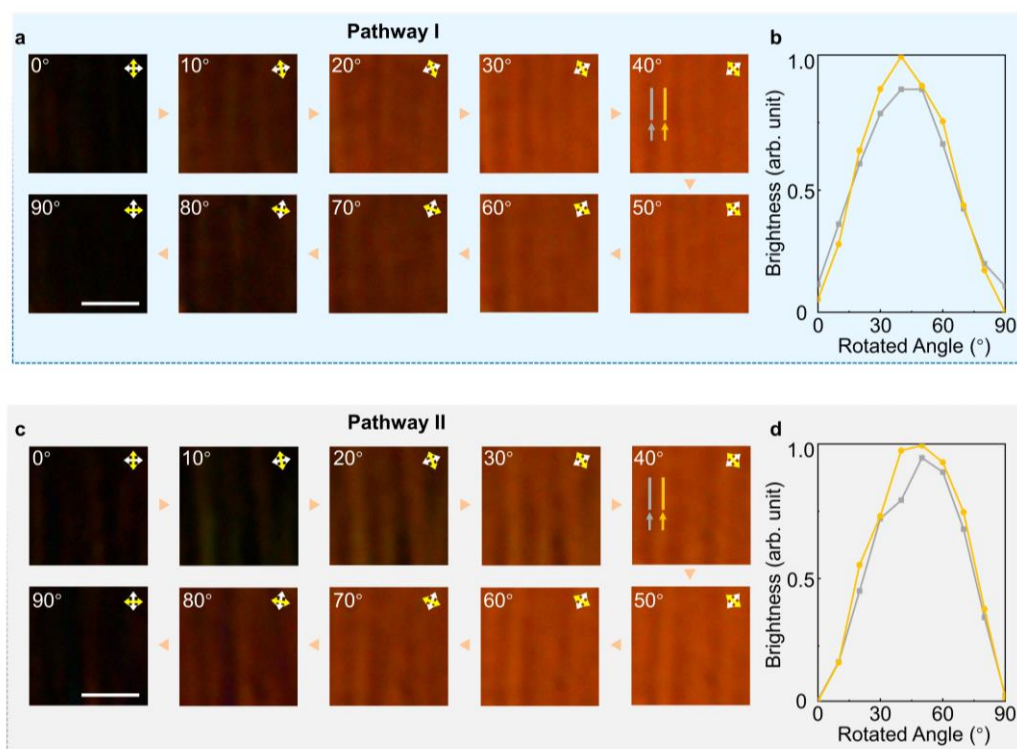


Fig. S14. PLM images of the sample in the Nx phase rotated under crossed polarizers and the brightness analysis. **a,c**, PLM textures under different rotation angles in Pathway I and Pathway II. The temperature is at 65 °C. The white and yellow arrows denote crossed polarizers. Scale bar: 5 μm . **b,d**, Brightness profiles extracted from one of the Nx stripes (yellow) and the transition region (grey) between two stripes. Source data are provided as a Source Data file.

Fig. S15.

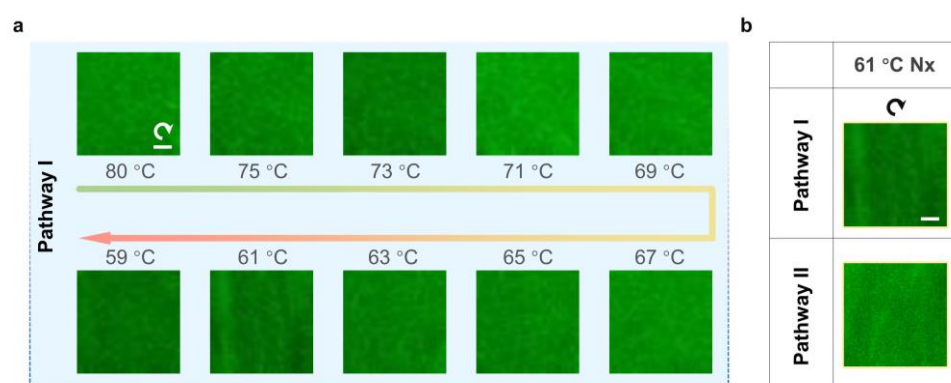


Fig. S15. FCPM images taken under circularly polarized light at different temperatures. Scale bar: 5 μm . Source data are provided as a Source Data file.

Fig. S16.

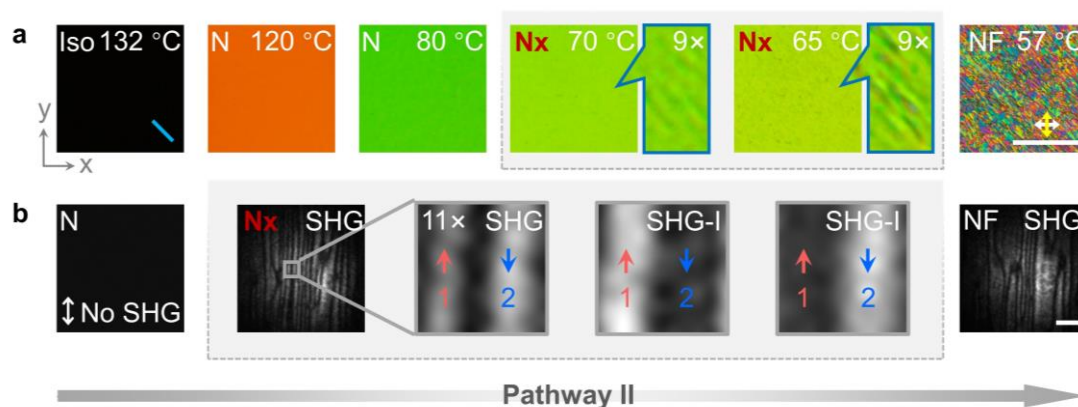


Fig. S16. Polar and orientational ordering of the Nx phase in Pathway II. **a**, PLM texture evolution as the temperature decreases. The white and yellow arrows denote crossed polarizers. The blue bar represents the alignment direction. Scale bar: 100 μm. **c**, SHG and SHG-I analysis of the polar ordering of the NJU001 material for Pathway II. The SHG images in the N and NF phases are at 80 °C and 57 °C, respectively; the rest of the SHG and SHG-I images are at 65 °C. The double-headed white arrows indicate the incident polarization. The red and blue arrows denote the polarization vectors in these regions. The Scale bar: 25 μm. Source data are provided as a Source Data file.

Fig. S17.

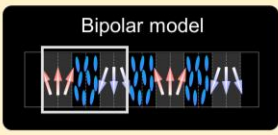
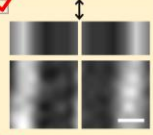
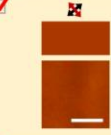
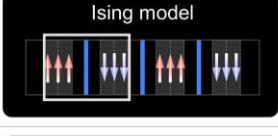
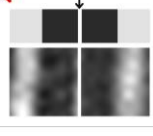
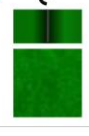
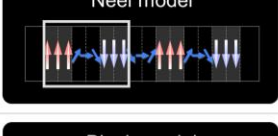
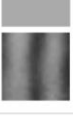
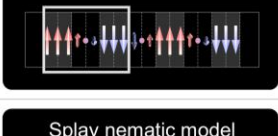
	Model for Pathway II	SHG	SHG-I	FCPM	PLM
1					
2					
3					
4					
5					

Fig. S17. Possible models (Bipolar model, Ising model, Néel model, Bloch model, and Splay nematic model) for the polar ordering of the Nx phase in Pathway II. We employ SHG, SHG-I, FCPM, and PLM to characterize the polar ordering in the Nx phase in Pathway II. Both the schematics and experimental results are provided in the corresponding cell. The black and red arrows denote crossed polarizers. The experimental results correspond to the schematics of the ordering in white boxes in the second column. Scale bar: 2 μm . Source data are provided as a Source Data file.

Fig. S18.

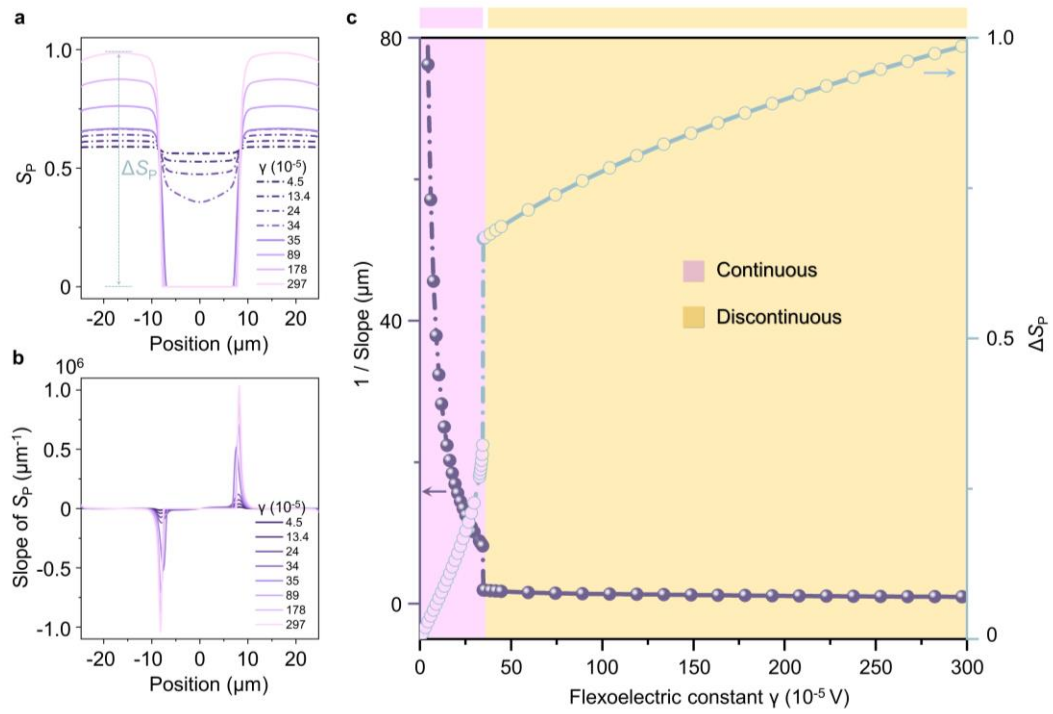


Fig. S18. Flexoelectric interaction merely competes against the polar Landau energy when S and S_P are decoupled. **a**, Polar orientational order parameters as a function of the coordinate with varied γ . $\Delta S_P = S_{P_{\text{max}}} - S_{P_{\text{min}}}$. **b**, Slope of S_P as a function of the coordinate corresponding to (a). **c**, Relationships between the 1/slope and the flexoelectric constant, and ΔS_P and the flexoelectric constant. Quasi-continuity and discontinuity of the variation of polar orientational order parameters can be found. The maximum slope values of the lines in (b) with specific γ s are plotted in (c). Source data are provided as a Source Data file.

Fig. S19.

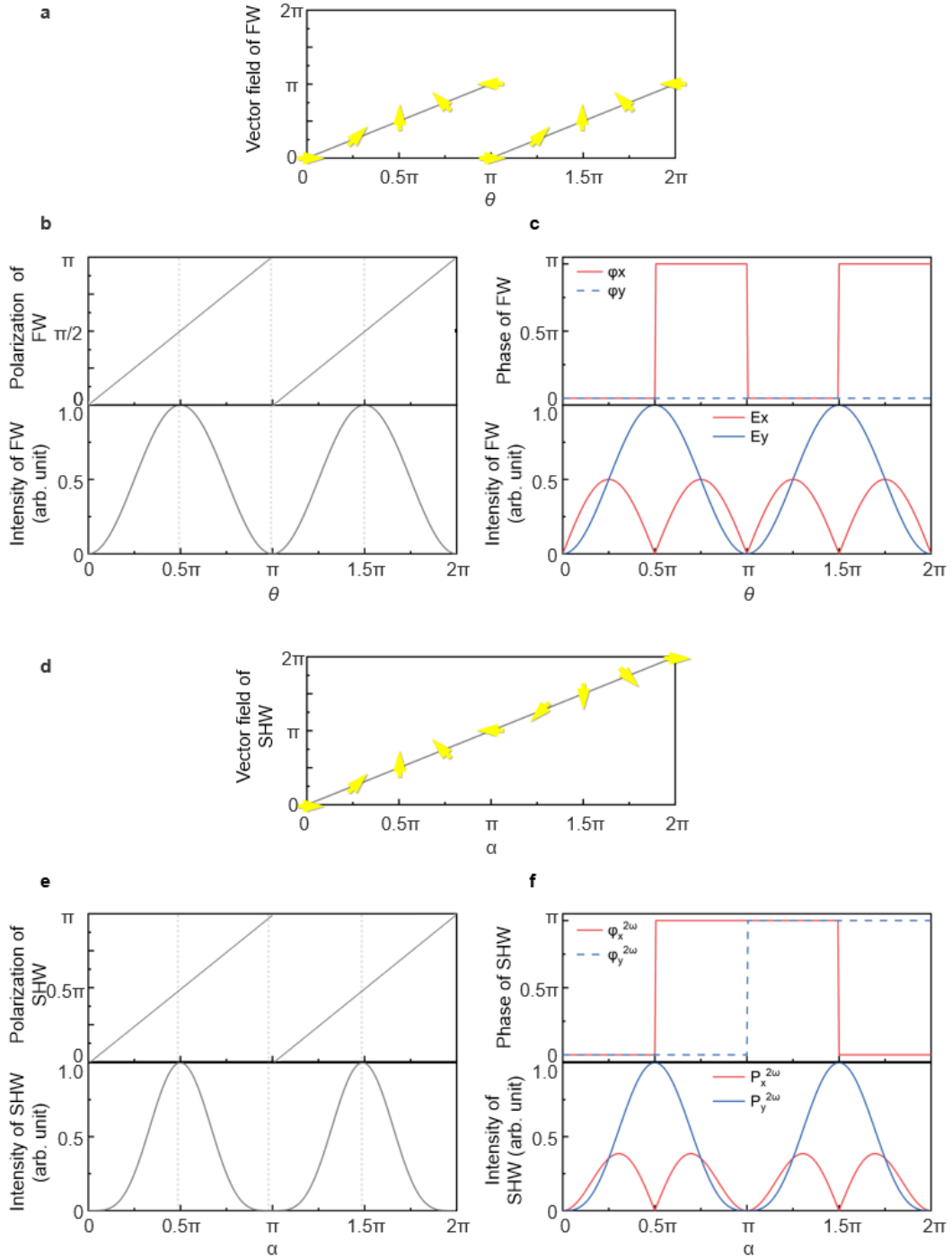


Fig. S19. Light field after passing through a linear polarizer and nonlinear polarization excited from an LC dipole, upon a linearly polarized FW excitation ($\phi = 90^\circ$) **a**, Instantaneous electric field vector (yellow arrows) of the FW depending on the orientation θ of the polarizer. **b**, Dependencies of polarization angle and intensity of the FW on the orientation θ of the polarizer. The polarization is head-tail equivalent. **c**, Dependencies of the phases and intensities of the FW components (E_x and E_y) on the orientation θ of the polarizer. **d**, Dependencies of the instantaneous electric field vector

of the SH wave ($\mathbf{P}_\alpha^{2\omega}$) on the orientation α of the dipole. The yellow arrows represent the vector orientation of SH wave. **b**, Dependencies of the phases and intensities of the SH wave components ($\mathbf{P}_x^{2\omega}$ and $\mathbf{P}_y^{2\omega}$) on the orientation α of the dipole. Source data are provided as a Source Data file.

Fig. S20.

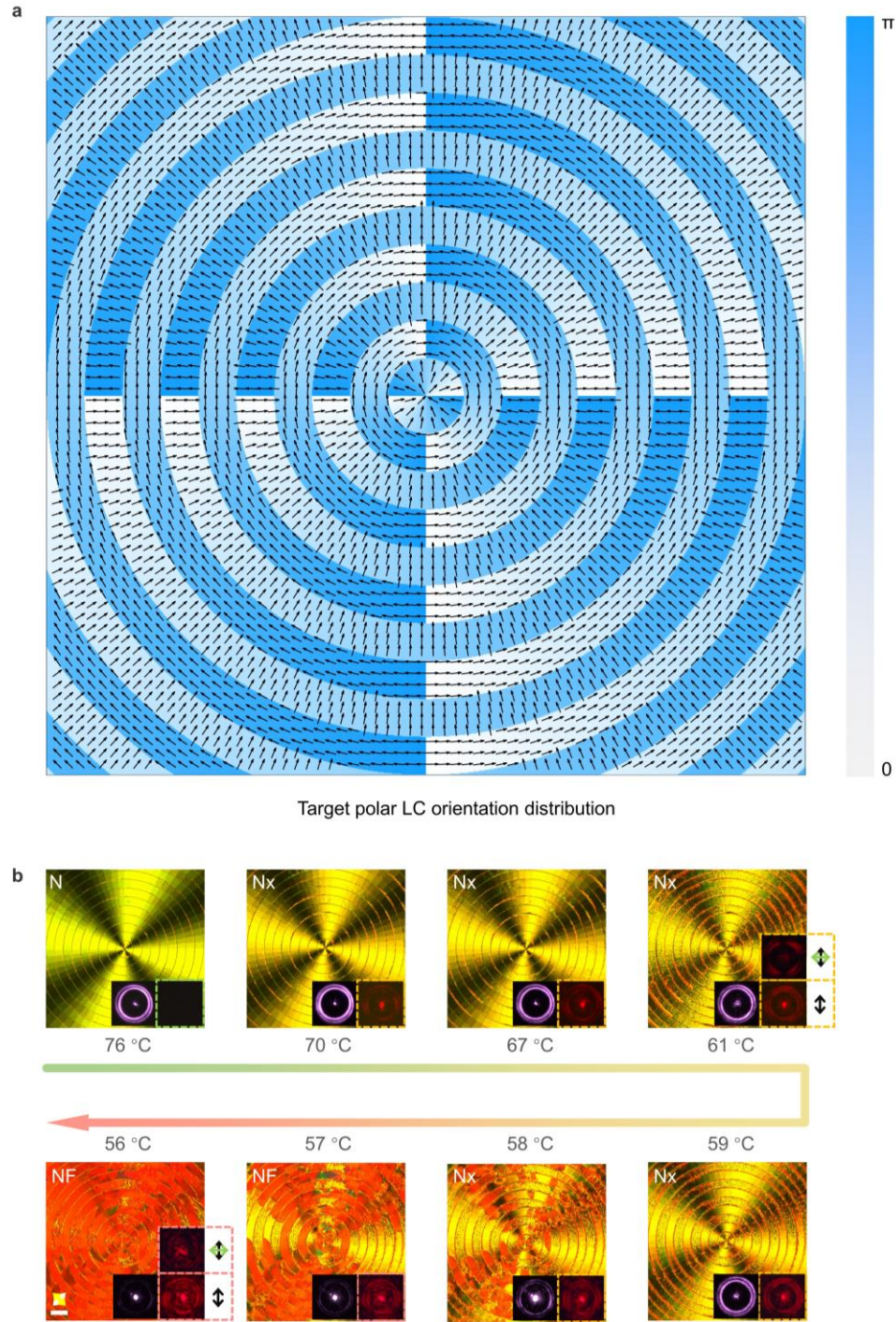


Fig. S20. a, Target orientation distribution α of polar LCs. **b**, Evolutions of PLM textures and corresponding nonlinear light fields generated by the topological polar superstructure. The white and yellow arrows indicate the crossed polarizers. The SH PVB is generated once the sample enters the Nx phase. Notably, the vectorial light field largely degrades when the sample transitions to the NF phase, which can be seen from the analyzed intensity profile at 56 °C. The black and green double-headed arrows indicate the incident polarization of FW and the direction of the analyzer, respectively. Scale bar: 100 μm . Source data are provided as a Source Data file.

Fig. S21.

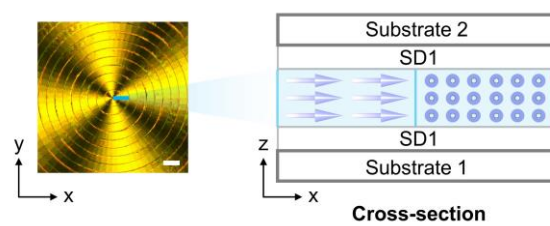


Fig. S21. A schematic of a cross-sections of the LC cell. Scale bar: 100 μm . Source data are provided as a Source Data file.

Fig. S22.

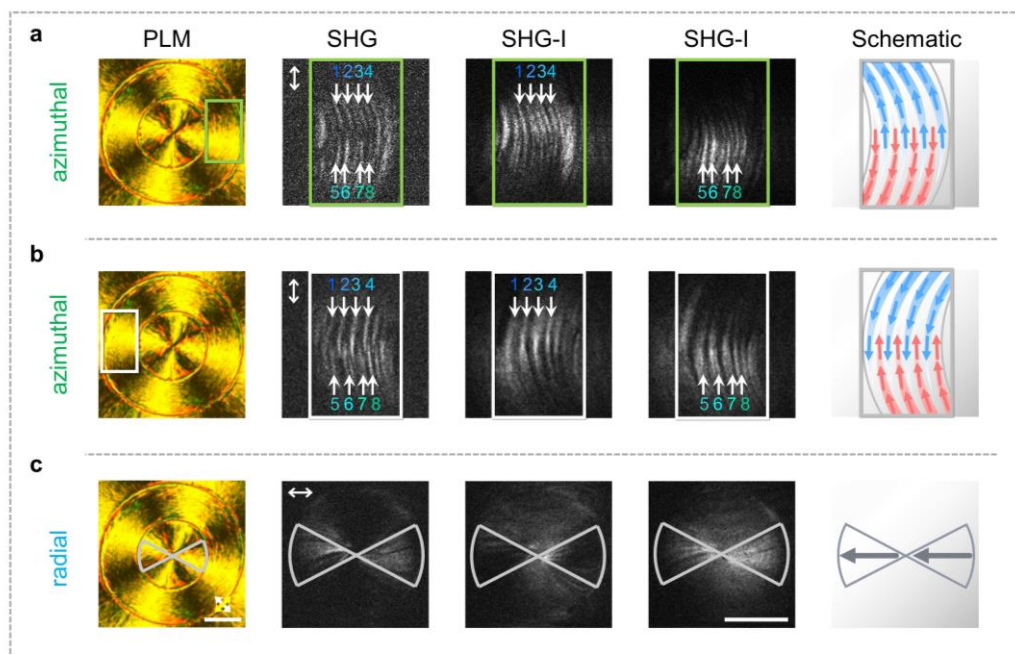


Fig. S22. Polar ordering characterization of topological LC superstructure in the Nx phase by PLM, SHG, SHG-I imaging. Different geometric figures are used to indicate the regions for imaging, which include the radial and azimuthal alignments. Representative Nx stripes are numbered and indicated by single-headed white arrows. Their polarization vectors are characterized and represented by red and blue arrows in the schematics in the last column. The double-headed white arrows indicate the incident linear polarization. White and yellow arrows denote the crossed polarizers. Scale bar: 50 μm . Here, the relative orientations of regional dipoles are deduced from the constructive or destructive interference observations, while the exact dipole orientations (e.g., 0 or π) or relative dipole orientations among different rings are still unknown due to the limited interference area in our experiment. According to the above analysis, there are two possible polar configurations provided in Fig. S24. Source data are provided as a Source Data file.

Fig. S23.

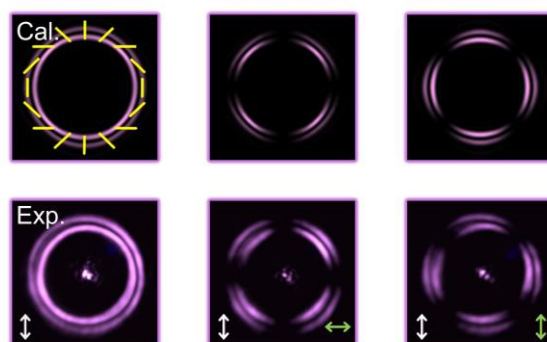


Fig. S23. Simulated and experimental results of the generated linear PVB. The white and green double-headed arrows indicate the incident polarization of FW and the direction of analyzer, respectively. The yellow bars represent the vector field of the linear PVB. Source data are provided as a Source Data file.

Fig. S24.

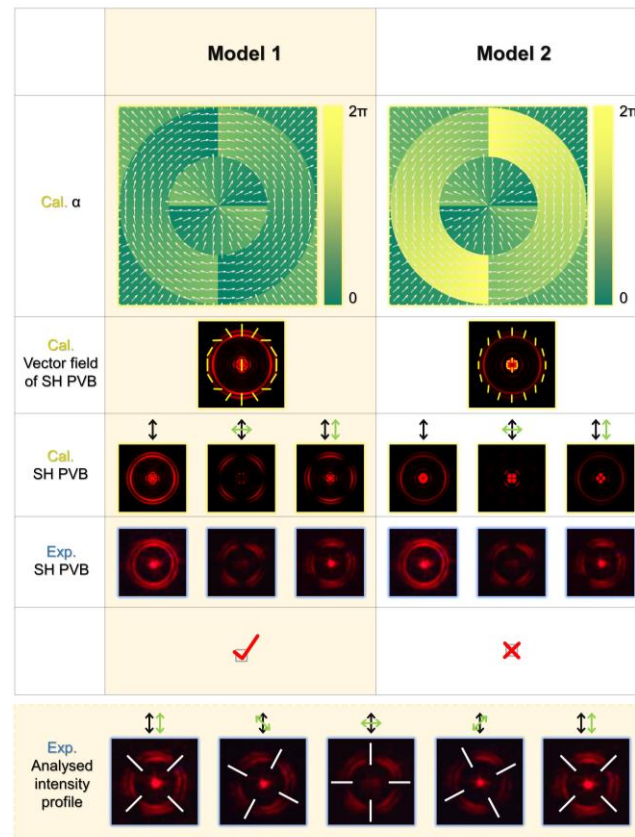


Fig. S24. Simulation of PVBs and their analyzed intensity profiles based on the structural Model 1 and 2. The black and green double-headed arrows indicate the incident polarization of FW and the direction of analyzer, respectively. The yellow bars represent the vector field of SH wave. Source data are provided as a Source Data file.

Fig. S25.

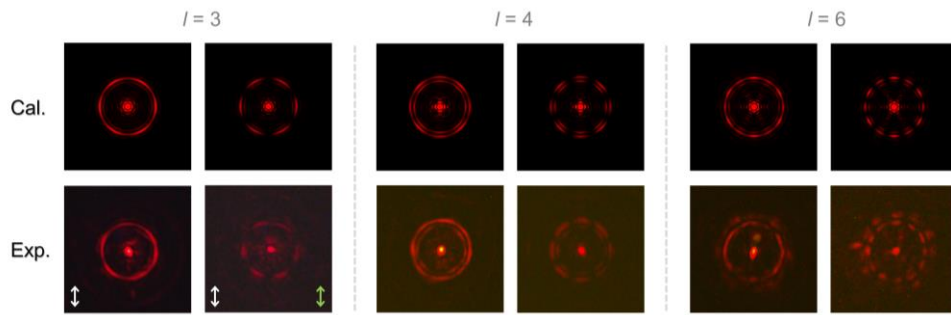


Fig. S25. Simulated and experimental results of the high-order PVBs with the polarization topological charge $l = 3, 4$, and 6 . The white and green double-headed arrows indicate the incident polarization of FW and the direction of the analyzer, respectively. Source data are provided as a Source Data file.

Fig. S26.

Figs in Manuscript	Anchoring Condition	Alignment pattern
Fig. 2b	Photopatterning	homogeneous alignment
Fig. 3a-c	Photopatterning	
Fig. 3d-f	Photopatterning	
Fig. 3h	Photopatterning	
Fig. 3i	Photopatterning	
Fig. 4b	Photopatterning	

Fig. S26. Summarized alignment patterns. In the third row: the school badge pattern of Nanjing University is reproduced with permission of Nanjing University. In the fourth and fifth rows: reproductions of “Girl with a Pearl Earring” by Johannes Vermeer (c. 1665) formed by converting it to grayscale images. The original artwork is in the public domain [Vermeer, J. Girl with a Pearl Earring. *c. 1665* <https://www.mauritshuis.nl/en/explore/the-collection/artworks/girl-with-a-pearl-earring-670/>]. The grayscale values from 0 to 255 are proportionally mapped to the distribution of α . Source data are provided as a Source Data file.

Fig. S27.

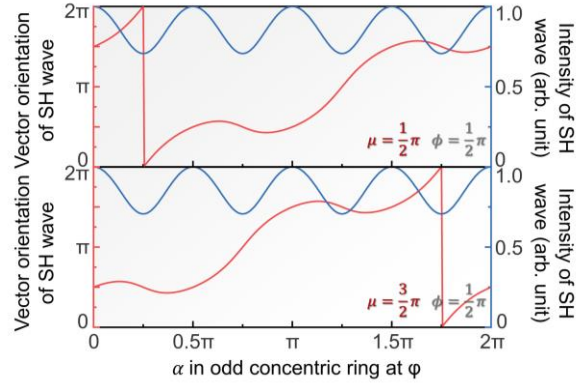


Fig. S27. Designing principle. We provide the relationships between the properties of far-field SH wave and the dipole orientation in the odd concentric rings in the radial direction of φ for $\phi = \frac{\pi}{2}$.

The dipoles in adjacent rings are orthogonally aligned to facilitate the manipulation of both linear and nonlinear PVBs. We set $\mu = \theta_{\text{even}} - \theta_{\text{odd}}$, $\theta \in (0, 2\pi)$ as the included angle between the dipoles in even and odd concentric rings, which has two choices, i.e., $\mu = \frac{1}{2}\pi$ (upper panel) and

$\mu = \frac{3}{2}\pi$ (lower panel), to determine all the dipoles in the radial direction of φ . Here, although the intensity of SH wave exhibits a periodic modulation as α changes, which stems from the polarization dependency of the nonlinear polarization generation, it always remains at a relatively high level (ranging from 0.71 to 1). The vector orientation of SH wave covers from 0 to 2π by engineering the orthogonally aligned dipoles in even and odd concentric rings. For a certain target vector orientation in a specific φ , there can be multiple choices of dipole orientation combinations. By leveraging the two cases with $\mu = \frac{1}{2}\pi$ and $\mu = \frac{3}{2}\pi$, the design of vector distribution of SH wave in the range of 0 to 2π can be achieved in a more flexible manner. Source data are provided as a Source Data file.