Nano-Clustering Stabilization of Ferroelectric Nematic Phases

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\textbf{Abstract}
During a half-decade, a new class of ferroic-fluid, ferroelectric nematic liquid crystals (N\textsubscript{F}LCs), creates a noise owing to its exceptional properties such as a colossal polarization, high electro-optic activity plus high fluidity. Regardless recent huge efforts on design and development of new N\textsubscript{F}LC molecules based on molecular parameters, the control of polymorphic N\textsubscript{F} phase transition and the stabilization of N\textsubscript{F} phase are in unexplored territory. Here we present a diastereomeric-controlled N\textsubscript{F} system employing DIO diastereomer [{\textit{trans}}DIO (1) and {\textit{cis}}DIO (2)], which is an indication of exchange of N\textsubscript{F}LC 1 by non-LC 2 both with similar dipole and molecular backbone. This new way successfully provides three types of polymorphic N\textsubscript{F} phase transition, thermodynamically stable N\textsubscript{F} phase and no sacrifice of polarization behavior in the 1/2 system. The unique characteristic is investigated by a combination of X-ray diffraction measurement, optical and polarization studies.
Introduction

Since a discovery of a true 3D-fluid ferroelectric nematic (N\textsubscript{f}) phase showing the field-induced polarization reversal via a domain wall motion in liquid crystals (LCs), great interest has been dedicated for both fundamental science and applications.[1–33] In the N\textsubscript{f} phase, the inversion symmetry of the paraelectric N phase is broken, forming the macroscopic domains with a uniform polarization (\(P\)) along director, \(n\) (Fig. 1a). The striking features of the N\textsubscript{f} LCs are gigantic polarization \([2,8,13,22]\), high nonlinear-optical activity \([2,9,24,32]\), high electro-optical activity \([8,12,13,15,17,20,22,29]\) as well as high fluidity \([2,8,27]\) that may engender a paradigm shift in materials science and revolutionize soft matter technologies. According to the simple model by Born, the electric-dipolar interaction (is proportional to square of dipole moment, \(\mu\)), which should be strong enough to withstand thermal fluctuation (\(k\textsubscript{B}T\)), is the most important to emerge the N\textsubscript{f} phase. [34,33] Indeed, such a unique N\textsubscript{f} phase was ascertained in the specific molecules as a 1,3-dioxane-tethered fluorinated molecule (DIO) \([2]\), a pear-shaped molecule (RM734) \([1,3]\), a fluorinated bearing a terminal cyano group molecule (UUQU-4-N) \([14]\) and another generic, \([13,21,24]\) whose \(\mu\) are very large (> 9 Debye). However, although the present systemized molecular parameters including \(\mu\) (another are the oblique dipole angle and the geometrical aspect ratio of molecular shape etc.) are confirmed for the N\textsubscript{f} emergence, there is no consideration of the effects on the phase sequence passing the N\textsubscript{f} phase. Archetypal phase behavior of the N\textsubscript{f} molecules are as follows: (1) DIO experiences three mesophases: the N–M–N\textsubscript{f} phase transition, where M is a phase possessing an antiferroelectric order;\([21,25]\) (2) RM734 exhibited the N–N\textsubscript{f} phase transition which corresponds with ferroelectric–ferroelastic phase transition as seen in inorganic solids;\([9]\) (3) the latest key is UUQU-4-N showing the direct N\textsubscript{f} phase transition from isotropic liquid (IL), i.e., IL–N\textsubscript{f} phase transition, which has been observed in some molecules.\([21,24]\) Additionally, the N\textsubscript{f} phase is thermodynamically unstable below room temperature, in most cases irrespective of a single molecule or LC blends. Under the circumstances, despite huge efforts on design and development of new N\textsubscript{f} LC molecules based on molecular parameters, the control of phase sequences involving the N\textsubscript{f} emergence and the successful way for stabilizing N\textsubscript{f} are still ambiguous.

In this work, we introduce a new concept based on the dipole equivalent for controlling emergence and stability of the N\textsubscript{f} phase. Thus, the exchange molecules with almost equivalent dipole moment and analogous structure, generating the macroscopic polarization. For our strategy, although two components including a N\textsubscript{f} molecule are treated, the counter molecule need not be of a liquid crystalline. This point is entirely different compared to conventional LC mixing approach.\([22,38,39]\) We herein adopt DIO diastereomer, \textit{trans}DIO (1) and \textit{cis}DIO (2), which are a ferroelectric nematogen
and a non-liquid crystalline, respectively (Fig. 1b), investigate effect of diastereomeric-controlling on nature of N\textsubscript{F} phase. Recently, the same binary trans-cis system was coincidently introduced by Zhou et al. and indeed, proving that this strategy works well. However, in this paper, we focus on the nanoscopic structure in the present binary system and discuss the emergence and stabilization of the N\textsubscript{F} phase in terms of cybotactic cluster formation.
Results and discussion

Control of the variant N_F phase transition in trans/cis-C3DIO system.

A stereoisomer with an equivalent topological structure with yet different geometric configuration is a.k.a. diastereomer. [40] C3DIO has also diastereomer because 1,3-dioxane moiety with alkyl chain in C3DIO can have two geometric configurations. Such a C3DIO diastereomer, \textit{trans} C3DIO (1) and \textit{cis} C3DIO (2), exhibit different physical properties (Fig. 1b). 1 is typical ferroelectric nematogen and exhibits the ferroelectric nematic (N_F) phase on cooling [2] whereas 2 is not a LC material despite similar large dipole moment to 1 (\(\mu_1 = 9.84\) D; \(\mu_2 = 9.85\) D. See also Supplementary Fig. 1) but a polar crystal (the single crystal X-ray crystallographic structures of 1 and 2 are Supplementary Fig. 2). If the diastereomeric ratio (\(dr\)) of 2 in 1/2 mixture is increased (i.e. exchanging 1 by 2), intuitively, the N_F phase is expected to be destabilized because the molecule (2) may collapse the strong dipole-dipole interaction between 1–1 molecule. Fig. 1c shows the polarizing optical microscope images via the variant phase sequence in the diastereomeric mixture (1/2). For \(dr\) (1/2 = 100/0), a uniform texture (in green-highlighted area) was changed to the inhomogeneous one (in blue-highlighted area), and finally to the stripe texture due to the 2\(\pi\) twist-wall [12] (in yellow-highlighted area) during cooling. These three phases are characterized as the N, M (antiferroelectric N or SmZA [21,25]) and N_F phase in the order of high to low of temperature. With increasing \(dr\), the intermediate M phase was vanished at \(dr = 70/30\). Thus, the mixture with \(dr\) (70/30) experienced the N–N_F phase transition as in the common generic N_F molecules including RM734.[1,3] Further increment of \(dr\) (> 60/40) eliminated the N and M phases, instead, the direct phase transition between an isotropic liquid and N_F phase was occurred. For instance, in case of \(dr = 60/40\), small droplets of the N_F phase emerged in the isotropic liquid and conglomerated each other, resulting the complete formation of N_F phase. This direct IL–N_F transition type is scarce case which has been observed in UUQU-4-N etc.[14,21,24] Thus, against expectation, the doping of 2 probably contributes the control of the phase transition related with the stability of the N_F phase. To explore the stabilization of the N_F phase by the diastereomeric control of DIO, the phase diagram of 1/2 system was constructed (Fig. 1d). At \(dr = 90/10\), the temperature range of the M phase was reduced, and instead the N_F phase regime was expanded. Furthermore, the N_F phase regime expanded to lower temperature range across room temperature. This trend was observed increasing doping level of 2 up to \(dr = 70/30\), yielding the maximum temperature range of the N_F phase. Interestingly, at \(dr = 70/30\), the N_F phase still stand at 0 °C and the wide regime was 80 K, which is approximately four times larger than that of pure DIO (1). More interestingly, we found that the mixture with \(dr = 70/30\) exhibited the enantiotropic N_F phase, which was thermodynamically stable, unlike the monotropic N_F phase in 1 (Fig. 1e). Similarly, at the regime with high doping level of 2 (\(dr = 70/30\))
≥ 40/60), the N_F phase persisted wide temperature range (~-50–20 K) across room temperature. The dielectric permittivity of the N_F and N phases were comparable to those of pure DIO; N_F and N phases showed dielectric permittivity of the order of 10^4 and 10, respectively (Fig. 1f, details discussed later). The complete DSC curves are shown in Supplementary Fig. 3 and the corresponding enthalpies were summarized in Supplementary Table 1.

**Structure analysis of the diastereomeric-controlled N_F phase.**

As mentioned above, the diastereomeric combination probably contributes the tuning the stability of the N_F phase. Here, we discuss how the doping level of 2 in 1 has effect on the structure of N_F phase mainly with the aid of X-ray diffraction (XRD) analysis. Fig. 2a displays a 2D wide-angle XRD pattern of the N_F phase (T−T_c = −10 °C) in 1 under the magnetic field (B ~ 0.5 T) (The complete data are shown in Supplementary Fig. 4). The unique diffraction patterns consist of: (i) a pair of skewed peaks (corresponds with the molecular length, ~ 2.2 nm) at a small-angle region on the equatorial direction (parallel to n); (ii) a series of weak overtone ones spanning the small- to wide-angle region on the equatorial direction; (iii) the halo peaks due to the intermolecular stacking on the meridional direction (normal to n). To analyzed the XRD profile in detail, the horizontal and vertical scan were carried out within the angle \( \varphi_1 = 80^\circ, \varphi_2 = 60^\circ \), generating the 1D XRD pattern. For the fitted skewed/halo peaks (Supplementary Fig. 5,6), the relative intensity \( (I_{rel}) \) and the full width at half maximum (FWHM) in \( q \)-space (i.e., \( q_{FWHM} \)) as a function of \( dr \) are shown in Fig. 2b and 2c. For the halo peak, the all \( q_{FWHM} \) was comparable while the intensity was slightly decreased with increasing doping level of 2. On the other hand, the \( q_{FWHM} \) of the skewed peaks slightly decreased as \( dr \) increases. Notably, the intensity of the skewed peak showed a significant dependence of \( dr \). It suggests that the doping of 2 may promote the growth of macroscopic polar region in the N_F phase. In addition, the peak separation on the equator direction was performed, providing the six peaks (Fig. 2c). The data of primary peak (p1) are displayed in Fig. 2c. As shown in Fig 2d,e, for the \( q_{FWHM} \) and intensity of the peaks (p2–p6), although both was on a downward trend at \( dr = 60/40 \), there was no remarkable difference on any \( dr \). Let us consider the unusual anisotropic diffraction pattern in the N_F phase of 1/2 system. For the diffraction on (i) (**vide supra**), the skewed peak is reflected on the normal cybotaxis, in which SmC-like stratification within clusters of mesogens, floating in the N phase. [35,36] The diffraction on (ii) is maybe due to the anomalously large correlation length in cybotactic clusters, which has been observed in the N phase in a rigid lath molecule. [37] Notably, Mandle et al. confirmed that a series of weak overtone observed in the N_F phase of RM734 was a consequence of polar nematic order with the aid of MD calculation. [18] By considering these important tips, in 1/2 system, the SmC-type cybotactic cluster may coexist
in the N\textsubscript{F} phase (Fig. 3a). In that case, the anomalous changes in intensity of diffractions may indicate growth of the size of cluster with polar order, depending on the doping level of 2.

To gain more information on the cluster in the N\textsubscript{F} phase in detail, we analyze 2D small-angle XRD pattern in the N\textsubscript{F} phase. Fig. 3a shows the schematic illustration connecting the structural parameters of a SmC-type cybotactic domain. The magnetic field aligns the clusters, in which the director \( \mathbf{n} \) is parallel to \( \mathbf{B} \). In the magnetic field, the normal to the smectic layer, \( \mathbf{k} \), is randomly distribute on \( \mathbf{B} \) at the tilt angle \( \beta \). Consequently, the XRD profile resulting from such distribution of microscopic SmC-type cluster is observed (Fig. 3b). According to reference.\textsuperscript{35,36}, we estimated the average size of the cybotactic clusters in the N\textsubscript{F} phase and its temperature and \( dr \) dependence. The average size of the clusters can be estimated from the longitudinal (\( \parallel \mathbf{B} \)) and transversal (\( \perp \mathbf{B} \)) intensity profiles of the skewed (four-spot) pattern (Fig 3b). Fig. 3c shows an example of diffraction intensity as a function of \( \Delta q_{\perp} = |q - q_{\perp}| \) of the 1/2 mixture with \( dr \) (70/30). The full width at half maximum of \( q_{\perp} \) correlates with the anisotropic short-range positional order of the cluster, which can be characterized by the correlation length \( \xi_{\perp} \), \( i.e., \xi_{\perp} = \alpha q/(\text{FWHM})_{\perp} \), where \( q_{\text{FWHM}} \) is full width at half maximum at the H-/V-scan profiles and \( \alpha = 2 \) (for Lorentzian fitting case) (Fig. 3b,c and Supplementary Fig. 7–14). Besides, the longitudinal and transversal dimension of the cluster, \( L_{\parallel} \) and \( L_{\perp} \) are given as \( L_{\parallel} = 3\xi_{\parallel} \) and \( L_{\perp} = 3\xi_{\perp} \). Fig. 3d shows the temperature evolution of the small-angle XRD pattern with various \( dr \). The four-spot pattern emerged below the critical point (\( T_{c} \)) for 1/2 mixtures with various \( dr \) (100/0–50/50), indicating the presence of the SmC-type cybotactic cluster over the entire range of the N\textsubscript{F} phase. With increasing doping level of 2, the contrast of the four-spot tends to be strong and its intensity drastically increased. From H-/V-scan profiles 1/2 mixtures with various \( dr \) (100/0–50/50), we estimated the corresponding \( L_{\parallel} \) and \( L_{\perp} \) as a function of temperature which are shown in Supplementary Fig. 15. For the 1/2 mixtures with high \( dr \), \( L_{\parallel} \) and \( L_{\perp} \) monotonically increase with similar slope toward low temperature whereas the value of \( L_{\parallel} \) elevated significantly compared to \( L_{\perp} \) in a series of 1/2 with low \( dr \) (> 65/35). The fact indicates that the growth anisotropy of the cluster (\( L_{\parallel}/L_{\perp} \)) should be different with respective to \( dr \) of 1/2 mixtures. Fig. 3e clearly evidences the striking difference of the grow process of the cluster. In case A, up to \( T - T_{c} \sim -30 \) °C, the cluster almost isotopically grew and then the cluster tended to grow transversally beyond the temperature. On contrary, in case B, a tendency of longitudinal growth of the cluster was observed over the entire range of the N\textsubscript{F} phase. It is noted that the case B occurred in the 1/2 mixture with \( dr \) (> 65/35), which experienced the direct IL–N\textsubscript{F} phase transition. A similar tendency was observed in UUQU-4-N exhibiting the direct IL–N\textsubscript{F} phase transition, in which SmA-like cybotactic cluster coexists in the N\textsubscript{F} phase (not shown here). Thus, the cybotactic cluster in a series of molecule showing the direct IL–N\textsubscript{F}
phase transition may grow inherently, irrespective cybotactic cluster types via the case B. Next, we investigated the internal molecular environment in the cluster. Fig. 4a shows schematic illustration of the SmC-like stratification within the cluster in the N\textsubscript{F} phase with the \( dr \) variation at fixed temperature (\( T-T_c = -10 \) °C). At \( dr = 100/0 \), the constituent molecules (1) arranged in a smectic layer with tilt angle \( \beta = 24.9^\circ \) are occupied in the cluster. With increasing doping of 2, substitution of 1 leads to generation of the scrambled dipoles of 1 and 2 with changing in the cluster anisotropy (see the middle panel in Fig.4a). Finally, the majority of cluster is colonized by the equimolar molecules. Although \( \beta \) increased nonlinearly by cooling, reflecting on the SmC feature at each \( dr \), at fixed temperature, the value of \( \beta \) was reduced slightly up to 19.5° with \( dr \) increases (Supplementary Fig. 16). With considering the volume of the cybotactic cluster (i.e. \( L_{\perp} \times L_{\perp} \times L_{\perp} \)), we estimated the average molecular numbers in the cluster of a series of 1/2 mixture. The average molecular numbers in the longitudinal dimension (\( N_l \)) or transversal one (\( N_{\perp} \)) are given as follows:

\[
N_l = L_{\parallel} / l = 3\xi_{\parallel} / l \\
N_{\perp} = L_{\perp} / w = 3\xi_{\perp} / w
\]

, where \( l \) and \( w \) are the molecular length (ca. 2.23 nm) of DIO and typical intermolecular distance (ca. 0.47 nm), respectively. Thus, the average molecular numbers (\( \bar{N} \)) in the cluster is expressed as \( N_l \times N_{\perp} \times N_{\parallel} \). For instance, in case of 1 at \( T-T_c = -10 \) °C, \( \bar{N} \) were calculated to be 1036, i.e., one thousand molecules are occupied in the cluster. The estimated \( \bar{N} \) for all 1/2 series as a function of temperature are summarized in Fig. 4b. At low \( dr \) regime (<70/30), the \( \bar{N} \) increased monotonically and reached to be approximately two thousand. By contrast, the 1/2 series with high \( dr \) regime (\( \geq 70/30 \)) showed tendency of the nonlinear increment of \( \bar{N} \), reaching to ca. 2,000–4,000. The relationship at \( T-T_c = -10 \) °C is highlighted in Fig. 4c. The value of \( \bar{N} \) increased at the threshold of \( dr \) (85/15), being 1.5–2 times at maximum \( dr \). Interestingly, the \( dr \) dependence of enthalpy related with phase transition via the N\textsubscript{F} phase showed quite similar relationship between \( \bar{N} \) and \( dr \) (Fig. 4d). It suggests that the anomalous latent heat have a strong association with the formation of the cybotactic cluster and its size. Besides, we found out that at threshold of \( dr \) (70/30), two regimes (IL–N–M–N\textsubscript{F} or IL–(N)–N\textsubscript{F}) were classified. The threshold of \( dr \) was good agreement with \( dr \) classifying cases, the trend of cluster growth as shown in Fig. 3e.

**Polarization behavior of the diastereomeric-controlled N\textsubscript{F} phase.**

As early prediction, the replacement of N\textsubscript{F} molecule (1) with non-LC molecule (2) probably causes destruction of the strong dipole-dipole interaction between 1–1 molecule so that the N\textsubscript{F} phase should be destabilized. Contrary to expectation, by diastereomeric control using 2, we succeeded in realizing
the N\textsubscript{F} state operating over an extended temperature range from 80 °C to 0 °C and control the various phase transition sequence, as mentioned above. If the diastereomeric-controlled N\textsubscript{F} phase is truly stabilized state, the corresponding polarization properties also should be equal to or greater than original ones. Therefore, we investigated the polarization behavior of the N\textsubscript{F} phase 1/2 system by dielectric relaxation, P-E hysteresis as well as SHG studies. The comparable temperature was fix to be −10 °C of T−T\textsubscript{c}. Fig. 5a shows the dielectric permittivity as a function of frequency of 1/2 mixture with various dr. All mixtures exhibited similar order of the dielectric permittivity (i.e. 10\textsuperscript{3}) and the corresponding relaxation peak moved toward low frequency range (complete data are shown in Supplementary Figs. 17, 18). It is noted that with increasing doping level of 2, although the relaxation frequency (f\textsubscript{r}) decreased, the order of the dielectric strength was maintained (Fig. 5b). For P-E hysteresis variation, a typical parallelogram-like P-E loops, which often appears in ferroelectrics, were obtained in the all mixtures (Fig. 5c). The corresponding coercive electric field was increased toward high dr. Notably, polarization density (P \sim 4 \mu C/cm\textsuperscript{2}) of the 1/2 mixture was increased and the maximum P was marked at dr = 70/30 (Fig. 5d). Complete data on P-E hysteresis are summarized in Supplementary Fig. 19. The SHG is quickly recognized as a powerful tool to confirm the macroscopic polar order and its symmetry of the individual nanostructures. The SHG as a function of temperature under the electric field (0.7 V/\mu m) for all mixtures are shown in Fig. 5e (The optical setup is shown in Supplementary Fig. 20). For all mixtures, the high SHG activity was observed in the range of N\textsubscript{F} phase. For example, the SHG profile at dr = 70/30 was set as a master curve, the other SHG profiles were coincided well with the master curve. The dr-dependent SHG of all mixtures is summarized in Fig. 5f. The SHG intensities at dr ≥ 90/10 were larger than that at dr = 100/0. Hence, the combined results provide evidence that the diastereomeric-controlled N\textsubscript{F} phase is surly stabilized N\textsubscript{F} state without sacrificing polarization behavior. The counter molecule 2 against 1 play an important role as a N\textsubscript{F} phase stabilizer.

Finally, we demonstrated that the potential of a stabilizer (2) for boosting temperature range of the N\textsubscript{F} phase even in another host N\textsubscript{F} molecule. Here, we selected \textsuperscript{trans}C4DIO (3) exhibiting a monotropic N\textsubscript{F} phase of which temperature range is very narrow (~ 7 K) (Fig. 5g,h and Supplementary Fig. 21a). The molecule 3 was blended with a stabilizer 2 to yield the 3/2 mixture with dr (=70/30). As a result, the temperature range of the N\textsubscript{F} phase was extremely extended from 7 K to 40 K across room temperature (right bar graph in Fig. 5h and Supplementary Fig. 21b). Surprisingly, the N\textsubscript{F} phase was stably operated with temperature range of 26 K on heating (i.e. enantiotropic N\textsubscript{F} phase). The N\textsubscript{F} phase in the 3/2 mixture with dr (=70/30) also exhibited gigantic dielectric permittivity, large polarization as well as high SHG activity.
In conclusion, in this work, we demonstrated a new N\textsubscript{F} phase generative model based on the diastereomeric mixture of \textit{trans}\text{DIO} (1) and \textit{cis}\text{DIO} (2). In the 1/2 mixtures with various diastereomeric ratio, we successfully tuned three types of the phase sequences passing the N\textsubscript{F} phase: 1) IL–N–M–N\textsubscript{F}, 2) IL–N–N\textsubscript{F} and 3) IL–N\textsubscript{F} phase transitions. The 1/2 mixture with \textit{dr} = 70/30 exhibited the enantiotropic N\textsubscript{F} phase with wide temperature range (~50 K) across room temperature. The XRD analysis of 1/2 mixture clearly evidenced that the cybotactic cluster existed in the N\textsubscript{F} phase and the anisotropic growth of the cluster dominated the phase sequence types. Furthermore, the combination of dielectric, \textit{P-E} hysteresis as well as SHG studies confirmed that the diastereomeric-controlled N\textsubscript{F} phase had similar macroscopic polarization, indicating the replacing 1 with 2 was stabilizable the N\textsubscript{F} phase without sacrificing its macroscopic polarization. This model was also adapted in the monotropic N\textsubscript{F} molecule, \textit{trans}\text{C4DIO} collaborating with 2, giving rise to the enantiotropic nature and an expanding temperature range of the N\textsubscript{F} phase. We believe that this new approach allows new scope for N\textsubscript{F} matter engineering and/or new theories to be explored and conceptualized.

**Experimental Section**

**Fabrication methods for liquid crystalline (LC) cells.** Sandwich-type electrical cell (5 and 13 \textmu m-thickness): Pre-treated ITO-coated glass plates (EHC model D-type, electrode area: 5 × 10 mm\textsuperscript{2}) were silanized with a silane coupling reagent (octadecyltriethoxysilane, TCI) at 120 °C for 2 hours, and then were rinsed with EtOH and ultrapure water. The two resulting glass plates were fixed with drops of an UV-curable glue using polymeric beads (micropearl, SEKISUI) as a spacer. The cell gap was estimated by capacitance of the empty cell. For SHG measurement, we used ITO-coated glass plates (GEHOATEC, electrode area: 4 × 5 mm\textsuperscript{2}), which was pre-baked at 400 °C for 1 hour in the electronic furnace (SUPER100T, SHIROTA) prior to treatment.

**Preparation and measurement methods for LC cells.** Preparation of LC mixtures (1/2 or 3/2): the protocol is as follows: 1) a compound was precisely weighted using an electronic balance (MSE2.7S, sartorius); 2) a chloroform solution with appropriate concentration was prepared using an electronic micro-pipet (eVol, SGE Analytical Science); 3) the solution was evaporated at 40 °C in a jet oven overnight; 4) the resulting mixture was dried in vacuo at room temperature for 3 hours.

For experiments: The LC mixture was injected by capillary action into a LC cell (5 \textmu m- and 13 \textmu m-thickness).
**Polarized optical microscopy.** Polarized optical microscopy were performed on a polarizing microscope (Eclipse LV100 POL, Nikon) with controlling the temperature using a temperature controller and a hot stage (mK2000, INSTEC). Unless otherwise noted, the sample temperature was controlled using INSTEC model mK2000 temperature controller.

**Differential scanning calorimetry.** Differential scanning calorimetry (DSC) was performed on a calorimeter (DSC30, Mettler-Toledo). Cooling/heating profiles were recorded and analyzed using the Mettler-Toledo STAtRe software system.

**Dielectric microscopy.** Dielectric relaxation spectroscopy was performed ranging between 1 Hz and 1 MHz using an impedance/gain-phase analyzer (SI 1260, Solartron Metrology) and a dielectric interface (SI 1296, Solartron Metrology). Prior to starting measurement of the LC sample, the capacitance of the empty cell was determined.

**P-E hysteresis measurements.** P-E hysteresis measurements were performed in the temperature range of the NF phase under a triangular-wave electric field (10 kV/cm, 200 Hz) using FCE system (TOYO Corporation), which equipped with an arbitrary waveform generator (2411B), a IV/QV amplifier (model 6252) and a simultaneous A/D USB device (DT9832).

**SHG measurement.** The SHG investigation was carried out using a Q-switched Nd: YAG laser (FQS-400-I-Y-1064, Elforlight) at $\lambda = 1064$ nm with a 5 ns pulse width (pulse energy: 400 $\mu$J) and a 10 kHz repetition rate. The primary beam was incident on the LC cell following by the detection of the SHG signal. The electric field was applied normal to the LC cell. The optical setup is shown in Supplementary Fig. 20.

**Wide- and small-angle X-ray scattering (WAXS, SAXS) analysis.** Two-dimensional WAXS and SAXS measurements were carried out at BL38B1 in the SPring-8 synchrotron radiation facility (Hyogo, Japan). The samples held in a glass capillary (1.5 mm in diameter) were measured under a magnetic field at a constant temperature using a temperature controller and a hot stage (mk2000, INSTEC) with high temperature-resistance neodymium magnets (~0.5 T, MISUMI). The scattering vector $q$ ($q = 4\pi\sin(\theta)/\lambda; 2\theta$ and $\lambda =$ scattering angle and wavelength of an incident X-ray beam [1.0 Å (for WAXS) and 0.95 Å (for SAXS)], respectively) and position of an incident X-ray beam on the detector were calibrated using several orders of layer diffractions from silver behenate ($d = 58.380$ Å). The sample-to-detector distances were 2.5 m (for WAXS) and 0.29 m (for SAXS), where acquired
scattering 2D images were integrated along the Debye–Scherrer ring by using software (SAS 2D, Igor Pro), affording the corresponding one-dimensional profiles.
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Competing Interests

The authors declare no competing interests.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files. All other information is available from the corresponding authors upon reasonable request.

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Stabilizing $N_f$ phase without sacrificing polarization behavior

**Diagram a**: 
- Paraelectric nematic ($N$)
- Ferroelectric nematic ($N_f$)

**Diagram b**: 
- DIO diastereomer
  - $\text{C3DIO (1)}$: 9.84 D, 20.8°
  - $\text{C3DIO (2)}$: 9.85 D, 16.6°
- Non LC (Polar crystal)

**Diagram c**: 
- Temperature vs. $d_r (1/2)$

**Diagram d**: 
- Phase diagram
  - K
  - N
  - IL
  - $N_f$
  - $N_f + IL$

**Diagram e**: 
- Exothermic (a.u.)
  - K
  - $N_f$
  - N
  - IL

**Diagram f**: 
- Dielectric permittivity
  - $N_f$
  - N
**Fig.1 Diastereomeric-controlled ferroelectric nematic system.** a Schematic illustration of nematic and ferroelectric nematic phases. b Chemical structure of DIO diastereomer: \textit{trans}C3DIO (1) and \textit{cis}C3DIO (2). 1 and 2 has dipole moment of 9.84 and 9.85 D, and its direction angle with respect to the long axis of 20.8 and 16.6°, respectively. c Evolution of polarized optical microscope images, which were taken under the crossed polarizers, of the mixture 1/2 with various \textit{dr} (100/0–50/50). Scale bar: 100 µm. Thickness: 13 µm. d A phase diagram of the mixture 1/2 as a function of \textit{dr} and temperature. Symbols represent the phase transition temperature determined by DSC (circle), POM (square) and XRD (triangle) studies. Abbrev.: IL (isotropic liquid); N (nematic); M (mesophase); N\texttextit{F} (ferroelectric nematic); K (crystal). The coexistence area is indicated by gray shadow. e DSC curves of the mixture 1/2 with \textit{dr} (70/30) on cooling (upper line) and heating (bottom line). The bottom panel denotes the enlarged temperature range between 60–80 °C, in which a good match of temperatures due to the N\texttextit{F}–N phase transition (\textit{ca.} 72 °C) on cooling and heating because of a very weak 1st order or 2nd order phase transition. Temperature recorded on DSC was calibrated using a reference (8CB) exhibiting 2nd order phase transition (SmA–N). f Dielectric permittivity as a function of frequency in N\texttextit{F} phase (24 °C, left) and N phase (100 °C, right).
Fig. 2 Wide-angle XRD analysis of the 1/2 mixture with various $dr$. a Wide-angle 2D XRD profile of the 1/2 mixture ($dr = 100/0$). The azimuth angle $\phi_1 = 80^\circ$, $\phi_2 = 60^\circ$ represents the scanning range for generation of the 1D XRD profile. The value of $q_{\text{FWHM}}$ and relative intensity ($I_{\text{rel}}$) as a function of $dr$ for halo (b) and skewed peaks (c). $I_{\text{rel}}$ was calculated by dividing $I$ by $I_{\text{IL}}$ for halo and skewed peaks. c 1D XRD profile of the 1/2 mixture ($dr = 70/30$) with separated peaks (p1–p6). Insets denote the analyzed area for all entries ($dr = 100/0–50/50$). The value of $q_{\text{FWHM}}$ (e) and relative intensity ($I_{\text{rel}}$) (f) as a function of $dr$ for multiple peaks (p2–p6). $I_{\text{rel}}$ was calculated by dividing $I_{\text{obs}}$ by the corresponding $I_{\text{IL}}$. 
Fig. 3 Characterization of cybotactic cluster in the diastereomeric-controlled $N_F$ phase. 

**a** Schematic illustration of the $N_F$ phase of 1 or $1/2$ mixture. $L_1$ and $L_\perp$ are longitudinal and transversal dimension of the cybotactic cluster, respectively. $L$, $d$, $\beta$ denote the molecular length, $d$-spacing between layers and tilt angle, respectively.

**b** Small-angle XRD profile. A white-colored arrow denotes the direction of the applied magnetic field. The symbols are defined in the text.

**c** The horizontal (H) and vertical (V) scans of the four-spot pattern along the H-/V-dash lines indicated in the panel **b**. Intensity profiles $I(\Delta q_\parallel)$ (upper) and $I(\Delta q_\perp)$ (bottom) of the small-angle skewed spots measured via the maxima at $q_0$ long the longitudinal ($\parallel B$) and transversal ($\perp B$) direction, respectively.

**d** Evolution of the skewed peaks of the $1/2$ mixture with $dr = 100/0$, $70/30$ and $60/40$, as a function of the temperature, $T-T_c$.

**e** The relationship between growth anisotropy of cluster and $dr$, and its temperature-dependent. Inset cartoon depicts the two variation (case A and case B) of the growth of the cybotactic cluster in the $N_F$ phase.
Fig. 4 Clustering effect on the evolution of phase sequence. 

**a** The schematic illustration of the growth process of the cybotactic cluster in the N$_F$ phase for 1/2 mixture. The exchange of cisDIO with transDIO promotes the anisotropic cluster growth. 

**b** The average molecular numbers in the cluster ($\bar{N}$) as a function of $T-T_c$ of the 1/2 mixture with various $dr$ (100/0–50/50). 

**c** The corresponding $\bar{N}$ as a function of $dr$ ($T-T_c = -10$ °C). 

**d** The relationship between latent heat ($\Delta H$) and $dr$ at $T-T_c = -10$ °C. 

Note: two distinct section of the phase transition types are indicated by color bands: IL–N–M–N$_F$ regime (blue), IL–(N)–N$_F$ regime (orange) in the panel c and d.
Fig. 5 Polarization behavior of the 1/2 mixture with various \( dr \).  

a Dielectric spectra.  

b Dielectric strength and the corresponding relaxation frequency (\( \log f \)) vs. \( dr \) (\( T-T_c = -10 \, ^\circ C \)).  
c \( P-E \) hysteresis loops (\( V_{\text{max}} = 10 \, \text{kV/cm} \)).  
d Polarization density vs. \( dr \) (\( T-T_c = -10 \, ^\circ C \)).  
e Field-induced \( p\)-in/\( p\)-out SHG at a 45° incident angle as a function of temperature (0.7 V/\( \mu \text{m} \)).  
f The SHG intensity vs. \( dr \) (\( T-T_c = -10 \, ^\circ C \)).  

Notes: LC-cell conditions: thickness of 13 \( \mu \text{m} \); silanized coated ITO electrode (5 × 10 mm) for dielectric and \( P-E \) hysteresis studies; thickness of 5 \( \mu \text{m} \); silanized coated baked-ITO electrode (4 × 5 mm) for SHG study.  
g Chemical structures of \( \text{trans} \)C4DIO (3) and \( \text{cis} \)C3DIO (2).  
h Temperature-dependent phase behaviors of the 3/2 mixture with \( dr = 100/70 \) (upper) and 70/30 (bottom) on cooling and heating.
Supplementary Information

Nano-Clustering Stabilization of Ferroelectric Nematic Phases

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Methods

1. General and materials

**General:** Analytical thin layer chromatography (TLC) was performed on silica gel layer glass plate Merck 60 F254 and visualized by UV irradiation (254 nm). Column chromatography was performed on a Biotage Isolera™ Prime flash system (Biotage) using Biotage SNAP Ultra (25 g; particle size 25 µm; HP-spherical silica) column cartridge. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on Ascend 600 (600 MHz, BRUKER) operating at 600.00 MHz and 150.00 MHz for $^1$H and $^{13}$C NMR, respectively, using the TMS (trimethylsilane) as an internal standard for $^1$H NMR and the deuterated solvent for $^{13}$C NMR. The absolute values of the coupling constants are given in Hz, regardless of their signs. Signal multiplicities were abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), dd (double–doublet), respectively.

**Materials:** All of reagents and solvents were purchased from Kanto Chemical Co., Inc., Tokyo Chemical Industry Co., Ltd., FUJIFILM Wako Pure Chemical Corporation, Sigma-Aldrich Co., LLC. and Combi-Blocks Inc. and used without further purification. A series of DIO molecule was synthesized in our laboratory.
Supplementary Fig. 1 | Optimized molecular structures of 1 and 2 optimized by DFT/B3LYP method.
Supplementary Fig. 2 | Single crystal X-ray crystallographic structures of 1 and 2. Z denotes the molecular numbers in a unit cell.
Supplementary Fig. 3 | DSC curves of 1/2 mixture with various $dr$.

The baseline estimated by a polynomial fitting was subtracted from the original DSC curve.
Supplementary Fig. 4 | 2D wide-angle XRD profiles of 1/2 mixture with various \( dr \).
Supplementary Fig. 5 | XRD analysis of 1/2 mixture with various $dr$. The X-ray diffractogram on the meridional direction (normal to $n$) were fitted by Voigt function.
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Supplementary Fig. 7 | 2D XRD profiles of 1/2 mixture with $d\tau = 100/0$ at various temperature.
Supplementary Fig. 8 | 2D XRD profiles of 1/2 mixture with $dr = 90/10$ at various temperature.
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Supplementary Fig. 20 | The optical setup for SHG studies. The electric field ($E$-field) was applied normal to the sample cell (thickness: 5 µm), generating the $p$-in/$p$-out polarization combination.
Supplementary Fig. 21 | DSC curves for 3/2 mixture with $dr = 100/0$ (a) and $=70/30$ (b).
Supplementary Table 1 | Thermal properties of the 1/2 mixture with various $dr$.

| $dr$ | $\Delta H_x^{[a]}$ [kJ mol$^{-1}$] | $\Delta H_y^{[b]}$ [kJ mol$^{-1}$] | $\Delta H_{tot}^{[c]}$ [kJ mol$^{-1}$] |
|------|-------------------------------|-------------------------------|-----------------------------------|
| 100/0| 0.750                         | 0.281                         | 1.03                              |
| 90/10| 0.480                         | 0.526                         | 1.01                              |
| 85/15| 0.383                         | 0.704                         | 1.09                              |
| 80/20| 0.367                         | 0.970                         | 1.34                              |
| 70/30| 0.219                         | 1.34                          | 1.56                              |
| 65/35| -                             | 2.22                          | 2.22                              |
| 60/40| -                             | 2.73                          | 2.73                              |
| 55/45| -                             | 2.95                          | 2.95                              |
| 50/50| -                             | 2.94                          | 2.94                              |

[a] $\Delta H_x$ denotes enthalpy of IL–N phase transition, [b] $\Delta H_y$ denotes enthalpy of IL–N$_F$ phase transition, [c] $\Delta H_{tot} = \Delta H_x + \Delta H_y$. Note: the enthalpy of N–N$_F$ was omitted because it was negligibly smaller than those of IL–N and IL–N$_F$ phase transition.