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Supporting Information

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Molecular Wires from Contorted Aromatics

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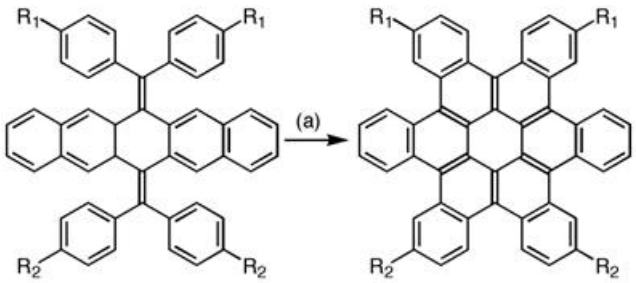
I. Synthesis

General. Anhydrous and anaerobic THF and toluene were obtained from a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). Unless otherwise noted, all reactions were run in oven-dried glassware, and monitored by TLC using silica gel 60 F_{254} precoated plates (EM Science). Column chromatography was performed on a CombiFlash® Sg100c system using RediSepTM normal phase silica columns (ISCO, Inc., Lincoln, NE). ^{1}H-NMR (300MHz, 400MHz) and ^{13}C-NMR (75MHz, 100MHz) spectra were recorded on a Bruker DRX-300 and Bruker DRX-400 spectrometers at room temperature unless otherwise noted. High resolution mass spectra were recorded on a JEOL JMS-HX110A/110A tandem mass spectrometer. The photochemistry was carried out according to a reported procedure. (Liu, L; Yang B; Katz, T. J; Poindexter, M. K. *J. Org. Chem.* **1991,** 56, 3769-3775).

The key for the synthesis of **1a**–**1c** is shown below in Scheme S1 where the bisolefins **2a-c** are photocyclized. The bis-olefins (**2a-c**) were prepared through two step-wise Barton-Kellogg olefination [(a) D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Chem. Commun.*, **1970**, 1225; (b) D.H.R. Barton, E. H. Smith and B. J. Willis, *J. Chem. Soc., Chem. Commun.*, **1970**, 1226 (c) J. Buter, S. Wassenaar and R. M. Kellogg, *J. Org. Chem.*, **1972**, *37*, 4045.4060.] procedures detailed in Scheme S2.

Scheme S1. Photocyclization to form contorted hexabenzocoronenes (**1a-c**) substituted with dodecyloxy-substituents.

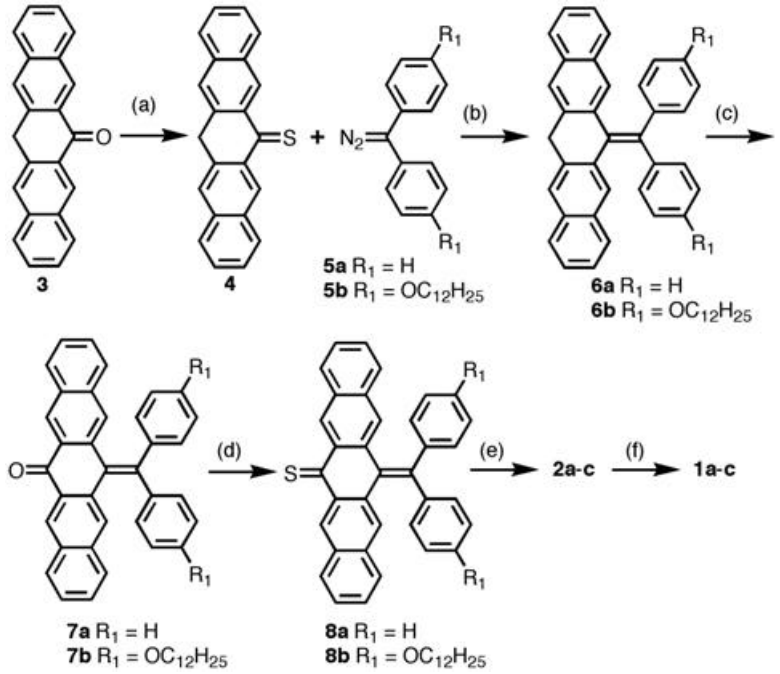


2a $R_1 = R_2 = H$
2b $R_1 = H$, $R_2 = O\text{-}C_{12}H_{25}$
2c $R_1 = R_2 = O\text{-}C_{12}H_{25}$

1a $R_1 = R_2 = H$
1b $R_1 = H$, $R_2 = O\text{-}C_{12}H_{25}$
1c $R_1 = R_2 = O\text{-}C_{12}H_{25}$

key: (a) hν, I_2, propylene oxide.

Scheme S2. Synthesis of the contorted hexabenzocoronenes (**1a-c**).



key: (a) Lawesson's reagent; (b) THF, then PPh_3; (c) $KMnO_4$; (d) Lawesson's reagent; (e) THF, then PPh_3; (f) hν, I_2, propylene oxide.

Preparation of starting materials. Ketone **3** was synthesized according to a literature procedure. (Clar, E. *Chemische Berichte* **1949**, 82, 495-514). Diphenyldiazomethane **(5a**) was synthesized according to a literature procedure (De Meijere, A; Teichmann, S; Yu, D; Kopf, J; Oly, M; Von Thienen, N. *Tetrahedron* **1989**, 45(10), 2957-68).

Synthesis of thioketone 4. 3 (4.4 g, 14.9 mmol) and Lawesson's reagent (0.7 eq, 4.2 g, 10.4 mmol) were added to 500 mL of toluene. The solution was heated to 80ºC for 2 hours. The dark green solution was allowed to cool to room temperature and 1200 mL of a 4:1 v/v mixture of hexanes and CH_2Cl_2 was added. Filtration through a plug of silica gel and a small amount of the same mixture of hexanes and CH_2Cl_2 was used to wash the remaining product from the silica gel. **4** was isolated as a green solid (2.2 g, 47%) after removal of the solvent and triturating with cold hexanes. ^{1}H-NMR (300 MHz, $CDCl_3$) *d* (ppm): 4.62 (s, 2H), 7.58 (dt, *J* = 6.9Hz, 1.3 Hz, 2H), 7.68 (dt, *J* = 6.9, 1.3 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.95 (s, 2H), 8.13 (d, *J* = 8.2 Hz, 2H), 9.19 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) *d* (ppm): 223.1, 139.1, 135.1, 132.3, 131.1, 130.9, 130.8, 130.2, 128.6, 127.0, 126.1, 125.8; HRMS (FAB+) : cald. for $C_{22}H_{15}S$: 311.0894, found: 311.0904.

Synthesis of olefin 6a. 1.1 eq. of diphenyldiazomethane (**5a**) dissolved in THF was added dropwise to a solution 1.0 g of thioketone **4** in 100 mL of THF. The diphenyldiazomethane was added until the green color of thioketone disappeared. After addition, the reaction was stirred for 1 hr. The thioepoxide was obtained by column chromatography (SiO_2, 3:1 hexanes:CH_2Cl_2, Rf=0.15) in quantitative yield (1.55g, 100%). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 4.58 (d, *J* = 16.8 Hz, 1H), 4.91 (d, *J* = 16.8 Hz, 1H), 6.98 (t, *J* = 6.0 Hz, 2H), 7.08 (t, *J* = 5.7 Hz, 4H), 7.45 (m, 6H), 7.53 (td, *J* = 6.9 Hz, 1.3 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 5.0 Hz, 4H), 8.00 (s, 2H);

^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 141.6, 136.6, 135.0, 133.0, 132.4, 129.6, 128.4, 128.0, 127.9, 127.3, 127.1, 126.5, 125.8, 125.3, 84.0, 72.5, 63.2, 38.6; HRMS (FAB+) cald. for $C_{35}H_{24}S$: 476.1599, found: 476.1608. A solution of the thioepoxide (1.55 g, 0.35 mmol) was then heated at reflux with triphenylphosphine (1.01 g, 0.39mmol) in 200 mL of anhydrous *p*-xylene for 12 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The solid residue was dissolved in 200 mL of CH_2Cl_2 and concentrated under reduced pressure to 50 mL. Upon cooling on an ice/water bath, **6a** precipitates from solution. The solids were isolated by vacuum filtration and washed with cold CH_2Cl_2. Compound **6a** was isolated as a white solid (1.35 g, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$) *d* (ppm): 4.34 (s, 2H), 7.10-7.45 (m, 16H), 7.52 (s, 2H), 7.72 (d, *J* = 2.2 Hz, 2H), 7.76 (s, 2H); HRMS (FAB+) cald. for $C_{35}H_{24}$: 444.1878, found: 444.1877.

Synthesis of ketone 7a. $KMnO_4$ (460 mg, 2.91 mmol) was added as a solid to **6a** (640 mg, 1.46 mmol) dissolved in 1 L of acetone. The solution was stirred for 2 hours at room temperature and then filtered. The solids were washed with 200 mL of CH_2Cl_2. The combined organic solutions were washed with 800 mL of water. The phases were separated and the aqueous phase was back extracted with CH_2Cl_2 (3 x 100 mL). Removal of the solvent followed by column chromatography (SiO_2, 45% CH_2Cl_2 in hexanes, Rf = 0.20) provided pure **7a** (380 mg, 56.7%). The first fraction from the column was unreacted starting material (20% CH_2Cl_2 in hexanes, Rf = 0.20). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 4.58 (d, *J* = 16.8 Hz, 1H), 7.25 (m, 10H), 7.50 (m, 6H), 7.67 (s, 2H), 8.00 (d, *J* = 6.3 Hz, 2H), 8.69 (s, 2H); ^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 186.2, 145.6, 143.5, 135.0, 134.5, 132.0, 131.9, 131.2, 129.6, 129.4, 128.9, 128.6, 128.2, 127.9, 127.2, 127.1; HRMS (FAB+) cald. for $C_{35}H_{22}O$: 458.1671, found: 458.1676.

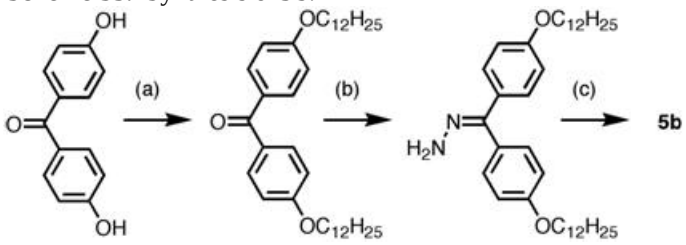
Synthesis of thioketone 8a. Ketone **7a** (757 mg, 1.65 mmol) and Lawesson's reagent (368 mg, 0.91 mmol, 0.55 eq) were dissolved in 300 mL toluene. The solution was heated for 30 minutes at 80ºC. After cooling to room temperature, the solution was filtered through a plug of silica gel and washed with 4:1 hexanes:CH_2Cl_2. The solvent was removed under reduced pressure to yield analytically pure compound **8a** (774 mg, 1.63 mmol, 98%). ^{1}H-NMR (300 MHz, CD_2Cl_2) *d* (ppm): 7.20-7.50 (m, 16H), 7.65 (s, 2H), 8.01 (t, *J* = 4.6 Hz, 2H), 8.95 (s, 2H).

Synthesis of bisolefin 2a. 1.1 eq. of diphenyldiazomethane (**5a**) dissolved in THF was added dropwise to **8a** (774 mg, 1.63 mmol) in 350 mL of THF. The diazomethane was added until the green color disappeared. The reaction was stirred at room temperature for 1 hr. The solvent was removed and the thioepoxide was purified by column chromatography (SiO_2, 3:1 hexanes:CH_2Cl_2, Rf=0.20) to yield 928 mg, 1.45mmol, 88%. ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 7.10 (m, 6H), 7.30 (m, 10H), 7.42 (d, *J* = 8.8Hz, 2H), 7.52 (d, *J* = 8.4Hz, 4H), 7.57 (d, *J* = 8.0Hz, 4H), 7.65 (d, *J* = 8.0Hz, 2H), 7.76 (s, 2H), 8.00 (s, 2H); ^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 142.4, 141.3, 140.8, 136.7, 134.7, 134.0, 132.1, 131.8, 130.8, 130.3, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.2, 126.4, 126.3, 71.9, 64.8; HRMS (FAB+) cald. for $C_{48}H_{32}S$: 640.2225, found: 640.2227. A solution of this thioepoxide (928 mg, 1.45 mmol) and triphenylphosphine (456 mg, 1.74 mmol) in 130 mL of anhydrous *p*-xylene was heated at reflux for 12 hours. The

solvent was removed under reduced pressure. Recrystallization from 2:1 v/v methanol:CH_2Cl_2 provided pure **2a** (859 mg, 98%). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 7.27 (m, 8H), 7.40 (m, 12H), 7.42 (m, 12H); ^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 142.8, 141.5, 136.2, 135.7, 131.7, 129.9, 128.6, 127.7, 127.3, 127.0, 126.0; HRMS (FAB+) cald. for $C_{48}H_{32}$: 608.2504, found: 608.2487.

Synthesis of contorted hexabenzocoronene 1a. The photolysis setup has been previously described (see: Liu, L; Yang B; Katz, T. J; Poindexter, M. K. *J. Org. Chem.* **1991,** 56, 3769-3775). A mixture of compound **2a** (500 mg, 0.82 mmol), iodine (965 mg, 3.78 mmol), propylene oxide (20mL) in 350 mL of anhydrous benzene were irradiated with UV light (Hanovia 450 W high-pressure quartz Hg-vapor lamp) in an immersion well. Argon was bubbled through the reaction vessel during the photolysis. To maintain a constant temperature, the whole apparatus is submerged in a large bath of circulating water. After 12 hours of irradiation, the solvent is reduced to 15 mL under reduced pressure and a yellow powder precipitates. Compound **1a** is isolated by vacuum filtration and washed with 100 mL of 20% CH_2Cl_2 in hexanes to yield 410 mg of **1a** (83% yield). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 9.24 (q, *J* = 3.0 Hz, 12H), 7.58 (q, *J* = 3.2 Hz, 12H); MS (TOF-MALDI M+H$^+$) cald. For $C_{48}H_{24}$: 600.7042, found: 601.2.

Scheme S3. Synthesis of **5b**.



key: (a) $C_{12}H_{25}Br$, K_2CO_3; (b) $NH_2NH_2 \cdot H_2O$; (c) HgO.

Synthesis of 4,4'-didodecyloxybenzophenone. A mixture of 4,4'-dihydroxybenzophenone (21.4 g, 100 mmol), 1-bromododecane (49.8g, 200 mmol), K_2CO_3 (50g) in 500 mL of DMF were heated with stirring at 120 ºC for 60 hours. After the mixture was cooled to room temperature, 1 L of water was added. The solution was extracted with CH_2Cl_2 (4 x 500 mL). The combined organic layers were dried with $MgSO_4$ and the most of the solvent removed under reduced pressure as a white solid formed. The solids were collected by filtration, washed with cold hexanes, and air dried to give 4,4'-didodecyloxybenzophenone (41.2 g, 75%). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 0.90 (m, 6H), 1.25-1.50 (m, *J* = 3.0 Hz, 36H), 1.83 (m, 4H), 4.04 (t, *J* = 6.5 Hz, 4H), 6.93 (d, *J* = 5.8 Hz, 4H), 7.76 (d, *J* = 5.8 Hz, 4H).

Synthesis of the hydrazone from 4,4'-didodecyloxybenzophenone. A mixture of 4,4'-didodecyloxybenzophenone (20.6 g) and hydrazine monohydrate (20 mL) in 150 mL of pentanol were heated at reflux for 24 hours. After cooling to room temperature, a white solid precipitated which is collected by vacuum filtration, washed with 20mL of cold ethanol, and air dried (19.4 g, 92%) ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 0.90 (m, 6H), 1.25-1.50 (m, *J* = 3.0 Hz, 36H), 1.83 (m, 4H), 4.04 (t, *J* = 6.5 Hz, 4H), 6.78 (d, *J* = 5.7 Hz, 2H), 6.98 (d, *J* = 5.4 Hz, 2H), 7.17 (d, *J* = 5.4 Hz, 2H), 7.35 (d, *J* = 5.7 Hz, 2H).

Diaryldiazomethane 5b. To a mixture of compound 4,4'-didodecyloxybenzophenone hydrazone (10 g), yellow HgO (20 g) in 150 mL of THF, 0.5 mL saturated sodium hydroxide in ethanol was added. After stirring overnight the solution turned a dark purple color and the solution was filtered. The resulting solution was stored at –20ºC for future usage.

Synthesis of olefin 6b. To 1.0 g of thioketone **4** dissolved in 100 mL of THF was added dropwise a solution of compound the diaryldiazomethane **5b** until the green color disappeared. The solution was stirred for 1 hr. The thioepoxide (1.79 g, 61%) was obtained by column chromatography (SiO_2, 3:1 hexanes:CH_2Cl_2, Rf=0.20). ^{1}H-NMR (300 MHz, CD_2Cl_2) *d* (ppm): 1.01 (m, 6H), 1.38 (m, 36H), 1.70 (m, 4H), 3.79 (t, *J* = 6.6 Hz, 4H), 4.60 (d, *J* = 16.8 Hz, 1H), 4.87 (d, *J* = 16.8 Hz, 1H), 6.56 (d, *J* = 9.7 Hz, 4H), 7.27 (d, *J* = 9.7 Hz, 4H), 7.50 (m, 4H), 7.77 (d, *J* = 7.9Hz, 2H), 7.89 (d, *J* = 7.9Hz, 2H), 7.92 (s, 2H), 7.99 (s, 2H); ^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 158.0, 136.7, 135.4, 133.9, 132.9, 132.3, 130.40, 128.3, 127.9, 127.1, 126.3, 125.7, 125.1, 113.6, 71.6, 68.3, 64.5, 38.6, 32.6, 30.3, 30.20, 30.16, 30.0, 27.7, 26.5, 23.4, 14.6. A mixture of this thioepoxide (895mg, 1.06 mmol) and triphenylphosphine (334 mg, 1.27 mmol) in 100 mL of *p*-xylene were heated at reflux for 12 hours. The solvent was removed under reduced pressure. Pure **6b** (800 mg, 93%) was obtained after column chromatography (SiO_2, 4:1 hexanes:CH_2Cl_2, Rf=0.20) as a white solid. ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 1.01 (m, 6H), 1.45 (m, 36H), 1.80 (m, 4H), 3.95 (t, *J* = 6.6 Hz, 4H), 4.39 (s, 2H), 6.85 (d, *J* = 6.8 Hz, 4H), 7.30-7.50 (m, 8H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.69 (s, 2H), 7.82 (d, *J* = 7.0 Hz, 4H); ^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 156.0, 141.7, 136.9. 136.8, 135.5, 135.0, 132.4, 132.2, 131.1, 128.2, 128.0, 127.2, 126.1, 125.5, 124.5, 114.5, 68.5, 38.6, 32.7, 30.4, 30.3, 30.1, 30.0, 26.7, 23.4, 14.7; HRMS (FAB+) cald. for $C_{59}H_{72}O_2$: 812.5532, found: 812.5514.

Synthesis of ketone 7b. Olefin **6b** (250 mg, 0.31 mmol) was dissolved in 500 mL of acetone and added $KMnO_4$ (194 mg, 1.23 mmol). The mixture was stirred at room temperature for 2 hours. The solution was filtered using vacuum filtration and the solids washed with 200 mL of CH_2Cl_2. The organic washings were back washed with 800 mL of water. The aqueous washings were extracted with CH_2Cl_2 (3 x 100 mL). After removal of the volatiles, the ketone (150 mg, 59%) was purified using column chromatography (SiO_2, 40% CH_2Cl_2 in hexanes, Rf = 0.20). The first fraction from the column was primarily starting material (20% CH_2Cl_2 in hexanes, Rf=0.20). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 0.93 (m, 6H), 1.32-1.50 (m, 36H), 1.75 (m, 4H), 3.91 (t, *J* = 6.6 Hz, 4H), 6.80 (dd, *J* = 6.8 Hz, 2.0Hz, 4H), 7.18 (dd, *J* = 6.8 Hz, 2.0Hz, 4H), 7.51 (m, 6H), 7.73 (s, 2H), 8.0 (m, 2H), 8.68 (s, 2H); ^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 186.0, 158.0, 145.5, 135.9, 135.5, 134.5, 132.1, 131.8, 130.7, 130.6, 129.5, 129.3, 128.6, 128.3, 127.7, 126.9, 114.8, 68.5, 32.6, 30.3, 30.2, 30.0, 29.8, 26.6, 23.4, 14.6; HRMS (FAB+) cald. for $C_{59}H_{70}O_3$: 826.5325, found: 826.5369.

Synthesis of thioketone 8b. To **7b** (147.4 mg, 0.178 mmol) in 80 mL toluene was added Lawesson's reagent (43.3 mg, 0.107 mmol). The solution was heated for 30 minutes at 80 ºC, and the reaction was monitored by TLC. After cooling to room temperature, the

solution was filtered through a plug of silica gel and washed with 4:1 hexanes:CH_2Cl_2. The solvent was removed under reduced pressure to yield analytically pure compound **8b** (150 mg, 98%). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 0.94 (m, 6H), 1.2-1.5 (m, 36H), 1.75 (m, 4H), 3.91 (t, *J* = 6.6 Hz, 4H), 6.77 (d, *J* = 8.6 Hz, 4H), 7.13 (d, *J* = 8.6 Hz, 4H), 7.51 (m, 6H), 7.62 (s, 2H), 8.0 (d, *J* = 8.0 Hz, 2H), 8.82 (s, 2H); ^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 158.0, 145.0, 140.9, 135.5, 134.2, 132.4, 132.0, 131.7, 131.1, 130.8, 129.8, 128.5, 128.4, 128.3, 128.2, 126.9, 114.8, 113.9, 68.5, 32.6, 30.3, 30.3, 30.0, 29.8, 26.6, 26.2, 23.4, 14.6; HRMS (FAB $[M+H]^+$) cald. for $C_{59}H_{70}O_2S$: 842.5097, found: 843.5163.

Synthesis of bisolefin 2c. A THF solution of the diaryldiazomethane (**5b**) was added to thioketone **8b** (700 mg, 0.83 mmol) in 350 mL of THF until the green color disappeared. The solution was stirred for an additional hour. The THF was removed under reduced pressure. The thioepoxide was obtained (928 mg, 0.67 mmol, 81%) was obtained by column chromatography (SiO_2, 3:1 hexanes:CH_2Cl_2, R_f = 0.2). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 0.93 (m, 12H), 1.30-1.50 (m, 72H), 1.68 (t, *J* = 6.6 Hz, 4H), 1.79 (t, *J* = 6.6 Hz, 4H), 3.81 (m, 4H), 3.95 (m, 4H), 6.57 (d, *J* = 8.8 Hz, 4H), 6.78 (d, *J* = 6.8 Hz, 4H), 7.26 (d, *J* = 8.7 Hz, 4H), 7.43 (m, 8H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.78 (s, 2H), 8.02 (s, 2H); ^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 158.2, 140.6, 137.6, 135.33, 134.5, 133.1, 132.2, 131.9, 131.8, 127.93, 127.88, 127.84, 127.75, 126.17, 126.14, 114.1, 113.3, 70.7, 68.4, 68.3, 65.5, 32.6, 30.3, 30.2, 30.1, 30.0, 29.95, 29.9, 26.7, 26.6, 23.4, 14.6; HRMS (FAB+) cald. for $C_{96}H_{128}O_4S$: 1376.9533, found: 1376.9563. This thioepoxide (928 mg, 1.45 mmol) and triphenylphosphine (456 mg, 1.74 mmol) were mixed in 130 mL of *p*-xylene and heated under reflux for 12 hours. The solvent was removed under reduced pressure. Pure compound **2c** (859 mg, 98%) was obtained by column chromatography (4:1 CH_2Cl_2:hexanes, Rf = 0.2). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 0.94 (m, 12H), 1.33 (m, 64H), 1.46 (m, 8H), 1.78 (m, 8H), 3.95 (t, *J* = 6.6 Hz, 8H), 6.86 (d, *J* = 8.7 Hz, 8H), 7.28 (dd, *J* = 6.3, 3.2Hz, 4H), 7.39 (d, *J* = 8.6 Hz, 8H), 7.48 (dd, *J* = 6.2, 3.2 Hz, 4H), 7.61 (s, 4H); ^{13}C-NMR (100 MHz, CD_2Cl_2) *d* (ppm): 158.1, 140.7, 163.9, 135.3, 135.2, 131.7, 131.1, 127.8, 127.0, 125.8, 114.5, 68.5, 32.56, 30.27, 30.24, 30.04, 29.99, 29.91, 26.7, 23.4, 14.6; HRMS (FAB+) cald. for $C_{96}H_{128}O_4$: 1344.9813, found: 1344.9768.

Synthesis of contorted hexabenzocoronene 1c. The photolysis setup has been previously described (Liu, L; Yang B; Katz, T. J; Poindexter, M. K. *J. Org. Chem.* **1991,** 56, 3769-3775). A mixture of compound **2c** (394 mg, 0.29 mmol), iodine (340 mg, 1.33 mmol), propylene oxide (20mL) in 350 mL of anhydrous benzene were irradiated with UV light (Hanovia 450 W high-pressure quartz Hg-vapor lamp) in an immersion well. Argon was bubbled through the reaction vessel during the photolysis. To maintain a constant temperature, the whole apparatus is submerged in a large bath of circulating water. After 12 hours of irradiation, the solvent is removed under reduced pressure, and a yellow powder precipitates. Compound **1c** (329 mg, 85%) is isolated by column chromatography (SiO_2, 4:1 hexanes:CH_2Cl_2, Rf=0.25). ^{1}H-NMR (400 MHz, C_6D_6) *d* (ppm): 0.90 (m, 12H), 1.33 (m, 64H), 1.48 (m, 8H), 1.80 (m, 8H), 4.05 (m, 8H), 7.42 (dd, *J* = 9.1, 2.4Hz, 4H), 7.56 (dd, *J* = 6.3, 3.3 Hz, 8H), 8.87 (s, 4H), 9.16 (d, *J* = 9.0 Hz, 4H), 9.38 (d, *J* = 6.2, 3.4 Hz, 4H); ^{13}C-NMR (100 MHz, C_6D_6) *d* (ppm): 158.1, 132.0, 131.2,

130.6, 128.6, 128.1, 127.9, 127.7, 127.3, 126.0, 125.3, 122.8, 119.8, 116.9, 111.4, 68.7, 32.5, 30.3, 30.2, 30.1, 30.0 ,26.8, 23.3, 14.5; HRMS (TOF-MALDI M+6H$^+$) cald. for $C_{96}H_{120}O_4$: 1336.9187, found: 1342.5.

Synthesis of bisolefin 2b. To thioketone **8a** (327 mg, 0.69 mmol) in 350 mL of THF was added dropwise a THF solution of the diaryldiazomethane **5b** until the green color disappeared. The reaction was stirred for an additional hour. The THF was removed under reduced pressure. The thioepoxide (600 mg, 0.60 mmol, 88%) was obtained by column chromatography (SiO_2, 3:1 hexanes:CH_2Cl_2, Rf = 0.2). ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 1.04 (m, 6H), 1.41 (m, 36H), 1.78 (m, 4H), 3.90 (t, *J* = 6.6 Hz, 4H), 6.68 (d, *J* = 8.0 Hz, 4H), 7.30-7.59 (m, 20H), 7.77 (d, *J* = 10 Hz, 2H), 7.81 (s, 2H), 8.09 (s, 2H). To this thioepoxide (600 mg, 0.60 mmol) in 100 mL of *p*-xylene was added triphenylphosphine (189 mg, 0.72 mmol). The mixture was heated at reflux for 10 hours. The solvent was removed under reduced pressure. Pure compound **2b** (510 mg, 0.52 mmol, 87%) was obtained by column chromatography (4:1 CH_2Cl_2:hexanes, Rf = 0.2) ^{1}H-NMR (400 MHz, CD_2Cl_2) *d* (ppm): 1.00 (m, 6H), 1.38-1.61 (m, 36H), 1.83 (m, 4H), 4.00 (t, *J* = 6.6 Hz, 4H), 6.92 (d, *J* = 8.7Hz, 4H) , 7.26-7.55 (m, 18H), 7.60 (m, 6H), 7.65 (s, 2H).

Synthesis of contorted hexabenzocoronene 1b. The photolysis setup has been previously described (Liu, L; Yang B; Katz, T. J; Poindexter, M. K. *J. Org. Chem.* **1991,** 56, 3769-3775). A mixture of compound **2b** (510 mg, 0.52 mmol), iodine (602 mg, 2.35 mmol), propylene oxide (10mL) in 350 mL of anhydrous benzene were irradiated with UV light (Hanovia 450 W high-pressure quartz Hg-vapor lamp) in an immersion well. Argon was bubbled through the reaction vessel during the photolysis. To maintain a constant temperature, the whole apparatus is submerged in a large bath of circulating water. After 12 hours of irradiation, the solvent is removed under reduced pressure. and a yellow powder precipitates. Compound **1b** (440 mg, 87%) is isolated by column chromatography (SiO_2, 4:1 hexanes:CH_2Cl_2, Rf=0.20). ^{1}H-NMR (400 MHz, C_6D_6) *d* (ppm): 1.00 (t, *J* = 6.9 Hz, 6H), 1.39 (m, 32H), 1.58 (m, 4H), 1.89 (m, 4H), 4.00 (m, 2H), 4.20 (m, 2H), 6.92 (dd, *J* = 9.0, 2.5 Hz, 2H) , 7.56-7.70 (m, 8H), 8.97 (d, *J* = 1.7 Hz, 2H), 9.20-9.37 (m, 8H), 9.48 (m, 2H); HRMS (FAB+) cald. for $C_{72}H_{72}O_2$: 968.5532, found: 968.5589.

II. Device Fabrication and Testing

Wafer cleaning and OTS functionalization. Electrical measurements were performed on a highly n-type doped (<0.005 Ωcm) Si wafer, used as a shared common gate, for the contorted HBC semiconductor thin films. A 300 nm thick, thermally grown SiO_2 served as the gate dielectric. Two surface treatments of the SiO_2 were performed on the dielectric surface before spin coating of the semiconductor film: (a) exposure to an oxidative plasma, and (b) a 10 min sonication in acetone, followed by a 70:30 H_2SO_4/H_2O_2 (piranha) etch for 1 hour at 100ºC, then a 1:1:5 $NH_3 \cdot H_2O/H_2O_2$/DI H_2O wash for 20 min at 70ºC, and finally a soak in a 25 μM solution of octadecyltrichlorosilane (OTS) in toluene at 28ºC for 1 hour. The dielectric surface was characterized using contact angle measurements, which were <5º after cleaning and

>105º after OTS monolayer formation. The contact angle of the OTS monolayer confirms a tight-packed hydrophobic surface.

Transistor fabrication and measurements. Top-contact geometry was used in the transistor devices. An n-doped Si wafer was used as substrate, with an indium contact that functioned as the gate and an oxide layer as the gate dielectric. The OTS treated silicon oxide layer of 300 nm has a capacitance per unit area of 11.3 nF/cm^2. Films were deposited by spin casting from 1,2-dichloroethane (concentration 1 mg/ml, 1200 rpm, 20 seconds). The drain and source electrodes were vacuum-deposited through a shadow mask, and the resulting semiconducting channels were measured with an optical microscope and are 75 μm long and 2 mm wide. The thin-film transistor characterization was carried out at room temperature in the ambient atmosphere using an Agilent 4155C semiconductor characterization system and a Karl Suss (PM5) manual probestation.

III. Liquid Crystal Analysis

Polarized Light Microscopy. Polarized light microscopy was performed on a Leica DMLP polarized light microscope with a 10X, 20X, or 40X objective, and an Optronics MagnaFire Model S99802 digital camera system and power supply. Digital images where collected and analyzed with Image-Pro Express software version 4.0 by Media Cybernetics. Samples were placed between a cover slip and glass slide. Photographic images were captured as the samples were cooled from their clearing temperature. The temperature was varied with a Linkam TMS 350E heating and cooling stage, with a Linkam TMS 94 heat controller and a Linkam LNP cooling system.

Capillary Tube X-ray Diffraction. The samples were loaded into Lindemann capillary tubes 1 mm in diameter. They were heated in a thermostatically controlled furnace equipped with Kapton windows. Samples were rotated around the long axis of the capillary to average out any effects of preferential orientation. The X-ray diffraction measurements were preformed on an Inel CPS 120 diffractometer using Ni filtered Cu Kα X-rays. The instrument was calibrated using a Y_2O_3/Silver Behenate mixture.

Differential Scanning Calorimetry. DSC was performed on a Perkin-Elmer Pyris 1 Calorimeter. The samples were weighed into aluminum calorimetry pans. The pans were then sealed and analyzed. The scan rate was 5°C/min.