

## Surface-Segregated Monolayers: A New Type of Ordered Monolayer for Surface Modification of Organic Semiconductors

Qingshuo Wei,<sup>†</sup> Keisuke Tajima,<sup>\*,†</sup> Yujin Tong,<sup>‡</sup> Shen Ye,<sup>\*,‡,§</sup> and Kazuhito Hashimoto<sup>\*,†,||</sup>

*Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan, PRESTO, Japan Science and Technology Agency (JST), and HASHIMOTO Light Energy Conversion Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Japan*

Received July 10, 2009; E-mail: k-tajima@light.t.u-tokyo.ac.jp; ye@cat.hokudai.ac.jp; hashimoto@light.t.u-tokyo.ac.jp

**Abstract:** We report a new type of ordered monolayer for the surface modification of organic semiconductors. Fullerene derivatives with fluorocarbon chains ([6,6]-phenyl-C<sub>61</sub>-butyric acid 1H,1H-perfluoro-1-alkyl ester or FC<sub>n</sub>) spontaneously segregated as a monolayer on the surface of a [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) film during a spin-coating process from the mixture solutions, as confirmed by X-ray photoelectron spectroscopy (XPS). Ultraviolet photoelectron spectroscopy (UPS) showed the shift of ionization potentials (IPs) depending on the fluorocarbon chain length, indicating the formation of surface dipole moments. Surface-sensitive vibrational spectroscopy, sum frequency generation (SFG) revealed the ordered molecular orientations of the C<sub>60</sub> moiety in the surface FC<sub>n</sub> layers. The intensity of the SFG signals from FC<sub>n</sub> on the surface showed a clear odd–even effect when the length of the fluorocarbon chain was changed. This new concept of the surface-segregated monolayer provides a facile and versatile approach to modifying the surface of organic semiconductors and is applicable to various organic optoelectronic devices.

### Introduction

Well-ordered ultrathin films of organic molecules have been extensively studied due to their potential applications in various fields such as molecular electronics, nonlinear optical materials, and biological sensors.<sup>1</sup> To control the chemical and physical properties of materials such as metals, metal oxides, and inorganic semiconductors, Langmuir–Blodgett (LB) films and self-assembled monolayers (SAMs) are frequently used for their surface modifications.<sup>1–3</sup> However, the surface of organic semiconductors is difficult to modify using these methods due to the instability of the organic substrates in solution and the lack of specific interaction between the head groups of the modifying molecules and the organic semiconductor surfaces.<sup>4</sup> Since control of the surface and interfacial properties is of critical importance for the realization of high-performance all-organic electronic devices, the development of a novel and simple approach to the surface modification of organic semiconductors is strongly desired.

Recently, we have reported the formation process of a self-organized layer on organic semiconducting materials, which utilized the phenomenon of surface segregation.<sup>5,6</sup> A novel fullerene derivative with a fluorocarbon chain (phenyl-C<sub>61</sub>-butyric acid 1H,1H-perfluoro-1-octyl ester or FC<sub>7</sub> in Figure 1a) was designed and synthesized. When a small amount of FC<sub>7</sub> was mixed in a solution of another fullerene derivative, [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) (Figure 1b), and the solution was spin-coated on a substrate, FC<sub>7</sub> spontaneously migrated to the surface as a result of the low surface energy of the fluorocarbon and formed a very thin layer on the PCBM surface in a single step (Figure 1c). By using the FC<sub>7</sub> layers as buffer layers between the organic and metal layers, an improvement in the performance of organic solar cells was achieved. Interestingly, the FC<sub>7</sub> layer on the PCBM film induced a large shift in ionization potential (IP), suggesting the alignment of the molecular dipole moment at the surface. This observation raised the notion that the layer of FC<sub>7</sub> could have a well-oriented, ordered structure on the surface, despite the great ease of the procedure. Although the surface segregation has been well studied in the research field of polymer film structure and coating process,<sup>7–10</sup> there has been no report to control the surface

<sup>†</sup> The University of Tokyo.

<sup>‡</sup> Hokkaido University.

<sup>§</sup> PRESTO, Japan Science and Technology Agency.

<sup>||</sup> ERATO, Japan Science and Technology Agency.

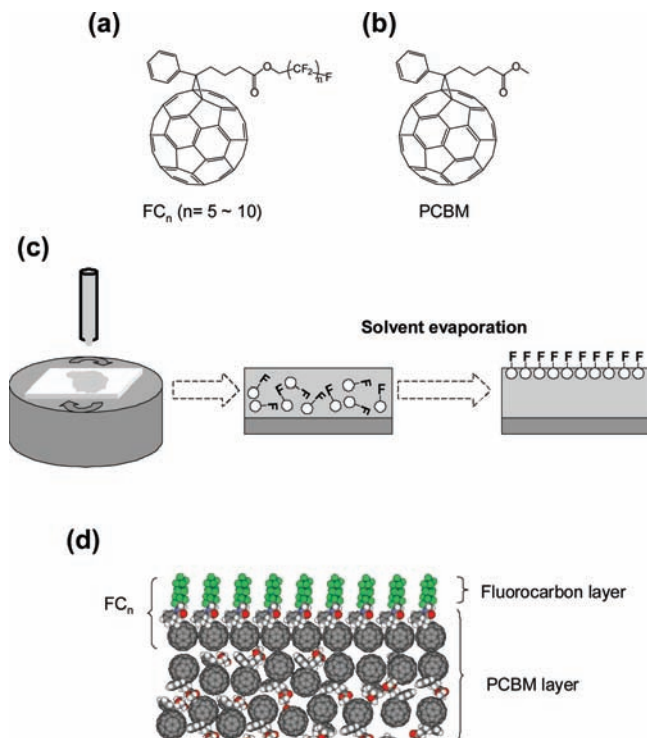
- (1) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic: New York, 1991.
- (2) Kuzmenko, I.; Rapaport, H.; Kjaer, K.; Als-Nielsen, J.; Weissbuch, I.; Lahav, M.; Leiserowitz, L. *Chem. Rev.* **2001**, *101*, 1659–1696.
- (3) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103–1169.
- (4) Calhoun, M. F.; Sanchez, J.; Olaya, D.; Gershenson, M. E.; Podzorov, V. *Nat. Mater.* **2008**, *7*, 84–89.

- (5) Wei, Q. S.; Nishizawa, T.; Tajima, K.; Hashimoto, K. *Adv. Mater.* **2008**, *20*, 2211–2216.

- (6) Yamakawa, S.; Tajima, K.; Hashimoto, K. *Org. Electron.* **2009**, *10*, 511–514.

- (7) Benrashed, R.; Nelson, G. L.; Linn, J. H.; Hanley, K. H.; Wade, W. R. *J. Appl. Polym. Sci.* **1993**, *49*, 523–537.

- (8) Chen, X.; Gardella, J. A. *Macromolecules* **1994**, *27*, 3363–3369.



**Figure 1.** (a) Chemical structure of  $FC_n$ , where  $n$  represents the number of fluorocarbons; (b) chemical structure of PCBM; (c) schematic representation of surface-segregated monolayer formation; (d) schematic representation of a model of PCBM film with a densely packed surface-segregated  $FC_n$  monolayer.

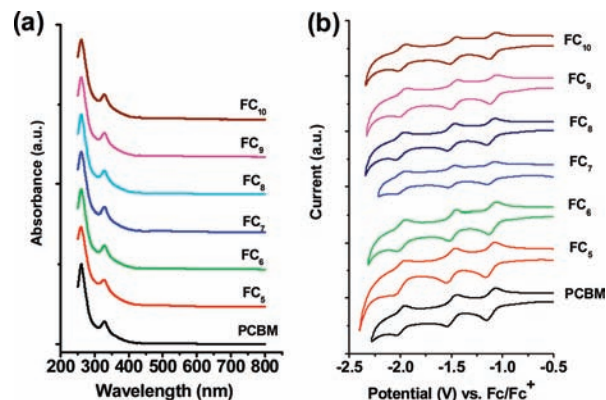
properties of the organic semiconductors such as ionization potential by utilizing this phenomenon.

In this study, we synthesized a series of fullerene derivatives with different lengths of fluorocarbon chains ( $FC_n$  in Figure 1a) and studied in detail the structure of the surface-segregated  $FC_n$  thin layer by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and sum frequency generation (SFG) vibrational spectroscopy. As a second-order nonlinear vibrational spectroscopy, SFG vibrational spectroscopy is now widely used to investigate the structure, symmetry, and ordering of molecules on various interfaces, given that such structural information is difficult to obtain by conventional infrared (IR) and Raman scattering methods.<sup>11–14</sup> This technique was successfully employed in this work to characterize the molecular structures on the surface of the  $FC_n$  thin film in combination with other measurements.

## Results and Discussion

**Electronic Properties of  $FC_n$  Molecules.**  $FC_n$  were synthesized by utilizing the synthetic protocol developed by Hummelen et

- (9) Affrossman, S.; Bertrand, P.; Hartshorne, M.; Kiff, T.; Leonard, D.; Petrick, R. A.; Richards, R. W. *Macromolecules* **1996**, *29*, 5432–5437.
- (10) Iyengar, D. R.; Perutz, S. M.; Dai, C. A.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1996**, *29*, 1229–1234.
- (11) Shen, Y. R. *The Principles of Nonlinear Optics*; John Wiley & Sons, Inc.: New York, 1984.
- (12) (a) Bain, C. D. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1281–1296. (b) Richmond, G. L. *Chem. Rev.* **2002**, *102*, 2693–2724. (c) Chen, Z.; Shen, Y. R.; Somorjai, G. A. *Annu. Rev. Phys. Chem.* **2002**, *53*, 437–465. (d) Holman, J.; Davies, P. B.; Nishida, T.; Ye, S.; Neivandt, D. J. *J. Phys. Chem. B* **2005**, *109*, 18723–18732. (e) Shen, Y. R.; Ostroverkhov, V. *Chem. Rev.* **2006**, *106*, 1140–1154. (f) Ye, S.; Osawa, M. *Chem. Lett.* **2009**, *38*, 386–391.

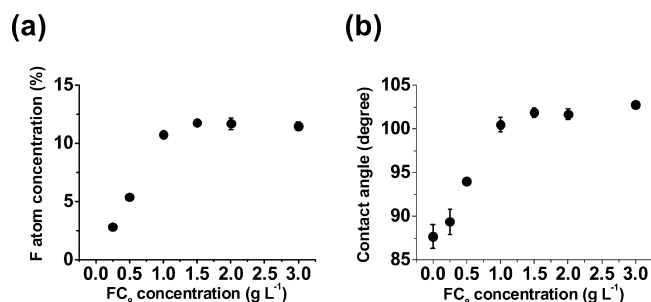


**Figure 2.** (a) UV-vis absorption spectra of PCBM and  $FC_n$  in  $CHCl_3$ ; concentration is  $1.6 \times 10^{-5}$  mol  $L^{-1}$ ; (b) cyclic voltammograms of PCBM and  $FC_n$ . Anhydrous dichloromethane was used as an electrolyte, containing 0.1 M tetrabutylammonium perchlorate and approximately  $1.0 \times 10^{-3}$  mol  $L^{-1}$   $FC_n$  or PCBM. The scan rate is 50 mV/s.

al.<sup>15</sup> Molecular electronic properties of the fullerene derivatives  $FC_n$  ( $n = 5-10$ ) in solution were investigated by UV-vis absorption spectroscopy and cyclic voltammetry. As shown in Figure 2a,  $FC_n$  ( $n = 5-10$ ) and PCBM had identical UV-vis absorption profiles in chloroform ( $CHCl_3$ ) with the absorption maxima of 260 and 330 nm attributed to the fullerene absorption. Cyclic voltammograms of  $FC_n$  (Figure 2b) and PCBM in dichloromethane ( $CH_2Cl_2$ ) were also identical with three reversible reduction peaks with half potentials at  $-1.1$ ,  $-1.5$ , and  $-2.0$  V (vs  $Fc/Fc^+$ ) corresponding to the one-, two-, three-electron reduction of the fullerene moieties, respectively.<sup>15</sup> These results indicate that the fluorocarbon moieties have little effect on the electronic properties of the methanofullerenes. This could be rationalized by the fact that the electron withdrawing fluorocarbon chains were attached via an ester group and therefore electronically isolated from the fullerene. Since the molecular electronic properties of the fullerene groups are the same, differences in the surface properties and spectra of  $FC_n$  and PCBM can be compared in the following sections.

**Surface Segregation in  $FC_n$ /PCBM Films.** In the spin-coated films from the mixture of  $FC_n$  and PCBM,  $FC_n$  molecules are expected to segregate to the film surface during spin-coating due to their lower surface energy.<sup>10</sup> To elucidate the surface segregation behavior of  $FC_n$ , the mixing ratio was changed in the  $FC_8$ /PCBM blend solution and the atomic concentration of F at the film surface was monitored by XPS. Films were

- (13) (a) Liu, J.; Conboy, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 8376–8377. (b) Chen, X.; Tang, H.; Even, M. A.; Wang, J.; Tew, G. N.; Chen, Z. *J. Am. Chem. Soc.* **2006**, *128*, 2711–2714. (c) Roke, S.; Roeterdink, W.; Wijnhoven, J.; Petukhov, A.; Kleyn, A.; Bonn, M. *Phys. Rev. Lett.* **2003**, *91*, 258302. (d) Tyrode, E.; Rutland, M. W.; Bain, C. D. *J. Am. Chem. Soc.* **2008**, *130*, 17434–17445. (e) Ma, G.; Allen, H. C. *Photochem. Photobiol.* **2006**, *82*, 1517–1529. (f) Stokes, G. Y.; Buchbinder, A. M.; Gibbs-Davis, J. M.; Scheidt, K. A.; Geiger, F. M. *J. Phys. Chem. A* **2008**, *112*, 11688–11698.
- (14) (a) Nishida, T.; Johnson, M.; Holman, J.; Osawa, M.; Davies, P. B.; Ye, S. *Phys. Rev. Lett.* **2006**, *96*, 77402. (b) Ye, S.; Noda, H.; Morita, S.; Uosaki, K.; Osawa, M. *Langmuir* **2003**, *19*, 2238–2242. (c) Ye, S.; Noda, H.; Nishida, T.; Morita, S.; Osawa, M. *Langmuir* **2004**, *20*, 357–365. (d) Li, G.; Morita, S.; Ye, S.; Tanaka, M.; Osawa, M. *Anal. Chem.* **2004**, *76*, 788–795. (e) Ye, S.; Morita, S.; Li, G.; Noda, H.; Tanaka, M.; Uosaki, K.; Osawa, M. *Macromolecules* **2003**, *36*, 5694–5703.
- (15) Hummelen, J. C.; Knight, B. W.; Lepeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532–538.



**Figure 3.** (a) F atom concentrations and (b) water contact angles on the surfaces of FC<sub>8</sub>/PCBM thin films plotted as a function of FC<sub>8</sub> concentrations in the spin-coating solutions.

prepared on ITO substrates by spin-coating chlorobenzene solutions of FC<sub>8</sub>/PCBM blends with various concentrations of FC<sub>8</sub> from 0 to 3 g L<sup>-1</sup> ( $2.3 \times 10^{-3}$  mol L<sup>-1</sup>), while the concentration of PCBM was fixed to 40 g L<sup>-1</sup> (0.044 mol L<sup>-1</sup>). F atom concentrations on the surface are plotted in Figure 3a as a function of the FC<sub>8</sub> concentrations in the solution. As the FC<sub>8</sub> concentration in the solution increased, the F atom concentration on the surface first linearly increased but clearly saturated at around 1 g L<sup>-1</sup> ( $8 \times 10^{-4}$  mol L<sup>-1</sup>). This result suggests that, when the amount of FC<sub>8</sub> in the solution is smaller than the saturation point, all the FC<sub>8</sub> molecules in the solution segregate to the surface to partly cover the film surface. With higher concentrations of FC<sub>8</sub> than the saturation point, the surface of the films is completely covered by the FC<sub>8</sub> molecules. In fact, XPS depth profiles of the films (see below) showed the absence of F atoms in the bulk below the saturated concentration, while F 1s peaks with a constant intensity were observed even in the bulk above the saturated concentration. This simple picture of the segregation behavior was also confirmed by the water contact angles of the film surface (Figure 3b). Increase of the contact angles at the low FC<sub>8</sub> concentration and clear saturation behavior at the FC<sub>8</sub> concentration of around 1 g L<sup>-1</sup> were observed, which coincides well with the surface concentration of F atoms in Figure 3a. The contact angle at the saturated region (102°) is close to the typical values of fluorocarbon SAMs on flat substrates (105–125°)<sup>16</sup> and larger than that of fullerene-based SAMs (70–90°).<sup>17–19</sup> This suggests dense coverage of the surface with the FC<sub>8</sub> molecules at the saturation point.<sup>20</sup>

**XPS Depth Profiles.** To further confirm the surface segregation of FC<sub>n</sub> molecules, depth profiles of the atomic components was evaluated by XPS and Ar<sup>+</sup> plasma etching. The FC<sub>n</sub>/PCBM films are prepared by spin-coating the blended solutions at the saturated concentration ( $8 \times 10^{-4}$  mol L<sup>-1</sup>) on glass substrates. From the atomic force microscopy (AFM) height images (Figure S3 of the Supporting Information), all the surfaces were found to be very flat with a mean roughness less than 2 nm. As shown in Figure 4, F 1s peaks were observed in the XPS spectra from

the surfaces of all FC<sub>n</sub>/PCBM films at 690 eV. After 5 s of Ar<sup>+</sup> etching on the surfaces (corresponding to an etching depth of approximately 2 nm), the F 1s peaks completely disappeared. Etching was carried out until the entire organic layer was removed, but no F 1s peaks were detected except at the surface. On the basis of the XPS results given above, it was concluded that the fluorocarbon chains of FC<sub>n</sub> were present to a depth of less than 2 nm from the surface.

**Surface Density of FC<sub>n</sub> Molecules.** To quantitatively investigate the surface coverage of FC<sub>n</sub> on PCBM films, we constructed a model with a densely packed FC<sub>n</sub> layer on a PCBM film, as shown in Figure 1d. In this model, the molecular conformation was optimized by density functional theory (DFT) calculations with extended fluorocarbon chains (Figure 5a). The center-to-center distance of the fullerene groups of FC<sub>n</sub> in the monolayer was assumed to be 0.985–1.013 nm by using the shortest distance between neighboring fullerenes in PCBM single crystals previously reported.<sup>21</sup> The packing density of FC<sub>n</sub> was estimated to be  $1.6\text{--}1.7 \times 10^{-10}$  mol cm<sup>-2</sup> in the model. These values are comparable to those of the fullerene-based SAMs on Au surfaces previously reported ( $1.0\text{--}1.8 \times 10^{-10}$  mol cm<sup>-2</sup>)<sup>19</sup> but lower than fluorocarbon-based SAMs on a Au surface ( $5.0 \times 10^{-10}$  mol cm<sup>-2</sup>).<sup>16</sup> A comparison of the F/C atom ratios observed by XPS measurement and calculated from this model could provide an estimation of the packing density of FC<sub>n</sub>. The fluorine to carbon atomic ratio from the surface can be calculated as

$$\text{F/C ratio} = \frac{L \times X_F}{(\lambda - L) \times X_C} \quad (1)$$

where  $\lambda$  is the attenuation length of photoelectrons that was assumed to be 2.5 nm based on the previous report by Lee et al.,<sup>22,23</sup>  $L$  is the length of the fluorocarbon layer, and  $X_F/X_C$  is the density ratio of fluorine to carbon. Since most photoelectrons originate from the first one or two layers of molecules at the surface,  $X_F/X_C$  was calculated from molar fractions of fluorine and nonfluorinated carbon in FC<sub>7</sub> molecules. The density ratio of fluorine to carbon was

$$\frac{X_F}{X_C} = \frac{15/0.89}{72/1.26} = 0.295 \quad (2)$$

As summarized in Table 1, the observed F/C atom ratios agree well with the calculated values for all the FC<sub>n</sub> molecules. Although some approximations are involved in the calculation, this result indicates that FC<sub>n</sub> molecules packed densely on the surface to cover the whole surface of the PCBM layer.

**Angle-Dependent XPS.** Angle-dependent XPS (ADXPS) was performed on the films to quantitatively determine the thickness of the segregated fluorinated carbon layer, following the technique previously reported for SAMs, LB films, and spin-coated polymer thin films.<sup>24–28</sup> The F 1s peak of fluorocarbons

(16) Colorado, R.; Lee, T. R. *Langmuir* **2003**, *19*, 3288–3296.

(17) Lee, S. W.; Shon, Y. S.; Lee, T. R.; Perry, S. S. *Thin Solid Films* **2000**, *358*, 152–158.

(18) Sahoo, R. R.; Patnaik, A. J. *Colloid Interface Sci.* **2003**, *268*, 43–49.

(19) Bonifazi, D.; Enger, O.; Diederich, F. *Chem. Soc. Rev.* **2007**, *36*, 390–414.

(20) The molar ratio between FC<sub>n</sub> and PCBM in the total film can be calculated based on the model in Figure 1d. By using the packing density of FC<sub>n</sub> on the surface ( $1.6\text{--}1.7 \times 10^{-10}$  mol cm<sup>-2</sup>, see below) and the film thickness (100 nm), the molar ratio between FC<sub>n</sub> and PCBM was estimated as approximately 0.02 in the film. This value is close to the molar ratio in the blended solution (0.018).

(21) Rispens, M. T.; Meetsma, A.; Rittberger, R.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Chem. Commun.* **2003**, 2116–2118.

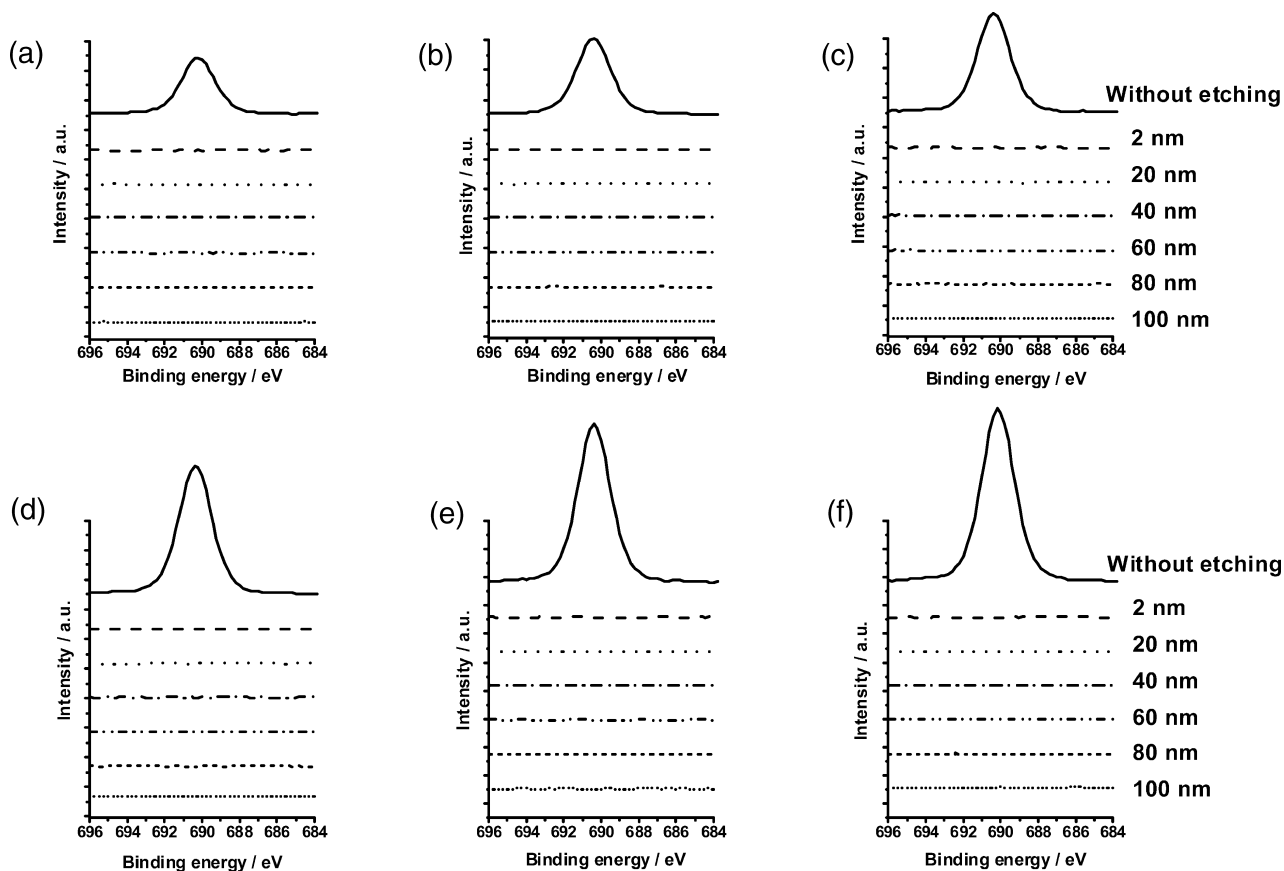
(22) Colorado, R.; Lee, T. R. *J. Phys. Chem. B* **2003**, *107*, 10216–10220.

(23) Mg K $\alpha$  radiation was used in this measurement, and the KE of C 1s was 968.6 eV.

(24) Fadley, C. S. *Prog. Surf. Sci.* **1984**, *16*, 275–388.

(25) Ton-That, C.; Shard, A. G.; Bradley, R. H. *Langmuir* **2000**, *16*, 2281–2284.

(26) Gerenser, L. J.; Pochan, J. M.; Mason, M. G.; Elman, J. F. *Langmuir* **1985**, *1*, 305–312.



**Figure 4.** XPS spectra of  $FC_n/PCBM$  films in F 1s region without etching, after etching for 2, 20, 40, 60, 80, and 100 nm. (a)  $FC_5/PCBM$ ; (b)  $FC_6/PCBM$ ; (c)  $FC_7/PCBM$ ; (d)  $FC_8/PCBM$ ; (e)  $FC_9/PCBM$ ; (f)  $FC_{10}/PCBM$ . The total film thickness was approximately 100 nm, as determined by profilometry.

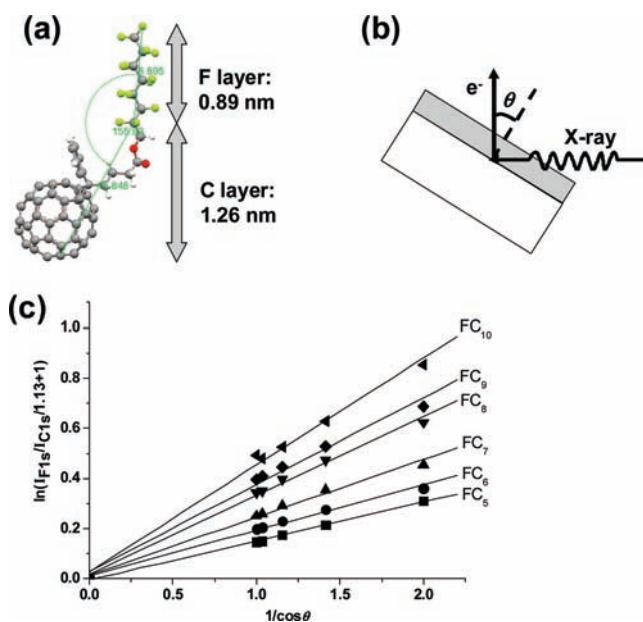
(690 eV) and the C 1s peak of nonfluorinated carbons (285 eV) were used for the measurement so that there was no contribution of the elements from one layer to the other. According to previous reports,<sup>24–28</sup>

$$\ln\left(\frac{I_{F1s}}{I_{C1s}} \frac{1}{K} + 1\right) = \frac{d}{\lambda} \sec \theta \quad (3)$$

where  $I_{F1s}$  and  $I_{C1s}$  are the XPS signal intensities of F 1s and C 1s, respectively,  $K$  is a constant determined by the relative sensitivity factor (RSF) for XPS and the atom density ratio of F to C,  $\lambda$  is the attenuation length of photoelectrons,  $\theta$  is the takeoff angle of the measurement (Figure 5b), and  $d$  is the film thickness.  $K$  was calculated from the RSF ratio and the density ratio of fluorine to carbon. The RSF ratio, which was obtained by XPS measurements, was 3.82. Thus,

$$K = \frac{F_{RSF} X_F}{C_{RSF} X_C} = 3.82 \times 0.295 = 1.13 \quad (4)$$

A plot of  $\ln((I_{F1s}/I_{C1s})/(1/(K) + 1))$  as a function of  $\sec \theta$  is expected to produce a straight line through the origin if the assumed model is valid. The slope of this line is equal to the thickness of the film in units of attenuation length. As shown



**Figure 5.** (a) Calculated optimized structure of  $FC_7$  molecule; (b) general geometry for angle-dependence XPS measurement; (c) plot of  $\ln(I_{F1s}/I_{C1s}/1.13 + 1)$  vs  $1/\cos \theta$  for a  $FC_n/PCBM$  film.

- (27) Evans, S. D.; Goppert-Berarducci, K. E.; Urankar, E.; Gerenser, L. J.; Ulman, A.; Snyder, R. G. *Langmuir* **1991**, *7*, 2700–2709.  
 (28) Solletti, J. M.; Botreau, M.; Sommer, F.; Brunat, W. L.; Kasas, S.; Duc, T. M.; Celio, M. R. *Langmuir* **1996**, *12*, 5379–5386.

in Figure 5c, good correlation was achieved by fitting a straight line for all the  $FC_n/PCBM$  films, which indicates the validity of the model. The slopes of these lines increase from  $FC_5$  to

**Table 1.** Experimental and Calculated Data for FC<sub>n</sub>/PCBM Films

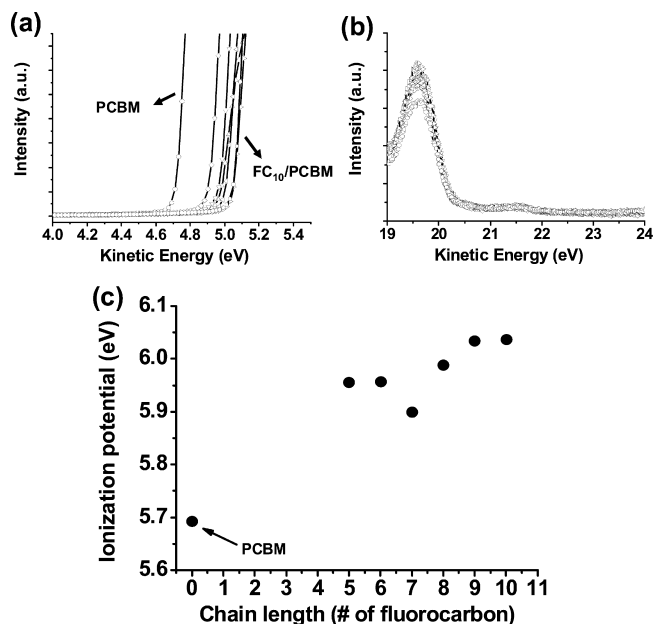
composition	calculated F/C atom ratio <sup>a</sup>	measured F/C atom ratio (by XPS) <sup>a</sup>	estimated length of fluorinated carbon chain (nm) <sup>b</sup>	film thickness (by ADXPS) (nm)	ionization potential (eV)
PCBM	-	-	-	-	5.69
FC <sub>5</sub> /PCBM	0.10	0.08	0.63	0.38	5.95
FC <sub>6</sub> /PCBM	0.13	0.11	0.75	0.48	5.96
FC <sub>7</sub> /PCBM	0.16	0.15	0.88	0.60	5.90
FC <sub>8</sub> /PCBM	0.20	0.20	1.00	0.82	5.99
FC <sub>9</sub> /PCBM	0.24	0.25	1.13	0.92	6.03
FC <sub>10</sub> /PCBM	0.30	0.27	1.25	1.11	6.04

<sup>a</sup> Fluorinated carbons were not considered here because fluorinated carbon has a binding energy different from nonfluorinated carbon.

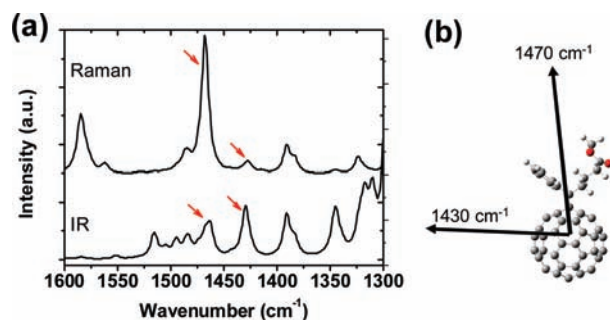
<sup>b</sup> Molecular length was estimated with the Cambridge Scientific Chem 3D software.

FC<sub>10</sub>, which suggests an increase in the thickness of the fluorocarbon layer with increasing fluorocarbon chain length. The thickness of the fluorocarbon layer was calculated by using equation  $d = \lambda\tau$ , where  $\tau$  was the slope. As shown in Table 1 and Figure S4 of the Supporting Information, the thickness of the fluorocarbon layer determined by ADXPS increases with increasing fluorocarbon chain length. This result indicates that FC<sub>n</sub> molecules formed densely packed monolayers on the surface of PCBM with the fluorocarbon chains pointing in the direction of the air. The thickness is less than that calculated from the molecular models based on the assumption of the extended conformation and orientation of fluorocarbons being completely perpendicular to the surface (Figure 1d). This suggests the tilting of fluorocarbons or the formation of a helical structure of fluorocarbon in the monolayer.<sup>29,30</sup> We could also see a slight deviation from the linear relationship in Figure S4 of the Supporting Information when the fluorocarbon chains get longer. This might be attributed to the change in the tilting angle or the conformations of the fluorocarbon chains due to the change of the interchain interactions on the surface.

**UPS Measurements.** XPS depth profiles and angle-dependent XPS clearly show that FC<sub>n</sub> molecules spontaneously migrate to the surface of PCBM during spin-coating and form a monolayer in a single step. In these structures, the perfluoroalkyl chains could form interfacial dipole moments that shift the vacuum level of the solid state. To confirm the formation of this dipole layer, UPS measurements were carried out on PCBM and FC<sub>n</sub>/PCBM films. Figure 6a and b show the UPS data for PCBM and FC<sub>n</sub>/PCBM films at the cutoff and Fermi edge regions, respectively, using the He (I) irradiation. As the fluorocarbon chain length increases, the cutoff of the photoemission spectra continuously shifts to higher kinetic energy. By using the spectrum width determined from the distance between the cutoff to the Fermi edge, the ionization potential (IP) of the films can be extracted.<sup>31</sup> As summarized in Figure 6c and Table 1, the IP of PCBM film was determined to be 5.69 eV. When a monolayer of FC<sub>n</sub> was introduced on the surface of the PCBM films, the IP shifted to 5.90–6.04 eV. This IP shift was also observed previously for the FC<sub>7</sub>/PCBM film by using photoelectron yield spectroscopy.<sup>5</sup> Since the same reduction potential of FC<sub>n</sub> and PCBM was observed by CV,



**Figure 6.** UPS data for PCBM and FC<sub>n</sub>/PCBM films at (a) cutoff and (b) Fermi edge regions using He (I) irradiation. (c) Ionization potentials plotted as the function of the number of fluorocarbons in FC<sub>n</sub>.



**Figure 7.** (a) Calculated Raman and IR spectra of PCBM; red arrows indicate the peaks at 1470 cm<sup>-1</sup> and 1430 cm<sup>-1</sup>, respectively. (b) Optimized structure of PCBM by DFT calculation. Arrows represent the dipole derivative vectors of the vibration modes at 1470 cm<sup>-1</sup> (A<sub>g</sub>(2) mode) and 1430 cm<sup>-1</sup> (F<sub>1u</sub>(4) mode), respectively.

the increase in IP can be attributed to a dipole layer induced by the molecular alignment of FC<sub>n</sub> at the film surface. From the direction of the IP shift, we conclude that the perfluoroalkyl chain points toward the direction of air to increase the ionization potential of the films.

**SFG Measurements.** As a second-order nonlinear vibration spectroscopy, SFG is sensitive to the molecular structure on the surface of materials.<sup>11</sup> Since the intensity of the SFG signal from a vibration mode is proportional to the product of its Raman polarizability tensor and IR dipole moment,<sup>11</sup> we first calculated IR and Raman spectra for PCBM and FC<sub>n</sub> obtained by using the density functional theory (DFT). The calculations were carried out at the B3LYP/6-31G\* level following the previous report by Schettino et al.<sup>32</sup> The same scaling factor (0.98) for frequency as that in the paper was also used in our calculation.

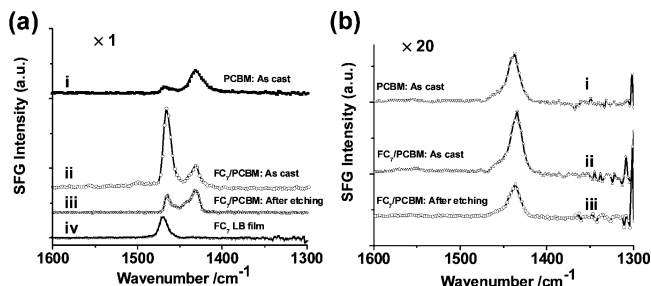
Figure 7a shows calculated IR and Raman spectra of PCBM. Reasonable agreements have been reached between the calcu-

(29) Genzer, J.; Kramer, E. J.; Fischer, D. A. *J. Appl. Phys.* **2002**, *92*, 7070–7079.

(30) Ji, N.; Ostroverkhov, V.; Lagugne-Labarthe, F.; Shen, Y. R. *J. Am. Chem. Soc.* **2003**, *125*, 14218–14219.

(31) Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. *Adv. Mater.* **1999**, *11*, 605–625.

(32) Schettino, V.; Pagliai, M.; Ciabini, L.; Cardini, G. *J. Phys. Chem. A* **2001**, *105*, 11192–11196.



**Figure 8.** (a) SFG spectra (*ssp*) of PCBM films, as-cast FC<sub>7</sub>/PCBM films, FC<sub>7</sub>/PCBM films after plasma etching, and FC<sub>7</sub> LB films. (b) SFG spectra (*sps*) of PCBM films, as-cast FC<sub>7</sub>/PCBM films, and FC<sub>7</sub>/PCBM films after plasma etching.

lated and experimentally observed IR and Raman spectra for PCBM (Figure S5 of the Supporting Information) and FC<sub>7</sub> (Figure S6 of the Supporting Information). Two vibration modes for the C<sub>60</sub> moiety in PCBM at 1470 and 1430 cm<sup>-1</sup> with different intensities can be found in both calculated Raman and IR spectra (indicated by red arrows in Figure 7a). The peak at 1470 cm<sup>-1</sup> can be assigned to the A<sub>g</sub>(2) mode of the C<sub>60</sub> moiety, which is a symmetry-forbidden vibration in C<sub>60</sub> but becomes active due to symmetry breaking in PCBM. This mode has also been observed in several C<sub>60</sub> derivatives with substitutions.<sup>33,34</sup> The peak at 1430 cm<sup>-1</sup> is attributed to an IR-active F<sub>1u</sub>(4) mode of C<sub>60</sub>,<sup>33–36</sup> which has often been reported in the IR spectra of C<sub>60</sub> compounds. A similar peak has also been observed in the SFG spectra of a C<sub>60</sub> monolayer adsorbed on a Ag(111) surface.<sup>37,38</sup> As indicated by the arrows in Figure 7b, the dipole moment of the A<sub>g</sub>(2) mode is pointing from the center of C<sub>60</sub> to the functionalized position of methanofullerene. On the other hand, the dipole direction of the F<sub>1u</sub>(4) mode is almost perpendicular to that of the A<sub>g</sub>(2) mode (see also the animations in the Supporting Information).

The DFT calculations showed that IR and Raman peaks for the C<sub>60</sub> moiety in FC<sub>n</sub> have quite similar peak positions and intensity to those of PCBM (see Table S1 of the Supporting Information). This insensitivity of the vibration properties to the substitution can be explained by the weak electronic coupling between C<sub>60</sub> and ester moieties in the molecules, which coincides with the identical electronic properties of the C<sub>60</sub> moiety observed by UV–vis absorption and the electrochemical measurements described in the previous section.

On the basis of the spectral information of IR and Raman spectra, we are able to understand and discuss our SFG observations on PCBM and FC<sub>7</sub>/PCBM thin films. Figure 8a-i shows a SFG spectrum for a spin-coated PCBM film (20 nm thick for all the following samples unless otherwise stated) obtained in the IR frequency region between 1300 cm<sup>-1</sup> and 1600 cm<sup>-1</sup>. The spectrum was collected with an *ssp* polarization combination (i.e., *s*-SFG, *s*-visible, *p*-IR), which is sensitive to

vibrational modes with IR dipole moments that contain a component perpendicular to the surface. Two peaks were clearly observed at 1470 and 1430 cm<sup>-1</sup>, which can be attributed to the A<sub>g</sub>(2) and F<sub>1u</sub>(4) vibration modes of C<sub>60</sub> moiety in PCBM, respectively, as expected from the DFT calculations. The peak intensity at 1430 cm<sup>-1</sup> is higher than that at 1470 cm<sup>-1</sup>.

Figure 8a-ii shows the *ssp*-polarized SFG spectrum of FC<sub>7</sub>/PCBM film. Two peaks at 1470 cm<sup>-1</sup> and 1430 cm<sup>-1</sup> were also observed as in the case of the PCBM films. Interestingly, the intensity of the peak at 1470 cm<sup>-1</sup> from the FC<sub>7</sub>/PCBM film is about ten times higher than that from the PCBM film. In contrast, the peak intensity at 1430 cm<sup>-1</sup> is comparable with that of the PCBM film. Since the vibrational properties of the C<sub>60</sub> moiety in FC<sub>7</sub> and PCBM obtained by the IR and Raman measurements are very similar from the aforementioned DFT calculations, the difference in SFG spectra in Figure 8a-i and 8a-ii can be attributed to the different surface structures between the PCBM and the FC<sub>7</sub>/PCBM films. The SFG spectrum after the removal of the surface FC<sub>7</sub> layer by Ar<sup>+</sup> plasma etching gave further support for this attribution. As shown in Figure 8a-iii, after ~2 nm of the surface on the FC<sub>7</sub>/PCBM film was etched away, the intensity of the peak at 1470 cm<sup>-1</sup> decreased substantially, and the SFG spectrum became similar to that of the pure PCBM film. These results again confirm that the SFG signals from the FC<sub>7</sub>/PCBM film are mainly contributed by FC<sub>7</sub> molecules segregated on the FC<sub>7</sub>/PCBM surface. The FC<sub>7</sub> structure on the surface of the FC<sub>7</sub>/PCBM film that produced the higher intensity of the peak at 1470 cm<sup>-1</sup> was removed by Ar<sup>+</sup> plasma etching, and the newly produced surface consisting of pure PCBM had a structure similar to that of the spin-coated film of pure PCBM. These SFG spectral changes correspond well to the surface segregation process of FC<sub>7</sub> molecules to the surface of the FC<sub>7</sub>/PCBM film proposed by the aforementioned XPS measurements (Figure 4).

We also measured the SFG spectrum of a crystalline FC<sub>7</sub> thin layer prepared by the LB method.<sup>39</sup> As shown in Figure 8a-iv, a peak is clearly observed at 1470 cm<sup>-1</sup> while the peak at 1430 cm<sup>-1</sup> is very faint. These results support the conclusion that the strong peak at 1470 cm<sup>-1</sup> is attributed to the well-ordered structure of FC<sub>7</sub> molecules on the surface.

#### Molecular Orientation at the Surface of FC<sub>7</sub>/PCBM Film.

The orthogonality of the dipole moments of the A<sub>g</sub>(2) and F<sub>1u</sub>(4) modes confirmed by the DFT calculation (Figure 7b) is important in understanding the SFG spectra and the molecular orientation of the FC<sub>7</sub>/PCBM and PCBM films, considering the interaction between the electric field of the incident IR pulse and the vibration dipole moments of the C<sub>60</sub> moiety. The higher SFG signal of the A<sub>g</sub>(2) mode at 1470 cm<sup>-1</sup> from FC<sub>7</sub>/PCBM shows a stronger interaction between the electric field of the incident *p*-polarized IR pulse and the dipole moment of the vibration mode. This indicates that the dipole moment of the A<sub>g</sub>(2) mode in the FC<sub>7</sub> monolayer contains a component perpendicular to the surface. In contrast, the intensity of the SFG peaks at 1430 cm<sup>-1</sup> are comparable between the FC<sub>7</sub>/PCBM and PCBM films. This is reasonable if the F<sub>1u</sub>(4) mode is in a direction that has a weaker interaction with the *p*-polarized IR pulse. To

(33) Konarev, D. V.; Lyubovskaya, R. N.; Drichko, N. V.; Yudanov, E. I.; Shul'ga, Y. M.; Litvinov, A. L.; Semkin, V. N.; Tarasov, B. P. *J. Mater. Chem.* **2000**, *10*, 803–818.

(34) Pichler, T.; Winkler, R.; Kuzmany, H. *Phys. Rev. B* **1994**, *49*, 15879–15889.

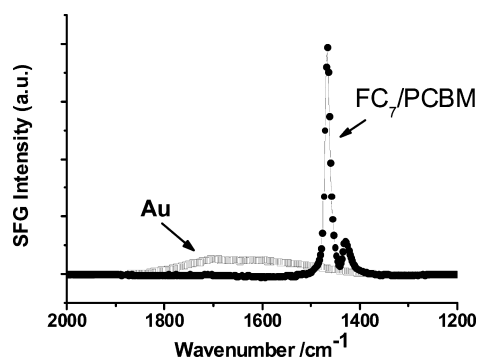
(35) Winkler, R.; Pichler, T.; Kuzmany, H. *Z. Phys. B* **1994**, *96*, 39–45.

(36) Semkin, V. N.; Drichko, N. V.; Kumzerov, Y. A.; Konarev, D. V.; Lyubovskaya, R. N.; Graja, A. *Chem. Phys. Lett.* **1998**, *295*, 266–272.

(37) Peremans, A.; Caudano, Y.; Thiry, P. A.; Dumas, P.; Zhang, W. Q.; LeRille, A.; Tadjeddine, A. *Phys. Rev. Lett.* **1997**, *78*, 2999–3002.

(38) Silien, C.; Caudano, Y.; Longueville, J. L.; Bouzidi, S.; Wiame, F.; Peremans, A.; Thiry, P. A. *Surf. Sci.* **1999**, *428*, 79–84.

(39) A Langmuir trough was employed for the preparation of the FC<sub>7</sub> LB films. An FC<sub>7</sub> chloroform solution having a concentration of 1 mg/mL was carefully spread on pure water at room temperature. The insoluble Langmuir film of FC<sub>7</sub> was formed by slowly compressing the barrier after waiting for more than 30 min for the solvent to evaporate. After a thin crystalline film formed on the surface of water, the films were transferred onto CaF<sub>2</sub> substrates.



**Figure 9.** SFG spectra (*ssp*) of an as-cast FC<sub>7</sub>/PCBM film and gold surface (before normalization).

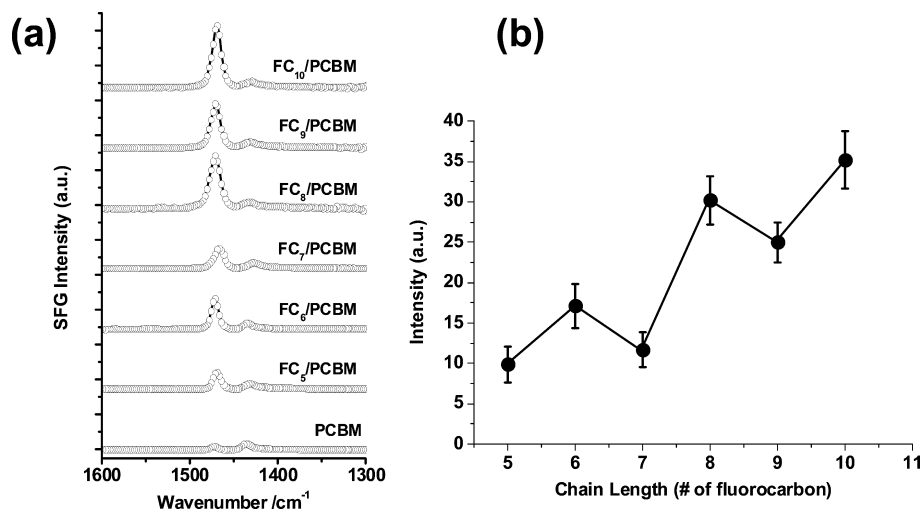
support this model, SFG measurements were also carried out with an *sps* polarization combination (i.e., *s*-SFG, *p*-visible, *s*-IR) that is sensitive to vibrational modes with IR dipole moments that contain a component parallel to the surface. As shown in Figure 8b, the SFG spectra of PCBM, FC<sub>7</sub>/PCBM, and etched FC<sub>7</sub>/PCBM thin films were similar to each other in this case, and only one peak at 1430 cm<sup>-1</sup> was observed with a small shoulder at 1470 cm<sup>-1</sup>. These results indicate that the C<sub>60</sub> moiety of the FC<sub>7</sub> monolayer aligned on the surface in an orientation with A<sub>g</sub>(2) mode more perpendicular to the surface. Considering the relative directions of the dipole moment of the A<sub>g</sub>(2) mode and fluorocarbon chains, one can expect that the fluorocarbon chains point in the direction of the air as that schematically proposed in Figure 1d. All the experimental observations (XPS, UPS, and SFG) independently support the structural model (Figure 1d).

On the other hand, neither SFG peaks from the carbonyl (C=O) stretching mode in the ester moiety nor the C–F stretching mode in the fluorocarbon chain from the FC<sub>7</sub>/PCBM surface were observed in the present experiments although the DFT calculation and the IR and Raman spectra in bulk predict the appearance of such bands (Figures S5 and S6 of the Supporting Information). Recently, Tyrode et al. reported an SFG study on adsorption of ammonium perfluorononanoate at the air–liquid interface and found reasonably strong C–F bands in their SFG observations.<sup>40</sup> This may be attributed to several possible reasons: (1) The packing density of fluorocarbon chains

on the FC<sub>7</sub>/PCBM film was  $1.6\text{--}1.7 \times 10^{-10}$  mol cm<sup>-2</sup>, which is lower than that of the fluorinated carbon SAMs on Au surface ( $5 \times 10^{-10}$  mol cm<sup>-2</sup>).<sup>16</sup> This should be related to the large footprints of C<sub>60</sub> molecules compared to the cross-section area of the fluorocarbon chain. Since SFG signal is proportional to the square of the molecular numbers on the surface, the lower surface coverage will largely reduce the relative SFG intensity. (2) Because of the same reason for (1), the van der Waals interaction between the fluorocarbon chains of FC<sub>7</sub> molecules is expected to be much weaker than the fluorinated carbon SAMs on Au surfaces. Although all the fluorocarbon chains averagely point to air, they may have some disordered conformation that can also significantly reduce the relative SFG intensities from the C=O group and fluorocarbon chains. (3) A technical problem of the tunable IR half-wave plate (PO-TWP-L2–25-IR, Alphalas GmbH) used in the present SFG system, which starts to absorb IR light as the frequency is lower than approximately 1400 cm<sup>-1</sup>, can affect our SFG spectral behaviors in lower wavenumber region. Detailed studies are still in progress.

It should be emphasized here that the SFG peak intensity at 1470 cm<sup>-1</sup> in the *ssp*-polarized SFG spectrum for the FC<sub>7</sub>/PCBM films is so strong that it is comparable to that of nonresonant signals from a gold substrate, which is normally used for the optical alignment and normalization procedures of SFG measurements (Figure 9). In addition to the molecular density, packing structures, and ordering of the C<sub>60</sub> moiety of FC<sub>7</sub> at the surface, very high second-order nonlinear susceptibility of the molecule should also significantly contribute to the strong SFG signal. These features can be applied for development of new nonlinear optical materials.

**SFG Signal Intensity Dependence on Fluorocarbon Chain Length.** SFG vibrational spectroscopy has been shown above to be a powerful tool for investigating molecular orientation in the surface-segregated monolayer of FC<sub>7</sub>. To investigate the orientation dependence on the fluorocarbon chain length, the SFG spectra of the FC<sub>*n*</sub>/PCBM films were collected with an *ssp* polarization combination, as shown in Figure 10a. The intensity of the peak at 1470 cm<sup>-1</sup> was plotted as a function of the number of fluorinated carbons.<sup>41</sup> As shown in Figure 10b, a longer fluorocarbon chain gives a higher intensity of the SFG signal from the vibration mode corresponding to the A<sub>g</sub>(2) mode



**Figure 10.** (a) SFG spectra (*ssp*) of PCBM, FC<sub>5</sub>/PCBM, FC<sub>6</sub>/PCBM, FC<sub>7</sub>/PCBM, FC<sub>8</sub>/PCBM, FC<sub>9</sub>/PCBM, and FC<sub>10</sub>/PCBM films; (b) plot of SFG signal intensity for the peak at 1470 cm<sup>-1</sup> as a function of the number of the fluorocarbons in FC<sub>*n*</sub>.

in C<sub>60</sub>. The DFT calculation shows that the length of fluorocarbon chain did not significantly affect the IR and Raman intensities for these vibration modes (Table S1 of the Supporting Information). Therefore, the increase in the peak intensity with the chain length should be attributed to the better packing of molecules with long chains owing to the stronger van der Waals interactions between the fluorocarbon chains, which can further improve the packing and orientation of the C<sub>60</sub> moiety in FC<sub>n</sub> molecules.

Interestingly, the molecules with even numbers of the fluorinated carbons give a higher intensity of the signal than those with odd numbers. The similar “odd–even” trend of the SFG signal intensity was also observed in FC<sub>n</sub>/PCBM thin films with a different film thickness of 100 nm (Figure S8 of the Supporting Information), suggesting that this effect is due to the surface structure. This so-called “odd–even effect” has been observed in other monolayer systems<sup>42</sup> where the layers have a densely packed, well-oriented structure. The observation of the odd–even effect for the surface-segregated FC<sub>n</sub> monolayer supports our hypothesis that FC<sub>n</sub> molecules are well oriented and densely packed on the surface. On the other hand, as discussed above, the density of fluorocarbon chains in FC<sub>n</sub>/PCBM is not as high as the fluorinated carbon SAMs on a Au surface<sup>16</sup> due to the large footprint of the C<sub>60</sub> moieties. At this point, the mechanism of the odd–even effect in the SFG signals from FC<sub>n</sub>/PCBM is not yet clear; the extremely high sensitivity of SFG vibration spectroscopy to the molecular alignment at the interface might enable the detection of structural difference between FC<sub>n</sub> with odd and even numbers of fluorinated carbons, which might be too subtle to be detected by other measurements

such as UPS or XPS. Detailed investigations of the origin of this odd–even effect are underway.

## Conclusion

In conclusion, we have presented a new type of ordered monolayer driven by surface segregation. It is worth emphasizing that the monolayers are spontaneously formed *during a spin-coating process from a mixture solution*; this process has not yet been considered to induce the formation of such oriented, ordered monolayers. The surface-segregated FC<sub>n</sub> monolayer can be easily applied to the control of the chemical or physical properties of the PCBM film surface such as ionization potential (IP). This concept is potentially applicable to other types of organic semiconductors and therefore could be useful for various organic devices. The surface-segregated FC<sub>n</sub> monolayers could also provide a new perspective for understanding the relationships between structural ordering, the local electric field, and the SFG signal; therefore, it may also lead to a new strategy for designing nonlinear optical materials.<sup>43,44</sup>

**Acknowledgment.** We thank Dr. Takeshi Nishizawa, Dr. Ryuhei Nakamura (The University of Tokyo), Dr. Chunhe Yang, and Dr. Erjun Zhou (ERATO project, JST) for helpful discussion, Dr. Koji Nakano (The University of Tokyo) for <sup>19</sup>F NMR measurements, and Dr. Kiyoshi Yagi (The University of Tokyo) for his support in the DFT calculations. This work was supported in part by the Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering), MEXT, Japan. This work was partly supported by JST (PRESTO) and a Grant-in-Aid for Scientific Research (B) 19350099 and Exploratory Research 21655074 from MEXT, Japan.

**Supporting Information Available:** General methods, characterization, spectra, images, and animations of vibration modes (.ppt file). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA9057053

(40) Tyrode, E.; Johnson, C. M.; Rutland, M. W.; Day, J. P. R.; Bain, C. D. *J. Phys. Chem. C* **2007**, *111*, 316–329.

(41) To eliminate the effects of the differences in CaF<sub>2</sub> substrates and laser intensity during different measurements, the peak at 1430 cm<sup>-1</sup> was normalized for comparison. When the FC<sub>7</sub>/PCBM films have been prepared and measured independently three times, the deviation in peak intensity ratio between 1430 and 1470 cm<sup>-1</sup> was smaller than 20% (Figure S7 of the Supporting Information).

(42) Tao, F.; Bernasek, S. L. *Chem. Rev.* **2007**, *107*, 1408–1453.

(43) Kaino, T.; Tomaru, S. *Adv. Mater.* **1993**, *5*, 172–178.

(44) Marder, S. R.; Perry, J. W. *Adv. Mater.* **1993**, *5*, 804–815.