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5′,5″-(9,10-Bis((4-hexylphenyl)ethynyl) anthracene-2,6-diyl)bis(5-hexyl-2,2′-bithiophene) as an Organic Semiconductor and its Application to Thin Film Transistors

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5′,5″-(9,10-Bis((4-hexylphenyl)ethynyl) anthracene-2,6-diyl)bis(5-hexyl-2,2′-bithiophene) as an Organic Semiconductor and its Application to Thin Film Transistors

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*New anthracene-containing conjugated molecules have been synthesized through Stille coupling reaction. 2,6-Dibromo-9,10-bis(4-hexylphenyl)ethynyl)anthracene and 2,6-dibromo-9,10-bis(phenylethynyl)anthracene were reacted with tributyl (5′-hexyl-2,2′-bithiophen-5-yl)stannane to yield 5′,5″-(9,10-bis(phenylethynyl) anthracene-2,6-diyl)bis(5-hexyl-2,2′-bithiophene), **1** and 5′,5″-(9,10-bis((4-hexyl phenyl)ethynyl) anthracene-2,6-diyl)bis(5-hexyl-2,2′-bithiophene), **2**. The molecule, **2** only exhibit good solubility in common organic solvents and good self-film-forming properties. The semiconducting properties of the molecule, **2** were evaluated in organic thin film transistors (OTFTs). The molecule, **2** exhibits charge carrier mobilities—as high as* $5.3 \times 10^{-3}\ cm^2\ V^{-1}\ s^{-1}$ *(*$I_{ON}/I_{OFF} = 2.43 \times 10^5$*) without thermal annealing process.*

Keywords Anthracene; bithiophene; conjugated molecules; mobility; organic thin film transistor; semiconductor

1. Introduction

p-Type organic semiconductors such as pentacene, rubrene, anthracene, thiophene, or their derivatives have attracted a great deal of attention for applications in high-performance OTFTs [1–3]. However, the preparation methods for the thin films of these molecules—under vacuum or inert atmospheric conditions—suffer severe limitations during large-scale device fabrication, due to the complexity of the process.

Organic semiconductors that are soluble in organic solvents facilitate the use of low-cost spin-coating or drop-casting techniques for OTFT device fabrication [3–5]. Therefore, the development of solution-processable p-type semiconductor materials is an important issue in the further development of OTFTs.

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Highly soluble, high-mobility low-molar-mass molecules such as [1]benzothieno-[3,2-b]benzothiophene derivatives, selenophene-containing heteroacene, and silylethynylated polyacenes are not capable of achieving large-area devices since their molecular weights are not sufficient for achieving a uniform film with favorable interfacial contact and coverage on the substrate [6,7]. Although some soluble anthracene-based semiconducting molecules have been reported, they exhibit poor performance in OTFT devices [8].

In this article, we present two different π- conjugated molecules and demonstrate a promising new class of medium-sized molecules for OTFTs. We investigated the optical, thermal, and electrochemical properties of the new conjugated molecules. The solution-processable molecule, **2** was employed to fabricate OTFTs and the performance of the devices was investigated. The newly synthesized crystalline molecule, **2** containing an anthracene moiety offers not only a high carrier mobility, of the order of $10^{-3}\,cm^2/V\,s$, but also a high on/off current ratio in a bottom gate and top contact device configuration.

Experimental

The detailed synthetic procedures of the molecules, **1** and **2** will be reported elsewhere. The spectroscopic and other characterization data are described in this section.

5′,5″-(9,10-bis(phenylethynyl)anthracene-2,6-diyl)bis(5-hexyl-2,2′-bithiophene) (1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) 8.89 (s, 2H), 8.69 (d, $J = 9.0$ Hz, 2H), 7.94 (d, $J = 9.0$ Hz, 2H), 7.88 (d, $J = 7.8$ Hz, 4H), 7.50–7.56 (m, 6H), 7.29 (d, $J = 7.8$ Hz, 2H), 7.21 (d, $J = 3.9$ Hz, 2H), 7.13 (d, $J = 3.5$ Hz, 2H), 6.79 (d, $J = 3.5$ Hz, 2H), 2.88 (t, 4H), 1.74–1.81 (m, 4H), 1.39–1.48 (m, 12H), 0.97 (t, 6H). Anal. Calcd. for $C_{58}H_{50}S_4$: C, 79.59; H, 5.76; S, 14.65, found: C, 79.59; H, 5.61; S, 14.54.

5′,5″-(9,10-bis((4-hexylphenyl)ethynyl)anthracene-2,6-diyl)bis(5-hexyl-2,2′-bithiophene) (2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) 8.86 (s, 2H), 8.66 (d, $J = 8.6$ Hz, 2H), 7.90 (d, $J = 8.6$ Hz, 2H), 7.78 (d, $J = 8.2$ Hz, 4H), 7.49 (d, $J = 3.9$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 4H), 7.20 (d, $J = 3.5$ Hz, 2H), 7.13 (d, $J = 3.5$ Hz, 2H), 6.78 (d, $J = 3.5$ Hz, 2H), 2.88 (t, 4H) 2.75 (t, 4H), 1.71–1.80 (m, 8H), 1.39–1.48 (m, 24H), 0.97 (t, 12H). Anal. Calcd. for $C_{70}H_{74}S_4$: C, 80.56; H, 7.15; S, 12.90, found: C, 80.58; H, 7.16; S, 12.40.

Instrumental Analysis

^{1}H NMR spectra were recorded on a Varian Mercury NMR 400 Hz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer.

X-ray diffraction (XRD) experiment was performed using the synchrotron radiation (1.542 Å) of the 3C2 beam line at the Pohang Synchrotron Laboratory, Pohang, Korea. The film samples were fabricated by drop-casting on silicon wafer, followed by drying at 70°C under vacuum (solvent: chloroform, concentration of the solution: 10 mg/mL). The measurements were obtained in a scanning interval of 2θ between 1° and 40°.

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 0.2 μm) and subsequently spin-cast on the quartz glass. The films were dried overnight at 70°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.

For the characterization of TFT performance, bottom gate top contact device geometry was employed. On the heavily n-doped Si/SiO_2 substrate the spin-coated films (thickness ~40–50 nm) were prepared with chloroform as a solvent. Surface modification was carried out with OTS to make hydrophobic dielectric surface. Source and drain electrodes were then thermally evaporated (100 nm) through shadow mask with the channel width and length of 1500 μm and 150 μm, respectively. We followed the fabrication and measurement methods reported in our previous literature [9].

Results and Discussion

Materials

We report here the facile and high-yield synthesis of new p-type anthracene-based semiconducting molecules. Figure 1 illustrates the simplified synthetic routes for the two molecules. Using tributyl(5′-hexyl-2,2′-bithiophen-5-yl)stannane, we performed Stille coupling by the addition of tetrakis(triphenylphosphine) palladium(0) in freshly distilled DMF to yield **1** and **2** in a fairly high yield.

Acting as solubilizing groups and crystallization-promoting moieties, two or four hexyl chains were substituted into the phenyl and thiophene groups. In molecule **1**, two hexyl groups were aligned in a unidirectional manner. In molecule **2**, four hexyl groups were introduced in a biaxial manner. The molecule **2** was only found

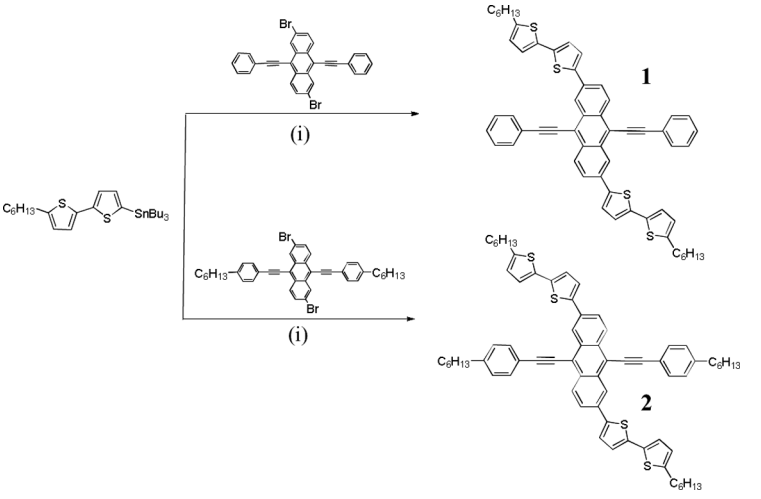

Figure 1. Synthesis of the anthracene-based molecules. (i) $Pd(PPh_3)_4$, DMF, 90°C, 12 h.

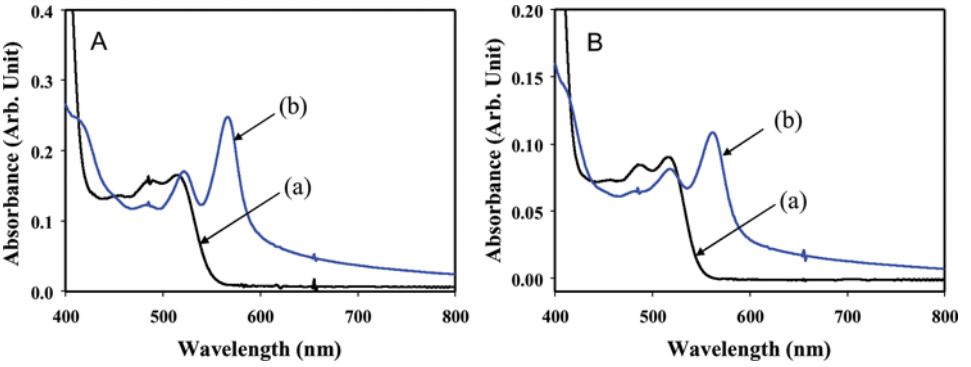

Figure 2. UV-Vis absorption spectra of **1** (A) and **2** (B). (a) Solution (b) as-coated film.

to have good self-film-forming properties and dissolved well in various organic solvents such as chloroform, xylene, MC, chlorobenzene, and THF.

UV–Vis Absorption Spectroscopy. In order to study the interaction between the molecules, the absorption spectra of the samples in chloroform (conc. 1×10^{-5} mol/L) and in thin films were obtained. Figure 2 shows the UV-Vis absorption spectra for the solutions and as-coated thin films prepared using the two molecules (see Table 1). The solution spectra for the two molecules are almost identical and the number of hexyl group does not influence the spectra.

In two samples, we observed a significant bathochromic shift in the absorption spectra upon film formation, which indicated the possible generation of J-aggregated intermolecular interactions. From the absorption edge, we were able to calculate the optical bandgap energies for the thin films of the two molecules. Molecules **1** and **2** showed similar bandgap energies together with similar intermolecular interactions.

X-Ray Diffraction Analysis. In order to study the crystallinity and preferred orientations of the two molecules, X-ray diffraction (XRD) was performed in an out-of-plane mode at room temperature. The molecular layers are thought to be associated with the layered stacking properties resulting from the inclusion of the terminal hexyl groups, which are already known to induce long-range ordering.

Table 1. Measured and calculated parameters for the two conjugated molecules

	T_d (°C)	T_m (°C)	T_c (°C)	Solution λ_{max} (nm)	Film λ_{max} (nm) Before annealing	$\lambda_{cut\ off}$ (nm)	E_g^{opt} (eV)	Energy level HOMO (eV)	Energy level LUMO (eV)[b]
1	420	260	191	394, 489, 514	388, 483, 521, 566	596[a]	2.08[a]	−5.65	−3.57[a]
2	414	235	223	396, 485, 517	388, 518, 562	588[a]	211[a]	−5.40	−3.29[a]

[a]Before annealing.
[b]HOMO(eV) – E_g^{opt}(eV).

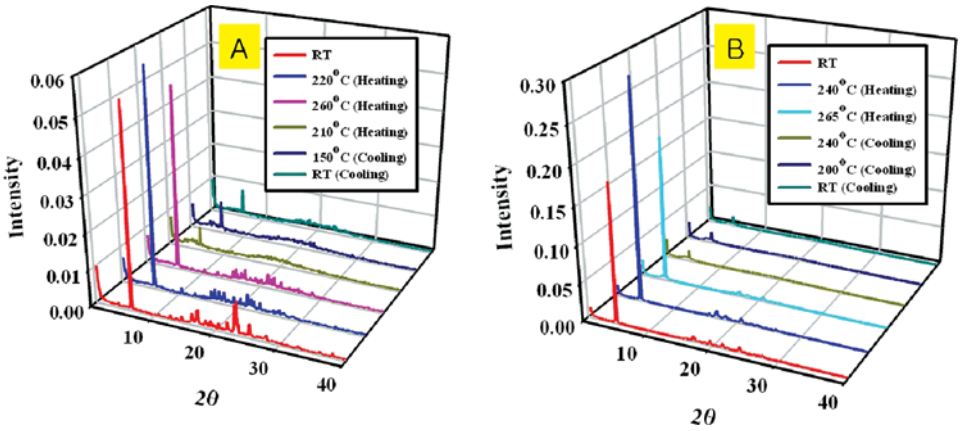

Figure 3. XRD patterns for as-cast thin films of the two conjugated molecules with the temperature: (A) **1** and (B) **2**.

X-ray diffraction scans of as-cast films of **1** and **2** revealed very distinctive crystalline peaks, indicating intermolecular stacking. The edge-on orientation of molecule **2** relative to the substrate is evidenced by the absence of diffraction at around 20–25° (see Figure 3). The preferred orientation is inferred through the high reflection (100) intensity of the peaks at $2\theta = 4.30-6.15°$. This result implies that most of the crystallites are preferentially oriented along the (100)-axis in the plane.

When comparing the d-spacing of the two molecules, it is clear that molecules of **2** containing four hexyl peripheral moieties exhibit larger d-spacing than those of **1**. The larger lamella ordering distance of **2** is attributed to the two-dimensional ordering induced by the interaction between the biaxial hexyl peripheral moieties.

Properties of OTFTs Made of Molecule 2. Bottom-gate, top-contact OTFT devices were fabricated under ambient conditions *without thermal annealing*. The channel length was $L = 100\,\mu m$ and the channel width was $W = 1500\,\mu m$. It should be noted that we did not anneal the molecular films before measuring the TFT performances, and all measurements were performed under atmosphere. Unfortunately, the molecule **1** showed very poor solubility in organic solvents and poor film formation occurred. The device containing the molecule **1** could not exhibit the dependence of drain current (I_{DS}) on the gate voltages.

The OTFTs of the molecule **2** exhibited typical p-channel field-effect transistor (FET) characteristics. The output characteristics showed very good saturation behaviors and clear saturation currents that were quadratically related to the gate bias (see Figure 4). The mobilities were obtained from the source (S)-drain (D) current-voltage curves (I_{DS} vs. V_{DS}) in well-resolved saturation regions.

The saturated field-effect mobility μ_{FET} can be calculated from the amplification characteristics using established equations describing field-effect transistors [9]. When using OTS treated SiO_2 insulator, the transistor devices made of **2** provided a field effect mobility of $5.3 \times 10^{-3}\,cm^2\,V^{-1}\,s^{-1}$, together with a high current on/off ratio ($>10^4$) and a threshold voltage ($V_{th} < -35\,V$).

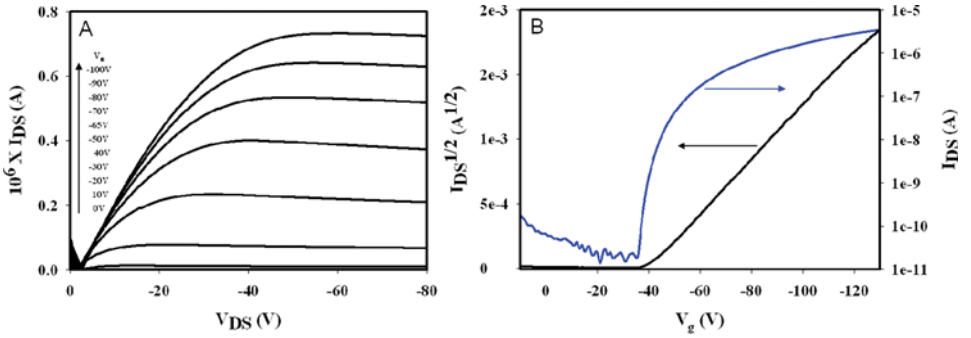

Figure 4. Electrical characterization of OTFT. Left: plot of drain current (I_{DS}) versus drain-source voltage (V_{DS}). Right: plot of I_{DS} and $I_{DS}^{1/2}$ versus gate voltage (V_g); $V_{DS} = -100$ V. (A) device A, (B) device B. *Insulator: OTS treated SiO_2 *Performance was measured under atmosphere.

Conclusion

We have successfully synthesized and characterized new anthracene-based conjugated molecules as semiconducting materials. The molecules with hexyl-substituted bithiophene peripheral units not only formed smooth films on large surfaces but also showed better homogeneous layer formation with relatively small crystallites. The thin film transistor device made of **2** provided a field effect mobility of $5.3 \times 10^{-3}\,cm^2\,V^{-1}\,s^{-1}$, together with a high current on/off ratio ($>10^4$) and a threshold voltage ($V_{th} < -35$ V). Our study unambiguously demonstrates that anthracene-based 2-D conjugated molecules with a high degree of molecular arrangement and high solubility can be utilized for fabricating and significantly improving OTFT devices.

Acknowledgment

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