Supplementary information for:

Liquid Crystal Stepwise Electropolymerization – An Approach to Create Insect Photonic Structure

Hiromasa Goto

Division of Materials Science, Faculty of Pure and Applied Sciences,
University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Correspondence to H. Goto, Tel: +81-298-53-5128, fax: +81-298-53-4490
Email: gotoh@ims.tsukuba.ac.jp

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Figure S1. Appearance of a blue mountain butterfly (Papilio Ulysses).

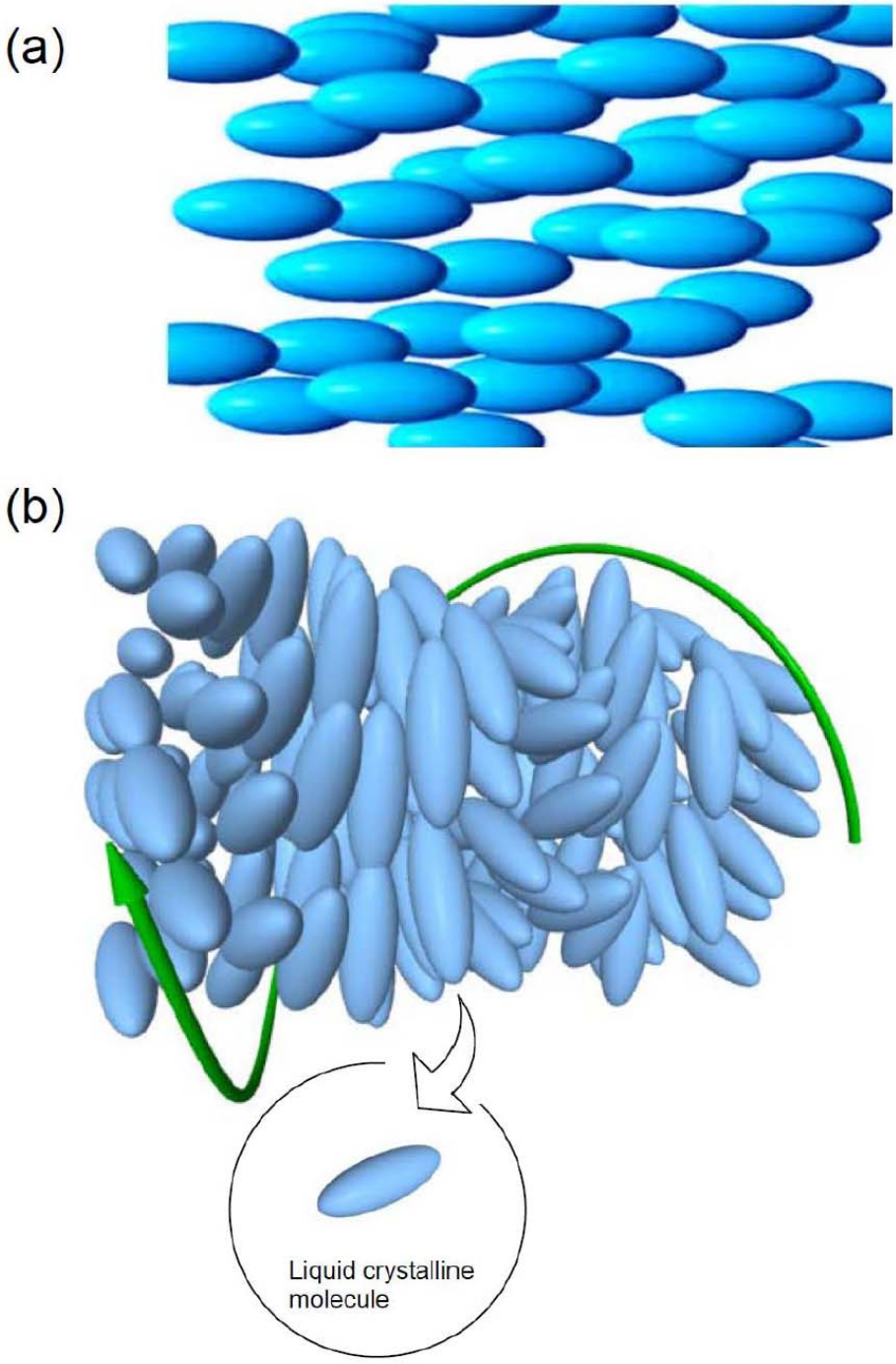

Figure S2. (a) Molecular aggregation structure of nematic phase, and (b)cholesteric phase.

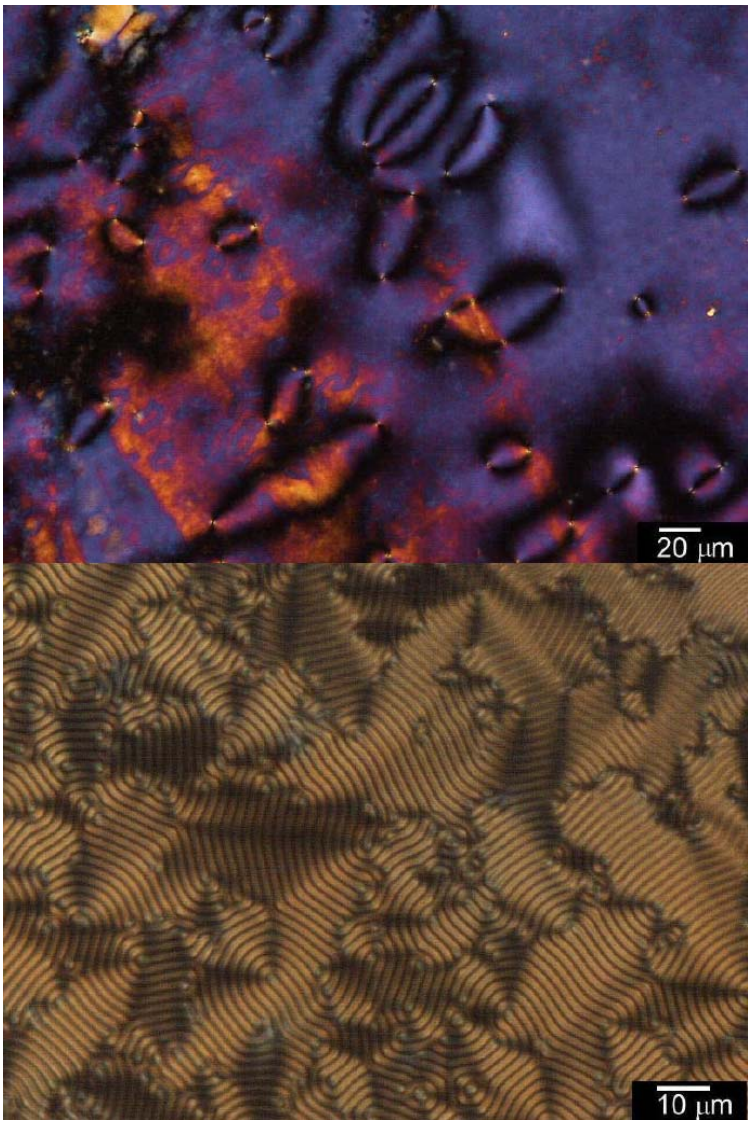

Figure S3. Photographs are polarized optical microscopy images of LC electrolyte solutions. (a) Nematic liquid crystal electrolyte solution, (b) cholesteric liquid crystal electrolyte solution.

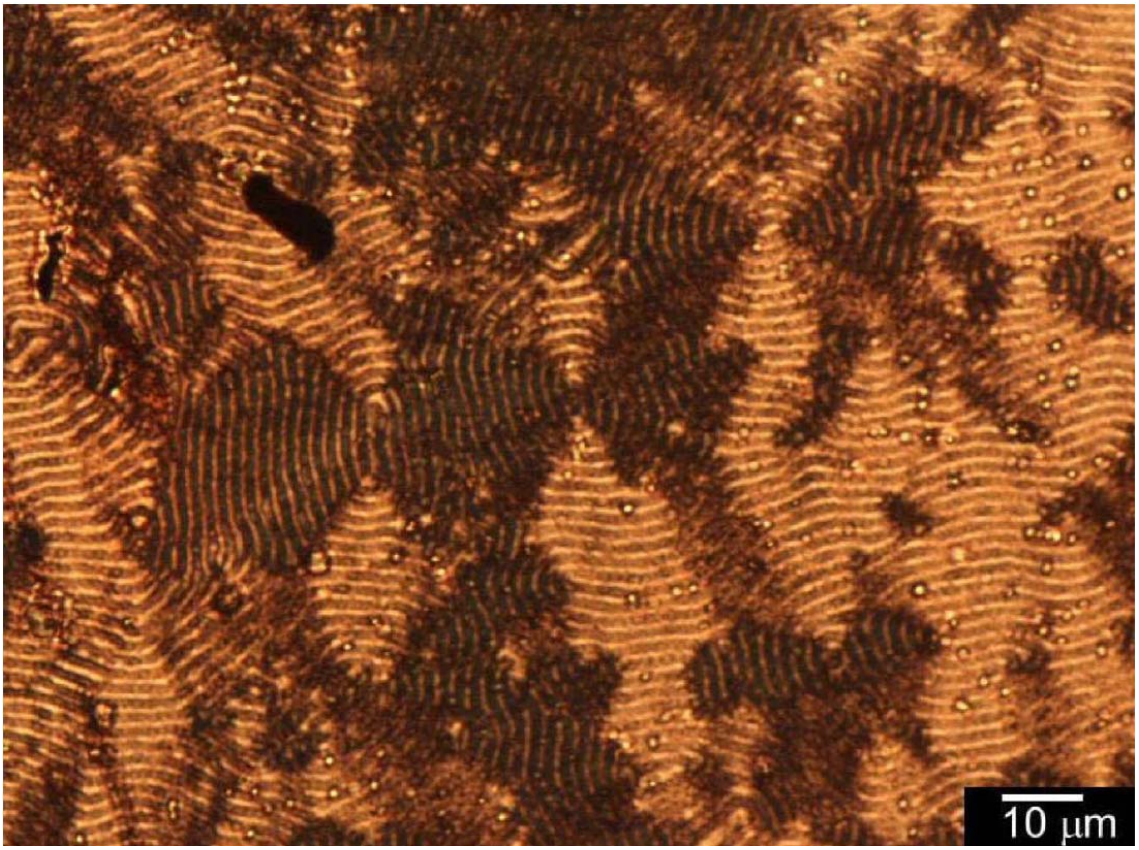

Figure S4. POM image of bottom layer of PBT(Ch*-N-Ch*) in reduced (de-doped) state. 500x.

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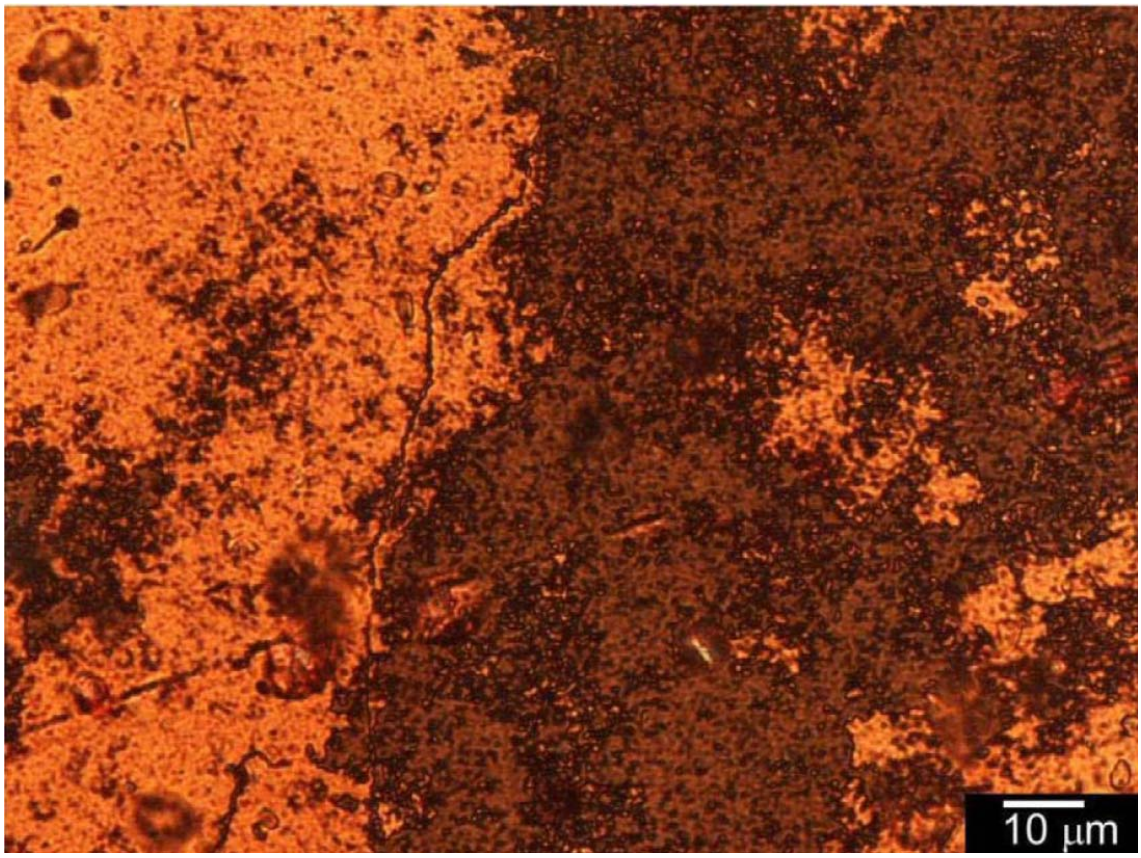

Figure S5. POM image of the middle layer of PBT(Ch*-N-Ch*) in reduced (de-doped) state showing threaded like texture. 500x.

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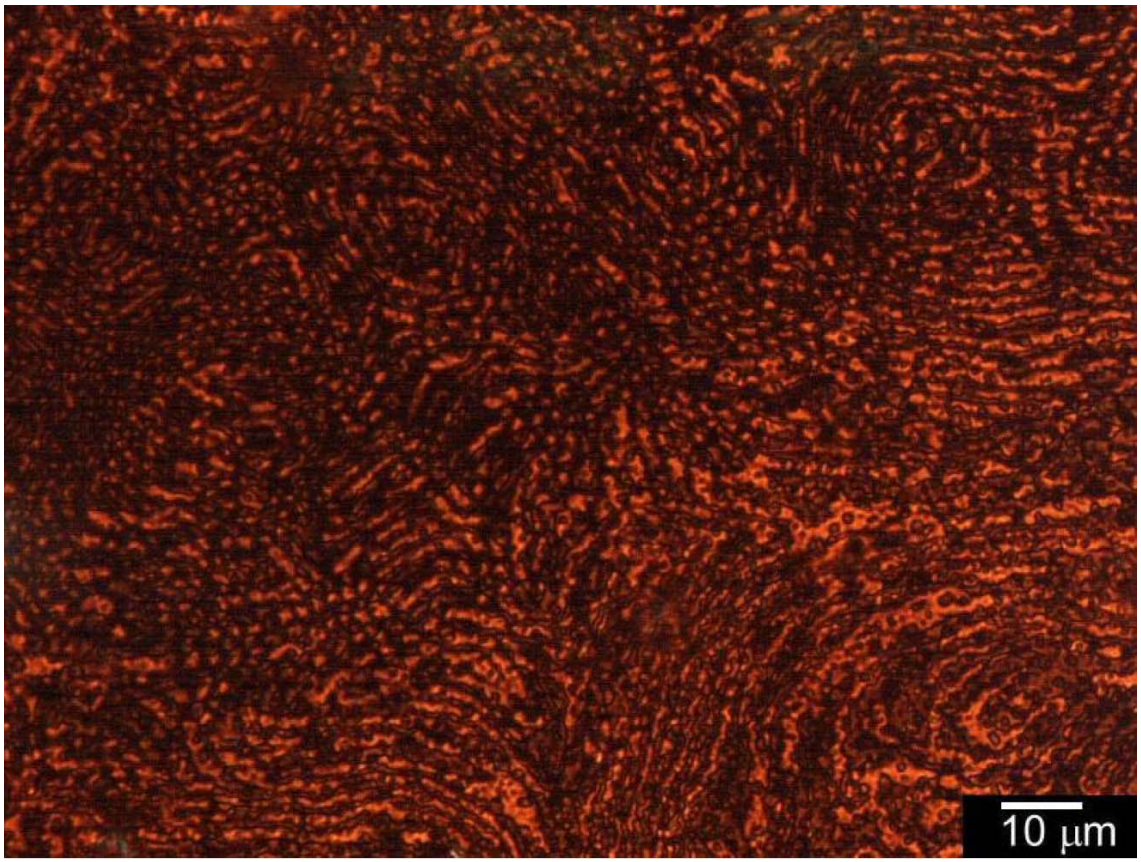

Figure S6. POM image of the top layer of PBT(Ch*-N-Ch*) in reduced (dedoping) state. 500x.

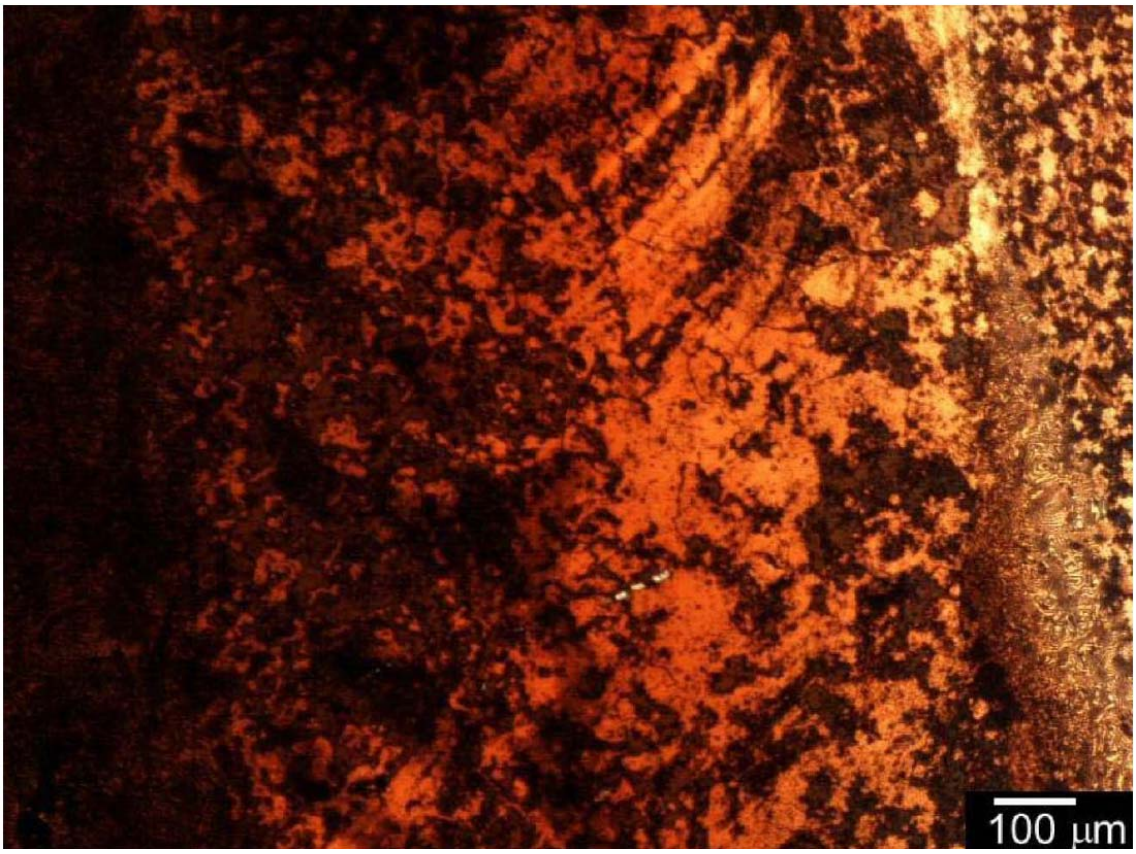

Figure S7. POM image of the entire area (an edge part of the sample on the ITO) of PBT(Ch*-N-Ch*) in reduced (de-doped) state. 500 x.

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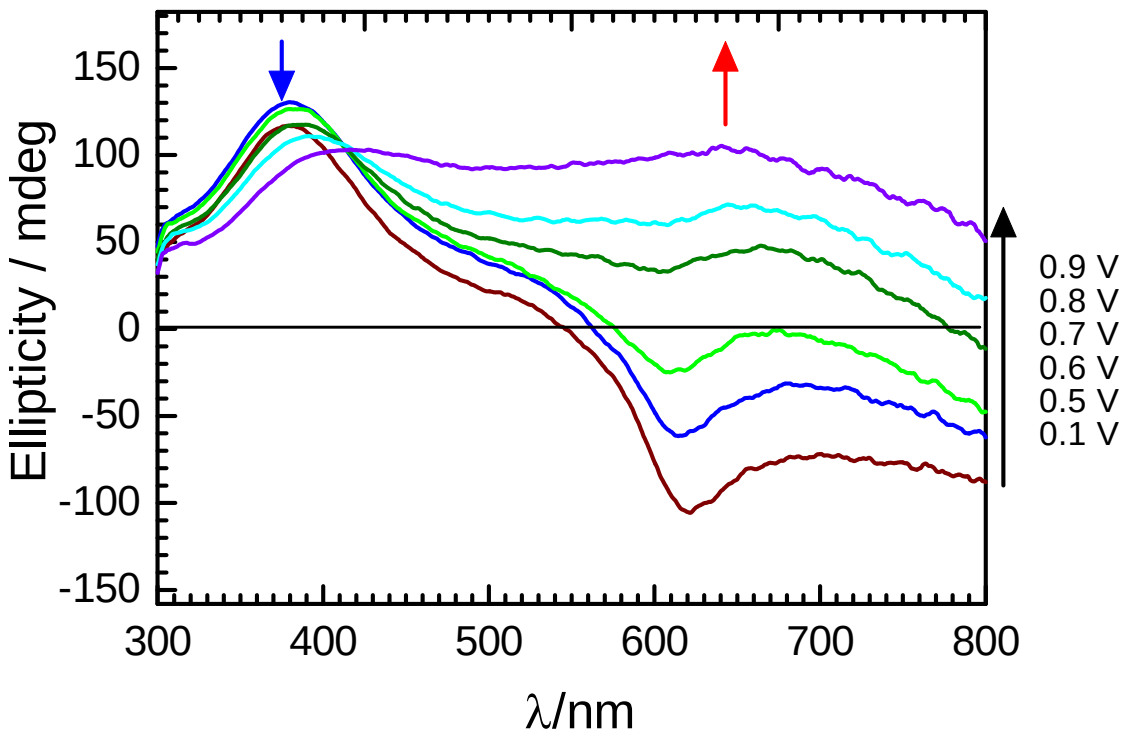

Figure S8. CD spectra of monomer-free triple-layer PBT(Ch*–N–Ch*) film at various potentials vs. Ag/Ag^{+} reference electrode from 300 -800 nm.

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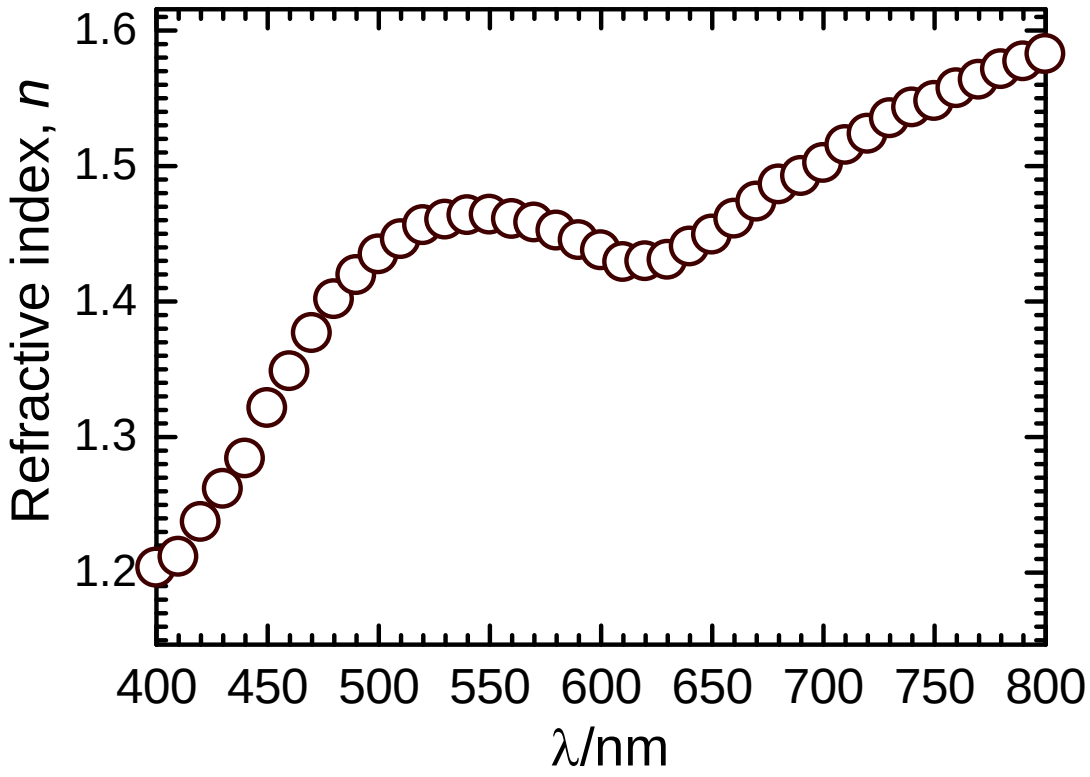

Figure S9. Refractive index (*n*) vs. wavelength as prepared PBT(Ch*-N-Ch*).

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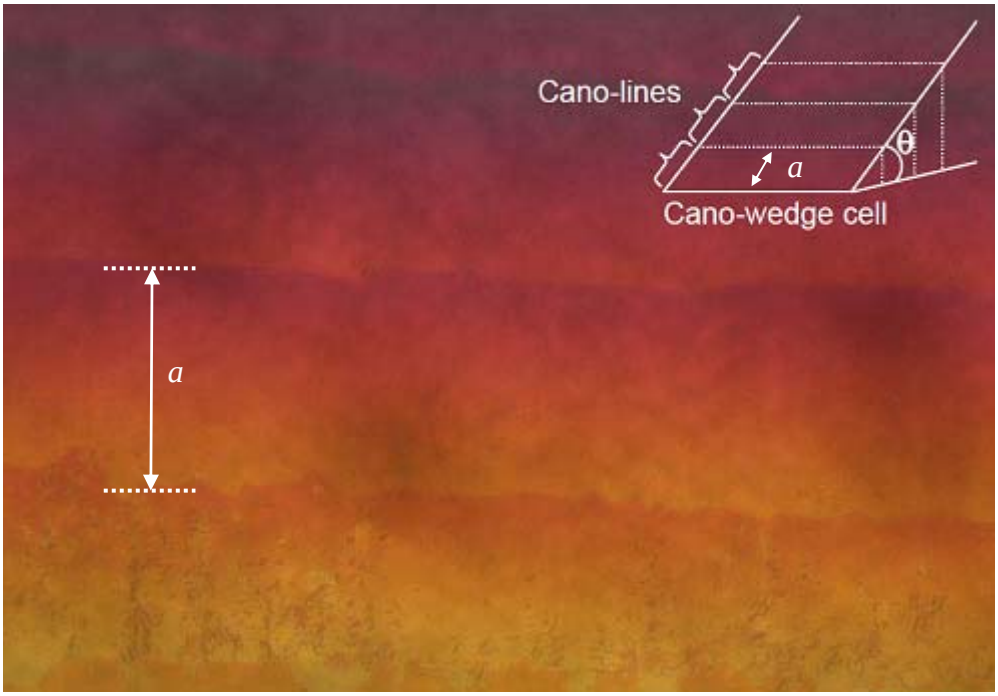

Figure S10. Cano-lines of cholesteric electrolyte solution containing monomer, electrolyte, and the chiral inducer in Cano wedge cell. The parameters a, and θ are length of Cano-line in the cell, degree of the Cano-wedge, respectively. a = 294 μm.

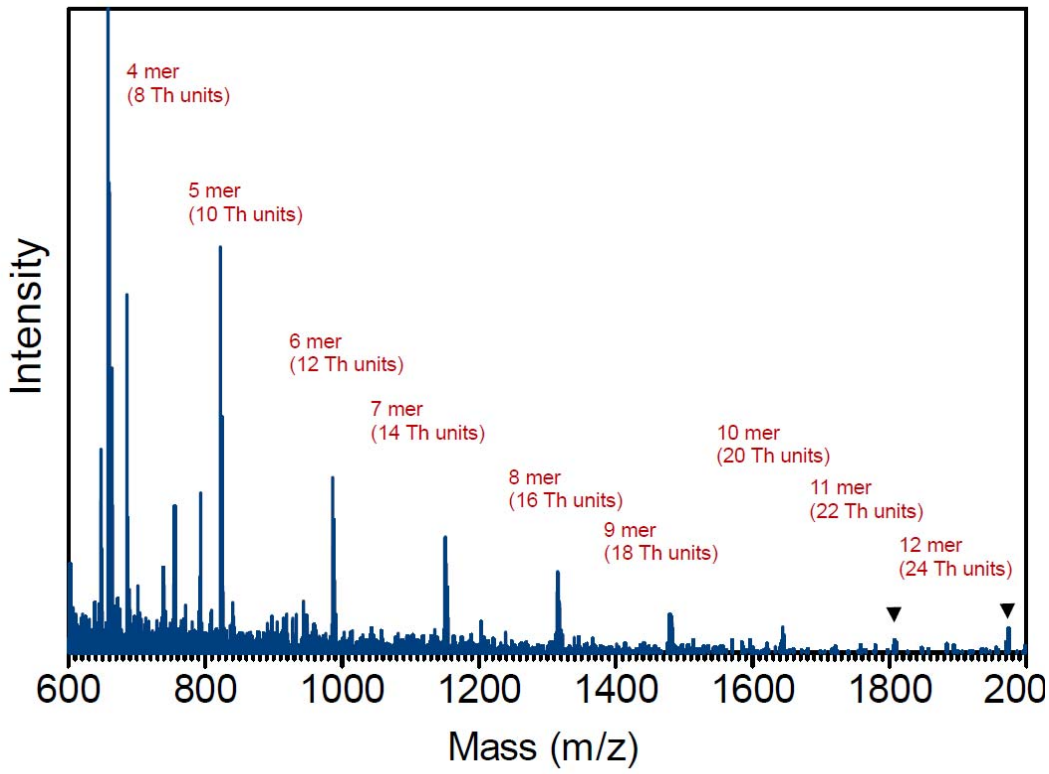

Figure S11. Matrix assisted laser desorption ionization, time of flight-mass (MALDI TOFF-MS) result of the polymer prepared in cholesteric liquid crystal electrolyte solution.

MOLECULAR WEIGHTS

Ionization of high molecular weight fractions of the polymer may not be performed completely in the TOFF-MS measurements. Also, high molecular weight molecules tend to decrease of arrival probability at the detector of the TOFF-MS. Therefore, the signal intensity of the TOFF-MS may be not always proportional to real amounts of the molecular weights of each fraction of the polymers.

The molecular weights obtained from the TOFF-MS measurements may be reference indexes. In the present study, the MALDI TOFF-MS results imply that M_n, M_w, and dispersity values of the polymer are to be 806 g/mol, 913 g/mol, and 1.13, respectively, with an assumption of the signal intensity was proportional to number of the molecules, although only the low molecular weight parts of the polymer can be estimated by the present TOFF-MS spectroscopy measurements. So, these values express molecular weights of only low molecular mass fractions in the polymer.

The TOFF-MS results exactly indicate sequence of the molecular repeat units.

PLAUSIBLE REFLECTION MECHANISM

Exoskeleton of beetles with cholesteric-nematic-cholesteric order reflects circular polarized light by using multilayer structure. The multilayer polymer film thus prepared in this study is comparable to reflection functionality of the photonic insects.

The multilayer polymer may have the same light reflection mechanism as natural photonic insects with LC order (Caveney, S, *Proc. R. Soc. London*, 1971, Ser. **B178**, 205–225). Plausible mechanism of the reflection is described as follows.

Firstly, the top layer of the film with cholesteric order may reflect right-handed circular polarized light (R-CPL), and left-handed circular polarized light (L-CPL) passes through the top layer with incidence of natural non polarized light (mix of R-CPL and L-CPL light). Subsequently, the middle layer with nematic order converts L-CPL into R-CPL. Finally, bottom cholesteric ordered layer reflects R-CPL (Figure S12). Therefore, the CD shows negative signals (right-handed polarized direction), as a result of gain loss of R-CPL due to reflection at low voltage (dedoped state). Also, the gain loss due to absorption occurs. In the doped state, the helical state of the cholesteric ordered layer is changed, and L-CPL may be reflected from the polymer. In this case, optical absorption may also occur as a gain loss.

This process may not be perfect for the PBT(Ch*-N-Ch*) having fingerprint pattern (homogeneous structure, helical axis is parallel to the layer) because this process is effective for Grandjean cholesteric LC alignment (planar structure, helical axis is

perpendicular direction to the substrate).

Incompleteness of the light reflection functionality of the triple layer allows passage of residual light through polymer as an output, although optical absorption of the polymer decreases transmission of light at a certain wavelengths. The multilayer polymer may reflect R-CPL, and L-CPL passes through the film at the low voltage. Also, optical rotation of the polymer occurs for left direction (positive values in the ORD), as shown in Figure 7(b).

The trough of the CD corresponds to peak top of the ORD signal in this case, although a maximum in the ORD corresponds to inflection point of the CD in general. The CD and the ORD signals do not well correspond to the optical absorption of the multilayer polymer because both the multilayer structure and optical absorption derived from π-conjugation affect the light reflection.

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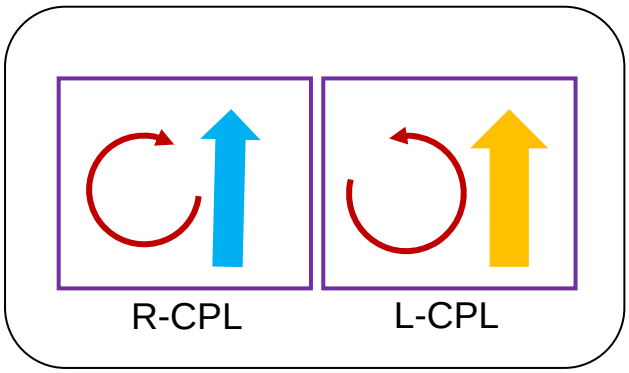
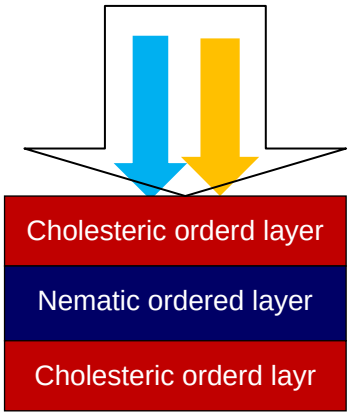
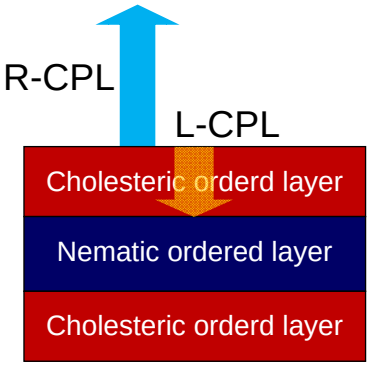


a)



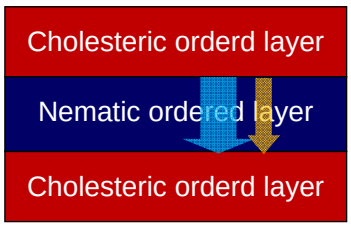
Incidence of light, which consists of right-handed (R-CPL) and left-handed circular polarized light (L-CPL).

b)



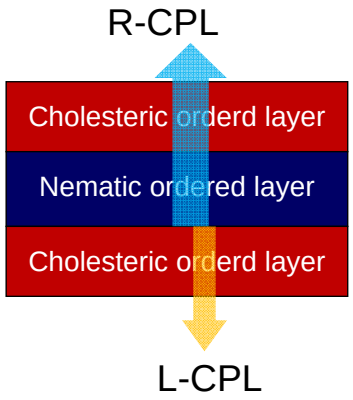
The top layer of the film with cholesteric order reflects R-CPL, and L-CPL passes through the top layer.

c)



The middle layer with nematic order converts L-CPL into R-CPL. The incompleteness of the conversion functionality allows passage of L-CPL.

d)



The bottom cholesteric ordered layer reflects R-CPL at visible range. The incompleteness of the light reflection functionality of the triple-layer polymer passes L-CPL as an output.

Figure S12. Possible model of light reflection function of the triple-layer polymer having cholesteric-nematic-cholesteric order with light passage process from (a) to (d).