Supplementary and supporting information for:

A survey of electron-deficient pentacenes as acceptors in polymer bulk heterojunction solar cells

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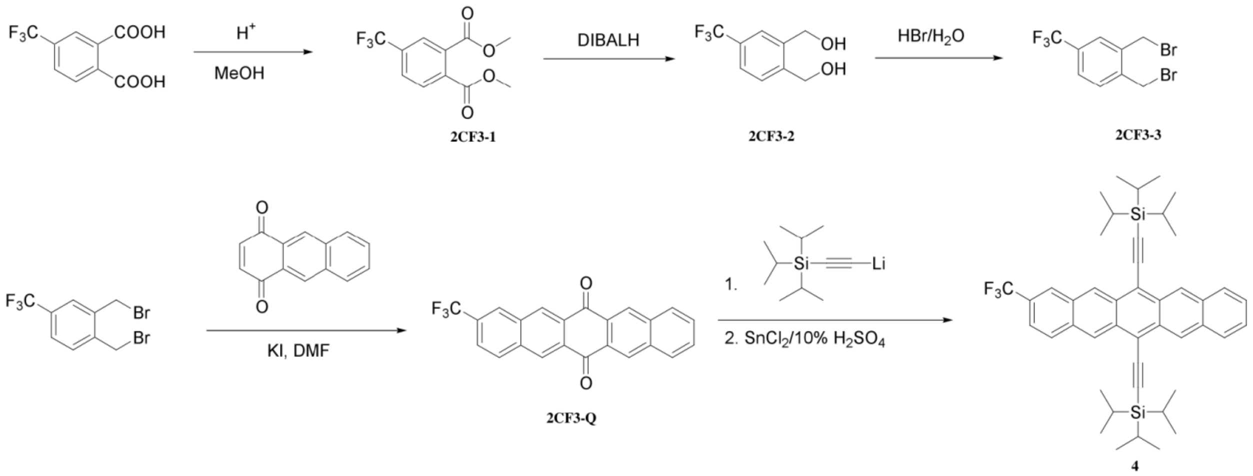
Synthesis

General:

Bulk solvents (hexanes, dichloromethane, acetone) were purchased from Pharmco-Aaper. Anhydrous THF was purchased from Aldrich. Triisopropylsilyl acetylene was purchased from GFS Chemicals. 4-trifluoromethyl phthalic acid was purchased from TCI America. Silica gel 230-400 mesh was purchased from Sorbent Technologies. All other chemicals were used as supplied from Aldrich, or prepared by literature methods. The NMR spectra were measured on a Varian (Gemini 200 Mhz or Unity 400 MHz) spectrometers. Chemical shifts are reported in ppm relative to $CDCl_3$ as an internal standard (^{1}H NMR: $CDCl_3$ at 7.24 ppm; ^{13}C NMR: $CDCl_3$ at 77.23 ppm). The UV-Vis spectra was measured on a UV-2501PC Shimadzu instrument. Mass spectroscopy was analyzed in EI mode at 70 eV on a JEOL (JMS-700T) mass spectrometer. GC-MS data were collected using an Agilent technologies 6890N GC with 5973 MSD, or a Hewlett-Packard G1800A GCD system. Melting and decomposition points were determined by differential scanning calorimetry on a TA DSC-Q100 at a rate of 8 °C/minute. Differential pulse voltammetry was carried out on a BAS CV-50W potentiostat under a blanket of N_2, at a scan rate of 20 mV/s and Fc/Fc^+ as an internal standard. A 0.1M Bu_4NPF_6 solution in dichloromethane was used as the supporting electrolyte solution, with a platinum button working electrode, a platinum wire counter electrode and a silver wire pseudo-reference electrode. Combustion analysis performed by Columbia Analytical Services. Single-crystal X-ray diffraction measurements, to determine the solid-state crystal packing arrangement of the acceptor molecules, was performed on solution-grown crystals of material. The date were collected on either a Bruker-Nonius KappaCCD diffractometer, or a Bruker-Nonius X8 Proteum diffractometer. The data were refined and the structures solved as described in the accompanying cif files.

Synthesis of 2-trifluoromethyl derivatives 4 and 12



4-Trifluoromethyl-phthalic acid dimethyl ester (2CF3-1)

4-Trifluoromethylphthalic acid (5 g, 21.36 mmol) was dissolved in 200 mL of methanol, followed by 10 mL of conc. H_2SO_4. The reaction was stirred at reflux for 1 day. The reaction was then cooled to room temperature, and the solvent removed under vacuum. The liquid was dissolved in diethyl ether, and extracted with water several times. The organic layer was dried with magnesium sulfate, filtered, and the solvent evaporated to yield 4-trifluoromethyl-1,2-dimethylphthalate (4.87 g, 18.57 mmol, 87%) as a clear liquid. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.86 (2 s, 6H), 7.73 (d, J = 1 Hz, 2H), 7.97 (s, 1H). ^{3}C-NMR ($CDCl_3$, 50 MHz) δ 53.020, 126.189, 128.101, 128. 313, 129.489, 132.273, 132.691, 135.855, 166.438, 167.211. MS (EI, 70 eV): *m/z*: 262 ($C_{11}H_9F_3O_4$).

4-trifluoromethylbenzene-1,2-dimethanol (2CF3-2)

To a flame dried round bottom flask cooled under nitrogen was added 25.9 g of 4-trifluoromethyl-phthalic acid dimethyl ester (98.9 mmol) and 200 mL of anhydrous dichloromethane. The flask was placed in an ice bath and cooled to 0 °C. 415.5 mL of DIBAlH (1.0 M in hexanes) was added slowly over the course of two hours. The reaction mixture was gradually warmed to room temperature and stirred for an additional 16 hours. The next day, the reaction mixture was quenched slowly with ice water, and the solids filtered and rinsed with dichloromethane. The dichloromethane layer was extracted twice with water and dried with magnesium sulfate. The quenched DIBAlH salts were rinsed with hot ethyl acetate and combined with previously collected product from dichloromethane extraction to give the product as a clear viscous oil after solvent was evaporated. 19.7 g (97% yield) of product was collected. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ4.677 (s, 6H), 7.441 (d, J = 7.8 Hz, 1H), 7.566 (d, J = 8.5 Hz, 1H), 7.645 (s, 1H). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ62.617, 121.418, 124.969, 125.029, 125.576, 126.820, 129.202, 139.779, 142.814. MS (EI, 70 EV): *m/z*: 204 ($C_9H_9F_3O_2{}^{+}$-H).

1,2-Bis-bromomethyl-4-trifluoromethyl-benzene (2CF3-3)

To a round bottom flask was added 4-trifluoromethylbenzene-1,2-dimethanol (19.7g), and 300 mL of aqueous HBr (48% in water). The reaction mixture was heated at reflux for 16 hours and then cooled to room temperature. The desired product was extracted with hexanes. The organic layer was dried with magnesium sulfate, filtered and the solvent evaporated off to yield the desired product as an orange liquid. 25.9 g (82% yield). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 5.126 (2 s, 4H), 7.480 (m, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 31.799, 118.397, 121.591, 124.899, 131.780, 140.247. MS (EI, 70 EV): *m/z*: 332 ($C_9H_7Br_2F_3$).

2-Trifluoromethyl pentacenequinone (2CF3-Q)

To a nitrogen purged round bottom flask was added 11 g of 1,4-anthraquinone (52.8 mmol) and 13.29g (40 mmol) 1,2-Bis(bromomethyl)-4-trifluoromethylbenzene. 100 mL of degassed DMF was added to the flask under nitrogen and the reactants heated to 90 °C. 58.7 g of KI (353.6 mmol) was then slowly added to the reaction, and the temperature was raised to 130 °C. The reaction mixture was stirred for 32 hours. The reaction mixture was subsequently cooled to room temperature and the solids filtered and washed with acetone, followed by copious amounts of THF and ether. The insoluble yellow solid was then allowed to air dry for several hours to yield 6.9 g (46%) of quinone. MS (EI 70 eV) *m/z* 376 (100%, M$^+$).

2-Trifluoromethyl-6,13-bis-[triisopropylsilylethynyl]-pentacene (4)

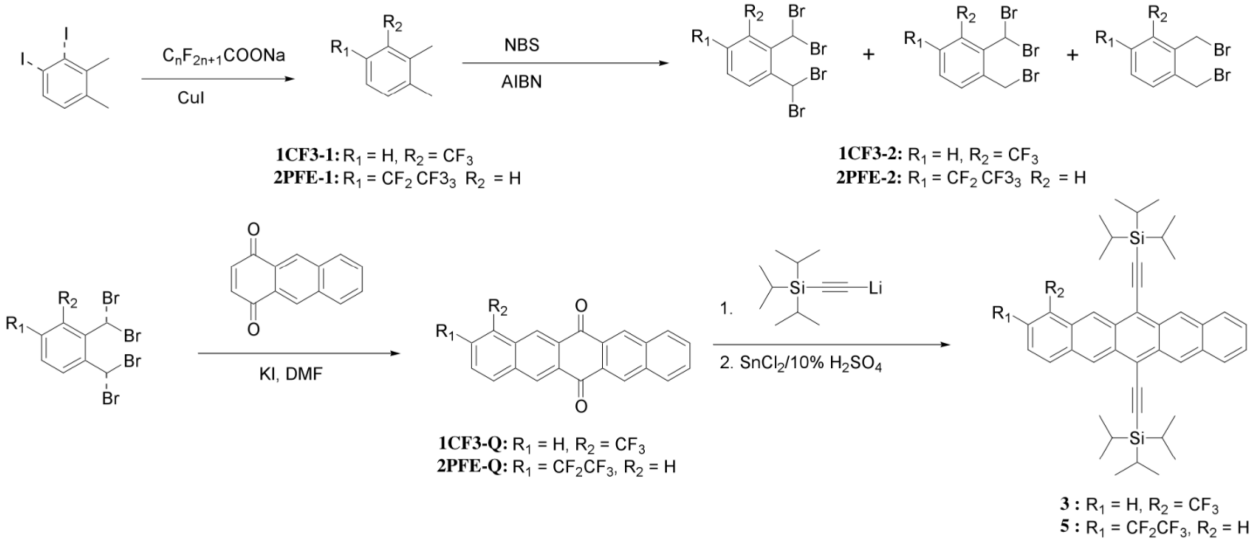
To a flame dried, nitrogen cooled round bottom flask was added hexanes (10 mL), followed by triisopropylsilylacetylene (1.04 mL, 4.65 mmol). 1.6 mL (3.98 mmol) of n-BuLi (2.5M in hexanes) was added slowly to the flask and the contents stirred for one hour. 2-Trifluoromethyl pentacene quinone (0.5 g, 1.33 mmol) was then added to that flask followed by 20 mL of anhydrous THF, and the contents stirred for one hour (until all the solids have dissolved). Deoxygenation proceeded with the addition of 3 mL of 10% H_2SO_4 and stannous chloride dihydrate, and the reaction stirred vigorously for 1 hour. The reaction mixture was then worked up and purified by silica gel column chromatography, using hexanes as an eluent. The product was further purified by recrystallization from acetone. The resulting product was filtered and dried in air to obtain 0.60g (64 % yield) of pure product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.368 (s, 42H), 7.401 (dd, J = 3.0 Hz, J = 6.6 Hz, 2H), 7.464 (dd, J = 1.4 Hz, J = 8.6 Hz, 1H), 7.947 (dd, J = 3.2 Hz, J = 6.6 Hz, 2H), 8.022 (d, J = 9.2 Hz, 1H), 8.237 (s, 1H), 9.310 (s, 2H), 9.327 (s, 1H), 9.385 (s, 1H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.863, 19.198, 104.412, 104.524, 108.108, 108.318, 118.987, 119.189, 121.083, 121.111, 123.113, 125.814, 126.556, 126.612, 126.640, 126.752, 127.060, 127.232 (q, $J_{c\text{-}F}$ = 5.6 Hz), 127.634, 127.956, 128.809, 128.893, 130.349, 130.461, 130.979, 131.021, 131.161, 132.085, 132.757, 132.827. MS (EI 70 eV) *m/z* 706 (100%, M$^+$ - 1) 707 (59%, M$^+$). MP: 228 °C. Elemental analysis calculated for $C_{45}H_{53}F_3Si_2$: C 76.44, H 7.56. Found: C 76.22, H 7.67.

2-Trifluoromethyl-6,13-bis-[(triisobutylsilyl)-ethynyl]-pentacene (12)

To a flame dried, nitrogen cooled round bottom flask was added hexanes (10 mL), followed by triisobutylsilylacetylene (1.52 g, 6.76 mmol). 2.32 mL (5.8 mmol) of n-BuLi (2.5M in hexanes) was added to the flask and the contents allowed to stir for one hour. 2-Trifluoromethyl pentacene quinone (0.75 g, 1.93 mmol) was added to that flask and 20 mL of anhydrous THF was added and the contents were stirred until all solids have dissolved. Deoxygenation proceeded with the addition of 3 mL of 10% H_2SO_4 and stannous chloride dihydrate for 1 hour. The reaction mixture was then worked up and purified by silica gel column chromatography, using hexanes as an eluent. The product was further purified by recrystallization from acetone. The resulting product was filtered and dried in air to obtain 0.31g (20 % yield) of pure product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.961 (d, J = 6.4 Hz, 36H), 1.182 (d, J = 6.4 Hz, 12H), 2.154 (sept, J = 7.4Hz, 6H), 7.420 (dd, J = 6.4, J = 3.2, 2H), 7.478 (d, J = 8.8 Hz, 1H), 7.953 (dd, J = 6.4, J = 3.2, 2H), 8.026 (d, J = 8.8, 1H), 8.244 (s, 1H), 8.263 (s, 2H), 8.285 (s, 1H), 9.361 (s, 1H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 25.077, 25.217, 25.581, 25.679, 26.262, 26.770, 89.743, 94.894, 104.412, 104.510, 110.809, 111.005, 118.955, 119.249, 121.129, 126.570, 126.640, 126.948, 127.186, 128.795, 130.293, 130.363, 131.021, 131.217, 131.553, 132.099, 132.757, 132.841. MS (EI 70 eV) *m/z* 790 (M^+ - 1), 791 (M^+), 454 (100%). MP: 173 °C. Elemental analysis calculated for $C_{51}H_{65}F_3Si_2$: C 77.42, H 8.28. Found: C 77.55, H 8.43.

Synthesis of 1-trifluoromethyl and 2-perfluoroethyl pentacenes 3 and 5



1CF3-1: R_1 = H, R_2 = CF_3
2PFE-1: R_1 = CF_2CF3_3 R_2 = H

1CF3-2: R_1 = H, R_2 = CF_3
2PFE-2: R_1 = CF_2CF3_3 R_2 = H

1CF3-Q: R_1 = H, R_2 = CF_3
2PFE-Q: R_1 = CF_2CF_3, R_2 = H

3 : R_1 = H, R_2 = CF_3
5 : R_1 = CF_2CF_3, R_2 = H

1,2-Dimethyl-3-trifluoromethyl-benzene (1CF3-1)

To a nitrogen purged, flame dried round bottom flask was added 25 g of 1-iodo *o*-xylene (107.7 mmol), 117.2 g of sodium trifluoroacetate (861.8 mmol), 41 g of CuI (215.4 mmol) and 200 mL of anhydrous NMP. The reaction contents were heated at 160 °C for 16 hours. After 16 hours, the reaction flask was allowed to cool to room temperature and the reaction mixture run through a thick silica gel plug with hexanes. The collected yellow liquids were then evaporated to dryness on a rotary evaporator and the oil distilled at 65 °C (10^{-1} Torr) to collect the desired product. 8.8 g of the product, a clear colorless liquid, was collected (47%). ^1H NMR (200 MHz, $CDCl_3$): δ 2.281 (s, 3H), 2.329 (s, 3H), 7.073 (t, J = 7.8 Hz, 1H), 7.249 (d, J = 7.6 Hz, 1H), 7.423 (d, J = 8.0, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.417, 22.981, 132.618, 125.591, 133.482, 138.868. MS (EI, 70 EV): *m/z*: 174 ($C_9H_9F_3$).

1,2-Bis-bromomethyl-3-trifluoromethyl-benzene, 2-Bromomethyl-1-dibromomethyl-3-trifluoromethyl-benzene, 1,2-Bis-dibromomethyl-3-trifluoromethyl-benzene (1CF3-2)

To the 8.8 g (50.6 mmol) 1,2-dimethyl-3-trifluoromethyl-benzene (**1CF3-1**) was added 40.5 g (227.5 mmol) of NBS. 150 mL of 1,2-dichloroethane was added as well as a catalytic amount of AIBN. The reaction was refluxed at 75 °C for 16 hours. The reaction flask was then cooled to room temperature and the reaction mixture filtered through a thin pad of silica gel, washing with hexanes. 21.0 g of liquid product was collected, and shown to be a mixture of products by GC/MS. The product was used in the next step without further purification. MS (EI, 70 EV): *m/z*: 330 ($C_9H_7Br_2F_3{}^+$-H), 411 ($C_9H_6Br_3F_3$), 409 ($C_9H_5Br_4F_3{}^+$-Br).

1-Trifluoromethyl pentacenequinone (1CF3-Q)

To a nitrogen purged round bottom flask was added 10.4 g of 1,4 anthraquinone (49.9 mmol) and approximately 50 mmol of the mixture of brominated 1-trifluoromethyl *o*-xylenes. 40 mL of degassed DMF was added to the flask under nitrogen and the reactants heated to 90 °C. 55.6 g of KI (335 mmol) was then slowly added to the reaction, and the temperature raised to 130 °C. The reaction mixture stirred for 32 hours, and then cooled to room temperature. The solids were filtered and washed with acetone, followed by THF and ether. The insoluble yellow solid was then allowed to air dry for several hours to yield 4.9 g (26%). MS (EI 70 eV) *m/z* 376 (100%, M^+).

1-Trifluoromethyl-6,13-bis-[triisopropylsilylethynyl]-pentacene (3)

To a flame dried, nitrogen cooled round bottom flask was added hexanes (10 mL), followed by triisopropylsilylacetylene (1.6 mL, 7 mmol). 2.4 mL (6 mmol) of n-BuLi (2.5M in hexanes) was added to the flask and the contents stirred for one hour at room temperature. 1-Trifluoromethyl pentacene quinone (0.75g, 2 mmol) was added to that flask, followed by 20 mL of anhydrous THF and stirred for one hour (until all solids have dissolved). Deoxygenation proceeded with the addition of 3 mL of 10% H_2SO_4 and stannous chloride dihydrate for 1 hour. The reaction mixture was then worked up and purified by silica gel column chromatography, using hexanes as eluent. The product was further purified by recrystallization from acetone. The resulting product was filtered and dried in air to obtain 0.85g (61 %) of pure product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.369 (s, 42H), 7.367 (t, J= 3.8 Hz, 1H), 7.406 (dd, J = 1.6 Hz, J = 3.4 Hz, 2H), 7.797 (d, J = 3.6 Hz, 1H), 7.969 (m, 2H), 8.110 (d, J = 4.4 Hz, 1H), 9.315 (s, 1H), 9.364 (d, 3.2 Hz, 2H), 9.687 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.91, 19.114, 104.23, 104.53, 107.91, 108.64, 118.550, 119.669, 125.232, 125.996 (q, $J_{C\text{-}F}$ = 7.0 Hz), 126.500, 126.500, 126.556, 126.836, 126.892, 127.956, 128.851, 128.949, 130.545, 130.951, 131.105, 131.357, 132.211, 132.757, 133.946. MS (EI 70 eV) *m/z* 706 (100%, M^+ - 1) 707 (57%, M^+). MP: 275 °C (decomp).

1,2-Dimethyl-4-pentafluoroethyl-benzene (2PFE-1)

To a nitrogen purged, flame dried round bottom flask was added 15 g of 4-iodo *o*-xylene (64.7 mmol), 16.8g of sodium pentafluoropropionic acid (90.5 mmol), 12.3 g of CuI (64.6 mmol) and 100 mL of anhydrous NMP. The reaction mixture was heated at 170 °C for 16 hours, then cooled to room temperature and run through a thick silica gel plug with hexanes. The collected yellow liquids were then evaporated to dryness on a rotary evaporator and the oil distilled at 60 °C (10^{-2} Torr) to collect the desired product. 9.14 g of the product, a clear colorless liquid, was collected (63%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.347 (s, 6H), 7.247 (d, J = 7.8 Hz, 1H), 7.357 (s, 1H), 7.401 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ

19.810, 19.840, 124.013 (t, J = 6.1 Hz), 127.472 (t, J = 6.1 Hz), 130.158, 137.563, 141.205. MS (EI, 70 EV): *m/z*: 224 ($C_{10}H_9F_5$).

1,2-Bis-bromomethyl-4-pentafluoroethyl-benzene, 1-Bromomethyl-2-dibromomethyl-4-pentafluoroethyl-benzene, 1,2-Bis-dibromomethyl-4-pentafluoroethyl-benzene (2PFE-2)

To a nitrogen purged, flame dried two neck round bottom flask was added 9.14 g (40.8 mmol) of 1,2-dimethyl-4-pentafluoroethyl-benzene **(3a)** and 36.3 g (204 mmol) of NBS. 200 mL of 1,2-dichloroethane was added as well as a catalytic amount of AIBN. The reaction was heated at reflux (75 °C) for 16 hours. The reaction mixture was then cooled and filtered through a thin pad of silica gel, washing with 1:1 dichlormethane:hexanes. 28.16 g of liquid product was collected, and shown to be a mixture of products by GC/MS. The product mixture was used in the next step without further purification. MS (EI, 70 EV): *m/z*: 382 ($C_{10}H_7Br_2F_5$), 379 ($C_{10}H_6Br_3F_5{}^+$ -Br), 420 ($C_{10}H_5Br_4F_5{}^+$-Br,-2F),

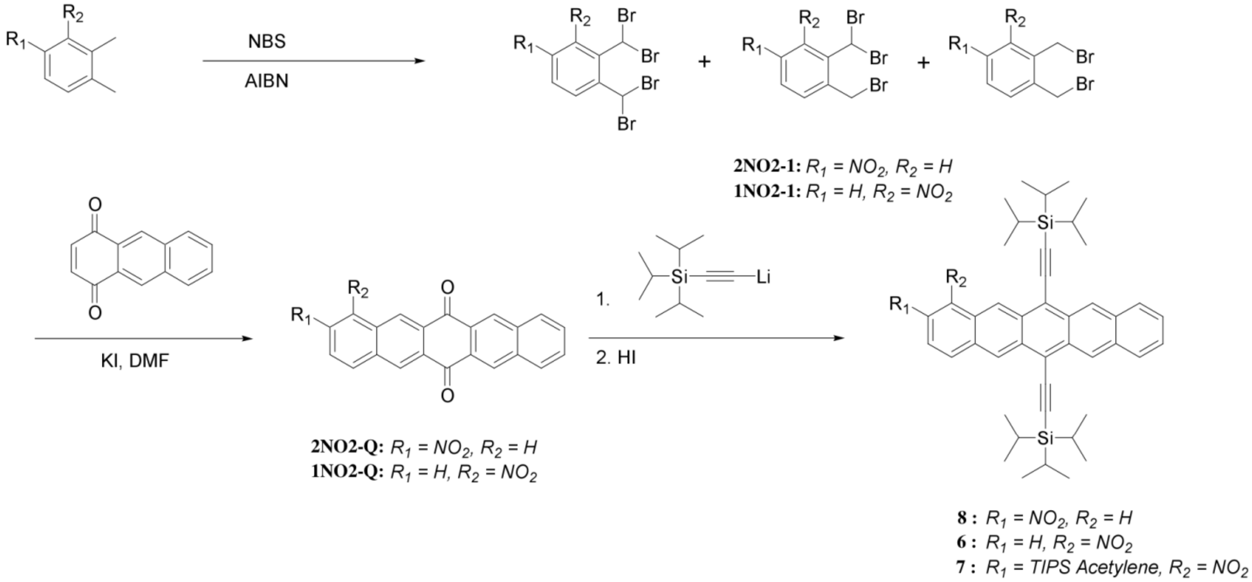
2-Pentafluoroethyl pentacenequinone (2PFE-Q)

To a nitrogen purged round bottom flask was added 8.5 g of 1,4 anthraquinone (40.9 mmol) and approximately 40 mmol of the mixture of brominated 2-pentafluoroethyl *o*-xylenes. 30 mL of degassed DMF was added to the flask under nitrogen and the reactants heated to 90 °C. 45.4 g of KI (274 mmol) was then slowly added to the reaction, and the temperature was raised to 130 °C. The reaction mixture was stirred for 32 hours, then cooled to room temperature and the solids filtered and washed with acetone, followed by copious amounts of THF and ether. The insoluble yellow solid was then allowed to air dry for several hours to yield 5.9 g (34%). MS (EI 70 eV) *m/z* 426 (100%, M^+).

2-Pentafluoroethyl-6,13-bis-[triisopropylsilylethynyl]-pentacene (5)

To a flame dried, nitrogen cooled round bottom flask was added hexanes (10 mL), followed by triisopropylsilylacetylene (1 mL, 4.40 mmol). 1.55 mL (3.87 mmol) of n-BuLi (2.5M in hexanes) was added to the flask and the contents stirred for one hour. 2-pentafluoroethyl pentacene quinone (0.5 g, 1.76 mmol) was added to that flask followed by 20 mL of anhydrous THF, and the contents stirred until all solids have dissolved. Deoxygenation proceeded with the addition of 3 mL of 10% H_2SO_4 and stannous chloride dihydrate followed by stirring for 1 hour. The reaction mixture was then worked up and purified by silica gel column chromatography, using hexanes as an eluent. The product was further purified by recrystallization from acetone. The resulting product was filtered and dried in air to obtain 0.32g (36%) of pure product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.369 (s, 42H), 7.414 (dd, J= 1.6, J = 3.4 Hz, 2H), 7.449 (d, J = 4.8 Hz, 1H), 7.957 (dd, J = 3.4 Hz, J = 5.6 Hz, 2H) 8.040 (d, J = 4.8 Hz, 1H), 8.224 (s, 1H), 9.299 (d, J = 2.4, 2H), 9.337 (s, 1H), 9.394 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.863, 19.198, 104.384, 104.510, 108.150, 108.416, 118.941, 119.291, 120.9, 121.1, 122.3, 126.024 (m), 126.640, 126.780, 127.088 (t, $^1J_{C\text{-}F}$ = 6) , 128.949, 129.425, 130.433, 130.951, 131.049, 131.189, 131.539, 132, 132, 132.785 (t, $^2J_{C\text{-}F}$ = 6) MS (EI 70 eV) *m/z* 756 (100%, M^+ - 1) 757 (62%, M^+). MP (decomp): 148 °C. Elemental analysis calculated for $C_{46}H_{53}F_5Si_2$: C 72.98, H 7.06. Found: C 73.21, H 7.10.

Synthesis of nitropentacenes 6, 7 and 8.



1,2-Bis-bromomethyl-4-nitro-benzene, 1-Bromomethyl-2-dibromomethyl-4-nitro-benzene, 1,2-Bis-dibromomethyl-4-nitro-benzene (2NO2-1)

To a nitrogen purged, flame dried two neck round bottom flask was added 10 g (66.2 mmol) of 1,2-dimethyl-4-nitro-benzene and 47.1 g (265 mmol) of NBS. 200 mL of 1,2-dichloroethane was added as well as a catalytic amount of AIBN. The reaction was heated at reflux at 70 °C for 16 hours. The reaction was then cooled and filtered through a thin pad of silica gel, washing with 1:1 dichlormethane:hexanes. 29.8 g of liquid product was collected, and shown to be a mixture of products by GC/MS. The products were used in the next step without further purification. MS (EI, 70 EV): *m/z*: 305 ($C_8H_7Br_2NO_2^+$-H), 307 ($C_8H_6Br_3NO_2^+$ -Br), 387 ($C_8H_5Br_4NO_2$ -Br),

2-Nitro pentacenequinone (2NO2 - Q)

To a nitrogen purged round bottom flask was added 13.7 g of anthraquinone (66 mmol) and approximately 66 mmol of a mixture of brominated 1,2-dimethyl-4-nitrobenzenes. 75 mL of degassed DMF was added to the flask under nitrogen and the reactants heated to 90 °C. 166 g of KI (442 mmol) was then slowly added to the reaction, and the temperature was raised to 130 °C. The reaction was stirred for an additional 32 hours. The reaction mixture was subsequently cooled to room temperature and the solids filtered and washed with hot acetone, followed by hot THF and finally ether. The brown solid was then air dried at ambient conditions for several hours to yield 16.6 g of a light brown solid (71 % yield). MS (EI 70 eV) *m/z* 353 (100%, M^+).

2-Nitro-6,13-bis-[triisopropylsilylethynyl]-pentacene (8)

To a flame dried, nitrogen cooled round bottom flask was added hexanes (10 mL), followed by triisopropylsilylacetylene (3.33 mL, 14.86 mmol). 5.1 mL (12.74 mmol) of n-BuLi (2.5M in hexanes) was added to the flask and the contents stirred for one hour. 2-nitro pentacene quinone (1.5 g, 4.25 mmol) was added to that flask followed by 20 mL of anhydrous THF, and the contents stirred for one hour, until all solids have dissolved. Deoxygenation proceeded with the addition of 3 mL of HI (48% in water) and stirring for 2 hours. The reaction mixture was then worked up and purified by silica gel column chromatography, using 9:1 hexanes:dichloromethane as an eluent. The product was further purified by recrystallization from acetone. The resulting product was filtered and dried in air to obtain 0.22 g (8 %) of pure product. ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.362 (s, 42H), 7.421 (q, J = 3.8 Hz, J = 7.0 Hz, 2H), 7.955 (q, J = 3.2 Hz, J = 6.6 Hz, 2H), 8.053 (m, 2H), 8.948 (d, J = 1.2 Hz, 1H), 9.309 (d, J = 3.6 Hz, 1H), 9.352 (s, 1H), 9.521 (s, 1H) . ^{13}C NMR (100 MHz, CDCl$_3$): δ 11.849, 19.198, 104.077, 104.188, 108.584, 109 12.171, 118.788, 119.235, 119.795, 126.808, 126.976, 127.298, 127.508, 128.879, 128.921, 129.691, 131.049, 131.147, 131.329, 131.441, 132.071, 132.939, 133.121, 145.760. MS (EI 70 eV) *m/z* 683 (100%, M$^+$), 653 (M$^+$-NO). MP (decomp): 274 °C. Elemental analysis calculated for $C_{44}H_{53}NO_2Si_2$: C 77.25, H 7.81. Found: C 76.88, H 7.85.

1,2-Bis-bromomethyl-3-nitro-benzene, 1-Bromomethyl-2-dibromomethyl-3-nitro-benzene, 1,2-Bis-dibromomethyl-3-nitro-benzene (1NO2-1)

To a nitrogen purged, flame dried two neck round bottom flask was added 10 g (66.2 mmol) of 1,2-Dimethyl-3-nitro-benzene and 47.1 g (265 mmol) of NBS. 200 mL of 1,2-dichloroethane was added, as well as a catalytic amount of AIBN. The reaction was heated to reflux at 70 °C for 16 hours. The reaction was then cooled and filtered through a thin pad of silica gel, washing with 1:1 dichlormethane:hexanes. 29.9 g of liquid product was collected, and shown to be a mixture of products by GC/MS. The product was used in the next step without further purification.

1-Nitro pentacenequinone (1NO2-Q)

To a nitrogen purged round bottom flask was added 13.8 g of 1,4-anthraquinone (66.3 mmol) and approximately 66 mmol of an unresolved mixture of di-, tri-, and tetra- brominated 1,2-dimethyl-3-nitro-benzene. 100 mL of degassed DMF was added to the flask under nitrogen and the reactants heated to 90 °C. 73.6 g of KI (443.4 mmol) was then slowly added to the reaction, and the temperature was raised to 130 °C. The reaction was stirred for 32 hours. The reaction mixture was subsequently cooled to room temperature and the solids filtered and washed with acetone, followed by copious amounts of THF and ether. The insoluble yellow solid was then allowed to air dry at ambient conditions for several hours to yield 12.3 g of a light brown solid (53 % yield). MS (EI 70 eV) *m/z* 353 (100%, M$^+$ - 1) 354 (25%, M$^+$).

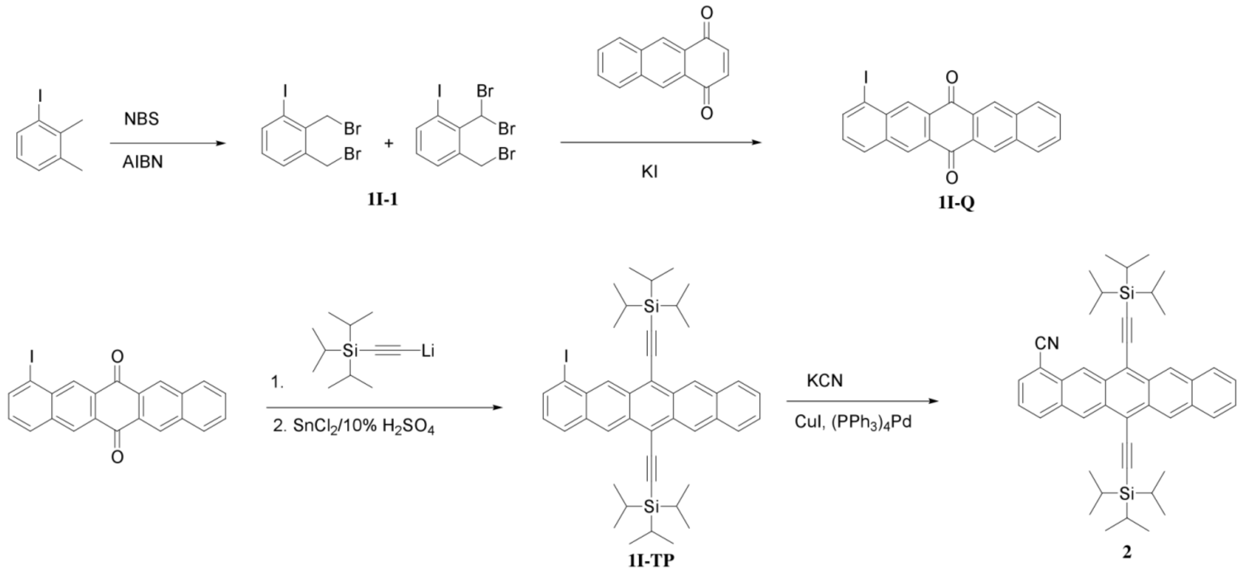
1-Nitro-6,13-bis-[triisopropylsilylethynyl]-pentacene (6)

To a flame dried, nitrogen cooled round bottom flask was added hexanes (10 mL), followed by triisopropylsilylacetylene (1.27 mL, 5.66 mmol). 2.1 mL (5.23 mmol) of n-BuLi (2.5M in hexanes) was added to the flask and the contents stirred for one hour. 1-nitro pentacenequinone (0.5 g, 1.42 mmol) was added to that flask and 20 mL of anhydrous THF was added and the contents stirred until all solids dissolve. Deoxygenation proceeded with the addition of 3 mL of HI (48% in water) for 2 hours. The reaction mixture was then worked up and purified by silica gel column chromatography, using 9:1 hexanes:dichloromethane as an eluent. The product was further purified by recrystallization from acetone. The resulting product was filtered and dried in air to obtain 0.46 g (48%) of pure product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.359 (m, 42H), 7.403 (s, 1H), 7.424 (dd, J = 3.2 Hz, 6.8 Hz, 2H), 7.962 (dd, J = 3.2 Hz, 6.8 Hz, 2H), 8.216 (dd, J = 0.8 Hz, 4.4 Hz, 1H), 8.277 (d, J = 7.6 Hz, 1H), (9.293 (s, 1H), 9.365 (s, 1H), 9.389 (s, 1H), 10.148 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ11.821, 11.849, 19.198, 104.035, 104.214, 108.388, 109.409, 118.788, 120.243, 123.155, 123.253, 124.064, 125.884, 126.626, 126.710, 126.766, 127.032, 128.348, 128.851, 128.963, 120.559, 131.301, 131.497, 131.693, 132.477, 132.925, 132.953, 146.936. MS (EI 70 eV) *m/z* 683 (100%, M^+ - 1) 684 (61%, M^+). MP (decomp) 260 °C. Elemental analysis calculated for $C_{44}H_{53}NO_2Si_2$: C 77.25, H 7.81. Found: C 77.15, H 7.90.

1-Nitro-2,6,13-tris-[triisopropylsilylethynyl]-pentacene (7)

This material was obtained as a reaction side product during the synthesis of 1-Nitro-6,13-bis-[triisopropylsilylethynyl]-pentacene. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.151 (m, 21H), 1.328 (m, 42H), 7.352 (d, J=8.8 Hz, 1H), 7.422 (dd, J =3.2 Hz, 6.8 Hz), 7.953 (m, 3H), 9.227 (s, 1H), 9.284 (s, 2H), 9.310 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.457, 11.765, 11.849, 18.834, 19.184, 100.857, 103.363, 103.825, 104.216, 108.346, 109.521, 114.266, 118.899, 119.949, 122.077, 122.973, 126.654, 126.724, 126.808, 126.962, 127.186, 127.634, 128.851, 128.963, 130.727, 130.937, 131.287, 132.939, 133.009, 151.359 . MS (EI 70 eV) *m/z* 863 (100%, M^+ - 1) 862 (73%, M^+). MP (decomp): 187 °C. Elemental analysis calculated for $C_{55}H_{73}NO_2Si_3$: C 76.42, H 8.51. Found: C 76.64, H 8.82.

Synthesis of 1-cyanopentacene 2



1,2-Bis-bromomethyl-3-iodo-benzene, 2-Bromomethyl-1-dibromomethyl-3-iodo-benzene (1I-1)

To a nitrogen purged, flame dried two neck round bottom flask was added 10 g (43 mmol) of 1-Iodo-2,3-dimethyl-benzene and 34.5 g (194 mmol) of NBS. 200 mL of 1,2-dichloroethane was added as well as a catalytic amount of AIBN. The reaction was heated to reflux at 75 °C for 16 hours. The reaction mixture was then cooled and filtered through a thin pad of silica gel, washing with hexanes. 15 g of liquid product was collected, and shown to be a mixture of products by GC/MS. The product was used in the next step without further purification. MS (EI, 70 EV): *m/z*: 388 ($C_8H_7Br_2I^+$-H), 387 ($C_8H_7Br_3I^+$-Br).

1-iodo Pentacenequinone (1I-Q)

1-Bromomethyl-2-dibromomethyl-3-iodo-benzene and 1,4 anthraquinone was heated in DMF to 90°C under N_2. Potassium iodide (6.7 equivalents) was then added to the reaction vessel, and the reaction mixture was stirred under nitrogen for 16 hours. The product was then filtered and rinsed with acetone, THF, and ether to yield an insoluble yellow solid. MS (LD-MS) *m/z* 434 (100%, M^+).

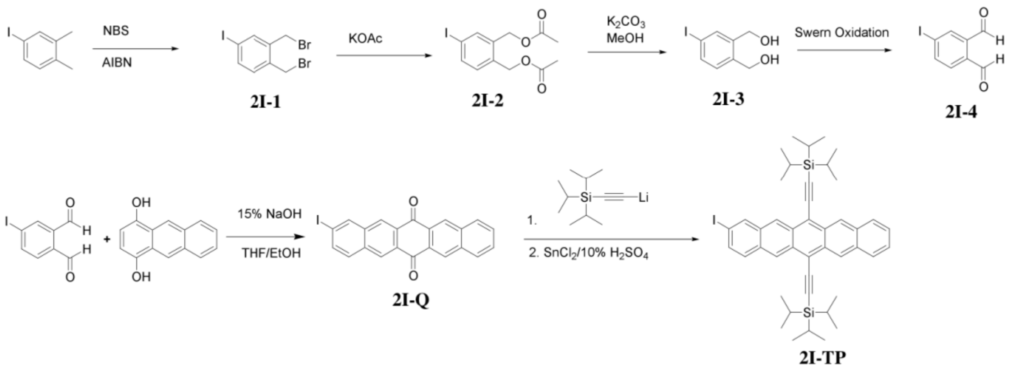
6,13-Bis-[triisopropylsilylethynyl]-1-iodo pentacene (1I-TP)

To a flame dried, nitrogen cooled round bottom flask was added hexanes (10 mL), followed by triisopropylsilylacetylene (1.81 mL, 8.05 mmol). 2.76 mL (6.90 mmol) of n-BuLi (2.5M in hexanes) was added to the flask and the contents stirred for one hour. **(1I-Q)** 1-iodo pentacene quinone (1 g, 2.30 mmol) was added to that flask along with 20 mL of anhydrous THF, and the contents stirred for one hour, until all solids have dissolved. Deoxygenation proceeded with the addition of 3 mL of 10% H_2SO_4 and stannous chloride dihydrate for 1 hour. The reaction mixture was then worked up and purified by silica gel column chromatography, using hexanes as an eluent. The product was further purified by recrystallization from acetone. The resulting product was filtered and dried in air to obtain 1.05 g (60%) of pure product. ^1H NMR (200 MHz, $CDCl_3$): δ 1.343 (m, 42H), 7.022 (dd, J =8.4, J = 7.0, 1H), 7.392 (dd, J = 6.8, J = 3.4, 2H), 7.916 (m, 3H), 8.019 (d, J = 6.8, 1H), 9.218 (s, 1H), 9.292 (s, 1H), 9.358 (s, 1H), 9.511 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 11.889, 19.203, 100.265, 104.529, 104.756, 107.731, 108.307, 118.309, 119.309, 126.456, 126.562, 126.668, 126.805, 127.806, 128.869, 128.914, 130.143, 131.069, 131.251, 131.418, 131.994, 132.359, 132.677, 132.996, 138.110. *m/z* 764 (100%, M^+ - 1), 765 (59%, M^+).

6,13-Bis-[triisopropylsilylethynyl]-pentacene-1-carbonitrile (2)

To a flame dried, nitrogen purged round bottom flask was added (**1I-TP)** 6,13-Bis-[triisopropylsilylethynyl]-pentacene-1-iodide, along with KCN, CuI, $(PPh_3)_4Pd$ and 40 mL of THF. The reaction was heated to reflux under nitrogen for 16 hours. The product was extracted from the reaction mixture with ether, the solvent was evaporated and the desired product was isolated via silica gel column chromatography with 1:1 hexanes:dichloromethane, and then recrystallized from acetone. ^1H NMR (400 MHz, $CDCl_3$): δ 1.342 (m, 42H), 7.381 (dd, J = 8.4, J = 6.4, 1H), 7.425 (dd, J = 6.4, J = 2.8 Hz, 2H), 7.884 (d, J = 6.8 Hz, 1H), 7.964 (dd, J = 6.8, J = 3.2, 2H), 8.148 (d, J = 8.8, 1H), 9.301 (s, 1H), 9.367 (s, 2H), 9.643 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.793, 19.198, 103.979, 104.398, 108.262, 108. 283, 111.509, 117.738, 118.899, 119.557, 124.372, 124.932, 126.668, 126.920, 128.418, 128.935, 129.495, 130.923, 131.021, 131.133, 131.343, 132.869, 134.450, 134.744. MS (EI 70 eV) *m/z* 663 (100%, M^+ - 1) 664 (59%, M^+). Elemental analysis calculated for $C_{45}H_{53}NSi_2$: C 81.39, H 8.04. Found: C 81.48, H 7.94.

Synthesis of 2-iodopentacene



1,2-Bis-bromomethyl-4-iodo-benzene (2I-1)

To a flame dried, nitrogen purged two neck round bottom flask was added 20 mL of 4-Iodo-1,2-dimethyl-benzene (175.9 mmol) and 125 g of NBS (703.6 mmol) as well as 300 mL of carbon tetrachloride. A catalytic amount of AIBN was then added and the reactants heated to reflux at 75 °C for 16 hours, under nitrogen. The reaction flask was then cooled to room temperature, NBS was filtered off and carbon tetrachloride was evaporated off in a rotary evaporator. The remaining liquid was run through a thick pad of silica gel with 2:1 hexanes:dichloromethane as eluent to give a mixture of bromination products (47.09 g) as determined by GC/MS. The product was used in the next step without further purification. MS (EI, 70 EV): *m/z*: 308 ($C_8H_8BrI^+$-H), 388 ($C_8H_7Br_2I^+$-H).

(4-iodo-1,2-phenylene)bis(methylene) diacetate (2I-2)

To a round bottom flask was added the crude reaction mixture from the synthesis of 1,2-bis-bromomethyl-4-iodobenzene (47.09 g), as well as 47.3g of potassium acetate (482 mmol) and 140 mL of DMF. The reaction flask was heated to 60 °C for 2 days with constant stirring. The reaction was then cooled to room temperature and extracted with diethyl ether. The product mixture was purified via silica gel column chromatography with 4:1 hexanes:ethyl acetate. 32.9 g of a light yellow liquid was collected (78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.929 (dd, J = 0.6 Hz, 3.6 Hz, 6H), 4.976 (s, 4 H), 6.969 (d, J = 4.0 Hz, 1H), 7.476 (d, J = 4.0 Hz, 1H), 7.597 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.573, 62.404, 62.831, 94.017, 131.086, 133.833, 136.473, 137.236, 137.816, 169.933 169.964. MS (EI, 70 EV): *m/z*: 348 ($C_{12}H_{13}IO_4$).

4-iodobenzene-1,2-dimethanol (2I-3)

To a round bottom flask was added 32.9 g of (4-iodo-1,2-phenylene)bis(methylene) diacetate (**2I-2**) (94.5 mmol) and 52.2 g (378.2 mmol) of potassium carbonate. To this was added 250 mL of THF and 125 mL of ethanol. The reaction mixture was heated to 87 °C and refluxed for 16 hours. Once cooled, the reaction mixture was extracted with dichloromethane several times and the organic layers dried with magnesium sulfate. After evaporating to dryness on a rotary evaporator, 10.42 g (42% yield) of a light pink to light orange solid was obtained. ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.451 (d, J = 6.6 Hz, 4 H), 5.201 (s, broad, alcohol), 7.155 (d, J = 8.0 Hz, 1H), 7.559 (dd, J = 2.0 Hz, 8.2 Hz, 1H), 7.715 (s, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ59.343, 59.669, 128.904, 134.740, 135.066, 139.073, 142.131.

4-Iodobenzene-1,2-dicarbaldehyde (2I-4)

To a nitrogen cooled, flame dried round bottom flask was added 200 mL of anhydrous dichloromethane. The flask was placed in a dry ice – isopropanol bath and allowed to cool to -78 °C over ten minutes. Oxalyl chloride (7.9 mL, 90.8 mmol) was added to the flask and stirred for five minutes. 12.9 mL of DMSO (181.6 mmol) mixed with 10 mL of dichloromethane was slowly added to the reaction flask at -78 °C in a dropwise manner using an addition funnel. After all of the DMSO solution had been added, the reaction was stirred for an additional 15 minutes at -78 °C. 6 g of **(2I-3)**4-iodobenzene-1,2-dimethanol (22.7 mmol) was dissolved in a minimal amount of DMSO and added to the reaction flask in a drop wise manner at -78 °C, and the reaction stirred for an additional 15 minutes after the diol has been completely added. 53.8 mL of triethylamine (385.9 mmol) was then added slowly to the reaction flask and the reactants allowed to warm to room temperature slowly over 16 hours. The product mixture was extracted with dichloromethane and ice cold water. The organic layer was dried with magnesium sulfate, and then purified by column chromatography with dichloromethane to yield an off-white solid. The solid was recrystallized from hexanes to give 3.5 g of pure product (59% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.627 (d, J = 8.0 Hz, 1H), 8.092 (dd, J = 1.8 Hz, 8.0 Hz, 1H), 8.272 (d, J = 1.4 Hz, 1H), 10.426 (2s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 101.532, 132.468, 135.488, 137.233, 138.828, 142.833, 190.736, 190.540.

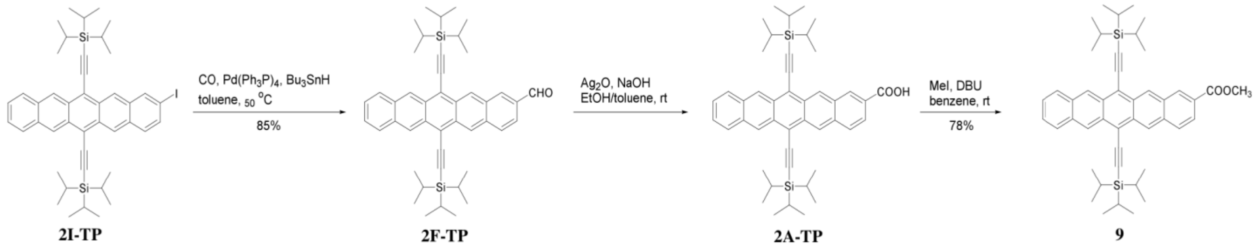
2-Iodo pentacenequinone (2I-Q)

To a small round bottom flask was added 3.07 g of **(2I-4)** 4-Iodobenzene-1,2-dicarbaldehyde (11.8 mmol) and 2.48 g of 1,4 dihydroxyanthracene (11.8 mmol). The solids were dissolved in a minimal amount of hot THF (30 mL) and ethanol (15 mL). Several drops of 15% aqueous NaOH was added dropwise to the reactants until a vigorous reaction occurred and a yellow precipitate appeared. The reaction was stirred for a half an hour, and then the solids were filtered and washed with methanol, THF and diethyl ether. The solids were then dried overnight under ambient conditions. 4.23 g of light beige colored solids were collected (83% yield). MS (MALDI, TCNQ matrix) *m/z* 434 (100%, M^+)

6,13-Bis-[triisopropylsilylethynyl]-pentacene-2-iodide (2I-TP)

To a flame dried, nitrogen cooled round bottom flask was added hexanes (10 mL), followed by triisopropylsilylacetylene (1.81 mL, 8.05 mmol). 2.76 mL (6.90 mmol) of n-BuLi (2.5M in hexanes) was added to the flask and the contents stirred for one hour. **(2I-Q)** 2-iodo pentacene quinone (1 g, 2.30 mmol) was added to that flask followed by 20 mL of anhydrous THF, and the contents stirred until all solids dissolved. Deoxygenation proceeded with the addition of 3 mL of 10% H_2SO_4 and stannous chloride dihydrate for 1 hour. The reaction mixture was then worked up and purified by silica gel column chromatography, using hexanes as an eluent. The product was further purified by recrystallization from acetone. The resulting product was filtered and dried in air to obtain 1.05 g (60%) of pure product. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.077 (s, 6H), 1.364 (d, J = 2.2 Hz, 36 H), 7.392 (dd, J = 3.0 Hz, J = 3.6 Hz, 2H), 7.564 (q, J = 9.2 Hz, 2H), 7.947 (dd, J = 3.2 Hz, J = 3.4 Hz, 2H), 8.378 (s, 1H), 9.149 (s, 1H), 9.239 (s, 1H) 9.280 (d, J = 3.4 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 11.207, 11.867, 18.613, 19.167, 92.505, 95.001, 104.744, 107.817, 107.992, 118.865, 119.040, 125.626, 126.491, 126.666, 127.121, 128.972, 130.346, 130.657, 130.976, 131.044, 131.234, 132.782, 133.586, 134.542, 137.683. MS (EI 70 eV) *m/z* 764 (100%, M^+ - 1) 765 (61%, M^+).

Synthesis of pentacene methyl ester 9



2-Formyl-6,13-bis((triisopropylsilyl)ethynyl) pentacene (2F-TP).

2-Iodo-TIPS pentacene (**2I-TP**) (1.15 g, 6.1 mmol) was dissolved in 5 mL of toluene. The resulting solution was degassed for 30 min by N_2 purging followed by bubbling in CO. The reaction was heated to 50 °C after tetrakis(triphenylphosphine)palladium (40 mg, 0.035 mmol) was added. A solution of Bu_3SnH in 10 mL of degassed toluene was added very slowly to the reaction mixsture by syringe pump over 10 hr. The reaction was then cooled to room temperature and the solvent was pulled off *in vacuo*. The residue was purified by flash chromatography (1.5:1 hexanes : DCM) to afford aldehyde (**2F-TP**) (0.57 g, 85 %) as deep blue crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ10.20 (s, 1H), 9.49 (s, 1H), 9.34 (s, 1H), 9.33 (s, 1H), 9.31 (s, 1H), 8.44 (s, 1H), 8.03-7.99 (m, 3H), 7.84 (dd, 1H, *J* = 1.2, 9.2 Hz), 7.47 (dd, 2H, *J* = 4, 4 Hz), 1.41-1.37 (m, 42H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.81, 138.44, 134.53, 133.10, 132.71, 132.53, 131.66, 131.05, 130.89, 130.75, 130.71, 130.09, 129.86, 128.66, 126.89, 126.59, 126.48, 126.44, 126.38, 121.11, 119.39, 118.81, 108.23, 107.93, 104.15, 19.01, 18.89, 11.65.

6,13-Bis((triisopropylsilyl)ethynyl)pentacene-2-carboxylic acid (2A-TP).

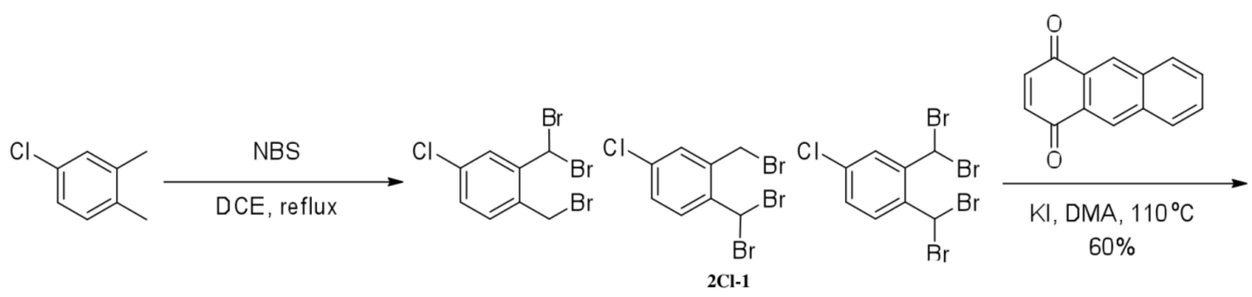
Freshly prepared Ag_2O (0.51 g, 2.2 mmol) was added to a suspension of NaOH powder (0.48 g, 12.1 mmol) in 10 mL of EtOH. To the mixture was added a solution of aldehyde (**2F-TP**) (0.15 g, 0.22 mmol) in 5 mL of toluene, and the suspension was stirred at room temperature for 2 hr. After quenching by careful addition of 10% H_2SO_4, the reaction mix was extracted with Et_2O. The organic phase was the dried over $MgSO_4$ and concentrated *in vacuo* to afford crude acid as deep blue solid, which was used directly in the next step without further purification.

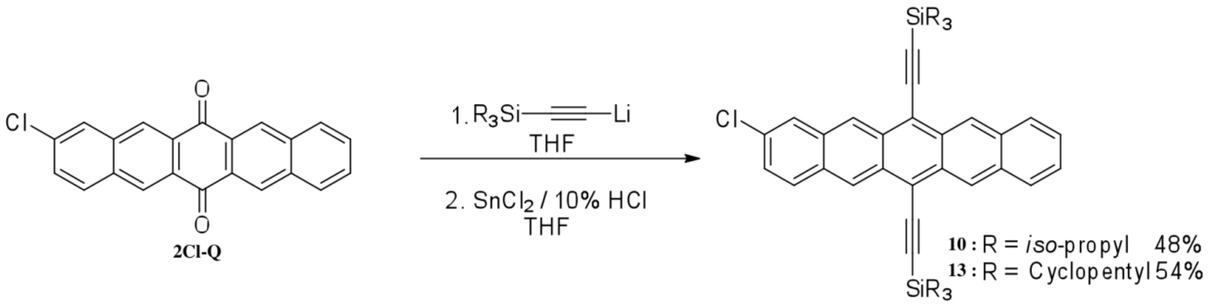
Methyl 6,13-bis((triisopropylsilyl)ethynyl)pentacene-2-carboxylate (9).

To a suspension of crude acid (**2A-TP**) in 5 mL of benzene was added methyl iodide (78 mg, 0.55 mmol) and DBU (67 mg, 0.44 mmol). The mixture was stirred at room temperature overnight and a homogeneous solution was formed. The reaction mix was then concentrated *in vacuo* and the residue was purified by flash chromatography (3:1 hexanes:DCM) to afford ester (**9**) (0.12 g, 78 % over two steps) as deep blue crystals. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 9.33-9.31 ($b_{overlap}$, 3H), 8.76 (s, 1H), 8.01- 7.97 (m, 3H), 7.92 (dd, 1H, *J* = 1.2, 8 Hz), 7.43 (dd, 2H, *J* = 4, 8 Hz), 4.04, (s, 3H), 1.42-1.37 (m, 42H);

^{13}C-NMR (100 MHz, CDCl$_3$) δ 167.05, 133.09, 132.57, 132.44, 131.40, 130.95, 130.89, 130.74, 130.63, 129.24, 129.02, 128.65, 127.48, 126.52, 126.40, 126.36, 126.31, 126.23, 124.34, 119.10, 118.57, 108.01, 107.64, 104.36, 104.28, 52.34, 19.00, 11.65. MS (EI 70 eV) *m/z* 696 (100%, M$^+$ - 1) 697 (59%, M$^+$). MP: 238 °C (decomp).

Synthesis of chloropentacenes 10 and 13





Mixture of brominated 4-chloroxylenes (2Cl-1):

5ml (5.235g, 37.23mmol) of 4-chloro-*o*-xylene was dissolved in 300ml of 1,2-dichloroethane. 14.6g (81.9mmol) of NBS and 200mg of AIBN were added and the reaction mixture was heated to 97 ˚C. 29.2g of NBS was added in 2 portions at 4h intervals and the reaction mixture was refluxed overnight. The next day the reaction mixture was cooled to 0˚C and the precipitated succinimide was filtered and washed with chloroform. The filtrate was extracted with sodium thiosulfate solution followed by water, dried over MgSO$_4$ and the solvent was removed under vacuum to give crude dark yellow solid. The crude product was purified further by running a short plug using hexanes to give 16g of a mixture of tribromo and tetrabromo chloroxylene (**2Cl-1**) which was used without further purification in the next step.

2-chloropentacene-6,13-dione (**2Cl-Q**)

To a 100ml round bottom flask equipped with a stir bar and reflux condenser were added 4.4g of the mixture of brominated chloroxylenes (**2Cl-1**) and 2.5g (12 mmol) of 1,4-anthraquinone. 35 ml of degassed DMA was added and the reaction mixture was heated to 70˚C. 16.56g (64.35mmol) of KI was added and the temperature was raised to 110˚C. The reaction mixture was allowed to stir for 24h. During the course of the reaction yellow precipitate crashes out from solution. The hot reaction mixture was poured into 800 ml of water and allowed to stir for 30 min. The precipitate was filtered and washed with plenty of water, followed by acetone and finally with 200 ml THF. 1.93 g (60% based on 4-chloro-

1,2-bis(dibromomethyl)benzene) of the insoluble chloro pentacenequinone (**2Cl-Q**) was obtained as a light golden brown solid. MS (EI 70 eV) *m/z* 342 (M^+, 100%)

General procedure for the synthesis of 6,13-Trialkylsilylethynyl-substituted 2-chloropentacenes (**10** and **13**):

To a flame dried 100 ml flask cooled under nitrogen was added 4.38 mmol of acetylene, followed by 5 ml of THF. The reaction mixture was then placed in an ice bath. 1.6 ml of n-BuLi (4 mmol, 2.5 M solution in hexanes) was added dropwise and the reaction mixture stirred at 0 ºC for an hour. 15 ml of anhydrous THF was added followed by 500 mg (1.46 mmol) of 2-chloropentacene quinone (**2Cl-Q**). The reaction mixture was allowed to stir overnight at room temperature and was quenched with 2ml of saturated NH_4Cl solution the next day. 2ml of 10% HCl was added followed by 5g of $SnCl_2•2H_2O$. The reaction mixture was monitored by TLC by following the disappearance of intermediate diol. The reaction mixture was then poured on to thick pad of silica gel and the acene was eluted using 100% hexanes. The solvent was removed under vacuum to give trialkylsilylethynyl 2-chloropentacenewhich was further purified by recrystallization from acetone.

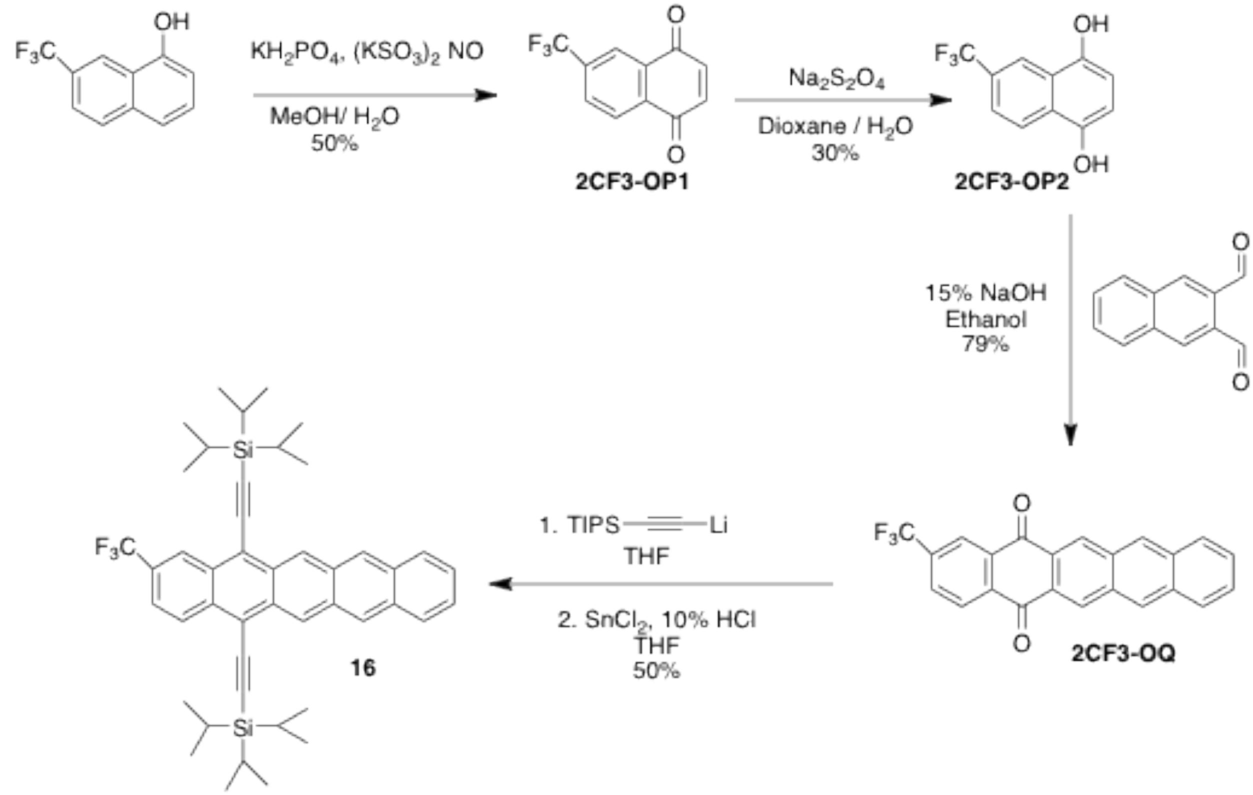
6,13-bis((triisopropylsilyl)ethynyl)-2-chloropentacene (**10**) – 472 mg (48%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 – 9.24 (m, 3H), 9.18 (s, 1H), 8.02 – 7.94 (m, 2H), 7.94 – 7.88 (m, 2H), 7.46 – 7.38 (m, 2H), 7.31 (dd, 9.2 Hz, 2 Hz, 1H), 1.37-1.34 (m, 42H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.69, 132.59, 132.29, 131.97, 131.06, 130.87, 130.74, 130.71, 130.43, 128.88, 127.56, 127.02, 126.84, 126.61, 126.57, 126.43, 126.39, 125.7, 118.89, 118.61, 107.8, 107.74, 104.64,19.21, 11.86. MS (EI 70 eV) *m/z* 672(M^+, 100%). Anal calc. for $C_{44}H_{53}ClSi_2$ C 78.46%, H 7.93% Found: C 78.54%, H 8.07%. Decomposition temperature: 255˚C (DSC)

6,13-bis((tricyclopentylsilyl)ethynyl)- 2-chloropentacene (**13**) – 650 mg (54%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 – 9.23 (m, 3H), 9.17 (s, 1H), 8.01 – 7.94 (m, 2H), 7.94 – 7.89 (m, 2H), 7.47 – 7.41 (m, 2H), 7.34 (dd, *J* = 9.1, 1.9 Hz, 1H), 2.17 – 1.99 (m, 12H), 1.92 – 1.57 (m, 36H), 1.45 – 1.25 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.66, 132.57, 132.28, 131.92, 131.03, 131.00, 130.81, 130.70, 130.63, 130.42, 128.82, 127.57, 127.01, 126.81, 126.60, 126.55, 126.42, 126.38, 125.69, 118.88, 118.61, 108.40, 108.33, 103.66, 29.63, 27.32, 24.13. MS (EI 70 eV) *m/z* 828 (M^+, 100%). Anal calc. for $C_{56}H_{65}ClSi_2$ C 81.06%, H 7.90% Found: C 80.88%, H 8.01% Decomposition temperature: 263˚C (DSC)

Synthesis of "offset" pentacene 16



6-(trifluoromethyl)-1,4-naphthoquinone (2CF3-OP1): To a 2L Erlenmeyer flask was added 250 ml KH_2PO_4(0.167M in water), potassium nitrodisulfonate (10 g, 40 mmol), **7-trifluorometyl-1-naphthol**,[1] (4.28g, 20mmol)**,** and 300 ml of methanol, and the mixture was stirred at room temperature for 2 hours. The organic products were extracted with ether, which was then washed with water 5 times. The ether layer was dried using $MgSO_4$, filtered and concentrated at reduced pressure. The crude product was purified using column chromatography (silica gel, 1:1 hexanes/DCM), and recrystallized from hexanes to give 2.05 g (50% yield) of **2CF3-OP1** as yellow crystals. MS (EI, 70eV) 226 (M^+). ^1H NMR (400MHZ, $CDCl_3$): δ 8.356 (s,1H), 8.22 (d, J= 8Hz,1H), 8.01 (d, J= 8Hz, 1H), 7.07(t,J= 10.4Hz, 2H).^{13}C NMR (100MHz, $CDCl_3$): δ 184, 183.8, 139.1, 139, 135.8 (q, J= 33.5Hz), 134.1, 132.4, 130.6 (q, J= 3.5Hz), 127.47 (q, J= 2.1Hz), 123.9 (q, J=4Hz), 121.9 (t, J= 271.7Hz).

6-trifluoromethyl-1,4 dihydroxynaphthalene (2CF3-OP2): To a dry round-bottom flask was added 1,4-dioxane (37 ml) and water (37ml). The solvents were degassed by sparging with nitrogen for 30 min. Trifluoromethyl naphthoquinone (2.05g, 9.6 mmol) was then added, along with $Na_2S_2O_4$ (6.63g, 38.09 mmol) and the mixture was stirred under nitrogen over night. 200ml of deoxygenated water was added to the mixture, which was then extracted exhaustively with ether (3*100ml). The combined ether layers were washed one more time with 100ml of deoxygenated water. The ether solution was dried ($MgSO_4$), filtered and concentrated. The crude product was purified using silica gel chromatography with

1:1 (hexane/ethyl acetate) to yield 0.75g (28%) of a sensitive purple solid which was used immediately without further purification. MS (EI, 70 eV) 228 (M^+). ^{1}H NMR (400 MHz, DMSO-D6): δ 6.837 (dd, J= 8, ? Hz, 2H), 7.63 (d, J= 8Hz, 1H), 8.23 (d, J= 8Hz, 1H), 8.36 (s, 1H), 9.70 (s, 1H), 9.84 (s, 1H). ^{13}C NMR (100 MHz, DMSO-D6): δ 157.6, 156.9, 140.2, 137.8, 137.6, 136.6 (q,J= 31.5Hz), 135.3 (q, J= 7.7Hz), 134.9, 132.2, 131.2 (q, J= 8Hz), 122.4 (t, J= 7Hz), 121.2 (q, J= 6Hz).

2-trifluoromethyl-5,14-pentacenedione (2CF3-OQ): To a round bottom flask equipped with a stir bar, was added the trifluoromethyl dihydroxynaphthalene (0.6g, 3.28mmol), naphthalene 2,3-dialdehyde[2] (0.75g, 3.28mmol), and ethanol (10ml). A few drops of 15% aqueous NaOH were added to the mixture, until a precipitate began to form. After 30 minutes, the insoluble quinone was recovered by filtration, and the solids washed with ether to remove any residual ethanol. This material was used without any purification in the subsequent step. Yield=0.968, 78%. MS (EI, 70 eV) 376 (M^+).

2-trifluoromethyl-5,14-bis(triisopropylsilylethynyl)pentacene (16): To a flame-dried round bottom flask with stir bar was added triisopropylsilyl acetylene (0.894g, 3.987mmol) and 2 ml anhydrous THF. After cooling this solution to 0^{o}C, n-BuLi (0.0229g, 3.588 mmol) was added, and the mixture stirred for 1 hour. At this time, 2CF3-OQ (0.5g,1.33 mmol) was added all at once, followed by an additional 5 ml of anhydrous THF, and the suspension was stirred until all quinone had dissolved. After an additional hour, the reaction was quenched with 1 ml of saturated aqueous solution of ammonium chloride, followed by addition of 3 ml of 10% aqueous HCl and 5 equivalents of solid $SnCl_2$•$2H_2O$. $MgSO_4$ was then added, filtered and solvent removed under reduced pressure. The resulting crude material was purified by column chromatography (silica gel, hexanes), followed by recrystallization from acetone. Yield= 50 %. For X-ray diffraction, crystals were grown by slow diffusion in methanol/ chloroform. ^{1}H NMR (400MHz, $CDCl_3$): δ 1.38 (m, 18H), 7.37 (dd, J= 6.8, 2.8Hz, 2H), 7.59 (dd, J= 16, 1.6Hz, 1H), 7.99 (dd, J= 6.8, 4Hz, 2H), 8.66(dd, J= 3.4, 0.4Hz, 2H), 8.68 (s, 1H), 8.96 (s, 1H), 9.57 (d, J= 2Hz, 1H), 9.58 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 132.9, 132.6, 132.5, 131.3, 131.1, 130.8, 130.4, 129.9, 129.2, 128.6, 128.4, 128.12, 127.4, 127.2, 127.1, 127.0, 126.38, 126.4 (q. J= 5.3Hz), 125.9 (q, J= 5.3Hz), 123.1, 121.8 (q, J= 3.1Hz), 120.9, 119.2 (t, J= 6Hz), 108.3, 107.5, 103.7, 103.4, 19.2, 19.1, 11.8, 11.7. Anal. Calc. For $C_{45}H_{53}F_3Si_2$: C 76.44%, H 7.56%. Found: C 76.38%, H 7.75%. MS (EI, 70 eV) xxx (M^+) .Decomposition temperature: 226°C

[1]Bailly, F.; Cottet, F.; Schlosser, M. *Synthesis*, **2005**, *5*, 791-797.

[2]Lin, C.H.; Lin, K.H.; Pal, B.; Tsou, L.D. *Chem. Comm*, **2009**, *7*, 803-805.

Device Fabrication and characterization

Materials:

P3HT was purchased from American Dye Source and used without further purification. PEDOT:PSS (Clevios PH 500) was purchased from H. C. Starck. All solvents were purchase from Sigma-Aldrich. Pre-patterned indium tin oxide (ITO) coated glass substrates were purchased from Kintec.

Fabrication:

Solar cells were fabricated on pre-patterned ITO coated glass substrates, which were cleaned by sonication in a mild detergent, rinsed in de-ionized water, dried in a nitrogen stream, and treated with a 10-minute UV-ozone exposure. PEDOT:PSS was filtered through a 0.45 μm PVDF syringe filter, and then deposited by spin-coating at 6000 rpm for 60 seconds. The PEDOT:PSS layer was baked on a hot-plate at 170 ^{o}C for 4 minutes to remove residual solvent. The samples were then transferred into a nitrogen-filled glovebox, in which all subsequent processing steps were carried out. P3HT and a pentacene acceptor were dissolved in toluene at a ratio of 1:1 by weight to give a total concentration of 20 mg/ml. 1,2-dichlorobenzene (DCB, 30 % by volume) was added just before spin-coating on top of the PEDOT:PSS layer at 1000 rpm for 60 seconds.. Finally, 4 Å of CsF and 400 Å of Al were thermally evaporated under high vacuum (~10^{-6} Torr) to form the cathode for the devices. A shadow mask was used in the evaporation to define a device active area of 3 mm^2.

Characterization:

Solar cell current-voltage (I-V) curves were obtained with a Keithley 236 source-measurement-unit (SMU) under AM 1.5 100 mW/cm^2 illumination from a Solar Light 16S-002 solar simulator. Light output power was calibrated using a Newport 818P-010-12 thermopile high power detector, which has a flat response over a broad spectral range. Spectral mismatch was not taken into account in these measurements. At least six devices were measured for each material to obtain device statistics. External quantum efficiency **(**EQE) measurements were performed using a Newport 1000 W xenon lamp coupled to an Oriel Cornerstone 260 ¼ m monochromator as the light source, a Keithley 236 SMU to measure short circuit current, and a Newport 918D-UV3-OD3 low power detector to monitor the light intensity. Tapping mode AFM images were taken with a Digital Instruments Dimension 3100 Atomic Force Microscope, with a scan area of 5 μm by 5 μm.

Representative JV curves of P3HT/12 and P3HT/13