

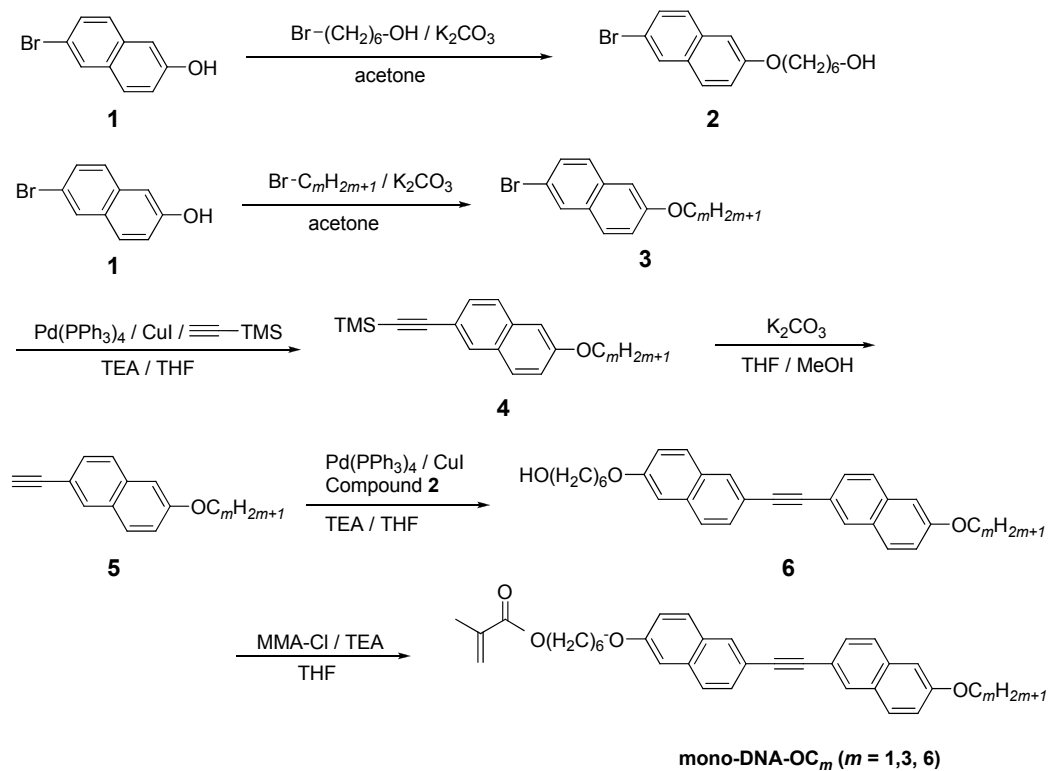
Supporting Information

Highly-Birefringent side-chain LC polymethacrylate with a dinaphthyl-acetylene mesogenic unit[†]

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Experimental (synthetic procedures)





Instruments

The ^1H NMR and ^{13}C NMR spectra were measured using a JEOL LNM-EX 400 at room temperature. CDCl_3 and tetramethylsilane (TMS) were used as a measurement solvent and an internal standard, respectively.

Materials

Unless otherwise noted, all chemicals were commercially available and use as received. Compound **2-5** were prepared according to our previous report (Y. Arakawa, S. Nakajima, S. Kang, M. Shigeta, G. Konishi, J. Watanabe, “Synthesis and evaluation of dinaphthylacetylene nematic liquid crystals for high-birefringence materials” *Liq. Cryst.*, **39**, 1063-1069 (2012). [DOI:10.1080/02678292.2012.696730]).

6-((6-((6-(hexyloxy)naphthalen-2-yl)ethynyl)naphthalen-2-yl)oxy)hexan-1-ol (6)

Argon-degassed THF (50 ml) and triethylamine (50 ml) were added to a mixture of 2-bromo-6-(hexyloxy)naphthalene (**3**) (4.2 g, 16.8 mmol), 2-ethynyl-6-(hexyloxy)naphthalene (**5**) (4.4 g, 13.6 mmol), Pd(PPh₃)₄ (0.52 g, 0.45 mmol), CuI (0.14 g, 0.75 mmol), and PPh₃ (0.2 g, 0.75 mmol) under argon atmosphere; then, the resulting mixture was stirred at 40 °C for 1 day. Subsequently, ether was added to the mixture, and insoluble salts were removed from it by filtration. The solution was washed HCl_{aq} and water. The resulting solution was evaporated. The residue was extracted by CHCl₃ and then washed with water. After removal of the solvent,

the crude product was purified by silica gel column (eluent: hexane : ethyl acetate = 3 : 1) to give **6** (95%). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 2H), 7.72 (d, 2H, *J* = 9.0 Hz), 7.79 (d, 2H, *J* = 8.68 Hz), 7.57 (d, 2H, *J* = 8.5 Hz), 7.18-7.14 (m, 2H), 7.11 (s, 2H), 4.12-4.06 (m, 4H), 3.68 (dt, 2H, *J* = 5.3, 5.4 Hz), 1.92-1.81 (m, 4H), 1.68-1.45 (m, 8H), 1.41-1.33 (m, 4H), 1.25 (t, 1H, *J* = 5.4 Hz), 0.92 (t, 3H, *J* = 7.1 Hz) ppm.

6-(((6-((hexyloxy)naphthalen-2-yl)ethynyl)naphthalen-2-yl)oxy)hexyl methacrylate
(mono-DNA-OC6)

Methacryloyl chloride (1.2 g, 11.8 mmol) was added dropwise to the THF (20 ml) solution of **6** (2.9 g, 5.9 mmol), triethylamine (2.6 ml, 17.6 mmol), and THF. The resulting solution was stirred for 13 h at room temperature. The resulting solution was evaporated. The residue was extracted by CHCl₃ and then washed with water. The resulting organic layer was dried over MgSO₄. After removal of the solvent, the crude product was purified by silica gel column (eluent: hexane : ethyl acetate = 5 : 1). Further purification was carried out by recrystallization in methanol to give **mono-DNA-OC6** (90%). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 2H), 7.75-7.65 (m, 4H), 7.61-7.54 (m, 2H), 7.20-7.13 (m, 2H), 7.12-7.08 (m, 2H), 6.10 (s, 1H), 5.51 (s, 1H), 4.16 (t, 2H, *J* = 6.6 Hz), 4.07 (t, 2H, *J* = 6.5 Hz), 3.02 (s, 3H), 1.94 (s, 3H), 1.86 (dd, 2H, *J* = 6.6 and 7.4 Hz), 1.79 (dd, 2H, *J* = 6.5 and 7.3 Hz), 1.53 (dd, 4H, *J* = 7.3 and 7.4 Hz) ppm.; ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 158.2, 157.7, 136.4, 134.1, 134.0, 131.1 (131.1), 129.30, 129.26, 129.02, 128.96, 128.5, 128.4, 126.79, 126.75, 125.3, 119.6, 119.4, 118.3, 118.2, 106.5, 105.8, 89.7, 89.6, 67.8, 64.6, 55.3, 31.6, 29.1, 28.5, 25.8, 18.3 ppm.

Poly-DNA-OC6

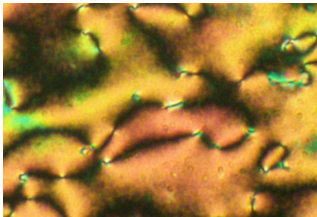
A dry NMP (0.7 g) solution of **mono-DNA-OC6** (0.3 g, 0.53 mmol) and AIBN (4.0 mg, 0.026 mmol) was heated at 80 °C for 3 days. After cooling to room temperature, the resulting solution was poured into methanol. The corrected precipitate was purified by reprecipitation from

MeOH/ system 5 times to give **P6MA-DNA-OC6** (50%). **¹H NMR** (400 MHz, CDCl₃) δ
8.08-7.82 (brm, 2H), 7.78-7.38 (brm, 6H), 7.22-6.83 (brm, 4H), 4.26-3.71 (brm, 6H), 2.25-0.66
(brm, 24H) ppm.

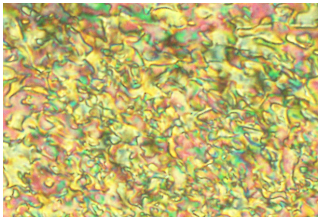
Figure Captions

Fig. S1 Photomicrographs obtained by POM observations for (a) poly-DNA-OC1, (b) and (c) poly-DNA-OC6. (a) Schlieren texture of nematic phase at 240 °C, (b) marble texture of nematic phase at 220 °C and (c) broken fan-shape texture of smectic C phase at 160 °C.

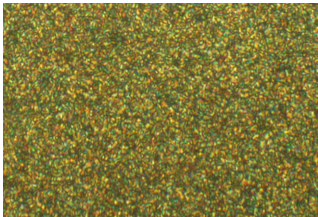
Fig. S2 An oriented WAXD profile for poly-DNA-OC6 at 160 °C under a magnetic field. In the small angle region, split layer reflections with respect to the meridional line appear up to third orders in addition to the diffuse scattering of outer reflections at $q = 1/4.4 \text{ \AA}^{-1}$ on the equatorial line, which strongly indicates a tilted layered structure, smectic C phase.



(a)



(b)



(c)

Figure S1

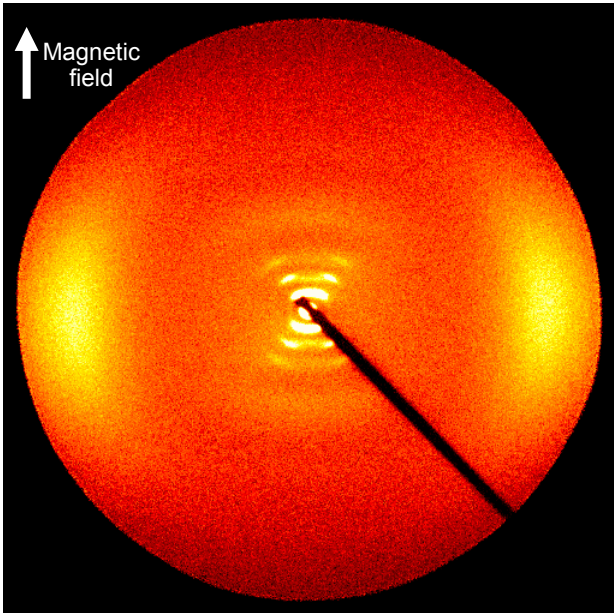


Figure S2