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Electronic Supplementary Information for

Sub-5 nm Homeotropically Aligned Columnar Structures of Hybrids Constructed by Porphyrin and Oligo(Dimethylsiloxane)

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Experimental Section

Materials

Benzyl 4-hydroxybenzoate (99%, Innochem), allyl bromide (98%, Macklin), 5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine (95%, Mreda), potassium carbonate (AR, Acros), Karstedt catalyst solution (Pt(dvs), Pt 2.7% in Xylene, Energy Chemical), 1-(3-(99%, dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride Innochem), 4dimethylaminopyridine (99%, Aladdin), 1,1,1,3,3,5,5-heptamethyltrisiloxane (90%, Adamas), hexamethylcyclotrisiloxane (98%, Energy Chemical), chlorodimethylsilane (95%, Energy Chemical), palladium on activated charcoal (10% on carbon, TCI), sodium phosphate monobasic dehydrate (99%, Greagent), sodium phosphate dibasic dodecahydrate (99%, Greagent), PVA 89 (Aldrich, Mn 13000 Da), o-dichlorobenzene (99%, Energy Chemical), 1,4dioxane (99%, Sigma-Aldrich), ethanol (HPLC, Fisher), acetonitrile (HPLC, J&K Chemical), N,N-dimethylformamide (HPLC, J&K Chemical), pyridine (HPLC, Concord), ethanol (HPLC, J&K Chemical), and ethyl acetate (HPLC, J&K Chemical) were used as received. Dichloromethane (DCM, HPLC, J&K Chemical), toluene (HPLC, J&K Chemical), and acetone (HPLC, J&K Chemical) were purified using the M Braun SPS-800 solvent purification system. Other chemical reagents were commercially available and used without further purification.

Synthetic Procedures

The general synthetic routes for the preparation of the intermediates $Si_3-C_3-Ph-COOH$, $Si_7-C_3-Ph-COOH$, and $Si_{11}-C_3-Ph-COOH$ are shown in Scheme S1 referring to Schenning's publication.^[1] Benzyl paraben was reacted with allyl bromide in a Williamson ether synthesis to form benzyl 4-(allyloxy)benzoate (intermediate 1). Monodisperse heptasiloxane monohydride (Me-Si₇-H) and undecsiloxane monohydride (Me-Si₁₁-H) were synthesized from trisiloxane monohydride (Me-Si₃-H) following the procedure in Meijer *et al.*'s work.^[2] Then Me-Si₃-H, Me-Si₇-H and Me-Si₁₁-H were coupled to 1 separately using Karstedt's catalyst to yield intermediate 2, 3, and 4. Finally, intermediate 2, 3, and 4 were deprotected using catalytic hydrogenation with palladium on carbon to produce the intermediates 5, 6, and 7, named Si₃-C₃-Ph-COOH, Si₇-C₃-Ph-COOH, and Si₁₁-C₃-Ph-COOH, respectively. The full synthetic

procedure and characterization data are provided below.



Scheme S1 Synthetic route of Si₃-C₃-Ph-COOH, Si₇-C₃-Ph-COOH, and Si₁₁-C₃-Ph-COOH.

Synthesis of Benzyl 4-(Allyloxy)benzoate (1)

A solution of benzyl paraben (4.20 g, 18.4 mmol), potassium carbonate (7.50 g, 54.3 mmol), allyl bromide (2.27 g, 18.8 mmol), and potassium iodide (0.0100 g, 0.0600 mmol) in 100 mL of acetone in a round-bottomed flask is stirred and refluxed under argon for 48 h. After acetone was removed under vacuum, the residue was dissolved in 100 mL of DCM and washed with 1 M NaOH and saturated brine for three times. The organic layer was collected and dried over anhydrous magnesium sulfate. DCM was removed under a reduced pressure, and the crude product was purified by column chromatography (eluent: petroleum ether (PE)/ ethyl acetate = 20:1, v:v) on silica gel to afford 3.49 g (13.0 mmol) of benzyl 4-(allyloxy)benzoate as a transparent liquid. Yield: 71%. ¹H NMR (400 MHz, Chloroform-*d*, δ , ppm) 8.07 – 7.99 (m, 2H), 7.47 – 7.31 (m, 5H), 6.97 – 6.88 (m, 2H), 6.05 (ddt, *J* = 17.3, 10.6, 5.3 Hz, 1H), 5.42 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.34 (s, 2H), 5.33 – 5.28 (m, 1H), 4.59 (dt, *J* = 5.3, 1.6 Hz, 2H).

Synthesis of Benzyl 4-(3-(1,1,3,3,5,5,5-Heptamethyltrisiloxanyl)propoxy)benzoate (2) Benzyl 4-(allyloxy)benzoate (1.34 g, 5.00 mmol) and Me-Si₃-H (1.34 g, 6.00 mmol) were added to a 25 mL Schlenk flask and kept under a nitrogen atmosphere. Then 5 mL of DCM and two drops of Karstedt's catalyst (2.7% in xylene) were subsequently added through a syringe. The reaction mixture was stirred at ambient temperature overnight. After the reaction finished, 0.5 mL of methanol was added to quench the reaction. Then the organic solvent was removed by rotary evaporator. And the crude product was purified by column chromatography (eluent: PE/DCM = 3:1, v:v) to afford 1.77 g of **2** as a transparent liquid. Yield: 72%. ¹H NMR (400 MHz, Chloroform-*d*, δ , ppm) 8.05 – 7.98 (m, 2H), 7.49 – 7.29 (m, 5H), 6.93 – 6.86 (m, 2H), 5.34 (s, 2H), 3.97 (t, *J* = 6.8 Hz, 2H), 1.89 – 1.78 (m, 2H), 0.70 – 0.62 (m, 2H), 0.10 (d, *J* = 9.9 Hz, 21H).

Synthesis of Benzyl 4-(3-(1,1,3,3,5,5,7,7,9,9,11,11,13,13,13 Pentadecamethylheptasiloxanyl)propoxy)benzoate (3)

The synthetic procedure of **3** was similar to that of **2**. Yield: 71%. ¹H NMR (400 MHz, Chloroform-*d*, δ , ppm) 8.04 – 7.99 (m, 2H), 7.48 – 7.29 (m, 5H), 6.92 – 6.87 (m, 2H), 5.33 (s, 2H), 3.96 (t, *J* = 6.8 Hz, 2H), 1.87 – 1.79 (m, 2H), 0.70 – 0.63 (m, 2H), 0.10 (m, 45H).

Synthesis of Benzyl 4-(3-(1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,21-Tricosamethylundecasiloxanyl)propoxy)benzoate (4)

The synthetic procedure of **4** was similar to that of **2**. Yield: 73%. ¹H NMR (400 MHz, Chloroform-*d*, δ , ppm) 8.04 – 7.99 (m, 2H), 7.47 – 7.29 (m, 5H), 6.91 – 6.87 (m, 2H), 5.33 (s, 2H), 3.95 (t, *J* = 6.8 Hz, 2H), 1.86 – 1.79 (m, 2H), 0.70 – 0.62 (m, 2H), 0.10 (m, 69H).

Synthesis of Si₃-C₃-Ph-COOH (5)

The intermediate 2 (1.77 g, 3.61 mmol) and palladium on activated charcoal (10% on carbon, 1.15 g, 1.08 mmol) were added into a Schlenk flask and kept under Argon atmosphere. Then 2 mL of ethyl acetate and 6 mL of ethanol were added into the flask through a syringe. After dissolution, hydrogen was blown up into the reaction mixture for half an hour. The reaction mixture was stirred at ambient temperature for 8 h under a hydrogen atmosphere. After the reaction finished, palladium on activated charcoal was removed by filtration. The crude product was collected by removing the organic solvent using rotary evaporator and then purified by column chromatography (eluent: petroleum ether (PE)/ethyl acetate (EA) = 10:1, v:v) on silica gel to afford 1.13 g (2.82 mmol) of **5** as a colorless waxy solid. Yield: 78%. ¹H NMR (400

MHz, Chloroform-*d*, *δ*, ppm) 8.09 – 8.01 (m, 2H), 6.97 – 6.90 (m, 2H), 4.00 (t, *J* = 6.8 Hz, 2H), 1.91 – 1.79 (m, 2H), 0.71 – 0.62 (m, 2H), 0.04 (d, *J* = 9.9 Hz, 21H).

Synthesis of Si₇-C₃-Ph-COOH (6)

The synthetic procedure of **6** was similar to that of **5**. Yield: 76%. ¹H NMR (400 MHz, Chloroform-*d*, δ , ppm) 8.07 – 8.01 (m, 2H), 6.96 – 6.89 (m, 2H), 3.99 (t, J = 6.8 Hz, 2H), 1.90 – 1.80 (m, 2H), 0.70 – 0.63 (m, 2H), 0.13 – 0.03 (m, 45H).

Synthesis of Si₁₁-C₃-Ph-COOH (7)

The synthetic procedure of 7 was similar to that of 5. Yield: 74%. ¹H NMR (400 MHz, Chloroform-*d*, δ , ppm) 8.06 – 8.01 (m, 2H), 6.95 – 6.88 (m, 2H), 3.9 7 (t, *J* = 6.8 Hz, 2H), 1.89 – 1.81 (m, 2H), 0.69 – 0.62 (m, 2H), 0.12 – 0.02 (m, 69H).

Synthesis of TPP-4Si₃

TPP-4Si₃ was synthesized by esterification reaction. A solution of 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine (31.0 mg, 0.0460 mmol), Si₃-C₃-Ph-COOH (129 mg, 0.322 mmol), 4-(dimethylamino)pyridine (7.8 mg, 0.064 mmol), Porphyrin-OH (1 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (123 mg, 0.644 mmol) in dry acetone was stirred at ambient temperature for 48 h. After reaction, CHCl₃ was poured into the mixture, and the resulting mixture was washed with distilled water and saturated NaOH several times. The organic layer was dried over MgSO₄ and was purified by column chromatography (eluent: petroleum ether (PE)/ tetrahydrofuran (THF) = 8:1, v:v) on silica gel to afford 62.0 mg (0.0280 mmol) of **TPP-4Si**₃ as a purple solid. Yield: 61%. ¹H NMR (400 MHz, Benzene-*d*₆, δ , ppm) 8.93 (s, 8H), 8.51 – 8.47 (m, 8H), 8.11 – 8.06 (m, 8H), 7.51 (d, *J* = 8.4 Hz, 8H), 6.93 – 6.88 (m, 8H), 3.64 (t, *J* = 6.7 Hz, 8H), 1.80 (dt, *J* = 15.5, 6.8 Hz, 8H), 0.69 – 0.61 (m, 8H), 0.22 – 0.16 (m, 84H), -2.16 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*, δ , ppm) 163.27, 161.83, 149.19, 137.62, 133.53, 130.62, 119.73, 118.29, 117.48, 112.59, 68.94, 21.27, 12.32, -1.68. MALDI-TOF MS: [M + H]⁺/z, Calcd, 2208.81; Found, 2208.35.

Synthesis of TPP-4Si7

The synthetic procedure of **TPP-4Si**₇ was similar to that of **TPP-4Si**₃. Yield: 53%. ¹H NMR (400 MHz, Benzene-*d*₆, δ , ppm) 8.93 (s, 8H), 8.52 – 8.46 (m, 8H), 8.12 – 8.04 (m, 8H), 7.51 (d, *J* = 8.4 Hz, 8H), 6.95 – 6.87 (m, 8H), 3.66 (t, *J* = 6.7 Hz, 8H), 1.81 (dt, *J* = 15.0, 6.6 Hz,

8H), 0.73 - 0.62 (m, 8H), 0.31 - 0.19 (m, 181H), -2.16 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*, δ , ppm) 205.86, 164.02, 162.59, 149.95, 138.37, 134.29, 131.37, 120.48, 119.05, 118.25, 113.33, 69.69, 29.83, 22.02, 13.06. MALDI-TOF MS: [M + H]⁺/z, Calcd., 3394.11; Found, 3395.59.

Synthesis of TPP-4Si₁₁

The synthetic procedure of **TPP-4Si**₁₁ was similar to that of **TPP-4Si**₃. Yield: 46%. ¹H NMR (400 MHz, Benzene-*d*₆, δ , ppm) 8.93 (s, 8H), 8.52 – 8.47 (m, 8H), 8.12 – 8.06 (m, 8H), 7.51 (d, *J* = 8.2 Hz, 8H), 6.94 – 6.88 (m, 8H), 3.66 (t, *J* = 6.6 Hz, 8H), 1.83 (dt, *J* = 15.2, 6.4 Hz, 8H), 0.79 – 0.58 (m, 8H), 0.31 – 0.19 (m, 276H), -2.16 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*, δ , ppm) 164.05, 162.62, 149.98, 138.40, 134.32, 131.40, 120.52, 119.08, 118.27, 113.36, 69.73, 22.06, 13.09. MALDI-TOF MS: [M + H]⁺/z, Calcd., 4579.41; Found, 4581.50.

Instrumentation and Characterization

NMR spectroscopy. ¹H and ¹³C NMR spectra were acquired by a Bruker-400 (400 MHz) spectrometer with CDCl₃ as a solvent. The determination of chemical displacement (ppm) was based on the internal standard of tetramethylsilane (TMS). The chemical shift of CDCl₃ was 7.27 ppm in ¹H NMR spectra and 77.00 ppm in ¹³C NMR spectra.

Mass spectrometry. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on an AB Sciex 5800 MALDI-TOF spectrometer using 2,5-dihydroxybenzoic acid (DHB) matrix.

Thermal analysis. Thermogravimetric analysis (TGA) was carried out on a Q600 SDT analyzer under a N₂ gas with a flow rate of 100 mL min⁻¹ and a heating rate of 10 °C min⁻¹ from ambient temperature to 600 °C. Differential scanning calorimetry (DSC) experiments were carried out on a Q2000 DSC calorimeter under a N₂ atmosphere with a flow rate of 50 mL min⁻¹ and a scanning rate of 10 °C min⁻¹ during both the heating and cooling processes. The data of the first cooling and the second heating processes were recorded.

Polarized light microscopy (PLM). PLM experiments were carried out on a Nikon DS-Ril microscopy with an Instec HCS302 hot stage. A small amount of sample was placed on a glass slide and pressed into a thin film with cover glass for testing. The temperature was first raised

so that the sample was in the isotropic state, and then the texture changes were observed during the cooling process.

X-Ray Diffractions (XRD). Wide-angle X-ray scattering (WAXS) profiles and grazingincidence wide-angle X-ray diffraction (GI-WAXD) patterns were acquired using Ganesha SAXS produced by SAXS LAB. The wavelength of the X-ray is 0.154 nm.

Cross-section scanning electron microscopy (SEM). SEM image of thin film was taken using Hitachi S-4800 cold-field emission scan electron microscopy.

Atomic-force microscopy (AFM). AFM images before etching were recorded in the tapping mode under ambient conditions using a NanoScope Analysis 1.5 Atomic force microscope fitted with a silicon probe (Bruker, RTESP, spring constant 42 N/m and a resonance frequency 320 kHz), and AFM images after etching were recorded in the ScanAsyst mode under ambient conditions using a NanoScope Analysis 1.5 Atomic force microscope fitted with a silicon probe (Bruker, Scanasyst-Air, spring constant 0.4 N/m and a resonance frequency 70 kHz).

Modification of Si Substrate

The Si substrate was decorated with a polydimethylsiloxane (PDMS) brush by hydrophilic modification and PDMS modification. A heptane solution of 1.5 wt% hydroxyl-terminated PDMS homopolymer ($M_n = 5000$ Da) was coated onto the hydrophilically modified Si wafer at 3000 rpm for 45 s and baked at 150 °C for 24 h.

Preparation of Parallel Oriented Thin Films

Uniform thin films were obtained by spinning-coating a solution of 1 wt% LCs in *n*-heptane onto PDMS-modified Si substrates at a spinning speed of 1500 rpm for 45 s. Then thermal annealing was carried out: The films were first heated to the isotropizaiton point of each LC and then cooled to ambient temperature at a rate of 1 °C min⁻¹.

Preparation of Glass Cells

Glass slides were spin-coated with 5 wt% PSS previously. Then a small piece of 1 µm-thick film was placed between two decorated glass slides. Finally, AB glue was used to stick the edge of the glass slides to obtain a cell with a 1 µm thickness.

Preparation of Homeotropically-aligned Thin Films

The TPP-4Si₁₁ thin film was firstly prepared onto a hydrophilically modified Si substrate by

spin-coating at a speed of 1500 rpm for 45 s. Then an approximately 100 nm- thick poly(vinyl alcohol) (PVA) 89 ($M_n = 13000$ Da) top coat was placed on the top of the as-casting **TPP-4Si**₁₁ thin film by spin-coating a 4.6 wt% PVA 89 solution in deionized water at a spinning speed of 1500 rpm for 45 s and drying at 50 °C on a hot plate for 30 minutes to remove the residual water. The LC film was confined between a PVA top coat and a bottom Si wafer, and then it was exposed to saturated solvent vapor (*o*-dichlorobenzene) in a closed solvent annealing chamber at 25 °C for 60 min. Following the completion of the solvent diffusion, the film was removed from the annealing chamber to allow the solvent evaporation throughout the top coat and edges of the sample at 50 °C in air for 60 min. Then, the top layer was removed by rinsing in water for ~10 sec. This treatment did not damage the underlying ordered LC film because of the high solubility of PVA 89 in water; in contrast, the LC film is not soluble in water.

Plasma Etching

Two-step plasma etching (RIE, LCCP-6A) was used to convert the vertically-aligned patterns to oxidized ODMS patterns. This consisted of a 50W CF₄ plasma at 20 mTorr for 6 seconds to remove the ODMS wetting layer on the surface and a 90 W O₂ plasma at 20 mTorr for 25 seconds to selectively remove the porphyrin matrix.

Results

Sample	First cooling	Second heating
TPP-4Si ₃	Iso-160-Colob	Colob-206-Iso
TPP-4Si7	Iso-88-Lam	Lam-130-Iso
TPP-4Si ₁₁	Iso –78–Col _h	Col _h -119-Iso

Table S1 Thermal transition data of TPP-4Si₃, TPP-4Si₇, and TPP-4Si_{11.^a}

^a Phase transition temperatures in $^{\circ}$ C; Col_{ob} = oblique columnar phase, Lam = lamellar phase, Col_h = hexagonal columnar phase, Iso = isotropic phase.



Fig. S2 ¹³C NMR spectrum of TPP-4Si₃.



Fig. S3 ¹H NMR spectrum of TPP-4Si₇.



Fig. S4 ¹³C NMR spectrum of TPP-4Si₇.



Fig. S5 ¹H NMR spectrum of TPP-4Si₁₁.



Fig. S6 ¹³C NMR spectrum of TPP-4Si₁₁.



Fig. S7 MALDI-TOF mass spectra of the LCs. Experimental results of **TPP-4Si**₃ (a), **TPP-4Si**₇ (c), and **TPP-4Si**₁₁ (e) and theoretical isotropic distribution of **TPP-4Si**₃ (b), **TPP-4Si**₇ (d), and **TPP-4Si**₁₁ (f). Theoretical results were simulated by using Chemputer: isotope pattern calculator from Prof Mark J. Winter's website: "https://winter.group.shef.ac.uk/chemputer/isotope pattern.html".



Fig. S8 TGA thermograms of **TPP-4Si₃** (black), **TPP-4Si₇** (orange), and **TPP-4Si₁₁** (blue) at a heating rate of 10 $^{\circ}$ C min⁻¹ under a nitrogen atmosphere (decomposition temperatures in $^{\circ}$ C at 5% weight loss are marked).



Fig. S9 DSC first-cooling and second-heating thermograms of **TPP-4Si₃** (black), **TPP-4Si₇** (orange), and **TPP-4Si₁₁** (blue) at a cooling and heating rate of 10 °C min⁻¹ under a nitrogen atmosphere (onset phase transition temperatures in °C are marked)



Fig. S10 PLM micrographs of **TPP-4Si**₃ at 240 °C (a), **TPP-4Si**₇ at 150 °C (b), and **TPP-4Si**₁₁ at 150 °C (c); PLM micrographs of **TPP-4Si**₃ (d), **TPP-4Si**₇ (e), and **TPP-4Si**₁₁ (f) at ambient temperature.



Fig. S11 Temperature-dependent WAXD profiles of TPP-4Si₃.



Fig. S12 Temperature-dependent WAXD profiles of TPP-4Si₇.



Fig. S13 Temperature-dependent WAXD profiles of $TPP-4Si_{11}$.



Figure S14. Schematic diagram of the phase transition of the three LCs during the heating process.



Fig. S15 Water contact angels of the original and modified substrates (a) and cross-sectional SEM image of **TPP-4Si**₁₁ thin film (b).



Fig. S16 AFM cross-sectional scanning curve of TPP-4Si7.



Fig. S17 AFM cross-sectional scanning curve of TPP-4Si₁₁.



Fig. S18 Large-area AFM phase image of TPP-4Si₁₁.



Fig. S19 AFM height image (a) and GI-WAXD pattern (b) of TPP-4Si₁₁ after plasma etching.

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