

Supplementary data

Control and modulation of Chirality for Azobenzene-substituted Polydiacetylene LB films with circularly polarized light

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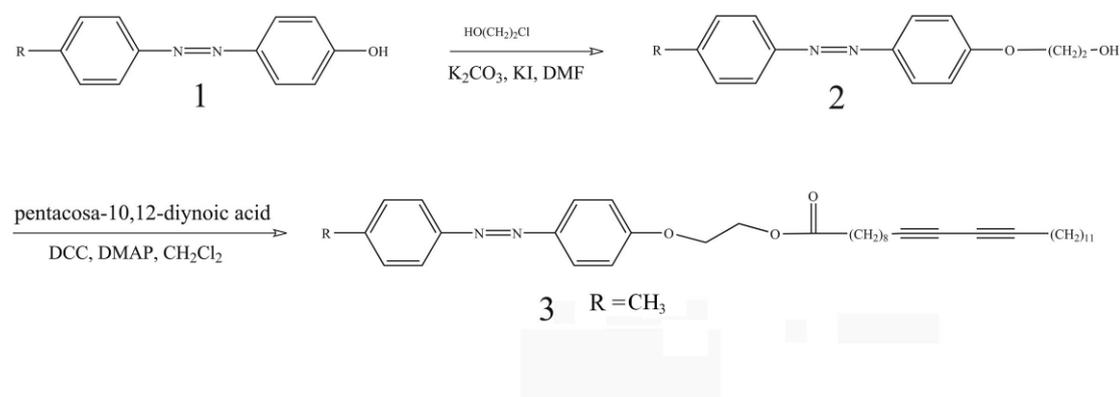
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Materials and Characterization:

10,12-pentacosadiynoic acid (DA) was purchased from Tokyo Chemical Industry Co., Ltd., and used as received. Diacetylene monomer containing *p*-methyl azobenzene moiety (MADA) was synthesized in analogy to the previous procedure [1S]. Monolayer at the air-water interface was compressed with aid of two barriers moving at the same speed of 10 mm/min in opposite direction. Subphase is pure water (18.2 M Ω). All experiments were carried out on a computer-controlled Langmuir film balance (600mm \times 150mm in length and width, 10mm in depth) in laboratory atmosphere at 20 $^{\circ}$ C (\pm 0.5 $^{\circ}$ C). A 16 W UV lamp (λ = 254 nm), hung 10 cm above the LB films, was used for normal UV-polymerization. And the circularly polarized UV light (CPUL) (313 nm) generated using Babinet-Soleil prism from ultra-high pressure mercury lamp was used for enantioselective polymerization [2S]. The laser (2mJ/pulse, 10 ns pulse duration and 10 Hz repetition rate at 520 nm) was obtained by using an optical parametric oscillator (OPO: Continuum Surelite OPO) pumped by a frequency-doubled of a Q-switched Nd-YAG Laser. The pump beam (20 mW/cm²) can be polarized circularly left or right using a Babinet-Soleil compensator. CD spectrum was measured using

JASCO CD spectrometer J-715.

An azobenzene mesogen-substituted diacetylene monomers was synthesized according to scheme 1.



Scheme 1. Synthetic routes of diacetylenic monomers containing azobenzene chromophores.

The detailed experimental procedures were given below. A mixture of **1** (2.23g, 10 mmol), potassium carbonate (4.14 g) and potassium iodide (0.01 g) was dissolved in DMF 50 mL, and 2-chloroethanol (0.89 g, 11 mmol) dissolved in DMF 10 mL was added drop wise. The resulting mixture was stirred at 120 °C for 72 h. The reaction was stopped by the addition of excess water to the mixture. The crude product was precipitated. The precipitate was filtered off and recrystallized twice from ethanol to give a yellow powder. Yield 80 %. mp: 147 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.90 (d, J = 9.0Hz, 2H), 7.77 (d, J = 9.0Hz, 2H), 7.29 (d, J = 9.0Hz, 2H), 7.01(d, J=9.0Hz, 2H), 4.16 (t, J = 4.5Hz, 2H), 4.00 (t, J = 4.5Hz, 2H).

A solution of N, N'-dicyclohexylcarbodiimide (DCC) (0.275 g, 1.3 mmol) and dry CH₂Cl₂ 20 mL was added dropwise at room temperature to a mixture of Pentacosano-10,12-dienoic acid (0.1 g, 0.27 mmol), **2** (0.08 g, 0.3 mmol) and a small quantity of 4-dimethylamino pyridine (DMAP) in dry CH₂Cl₂ 40 mL. The mixture was stirred at 25 °C for 72 h. The resulting mixture was filtered with suction and repeatedly washed with water, 1.2 M HCl, 5% aqueous NaHCO₃, and water in order. The crude product was purified by silica gel column. After the solvent was removed, a yellow solid was obtained. **3** Yield 63 %. mp: 83-84°C. ¹H NMR (300 MHz, CDCl₃) δ: 7.84 (d, J = 9.0Hz, 2H), 7.73 (d, J = 8.4Hz, 2H), 7.22 (d, J=8.4Hz, 2H), 6.95 (d, J =

9.0Hz, 2H), 4.40 (t, $J = 4.6\text{Hz}$, 2H), 4.19 (t, $J = 4.6\text{Hz}$, 2H), 2.36 (s, 3H), 2.32 (t, $J=7.5\text{Hz}$, 2H), 2.19 (m, 4H), 1.57 (m, 2H), 1.47 (m, 4H), 1.44-1.33 (m, 26H), 0.81 (t, $J = 6.7\text{Hz}$, 3H). The ^1H NMR spectra of **3** was given below.

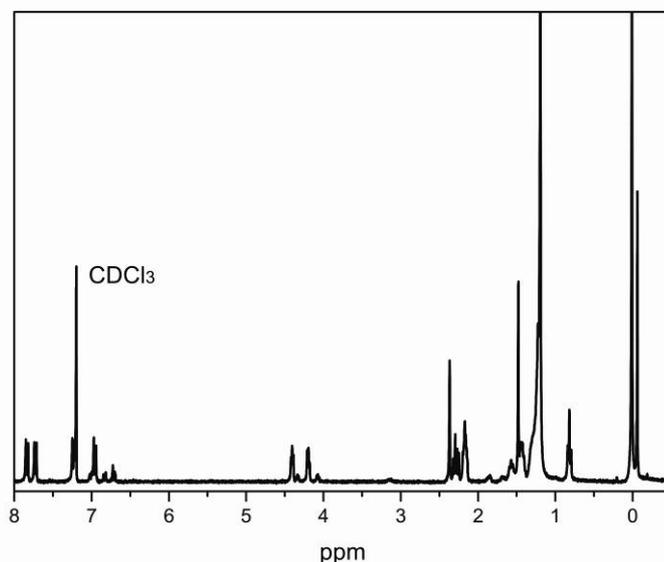


Figure S1. ^1H NMR spectra of the azobenzene mesogen-substituted diacetylene monomers

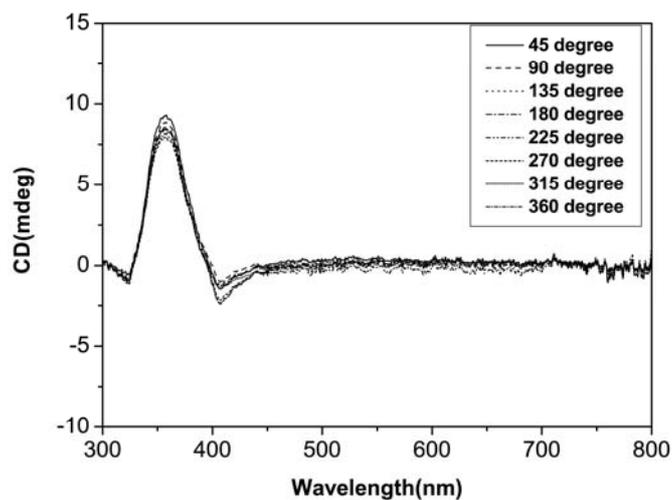


Figure S2. CD spectra of the MADA LB films before polymerization rotated as, 45°; 90°; 135°; 180°; 225°; 270°; 315°; 360°.

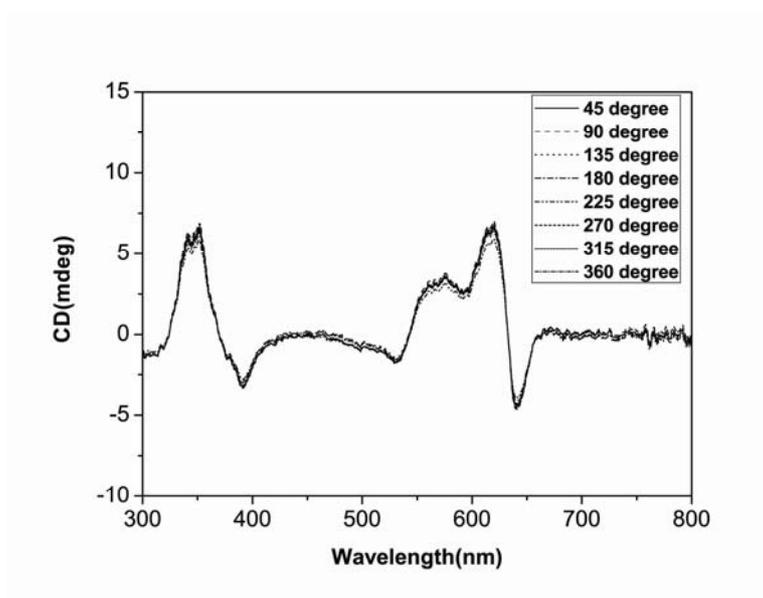


Figure S3. CD spectra of the PMADA LB films after polymerization upon left-handed CPUL rotated as, 45°; 90°; 135°; 180°; 225°; 270°; 315°; 360°.

References

- 1S Q. Ye, X. You, G. Zou, X.W. Yu, Q.J. Zhang, *J. Mater. Chem.*, 2008, **18**, 2775
- 2S a) T. Manaka, H. Kon, Y. Ohshima, G. Zou and M. Iwamoto, *Chem. Lett.*, 2006, **35**(9), 1028; b) G. Zou, H. Kon, Y. Ohshima, T. Manaka, M. Iwamoto, *Chem. Phys. Lett.* 2007, **442**: 97 .