

## Electronic Supplementary Information

### Electrically-stabilized liquid-crystalline phase: origin and application

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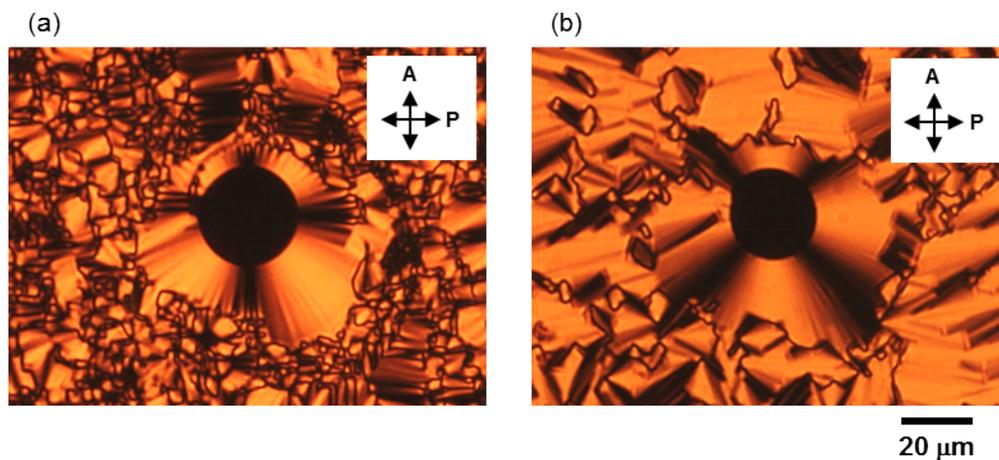
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## Synthesis of (*S,S*)-AZO-PB

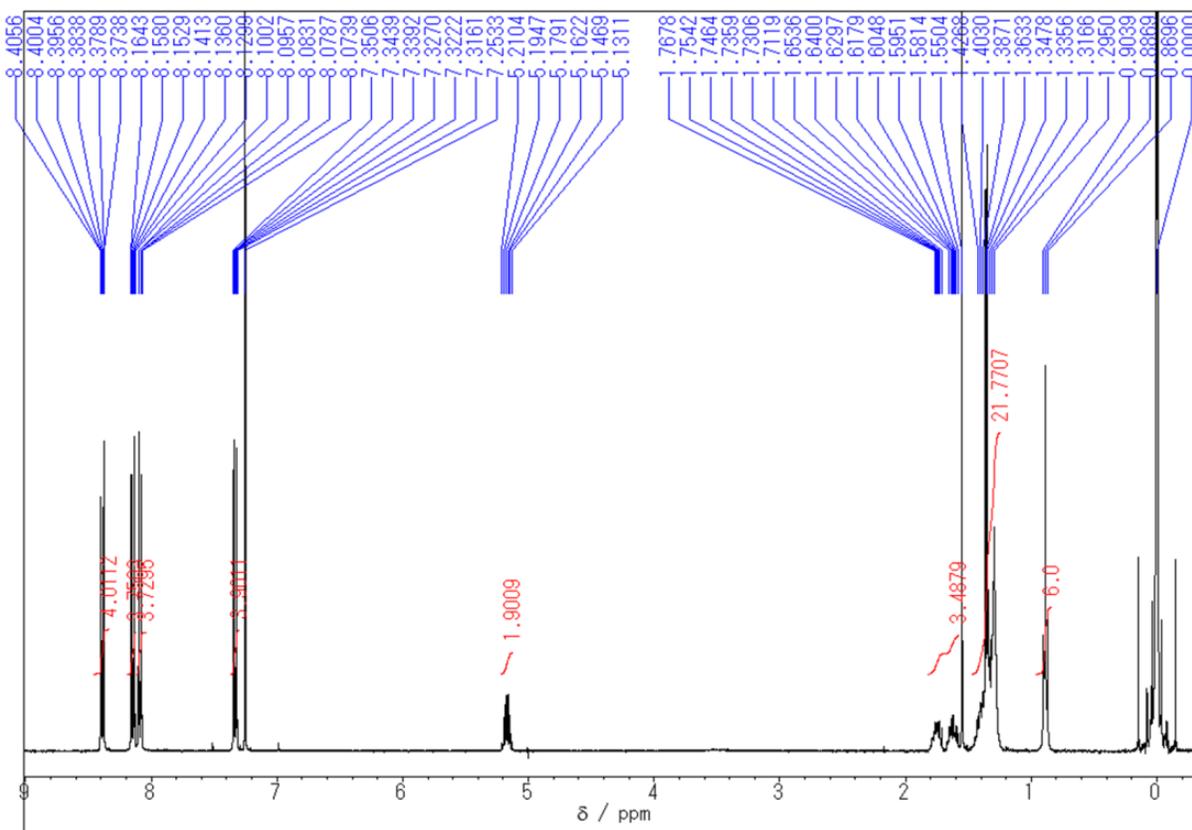
(*S,S*)-AZO-PB (Figure 1) was synthesized by a simple esterification, using *N,N'*-Dicyclohexylcarbodiimide (0.61 mg, 3.0 mmol) and *N,N*-dimethyl-4-aminopyridine in dry dichloromethane (10 ml), between 4,4'-azodibenzoic acid (Tokyo Chemical Industry Co., Ltd. Japan) (0.27 mg, 1.0 mmol) and [(1*R*)-1-methylheptyl] 4-hydroxybenzoate (0.55 mg, 2.2 mmol) prepared according to the standard procedures. The crude product was purified by column chromatography using dichloromethane as the eluent, and recrystallized from ethanol (50 ml), giving a light orange solid. Yield = 0.33 g (46%). The structure was confirmed by <sup>1</sup>H NMR and elemental analysis: Elemental analysis found (%): C 72.0, H 6.9, N 3.8; calculated for C<sub>44</sub>H<sub>50</sub>N<sub>2</sub>O<sub>8</sub> (%): C 72.0, H 6.9, N 3.8. δH (400 MHz, CDCl<sub>3</sub>, TMS); 8.39 (m, 4H, Ar-H), 8.15 (m, 4H, Ar-H), 8.08 (m, 4H, Ar-H), 7.33 (m, 4H, Ar-H), 5.18 (m, 2H, -COO-CH(-CH<sub>3</sub>)-CH<sub>2</sub>-), 1.74 (t, 4H, -COO-CH(-CH<sub>3</sub>)-CH<sub>2</sub>-), 1.40 (m, 22H, -COO-CH(-CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, -COO-CH(-CH<sub>3</sub>)-CH<sub>2</sub>-), 0.89 (t, 6H, -CH<sub>3</sub>).

## Electro-optical measurements

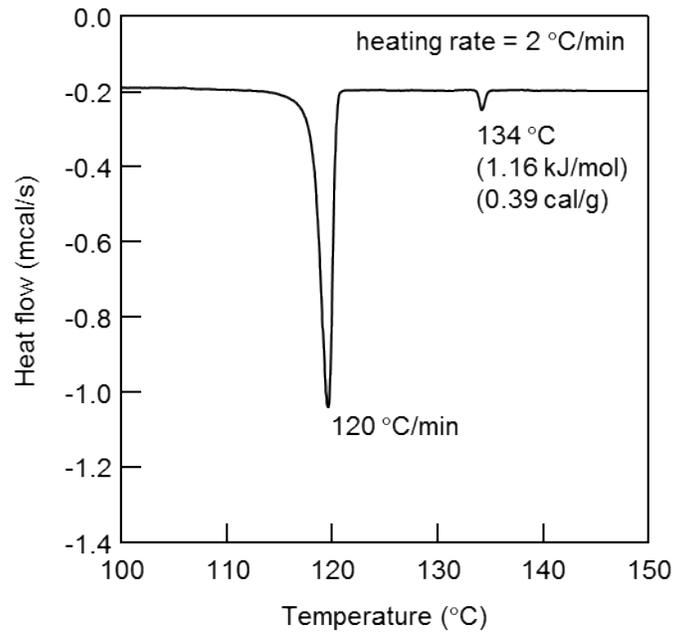
The electro-optical measurements were conducted in commercially available in-plane switching cells (E.H.C. Corp.) by the application of ac fields at frequency of 100 Hz. The spacing between ITO electrodes was 10 μm. The cell gap was 5 μm. The glass substrates were treated with no alignment layers. The switching polarization of (*S,S*)-AZO-PB was investigated by the triangular wave voltage method using a current-to-voltage converter (Toyo Corp., Model 6250). The switching polarization obtained by integrating area under the current peaks was found to be approximately 210 nC/cm<sup>2</sup>.



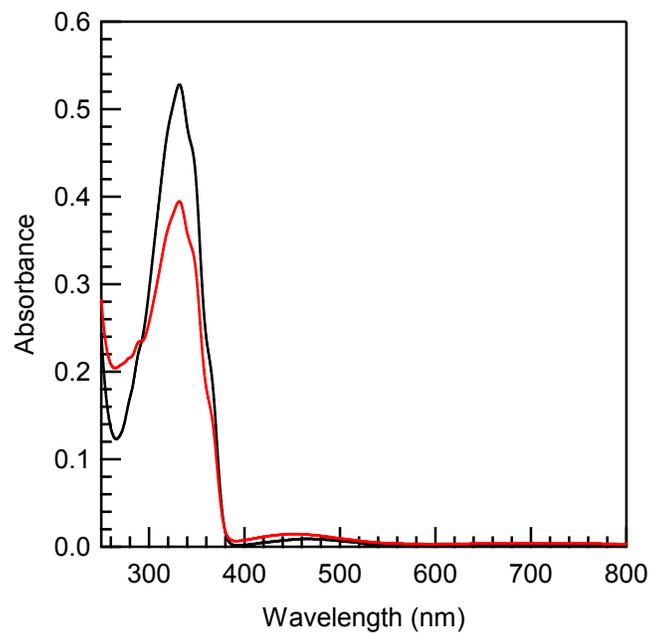
**Figure S1.** Typical textural change of antiferroelectric-ferroelectric phase transition of (*S, S*)-AZO-PB at 126 °C, showing the textures of (a) the antiferroelectric phase ( $E = 0 \text{ V}_{0-p}/\mu\text{m}$ ) and (b) the electrically-induced ferroelectric phase ( $E = 10 \text{ V}_{0-p}/\mu\text{m}$  (frequency = 100 Hz)), respectively. (*S, S*)-AZO-PB was placed in a conventional sandwiched cell (gap = 3  $\mu\text{m}$ ). The glass substrates of the cell were treated without alignment layers.



**Figure S2.** NMR spectrum of (*S, S*)-AZO-PB in  $\text{CDCl}_3$ .



**Figure S3.** DSC chart of (*S,S*)-AZO-PB in heating process (+2 °C/min).



**Figure S4.** UV-vis spectra of (*S,S*)-AZO-PB in THF ( $1.2 \times 10^{-5}$  mol/L) before (black) and after (red) irradiation of UV light ( $50 \text{ mW/cm}^2$ ) at 25 °C for 10 min.

