Supporting information for:

Synthesis and characterization of electron-deficient pentacenes

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General experimental: All reagents were obtained from the Aldrich Chemical Company (Milwaukee, WI) or Acros Organics (Pittsburgh, PA). Triisopropylsilyl acetylene was purchased from GFS Chemicals (Powell, OH). Tetrahydrofuran and diethyl ether were purified by passage through activated alumina columns under nitrogen. TLC was carried out on *MERCK Silica Gel 60* thin layer plates. Silica gel chromatography was performed on *Sorbent Technologies* silica gel (230-450 mesh). Flame-dried glassware was used in the appropriate steps, and cooled under dry nitrogen. Melting points were recorded on a Thomas-Hoover Capillary Melting Point apparatus, and are uncorrected. UV-Vis absorbance spectra were recorded using a Shimadzu UV-Vis spectrophotometer model UV-2501PC. NMR spectra were recorded on either a Varian Inova 400 MHz NMR, or a Varian Gemini 200 MHz NMR.

9,10-dibromo-6,13-pentacenequinone (2): To a flame-dried round bottom flask cooled under nitrogen at room temperature was added 100 mL of dry N,N-dimethylacetamide. The solvent was purged for 30 minutes with nitrogen. 4,5-Dibromo- $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene (1.08 g, 1.86 mmol) was added to the mixture, followed by 1,4-anthraquinone (0.387 g, 1.86 mmol, 1 eq.), and NaI (1.42 g, 9.48 mmol, 5.1 eq.). The flask was capped with a rubber septum and bubbler, and stirred vigorously at 90 °C overnight. The reaction mixture was then filtered, and the crude yellow solid was rinsed with acetone and water. The solid was then triturated with chloroform, filtered, and dried to yield 9,10-dibromo-6,13-pentacenequinone (0.554 g, 1.19 mmol, 64%) as an insoluble yellow solid. MS (EI, 70 eV) 466 (M^+ , 100%, showing expected bromine isotope peaks). Anal. calc. C 56.68%, H 2.16%. Found: C 56.66%, H 2.09%.

9,10-dibromo-6,13-bis-tri(isopropylsilylethynyl)pentacene (4): To a flame-dried round bottom flask and stir bar cooled under nitrogen was added 100 mL of anhydrous ether. Triisopropylsilyl acetylene (0.66 mL, 2.95 mmol, 5 eq.) was then added to the flask, followed by *n*-BuLi (2.46M in hexanes, 0.72 mL, 1.77 mmol, 3 eq.). The mixture was stirred for 30 minutes, and then 9,10-dibromo-6,13-pentacenequinone (0.275 g, 0.590 mmol, 1 eq.) was added to the mixture, followed by 15 mL of anhydrous THF. The mixture was stirred for several hours at room temperature, until complete dissolution of the quinone occurred. The mixture was then quenched with wet ether, and the solvent was removed by evaporation. The residue was dissolved in hexanes, and flushed through a silica plug with hexanes to remove excess triisopropylsilyl acetylene. The diol was then removed by flushing the plug with diethyl ether. The solvent was evaporated to yield the crude diol, which was then dissolved in 1:1 CH₃CN/THF, and stannous chloride dihydrate was added until the mixture turned dark blue. The mixture was stirred for one

hour at 25 °C, and the blue solid was filtered off, dissolved in CH₂Cl₂, and filtered through a silica plug. The solvent was evaporated to yield 9,10-dibromo-6,13-bis-tri(*isopropylsilylethynyl*)pentacene (0.230 g, 0.289 mmol, 49%) as a dark blue solid which was further purified by recrystallization from dichloromethane. ¹H NMR (400 MHz, CDCl₃) δ 9.30 (s, 2H), 9.20 (s, 2H), 8.30 (s, 2H), 7.98 (dd, *J* = 6.7 Hz, 3.2 Hz, 2H), 7.44 (dd, *J* = 6.9 Hz, 3.2 Hz, 2H), 1.40 (s, 42H). ¹³C NMR (100 MHz CDCl₃) δ 132.7, 132.6, 131.1, 130.9, 130.7, 128.7, 126.5, 126.4, 125.9, 122.3, 118.8, 108.1, 104.2, 19.0, 11.6. MS (EI, 70 eV) 796 (M⁺, 100%). Anal. calc. C 66.32%, H 6.57%. Found: C 66.80%, H 6.35%. MP: 258 °C.

2,3-dicyano-6,13-bis-(triisopropylsilylethynyl)pentacene (15): To a flame-dried threaded sealed tube reactor cooled under nitrogen was added 50 mL of dioxane, which was sparged with nitrogen for 20 minutes at room temperature. After sparging, 2,3-dibromo-6,13-bis-tri(*isopropylsilylethynyl*)pentacene (0.380 g, 0.477 mmol, 1 eq.) was added to the mixture, followed by Pd(PPh₃)₄ (0.110 g, 0.095 mmol, 0.2 eq.), and CuCN (0.256 g, 2.86 mmol, 6 eq.). The vessel was then capped and heated in an oil bath at 120 °C for 14 hours. The mixture was then cooled to room temperature, diluted with ethyl acetate, and filtered through a silica plug. The solvent was evaporated to yield a crude blue-green solid. The product was purified by silica column chromatography (1:1 hexanes/CH₂Cl₂) to yield 2,3-dicyano-6,13-bis-tri(*isopropylsilylethynyl*)pentacene (0.120 g, 0.160 mmol, 33%) as a blue-green solid. The product was recrystallized from toluene to yield blue needles. ¹H NMR (400 MHz, CDCl₃) δ 9.40 (s, 2H), 9.38 (s, 2H), 8.48 (s, 2H), 8.03 (dd, *J* = 6.6 Hz, 3.1 Hz, 2H), 7.52 (dd, *J* = 6.6 Hz, 3.1 Hz, 2H), 1.40 (m, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 138.8, 133.2, 131.5, 131.3, 129.7, 128.9, 128.7, 127.1, 126.8, 120.1, 116.2, 109.7, 108.1, 103.4, 19.0, 11.6. MS (EI, 70 eV) 688 (M⁺, 100%). Anal. calcd. C 80.17%, H 7.60%, N 4.06%. Found: C 80.05%, H 7.38%, N 3.94%. MP: 327 °C.

2,3,9,10-tetrabromo-6,13-pentacenequinone (3): To a flame-dried round bottom flask cooled under nitrogen was added 100 mL of dimethylacetamide. The solvent was sparged for 30 minutes with nitrogen. 4,5-Dibromo- $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene (10 g, 17.26 mmol) was added to the flask with vigorous stirring, followed by *p*-benzoquinone (0.933 g, 8.63 mmol, 0.5 eq.), and sodium iodide (13.19 g, 88.02 mmol, 5.1 eq.). The mixture was then capped with a rubber septum and bubbler and was stirred at 90 °C for 48 hours. The mixture was then filtered, and the yellow-brown solid was rinsed with acetone and water. The solid was then triturated with chloroform, filtered, and dried under vacuum to yield 2,3,9,10-tetrabromo-6,13-pentacenequinone as a yellow solid (1.55 g, 2.28 mmol, 29%). MS (MALDI): 623 (M⁺, 100%). Anal. calc. C 42.35%, H 1.29%. Found: C 42.03%, H 1.48%.

2,3,9,10-tetrabromo-6,13-bis-(triisopropylsilylethynyl)pentacene (5): To an oven-dried round-bottom flask cooled under nitrogen was added 80 mL of anhydrous ether at 0 °C. Triisopropylsilylacetylene (2.41 mL, 10.75 mmol, 5 eq.) was added to the flask, followed by *n*-butyllithium (2.62 mL, 6.54 mmol, 3 eq.). The mixture was stirred for 30 minutes, and then 2,3,9,10-tetrabromo-6,13-pentacenequinone (1, 2.15 mmol, 1 eq.) was added to the mixture, followed by 30 mL of anhydrous tetrahydrofuran. The mixture was

then removed from the ice bath, and allowed to warm to room temperature overnight. The reaction was quenched with wet diethyl ether, and evaporated to dryness. The crude oil was dissolved in hexanes, and flushed with hexanes on a silica plug to remove excess triisopropylsilylacetylene. The plug was then flushed with ethyl acetate to remove the diol. After the solvent was evaporated, the diol was dissolved in THF/CH₃CN, and stannous chloride was added until the mixture turned a dark blue color. The reaction was stirred for one hour at room temperature, and then the solvent was evaporated. The residue was dissolved in 1:1 hexanes/CH₂Cl₂ and filtered through a silica plug. The solvent was evaporated to yield 2,3,9,10-tetrabromo-6,13-bis-tri(isopropyl - silylethynyl)pentacene (1.31 g, 0.419 mmol, 64%) as a dark blue solid. The solid was recrystallized from 1,2-dichloroethane to yield blue needles. ¹H-NMR (400 MHz, CDCl₃) δ 9.20 (s, 4H), 8.25 (s, 4H), 1.4 (s, 42H). ¹³C NMR (100 MHz, CDCl₃) δ 132.7, 131.4, 131.1, 126.0, 122.8, 119.2, 108.9, 103.8, 19.0, 11.9. MS (EI, 70 eV) 954.5 (M⁺, 100%). Anal. calc. C 55.35%, H 5.27%. Found: C 55.86%, H 5.40%. MP: 332 °C.

2,3,9,10-tetracyano-6,13-bis-tri(isopropylsilyl)ethynylpentacene (16): To a flame-dried pyrex tube with glass-thread mouth was added 50 mL of DMF, and the solvent was sparged with nitrogen for 30 minutes. 2,3,9,10-tetrabromo-6,13-bis-tri(isopropylsilyl)ethynylpentacene (0.300 g, 0.314 mmol) was added to the flask, followed by Pd(PPh₃)₄ (0.073 g, 0.063 mmol, 2 eq.), and CuCN (0.377 g, 3.76 mmol, 12 eq.). The flask was capped and placed inside a microwave reactor. The reaction was stirred and heated at 140 °C for 18 minutes (power=150 W). The mixture was allowed to cool to room temperature, and was then diluted with CH₂Cl₂. The organic layer was then added to a 50% (v/v) NH₄OH /H₂O solution, and the organic layer was then extracted several times with ice water, dried over MgSO₄, filtered, and the solvent removed to yield a crude green solid. The solid was purified by column chromatography (silica / CH₂Cl₂) to yield 2,3,9,10-tetracyano-6,13-bis-tri(isopropylsilyl)ethynylpentacene (0.095 g, 0.129 mmol, 41%) as a blue solid. The material was recrystallized from CH₂Cl₂ to yield blue needles. ¹H-NMR (200 MHz, CDCl₃) 9.50 (s, 4H), 8.50 (s, 4H), 1.60 (s, 6H), 1.40 (s, 36H). ¹³C-NMR (50 MHz, CDCl₃) δ 138.6, 132.9, 130.1, 129.9, 121.6, 115.8, 112.49, 109.4, 102.4, 19.1, 11.6. Anal. calc. C 78.00%, H 6.81%, N 7.58%. Found C 77.86%, H 6.63%, N 7.03%. MP: 355°C.

1,2-Bis-bromomethyl-3,4,5,6-tetrafluoro-benzene (8): 5.5 g, (26 mmol) of tetrafluoro benzenedimethanol¹ was added to 200 mL concentrated hydrobromic acid. The mixture was allowed to reflux overnight, by which time all solid had disappeared and an oil formed at the bottom of the flask. The mixture was diluted with water and extracted with hexanes. Drying and evaporation gave **8** as a yellow oil (8.7 g, 99 % yield). MS (EI, 70 eV) 336 (M⁺), 255 (M⁺ - Br). ¹H-NMR (400 MHz, CDCl₃) 4.63 (s, 4H).

1,2,3,4-tetrafluoro-pentacene-6,13-dione (9): Dibromide **8** (4.7 g, 14.0 mmol), 1,4-anthraquinone (2.91 g, 14.0 mmol), and KI (15.56 g, 93.7 mmol), were dissolved in dry DMF and stirred in a vessel capped with a threaded Teflon plug at 110 °C for two days. The reaction mixture was cooled to room temperature and filtered, and the collected solid

¹ Coe, P. L.; Croll, B. T.; Patrick, C. R. *Tetrahedron* **1967**, 23, 505.

washed with methylene chloride to remove any soluble organic contaminants. The dark solid was then stirred in an Erlenmeyer flask with water to remove excess KI. The remaining brown solid was filtered once again, washed with acetone and dried in air to yield 4.0 g of an insoluble powder (75 % yield). MS (EI, 70 eV) 380 (M^+).

1,2,3,4-tetrafluoro-6,13-bis-(triisopropylsilylethynyl) pentacene (13): In a dried flask triisopropylsilyl acetylene (3.07 g, 16.84 mmol) was dissolved in dry hexanes. A 2.5 M solution of n-butyllithium (5.9 mL, 14.7 mmol) was added slowly under dry nitrogen, and the mixture allowed to stir for thirty minutes. Pentacenequinone **9** was added quickly, and the mixture was stirred at room temperature for 5 d, until all of the quinone had dissolved. The reaction mixture was quenched with 10 % HCl, which caused a brown precipitate to form. The precipitate was filtered and dissolved in acetonitrile. Tin (II) chloride (2.85 g, 12.63 mmol) was added to the solution and it was heated at reflux overnight under nitrogen. The light-blue precipitate was filtered and washed with acetone. Recrystallizing twice from hexanes gave dark blue needles of **13** (0.6 g, 20 % yield). ^1H NMR (400 MHz, CDCl_3) δ 9.52 (s, 2 H), 9.28 (s, 2 H), 7.97 (dd, 2 H, $J = 3.6$ Hz, 6.8 Hz), 7.44 (dd, 2 H, $J = 3.2$ Hz, 6.8 Hz), 1.35 (m, 42 H). MS (EI, 70 eV) 710 (100%, M^+), 691 (20%, $M^+ - \text{F}$). Anal. Calcd. for $\text{C}_{44}\text{H}_{50}\text{F}_4\text{Si}_2$: C 74.32%, H 7.08%. Found: C 74.23%, H 7.06%. M.P. 275 °C.

5,6,7,8-tetrafluoro-1,4-anthraquinone (11): In a dry flask, 1,2-bis-bromomethyl-3,4,5,6-tetrafluoro-benzene **8** (2.0 g, 6.0 mmol), benzoquinone (0.64 g, 6.0 mmol), and KI (6.6 g, 40.0 mmol), were dissolved in dry DMF (60 mL). The mixture was heated at 110 °C for two days. The dark mixture was cooled to room temperature and extracted with ice water and methylene chloride. The organic layer was dried and all organic solvents were evaporated. The product was isolated on a plug eluted with 1:1 hexanes/methylene chloride to yield a yellow solid (**10**) which turned brown on exposure to air overnight to yield quinone **11** (1.0 g, 60 % yield), and was used without further purification in the next reaction step. ^1H NMR (400 MHz, CDCl_3) δ 6.82 (s, 2 H), 3.74 (s, 2 H). MS (EI, 70 eV) 280 (100%, M^+).

1,2,3,4,8,9,10,11-octafluoro-6,13-pentacene quinone (12): In a dried, round bottom flask, 5,6,7,8-tetrafluoro-1,4-anthraquinone **11** (3.15 g, 11.3 mmol), 1,2-bis-bromomethyl-3,4,5,6-tetrafluoro-benzene **8** (3.78 g, 11.3 mmol), and KI (12.51 g, 75.4 mmol) were dissolved in dry DMF (60 mL) and heated at 110 °C for two days. The workup was identical to that described for 1,2,3,4-tetrafluoro-6,13-pentacenequinone **9**, yielding a highly insoluble light yellow-green solid (1.17 g, 23 % yield). MS (EI, 70 eV) 458 (100%, M^+), 441 (70%, $M^+ - \text{F}$), 422 (40%, $M^+ - 2\text{F}$).

1,2,3,4,8,9,10,11-tetrafluoro-bis-(triisopropylsilylethynyl) pentacene (14): The procedure used to make tetrafluoro compound **13** was used on 1.13 g (2.5 mmol) of **12** to prepare **14**. The crude product was recrystallized twice from methylene chloride to give dark square plates (0.58 g, 30 % yield). ^1H NMR (400 MHz, CDCl_3) δ 9.65 (s, 4H), 1.41 (s, 42 H). MS (EI, 70 eV) 782 (30%, M^+), 638 (30%, $M^+ - 2(i\text{-Pr})$ and 3 F). Anal. Calcd. for $\text{C}_{44}\text{H}_{46}\text{F}_8\text{Si}_2$: C 67.89%, H 5.92%. Found: C 68.37%, H 5.99%. M.P. 279 °C.

UV-Vis spectra for compounds **13** – **17**.

Numerical UV-Vis data for **13** – **16**:

Tetrafluoro **13** λ_{nm} (ϵ) in CH_2Cl_2 : 640 (15418), 590 (10008), 546.5 (4928), 440 (4184), 416 (3903), 392 (4041), 349 (sh, 9569), 327 (sh, 27715), 310 (153903), 270.5 (21075)

Octafluoro **14** λ_{nm} (ϵ) in CH_2Cl_2 : 635 (13090), 586 (9045), 544.5 (4415), 505.5 (2337), 440 (2382), 417 (2485), 392 (3131), 348 (sh, 7781), 326 (sh, 22111), 308 (174045), 269 (15452)

Dicyano **15** λ_{nm} (ϵ) in CH_2Cl_2 : 675 (11684), 621 (7731), 570.5 (3612), 527.5 (1963), 445 (4391), 417 (5782), 339 (113612), 293 (39210)

Tetracyano **16** λ_{nm} (ϵ) in CH_2Cl_2 : 668 (8980), 613 (5788), 566.5 (3418), 471 (3369), 382 (sh, 8532), 342 (116236), 327.5 (sh, 31270), 275.5 (13753)