Effects of Perfluoroalkyl Chain Lengths Introduced to Buckminsterfullerene Derivatives on Their Field-Effect Transistor Performances

Makoto Karakawa[1], Takabumi Nagai[2], Kenji Adachi[2], Yutaka Ie[1], and Yoshio Aso[1]

[1] The Institute of Scientific and Industrial Research, Osaka University,
Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan
Phone: +81-6-6879-8476 E-mail: karakawa@sanken.osaka-u.ac.jp
[2] Fundamental Technology Group, Chemical R&D Center, Daikin Industries, LTD,
1-1 Nishi Hitotsuya, Settsu-shi, Osaka, 566-8585, Japan

1. Introduction

Solution-processable *n*-type organic semiconductors have attracted great attention owing to their potentials for low cost and printable device applications, such as organic CMOS-like inverters and ring-oscillators.[1] C_{60} derivatives are one of the promising candidates for organic field-effect transistor (FET) application. The introduction of perfluoroalkyl substituents into C_{60} is an effective method to realize high-performance organic FET devices.[2] However, perfluoroalkyl chains longer than the number of carbon atoms of C_8 will not be able to use for any products in the world after 2015.[3] The world-major fluorochemical companies, Arkena, Asahi, BASF corporation, Clariant, Daikin, 3M/Dyneon, DuPont, and Solvay Solexis, have worked toward an elimination of the chemicals containing long perfluoroalkyl chains by 2015 according to a regulation. In the foreseeable future, we cannot thus use long perfluroalkyl-substituted materials, such as long perfluoroalkyl-substituents on C_{60} derivatives. Alternative materials to the current compounds will be required and should be developed as rapidly as possible.

Industrially available short perfluoroalkyl groups are one of alternative candidates for substituent groups to develop new solution-processable fullerene derivatives. We predict that oil- and water-shedding properties derived from perfluoroalkyl chain interactions are somewhat relieved in short perfluoroalkyl chains.

In this paper, we report on the new solution-processable fulleropyrrolidine derivatives with perfluoroalkyl group, exhibiting good *n*-type FET characteristics. We demonstrate an extensive investigation about the influence of the fluoroalkyl chain length affecting the thin-film transistor performances. The results clearly show the relationship between perfluoroalkyl chain length and FET properties.

2. Experimental

FET devices were constructed on a highly doped *n*-type silicon wafer covered with 300-nm-thick SiO_2 (having a capacitance per unit area of 10 nF/cm^2). The substrates were cleaned by using organic solvents in an ultrasonic bath and exposed to an UV−ozone ambient. They were treated with octadecyltrichlorosilane (OTDS) used to fabricate mono-layered hydrophobic surfaces according to the literature procedure.[4] The substrates were soaked in a toluene solution of ODTS for 1 h at room temperature and then

rinsed with toluene in an ultrasonic bath. To fabricate thin-films of fulleropyrrolidine derivatives, chloroform solutions containing 1.0 wt.% of fulleropyrrolidine derivatives were spin-coated on the substrate under the ambient atmosphere. The substrates were then transferred in a vacuum chamber to deposit gold source and drain electrodes. OFET characteristics were measured with several annealing temperatures using a Keithley 4200 semiconductor parameter analyzer. Field-effect mobilities for saturated regimes were determined using the following equation: $I_{DS} = (WC/2L)\mu(V_G-V_t)^2$, where μ is the field-effect mobility, W (35 mm) is the channel width, L (5 μm) is the channel length, C is the capacitance per unit area of the insulating layer, and V_G and V_t are the gate voltage and the extrapolated threshold voltage, respectively.

3. Result and discussion

New perfluoroalkylated fulleropyrrolidine derivatives shown in Figure 1 were synthesized according to our previously reported methods.[5] Perfluoroalkyl groups on the derivatives vary in length of C_4, C_6 and C_8. The *N*-1 position of pyrrolidine ring was substituted with dodecyl or methyl group. PC$_{61}$BM was used as a reference compound in this study.
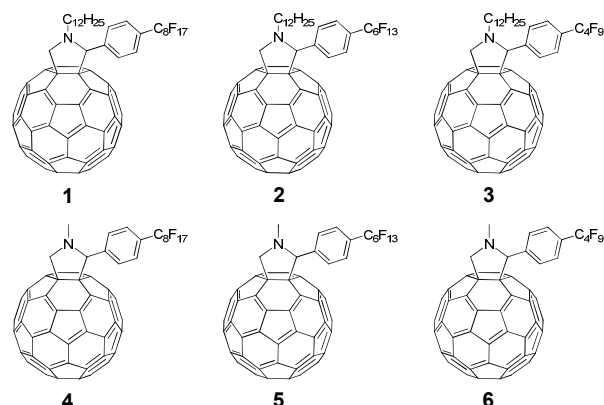

Fig. 1 Chemical structures of fulleropyrrolidine derivatives, **1-6**.

The UV−vis absorption spectra for fulleropyrrolidine derivatives, **1−6**, and PC$_{61}$BM in chloroform solutions are very similar in shape and in molar extinction coefficiency. The UV−vis spectra clearly show that the absorption prop-

erties of the fulleropyrrolidine derivatives are derived from the π-system of the fullerene. On the CV measurements, the fullerene derivatives underwent reversible redox processes and the CV curves were unchanged during successive multiple potential scans, indicating a high stability of the materials for electron injections.

The FETs based on the compounds showed excellent n-channel characteristics. The highest electron mobility among the fulleropyrrolidine derivatives was observed on the device of compound **5**, which have field-effect electron mobility (μ_e) about 0.03 cm^2/Vs with an on/off ratio of 10^{-6} and a threshold voltage of 13 V. Transfer characteristics of the FET based on the compound **5** are shown in Figure 2. The OFET parameters of the devices were summarized in Table 1. Crystal-like film morphology of compound **5** observed by AFM measurements contributes to the good mobility of the FET device. Whereas, although compounds **1**, **2**, and **3** also showed typical n-channel characteristics with good output and transfer characteristics, μ_es of the devices are relatively lower values than those of the compounds **4**, **5**, and **6**. This deterioration of the field-effect mobility in **1**, **2**, and **3** can be attributed to the bulkiness of the long alkyl (dodecyl) substituent at the N-1 position, which can suppress desirable ordering required for electron transporting π–π intermolecular overlaps between C$_{60}$ π-orbital in the films.
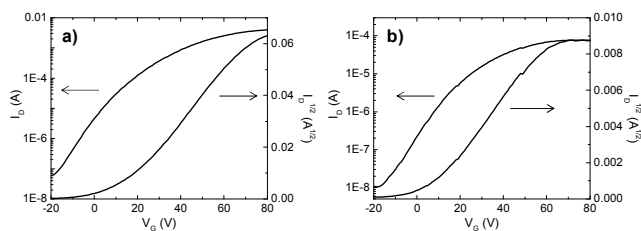

Figure 2 Transfer characteristics of a TFT based on fulleropyrrolidine derivative, **5**; a) in vacuum, b) in air.

The FET devices based on the compounds **1-6** exhibited n-channel characteristics after exposure to the air. In contrast, the PC$_{61}$BM-based device did not operate in identical conditions. The LUMO energy levels of the compounds **1-6** are between −3.69 and −3.63 eV as with PC$_{61}$BM. These results are indicative that the three different fluoroalkyl groups introduced C$_{60}$ frameworks have positive effect to acquire the air durability as a functional group for the fullerene. Thus, the perfluoroalkyl group as a substituent for fullerene framework is one of the strategies to bring an enhancement of tolerability to ambient conditions.

4. Conclusions

New fluoroalkylated fulleropyrrolidine derivatives were subjected to investigate their optical, electrochemical, and FET characteristics. The fulleropyrrolidine derivatives show very close absorption ranges and reduction potentials to those of PC$_{61}$BM, exhibiting the fundamental properties of the derivatives as same as those of PC$_{61}$BM. Regardless of the fundamental properties, it is worth noting that the FET devices based on the fluoroalkylated fullerenes have higher electron mobilities than that of PC$_{61}$BM and are able to operate in the air as n-channel transistors. These results show that the fluoroalkyl chain lengths have an effect to enhancing FET performances and to inducing the air durability by kinetic barriers. On the basis of the findings of this work, we can thus choose short perfluoroalkyl groups as an alternative substituent group to construct crystalline film structures for OFET devices and to lead the air durability of the buckminster fullerenes.

Table I   Field-Effect Transistor Characteristics Measured in a Vacuum and in the Air

Compound	Mobility (cm^2/Vs)		V_t (V)	
	in vac.	in air[a]	in vac.	in air[a]
1	0.008	3 x 10^{-5}	50	35
2	0.009	7 x 10^{-6}	42	19
3	0.007	7 x 10^{-5}	44	41
4	0.011	2 x 10^{-4}	30	23
5	0.030	8 x 10^{-4}	25	35
6	0.016	7 x 10^{-5}	48	40
PC$_{61}$BM	0.006	NA[b]	50	NA[b]

[a] After exposure to air for 1 h. [b] Not active.

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