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Macrocyclic 1,8-Anthrylene—Ethynylene Oligomers: A Novel Three-Dimensional π Conjugated Architecture

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Experimental Details

Melting points are uncorrected. Elemental analyses were performed by a Perkin-Elmer 2400 series analyzer. NMR spectra were measured on a Varian Gemini-300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) or a JEOL Lambda-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometer. High-resolution FAB mass spectra were measured on a JEOL MStation-700 spectrometer. MALDI-TOF mass spectra were measured on a Voyager-biocad spectrometer. UV spectra were measure on a Hitachi U-3000 spectrometer with a 10 mm cell. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer with a 10 mm cell. GPC was carried out on a Japan Analytical Industry Co. LC-908 recycling preparative HPLC system with 20 mm ϕ × 600 mm JAIGEL-1H, 2H columns with chloroform eluent.

1,8-Bis[(triisopropylsilyl)ethynyl]anthracene (**4a**). This compound was prepared in a similar manner as the procedure described in the literature.[1] A solution of [(triisopropylsilyl)ethynyl]magnesium bromide was prepared by the treatment of (triisopropylsilyl)ethyne (7.29 mL, 32.5 mmol) and 10.0 mL (30 mmol) of 3.0 mol L^{-1} diethyl ether solution of ethylmagnesium bromide in 100 mL of THF. This solution was added dropwise to a solution of 1,8-dichloroanthracene.[2] (2.00 g, 8.13 mmol), [Ni(acac)$_2$] (14.6 mg, 0.057 mmol), and triphenylphosphine (53.2 mg, 0.033 mmol) in 50 mL of THF. The mixture was refluxed for 2 days under Ar atmosphere, and then quenched by slow addition of 20 mL of water. The organic layer was separated, dried over magnesium sulfated, and evaporated. The crude produced was purified by chromatography on silica gel with hexane eluent to give yellow crystals. An analytical sample was obtained by recrystallization from ethanol. Yield 4.39 g (99%); m.p. 176–177 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ= 1.19-1.28 (m, 42H, ^{i}Pr), 7.42 (dd, J = 1.5, 8.5 Hz, 2H, H-3,6), 7.82 (d, J = 7.0 Hz, 2H, H-4,5), 7.97 (d, J = 8.6 Hz, 2H, H-2,7), 8.42 (s, 1H, H-10), 9.27 (s, 1H, H-9); ^{13}C NMR (75 MHz, CDCl$_3$): δ= 11.61, 18.87, 96.74, 105.81, 121.74, 123.69, 124.93, 127.78, 129.06, 131.04, 131.37,

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[1] H. E. Katz, *J. Org. Chem.* **1989**, 54, 2179-2183.
[2] H. O. House, D. G. Koepsell and W. J. Campbell, *J. Org. Chem.*, **1972**, 37, 1003-1009.

133.37. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 263 (151000), 292 (10600), 305 (14100), 353 (4770), 371 (10300), 392 (18000), 414 nm (17700); Anal. Calcd for $C_{36}H_{50}Si_2$: C, 80.23; H, 9.35. Found: C, 80.21; H, 9.55.

1-Ethynyl-8-[(triisopropylsilyl)ethynyl]anthracene (**5a**). To a solution of 1,8-bis[(triisopropylsilyl)ethynyl]anthracene (100 mg, 186 mmol) in 50 mL of dichloromethane was added 186 mL (186 mmol) of 1.0 mol L^{-1} solution of tetrabutylammonium fluoride (TBAF) in THF. The solution was stirred for 20 min at room temperature. The solvent was removed by evaporation, and the residue was extracted with dichloromethane. The organic solution was washed with brine, dried over magnesium sulfate, and evaporated. The products were separated by chromatography on silica gel with hexane eluent. The desired compound (R_f 0.20, hexane) was obtained as yellow oil with the recovery of 31 mg (31%) of the starting material (R_f 0.29, hexane). Yield 33 mg (33%); m.p. 176-177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.16-1.24 (m, 21H, ^{i}Pr), 3.49 (s, 1H, C≡CH), 7.43 (d, J = 6.9 Hz, 1H), 7.45 (d, J = 6.9 Hz, 1H), 7.79 (d, J=7.0 Hz, 2H), 8.01 (t, J = 8.8 Hz, 2H,), 8.45 (s, 1H, H-10), 9.64 (s, 1H, H-9); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 11.44, 18.93, 81.79, 82.48, 96.28, 105.00, 120.24, 121.61, 123.90, 124.75, 124.98, 127.46, 128.92, 129.04, 129.43, 131.18, 131.30, 131.42, 131.50, 131.60; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 261 (121000), 287 (9910), 300 (11800), 349 (4300), 367 (9350), 387 (15800), 409 nm (15400); HR FAB MS: *m/z* 383.2166 [M+H$^+$]; calcd for $C_{27}H_{30}Si$; *m/z* 383.2195 [M+H$^+$].

1^8,7^8-Bis[(triisopropylsilyl)ethynyl]-1,7(1),4(1,8)-trianthracenaheptan-2,5-diyne (**6a**). To a degassed solution of 1-ethynyl-8-[(triisopropylsilyl)ethynyl]anthracene (1.02g, 2.68 mmol), 1,8-diiodoanthracene[3] (383 mg, 0.892 mmol) in a mixture of 50 mL of THF and 50 mL of triethylamine were added [Pd(PPh_3)$_4$] (154 mg, 0.134 mmol), CuI (25.4 mg, 0.134 mmol), and PPh_3 (40.2 mg, 0.132 mmol). The solution was refluxed for 48 h under Ar atmosphere. After the solvent was removed by evaporation, the residue was chromatographed on silica gel with hexane/dichloromethane (10:1) as eluent. Recrystallization from hexane-dichloromethane gave the desired compound as yellow crystal. Yield 769 mg (92%); m.p. 281—282 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.62–0.77 (m, 42H, ^{i}Pr), 6.53 (m, 2H), 7.31–7.54 (m, 8H), 7.66 (d, J = 7.3 Hz, 2H), 7.85 (m, 4H), 8.54 (s, 1H), 9.22 (s, 2H), 9.96 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 11.31, 18.41, 92.07, 93.18, 96.39, 104.91, 120.76, 121.85, 122.36, 123.57, 124.42, 124.58, 125.10, 127.08, 127.11, 128.20, 128.74, 128.76, 130.08, 130.77, 131.03, 131.08, 131.52, 131.67, 132.03; λ_{max} (ε) = 252 (157000), 305 (15300), 394 (26000), 413 nm (29400); Anal. Calcd for $C_{68}H_{66}Si_2$: C, 86.94; H, 7.08. Found: C, 86.76; H, 7.00. MALDI-TOF MS: *m/z* 938.43 [M^+]; calcd for $C_{68}H_{66}Si_2$; *m/z* 938.47 [M^+].

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[3] J. M. Love II and J. A. Joule, *Syn. Commun.*, **1997**, 27, 1209-1215.

1^8-Ethynyl-7^8-(triisopropylsilyl)ethynyl-1,7(1),4(1,8)-trianthracenaheptan-2,5-diyne (**7a**). To a solution of **6a** (100 mg, 0.106 mmol) in 180 mL of dichloromethane was added 30 mL (0.030 mmol) of a 1.0 mol/L THF solution of TBAF. The solution was stirred for 60 min at room temperature with monitoring the course of reaction by TLC. The reaction mixture was quenched by addition of 5 mL of water. The organic layer was separated, dried over magnesium sulfate, and evaporated. The residue was chromatographed on silica gel with hexane-dichloromethane (2:1) as eluent. The second fraction (R_f 0.38, hexane-dichloromethane 2:1) was collected, and the subsequent recrystallization from chloroform afforded 39 mg (47%) of the mono desilylated product as yellow solid. The starting material was recovered as the most easily eluted fraction (15 mg, 30%, R_f 0.47), and a small amount of the completely desilylated product was obtained as the third fraction (R_f 0.21). m.p. 133—136 °C (dec); ^{1}H NMR (300 MHz, CDCl$_3$): δ= 0.52–0.77 (m, 21H, ^{i}Pr), 2.98 (s, 1H, C≡CH), 6.60–6.56 (m, 1H), 6.80–6.85 (m, 1H), 7.15–8.13 (m, 20H), 8.57 (s, 1H), 9.33 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ= 11.3, 18.4, 81.6, 82.5, 92.5, 92.8, 93.3, 93.5, 96. 3, 104.95, 120.44, 120.87, 120.92, 121.75, 122.25, 123.70, 124.27, 123.31, 124.45, 124.55, 124.63, 125.16, 125.19, 125.27, 126.71, 127.06, 127.26, 128.10, 128.38, 128.72, 128.80, 128.89, 129.75, 130.75, 130.18, 130.27, 130.57, 130.66, 130.74, 130.78, 130.90, 130.97, 131.04, 131.58, 131.68, 131.77, 131.94. HR FAB MS: *m/z* 782.3356 [M+H$^+$]; calcd for $C_{59}H_{46}Si$; *m/z* 782.3369 [M+H$^+$]. Data of 1,8-bis[(8-ethynyl-1-anthryl)ethynyl]anthracene. Yellow powder; m.p. 259—263 °C (dec); ^{1}H NMR (300 MHz, CDCl$_3$): δ= 2.79 (s, 2H), 6.75-6.81 (m, 2H), 7.17-7.21 (m, 4H), 7.48-7.69 (m, 6H), 7.93-7.96 (m, 4H), 8.11 (d, J = 8.3 Hz, 2H), 8.58 (s, 1H), 9.39 (s, 2H), 10.29 (s, 1H).

1^8-Iodo-10^8-(triisopropylsilyl)ethynyl-1,10(1),4,7(1,8)-tetraanthracenadecan-2,5,8-triyne (8a). To a degassed solution of **7a** (78.2 mg, 100 mmol) and 1,8-diiodoanthracene (129 mg, 300 mmol) in a mixture of 15 mL of THF and 35 mL of triethylamine were added [Pd(PPh$_3$)$_4$] (23.2 mg, 0.020 mmol), CuI (1.9 mg, 0.010 mmol), and PPh$_3$ (5.3 mg, 0.020 mmol). The solution was refluxed for 48 h under Ar atmosphere. The solvent was removed by evaporation and the crude product was purified by chromatography on silica gel with hexane/dichloromethane (2:1) as eluent to give yellow solid. Yield 51 mg (47%); m.p. 182—186 °C (dec); ^{1}H NMR (300 MHz, CDCl$_3$): δ= 0.37 (septet, J = 7.3 Hz, 3H), 0.62 (d, J = 7.3 Hz, 18H), 6.51–6.65 (m, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.80 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 7.3Hz, 1H), 7.17-7.79 (18H, m), 7.87 (1H,s), 7.92-7.95 (2H, m), 8.00 (s, 1H), 8.02 (s, 1H), 8.88 (s, 1H), 8.97 (s, 1H), 9.58 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ= 11.23, 18.27, 92.49, 92.81, 92.98, 93.23, 93.33, 93.41, 96.11, 100.69, 104.98, 120.78, 120.90, 121.30, 121.51, 121.77, 121.92, 122.16, 123.41, 124.19, 124.24, 124.39, 124.42, 124.53, 124.56, 124.58, 125.68, 126.48, 126.57, 126.87, 127.01, 127.49, 127.84, 127.86, 127.89, 128.37, 128.65, 128.76, 128.85, 129.38, 129.52, 129.75, 129.78, 130.10, 130.37, 130.50, 130.68, 130.71, 130.73, 130.79, 130.87, 130.96, 131.01, 131.06, 131.26, 131.45, 131.91, 136.76; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 248 (268000), 413 (36700), 436 nm (33100); MALDI-TOF MS: *m/z* 1084.29 [M^+]; calcd for $C_{73}H_{53}ISi$; *m/z* 1084.30 [M^+]. Chromatographic separation also gave the homodimer as a by product (1^8,18^8-bis[(triisopropylsilyl)ethynyl]-1,18(1),4,7,12,15(1,8)-hexaanthracenaoctadecan-2,5,8,10,13,16-hexayne). Yield 9.6 mg; m.p. 289—292 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.42 (septet, J = 7.2 Hz, 6H), 0.62 (d, J = 7.3 Hz, 36H), 5.91 (dd, J = 7.0, 8.5 Hz, 2H), 6.29–6.34 (m, 4H), 6.73 (d, J = 6.2 Hz, 2H), 6.80 (dd, J = 6.9, 8.4 Hz, 2H), 7.08–7.11 (m, 6H), 7.23 (dd, J = 6.8, 8.5 Hz, 2H), 7.30 (dd, J = 6.9, 8.6 Hz, 2H), 7.39–7.52 (m, 10H), 7.59 (d, J = 6.8 Hz, 2H), 7.72–7.77 (m, 4H), 7.83 (d, J = 8.8 Hz, 2H), 8.00 (s, 2H), 8.05 (s, 2H), 8.37 (s, 2H), 9.29 (s, 2H), 9.75 (s, 2H),

Synthesis of Cyclic Oligomer 1a (1,4,7,10(1,8)-tetraanthracenadodecan-2,5,8,11-tetrayne). To a solution of **8a** (19.6 mg, 0.018 mmol) in 5 mL of THF was added 27 μL of a 1.0 mol/L solution of TBAF in THF under Ar atmosphere. After the mixture was stirred for 20 min., 5 mL of triethylamine, $[Pd(PPh_3)_4]$ (10.4 mg, 0.018 mmol) and copper(I) iodide (0.85 mg, 0.0045 mmol) were added. The solution was refluxed for 40 min, and the solvent was removed by evaporation. The crude product was purified by a short chromatography on alumina with hexane/dichloromethane 2:1 as eluent. Recrystallization from chlorobenzene afforded the pure product as orange crystal. Yield 3.3 mg (23%); m.p. >350 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ= 6.86 (m, 8H), 7.28 (d, J = 6.7 Hz, 8H), 7.72 (d, J = 7.8 Hz, 8H), 8.23 (s, 4H), 9.87 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 93.14, 121.23, 124.36, 126.98, 129.02, 129.71, 130.94. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 262 (68400), 390 (7100), 411 (11800), 439 nm (12000); MALDI-TOF MS: *m/z* 800.27 [M^+]; calcd for $C_{64}H_{32}$; *m/z* 800.25 [M^+].

10-Butyl-1,8-dichloroanthracene (3b). To a solution of 4,5-dichloro-9-anthrone[4] (1.00 g, 3.80 mmol) in 30 mL of benzene was added 4.87 mL (7.60 mmol) of a 15% butyllithium solution in hexane at –78 °C under Ar atmosphere. The mixture was allowed to warm up to room temperature, and stirred for 15 h. After the addition of 15 mL of 10% hydrochloric acid, the mixture was refluxed for 30 min. The organic materials were extracted with benzene. The benzene solution was washed with brine, dried over magnesium sulfate, and evaporate. The crude product was purified by chromatography on silica gel with hexane eluent to give yellow crystal. Yield 0.51 g (44%); m.p. 80.5-81.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.03 (t, J = 7.3 Hz, 3H), 1.59 (sextet, J = 7.3 Hz, 2H), 1.78 (m, 2H), 3.60 (t, J = 8.2 Hz, 2H), 7.44 (dd, J = 7.3, 8.9 Hz, 2H), 7.63 (d, J = 7.0 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H), 9.27 (s, 1H); ^{13}C NMR

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[4] 4,5-Dichloro-9-anthrone was prepared by reduction of 1,8-dichloroanthraquinone with various reductants. $Na_2S_2O_4$: H. Prinz, W. Wiegrebe, K. Mueller, *J. Org. Chem.*, **61**, 2853-6 (1996). Al/H_2SO_4; H. O. House, J. A. Hrabie, D. VanDerveer, *J. Org. Chem.*, **51**, 921-9 (1986). $SnCl_2$: H. O. House, N. I. Ghali, J. L. Haack, D. VanDerveer, *J. Org. Chem.*, **45**, 1807-17 (1980).

(75 MHz, $CDCl_3$): δ= 14.61, 23.93, 29.08, 34.22, 120.31, 124.32, 125.99, 126.17, 129.88, 131.18, 133.87, 137.74; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 261 (85800), 343 (2760), 360 (5890), 380 (9520), 401 nm (8840); HR FAB MS: *m/z* 303.0686 [*M*+H$^+$]; calcd for $C_{18}H_{17}{}^{35}Cl_2$; *m/z* 303.0707 [*M*+H$^+$]. Anal. Calcd for $C_{18}H_{17}Cl_2$; C, 71.30; H, 5.32. Found: C, 70.94; H, 5.38.

10-Butyl-1,8-bis[(trimethylsilanyl)ethynyl]anthracene. A solution of [(trimethylsilyl)ethynyl]magnesium bromide was prepared by the treatment of (trimethylsilyl)ethyne (1.73 ml, 24.8 mmol) and 7.41 ml (22.3 mmol) of 3.0 mol/L diethyl ether solution of ethylmagnesium bromide in 100 mL of THF. This solution was slowly added to a suspension of 10-butyl-1,8-dichloroanthracene (1.25 g, 4.14 mmol), [Ni(acac)$_2$] (7.4 mg, 0.028 mmol), and triphenylphosphine (27.0 mg, 0.103 mmol) in 30 mL of THF at room temperature. The mixture was refluxed for 2 days under Ar atmosphere, and then quenched by slow addition of 20 mL of aqueous ammonium chloride. The organic layer was separated, washed with brine, and dried over magnesium sulfated, and evaporated. The crude produced was purified by chromatography on silica gel with hexane eluent to give yellow crystals. An analytical sample was obtained by recrystallization from ethanol. Yield 1.02 g (58%); m.p. 151.5-152.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 0.38 (s, 18H), 1.01 (t, *J* = 7.3 Hz, 3H), 1.55 (sextet, *J* = 7.3 Hz, 2H), 1.73 (m, 2H), 3.54 (t, *J* = 8.2 Hz, 2H), 7.42 (dd, *J* = 7.0, 8.9 Hz, 2H), 7.77 (d, *J* = 6.7 Hz, 2H), 8.22 (d, *J* = 9.2 Hz, 2H), 9.30 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 0.44, 14.03, 23.32, 28.04, 33.68, 99.73, 104.02, 122.06, 122.72, 124.75, 125.56, 129.22, 131.10, 131.97, 136.67; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 266 (79500), 294 (6640), 308 (8450), 363 (3170), 381 (7380), 402 (13600), 426 nm (13800); HR FAB MS: *m/z* 426.2180 [*M*$^+$]; calcd for $C_{28}H_{34}Si_2$; *m/z* 426.2199 [*M*$^+$]; Anal. Calcd for $C_{28}H_{34}Si_2$: C, 78.81; H, 8.03. Found: C, 78.44; H, 8.15.

10-Butyl-1,8-diethynylanthracene. 10-Butyl-1,8-bis[(trimethylsilanyl)ethynyl]anthracene (2.23 g, 5.24 mmol) was heated in 200 mL of ethanol with potassium fluoride (1.51 g, 26.2 mmol) under reflux for 1 h. The solvent was evaporated, and the residue was extracted with dichloromethane. The organic solution was washed with brine, dried over magnesium bromide, and evaporated. The crude product was purified with chromatography on silica gel with hexane eluent. Recrystallization from ethanol gave the desired compound as yellow solid. Yield 1.35 g (90%); m.p. 98–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.02 (t, *J* = 7.2 Hz, 3H), 1.58 (sextet, *J* = 7.3 Hz, 2H), 1.77 (m, 2H), 3.57-3.61 (m, 3H, α-CH_2 and C≡CH), 7.47 (dd, *J* = 7.0, 9.2 Hz, 2H), 7.78 (d, *J* = 7.0 Hz, 2H), 8.29 (d, *J* = 9.2 Hz, 2H), 9.44 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 14.54, 23.85, 28.49, 34.25, 82.47, 83.09, 121.57, 123.09, 125.33, 126.36, 129.69, 131.61, 131.97,137.33; HR FAB MS: *m/z* 282.1390 [*M*$^+$]; calcd for $C_{22}H_{18}$; *m/z* 282.1409 [*M*$^+$].

10-Butyl-1-ethynyl-8-[(triisopropylsilyl)ethynyl]anthracene (5b). To a solution of 10-butyl-1,8-diethynylanthracene (1.33 g, 4.69 mmol) in 125 mL of THF was added 3.71 ml (5.70 mmol) of 15% butyllithium solution in hexane at –78 °C under Ar atmosphere. The solution was stirred at the temperature for 1.5 h, and then allowed to warm up to 0 °C. Chlorotriisopropylsilane (3.71 ml, 5.70 mmol) was added, and the solution was stirred for 3 h at the temperature and then for 14 h at room temperature. The reaction mixture was quenched by addition of 20 mL of water, and the solvent was evaporated. The residue was extracted with dichloromethane. The extract was washed with brined, dried over magnesium sulfate, and evaporated. The crude products were separated by chromatography on silica gel with hexane eluent. The order of elutions was bis-silylated compound (R_f 0.52, hexane eluent), mono-silylated compound (0.42), and the starting compound (0.35). The desired product was obtained as yellow oil. Yield 1.10 g (53%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.3 Hz, 3H), 1.23-1.24 (m, 21H), 1.57 (sextet, J = 7.3 Hz, 2H), 1.76 (m, 2H), 3.48 (s, 1H), 3.54 (t, J = 7.9 Hz, 2H), 7.43 (t, J = 7.0 Hz, 1H), 7.78 (d, J = 6.9 Hz, 2H), 8.25 (t, J = 9.2 Hz, 1H), 8.29 (t, J = 8.9 Hz, 1H), 9.46 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.97, 14.54, 19.44, 23.82, 28.46, 34.22, 82.60, 83.00, 96.82, 105.8, 121.5, 122.9, 123.3, 125.1, 125.4, 125.8, 126.3, 129.6, 129.7, 131.6, 131.7, 131.9, 132.0, 137.2; HR FAB MS: *m/z* 438.2708 [M^+]; calcd for $C_{31}H_{38}Si$; *m/z* 438.2743 [M^+].

1^{10},7^{10}-Dibutyl-1^8,7^8-bis[(triisopropylsilyl)ethynyl]-1,7(1),4(1,8)-trianthracenaheptan-2,5-diyne (**6b**). To a degassed solution of **5b** (1.10g, 2.50 mmol) and 1,8-diiodoanthracene (484 mg, 1.13 mmol) in a mixture of 80 mL of THF and 200 mL of triethylamine were added [$Pd(PPh_3)_4$] (173.3 mg, 0.150 mmol) and CuI (14.2mg, 0.075 mmol). The reaction mixture was refluxed for 19 h under Ar atmosphere. After the solvent was evaporated, the crude material was purified by chromatography on silica gel with hexane/dichloromethane (6:1) as eluent to give yellow powder. Yield 0.69 g (59%); m.p. 217–219 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.70-0.83 (s, 42H), 1.03 (t, J = 8.3 Hz, 3H), 1.06-1.70 (m, 4H), 3.51(t, J = 7.7 Hz, 2H), 6.53 (dd, J = 6.9, 9.0 Hz, 2H), 7.36-7.53 (m, 6H), 7.70 (d, J = 6.4 Hz, 2H), 7.85-7.88 (m, 4H), 8.08 (d, J = 8.6 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H), 8.54 (s, 1H), 9.40 (s, 2H), 9.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.88, 14.66, 19.05, 23.92, 28.60, 34.27, 92.91, 94.10, 97.14, 105.98, 122.39, 122.83, 123.20, 123.39, 125.10, 125.19, 125.24, 125.55, 125.64, 127.75, 129.33, 129.51, 129.62, 130.87, 131.50, 131.60, 131.70, 131.96, 132.30, 132.50, 136.57; MALDI-TOF MS: *m/z* 1050.59 [M^+]; calcd for $C_{76}H_{82}Si_2$; *m/z* 1050.60 [M^+].

1^{10},7^{10}-Dibutyl-1^8,7^8-diethynyl-1,7(1),4(1,8)-trianthracenaheptan-2,5-diyne. To a solution of **6b** (153.2 mg, 0.145 mmol) in 20 mL of THF was added 0.30 mL (0.30 mmol) of a 1.0 mol/L THF solution of TBAF. The solution was stirred for 1.5 h at room temperature. The solvent was evaporated, and the residue was extracted with dichloromethane. The organic solution was washed with brine, dried over magnesium sulfate, and evaporate. The crude material was purified by chromatography on silica gel with hexane eluent to give yellow power. Yield 93.5 mg (86%); m.p. 203—236 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.03 (t, *J* = 7.3 Hz, 6H), 1.57 (sextet, *J* = 7.3 Hz, 4H), 1.67 (m, 4H), 2.83 (s, 2H), 3.39 (t, *J* = 7.3 Hz, 4H), 6.83 (dd, *J* = 6.7, 8.9 Hz, 2H), 7.19–7.24 (m, 4H), 7.55–7.58 (m, 4H), 7.81 (d, *J* = 9.2 Hz, 2H), 7.95–7.98 (m, 4H), 8.09 (d, *J* = 8.5 Hz, 2H), 8.56 (s, 1H), 9.46 (s, 2H), 10.26 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 14.08, 23.41, 28.00, 33.64, 81.98, 82.54, 93.22, 94.02, 121.35, 121.77, 122.48, 122.93, 124.21, 124.29, 124.36, 125.23, 125.37, 125.70, 127.30, 128.52, 128.65, 128.74, 129.33, 130.23, 130.30, 130.75, 131.68, 135.50; HR FAB MS: *m/z* 738.3241 [M^+]; calcd for $C_{58}H_{42}$; *m/z* 738.3287 [M^+].

1^{10},7^{10}-Dibutyl-1^8-ethynyl-7^8-(triisopropylsilyl)ethynyl-1,7(1),4(1,8)-trianthracenaheptan-2,5-diyne (7b). To a solution of 1^{10},7^{10}-dibutyl-1^8,7^8-diethynyl-1,7(1),4(1,8)-trianthracenaheptan-2,5-diyne (70 mg, 0.095 mmol) in 30 mL of THF was added 68 μL (0.11 mmol) of 15% butyllithium solution in hexane at –78 °C under Ar atmosphere. The solution was stirred at the temperature for 1.5 h, and then allowed to warm up to 0 °C. After the addition of chlorotriisopropylsilane (16 μL, 0.095 mmol), the solution was stirred for 3 h at the temperature and then for 14 h at room temperature. The reaction mixture was quenched by addition of 5 mL of water, and the solvent was evaporated. The residue was extracted with dichloromethane. The extract was washed with brined, dried over magnesium sulfate, and evaporated. The crude products were roughly purified by chromatography on silica gel with hexane eluent. The desired product was separated by GPC with chloroform eluent to give yellow powder. Yield 31 mg (37%); m.p. 207—211 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 0.58 (septet, *J* = 7.3 Hz, 3H), 0.75 (d, *J* = 7.3 Hz, 18H), 1.02 (t, *J* = 7.3 Hz, 3H), 1.06 (t, *J* = 7.3Hz, 3H), 1.55 (sextet, *J* = 7.6 Hz, 2H), 1.60 (sextet, *J* = 7.3 Hz, 2H), 1.64–1.76 (m, 4H), 3.11 (s, 1H), 3.44 (t, *J* = 8.2 Hz, 2H), 3.50 (t, *J* = 8.2 Hz, 2H), 6.51 (dd, *J* = 7.0, 9.2 Hz, 1H), 6.97 (dd, *J* = 6.7, 8.9 Hz, 1H), 7.17 (d, *J* = 6.7 Hz, 1H), 7.24 (dd, *J* = 6.7, 8.9 Hz, 1H), 7.29 (dd, *J* = 6.7, 8.9 Hz, 1H), 7.54–7.59 (m, 4H), 7.64 (d, *J* = 6.4 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.91–7.96 (m, 3H), 8.03 (d, *J* = 8.9 Hz, 1H), 8.08–8.11 (m, 3H), 8.55 (s, 1H), 9.43 (s, 1H), 9.46 (s, 1H), 10.07 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 11.28, 14.05, 14.12, 18.42, 23.37, 23.40, 27.97, 28.10, 33.65, 33.71, 82.04, 82.52, 92.58, 92.95, 93.70, 92.72, 96.48, 105.37, 121.22, 121.77, 121.96, 122.31, 122.34, 122.64, 122.83, 122.98, 124.33, 124.35, 124.47, 124.55, 124.67, 124.69, 124.94, 125.19, 125.28, 125.31, 127.25, 128.78, 128.82, 128.97, 129.61, 130.26, 130.35, 130.80, 130.84, 130.94, 131.03, 131.16, 131.35, 131.68, 131.70, 131.73, 131.89, 135.72, 135.87; HR FAB MS: *m/z* 894.4626 [M^+]; calcd for $C_{67}H_{62}Si$; *m/z* 894.4621 [M^+].

1^{10},7^{10}-Dibutyl-10^8-iodo-1^8-(triisopropylsilyl)ethynyl-1,10(1),4,7(1,8)-tetraanthracenadecan-2,5,8-triyne (8b). To a degassed solution of **7b** (31.2 mg, 0.035 mmol) and 1,8-diiodoanthracene (17.9 mg, 0.042 mmol) in a mixture of 8 mL of THF and 20 mL of triethylamine were added [$Pd(PPh_3)_4$] (9.6 mg, 8.3 μmol) and CuI (0.79 mg, 4.2 μmol). The solution was refluxed for 5 h under Ar atmosphere. The solvent was removed by evaporation and the crude product was purified by chromatography on silica gel with hexane/dichloromethane (10:1—4:1) as eluent. The desired product was separated from the by-product by GPC with chloroform eluent to give yellow oil. Yield 16 mg (38%); m.p. 138—142 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 0.41 (septet, J = 7.6 Hz, 3H), 0.66 (d, J = 7.6 Hz, 18H), 1.05 (t, J = 7.3Hz, 3H), 1.07 (t, J = 7.3 Hz, 3H), 1.56–1.76 (m, 8H), 3.46 (t, J = 8.2 Hz, 2H), 3.51 (t, J = 8.2 Hz, 2H), 6.72–6.83 (m, 4H), 6.96 (dd, J = 6.7, 8.2 Hz, 2H), 7.22–7.28 (m, 4H), 7.35–7.45 (m, 3H), 7.54–7.57 (m, 2H), 7.63–7.65 (m, 2H), 7.73–7.83 (m, 4H), 7.89–7.95 (m, 3H), 8.05 (s, 1H), 8.10–8.14 (m, 2H), 9.01 (s, 1H), 9.22 (s, 1H), 9.67 (s, 1H), 9.77 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 11.87, 14.49, 18.75, 23.96, 24.03, 28.67, 28.70, 34.26, 34.30, 93.21, 93.28, 93.70, 93.91, 94.13, 94.21, 96.88, 100.89, 106.03, 121.27, 121.72, 122.03, 122.54, 122.85, 122.95, 123.88, 124.76, 124.79, 124.82, 124.90, 125.10, 125.14, 125.21, 125.68, 125.70, 126.21, 127.23, 127.71, 128.20, 128.52, 128.89, 128.92, 129.00, 129.11, 129.19, 129.24, 129.38, 129.44, 129.69, 130.10, 130.12, 130.27, 130.30, 131.05, 131.20, 131.23, 131.28, 131.36, 131.55, 131.68, 131.77, 131.80, 132.33, 132.43, 136.22, 136.35, 137.36; MALDI-TOF MS: m/z 1197.5 [M+H$^+$]; calcd for $C_{81}H_{69}ISi$; m/z 1197.4 [M+H$^+$]. Data of the 1:2 coupling product (**9: $1^{10},7^{10},13^{10},19^{10}$-Tetrabutyl-$1^{8},19^{8}$-bis[(triisopropylsilyl)ethynyl]-1,10(1),4,7,16,19(1,8)-heptaanthracenanonadecan-2,5,8,11,14,17-hexayne**): Yellow powder. Yield 4.5 mg. m.p. 237—242 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 0.47-0.56 (m, 6H), 0.63-0.65 (m, 36H), 1.00-1.04 (m, 6H), 1.10 (t, J = 7.1 Hz, 6H), 1.58-1.79 (m, 16H), 3.16-3.17 (m, 4H), 3.55-3.60 (m, 4H), 6.03 (dd, J = 6.8, 9.0 Hz, 2H), 6.19 (dd, J =6.8, 9.0 Hz, 2H), 6.28 (dd, J = 7.0, 8.7 Hz, 2H), 6.50 (dd, J = 7.0, 8.5 Hz, 2H), 6.70-6.82 (m, 6H), 7.00 (d, J = 6.6 Hz, 2H), 7.14-7.18 (m, 4H), 7.31-7.41 (m, 12H), 7.65 (t, J = 6.2Hz, 4H), 7.72 (d, J = 6.6 Hz, 2H), 7.85 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 9.3 Hz, 2H), 8.05 (s, 2H), 8.22 (d, J = 9.3 Hz, 2H), 9.32 (s, 2H), 9.46 (s, 2H), 9.49 (s, 2H). 9.56 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 11.18, 14.11, 14.22, 18.31, 23.41, 23.44, 27.91, 28.12, 33.52, 33.84, 92.76, 92.77, 92.89, 93.10, 93.18, 93.42, 96.75, 105.23, 121.34, 121.45, 121.86, 122.04, 122.18, 122.25, 122.73, 123.08, 123.10, 123.25, 123.70, 123.78, 123.93, 123.97, 124.28, 124.33, 124.38, 124.43, 124.46, 124.70, 124.85, 125.01, 126.13, 126.35, 127.30, 127.51, 127.99, 128.17, 128.55, 129.01, 129.08, 129.21, 129.33, 129.63, 129.98, 130.20, 130.24, 130.34, 130.61, 130.80, 131.00, 131.14, 131.16, 131.19, 131.37, 134.19, 135.93; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 266 (270000), 377 (26300, sh), 404 (41300), 426 (45900), 449 (31700, sh) nm; MALDI-TOF MS: m/z 1962.83 [M^+]; calcd for $C_{148}H_{130}Si_2$; m/z 1962.97 [M^+]. Data of homodimer (**$1^{10},7^{10},12^{10},18^{10}$-Tetrabutyl-$1^{8},18^{8}$-bis[(triisopropylsilyl)ethynyl]-1,18(1),4,7,12,15(1,8)-hexaanthracenaoctadecan-2,5,8,10,13,16-hexayne**). Yellow powder. Yield 2.8 mg. m.p. 159—161 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 0.46 (septet, J = 7.3 Hz, 6H), 0.66 (d, J = 7.6 Hz, 18H), 1.08 (t, J = 7.3 Hz, 6H), 1.19 (t, J = 7.3 Hz, 6H), 1.61 (sextet, J = 7.3 Hz, 4H), 1.70–1.77 (m, 8H), 1.88 (m, 4H), 3.45–3.51 (m, 8H), 5.81 (dd, J = 7.0, 8.2 Hz, 2H), 6.20 (dd, J = 6.7, 8.5 Hz, 2H), 6.26 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 6.4 Hz, 2H), 6.86 (dd, J = 7.0, 8.9 Hz, 2H), 7.10–7.15 (m, 6H), 7.26 (dd, J = 6.7, 8.2 Hz, 2H), 7.36 (dd, J = 6.7, 8.9 Hz, 2H), 7.44–7.47 (m, 4H), 7.55 (d, J = 6.4 Hz, 2H), 7.62 (d, J = 6.7 Hz, 2H), 7.68 (d, J = 9.2 Hz, 2H), 7.77 (d, J = 6.7 Hz, 2H), 7.84 (d, J = 8.9 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H), 8.14 (d, J = 8.9 Hz, 2H), 8.49 (s, 2H), 9.39 (s, 2H), 9.74 (s, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ= 11.22, 14.17, 14.24, 18.35, 23.43, 23.60, 28.01, 28.08, 33.74, 34.02, 79.52, 80.90, 92.61, 92.94, 93.25, 93.67, 96.63, 105.23, 120.93, 121.43, 122.06, 122.25, 122.27, 122.68, 122.81, 123.08, 124.00, 124.30, 124.49, 124.52, 124.61, 124.94, 124.98, 125.84, 126.61, 128.24, 128.61, 128.64, 128.73, 128.87, 128.92, 129.78, 129.86, 130.44, 130.57, 130.76, 130.88, 130.92, 130.94, 131.12, 131.27, 131.52, 134.68, 135.69; MALDI-TOF MS: *m/z* 1786.82 [M^+]; calcd for $C_{130}H_{122}Si_2$; *m/z* 1786.91 [M^+].

Synthesis of Cyclic Oligomer 1b (1^{10}, 7^{10}-dibutyl-1,4,7,10(1,8)-tetraanthracenadodecan-2,5,8,11-tetrayne). To a solution of **8b** (21.5 mg, 0.018 mmol) in 10 mL of THF was added 36 μL (0.036 mmol) of a 1.0 mol/L THF solution of TBAF under Ar atmosphere. After the mixture was stirred for 1 h., 10 mL of triethylamine, $[Pd(PPh_3)_4]$ (20.7 mg, 0.018 mmol) and copper(I) iodide (1.7 mg, 9.0 μmol) were added. The solution was refluxed for 14 h at room temperature, and the solvent was removed by evaporation. The crude product was purified by a short chromatography on alumina with hexane/dichloromethane (1:1) as eluent. Recrystallization from chlorobenzene afforded the pure product as orange crystal. Yield 3.0 mg (18%); m.p. 338—342 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.13-1.93 (m, 14H), 3.51-3.57 (m, 4H), 6.81-6.88 (br m, 8H), 7.28-7.31 (m, 8H), 7.69 (d, J = 8.4 Hz, 4H), 7.98 (d, J = 8.8 Hz, 4H), 8.19 (s, 2H), 9.86 (s, 2H), 9.90 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 93.15, 93.54, 121.39, 122.03, 123.59, 124.29, 124.40, 124.51, 124.59, 126.25, 126.99, 128.25, 128.80, 128.92, 129.53, 129.79, 130.88; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 448 (25300), 422 (23400), 265 nm (126000); MALDI-TOF MS: *m/z* 912.35 [M^+]; calcd for $C_{72}H_{48}$; *m/z* 912.38 [M^+].