Supplementary Information

Sequential Phase Transformation of Propeller-like C_3 -Symmetric Liquid Crystals from a Helical to Ordered to Disordered Hexagonal Columnar Structure

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Experimental Details

Materials. Pyrogallol, nitrocatechol, *t*-butylnitrite, trimethylsilylazide (TMS-azide), 1,3,5tribromobenzene, CuI (98%), 2-methyl-3-butyn-2-ol, (+)-sodium L-ascorbate, CuSO₄·5H₂O were purchased from Sigma-Aldrich Chemical Co. Anhydrous MgSO₄ (min. 99%), anhydrous potassium carbonate (min. 99%), graphite powder were purchased from Duksan Pure Chemical, Korea. Bis(triphenylphosphine)palladium(II) dichloride, 1-bromooctane, hydrazine (99%) were purchased from Tokyo Chemical Industry. Nitric acid and silica gel were purchased Samchun Chemical. Ethanol, acetonitrile (ACN) and dichloromethane (DCM) were stored over a type 4 Å molecular sieve. *N*,*N*'-Dimethylformamide (DMF) was distilled under vacuum, and stored over a type 4 Å molecular sieve. Tetrahydrofuran (THF) was dried by distillation from sodium metal, and stored over a type 4 Å molecular sieve. Triethylamine and pyridine were distilled from calcium hydride, and stored over a type 4 Å molecular sieve.

Methods. ¹H-, and ¹³C-NMR spectra were recorded from a CDCl₃ solution using Varian 200 and Bruker AM 400 spectrometers. The purity of the compounds was checked by thin-layer chromatography (TLC; Merck, silica gel 60). Gel permeation chromatography (GPC) measurements were conducted in THF and N,N'-dimethylacetamide (99.9%) (40:1 volume ratio) using a Waters 401 instrument equipped with Stragel HR 2,3 columns and Shodex AT-8045 at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) measurements were performed using a Perkin Elmer DSC-7 with the 1020 thermal analysis equipment at a rate of 10 °C/min. Indium (melting temperature = 429 K and ΔH = 28.45 J/g) was used as a calibration standard. X-ray scattering measurements using the bulk samples were performed in transmission mode with synchrotron radiation at the 9A beamline of the Pohang Accelerator Laboratory (PAL), Korea. The sample was held in an aluminum sample holder with polyimide films on both sides. Grazing incidence X-ray scattering (GIXS) experiments were also conducted at the 9A beamline of the PAL. For the GIXS experiments, the surfacealigned samples were prepared by spin-casting the sample solutions (dissolved in chloroform, ~3 wt%) on Si-wafers functionalized with 3-aminopropyltriethoxysilane (APS). The aligned samples were held in vacuum chamber with temperature-controlled heating stage and the diffraction patterns were recorded with a 2-D imaging detector. The X-ray spectra were plotted against q value (= $4\pi \sin\theta/\lambda$). Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at the Organic Chemistry Research Center, Sogang University, Korea. A Nikon eclipse LV100 optical polarized microscopy equipped with a Linkam TMS 94 heating system was used to observe the thermal transitions and to analyze the anisotropic texture. The density measurement was performed using a floating and sinking method in water/methanol mixture solutions. The density was determined when the particle was in the middle of the solution. By repeating the measurement several times, the average value (0.857 g/cm³ for 1 and 0.842 g/cm³ for **2**) was used.

Synthesis of azide and ethynyl precursors for click chemistry. 1,3,5-Triethynylbenzene was prepared by following a previous procedure.^{S1} 4-Azido-1,2,3-tris(octyloxy)benzene and 4-azido-1,2-bis(octyloxy)benzene were synthesized by following a previous procedure.^{S2}



Scheme S1. Synthesis of the final mesogenic compounds (1 and 2) by a click reaction of the azide and ethynyl precursors.

Synthesis of the final molecules (1 and 2). The final compounds were synthesized via a click reaction as outlined in Scheme S1. Molecules 1 and 2 were synthesized using an identical procedure. A representative synthesis is described for 1. 1,3,5-Triethynylbenzene (0.30 g, 2.00 mmol), compound a (3.32 g, 6.59 mmol), copper(II) sulfate pentahydrate (0.50 g, 2.00 mmol) and sodium L-ascorbate (0.39 g, 4.00 mmol) were dissolved in 20 mL of dry THF and 2 mL of water. The mixture was stirred at room temperature for 12 h under N₂ atmosphere. After removing THF using a rotary evaporator, the mixture was extracted with deionized water and dichloromethane. The dichloromethane layer was washed with deionized water several times, and then dried over anhydrous MgSO₄. After removing dichloromethane using a rotary evaporator, the resulting mixture was purified by silica gel column chromatography using dichloromethane:ethyl acetate = 10:1 as the eluent, yielding 2.69 g (81.3%) of a yellowish solid. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 8.50 (s, 3H, triazole-*H*), 8.42 (s, 3H, Ar-*H*), 7.02 (s, 3H, Ar-*H*), 4.06 (t, 18H, *J* = 6.4 Hz, OCH₂CH₂(CH₂)₅CH₃), 1.90-1.76 (m, 18H, OCH₂CH₂(CH₂)₅CH₃), 1.57-1.30 (m, 90H, OCH₂CH₂(CH₂)₅CH₃), 0.88 (t, 18H, J = 6.8 Hz, OCH₂CH₂(CH₂)₅CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 153.97, 147.39, 138.55, 132.36, 131.57, 122.61, 118.97, 99.33, 73.79, 69.60, 32.05, 30.47, 29.51, 26.22, 22.83, 14.21. Anal. Calcd for C₁₀₂H₁₆₅N₉O₉: C, 73.74; H, 10.01; N, 7.59, Found: C, 73.75; H, 10.07; N, 7.59. $M_w/M_n = 1.01$ (GPC).

2. Yield: 76.3%. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 8.42 (s, 3H, triazole-*H*), 8.36 (s, 3H, Ar-*H*), 7.35 (s, 3H, Ar-*H*), 7.22 (d, 3H, *J* = 8.8 Hz, Ar-*H*), 6.95 (d, 3H, *J* = 8.8 Hz, Ar-*H*), 4.06 (t, 12H, *J* = 6.4 Hz, OCH₂CH₂(CH₂)₅CH₃), 2.11-1.81 (m, 12H, OCH₂CH₂(CH₂)₅CH₃), 1.67-1.29 (m, 60H, OCH₂CH₂(CH₂)₅CH₃), 0.88 (t, 18H, *J* = 6.8 Hz, OCH₂CH₂(CH₂)₅CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 149.99, 149.58, 147.41, 131.67, 130.51, 122.54, 118.74, 113.68, 112.54, 106.51, 69.56, 31.91, 29.37, 26.11, 22.76, 14.18. Anal. Calcd for C₇₈H₁₁₇N₉O₆: C, 73.37; H, 9.24; N, 9.87, Found: C, 73.37; H, 9.27; N, 9.88. M_w/M_n = 1.01 (GPC).

Reference

(S1) M.-H. Ryu, J.-W. Choi and B.-K. Cho, J. Mater. Chem., 2010, 20, 1806-1810.
(S2) J. Kim, S. Cho and B.-K. Cho, Chem. Eur. J., 2014, 20, 7588-7594.



Fig. S1 (a) 1 H- and (b) 13 C-NMR spectra of 1, and (c) 1 H- and (d) 13 C-NMR spectra of 2.



Fig. S2 GPC elugrams of 1 and 2.



Fig. S3 Optical textures of (a,b) **1** at 30 °C and 170 °C, and (c,d,e) **2** at 30 °C, 85 °C and 160 °C.



Fig. S4 GIXS data of 1 at 30 °C,



Fig. S5 Gaussian peak separation of the WAXS data of 1 at 30 °C, 140 °C and 150 °C.