Nano-clustering mediates phase transitions in a diastereomerically-stabilized ferroelectric nematic system

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In recent years, ferroelectric nematic liquid crystals have attracted considerable attention owing to their unique properties such as a colossal polarization, high electro-optic activity, and high fluidity. However, despite large efforts in designing and developing new ferrofluid molecules based on molecular parameters, the control and stabilization of ferroelectric nematic phase transitions remain challenging. Here, we discuss the impact of mixing 1,3-dioxane-tethered fluorinated (DIO) diastereomer molecules, namely transDIO and cisDIO, in controlling the ferroelectric nematic phase transition, using X-ray diffraction to investigate the effect of smectic cybotactic cluster formation. Our results show that the ferroelectric nematic phase transition can be tuned by a smooth exchange of the ferroelectric nematic transDIO and non-liquid crystal cisDIO components, where the similar dipole and molecular backbone of the two components ensures a consistent macroscopic polarization of the diastereomeric-controlled ferroelectric nematic phase.
Since the discovery of a true three-dimensional (3D) fluid ferroelectric nematic (N$_f$) phase showing a field-induced polarization reversal via a domain wall motion in liquid crystals (LCs), great interest has been dedicated to both fundamental science and applications$^{1-35}$. In the N$_f$ phase, the inversion symmetry of the nematic (N) director is broken, forming macroscopic domains with a uniform polarization ($P$) along the director, $n$ (Fig. 1a). The striking features of N$_f$-LCs are their large spontaneous polarization, gigantic dielectric permittivity$^{3,13,14,18,21,24,28}$, high nonlinear optical activity$^{3,9,24,31}$, electro-optic response with very low or zero threshold voltage$^{8,12,13,15,17,20,22}$, and high fluidity$^{3,8,27}$ that may lead to unconventional soft matter technologies. According to the simple model by Born, the electric–dipolar interaction proportional to the square of the dipole moment, $\mu$, which should be...
strong enough to withstand a thermal fluctuation ($k_B T$), is the most important to emerge from the $N_\psi$ phase.35,36. This unique $N_\psi$ phase has been ascertained in specific molecules as a 1,3-dioxane-tethered fluorinated molecule (DIO), a $d$-shape-pershared molecule (RM734)1,2, a fluorinated molecule bearing a terminal cyanogroup (UUQU-4-N)14, and other generics13,23,24 with very large $\mu$ (i.e., > 9 Debye). However, although the present systemized molecular parameters, including $\mu$, oblique dipole angle, and geometrical aspect ratio of a molecular shape, are confirmed for the $N_\psi$ emergence, the effects on the phase sequence passing the $N_\psi$ phase have not been considered. The archetypal phase behavior of $N_\psi$ molecules is described as follows: (1) DIO experiences three mesophases: the $N$–$M$–$N_\psi$ phase transition (i.e., $M$ is antiferroelectric $N$, $SmA_o$, or $Ns$ with periodic density modulation in the direction perpendicular to $n$; the nomenclature is under debate21,23,27); (2) RM734 exhibits the $N$–$N_\psi$ phase transition that corresponds with the ferroelectric–ferroelastic phase transition seen in inorganic solids;9 and (3) the latest key is UUQU-4-N showing the direct $N_\psi$ phase transition from isotropic liquid (IL) (i.e., IL–$N_\psi$ phase transition observed in some molecules)1,2,3,24. In most cases, the $N_\psi$ phase is thermodynamically unstable below room temperature, irrespective of a single molecule or LC blends. Considering the results of the single-crystal X-ray diffraction4,21,24, the two adjacent $N_\psi$ molecules with a synparallel arrangement may flip each other, destroying the $N_\psi$ state and undergoing crystallization below room temperature. Under this circumstance, the control of the phase sequences involving the $N_\psi$ emergence and the successful way of stabilizing $N_\psi$ remain ambiguous despite huge efforts on the design and development of new $N_\psi$-LC molecules based on molecular parameters. Note that a new-found ferroelectric state, that is, a uniaxial ferroelectric smectic A ($SmA_\psi$) phase37,38 that appears just below the $N_\psi$ phase, just emerged, offering an important clue. $SmA_\psi$ looks highly correlated with the $N_\psi$ phase; hence, the smectic cluster floating in the $N_\psi$ media may influence the $N_\psi$ phase characteristic.

In this work, we report a ferrofluid matter engineering concept based on the dipole equivalent for controlling the $N_\psi$ phase transition and its possible impact to cluster formation. Very recently, almost the same diastereomeric system had been coincidently introduced by another group; however, the mechanism behind this well-controlled $N_\psi$ phase has remained unknown39. In this study, we focus on the nanoscopic structure in the present diastereomeric binary system and discuss the alteration of the $N_\psi$ phase transition in terms of the cybotactic cluster formation. The result suggests that the molecule exchange with an almost equivalent dipole moment and an analogous structure occurs without reducing the macroscopic crystallization. For this strategy, although two components, including a $N_\psi$ molecule, are treated, the counter molecule need not be liquid crystalline. This point is unique compared to the conventional approach22,40,41. We herein adopt DIO diastereomers, $trans$-DIO (1) and $cis$-DIO (2), which are a ferroelectric nematogen and a non-liquid crystalline, respectively (Fig. 1b), to investigate the effect of diaster-ecomical control and the $N_\psi$ phase structure in view of the X-ray diffraction (XRD) analysis and computer simulation.

Results and discussion

Control of the variant $N_\psi$ phase transition in $trans/cis$-DIO system. A stereoisomer with an equivalent topological structure, but a different geometric configuration, is also known as a diastereomer42. DIO has a diastereomer because its 1,3-dioxane moiety with alkyl chain can have two geometric configurations. This DIO diastereomer (i.e., $trans$/cis-DIO (1) and $cis$/cis-DIO (2)) exhibit different physical properties (see Fig. 1b and Supplementary Figs. 1–6 for the characterization data). 1 is a typical ferroelectric nematogen that exhibits the ferroelectric nematic (N$_\psi$) phase on cooling3. Despite a similar large dipole moment to $\mu_1 = 9.36$ D; $\mu_2 = 9.04$ D; see Supplementary Fig. 7), 2 is not an LC material, but a polar crystal (instead of an apolar one like 1). Supplementary Fig. 8 (Supplementary Data 1 and 2) shows the single-crystal X-ray crystallographic structures of 1 and 2. If the diastereomeric ratio ($d_r$) of 2 in the 1/2 mixture is increased (i.e., exchanging 1 by 2), the $N_\psi$ phase is intuitively expected to destabilize because molecule (2) may collapse the strong dipole–dipole interaction between the 1–1 molecule. Figure 1c and Supplementary Figs. 9–14 depict the polarizing optical microscope images via the variant phase sequence in the diastereomeric mixture (1/2). For $d_r = 100/0$, the uniform texture (green-highlighted area in the figure) is first changed to an inhomogeneous one (blue-highlighted area in the figure) and finally to a stripe texture because of the polar defect (e.g., $2\pi$ twist-wall15) (yellow-highlighted area in the figure) during cooling.

These three phases are characterized as the N, M, and $N_\psi$ phases in the order of high to low temperature. With an increasing $dr$, the intermediate M phase vanishes at $dr = 70/30$. Thus, the mixture with $dr = 70/30$ experiences the N–$N_\psi$ phase transition like the common generic $N_\psi$ molecules, including RM734. A further increment of $dr = 60/40$ eliminates the N and M phases, and a direct phase transition between isotropic liquid and $N_\psi$ phase instead occurs. In the case of $dr = 60/40$, small $N_\psi$ phase droplets emerge in the isotropic liquid and conglomerate, resulting in a complete $N_\psi$ phase formation. This direct IL–$N_\psi$ transition type is a scarce case observed in UUQU-4-N, etc.14,21,24. Thus, against expectation, the 2 doping probably contributes to the phase transition control related to the $N_\psi$ phase stability. The phase diagram of the 1/2 system is constructed (Fig. 1d) to explore the $N_\psi$ phase stabilization by the diastereomeric control of DIO. The temperature range of the M phase is reduced at $dr = 90/10$. In addition, the $N_\psi$ phase regime expands to a lower temperature range across the room temperature. This trend is observed when increasing the doping level of 2 up to $dr = 70/30$, which yields the maximum temperature range of the $N_\psi$ phase. Interestingly, at $dr = 70/30$, the $N_\psi$ phase still stands at 0 °C, and the wide regime is 80 °C, which is approximately four times larger than that of pure DIO (1). More interestingly, the mixture with $dr = 70/30$ exhibits an enantiotropic $N_\psi$ phase that is thermodynamically stable, unlike the monotropic $N_\psi$ phase in 1 (Fig. 1e).

Similarly, at the regime with a high doping level of 2 ($dr \geq 40/60$), the $N_\psi$ phase maintains a wide temperature range of 50–20 K.
across the room temperature. The dielectric permittivity of the NF and N phases in the 1/2 system is comparable to that of pure DIO. The N and N phases show a dielectric permittivity of the orders of 10^4 and 10 at 1 kHz frequency, respectively (Fig. 1f). Supplementary Fig. 15 depicts the complete DSC curves. Supplementary Table 1 summarizes the corresponding enthalpies.

**Structure analysis of the diastereomeric-controlled NF phase.** As mentioned above, the diastereomeric combination probably alters the nature of the NF phase transition. We discuss here how the doping level of 2 in 1 affects the NF phase structure mainly with the aid of a X-ray analysis. Figure 2a displays a two-dimensional (2D) wide-angle X-ray diffraction (WAXD) pattern of the NF phase (T = Tc = 70 °C) in 1 under the magnetic field (B = 0.5 T). Supplementary Fig. 16 provides the complete data. The unique diffraction patterns consist of (i) a pair of skewed peaks corresponding to a molecular length of ~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, and (iii) halo peaks caused by the intermolecular stacking on the meridional direction (normal to n). The WAXD profile is analyzed in detail by performing horizontal and vertical scans within angles φ1 = 80° and φ2 = 60°, generating a one-dimensional XRD pattern. Figure 2b, c shows the relative intensity (Irel) and the full width at half maximum (FWHM) in the q-space (i.e., qFWHM) as a function of dr for the fitted halo/skewed peaks (Supplementary Figs. 17 and 18). For the halo peak, all qFWHM are comparable, while the intensity slightly decreases with the increasing doping level of 2. By contrast, the qFWHM of the skewed peaks slightly decreases as dr increases. The intensity shows a significant dependence on dr, suggesting that the doping of 2 may promote the cybotactic cluster growth in the NF phase. The peak separation on the equator direction is also performed, providing peaks (Fig. 2d). For the qFWHM and intensity of peaks p2–p6, although both are on a downward trend at dr = 60/40, no remarkable difference is found on any dr (Fig. 2e and f). Let us consider the unusual anisotropic diffraction pattern in the NF phase of the 1/2 system. For the diffraction on (i) (vide supra), the skewed peak is reflected on the normal cybotaxis, in which an SmC-like stratification exists within the mesogen clusters, floating in the N phase43,44. The diffraction on (ii) may be caused by the anomalously large correlation length in the cybotactic clusters observed in the N phase in a rigid nematic DIO molecule45. With the aid of molecular dynamics (MD) calculations, Mandle et al. confirmed that a series of weak overtones observed in the NF phase of RM734 was a consequence of the polar nematic order18. Considering these important tips, in the 1/2 system, the SmC-type cybotactic cluster may coexist in the NF phase (Fig. 3a). In this case, the anomalous changes in the diffraction intensity may indicate the growth of the cluster size with a polar order depending on the doping level of 2.
Fig. 3 Characterization of the cybotactic clusters in the diastereomeric-controlled NF phase. a Schematic illustration of the NF phase of 1 or 1/2 mixture. \(L_\parallel\) 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 X-ray scattering profile. A white-colored arrow denotes the direction of the applied magnetic field. The symbols are defined in the text. 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 \(q_\|\) 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 NF phase.

We analyze in detail the 2D small-angle X-ray scattering (SAXS) patterns in the NF phase to gain more information on the cluster in the NF phase. Figure 3a shows a schematic illustration connecting the structural parameters of the SmC-type cybotactic domain. The magnetic field aligns the clusters, in which the director n is parallel to B. In the magnetic field, the normal to smectic layer, \(k\), is randomly distributed on B at the tilt angle \(\beta\). As a result, the SAXS profile resulting from this distribution of microscopic SmC-type clusters is observed (Fig. 3b and Supplementary Figs. 19–26). Based on refs. 43,44, we estimated the average size of the cybotactic clusters in the NF phase and its temperature and \(dr\) dependence. The average cluster size can be estimated from the longitudinal (\(\parallel\) B) and transversal (\(\perp\) B) intensity profiles of the skewed (four-spot) pattern (Fig. 3b). Figure 3c shows an example of the diffraction intensity as a function of \(\Delta q_\parallel\) (Fig. 3b, c). 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 NF phase.
occurs in the 1/2 mixture with $dr$ (>65/35), which experiences a direct IL–Nf phase transition. A similar tendency is observed in UUQU-4-N exhibiting the direct IL–Nf phase transition, in which SmA-like cybotactic cluster coexists in the Nf phase (Supplementary Fig. 28). Thus, the cybotactic cluster in a series of molecules showing the direct IL–Nf phase transition may inherently grow, irrespective of the cybotactic cluster types, via Case B. We next investigate the internal molecular environment in the cluster. The left panel in Fig. 4a is a schematic illustration of the SmC-like stratification within the cluster in the Nf phase with the $dr$ variation at a fixed temperature ($T − T_{c1} = −10 ^\circ C$). At $dr = 100/0$, the constituent molecules (I) arranged in a smectic layer with the tilt angle $\beta = 24.9 ^\circ$ (Supplementary Fig. 29) are occupied in the cluster (the left panel in Fig. 4a). With the increasing doping of 2, the substitution of 1 leads to the generation of scrambled dipoles of 1 and 2 with a changing cluster anisotropy (the middle and right panels in Fig. 4a). At $dr = 50/50$, the majority of clusters is colonized by equimolecular molecules. Although $\beta$ is nonlinearly increased by cooling, reflecting on the SmC-Sm feature at each $dr$, the $\beta$ value at a fixed temperature is slightly reduced to 19.5 $^\circ$ (Supplementary Fig. 29) with the increasing $dr$. Considering the cybotactic cluster volume (i.e., $L_2 \times L_1 \times L_3$), we estimate the average molecular numbers in the cluster of a series of 1/2 mixtures. The average molecular numbers in the longitudinal ($N_2$) or transversal ($N_1$) dimension are given as follows:

$$N_1 = L_1 / l = 3 \xi l / l,$$

$$N_2 = L_2 / w = 3 \xi l / w,$$

where $l$ and $w$ are the molecular length (ca. 2.23 nm) of DIO and the typical intermolecular distance (ca. 0.47 nm), respectively. The average molecular numbers ($N$) in the cluster are expressed as $N_2 \times N_1 \times N_3$. In the case of 1 at $T − T_{c1} = −10 ^\circ C$, $N$ is calculated as 1036 (i.e., one thousand molecules are occupied in the cluster). Figure 4b summarizes the estimated $N$ for all the 1/2 series as a function of the temperature. At a low $dr$ regime (<70/30), the $N$ monotonically increases and reaches approximately 2000. By contrast, the 1/2 series with a high $dr$ regime (>70/30) expresses the tendency of a nonlinear increment of $N$ reaching to ca. 2000–4000. Figure 4c highlights the relationship at $T − T_{c1} = −10 ^\circ C$. The $N$ value increases at the $dr$ threshold (85/15), being 1.5–2 times at the maximum $dr$. Interestingly, the $dr$ dependence of enthalpy related with the phase transition via the Nf phase shows a quite similar relationship between $N$ and $dr$ (Fig. 4d). This suggests that the anomalous latent heat has a strong association with the formation of the cybotactic cluster and its size. At the $dr$ threshold (70/30), two regimes (i.e., IL–N–M–Nf and IL–(N–N–Nf)) are also classified. The $dr$ threshold shows a good agreement with the $dr$ classifying cases, depicting the cluster growth trend in Fig. 3c.

We assess the cluster model validation in the Nf phase for the 1/2 system by performing an MD simulation using all-atom models with GROMACS 2020.5. Here we simulate four systems: compound 1 arranged all in parallel (System 1) and half in anti-parallel (System 2) and 50:50 compositions of 1 and 2 all in parallel (System 3) and half in anti-parallel (System 4). The initial structures are built with six layers containing 100 molecules each. Hence, the total number of molecules in the simulation box is 600. Supplementary Note 1 provides the relevant details for this. Figure 4e compares the time-averaged total energy of the four systems and the corresponding MD snapshots in the Nf regime ($T − T_{c1} = −15 ^\circ C$). The calculated energies ($G$) of Systems 1 and 2 are ~6087 kcal mol$^{-1}$ and ~7285 kcal mol$^{-1}$, respectively. Thus, the parallel (or) orientation may predominately occur in the 1-only system. This result corresponds with that of previous reports.$^{8,18}$ By a sharp contrast, the time-averaged total energies of Systems 3 and 4 are extremely lower (i.e., $G_{\text{System 3}} = −6879$ kcal mol$^{-1}$ and $G_{\text{System 4}} = −6306$ kcal mol$^{-1}$); hence, it is natural to consider that the doping of 2 stabilizes the system. Interestingly, closely looking at the MD simulation snapshots shows a pairing of 1 and 2, which means a plausible dimerization (Supplementary Fig. 33) confirmed by the peak differences on the 2D radial distribution function profiles of 1 only, 2 only, and both 1 and 2 in the one layer for System 3 (Supplementary Fig. 37). The possibility of dimerization is also discussed through the density functional theory calculation$^{46}$ (Supplementary Note 1, Supplementary Table 2, Supplementary Figs. 30–32, 34–36, and 38–39). A rough estimate of the energetic difference of the pair interaction in Systems 3 and 4 provided 573/300 ~2 kcal mol$^{-1}$, which is comparable with the thermal agitation energy above the room temperature (e.g., $k_B T = 2.4$ kcal mol$^{-1}$ at 300 K). The total energy in MD tends to be reduced by the size limitation of the simulation box. It looks reasonable that the pair orientation of 1–2 dimers in a cluster is energetically preferable than the apolar 1–2 configuration. The tilt angles ($\phi$) of Systems 1 and 3 are well accorded with those obtained by the X-ray analysis (Fig. 4e and Supplementary Fig. 29). Hence, the MD simulation results strongly support our polar configuration model.

**Polarization behavior of the diastereomeric-controlled Nf phase.** As an early prediction, the replacement of the Nf molecule (1) with a non-LC molecule (2) will probably cause a destruction of the strong dipole–dipole interaction between the 1–1 molecule, such that the Nf phase should be destabilized. Contrary to expectation, by diastereomeric control using 2, we succeeded in realizing the Nf state operating over an extended temperature range from 80 °C to 0 °C and controlled various phase transition sequences, as mentioned above. If the diastereomeric-controlled Nf phase is a truly stabilized state, the corresponding polarization properties should also be equal to or greater than the original ones. Accordingly, we investigated the polarization behavior of the Nf phase 1/2 system by dielectric relaxation, $P$–$E$ hysteresis, and SHG studies. The comparable temperature was fixed to $−10 ^\circ C$ of $T − T_{c1}$. Figure 5a shows the dielectric permittivity as a function of the frequency of the 1/2 mixture with various $dr$. All mixtures exhibited a similar order of dielectric permittivity (i.e., 10$^5$), and the corresponding relaxation peak moved toward a low frequency range. Supplementary Figs. 40 and 41 provide the complete data for this. With an increasing doping level of 2, although the relaxation frequency ($\tilde{f}$) decreased, the dielectric strength order was maintained (Fig. 5b). The $dr$ dependence of frequency was discussed in Supplementary Note 2 and Supplementary Fig. 46. For the $P$–$E$ hysteresis variation, typical parallelogram-like $P$–$E$ loops that often appear in ferroelectrics were obtained in all mixtures (Fig. 5c). The corresponding coercive electric field was increased toward a high $dr$. Notably, the polarization density ($P \sim 4 \mu C \ cm^{-2}$) of the 1/2 mixture was increased, and the maximum $P$ was marked at $dr = 70/30$ (Fig. 5d). Supplementary Fig. 42 provides the complete data on the $P$–$E$ hysteresis. The SHG is quickly recognized as a powerful tool for confirming the macroscopic polar order and its symmetry of individual nanostructures. Figure 5e presents the SHG as a function of the temperature under the electric field (0.7 V μm$^{-1}$) for all mixtures. Supplementary Fig. 43 presents the optical setup. For all mixtures, the high SHG activity was observed in the NF phase, in which SmA-like cybotactic cluster coexists in the NF phase transition, in Supplementary Fig. 28. By a sharp contrast, the time-averaged total energies of Systems 3 and 4 are extremely lower (i.e., $G_{\text{System 3}} = −6879$ kcal mol$^{-1}$ and $G_{\text{System 4}} = −6306$ kcal mol$^{-1}$); hence, it is natural to consider that the doping of 2 stabilizes the system. Interestingly, closely looking at the MD simulation snapshots shows a pairing of 1 and 2, which means a plausible dimerization (Supplementary Fig. 33) confirmed by the peak differences on the 2D radial distribution function profiles of 1 only, 2 only, and both 1 and 2 in the one layer for System 3 (Supplementary Fig. 37). The possibility of dimerization is also discussed through the density functional theory calculation$^{46}$ (Supplementary Note 1, Supplementary Table 2, Supplementary Figs. 30–32, 34–36, and 38–39). A rough estimate of the energetic difference of the pair interaction in Systems 3 and 4 provided 573/300 ~2 kcal mol$^{-1}$, which is comparable with the thermal agitation energy above the room temperature (e.g., $k_B T = 2.4$ kcal mol$^{-1}$ at 300 K). The total energy in MD tends to be reduced by the size limitation of the simulation box. It looks reasonable that the pair orientation of 1–2 dimers in a cluster is energetically preferable than the apolar 1–2 configuration. The tilt angles ($\phi$) of Systems 1 and 3 are well accorded with those obtained by the X-ray analysis (Fig. 4e and Supplementary Fig. 29). Hence, the MD simulation results strongly support our polar configuration model.
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 (N) as a function of T – T_c of the 1/2 mixture with various dr (100/0–50/50). c The corresponding N as a function of dr (T – T_c = −10 °C). d The relationship between latent heat (ΔH) 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. e Energy diagram of the N_F phase in 1/2 system generated by MD simulation. The snapshots (after 300 ns equilibration run) of four system consisting of parallel 1–1, anti-parallel 1–1, parallel 1–2 and anti-parallel 1–2 dimers obtained by all-atom MD simulation (for 1–1 dimer, 323 K; for 1–2 dimer, 288 K) are inserted. β denotes the average tilt angle of molecules in a smectic layer. The bottom values are the average total energy (simulation time: 200–300 ns).
at $dr = 100/0$. Hence, the combined results provided evidence that the diastereomeric-controlled $N_F$ phase was in a stabilized $N_F$ state without sacrificing the polarization behavior. The counter molecule 2 against 1 plays an important role as a $N_F$ phase stabilizer.

Finally, we demonstrated the potential of a stabilizer (2) for boosting the temperature range of the $N_F$ phase, even in another host $N_F$ molecule. We selected herein transC4DIO (3) that exhibits a monotropic $N_F$ phase, of which the temperature range is very narrow ($\sim 7$ K) (Fig. 5g, h and Supplementary Fig. 44a). 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 $N_F$ phase was extremely extended from 7 to 40 K across the room temperature. Surprisingly, the $N_F$ phase was stably operated with a temperature range of 26 K on heating (i.e., enantiotropic $N_F$ phase) (Fig. 5g, h and Supplementary Fig. 44b). Supplementary Fig. 45 summarizes the $N_F$ phase characterization in the 3/2 mixture with $dr = 70/30$.

**Conclusion**

In conclusion, we demonstrate herein the alteration of the $N_F$ phase transition and the nano-cluster formation in the diastereomeric mixture of transDIO (1) and cisDIO (2). In the 1/2 mixtures with various diastereomeric ratios, we successfully tune three types of phase sequences passing the $N_F$ phase, namely the IL–N–M–$N_F$, IL–N–$N_F$ and IL–$N_F$ phase transitions. The 1/2 mixture with $dr = 70/30$ exhibited an enantiotropic $N_F$ phase with a wide temperature range ($\sim 50$ K) across the room temperature. The SAXS analysis of the 1/2 mixture clearly and evidently showed that the cybotactic cluster exists in the $N_F$ phase, and the anisotropic growth of the cluster dominates the phase sequence types. The computer simulation clarified that in the nano-cluster, the substitution of 1 with 2 without energetic penalty in the polar configuration was allowed, and 1–2 (parallel polar arrangement) was the energetically most stable configuration in another pair case. Furthermore, the combination of
dielectric, P–E hysteresis, and SHG studies confirmed that the diasteroemeric-controlled Nf phase had a similar macroscopic polarization, indicating that replacing 1 with 2 stabilized the Nf phase without sacrificing its macroscopic polarization. This model was also adapted in the monotropic Np molecule, trans-C4DIO, collaborating with 2. The results led to the enantiotropic nature and an extended temperature range of the Nf phase (24 K) on heating. We believe that this proposed approach allows for a new scope of Np matter engineering and/or new theories to be explored and conceptualized.

**Method**

**General and materials.** See Supplementary Methods

**Fabrication methods for liquid crystalline (LC) cells.** Sandwich-type electrical cell (5 and 13 μm-thickness): Pre-treated ITO-coated glass plates (EHC model D-type, electrode area: 5 × 10 mm²) were silanized with a silane coupling reagent (octa-[(trimethoxysilyl)]-1,1,1-trifluoroethane, TOYO Corporation), equipped with an arbitrary waveform generator (2411B, A/VQ/V amplifier (model 6252) and a simultaneous A/D USB device (DT9832).

**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 added in a vial (6 mL) and precisely weighted using an electronic balance (MSE2.7 S, sartorius); 2) a chloroform was added into this vial, preparing a mother liquor; 3) Two kind of mother liquors (chloroform solution of 1 or 3 and 2) were mixed with appropriate concentration using an electronic micro-pipet (eVol, SGE Analytical Science); 4) the solution mixture was vortexed and then evaporated at 40 °C in a jet oven overnight; 5) the resulting mixture was dried in vacuo at room temperature for 3 h and then mechanically stirred at 120 °C by a magnetic stirrer followed by cooling to room temperature.

For experiments: The LC mixture was injected by capillary action into a LC cell (5 μm- and 13 μm-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 INSECT model mk2000 temperature controller and a liquid nitrogen cooling system pump (LN2-P/LN2-D2, INSTEC).

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

**Dielectric spectroscopy.** 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 Nc phase under a triangular-wave electric field (10 kV cm⁻¹, 200 Hz) using FCE system (TOYO Corporation), 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 (FSQ-400-1-1064, Eloflouright) at λ = 1064 nm with a 5 ns pulse width (pulse energy: 400 μJ) and a 2 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. 43.

**Wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) analyses.** Two-dimensional WAXD and SAXS measurements were carried out at BL38B1 in the SPring-8 synchrotron radiation facility (Hyogo, Japan). The samples held in a glass capillary (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 = 4πsinθ/λ, 2θ = scattering angle and wavelength of an incident X-ray beam [1.0 Å (for WAXD) and 0.95 Å (for SAXS)]) 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 WAXD) and 0.29 m (for SAXS), where acquired scattering 2D images were integrated along the Debye-Scherrer ring by using software ( Igor Pro with Nika-plugin), affording the corresponding one-dimensional profiles.

**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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Author contributions
H.N. conceived the project and performed all the experiments. F.A. co-designed the work. K.S. and F.A supported XRD measurements and analyses. S.K. and G.W. performed MD and DFT calculations. A.N. synthesized compounds. B.D. helped and analyzed the single crystal XRD. H.N., K.S. and F.A. analyzed data and discussed the results. H.N. and F.A wrote the manuscript and all authors approved the final manuscript.

Competing interests
The authors declare no competing interests.

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