Supporting Information for:

Scalable, Divergent Synthesis of a High Aspect Ratio Carbon Nanobelt

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General Details

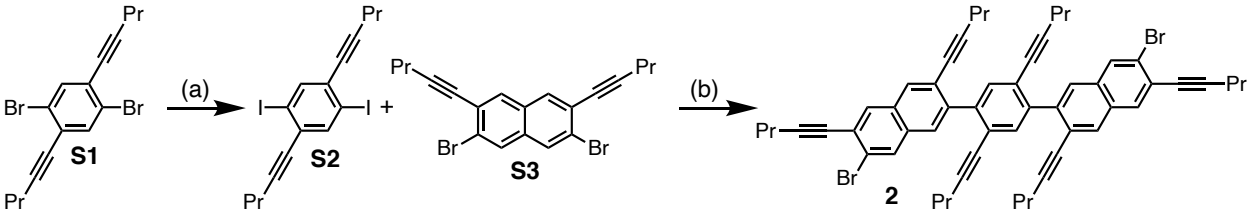
Unless otherwise stated, all manipulations were conducted in dry solvents under an inert atmosphere of nitrogen, using either standard Schlenk techniques or a glovebox. Pentane, toluene, tetrahydrofuran (THF), diethyl ether, dimethylformamide (DMF), and dichloromethane (CH_2Cl_2) were dried using a JC Meyers Phoenix SDS solvent purification system. Benzene-d_6 and $CDCl_3$ were freed from oxygen with vigorous nitrogen bubbling for 30 minutes, and then dried for at least 48 h over 3 Å molecular sieves (5% by mass). CD_2Cl_2 was freed from oxygen via freeze-pump-thaw three times, and then dried for at least 48 h over 3 Å molecular sieves (5% by mass). All reaction solvents were stored over 3 Å molecular sieves. **S1** and **S3**,[1] and $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$[2] were synthesized by literature procedures. All other reagents were purchased from commercial suppliers and used as received. *N*-Butyllithium and *tert*-butyllithium* were titrated by ^{1}H-NMR before use.[3] "Room temperature" or "RT" refers to ~22 ˚C. Reaction temperatures represent the oil bath temperature unless otherwise stated.

Mass spectrometry of all compounds was performed *via* MALDI at the Mass Spectrometry Facility at UC Riverside, using α-cyano-4- hydroxycinnamic acid as the matrix. Column chromatography was carried out using Fisher Chemical 40–63μm, 230–400 mesh silica gel. NMR (^{1}H and ^{13}C) spectra were obtained at room temperature on Bruker AV-600, AV-500, and AVB-400 spectrometers. Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks for ^{1}H-NMR spectra (δ = 7.26 ppm for $CDCl_3$, = 5.32 ppm for CD_2Cl_2 and δ = 7.16 for C_6D_6) and ^{13}C-NMR spectra (δ = 77.16 ppm for $CDCl_3$, δ = 128.06 for C_6D_6).

*CAUTION: *tert*-butyllithium is highly pyrophoric and should be handled with extreme care.

Synthetic procedures and basic characterization data

Scheme S1. Synthesis of compound 2

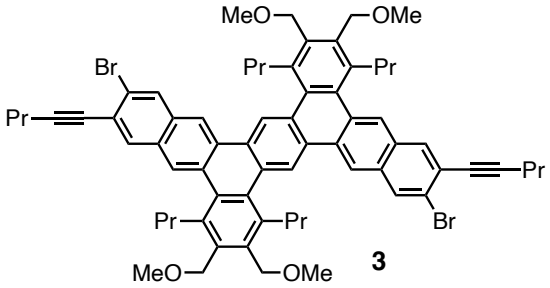


Reagents and conditions: (a) i) tBuLi (4.0 eq), THF, -78 ˚C, ii) I_2, -78 ˚C to 23 ˚C, 85%; (b) i) nBuLi (2.0 eq), THF, -78 ˚C, ii) $Pd(PPh_3)_4$, -78 ˚C to 23 ˚C, 53%

1,4-diiodo-2,5-di-1-pentyn-1-yl-benzene (S2). A 250 mL Schlenk flask was charged with **S1** (4.00 g, 10.9 mmol, 1 equiv) and tetrahydrofuran (80 mL) and the solution was cooled to –78 °C with a CO_2(s)/acetone bath. To this solution was added *tert*-butyllithium (1.68 M in hexanes, 25.6 mL, 43.5 mmol, 4.00 equiv) by syringe over 20 min and the resulting mixture was stirred for a further 10 min at –78 °C. The flask was then transferred to an ice water bath and the mixture was warmed to 0 ˚C over 1 h. Iodine (13.8 g, 54.4 mmol, 5.00 equiv) was then added against a flow of N_2, the ice bath was removed, and the reaction mixture was allowed to warm to RT with stirring over 2 h. The solution was then exposed to air and diluted with aqueous ammonium chloride (80 mL). The crude product was extracted with hexanes (3 x 60 mL), washed with sodium thiosulfate (3x 60 mL), dried over Mg_2SO_4, and solvents were removed by rotary evaporation. The crude solid was then dissolved in hexanes and passed through a short plug of silica gel (20 g) with hexanes. The solvent was removed by rotary evaporation, and the resulting pale yellow crystalline solid was recrystallized from ethanol to afford **S2** (4.27 g, 85%) as colorless crystals. ^{1}H NMR (chloroform-*d*, 600 MHz): δ = ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 2H), 2.45-2.43 (m, 4H), 1.69-1.53 (m, 4H), 1.09-1.07 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.43, 131.12, 99.62, 97.35, 81.77, 22.03, 21.77, 13.82. MS-MALDI (m/z): [M]+ calcd. for $C_{16}H_{16}I_2$, 461.9341; found, 461.89.

Hexayne 2. A 250 mL Schlenk flask was charged with **S3** (6.60 g, 15.7 mmol, 2.50 equiv) and tetrahydrofuran (100 mL) and the solution was cooled to –78 °C with a CO_2(s)/acetone bath. To this solution was added *n*-butyllithium (2.12 M in hexanes, 7.10 mL, 15.1 mmol, 2.40 equiv) by syringe over 20 min and the resulting mixture was stirred for a further 10 min at –78 °C. To this mixture was added $ZnCl_2$ (1.05 M in THF, 17.2 mL, 18.1 mmol, 2.9 equiv) by syringe over 5 min, and subsequently the flask was removed from the cold bath and warmed to RT over 1 h. At this time **S2** (2.90 g, 6.28 mmol, 1 equiv), $Pd_2(dba)_3$ (230 mg, 0.251 mmol, 0.04 equiv), and tris(*o*-tolyl)phosphine (153 mg, 0.502 mmol, 0.08 equiv) were added against a flow of N_2, the Schlenk flask was sealed, and the mixture was stirred at RT for 18 h. The solution was then exposed to air and diluted with aqueous ammonium chloride (80 mL). The crude product was extracted with CH_2Cl_2 (3x 60 mL), dried over Mg_2SO_4, and solvents were removed by rotary evaporation. The crude product was purified by column chromatography (1:5 CH_2Cl_2:hexanes) and solvent was removed by rotary evaporation. The product was then dissolved in CH_2Cl_2 (20 mL), precipitated from the solution by addition of MeOH (40 mL), and collected via vacuum filtration to afford **2** (3.31 g, 53%) as an off-white powder. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02

(s, 2H), 7.90 (s, 4H), 7.74 (s, 2H), 7.61 (s, 2H), 2.52-2.50 (m, 4H), 2.30-2.27 (m, 4H), 2.14-2.11 (m, 4H), 1.75-1.69 (m, 4H), 1.54-1.48 (m, 4H), 1.33-1.27 (m, 4H), 1.15-1.12 (m, 6H), 0.92-0.88 (m, 6H), 0.72-0.70 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.35, 140.79, 134.05, 132.08, 132.04, 131.06, 130.93, 130.81, 128.01, 123.98, 123.03, 122.95, 122.47, 95.68, 95.05, 94.80, 80.07, 79.95, 79.85, 22.26, 22.07, 22.02, 21.84, 21.77, 21.56, 13.80, 13.63, 13.33. MS-MALDI (m/z): [M]+ calcd. for $C_{56}H_{52}Br_2$, 882.2436; found, 882.12.



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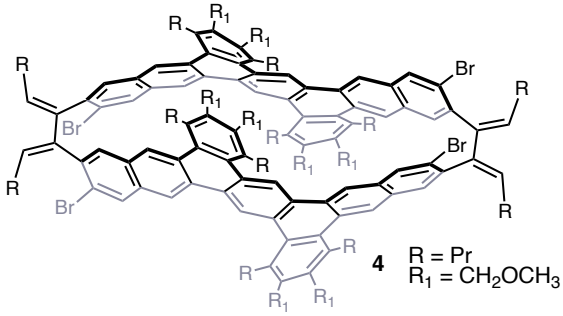
Monomer 3. To a solution of $[Ir(COD)Cl]_2$ (54.7 mg, 0.0814 mmol, 0.040 equiv) in benzene (4 mL) was added (dropwise over ~1 min) a solution of dppe (64.8 mg, 0.163 mmol, 0.080 equiv) in benzene (2 mL). This mixture was immediately added to a flask containing a solution of hexayne **2** (1.80 g, 2.03 mmol, 1.0 equiv) and 1,4-dimethoxy-2-butyne (0.929 g, 8.14 mmol, 4 equiv) in benzene (24 mL). The flask was sealed with a Teflon stopper and the stirred reaction mixture was heated at 80 °C for 2 h. The mixture was allowed to cool to RT and concentrated to dryness via rotary evaporation. The dark red solid was then suspended in boiling benzene (10 mL) and hexanes (50 mL) was added to the hot, stirred solution to produce an immediate precipitate. The mixture was allowed to cool to RT, then the precipitate was collected via filtration, washed with hexanes (10 mL), and dried under high vacuum to afford pure **3** (1.83 g, 81%) as a light pink solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.05 (s, 2H), 8.70 (s, 2H), 8.42 (s, 2H), 8.26 (s, 2H), 8.04 (s, 2H), 4.81 (s, 4H), 4.78 (s, 4H), 3.64 (s, 6H), 3.59 (s, 6H), 3.57 (m, 4H), 3.40-3.37 (m, 4H), 2.55-2.53 (m, 4H), 2.07- 2.03 (4H), 1.82-1.76 (m, 4H), 1.75-1.72 (m, 4H), 1.17-1.12 (m, 12H), 0.97-0.95 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.63, 136.46, 136.35, 136.31, 134.36, 134.19, 133.06, 131.80, 131.67, 131.17, 131.02, 130.61, 130.33, 130.15, 127.83, 124.94, 123.47, 122.78, 121.12, 95.72, 80.07, 69.15, 69.06, 59.08, 58.97, 34.97, 34.73, 26.14, 25.99, 22.29, 21.90, 15.00, 14.71, 13.83. MS-MALDI (m/z): [M]+ calcd. for $C_{68}H_{72}Br_2O_4$, 1110.3797; found, 1110.36.



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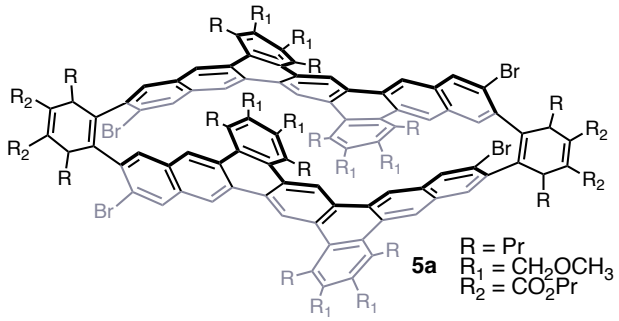
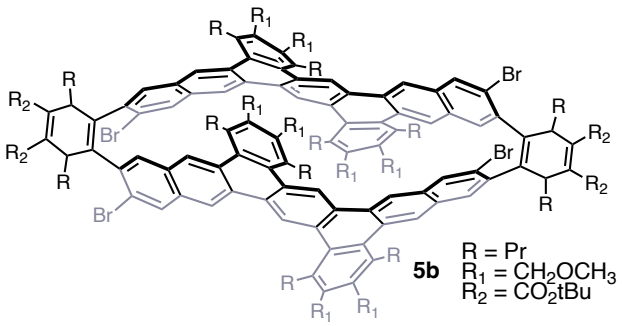
Macrocycle 4. To a 500 mL flask containing a vigorously stirred solution of **3** (1.75 g, 1.57 mmol, 1 equiv) in toluene (70 mL) was added a solution of $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (1.04 g, 2.20 mmol, 1.4 equiv) in toluene (35 mL) dropwise over 20 min.* The stirred reaction mixture was then cooled to -78 ˚C in a dry ice/acetone bath, and HCl (2 M in Et_2O, 3.30 mL, 4.2 equiv)

was added dropwise over 5 min. The mixture was allowed to stir for 5 min, then removed from the cold bath and warmed to RT over 40 min. The flask was opened to air and the product was precipitated by the addition of 200 mL MeOH. The precipitate was collected via vacuum filtration, washed with MeOH (3x10 mL) and dried under high vacuum. The crude product was then recrystallized from boiling *o*-dichlorobenzene (10 mL) to afford **4** (1.05 g, 60%) as a 90% pure beige solid that was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 4H), 8.12 (s, 4H), 8.01 (s, 4H), 7.83 (s, 4H), 7.30 (s, 4H), 6.51- 6.47 (m, 4H), 4.65 (s, 16H), 3.64 (s, 12H), 3.62 (s, 12H), 3.04 (b, 8H), 2.90 (b, 8H), 2.72 (b, 8H), 2.30- 2.24 (m, 8H), 2.14- 2.08 (m, 8H), 2.05-1.86 (b, 8H), 1.85-1.68 (b, 8H), 1.64-1.58 (m, 8H), 1.11-1.08 (m, 12H), 0.98-0.94 (m, 24H). MS-MALDI (m/z): [M]+ calcd. for $C_{136}H_{148}Br_4O_8$, 2224.7908 ; found, 2224.93.

*Note: On small scale (≤100 mg) dropwise addition is unnecessary, but as the reaction is scaled it becomes necessary to maintain high yields.

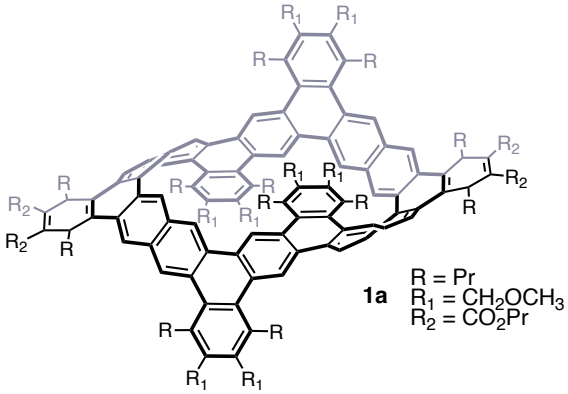


Macrocycle 5a. A 125 mL flask was charged with **4** (600 mg, 0.258 mmol, 1.00 equiv), dipropylacetylenedicarboxylate (255 mg, 1.29 mmol, 5 equiv), and toluene (40 mL) and sealed with a Teflon stopper. The reaction mixture was heated to 110 ˚C for 16 h, cooled to RT, and solvent was removed by rotary evaporation. The crude solid was triturated with hexanes (20 mL), and the solid was collected by vacuum filtration and washed with hexanes (3x10 mL) to afford **5a** (606 mg, 86%) as a pale yellow-green solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (s, 4H), 8.21 (s, 4H), 8.15 (s, 4H), 7.88 (s, 4H), 7.50 (s, 4H), 4.70-4.63 (20H), 4.23- 4.21 (m, 8H), 3.94-3.92 (4H), 3.56 (s, 12H), 3.55 (s, 12H), 3.50, 3.23-3.18 (m, 8H), 3.02- 2.95 (m, 8H), 1.92-1.90 (m, 8H), 1.87-1.81 (m, 8H), 1.79-1.73 (m, 8H), 1.70-1.58 (b, 8H), 1.55-1.51 (m, 8H), 1.40-1.36 (m, 8H), 1.06-1.04 (m, 12H), 1.02-1.00 (m, 12H) 0.89-0.86 (m, 12H), 0.75-0.60 (b, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.23, 139.43, 137.74, 137.30, 136.88, 136.35, 133.63, 133.17, 132.05, 131.64, 131.30, 131.17, 130.85, 130.06, 128.58, 126.61, 124.29, 120.92, 69.13, 66.99, 59.01, 58.95, 42.34, 36.89, 34.11, 33.88, 26.29, 25.46, 22.09, 21.22, 14.79, 14.49, 14.38, 10.73. MS-MALDI (m/z): [M]+ calcd. for $C_{156}H_{176}Br_4O_{16}$, 2620.9692; found, 2620.57.



Macrocycle 5b. A 125 mL flask was charged with **4** (600 mg, 0.258 mmol, 1.00 equiv), ditertbutylacetylenedicarboxylate (584 mg, 2.58 mmol, 10 equiv), and toluene (40 mL) and sealed with a Teflon stopper. The reaction mixture was heated to 110 ˚C for 72 h, cooled to RT, and solvent was removed by rotary evaporation. The crude solid was triturated with hexanes (20 mL), and the solid was collected by vacuum filtration and washed with hexanes (3x10 mL) to afford **5b** (615 mg, 85%) as a pale yellow-green solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 4H), 8.20 (s, 4H), 8.14 (s, 4H), 7.87 (s, 4H), 7.49 (s, 4H), 4.70-4.62 (m, 20H), 3.84-3.82 (m, 4H), 3.56 (s, 12H), 3.55 (s, 12H), 3.29-3.12 (b, 8H), 3.07-2.87 (b, 8H), 1.97-1.77 (b, 24H), 1.83, 1.62, 1.57, 1.56, 1.53, 1.53, 1.50 (s, 36H), 1.06-1.04 (12H), 0.89-0.85 (m, 12H), 0.73-0.63 (12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.50, 139.88, 138.15, 137.31, 136.86, 136.78, 136.72, 133.62, 133.21, 131.97, 131.62, 131.23, 131.16, 130.79, 130.01, 128.73, 128.59, 126.62, 124.29, 121.10, 118.77, 69.13, 67.58, 59.00, 58.93, 42.64, 37.39, 34.13, 33.87, 28.25, 26.29, 25.4, 22.34, 21.40, 14.78, 14.58, 14.37. MS-MALDI (m/z): [M]+ calcd. for $C_{160}H_{184}Br_4O_{16}$, 2677.0318; found, 2677.01.

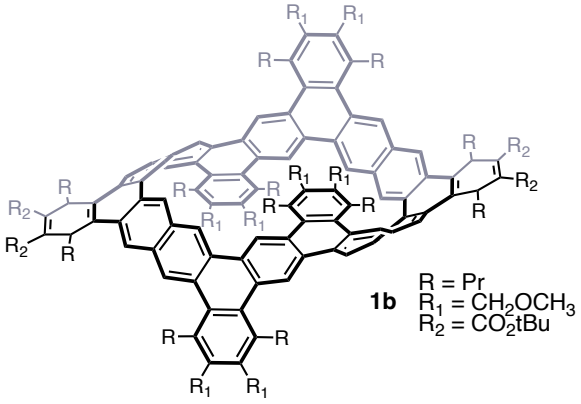
Note: the concentration of this reaction is extremely important for achieving reliable reaction times. This cycloaddition is fairly sluggish and **4** is only sparingly soluble in the reaction solvent. Thus, lower concentrations decrease reaction rate, but higher concentrations *also* slow the reaction because the reaction mixture becomes significantly heterogeneous.



CNB 1a. To a stirred suspension of $Ni(COD)_2$ (337 mg, 1.37 mmol, 6.00 equiv) in DMF (5 mL) was added a solution of 2,2'-bipyridine (214 mg, 1.37 mmol, 6.00 equiv) in DMF (5 mL) dropwise over 2 min, during which time the solution became deep purple. This solution was then transferred to a flask containing a stirred solution of **5a** (600 mg, 0.228 mmol, 1.00 equiv) in DMF (40 mL). The flask was sealed with a Teflon stopper, and the mixture was heated at 85 ˚C for 12 h. The reaction mixture was then exposed to air and the crude product precipitated with MeOH (100 mL). This suspension was filtered through celite and washed with MeOH (3x15

mL). The crude product was extracted from the celite with THF (75 mL) and solvent was removed by rotary evaporation. The crude product was then recrystallized from boiling toluene (15 mL) to afford **1a** (348 mg, 66%) as a bright yellow powder. Single crystals suitable for x-ray diffraction were grown via diffusion of hexamethyldisiloxane into a saturated solution of **1a** and *p*-terphenyl* in THF at -30 ˚C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.87 (s, 4H), 8.46 (s, 4H), 8.36 (s, 4H), 8.26 (s, 4H), 7.99 (s, 4H), 4.69-4.53 (m, 16H), 4.34-4.31 (m, 4H), 4.26-4.23 (m, 8H), 3.55 (s, 12H), 3.46 (s, 12H), 3.23-3.12 (m, 8H), 2.37-2.28 (m, 4H), 2.15-1.86 (m, 24H), 1.86-1.77 (m, 12H), 1.20-1.12 (m, 32H), 1.08-1.04 (m, 12H). MS-MALDI (m/z): [M]+ calcd. for $C_{156}H_{176}O_{16}$, 2305.2958; found, 2305.10.

*Note: *p*-terphenyl was initially screened during crystal growth in an attempt to observe host-guest complexation crystallographically. It was discovered that its presence was necessary for the growth of diffraction quality crystals, but due to significant disorder it could not be located within the crystal lattice.



CNB 1b. To a stirred suspension of $Ni(COD)_2$ (337 mg, 1.37 mmol, 6.00 equiv) in DMF (5 mL) was added a solution of 2,2'-bipyridine (214 mg, 1.37 mmol, 6.00 equiv) in DMF (5 mL) dropwise over 2 min, during which time the solution became deep purple. This solution was then transferred to a flask containing a stirred solution of **5b** (612 mg, 0.228 mmol, 1.00 equiv) in DMF (40 mL). The flask was sealed with a Teflon stopper, and the mixture was heated at 85 ˚C for 12 h. The reaction mixture was then exposed to air and the crude product precipitated with MeOH (100 mL). This suspension was filtered through celite and washed with MeOH (3x15 mL). The crude product was extracted from the celite with THF (75 mL) and solvent was removed by rotary evaporation. The crude product was then recrystallized from boiling toluene (15 mL) to afford **1b** (339 mg, 63%) as a bright yellow powder. Single crystals suitable for x-ray diffraction were grown via diffusion of hexamethyldisiloxane into a saturated solution of THF at -30 ˚C. ^{1}H NMR (600 MHz, C_6D_6) δ 8.97 (s, 4H), 8.66 (s, 4H), 8.44 (s, 4H), 8.42 (s, 4H), 8.34 (s, 4H), 4.78-4.72 (m, 8H), 4.61-4.58 (m, 12H), 3.59-3.52 (b, 8H), 3.35-3.31 (b, 8H), 3.29 (s, 12H), 3.24 (s, 12H), 2.53- 2.48 (b, 4H), 2.38-2.32 (b, 4H), 2.27-2.21 (b, 4H), 2.16-2.09 (b, 8H), 2.02-1.95 (b, 8H), 1.93-1.89 (b, 4H), 1.54 (s, 36H), 1.15-1.13 (m, 12H), 1.08-1.02 (m, 24H), 0.89-0.86 (m, 4H). ^{13}C NMR (151 MHz, C_6D_6) δ 167.62, 141.85, 137.88, 137.58, 137.15, 135.81, 135.10, 134.15, 132.27, 132.05, 131.95, 131.69, 131.60, 131.54, 130.09, 129.12, 125.55, 123.57, 122.69, 118.21, 81.32, 69.49, 69.10, 58.36, 58.20, 42.91, 41.65, 34.82, 34.45, 33.53, 28.17, 26.47, 23.32, 22.73, 14.94, 14.45, 14.36, 14.27. MS-MALDI (m/z): [M]+ calcd. for $C_{160}H_{184}O_{16}$, 2361.3854; found, 2361.32.

General Notes on the Sensitivity of Nanobelt 1

Nanobelts **1a** and **1b** are kept in a glovebox under N_2 for long term storage, but appear to be stable as solids under ambient conditions for at least a week. The nanobelts display varying degrees of sensitivity in several solvents even under N_2. Both **1a** and **1b** have a half-life of approximately 2 h in chlorinated solvents ($CDCl_3$ and CD_2Cl_2), and 6 h in THF. By contrast, they display a lack of measurable decomposition in aromatic solvents (C_6D_6 and toluene-*d8*) over 18 h, although **1a** is only very sparingly soluble. In all cases, the presence of O_2 appreciably increases the rate of decomposition. Thus, rapid manipulations of the nanobelt in solution may be carried out under ambient conditions (especially if care is taken to exclude light), but it is recommended that any prolonged manipulation of the nanobelts in solution be performed in an O_2-free environment.

Determination of bromide orientation of 4 via NMR

Assignment of **4** as the syn-bromide rotamer was made based on the observed symmetry of the zirconacycle intermediate (pictured below) by ^1H NMR. The anti-bromide isomer belongs to the D_2 point group, and consequently all four Cp rings should be chemically equivalent. Conversely, the syn-rotamer belongs to the lower symmetry C_{2h} point group and thus has two sets of chemically inequivalent Cp rings. The ^1H NMR spectrum of the intermediate zirconacycle *in-situ* clearly indicates the presence of two chemically inequivalent Cp rings, confirming that the dimer formed is the syn-rotamer. The underlying reason for the observed *syn*-selectivity of this transformation is unknown, but is under current investigation in this laboratory.

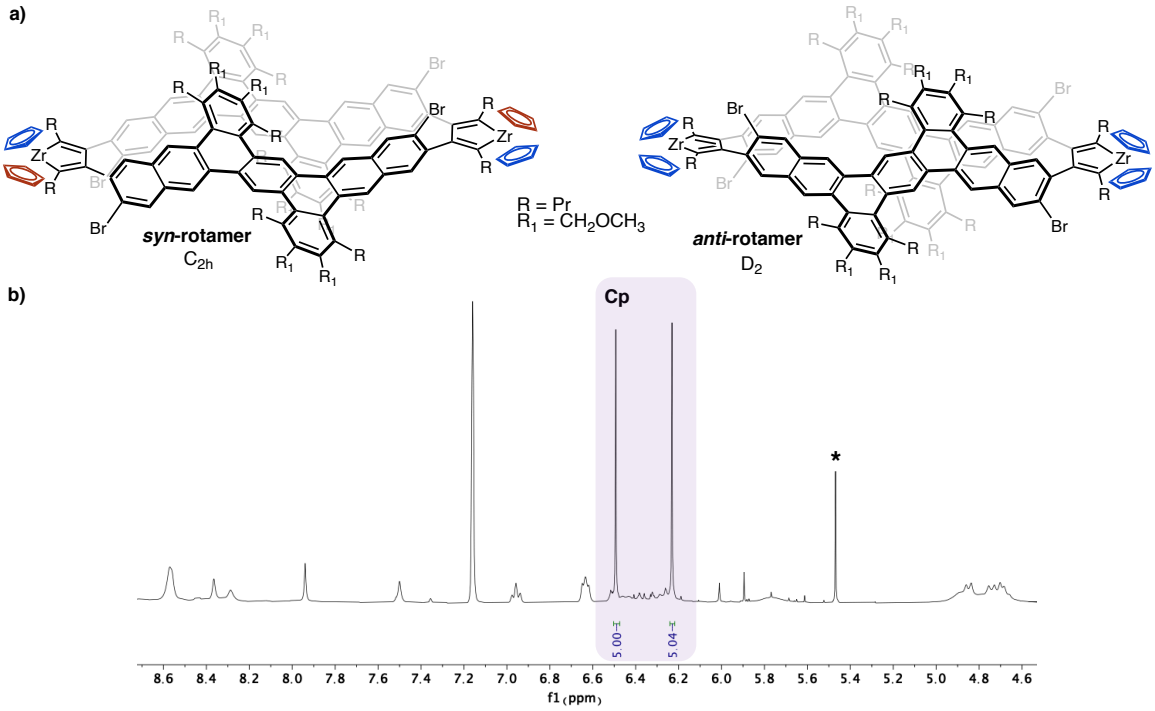


Figure S1. Evidence supporting formation of the *syn*-rotamer of macrocycle **4**. a) depictions of the *syn* and *anti*-rotamers of the zirconacycle intermediate of macrocycle **4**, with Cp rings color coded to highlight chemically equivalent sets; b) a partial ^{1}H NMR spectrum of the *in-situ* reaction mixture, with the region containing two Cp resonances highlighted. * denotes excess $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$.

^{1}H, ^{13}C{^{1}H}, and Selected 2D NMR spectra

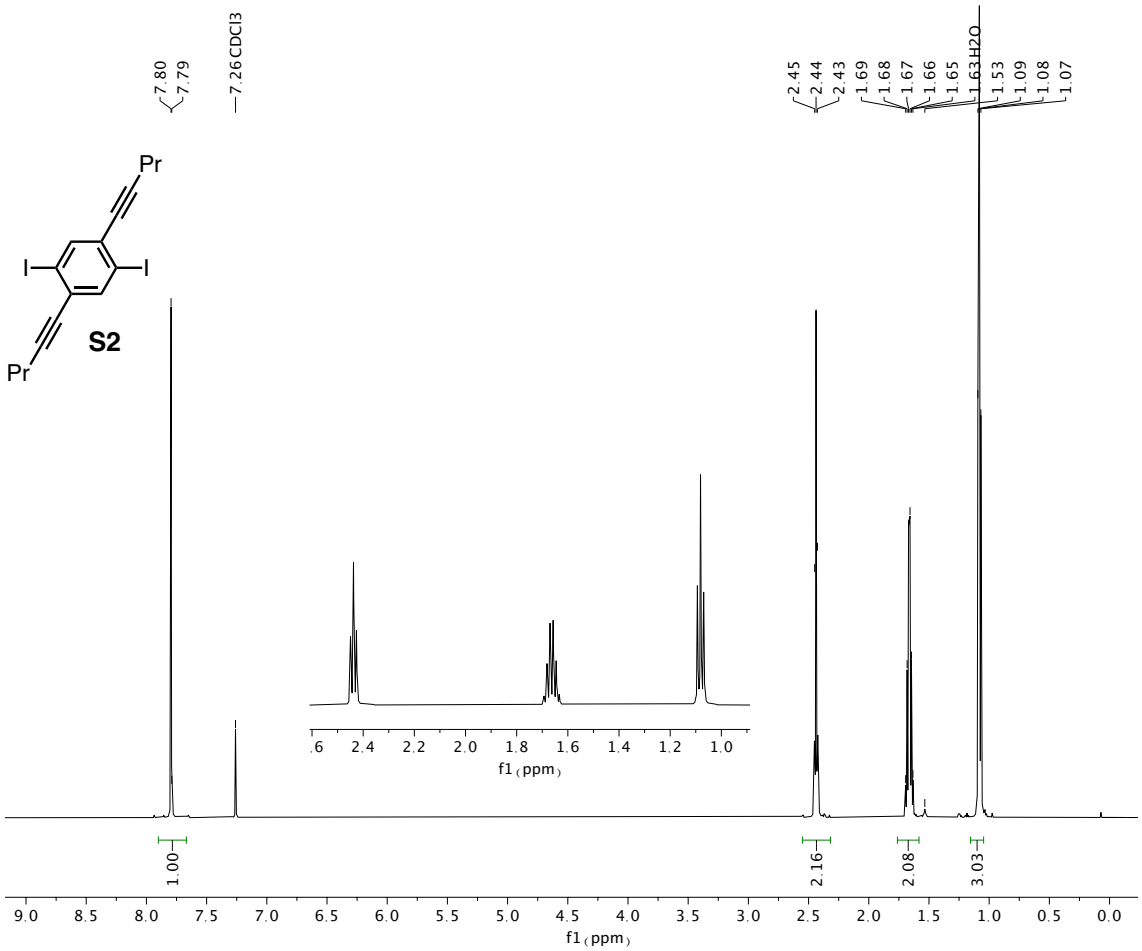


Figure S2. ^{1}H NMR Spectrum (500 MHz, chloroform-d) of **S2**.

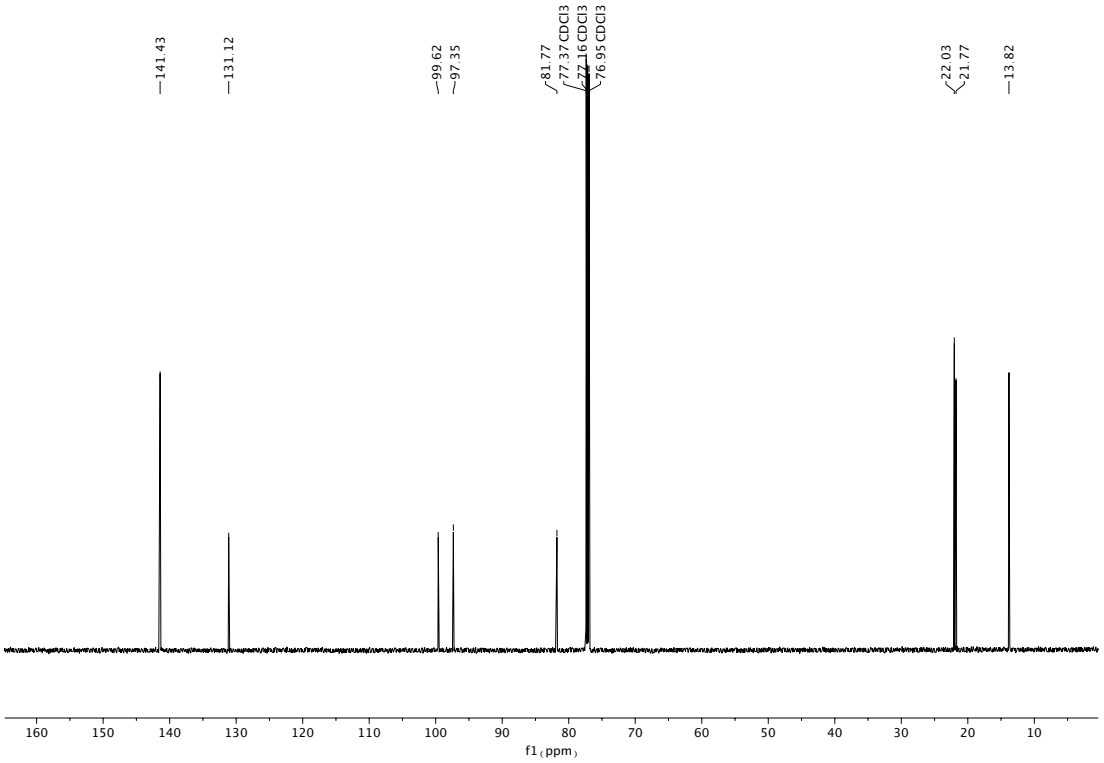


Figure S3. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-d) of **S2**.

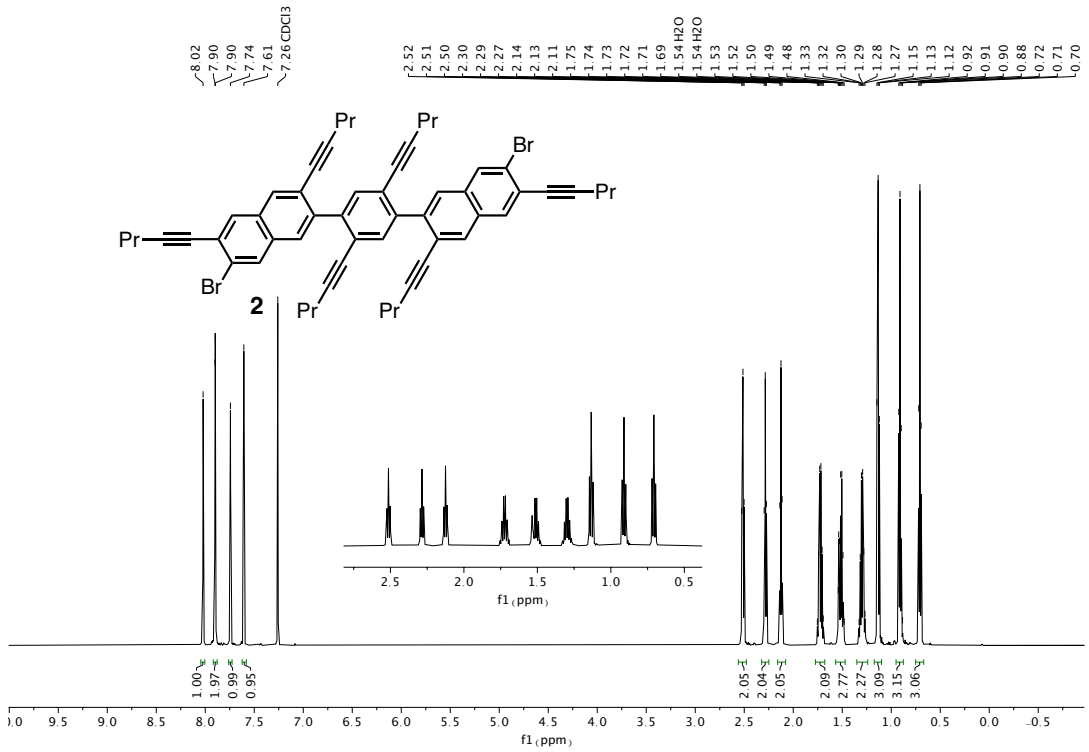


Figure S4. ^{1}H NMR Spectrum (500 MHz, chloroform-d) of **2**.

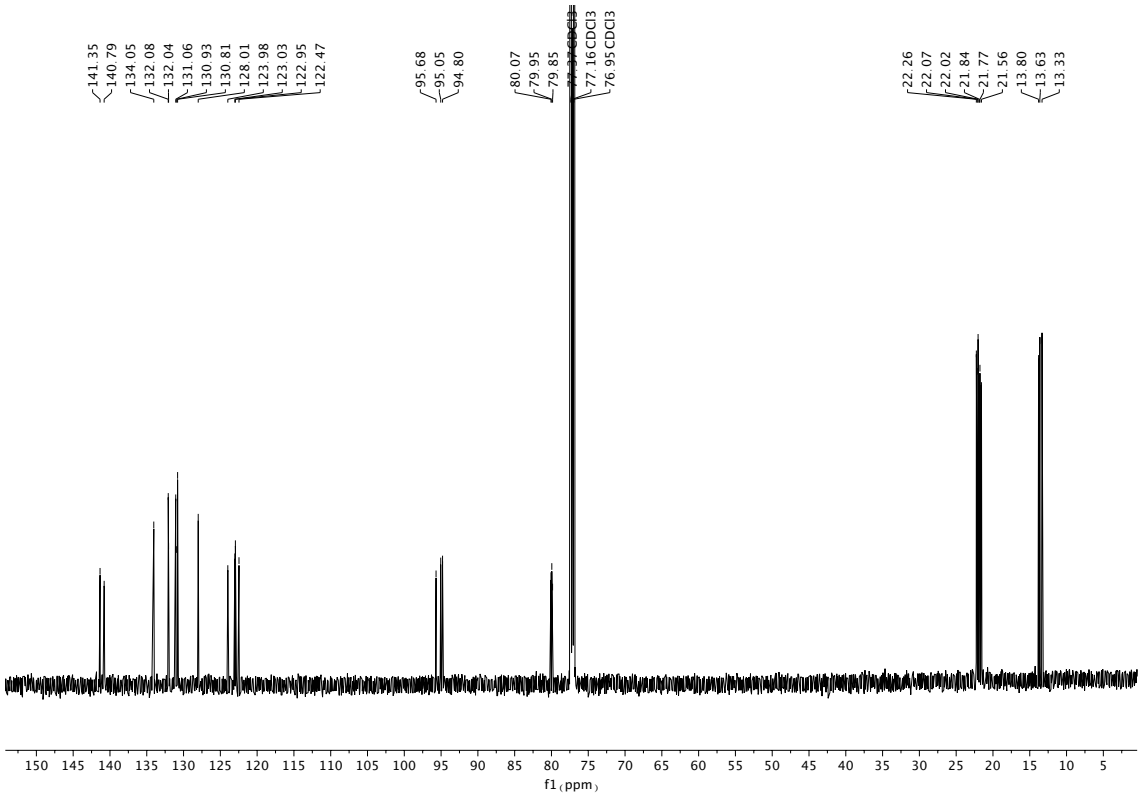


Figure S5. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-d) of **2**.

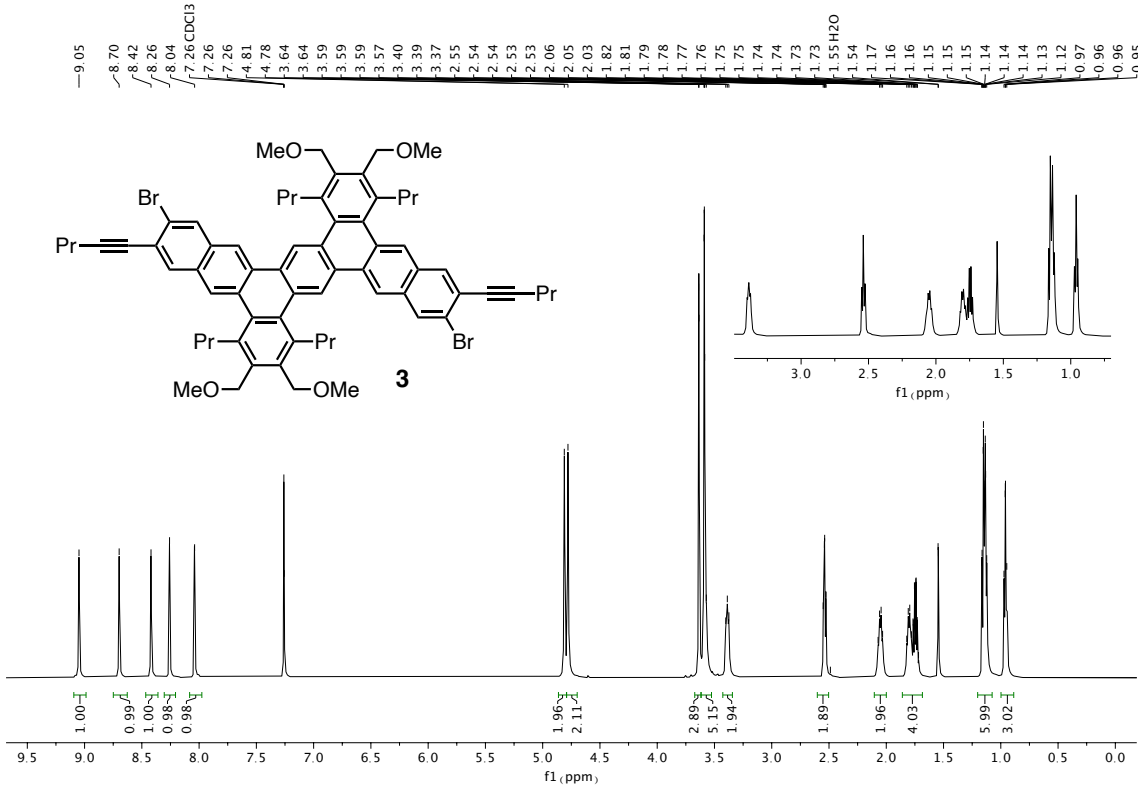


Figure S6. ^{1}H NMR Spectrum (500 MHz, chloroform-d) of **3**.

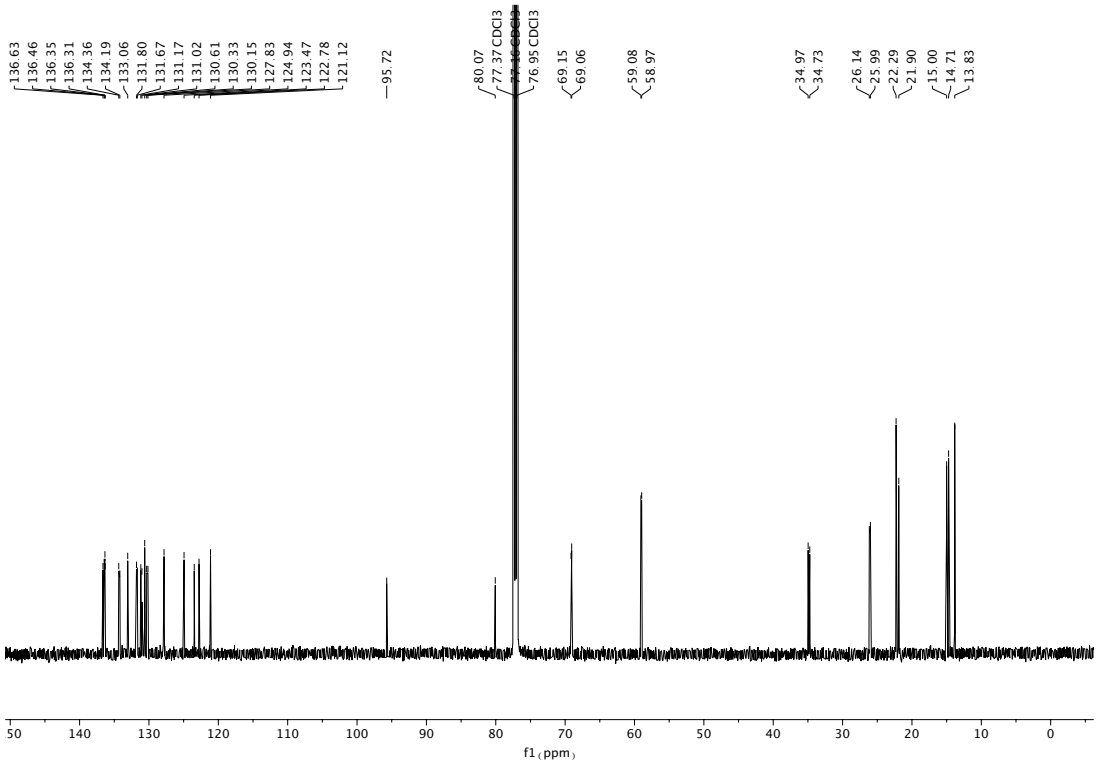


Figure S7. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-d) of **3**.

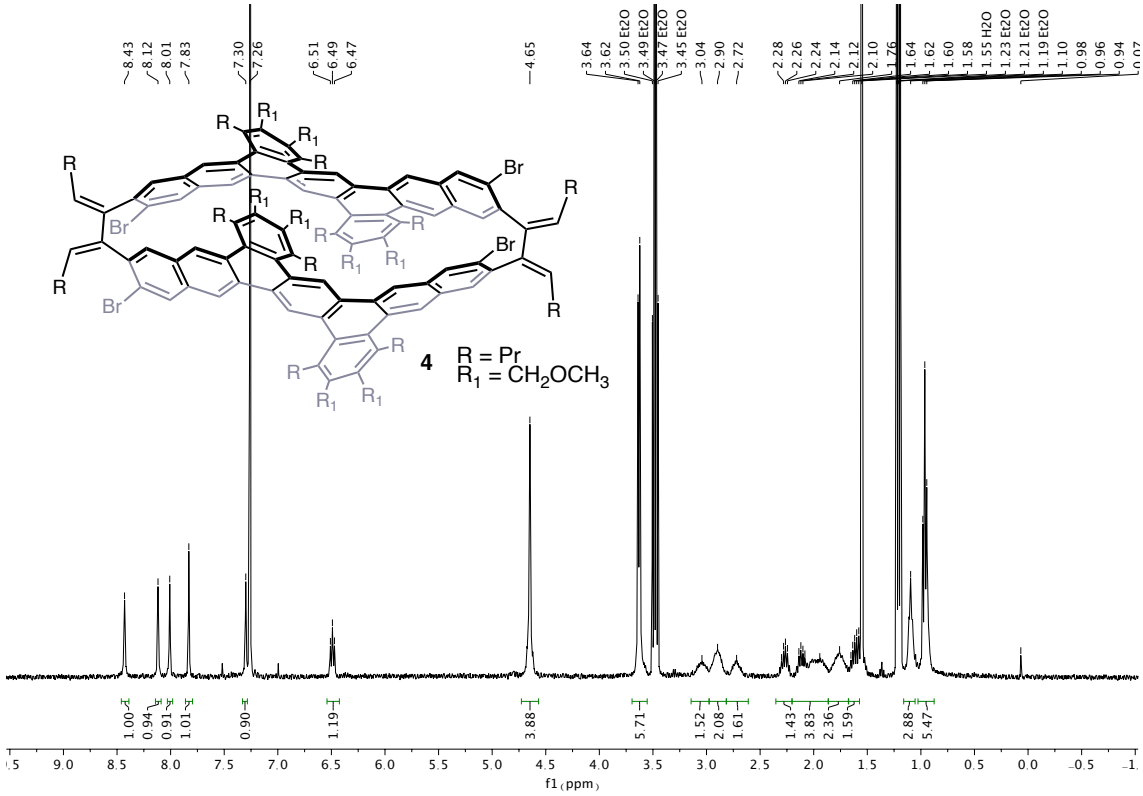


Figure S8. ^{1}H NMR Spectrum (500 MHz, chloroform-d) of **4**.

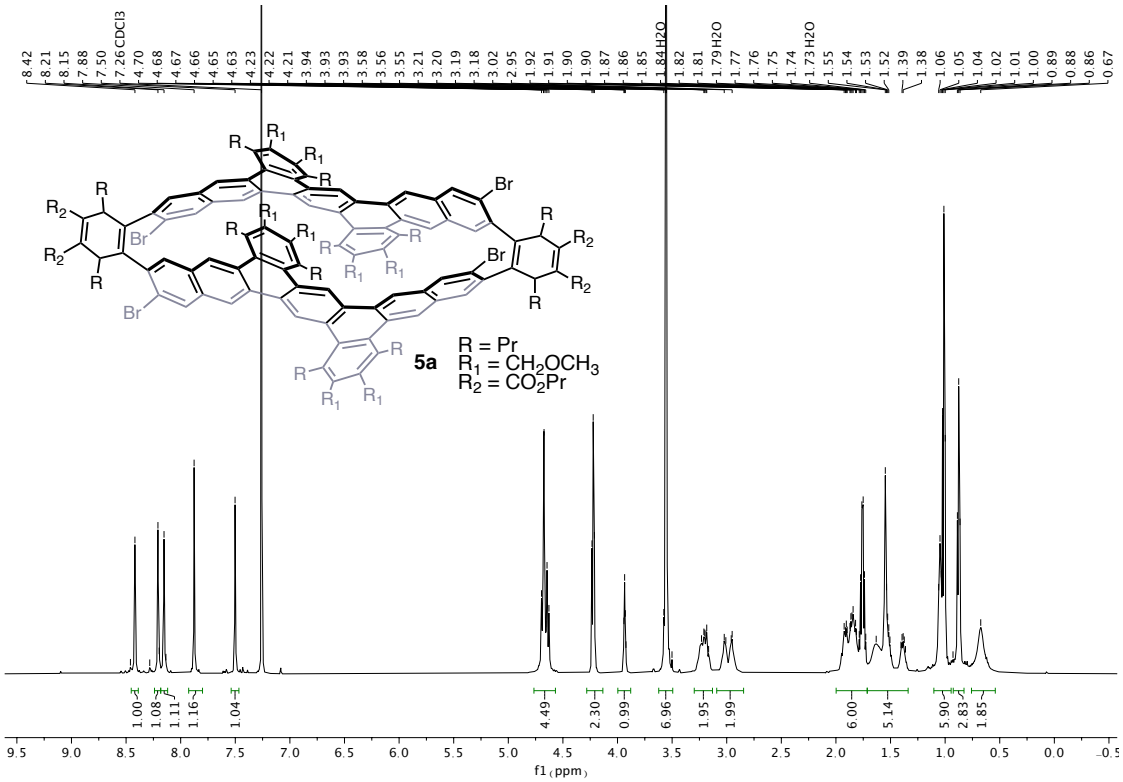


Figure S9. ^{1}H NMR Spectrum (500 MHz, chloroform-d) of **5a**.

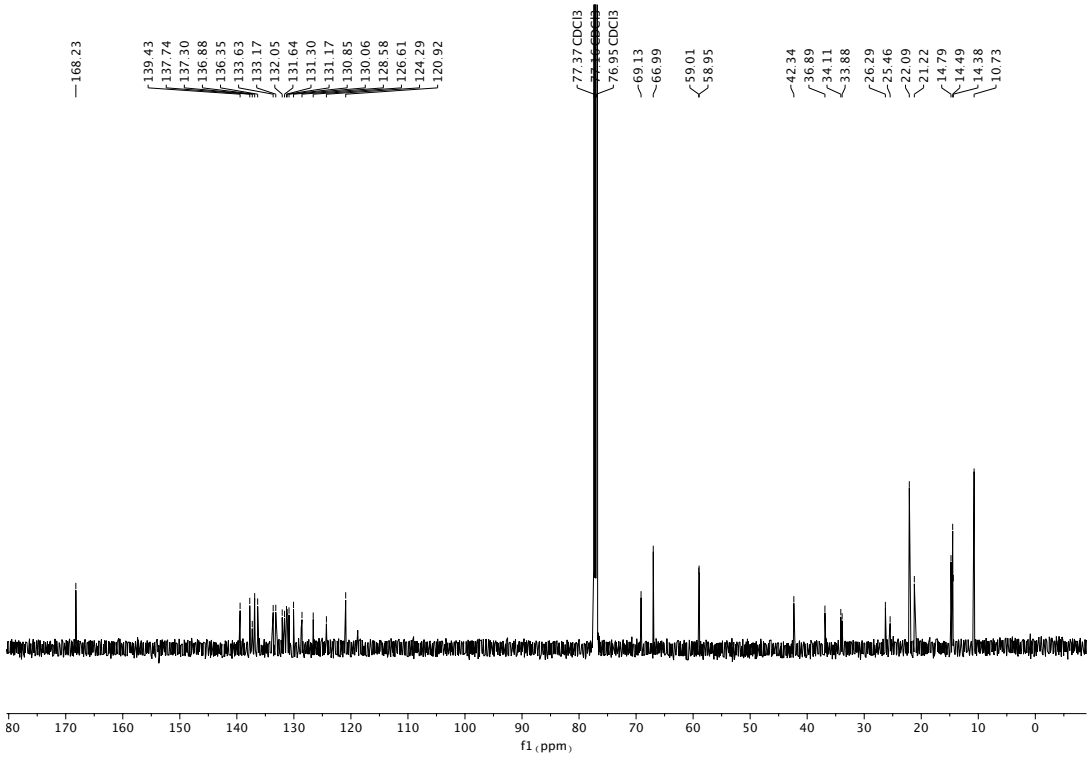


Figure S10. ^{13}C{^{1}H} NMR Spectrum (101 MHz, chloroform-d) of **5a**.

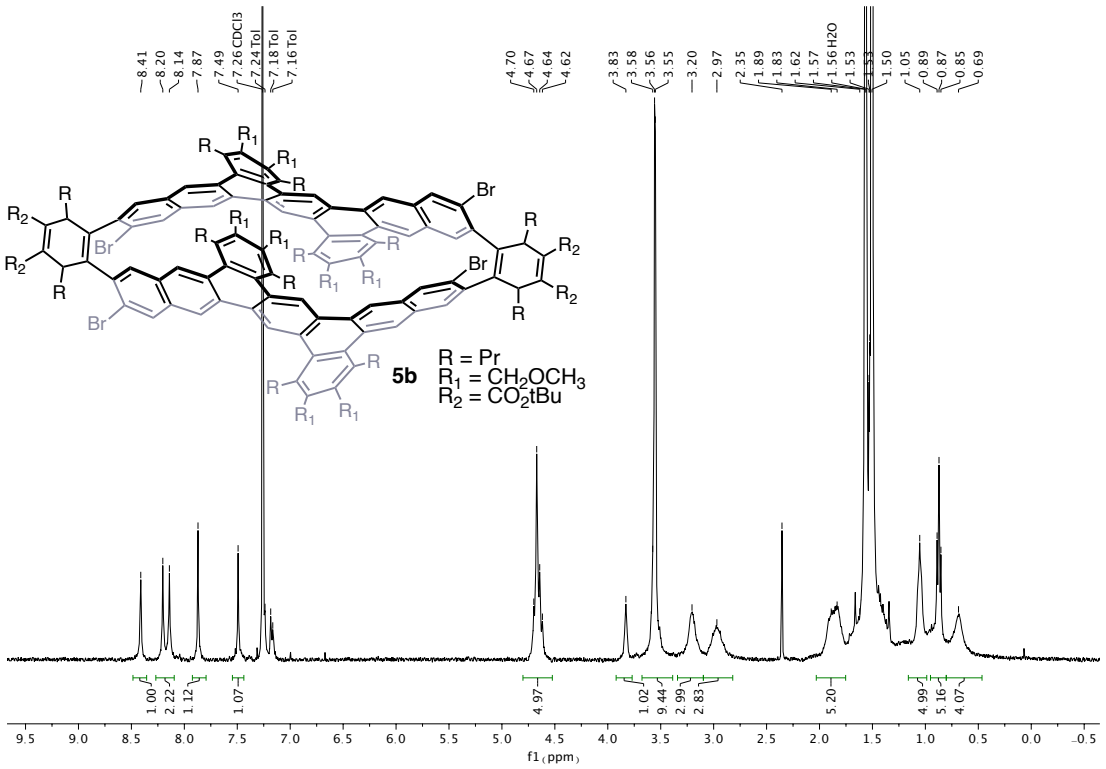


Figure S11. ^{1}H NMR Spectrum (500 MHz, chloroform-d) of **5b**.

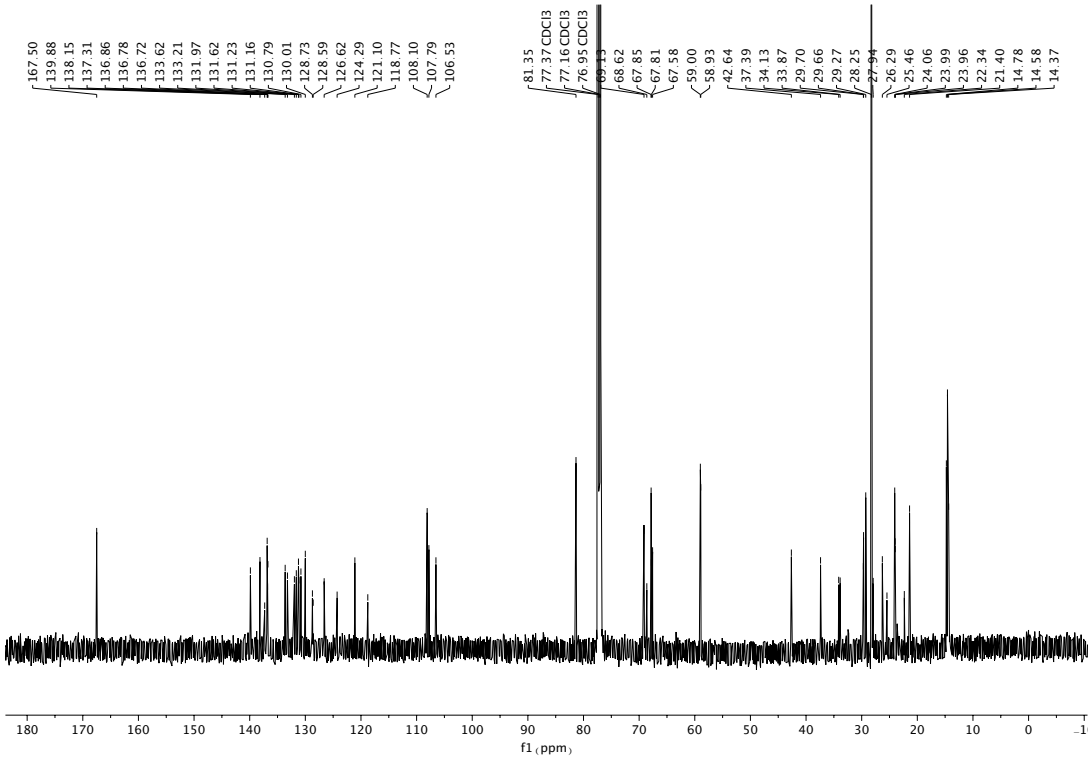


Figure S12. ^{13}C{^{1}H} NMR Spectrum (101 MHz, chloroform-d) of **5b**.

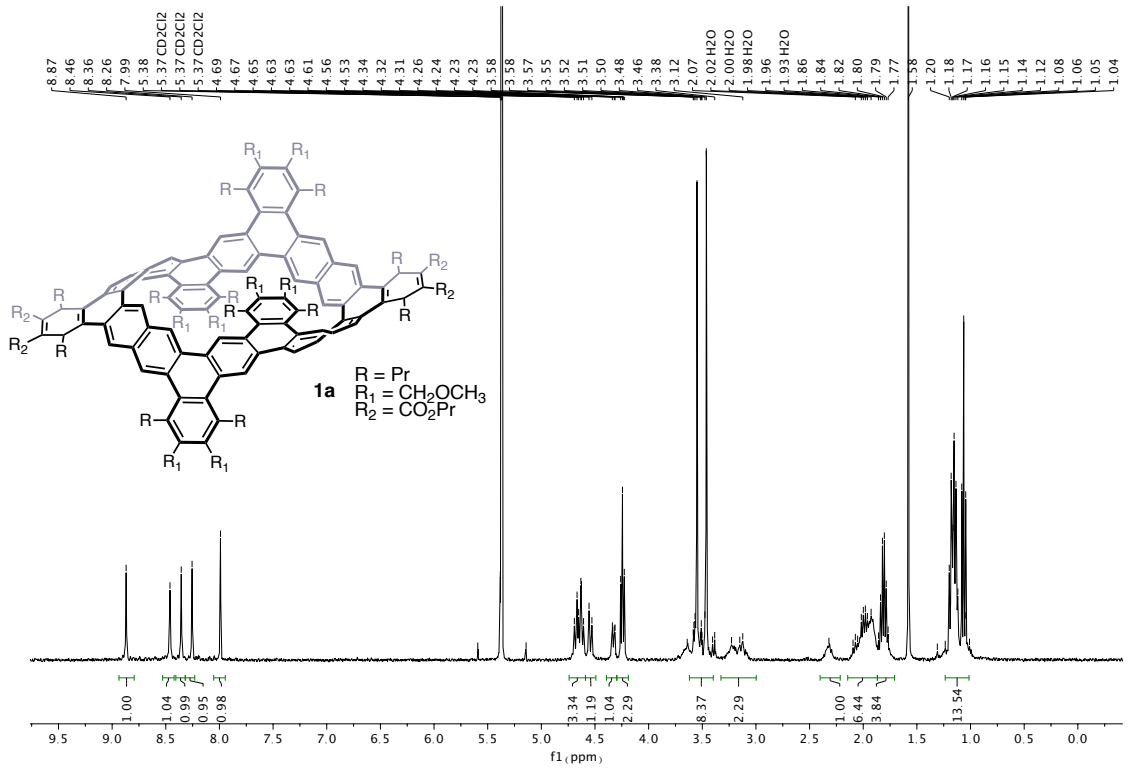


Figure S13. ^{1}H NMR Spectrum (500 MHz, CD_2Cl_2) of **1a**.

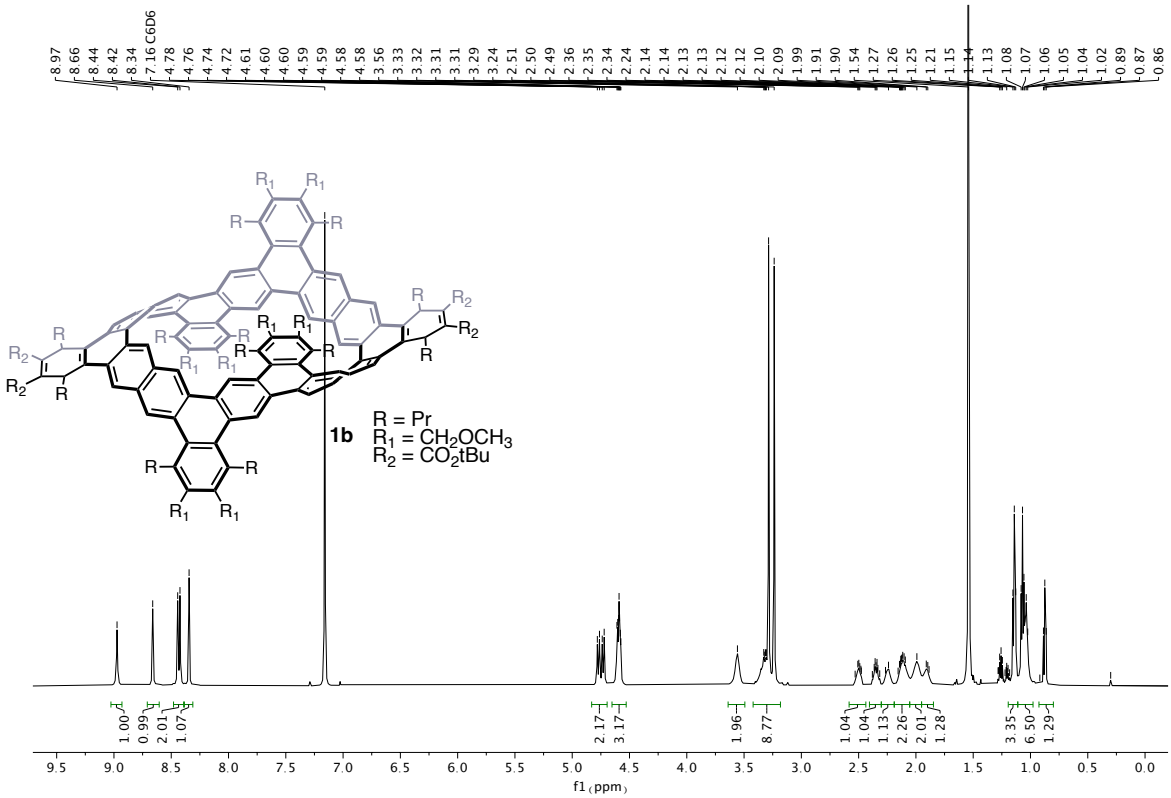


Figure S14. ^{1}H NMR Spectrum (500 MHz, C_6D_6) of **1b**.

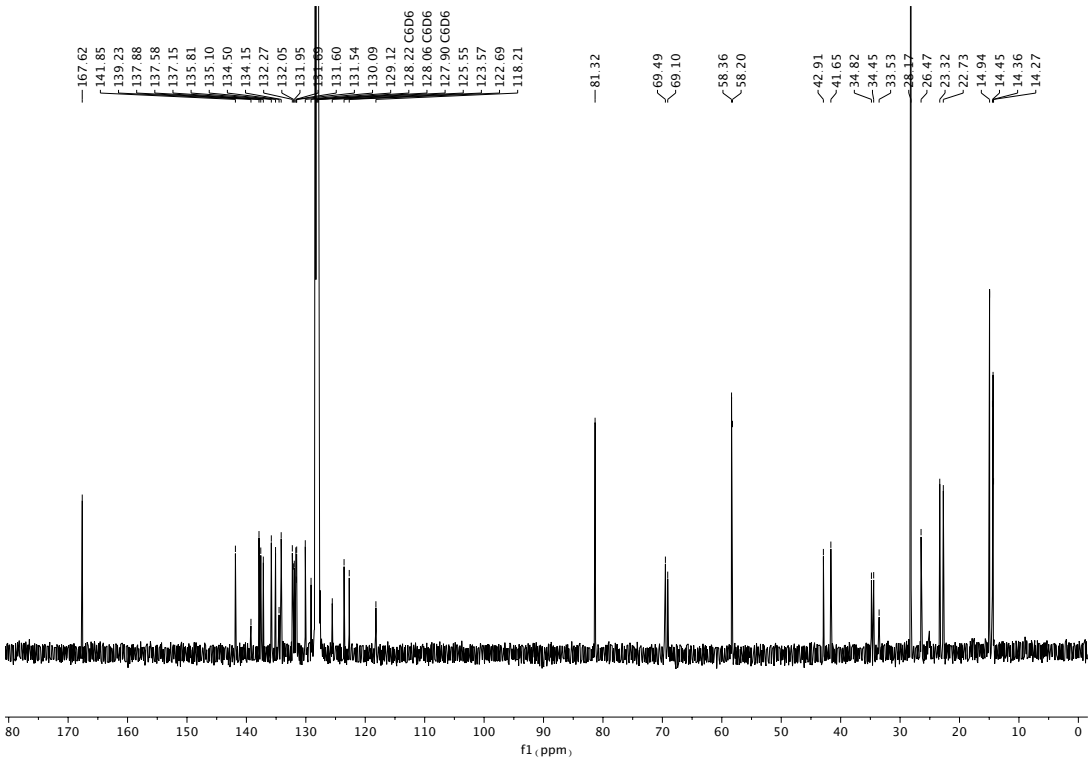


Figure S15. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, C_6D_6) of **1b**.

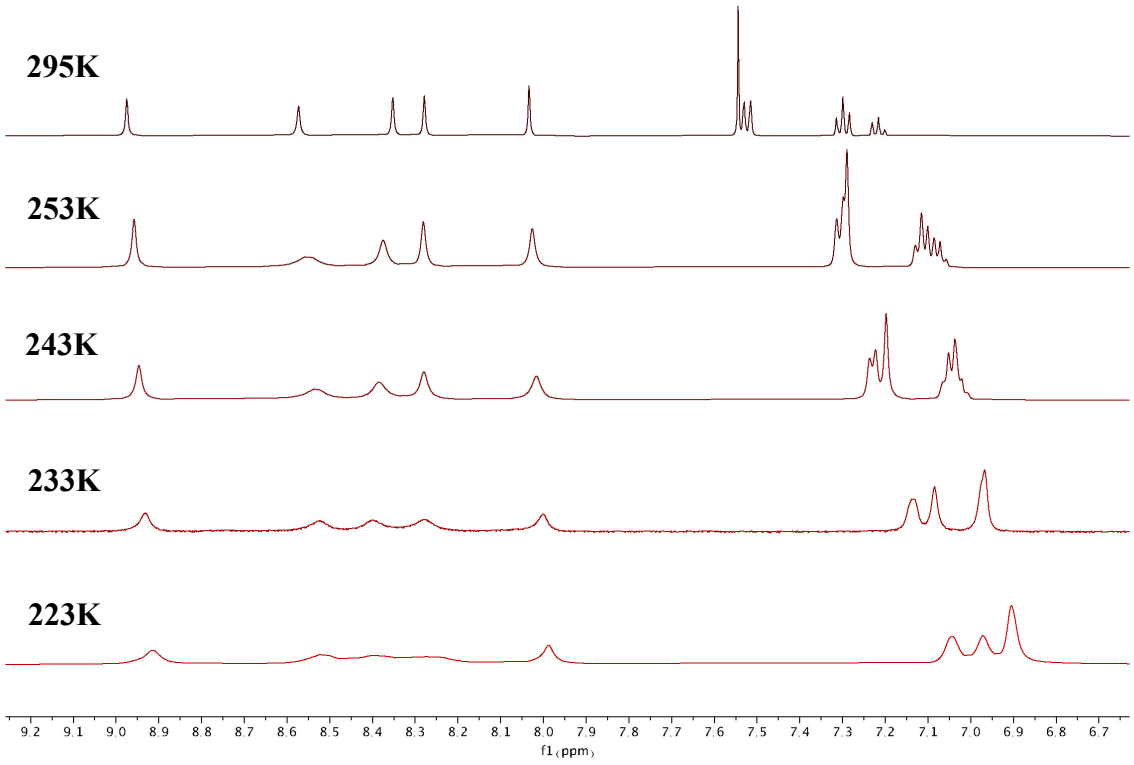


Figure S16. Variable Temperature ^{1}H NMR Spectrum (500 MHz, THF-*d8*) of a 1:1 mixture of **1b** and *p*-terphenyl.

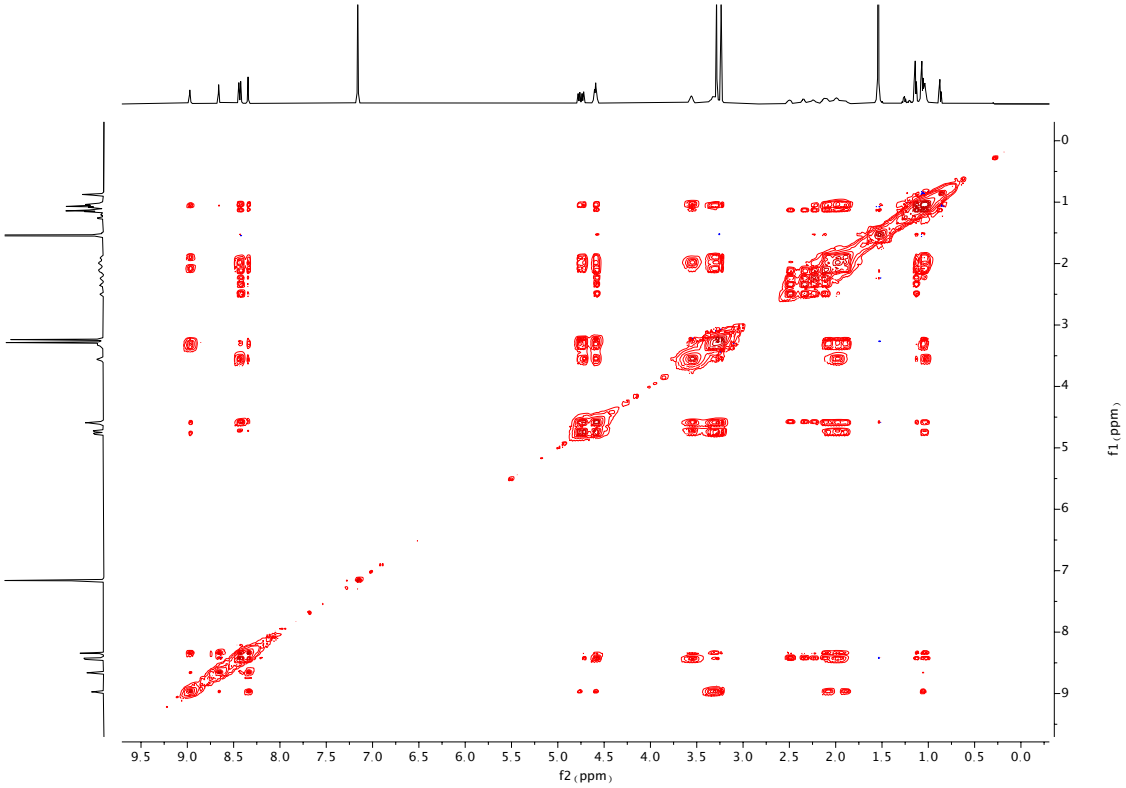


Figure S17. ^{1}H-^{1}H NOESY Spectra (600 MHz, C_6D_6) of **1b**.

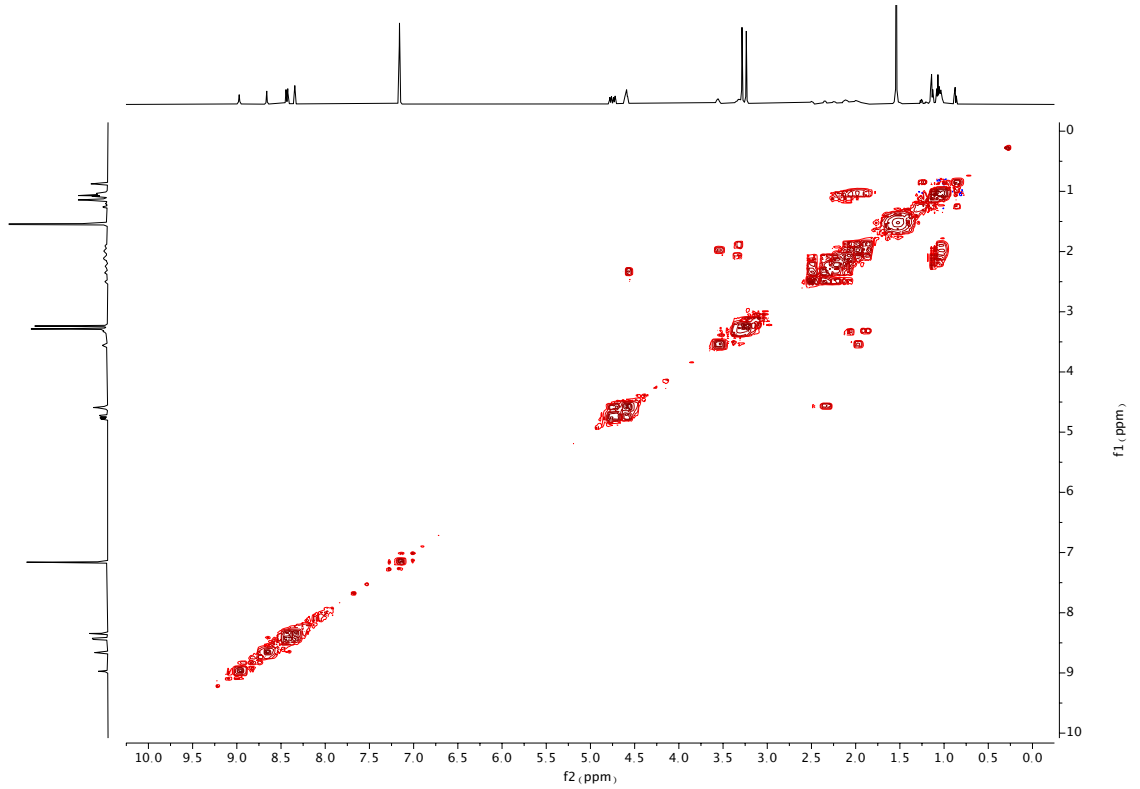


Figure S18. ^{1}H-^{1}H COSY Spectrum (600 MHz, C_6D_6) of **1b**.

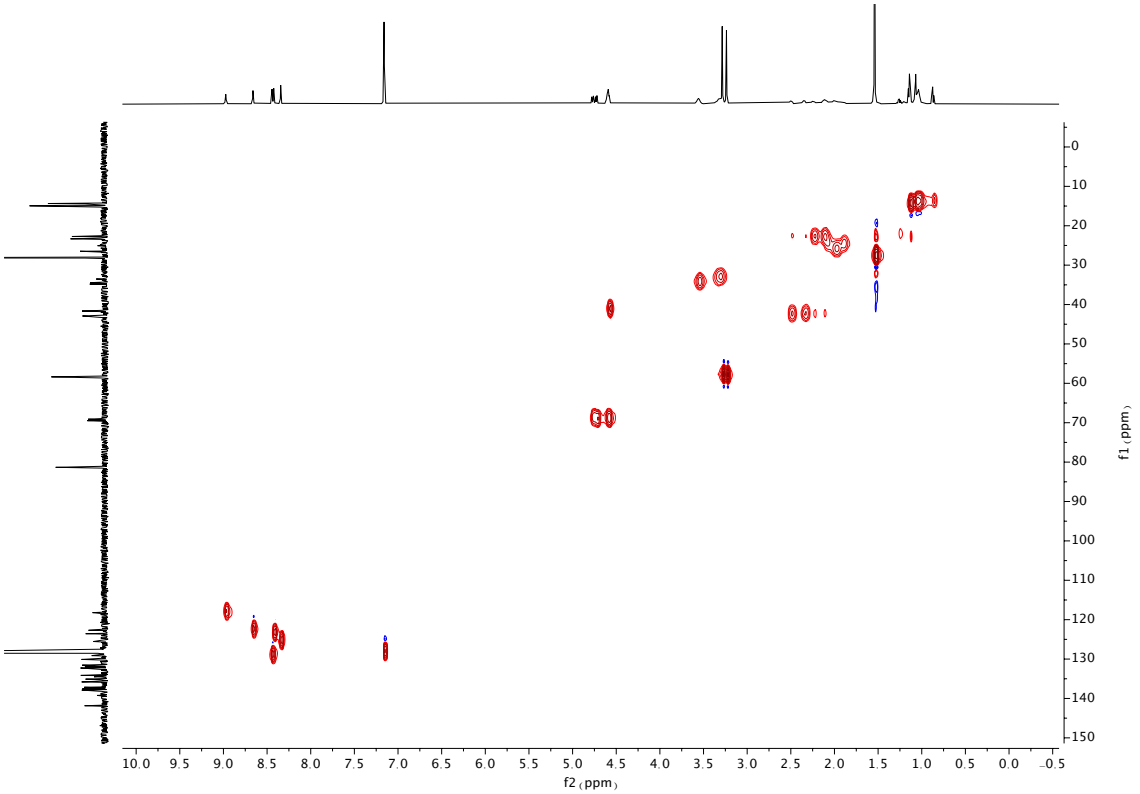


Figure S19. ^{1}H-^{1}H HSQC Spectrum (600 MHz, C_6D_6) of **1b**.

Determination of Association Constants via NMR Titration

Association constants were determined by NMR titration where the concentration of guest was held constant at 0.10 mM, while the concentration of CNB **1b** was varied. All titrations were performed in C_6D_6 at 25 ˚C. Each experiment was run in duplicate. The data was then fitted via non-linear regression using Thordarson's BindFit program[4-6] to determine the association constant. The full details of association constant determination, including the raw data, plots of chemical shift vs. host-guest ratio, curve fitting, and error analysis can be found at the following URLs:

1b•QT - http://app.supramolecular.org/bindfit/view/b7ebe40f-8e22-418e-b634-5ad1921b83ea
1b•pTP - http://app.supramolecular.org/bindfit/view/137f8d7e-011b-4129-bd2a-07640e1b911f

Note that this program treats whichever species has a fixed concentration as the host, and the species that is varying in concentration as the guest. Because these experiments were performed in the opposite manner, all data from BindFit reverses the actual roles of these compounds, such that "Host" refers to pTP/QT concentration and "Guest" refers to CNB **1b** concentration.

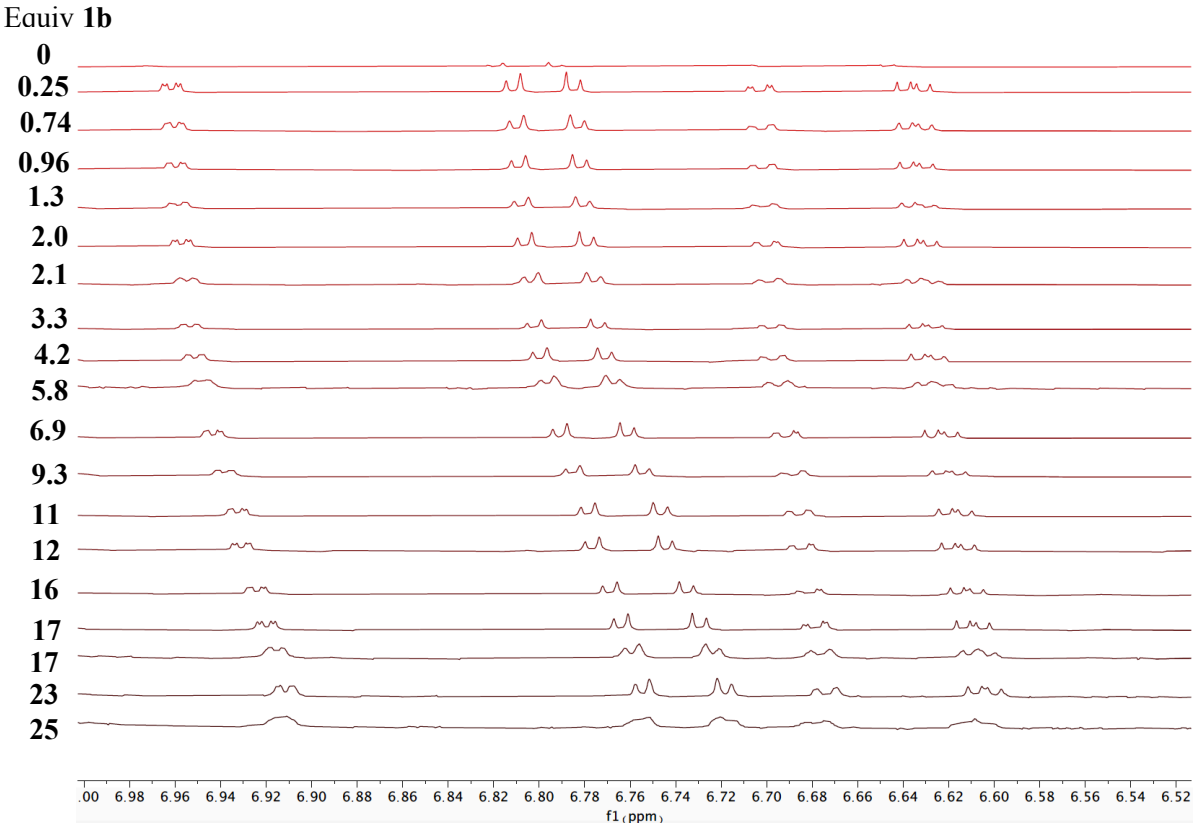


Figure S20. Partial ^{1}H NMR Titration of α-quaterthiophene with CNB **1b**. $K_a = 148 \pm 3\ M^{-1}$.

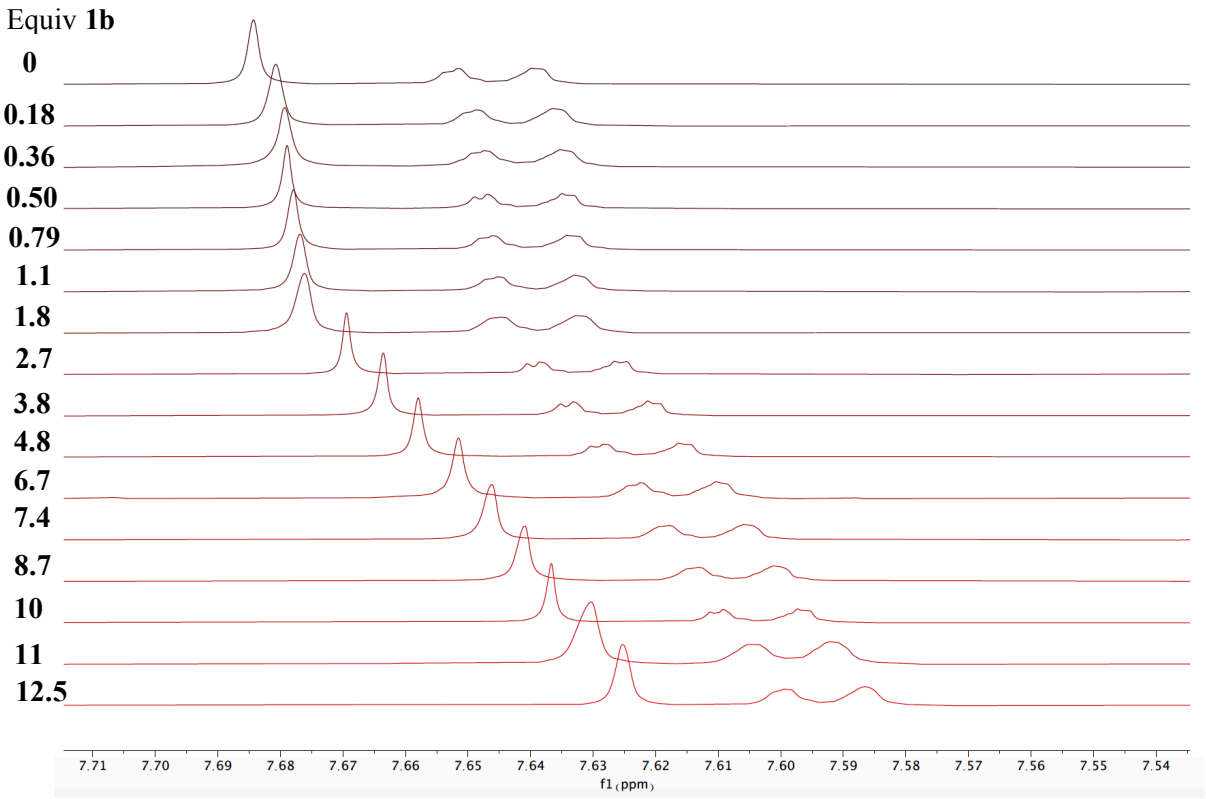


Figure S21. Partial ^{1}H NMR Titration of *p*-terphenyl with CNB **1b**. $K_a = 54 \pm 1\ M^{-1}$.

Steady-State Spectroscopy

UV-Vis and fluorescence spectroscopies were performed on a Varian 5000 UV-Vis-NIR spectrometer and Nanolog Spectrofluorimeter respectively using quartz cuvettes with a path length of 1 cm. Dry, degassed THF was used as the solvent in all cases. UV-vis spectra for CNB **1b** were acquired at 1.95×10^{-6} M, 3.25×10^{-6} M, and 1.95×10^{-5} M (each in duplicate), and absorbance was found to be linear as a function of concentration. The molar absorptivity was calculated at each concentration using the Beer-Lambert Law and averaged to afford a value of $2.63 \times 10^{5}\ M^{-1}\ cm^{-1}$. The optical bandgap was determined by finding the intersection of a tangent line along the broad transition starting at 400 nm with the x-axis.

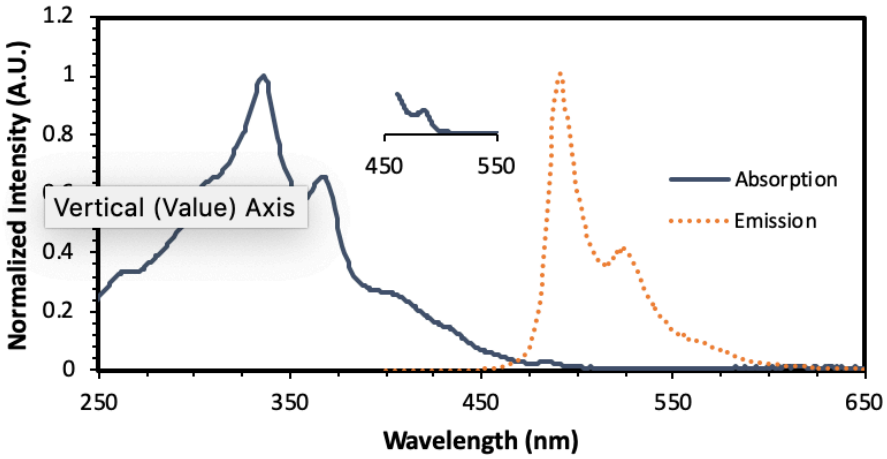


Figure S22. Normalized absorption (solid blue) and emission (dotted orange) spectra for CNB **1b** in THF at 3.25×10^{-6} M. The inset depicts the absorption onset, magnified 10x for ease of visualization.

Cyclic Voltammetry

Cyclic voltammetry was performed on a BASi EC Epsilon potentiostat/galvanostat and a PWR-3 Power Module using dry, oxygen-free solvents, a glassy carbon working electrode, Pt counter electrode, and Ag/Ag+ reference electrode.

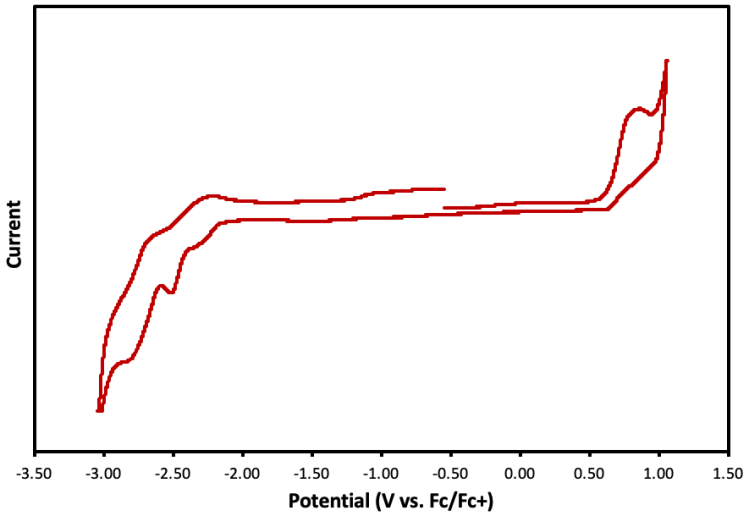


Figure S23. Cyclic voltammogram of a solution (0.2 mM) of CNB **1b** in THF with 0.1 M $[nBu_4N][PF_6]$ as supporting electrolyte. Scan rate: 100 mV/s.

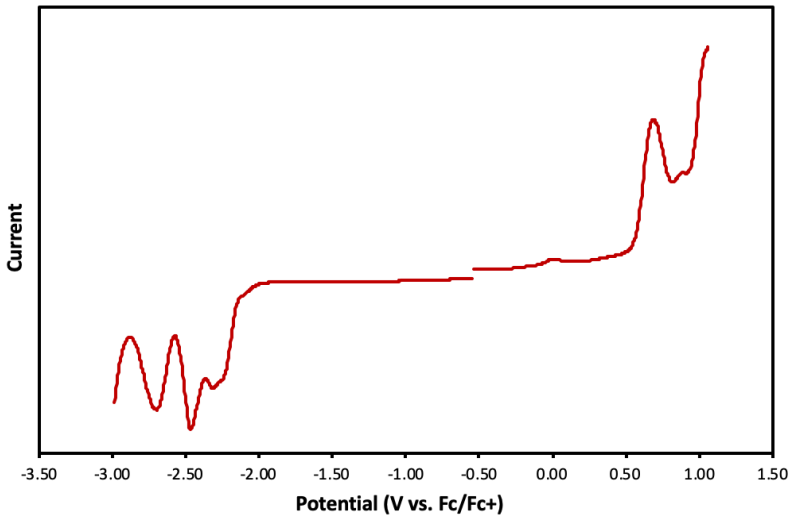


Figure S24. Square wave voltammogram of a solution (0.2 mM) of CNB **1b** in THF with 0.1 M [nBu_4N][PF_6] as supporting electrolyte. Scan rate: 100 mV/s.

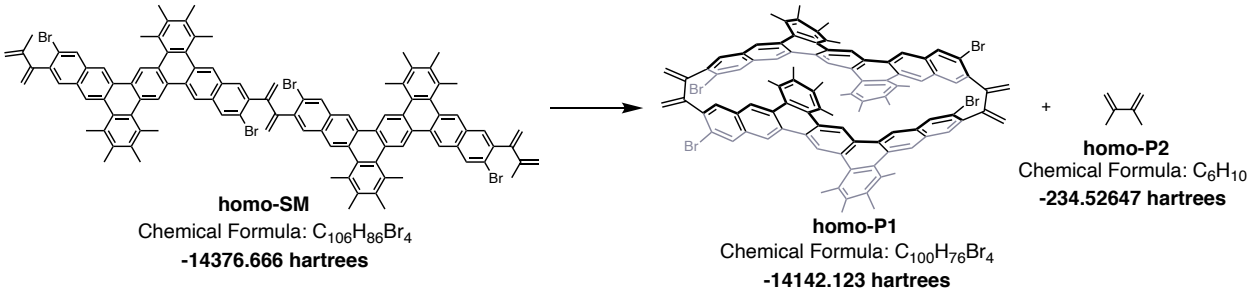
DFT Calculations

Density functional theory (DFT) calculations were performed using the Gaussian 16 software package.[7] Molecular mechanics was used to generate starting geometries, and DFT optimization was carried out in unconstrained C1 symmetry. Geometries were refined to meet standard convergence criteria, and confirmed to be local minima by normal mode frequency calculations. In all cases, to minimize computation time, all sidechains were truncated from CNB **1**.

Strain Energy Calculations

Strain energy calculations were performed using the hybrid functional B3LYP, and the 6-31G(d,p) basis set. The strain energy of macrocycle **4** was calculated via a homodesmotic reaction (Scheme S2) and determined to be 10.2 kcal/mol. The strain energy of CNB **1** was determined using the program Strainviz[8] from two fragments (Figure S25a) and determined to be 73.4 kcal/mol. The strain energy referenced in the main text as the strain incorporated by the final Yamamoto coupling (63.2 kcal/mol) was calculated by subtracting the strain energy of macrocycle **4** from that of CNB **1**.

Scheme S2. Homodesmotic reaction used to determine strain energy in macrocycle 4.



C	10.650346	0.879496	-0.129585	C	10.052392	-5.284806	0.02299
C	11.094048	-0.447028	-0.125464	C	9.763193	-4.013829	-0.497673
C	10.148802	-1.499121	-0.248265	C	-0.142539	1.403597	-1.723707
C	8.79898	-1.131542	-0.332829	C	-0.380966	1.221257	0.736249
C	8.355249	0.1949	-0.335781	C	0.208456	1.230547	1.941493
C	9.30056	1.247199	-0.214443	C	19.44979	-2.450461	-0.61449
C	6.933967	0.52892	-0.464903	C	-10.377251	-0.880371	-0.313589
C	5.933303	-0.399876	-0.212268	C	-11.134951	0.246867	0.020757
C	4.5651	-0.076866	-0.307775	C	-10.477997	1.415733	0.487285
C	4.204699	1.264639	-0.638914	C	-9.078597	1.372653	0.552418
C	5.22836	2.204912	-0.879455	C	-8.320947	0.245456	0.218137
C	6.580271	1.873654	-0.84152	C	-8.977883	-0.923276	-0.248712
C	3.533829	-1.022511	-0.057348	C	-6.860379	0.237478	0.34234
C	2.217348	-0.643636	-0.127604	C	-6.121959	1.410009	0.421639
C	1.824015	0.693482	-0.442148	C	-4.715467	1.409542	0.517366
C	2.827098	1.610269	-0.689267	C	-4.033119	0.154676	0.490064
C	12.514912	-0.781116	0.007649	C	-4.792076	-1.031055	0.392438
C	13.51637	0.148339	-0.239645	C	-6.183473	-1.034706	0.356626
C	14.883941	-0.174541	-0.137258	C	-3.952074	2.604532	0.599905
C	15.243747	-1.515963	0.19248	C	-2.581471	2.545371	0.66158
C	14.219329	-2.457026	0.428493	C	-1.873449	1.307634	0.642079
C	12.867588	-2.126266	0.384843	C	-2.614295	0.14627	0.543644
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C	17.235367	0.392011	-0.302124	C	-13.333904	-0.919025	-0.180716
C	17.632576	-0.942626	0.024186	C	-14.739821	-0.917873	-0.272079
C	16.620423	-1.857827	0.257026	C	-15.422984	0.335139	-0.241844
C	19.057152	-1.390197	0.112941	C	-14.665158	1.521301	-0.144493
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C	0.390702	1.108167	-0.526691	C	-15.506732	-2.110357	-0.359226
Br	0.87498	-1.979407	0.17442	C	-16.876914	-2.054229	-0.409471
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C	8.877105	2.656885	-0.343818	C	-16.842314	0.340532	-0.282693
C	7.419356	4.15197	-1.626903	C	-19.086559	-0.718161	-0.422423
C	8.307774	5.20953	-1.377242	Br	-17.830104	-3.706568	-0.574506
C	9.396064	5.032578	-0.492222	Br	-1.599459	4.186353	0.755935
C	9.686616	3.762552	0.030044	C	-6.94753	-2.281686	0.142067
C	11.815957	-3.15536	0.524824	C	-8.218625	-2.168357	-0.486886
C	10.571945	-2.908924	-0.119955	C	-6.430648	-3.573841	0.425644
C	12.025863	-4.405905	1.164702	C	-7.031799	-4.696782	-0.164123
C	11.138153	-5.463069	0.910829	C	-8.134492	-4.540519	-1.035069

C	-8.732481	-3.281873	-1.203468	H	-6.622817	2.370957	0.37154
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C	-11.237378	2.660674	0.72552	H	-4.457061	3.564397	0.612525
C	-13.028069	4.064691	-0.184677	H	-2.08662	-0.802676	0.509778
C	-12.426344	5.188505	0.40261	H	-12.832625	-1.879839	-0.13358
C	-11.32216	5.033354	1.271952	H	-15.212009	2.449028	-0.043412
C	-10.723427	3.775122	1.440787	H	-15.002831	-3.070153	-0.397285
C	-19.650342	0.066741	-1.357097	H	-17.362676	1.292506	-0.233577
C	-19.911182	-1.396453	0.62269	C	-5.331486	-3.783427	1.454143
C	-19.327118	-1.486419	2.013635	C	-6.47949	-6.086872	0.079445
C	-21.123691	-1.891923	0.338306	C	-8.689097	-5.760147	-1.743566
C	19.980908	-0.727708	1.082533	C	-9.821587	-3.12004	-2.251228
C	19.383075	-0.232634	2.379274	C	-14.129235	4.272434	-1.211491
C	21.287332	-0.590759	0.815976	C	-12.979112	6.578272	0.158221
H	11.395067	1.656995	-0.078501	C	-10.76679	6.253897	1.978267
H	8.054293	-1.909148	-0.384139	C	-9.633137	3.614824	2.487521
H	6.192926	-1.403011	0.108706	H	-19.055064	0.537365	-2.132788
H	4.926229	3.229359	-1.049886	H	-20.719353	0.251212	-1.367844
H	3.793839	-2.048316	0.180783	H	-18.990272	-0.507869	2.374187
H	2.549522	2.633653	-0.925088	H	-18.45651	-2.151611	2.024654
H	13.25814	1.151618	-0.561228	H	-20.061032	-1.882289	2.719907
H	14.521037	-3.481389	0.600313	H	-21.519399	-1.890756	-0.671816
H	15.66172	1.787043	-0.65134	H	-21.744855	-2.336497	1.110118
H	16.894141	-2.875147	0.520725	H	18.804686	-1.015873	2.882319
C	6.33657	4.333699	-2.677871	H	18.700736	0.604637	2.194796
C	8.087404	6.569661	-2.008259	H	20.163381	0.114143	3.061202
C	10.270782	6.223812	-0.156296	H	21.709566	-0.882199	-0.139901
C	10.771552	3.633614	1.086645	H	21.967514	-0.1579	1.543407
C	13.104879	-4.589134	2.219318	H	10.692089	4.460513	1.798377
C	11.356487	-6.824106	1.540666	H	11.79161	3.664932	0.682163
C	9.178759	-6.475585	-0.31739	H	10.668368	2.710558	1.656828
C	8.680727	-3.882471	-1.556521	H	10.48831	6.818366	-1.048009
H	0.444195	1.321666	-2.632203	H	11.228331	5.930262	0.272626
H	-1.172285	1.727973	-1.824719	H	9.783572	6.897628	0.561582
H	1.28494	1.15833	2.052065	H	7.085153	6.680569	-2.420714
H	-0.377741	1.321336	2.849492	H	8.799239	6.760971	-2.822758
H	18.788112	-2.914327	-1.338736	H	8.223172	7.371566	-1.27705
H	20.442604	-2.873443	-0.503391	H	5.943148	3.375846	-3.017605
H	-10.907174	-1.766211	-0.623926	H	6.754134	4.840071	-3.553153
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H	13.496685	-3.631682	2.562049	H	-8.050704	-6.069677	-2.58225
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H	12.684332	-5.097175	3.092212	H	-8.753755	-6.615692	-1.065316
H	8.762349	-4.707217	-2.270526	H	-9.54392	-3.665654	-3.157788
H	8.784659	-2.95765	-2.12367	H	-9.953386	-2.075988	-2.534696
H	7.659735	-3.915501	-1.154561	H	-10.799856	-3.508042	-1.93891
H	9.668997	-7.149448	-1.033162	H	-9.909686	4.161919	3.39353
H	8.223394	-6.181508	-0.750771	H	-8.655208	4.002127	2.173371
H	8.95677	-7.070352	0.573135	H	-9.501137	2.571196	2.772392
H	12.357809	-6.936033	1.955172	H	-10.704123	7.108922	1.299189
H	11.22184	-7.6251	0.808245	H	-9.765637	6.087263	2.374433
H	10.642868	-7.016118	2.353456	H	-11.403532	6.563727	2.818104
H	-5.18518	-2.896693	2.070539	H	-13.979842	6.559498	-0.272091
H	-4.360607	-4.048044	1.016015	H	-12.340794	7.156536	-0.523617
H	-5.606621	-4.602053	2.12578	H	-13.041596	7.148318	1.089543
H	-5.478761	-6.068546	0.509738	H	-14.276725	3.384477	-1.825872
H	-6.417116	-6.656309	-0.852232	H	-13.855289	5.089653	-1.885325
H	-7.118016	-6.665334	0.760946	H	-15.099279	4.538234	-0.772079

EE + Thermal Free Energy Correction: -14376.666 Hartree

Table S1. Cartesian coordinates of calculated **homo-SM**.

C	0.967845	0.869382	3.334587	C	5.197329	0.255237	2.482361
C	1.498342	-0.394152	3.051375	C	5.637572	-1.068445	2.177929
C	0.613394	-1.477069	2.775084	C	4.744508	-2.141193	2.383011
C	-0.75942	-1.194453	2.820925	C	3.429772	-1.949872	2.797496
C	-1.281848	0.085066	3.036208	C	6.115404	1.327395	2.32761
C	-0.403457	1.15412	3.329731	C	7.365071	1.11058	1.799733
C	-2.707351	0.369992	2.855683	C	7.783222	-0.18417	1.352107
C	-3.670988	-0.624821	2.931573	C	6.920651	-1.238145	1.598486
C	-5.021497	-0.385667	2.604887	C	2.495868	-3.086922	2.904419
C	-5.400134	0.934766	2.221315	C	1.135571	-2.84647	2.565647
C	-4.433206	1.964011	2.259391	C	2.926294	-4.402144	3.217436
C	-3.090552	1.725612	2.535059	C	2.068323	-5.482406	2.959444
C	-6.014981	-1.39868	2.617559	C	0.811572	-5.256281	2.353618
C	-7.292161	-1.136876	2.181751	C	0.349342	-3.949028	2.127416
C	-7.672906	0.149607	1.679381	C	-2.101477	2.819541	2.67245
C	-6.724156	1.154971	1.766654	C	-0.910725	2.538662	3.400115
C	2.945638	-0.602622	2.927967	C	-2.314146	4.147816	2.213254
C	3.846361	0.451645	2.832204	C	-1.537494	5.190217	2.745258

C	-0.534197	4.922684	3.704635	C	-2.635042	4.575756	-3.376315
C	-0.202571	3.596768	4.023243	C	-1.710806	5.603476	-3.13317
C	-8.965525	0.441197	0.983656	C	-0.47423	5.308111	-2.515429
C	9.017001	-0.436895	0.542503	C	-0.096908	3.97811	-2.265077
Br	8.518808	2.631396	1.652703	C	-8.866641	1.079387	-0.373966
Br	-8.536119	-2.592031	2.255048	C	8.806705	-1.090384	-0.793869
C	0.830194	1.136205	-2.90568	Br	8.673337	1.922917	-1.935872
C	1.262925	-0.176973	-3.123904	Br	-8.621642	-1.999523	-1.328872
C	0.314363	-1.175175	-3.447214	C	-9.744106	2.013888	-0.776288
C	-1.034966	-0.798134	-3.443274	C	-10.156139	0.173718	1.541905
C	-1.475535	0.493593	-3.139085	C	10.243046	-0.117986	0.98218
C	-0.518889	1.51582	-2.871113	C	9.632229	-2.046765	-1.247925
C	-2.902115	0.795982	-2.985079	H	1.656334	1.683753	3.499407
C	-3.856366	-0.199012	-2.808713	H	-1.463147	-1.989578	2.646984
C	-5.180907	0.091809	-2.428013	H	-3.389087	-1.626764	3.239419
C	-5.542997	1.454327	-2.198341	H	-4.785398	2.969108	2.079911
C	-4.594759	2.461311	-2.474947	H	-5.756682	-2.396869	2.953886
C	-3.298873	2.173273	-2.896029	H	-6.989491	2.148903	1.418267
C	-6.144089	-0.921085	-2.169847	H	3.505832	1.475144	2.941652
C	-7.349926	-0.60134	-1.600753	H	5.090053	-3.138044	2.137054
C	-7.686027	0.737659	-1.227627	H	5.81591	2.332178	2.605113
C	-6.797998	1.732687	-1.592777	H	7.220018	-2.236206	1.29027
C	2.660605	-0.56774	-2.921223	C	4.237288	-4.652748	3.944472
C	3.690399	0.362504	-2.920248	C	2.495315	-6.903161	3.269789
C	5.009307	0.022087	-2.560014	C	-0.054	-6.445953	1.984557
C	5.293945	-1.34011	-2.245103	C	-0.905614	-3.769037	1.288837
C	4.264096	-2.298047	-2.361885	C	-3.256734	4.457688	1.062258
C	2.945343	-1.957555	-2.650469	C	-1.789997	6.625347	2.327322
C	6.058633	0.975822	-2.47308	C	0.21341	6.082	4.33155
C	7.288326	0.608448	-1.987434	C	0.817629	3.321933	5.115293
C	7.56987	-0.723762	-1.553512	H	1.585937	1.879476	-2.722864
C	6.585649	-1.672883	-1.756134	H	-1.779459	-1.558858	-3.623078
C	1.888015	-2.976526	-2.839958	H	-3.572298	-1.243911	-2.866079
C	0.723908	-2.588313	-3.56061	H	-4.876779	3.487188	-2.270686
C	2.006482	-4.33311	-2.430183	H	-5.914065	-1.954285	-2.406867
C	1.164311	-5.299212	-3.004649	H	-7.031405	2.76031	-1.328855
C	0.186246	-4.927824	-3.955684	H	3.486034	1.395209	-3.183474
C	-0.052514	-3.571442	-4.22453	H	4.544345	-3.33195	-2.225451
C	-2.291785	3.242495	-3.035913	H	5.879741	2.002153	-2.775161
C	-0.950917	2.920303	-2.685419	H	6.777191	-2.695838	-1.445227

C	2.916295	-4.750596	-1.286729	H	-3.497406	3.561815	0.490104
C	1.317429	-6.763411	-2.642585	H	-2.774533	5.153788	0.370233
C	-0.635362	-6.00896	-4.628065	H	-2.771939	6.759712	1.873962
C	-1.046075	-3.186913	-5.308074	H	-1.044072	6.977026	1.600661
C	-3.925738	4.893606	-4.113194	H	-1.737236	7.302627	3.183773
C	-2.043978	7.042693	-3.471763	H	0.527947	6.806998	3.574496
C	0.461632	6.446864	-2.15847	H	1.110398	5.762999	4.860798
C	1.144118	3.732454	-1.422872	H	-0.412675	6.628158	5.04977
H	-9.692747	2.440817	-1.772586	H	-0.885033	-3.805085	-6.196596
H	-10.534819	2.367201	-0.122778	H	-0.923956	-2.148139	-5.613867
H	-10.235652	-0.236201	2.541579	H	-2.093959	-3.326204	-5.013041
H	-11.080078	0.334059	0.996265	H	-1.00533	-6.737022	-3.899495
H	10.399519	0.312615	1.964511	H	-0.043324	-6.571217	-5.362522
H	11.116954	-0.255878	0.354042	H	-1.503952	-5.609329	-5.149828
H	9.493015	-2.491023	-2.22825	H	2.287523	-6.982097	-2.19648
H	10.467811	-2.400761	-0.652808	H	1.219904	-7.401701	-3.524615
H	-4.407596	3.990473	-4.486315	H	0.547827	-7.091817	-1.929824
H	-3.713346	5.529326	-4.9783	H	3.205091	-3.897064	-0.673745
H	-4.659956	5.430428	-3.499225	H	3.83313	-5.260499	-1.611188
H	-3.100065	7.183167	-3.698654	H	2.38586	-5.444333	-0.628894
H	-1.473845	7.398293	-4.340466	H	4.659321	-3.730022	4.341223
H	-1.802296	7.712791	-2.641253	H	5.004143	-5.122518	3.315582
H	0.43793	7.231937	-2.917878	H	4.070054	-5.324374	4.79211
H	1.49795	6.119886	-2.071282	H	3.562987	-6.982134	3.470982
H	0.188103	6.91995	-1.204792	H	2.275723	-7.575736	2.435353
H	2.085481	3.792033	-1.985149	H	1.967943	-7.304233	4.145806
H	1.107792	2.760957	-0.930182	H	0.01841	-7.235839	2.736008
H	1.204302	4.485198	-0.632449	H	0.245511	-6.892409	1.025846
H	0.617526	3.961148	5.980694	H	-1.108264	-6.181105	1.901974
H	1.853025	3.52062	4.80999	H	-0.913486	-4.50604	0.48137
H	0.766716	2.289646	5.460801	H	-0.935148	-2.786462	0.818267
H	-4.200734	4.923511	1.375052	H	-1.841296	-3.90459	1.847245

EE + Thermal Free Energy Correction: -14142.123 Hartree

Table S2. Cartesian coordinates of calculated **homo-P1**.

C	-1.45955	-1.128628	-0.427771	C	1.425446	1.188929	-0.476268
C	-0.745316	0.124705	0.026961	C	1.459567	-1.12861	0.427764
C	-1.425467	1.188908	0.476269	H	-2.54365	-0.99229	-0.40709
C	0.745321	0.12471	-0.026949	H	-1.217529	-1.985086	0.212701

H	-1.1679	-1.404738	-1.448471	H	2.511674	1.200065	-0.494511
H	-2.511696	1.200032	0.494467	H	1.217461	-1.985106	-0.212617
H	-0.916961	2.072003	0.848898	H	1.168023	-1.404658	1.448517
H	0.916906	2.072003	-0.848893	H	2.54367	-0.992307	0.40696

EE + Thermal Free Energy Correction: -234.52647 Hartree
Table S3. Cartesian coordinates of calculated **homo-P2**.

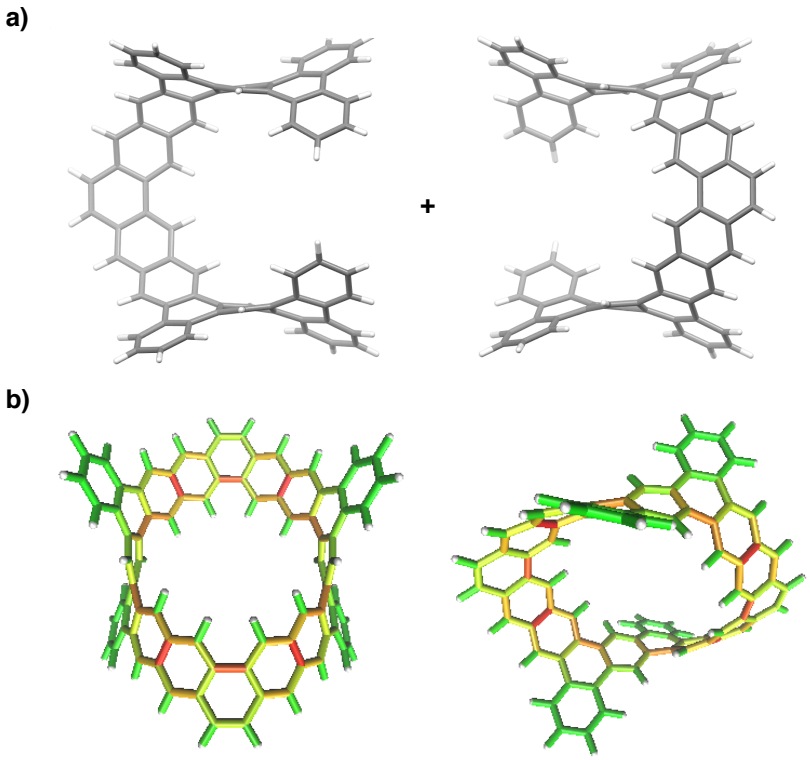

Figure S25. Strainviz strain energy calculation of CNB **1**. a) input fragments; b) strain visualization map (red – high strain, green – low strain).

Host-Guest Complex Calculations

DFT calculations on both host-guest complexes were performed using the hybrid functional TPSS with D3 dispersion corrections by Grimme,[9] and the def2-TZVP basis set.

C	1.179506	-4.775891	1.43717	C	-1.887544	-4.868493	-0.603907
C	2.145228	-4.440813	0.483624	C	-2.309703	-3.940788	-1.546802
C	1.886099	-4.721827	-0.88587	C	-3.670677	-3.569982	-1.65101
C	0.544145	-4.879943	-1.259259	C	-4.644422	-4.363365	-0.952314
C	-0.466184	-5.012534	-0.302706	C	-4.198538	-5.323388	-0.017538
C	-0.102687	-5.195681	1.06014	C	-2.849629	-5.493031	0.263029

C	-4.068575	-2.334278	-2.207072	C	-4.735914	0.562062	-2.337444
C	-5.365182	-1.851721	-2.060681	C	-5.694843	-0.4228	-2.125487
C	-6.375762	-2.761826	-1.572286	C	-7.007337	-0.005172	-1.687925
C	-6.002348	-3.996279	-1.05753	C	-7.210223	1.301498	-1.263449
C	3.372693	-3.719187	0.803619	C	1.429487	4.858688	0.833352
C	3.360179	-2.730481	1.778454	C	1.828455	3.954092	1.807923
C	4.42953	-1.813887	1.902598	C	3.192068	3.612043	1.971942
C	5.650166	-2.09807	1.198807	C	4.178041	4.432413	1.322188
C	5.654421	-3.123319	0.229116	C	3.753408	5.380322	0.364796
C	4.503615	-3.837742	-0.076421	C	2.41663	5.504403	0.010112
C	4.252818	-0.533144	2.471898	C	3.587146	2.364889	2.506231
C	5.214207	0.462446	2.332223	C	4.889471	1.893805	2.365514
C	6.525026	0.07688	1.862483	C	5.906797	2.832626	1.950612
C	6.721268	-1.189699	1.330334	C	5.537521	4.083795	1.474375
C	4.333621	-4.538532	-1.353425	C	1.993332	6.105805	-1.258913
C	3.017799	-4.83848	-1.807137	C	0.705984	5.787622	-1.776205
C	5.419029	-4.810238	-2.207557	C	2.859295	6.893722	-2.039471
C	5.228696	-5.321363	-3.482681	C	2.501421	7.323647	-3.308697
C	3.931249	-5.577479	-3.943974	C	1.253751	6.969951	-3.837031
C	2.847912	-5.346042	-3.11012	C	0.370725	6.221661	-3.073366
C	-2.380281	-6.117937	1.504318	C	-4.829295	4.727035	1.303412
C	-1.062629	-5.834735	1.961699	C	-3.521793	4.956473	1.816496
C	-3.225822	-6.892177	2.320355	C	-5.93766	5.127319	2.071907
C	-2.816687	-7.341744	3.567359	C	-5.780601	5.694846	3.327965
C	-1.536142	-7.023776	4.036583	C	-4.495408	5.875964	3.853807
C	-0.673772	-6.289274	3.236545	C	-3.38706	5.519342	3.100309
C	-7.744031	-2.31284	-1.470429	C	-8.047077	-0.993801	-1.526668
C	7.570447	1.069074	1.788586	C	7.276888	2.390003	1.840928
C	-1.026342	4.857153	1.383454	H	1.445763	-4.71109	2.487979
C	0.0211	4.970509	0.465157	H	0.267594	-4.897311	-2.309174
C	-0.285153	5.144	-0.912358	H	-1.567438	-3.361584	-2.090698
C	-1.557383	4.736294	-1.335379	H	-4.950509	-5.803714	0.602219
C	-2.568678	4.443777	-0.41671	H	-3.286788	-1.694254	-2.60594
C	-2.356309	4.736338	0.958739	H	-6.76096	-4.630495	-0.602184
C	-3.817149	3.775779	-0.77474	H	2.439799	-2.537605	2.32363
C	-3.816986	2.768644	-1.730649	H	6.535485	-3.208722	-0.399792
C	-4.90875	1.876346	-1.849056	H	3.269025	-0.295765	2.8668
C	-6.136141	2.21401	-1.181861	H	7.67994	-1.428179	0.873909
C	-6.141013	3.288267	-0.264531	H	6.430475	-4.616859	-1.863834
C	-4.975663	3.973569	0.053749	H	6.085788	-5.523503	-4.119061

H	3.772664	-5.976722	-4.941737	C	2.260745	0.128544	-0.872205
H	1.850501	-5.594213	-3.45974	C	1.462093	1.199542	-0.430801
H	-4.220402	-7.148596	1.968154	C	0.186107	0.991547	0.084778
H	-3.489179	-7.940909	4.174915	C	-0.3651	-0.300282	0.179607
H	-1.208092	-7.370403	5.012466	C	0.425938	-1.365299	-0.283833
H	0.334655	-6.093383	3.587886	C	1.699146	-1.156029	-0.792344
H	-0.791581	4.893392	2.443189	C	-1.720935	-0.549945	0.721409
H	-1.785047	4.666034	-2.394876	C	-2.058706	-1.79653	1.281449
H	-2.891298	2.531967	-2.249972	C	-2.720545	0.43605	0.668287
H	-7.038646	3.433348	0.330017	C	-4.010286	0.181071	1.128686
H	-3.749818	0.295757	-2.706698	C	-4.335022	-1.06961	1.654899
H	-8.174262	1.575552	-0.838638	C	-3.348882	-2.054778	1.736565
H	1.075681	3.360028	2.32005	H	6.034645	-1.269605	-3.221828
H	4.522355	5.879685	-0.217722	H	3.716521	-1.536434	-2.484457
H	2.79956	1.702269	2.853078	H	6.261257	2.499273	-1.158
H	6.302889	4.738865	1.061832	H	7.341356	0.754375	-2.573164
H	3.829635	7.175859	-1.6423	H	3.953548	2.220283	-0.390265
H	3.188767	7.933327	-3.888473	H	1.836555	2.216777	-0.490591
H	0.966334	7.299161	-4.831596	H	-0.382598	1.851673	0.428964
H	-0.613496	5.998168	-3.473228	H	0.03974	-2.379208	-0.252869
H	-6.939444	4.994506	1.674399	H	2.275121	-2.017638	-1.110489
H	-6.653591	5.998983	3.89869	H	-2.499854	1.404698	0.232066
H	-4.363021	6.317239	4.837634	H	-4.76642	0.956988	1.053185
H	-2.395034	5.714108	3.496065	H	-5.346754	-1.275824	1.993166
C	5.704773	1.616758	-1.460011	H	-1.303728	-2.572382	1.367441
C	6.311881	0.636297	-2.245576	H	-3.582898	-3.031937	2.149949
C	5.581292	-0.497637	-2.60497	H	-8.513367	-3.05159	-1.258103
C	4.264649	-0.650221	-2.179385	H	8.586746	0.732319	1.598401
C	3.641777	0.320464	-1.373008	H	-9.06467	-0.648592	-1.359446
C	4.390241	1.460087	-1.029242	H	8.050835	3.139577	1.693478

EE + Thermal Free Energy Correction: -3768.208967 Hartree

Table S4. Cartesian coordinates of calculated **1•pTP**.

C	-1.622793	-4.825756	1.299853	C	-4.139475	-3.360202	-0.959951
C	-0.540084	-5.011855	0.436013	C	-3.963286	-2.314899	-1.855024
C	-0.783412	-5.109969	-0.961853	C	-4.959506	-1.325654	-2.023857
C	-1.976357	-4.551409	-1.437911	C	-6.261749	-1.570605	-1.467237
C	-3.000028	-4.180277	-0.563628	C	-6.436067	-2.667071	-0.59463
C	-2.905367	-4.549034	0.805892	C	-5.369706	-3.476156	-0.226656

C	-4.647326	-0.030971	-2.492231	C	-3.781879	2.808488	-2.413218
C	-5.546853	1.023443	-2.375277	C	-5.115957	2.425683	-2.319541
C	-6.91273	0.713009	-2.022667	C	-6.074761	3.414993	-1.884475
C	-7.246554	-0.571714	-1.614086	C	-5.630641	4.617368	-1.349601
C	0.853867	-5.032377	0.871718	C	3.522516	3.41778	1.097716
C	1.283884	-4.176657	1.878176	C	3.352654	2.403693	2.030338
C	2.662829	-3.93649	2.091618	C	4.333295	1.397097	2.198277
C	3.608931	-4.813426	1.457427	C	5.624392	1.603683	1.601318
C	3.149745	-5.715583	0.472913	C	5.790517	2.661056	0.681242
C	1.820554	-5.737448	0.072921	C	4.728902	3.477867	0.318362
C	3.128789	-2.728902	2.658645	C	4.013077	0.115703	2.699163
C	4.46535	-2.351737	2.570452	C	4.901888	-0.950366	2.59467
C	5.426446	-3.355765	2.173494	C	6.269454	-0.659658	2.230472
C	4.984087	-4.565989	1.656397	C	6.605104	0.604237	1.765443
C	1.40486	-6.2809	-1.224082	C	4.721612	4.233782	-0.937795
C	0.181227	-5.83066	-1.793454	C	3.473499	4.631661	-1.494719
C	2.227894	-7.136878	-1.978505	C	5.895849	4.463302	-1.679334
C	1.891798	-7.50872	-3.272087	C	5.853876	5.019498	-2.949456
C	0.711383	-7.025984	-3.850682	C	4.621243	5.365371	-3.51727
C	-0.131746	-6.207876	-3.113635	C	3.454022	5.181448	-2.791034
C	-5.38179	-4.279136	1.000485	C	-1.990278	6.394438	1.435283
C	-4.140618	-4.664108	1.583873	C	-0.745408	5.968199	1.976697
C	-6.57147	-4.567823	1.694371	C	-2.797028	7.260752	2.195414
C	-6.554576	-5.171118	2.943659	C	-2.423269	7.667113	3.46819
C	-5.331567	-5.504929	3.538747	C	-1.21994	7.210179	4.019749
C	-4.14734	-5.261966	2.85894	C	-0.393329	6.381125	3.276121
C	-7.878265	1.781586	-1.922567	C	-7.477221	3.073608	-1.850835
C	6.830936	-3.02373	2.151464	C	7.233899	-1.731507	2.178582
C	1.395151	4.666717	1.59515	H	-1.454983	-4.920734	2.368767
C	2.390061	4.250964	0.706135	H	-2.131833	-4.417915	-2.504349
C	2.263942	4.580502	-0.671958	H	-2.980946	-2.149874	-2.290088
C	0.975372	4.877298	-1.137788	H	-7.38546	-2.742476	-0.072379
C	-0.082917	5.103518	-0.252814	H	-3.617062	0.156383	-2.780909
C	0.197088	5.22889	1.135794	H	-8.256535	-0.766272	-1.257646
C	-1.486508	5.120218	-0.65588	H	0.558131	-3.534446	2.371735
C	-1.93403	4.257184	-1.647518	H	3.899565	-6.25981	-0.094515
C	-3.31437	4.007897	-1.831185	H	2.380795	-2.018427	2.998882
C	-4.254279	4.872535	-1.171428	H	5.713772	-5.269579	1.259608
C	-3.779272	5.78071	-0.199696	H	3.145086	-7.519606	-1.540933
C	-2.439127	5.823	0.161243	H	2.543442	-8.17401	-3.831619

H	0.441962	-7.309938	-4.86406	C	7.265769	0.758701	-2.437805
H	-1.070205	-5.883727	-3.55286	S	6.594381	-1.532995	-1.495427
H	-7.526453	-4.314211	1.244006	C	7.795717	-0.467845	-2.116988
H	-7.488874	-5.384727	3.455391	C	5.874281	0.837916	-2.185862
H	-5.30845	-5.974874	4.517883	H	5.27647	1.722825	-2.375128
H	-3.208244	-5.572231	3.30685	H	-6.801855	0.830952	1.982409
H	1.574597	4.557245	2.660589	H	7.851348	1.573744	-2.849383
H	0.781826	4.945469	-2.204182	H	-5.931823	-1.624239	2.468133
H	-1.217044	3.618615	-2.15736	H	8.817201	-0.807968	-2.220759
H	-4.519101	6.319825	0.385304	H	-3.417924	-1.902002	1.776876
H	-3.035007	2.110734	-2.781023	C	-3.422583	0.170915	1.131952
H	-6.358186	5.31019	-0.930474	C	-3.978739	-0.981383	1.659881
H	2.379536	2.271166	2.497104	S	-4.607835	1.450196	1.099335
H	6.723931	2.695131	0.128128	C	-5.810607	0.43852	1.800712
H	2.98609	-0.054772	3.009763	C	-5.334533	-0.826997	2.040251
H	7.607581	0.775874	1.378676	H	-1.872832	2.557244	0.701984
H	6.857213	4.19443	-1.252431	H	0.584745	2.289266	-0.128393
H	6.776053	5.186329	-3.499263	H	3.914998	-2.760045	-0.979567
H	4.578294	5.797952	-4.5128	H	1.42465	-2.527492	-0.250227
H	2.509643	5.500377	-3.221236	C	1.583318	-0.379066	-0.541971
H	-3.731017	7.624878	1.777993	S	2.848123	0.701633	-1.068869
H	-3.063012	8.340304	4.032029	C	3.388641	-1.812399	-0.940394
H	-0.920274	7.522551	5.016137	C	2.042612	-1.687674	-0.545766
H	0.562306	6.076608	3.691889	S	-1.032936	-0.937118	0.231484
H	-8.927679	1.51828	-1.811959	C	3.986689	-0.604004	-1.260121
H	7.548418	-3.828996	2.013106	C	-2.079041	0.396977	0.658537
H	-8.196827	3.871001	-1.680345	C	0.298896	0.133966	-0.144194
H	8.283256	-1.472927	2.060144	C	-1.414887	1.599239	0.483592
C	5.342982	-0.331528	-1.667457	C	-0.087468	1.453788	0.034806

EE + Thermal Free Energy Correction: -5282.509729 Hartree
Table S5. Cartesian coordinates of calculated **1•QT**.

X-ray Crystallography

X-ray diffraction data for **1a** was collected at the UC Berkeley CheXRay crystallographic facility on a Rigaku Pilatus 200K diffractometer using Cu Kα radiation with a wavelength of 1.5418 Å. X-ray diffraction data for **1b** was collected at beamline 12.2.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory. Frames were collected on a shutterless PHOTON II detector using radiation with a wavelength of 0.7288 Å selected by a Si(111) monochromator and focused to 200 μm^2 with a toroidal mirror. Crystals of **1a** and **1b** were kept at 100 K throughout collection. Data collection, integration, scaling, and space group determination for **1a** was

performed with Rigaku CrysAlis Pro (v. 40_64.84a) software. Data collection, integration, scaling, and space group determination for **1b** was performed with Bruker APEX3 (v. 2016.5-0) software. Structures were solved by SHELXT-2014[10] and refined with SHELXL-2014,[11] with refinement of F^2 on all data by full-matrix least squares, using the OLEX2 interface.[12] The 3D molecular structure figures were visualized with Mercury 3.7.

Details of structure solution and refinement for 1a:
Crystals of **1a** were formed as two component twins. Reflections from both domains were integrated, and the structure was solved by SHELXT using a single-domain HKLF4 format reflection file. Structure refinement was carried out with reflection data from both domains using a HKLF5 format reflection file. A large channel occupied by highly disordered solvent molecules was modeled with a solvent mask; the number of electrons in the void region is consistent with the presence of three molecules of hexamethyldisiloxane per asymmetric unit. All carbon and oxygen atoms were modeled anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model. Occupancies of disordered atoms were modeled with free variables. RIGU, SADI, and EADP constraints / restraints were used to maintain reasonable anisotropic displacement parameters.

Empirical formula	$C_{156}H_{176}O_{16} + 6[C_6H_{18}OSi_2]$
Formula weight	2306.96
Temperature/K	100.15
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	22.2409(7)
b/Å	17.6565(6)
c/Å	25.9714(10)
α/°	90
β/°	107.002(4)
γ/°	90
Volume/Å^3	9753.1(6)
Z	2
ρ_{calc}g/cm^3	0.786
μ/mm^{-1}	0.390
F(000)	2480.0
Crystal size/mm^3	0.04 × 0.04 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.142 to 101.196
Index ranges	$-22 \le h \le 22$, $-17 \le k \le 17$, $-25 \le l \le 25$
Reflections collected	16284

Table S6. Crystal data and structure refinement for **1a**.

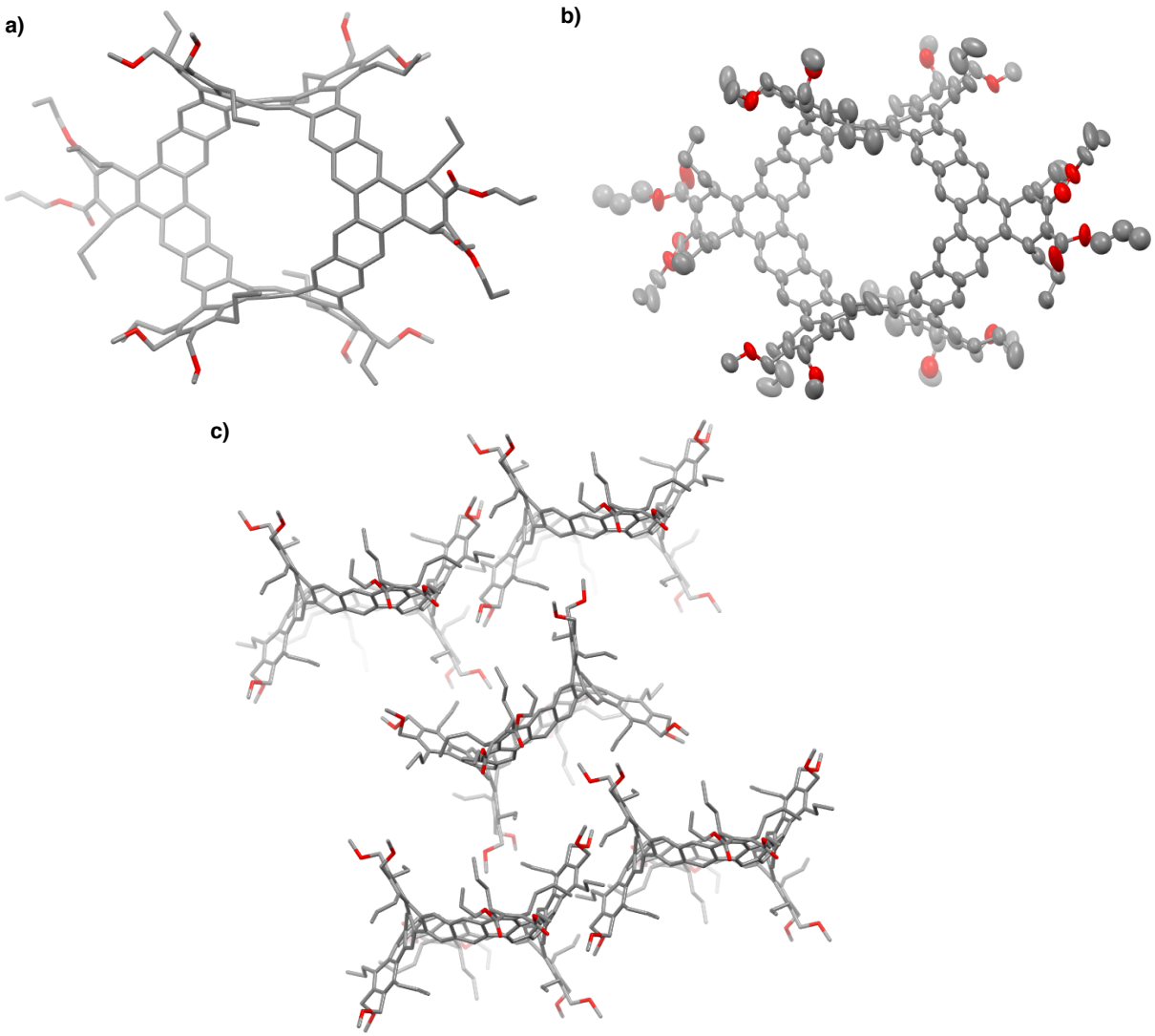

Figure S26. Solid state structure of **1a** as determined by single-crystal X-ray diffraction with hydrogen atoms omitted for clarity. a) top-down view; b) top-down view with 50% probability ellipsoids; c) crystal packing of **1a**.

Details of structure solution and refinement for 1b:
Crystals of **1b** showed no evidence of twinning upon inspection of the diffraction images. A large channel occupied by highly disordered solvent molecules was modeled with a solvent mask; the number of electrons in the void region is consistent with the presence of 0.75 molecules of hexamethyldisiloxane per asymmetric unit. All carbon and oxygen atoms were modeled anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model.

Empirical formula	$C_{160}H_{184}O_{16}$ + 2[C_4H_8O] + 1.5[$C_6H_{18}Si_2O$]
Formula weight	2507.27
Temperature/K	100.15

Crystal system	triclinic
Space group	*P*–1
a/Å	13.3999(13)
b/Å	18.2674(17)
c/Å	18.3598(17)
α/°	109.836(3)
β/°	91.981(3)
γ/°	111.083(3)
Volume/Å^3	3881.2(6)
Z	1
ρ_{calc}g/cm^3	1.073
μ/mm^{-1}	0.071
F(000)	1352.0
Crystal size/mm^3	0.06 × 0.05 × 0.05
Radiation	synchrotron (λ = 0.7288)
2θ range for data collection/°	2.458 to 47.32
Index ranges	$-14 \le h \le 14$, $-20 \le k \le 20$, $-20 \le l \le 20$
Reflections collected	36165

Table S7. Crystal data and structure refinement for **1b**.

References

(1) Kiel, G. R.; Bergman, H. M.; Tilley, T. D. *Chem. Sci.* **2020**, *11*, 3028–3035.
(2) Nitschke, J. R.; Zu, S.; Tilley, T. D. *J. Am. Chem. Soc.*, **2000**, *122*, 10345–10352.
(3) Hoye, T. R.; Eklov, B. M.; Voloshin, M. *Org. Lett.* **2004**, *6*, 2567.
(4) Thordarson, P. *Chem. Soc. Rev.* **2011**, *40*, 1305–1323.
(5) Hibbert, D. B.; Thordarson, P. *Chem. Commun.*, **2016**, *52*, 12792-12805.
(6) http://supramolecular.org
(7) Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
(8) Colwell, C. E.; Price, T. W.; Stauch, T.; Jasti, R. *Chem. Sci.*, **2020**, *11*, 3923-3930.
(9) Grimme, S.; Antony, J.; Ehrlich, S.; Kriege, H. *J. Chem. Phys.* **132**, 154104 (2010
(10) Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8.
(11) Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

(12) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.