Electronic Supplementary Information

Spin Crossover Characteristics of Nanofibrous Fe^{II}-1,2,4-Triazole Complexes in Liquid Crystals

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[1] Experimental

Materials: [Fe(**1**)$_3$]Cl$_2$ was synthesized according to the literature. Nematic liquid crystals **JC-1041XX** and **JD-1002XX** were gifts from Chisso Co. Ltd. The [Fe(**1**)$_3$]Cl$_2$/liquid crystal hybrids were prepared by mixing chloroform solutions of liquid crystals (0.9 g in 1 mL) and [Fe(**1**)$_3$]Cl$_2$ (0.1 mg in 1 mL chloroform) in a sealed sample tube at 0 °C. The mixtures were lyophilized and kept at room temperature.

***Measurement*:** In optical microscopic observation, homogeneous mixtures of [Fe(**1**)$_3$]Cl$_2$ and low-molecular-weight liquid crystals was filled into glass cells. The cell thickness was adjusted to 20 μm by using poly(ethylene terephthalate) film spacers. Optical textures of the cells were observed under a polarizing optical microscope (ECLIPSE E600 POL, Nikon Co.) equipped with a hot stage calibrated to an accuracy of ± 0.1 K. Reflectance spectra of [Fe(**1**)$_3$]Cl$_2$/liquid crystals were measured by using Multichannel Photodetector System (MCPD-7000, Otsuka electronics Co. Ltd.)). Transmission electron microscopy was conducted on a JEOL JEM-2010, operating at 120 kV with cryo-system (77 K). Specimens of transmission electron microscope were prepared by transferring the surface layer of liquid crystal gels on carbon-coated TEM grids.[44] Differential scanning calorimetry (DSC) was conducted on a Seiko Electronics SSC-5200H instrument (heating rate = 1 K min^{-1}). Sample for DSC measurements were placed in aluminium pan (SSC000E33, Seiko Instruments Inc.). Magnetic susceptibility measurements were performed on a Quantum Design model MPMS-7XL superconducting quantum interference device (SQUID) magnetometer in a temperature range of 210 – 400 K. Magnetic data were corrected for diamagnetic contributions from triazole ligands and sample holders. The Pascal constants of the ligands and susceptibilities of the holders, which were measured separately, were used for the correction. The wide angle X-ray diffraction (WAXD) data of the hybrids were recorded on a powder X-ray diffractometer at BL02B2 in SPring-8 (operation energy = 8 GeV, stored current = 100 mA, λ = 1Å). For XRD, samples are placed in a capillary (Markrohrchen aus Glas Nr. 14, 80 mm(long) × 0.7 mm(diameter) × 0.01 mm(thick)), Hilgenberg GmbH).

[2] Reflectance spectra of $[Fe^{II}(\mathbf{1})_3]Cl_2$/**JC-1041XX** and their temperature dependence.

Reflectance spectra were measured for $[Fe^{II}(\mathbf{1})_3]Cl_2$/**JC-1041XX** cast on a quartz plate. At 294K, an absorption peak centered at 529 nm is observed (Figure S1a), which is a characteristic of the LS Fe^{II} complex ($^1A_1 \rightarrow {}^1T_1$ d-d transition in the $S = 0$ state). When the liquid crystal gel is heated above 294 K, the absorption intensity at 529 nm showed gradual decrease and a pale-yellow gel was obtained at ca. 359 K (HS state). The observed spin crossover is completely reversible, as indicated by the temperature dependence of the reflectance intensity at 529 nm (Figure S1b). In Figure S1b, it is clearly seen that changes in the absorption intensity (temperature range, 294 K to 350K) are accompanied by thermal hysteresis.

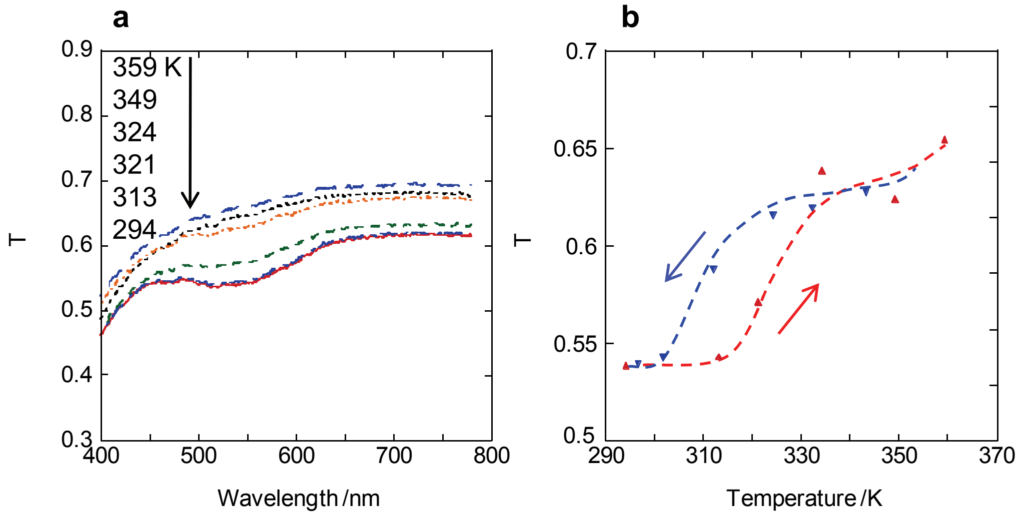

Figure S1. (a) Temperature dependence of reflectance spectra for $[Fe^{II}(\mathbf{1})_3]Cl_2$/**JC-1041XX** liquid crystal gels (b) Dependence of reflectance intensity (at 529 nm) on temperature.
Both of the heating and cooling cycles are shown.

[3] Temperature dependence of $\chi_M T$ and DSC data for $[Fe^{II}(\mathbf{1})_3]Cl_2$ /**JD-1002XX** liquid crystal gel.

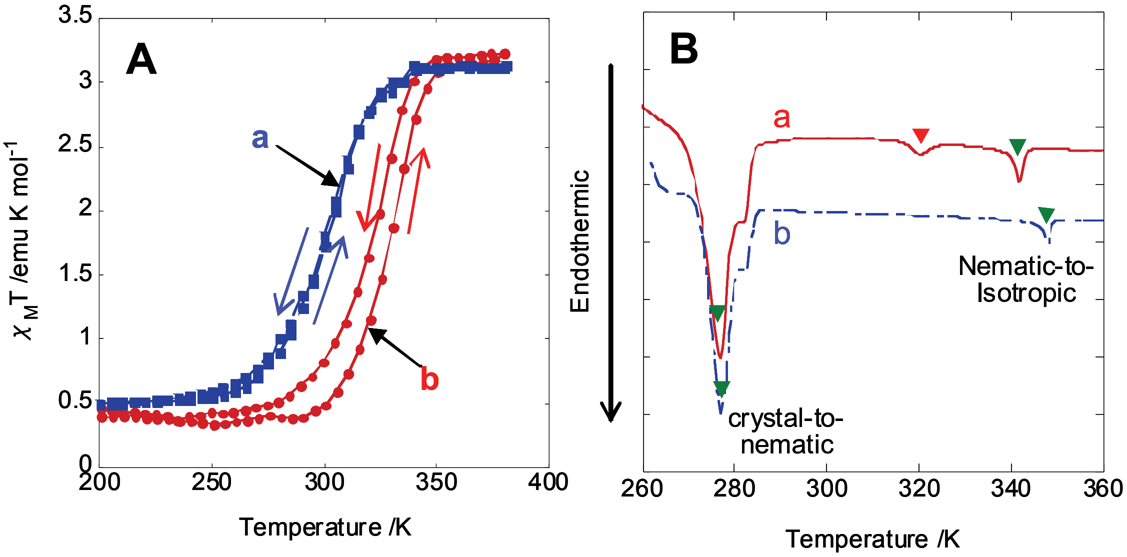

Figure S2. **A**, Temperature dependence of $\chi_M T$. (a) crystalline $[Fe(\mathbf{1})_3]Cl_2$ (b) $[Fe(\mathbf{1})_3]Cl_2$ /**JD-1002XX** liquid crystal gel. $[Fe^{II}(\mathbf{1})_3]Cl_2$: **JD-1002XX** = 1 : 9 (wt%). Temperature of the specimens was changed at the rate of 1 K min^{-1}. **B**, DSC Thermgrams of (a) $[Fe(\mathbf{1})_3]Cl_2$ /**JD-1002XX** liquid crystal gel, (b) **JD-1002XX** alone.

The crystalline $[Fe(\mathbf{1})_3]Cl_2$ shows abrupt spin transition without thermal hysteresis (curve a in Figure S2A), which is indicative of small interchain interactions (and cooperativity) among 1-D Fe(II)(triazole)$_3$ coordination chains. This would results from the introduction of long alkyl substituents. In contrast, $[Fe(\mathbf{1})_3]Cl_2$/**JD-1002XX** liquid crystal gel showed spin crossover with thermal hysteresis at higher temperatures compared to that observed for crystalline $[Fe(\mathbf{1})_3]Cl_2$ (curve b in Figure S2A). In Figure 4A and Figure S2A, temperature of the specimens was changed slowly at the rate of 1 K min^{-1}. Both of the liquid crystal gels ($[Fe(\mathbf{1})_3]Cl_2$ /**JD-1002XX** and $[Fe(\mathbf{1})_3]Cl_2$ /**JC-1041XX)** gave similar thermal hysteresis when temperature was changed at much slower rate of 0.1 K min^{-1}.

In DSC thermograms (Figure S2B), spin crossover temperature was observed at 319 K (curve a), which is in contrast to the broad endothermic peak observed for crystalline $[Fe(\mathbf{1})_3]Cl_2$ at lower temperature range (280-313 K, curve a in Figure 4B). On the other hand, the liquid crystal-to-isotropic transition temperature of **JC-1041XX** was lowered to 342 K from 348 K observed for the bulk liquid crystals (curve b in Figure S2B). These changes indicate that the both components influence each other in the bicontinuous structure.

[4] FT-IR spectra.

In FT-IR spectra, solid [Fe(**1**)$_3$]Cl$_2$ gave C-H stretching bands of ligand molecules at 2920 cm^{-1} (ν_{anti}) and 2850 cm^{-1} (ν_{sym}) in the temperature range of 273–333 K, which are assigned to all-trans conformation of hydrocarbon chains.[1,2] The frequencies of asymmetric and symmetric methylene stretching vibrations are conformation sensitive due to the perturbation by Fermi-resonance interaction with the methylene bending vibration, and they are empirically correlated with the order. When the sample was further heated to 353 K, the C-H stretching bands exhibited blue shifts to 2925 cm^{-1} and 2854 cm^{-1}, respectively.[3] The observed changes in IR spectra are related to the endothermic peak at 337 K (curve a in Fig. 4B), which is therefore associated with the order-disorder transition of ligand alkyl chains.

Evidence for the solvation of ligand alkylchains by liquid crystals.

FT-IR spectra of [Fe(**1**)$_3$]Cl$_2$/**JC-1041XX** showed C-H stretching bands at 2925 and 2854 cm^{-1} (temperature range, 273 K to 373 K), which are blue-shifted compared to those observed for [Fe(**1**)$_3$]Cl$_2$ (at 2920 and 2850 cm^{-1}). The blue shifts in C-H stretching bands observed for liquid crystal gels indicate that the conformation of ligand-alkylchains is disordered due to interactions with liquid crystal molecules. This is consistent with the disappearance of the order-disorder transition of alkylchains in the liquid crystal gel [Fe(**1**)$_3$]Cl$_2$/**JC-1041XX**, which was observed for crystalline [Fe(**1**)$_3$]Cl$_2$ sample at 337 K (Fig. 4B, curve a). It gives a reasonable account for the miscibility observed for these components.

[5] Wide-angle X-ray diffraction (WAXD) data and molecular orientation.

Figure S3 compares WAXD data obtained for $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$/**JC-1041XX** (left) and $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$/**JD-1002XX** (right) at 293 and 353 K, respectively. At room temperature, $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$/**JC-1041XX** showed intense (001), (002), and (003) diffraction peaks at 1.58 Å, 3.04 Å and 4.57 Å, respectively (Figure S3a). These diffraction peaks are originated from fibrous nano-assemblies of $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$ dispersed in liquid crystals. and indicate the presence of regular lamellar structure with a long spacing of 37.2 Å (Figure S4, page S6). This d-spacing is by ca. 1.2 Å larger than that observed for the powdery sample of $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$ (d = 36.0 Å)[4]. The observed increase in d-spacing (d = 36.0 Å in powdery $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2 \rightarrow$ 37.2 Å in $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$/**JC-1041XX**) indicates that lipophilic alkylchains of $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$ are miscible with liquid crystal molecules, and they adopt more perpendicular orientation upon the uptake of liquid crystal molecules. This is also supported by the blue-shift in C-H stretching bands (FT-IR) as discussed in page S4. Upon heating to 353 K, the long spacing of $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$/**JC-1041XX** showed further increase from 37.2 Å to 39.2 Å (Figure S3b). It reflects thermally enhanced motion of alkyl chains in $[\mathrm{Fe}^{\mathrm{II}}(\mathbf{1})_3]\mathrm{Cl}_2$ at elevated temperatures, which would be accompanied by enhanced solvation by liquid crystal molecules **JC-1041XX** (Figure S4, top).

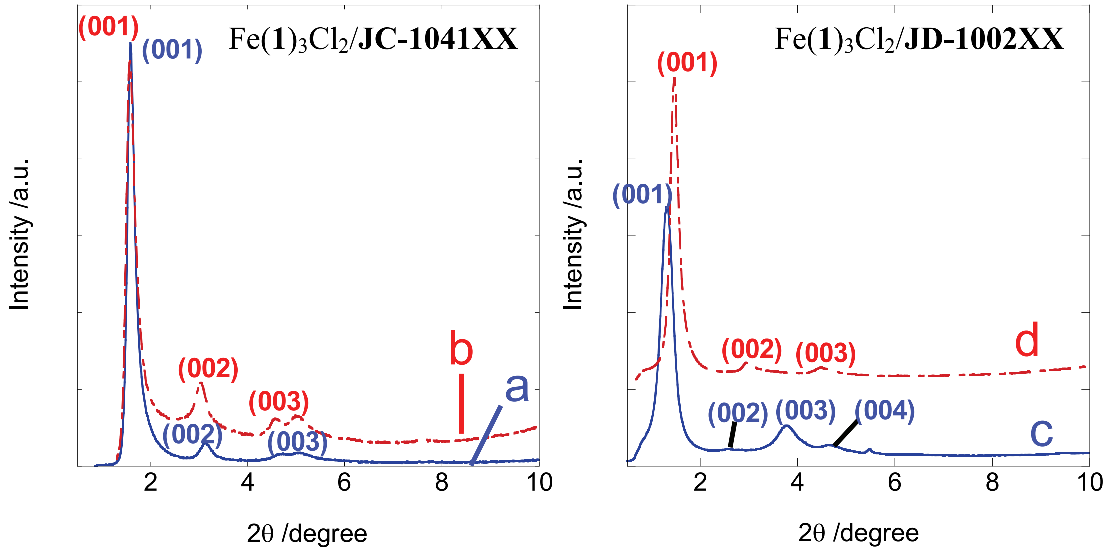

Figure S3. Wide-angle X-ray diffraction (WAXD) data for liquid crystal gel $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$ /**JC-1041XX** at 293 K (a) and 353 K (b), $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$ /**JD-1002XX** liquid crystal gel at 293 K (c) and 353 K (d). $[\mathrm{Fe}(\mathbf{1})_3]\mathrm{Cl}_2$: Liquid crystals = 1 : 9 (wt%).

The peaks around at $2\theta = 5$ ° show two peaks (in Fig. S3a,b), one of which could be ascribed to periodicity due to metal ions in a polymeric structure (i. e., Fe-Fe-Fe = 7.3 Å). Similar diffraction peaks have been observed in powder X-ray diffraction patterns of $\mathrm{Fe(Htrz)_3(BF_4)_2}$ (Htrz; 1,2,4-4*H*-triazole).[3]

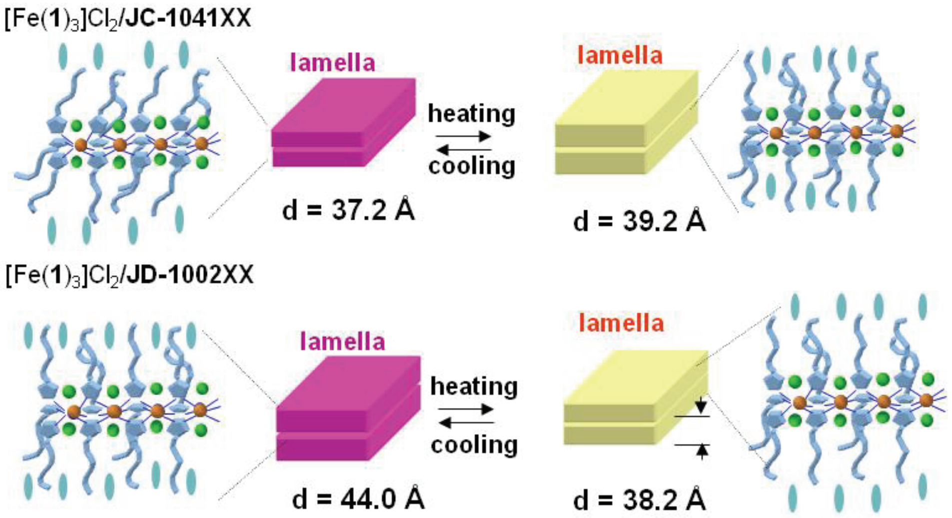

Figure S4. Schematic illustrations of thermal structural changes observed for lamellar nanofibers of [Fe(**1**)$_3$]Cl$_2$ dispersed in liquid crystal gels.

In the case of [Fe(**1**)$_3$]Cl$_2$/**JD-1002XX**, a lamellar long spacing of 44.0 Å was observed at 293 K (Figure S3c). The increase in long spacings (d = 36.0 Å for powdery [Fe(**1**)$_3$]Cl$_2$ → 44.0 Å in [Fe(**1**)$_3$]Cl$_2$/**JD-1002XX**) also reflect the solvation of alkylchain layer by **JD-1002XX** molecules.

In contrast, the long period of [Fe(**1**)$_3$]Cl$_2$/**JD-1002XX** showed decrease from 44.0 Å (at 293 K) to 38.2 Å (at 353 K). The smaller diffraction intensity obtained at 293 K (Fig. S3c) compared to that at 353 K (Fig. S3d) implies that the alkylchain layer of [Fe(**1**)$_3$]Cl$_2$ well accommodate **JD-1002XX** molecules and show better solvation at lower temperature. Upon heating, however, **JD-1002XX** molecules become segregated from the alkylchain layer, leaving tilt-oriented alkylchain layer which exerted the decrease in long spacing (Figure S4, bottom).

Thus, thermal changes in lamellar structures of nanofibrous [Fe(**1**)$_3$]Cl$_2$ are dependent on the chemical structure of liquid crystal molecules. The observed structural transitions are thermally reversible, and regular lamellar structures are maintained even in liquid crystals.

References

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