

## Magnetic properties of organic radical fibers aligned in liquid crystals

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**Abstract** – Liquid crystalline (LC) gels composed of an amino acid-based gelator having a (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) moiety (**1**) and a cyanobiphenyl compound (**2**) were developed to obtain organic radical fiber aligned in one direction. The magnetic properties of the LC gels were examined with superconducting quantum interference device (SQUID) magnetometer, while LC gels of amino acid-based gelators without TEMPO moieties (**Ref**) have been also measured for a reference. Magnetic susceptibility measurement of non-oriented sample suggested that **1** + **2** is a paramagnet with antiferromagnetic interaction between spins in TEMPO moieties. The super-exchange interaction constant  $J$  was estimated as  $-0.88(6) \text{ cm}^{-1}$ . Decrease of diamagnetic susceptibility by magnetic field orientation was observed: 9.9(2)% for **1** + **2** and 5.6(1)% for **Ref** + **2**. On the other hand, no change of spin magnetic susceptibility was observed. The origin of this change was found to be orientated liquid crystal molecules along applied magnetic field. The change ratio of diamagnetic component showed dependence on the combined gelator: the value of **1** + **2** is approximately twice as large as that of **Ref** + **2**. The origin of gelator dependency was expected to be the difference in the orientation degree induced by dissimilar viscosity or assembled structure, whereas the interaction between spins are maintained.

**About authors** – Yoshikazu Umeta: His research interest lies in synthesis and physical property measurements of metal complexes. In this study, Y. U. performed magnetic field orientation experiments and magnetization measurements. Hiroki Eimura: His research interest lies in organic synthesis, supramolecular chemistry. In this study, H. E. performed preparation of materials, ESR measurements, and discussion related to magnetic field orientation of liquid crystals.

**Trigger for this research** – H. E. gave presentations about materials in this research in MERIT camp and Colloquium. Then, Y. U. was interested in them and proposed measuring the magnetic properties of these samples.

### 1. Introduction

Self-organization process is a promising approach to control assembled structures of functional organic materials, which critically determine material properties.

It is notable that the ordered structure at nano-meter scale can be spontaneously obtained in self-organization without high energy consumption.<sup>[1]</sup> In the past dozen years, it has been demonstrated that self-assembly of

liquid crystals and fibrous aggregates enables us to develop a variety of functional soft materials including anisotropic charge transport and stimuli responsive fluorescence materials. Recently, research interest in molecular assembly has gradually shifted from nano to micro scales, in order to significantly reduce the properties of molecules. For example, macroscopic alignment of self-assembled fibers was achieved by using liquid crystals as an anisotropic solvent.<sup>[2]</sup>

From another point of view, organic radicals are expected as organic magnetic materials due to magnetic moments derived from these odd electrons. Magnetic properties of organic radicals in bulk are expected to be highly dependent on arrangement of radical moieties, which is incorporated into self-assembled structures of organic radical molecules.

Our groups reported that an amino acid derivative having a (2,2,6,6-Tetramethylpiperidin-1-yl) oxyl (TEMPO) moiety self-organize into fibrous aggregates in dodecane solution, which resulted in formation of gels. In the study, magnetic measurements of the gels were performed, which showed that magnetic interactions between the organic radical molecules are induced by formation of the fibrous nanostructure via self-assembly.<sup>[3]</sup> Significantly, the previous research propose that self-assembly into fibrous structures is effective for tuning of magnetic properties of organic radicals. However, effect of the macroscopic structures on magnetic properties is unexplored.

Here, we developed macroscopically aligned self-assembled radical fibers in liquid crystals. The oriented organic radical assembly was obtained by using a new amino acid derivative having a rigid phenyl group as linker between organic radical and hydrogen bonding moieties. In order to reveal effect of the macroscopic structures on magnetic properties, we measured the

magnetic properties of aligned self-assembled fiber having organic radical moieties in liquid crystals.

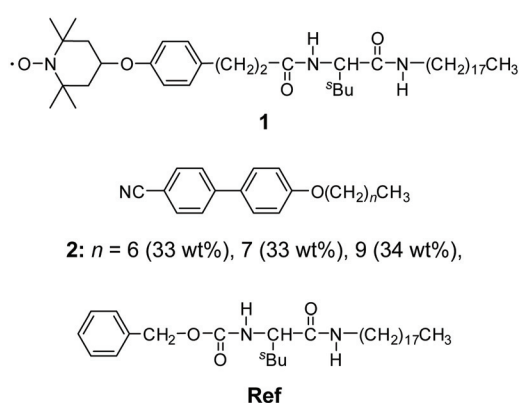
## 2. Experimental

### 2.1. Material

Figure 1 shows materials used in this study. An amino acid-based gelator having (2,2,6,6-Tetramethyl-piperidin-1-yl) oxyl (TEMPO) moiety (**1**) was synthesized through Mitsunobu reaction, hydrolysis reaction, and EDC coupling. Mixtures of compound **1** and liquid crystal **2** were stirred for 30 minutes at 383 K to yield homogeneous mixtures (**1** + **2**). Mixtures (**Ref** + **2**), which contains **Ref** instead of **1** as a gelator, were also prepared in the same procedure. A differential scanning calorimetry measurement indicated that LC gel **1** + **2** exhibits phase transition to isotropic phase (liquid) at 348 K on heating.

### 2.2. Magnetic property measurement

Electron paramagnetic resonance (ESR) spectra were recorded using a JEOL JES-FA200 X-band ESR spectrometer at room temperature and 373 K with center field of 322 mT, sweep time of 2 minute, sweep width 25 mT, microwave frequency of 9 GHz, modulation width



**Figure 1.** Chemical structures of compounds used in this study. Compound **1** is an amino acid-based gelator bearing a TEMPO moiety as an organic radical moiety. Compound **2** is a smectic liquid crystalline mixture. Compound **Ref** has no organic radical group and was used for estimation of magnetic susceptibility derived from diamagnetism in mixtures (**1** + **2**).

of 0.1 mT, and power of 50 mW. Manganese oxide was used as an external standard. Magnetic susceptibility measurements were performed using a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer. Temperature sweep measurements from 280 K to 2 K were conducted with external magnetic field of 0.5 T. Samples were held in aluminum cells.

### 2.3. Sample preparation

We macroscopically oriented liquid crystals and organic radical fibers by the following method using magnetic field. The samples were heated on a hot plate set 403 K to prepare isotropic phase samples. To realize magnetic field orientation of LC gels, the isotropic phase samples (liquid) were inserted into a 8 T superconducting magnet and then kept for 2 hours to cool the samples to room temperature. This thermal treatment using magnet allows appearance of nematic phase under magnetic field, which is important for magnetic field orientation of LC gels. We carried out this procedure without magnetic field to evaluate magnetic property of non-oriented sample. And then, we applied a magnetic field of 8 T with the superconducting magnet. These processes were repeated three times to confirm repeatability. Magnetic property measurements was conducted the same samples passing each process.

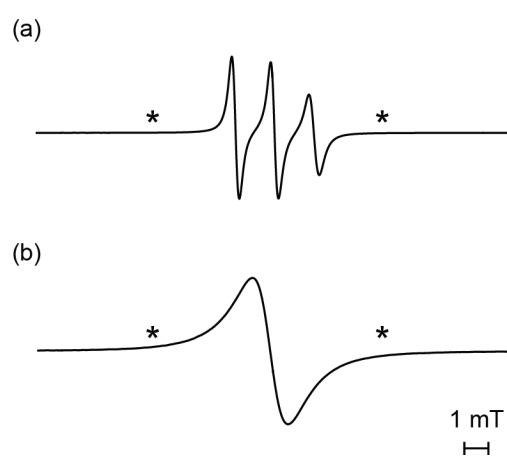
### 2.4. Correction of magnetic susceptibility

Observed magnetic susceptibility  $\chi_{\text{obs}}$  was assumed to be a summation of spin magnetic susceptibility  $\chi_{\text{spin}}$  and diamagnetic susceptibility  $\chi_{\text{dia}}$  ( $\chi_{\text{obs}} = \chi_{\text{spin}} + \chi_{\text{dia}}$ ). Spin magnetic susceptibility of **1 + 2** was calculated by subtracting observed magnetic susceptibility of **Ref + 2**. In order to estimate change ratio by magnetic orientation, differences of magnetic susceptibility in a range of 50 K to 280 K, where there is no interaction between spins.

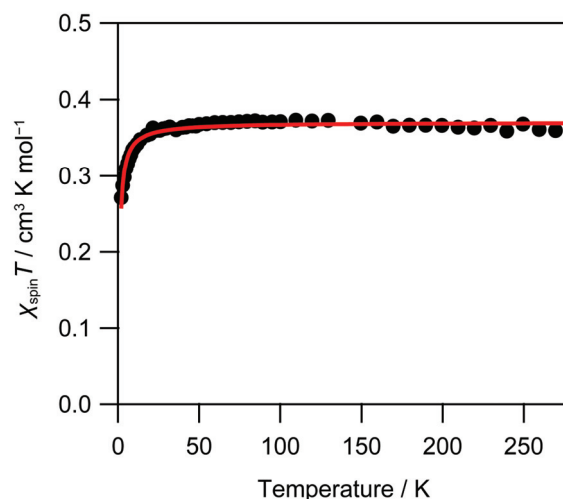
## 3. Results and discussion

### 3.1. Magnetic properties of non-oriented sample

Figure 2 shows electron paramagnetic resonance (ESR) spectrum of **1 + 2**. Three non-equivalent peaks were observed at 373 K, while only one broad peak at room temperature.  $g$  value at 373 K was estimated to be 2.006. The peak splitting at 373 K is due to hyperfine coupling splitting which is observed in a TEMPO moiety. **1 + 2** shows isotropic phase (liquid) at 373 K and



**Figure 2.** ESR spectra of **1 + 2** (a) at 373 K and (b) at room temperature. Asterisks show positions of signals from  $\text{Mn}^{2+}$  as an external standard.



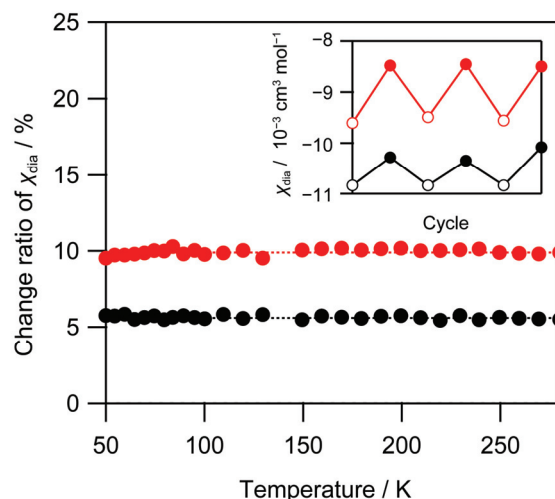
**Figure 3.** Temperature dependence of  $\chi_{\text{spin}}T$  of **1 + 2**. Black close circles show observed value and a red line shows the fitting curve by Bonne-Fisher model.

crystalline phase (solid) at room temperature. The extinction of hyperfine coupling splitting was expected to be due to an interaction between spins arising from alignments of TEMPO moieties and restraint of molecular motion in a highly viscous environment.

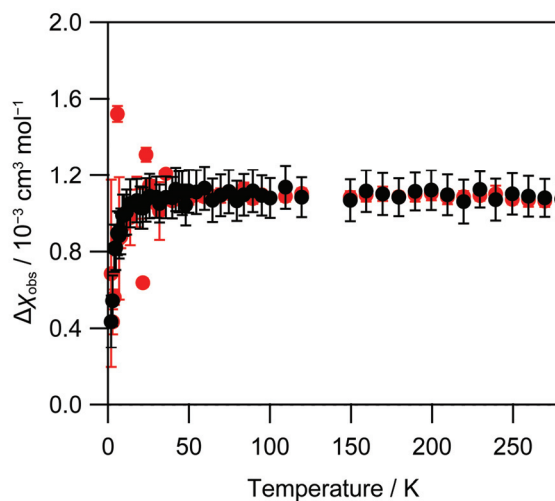
Figure 3 describes the temperature dependence of  $\chi_{\text{spin}}T$  values.  $\chi_{\text{spin}}T$  values show an almost constant value in a range of 280 to 50 K and decrease below 50 K. The constant  $\chi_{\text{spin}}T$  value in the range of 280 to 50 K was considered to be a result of a Curie-Weiss-like behavior and the  $\chi_{\text{spin}}T$  value was  $0.359 \text{ cm}^3 \text{ K mol}^{-1}$  at 280 K. The value is 95.7% of  $0.375 \text{ cm}^3 \text{ K mol}^{-1}$ , which is expected in a  $S = 1/2$  paramagnet. The decrease of the  $\chi_{\text{spin}}T$  value below 50 K indicated antiferromagnetic interaction between spins in **1 + 2**. The organic radical parts in **1** are revealed to make one-dimensional alignment in complexes with **2** in nano-scale. Bonner-Fisher model, which is known as a model describing a paramagnet with antiferromagnetic interaction between the nearest sites ( $H = -J \sum S_i S_{i+1}$ ) in one-dimensional alignment like this system.<sup>[4]</sup> Then, in order to estimate the strength of antiferromagnetic interaction (superexchange interaction constant  $J$ ) between spins in TEMPO moieties, the experimental value was fitted to the Bonner-Fisher model with a spin value of  $S = 1/2$  on each site, written as follows.

$$\chi_{\text{spin}} = \frac{Ng^2\mu_B^2}{kT} \cdot \frac{0.25 + 0.074975x + 0.075235x^2}{1 + 0.9931x + 0.172135x^2 + 0.757825x^3}$$

Here,  $x$  is  $|J|/kT$  and the  $g$  value is 2.006, which was obtained by the ESR measurement. The  $J$  value and a residue factor ( $R = \sum[(\chi_{\text{spin}})_{\text{exp}} - (\chi_{\text{spin}})_{\text{calc}}]^2 / \sum[(\chi_{\text{spin}})_{\text{exp}}]^2$ ) are estimated as  $-0.88(6) \text{ cm}^{-1}$  and  $1.2 \times 10^{-3}$ , respectively. The  $J$  value is almost identical with that of self-organization fiber analogue ( $J = 0.99(1) \text{ cm}^{-1}$ ) in a previous study.<sup>[3]</sup> This  $J$  value consistency suggests the existence of the same interaction between spins.



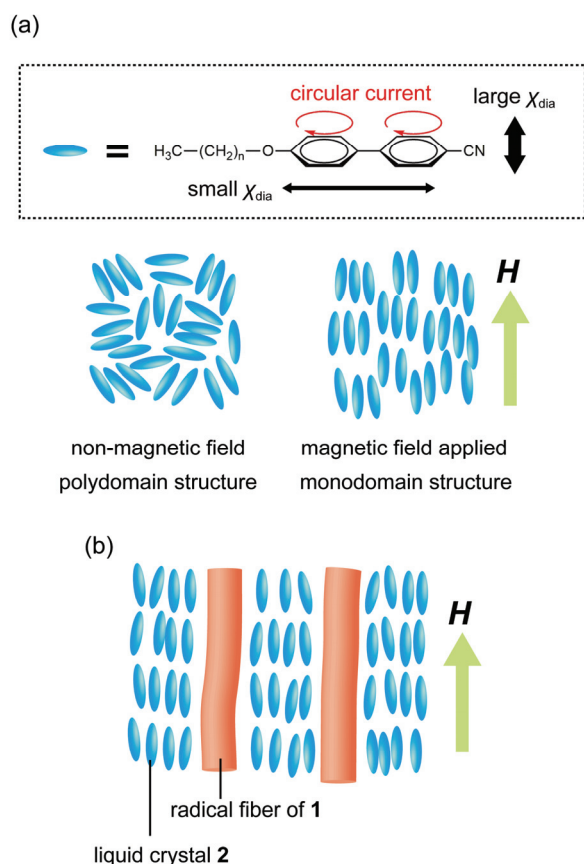
**Figure 4.** Temperature dependence of the fraction of diamagnetic susceptibility change by magnetic field orientation of **1 + 2** and **Ref + 2**. The close red and black circles describe the fraction of change of diamagnetic susceptibility of **1 + 2** and **Ref + 2**, respectively. Inset: diamagnetic susceptibility ( $\chi_{\text{dia}}$ ) of **1 + 2** and **Ref + 2** in each cycle. Open red circle: **1 + 2** (non-orientated); open black circle: **Ref + 2** (non-orientated); Open red circle: **1 + 2** (orientated); open black circle: **Ref + 2** (orientated).



**Figure 5.** Temperature dependence of the magnetic susceptibility ( $\chi_{\text{obs}}$ ) change by magnetic field orientation of **1 + 2** (red circle) and  $1.8 \times$  scaled that of **Ref + 2** (black circle).

### 3.2. Magnetic properties of oriented sample

Figure 4 shows the temperature dependences of diamagnetic susceptibility of non-orientated and orientated samples in a range of 50 to 280 K. Both **1 + 2** and **Ref + 2** show a decrease of diamagnetic susceptibility,



**Figure 6.** Schematic illustrations of response behaviors of liquid crystal alone (a) and LC gel of smectic liquid crystal and amino acid-based gelator (b) to magnetic field.

whereas change ratio are different (Figure 4). The change ratio are estimated as 9.9(2)% and 5.6(1)% for **1 + 2** and **Ref + 2**, respectively.

The temperature dependence of the magnetic susceptibility change of **1 + 2** and **Ref + 2** in an assumption, in which **1 + 2** and **Ref + 2** has a same fraction of change, are depicted in Figure 5. Dispersing values of **1 + 2** below 50 K are thought to be caused by the difference of measurement range: **1**'s paramagnetic component and **2**'s diamagnetic one are different. The change ratio for **1 + 2** and **Ref + 2** agree within error margin. Therefore, the change induced by magnetic field orientation is derived from not organic radical component but diamagnetic one. This result indicates that the changes of organic radical moieties alignments

in nanoscale are limited enough to maintain the interaction between spins. In addition, the change ratio is significantly larger than the amount of gelling agent (2 mol%). This exceedance suggests that the changes of observed magnetic susceptibility are derived from a response of liquid crystal molecules.

Figure 6 shows change mechanism of magnetic susceptibility by magnetic field orientation. Liquid crystals are known to respond to magnetic field and align parallel to the magnetic field direction.<sup>[5]</sup> Phenyl group shows larger diamagnetism in the out-plane direction than in-plane because diamagnetic ring current on the phenyl ring is induced under magnetic field. In the magnetic susceptibility measurements, magnetic susceptibility in the magnetic field direction was observed. The decrease of magnetic susceptibility by magnetic field orientation is consistent with innate response properties of liquid crystals to magnetic field. Therefore, we conclude that the thermal treatments under magnetic field lead to macroscopic alignment of LC mixtures in the sample. The fraction of the magnetic susceptibility change for **1 + 2** was approximately twice as large as for **Ref + 2**, suggesting different orientation between **1 + 2** and **Ref + 2**. This effect of gelators on the orientation degree may result from difference of viscosity between **1 + 2** and **Ref + 2** or self-assembled structures between **1** and **2**.

#### 4. Conclusion

Magnetic susceptibility of amino acid-based gelators with and without an organic radical moiety **1** and **Ref** in liquid crystals **2** was measured. Macroscopically aligned LC mixtures were obtained by thermal treatment under magnetic field using superconductive magnet. Magnetic properties of the oriented samples were also examined with SQUID measurements in order to reveal effect of magnetic field orientation on magnetic properties.

Magnetic susceptibility measurements of non-oriented sample suggested that **1 + 2** is a paramagnet with antiferromagnetic interaction between spins in TEMPO moieties. The super-exchange interaction constant  $J$  is estimated as  $-0.88(6) \text{ cm}^{-1}$ . Decrease of diamagnetic susceptibility by magnetic field orientation was observed: 9.9(2)% for **1 + 2** and 5.6(1)% for **Ref + 2**. On the other hand, no changes of spin magnetic susceptibility were observed. This change is found to be due to orientation of liquid crystal molecules along applied magnetic field. The change ratio of diamagnetic component showed dependence on the combined gelator: the value of **1 + 2** is approximately twice as large as that of **Ref + 2**. The gelator dependency was probably caused by the difference in the orientation degree due to dissimilar viscosity or assembled structure, whereas the interactions between spins are maintained.

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