Supporting Information

The Functionalized Hexa-*peri*-hexabenzocoronenes by Sonogashira

Coupling Method to Modify the Columnar Mesophase Behavior

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1. Experimental Section

1.1 General methods

^1H -NMR and ^{13}C -NMR spectra were recorded in CDCl_3 and $\text{CDCl}_3/\text{CS}_2$ 10:1 on an Agilent Technologies 400-MR NMR spectrometer with use of the solvent proton or carbon signal as the internal standard (^1H : 7.25 ppm; ^{13}C : 77.0 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Mass spectra were obtained on a Bruker Microflex by using MALDI.

Differential scanning calorimetry (DSC) was measured on a Mettler Toledo DSC822ew with heating and cooling rates of 10 and 20 $^{\circ}\text{C min}^{-1}$. First-order transition temperatures were reported as the minima of their endothermic peaks during heating. Polarizing optical microscopy (POM) was carried out on a Zeiss Axio Imager A1m with a Mettler FP90/FP82HT hot stage system that was used to characterize the polarization microscopy textures and to estimate clearing temperatures. Heating and cooling rates varied between 10 and 20 $^{\circ}\text{C min}^{-1}$. X-ray diffraction experiments were measured on the wiggler beam line BL17A of the National Synchrotron Radiation Research Center (NSRRC, Taiwan), using a triangular bent Si (111) monochromator and a wavelength of 1.3213 Å. The sample in a 1-mm capillary or an extruded filament was mounted on the Huber 5020 diffractometer. The BL17A beamline was equipped

with an air-stream heater, and the temperature controller was programmed by a PC with a PID feedback system.

1.2 Materials

All chemicals and solvents were reagent grade and were used without further purification. The chemicals and their purities (as received) are listed: [1,1']-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (98.0%), bromine (99.0%), 1-bromo-4-iodobenzene (98.0%), 1-bromobutane (98.0%), 1-bromohexane (99.0%), 1-bromodecane (98.0%), 1-bromododecane (98.0%), 4-bromobenzaldehyde (98.0%), 4-bromophenylacetic acid (99.0%), copper(I) iodide (99.5%), dicyclohexylcarbodiimide (99.0%), 4-dimethylaminopyridine (99.0%), 1-dodecanol (98.0%), ethynyltrimethylsilane (98.0%), hydrochloric acid (37.4%), iodine (99.5%), iron(III) chloride (97.0%), magnesium (99.5%), magnesium sulfate (99.0%), 2-methylbut-3-yn-2-ol (98.0%), potassium-*tert*-butanolate (97.0%), potassium hydroxide (85.0%), sodium bicarbonate (99.0%), sodium chloride, sodium hydroxide (97.0%), sodium lumps (100%), sodium thiosulfate (98.0%), sulfuric acid (97.0%), tetrabutylammonium fluoride in 1 M THF, tetrabutylammonium hydroxide in 1 M methanol, titanium(IV) chloride in 1 M toluene, *p*-toluenesulfonic acid (99.0%), zinc flake (99.9%), *t*-butanol (99.5%), carbon disulfide (99.9%), chloroform (99.8%), dichloromethane (99.5%), dimethyl sulfoxide (99.9%), diphenyl ether (99.0%), ethanol

(99.5%), ethyl acetate (99.5%), ethylene glycol (99.0%), *n*-hexane (98.0%), methanol (99.5%), nitromethane (98.0%), tetrahydrofuran (99.0%), toluene (99.5%), and triethylamine (98.0%)

1.3 Syntheses

Scheme S1. The synthesis of *mono*-bromohexabenzocoronene **1**. i) 0.8 M tetrabutylammonium hydroxide in MeOH, *t*-BuOH, Ar, 85 °C, 78%; ii) diphenyl ether, dialkyldiphenylacetylene, Ar, reflux, 61%.; (iii) FeCl₃, CH₂Cl₂, CH₃NO₂, 30 °C, 43%

1.3.1 3-(4-Bromophenyl)-2, 4, 5-tris(4-dodecylphenyl)cyclopenta-2,4-dienone .

For this synthesis, 1.72 g (3.15 mmol) of 1,3-bis(4-dodecylphenyl)propan-2-one and

1.45 g (3.15 mmol) of 4-bromo-4'-dodecylbenzil were dissolved in *t*-butanol (35 mL) under an Ar atmosphere and stirred at 85 °C. A solution prepared from 0.6 mL of 0.8 M tetrabutylammonium hydroxide in methanol (0.6 mL) and 2 mL of *t*-butanol was added. After 30 min. the reaction mixture was quenched by addition of 50 mL H₂O. The product was extracted with CH₂Cl₂, concentrated, and purified using column chromatography on silica gel with *n*-hexane/CH₂Cl₂ (6:1) to give a purple oil product 2.37 g (2.45 mmol). Yield: 78%. ¹H NMR (400 MHz, CDCl₃): δ = 7.29 (d, *J* = 8 Hz, 2 H), 7.17-6.75 (m, 14 H), 3.64-2.50 (m, 6 H), 1.38-1.20 (m, 52 H), 0.89 (t, *J* = 12 Hz, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ = 200.61, 153.62, 152.30, 143.52, 142.52, 142.23, 132.35, 131.10, 130.25, 129.89, 129.17, 128.21, 128.10, 128.04, 127.74, 125.52, 124.76, 122.57, 35.78, 35.72, 31.92, 31.19, 30.99, 29.66, 29.50, 29.39, 29.36, 29.21, 22.68, 14.12.

1.3.2 1-(4-Bromophenyl)-2,3,4,5,6-pentakis(4-dodecylphenyl)benzene (4)

For this synthesis, 1.41 g (2.74 mmol) of 1,2-bis(4-dodecylphenyl)ethyne and 2.65 g (2.74 mmol) of 3-(4-bromophenyl)-2,4,5-tris(4-dodecylphenyl)cyclopenta-2,4-dienone were suspended in a minimal amount of diphenyl ether and refluxed for 5 h under an Ar atmosphere. After cooling, diphenyl ether was removed under reduced pressure. The reaction product was purified using column chromatography on silica gel with *n*-hexane to give yellow oil product 2.42 g (1.67 mmol). Yield: 61%. ¹H NMR (400 MHz, CDCl₃): δ = 6.95 (d, *J* = 8 Hz, 2 H), 6.68-6.61 (m, 22 H), 2.39-2.32 (m, 10 H), 1.51-1.12 (m, 100

H), 0.89 (t, J = 12 Hz, 15 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 140.80, 140.52, 140.20, 140.07, 139.44, 139.16, 138.79, 138.02, 137.95, 137.79, 133.21, 131.26, 129.54, 126.75, 126.49, 119.05, 35.34, 35.31, 31.94, 31.23, 31.13, 29.75, 29.69, 29.55, 29.39, 28.78, 28.80, 22.69, 14.11.

1.3.3 2-Bromo-5,8,11,14,17-pentadodecylhexa-peri-hexabenzocoronene.

A 250 mL two-necked round bottom flask was charged with 0.38 g (0.26 mmol) of 1-(4-bromophenyl)-2,3,4,5,6-pentakis(4-dodecylphenyl)benzene and 400 mL of dry CH_2Cl_2 . A constant stream of Ar was bubbled through the solution for 15 min. Then, 0.81 g (4.97 mmol) of FeCl_3 dissolved in CH_3NO_2 (10 mL) was added dropwise using a syringe. After 30 min, the mixture was quenched with 400 mL of methanol, and the precipitate was filtered. The resulting yellow solid was dissolved in CH_2Cl_2 and dried under vacuum to yield yellow powder 0.16 g (0.11 mmol). Yield: 43%. ^1H NMR (400 MHz, CDCl_3): δ = 7.96 (s, 2 H), 7.84 (s, 2 H), 7.69 (s, 2 H), 7.59 (s, 2 H), 7.51 (s, 2 H), 7.36 (s, 2 H), 2.94 (t, J = 16 Hz, 2 H), 2.75 (t, J = 16 Hz, 4 H), 2.53 (t, J = 16 Hz, 4 H), 2.04 (m, J = 16 Hz, 4 H), 1.89 (m, J = 16 Hz, 4 H), 1.74 (m, J = 16 Hz, 6 H), 1.62-1.26 (m, 90 H), 0.91 (t, J = 12 Hz, 15 H). ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2$): δ = 138.86, 138.71, 138.64, 130.10, 128.82, 128.58, 128.29, 128.17, 127.03, 122.24, 121.99, 121.86, 127.76, 121.70, 120.64, 120.38, 120.22, 120.14, 120.00, 119.91, 118.40, 118.06, 117.81, 117.10, 37.40, 37.20, 36.86, 32.67, 32.50, 32.21, 32.08, 31.96, 30.43, 30.34, 30.27, 30.18, 30.11, 30.08, 30.02, 29.99, 29.91, 29.56, 22.86, 14.19.

1.3.3 2-(4-Butylphenyl)ethynyl-5,8,11,14,17-pentadodecylhexa-*peri*-hexabenzocoronene (5a)

A mixture of 0.35 g (0.24 mmol) 2-bromo-5,8,11,14,17-pentadodecylhexa-*peri*-hexabenzocoronene, 0.13 mL (0.74 mmol) 1-butyl-4-ethynylbenzene, and 0.01 g (0.005 mmol) CuI in 50 mL trimethylamine and 0.36 g (0.05 mmol) bis(triphenylphosphine) palladium(II) chloride were added consecutively under argon. The reaction mixture was stirred overnight at 80 °C, quenched with brine, and extracted with CH₂Cl₂. The extract was concentrated under reduced pressure and purified by column chromatography with hexane/dichloromethane (10/1) as eluent to give yellow powder 0.29 g (0.19 mmol). Yield: 80%. ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (s, 2H), 7.86 (s, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.77 (s, 2H), 7.67 (s, 2H), 7.65 (s, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.78-2.45 (m, 10H), 2.10-1.15 (m, 104H), 1.10 (t, *J* = 8 Hz, 3H), 1.00-0.80 (m, 15H). ¹³C NMR (100 MHz, CDCl₃/CS₂): δ = 143.03, 138.66, 138.53, 131.77, 128.56, 128.23, 123.23, 122.89, 121.97, 121.72, 121.64, 121.48, 121.44, 121.40, 120.36, 120.03, 119.93, 118.99, 118.44, 118.20, 117.91, 117.47, 117.96, 117.73, 117.47, 116.14, 114.66, 91.10, 88.91, 37.23, 37.04, 36.98, 35.85, 33.61, 32.39, 32.36, 32.01, 30.37, 30.31, 30.15, 30.09, 30.05, 30.01, 29.97, 29.94, 29.87, 29.84, 29.52, 29.49, 22.74, 22.57, 14.13, 14.07. MALDI-MS: *m/z* (%): calcd. for C₁₁₄H₁₅₀: 1520.4; found 1521.1 [M+H]⁺.

Compound **5b**: Yield: 85%. ^1H NMR (400 MHz, CDCl_3): δ = 8.07 (s, 2H), 7.90 (s, 2H), 7.82 (s, 2H), 7.81 (d, J = 8 Hz, 2H), 7.76 (s, 2H), 7.72 (s, 2H), 7.69 (s, 2H), 7.40 (d, J = 8 Hz, 2H), 2.87-2.80 (m, 10H), 2.74-2.66 (m, 2H), 2.08-1.15 (m, 108H), 1.71-1.16 (m, 96 H), 1.03-1.00 (t, J = 6 Hz, 2H), 1.00-0.87 (m, 15H). ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2$): δ = 143.19, 138.96, 138.84, 131.82, 128.86, 128.64, 128.60, 128.55, 128.47, 127.85, 123.39, 123.08, 121.99, 121.92, 121.89, 121.34, 120.59, 120.29, 120.22, 119.26, 118.68, 118.44, 118.15, 117.45, 91.06, 89.13, 37.31, 37.15, 37.06, 36.21, 32.62, 32.44, 32.38, 32.03, 31.89, 31.59, 31.48, 30.39, 30.31, 30.11, 30.06, 30.02, 29.96, 29.86, 29.70, 29.52, 29.26, 22.75, 22.85, 14.20, 14.15. MALDI-MS: m/z (%): calcd. for $\text{C}_{116}\text{H}_{154}$: 1548.5; found 1549.2 $[\text{M}+\text{H}]^+$.

Compound **5c**: Yield: 79%. ^1H NMR (400 MHz, CDCl_3): δ = 7.96 (s, 2H), 7.80 (d, J = 8.0, 2H), 7.77 (s, 2H), 7.68 (s, 2H), 7.64 (s, 2H), 7.57 (s, 2H), 7.54 (s, 2H), 7.40 (d, J = 8.0, 2H), 2.90-2.50 (m, 12H), 2.05-1.15 (m, 116H), 1.00-0.80 (m, 18H). ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2$): δ = 143.15, 138.94, 138.81, 131.81, 128.65, 128.57, 128.49, 123.07, 121.91, 120.27, 119.28, 118.47, 118.18, 117.48, 91.09, 91.08, 37.30, 37.14, 37.05, 32.43, 32.01, 30.02, 29.85, 29.50, 29.43, 22.74, 14.13. MALDI-MS: m/z (%): calcd. for $\text{C}_{120}\text{H}_{162}$: 1604.6; found 1605.1 $[\text{M}+\text{H}]^+$.

Compound **5d**: Yield: 92%. ^1H NMR (400 MHz, CDCl_3): δ = 8.07 (s, 2H), 7.86 (s, 2H), 7.81 (s, 2H), 7.79 (s, 4H), 7.75 (s, 2H), 7.67 (d, J = 8.0, 2H), 7.38 (d, J = 8.0, 2H), 2.95-

2.90 (m, 2H), 2.75-2.55 (m, 10H), 2.0-1.9 (m, 2H), 1.9-1.7 (m, 10H), 1.7-1.1 (m, 108H), 0.95-0.85 (m, 18H). ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2$): δ = 143.17, 138.94, 138.82, 131.79, 128.83, 128.58, 128.45, 127.83, 123.06, 121.97, 121.87, 121.32, 120.57, 120.27, 119.23, 118.66, 118.42, 118.13, 117.75, 117.43, 91.03, 89.11, 37.29, 37.13, 37.04, 36.19, 32.60, 32.42, 32.01, 31.87, 31.57, 30.37, 30.29, 30.09, 30.04, 30.00, 29.93, 29.84, 29.49, 29.24, 22.73, 22.63, 14.18, 14.13. MALDI-MS: m/z (%): calcd. for $\text{C}_{122}\text{H}_{166}$: 1632.6; found 1633.1 $[\text{M}+\text{H}]^+$.

Compound **6**: Yield: 81%. ^1H NMR (400 MHz, CDCl_3): δ = 8.22 (s, 2H), 8.07 (s, 2H), 8.02 (s, 2H), 7.95 (s, 2H), 7.93 (s, 2H), 7.84 (d, J = 8 Hz, 2H), 7.74 (s, 2H), 7.11 (d, J = 8 Hz, 2H), 4.14 (t, J = 8 Hz, 2H), 2.88-2.56 (m, 10H), 2.00-1.20 (m, 120H), 0.95-0.80 (m, 15H). ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2$): δ = 159.23, 138.74, 138.58, 138.49, 138.42, 138.35, 133.25, 129.90, 128.61, 128.45, 128.29, 128.04, 127.92, 127.74, 126.76, 123.21, 122.88, 121.97, 121.78, 121.68, 121.48, 120.40, 120.11, 119.96, 119.86, 119.73, 119.57, 119.29, 118.46, 118.24, 117.96, 117.73, 117.47, 116.14, 114.66, 90.25, 88.83, 68.23, 37.35, 37.24, 37.13, 37.04, 36.80, 32.69, 32.60, 32.51, 32.41, 32.24, 32.05, 32.03, 29.55, 29.52, 29.45, 29.35, 26.25, 22.76, 22.69, 14.16. MALDI-MS: m/z (%): calcd. for $\text{C}_{122}\text{H}_{166}\text{O}$: 1648.6; found 1649.6 $[\text{M}+\text{H}]^+$.

Compound **7**: Yield: 83%. ^1H NMR (400 MHz, CDCl_3): δ = 8.25 (d, J = 8 Hz, 2H), 8.13 (s, 2H), 8.01 (s, 2H), 7.95 (s, 2H), 7.91 (d, J = 8 Hz, 2H), 7.85 (s, 6H), 4.46 (t, J = 6 Hz,

2H), 2.95-2.65 (m, 10H), 1.70-1.13 (m, 100H), 0.97-0.88 (m, 18H). ¹³C NMR (100 MHz, CDCl₃/CS₂): δ = 166.14, 139.02, 138.88, 131.61, 129.69, 128.87, 128.72, 128.62, 128.47, 127.73, 123.79, 123.04, 121.94, 120.59, 120.27, 118.89, 118.55, 118.32, 118.20, 117.33, 94.79, 88.20, 65.42, 41.34, 37.27, 37.12, 36.07, 34.66, 34.52, 32.59, 32.43, 32.02, 31.59, 30.31, 30.11, 30.07, 30.02, 29.95, 29.85, 29.51, 29.44, 29.06, 28.90, 27.66, 26.72, 26.16, 25.27, 22.75, 22.66, 22.59, 20.67, 20.45, 19.40, 18.72. MALDI-MS: *m/z* (%): calcd. for C₁₂₃H₁₆₆O₂: 1675.3; found 1675.3 [M+H]⁺

1.4 The Mesophase characterization

Fig. S1 Powder X-ray diffraction pattern and partial enlarged drawing of compound **5a** at 180 °C.

Fig. S2 Powder X-ray diffraction pattern and partial enlarged drawing of compound **5b** at 180 °C.

Fig. S3 Powder X-ray diffraction pattern and partial enlarged drawing of compound **5c** at 180 °C.

Fig. S4 Powder X-ray diffraction pattern and partial enlarged drawing of compound **5d** at 180 °C.

Fig. S5 Powder X-ray diffraction pattern and partial enlarged drawing of compound **6** at 180 °C.

Fig. S6 Powder X-ray diffraction pattern and partial enlarged drawing of compound **7** at 180 °C.

^exo

Lab: METTLER

STAR^e SW 9.10

Fig. S7 The DSC of compound **5a** at 10 °C/min.

exo

HBC-C12-PH-C6

30.09.2014 16:17:56

Lab: METTLER

STAR^e SW 9.10

Fig. S8 The DSC of compound **5b** at 10 °C/min.

^exo

Fig. S9 The DSC of compound **5c** at 10 °C/min.

^exo

Lab: METTLER

Fig. S10 The DSC of compound 5d at 10 °C/min.

STAR[®] SW 9.10

^exo

Lab: METTLER

Fig. S11 The DSC of compound **6** at 10 °C/min.

STAR[®] SW 9.10

^exo

Lab: METTLER

Fig. S12 The DSC of compound 7 at 10 °C/min.

STAR^e SW 9.10