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Communications

High-Performance n-Type Organic Thin-Film Transistors Based on Solution-Processable Perfluoroalkyl-Substituted C₆₀ Derivatives

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In recent years, organic thin-film transistors (TFTs) based on solution-processable organic semiconductors have been attracting interest concerning both fundamental research and practical application for low-cost, large-area, and flexible devices.¹⁻⁴ Development of high-performance p-type and n-type materials is crucial for realizing not only p-n junction devices such as organic light-emitting diodes and photovoltaic cells but also organic complementary metal-oxide-semiconductor (CMOS). However, variation of solution-processable n-type materials with high carrier mobility and stability is limited compared with that of p-type materials. Therefore, development of high performance n-type materials is important for further progress of organic electronic devices.⁵⁻¹⁸

In our previous study, we developed long-chain alkyl-substituted C₆₀ derivatives. C₆₀-fused *N*-methylpyrrolidine-*meta*-dodecyl phenyl, C60MC12 (**2**), forms highly ordered crystalline film by solution process and exhibits high electron mobility of 0.06–0.09 cm²/Vs,^{17,18} which is superior compared with a well-known solution-processable n-type material, [6,6]-phenyl C61-butyric acid methyl ester, PCBM (**1**), that tends to take an amorphous-like structure. However, these compounds do not exhibit TFT performance in air, because O₂ and H₂O diffuse into channel region and act as trap species of electron transport. To realize both high electron mobility and air stability, we have focused on long-chain perfluoroalkyl-substituted C₆₀ derivatives. Since perfluoroalkyl chains are known to act as an efficient gas barrier, TFTs

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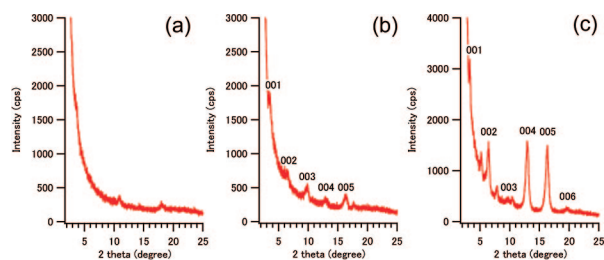


Figure 1. XRD patterns of spin-coated (a) C60MC8F17, (b) C60PC8F17, and (c) C60PC12F25 films.

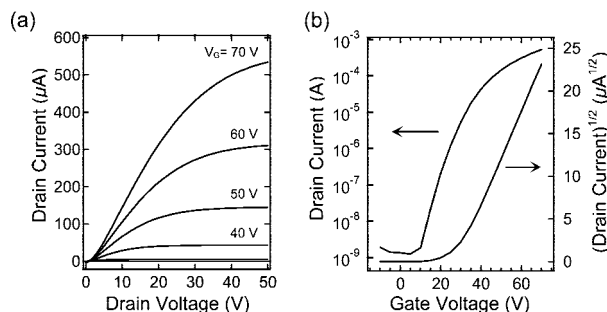
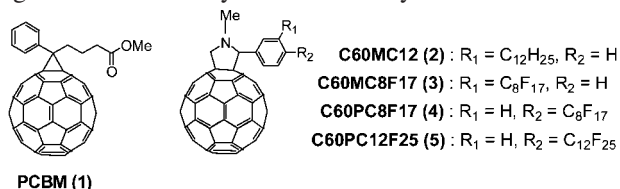


Figure 2. (a) Output and (b) transfer characteristics of a TFT based on C60PC12F25.

based on these compounds are expected to exhibit *n*-channel characteristics in air.

In this communication, we report new solution-processable perfluoroalkyl-substituted C₆₀ derivatives **3–5**, which exhibit high electron mobility and air stability.



New C₆₀ derivatives **3–5** were synthesized according to Scheme S1 (see the Supporting Information). The electronic state of the C₆₀ portion in **1–5** is almost the same, because each of the functional groups in **1–5** adds to a 6:6 ring juncture of C₆₀. Each film of **3–5** was fabricated on HMDS-treated SiO₂/p⁺-Si by spin coating from a chloroform solution under ambient condition. The microstructure of spin-coated films was investigated by X-ray diffraction (XRD) measurement (Figure 1). The spin-coated films of perfluoroalkyl substituted C₆₀ via the para position of phenyl group (C60PC8F17, C60PC12F25) exhibited high crystallinity compared to that via the meta position of phenyl group (C60MC8F17). The XRD patterns of C60PC8F17 and C60PC12F25 films showed 00*L* reflections up to higher-order, indicating formation of ordered structure. The spacings of the (001) planes of C60PC8F17 and C60PC12F25 films are calculated to be 2.57 and 2.70 nm, respectively. These results indicate that the film crystallinity strongly depends on both fluoroalkyl-chain orientation and length.

Figure 2 shows output and transfer characteristics of the TFT based on C60PC12F25 in a vacuum at room temperature. The device showed excellent *n*-channel characteristics. The field-effect electron mobility (μ_e) in saturation regime is calculated to be 0.25 cm²/Vs. The average μ_e of four devices is 0.23 cm²/Vs, which is one of the highest value

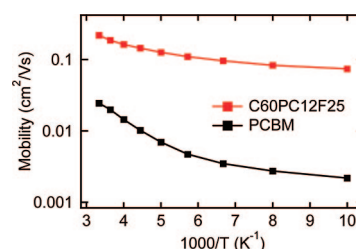


Figure 3. Temperature dependence of the field-effect mobility extracted from the characteristics of C60PC12F25- and PCBM-TFT in the saturation regime ($V_D = 50$ V).

Table 1. Field-Effect Electron Mobilities (μ), Threshold Voltage (V_T), and Current On/Off Ratios (I_{on}/I_{off}) for TFTs Measured in a Vacuum and Air

compound	vacuum			air ^a		
	μ (cm ² /Vs)	V_T (V)	I_{on}/I_{off}	μ (cm ² /Vs)	V_T (V)	I_{on}/I_{off}
C60MC8F17	0.024	21	5×10^4	4×10^{-4}	55	1×10^2
C60PC8F17	0.067	22	2×10^5	0.008	46	7×10^3
C60PC12F25	0.25	28	4×10^5	0.078	51	4×10^4
PCBM	0.025	33	2×10^4	NA ^b		
C60MC12	0.090	24	2×10^5	NA ^b		

^a After exposure to air for 5 h. ^b Not active.

among those of previously reported solution-processed *n*-type organic TFTs.^{10–14} C60MC8F17- and C60PC8F17-TFTs also exhibited typical *n*-channel characteristics (Figures S2 and S3 in the Supporting Information) and high mobilities of 0.024 and 0.067 cm²/(V s), respectively.

Figure 3 shows temperature dependence of field-effect electron mobility between 100 and 300 K in a vacuum. From the result of XRD measurement, the microstructure of the PCBM film is amorphous-like, whereas that of the C60PC12F25 film is crystalline. The mobilities of C60PC12F25- and PCBM-TFT decreased with decreasing temperature. The dependence of the mobility of the C60PC12F25-TFT is more moderate than that of the PCBM-TFT. The activation energy (E_a) of the C60PC12F25-TFT given by $\mu \propto \exp(-E_a/kT)$ is 27 meV in the range 225–275K, which is small compared with that of the PCBM-TFT (71 meV). Trap density (N_{trap}) can be estimated by $N_{trap} = C_i(V_T - V_{TO})/e$, where C_i is the capacitance per unit area of gate dielectric, V_T is the threshold voltage, V_{TO} is the turn-on voltage, e is the elementary charge.^{24,25} Estimated trap density of C60PC12F25 film (1.2×10^{12} cm⁻²) was comparable with that of PCBM film (1.3×10^{12} cm⁻²). However, the C60PC12F25 film shows higher μ_e and smaller E_a . The results indicate that C60PC12F25 molecules in the crystalline grain form stronger π - π interaction compared with PCBM molecules in the amorphous-like domain because of the improvement in structural order. The results also indicate that electron traps between grain boundaries in the C60PC12F25 film are very shallow.

After exposure to air, TFTs based on **3–5** exhibited *n*-channel characteristics (Figures S6–S8 in the Supporting Information), whereas the TFTs employing C₆₀ derivatives with a hydrocarbon chain (PCBM and C60MC12) did not operate (Figure S9). TFT performance of each device is summarized in Table 1. Electrochemical properties of the C₆₀ derivatives were investigated by cyclic voltammetry (see the Supporting Information). The lowest unoccupied molecular orbital (LUMO) levels of the C₆₀ derivatives were calculated by using the onset of the reduction peak

Table 2. Electrochemical Properties^a and the Corresponding LUMO Energies

compd	E_{red}^1 (V)	$E_{\text{red/onset}}$ (V)	LUMO (eV)
C60MC8F17 (3)	-0.61	-0.55	-3.63
C60PC8F17 (4)	-0.61	-0.55	-3.63
C60PC12F25 (5)	-0.61	-0.55	-3.63
PCBM (1)	-0.59	-0.52	-3.66
C60MC12 (2)	-0.63	-0.57	-3.61

^a V vs Ag/AgCl, 0.05 M *n*-Bu₄NPF₆ in ODCB.

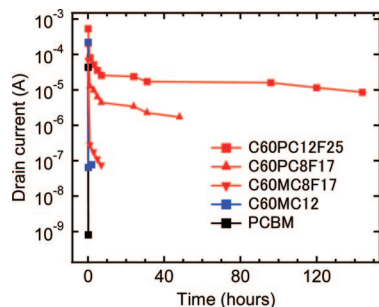


Figure 4. Time dependence of drain current of TFTs after exposure to air ($V_D = 50$ V, $V_G = 70$ V).

($E_{\text{red/onset}}$) according to the empirical equation,^{8,11,20} LUMO (eV) = $-[E_{\text{red/onset}} - E_{1/2}(\text{Fc}/\text{Fc}^+) + 4.8]$. The LUMO energies of the five different materials are almost the same with one another as shown in Table 2 (-3.61 eV to approximately -3.66 eV).

There are several reports concerning the correlation between electron affinity of n-type materials and air stability.^{19–21} Anthopoulos et al. reported that n-type materials with electron affinity <4 eV are unstable in air.¹⁹ However, in spite of the perfluoroalkyl-substituted C₆₀ derivatives (3–5) with low electron affinity (3.63 eV), the TFTs showed n-channel characteristics in air. These results indicate that air stability of C₆₀-based TFTs is attributed to introduction of a long-chain perfluoroalkyl group to C₆₀. Because fluorocarbon chains tend to be packed densely, diffusion of O₂ and H₂O into the channel region can be prevented, leading to improvement of air stability.^{5,21–23}

Figure 4 shows the time dependence of drain current of the TFTs after exposure to air. Difference in air stability of the

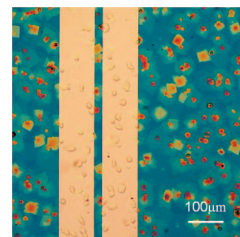


Figure 5. An optical microscopic image of a C60PC12F25 film. Two gold lines are source and drain electrodes.

TFTs was observed. The air stability is in the order of C60PC12F25 > C60PC8F17 > C60MC8F17, which agrees with the order of the film crystallinity. In particular, C60PC12F25-TFT exhibits high air stability and good n-channel characteristics even after exposure to air for 144 h. From the results of XRD and TFT measurement, it was found that fabrication of ordered crystalline film is important for realizing both high electron mobility and air stability of TFTs based on perfluoroalkyl-substituted C₆₀ derivatives.

However, in the case of perfluoroalkyl-substituted C₆₀ derivatives, a quick drop of the drain current was observed before reaching the steady state (Figure 4), which leads to V_T shifts to positive voltage and decrease of mobility in air (Table 1). These results can be explained by diffusion of O₂ and H₂O into the channel from amorphous regions or grain boundaries. An optical microscopic image of a C60PC12F25 film shows an inhomogeneous microstructure that has large crystalline domains from 10 to 30 μm dispersed in the film (Figure 5). By optimizing thin-film fabrication condition, further improvement of crystallinity and air-stability is expected.

In summary, we have demonstrated n-type organic TFTs based on solution-processable perfluoroalkyl-substituted C₆₀ derivatives. C60PC12F25-TFTs exhibit high electron mobility of 0.25 $\text{cm}^2/(\text{V s})$ and can operate in air. The mobility is one of the highest value among those of previously reported solution-processed n-type organic TFTs. We found that introduction of a long-chain perfluoroalkyl group to C₆₀ is effective for fabrication of stable and high performance n-type organic TFTs.

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Supporting Information Available: Experimental procedures and additional data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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