

Supplementary Material

Double Diels-Alder Strategies to Soluble 2,9- and 2,9,6,13-Tetraethynylpentacenes; Photolytic [4+4] Cycloadditions; and Pentacene Crystal Packing

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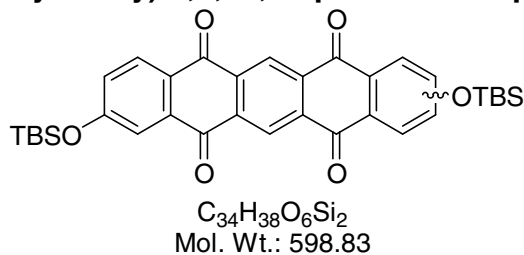
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All non-aqueous reactions were performed under nitrogen in flame-dried glassware using dry solvents. Tetrahydrofuran, diethyl ether was distilled from sodium/benzophenone. Dichloromethane, toluene, diisopropylethylamine and triethylamine were distilled from calcium hydride. *n*-Butyllithium solutions in hexanes were titrated prior to use against diphenylacetic acid and used directly.

Reactions were monitored by thin layer chromatography (TLC) using commercial aluminum-backed silica gel sheets coated with silica gel 60 F₂₅₄. TLC spots were developed by heating the plate after treatment with a 5% solution of phosphomolybdic acid in ethanol or a solution of KMnO₄ in aqueous potassium hydroxide. Room temperature corresponds to 21 °C. Anhydrous magnesium sulfate (MgSO₄) was used to dry solutions in organic solvents. Excess solvents were removed (concentrated) *in vacuo* at pressures obtained by a water or air aspirator connected to a Büchi rotary evaporator. Trace solvents were removed on a vacuum pump. Product purification by flash chromatography was performed with Silica Gel 60 (230-400 mesh). Petroleum ether refers to a mixture of hydrocarbons with a boiling range of 30-60 °C.

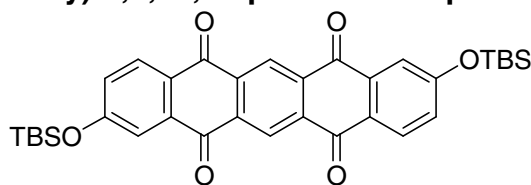
Melting points were determined with a capillary melting point apparatus and are uncorrected. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded as indicated, ¹H NMR (400 or 300 MHz) and ¹³C NMR (100 or 75 MHz). Chemical shifts are reported downfield from tetramethylsilane (δ scale) in ppm. ¹H NMR data are reported as follows: Chemical shift (multiplicity, coupling constants (Hz), and integration). Low resolution mass spectroscopy (MS) using electron impact (EI), mass spectrometry with an electron beam energy of 70 eV. High resolution mass spectroscopy (HRMS) was performed with an electron beam energy of 70 eV. The purity of all title compounds was judged to be >95% as determined by a combination of ¹H NMR and ¹³C NMR analyses.

2,9/2,10-Bis(*t*-butyldimethylsiloxy)-5,7,12,14-pentacenediquinone (**4**, **5**)



1,4,5,8-Anthradiquinone (**3**) (2.45 g, 10.3 mmol, 1 eq) and *trans*-3-(*t*-butyldimethylsiloxy)-1-methoxy-1,3-butadiene (**2**) (5.14 mL, 21.6 mmol, 2.1 eq) were combined in CH₂Cl₂ and stirred at room temperature (22 °C) for 20 h. The reaction was concentrated, taken up in THF, silica gel was added, and the suspension was stirred open to air for 24 h. The reaction was filtered through a silica gel plug with CH₂Cl₂ to afford **4** and **5**. The plug was flushed with THF to recover unaromatized material. Silica gel was added to the THF fraction and this slurry was stirred open to air for 24 h. Filtration through a silica gel plug with CH₂Cl₂ afforded additional **4** and **5**. The silica gel oxidation/filtration was repeated until all of the unaromatized material was converted to **4** and **5**. The diquinones were isolated as a yellow solid (3.72 g, 60%) as mixture of **4** and **5** (1:1). Isomers **4** and **5** could be separated by preparative HPLC (CH₂Cl₂/hexane 70:30) or preferably by fractional crystallization from chloroform.

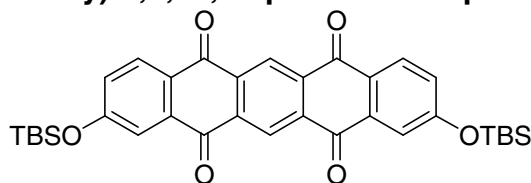
2,9-Bis(*t*-butyldimethylsiloxy)-5,7,12,14-pentacenediquinone (4)



$C_{34}H_{38}O_6Si_2$
Mol. Wt.: 598.83

mp: > 270 °C; 1H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 2H), 8.28 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 2.5 Hz, 2H), 7.24 (dd, J = 8.5, 2.6 Hz, 2H), 1.01 (s, 18 H), 0.30 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.8 (s), 180.7 (s), 161.9 (s), 136.9 (s), 136.7 (s), 135.6 (s), 130.4 (d), 127.5 (s), 127.0 (d), 126.5 (d), 117.7 (d), 25.5 (q), 18.3 (s), -4.3 (q); MS (EI) m/z 541.2 (M^+ - *t*-Bu, 100), 485.1 (8), 242.0 (19), 162.0 (34); IR ($CDCl_3$) ν 2957.6, 2930.7, 1677.7, 1591.9 cm^{-1} ; HRMS calcd for $C_{30}H_{29}O_6Si_2$ 541.1502 (M^+ - *t*-Bu), found 541.1510.

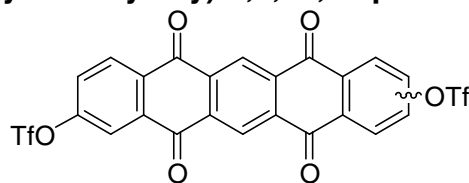
2,10-Bis(*t*-butyldimethylsiloxy)-5,7,12,14-pentacenediquinone (5)



$C_{34}H_{38}O_6Si_2$
Mol. Wt.: 598.83

mp: > 270 °C; 1H NMR (500 MHz, $CDCl_3$) δ 9.18 (s, 1H), 9.14 (s, 1H), 8.28 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 2.4 Hz, 2H), 7.24 (dd, J = 8.2, 2.6 Hz, 2H), 1.01 (s, 18 H), 0.30 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.8 (s), 180.7 (s), 161.9 (s), 137.0 (s), 136.6 (s), 135.6 (s), 130.4 (d), 127.5 (s), 127.1 (d), 127.0 (d), 126.5 (d), 117.7 (d), 25.5 (q), 18.3 (s), -4.3 (q); IR ($CDCl_3$) ν 2955.8, 2927.2, 1675.0, 1590.9 cm^{-1} ; MS (EI) m/z 541.2 (M^+ - *t*-Bu, 15), 504.9 (3), 162.0 (18), 57.1 (100); HRMS calcd for $C_{30}H_{29}O_6Si_2$ 541.1502 (M^+ - *t*-Bu), found 541.1516.

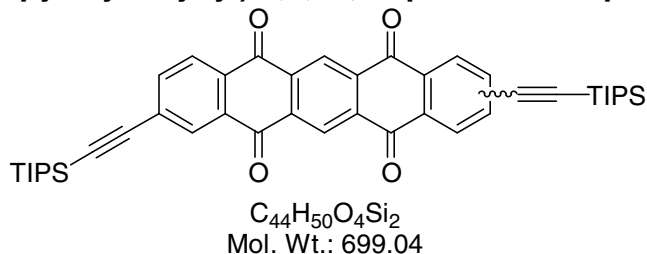
2,9/2,10-Bis(trifluoromethylsulfonyloxy)-5,7,12,14-pentacenediquinone (6, 7)



$C_{24}H_8F_6O_{10}S_2$
Mol. Wt.: 634.44

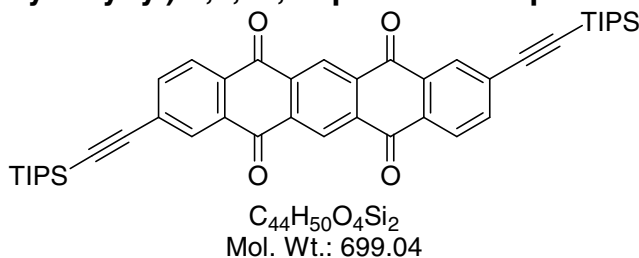
A solution of TBAF (1 M in THF, 1.81 mL, 1.81 mmol, 2.2 eq) was added to a 0 °C solution of diquinone **4** or **5** (493 mg, 0.823 mmol, 1 eq) in THF (400 mL). The yellow solution turned deep blue immediately upon addition of TBAF. The reaction was stirred at 0 °C for 15 min followed by the addition of a solution of Tf_2NPh (882 mg, 2.47 mmol, 3 eq) in THF (5 mL). The reaction was warmed to room temperature and stirred for 18 h, concentrated to ~ 100 mL and diluted with Et_2O (200 mL). The organic suspension was washed with HCl (10% aq), $NaHCO_3$ (sat. aq.), and water, concentrated to ~50 mL, and filtered to afford crude **6** or **7** (depending on the starting material) as a nearly colourless solid (518 mg, 98%). This compound was not further purified or characterized, but used directly in subsequent reactions.

2,9/2,10-Bis(triisopropylsilylethynyl)-5,7,12,14-pentacenediquinone (8, 9)



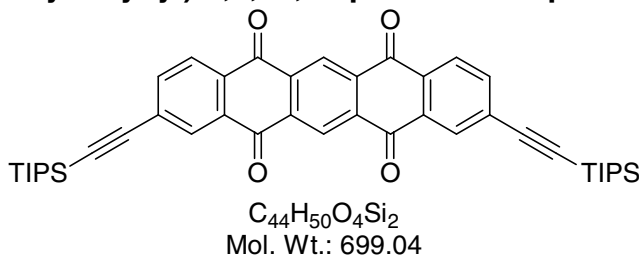
A solution of ditriflate **6** or **7** (500 mg, 0.788 mmol, 1 eq) in THF (250 mL) was degassed by bubbling argon through the solution for 30 min. CuI (30 mg, 20 mol%), Pd(PPh₃)₂Cl₂ (60 mg, 10 mol %), and Et₃N (7.5 mL) were added to the degassed solution and stirred at room temperature for 10 min. Triisopropylsilylacetylene (438 μ L, 1.97 mmol, 2.5 eq) was added to the solution and the reaction was heated to reflux for 16 h. The reaction was cooled to room temperature and concentrated. The residue was taken up in CH₂Cl₂ and washed with HCl (10% aq), NaHCO₃ (sat. aq), and water, dried, and concentrated. Chromatography (petroleum ether/CH₂Cl₂, 7:3) afforded **8** or **9** as a yellow solid (400 mg, 73% over two steps). If conducted on the mixture of isomers **8** or **9** could be separated by fractional crystallization from Et₂O.

2,9-Bis(triisopropylsilylethynyl)-5,7,12,14-pentacenediquinone (8)



mp: > 272-273 °C; IR (neat) ν 2945.3, 2866.9, 1679.8, 1595.5 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.22 (s, 2H), 8.41 (d, J = 1.6 Hz, 2H), 8.31 (d, J = 8.1 Hz, 2H), 7.88 (dd, J = 8.1, 1.7 Hz, 2H), 1.15 (s, 42H); ¹³C NMR (125 MHz, CDCl₃) δ 181.2 (s), 181.0 (s), 137.7 (d), 136.8 (s), 136.7 (s), 133.3 (s), 132.3 (s), 131.0 (d), 130.5 (s), 127.7 (d), 127.5 (d), 104.9 (s), 98.2 (s), 18.3 (q), 11.7 (d); MS (FAB) m/z 699.3 (M⁺), 307.2, 154.1.

2,10-Bis(triisopropylsilylethynyl)-5,7,12,14-pentacenediquinone (9)



mp: > 247-248 °C; IR (neat) ν 2945.7, 2866.9, 1679.2, 1595.8 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.22 (s, 1H), 9.21 (s, 1H), 8.41 (d, J = 1.3 Hz, 2H), 8.31 (d, J = 8.0 Hz, 2H), 7.88 (dd, J = 8.1, 1.2 Hz, 2H), 1.15 (s, 42H); ¹³C NMR (125 MHz, CDCl₃) δ 181.2 (s), 181.0 (s), 137.0 (d), 136.9 (s), 136.7 (s), 133.3 (s), 132.3 (s), 131.0 (d), 130.5 (d), 130.2 (s), 127.7 (d), 127.6 (d), 104.9 (s), 98.2 (s), 18.6 (q), 11.3 (d); MS (FAB) m/z 699.3 (M⁺), 307.2, 154.1.

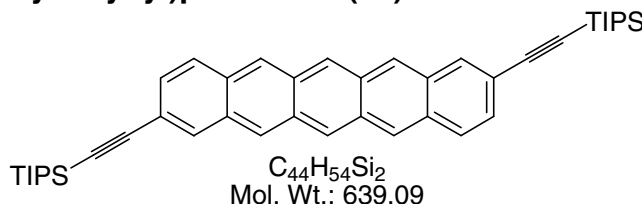
Meerwein-Ponndorf-Verley Aromatization-Photolytic Dimerization

2,9/2,10-Bis(triisopropylsilyl)ethynyl)pentacene (10, 11)



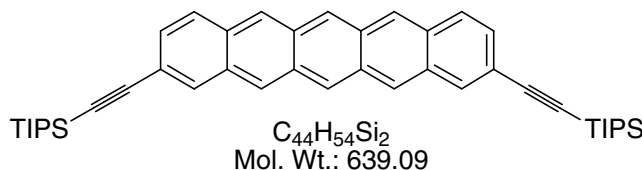
A mixture of aluminium (168.0 mg, 6.227 mmol, 43 eq), carbon tetrabromide (16.8 mg, 0.062 mmol, 0.43 eq) and mercuric chloride (3.4 mg, 0.010 mmol, 0.07 eq) in cyclohexanol (2.5 mL) was heated to reflux for 1.5 h under argon atmosphere in a Schlenk tube. After formation of a dark grey mixture, the reaction flask was cooled to room temperature and the diquinone **8** or **9** (100 mg, 0.143 mmol, 1 eq) was added as a solid and the mixture was reheated to reflux for 2 h. The resulting purple mixture was cooled to 50 °C and the residue rinsed with degassed hexane (4 x 10 mL) added via a syringe. The filtrate was then transferred to a round-bottom-flask via syringe and the solvent was removed under vacuum. The dark purple residue was dissolved in hexane and transferred to a silica gel column with rigorous exclusion of air. Elution under an inert atmosphere of argon with hexanes/dichloromethane (20:1) afforded a purple band of eluent of the expected pentacene as a blue solid.

2,9-Bis(triisopropylsilyl)ethynyl)pentacene (10)



1H NMR (500 MHz, acetone- d_6) δ 9.14 (s, 2H), 8.86 (s, 2H), 8.83 (s, 2H), 8.25 (s, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 1.20 (s, 42H).

2,10-Bis(triisopropylsilyl)ethynyl)pentacene (11)



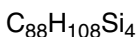
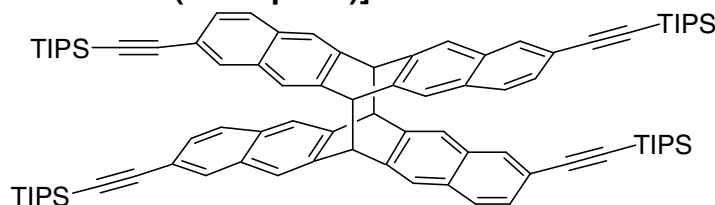
1H NMR (500 MHz, acetone- d_6) δ 9.15 (s, 1H), 9.14 (s, 1H), 8.88 (s, 2H), 8.83 (s, 2H), 8.26 (s, 2H), 8.04 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 1.21 (s, 42H).

Photocycloaddition Adducts (Pentacene based numbering)

Dimers from 2,9/2,10-bis(triisopropylsilyl)ethynyl)-5,7,12,14-pentacenediquinone (8**, **9**)**

A mixture of aluminum (840 mg), carbon tetrabromide (84 mg) and mercuric chloride (17 mg) in dry cyclohexanol (12.5 ml) was heated to reflux for 1.5 h under an argon atmosphere in a Schlenk tube. After the formation of a dark grey mixture, the reaction flask was cooled to room temperature. Either 2,9- or 2,10-bis(triisopropylsilyl)ethynyl)-5,7,12,14-pentacenediquinone (500 mg, 0.715 mmol) was added and the mixture was heated again to reflux for 2 h to afford a purple solution. The reaction flask was cooled to room temperature and the dark grey residue washed with degassed hexane (4 x 10mL) added via a syringe. The mixture was transferred to a round-bottom-flask and both hexane and cyclohexanol were distilled under vacuum to afford a dark purple residue. Degassed hexane (5 mL) was added to this residue under argon. Photolysis with a 60W lamp for 12 h afforded 169 mg (37%, 2 steps) of the expected dimers as a mixture (1:1). These products were separated by preparative TLC (silica gel) three elutions with petroleum ether/dichloromethane (10:1).

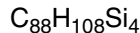
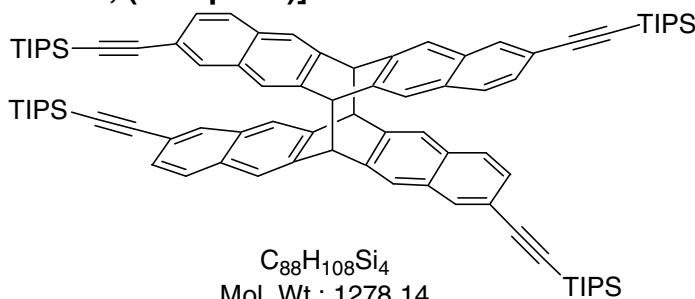
Syn-2,2',9,9'-tetra(triisopropylsilyl)ethynyl)tetrakisnaphthotricyclo[4.2.2.2^{2,5}]-dodecane (12) [2,9-Dimer 12 (more polar)]



Mol. Wt.: 1278.14

White solid. mp: 203-205 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.67 (br. s, 4H), 7.43 (d, *J* = 8.5 Hz, 4H), 7.39 (s, 4H), 7.34 (s, 4H), 7.26 (dd, *J* = 8.5, 1.5 Hz, 4H), 5.06 (s, 4H), 1.12 (s, 84H); ¹³C NMR (125 MHz, CDCl₃) δ 140.9, 140.5, 131.4, 131.2, 128.4, 127.0, 125.4, 125.3, 120.1, 107.4, 90.4, 53.7, 18.6, 11.2; MS (*m/z*, ES) 1316 (*M* + K⁺).

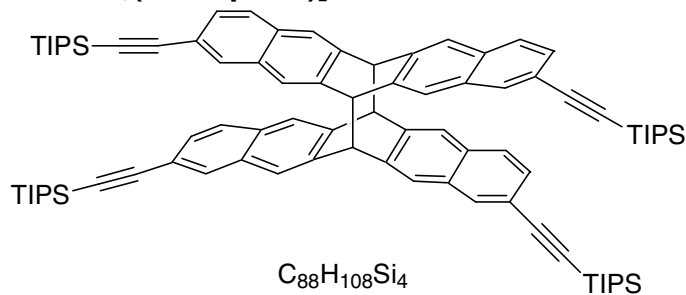
Anti-2,2',9,9'-tetra(triisopropylsilyl)ethynyl)tetrakisnaphthotricyclo[4.2.2.2^{2,5}]-dodecane (13) [2,9-Dimer, (less polar)]



Mol. Wt.: 1278.14

White solid. mp: 194-196 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.66 (br. s, 4H), 7.44 (d, *J* = 8.5 Hz, 4H), 7.38 (s, 4H), 7.35 (s, 4H), 7.27 (dd, *J* = 8.5, 1.4 Hz, 4H), 5.06 (s, 4H), 1.13 (s, 84H); ¹³C NMR (125 MHz, CDCl₃) δ 140.9, 140.5, 131.4, 131.1, 128.4, 127.1, 125.4, 125.3, 120.1, 107.5, 90.4, 53.7, 18.6, 11.3; MS (*m/z*, ES) 1316 (*M* + K⁺).

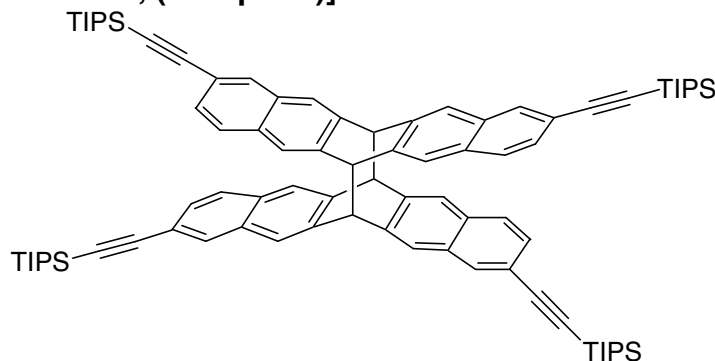
Syn-2,2',10,10'-tetra(triisopropylsilylethynyl)tetrakisnaphthotricyclo[4.2.2.^{2,5}]-dodecane (14) [2,10-Dimer,(more polar)]



$C_{88}H_{108}Si_4$
Mol. Wt.: 1278.14

White solid. mp: 190-192 °C; 1H NMR (500 MHz, $CDCl_3$) δ 7.68 (br. s, 4H), 7.41 (d, J = 8.4 Hz, 4H), 7.37 (s, 4H), 7.35 (s, 4H), 7.25 (dd, J = 8.4, 1.5 Hz, 4H), 5.06 (d, J = 6.1 Hz, 4H), 1.12 (s, 84H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 140.6, 131.4, 131.2, 128.4, 127.0, 125.4, 125.3, 120.1, 107.4, 90.4, 53.8, 53.6, 18.6, 11.2; MS (m/z , ES) 1316 ($M + K^+$).

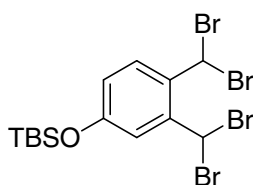
Anti-2,2',10,10'-tetra(triisopropylsilylethynyl)tetrakisnaphthotricyclo[4.2.2.^{2,5}]-dodecane (15) [2,10-Dimer, (less polar)]



$C_{88}H_{108}Si_4$
Mol. Wt.: 1278.14

White solid. mp: 208-210 °C; 1H NMR (500 MHz, $CDCl_3$) δ 7.66 (br. s, 4H), 7.42 (d, J = 8.3 Hz, 4H), 7.37 (s, 4H), 7.37 (s, 4H), 7.25 (dd, J = 8.5, 1.5 Hz, 4H), 5.07 (s, 4H), 1.11 (s, 84H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 140.6, 131.4, 131.1, 128.4, 127.0, 125.4, 125.3, 120.1, 107.4, 90.3, 53.7, 53.6, 18.6, 11.2; MS (m/z , ES) 1316 ($M + K^+$).

(3,4-Bis(dibromomethyl)phenoxy)(*tert*-butyl)dimethylsilane (17)

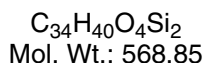
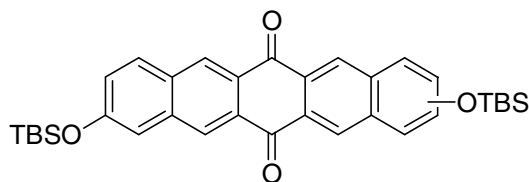


$C_{14}H_{20}Br_4OSi$
Mol. Wt.: 552.01

tert-Butyl(3,4-dimethylphenoxy)dimethylsilane (**16**) (9.747 g, 41.23 mmol) and NBS (31.56 g, 177.3 mmol, 4.3 eq.) were added to CCl_4 and heated at a gentle reflux. A catalytic amount of

AIBN was added and the solution gradually turned from colourless to red. After 5 days the reaction was cooled to rt and the organics were washed with sat. NaHCO₃ (3X), dried, filtered and concentrated. The crude product was filtered through a silica gel plug (10 cm high, petroleum ether/ethyl acetate, 10:1) to provide compound **17** as a white solid. mp: 81-82°C; ¹H NMR (300 MHz, CDCl₃) δ 7.46 (b, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.00 (s, 1H), 6.77 (dd, *J* = 8.4 and 2.7 Hz, 1H), 0.97 (s, 9H), 0.24 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 157.5 (C), 139.8 (C), 130.9 (CH), 130.4 (C), 122.1 (CH), 121.3 (CH), 36.7 (CH), 36.7 (CH), 25.8 (CH₃), 18.6 (C), -3.9 (CH₃); IR (thin-film): ν = 3052, 2954; MS (EI) *m/z* 551 (M⁺) (9), 473 (100), 392 (8), 335 (19), 254 (10), 139 (4), 73 (46); HRMS calculated for C₁₄H₂₀⁷⁹Br₄OSi (M⁺) 547.80169, found 547.79231.

2,9/2,10-Bis(*t*-butyldimethylsiloxy)-6,13 –pentacenequinone(s) (**21**, **22**)



Tetrabromide **17** (1.10 g, 2 mmol) and benzoquinone (218 mg, 2 mmol) were added to the stirred ionic liquid **18** (1-butyl-3-methylimidazolium iodide) (5 g). The mixture was heated to 60 °C and stirred for a further 2 hours. The mixture was washed four times with ether, and the ether layers combined. The ether solution was concentrated under reduced pressure and the solid washed with acetone to afford a mixture (1:1) of **21** and **22** (436 mg, 77%) as a yellow solid. The remaining ionic liquid phase was dried under vacuum and directly reused in the subsequent experiments. Fractional recrystallization from CH₂Cl₂ gave the pure 2, 9 adduct (**22**) as yellow needles. mp:<270 °C.

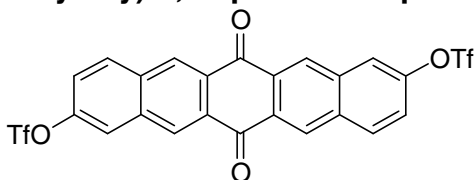
2,9-Bis(2-(triisopropylsilyl)ethynyl)pentacene-6,13-dione (22**):** ¹H NMR (300 MHz, CDCl₃) δ 8.83 (s, 2H), 8.73 (s, 2H), 7.98 (d, *J* = 9 Hz, 2H), 7.41 (d, *J* = 2.1 Hz, 2H), 7.27 (m, 2H), 1.02, (s, 18H), 0.29 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 183.5, 157.1, 137.4, 132.2, 131.4, 131.2, 130.0, 129.3, 128.4, 126.2, 116.9, 26.0, 18.7, -3.9; IR (CH₂Cl₂) ν 3055, 3005, 1712 cm⁻¹; MS (EI) *m/z* 568 (M⁺) (63), 545 (4.6), 511 (100), 455 (14), 227 (28); HRMS calculated for (M⁺) 568.24651, found 568.24548.

2,10-Bis(2-(triisopropylsilyl)ethynyl)pentacene-6,13-dione (21**):** yellow powder mp: >270 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.82 (s, 2H), 8.73 (s, 2H), 7.99 (d, *J* = 9 Hz, 2H), 7.42 (d, *J* = 2.1 Hz, 2H), 7.27 (m, 2H), 1.06 (s, 18H), 0.33 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 183.8, 183.1, 157.1, 137.3, 132.2, 131.3, 131.2, 129.9, 129.4, 128.5, 126.3, 117.0, 26.1, 18.8, -

3.8; IR (thin-film) ν 2955, 2857, 1672, 1619, 829 cm^{-1} ; MS (EI) m/z 568 (M^+) (54), 511 (100), 227 (28), 143 (12); HRMS calculated for (M^+) 568.24651, found 568.24910.

Benzoquinone (0.040 g, 0.368 mmol) was dissolved in dry dimethylacetamide (20 mL) and (3,4-bis(dibromomethyl)phenoxy)*tert*-butyl)dimethylsilane (0.407 g, 0.736 mmol, 2 eq.) was added, followed by $\text{Cu}(\text{OTf})_2$ (0.013 g, 0.037 mmol, 0.1 eq.) and NaI (0.717 g, 4.786 mmol, 13 eq.), respectively. The reaction was stirred at 65 °C for 8 hours. Once the absence of initial benzoquinone aliquot was confirmed by TLC, further aliquots of benzoquinone were added (0.010 g, 0.093 mmol, 0.25 eq., three further additions over the duration of reaction) until complete consumption of (3,4-bis(dibromomethyl)phenoxy)(*tert*-butyl)dimethylsilane was observed. The reaction was cooled to room temperature (22 °C) and the solution changed from brown to yellow upon the addition of cold sat. aqueous $\text{Na}_2\text{S}_2\text{O}_3$. The yellow precipitate that formed was filtered and washed with H_2O , then taken up with CH_2Cl_2 and concentrated. The impurities were dissolved in acetone and the product was filtered through a sintered glass funnel, which provided 2,9 and 2,10-bis-(*tert*-butyl-dimethylsilyloxy)-pentacene-6,13-dione as a yellow solid in 35-37% yield..

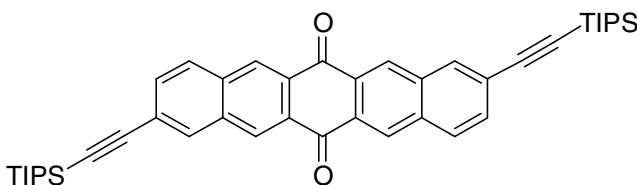
2,9-Bis(trifluoromethylsulfonyloxy)-6,13-pentacenequinone (23)



$\text{C}_{24}\text{H}_{10}\text{F}_6\text{O}_8\text{S}_2$
Mol. Wt.: 604.45

2,9-Bis-(*tert*-butyl-dimethyl-silyloxy)-pentacene-6-13-dione (**22**) (288 mg, 0.5 mmol) was dissolved in THF (150 mL), cooled to 0 °C and TBAF (1.1 mL, 1.1 mmol, 1M in THF) added. After 15 min., Tf_2NPh (500 mg, 1.4 mmol) in THF (10 mL) was cannulated into the reaction flask and warmed to 22 °C. After 18 h, the reaction was concentrated to 50 mL, diluted with ether, washed with 1 M HCl, 5% NaHCO_3 , and H_2O . The ether solution was concentrated to 30 mL and filtered through a sintered glass funnel to obtain the title compound **23** as a pale yellow solid (278 mg, 90%) that was used directly without further purification for the next step.

2,9-Bis(triisopropylsilylethynyl)-6,13-pentacenequinone (24)

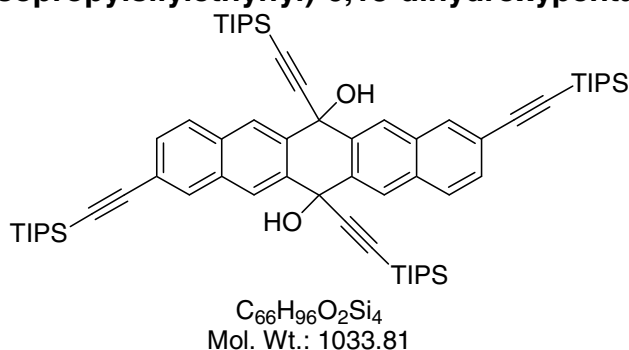


$\text{C}_{44}\text{H}_{52}\text{O}_2\text{Si}_2$
Mol. Wt.: 669.05

2,9-Bis(trifluoromethylsulfonyloxy)-6,13-pentacenequinone (**23**) (270 mg, 0.44 mmol) was dissolved in THF (100 mL), followed by the addition of CuI (16 mg, 0.09 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (32 mg, 0.045 mmol) and Et_3N (10 mL). After degassing for 30 min, TIPS-acetylene (0.26 mL, 1.16 mmol) was added and the reaction heated at reflux for 12 h. The reaction was cooled to 22

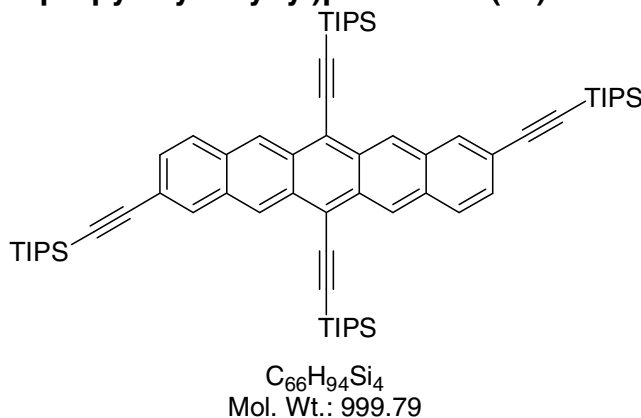
°C and filtered through a pad of silica gel (petroleum ether/EtOAc₂, 9:1) to afford the title compound **24** as a yellow solid (268 mg, 90%), mp: >270 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.83 (s, 4H), 8.20 (s, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 1.16 (s, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 182.5, 134.9, 134.4, 133.5, 132.3, 131.1, 130.8, 129.9, 129.5, 129.4, 124.8, 106.2, 94.8, 18.7, 11.3; IR (CH₂Cl₂) ν 3058, 2929, 2150, 1713 cm⁻¹; HRMS (EI, 20 eV) calcd for C₄₄H₅₂O₂Si₂: 668.3506; found 668.3500.

2,6,9,13-Tetrakis(triisopropylsilylethynyl)-6,13-dihydroxypentacene (25)



n-Buli (0.10 ml, 0.24 mmol, 2.5 M in hexanes) was added dropwise to triisopropylsilyl acetylene (45 mg, 0.25 mmol) in dry THF (3 mL) under argon at 0 °C and the mixture was stirred for 0.5 h. Compound **24** (40 mg, 0.06 mmol) in THF (3 mL) was added and the mixture was stirred for 3 h at 0 °C. The reaction was quenched with saturated aqueous NH₄Cl. The organic layer was separated and the aqueous layer was extracted with ether three times. The organic layers were combined, washed with brine, and dried over Na₂SO₄. Solvent was concentrated under reduced pressure and the residue was purified by silica gel chromatography (petroleum ether/EtOAc₂, 9:1) to give the title compound **25** (47 mg, 76%) as pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (s, 2H), 8.59 (s, 2H), 8.02 (s, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.55 (dd, *J* = 8.4, 1.5 Hz, 2H), 3.35 (s, 2H), 1.15 (m, 42H), 1.05 (m, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 137.0, 136.9, 132.7, 132.6, 132.0, 129.8, 128.1, 125.8, 121.9, 109.0, 107.2, 91.9, 90.0, 69.6, 18.7, 18.6, 11.4, 11.2; IR (film) ν 3489, 2941, 2864, 2154, 1463 cm⁻¹; MS (ESI) Calcd for C₆₆H₉₆KO₂Si₄: 1071.6 (M⁺ + K), Found 1071.6.

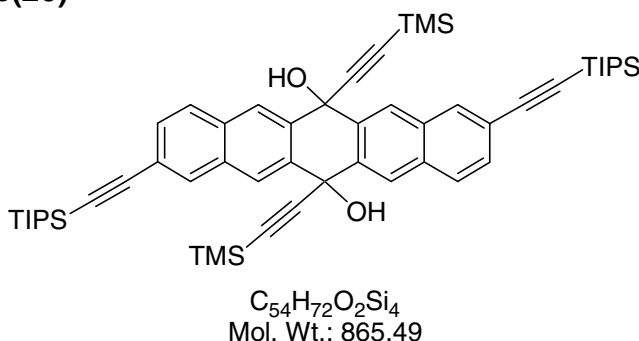
2,6,9,13-Tetrakis(triisopropylsilylethynyl)pentacene (28)



Compound **25** (38 mg, 0.04 mmol) in 1,4-dioxane (0.5 mL) was added to a solution of SnCl₂·2H₂O (0.18 g, 0.8 mmol) suspended in 50% acetic acid (0.5 mL). The mixture turned blue after the addition was complete. The reaction mixture was stirred at 22 °C for 30 min, ether (3

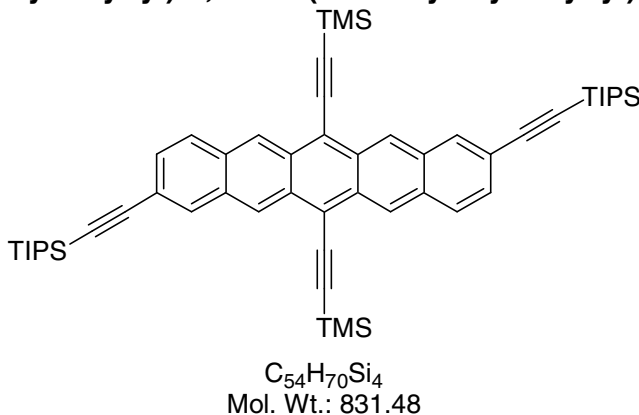
mL), and solid sodium bicarbonate added. The reaction mixture was stirred for another 10 min at 22 °C, filtered through a pad of Celite[®], and the solvent concentrated under reduced pressure. The residue was passed through a short pad of silica gel (hexane) to give **28** (34 mg, 92%) as a dark blue solid. ¹H NMR (400 MHz, CDCl₃) δ 9.22 (s, 2H), 9.20 (s, 2H), 8.09(s, 2H), 7.87 (d, *J* = 9.2, 2H), 7.36 (dd, *J* = 9.2, 1.2 Hz, 2H), 1.36 (s, 36H), 1.42-1.33 (m, 6H), 1.19 (s, 36H), 1.21-1.17 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 132.7, 131.6, 131.2, 131.0, 130.9, 128.6, 126.5, 126.4, 121.0, 118.8, 107.8, 107.7, 104.3, 93.1, 19.0, 18.7, 11.7, 11.4; IR (film) ν 2941, 2923, 2864, 2140, 2062, 1460, 1367 cm⁻¹.

2,9-Bis(triisopropylsilylethynyl)-6,13-bis(trimethylsilylethynyl)-6,13-dihydroxypentacene(26)



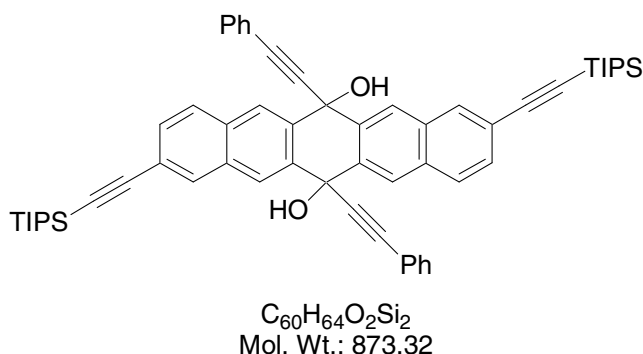
n-Buli (0.46 ml, 1.15 mmol, 2.5 M in hexanes) was added dropwise to trimethylsilyl acetylene (117 mg, 1.2 mmol) in dry THF (5 mL) under argon at 0 °C and the mixture was stirred for 0.5 h. Compound **24** (131 mg, 0.23 mmol) in THF (5 mL) was added and the mixture was stirred for 2 h at 0 °C. The reaction was quenched with saturated aqueous NH₄Cl. The organic layer was separated and the aqueous layer was extracted with ether three times. The organic layers were combined and washed with brine, dried over Na₂SO₄. Solvent was concentrated under reduced pressure and the residue was purified by chromatography (petroleum ether/EtOAc, 9:1) to give the diol **26** (158 mg, 80%) as pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 2H), 8.52 (s, 2H), 8.05 (s, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.57 (dd, *J* = 8.5, 1.5 Hz, 2H), 3.65 (s, 2H), 1.16 (m, 42H), 0.21 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 136.7, 132.7, 132.6, 132.0, 130.0, 128.2, 125.7, 125.6, 122.1, 107.2, 106.5, 93.9, 92.0, 69.6, 19.3, 11.6, -0.3; IR (film) ν 2295, 2943, 2864, 2152, 1464, 1251 cm⁻¹; MS (ESI) Calcd for C₅₂H₇₂KO₂Si₄: 903.4 (M⁺ + K), Found 903.5.

2,9-Bis(triisopropylsilylethynyl)-6,13-bis(trimethylsilylethynyl)-6,13-pentacene (29)



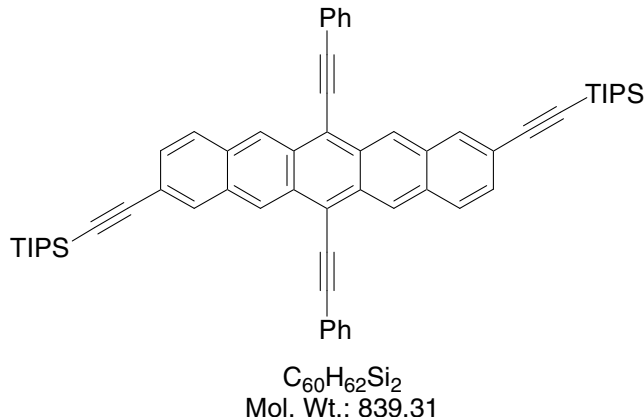
Compound **26** (138 mg, 0.16 mmol) in 1,4-dioxane (3 mL) was added to the solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.82 g, 3.2 mmol) suspended in 50% acetic acid (2 mL). The mixture turned blue after addition was complete. The reaction mixture was stirred at 22 °C for 30 min and ether (5 mL) plus solid sodium bicarbonate added. The reaction mixture was stirred for another 10 min and filtered to remove the solid. The solvent was concentrated under reduced pressure and the residue purified by filtration (hexane) through a pad of silica gel to give the pentacene **29** (125 mg, 93%) as a blue solid. ^1H NMR (400 MHz, CDCl_3) δ 9.00 (s, 2H), 8.92 (s, 2H), 8.13 (s, 2H), 7.86 (d, $J = 9.4$ Hz, 2H), 7.37 (dd, $J = 8.9, 1.2$ Hz, 2H), 1.19 (m, 42H), 0.54 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.7, 131.5, 131.1, 130.6, 130.5, 128.7, 128.5, 126.3, 126.1, 120.9, 118.3, 110.7, 107.7, 102.5, 92.9, 18.8, 11.4, 0.4; IR (film) ν 2957, 2941, 2864, 2138, 1464, 1369, 1248 cm^{-1} .

6,13-Bis(2-phenylethynyl)-2,9-bis(2-(triisopropylsilyl)ethynyl)-6,13-dihydropentacene-6,13-diol (27)



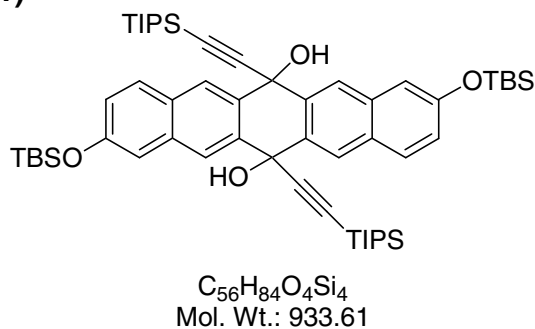
n-Buli (0.12 mL, 0.3 mmol, 2.5 M in hexanes) was added dropwise to phenyl acetylene (32 mg, 0.31 mmol) in dry THF (3 mL) under argon at 0 °C and the mixture was stirred for half an hour. Compound **24** (35 mg, 0.05 mmol) in THF (3 mL) was added and the mixture was stirred for 2 h at 0 °C. The reaction was quenched with saturated NH_4Cl . The organic layer was separated and the aqueous layer was extracted with ether three times. The organic layers were combined and washed with brine, dried over Na_2SO_4 . Solvent was removed and the residue was purified through chromatography (1:9; EA:PE) to give the title compound **27** (39.8 mg, 87%) as white solid. ^1H NMR (300 MHz, CDCl_3) δ 8.67 (s, 2H), 8.66 (s, 2H), 8.13 (s, 2H), 7.91 (d, $J = 8.5$ Hz, 2H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.55-7.52 (m, 4H), 7.37-7.31 (m, 6H), 1.19 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.2, 133.2, 133.0, 132.5, 132.2, 130.4, 129.4, 128.8, 128.6, 126.3, 126.3, 122.4, 122.2, 107.5, 92.3, 91.1, 88.7, 70.1, 19.1, 11.8; IR (film) ν 3330, 2941, 2864, 2150, 1488 cm^{-1} ; MS (ESI) Calcd for $\text{C}_{60}\text{H}_{64}\text{KO}_2\text{Si}_2$: 911.4 ($\text{M}^+ + \text{K}$), Found: 911.4

6,13-Bis(2-phenylethynyl)-2,9-bis(2-(triisopropylsilyl)ethynyl)pentacene (**30**)



Compound **27** (36 mg, 0.04 mmol) in 1,4-dioxane (0.5 mL) was added to the solution of $SnCl_2 \cdot 2H_2O$ (0.21 g, 0.8 mmol) suspended in 50% acetic acid (0.5 mL). The mixture turned to green blue after adding. The reaction mixture was then stirred at rt for 1 hour and ether (2 mL) and solid sodium bicarbonate was added. The reaction mixture was stirred for another 10 min at rt. Filter through a pad of celite to remove the solid and the solvent was removed under reduced pressure. The residue was purified by filtering through a short pad of silica gel (EA:PE; 1:4 to THF:PE; 1:2) to get **30** (27.8 mg, 78%) as a green blue solid. 1H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 2H), 8.95 (s, 2H), 8.15 (s, 2H), 7.91-7.84 (m, 6H), 7.60-7.51 (m, 6H), 7.41 (d, J = 11.6 Hz, 2H), 1.25 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8, 131.9, 131.5, 131.0, 130.3, 130.3, 128.9, 128.7, 128.6, 128.5, 126.2, 126.0, 123.5, 120.9, 118.2, 107.8, 104.7, 92.7, 87.6, 18.8, 11.4; IR (film) ν 2939, 2921, 2862, 2145, 1490, 1463 cm^{-1} .

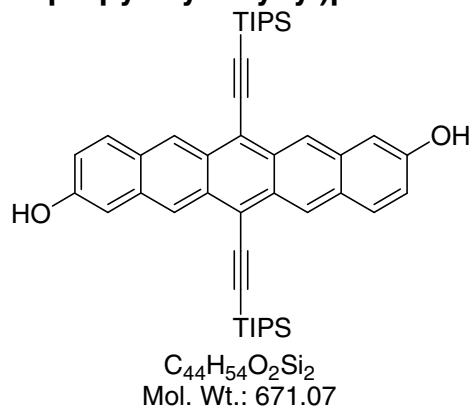
2,9-Bis(*t*-butyldimethylsiloxy)-6,13-bis(triisopropylsilylethynyl)-6,13-dihydropentacene (**31**)



n-BuLi (1.2 mL, 3 mmol, 2.5 M in hexanes) was added dropwise to triisopropylsilyl acetylene (583 mg, 3.2 mmol) in dry THF (10 mL) under argon at 0 °C and the mixture was stirred for 0.5 h. 2,9-Adduct **22** (262 mg, 0.46 mmol) in THF (5 mL) was added and the mixture stirred for 6 h at 0 °C. The reaction was quenched with saturated aqueous NH_4Cl . The organic layer was separated and the aqueous layer was extracted with ether 3 times. The organic layers were combined, washed with brine, and dried over Na_2SO_4 . Solvent was concentrated under reduced pressure and the residue was purified by chromatography (petroleum ether/ $EtOAc$, 9:1) to give compound **31** (374 mg, 87%) as pale yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 2H), 8.50 (s, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 2.0 Hz, 2H), 7.11 (dd, J = 8.8, 2.4 Hz, 2H), 3.28 (s,

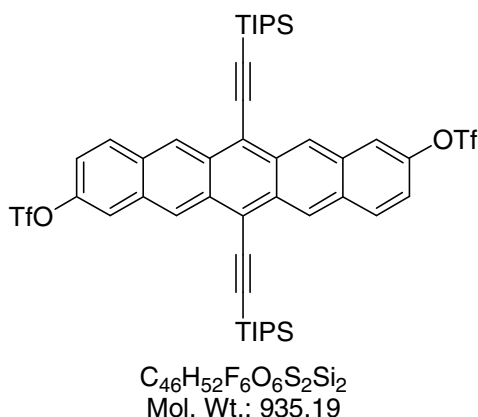
2H), 1.06 (m, 42H), 1.01 (s, 18H), 0.25(s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 136.8, 134.5, 134.2, 129.6, 128.9, 125.7, 124.6, 123.1, 114.9, 109.6, 89.2, 69.7, 25.7, 18.7, 18.3, 11.3, -4.3; MS (ESI) Calcd 971.5 ($\text{M}^+ + \text{K}$), Found 971.4; IR (film) ν 2943, 2864, 1605, 1464, 1383, 1254 cm^{-1} .

2,9-Dihydroxy-6,13-bis(triisopropylsilylethynyl)pentacene



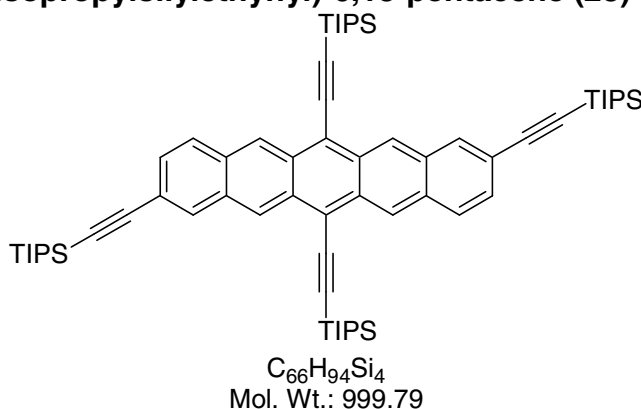
The diol ether **31** (374 mg, 0.41 mmol) in 1,4-dioxane (10 mL) was added to a solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2.32 g, 10 mmol) suspended in 50% acetic acid (6 mL). The mixture turned blue upon completion of the addition. The reaction mixture was then stirred at 22 $^\circ\text{C}$ for 30 min and THF (10 mL) and HCl (3M, 5 mL) were added. The reaction was stirred for ~15 h. Ether was added, the organic layer was separated, solid sodium bicarbonate was added, and stirred for 0.5 h. The reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether/ EtOAc , 9:1) to give the 2,9-diol (200 mg, 73%) as a green blue solid. ^1H NMR (400 MHz, CDCl_3) δ 9.20 (s, 2H), 9.03 (s, 2H), 7.89 (dd, $J = 9.16$, 2H), 7.17 (s, 2H), 7.10 (dd, $J = 9.16$, 2.24 Hz, 2H), 5.11 (s, broad, 2H), 1.34 (s, 36H), 1.37-1.32 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.1, 132.8, 131.1, 130.7, 129.9, 129.4, 126.4, 123.3, 120.8, 117.5, 107.1, 106.6, 104.8, 19.0, 11.7; IR (film) ν 3380 (br), 2952, 2923, 2862, 2135, 1703, 2631, 1460 cm^{-1} ; MS (EI, 70eV) m/z 670 (M^+ , 10%), 418 (4), 332 (2), 205 (13), 167(11), 57(100); HRMS (EI, 70 eV) Calcd for $\text{C}_{44}\text{H}_{54}\text{O}_2\text{Si}_2$: 670.3662, Found: 670.3664.

2,9-Bis(trifluoromethylsulfonyloxy)-6,13-bis(triisopropylsilylethynyl)pentacene (32)



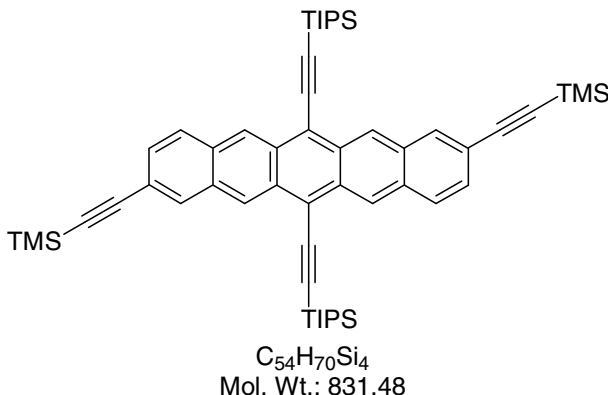
The diol above (113 mg, 0.17mmol) in THF (2 mL) was added to sodium hydride (15 mg, 0.38 mmol) in dry THF (2 mL) at 0 °C. The reaction mixture was stirred for 0.5 h and *N*-phenyl-trifluoromethanesulfonimide (134 mg, 0.37 mmol) was added. The mixture was then stirred for 1 h and saturated aqueous NH₄Cl was added to quench the reaction. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, and dried over Na₂SO₄. The solvent was concentrated under reduced pressure and the residue was filtered through a silica gel pad (petroleum ether) to give **32** (141 mg, 90%) as a blue solid. ¹H NMR (400 MHz, CDCl₃) δ 9.35 (s, 2H), 9.32 (s, 2H), 8.03 (d, *J* = 9.4, 2H), 7.83 (s, 2H), 7.30 (dd, *J* = 9.4, 2.1 Hz, 2H), 1.36 (s, 36H), 1.42-1.34 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 132.1, 131.2, 131.1, 131.0, 130.6, 127.6, 127.5, 120.8, 119.5, 119.2, 118.8 (q, *J* = 319Hz), 109.0, 103.7, 19.0, 11.6; IR (film) ν 2941, 2925, 2864, 2135, 1425, 1369, 1207 cm⁻¹.

2,6,9,13-Tetrakis(triisopropylsilyl)ethynyl)-6,13-pentacene (**28**)



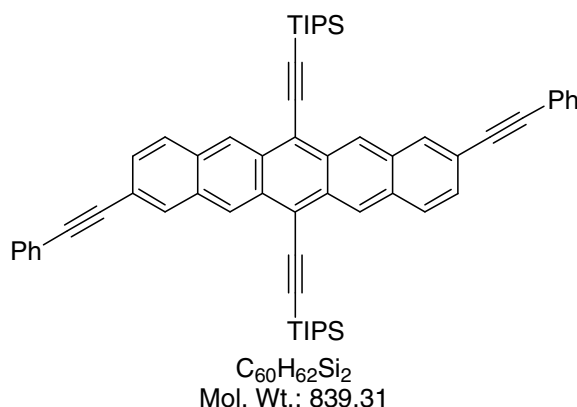
Compound **32** (136 mg, 0.15 mmol), Pd(PPh₃)₂Cl₂ (12 mg, 0.015 mmol) and CuI (6 mg, 0.03 mmol) were dissolved in a mixture of triethylamine (0.5 mL) and THF (5 mL) and degassed (argon) for 30 min. Triisopropylsilylacetylene (70 μL, 0.32 mmol) was added and the solution was stirred at room temperature for 1 h. The mixture was filtered through a pad of silica gel with ether as eluent and concentrated. The resultant organic residue was filtered through a second silica gel pad with petroleum ether as eluent. Removal of the solvent afforded the pentacene **28** (135 mg, 93%) as a blue solid.

6,13-Bis(2-(triisopropylsilyl)ethynyl)-2,9-bis(2-(trimethylsilyl)ethynyl)pentacene (**33**)



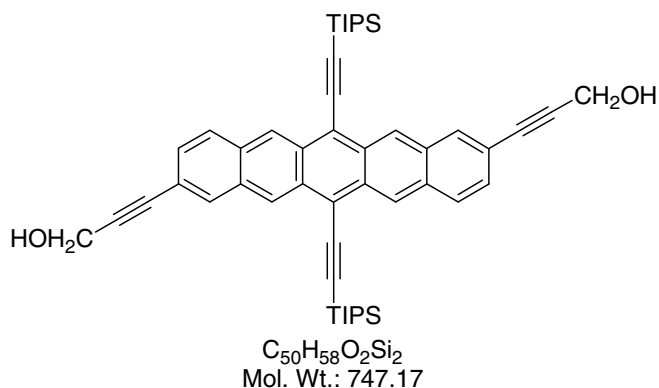
Compound **32** (18.3 mg, 0.02mmol) in THF (2 mL) was degassed for 20 min. CuI (1 mg, 0.005 mmol), Pd(PPh₃)₂Cl₂ (2 mg, 0.002mmol) and triethylamine (0.2 mL) was added and degassed for another 10 mins. TMS acetylene (5 mg, 0.05mmol) in THF (0.5 mL) was then added at room temperature. The reaction mixture was stirred at rt for 30 mins and was filtered through a short pad of silica gel. The solvents was removed under reduced pressure and the residue was purified by a short pad of silica (petroleum ether/EtOAc₂, 9:1) to afford the title compound **33** as a green-blue solid (14.3mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 9.21(s, 2H), 9.18 (s, 2H), 8.08 (s, 2H), 7.86 (d, *J* = 9.3 Hz, 2H), 7.36 (dd, *J* = 8.8, 1.2 Hz, 2H), 1.35 (s, 42H), 0.31 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 132.9, 131.6, 131.2, 131.1, 130.9, 128.7, 128.4, 126.6, 126.5, 120.6, 118.8, 107.8, 105.7, 104.2, 96.4, 19.0, 11.7, 0.0; IR (film) ν 2954, 2943, 2920, 2864, 2146, 1431, 1230 cm⁻¹.

2,9-Bis(2-phenylethynyl)-6,13-bis(2-(triisopropylsilyl)ethynyl)pentacene (34)



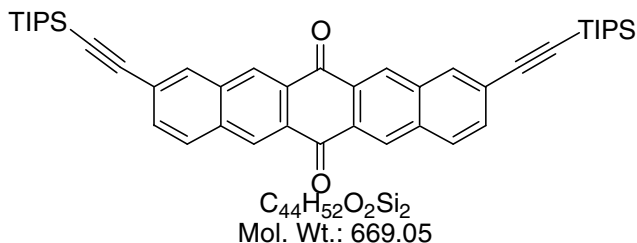
Compound **32** (18.5 mg, 0.02mmol) in THF (2 mL) was degassed for 20 min. CuI (1 mg, 0.005 mmol), Pd(PPh₃)₂Cl₂ (2 mg, 0.002mmol) and triethylamine (0.2 mL) was added and degassed for another 10 mins. Phenylacetylene (5.1 mg, 0.05mmol) in THF (0.5 mL) was then added at room temperature. The reaction mixture was stirred at rt for 30 mins and was filtered through a short pad of silica gel. The solvent was removed under reduced pressure and the residue was purified by a short pad of silica (petroleum ether/EtOAc₂, 9:1) to afford the title compound **34** as a green-blue solid (14.6mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 9.25 (s, 2H), 9.23 (s, 2H), 8.15 (s, 2H), 7.92 (d, *J* = 9.1 Hz, 2H), 7.63-7.60 (m, 4H), 7.45 (dd, *J* = 8.8, 1.3 Hz, 2H), 7.40-7.36 (m, 6H), 1.43-1.34 (m, 42H); ¹³C NMR (75 MHz, CDCl₃) δ 132.7, 132.2, 132.1, 131.6, 131.5, 131.4, 129.3, 129.0, 128.9, 128.6, 126.9, 126.9, 123.5, 121.2, 119.2, 108.1, 104.7, 91.8, 90.6, 19.5, 12.1; IR (film) ν 2941, 2864, 2135, 1909, 1599, 1491, 1463, 1369 cm⁻¹.

2,9-Bis(2-propargylethynyl)-6,13-bis(2-(triisopropylsilyl)ethynyl)pentacene (35)



Compound **32** (25.6 mg, 0.027mmol) in THF (3 mL) was degassed for 20 min. CuI (1 mg, 0.005 mmol), Pd(PPh₃)₂Cl₂ (2 mg, 0.002mmol) and triethylamine (0.2 mL) was added and degassed for another 10 mins. Propargyl alcohol (4.7 mg, 0.08mmol) in THF (0.5 mL) was then added at room temperature. The reaction mixture was stirred at rt for 30 mins and was filtered through a short pad of silica gel. The solvent was removed under reduced pressure and the residue was purified by a short pad of silica (petroleum ether/EtOAc, 4:1) to afford the title compound **35** as a green-blue solid (16.6mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ 9.26 (s, 2H), 9.24 (s, 2H), 8.11 (s, 2H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 4.63 (d, *J* = 6.0 Hz, 4H), 1.39 (s, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 132.7, 131.6, 131.2, 131.1, 131.0, 128.9, 128.0, 126.6, 126.5, 120.0, 118.8, 107.9, 104.2, 89.0, 86.4, 51.9, 19.0, 11.7; IR (film) ν 3361, 2941, 2864, 2135, 1464, 1367 cm⁻¹; MS(ESI) Calcd for C₅₀H₅₈KO₂Si₂: 785.4 (M⁺+K), Found: 785.5.

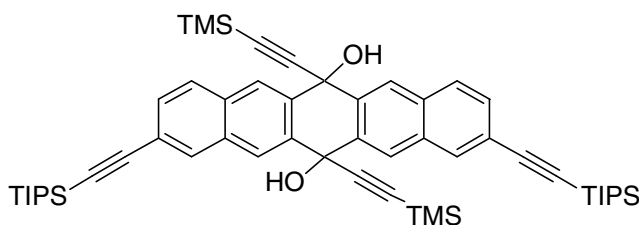
2,10-Bis(2-(triisopropylsilyl)ethynyl)pentacene-6,13-dione (**37**)



A mixture of 2,9-Bis(trifluoromethylsulfonyloxy)-6,13-pentacenequinone (**23**) and 2,10-Bis(trifluoromethylsulfonyloxy)-6,13-pentacenequinone (**36**) prepared as above by exposure to TBAF (1.1 mL, 1.1 mmol, 1M in THF, 0 °C) followed after 15 min. by cannulated addition of Tf₂NPh (500 mg, 1.4 mmol) in THF (10 mL) and warmed to 22 °C. After 18 h, the reaction was concentrated to 50 mL, diluted with ether, washed with 1 M HCl, 5% NaHCO₃, and H₂O. The ether solution was concentrated to 30 mL and filtered through a sintered glass funnel to obtain the mixture that was used directly without further purification. The triflates (620 mg, 1 mmol) were dissolved in THF (200 mL), followed by the addition of CuI (32 mg, 0.18 mmol), Pd(PPh₃)₂Cl₂ (64 mg, 0.09 mmol) and Et₃N (10 mL). After degassing for 30 min, TIPS-acetylene (0.60 mL, 2.3 mmol) was added and the reaction was heated at reflux for 6 h. The reaction was cooled to 22 °C and filtered through a pad of silica gel (petroleum ether/EtOAc₂, 9:1) to afford **24** and **37** as a yellow solid (616 mg, 90%). Fractional crystallization from CH₂Cl₂ gave **37** as a pale yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 8.86 (s, 2H), 8.85 (s, 2H), 8.23 (s, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.71 (dd, *J* = 8.5, 1.3 Hz, 2H), 1.20 (s, 42H); ¹³C NMR (75 MHz, CDCl₃) δ 182.5, 182.4, 134.8, 134.4, 133.5, 132.3, 131.0, 130.8, 129.9, 129.5, 129.4, 124.8, 106.2, 94.8,

18.7, 11.3; IR (film) ν 2939, 2862, 2148, 1684, 1612, 1456, 1386 cm^{-1} ; MS (EI) Calcd for $\text{C}_{44}\text{H}_{52}\text{O}_2\text{Si}_2$: 668.3506; Found: 668.3488.

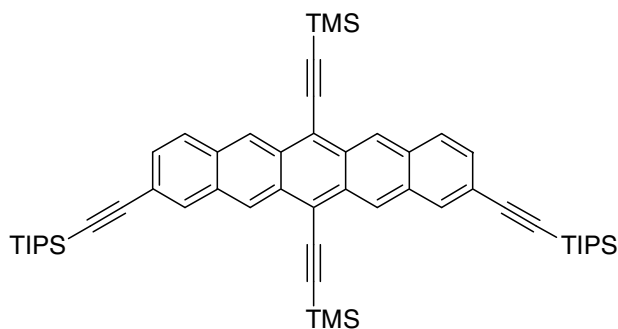
2,9-Bis(2-(triisopropylsilyl)ethynyl)-6,13-bis(2-(trimethylsilyl)ethynyl)-6,13-dihydropentacene-6,13-diol



$\text{C}_{54}\text{H}_{72}\text{O}_2\text{Si}_4$
Mol. Wt.: 865.49

n-Buli (0.38 ml, 0.96 mmol, 2.5 M in hexanes) was added dropwise to trimethylsilyl acetylene (98 mg, 1.0 mmol) in dry THF (5 mL) under argon at 0 °C and the mixture was stirred for 0.5 h. Compound **37** (109.5 mg, 0.19 mmol) in THF (5 mL) was added and the mixture was stirred for 2 h at 0 °C. The reaction was quenched with saturated aqueous NH_4Cl . The organic layer was separated and the aqueous layer was extracted with ether three times. The organic layers were combined and washed with brine, dried over Na_2SO_4 . Solvent was removed under reduced pressure and the residue was purified by chromatography (petroleum ether/ EtOAc , 9:1) to give the 6,13-diol. (131.6, 81%) as pale yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, 2H), 8.53 (s, 2H), 8.07 (s, 2H), 7.86 (d, J = 11.2 Hz, 2H), 7.38 (d, J = 11.4 Hz, 2H), 3.78 (br, 1H), 3.65 (br, 1H), 1.18 (s, 42H), 0.25 (s, 9H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.3, 136.8, 133.1, 132.9, 132.4, 130.4, 128.6, 126.3, 125.8, 122.4, 107.5, 107.2, 106.6, 94.5, 94.1, 92.4, 70.3, 69.7, 19.1, 11.8, 0.15, 0.08; IR (film) ν 3375, 2957, 2864, 2150, 1720, 1456, 1254 cm^{-1} ; MS (ESI) Calcd for $\text{C}_{52}\text{H}_{72}\text{KO}_2\text{Si}_4$: 903.4 ($\text{M}^+ + \text{K}$), Found 903.5.

2,10-Bis(2-triisopropylsilyl)ethynyl)-6,13-bis(2-(trimethylsilyl)ethynyl)pentacene (38)



$\text{C}_{54}\text{H}_{70}\text{Si}_4$
Mol. Wt.: 831.48

The 6,13-diol above (92.3 mg, 0.11 mmol) in 1,4-dioxane (2 mL) was added to the solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.50 g, 2.0 mmol) suspended in 50% acetic acid (2 mL). The mixture turned blue after addition was complete. The reaction mixture was stirred at rt for 30 min and ether (5 mL) plus solid sodium bicarbonate was added. The reaction mixture was stirred for another 10 min and filtered to remove the solid. The solvent was concentrated under reduced pressure and the

residue was purified by filtration through a pad of silica gel (petroleum ether/EtOAc, 95:5) to give the pentacene **38** (83.2 mg, 92%) as a green blue solid. ^1H NMR (400 MHz, CDCl_3) δ 9.02 (s, 4H), 8.12 (s, 2H), 7.89 (d, $J = 9.2$ Hz, 2H), 7.38 (dd, $J = 9.2, 1.2$ Hz, 2H), 1.19 (s, 42H), 0.54 (s, 9H), 0.52 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.7, 131.5, 131.2, 130.6, 128.6, 126.3, 126.1, 121.0, 118.5, 118.2, 111.0, 110.6, 107.7, 102.5, 92.9, 18.8, 11.4, 0.37, 0.33; IR (film) ν 2956, 2941, 2864, 2149, 1463, 1250 cm^{-1} .

X-Ray Figures

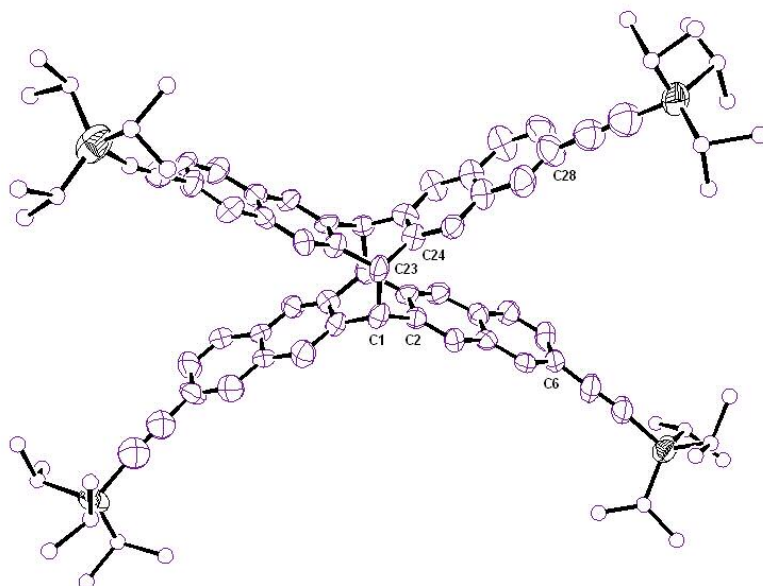


Figure A. X-Ray crystal structure of the [4+4] photochemical dimer **14**

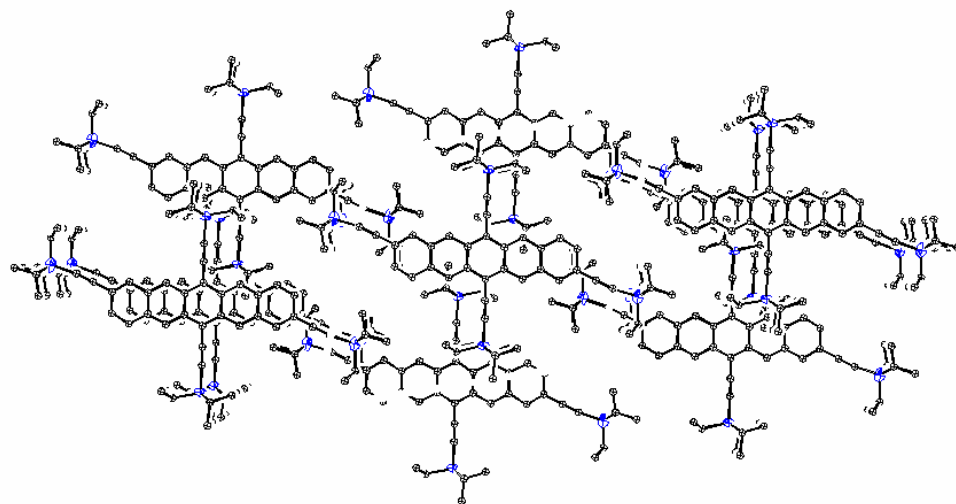


Figure B. Crystal Packing: Perpendicular View of 2,6,9,13-Tetrakis(triisopropylsilyl)ethynyl-6,13-pentacene (**28**)