Semiconducting 2,6,9,10-Tetrakis(phenyl ethynyl)anthracene Derivatives: Effect of Substitution Positions on Molecular Energies

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1. Experimental Details

1.1. Synthesis

**Materials:** All commercially available starting materials and solvents were purchased from Aldrich, TCI, and Acros Co. and used without further purification. Compounds 2 and 3 were synthesized by following the literature methods.\(^{1-3}\) All of the reactions and manipulations were carried out under N\(_2\) with the use of standard inert-atmosphere and Schlenk techniques unless otherwise noted. Solvent used in inert-atmosphere reactions were dried and degassed using standard procedures. Flash column chromatography was carried out with 230-400 mesh silica gel from Aldrich using wet-packing method. All deuterated solvent were purchased from Cambridge Isotope Laboratories, Inc.
2,6-Bis((4-hexylphenyl)ethynyl)anthracene-9,10-dione, 1. An oven dried, mag.-stirred, 250 mL round bottom flask (RBF) was charged with a solution of 2,6-dibromoanthracene-9,10-dione (3.00 g, 8.2 mmol), bis(triphenylphosphine) palladium(II) dichloride (0.29 g, 0.41 mmol), and copper iodide (0.078 g, 0.41 mmol) in a mixture of freshly distilled THF (80 mL), triethylamine (35 mL) and diisopropylamine (25 mL). 1-Ethynyl-4-hexylbenzene (3.35 g, 18.0 mmol) was then added and the mixture was heated at 80 °C for 16 hrs. After completing the reaction, the solution was poured into methanol to collect the precipitates. The crude solid was purified by silica-gel column chromatography using chloroform as an eluent. Further purification by precipitation afforded 2,6-
bis((4-hexylphenyl)ethynyl)anthracene-9,10-dione, 1. (Yield 3.6 g, 74 %); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.36 (s, 2H), 8.26 ~ 8.24 (d, $J = 7.8$ Hz, 2H), 7.85 ~ 7.83(d, $J = 8.0$ Hz, 2H), 7.47 ~ 7.45 (d, $J = 8.2$ Hz, 4H), 7.18 ~ 7.16 (d, $J = 7.8$ Hz, 4H), 2.61 ~ 2.65(t, $J = 7.8$ Hz, 4H), 1.57~1.64 (m, 4H), 1.29 ~ 1.34 (m, 12H), 0.87 ~ 0.91 (t, $J = 6.2$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 182.18, 144.77, 136.58, 133.68, 132.20, 132.05, 130.33, 130.26, 128.84, 127.61, 119.56, 95.17, 87.80, 34.09, 31.36, 29.15, 22.81, 14.30. LR-MS (EI) m/z (M$^+$): Calcd for C$_{42}$H$_{40}$O$_2$, 576.3 ; found, 576.3. EA analysis calcd for C$_{42}$H$_{40}$O$_2$: C, 87.46 ; H, 6.99, found : C, 87.30 ; H, 6.89.

2,6-Bis((4-hexylphenyl)ethynyl)-9,10-bis(phenylethynyl)anthracene, 4. In a 250 mL, oven dried, mag.-stirred RBF, 3 (0.43 g, 4.23 mmol) was dissolved in freshly distilled THF (50 mL). The solution was then cooled to $-78^\circ$C. $n$-BuLi (2.03 mL, 5.08 mmol, 2.5 M sol’n. in hexane) was then added dropwise over 15 minutes. This mixture was stirred for 30 min and 2,6-bis((4-hexylphenyl)ethynyl)anthracene-9,10-dione, 1 (1.0 g, 1.69 mmol) were added at -78 °C. The mixture was stirred at room temperature for 3 hrs, and then quenched with water, SnCl$_2$, and HCl. After completing the reaction, the solution was poured into methanol to collect the precipitates. (Yield 0.43 g, 34 %); $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$(ppm) 8.75 (s, 2H), 8.56 (d, $J = 9.0$ Hz, 2H), 7.81 (d, $J = 7.8$ Hz, 4H), 7.66 (d, $J = 8.6$ Hz, 2H), 7.56(d, $J = 8.2$ Hz, 4H), 7.45 (m, 6H), 7.21 (d, $J = 7.8$ Hz, 4H), 


2.64 (t, $J = 7.8$ Hz, 4H), 1.67-1.60 (m, 4H), 1.37-1.32 (m, 12H), 0.90 (t, $J = 7.0$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$(ppm) 144.25, 131.94, 131.89, 131.80, 131.63, 130.85, 129.35, 128.75, 128.49, 128.42, 127.56, 123.35, 121.90, 120.45, 118.48, 103.43, 91.54, 90.25, 85.45, 36.09, 31.76, 31.25, 28.99, 22.62, 14.12. HR-MS (FAB) m/z (M$^+$) : Calcd for C$_{58}$H$_{50}$, 746.3913; found, 746.3912. EA analysis calcd for C$_{58}$H$_{50}$: C, 93.25; H, 6.75; found: C, 94.03; H, 6.86.

9,10-Bis((4-hexylphenyl)ethynyl)-2,6-bis(phenylethynyl)anthracene, 5. An oven dried, mag.-stirred, 250 mL RBF was charged with a solution of 2,6-dibromo-9,10-bis((4-hexylphenyl)ethynyl)anthracene, 2 (1.00 g, 1.42 mmol), bis(triphenyl phosphine)palladium(II) dichloride (0.014 g, 0.071 mmol), and copper iodide (0.050 g, 0.071 mmol) in a mixture of freshly distilled THF (50 mL), triethylamine (20 mL) and diisopropylamine (10 mL). 3 (0.36 g, 3.55 mmol) was then added and the mixture was heated at 80 °C for 16 hrs. After completing the reaction, the solution was poured into methanol to collect the precipitates. The crude solid was purified by recrystallization from acetone to give 9,10-bis((4-hexylphenyl)ethynyl)-2,6-bis(phenylethynyl)anthracene, 5 (Yield 0.50 g, 47%); $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$(ppm) 8.79 (s, 2H), 8.60 (d, $J = 9.0$ Hz, 2H), 7.71 (d, $J = 7.8$ Hz, 4H), 7.67 (d, $J = 1.6$ Hz, 2H), 7.65(m, 4H) 7.41 (m, 6H), 7.25 (d, $J = 3.9$ Hz, 4H), 2.70(t, $J = 7.8$ Hz, 4H), 1.71-1.64 (m, 4H), 1.40-1.31 (m, 12H), 0.93 (t, $J = 7.0$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$(ppm) 144.25, 131.94, 131.89, 131.80, 131.63, 130.85,
129.35, 128.75, 128.49, 128.42, 127.56, 123.35, 121.90, 120.45, 118.48, 103.43, 91.54, 90.25, 85.45, 36.09, 31.76, 31.25, 28.99, 22.63, 14.08. HR-MS (FAB) m/z (M⁺) : Calcd for C₅₈H₅₀ , 746.3913; found, 746.3910. EA analysis calcd for C₅₈H₅₀ : C,93.25 ; H,6.75 , found : C, 93.27 ; H, 6.79.

1.2 Instrumentation

¹H NMR spectra were recorded on a Varian Mercury NMR 400Hz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. High resolution mass analysis was performed on a JMS-700 MStation mass spectrometer (JEOL, resolution 60,000, m/z range at full sensitivity 2,400). Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821e instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 (temperature rate 10°C/min under N₂). The redox properties of two molecules were examined by using cyclic voltammetry (Model: EA161 eDAQ). Thin films were coated on a platinum plate using chloroform as a solvent. The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in a freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV/s.

Atomic force microscopy (Digital Instruments Multimode equipped with a nanoscope IIIa
controller) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the samples. The film samples were fabricated by spin-coating (1500 rpm) on silicon wafer followed by drying at 70°C under vacuum (solvent: chloroform, conc. of the solution: 10 mg/mL).

In order to study absorption behavior, the films of two molecules were fabricated on quartz substrates as follows. The solution (1 wt%) of each molecule in chloroform was filtered through an acrodisc syringe filter (Millipore 0.45 µm) and subsequently spin-cast on the quartz glass. The films were dried overnight at 50°C for 24 hours under vacuum. Absorption spectra of samples in a film and solution state (chloroform, conc. 1×10⁻⁵ mole/L) were obtained using a UV-Vis spectrometer (HP 8453, photodiode array type) in the wavelength range of 190-1100 nm. PL spectra of the solutions were acquired on a Hitachi F-7000 fluorescence spectrophotometer.

1.3 Fabrication of Organic Thin Film Transistor

For the characterization of TFT performance, bottom gate top contact device geometry was employed. On the heavily n-doped Si/SiO₂ substrate the spin-coated films (thickness ~40-50 nm) were prepared with chloroform as a solvent. Surface modification was carried out with n-octyltrichlorosilane (OTS) to make hydrophobic dielectric surface. Source and drain electrodes were then thermally evaporated (100nm) through shadow mask with the channel width and length of 1500 µm and 100 µm,
respectively. All the field effect mobilities were extracted in the saturation regime using the relationship \( \mu_{\text{sat}} = \frac{2I_{DS}L}{WC(V_G - V_{th})^2} \), where \( I_{DS} \) means saturation drain current, \( C \) is capacitance of SiO\(_2\) dielectric, \( V_G \) is gate bias, and \( V_{th} \) is threshold voltage. The device performance was evaluated in air using Keithley 4200-SCS semiconductor characterization system at ambient conditions.

2. Results

2.1. DSC and TGA thermograms of 4 and 5.

![DSC thermograms of molecules 4 (a) and 5 (b).](image1.png)

Figure 1S. DSC thermograms of molecules 4 (a) and 5 (b).

![TGA thermograms of molecules 4 (a) and 5 (b).](image2.png)

Figure 2S. TGA thermograms of molecules 4 (a) and 5 (b).
2.2. Density Functional Theory (DFT) calculation

![Figure 3S](image)

Figure 3S. HOMO/LUMO levels of molecules 4 (a) and 5 (b) used to calculate the theoretical molecular orbitals.

To estimate the position and molecular energies of frontier orbitals for 4 and 5, Density Functional Theory (DFT) calculations were performed using the Spartan’06 program at the B3LYP/6-31G* level. The hexyl peripheral groups were sustained in calculation to observe the effect of substituents on the optimized geometries and theoretical energy levels. It could be found that the whole conjugated moieties are perfectly flat. As shown in Figure 1S, the largest coefficients in the HOMO orbitals are located on the 2-D \( \pi \)-system centered at anthracene unit. The coefficients in the LUMO orbital are mainly located on the anthracene unit along 9,10-substituted positions only. The calculated bandgap energies show identity, implying the properties of single molecule without considering intermolecular interaction.
2.3. Cyclic Voltammetry

Figure 4S. Cyclic voltammograms of 4 (a) and 5 (b). *sample: Films

2.4. Atomic Force Microscopic study of thin films made of 4 (a) and 5 (b).

Figure 5S. 2-D and 3-D AFM images of thin films made of 4 (a) and 5(b).
The surface topographies were investigated using atomic force microscope. The surface of spin-coated film with molecule 5 is much smoother than that of the film with 4. It implies that more dense polycrystallites were formed in the thin film of molecule 5.

2.5 Time correlated single-photon counting (TCSPC) measurement: Life-time measurement

Fluorescence lifetime measurements were performed by exciting solution, thin film, and crystalline microplate samples with 50 ps pulses at 375 nm, obtained by picosecond pulsed diode laser system (FluoroTime 200, PicoQuant GmbH, Germany). Fluorescence life-times for solutions, films, and crystalline objects were measured. The results from 4 indicated that the fluorescence decay of film ($\tau = 0.25-0.46$ ns at 525 (563) nm) and single-crystals ($\tau = 3.42$ ns at 594 nm) is much faster than that of the solution ($\tau = 5.43 – 5.67$ ns at 506 (539) nm). Same tendency could be observed in 5. (see Figures 6S and 7S)

Figure 6S. Fluorescence decay profiles of 4 monitored at each emission band. a: solution at 1 x 10^{-5} M, b: film and single-crystals.
Figure 7S. Fluorescence decay profiles of 5 monitored at each emission band. a: solution at 1 $\times$ 10$^{-5}$ M, b: film and single-crystals. The results from 5 indicated that the fluorescence decay of film ($\tau = 0.24$–0.31 ns at 557 (592) nm) and single-crystals ($\tau = 2.59$ – 3.24 ns at 560 (605) nm) is much faster than that of the solution ($\tau = 5.59$–6.03 at 513 (543) nm.)
3. $^1$H, $^{13}$C NMR spectra of 4 and 5.

3.1. $^1$H NMR spectra of compound 4

![1H NMR spectrum of compound 4](image1)

3.2. $^{13}$C NMR spectra of compound 4

![13C NMR spectrum of compound 4](image2)
3.3. $^1$H NMR spectra of compound 5

![H NMR spectra of compound 5]

3.4. $^{13}$C NMR spectra of compound 5

![C NMR spectra of compound 5]

4. References

