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Observation of positive and negative magneto-LC effects in all-organic nitroxide radical liquid crystals by EPR spectroscopy

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The generation of spin glass-like inhomogeneous magnetic interactions (the average spin-spin interaction constant: \( J > 0 \) or \( J < 0 \)), which we refer to as positive or negative “magneto-LC effects”, respectively, was observed in the bulk liquid crystalline (LC) phases of chiral all-organic radical compounds. This is most likely because of the highly viscous ligand-coordinated metal complex structure, which is in contrast to the small molecular size of 1 responsible for the swift coherent collective behavior of organic molecules in the LC state.

Several other rod-like or discotic all-organic LC nitroxide radical compounds with a DOXYL, TEMPO, or PROYLM group as the spin source at the peripheral position in the molecule had been synthesized and magnetically characterized. These achiral rod-like LCs showed no appreciable magnetic interaction, while the achiral discotic LCs exhibited a weak antiferromagnetic interaction; weak negative magneto-LC effects (\( J < 0 \))

As to the paramagnetic metallomesogens with permanent spins originating from the transition (d-orbital) or lanthanide (f-orbital) metal ion in the mesogen core, such positive magneto-LC effects (\( J > 0 \)) have not been observed. This is most likely because of the highly viscous ligand-coordinated metal complex structure, which is in contrast to the small molecular size of 1 responsible for the swift coherent collective behavior of organic molecules in the LC state.

Liquid crystals (LCs) are unique soft materials that can easily change the molecular orientation or superstructure by the application of external stimuli, such as heat, light and electric or magnetic field, or by adding a chiral dopant, respectively. In this context, paramagnetic liquid crystalline (LC) compounds are fascinating soft materials that can enhance the effect of magnetic fields on the electric, magnetic, and optical properties in LCs.

In fact, although the possibility of a ferromagnetic LC material had been considered to be unrealistic due to the inaccessibility of long-range spin-spin interactions between rotating molecules in the LC state, quite recently we have found that a sort of spin glass (SG)-like inhomogeneous magnetic interactions (the average spin-spin interaction constant \( J > 0 \)) in the vicinity of the mesophase transition were observed in the bulk LC (N, N*, SmC, and SmC*) phases of rod-like all-organic LC nitroxide radical compounds 1 with a positive dielectric anisotropy (\( \Delta \varepsilon < 0 \)) under weak magnetic fields, due most likely to the swift coherent collective properties of organic molecules with structural anisotropy in the LC state. Furthermore, this observation has proved to have nothing to do with the molecular reorientation effect arising from the simple molecular magnetic anisotropy (\( \Delta g \)) by means of variable temperature (VT)-EPR spectroscopy. Thus, we refer to this new magnetic phenomenon as positive “magneto-LC effects” (\( J > 0 \)). Remarkably, these radical LC droplets of 1 floating on water were attracted to a permanent magnet and moved freely on water under the influence of the magnet, whereas these fully crystallized particles never responded to the same magnet on water.
were predicted to have a positive dielectric anisotropy ($\Delta \varepsilon > 0$) by MO calculations (Fig. 1). Here, we report that positive magneto-LC effects ($\overrightarrow{J} > 0$) operate in the chiral nematic (N*) and smectic A (SmA*) phases of 2, whereas negative magneto-LC effects ($\overrightarrow{J} < 0$) are observed in the achiral nematic (N) phase of 2.

The origin of such different magnetic interactions in the LC phases of 2 is discussed on the basis of (i) the temperature dependence of molar magnetic susceptibility ($\chi_m$) measured on a SQUID magnetometer and (ii) the temperature dependence of relative paramagnetic susceptibility ($\chi_{rel}$), g-value, and peak-to-peak line width ($\Delta H_{pp}$) obtained by EPR spectroscopy, which has proved to be an excellent tool to analyze the magnetic interactions operating in the LC phases of all-organic nitroxide radical compounds.

**Derivation of relative paramagnetic susceptibility ($\chi_{rel}$) from EPR spectra**

The EPR spectra of 2a and 2b in the solid and LC states measured at a magnetic field of 0.33 T (X-band) by using a quartz tube (5 mm φ) were Lorentzian in an ambient temperature range (Fig. S2-S4, ESI†). Therefore, by using the parameters directly obtained from the differential curves, such as maximum peak height ($I'_m$ and $-I'_m$), g-value (g) and peak-to-peak line width ($\Delta H_{pp}$), paramagnetic susceptibility ($\chi_{para}$) could be derived from the following Bloch equation:

$$\chi_{para} = 2 \mu_B g I_m \Delta H_{pp} / (\sqrt{3} h v H_1)$$

where $\mu_B$ is Bohr magneton, $h$ is Planck’s constant, $v$ is the frequency of the absorbed electromagnetic wave, and $H_1$ is the amplitude of the oscillating magnetic field. For plotting the temperature dependence of $\chi_{para}$, the relative paramagnetic susceptibility ($\chi_{rel}$), which is defined as

$$\chi_{rel} = \chi_{para} / \chi_0$$

where $\chi_0$ is the standard paramagnetic susceptibility at 30°C in the heating run, was used in place of $\chi_{para}$ to simplify the treatment. The magnetic data are the mean values of five measurements at each temperature to estimate $\chi_{para}$ with maximum accuracy.

**Results and Discussion**

**Characterization of LC Phases of 2**

The LC phases of 2 were characterized by DSC analysis, polarized optical microscopy (POM), and VT-XRD analysis (Fig. 2-4 and S5, ESI†). Enantiomerically enriched (25,5S)-2a (96% ee) showed an enantiotropic N* phase between 75 and 106°C in...
behaviors of (±)2b could not be obtained. Since the calculated molecular length (43.2 Å) of 2b is shorter than those (51.7 and 50.8 Å) obtained from the XRD analyses of (2S,5S)-2b and (±)-2b (Fig. S5b,d, ESI†), it is anticipated that both the SmA* and SmA phases assume a deeply interdigitated molecular arrangement (see Fig. 12d). Thus, we could collect the magnetic data for the stable enantiotropic N*, N, and SmA* phases of (2S,5S)-2a, (±)-2a, and (2S,5S)-2b, respectively.

SQUID Magnetometry

To confirm that the magnetic behavior in the magnetic LC phases is different from that in their crystalline phases and to prove which magnetic interactions are operative in each LC phase, \( \chi > 0 \) or \( \chi < 0 \), we measured the temperature dependence of \( \chi_M \) for the above three samples at a magnetic field of 0.05 or 0.5 T (Fig. S6–S8, ESI†). Here we define the sum of \( \chi_{para} \) and \( \chi_{dia} \) as molar magnetic susceptibility \( \chi_M = \chi_{para} + \chi_{dia} \), because we cannot exactly determine the paramagnetic susceptibility \( \chi_{para} \) in the magnetic LC phases due to the temperature-dependent nature of diamagnetic susceptibility \( \chi_{dia} \) in LC phases. The \( \chi_M \) plots obeyed the Curie-Weiss law in the temperature range between 200 and 300 K \( [\chi_M = C(T - \theta) + \chi_{dia}] \). Weiss constants \( \theta = -0.5, -7.3, \) and \(-1.1 \) K and Curie constants \( C = 0.36, 0.38, \) and 0.36 e.m.u. K mol\(^{-1}\) for (2S,5S)-2a, (±)-2a, and (2S,5S)-2b, respectively, at 0.5 T (Fig. S6c, S7c, and S8c, ESI†), exhibiting the magnetic properties of ordinary paramagnetic radical crystals with weak antiferromagnetic interactions at low temperatures. On the contrary, between 25 and 120°C, we observed a considerable \( \chi_N \) increase (\( \chi > 0 \)) for (2S,5S)-2a and (2S,5S)-2b and a slight \( \chi_N \) decrease (\( \chi < 0 \)) for (±)-2a at the Cr-to-LC phase transition in the heating run (Fig. S6a,b, S7a,b, and S8a,b, ESI†). Since the scatter of the \( \chi_M \) plots for 2a and 2b at higher temperatures was too large to discuss the details of the temperature dependence of the magnetic interactions (Fig. S6–S8, ESI†) and it was impossible to accurately estimate the \( \chi_{para} \) values in the magnetic LC phases due to the variable \( \chi_{dia} \), we used the relative paramagnetic susceptibility \( \chi_{rel} \) value by EPR spectroscopy which allows us to ignore the \( \chi_{dia} \) term, according to our previous work.12

EPR Spectroscopy

The temperature dependence of EPR spectra of (2S,5S)-2a, (±)-2a, and (2S,5S)-2b in the solid and LC states was measured between 30 and 120°C. Although these magnetic data revealed the same tendency as those obtained by SQUID magnetization measurement (Fig. S6–S8, ESI†), those obtained by EPR spectroscopy could distinctly display a more detailed change in \( \chi_{para} \) with full reproducibility. The temperature dependence of relative paramagnetic susceptibility \( \chi_{rel} \) is shown in Fig. 5 (See Experimental section for the definition of \( \chi_{rel} \)).

Indeed, (2S,5S)-2a (96% ee) exhibited an explicit \( \chi_{rel} \) increase (positive magneto-LC effects, \( \chi > 0 \)) by 0.13 at the Cr-to-N* phase transition (75°C) in the heating run (Fig. 5a), while (±)-2a showed a small but a distinct \( \chi_{rel} \) decrease (negative magneto-LC effects, \( \chi < 0 \)) by 0.05 at the Cr-to-N transition (104°C) in the heating run (Fig. 5d). These results suggest that the formation of...
negative magneto-LC effects, or weak antiferromagnetic interactions, in the N phase of (±)-2a.

To prove this hypothesis and evaluate the relationship between the sign and magnitude of magneto-LC effects and the helical pitch length, a chiral dopant was added to (±)-2a to prepare a racemic helical N* phase. (S)-BICH was found to be a more powerful chiral dopant than (-)-TADDOL to induce an N* phase of (±)-2a; addition of 2.5 or 4.0 wt% of (S)-BICH to (±)-2a induced a N* phase with the pitch length of 1.8 or 1.1 μm at 100°C, respectively (Fig. 6 and S9e,f, ESI†), while 5 wt% of (-)-TADDOL led to that of 8 μm at 80°C (Fig. S9d, ESI†). Consequently, almost no influence of chiral dopants, or the helical pitch length, on the magneto-LC effects was noted (Fig. 7).

Next, to clarify the effects of the ee value of 2a on the sign and magnitude of magneto-LC effects, the temperature dependence of EPR spectra of 2a with 40% ee and 60% ee was measured. As the ee value decreased, the helical pitch elongated (Fig. 6 and S9a-c, ESI†). As a consequence, a χrel increase (positive magneto-LC effects) by 0.04 at the Cr-to-N* transition (77°C) was noted in the N* phase (the pitch length of 1.2 μm at 80°C) of 60% ee in the heating run (Fig. 5b), while the N* phase (the pitch length of 1.6 μm at 100°C) of 40% ee showed a χrel decrease (negative magneto-LC effects) by 0.02 at the Cr-to-N* transition (102°C) in the heating run (Fig. 5c). These results indicate that as the ee value increases, the RS magnetic dipolar interaction reduces in the N* phase and thereby the positive magneto-LC effects turn out to prevail over the negative ones.

Thus, the origin of the negative magneto-LC effects observed in the N phase could be understood in terms of the formation of the RS magnetic dipolar interaction due to the strong electric dipole interactions (Δε > 0), which results in the generation of weak antiferromagnetic interactions, even in the chiral dopant-induced racemic helical N* phase.

In the case of (2S,5S)-2b (89% ee), during the heating process, the χrel increased by as large as 0.20 at the Cr-to-SmA* transition (87°C) and by additional 0.07 at the SmA*-to-Isa transition (104°C) (Fig. 8a). The χrel values in the SmA* phase of (2S,5S)-

![Fig. 5](image1.png)

**Fig. 5** Temperature dependence of χrel value for 2a at a magnetic field of 0.33T. (a) (2S, 5S)-2a (96% ee), (b) (2S, 5S)-2a (60% ee), (c) (2S, 5S)-2a (40% ee), and (d) (±)-2a. The LC temperatures determined by DSC analysis in the heating run are shown in the lower sides inside panels. The insets indicate the magnification of χrel vs T plots. The LC temperatures inside the insets refer to the heating run.

either a non-helical superstructure or an RS magnetic dipolar interaction should be responsible for the generation of the weak

![Fig. 6](image2.png)

**Fig. 6** Temperature dependence of helical pitch length measured by using a wedge cell in the cooling run. Open and filled squares, and open circles correspond to (2S,5S)-enriched 2a of 96% ee, 60% ee, and 40% ee, respectively. Filled circles and open triangles denote (±)-2a doped with 2.5 and 4.0 wt% of (S)-BICH, respectively.
2b in the cooling run were much larger than those in the heating run, implying the large difference in the magnetic interactions in the same SmA* phase between the two processes. This unusual magnetic behavior in the SmA* phase of (2S,5S)-2b can be explained by the difference in the LC domain size between the heating and cooling runs (Fig. 9c); the larger the domain size, the larger the magnetic interactions. Meanwhile, as expected, almost no difference in the domain size was noted between the heating and cooling runs in the N* and N phase of 2a (Fig. 9a,b).

Thus, in the heating run, (2S,5S)-2a (96% ee) and (2S,5S)-2b (89% ee) showed a considerable net $\chi_{rel}$ increase (0.13 and 0.20) at the Cr-to-N* and Cr-to-SmA* phase transitions, respectively (Fig. 5a and 8a), whereas ($\pm$)-2a exhibited a small but distinct $\chi_{rel}$ decrease (0.05) at the Cr-to-N phase transition (Fig. 5d). In other words, larger positive magneto-LC effects ($J > 0$) operated in the SmA* phase of (2S,5S)-2b than in the N* phase of (2S,5S)-2a, whereas small negative magneto-LC effects ($J < 0$) was noted in the N phase of ($\pm$)-2a, compared to their crystalline phases. It is noteworthy that the $\chi_{rel}$ value of 1.4 observed in the SmA* phase of (2S,5S)-2b in the cooling run is the largest of all magnetic LC phases of 1 and 2 (Fig. 8a).12

![Fig. 7](image)

**Fig. 7** Temperature dependence of $\chi_{rel}$ value for ($\pm$)-2a in the presence of a chiral dopant at a magnetic field of 0.33T. (a) 5 wt% of (-)TADDOL, (b) 2.5 wt% of (S)-BICH, and (c) 4.0 wt% of (S)-BICH. The LC temperatures determined by DSC analysis in the heating run are shown in the lower sides inside panels. The insets indicate the magnification of $\chi_{rel}$ vs T plots. The LC temperatures inside the insets refer to the heating process.

![Fig. 8](image)

**Fig. 8** Temperature dependence of (a) $\chi_{rel}$, (b) $\Delta H_{pp}$, and (c) g values for (2S,5S)-2b (89% ee) by EPR spectroscopy at a magnetic field of 0.33 T. The LC temperatures determined by DSC analysis in the heating and cooling runs are shown in the lower and upper sides inside panels, respectively.
crystallized N droplet of (±)-2a floating on water was explicitly attracted by both the N and S poles of the magnet (Movies S1-S3), while these fully crystallized particles on water never responded to the same magnet. This behavior was fully reproducible, indicating that the threshold magnetic field required to attract crystalline paramagnetic particles by the magnet is much larger than that required for attracting magnetic LC droplets due to the increasing interfacial interaction between the crystalline particle and water.

Interestingly, the SmA* droplet of (2S,5S)-2b responded to the action of the magnet more quickly than the N* droplet of (2S,5S)-2a, while the partially crystallized N droplet of (±)-2a moved very slowly (Movies S1-S3). These results suggest that the difference in the response of these LC droplets to the magnet should depend not only on the interfacial interaction between the LC droplet and water but also on the sign and magnitude of applied magnetic field.

**Response of LC Droplets on Water to the Action of a Permanent Magnet**

To compare the extents of magneto-LC effects in these three LC phases visually, we watched how individual LC droplets and crystallized particles of (2S,5S)-2a (96% ee), (±)-2a, and (2S,5S)-2b (89% ee) on water behaved under the influence of a permanent magnet. The LC droplet with a diameter of 1~5 mm was prepared by floating the melted LC compound on hot water at 75°C by using a small plastic spatula. Generally, a sufficiently strong magnet can attract any paramagnetic materials. As an ordinary rod-like rare-earth magnet (maximum 0.5 T, 6 mm φ x 20 mm) approached (Fig. S10, ESI†), the respective N* and SmA* droplets of (2S,5S)-2a and (2S,5S)-2b, and the partially

![Image](https://repository.kulib.kyoto-u.ac.jp/)
magneto-LC effects. As expected, the difference in the $\chi_{\text{rel}}$ value of these three magnetic LC phases at 75°C on the cooling run was consistent with that in the response to the action of a permanent magnet in the increasing order of $N < N^* < \text{SmA}^*$ (Fig. 5 and 8), although the N droplet was partially crystallized on water.

**Origin of Magneto-LC Effects**

In our previous paper, it was proved that the generation of positive magneto-LC effects has nothing to do with the molecular reorientation effect arising from the magnetic anisotropy ($\Delta \gamma$). To gain an insight into the origin of the negative or positive magneto-LC effects ($\overline{J} < 0$ or $\overline{J} > 0$) operating in the N and doped-N* phases of (±)-2a or in the N* phase of (2S,5S)-2a and SmA* phase of (2S,5S)-2b, respectively, the temperature dependence of $\Delta H_{pp}$ and $g$ values was compared with that of $X_{\text{rel}}$ for these samples (Fig. 5, 7, 8, 10, and 11). This is because 1) the change in $\Delta H_{pp}$ reflects the following two competing factors, (a) spin-spin dipole interaction (the stronger the interaction is, the more the $\Delta H_{pp}$ increase is) and (b) spin-spin exchange interaction (the stronger the interaction is, the more the $\Delta H_{pp}$ decrease is) and 2) the change in $g$ value corresponds to that in the molecular orientation in the magnetic field.

In the case of (±)-2a, a slight increase in $\Delta H_{pp}$ occurred in concert with the slight decrease in $X_{\text{rel}}$ at the Cr-to-N transition in the heating run, irrespective of the presence of chiral dopants and the $g$ value change (Fig. 5d, 7, 10h, and 11), indicating the increase of spin-spin dipole interactions in both the N and chiral dopant-induced N* phases of (±)-2a. Accordingly, it is quite natural to consider that the negative magneto-LC effects operating in the N phase of (±)-2a originate from the generation of antiferromagnetic interactions due to the local SOMO-SOMO overlapping in the strong RS magnetic dipolar interaction in which the side-by-side spin-spin dipole interaction should operate (Fig. 12a,b).

In contrast, at the Cr-to-N transition of (2S,5S)-2a (96% ee), both $\Delta H_{pp}$ and $X_{\text{rel}}$ distinctly increased without no molecular reorientation in the magnetic field (Fig. 5a and 10a,b), reflecting the generation of the energetically favored ferromagnetic head-to-tail spin-spin dipole interactions (Fig. 12c), as observed in the N* phase of 1,12

In the case of (2S,5S)-2b (89% ee), the large $g$ value (2.0069) in the SmA* phase having a large LC domain size formed by cooling from the isotropic phase indicates that the majority of molecular long axes aligned perpendicular to the magnetic field (Fig. 8c). In harmony with this behavior, the substantial $X_{\text{rel}}$ increase occurred in the SmA* phase with a deeply interdigitated layer structure, together with a slight $\Delta H_{pp}$ decrease due to the

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**Fig. 11** Temperature dependence of $\Delta H_{pp}$ and $g$ values for (±)-2a in the presence of a chiral dopant at a magnetic field of 0.33T. (a,b) 5 wt% of (−)-TADDOL, (c,d) 2.5 wt% of (S)-BICH, and (e,f) 4.0 wt% of (S)-BICH. The LC temperatures determined by DSC analysis in the heating and cooling runs are shown in the lower and upper sides inside panels, respectively.

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**Fig. 12** Schematic illustration of spin-spin dipole interactions in LC phases. (a) N phase of (±)-2a, (b) N* phase of (±)-2a with a chiral dopant, (c) N* phase of (2S,5S)-2a, and (d) SmA* phase of (2S,5S)-2b.
increased spin-spin exchange interactions (Fig. 8a,b). Therefore, in the SmA* phase, ferromagnetic head-to-tail spin-spin dipole interactions should dominate, too (Fig. 12d).

Conclusions

Chiral all-organic LC nitroxide radical compounds 2 with a positive dielectric anisotropy (Δε > 0) showing a chiral N* or SmA* phase, or an achiral N phase exhibited unique magnetic behaviors which are different from those of LC compounds 1 with a negative dielectric anisotropy (Δε < 0) displaying chiral N* and/or SmC* phases, or an achiral N and/or SmC phases. Under weak magnetic fields, larger positive magneto-LC effects (∆< 0) operated in the SmA* phase of (25,55)-2b than in the N* phase of (25,55)-2a, while small negative magneto-LC effects (∆> 0) were observed in the N phase of (±)-2a, which was in contrast to the N phase of (±)-1 showing positive magneto-LC effects (∆> 0). The origin of such negative magneto-LC effects operating in the N phase of (±)-2a was interpreted in terms of the generation of antiferromagnetic interactions which is associated with the formation of the RS magnetic dipolar interaction due to the strong electric dipole interactions. Therefore, although addition of chiral dopants to the N phase resulted in the formation of the racemic N* phase of 2a, the sign and magnitude of the magneto-LC effects did not change. These experimental results strongly suggest that positive magneto-LC effects could be induced in discotic magnetic LC phases15,16 by introducing chirality into the molecules so as to avoid the discotic dimer formation.

Furthermore, among the bulk N*, SmC*, SmA*, N, and SmC phases of all-organic LC nitroxide radical compounds (1 and 2) which we have prepared thus far, the SmA* phase of (25,55)-2b displayed the largest positive magneto-LC effects (∆> 0). Moreover, it should be emphasized that VT-EPR spectroscopy is an excellent means to analyze the magnetic interactions operating in the LC phases of all-organic nitroxide radical compounds.

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Notes and references


