Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary information for

Liquid Crystal Electropolymerisation Under Magnetic Field and Resultant Linear Polarised Electrochromism

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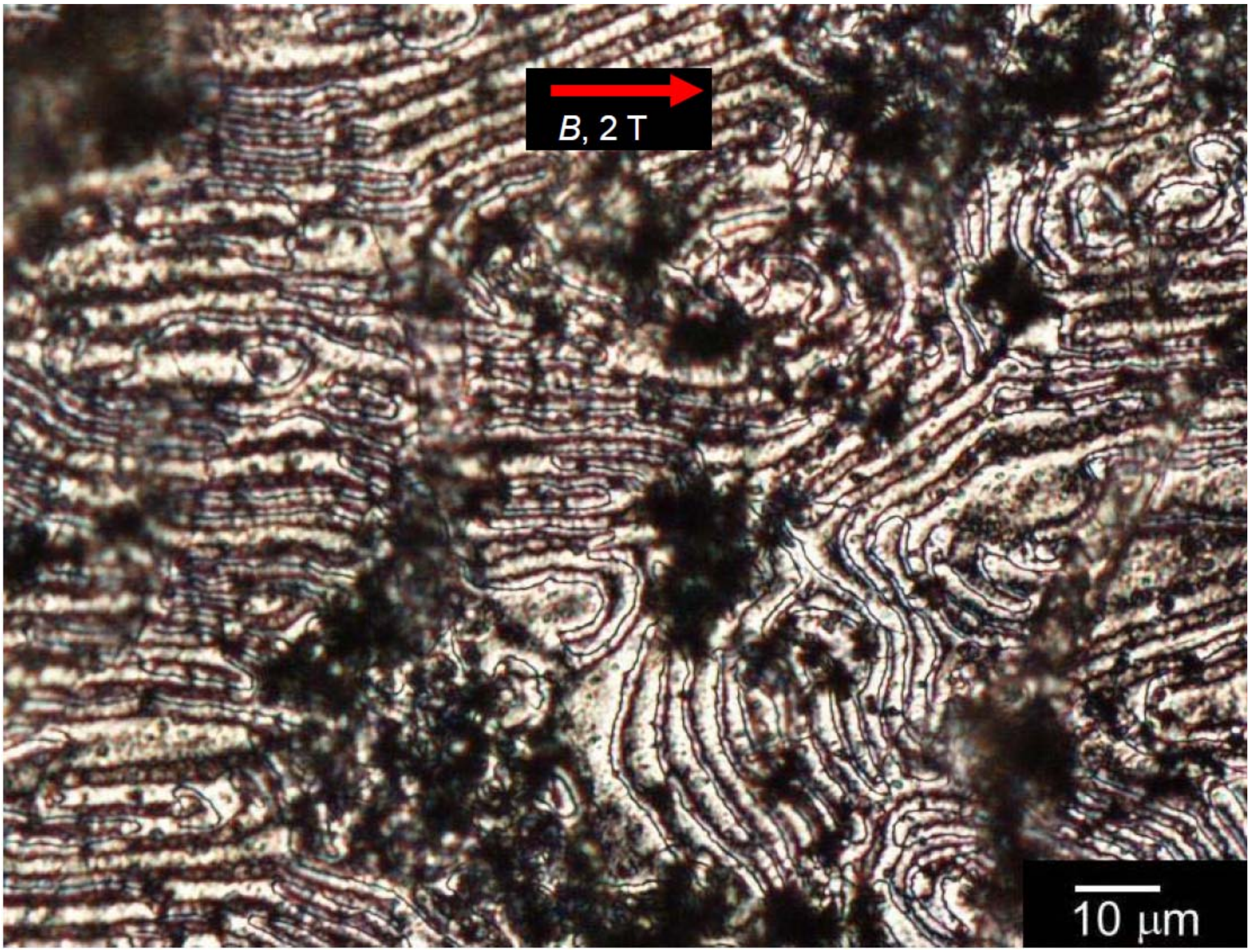

Fig. S1. Polarising optical microscopic image of PEDOT prepared in Ch*LC electrolyte under magnetic field of 2 T (PEDOT-Ch*$_{2T}$).

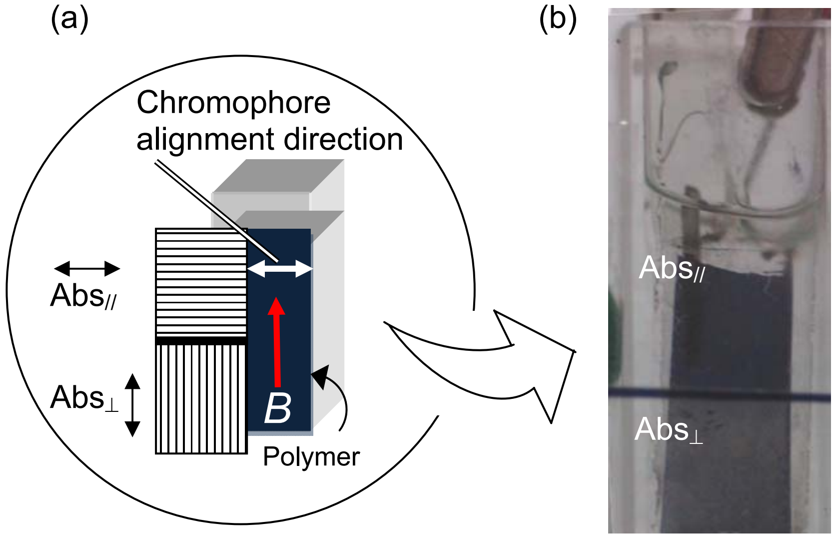

Fig. S2. Schematic illustration of PEDOT prepared in SmALC electrolyte under 4 T (PEDOT-SmA$_{4T}$). (a) Direction of the polariser setting for visual observation of the oriented sample. (b) Visual inspection through two polarisers (PEDOT-SmA$_{4T}$) in a quartz cuvette. Abs = absorption.

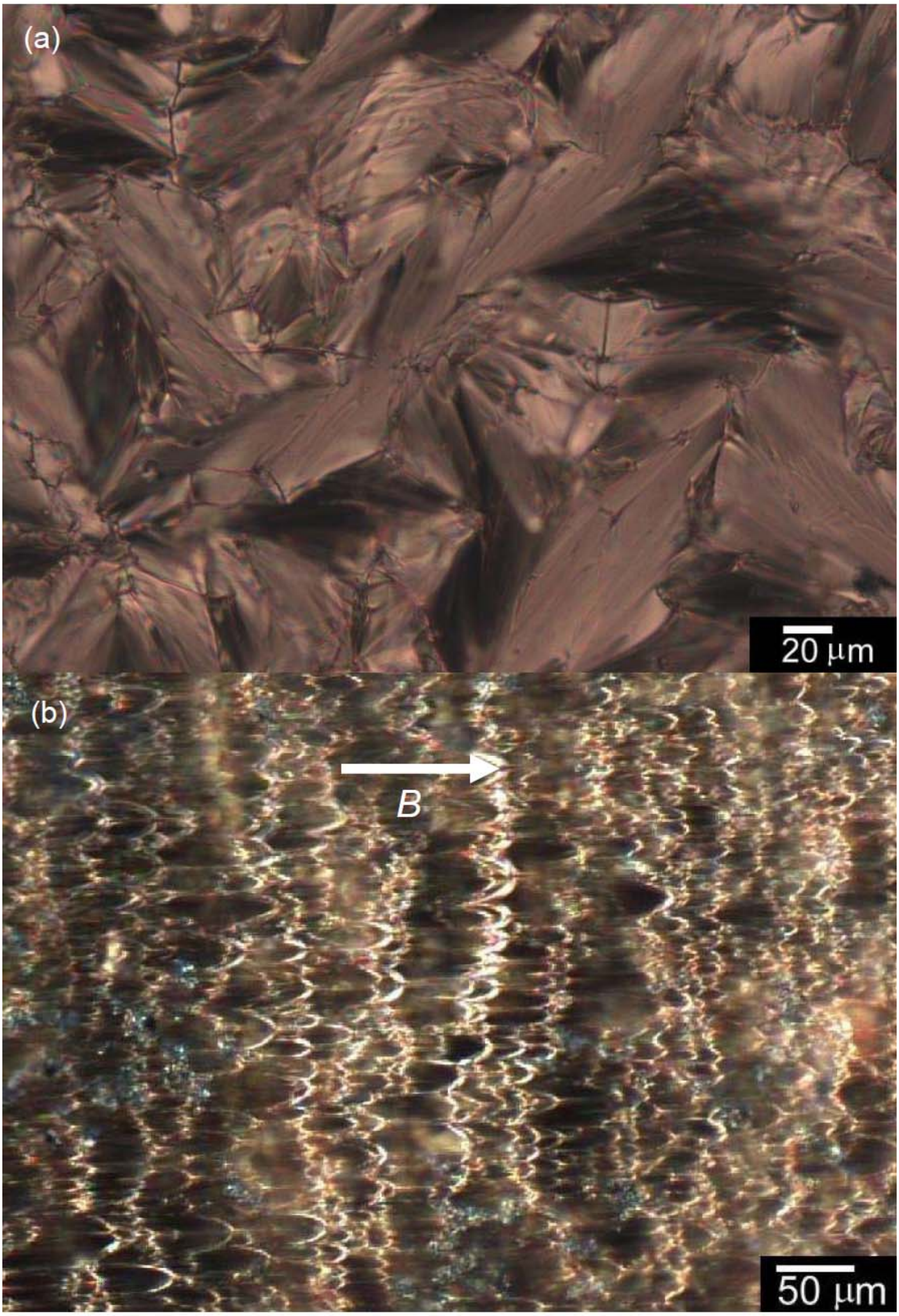

Fig. S3. POM images of SmALC electrolyte solution containing the monomer (2,3,2′,3′,2″,3′-hexahydro-[5,5′:7′,5″]*ter*[thieno[3,4-b]-[1,4]dioxine]; *ter*EDOT) and supporting salt (tetrabutylammonium perchlorate; TBAP) (a) showing random fan-shaped texture at 25 °C, and (b) under 4 T at 25 °C.

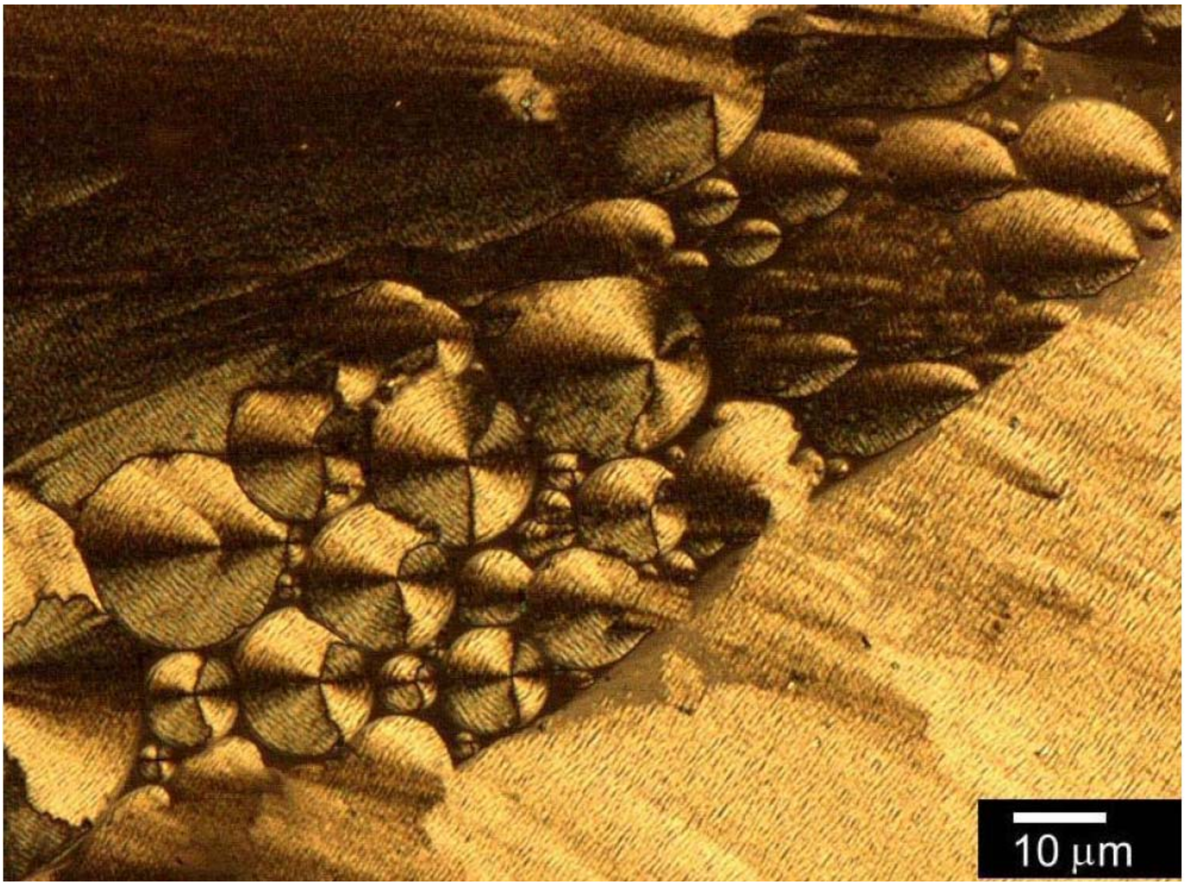

Fig. S4. POM image of PEDOT prepared in SmALC electrolyte solution under zero magnetic field, showing multi-domain structure without insertion of gypsum first-order red plate.

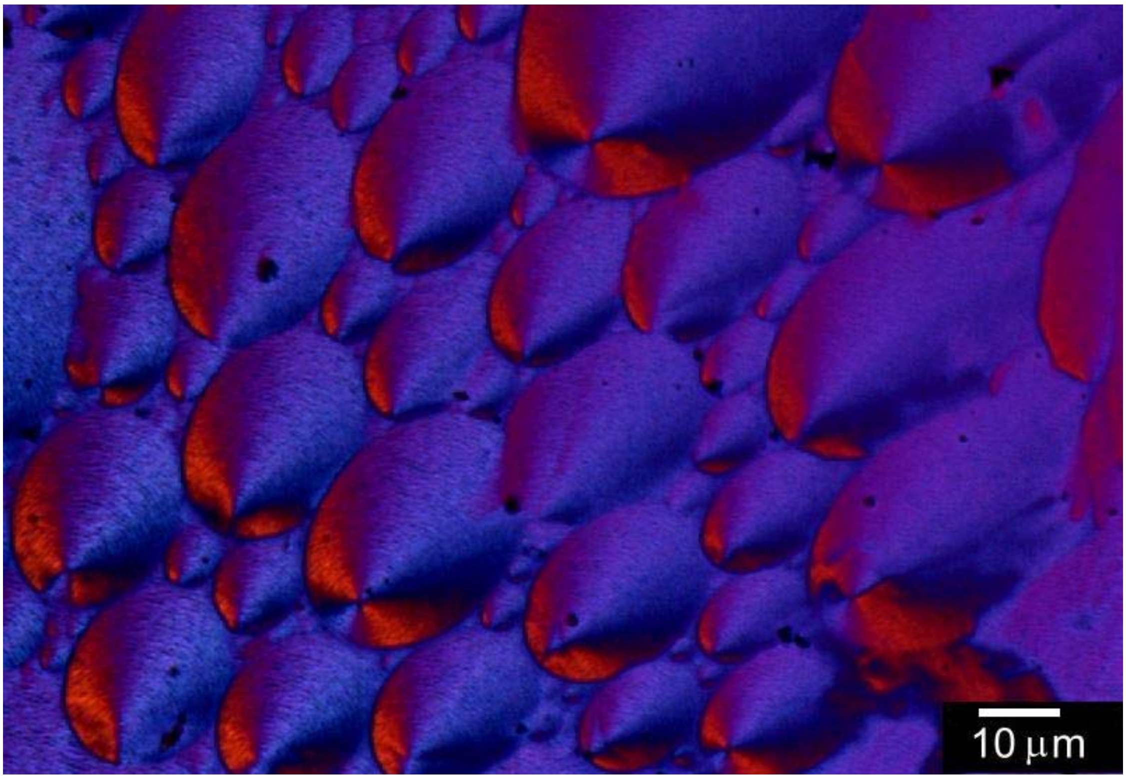

Fig. S5. POM images of PEDOT (LC free sample) prepared in SmA with insertion of gypsum first-order red plate under zero magnetic field.

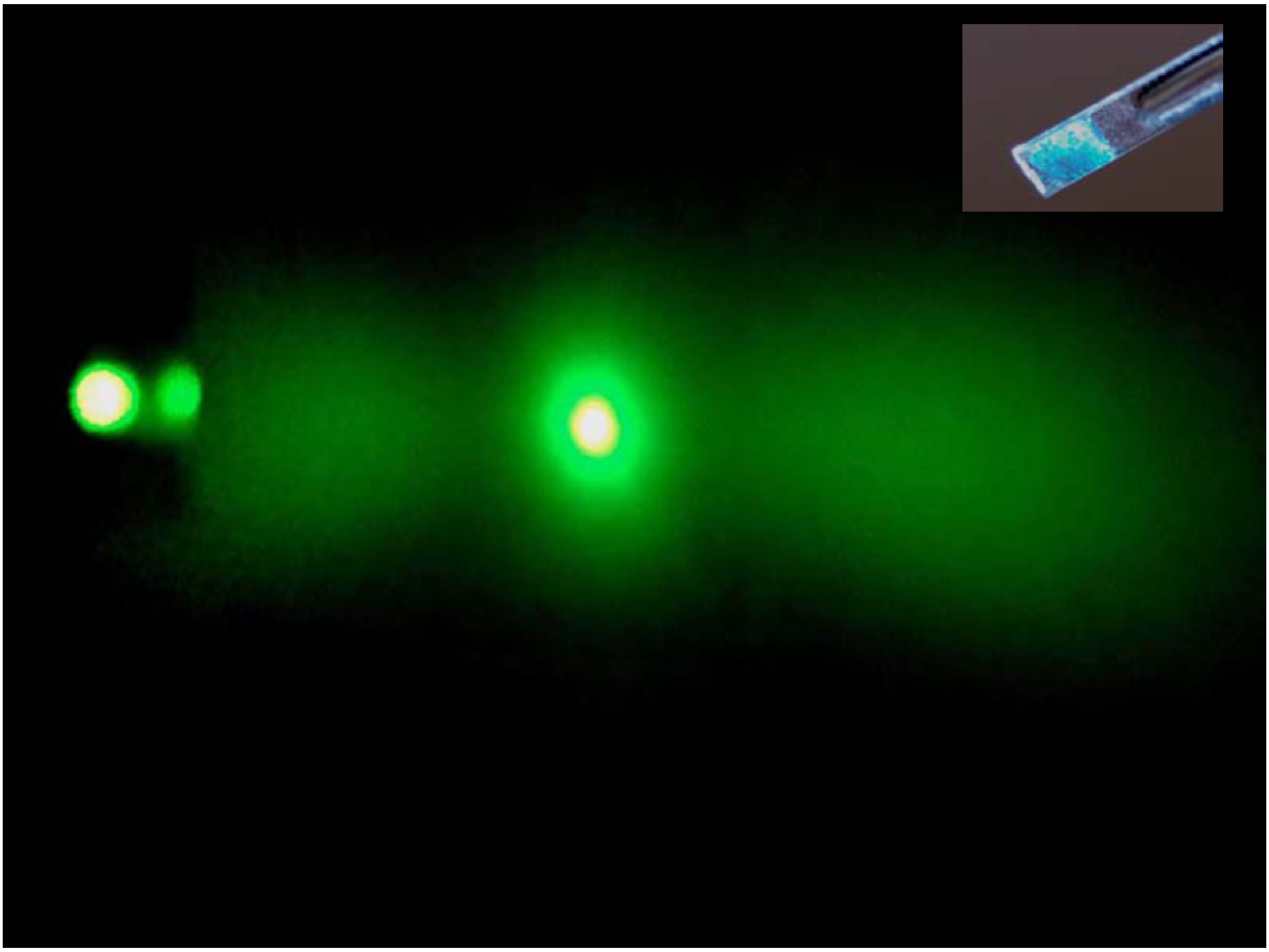

Fig. S6. Laser diffraction image of PEDOT prepared in SmALC electrolyte under zero magnetic field (PEDOT-SmA_{0T}). Inset shows the reflection colour of PEDOT with an oblique angle of incidence from a white light emitting diode beam.

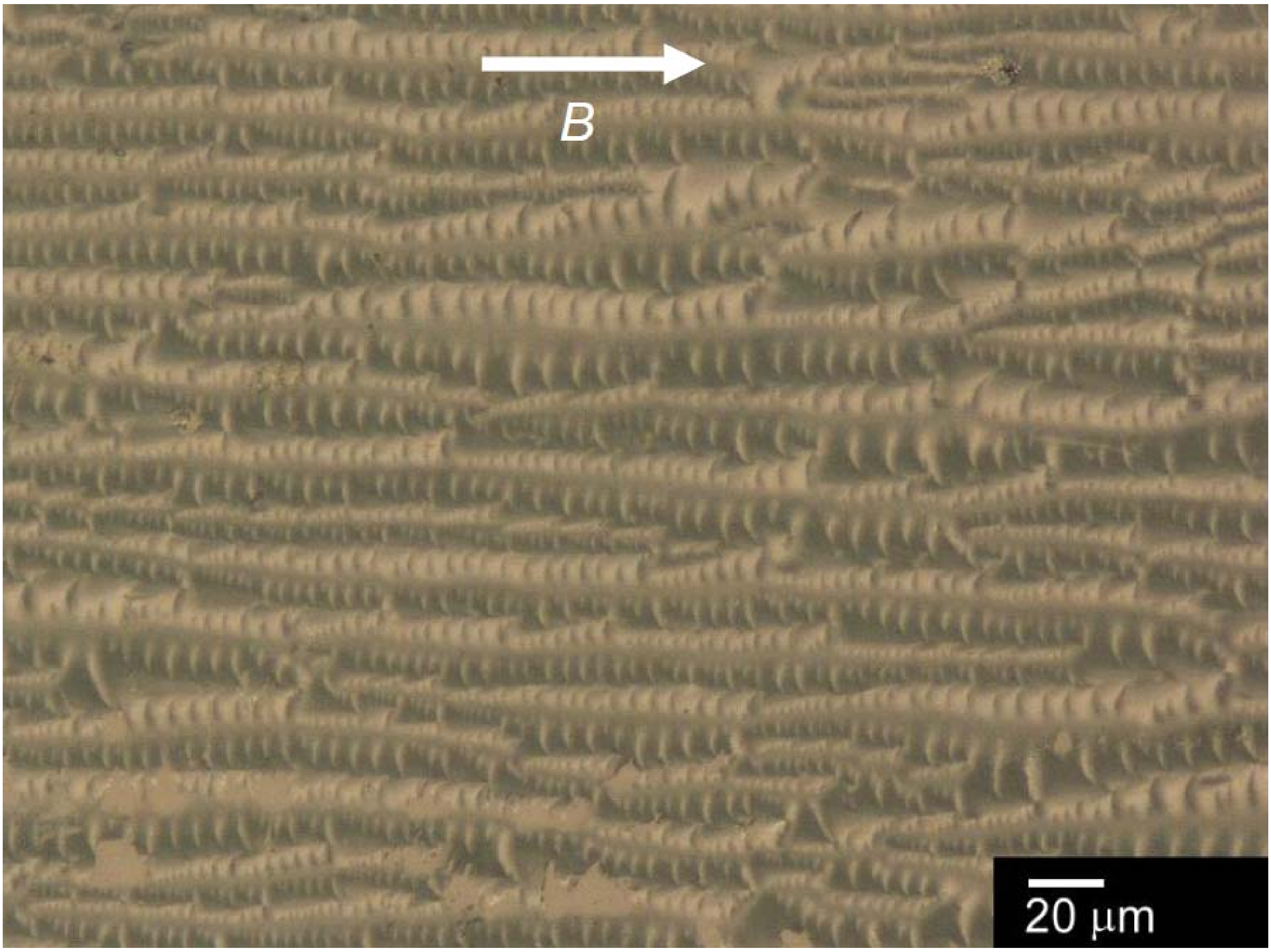

Fig. S7. POM image of PEDOT prepared in SmALC electrolyte solution under a magnetic field of 4 T, showing an aloe leaf-like structure.

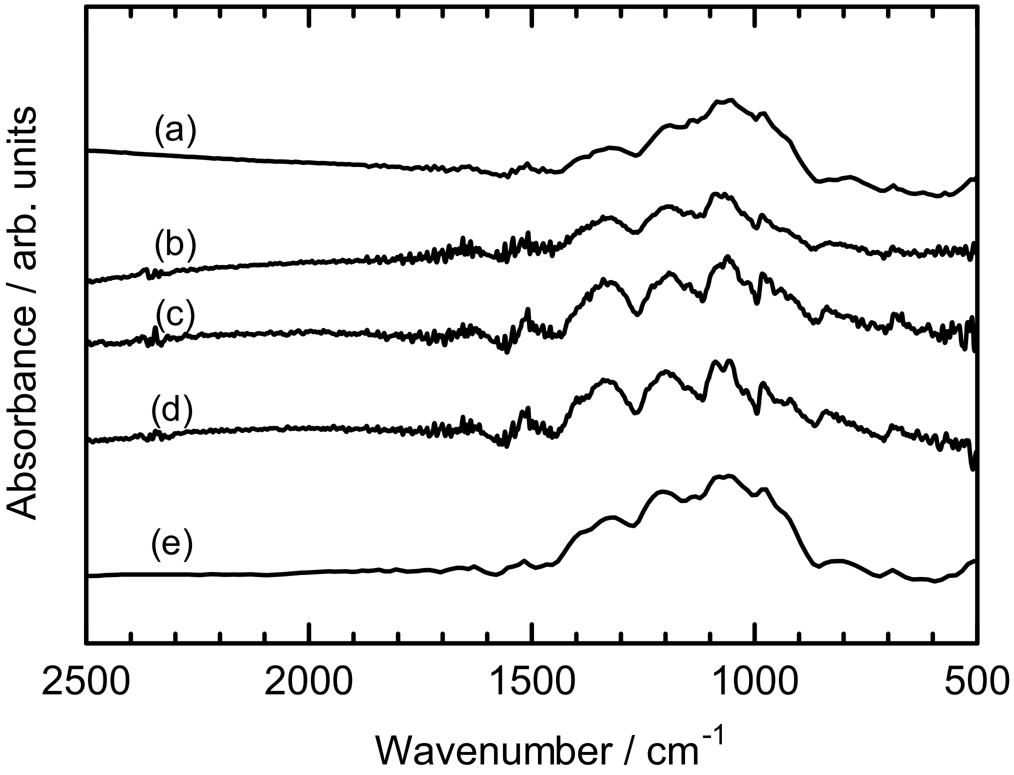

Fig. S8. Infrared (IR) spectra of PEDOT prepared in acetonitrile solution (PEDOT-ACN) (a), nematic liquid crystal (LC) (LC free sample) (PEDOT-N_{4T}) (b), cholesteric LC (LC free sample) (PEDOT-Ch^{*}_{4T}) (c), smectic A LC (LC free sample) (PEDOT-SmA_{4T}) (d), isotropic state of smectic A LC at 80 °C (LC free sample) (PEDOT-SmA_{0T}iso) (e).

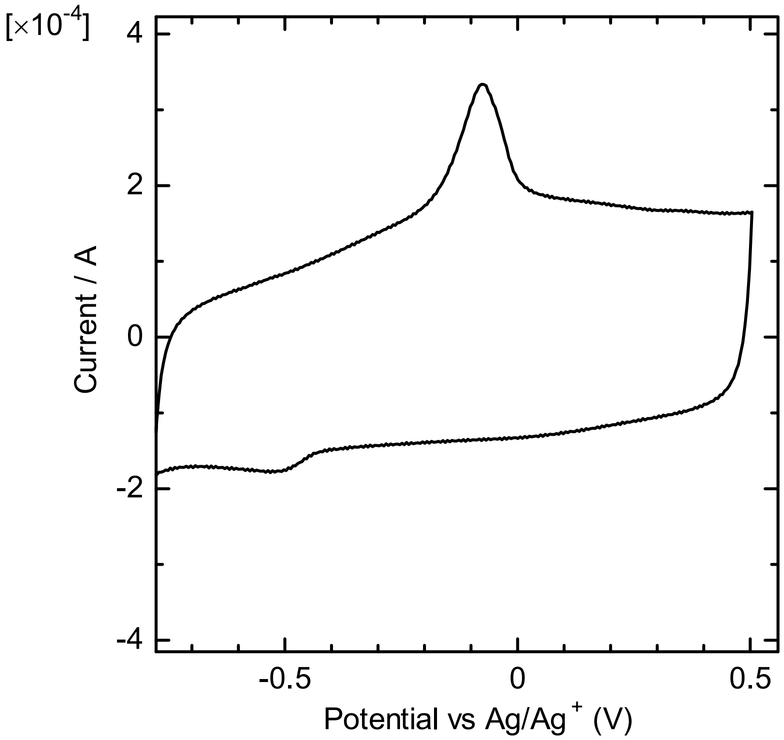

Fig. S9. Cyclic voltammogram of PEDOT prepared with SmALC (PEDOT-SmA$_{4T}$) at a scan rate of 100 mV/s in 0.1 M TBAP/acetonitrile solution.

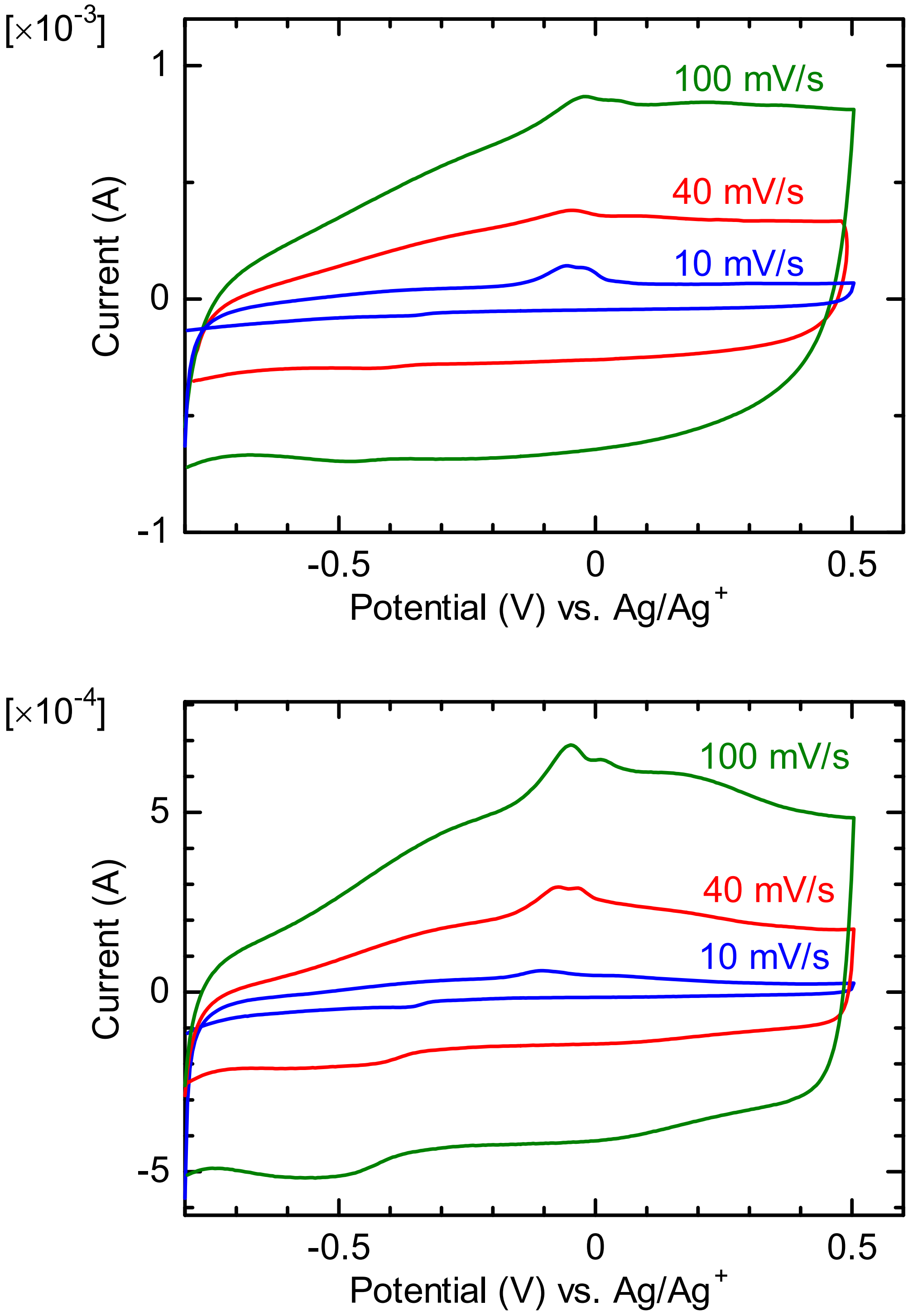

Fig. S10. Cyclic voltammogram of PEDOT in monomer free 0.1 M TBAP/acetonitrile solution. (a) PEDOT prepared in acetonitrile solution at room temperature (PEDOT-ACN). (b) PEDOT prepared in isotropic state (80 °C) of SmALC (PEDOT-SmA$_{0T}$iso).

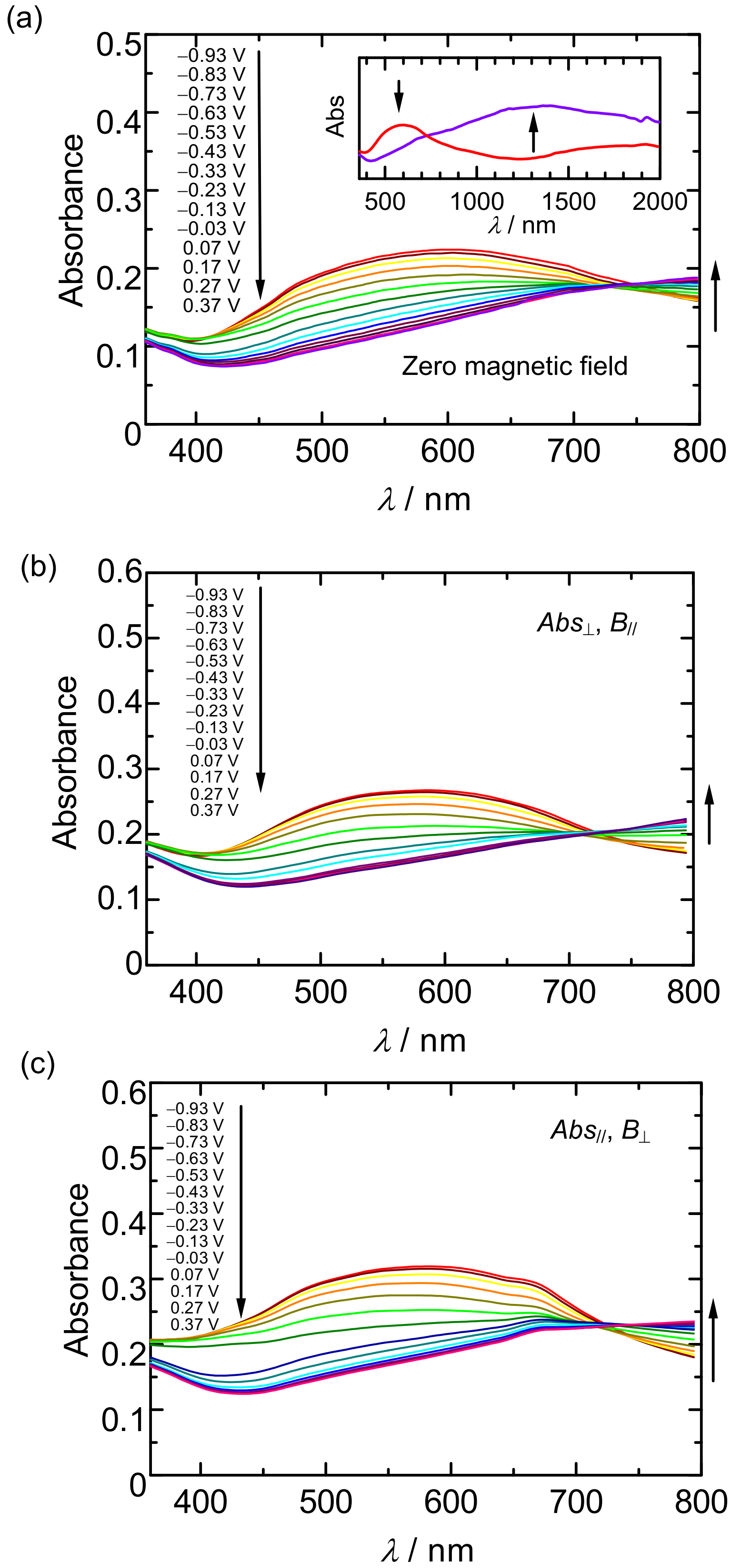

Fig. S11. Spectro-electrochemical analysis of PEDOT prepared in NLC electrolyte solution (a) under zero magnetic field and (b,c) under 4 T (PEDOT-N$_{4T}$). (a) Change in optical absorption during the doping (oxidation) process without the polariser. The inset shows the optical absorption at long wavelength. (b) Optical absorption during the doping (oxidation) process with the polariser set perpendicular to the direction of the oriented chromophore ($Abs_{\perp}$, $B_{//}$). (c) Optical absorption during the doping (oxidation) process with the polariser set parallel to the direction of the oriented chromophore ($Abs_{//}$, $B_{\perp}$)

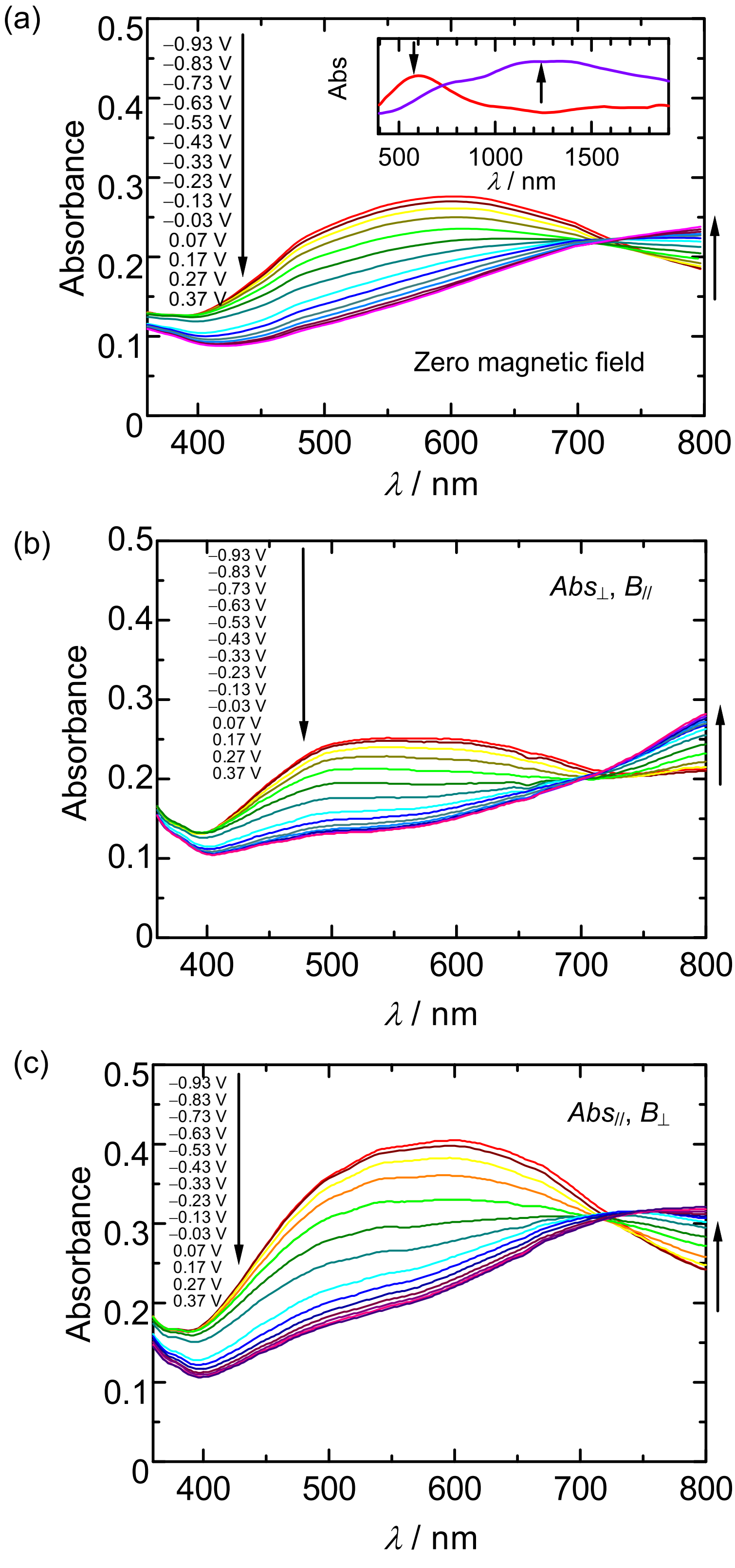

Fig. S12. Spectro-electrochemical analysis of PEDOT prepared in Ch*LC electrolyte solution (a) under zero magnetic field and (b,c) under 4 T (PEDOT-Ch*$_{4T}$). (a) Optical absorption spectra during the oxidation (doping) process without the polariser. The inset shows the optical absorption spectra at long wavelength. (b) Optical absorption spectra during the oxidation (doping) process with the polariser set perpendicular to the direction of the oriented chromophore ($Abs_{\perp}$, $B_{//}$). (c) Optical absorption spectra during the oxidation (doping) process with the polariser set parallel to the direction of the oriented chromophore ($Abs_{//}$, $B_{\perp}$).

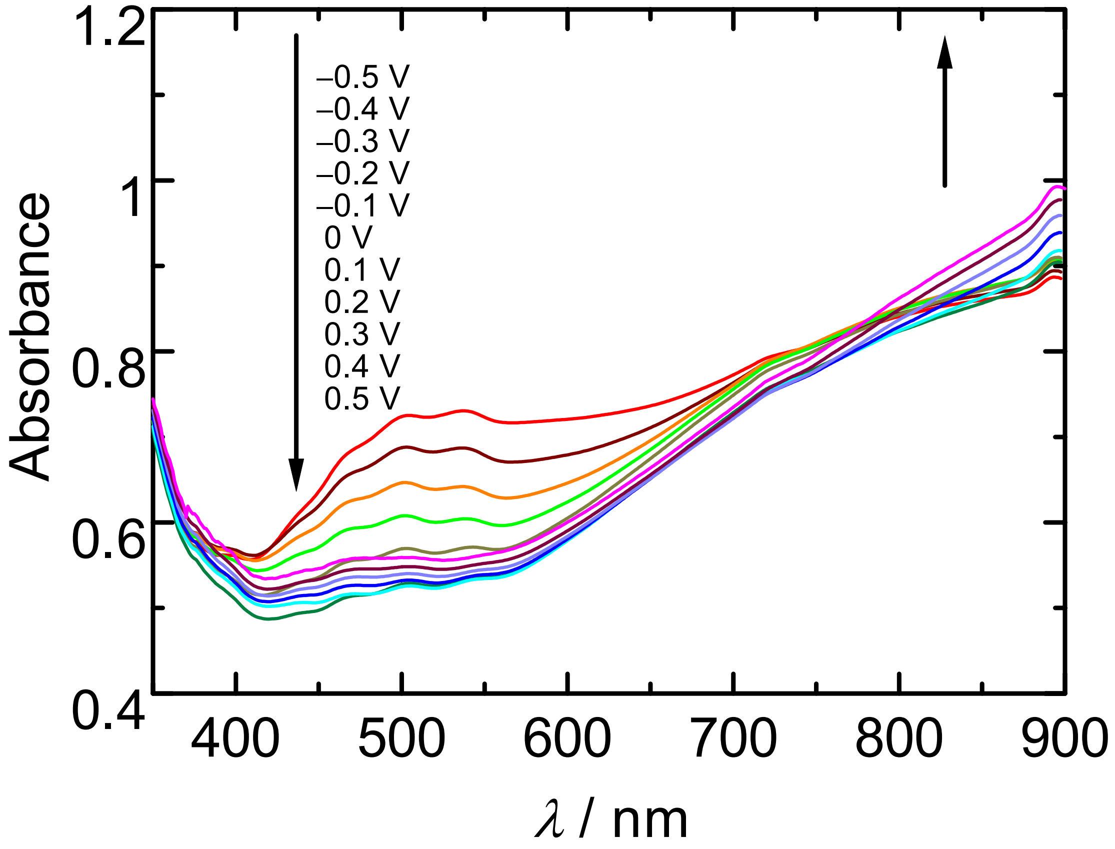

Fig. S13. Spectro-electrochemical analysis of PEDOT prepared from *ter*EDOT (PEDOT-ACN) in monomer-free 0.1 M acetonitrile solution under zero magnetic field. Optical absorption spectra during the oxidation (doping) process without the polariser.

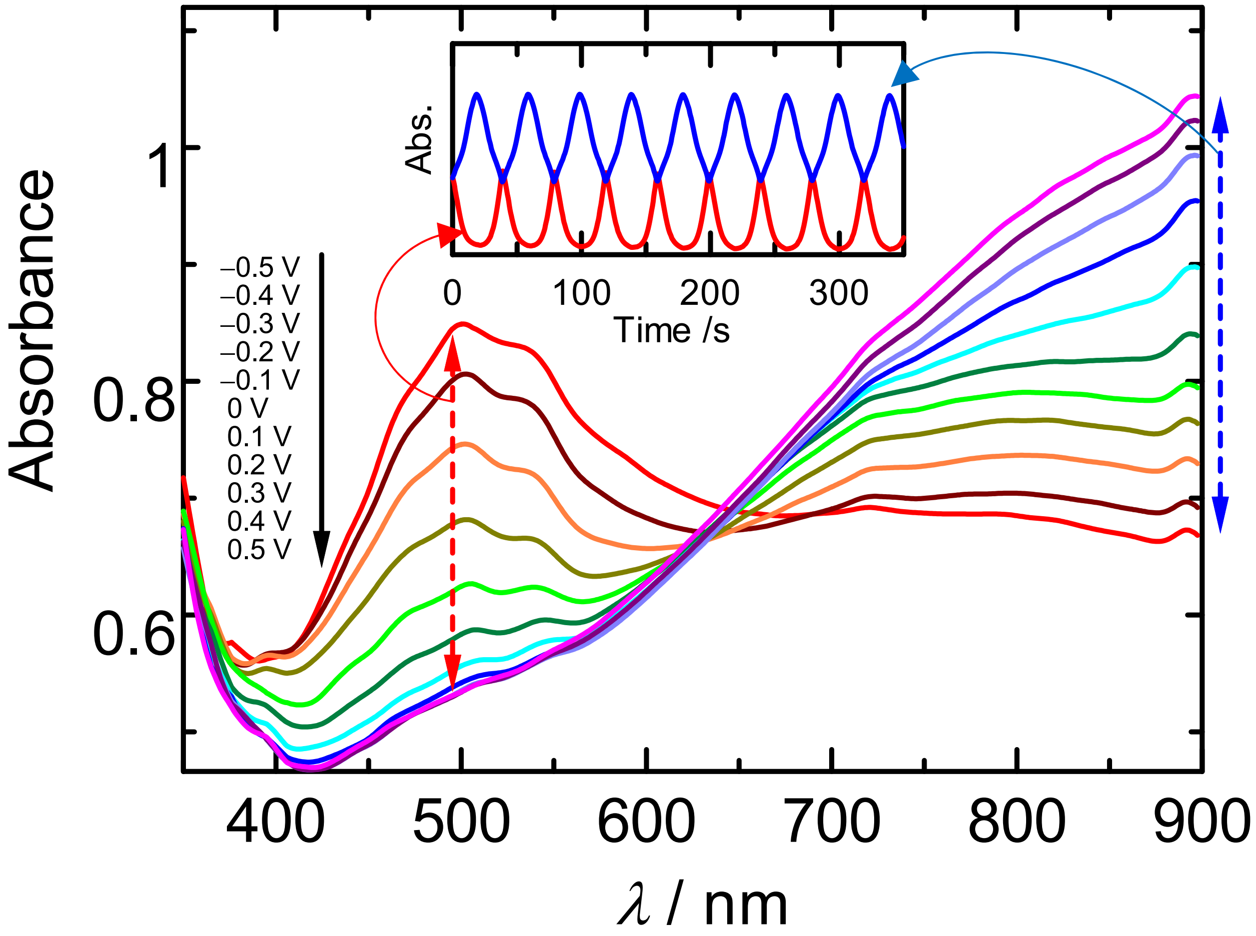

Fig. S14. Spectro-electrochemical analysis of PEDOT prepared from *ter*EDOT in an isotropic state SmA electrolyte solution under zero magnetic field (PEDOT-SmA$_{0T}$iso) in monomer-free 0.1 M acetonitrile solution (6CB: 0.165 g, 8OCB: 0.33 g, TBAP: 0.25 mg, *ter*EDOT: 2.5 mg). Optical absorption spectra during the oxidation (doping) process without the polariser. The inset shows the reversible change in intensity during the oxidation/reduction (doping/dedoping) process (CV scan, 50 mV/s) at 500 nm (red line) and 900 nm (blue line).

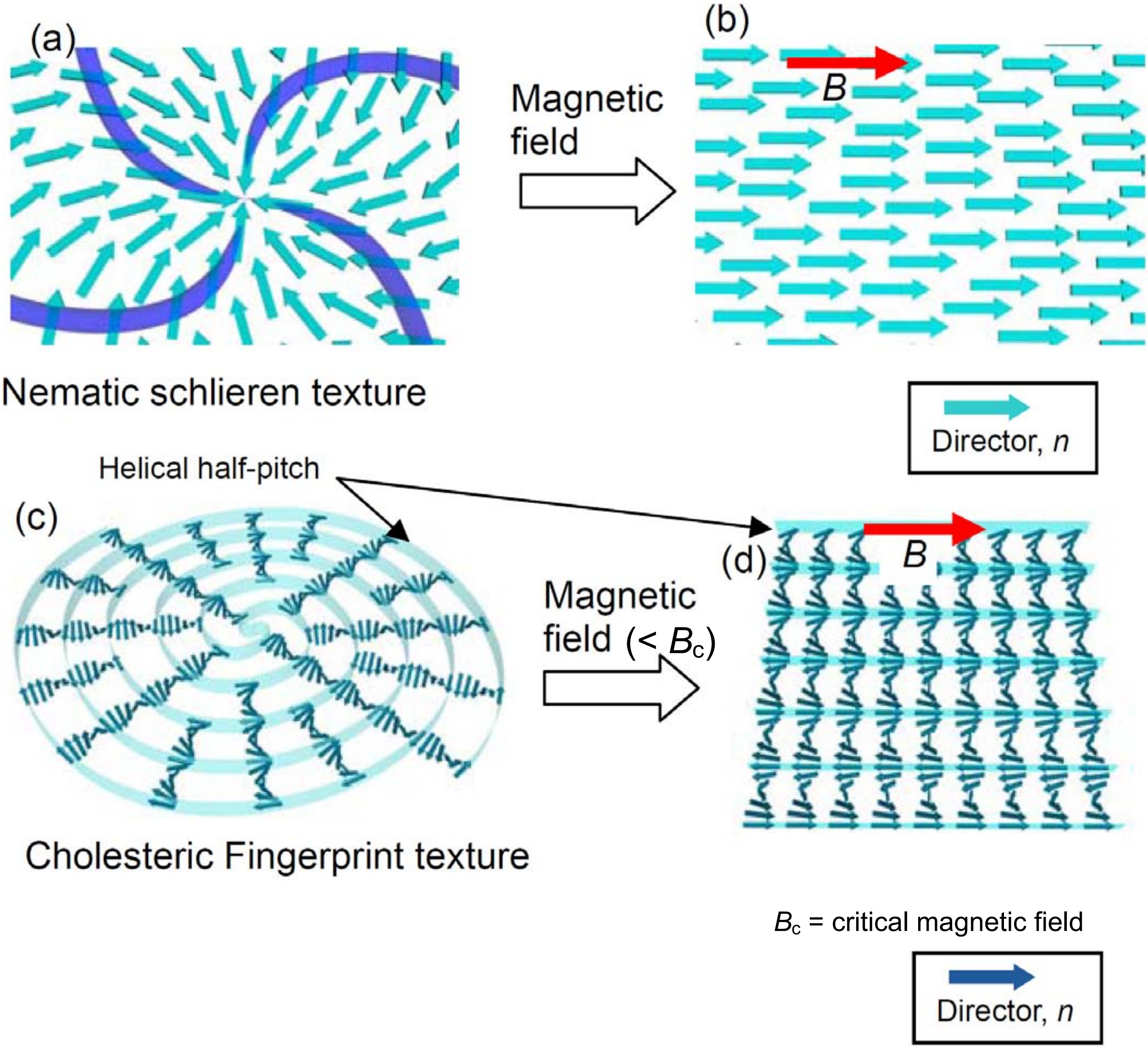

Fig. S15. (a) Molecular arrangement of the nematic schlieren texture. (b) Magnetic orientation of NLC. (c) Cholesteric fingerprint texture under zero magnetic field. (d) Magnetic orientation of Ch*LC (<B_c). Magnetic fields higher than B_c result in unwinding of the helical arrangement of Ch*LC. Arrows indicate the directors (n) of individual molecules in the LC state.

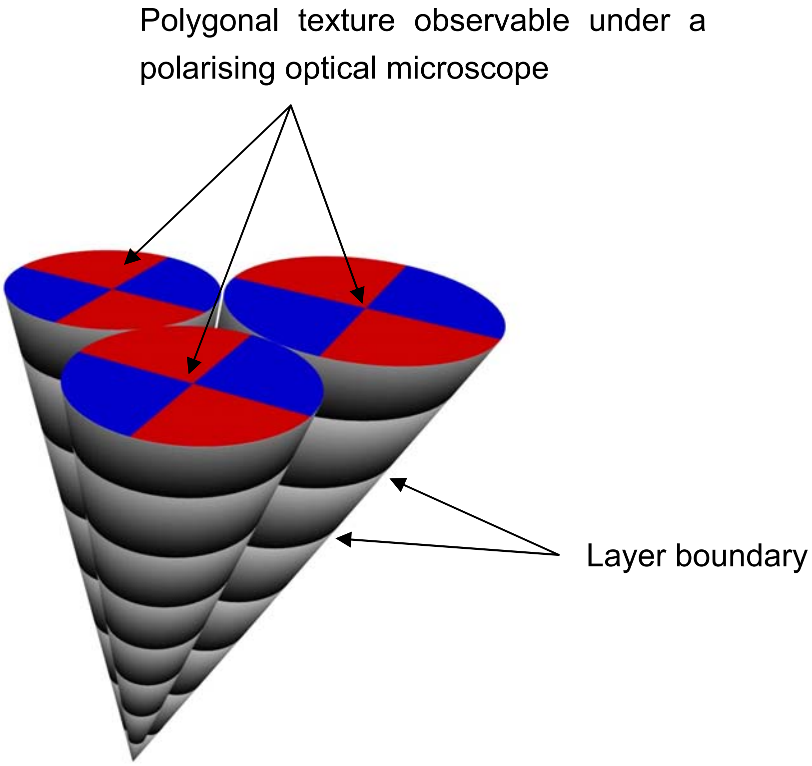

Fig. S16. Molecular arrangement of the polygonal texture of the SmA phase.

Experimental

4-Heptyloxy-4’-cyanobiphenyl (8OCB):

4-Hydroxy cyanobiphenyl (5 g, 25.6 mmol) and K_2CO_3 (3.5 g, 25.6 mmol) were added to 1-octylbromide (4.95 g, 25.6 mmol) in 30 mL of ethanol. A catalytic amount of dibenzo-crown-6 (1 mg) was added to the solution and the reaction mixture was then stirred and refluxed for 24 h. The reaction mixture was evaporated to remove the solvents, and washed several times with water. The organic layer was extracted with ether. The ether was evaporated and the crude product was recrystallised from acetone to yield 5.2 g of white powder. Yield = 66%. ^{1}H NMR (500 MHz, δ from TMS, $CDCl_3$): 0.89 (3H, CH_3, t, J = 6.0 Hz), 1.29-1.50 (10H, CH_2, m), 1.8 (2H, OCH_2CH_2, quint, J = 4.3 Hz), 4.00 (2H, OCH_2, t, J = 6.4 Hz), 6.99 (2H, d, ph, J = 8.0 Hz), 7.52 (2H, d, ph, J = 7.9 Hz), 7.64 (2H, d, ph, J = 7.9 Hz), and 7.68 (2H, d, ph, J = 7.6 Hz) ppm. ^{13}C NMR (125 MHz, δ from TMS, $CDCl_3$): 14.11, 22.67, 26.05, 29.23, 29.25, 29.36, 31.82, 68.20, 110.03, 115.10, 119.13, 127.08, 128.32, 131.25, 132.57, 145.31, and 159.83 ppm. The NMR spectra are shown in Fig. S17 (^{1}H NMR) and Fig. S18 (^{13}C NMR) (Supplementary Information).

Preparation of NLC electrolyte solution

NLC electrolyte solution was prepared by dissolving TBAP (0.1 mg) as a supporting salt and *ter*EDOT (monomer, 5 mg) in 6CB (matrix LC, 0.5 g) under argon flow. At room temperature, the NLC electrolyte solution exhibits a schlieren texture, as observed under the POM. The NLC electrolyte solution was heated once in a vial to 40 °C under an argon atmosphere, in order to completely dissolve the supporting salt and monomer in the 6CB LC solvent.

Preparation of Ch*LC electrolyte solution

Ch*LC electrolyte solution was prepared with the addition of a small amount of cholesteric pelargonate (an optically active material) as a Ch*LC inducer to 6CB as an NLC to induce the formation of Ch*LC with a mesoscopic helical structure.

The Ch*LC electrolyte solution was prepared as a reaction solvent by the addition of cholesteryl pelargonate (10 mg) to 6CB (0.5 g). TBAP (0.1 mg) was then added as a supporting salt. Liquid crystallinity was confirmed to be maintained after the addition of the monomer (*ter*EDOT, 5 mg). At room temperature, the Ch* electrolyte solution exhibits a fingerprint texture under the POM, typical of a Ch* phase. The distance between the stripes in the optical texture corresponds to the helical half-pitch ($P/2$) of the Ch*LC.

Preparation of SmA electrolyte solution

A mixture of 8OCB/6CB (= 1/5 by weight), which exhibited a stable SmA focal conic fan-shaped texture or polygonal texture under the POM at room temperature, was prepared prior to the preparation of SmALC. Although 8OCB exhibits the SmA phase between 54.5 and 67 °C, a mixed LC system of 6CB and 8OCB was employed for the SmALC electrolyte solution, in order to achieve depression of the viscosity and tuning of the LC temperature range for electropolymerisation under magnetic field at room temperature. The SmALC electrolyte solution was prepared by dissolving TBAP (0.1 mg) and *ter*EDOT (monomer, 5 mg) in the 8OCB/6CB mixture (1/5, w/w, matrix LC, 0.5 g) under argon flow.

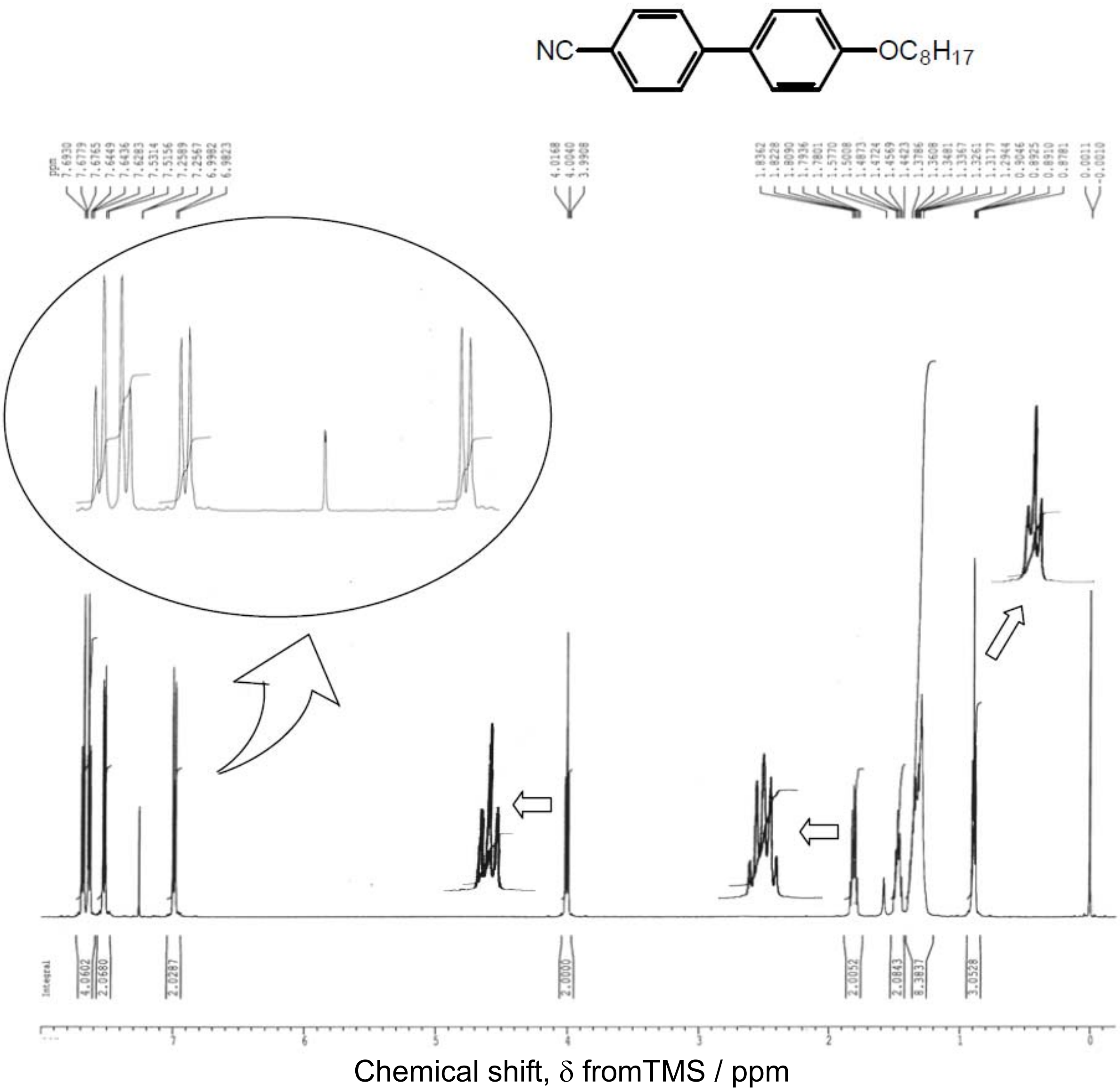

Fig. S17. ^{1}H NMR spectrum of 8OCB in $CDCl_3$.

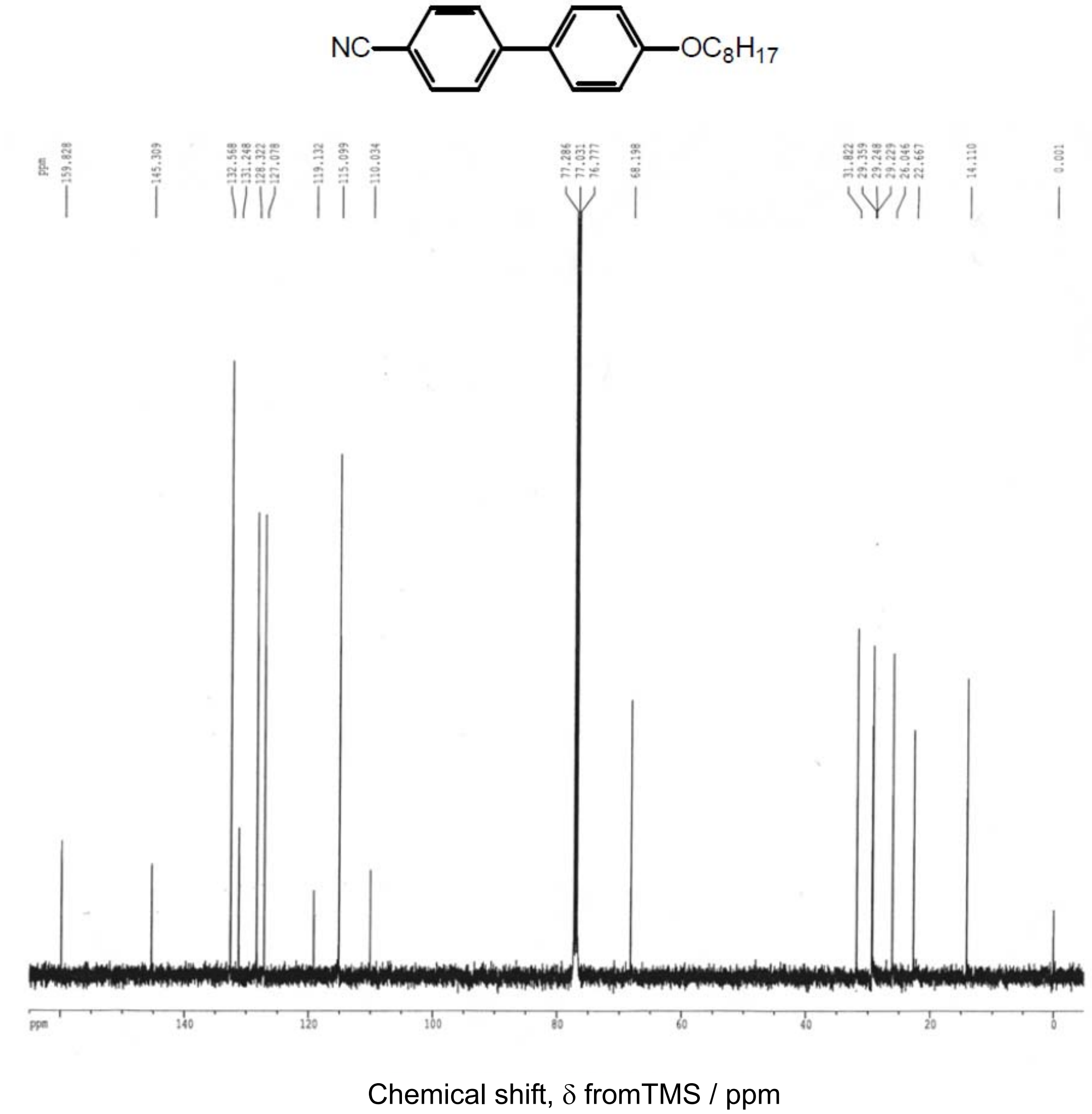

Fig. S18. ^{13}C NMR spectrum of 8OCB in $CDCl_3$.