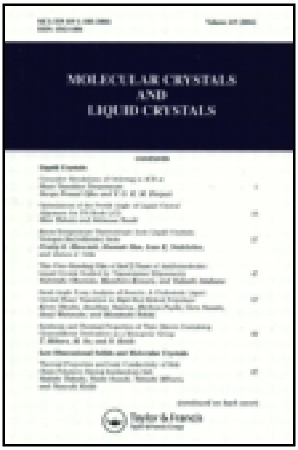

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Perfluoropentacene and Perfluorotetracene: Syntheses, Crystal Structures, and FET Characteristics

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Perfluoropentacene and Perfluorotetracene: Syntheses, Crystal Structures, and FET Characteristics

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The syntheses and FET characteristics of perfluoropentacene and perfluorotetracene are described. Both acenes are planar and crystalline materials that adopt π*-stack structures with the short interpalnar distances of 3.27 Å in perfluorotetracene and 3.21 Å in perfluoropentacene. The oxidation and reduction peak potentials of the perfluorinated acenes shift positively compared with those of the corresponding acenes, suggesting that the HOMO and LUMO energies are diminished by fluorine substituents. Organic field-effect transistors (OFETs) with perfluoropentacene exhibit n-type semiconducting properties with high electron mobility of 0.22* $cm^2/V\,s$.

Keywords: organic field-effect transistor; organic n-type semiconductors; perfluoropentacene; perfluorotetracene

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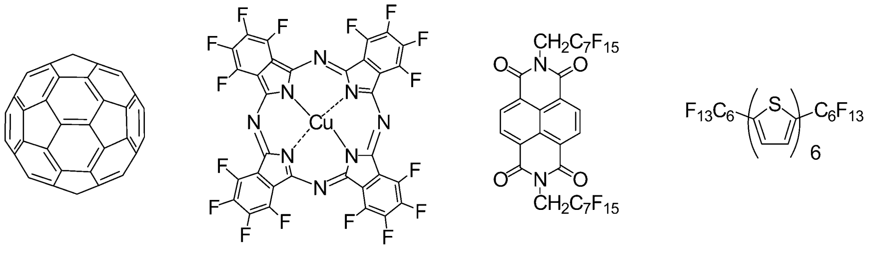
INTRODUCTION

Polycyclic aromatic hydrocarbons such as pentacene and tetracene have received considerable attentions because of the unique physical properties [1] and the potential applications to the active materials for organic field-effect transistors (OFETs). OFETs with pentacene exhibit p-type semiconducting properties with the highest hole mobility among the values reported so far (0.3–0.7 $cm^2/V\,s$ on SiO_2/Si substrates [2], 1.5 $cm^2/V\,s$ on chemically modified SiO_2/Si substrates [3], and 3 $cm^2/V\,s$ on polymer gate dielectrics [4]). In addition to acenes, π-conjugated oligomers such as oligothiophenes and their derivatives are known to be efficient p-type semiconductors [5]. Although organic n-type semiconductors with high electron mobilities are crucial for fabrication of bipolar transistors and complementary circuits, few n-type semiconductors have been developed to date. Some examples of n-type semiconductors are shown in Figure 1. OFETs with C_{60} [6], F16MPc [7], NTCDI [8], and DFH-6T [9] show n-type FET activities with electron mobility of 0.08, 0.03, 0.1, and 0.02 $cm^2/V\,s$, respectively.

We previously demonstrated that perfluorinated oligo (*p*-phenylene)s such as perfluoro-*p*-sexiphenyl function as n-type semiconductors for the electron-transport layer of organic light-emitting diodes [10]. However, OFETs with perfluoro-*p*-sexiphenyl show no FET activity. To develop efficient n-type semiconductors for OFETs, we have designed perfluorotetracene and perfluoropentacene [11] because they would have high electron affinity for the efficient electron injection from the electrodes and π-stack structures to achieve high charge carrier mobilities (Fig. 2). We report here the syntheses and properties of perfluorotetracene and perfluoropentacene as well as the applications of these acenes as the semiconductors in OFETs.



C_{60} **F16MPc** **NTCDI** **DFH-6T**

FIGURE 1 Organic n-type semiconductors for OFETs.

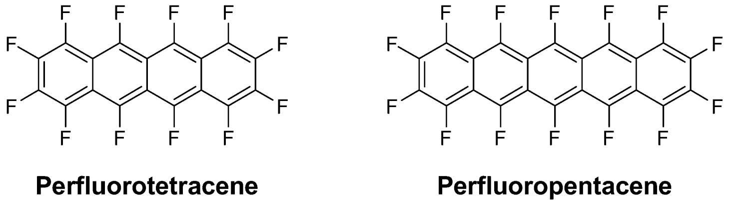


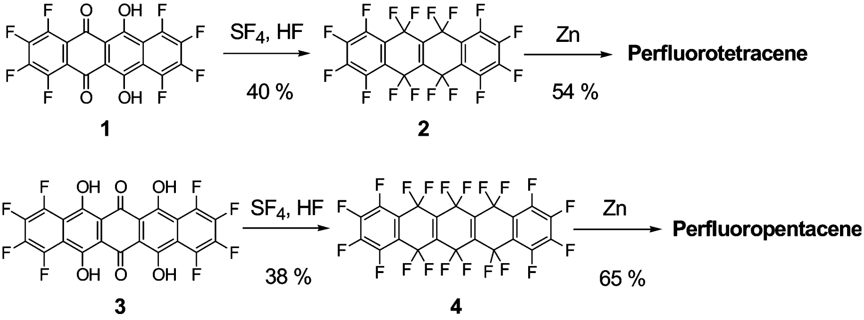
FIGURE 2 Chemical structures of perfluorotetracene and perfluoropentacene.

RESULTS AND DISCUSSION

Synthesis and Physical Properties

Although perfluoroanthracene was first prepared by fluorination of anthracene by cobaltic fluoride and subsequent defluorination of the resulting perfluoroperhydroanthracene in vapor phase over Ni turnings almost 40 years ago [12], higher perfluorinated acenes have not yet been reported because of the absence of convenient methods for their synthesis. Perfluorotetracene and perfluoropentacene have been prepared as shown in Scheme 1. Compounds **1** [13] and **3** [11] were fluorinated by SF_4 in the presence of HF [14] to afford perfluorotetrahydrotetracene **2** in 40% yield and perfluorohexahydropentacene **4** in 38% yield, respectively. Defluorinations of **3** and **4** by Zn in evacuated glass tubes [14] gave perfluorotetracene in 54% yield and perfluoropentacene in 65% yield, respectively. Both acenes are purified by train sublimation [15] and characterized by EI-MS and elemental analyses.

Single crystals of the perfluorinated acenes were grown by slow sublimation. The crystal structures of perfluorotetracene [16] and perfluoropentacene [17] exhibit the common feature of close cofacial packing. The minimum interplanar π–π distances in perfluorotetracene



SCHEME 1 Synthesis of perfluorotetracene and Perfluoropentacene.

(3.27 Å) and perfluoropentacene (3.21 Å) are shorter than the layer separation of graphite (3.35 Å) probably because of the electrostatic interaction between electropositive acene moieties and electronegative fluorine atoms.

Electrochemical measurements are conducted in 1,2-dichlorobenzene to examine the redox behaviors of the acenes. Differential plus voltammogram (DPV) of perfluorotetracene shows a reduction peak at –1.49 V and an oxidation peak at 1.02 V (versus the ferrocene/ferrocenium couple), which are more positive potentials than the values of tetracene (–2.13 and 1.02 V, respectively). The reduction (–1.13 V) and oxidation peaks (0.79 V) of perfluoropentacene also shift positively compared with those of pentacene (–1.87 and 0.22 V, respectively). These observations suggest the high electron affinity of the perfluorinated acenes relative to the unsubstituted ones.

To estimate frontier molecular orbitals (FMOs) energies of the acenes, the density functional theory (DFT) calculations (B3LYP) were performed using 6-31G (d) basis sets. Figure 3 depicts the FMOs energy calculated at a B3LYP/6-31G (d) level of theory for the acenes. As expected, the perfluorinated acenes have lower HOMO and LUMO energy levels relative to the corresponding acenes. The energy differences between HOMOs and LUMOs of the perfluorinated acenes are estimated to be 2.56 eV for perfluorotetracene and 2.02 eV for perfluoropentacene, which are smaller than those for the corresponding acenes.

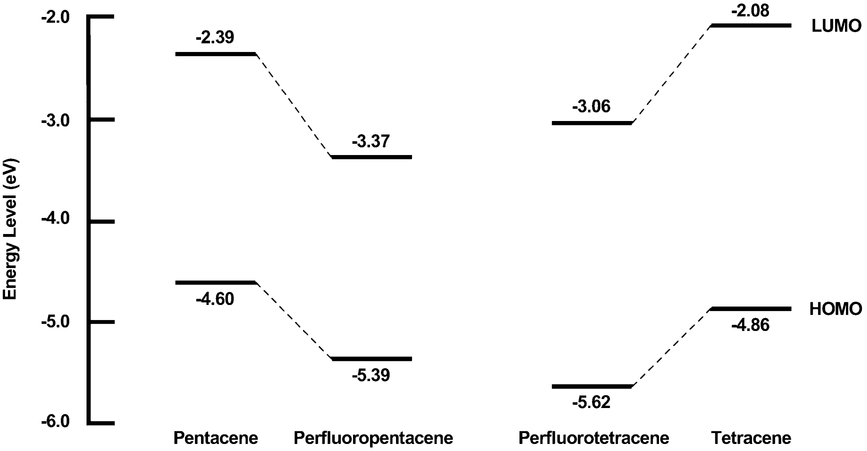


FIGURE 3 FMOs energy diagrams calculated at the B3LYP/6-31G (d) for tetracene, pentacene, perfluorotetracene, and perfluoropentacene.

FET Characteristics

The field-effect mobilities of the OFETs with perfluorotetracene and perfluoropentacene were determined by using top-contact geometries. Perfluorotetracene and perfluoropentacene were deposited on SiO_2 or SiO_2 treated with octadecyltrichlorosilane (OTS). Source and drain electrodes were formed on the organic layer through a shadow mask with a channel width (*W*) of 1000 μm and channel lengths (*L*) of 50 and 100 μm.

The field-effect mobilities were estimated in the saturated regime using Eq. (1)

$$I_D = (W/2L)\mu C_i(V_G - V_0)^2 \tag{1}$$

where I_D is the drain-source current in the saturation regime, *W* and *L* are the channel width and length, respectively, μ is the field-effect mobility, C_i is the capacitance per unit area of the insulating layer, and V_G and V_0 are the gate voltage and the threshold voltage.

Perfluorotetracene and perfluoropentacene operated as n-channel transistors in the accumulation mode. Figure 4 shows the current-voltage curves of a perfluorotetracene FET on an OTS-modified SiO_2/Si substrate at different gate voltages. The FET characteristics are unstable due to poor quality of the perfluorotetracene thin films,

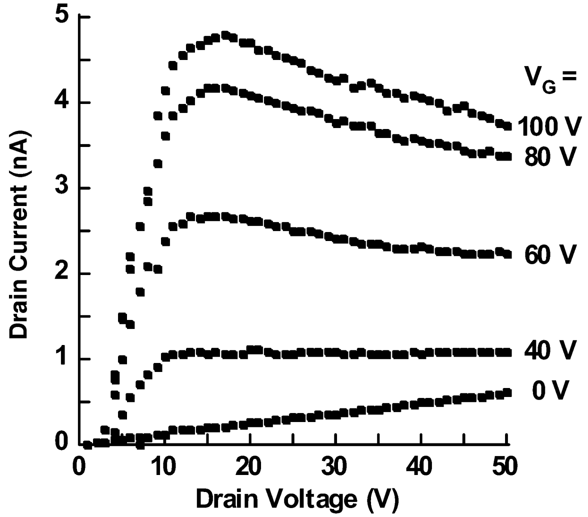


FIGURE 4 Drain current (I_D) versus drain voltage (V_D) characteristics of a perfluorotetracene FET on OTS-modified SiO_2 at different gate voltages.

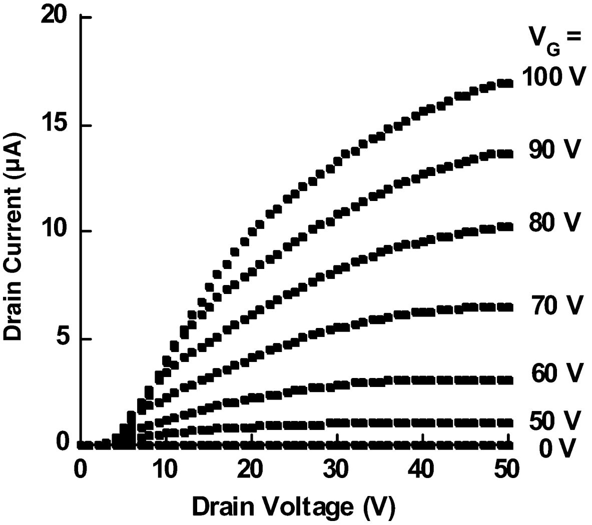


FIGURE 5 Drain current (I_D) versus drain voltage (V_D) characteristics of a perfluoropentacene FET on OTS-modified SiO_2 at different gate voltages.

resulting in the low electron mobility (0.00024 $cm^2/V\,s$). Further optimization of the fabrication conditions would improve the morphologies of the perfluorotetracene thin films and the perfluorotetracene FET performances. OFETs with perfluoropentacene exhibit better FET performances compared with those with perfluorotetracene (Fig. 5). Table 1 summarizes the electron mobilities for perfluoropentacene FETs fabricated under various conditions. The electron mobilities for the OFETs made on SiO_2 at different substrate temperatures range from 0.043 to 0.049 $cm^2/V\,s$. While the perfluoropentacene FET

TABLE 1 Electron Mobilities of Perfluoropentacene FETs Fabricated under Various Conditions

Substrate temp (°C)	Source and drain electrodes	Electron mobility ($cm^2/V\,s$)
25	Au	0.0488
25[a]	Au	0.0156
50	Au	0.0451
50[a]	Au	0.220
50	Au/Mg	0.0624
60	Au	0.0443

[a] OFETs were fabricated on OTS-modified SiO_2/Si substrates.

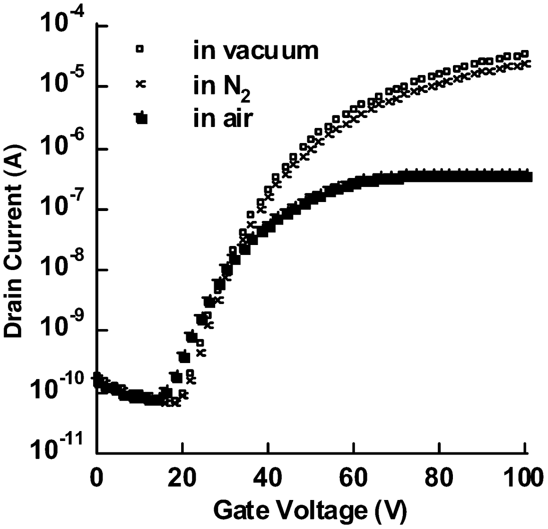


FIGURE 6 Drain current (I_D) versus gate voltage (V_G) characteristics of a perfluoropentacene FET on OTS-modified SiO_2 in air, nitrogen atmosphere, and vacuum.

performances are slightly dependent on the substrate temperatures, they are dramatically improved by the treatment of SiO_2 surface with OTS. A perfluoropentacene FET on OTS-modified SiO_2 exhibit the highest electron mobility of 0.22 cm^2/V s (at substrate temperature of 50°C) and the on/off ratio of 10^5. To test the stability of the perfluoropentacene FETs, the electrical measurements were carried out in air, nitrogen atmosphere, and vacuum. As shown in Figure 6, the FET performances are reduced in air presumably due to the carrier-trapping by oxygen and ambient humidity.

CONCLUSIONS

The perfluorinated acenes, perfluorotetracene and perfluoropentacene, have been prepared for the first time and the crystal structures, electrochemical properties, and electron mobilities of the acenes have been explored. Both acenes have the high electron affinity and the π-stack structures with the short interplanar distances. OFETs with perfluoropentacene exhibit the n-channel FET activities with the electron mobilities of ~0.22 cm^2/V s, which are comparable to the hole mobilities for the pentacene FETs. Combination of perfluoropentacene (n-channel) and pentacene (p-channel) offers bipolar OFETs and complementary circuits [11].

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[16] Crystal data for perfluorotetracene: monoclinic, space group $P21/c$, $a = 26.750(5)$ Å, $b = 4.5921(9)$ Å, $c = 11.482(2)$ Å, $\beta = 101.434(4)^\circ$, $V = 1382.5(5)$ Å^3, $T = 293$ K, $Z = 4$, $R = 0.034$, GOF $= 0.82$.

[17] Crystal data for perfluoropentacene: monoclinic, space group $P21/c$, $a = 15.51(1)$ Å, $b = 4.490(4)$ Å, $c = 11.449(11)$ Å, $\beta = 91.567(13)^\circ$, $V = 797.0(13)$ Å^3, $T = 173$ K, $Z = 2$, $R = 0.064$, GOF $= 1.02$.