

Supporting Information

Functionalized Pentacene: Improved Electronic Properties from Control of Solid-State Order

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Preparation of pentacenes **1** and **2**:

General Experimental: All reagents were obtained from the Aldrich Chemical Co. (Milwaukee, WI) or Acros Organics (Pittsburgh, PA). Triisopropylsilyl acetylene was purchased from GFS Chemicals (Powell, OH). Diethyl ether and tetrahydrofuran were purified by passage through activated alumina columns under nitrogen. Moisture sensitive reactions were carried out in flame dried glassware under dry nitrogen. TLC was carried out on *MERCK Silica Gel 60* thin layer plates. Silica gel chromatography was performed on *Fisher Brand* silica gel (170-400 mesh). The pentacene quinone precursors for these syntheses are known compounds,¹ and were purified by recrystallization from N,N-dimethylformamide.

General procedure: To a flame-dried 60 ml Teflon screw-stoppered glass tube was added 4.9 ml of a 2.0 M solution of isopropyl magnesium chloride in tetrahydrofuran. Triisopropylsilyl acetylene (1.8g, 9.87 mmol) was added via syringe, followed by an additional 10 ml of dry tetrahydrofuran. The cap was replaced and the tube placed in a 60 °C oil bath for 15 minutes. The tube was removed from heat and the solution was allowed to cool. 0.5g (1.62 mmol, .16 equivalents based on Grignard reagent) of the appropriate quinone was added to the solution, the cap was replaced and the tube placed back into the oil bath for 30 minutes (or until there was no solid quinone remaining in the tube). The tube was removed from heat and allowed to cool. A solution of 10% aqueous HCl saturated with SnCl₂ was added carefully until the tube contents no longer bubbled on addition of the tin chloride solution. The reaction solution turned a deep blue color. The cap was replaced and the tube returned to the oil bath for 15 minutes. The tube was removed and allowed to cool. The solution was filtered through a short pad of silica gel eluting with dichloromethane. The solvent was removed in vacuo. The resulting crude product was purified by chromatography on silica gel, first eluting excess (triisopropylsilyl)acetylene with hexane and then eluting a deep blue band with 90% hexane 10% dichloromethane.

6,13-bis(triisopropylsilylethynyl)pentacene (1**):** The product was synthesized from 6,13-pentacenequinone to give 0.85 g (1.33 mmol, 82%) of deep blue plates: mp. 210 °C (acetone); ¹H NMR (400 MHz, CDCl₃): δ 1.39 (s, 42H), 7.43 (dd, *J* = 6.6, 3.0 Hz, 4H), 7.99 (dd, *J* = 6.6, 3.0 Hz, 4H), 9.32 (s, 4H). ¹³C NMR (400 MHz, CDCl₃): δ 11.90, 19.22, 104.91, 107.39, 118.55, 126.24, 126.53, 128.90, 130.58, 132.49. MS (EI, 70 eV) *m/z* 638 (M⁺, C₄₄H₅₄Si₂ requires 638). UV/Vis (CH₂Cl₂): λ_{max} (ε) 307 (72000), 329 (32000), 350 (7000), 439 (3000), 550 (4000), 592 (10000), 643 (20000). Anal. Calcd for C₄₄H₅₄Si₂: C 82.69, H 8.51; Found C 83.04, H 8.26.

5,14-bis(triisopropylsilylethynyl)pentacene (2**):** The product was synthesized from 5,14-pentacenequinone to give 0.77 g (1.2 mmol, 74%) of deep blue truncated octahedra: mp. 246 °C (toluene); ¹H NMR (400 MHz, CDCl₃): δ 1.38 (s, 42H), 7.38 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.49 (dd, *J* = 6.8, 3.2 Hz, 2H), 8.00 (dd, *J* = 6.8, 3.2 Hz, 2H), 8.59 (dd, *J* = 6.8, 2.8 Hz, 2H), 8.69 (s, 2H), 9.60 (s, 2H). ¹³C NMR (400 MHz, CDCl₃): δ 11.61, 18.98, 104.07, 106.25, 118.51, 120.37, 123.51, 125.44, 126.68, 127.51, 128.44, 130.51, 132.08, 132.87, 137.72. MS (EI, 70 eV) *m/z* 638 (M⁺, C₄₄H₅₄Si₂ requires 638). UV/Vis (CH₂Cl₂): λ_{max} (ε) 301 (64000), 353 (50000), 374 (7000), 396 (7000), 543 (3000), 583 (8000), 632 (13000).

¹6,13-pentacenequinone: Ried, W.; Anthöfer, F. *Angew. Chem.* **1953**, 65, 601. 5,14-pentacenequinone: Serpaud, B.; Lepage, Y. *Bull. Chem. Soc. Fr.* **1977**, 539.

Electrical Measurements: All measurements were made on single crystals of the respective pentacenes. Electrical contacts were made by affixing 0.25 mm gold wire to the crystals with low temperature silver epoxy (Lake Shore Cryotronics, Westerville, OH) or silver acrylic paint (Delta Industries, Stillwater, MN). Current was supplied by a Keithley Model 220 Programmable Current Source (Keithley Instruments, Cleveland, OH) and voltage drops were measured with a Keithley Model 6517A Electrometer Voltmeter. Data was collected using LabView software (National Instruments, Austin, TX) on a personal computer equipped with an IEEE-488 interface card. Temperature was measured using a K-type bead thermocouple probe supplied with the voltmeter.

Measurements were made in a nitrogen atmosphere glove box to avoid air oxidation of samples when heated. Samples were heated to 80 °C on a hot plate with a ceramic dish covering the sample to exclude light. Once the samples came to temperature, the hot plate was turned off and the sample was allowed to cool. During this cooling period, the data collection system was set to automatically record current, voltage, and temperature values every 10 seconds.