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Author(s)	Uchida, Yoshiaki; Akita, Takuya; Hanada, Kazuki et al.
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Molecular Clustering Behaviour in Cybotactic Nematic Phase of Spin-labelled Liquid Crystal

Yoshiaki Uchida,* Takuya Akita, Kazuki Hanada, Daichi Kiyohara and Norikazu Nishiyama

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A newly synthesised liquid crystalline nitroxide radical (LC-NR) with a terminal trifluoromethyl group as spin-labelled LC compounds exhibits anomalous phase transition behaviour. It is likely attributed to non-covalent interactions between trifluoromethyl groups of adjacent molecules. X-ray diffractometry of the LC-NR suggests the existence of a cybotactic nematic (N_{cyb}) phase with a transient and local layer order between normal nematic (N) and smectic A (SmA) phases. EPR spectroscopy of the spin-labelled LC implies no discontinuity in magnetic susceptibility around the N-to- N_{cyb} phase transition. Intermolecular contacts between nitroxide radicals seem to change there continuously. These results imply that the interactions between trifluoromethyl groups induce the cybotactic clusters, which molecules go into and out of.

Introduction

The properties of liquid crystalline (LC) phases depend on the molecular orientation and intermolecular interactions.^{1,2} The origins of the properties can be discussed by synthesising analogous molecules and observing the LC superstructures using a polarised optical microscope and X-ray diffraction. It uncovers the correlation of the molecular structures with the molecular orientations and periodic superstructures. As one of the molecular modifications, fluorine substitution in LC structures affects the melting points, mesophase morphology, transition temperatures, and the many essential physical properties of LC materials, such as optical, dielectric and viscoelastic properties.³

Recently, LC nitroxide radicals containing a five-membered ring NR moiety in the mesogen core (LC-NRs) have been reported as metal-free magnetic soft materials.⁴ In contrast to inorganic solid-state materials, including transition metals (Fe, Co, Ni, etc.) and lanthanides, they are more favourable from the point of view of the elements strategy,^{5,6} and their magnetic properties are fine-tuneable. Some desired functions such as chirality and anisotropy can be easily added by molecular modification. In addition, these compounds exhibit some fascinating properties in the externally applied magnetic field;⁷ e.g., their molecular reorientation occurs in a uniform magnetic field,^{8,9} and they exhibit a sort of spin glass-like inhomogeneous ferromagnetic interactions in LC phases.^{10,11} LC-NRs can be analysed on both molecular orientation and intermolecular interactions. Therefore, electron paramagnetic resonance (EPR) spectroscopic research using LC-NRs as spin-labelled LC compounds has given us understanding of the phenomena from perspectives never seen before; e.g., the pretransitional change

of the molecular conformation ensemble in de Vries type SmA*-SmC* phase transition,¹² and the dimeric intermolecular interactions based on the electric dipole along the long axis of LC molecules.^{13,14}

As phenomena expected to originate from intermolecular interactions, unconventional LC phases have been reported. One is a nematic phase with transient local layer order (cybotactic cluster), called cybotactic nematic (N_{cyb}) phase.¹⁵ Whereas most of the research on cybotactic clusters has focused on bent-core molecules to date,¹⁶ some LC molecules with non-covalent interactions like hydrogen bonding have also been reported to show N_{cyb} phases.^{17,18} The previous discussion has concluded that the lateral interactions between rod-like molecules are important for cybotactic cluster formation. LC-NRs showing N_{cyb} phases could be used as spin-labelled LCs for EPR spectroscopy, which would clarify the cluster formation process in terms of the molecular orientation and intermolecular interactions. We focused on the specific substituents like hydroxy, ionic and fluorinated groups needed to induce the non-covalent interactions for the cybotactic cluster formation. We have already reported hydrogen-bonded LC-NRs,^{19,20} ionic LC-NRs²¹ and terminal fluorinated LC-NRs containing a mono-, di- or trifluorobenzene group.²² However, they do not exhibit N_{cyb} phases originating from fluorination. Here, we report synthesising a new series of LC-NRs with a trifluoromethyl group as a terminal unit. We discuss the molecular clustering behaviour based on EPR spectroscopy for one LC-NR showing an N_{cyb} phase.

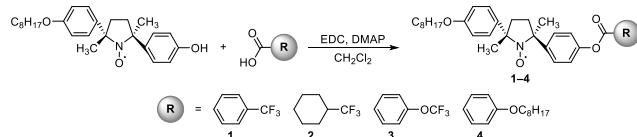
Results and discussion

Design and synthesis

An NR with a phenol moiety as the starting compound was prepared using the previously reported procedure.^{4,23} We synthesised LC-NRs with a terminal trifluoromethyl group (\pm)-1-

Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan. E-mail: y.uchida.es@osaka-u.ac.jp

3 by esterifying the starting compound with corresponding carboxylic acids, as shown in **Scheme 1** (see Experimental). We compare them with a previously reported analogue (\pm)-**4** for phase transition behavior.⁴



Scheme 1. Synthetic route and molecular structures of (\pm)-**1-4**.

To check the purity of (\pm)-**1-3**, we measured their magnetic properties using EPR spectroscopy and SQUID magnetometry, as summarised in **Table 1**. The EPR spectroscopy of their tetrahydrofuran (THF) solutions at a field of 0.33 T at room temperature displayed spectra with intense 1:1:1 triplet specific to NR compounds with normal g values and hyperfine coupling constants (a_N). Their paramagnetic susceptibilities (χ) measured on a SQUID magnetometer at a field of 0.5 T in the temperature range 2–300 K in the first heating depend on the temperature, as shown in **Figure 1**. The χT - T plots obeyed the Curie-Weiss law in the temperature range between 100 and 300 K (theoretical C is 0.375). It indicates that the LC-NRs are paramagnetically pure. They all show weak antiferromagnetic intermolecular interactions at low temperatures ($\theta_W < 0$).

Table 1. Magnetic properties of compounds (\pm)-**1-3**

Compound	EPR ^a		SQUID	
	g	a_N [mT]	C^b [emu K mol ⁻¹]	θ_W^c [K]
1	2.0059	1.34	0.375	-0.28
2	2.0059	1.34	0.379	-0.11
3	2.0059	1.33	0.387	-0.05

^aMeasured as THF solutions at room temperature. ^bCurie constant. ^cWeiss temperature.

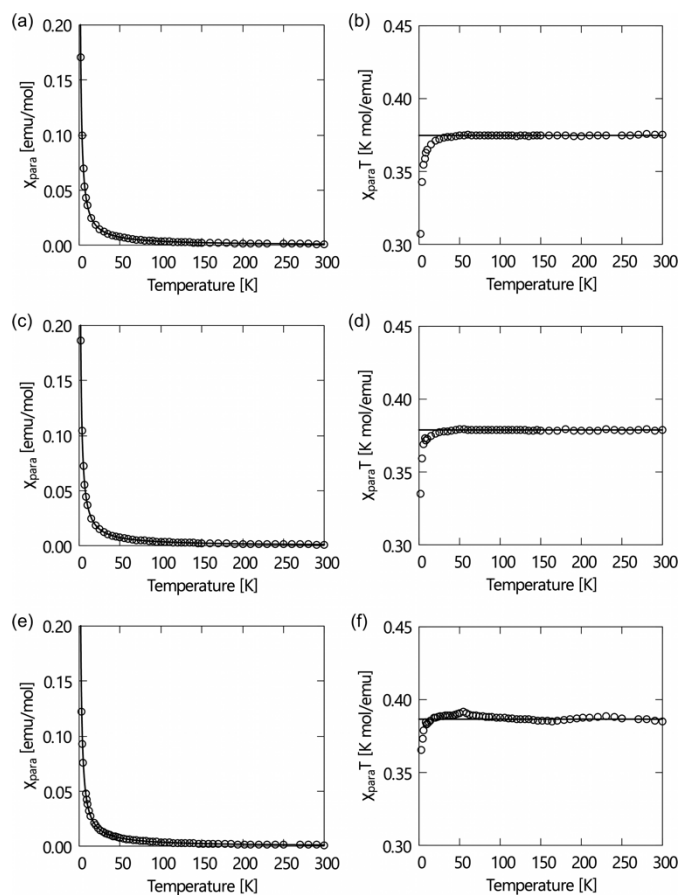


Figure 1. Magnetic properties of the newly synthesised compounds. Temperature dependences of molar paramagnetic susceptibility (X_{para}) and $X_{para}T$ - T plots of (a), (b) (\pm)-**1**, (c), (d) (\pm)-**2** and (e), (f) (\pm)-**3** at a field of 0.5 T in the heating process (2–300 K). Open circles represent the experimental data, solid lines in (a), (c) and (e) show Curie-Weiss fitting curves, and solid lines in (b), (d) and (f) are horizontal lines at 0.375.

Macroscopic phase transition behaviours

The phase transition behaviours of (\pm)-**1-3** are characterised by differential scanning calorimetry (DSC) analyses at a scanning rate of 5°C/min upon heating and cooling processes, as shown in **Figure 2** and polarised optical microscopy (POM), as shown in **Figure 3**. During the DSC cooling run, only (\pm)-**2** crystallised from the supercooled nematic (N) phase as soon as phase-transitioned from the isotropic phase, whereas (\pm)-**1**, (\pm)-**3** and (\pm)-**4** showed the supercooled LC phases, which were kept stable down to around room temperature. We found that (\pm)-**1** displays monotropic N and smectic A (SmA) phases; the POM image shows a Schlieren texture typical of the N phase between two exothermic peaks in the cooling run, as shown in **Figure 3a**. Under rather a weak peak at 51.4°C, as shown in **Figure 2a**, we observed a fan-shaped texture typical of the SmA phase as a natural texture, as shown in **Figure 3b**.²⁴ In addition, we prepared glass sandwich cells, whose inner surfaces of the two glass substrates were coated with CYTOP (AGC Chemicals, Japan) as a homeotropic alignment type aligning agent. No birefringence is displayed where the N and SmA directors orient perpendicular to the substrates; it is called pseudo-isotropic texture.²⁴ Since the pseudo-isotropic texture was maintained under this homeotropic boundary condition to the temperature

range where the crystallisation occurs, we conclude that this supercooled smectic phase is an SmA phase. In the case of (\pm)-**2**, only a monotropic N phase was observed. We found that the monotropic N phase exists in the narrow temperature range between 71.4 and 68.2°C, as shown in **Figure 3b**. The Schlieren texture was observed at 69°C, whereas this supercooled N phase is unstable and coexists with a crystalline (Cr) phase, as shown in **Figure 3c**. We found that (\pm)-**3** showed enantiotropic N and monotropic SmA phases; Schlieren texture was observed in both heating and cooling processes, as shown in **Figure 3d**, while the fan-shaped texture was observed only in the cooling process under weak exothermic peak (65.3°C), as shown in **Figure 3e**. It displayed a pseudo-isotropic texture in the homeotropic boundary condition until a Cr phase appears similar to (\pm)-**1**.

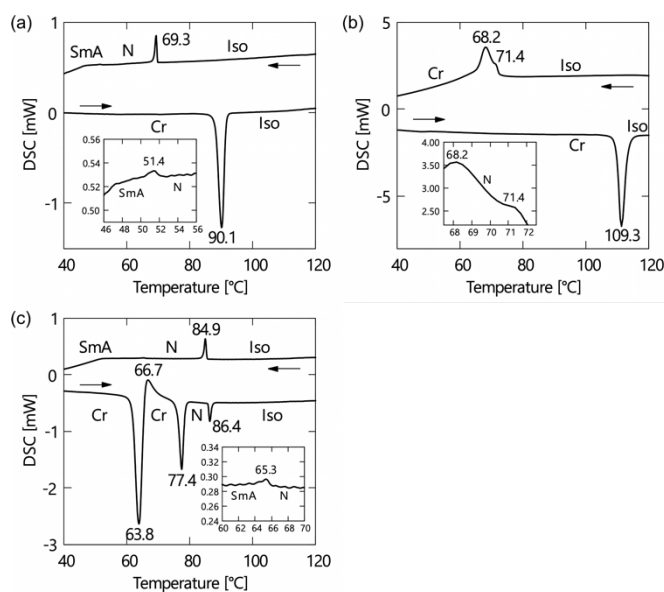


Figure 2. DSC curves of (a) (\pm)-**1**, (b) (\pm)-**2** and (c) (\pm)-**3**. Standard notation gives the transition temperatures between the crystalline (Cr), smectic A (SmA), nematic (N) and isotropic (Iso) phases.

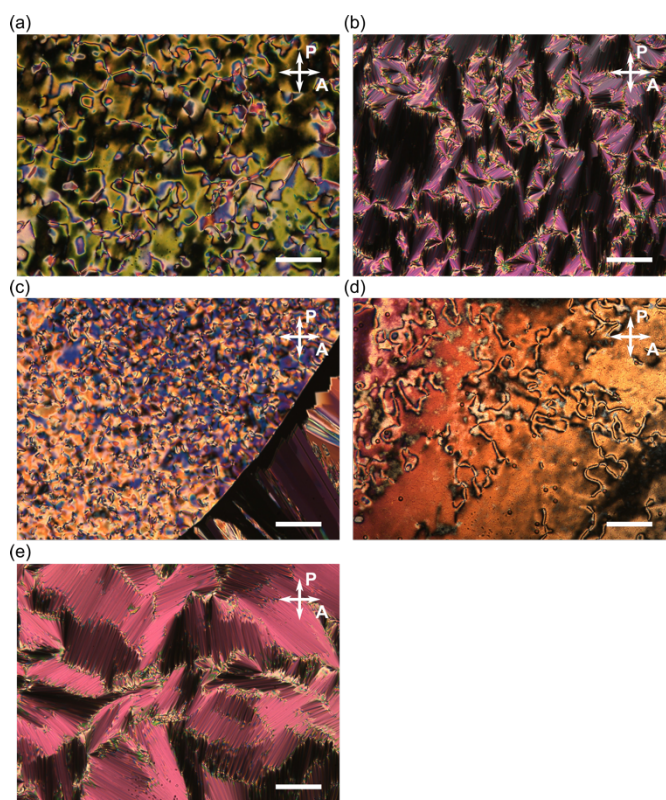


Figure 3. Polarised optical micrographs of (\pm)-**1–3** in the cooling run. (a) A Schlieren texture for the N phase of (\pm)-**1** at 65°C, (b) a fan-shaped texture for the SmA phase of (\pm)-**1** at 45°C and (c) A Schlieren texture for the N phase (centre), an isotropic phase (left) and a Cr phase (right) of (\pm)-**2** at 69°C. (d) A Schlieren texture for the N phase of (\pm)-**3** at 80°C, (e) a fan-shaped texture for the SmA phase of (\pm)-**3** at 55°C. The scale bars correspond to 100 μm .

The comparison of phase transition behaviours is summarised in **Figure 4**, and previously reported NR-LC compound (\pm)-**4** is quoted to discuss the substituent effects.⁴ We can obtain three kinds of information useful for the molecular design of NR-LC compounds; (a) trifluoromethyl group tends to induce a SmA phase, (b) cyclohexane ring promotes the crystallisation and (c) ether oxygen atom stabilises LC phases dramatically.

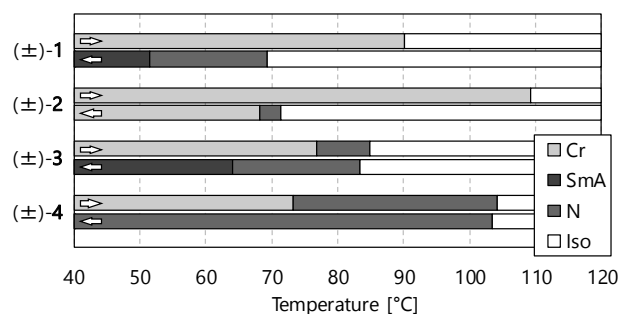
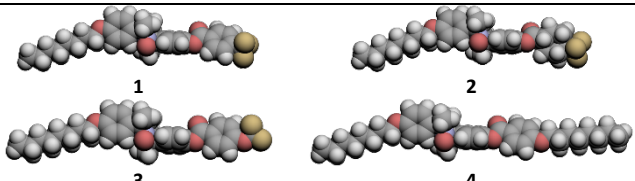


Figure 4. Phase transition behaviors of compounds (\pm)-**1–4**. DSC analyses determined transition temperatures at a scanning rate of 5°C/min upon the heating and cooling run.

Whereas (\pm)-**4** with terminal alkoxy groups shows only an N phase upon both heating and cooling processes, (\pm)-**1** and (\pm)-**3** with trifluoromethyl group as one of the terminal units show SmA phase in the cooling process. Generally, the longer the

terminal chains become, the more the SmA phase stabilises.²⁵ To compare their molecular lengths, we carried out the molecular modelling by DFT calculations at the B3LYP/6-31G** level using the Gaussian 09 program package.²⁶ The results show that the longest radii of the molecular ellipsoids of (\pm)-1–3 are smaller than that of (\pm)-4, as shown in **Table 2**. These results indicate that the trifluoromethyl group is smaller than the octyloxy group, drastically stabilising the SmA phase. We guess that fluorine atoms induce micro-phase separation structure because of their insolubility in hydrocarbon groups, favourable to layer structured SmA phases.²⁷

Table 2. Optimised structures and molecular ellipsoid properties of (\pm)-1–4. These structures were obtained from DFT calculations.



Compound	Long radius [nm]	Short radius [nm]	Aspect ratio [-]
1	3.6899	0.5645	6.537
2	3.7117	0.5992	6.195
3	3.7889	0.5046	7.509
4	4.4505	0.5012	8.879

Compound (\pm)-2 containing cyclohexane ring instead of benzene ring shows about 20°C higher melting point than analogue (\pm)-1. In addition, the temperature range of the supercooled N phase of (\pm)-2 is narrower than that of (\pm)-1. It is due to the difference in the crystallisation behaviours of those; N phase of (\pm)-2 crystallises quickly at 69°C, (\pm)-1 maintains supercooled N phase below 40°C. Considering the clearing points of (\pm)-1 and (\pm)-2 in the cooling process are almost the same, we can conclude that the stability of the N phase is not much different, and flexible cyclohexane ring stabilises only the Cr phase more strongly than rigid benzene ring.

Although structural change between (\pm)-1 and (\pm)-3 is the existence or absence of an ether oxygen atom bound to benzene ring with trifluoromethyl group at the molecular terminal, their phase transition behaviours are quite different from each other. The N phase of (\pm)-3 appears in even heating process, and the N-to-SmA phases transition temperatures of (\pm)-3 in the cooling process are about 14°C higher than that of (\pm)-1. These results indicate that the ether oxygen atom has an important role in the stability of LC phases of NR compounds. The aspect ratio should be considered the origin of this substituent effect; introducing oxygen atom increases the aspect ratio needed for stable LC phases. Furthermore, the change of the mobility and orientation of terminal units could influence the stability of LC phases. Additional works are needed to elucidate these ether oxygen effects.

Microscopic phase transition behaviours

The above analyses indicate that (\pm)-1 and (\pm)-3 exhibit N-to-SmA phase transitions. These phase transitions are further

characterised by X-ray diffraction (XRD) measurement upon the cooling processes (**Figure 5**). XRD measurements of compound (\pm)-3 were carried out in the temperature range of 70–90 °C in the heating process and 80–45 °C in the cooling process. No peak was observed in the N phase during the heating process and between 80 °C and 75 °C during the cooling process (**Figure 5a**). Meanwhile, a diffuse small angle scattering appeared around $2\theta = 3.15$ at 75 °C, and it increases in the N phase upon approaching the N-to-SmA phase transition, in line with a pretransitional formation and growth of some cybotactic clusters. Each correlation length was estimated as a reciprocal of the half-width at half maximum (HWHM) of the diffuse scattering in an XRD pattern in wavenumber space. The correlation lengths are omnidirectional average. The correlation lengths in the N phase are smaller than those in the SmA phase during the cooling process (**Figure 5a**). The *d*-spacing decreased to the N-to-SmA phase transition, though the correlation length steeply increased at the N-to-SmA phase transition, as shown in **Figure 5**. Besides, the correlation length decrease is probably due to the peak disappearing in the crystallization process. These results indicate that the layer order pretransitionally appears like an N-to-N_{cyb} phase transition.

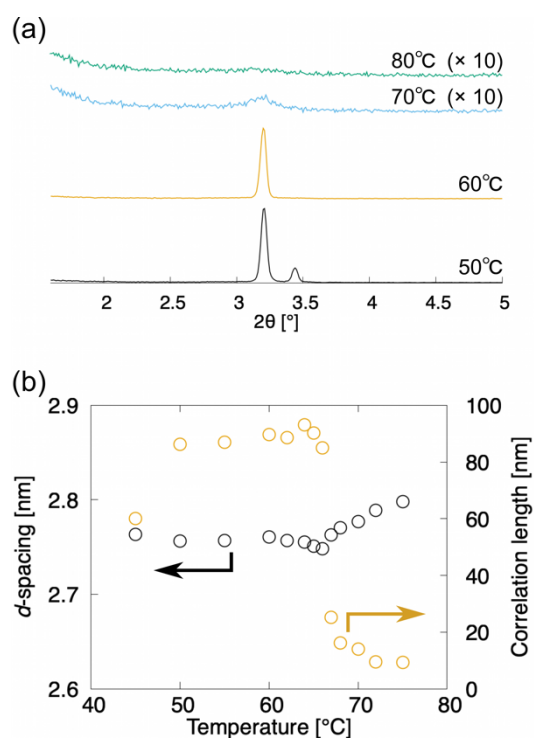


Figure 5. X-ray diffractometry of (\pm)-3 upon the cooling run. Black and orange circles denote the *d*-spacing and the correlation length of the layer structure, respectively.

To track the temperature-dependence of the orientational direction and order of the molecular cores at the appearance of the layer order, we estimated the temperature dependence of *g*-values from EPR spectra for compound (\pm)-3 during the cooling process (**Figure 6a**).^{8,12} The *g*-values continuously increase around 75 °C, as shown in **Figure 6b**, where the layered structure starts to appear, whereas the *g*-values steeply increase around the transition to the SmA phase at 65 °C.

Considering the POM texture did not change at 75 °C, the orientational order of molecular cores gradually increased like the macroscopic orientational order. In addition, although the molecular domains orientate almost randomly in the N and N_{cyb} phases, the molecular domains whose long axis is perpendicular to the magnetic field gradually increase due to the increase of the orientational order. Meanwhile, the natural homeotropic anchoring effect on the glass surface aligns the molecular long axis perpendicular to the magnetic field in the SmA phase.⁸ Although the XRD patterns and *g*-values reflect the direction of the nematic director and the orientational order, we do not know if the molecules belonging to the cybotactic clusters and the rest of the region are swapped or not.

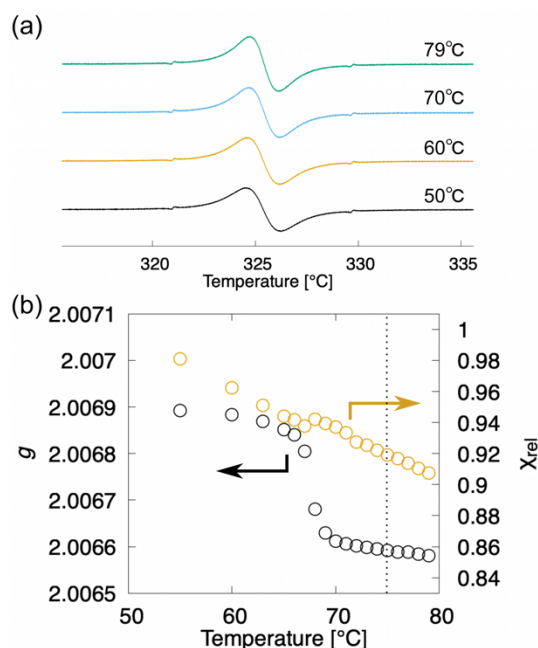


Figure 6. EPR spectroscopy of (±)-**3** upon the cooling run. Black and orange circles denote the *g*-value and χ_{rel} , respectively. Vertical dotted line denotes N-to-N_{cyb} phase transition point.

We focused on the magnetic susceptibility of LC-NRs to discuss the clustering behaviour in the N_{cyb} phase; it reflects molecular mobility and inhomogeneity of intermolecular interactions.²⁸ We estimated the temperature-dependence of relative magnetic susceptibility χ_{rel} during the cooling process from EPR spectra for compound (±)-**3**. As the temperature decreased, χ_{rel} gradually increased, as shown in **Figure 6b**. It looks like a natural behaviour for paramagnetic materials (Curie-Weiss law). Although there was no discontinuity in χ_{rel} around the N-to-N_{cyb} phase transition, χ_{rel} changes a little discontinuously in the N_{cyb}-to-SmA phase transition like previously reported compounds.^{11,29} In general, a certain molecule magnetically interacts with the other molecules at a certain moment. For solid phases, the magnetic susceptibility reflects spatial heterogeneity. In a liquid crystalline phase, the exchange interacting partner molecules are replaced from moment to moment (~ 0.1 ns), and the memory of the interaction remains in the molecules (~ 1 μ s).²⁸ The exchange interactions experimentally averaged out to give the continuous

change in χ_{rel} around the N-to-N_{cyb} phase transition. It indicates that the relaxation time of the memory is many orders of magnitude longer than that of the molecules staying in the clusters. These results indicate that the cybotactic clusters grow gradually, which molecules go into and out of, as shown in **Figure 7**. In addition, the discontinuity in χ_{rel} at the N_{cyb}-to-SmA phase transition is likely attributed to the molecular reorientation.¹¹

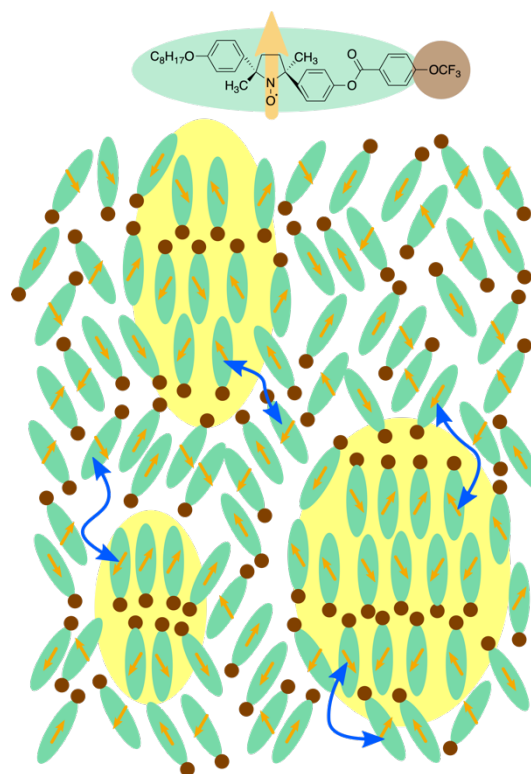


Figure 7. Molecular orientations in and out of the cybotactic cluster. Molecules of (±)-**3** have trifluoromethyl group (brown circles) and electron spins of nitroxide radical moieties (orange arrows). The molecules go into and out of the yellow-colored cybotactic clusters. Blue double-headed arrows denote molecular exchange inside and outside the cybotactic clusters.

Experimental

Instrumentation

Mass spectra were recorded on a JEOL JMS-700. IR spectra were recorded with a SHIMADZU IRAffinity-1 using KBr-pellet technique. Elemental analyses (CHN) were obtained on a PerkinElmer 2400II. The *g*-values and hyperfine coupling constants (a_N) were determined by the EPR spectra of tetrahydrofuran (THF) solution at room temperature. EPR spectra were recorded with a JEOL JES-FE1XG in a magnetic field of about 0.33 T (X-band). Magnetization was recorded with a QUANTUM DESIGN MPMS-3. Phase transition temperatures were determined by differential scanning calorimetry (SHIMADZU DSC-60), X-ray diffraction measurements, and polarized optical microscopy (Olympus BX51). A hot stage (Japan High Tech 10083) was used as the temperature control unit for the microscopy. For variable temperature X-ray diffraction measurements, the data

collections were performed on a Rigaku RINT2200/PC-LH diffractometer using Cu-K α radiation with 0.15418 nm. Unless otherwise noted, solvents and reagents were reagent grade and used without further purification. THF that was used for the EPR spectroscopy was distilled from sodium/benzophenone ketyl under nitrogen.

Materials and synthesis

Dichloromethane (50 mL) was charged with the phenol (0.3 mmol), the carboxylic acid (0.33 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 0.45 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.09 mmol). After the mixture was stirred for 12 h at room temperature, reaction solution was added saturated aqueous NaHCO₃ (50 mL), and extracted with diethyl ether (50 mL \times 2). The extract was dried over MgSO₄ and evaporated. The residue was purified by flash column chromatography on silica gel (hexane/diethyl ether = 8/2 for 1 and 3, and hexane/ethyl acetate = 8/2 for 2) and recrystallized from hexane to afford the ester (\pm)-1–3 as yellow crystals (yield 60–70% from NR-phenol, Scheme 1).

(\pm)-1: IR ν (KBr): 2930, 2859, 1740, 1609, 1508, 1263, 1202, 1074, 1015, 829 cm⁻¹; HRMS: Calcd. for C₃₄H₃₉F₃NO₄ [M]⁺: 582.2831, Found 582.2828; Anal. Calcd. for C₃₄H₃₉F₃NO₄: C, 70.08; H, 6.75; N, 2.40; Found: C, 70.08; H, 6.76; N, 2.41.

(\pm)-2: IR ν (KBr): 2930, 2870, 1749, 1609, 1508, 1339, 1206, 1086, 1003, 829 cm⁻¹; HRMS: Calcd. for C₃₄H₄₅F₃NO₄ [M]⁺: 588.3301, Found 588.3303; Anal. Calcd. for C₃₄H₄₅F₃NO₄: C, 69.36; H, 7.70; N, 2.38; Found: C, 69.31; H, 7.87; N, 2.37.

(\pm)-3: IR ν (KBr): 2930, 2860, 1740, 1508, 1260, 1204, 1171, 1072, 829 cm⁻¹; HRMS: Calcd. for C₃₄H₃₉F₃NO₅ [M]⁺: 598.2780, Found 598.2789; Anal. Calcd. for C₃₄H₃₉F₃NO₅: C, 68.21; H, 6.57; N, 2.34; Found: C, 68.29; H, 6.44; N, 2.25.

Conclusions

We synthesized several LC-NRs with a terminal trifluoromethyl group. The trifluoromethyl group probably induces smectic phases, having layer order. Furthermore, an ether oxygen atom binding the terminal benzene ring especially is likely to stabilise LC phases. One of the new LC-NRs with a trifluoromethoxy group as a terminal group exhibits N and SmA phases in the cooling process. Although POM observation does not suggest forming a layered structure in the N phase, X-ray diffractometry indicates that a pretransitional layer order starts to appear in the N phase. It seems an N_{cyb} phase. EPR spectroscopy uncovered that the interactions between trifluoromethyl groups induce the orientational order of the mesogen core, and the induced cybotactic clusters grow gradually. It also implied that molecules go into and out of the cybotactic clusters from moment to moment.

Author Contributions

Yoshiaki Uchida: Conceptualization, Investigation, Visualization, Writing – original draft.

Takuya Akita: Methodology, Investigation, Visualization, Writing – original draft.

Kazuki Hanada: Methodology, Investigation, Writing – review & editing.

Daichi Kiyohara: Methodology, Investigation, Writing – review & editing.

Norikazu Nishiyama: Supervision, Resources, Writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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