Supporting Information for:

Carbon Networks Based on Benzocyclynes. 6. Synthesis of Graphyne Substructures via Directed Alkyne Metathesis

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Experimental

**a. General Data.** $^1$H and $^{13}$C NMR spectra were recorded using a Varian Inova 300 ($^1$H 299.95 MHz, $^{13}$C 75.43 MHz) or Inova 500 ($^1$H 500.10 MHz, $^{13}$C 125.75 MHz) spectrometer. Chemical shifts ($\delta$) are expressed in ppm downfield from tetramethylsilane using the residual non-deuterated solvent as internal standard (CDCl$_3$: $^1$H 7.26 ppm, $^{13}$C 77.0 ppm). IR spectra were recorded using a Nicolet Magan-FTIR 550 spectrometer. UV-Vis spectra were recorded using a Hewlett-Packard 8453 spectrophotometer. Mass spectra were recorded using an Agilent 1100 Series LC/MSD or ION-TOF TOF-SIMS Model IV. Melting points were determined on a Meltemp II apparatus or using a TA Instruments 2920 Modulated DSC. THF was freshly distilled from potassium. 1,2,4,5-Tetraiodobenzene,$^1$ triazine 15,$^2$ 1,2-didecyl-4,5-diiodobenzene,$^3$ and 1,4-dibromo-2,5-diiodobenzene$^4$ were prepared according to literature. All other chemicals were of reagent grade and used as obtained from manufacturers. Pd-, Mo-, and W-catalyzed reactions were carried out in an inert atmosphere (dry N$_2$ or Ar). Column chromatography was performed on Whatman reagent grade silica gel (230-400 mesh). Rotary chromatography was performed on a Harrison Research Chromatotron model 7924T with EM-Science 60PF$_{254}$ silica gel. Precoated silica gel plates (Sorbent Technology, UV$_{254}$, 200 µm, 5 × 20 cm) were used for analytical thin-layer chromatography.

**General Deprotection/Cross-Coupling Procedure.** A suspension consisting of silyl-protected ethynylarene (1 equiv) and K$_2$CO$_3$ (3-5 equiv) in Et$_2$O (0.05 M) and MeOH (0.03 M) was stirred at rt for 1 h. The suspension was diluted with Et$_2$O and washed thrice with H$_2$O. The organic layer was dried over MgSO$_4$ and concentrated in vacuo. Without further purification, a syringe pump was used to deliver a deoxygenated solution of the free acetylene in THF (0.05 M) over 12 h to a stirred, deoxygenated suspension of haloarene, Pd(PPh$_3$)$_4$ (5 mol% per transformation), and CuI (10 mol% per transformation) in THF and i-Pr$_2$NH (1:1 ratio, 0.1 M) at 35-85 °C. The reaction was stirred an additional 12 h at rt under N$_2$, concentrated, and purified by silica gel chromatography.

**General Propyne Coupling Procedure.** A suspension consisting of iodoarene (1 equiv), PdCl$_2$(PPh$_3$)$_2$ (5 mol% per transformation), and CuI (10 mol% per transformation) in THF (0.1 M) and i-Pr$_2$NH (0.1 M) was degassed by bubbling argon. The reaction
mixture was placed under N₂ and heated between 40-50 °C. Propyne was bubbled through the stirred reaction mixture at a rate of ~75 mL/min for 5-10 min and stirring was continued for an additional 30 min. The reaction mixture was concentrated and purified by silica gel chromatography.

b. Synthesis of 6a and 6b.

![Chemical structures and reactions](image)

**4-Butyl-2-iodoaniline (12a).** A suspension consisting of 4-butylaniline (2 g, 13 mmol), BTEA·ICl₂ (5.2 g, 13 mmol), and CaCO₃ (1.6 g, 16 mmol) in CH₂Cl₂ (50 mL) and MeOH (25 mL) was stirred for 1 h. The mixture was filtered, concentrated by rotary evaporation, and dissolved in Et₂O. 5% NaHSO₃ (100 mL) was added and the mixture was extracted four times with Et₂O. The combined organic fractions were dried with MgSO₄, concentrated, and chromatographed on silica with 2:1 CH₂Cl₂:hexanes to afford iodoaniline 12a (2.81 g, 76%) as a red-brown oil. ¹H NMR (300 MHz, CDCl₃): δ 7.46 (d, J = 1.8 Hz, 1H), 6.95 (dd, J = 8.4, 1.8 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 3.95 (br s, 2H), 2.46 (t, J = 7.6 Hz, 2H), 1.60-1.47 (m, 2H), 1.39-1.26 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 144.34, 138.29, 134.60, 129.30, 114.57, 84.31, 34.05,
33.68, 22.12, 13.88. IR (neat): v 3460, 2962, 2903, 2866 cm⁻¹. MS (CI pos) m/z (%): 276 (MH⁺, 10), 275 (M⁺, 100); C₁₀H₁₄IN (275.13).

4-Tetradecyl-2-iodoaniline (12b). A red-brown oil (71%). ¹H NMR (300 MHz, CDCl₃): δ 7.46 (d, J = 1.8 Hz, 1H), 6.95 (dd, J = 8.4, 1.8 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 3.93 (br s, 2H), 2.45 (t, J = 7.5 Hz, 2H), 1.62-1.43 (m, 2H), 1.26 (br s, 22H), 0.89 (t, J = 6.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 144.38, 138.39, 134.83, 129.36, 114.62, 84.36, 34.45, 31.90, 31.63, 29.64 (5C), 29.56, 29.45, 29.33, 29.16, 22.67, 14.11. IR (neat): v 3458, 2959, 2910, 2867 cm⁻¹. MS (CI pos) m/z (%): 416 (MH⁺, 100), 415 (M⁺, 41); C₂₀H₃₄IN (415.17).

Triazene 13a. NaNO₂ (2.9 g, 42 mmol) in H₂O (15 mL) was added dropwise to a stirred, cooled solution (0 ℃) of iodoaniline 12a (10.58 g, 38 mmol) in conc. HCl (12 mL), H₂O (20 mL), CH₃CN (20 mL), and THF (50 mL). The reaction was stirred for an additional 20 min at 0 ℃. Maintaining temperature below 0 ℃, the reaction mixture was added slowly to a stirred solution of Me₂NH (40% aq, 6.5 g, 58 mmol) and K₂CO₃ (8 g, 58 mmol) in THF (20 mL) and H₂O (20 mL) at 0 ℃. The mixture was warmed to rt, extracted twice with Et₂O, and the combined organics were washed with H₂O thrice. The organic layer was dried over MgSO₄, concentrated by rotary evaporation, and filtered through a 2.5 cm silica plug with 1:1 CH₂Cl₂:hexanes to afford a red oil. Without further purification, the intermediate red oil was reacted according to General Propyne Coupling Procedure. The mixture was concentrated and filtered through a 2.5 cm silica plug with 2:1 hexanes:CH₂Cl₂ to afford 13a (8.6 g, 88%) as a red-brown oil. ¹H NMR (300 MHz, CDCl₃): δ 7.29-7.24 (m, 2H), 7.02 (dd, J = 8.3, 2.1 Hz, 1H), 3.37 (br s, 6H), 2.54 (t, J = 7.2 Hz, 2H), 2.10 (s, 3H), 1.62-1.52 (m, 2H), 1.39-1.26 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 149.68, 139.48, 132.61, 128.45, 128.32, 116.89, 89.23, 77.80, 34.81, 33.38, 31.51, 22.56, 22.12, 13.85, 4.61. IR (neat): v 2966, 2933, 2870 cm⁻¹. MS (CI pos) m/z (%): 245 (M⁺+2, 19), 244 (MH⁺, 100), 243 (M⁺, 40); C₁₅H₂₁N₃ (243.35).

Triazene 13b. An orange oil (67%). ¹H NMR (300 MHz, CDCl₃): δ 7.30 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 1.9 Hz, 1H), 7.02 (dd, J = 8.4, 1.9 Hz, 1H), 3.80 (br s, 4H), 2.53 (t, J = 7.8 Hz, 2H), 2.10 (s, 3H), 1.70 (br s, 6H), 1.61-1.52 (m, 2H), 1.25 (br s, 22H), 0.88 (t, J = 6.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 149.65, 139.87, 132.71, 128.50, 118.59, 116.77, 89.34, 77.87, 35.22, 31.89, 31.27, 29.64 (5C), 29.57, 29.49, 29.33, 29.16, 25.24.
Diyne 6a. Arene 13a (2.0 g, 8.2 mmol) in CCl₄ (100 mL) was added dropwise over 30 min to a stirred solution of I₂ (10.4 g, 41 mmol) and HI (48% aq, 7.2 mL, 41 mmol) in CH₃CN (100 mL) at 60 °C. The reaction mixture was stirred for an additional 10 min, diluted with CH₂Cl₂, and then washed successively with saturated NaHCO₃, H₂O, and 5% NaHSO₃. The organic layer was dried with MgSO₄ and concentrated in vacuo. The crude product was extracted with hexanes to afford a yellow oil. A suspension of the intermediate yellow oil (2.1 g, 7 mmol), Pd(PPh₃)₄ (410 mg, 0.35 mmol), and CuI (133 mg, 0.7 mmol) in THF (100 mL) and i-Pr₂NH (100 mL) was degassed by bubbling argon. TMSA (1.4 g, 14 mmol) was added and the mixture was stirred under N₂ for 12 h at 40 °C. The solvent was removed by rotary evaporation and the crude residue was filtered through a 2.5 cm silica plug with 2:1 hexanes:CH₂Cl₂. Silica gel chromatography (hexanes) of the concentrated filtrate afforded 6a (1.8 g, 83%) as a highly viscous, pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 7.34 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 1.5 Hz, 1H), 7.00 (dd, J = 8.3, 1.5 Hz, 1H), 2.54 (t, J = 7.5 Hz, 2H), 2.11 (s, 3H), 1.61-1.50 (m, 2H), 1.36-1.24 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H), 0.28 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 142.8, 131.3, 131.2, 126.9, 120.1, 113.6, 103.5, 95.6, 88.9, 86.9, 82.5, 35.2, 31.8, 30.9, 29.6 (5C), 29.5, 29.4, 29.2, 29.1, 22.5, 14.1, 4.4, 0.0. IR (neat): ν 2962, 2940, 2865 cm⁻¹. MS (Cl pos) m/z (%): 425 (M⁺+2, 39), 424 (MH⁺, 100); C₂₈H₄₅N₃ (423.68).

Diyne 6b. Triazene 13b (500 mg, 1.2 mmol) and MeI (6 mL) were combined in a sealed tube equipped with a stir bar. The reaction was stirred for 12 h at 135 °C and upon cooling, the suspension was filtered. The filtrate was concentrated and chromatographed on silica gel (hexanes) to afford a colorless oil. Without further purification, the intermediate was reacted with TMSA as per 6a to afford 6b as a pale yellow oil (328 mg, 66%). ¹H NMR (300 MHz, CDCl₃): δ 7.34 (d, J = 8.1 Hz, 1H), 7.20 (d, J = 1.5 Hz, 1H), 7.00 (dd, J = 8.1, 1.5 Hz, 1H), 2.54 (t, J = 7.5 Hz, 2H), 2.11 (s, 3H), 1.61-1.47 (m, 2H), 1.26 (br s, 2H), 0.89 (t, J = 6.9 Hz, 3H), 0.27 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 143.3, 131.7, 131.5, 127.5, 126.8, 122.7, 104.0, 97.01, 89.7, 85.5, 35.6, 31.9, 30.9, 29.6 (5C), 29.7, 29.4, 29.3, 29.1, 22.6, 14.1, 4.4, 0.0. IR (neat): ν
2924, 2853, 2159 cm\(^{-1}\). MS (CI pos) \(m/z\) (%): 481 (MH\(^+\)+THF, 13), 480 (M\(^+\)+THF, 37), 479 (M\(^+\)-1+THF, 100); C\(_{28}\)H\(_{44}\)Si (408.73).

c. Synthesis of 6c.

\[
\begin{array}{c}
\text{Dec} & \text{I} & \text{TMS} \\
\text{Dec} & \text{I} & \text{TMS}
\end{array}
\xrightarrow{\text{TMSA, Pd(PPh}_3)_4, \text{CuI, i-Pr}_2\text{NH, 80 °C}}
\begin{array}{c}
\text{Dec} & \text{TMS} & \text{propyne, Pd(PPh}_3)_4, \text{CuI, i-Pr}_2\text{NH, 45 °C}
\end{array}
\xrightarrow{51\%}
\begin{array}{c}
\text{Dec} & \text{TMS} \\
\text{Dec} & \text{TMS}
\end{array}
\xrightarrow{94\%}
\begin{array}{c}
\text{Dec} & \text{TMS} \\
\text{Dec} & \text{TMS}
\end{array}
\]

**Iodoarene 14.** A suspension of 1,2-didecyl-4,5-diiodobenzene (2.05 g, 3.4 mmol), Pd(PPh\(_3\))\(_4\) (194 mg, 0.2 mmol), and CuI (64 mg, 0.4 mmol) in i-Pr\(_2\)NH (25 mL) was degassed by bubbling argon. TMSA (333 mg, 3.4 mmol) was added and the mixture was stirred in a sealed tube at 80 °C for 3 h. The solvent was removed by rotary evaporation and the crude residue was filtered through a 2.5 cm silica plug with 5:1 hexanes:CH\(_2\)Cl\(_2\). Silica gel chromatography (hexanes) of the concentrated filtrate afforded 14 (1 g, 51%) as a pale yellow oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.58 (s, 1H), 7.25 (s, 1H), 2.59-2.41 (m, 4H), 1.60-1.53 (m, 4H), 1.27 (s, 28H), 0.89 (t, \(J = 6.6\) Hz, 6H), 0.28 (s, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 143.33, 140.64, 138.97, 133.30, 126.68, 106.90, 97.66, 97.17, 32.22, 32.09, 30.91, 29.60, 29.56, 29.47, 29.41, 29.33, 22.69, 14.13, -0.12. IR (neat): \(\nu\) 2960, 2943, 2866, 2158 cm\(^{-1}\). MS (CI pos) \(m/z\) (%): 580 (M\(^+\), 39), 579 (M\(^+\)-1, 100); C\(_{31}\)H\(_{53}\)Si (580.30).

**Diyne 6c.** Arene 14 (1.1 g, 1.9 mmol) was reacted according to General Propyne Coupling Procedure. The crude residue was successively filtered through two 2.5 cm silica plugs with Et\(_2\)O and then hexanes to afford 6c (870 mg, 94%) as a yellow oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.21 (s, 1H), 7.15 (s, 1H), 2.54 (t, \(J = 7.5\) Hz, 4H), 1.60-1.49 (m, 4H), 1.26 (s, 28H), 0.88 (t, \(J = 6.3\) Hz, 6H), 0.26 (s, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 141.28, 140.21, 132.44, 132.17, 124.18, 122.59, 104.35, 96.51, 88.79, 78.52, 32.40, 32.33, 31.90, 30.88, 30.82, 29.66, 29.60, 29.56, 29.50, 29.33, 22.69, 14.11, 4.44, 0.51. IR (neat): \(\nu\) 2956, 2925, 2853, 2155 cm\(^{-1}\). MS (CI pos) \(m/z\) (%): 565 (MH\(^+\)+THF, 39), 564 (M\(^+\)+THF, 100), 563 (M\(^+\)-1+THF, 100); C\(_{33}\)H\(_{56}\)Si (492.42).
e. Synthesis of 8.

**Tetrayne 16.** Diethynylarene 6b (500 mg, 1.2 mmol) was reacted with triazene 15 (266 mg, 0.55 mmol) according to General Deprotection/Cross-Coupling Procedure at 35 °C. The residue was filtered through a 2.5 cm silica plug with 2:1 hexanes:CH₂Cl₂ and the filtrate concentrated in vacuo. Purification via column chromatography (2:1 hexanes:CH₂Cl₂) afforded 16 (343 mg, 70%) as a bright yellow, amorphous solid. ¹H NMR (500 MHz, CDCl₃):  δ 7.81 (s, 1H), 7.67 (s, 1H), 7.48 (dd,  J = 7.8, 5 Hz, 2H), 7.26 (br s, 2H), 7.05 (d,  J = 7.8 Hz, 2H), 3.41 (br d, 6H), 2.57 (t,  J = 7.5 Hz, 4H), 2.03 (s, 3H), 2.01 (s, 3H), 1.65-1.58 (m, 4H), 1.27 (br s, 44H), 0.89 (t,  J = 7.3 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃):  δ 147.39, 143.22, 143.18, 136.37, 131.96, 131.91, 131.71, 131.63, 127.57 (2C), 126.46, 126.36, 125.40, 123.21, 122.93, 122.87, 121.35, 119.13, 93.20, 92.62, 90.78, 90.31, 90.04, 89.99, 78.73, 78.68, 42.50, 36.33, 35.66, 31.91, 31.01, 29.64, 29.55, 29.46, 29.35, 29.20, 22.67, 14.09, 4.51. IR (neat): ν 2943, 2833, 2156 cm⁻¹. MS (Cl pos) m/z (%): 968 (MH⁺+THF, 15), 900 (M⁺+5, 19), 898 (M⁺+3, 100), 897 (M⁺+2, 63), 896 (MH⁺, 87); C₅₈H₇₈BrN₃ (895.44).
Pentayne 17. A degassed suspension consisting of arene 16 (2.05 g, 2.3 mmol), TMSA (562 mg, 5.7 mmol), Pd(PPh₃)₄ (132 mg, 0.11 mmol), and CuI (50 mg, 0.23 mmol) in THF (50 mL) and i-Pr₂NH (50 mL) was stirred at 80 °C for 12 h in a sealed tube. After cooling of the reaction vessel, the mixture was concentrated, filtered through a 2.5 cm silica plug (2:1 hexanes:CH₂Cl₂), and purified by silica gel chromatography (2:1 hexanes:CH₂Cl₂) to afford 17 (1.97 g, 94%) as a yellow, amorphous solid. ¹H NMR (300 MHz, CDCl₃): δ 7.71 (s, 1H), 7.69 (s, 1H), 7.48 (dd, J = 8.1 , 5.8 Hz, 2H), 7.26 (br s, 2H), 7.05 (d, J = 8.1 Hz, 2H), 3.42 (br d, 6H), 2.57 (t, J = 7.5 Hz, 4H), 2.01 (s, 6H), 1.65-1.57 (m, 4H), 1.27 (br s, 44H), 0.89 (t, J = 6.6 Hz, 6H), 0.27 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 151.07, 143.20, 142.95, 136.87, 131.94 (2C), 131.70, 131.58, 127.51 (2C), 126.48, 126.25 (2C), 123.03, 122.90, 121.94, 120.29, 117.88, 102.32, 100.01, 93.44, 92.53, 91.33, 90.70, 89.99, 89.90, 78.70 (2C), 43.01, 35.99, 35.63, 31.88, 30.93, 29.64, 29.62, 29.52, 29.43, 29.32, 29.16, 22.65, 14.07, 4.47, 4.44, 0.016. IR (neat): ν 2955, 2924, 2850, 2150 cm⁻¹. MS (Cl pos) m/z (%): 916 (M⁺+2, 43), 915 (MH⁺, 82), 914 (M⁺, 100); C₆₃H₈₇N₃Si (914.47).

Hexayne 8. Pentayne 17 (1.05 g, 1.1 mmol) in CCl₄ (100 mL) was added dropwise over 30 min to a stirred solution of I₂ (1.5 g, 5.8 mmol) and HI (55% aq, 0.9 mL, 5.8 mmol) in CH₃CN (100 mL) at 60 °C. The reaction mixture was stirred for an additional 10 min, diluted with CH₂Cl₂, and then washed successively with saturated NaHCO₃, H₂O, and 5% NaHSO₃. The organic layer was dried with MgSO₄, concentrated in vacuo, and extracted with hexanes to afford a light brown, highly viscous oil. Without further purification, the intermediate oil was reacted according to General Propyne Coupling Procedure. Purification by silica gel chromatography (5:1 hexanes:CH₂Cl₂) afforded 8 (698 mg, 72%) as a light brown solid. Mp: 61-63 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.67 (s, 1H), 7.59 (s, 1H), 7.48 (dd, J = 7.8, 2.7 Hz, 2H), 7.26 (br s, 2H), 7.07 (d, J = 7.8 Hz, 2H), 2.58 (t, J = 8.1 Hz, 4H), 2.15 (s, 3H), 2.01 (s, 6H), 1.65-1.56 (m, 4H), 1.28 (br s, 44H), 0.91 (t, J = 7.2 Hz, 6H), 0.31 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 143.49, 143.43, 135.48, 135.05, 132.18, 132.12, 131.79, 131.76, 127.57 (2C), 126.44 (2C), 126.22, 125.59, 124.81, 124.78, 122.61, 122.56, 102.91, 99.90, 94.47, 94.15, 92.12, 90.18, 90.14 (2C), 90.11, 78.56, 78.54, 77.78, 35.67, 31.92, 31.58, 31.02, 29.64, 29.55, 29.46, 29.35, 29.20, 22.68, 14.10, 4.55, 4.49, 0.14. IR (neat): ν 2924, 2853, 2156 cm⁻¹.
MS (CI pos) m/z (%): 953 (M⁺+THF, 43), 883 (M⁺+2, 33), 882 (MH⁺, 51), 881 (M⁺, 64); C₆₄H₆₄Si (881.44).

e. Synthesis of 3a-c, 4, and 7-11.

Octayne 7a. Diethynylarene 6a (1.4 g, 5.2 mmol) was reacted with 1,2,4,5-tetraiodobenzene (500 mg, 0.86 mmol) according to General Deprotection/Cross-Coupling Procedure at 50 °C. The residue was filtered through a 2.5 cm silica plug with 1:1 hexanes:CH₂Cl₂ and the filtrate concentrated in vacuo. Purification via Chromatotron (5:1 hexanes:CH₂Cl₂) afforded 7a (536 mg, 73%) as a light yellow solid. Mp: 140-142 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.77 (s, 2H), 7.49 (d, J = 7.8 Hz, 4H), 7.27 (d, J = 1.5 Hz, 4H), 7.06 (dd, J = 7.8, 1.5 Hz, 4H), 2.59 (t, J = 7.5 Hz, 8H), 2.01 (s, 12H), 1.62-1.54 (m, 8H), 1.39-1.31 (m, 8H), 0.93 (t, J = 7.2 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 143.49, 135.63, 132.19, 131.84, 127.66, 126.43, 125.23, 122.62, 94.35, 90.38, 90.21, 78.58, 35.36, 33.17, 22.24, 13.92, 4.55. UV-Vis (CH₂Cl₂): λmax (ε) 233 (89,900), 266 (64,900), 270 (79,000), 367 (41,000) nm. IR (neat): ν 2955, 2929, 2858, 2207 cm⁻¹. MS (CI pos) m/z (%): 858 (M⁺+3, 25), 857 (M⁺+2, 66), 856 (MH⁺, 100), 855 (M⁺, 43); C₆₆H₆₂ (855.20).

Octayne 7b. A yellow solid (76%). Mp: 77-79 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.76 (s, 2H), 7.48 (d, J = 7.8 Hz, 4H), 7.26 (br s, 4H), 7.05 (d, J = 8.1 Hz, 4H), 2.57 (t, J = 7.5 Hz, 8H), 2.00 (s, 12H), 1.65-1.51 (m, 8H), 1.26 (br s, 88H), 0.88 (t, J = 6.3 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 143.53, 135.64, 132.18, 131.82, 127.65, 126.44, 125.24, 122.63, 94.35, 90.39, 90.21, 78.60, 35.70, 31.92, 31.06, 29.65 (5C), 29.56, 29.47, 29.36, 29.22, 22.69, 14.13, 4.55. IR (neat): ν 2923, 2850, 2199 cm⁻¹. MS (CI pos) m/z (%): 1419 (M⁺+3, 17), 1418 (M⁺+2, 83), 1417 (MH⁺, 98), 1416 (M⁺, 100); C₁₀₆H₁₄₂ (1416.26).

Octayne 7c. An amorphous, yellow solid (77%). ¹H NMR (300 MHz, CDCl₃): δ 7.76 (s, 2H), 7.37 (s, 4H), 7.21 (s, 4H), 2.63-2.45 (m, 16H), 1.98 (s, 12H), 1.63-1.51 (m, 16H), 1.26 (br s, 112H), 0.98-0.81 (m, 24H). ¹³C NMR (75 MHz, CDCl₃): δ 141.40, 140.22, 135.24, 133.05, 132.35, 125.38, 123.77, 122.66, 94.62, 90.11, 89.33, 32.52, 32.35, 31.94, 31.92, 30.95, 30.89, 29.76, 29.71, 29.67, 29.64, 29.60, 29.55, 29.39, 29.36, 22.70, 14.11,
4.66, 4.54. IR (neat): ν 2961, 2937, 2840, 2200 cm⁻¹. MS (CI pos) m/z (%): 1754 (M⁺+3, 100), 1753 (M⁺+2, 95), 1752 (MH⁺, 71); C₁₃₀H₁₉₀ (1751.49).

**Bis[12]cyclyne 3c.** A suspension of 7a (70 mg, 0.08 mmol) and (t-BuO)₃W≡C-t-Bu (50 mol%) in toluene was heated for 24 h at 80 °C under an Ar atmosphere. Concentration in vacuo, purification via Chromatotron (2:1 hexanes:CH₂Cl₂), and precipitation with cold Et₂O afforded 3c (28 mg, 46%) as a bright yellow solid. Mp: 225 °C (dec). ¹H NMR (500 MHz, CDCl₃): δ 7.30 (s, 2H), 7.22 (d, J = 8 Hz, 4H), 7.20 (br s 4H), 7.00 (d, J = 8 Hz, 4H), 2.59 (t, J = 7.5 Hz, 8H), 1.62-1.54 (m, 8H), 1.39-1.31 (m, 8H), 0.93 (t, J = 7.5 Hz, 12H). ¹³C NMR: insufficient solubility to obtain spectrum. UV-Vis (CH₂Cl₂): λ max (ε) 286 (49,100), 295 (61,600), 305 (119,300), 318 (64,700), 329 (70,300), 343 (97,800), 380 (10,600), 399 (10,800) nm. Fluorescent emission ([3c] ≤ 5 × 10⁻⁵ M in toluene; Φₑ = 0.19; 399 nm excitation): λ max 488, 525, 546 nm. IR (neat): ν 2955, 2934, 2861, 2217 cm⁻¹. MS (CI pos) m/z (%): 820 (MH⁺+THF, 52), 819 (M⁺+THF, 82), 748 (MH⁺, 33); C₅₈H₅₀ (747.02).

**Bis[12]cyclyne 3d.** A solution of 7b (50 mg, 0.035 mmol), EtC≡Mo[N(t-Bu)(3,5-C₆H₃Me₂)]₃ (7 mg, 0.01 mmol), and silanol-POSS (58 mg, 0.06 mmol) in 1,2,4-trichlorobenzene (1.1 mL) was heated for 30 min at 75 °C and 1 torr. Removal of solvent by distillation and trituration of the crude residue with cold Et₂O afforded 3d (40 mg, 87%) as a bright yellow solid. Mp: 110-112 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.30 (s, 2H), 7.22 (d, J = 7.9 Hz, 4H), 7.18 (d, J = 1.3 Hz, 4H), 7.00 (dd, J = 7.9, 1.3 Hz, 4H), 2.53 (t, J = 7.3 Hz, 8H), 1.65-1.50 (m, 8H), 1.26 (br s, 88H), 0.88 (t, J = 6.9 Hz, 12H). ¹³C NMR: insufficient solubility to obtain spectrum. UV-Vis (CH₂Cl₂): λ max (ε) 288 (58,000), 296 (70,600), 306 (115,500), 319 (70,200), 331 (72,200), 344 (97,600), 381 (16,100), 399 (13,100) nm. Fluorescent emission ([3d] ≤ 5 × 10⁻⁵ M in toluene; 399 nm excitation): λ max 488, 525, 546 nm. IR (neat): ν 2925, 2857, 2212 cm⁻¹. MS (CI pos) m/z (%): 1380 (MH⁺+THF, 43), 1379 (M⁺+THF, 79), 1309 (M⁺+2, 85), 1308 (MH⁺, 100), 1307 (M⁺, 83); C₉₈H₁₃₀ (1307.02).

**Bis[12]cyclyne 3e.** A solution of 7c (60 mg, 0.03 mmol), EtC≡Mo[N(t-Bu)(3,5-C₆H₃Me₂)]₃ (13.6 mg, 0.02 mmol), and silanol-POSS (112 mg, 0.12 mmol) in 1,2,4-trichlorobenzene (20 mL) was heated for 14 h at 75 °C under 1 torr. The solvent was removed by distillation and the crude material was purified by silica gel chromatography.
(3:1 hexanes:CH₂Cl₂) to afford 3e (44 mg, 91%) as a bright yellow solid. Mp: 111-112 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.28 (s, 2H), 7.11 (s, 4H), 7.07 (s, 4H), 2.51 (t, J = 7.5 Hz, 16H), 1.65-1.47 (m, 16H), 1.28 (br s, 112H), 0.89 (t, J = 7.2 Hz, 24H). ¹³C NMR (75 MHz, CDCl₃): δ 141.97, 141.37, 134.49, 132.55, 132.32, 126.45, 124.20, 123.43, 95.19, 92.19, 91.07, 32.44, 32.32, 31.90, 30.67, 30.56, 29.70, 29.63, 29.59, 29.52, 29.53, 27.25, 26.99, 22.69, 14.11. UV-Vis (CH₂Cl₂): λmax (ε) 292 (40,000), 300 (54,000), 311 (118,000), 322 (60,000), 333 (62,700), 347 (99,500), 381 (7,700), 401 (6,700) nm. Fluorescent emission ([3e] ≤ 5 × 10⁻⁵ M in toluene; Φₖ = 0.21; 399 nm excitation): λmax 495, 533, 553 nm. IR (neat): ν 2953, 2923, 2851, 2212 cm⁻¹. MS (TOF-SIMS, pos, Bi₃⁺) m/z: 1645.6 (M++2), 1644.6 (MH+), 1643.6 (M+); C₁₂₂H₁₇₈ (1643.39).

Polyyne 9. Hexayne 8 (200 mg, 0.23 mmol) was reacted with 1,2-didecyl-4,5-diodobenzene (55 mg, 0.09 mmol) according to General Deprotection/Cross-Coupling Procedure at 85 °C. The residue was filtered through a 2.5 cm silica plug with 3:1 hexanes:CH₂Cl₂ and the filtrate concentrated in vacuo. Purification via column chromatography (4:1 hexanes:CH₂Cl₂) afforded 9 (145 mg, 81%) as an amorphous orange-brown solid. ¹H NMR (300 MHz, CDCl₃): δ 7.79 (s, 2H), 7.62 (s, 2H), 7.48-7.39 (m, 6H), 7.26 (s, 2H), 7.22 (s, 2H), 7.06-7.00 (m, 4H), 2.71-2.43 (m, 12H), 2.01 (s, 6H), 1.98 (s, 6H), 1.87 (s, 6H), 1.67-1.53 (m, 12H), 1.26 (br s, 116H), 0.89 (t, J = 7.2 Hz, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 143.41, 143.33, 141.58, 135.65, 135.37, 132.98, 132.26 (2C), 131.71 (2C), 127.61, 127.57, 126.49, 126.39, 125.78, 125.27, 125.22, 124.86, 122.79, 122.75, 122.65, 94.21, 94.18, 93.66, 93.51, 92.41, 90.84, 90.52, 90.30, 90.23, 90.17, 78.57, 77.98, 35.71, 35.70, 32.52, 32.49, 31.92, 31.01, 30.88, 29.66, 29.59, 29.48, 29.36, 29.27, 29.24, 22.69, 14.11, 4.71, 4.51, 4.40. UV-Vis (CH₂Cl₂): λmax (ε) 248 (98,900), 266 (98,100), 314 (87,000), 366 (56,000) nm. IR (neat): ν 3056, 2934, 2852, 2195 cm⁻¹. MS (Cl pos) m/z (%): 1975 (M⁺+3, 33), 1974 (M⁺+2, 37), 1972 (M⁺, 63), 962 (100); C₁₄₈H₁₉₄ (1971.50).

Tris[12]cyclyne 4. a) Using W-catalyst: A suspension of polyyne 9 (140 mg, 0.07 mmol) and (t-BuO)₅W≡C-t-Bu (100 mol%) in toluene was heated for 4 h at 80 °C under an Ar atmosphere. Concentration in vacuo and purification via Chromatotron (5:1 hexanes: CH₂Cl₂) afforded 4 (25 mg, 19%) as a bright orange solid. b) Using Mo-catalyst: Reaction of 9 (40 mg, 0.02 mmol) with EtC≡Mo[N(t-Bu)(3,5-C₆H₃Me₂)]₃ (6
mg, 0.008 mmol) and silanol-POSS (49 mg, 0.05 mmol) in 1,2,4-trichlorobenzene (5 mL) for 3 h at 75 °C and 1 torr afforded 10 mg of 4 (31%). Mp: 183-185 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.21-7.15 (m, 12H), 7.07 (s, 2H), 6.98 (dd, $J = 7.0, 1.9$ Hz, 4H), 2.53 (br s, 12H), 1.62-1.54 (m, 12H), 1.26 (br s, 116H), 0.95-0.92 (m, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.90, 144.10, 144.05, 142.19, 134.71, 134.66, 132.49, 131.95 (2C), 128.86, 126.93, 126.75 (2C), 126.73, 126.65, 126.43, 125.89, 123.62, 123.59 (2C), 123.56, 95.36, 95.21, 95.05, 93.91, 92.74, 92.64, 91.50, 91.44, 91.13, 35.66, 31.93, 30.85, 30.42, 29.69, 29.66, 29.61, 29.56, 29.47, 29.36, 29.24, 22.69, 14.12. UV-Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$) 267 (54,000), 305 (71,300), 327 (128,000), 318 (64,700), 357 (135,700), 411 (25,200), 430 (10,500), 461 (6,800), 511 (2,700) nm. Fluorescent emission ([4] $\leq 5 \times 10^{-5}$ M in toluene or CH$_2$Cl$_2$; $\Phi_F = 0.27$; 411 nm excitation): $\lambda_{\text{max}}$ 515, 557, 579 nm. IR (neat): $\nu$ 2924, 2852, 2212 cm$^{-1}$. MS (tof-SIMS, pos, Bi$_3^+$) m/z: 1811.1 (M$^{++2}$), 1810.6 (MH$^+$), 1809.1 (M$^+$); C$_{136}$H$_{176}$ (1809.38).

**Tetrayne 10.** Diyne 6b (110 mg, 0.27 mmol) was reacted with 1,4-dibromo-2,5-diodobenzene (62 mg, 0.13 mmol) according to General Deprotection/Cross-Coupling Procedure at 30 °C. The residue was filtered through a 2.5 cm silica plug with 2:1 hexanes:CH$_2$Cl$_2$ and the filtrate concentrated in vacuo. Purification via column chromatography (3:1 hexanes:CH$_2$Cl$_2$) afforded 10 (103 mg, 90%) as a pale yellow solid. Mp: 109-110 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.78 (s, 2H), 7.45 (d, $J = 7.8$ Hz, 2H), 7.27 (br s, 2H), 7.09 (br d, $J = 8.1$ Hz, 2H), 2.57 (t, $J = 7.5$ Hz, 4H), 2.15 (s, 6H), 1.63-1.57 (m, 4H), 1.25 (br s, 44H), 0.88 (t, $J = 6.5$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.19, 136.33, 132.05, 127.79, 126.61, 126.53, 123.15, 121.77, 121.36, 95.99, 90.32, 89.38, 78.51, 35.71, 31.93, 31.00, 29.66, 29.54, 29.44, 29.36, 29.17, 22.70, 14.14, 4.89. IR (neat): $\nu$ 2935, 2874, 2165 cm$^{-1}$. MS (CI pos) m/z (%): 976 (M$^{++2}$+THF, 43), 906 (M$^{++4}$, 13), 905 (M$^{++3}$, 27), 903 (MH$^+$, 17), 743 (100); C$_{56}$H$_{72}$Br$_2$ (902.4).

**Polyyne 11.** Hexayne 8 (134 mg, 0.15 mmol) was reacted with tetrayne 10 (60 mg, 0.06 mmol) according to General Deprotection/Cross-Coupling Procedure at 85 °C. The residue was filtered through a 2.5 cm silica plug with 3:2 hexanes:CH$_2$Cl$_2$ and the filtrate concentrated in vacuo. Purification via Chromatotron (3:1 hexanes:CH$_2$Cl$_2$) afforded 11 (102 mg, 65%) as a bright yellow, waxy solid. Mp: >175 °C (dec). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.81 (s, 2H), 7.98 (s, 2H), 7.65 (s, 2H), 7.54-7.46 (m, 6H), 7.26 (br s, 6H), 7.07 (s, 2H), 6.98 (dd, $J = 7.0, 1.9$ Hz, 4H), 2.53 (br s, 12H), 1.62-1.54 (m, 12H), 1.26 (br s, 116H), 0.95-0.92 (m, 18H).
7.10-7.04 (m, 6H), 2.61 (t, J = 7.7 Hz, 8H), 2.52 (t, J = 7.9 Hz, 4H), 2.09 (s, 6H), 2.05 (s, 6H), 2.03 (s, 6H), 1.87 (s, 6H), 2.63-2.47 (m, 12H), 1.28 (br s, 132H), 0.90 (t, J = 6.9 Hz, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 143.82, 143.60, 143.48, 135.81, 135.62, 135.61, 135.44, 132.35, 132.21, 132.19, 131.95, 131.83, 131.50, 127.88, 127.64, 127.53, 126.60, 126.49, 126.39, 125.91, 125.79, 125.61, 125.18, 124.92, 124.72, 122.69, 122.61, 122.32, 94.99, 94.73, 94.22, 93.66, 92.72, 92.71, 90.43, 90.35, 90.23, 90.18, 90.09 (2C), 78.67, 78.58, 78.49, 77.85, 35.72, 35.70, 31.93, 31.06, 31.05, 30.94, 29.68, 29.57, 29.47, 29.36, 29.29, 29.27, 22.69, 14.11, 4.64, 4.56, 4.37. UV-Vis (CH$_2$Cl$_2$): $\lambda_{max}$ (e) 251 (117,000), 312 (72,300), 365 (59,800), 424 (36,900) nm. IR (neat): $\nu$ 2963, 2901, 2873, 2187 cm$^{-1}$. MS (Cl pos) m/z (%): 2361 (MH$^+$, 72), 2360 (M$^+$, 100); C$_{178}$H$_{222}$ (2359.74).

References
r^1 = C_{19}H_{37}\text{dec}

r^2 = \text{Dec}