Supporting information

Synthesis of diphenyl-diacetylene-based nematic liquid crystals and their high birefringence properties

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1-Iodo-4-hexyloxybenzene (1-OC6)

A mixture of 4-iodophenol (3.5 g, 16 mmol), 1-bromohexane (7.9 g, 48 mmol), potassium carbonate (6.6 g, 48 mmol) and acetonitrile (60 ml) was refluxed for 12 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 column chromatography on silica gel (eluent: hexane), an objective compound as a viscous liquid was obtained (4.9 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 9.0 Hz, Ar-H, 2H), 6.67 (d, J = 9.0 Hz, Ar-H, 2H), 3.91 (t, J = 6.6 Hz Ar-O-CH_2, 2H) 1.76 (tt, J = 6.6, 6.7 Hz, CH_2, 2H), 1.48-1.40 (m, CH_2, 2H), 1.37-1.30 (m, CH_2, 4H), 0.90 (t, J = 7.0 Hz, CH_3 3H) ppm.

1-Hexyloxy-4-[2-(trimethylsilyl)ethynyl]benzene (2-OC6)

The mixture of 4-hexyloxyiodobenzene (4.0 g, 13 mmol), trimethylsilylacetylene (2.2 ml, 0.016 mol), $Pd(PPh_3)_4$ (0.55 g, 0.48 mmol), *N*-ethyldiisopropylamine (33 ml), and CuI (91 mg, 0.48 mmol) was stirred and at 45 °C for 20 h. Ether was added to resulting mixture, and insoluble salts were removed by filtration. The solution was

washed with 2M HCl and water. The organic phase was dried by $MgSO_4$, and ether was evaporated. The crude product (viscous liquid) was purified by column chromatography on silica gel (eluent: hexane) and used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, Ar-H, 2H), 6.80 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.94 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 1.80-1.73 (m, CH_2, 2H), 1.48-1.31 (m, CH_2, 6H), 0.90 (t, *J* = 6.8 Hz, CH_3, 3H), 0.23 (s, -Si-CH_3, 9H) ppm.

1-Ethynyl-4-hexyloxybenzene (3-OC6)

A mixture of 1-hexyloxy-4-[2-(trimethylsilyl)ethynyl]benzene (2-OC6) (1.5 g 5.5 mmol), potassium carbonate (3.9 g, 28 mmol), THF (20 ml), and MeOH (20 ml) was stirred at room temperature for 1.5 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 yield 3-OC6 (69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, Ar-H, 2H), 6.83 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.95 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 2.99 (s, -C≡C-H, 1H), 1.77 (tt, *J* = 6.6, 7.5 Hz, CH_2, 2H), 1.49-1.31 (m, CH_2, 6H), 0.90 (t, *J* = 7.1 Hz, CH_3, 3H) ppm.

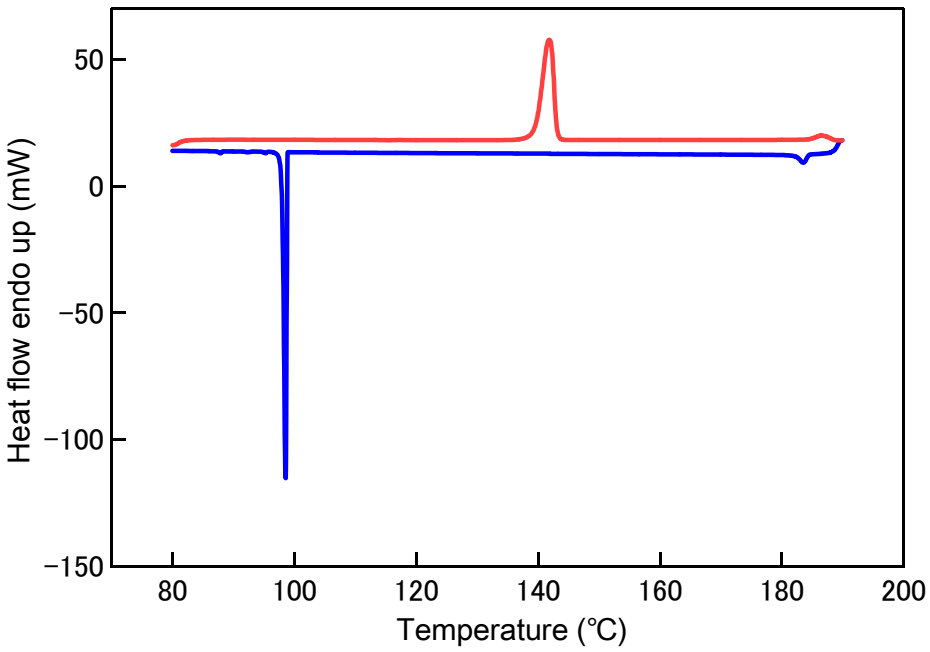

Figure S1. DSC thermograms of 1,4-bis(4-methoxyphenyl)buta-1,3-diyne **(4-OC1).**

Spectral Data

4-Iodo-1-propoxybenzene (1-OC3)

Yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, Ar-H, 2H), 6.67 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.88 (t, *J* = 6.6 Hz Ar-O-CH_2, 2H), 1.79 (tq, *J* = 6.6, 7.4 Hz, Ar-O-CH_2, 2H), 1.02 (t, *J* = 7.4 Hz, CH_3, 3H) ppm.

4-Butoxy-1-I-odobenzene (1-OC4)

Yield: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.8 Hz, Ar-H, 2H), 6.67 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.92 (t, *J* = 6.5 Hz Ar-O-CH_2, 2H), 1.75 (tt, *J* = 6.5, 7.5 Hz, -CH_2, 2H), 1.48 (tq, *J* = 7.5, 7.5 Hz, -CH_2, 2H), 0.97 (t, *J* = 7.5 Hz, CH_3, 3H) ppm.

4-Iodo-1-pentyloxybenzene (1-OC5)

Yield: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.0 Hz, Ar-H, 2H), 6.67 (d, *J* = 9.0 Hz, Ar-H, 2H), 3.91 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 1.80-1.73 (m, -CH_2, 2H), 1.47-1.33 (m, -CH_2, 4H) 0.93 (t, *J* = 7.1 Hz, -CH_3, 3H) ppm.

4-Heptyloxy-1-iodobenzene (1-OC7)

Yield: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.0 Hz, Ar-H, 2H), 6.67 (d, *J* = 9.0 Hz, Ar-H, 2H), 3.91 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 1.76 (tt, *J* = 6.6, 7.4 Hz, -CH_2, 2H), 1.47-1.40 (m, -CH_2, 2H), 1.38-1.27 (m, -CH_2, 6H), 0.89 (t, *J* = 7.0 Hz, -CH_3, 3H) ppm.

1-Methoxy-4-[2-(trimethylsilyl)ethynyl]benzene (2-OC1)

Yield: 31%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, Ar-H, 2H), 6.82 (d, *J* = 8.6 Hz, Ar-H, 2H), 3.81 (s, Ar-O-CH_3, 3H), 0.24 (s, -Si-CH_3, 9H) ppm.

1-Ethoxy-4-[2-(trimethylsilyl)ethynyl]benzene (2-OC2)

Yield: 38%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, Ar-H, 2H), 6.80 (d, *J* =

8.8 Hz, Ar-H, 2H), 4.02 (q, *J* = 7.1 Hz Ar-O-CH_2, 2H), 1.41 (t, *J* = 7.1 Hz, -CH_3, 3H), 0.23 (s, -Si-CH_3, 9H) ppm.

1-Propoxy-4-[2-(trimethylsilyl)ethynyl]benzene (2-OC3)

Yield: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39, (d, *J* = 8.8 Hz, Ar-H, 2H), 6.80 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.91 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 1.83-1.77 (tq, *J* = 6.6, 7.4 Hz, CH_2, 2H), 1.03 (t, *J* = 7.4 Hz, CH_3, 3H), 0.23 (s, -Si-CH_3, 9H) ppm.

1-Butoxy-4-[2-(trimethylsilyl)ethynyl]benzene (2-OC4)

Yield: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38, (d, *J* = 8.8 Hz, Ar-H, 2H), 6.80 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.95 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 1.79-1.72 (m, -CH_2, 2H), 1.51-1.46 (m, -CH_2, 2H), 0.97 (t, *J* = 7.4 Hz, CH_3, 3H), 0.23 (s, -Si-CH_3, 9H) ppm.

1-Pentyloxy-4-[2-(trimethylsilyl)ethynyl]benzene (2-OC5)

Yield: >99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38, (d, *J* = 8.5 Hz, Ar-H, 2H), 6.80 (d, *J* = 8.5 Hz, Ar-H, 2H), 3.94 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 1.77 (tt, *J* = 6.6, 6.7 Hz, -CH_2, 2H), 1.46-1.37 (m, -CH_2, 4H), 0.93 (t, *J* = 7.0 Hz, -CH_3, 3H), 0.23 (s, -Si-CH_3, 9H) ppm.

1-Heptyloxy-4-[2-(trimethylsilyl)ethynyl]benzene (2-OC7)

Yield: 37%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 9.0 Hz, Ar-H, 2H), 6.80 (d, *J* = 9.0 Hz, Ar-H, 2H), 3.94 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 1.81-1.72 (m, -CH_2, 2H), 1.48-1.26 (m, -CH_2, 8H), 0.89 (t, *J* = 6.7 Hz, -CH_3, 3H), 0.23 (s, -Si-CH_3, 9H) ppm.

1-Ethynyl-4-methoxybenzene (3-OC1)

Yield: 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 9.0 Hz Ar-H, 6H), 6.88 (d, *J* = 9.0 Hz, Ar-H, 2H), 3.85 (s, Ar-O-CH_3, 3H), 3.03 (s, -C≡C-H, 1H) ppm.

1-Ethoxy-4-ethynylbenzene (3-OC2)

Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz Ar-H, 2H), 6.83 (d, *J* =

8.8 Hz, Ar-H, 2H), 4.03 (q, *J* = 6.8 Hz, Ar-O-CH_2, 2H), 2.99 (s, -C≡C-H, 1H), 1.42 (t, *J* = 6.8 Hz, CH_3, 3H) ppm.

1-Ethynyl-4-propoxybenzene (3-OC3)

Yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz Ar-H, 2H), 6.83 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.92 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 2.99 (s, -C≡C-H, 1H), 1.81 (tq, *J* = 6.6, 7.4 Hz, CH_2, 2H), 1.03 (t, *J* = 7.4 Hz, CH_3, 3H) ppm.

1-Butoxy-4-ethynylbenzene (3-OC4)

Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 9.0 Hz Ar-H, 2H), 6.83 (d, *J* = 9.0 Hz, Ar-H, 2H), 3.95 (t, *J* = 6.5 Hz, Ar-O-CH_2, 2H), 2.98 (s, -C≡C-H, 1H), 1.77 (tt, *J* = 6.5, 7.4 Hz, CH_2, 2H), 1.52-1.44 (m, CH_2, 2H), 0.98 (t, *J* = 7.3 Hz, CH_3, 3H) ppm.

1-Ethynyl-4-pentyloxybenzene (3-OC5)

Yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, Ar-H, 2H), 6.83 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.95 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 2.99 (s, -C≡C-H, 1H), 1.78 (tt, *J* = 6.6, 7.4 Hz, -CH_2, 2H), 1.47-1.34 (m, -CH_2, 4H), 0.93 (t, *J* = 7.1 Hz, -CH_3, 3H) ppm.

1-Ethynyl-4-heptyloxybenzene (3-OC7)

Yield: >99%;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, Ar-H, 2H), 6.83 (d, *J* = 8.8 Hz, Ar-H, 2H), 3.95 (t, *J* = 6.6 Hz, Ar-O-CH_2, 2H), 2.99 (s, -C≡C-H, 1H), 1.77 (tt, *J* = 6.6, 7.6 Hz, -CH_2, 2H), 1.46-1.28 (m, -CH_2, 8H), 0.89 (t, *J* = 6.8 Hz, -CH_3, 3H) ppm.

1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (4-OC1)

Yield: 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz Ar-H, 4H), 6.86 (d, *J* = 8.6 Hz, Ar-H, 4H), 3.83 (s, Ar-O-CH_3, 6H) ppm.

1,4-Bis(4-ethoxyphenyl)buta-1,3-diyne (4-OC2)

Yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43, (d, *J* = 9.0 Hz, Ar-H, 4H), 6.82 (d, *J* = 9.0 Hz, Ar-H, 4H), 4.04 (q, *J* = 7.0 Hz, Ar-O-CH_2, 4H), 1.41 (t, *J* = 7.0 Hz, -CH_3, 6H)

ppm.

1,4-Bis(4-propoxyphenyl)buta-1,3-diyne (4-OC3)

Yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.8 Hz, Ar-H, 4H), 6.84 (d, J = 8.8 Hz, Ar-H, 4H), 3.93 (t, J = 6.6 Hz Ar-O-CH_2, 4H), 1.81 (tq, J = 6.6, 7.4 Hz, Ar-O-CH_2, 4H), 1.04 (t, J = 7.4 Hz, CH_3, 6H) ppm.

1,4-Bis(4-butoxybenzene-1-yl)buta-1,3-diyne (4-OC4)

Yield: > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz Ar-H, 4H), 6.84 (d, J = 8.3 Hz, Ar-H, 4H), 3.97 (t, J = 6.5 Hz, Ar-O-CH_2, 4H), 1.77 (tt, J = 6.5, 7.5 Hz –CH_2, 4H), 1.49 (tq, J = 7.5, 7.4 Hz, -CH_2, 4H), 0.96 (t, J = 7.4 Hz, -CH_3, 6H) ppm.

1,4-Bis(4-pentyloxyphenyl)buta-1,3-diyne (4-OC5)

Yield: 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 9.0 Hz Ar-H, 4H), 6.87 (d, J = 9.0 Hz, Ar-H, 4H), 3.98-3.93 (m, Ar-O-CH_2, 4H), 1.81-1.77 (m, -CH_2, 4H), 1.45-1.37 (m, -CH_2, 8H), 0.93 (t, J = 7.08 Hz, -CH_3, 6H) ppm.

1,4-Bis(4-heptyloxphenyl)buta-1,3-diyne (4-OC7)

Yield: 25%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.8 Hz Ar-H, 4H), 6.83 (d, J = 8.8 Hz, Ar-H, 4H), 3.96 (t, J = 5.9 Hz, Ar-O-CH_2, 4H), 1.81-1.72 (m, -CH_2, 4H), 1.47-1.26 (m, -CH_2, 16H), 0.90 (t, J = 7.7 Hz, -CH_3, 6H) ppm.