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Supporting information

Design of an Extremely High Birefringence Nematic Liquid Crystal Based on Dinaphthyl-diacetylene Mesogen

Yuki Arakawa,[a] Shunpei Nakajima,[a] Sungmin Kang,[a,*] Masayuki Shigeta,[a] Gen-ichi Konishi[a,*] and Junji Watanabe[a]

[a] 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan., Fax: +81-3-5734-2888; Tel: +81-3-5734-2321; E-mail: konishi.g.aa@m.titech.ac.jp, skang@polymer.titech.ac.jp

Experimental

Instruments

The ^{1}H NMR spectra was measured in $CDCl_3$ on a JEOL LNM-EX 400 at room temperature using tetramethylsilane (TMS) as an internal standard. The transition behavior was investigated by polarizing optical microscopy (POM) (Leica DM2500P microscopy with a Mettler FP90 hot stage) and differential scanning calorimetry (Perkin Elmer DSC7) with heating and cooling scans performed at 10 °Cmin^{-1}. The transmittance of light was observed by a microscope spectroscopic method using a Nikon LV100 Pol optical microscope equipped with a USB4000 (Ocean photonics) spectrometer.

Materials

Unless otherwise noted, all chemical were commercially available and use as received. Trimethylsilylacetylene and $Pd(PPh_3)_4$ (TCI), and alkylbromide, PPh_3, CuI, 1,8-diazacicyclo[5,4,0]-7-undecene (DBU), *N* ,*N* ,*N*' ,*N*'-tetramethylethylenediamine (TMEDA) and 2-bromo-6-naphthol (Wako), and CuCl (Nacalai tesque) were purchased, respectively.

General Procedure of 1,4-Bis(2-hexyloxy-2'-naphthyl)buta-1,3-diyne (4-OC*6*)

General procedure of 1,4-Bis(2-hexyloxy-2'-naphthyl)buta-1,3-diyne (4-OC*6*) is as follows. And other compounds (DNDA-OC*1*-*3*, *5*, *8*, *9*) were synthesized in a similar manner as DNDA-OC*6*.

2-bromo-6-hexyloxynaphthalene (1-OC*6*)

A mixture of 6-bromo-2-naphthol (1.5 g, 6.7 mmol), 1-bromohexane (3.3 g, 20 mmol), and potassium carbonate (2.8 g, 20 mmol) in acetonitrile (40 mL) was refluxed for 3 h. After cooling, the insoluble solids were removed by filtration with diethylether, and the filtrate was extracted with diethylether, washed with water, and dried over $MgSO_4$. After removal of solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: hexane) to afford the title compound as a colorless solid. **Yield**: 96%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, 1H, *J* = 2.0 Hz), 7.63 (d, 1H, *J* = 9.0 Hz), 7.58 (d, 1H, *J* = 8.8 Hz), 7.48 (dd, 1H, *J* = 2.0, 8.8 Hz), 7.16 (dd, 1H, *J* = 2.2, 9.0 Hz), 7.08 (d, 1H, *J* = 2.2 Hz), 4.06 (t, 2H, *J* = 6.5 Hz), 1.84 (tt, 2H, *J* = 6.5, 7.1 Hz), 1.52-1.29 (m, 6H), 0.92 (t, 3H, *J* = 6.9 Hz) ppm.

2-hexyloxy-6-[2-(trimethylsilyl)ethynyl]naphthalene (2-OC*6*)

To a mixture of 2-bromo-6-hexyloxynaphthalene (2.0 g, 6.4 m mol), $Pd(PPh_3)_4$ (0.22 g, 0.19 mmol), CuI (37 mg, 0.19 mmol), PPh_3 (50 mg, 0.19 mmol), and *N*-ethyldiisopropylamine (11 mL) in THF (10 mL) was added trimethylsilylacetylene (1.4 mL, 10 mmol), and the mixture was stirred at room temperature. After 15 h, insoluble salts were removed by filtration with diethylether. The filtrate was extracted with diethylether, washed 2 M HCl and water, and dried over $MgSO_4$. After removal of solvents under reduced pressure, the crude product was purified by silica gel column chromatography (EtOAc/hexane = 1/3) to afford the title compound as a colorless solid. **Yield**: 80%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* = 1.5 Hz), 7.67 (d, 1H, *J* = 9.0 Hz), 7.62 (d, 1H, *J* = 8.5 Hz), 7.44 (dd, 1H, *J* =

1.5, 8.5 Hz), 7.14 (dd, 1H, *J* = 9.0, 2.44 Hz), 7.07 (d, 1H, *J* = 2.4 Hz), 4.06 (t, 2H, *J* = 6.6 Hz), 1.84 (dt, 2H, *J* = 7.4, 6.6 Hz), 1.55-1.35 (m, 6H), 0.92 (t, 3H, *J* = 6.9 Hz), 0.27 (s, 9H) ppm.

2-ethynyl-6-hexyloxynaphthalene (3-OC*6*)

A mixture of 2-hexyloxy-6-[2-(trimethylsilyl)ethynyl]naphthalene (2-OC6) (1.2 g, 3.8 mmol), potassium carbonate (2.6 g, 19 mmol), THF (30 mL), and MeOH (30 mL) was stirred for 2 h. The solvent was removed under reduced pressure, and the obtained residue was extracted with ether, washed with water and dried over $MgSO_4$. The solvent was removed to afford the title compound as a colorless solid. Yield: 92%. 1H NMR (400 MHz, CDCl3) δ 7.94, (d, 1H, J = 1.0 Hz), 7.69 (d, 1H, J = 9.0 Hz), 7.65 (d, 1H, J = 8.5 Hz), 7.48 (dd, 1H, J = 1.0, 8.5 Hz), 7.16 (dd, 1H, J = 2.4, 9.0 Hz), 7.09 (d, 1H, J = 2.4 Hz), 4.07 (t, 2H, J = 6.5 Hz), 3.10 (s, 1H), 1.85 (tt, 2H, J = 6.5, 7.6 Hz), 1.53-1.29 (m, 6H), 0.92 (t, 3H, J = 6.70 Hz) ppm.

1,4-Bis(2-hexyloxy-2'-naphthyl)buta-1,3-diyne (4-OC*6*)

DBU (0.12 ml, 0.79 mmol), TMEDA (1.8 μL, 12 μmol), CuCl (1.6 mg, 16 μmol) and acetonitrile (15 mL) were bubbled with oxygen for 5 min, then 2-ethynyl-6-hexyloxynaphthalene (0.20 g, 0.79 mmol) was added to the mixture. And the reaction was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the obtained residue was extracted with ether, washed with water and dried over $MgSO_4$. After removing the solvent under reduced pressure and purifying by silica gel column chromatography (eluent: hexane) then, by recrystallization with methanol to afford the title compound as colorless solid.

Yield: 80%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00, (d, 1H, *J* = 1.7 Hz), 7.70 (d, 1H, *J* = 9.0 Hz), 7.66 (d, 1H, *J* = 8.8 Hz), 7.51 (dd, 1H, *J* = 1.7, 8.5 Hz), 7.51 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.10 (d, 1H, *J* = 2.4 Hz), 4.08 (t, 2H, *J* = 6.6 Hz), 1.85 (tt, 2H, *J* = 6.6, 7.6 Hz), 1.54-1.32 (m, 6H), 0.92 (t, 3H, *J* = 7.0 Hz) ppm. HRMS-DART (m/z): [M+H] calcd for $C_{36}H_{39}O_2$, 503.29500; found, 503.28103

Spectral Data

2-Bromo-6-ethoxy-naphthalene (1-OC*1*)

Yield: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, 1H, *J* = 2.0 Hz), 7.65 (d, 1H, *J* = 9.0 Hz), 7.61 (d, 1H, *J* = 8.8 Hz), 7.50 (dd, 1H, *J* = 2.0, 8.8 Hz), 7.16 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.10 (d, 1H, *J* = 2.4 Hz), 3.92 (s, 3H) ppm.

2-Bromo-6-ethoxynaphthalene (1-OC*2*)

Yield: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* = 2.0 Hz), 7.64 (d, 1H, *J* = 8.8 Hz), 7.59 (d, 1H, *J* = 8.8 Hz), 7.49 (dd, 1H, *J* = 2.0, 8.8 Hz), 7.16 (dd, 1H, *J* = 2.4, 8.8 Hz), 7.08 (s, 1H), 4.14 (q, 2H, *J* = 7.0 Hz), 1.48 (t, 3H, *J* = 7.0 Hz) ppm.

2-Bromo-6-propoxynaphthalene (1-OC*3*)

Yield: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* = 1.7 Hz), 7.64 (d, 1H, *J* = 9.0 Hz), 7.59 (d, 1H, *J* = 8.8 Hz), 7.49 (dd, 1H, *J* = 1.7, 8.8 Hz), 7.17 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.08 (d, 1H, *J* = 2.4 Hz), 4.03 (t, 2H, *J* = 6.6 Hz), 1.88 (tq, 2H, *J* = 6.6 and 7.5 Hz), 1.08 (t, 3H, *J* = 7.5 Hz) ppm.

2-Bromo-6-pentyloxynaphthalene (1-OC*5*)

Yield: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* = 2.0 Hz), 7.64 (d, 1H, *J* = 9.0 Hz), 7.58 (d, 1H, *J* = 8.8 Hz), 7.48 (dd, 1H, *J* = 2.0, 8.8 Hz), 7.16 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.09 (d, 1H, *J* = 2.4 Hz), 4.06 (t, 2H, *J* = 6.6 Hz), 1.85 (tt, 2H, *J* = 6.6 and 7.4 Hz), 1.52-1.39 (m, 4H), 0.95 (t, 3H, *J* = 7.2 Hz) ppm.

2-Bromo-6-octyloxynaphthalene (1-OC*8*)

Yield: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, 1H, *J* = 2.0 Hz), 7.64 (d, 1H, *J* = 9.0 Hz), 7.58 (d, 1H, *J* = 8.8 Hz), 7.48 (dd, 1H, *J* = 2.0, 8.8 Hz), 7.16 (dd, 1H, *J* = 2.4, 8.8 Hz), 7.08 (d, 1H, *J* = 2.4 Hz), 4.05 (t, 2H, *J* = 6.5 Hz), 1.84 (tt, 2H, *J* = 6.5, 7.7 Hz), 1.52-1.24 (m, 10H), 0.89 (t, 3H, *J* = 6.8 Hz) ppm.

2-Bromo-6-nonyloxynaphthalene (1-OC*9*)

Yield: 97%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* = 1.9 Hz), 7.64 (d, 1H, *J* = 9.0 Hz), 7.58 (d, 1H, *J* = 8.8 Hz), 7.48 (dd, 1H, *J* = 1.9, 8.8 Hz), 7.16 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.08 (d, 1H, *J* = 2.4 Hz), 4.05 (t, 2H, *J* = 6.6 Hz), 1.84 (tt, 2H, *J* = 6.6, 7.6 Hz), 1.53-1.13 (m, 12H), 0.89 (t, 3H, *J* = 6.8 Hz) ppm.

2-Methoxy-6-[2'-(trimethylsilyl)ethynyl]naphthalene (2-OC*1*)

Yield: 92%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, 1H, *J* = 1.5 Hz), 7.68 (d, 1H, *J* = 9.0 Hz), 7.65 (d, 1H, *J* = 8.8 Hz), 7.47 (dd, 1H, *J* = 1.5, 8.8 Hz), 7.14 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.09 (d, 1H, *J* = 2.4 Hz), 0.27 (s, 9H) ppm.

2-Ethoxy-6-[2'-(trimethylsilyl)ethynyl]naphthalene (2-OC*2*)

Yield: 64%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* = 1.7 Hz), 7.67 (d, 1H, *J* = 9.0 Hz), 7.62 (d, 1H, *J* = 8.6 Hz), 7.46 (dd, 1H, *J* = 1.7, 8.6 Hz), 7.14 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.07 (d, 1H, *J* = 2.4 Hz), 4.14 (q, 2H, *J* = 6.9 Hz), 1.48 (t, 3H, *J* = 6.9 Hz), 0.27 (s, 9H) ppm.

2-Propoxy-6-[2'-(trimethylsilyl)ethynyl]naphthalene (2-OC*3*)

Yield: 78%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* = 1.6 Hz), 7.67 (d, 1H, *J* = 8.80 Hz), 7.62 (d, 1H, *J* = 8.3 Hz), 7.46 (dd, 1H, *J* = 1.6, 8.3 Hz), 7.14 (dd, 1H, *J* = 2.4, 8.8 Hz), 7.08 (d, 1H, *J* = 2.4 Hz), 4.03 (t, 2H, *J* = 6.6 Hz), 1.87 (tq, 2H, *J* = 6.6, 7.4 Hz), 1.08 (t, 3H, *J* = 7.4 Hz), 0.27 (s, 9H) ppm.

2-Pentyloxy-6-[2'-(trimethylsilyl)ethynyl]naphthalene (2-OC*5*)

Yield: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* =1.5 Hz), 7.67 (d, 1H, *J* = 9.0 Hz), 7.62 (d, 1H, *J* = 8.5 Hz), 7.45 (dd, 1H, *J* = 1.5, 8.5 Hz), 7.14 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.08 (d, 1H, *J* = 2.4 Hz), 4.06 (t, 2H, *J* = 6.6 Hz), 1.84 (tt, 2H, *J* = 6.6, 7.4 Hz), 1.50-1.38 (m, 4H), 0.95 (t, 3H, *J* = 7.1 Hz), 0.27 (s, 9H) ppm.

2-Octyloxy-6-[2'-(trimethylsilyl)ethynyl]naphthalene (2-OC*8*)

Yield: 82%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* =1.5 Hz), 7.67 (d, 1H, *J* = 8.8 Hz), 7.62 (d, 1H, *J* = 8.5 Hz), 7.46 (dd, 1H, *J* = 1.5, 8.5 Hz), 7.14 (dd, 1H, *J* = 2.4, 8.8 Hz), 7.07 (d, 1H, *J* = 2.4 Hz), 4.06 (t, 2H, *J* = 6.5 Hz), 1.84 (tt, 2H, *J* = 6.5, 7.5 Hz), 1.56-1.24 (m, 10H), 0.89 (t, 3H, *J* = 6.7 Hz), 0.27 (s, 9H) ppm.

2-Nonyloxy-6-[2'-(trimethylsilyl)ethynyl]naphthalene (2-OC*9*)

Yield: 92%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* = 1.4 Hz), 7.67 (d, 1H, *J* = 9.0 Hz), 7.62 (d, 1H, *J* = 8.5 Hz), 7.46 (dd, 1H, *J* = 1.4, 8.5 Hz), 7.14 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.08 (d, 1H, *J* = 2.4 Hz), 4.06 (t, 2H, *J* = 6.3 Hz), 1.82 (tt, 2H, *J* = 6.3, 7.7 Hz), 1.49-1.16 (m, 12H), 0.88 (t, 3H, 6.3 Hz), 0.27 (s, 9H) ppm.

2-Ethynyl-6-methoxynaphthalene (3-OC*1*)

Yield: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, 1H, *J* = 1.8 Hz), 7.70 (d, 1H, *J* = 9.0 Hz), 7.68 (d, 1H, *J* = 8.6 Hz), 7.49 (dd, 1H, *J* = 1.8, 8.6 Hz), 7.48 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.11 (d, 1H, *J* = 2.4 Hz), 3.93 (s, 3H), 3.11 (s, 1H) ppm.

6-Ethoxy-2-ethynylnaphthalene (3-OC*2*)

Yield: 97%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, 1H, *J* = 1.5 Hz), 7.69 (d, 1H, *J* = 8.8 Hz), 7.65 (d, 1H, *J* = 8.5 Hz), 7.48 (dd, 1H, *J* = 1.5, 8.5 Hz), 7.16 (dd, 1H, *J* = 2.4, 8.8 Hz), 7.09 (d, 1H, *J* = 2.4 Hz), 4.15 (q, 2H, *J* = 7.0 Hz), 3.10 (s, 1H), 1.49 (t, 3H, *J* = 7.0 Hz) ppm.

2-Ethynyl-6-propoxynaphthalene (3-OC*3*)

Yield: 46%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, 1H, *J* = 1.4 Hz), 7.69 (d, 1H, *J* = 9.0 Hz), 7.65 (d, 1H, *J* = 8.5 Hz), 7.48 (dd, 1H, *J* = 1.4, 8.5 Hz), 7.16 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.09 (d, 1H, *J* = 2.4 Hz), 4.06 (t, 2H, *J* = 6.5 Hz), 3.10 (s, 1H), 1.88 (tq, 2H, *J* = 6.5, 7.3 Hz), 1.08 (t, 3H, *J* = 7.3 Hz) ppm.

2-Ethynyl-6-pentyloxynaphthalene (3-OC*5*)

Yield: 70%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, 1H, *J* = 1.6 Hz), 7.69 (d, 1H, *J* = 9.0 Hz), 7.65 (d, 1H, *J* = 8.5 Hz), 7.48 (dd, 1H, *J* = 1.6, 8.5 Hz), 7.16 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.10 (d, 1H, *J* = 2.4 Hz), 4.08 (t, 2H, *J* = 6.6 Hz), 3.11 (s, 1H), 1.84 (tt, 2H, *J* = 6.6, 7.5 Hz), 1.52-1.39 (m, 4H), 0.96 (t, 3H, *J* = 7.1 Hz) ppm.

2-Ethynyl-6-octyloxynaphthalene (3-OC*8*)

Yield: >99%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, 1H, *J* = 1.5 Hz), 7.69 (d, 1H, *J* = 9.0 Hz), 7.65 (d, 1H, *J* = 8.6 Hz), 7.47 (dd, 1H, *J* = 1.5, 8.6 Hz), 7.16 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.09 (d, 1H, *J* = 2.4 Hz), 4.07 (t, 2H, *J* = 6.6 Hz), 3.10 (s, 1H), 1.84 (tt, 2H, *J* = 6.6, 7.4 Hz), 1.52-1.24 (m, 10H), 0.89 (t, 3H, *J* = 6.7 Hz) ppm.

2-Ethynyl-6-nonyloxynaphthalene (3-OC*9*)

Yield: 96%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, 1H, *J* = 1.7 Hz), 7.69 (d, 1H, *J* = 9.0 Hz), 7.65 (d, 1H, *J* = 8.5 Hz), 7.48 (dd, 1H, *J* = 1.7, 8.5 Hz), 7.16 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.09 (d, 1H, *J* = 2.4 Hz), 4.07 (t, 2H, *J* = 6.6 Hz), 3.10 (s, 1H), 1.84 (tt, 2H, *J* = 6.6, 7.6 Hz), 1.53-1.25 (m, 12H), 0.88 (t, 3H, *J* = 6.8 Hz) ppm.

1,4-Bis(6-methoxynaphth-2-yl)buta-1,3-diyne (4-OC*1*)

Yield: 48%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, 1H, *J* = 1.7 Hz), 7.69 (d, 1H, *J* = 9.0 Hz), 7.66 (d, 1H, *J* = 8.5 Hz), 7.51 (dd, 1H, *J* = 1.7, 8.5 Hz), 7.16 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.11 (d, 1H, *J* = 2.4 Hz), 3.92 (s, 3H) ppm.

1,4-Bis(6-ethoxynaphth-2-yl)buta-1,3-diyne (4-OC*2*)

Yield: 50%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, 1H, *J* = 1.4 Hz), 7.69 (d, 1H, *J* = 9.0 Hz), 7.64 (d, 1H, *J* = 8.5 Hz), 7.50 (dd, 1H, *J* = 1.4, 8.5 Hz), 7.16 (dd, 1H, *J* = 2.2, 9.0 Hz), 7.09 (d, 1H, *J* = 2.2 Hz), 4.16 (q, *J* = 7.0 Hz, 2H), 1.47 (t, 2H, *J* = 7.0 Hz) ppm.

1,4-Bis(6-propoxynaphth-2-yl)buta-1,3-diyne (4-OC*3*)

Yield: 48%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, 1H, *J* = 1.4 Hz), 7.69 (d, 1H, *J* = 9.0 Hz), 7.64 (d, 1H, *J* = 8.5 Hz), 7.50 (dd, 1H, *J* = 1.4, 8.5 Hz), 7.17 (dd, 1H, *J* = 2.4, 8.80 Hz), 7.10 (d, 1H, *J* = 2.4 Hz), 4.05 (t, 2H, *J* = 6.6 Hz), 1.87 (tq, 2H, *J* = 6.6, 7.0 Hz), 1.08 (t, 3H, *J* = 7.0 Hz) ppm.

1,4-Bis(6-pentyloxynaphth-2-yl)buta-1,3-diyne (4-OC*5*)

Yield: 42%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, 1H, *J* = 1.5 Hz), 7.68 (d, 1H, *J* = 9.0 Hz), 7.64 (d, 1H, *J* = 8.6 Hz), 7.49 (dd, 1H, *J* = 1.5, 8.6 Hz), 7.16 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.09 (d, 1H, *J* =2.4 Hz), 4.08 (t, 2H, *J* = 6.6 Hz), 1.85 (tt, 2H, *J* = 6.6, 7.4 Hz), 1.53-1.37 (m, 4H), 0.95 (t, 3H, *J* = 7.2 Hz) ppm.

1,4-Bis(6-octyloxynaphth-2-yl)buta-1,3-diyne (4-OC*8*)

Yield: 86%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, 1H, *J* = 1.6 Hz), 7.70 (d, 1H, *J* = 9.0 Hz), 7.66 (d, 1H, *J* = 8.5 Hz), 7.51 (dd, 1H, *J* = 1.6, 8.5 Hz), 7.17 (dd, 1H, *J* = 1.7, 9.0 Hz), 7.10 (d, 1H, *J* =1.7 Hz), 4.08 (t, 2H, *J* = 6.6 Hz), 1.85 (tt, 2H, *J* = 6.6, 7.4 Hz), 1.51-1.24 (m, 10H), 0.90 (t, 3H, *J* = 6.6 Hz) ppm.

1,4-Bis(6-nonyloxynaphth-2-yl)buta-1,3-diyne (4-OC*9*)

Yield: 43%; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, 1H, *J* =1.7 Hz), 7.70 (d, 1H, *J* = 8.8 Hz), 7.66 (d, 1H, *J* = 8.5 Hz), 7.51 (dd, 1H, *J* = 1.7, 8.5 Hz), 7.17 (dd, 1H, *J* = 2.4, 8.8 Hz), 7.10 (d, 1H, *J* = 2.4 Hz), 4.08 (t, 2H, *J* = 6.6 Hz), 1.85 (tt, 2H, *J* = 6.6, 7.5 Hz), 1.52-1.21 (m, 12H), 0.89 (t, 3H, *J* = 6.8 Hz) ppm.

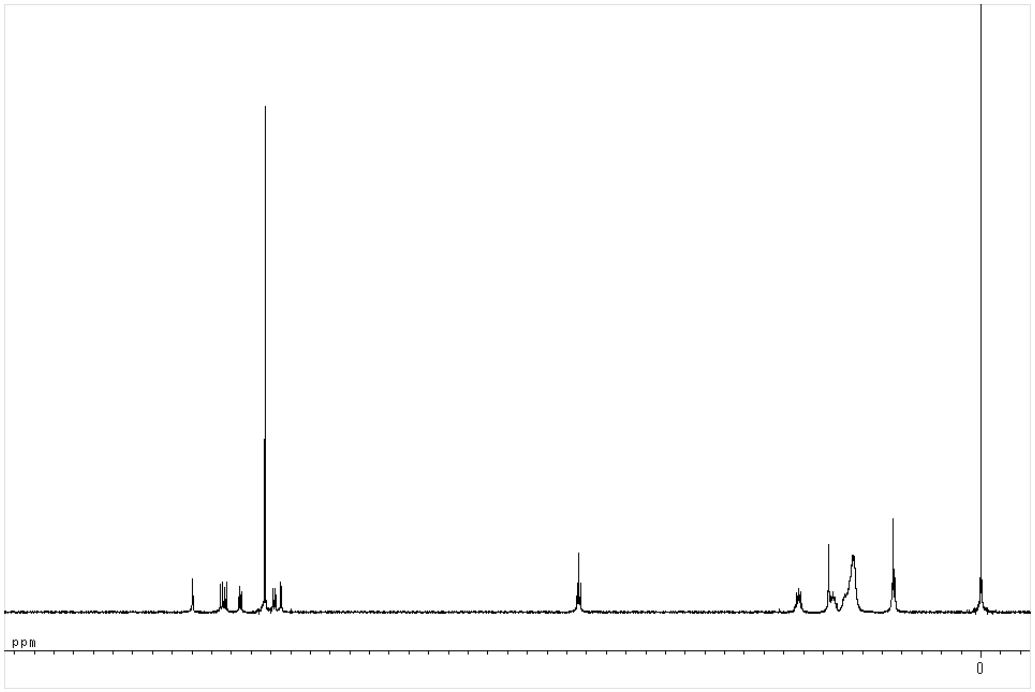

Figure S1. ^{1}H NMR spectrum of **4-OC9** (400 MHz, $CDCl_3$).

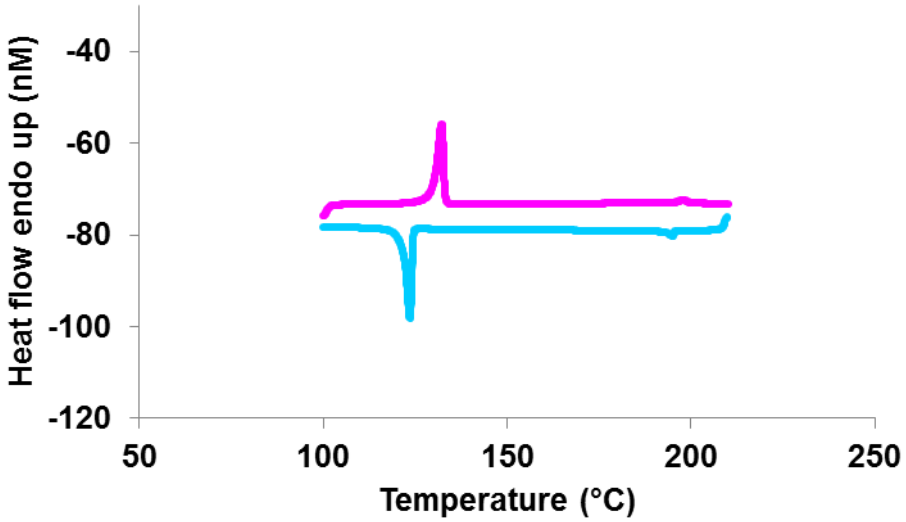

Figure S2. DSC thermogram of **4-OC9**

Table S1. Phase transition temperatures (°C) and enthalpies (*ΔH, kJ mol*$^{-1}$) (*in italics*) for compounds of the DNDA-OC*m* series.

Sample	Transition temperature / °C (enthalpy/kJmol-1)
DNDA-OC*1*	Cr 218.0 (26.9)[a] N decomposition[b] Iso T_m: 231.6
DNDA-OC*2*	Cr 201.5 (46.1)[a] N decomposition[b] Iso T_m: 213.9
DNDA-OC*3*	Cr 188.4 (55.5)[a] N decomposition[b] Iso T_m: 198.8
DNDA-OC*5*	Cr 151.1 (59.8)[a] N 238.0 (------)[c] Iso T_m: 163.3
DNDA-OC*6*	Cr 131.3 (41.6)[a] N 230.8 (------)[c] Iso T_m: 142.3
DNDA-OC*8*[a]	Cr 128.4 (*34.9*) N 207.2 (*1.74*) Iso T_m: 137.3
DNDA-OC*9*[a]	Cr 123.6 (*29.9*) N 195.0 (*1.54*) Iso T_m: 132.2

[a] Observed by DSC (on cooling at a rate of 10 °C min^{-1}). [b] Although we observed the transition temperature of the compounds by POM, we could not confirm their T_c because they decomposed at ~260 °C. [c] Observed by POM.

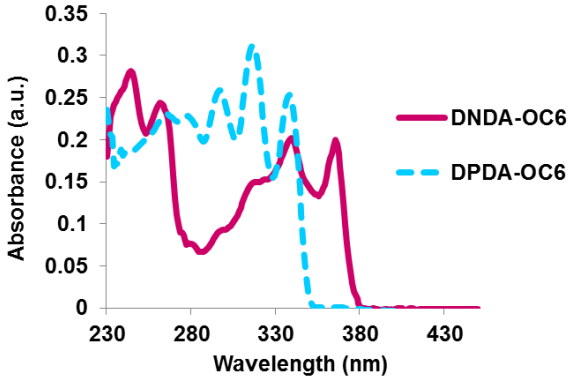

Figure S3. UV-vis spectra of DNDA-OC*6* and DPDA-C*6* (in THF).

A detailed calculation method of β, Δn_0 and T_i.

First, we measured wavelength dispersion of Δn for DNDA-OC*m*. Then, Δn values of respective compounds at wavelength of 550 nm are employed, using linear curve fitting approach of following equation. Thus, the β, Δn_0 and T_i values can be obtained

$$\Delta n = \Delta n_0 (1 - T / T_i)^{\beta}$$

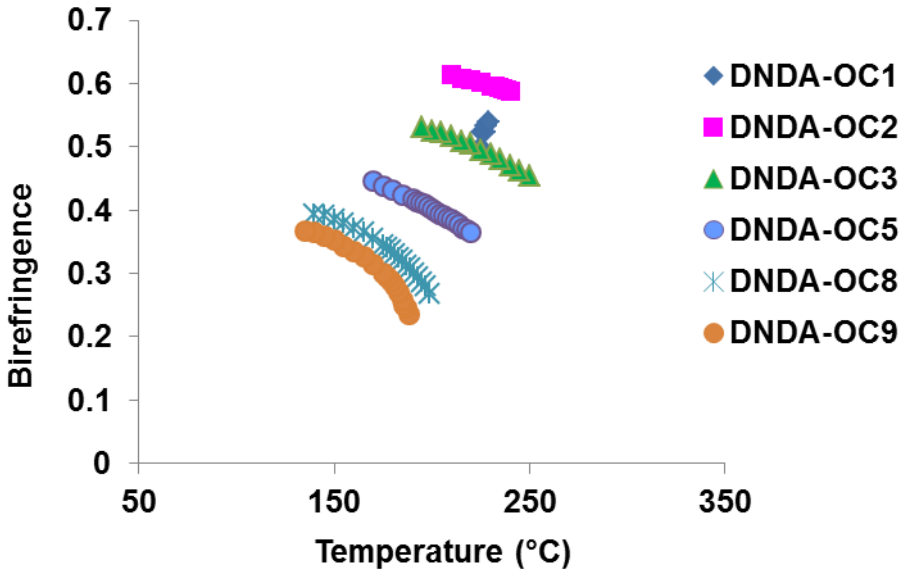

Figure S4. Temperature dependence of birefringence measured at wavelength of 550 nm for DNDA-OC*m*.