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Supporting Information for

Thermally tunable selective formation of self-assembled fibers into two orthogonal directions in oriented liquid-crystalline smectic templates

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Experimental

Gelator **1** and liquid crystal **MCB** were prepared according to previous reports.[1,2] Mixtures of gelator **1** and liquid crystal **MCB** were prepared by evaporation from chloroform solution of the LC molecules and the gelators. The LC mixtures were filled in glass sandwich cells (thickness: 5μm) with polyimide alignment layers. The rubbing direction of two surfaces was antiparallel. The mixtures in the cells were cooled from the isotropic states to certain temperatures at a cooling rate of 5 °C min^{-1}, which were controlled by a Linkam LTS350 hot stage. An Olympus BX51 polarizing optical microscope was used for optical microscope observation. For scanning electron microscopy (SEM) observations, xerogels of LC gels were prepared by immersing the LC gel mixtures in hexane to extract the LC molecules and finally dried at room temperature. SEM measurements were performed with a KEYENCE VE-9800 operated at 1 kV. For Infrared (IR) absorption spectroscopy, LC mixtures were put into CaF_2 plates with polyimide alignment layers rubbed in antiparallel manner. IR absorption spectra were recorded on a JASCO FT/IR-6100 and IRT-5000 equipped with Linkam T95-HS hot stage with and without polarizer. Microscopic infrared (IR) spectroscopy was conducted at BL43IR beamline of SPring-8 (Hyogo, Japan) with a Fourier transform IR microscope system (VERTEX 70 and HYPERION 2000, Bruker) equipped with an MCT detector. LC mixtures filled in CaF_2 sandwich cells were installed into a temperature-controlled stage (LINKAM 10036L). IR spectra were recorded in transmission mode with resolution of 4 cm^{-1} and 100 times integration with polarizer. X-ray diffraction (XRD) measurements were carried out on Rigaku RINT2500 diffractometer with a heating stage using Ni-filtered Cu Kα radiation (1.54 Å).

Supplemental Data

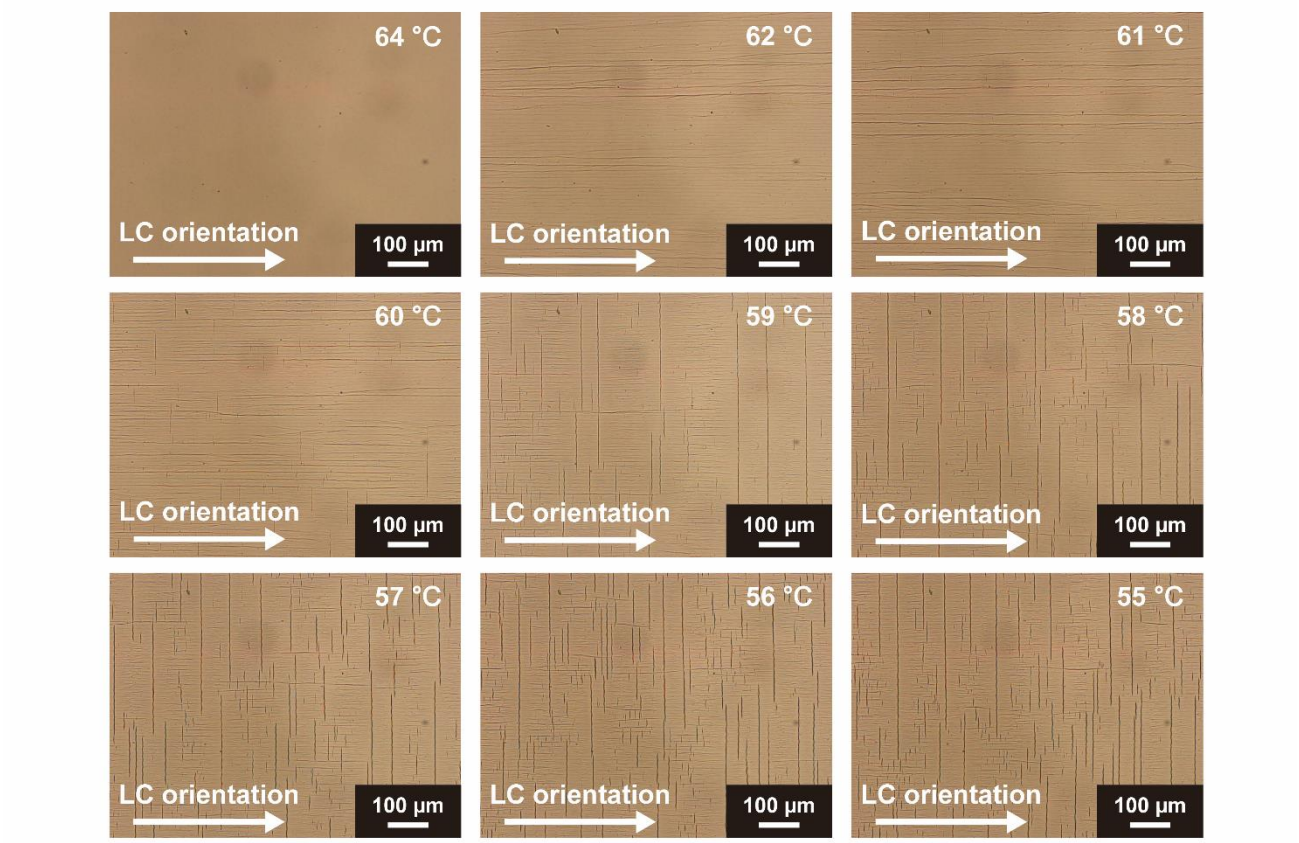

Fig. S1 Optical microscope images of the self-assembled fibers of **1** in homogenously oriented **MCB** prepared by isothermal annealing for 30 minutes after cooling to each temperature from the isotropic states at 90 ºC.

Optical microscope image at 64 ºC (Fig. S1) shows no fiber formation in the smectic A phase.

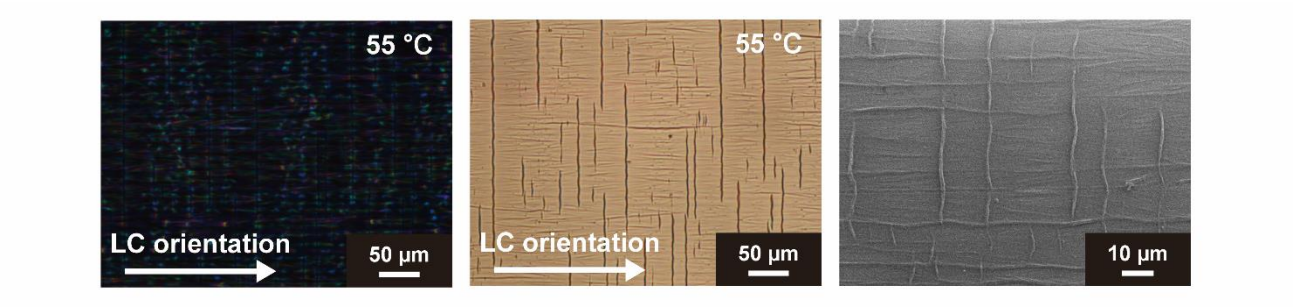

Fig. S2 Polarized optical, optical and scanning electron microscope images of self-assembled fibers of 1 mol% of **1** formed in **MCB** prepared at 55 ºC after cooling from the isotropic state at 90 ºC.

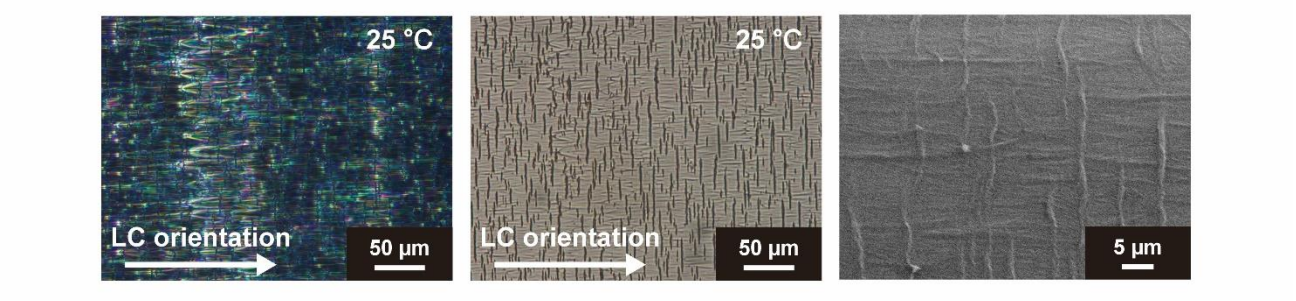

Fig. S3 Polarized optical, optical and scanning electron microscope images of self-assembled fibers of 1 mol% of **1** formed in **MCB** prepared by rapid quenching at 25 ºC from the smectic A phase at 64 ºC.

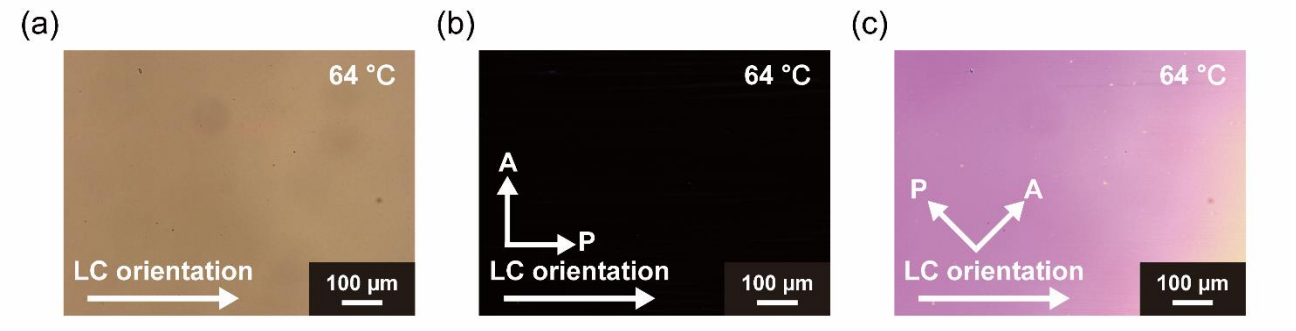

Fig. S4 (a) Optical and (b,c) polarized optical microscope images of the homogenous mixture of **1**/**MCB** (1.0 mol%) in the oriented smectic A phase at 64 ºC. P: polarizer. A: analyzer.

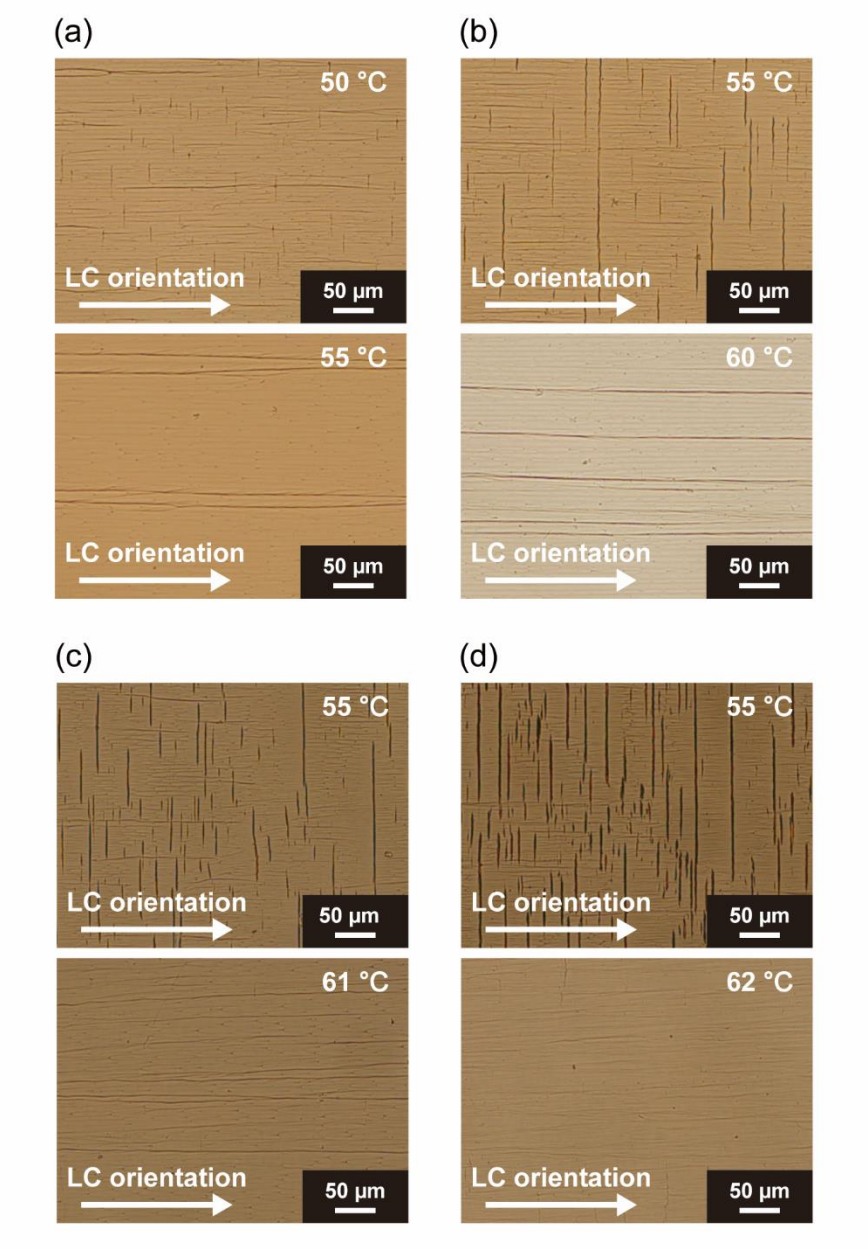

Fig. S5 Optical microscope images of the formation of self-assembled fibers in **MCB** with various concentrations of (a) 0.5, (b) 0.75, (c) 1.5 and (d) 2.0 mol% for **1** prepared by isothermal annealing at lower and higher temperatures. They were cooled from the isotropic states at 90 ºC.

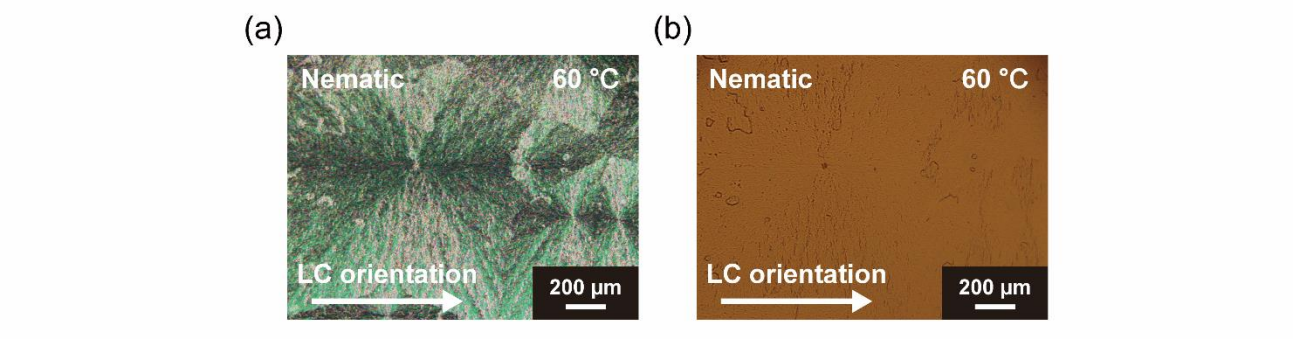

Fig. S6 (a) polarized optical and (b) optical microscope images of the self-assembled fibers of **1** (2.5 mol%) in homogenously oriented **MCB** prepared at 60 ºC after cooling from the isotropic states at 90 ºC.

Smectic-nematic phase transition temperatures of LC mixtures are decreased as the concentration of gelators increases.[3] The LC mixtures of 0.5-2.0 mol% of **1** formed fibers below the smectic-nematic phase transition temperature, while the LC mixture of 2.5 mol% of **1** shows smectic-nematic phase transition below 60 °C and fiber formation occurs in the nematic phase.

Table S1. Phase transition temperatures and fiber growth properties for the mixture **1**/**MCB** with different gelator concentration

Concentration [mol%]	0	0.5	0.75	1.0	1.5	2.0	2.5
$T_{iso\text{-}N}$ [°C]	80	77	77	75	75	74	73
$T_{N\text{-}SmA}$ [°C]	69	66	65	64	63	62	60
Fiber orientation In N phase	–	–	–	–	–	–	Spherulitic
Fiber orientation in SmA phase (in Higher *T*)	–	One directional (// LC)	One directional (// LC)	One directional (// LC)	One directional (// LC)	One directional (// LC)	–
Fiber orientation in SmA phase (in lower *T*)	–	Grid-like	Grid-like	Grid-like	Grid-like	Grid-like	–

N: menatic. SmA: smectic A.

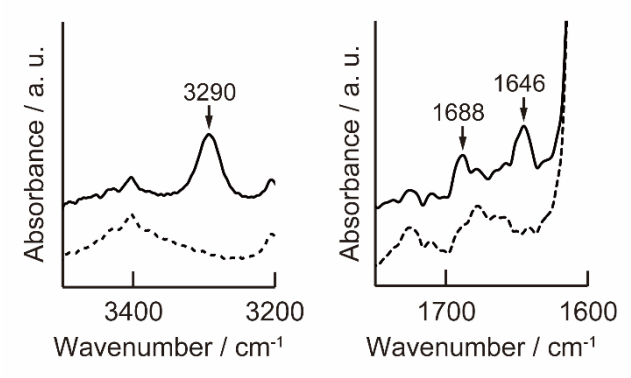

Fig. S7 IR spectra for the mixture of **1**/**MCB** (1 mol%) in the LC gel state (solid line: 55 ºC) and the LC state (dashed line: 63 ºC).

In IR spectra of **1**/**MCB** at the LC state, broad peaks appear around 3400 cm^{-1} corresponding to the N−H stretching bands, and C=O stretching bands of urethane and amide groups at 1720 and 1680 cm^{-1}. For the LC gel state, sharp peaks at 3290 (νN−H of urethane and amide), 1688 cm^{-1} (νC=O of urethane) and 1646 cm^{-1} (νC=O of amide) were observed for **1**/**MCB**. These lower peak shifts of stretching bands for urethane and amide groups show the formation of intermolecular hydrogen bonds in the fibrous aggregates.[2]

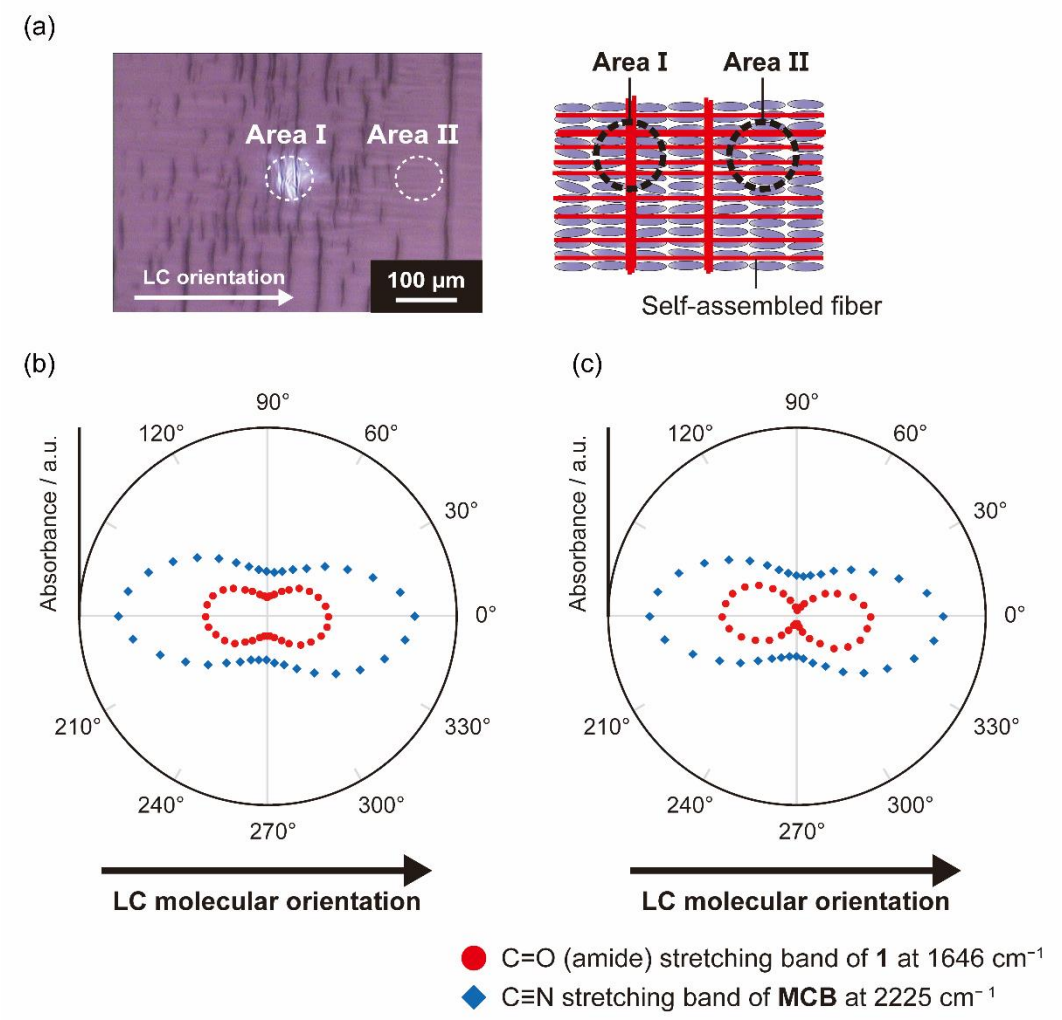

Fig. S8 (a) Optical microscopic image and a schematic illustration of the LC mixture of **1**/**MCB** (1.5 mol%) with grid-like fibrous structure prepared by isothermal annealing at 60 ºC. Polar plots of the microscopic IR absorbance for different sampling areas of (b) grid-like (area I) and (c) non-grid-like area (area II).

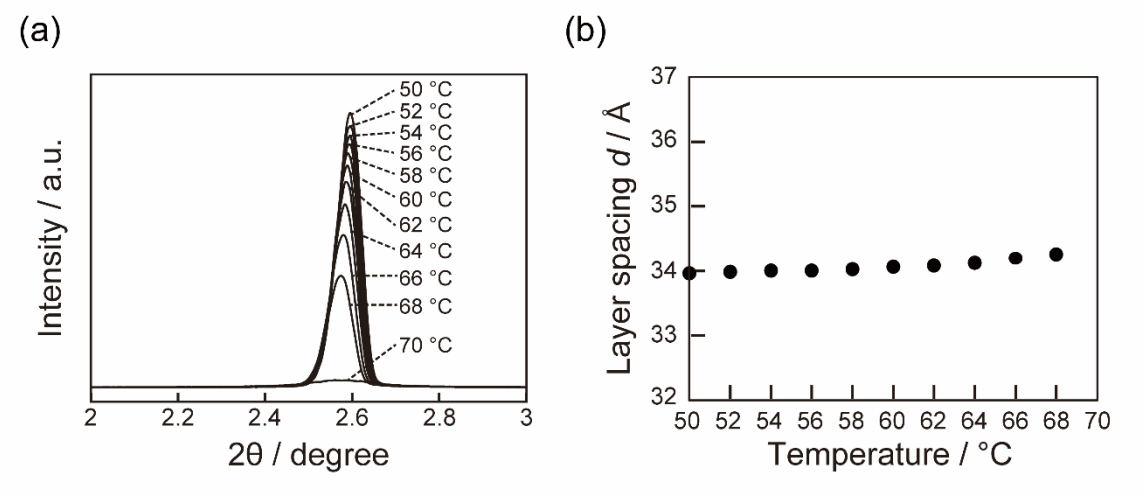

Fig. S9 (a) Temperature-dependent XRD patterns at the (001) diffraction peak for **MCB** in the smectic A phases from 50 to 70 ºC. (b) Temperature-dependent layer spacing *d* for the layered smectic structures.

Translational order parameter Σ was obtained according to a previous report.[4] For the smectic A phase, Σ is given by the equation $\Sigma = [1 - (T/T_c)]^{\beta}$, where *T*c and β is the nematic-smectic A transition temperature of **MCB** and the order-parameter exponent. *T*c was determined as 69 ºC by the polarized optical microscope observation. β was obtained as 0.140 by fitting the equation $I(T) = I_0[1 - (T/T_c)]^{2\beta}$ to the temperature-dependent intensity *I*(*T*) of the XRD data in a double-logarithmic plot. Integration of the peak areas at several temperatures *T* leads to the temperature-dependent intensity *I*(*T*). The integrated intensity was used instead of the peak maxima because the width of the layer peak is due to quasi-long-range order and instrumental resolution that is not infinitely small.[4]

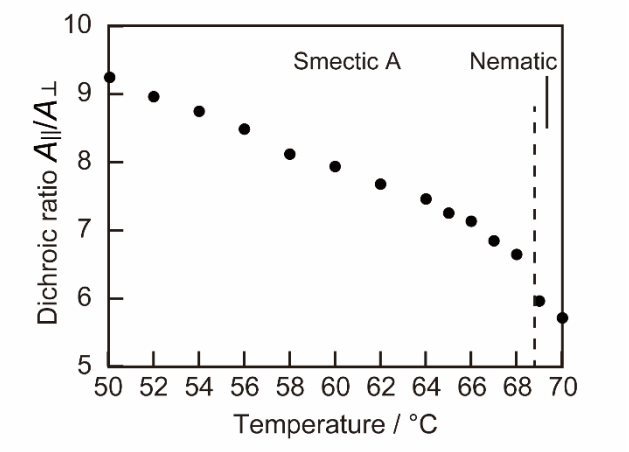

Fig. S10 Dichroic ratio of the absorbance of the CN stretching band for the homogenously oriented pure **MCB** with the infrared light polarization parallel ($A_{\parallel}$) to perpendicular ($A_{\perp}$) to the LC molecular orientation of **MCB**.

In the temperature-dependent polarized IR absorption analyses on pure **MCB** in the homogenously oriented LC states, the maximum intensity of the absorbance for the CN stretching band of **MCB** at 2225 cm^{-1} is obtained when the direction of polarized light is parallel to the LC molecular orientation. Dichroic ratio of the absorbance for the CN stretching band of **MCB** $A_{\parallel}/A_{\perp}$ as a function of temperature is shown in Fig. S10, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances of the band with the IR light polarization axis parallel and perpendicular to the LC molecular orientation. The dichroic ratio for the CN stretching band was increased with decreasing temperature. These results suggest that the LC smectic A molecules are more oriented as temperature is decreased. Suppression of the thermal fluctuation of the LC molecules should contribute to the formation of an ordered layered structure in the LC smectic phase. This behavior of **MCB** is compatible with the previous reports for smectic A phases of alkoxy-cyanobiphenyl molecules.[5,6]

References

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