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Novel p- and n-Type Organic Semiconductors with an Anthracene Unit

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Organic semiconductors have been widely studied from viewpoints of their fundamental optoelectronic properties and their potential applications such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and photovoltaic cells.[1] Usually hole-transporting (p-type) semiconductors have been prepared from electron-donating π-systems, whereas electron-transporting (n-type) semiconductors are prepared from electron-accepting ones.[2] However, unusual n-type materials for OFETs have recently been obtained by introduction of fluoroalkyl substituents[3] or a pentafluorophenyl substituent[4] to thiophen oligomers which are known as hole-trasporting systems. Marks et al. have reported that in OFETs with thiophene/perfluoroarene oligomers as active layers the terminal aryl groups have a great effect in determining the polarity of OFETs.[4] This result suggests that novel p- and n-type organic semiconductors would be produced by introducing electron-accepting or electron-donating groups as terminal groups into a common core unit like thiophene oligomers. In the case of acenes, pentacene is known to exhibit the highest mobility ($\mu = 3.0$ cm^2/Vs) among OFETs.[5] Some derivatives of pentacene show p-type semiconducting behavior,[6] and perfluorination of pentacene has been reported to induce n-type semiconducting behavior.[7] However, chemical modification of pentacene has a general difficulty caused by its low solubility in common organic solvents as well as instability in air. Therefore, we have paid our attention to anthracene[8] which can be more easily derivatized owing to its better solubility.

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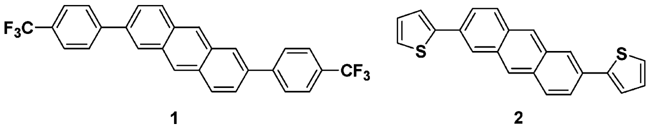
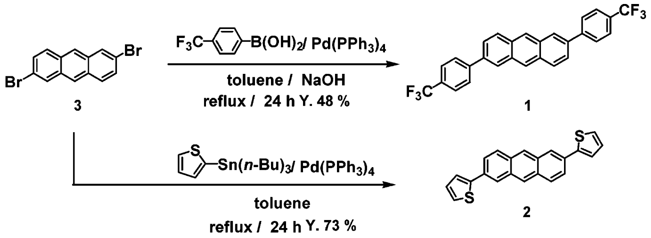
Chart 1. Structure of Anthracene Derivatives



1 **2**

Scheme 1. Synthesis of Compounds 1 and 2



The OFETs with anthracene dimers or trimers as active layers have exhibited good hole mobilities,[9] suggesting that the π-extension of the anthracene unit by introducing aryl groups would afford efficient charge transportation systems. In this context, we have now designed novel anthracene derivatives having thiophene and 4-trifluormethylphenyl rings as electron-donating and accepting parts, respectively, for p- and n-type transistor materials. We report herein the synthesis and characterization of 2,6-bis(4-trifluoromethylphenyl)anthracene (**1**) and 2,6-dithienylanthracene (**2**) (Chart 1). OFETs using these derivatives have been constructed and their performances as p- and n-type semiconductors are presented here.

The syntheses of anthracene derivatives **1** and **2** were conveniently achieved as outlined in Scheme 1. Trifluoromethylphenyl derivative **1** was synthesized by the Suzuki coupling reaction of 2,6-dibromoanthracene (**3**)[10] and 4-trifluromethylphenylboronic acid with $Pd(PPh_3)_4$ in refluxing toluene in 48% yield. On the other hand, thiophene derivative **2** was synthesized by the Stille coupling reaction using 2-tributylstannylthiophene in 73% yield. Compounds **1** and **2** were purified by sublimation and the structures were determined by the spectral data along with elemental anaylsis. Both compounds are bright-yellow color and have low solubility in common organic solvents. Differential scanning calorimetry (DSC) measurements showed a sharp melting endotherm peak at 289 °C for **1** and 322 °C for **2**, respectively.

The absorption and emission spectral data of these derivatives are summarized in Table 1. The absorption maximum of **1** with electron-withdrawing units is blue-shifted compared to that of **2** with electron-donating thienyl units. The HOMO−LUMO gaps obtained from the end-absorptions are 2.85 eV for **1** and 2.68 eV for **2**.[11] The lower gap for **2** is probably attributed to the less steric hindrance between the five-membered ring and anthracene unit, which leads to more effective π-conjugation. On the other hand, the emission maximum of **1** (439 nm) in chloroform appears at a longer wavelength than that of **2** (431 nm). The larger Stokes shift observed in **1** can be explained by considering that the geometry of **1** becomes more planar in the excited state. Moreover, **1** and **2** exhibited strong green photoluminescence in the solid state. The emission maxima were observed at longer wavelengths than those in solution (59−78 nm red shift), indicating the presence of strong intermolecular interactions in the solid state.

Table 1. Absorption and Fluorescene Maxima of 1 and 2 in the Chloroform Solution and Solid State[a]

	solution		solid
compound	λ_{abs} [nm]	λ_{em} [nm]	λ_{em} [nm]
1	379	439	517
2	392	431	490

[a] Excitation wavelength: 365 nm.

The electrochemical measurements of these derivatives **1** and **2** were performed in tetrahydrofuran.[12] The differential pulse voltammogram (DPV) of **1** with acceptor units exhibited one oxidation peak (+1.43 V vs SCE) and one reduction peak (−1.68 V vs SCE). DPV of **2** with donor units showed two oxidation peaks (+1.20 V, +1.58 V vs SCE) and one reduction peak (−1.76 V vs SCE). Both oxidation and reduction potentials of **1** are a little higher than those of **2**. This result indicates that **1** has a higher ionization potential and a higher electron affinity than **2**.

The single crystal of **1** was obtained by slow sublimation. To investigate the molecular structure and intermolecular interactions in the soild state, X-ray structure analysis of the single crystal of **1** was carried out. As expected, the molecule of **1** has a little twisted geometry, where a torsion angle of 32.2° is observed between the anthracene and 4-triflurometh-ylphenyl rings. In the crystal, the intermolecular short C−C contact of 3.43 Å is observed between the C4 positions of anthracene rings. The molecules of **1** are packed in a herringbone manner as shown in Figure 1c, where the anthracene ring is overlapped with the 4-trifluoromethylphenyl rings.

FETs with these derivatives were constructed on SiO_2/Si substrates using a top-contact geometry (Figure 2a). An n-type Si wafer and a 200 nm thick layer of thermally grown SiO_2 were used as the gate and gate insulator, respectively. The thin films of these derivatives (50 nm) were formed on the SiO_2 by high-vacuum evaporation at different substrate temperatures. Gold source and drain contacts (50 nm) were deposited on the organic layer through a shadow mask. The channel length (L) and width (W) are 100 and 1000 μm, respectively. The FET measurements were carried out at room temperature in a vacuum chamber (10^{-5} Pa) without

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(8) Hole mobilities in the anthracene single crystals were measured by the time-of-flight photocurrent technique and found to reach up to 3 cm^2 V^{-1} S^{-1} at 300 K. (a) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*; Oxford University Press: New York, 1999. (b) Karl, N.; Marktanner, J. *Mol. Cryst. Liq. Cryst.* **2001**, *355*, 149−173. (c) Aleshin, A. N.; Lee, J. Y.; Chu, S. W.; Kim, J. S.; Park, Y. W. *Appl. Phys. Lett.* **2004**, *84*, 5383.

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(11) This is in agreement with the result of PM3 calculations: The HOMO−LUMO energy gaps of **1** and **2** show 6.91 and 6.87 eV, respectively.

(12) Measured at a Pt electrode with 0.1 mol dm^{-3} Bu_4NPF_6 as a supporting electrolyte in THF.

(13) See Supporting Information for semilogarithmic plot of source-drain current versus gate voltage and plot of square root of source-drain current versus gate voltage, for OFETs using **1** and **2** as semiconducting material, from which field-effect mobility, I_{on}/I_{off} ratio, and threshold voltage can be calculated.

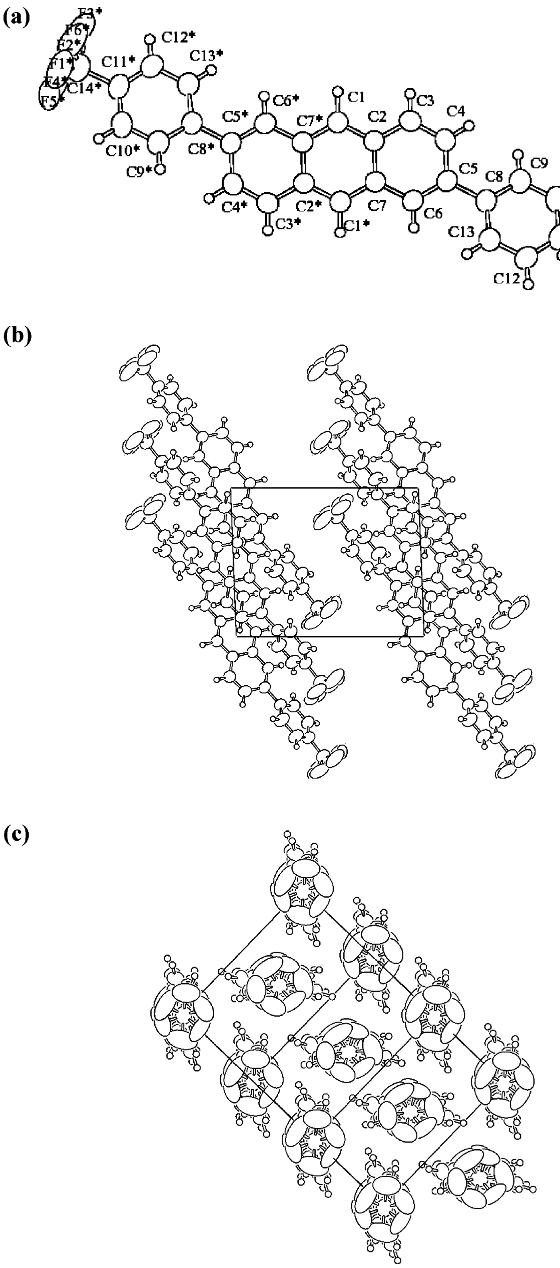

Figure 1. X-ray structure of anthracene derivative **1**: (a) ORTEP drawing of the molecular structure, (b) overlapping view along the *b*-axis, and (c) packing structure.

exposure to air. Transistor responses were observed only for positive bias for **1**, and for negative bias for 2 (Figures 2b and 2c), which means that **1** with acceptor units is an n-type semiconductor and **2** with donor units is a p-type semiconductor.[13] However, the FET behavior of **1** was not observed in air. The electron mobility and on/off ratio of the film of **1** prepared at 20 °C are 3.4×10^{-3} cm^2/V s and 10^4, respectively. On the other hand, the hole mobility and on/off ratio of the film of **2** prepared at 20 °C are 4.5×10^{-3} cm^2/V s and 10^3, respectively. It should be noted that almost similar mobilities with different polarity were realized by changing the terminal aryl groups. The threshold gate voltages were ca. +75 V for film **1** and ca. −40 V for film **2**, suggesting that generation of the charge carrier (electron) in **1** is more difficult. This is related to the high LUMO level of **1**.

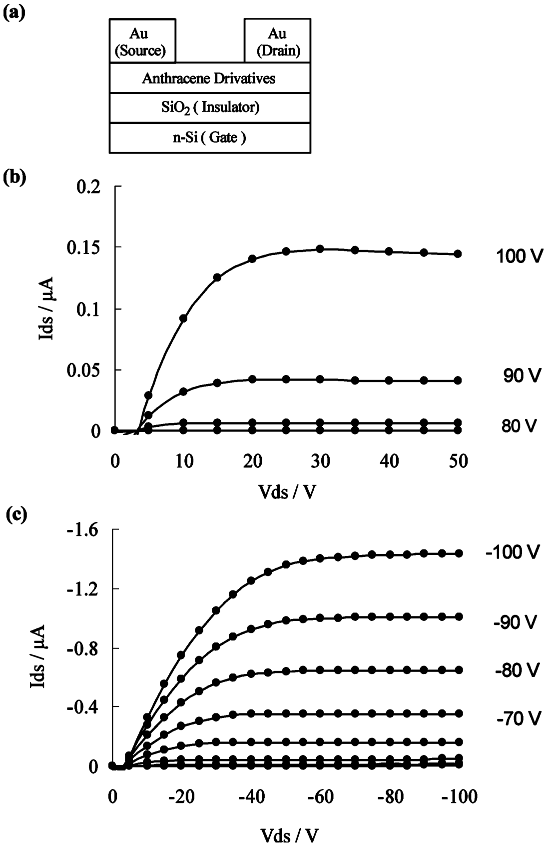

Figure 2. (a) Device structure. Output characteristics of FET devices based on films at the different gate bias: (b) for **1** and (c) for **2**.

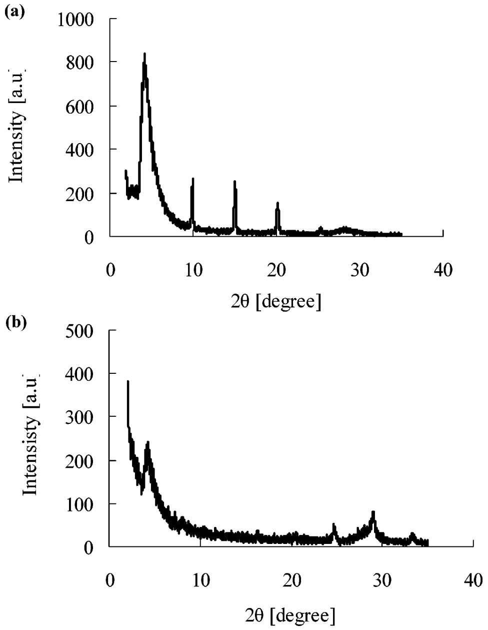

Figure 3. X-ray diffraction of films (50 nm thickness) deposited at room temperature: (a) for **1** and (b) for **2**.

The anthracene films deposited on SiO_2/Si substrates were investigated by X-ray diffraction in reflection mode. Figures 3a and 3b show the thin-film X-ray diffraction (XRD) patterns of **1** and **2** films deposited at 20 °C. In the case of film **1**, the sharp and strong reflections up to the fifth order indicate a high degree of lamellar ordering and crystallinity. The *d*-spacing obtained from the first reflection peak ($2\theta = 4.21$) is 2.09 nm. Since the molecular length of **1** obtained

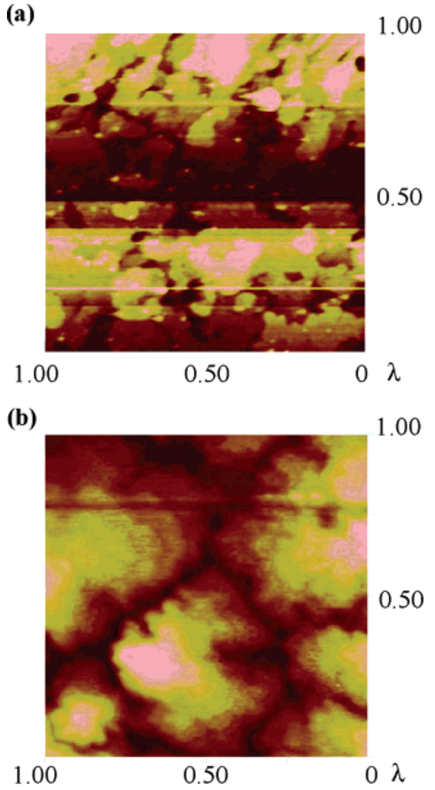

Figure 4. AFM images of films deposited onto Si/SiO$_2$: (a) for **1** and (b) for **2**.

from the single-crystal X-ray analysis is 2.02 nm, the molecule of **1** is considered to be almost perpendicular on the substrate. This is an ideal molecular arrangement for charge transport. On the other hand, the film **2** showed almost no reflection peak, suggesting a disorder orientation on the Si/SiO$_2$ substrate.

The sublimed films of compounds **1** and **2** are dark blue and shiny. Figure 4 shows noncontact mode atomic-force microscopy (AFM) images of the thin films deposited on Si/SiO$_2$. The AFM of **1** film shows a small grain size and rough surface. On the other hand, the AFM of **2** film shows a larger grain size which is estimated to be ca. 0.4−0.6 μm and each step appears from the surface in the grain. In general, the field-effect mobility for organic semiconductor films depends on the grain size as well as molecular orientation on the substrate. Therefore, the field-effect mobility of **1** film would be improved by making larger crystalline grains on the substrate.

In summary, new anthracene derivatives **1** and **2** were prepared as semiconductors for FETs to prove the effect of terminal groups on charge transport. The n- and p-type activities were achieved by introduction of acceptor or donor units into the anthracene structure. The film of **1** with electron-accepting 4-trifluoromethylphenyl units exhibited good n-type semiconducting behavior. This is the first n-type performance of anthracene derivatives. Since the trifluoromethylphenyl group can be easily introduced by the Suzuki coupling reaction, this group would be used for electron injection in π-conjugated electronic systems. In contrast, the film of **2** with electron-donating thiophene units exhibited p-type semiconducting behavior with the same mobility range observed for the film of **1**. This result indicates that the terminal substituents near the gate electrode have a great effect in determining the polarity of FET characteristics.

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Supporting Information Available: Detailed experimental procedures, elemental analyses of **1** and **2**, and X-ray structural information on compound **1** (PDF) and X-ray crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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