Electronic Supplementary Information for

Surface Functionalization of Organic Semiconductor Films by Segregated Monolayers

Seiichiro Izawa,[1,2,3] *Kazuhito Hashimoto*[1*] *and Keisuke Tajima*[3,4*]

[1]Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, [2]Research Fellow of Japan Society for the Promotion of Science, 5-3-1 Kohjimachi, Chiyoda-ku, Tokyo 102-0083, Japan, [3]RIKEN, Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako-shi, Saitama 351-0106, Japan, [4]Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science Technology Agency (JST), 4-1-8 Honcho, Kawaguchi-shi, Saitama 332-0012, Japan

E-mail: keisuke.tajima@riken.jp

Materials and instruments

All the chemicals were purchased from commercial suppliers and used without further purification. High-performance liquid chromatography was carried out on a system with a CBM-20A controller (Shimadzu), an LC-6AD pump (Shimadzu), an SPD-20A UV-vis detector and a Luna Silica column (particle size: 5 μm; column length: 250 mm; inner diameter: 21.2 mm) (Phenomenex). ^{1}H NMR spectra were measured in $CDCl_3$ containing 1% v/v TMS on an Oxford superconducting magnet system (500 MHz). MALDI-TOF-MS spectra were measured on Ultraflex RO (Bruker Daltonics) with dithranol as the matrix. Density functional theory (DFT) calculations were conducted using Gaussian 03 with the B3LYP functional and 6-31G(d) basis set. The molecular structures were optimized by minimizing the energy.

Synthesis

[6,6]-Phenyl-C_{61}-butyric acid was synthesized according to procedures in the literature.[1]

2-bromomethylthiophene

2-Thiophenemethanol (2.00 g, 17.5 mmol), anhydrous pyridine (100 μL), and anhydrous dichloromethane (75 mL) were added to a 100 mL two-neck round-bottom flask under N_2. The mixture was cooled to 0 °C and phosphorus tribromide (2.49 mL, 26.3 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h, and then at room temperature for 1 h. Water was added to quench the reaction and the mixture was extracted with dichloromethane. The organic layer was dried with sodium sulfate and filtered. The solvent was removed in vacuo, yielding the product as a pale yellow liquid (2.82 g, 91%).

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.31-7.32 (d, 1H), 7.11-7.12 (d, 1H), 6.94-6.95 (m, 1H), 4.75 (s, 2H).

General synthesis for the ω-functionalized semifluoroalkyl alcohols (1-4)

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluoro-1,10-decanediol (1.00 g, 2.16 mmol), NaH (oil dispersion 50~72%, 118 mg), and dry THF were added to a 100 mL two-neck round-bottom flask under N_2. The reaction mixture was stirred at room temperature for 1 h. Iodomethane, benzyl bromide, propargyl bromide, or 2-thiophenemethanol (3.24 mmol) was added for the synthesis of corresponding product **1-4**, respectively. The reaction mixture was stirred overnight at 60 °C. Water was added to quench the reaction and the mixture was extracted with ethyl acetate. The organic layer was dried with magnesium sulfate and filtered. The product was purified by column chromatography using silica gel and chloroform as the eluent, yielding a white solid.

12-Methoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1-dodecanol (1) (Yield: 31%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 4.06-4.15 (m, 2H), 3.86-3.93 (t, 2H), 3.52 (s, 3H), 2.03-2.07 (t, 1H).

12-Benzyloxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1-dodecanol (2) (Yield: 32%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.32-7.40 (m, 5H), 4.69 (s, 2H), 4.06-4.15 (m, 2H), 3.91-3.98 (t, 2H), 1.99-2.02 (t, 1H).

12-Propargyloxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1-dodecanol (3) (Yield: 30%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 4.32-4.33 (d, 2H), 4.02-4.14 (m, 4H), 2.54-2.55 (t, 1H), 2.06-2.10 (t, 1H).

12-(Thiophene-2-methoxy)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1-dodecanol (4) (Yield: 30%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.35-7.36 (d, 1H), 7.05-7.06 (d, 1H), 7.00-7.01 (m, 1H), 4.84 (s, 2H), 4.07-4.11 (m, 2H), 3.90-3.96 (t, 2H), 2.10-2.13 (t, 1H).

General synthesis for Me, Bn, A, and T

[6,6]-Phenyl-C_{61}-butyric acid (100 mg, 0.112 mmol) was added to a 50 mL two-neck round-bottom flask under N_2, and then distilled CS_2 (30 mL) and thionyl chloride (966 μL, 17.9 mmol) were added. The reaction mixture was refluxed overnight at 55 °C. The solvent was removed, and the crude product was dried at 80 °C for 3 h. Then, anhydrous toluene (10 mL) and NaH (oil dispersion 50–72%, 12.0 mg), which had been washed with hexane, were added. The flask was covered with aluminum foil, and **2**, **3**, **4**, or **5** (0.168 mmol) was added for **Me**, **Bn**, **A**, or **T**, respectively. The reaction mixture was stirred at room temperature for 48 h and then purified by column chromatography using silica gel and chloroform as the eluent and by HPLC using chloroform as the eluent. The product was reprecipitated in methanol and filtered, yielding a brown solid.

2,13-Dioxa-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-hexadecafluoro-14-carbonyl-18-phenyl-18-[6.6]-C_{61}-octadecane (Me) (Yield: 80%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.91-7.94 (m, 2H), 7.53-7.57 (m, 2H), 7.46-7.47 (m, 1H), 4.56-4.63 (t, 2H), 3.86-3.93 (t, 2H), 3.52 (s, 3H), 2.90-2.94 (m, 2H), 2.62-2.65 (m, 2H), 2.20-2.26 (m, 2H). MALDI-TOF-MS calcd. 1354.74, found 1354.24.

1-Phenyl-2,13-dioxa-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-hexadecafluoro-14-carbonyl-18-phenyl-

18-[6.6]-C_{61}-octadecane (Bn) (Yield: 70%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.92-7.94 (m, 2H), 7.53-7.57 (m, 2H), 7.48-7.50 (m, 1H), 7.33-7.38 (m, 5H), 4.69 (s, 2H), 4.56-4.63 (t, 2H), 3.91-3.98 (t, 2H), 2.90-2.94 (m, 2H), 2.61-2.65 (m, 2H), 2.20-2.24 (m, 2H). MALDI-TOF-MS calcd. 1430.77, found 1430.27.

1-Yne-4,15-dioxa-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-hexadecafluoro-16- carbonyl-20-phenyl-20-[6.6]-C_{61}-icosane (A) (Yield: 56%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.92-7.94 (m, 2H), 7.53-7.57 (m, 2H), 7.48-7.50 (m, 1H), 4.56-4.63 (t, 2H), 4.31-4.32 (d, 2H), 4.02-4.09 (t, 2H), 2.90-2.94 (m, 2H), 2.61-2.65 (m, 2H), 3.54-3.55 (t, 1H), 2.18-2.26 (m, 2H). MALDI-TOF-MS calcd. 1378.74, found 1378.23.

1-(Thiophene-2-yl)-2,13-dioxa-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-hexadecafluoro-14-carbonyl-18-phenyl-18-[6.6]-C_{61}-octadecane (T) (Yield: 58%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.92-7.94 (m, 2H), 7.53-7.57 (m, 2H), 7.48-7.50 (m, 1H), 7.34-7.36 (m, 1H), 7.05-7.06 (m, 1H), 7.00-7.02 (m, 1H), 4.84 (s, 2H), 4.56-4.63 (t, 2H), 3.90-3.97 (t, 2H), 2.90-2.94 (m, 2H), 2.61-2.65 (m, 2H), 2.20-2.26 (m, 2H). MALDI-TOF-MS calcd. 1436.73, found 1436.21.

General synthesis for F and OH[2]

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluoro-1-nonanol (4.94 g, 11.0 mmol) or 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-1,10-decanediol (5.08 g, 11.0 mmol), [6,6]-phenyl-C_{61}-butyric acid methyl ester (1.00 g, 1.10 mmol), *p*-toluenesulfonic acid monohydrate, and anhydrous *o*-dichlorobenzene (100 mL) were added to a 100 mL two-neck round-bottom flask under N_2. The reaction mixture was stirred at 180 °C for 3 days and then poured into methanol (2 L). The resulting solid was collected by vacuum filtration and the crude product was purified by column chromatography using silica gel and toluene as the eluent. The product was reprecipitated in methanol and filtered, yielding a brown solid.

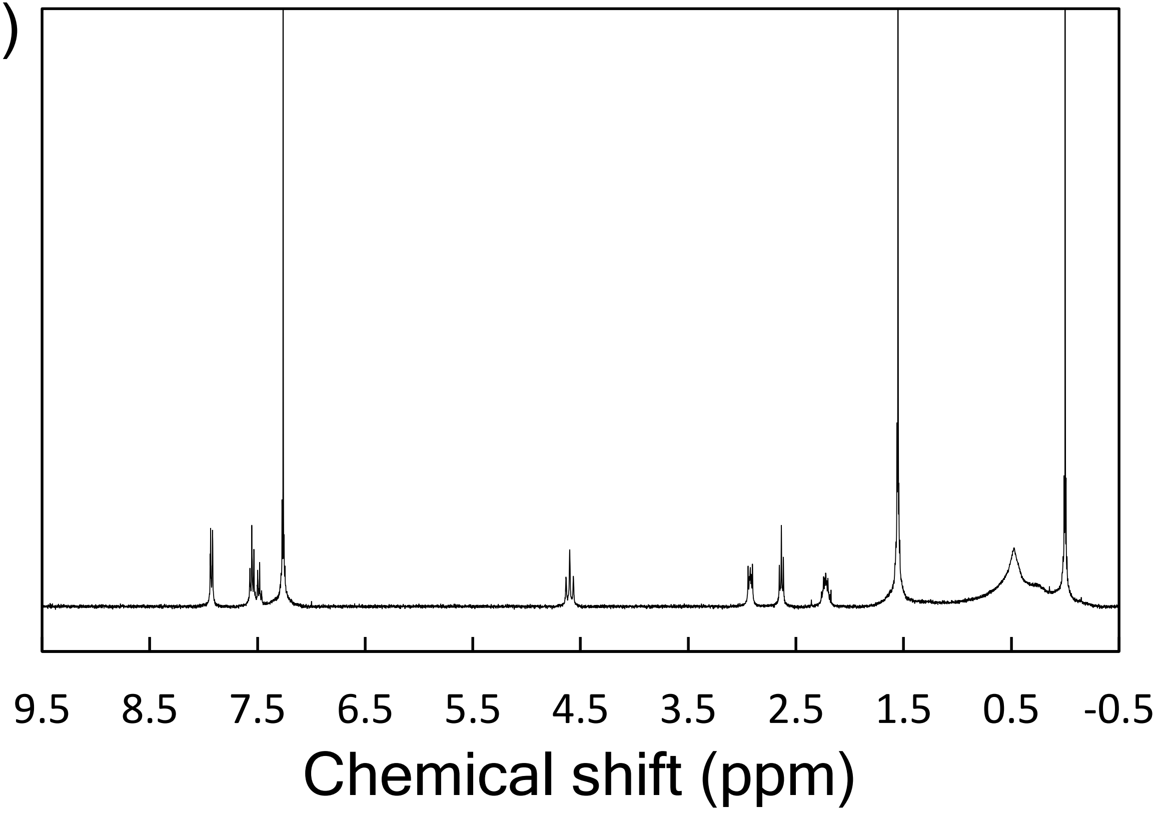
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-10-oxa-11-carbonyl-15-phenyl-15-[6.6]-C_{61}-pentadecane (F) (Yield: 90%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.92-7.94 (m, 2H), 7.53-7.57 (m, 2H), 7.46-7.49 (m, 1H), 4.57-4.64 (t, 2H), 2.90-2.94 (m, 2H), 2.62-2.65 (m, 2H), 2.17-2.26 (m, 2H). MALDI-TOF-MS calcd. 1328.21, found 1328.71.

1-ol-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluoro-11-oxa-12-carbonyl-16-phenyl-16-[6.6]-C_{61}-hexadecane (OH) (Yield: 46%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.91-7.93 (m, 2H), 7.53-7.57 (m, 2H), 7.46-7.50 (m, 1H), 4.56-4.63 (t, 2H), 4.06-4.15 (m, 2H), 2.90-2.96 (m, 2H), 2.61-2.65 (m, 2H), 2.18-2.26 (m, 2H), 1.99-2.02 (t, 1H). MALDI-TOF-MS calcd. 1340.73, found 1340.18.

(a)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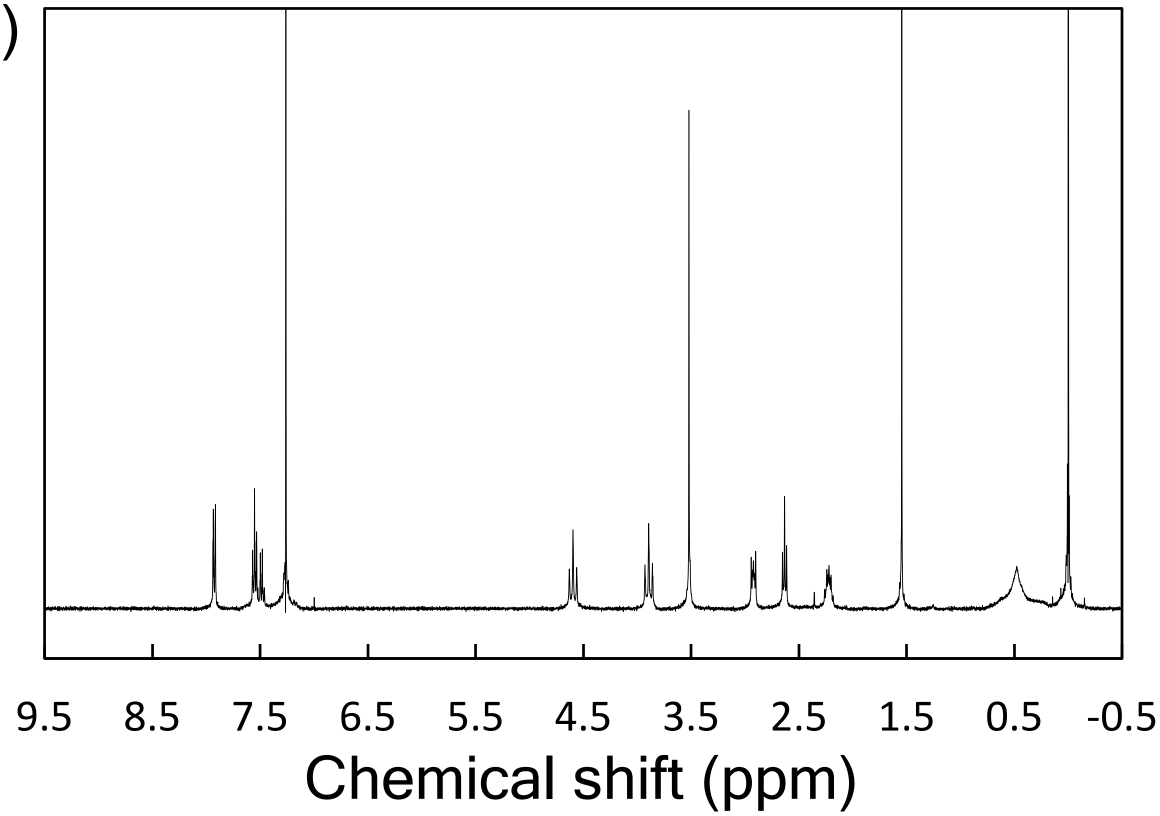
Chemical shift (ppm)

(b)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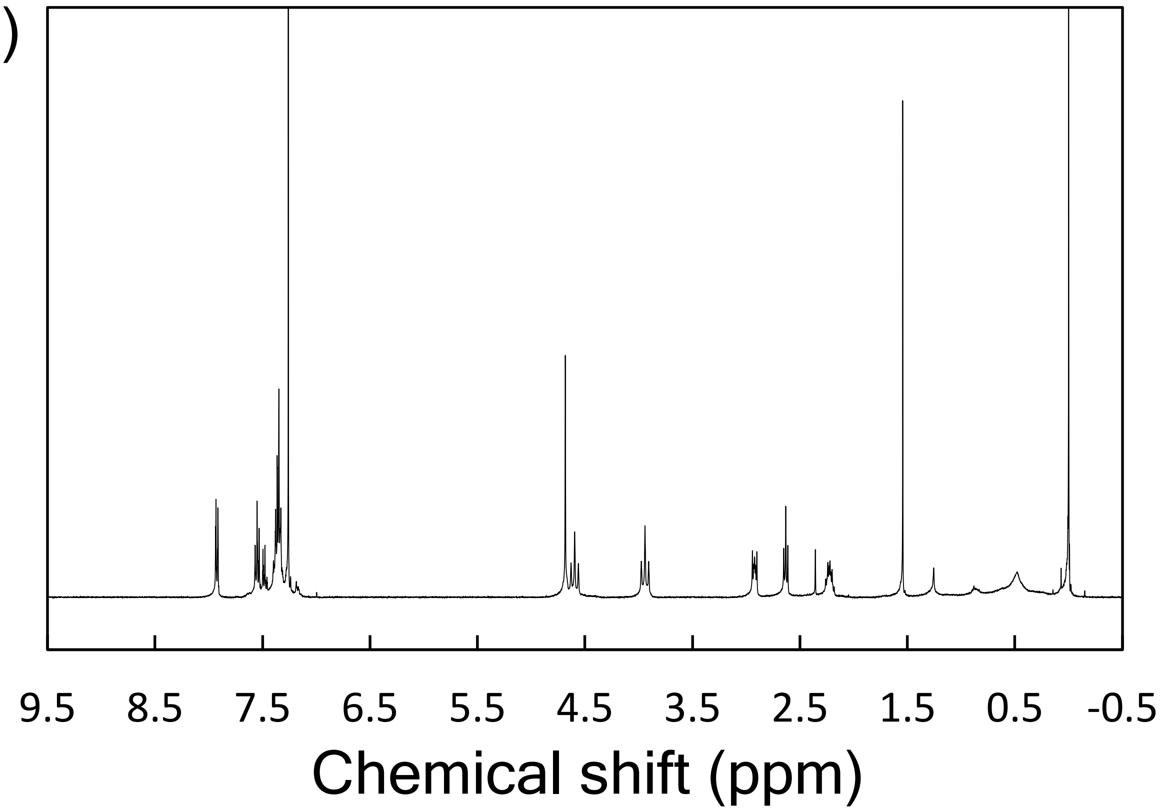
Chemical shift (ppm)

(c)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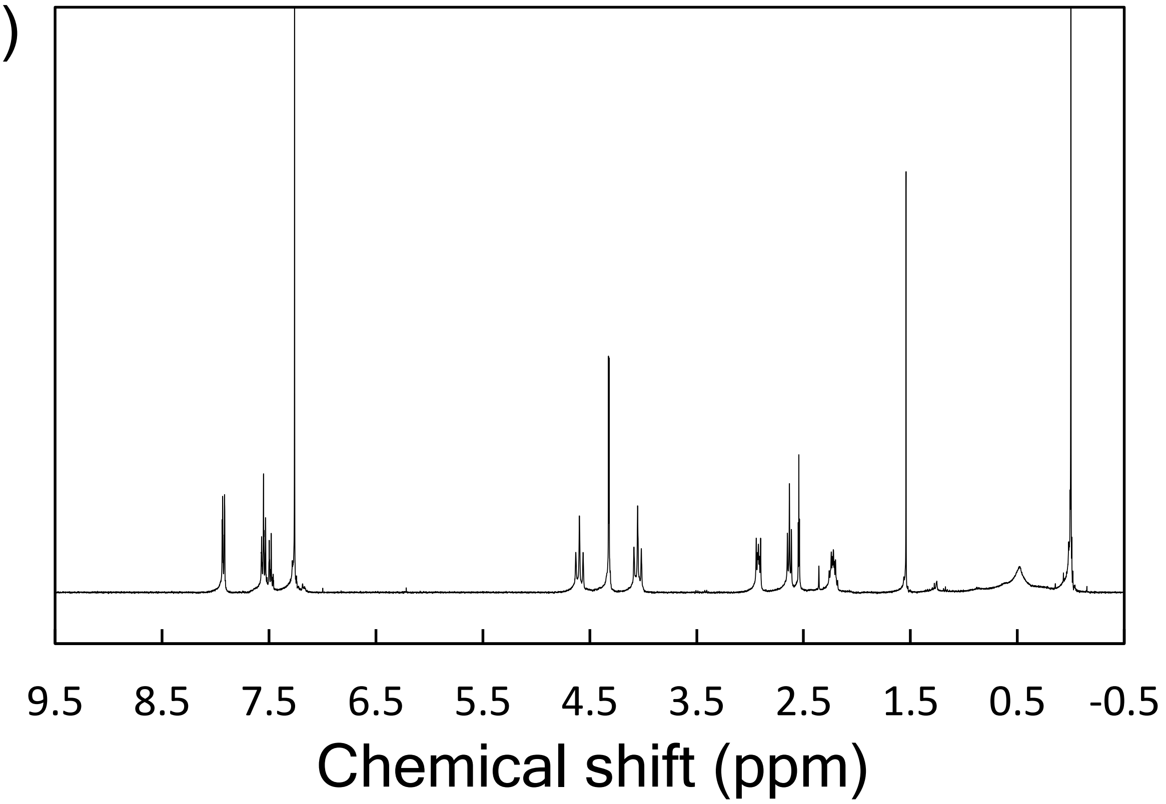
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Chemical shift (ppm)

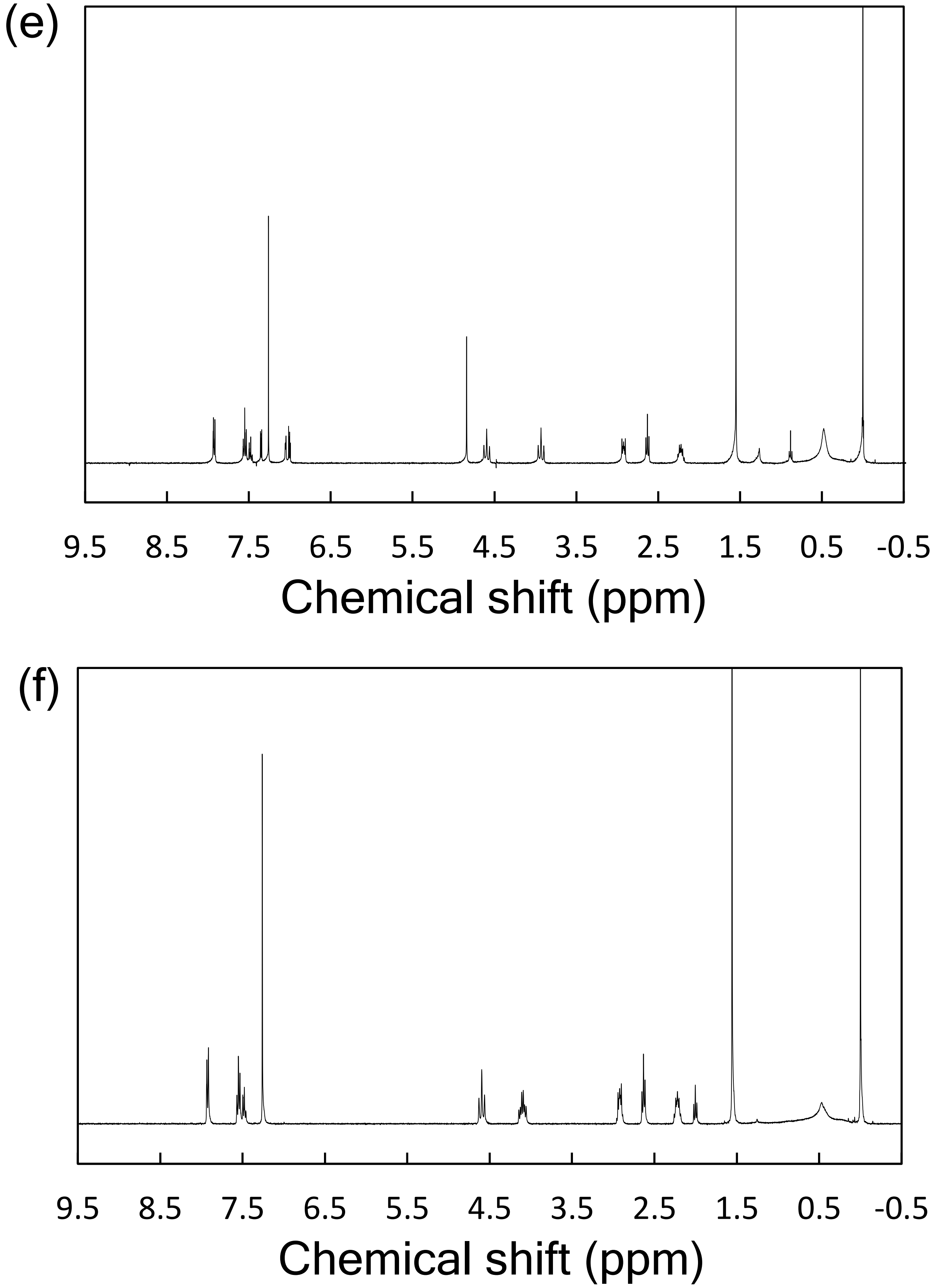
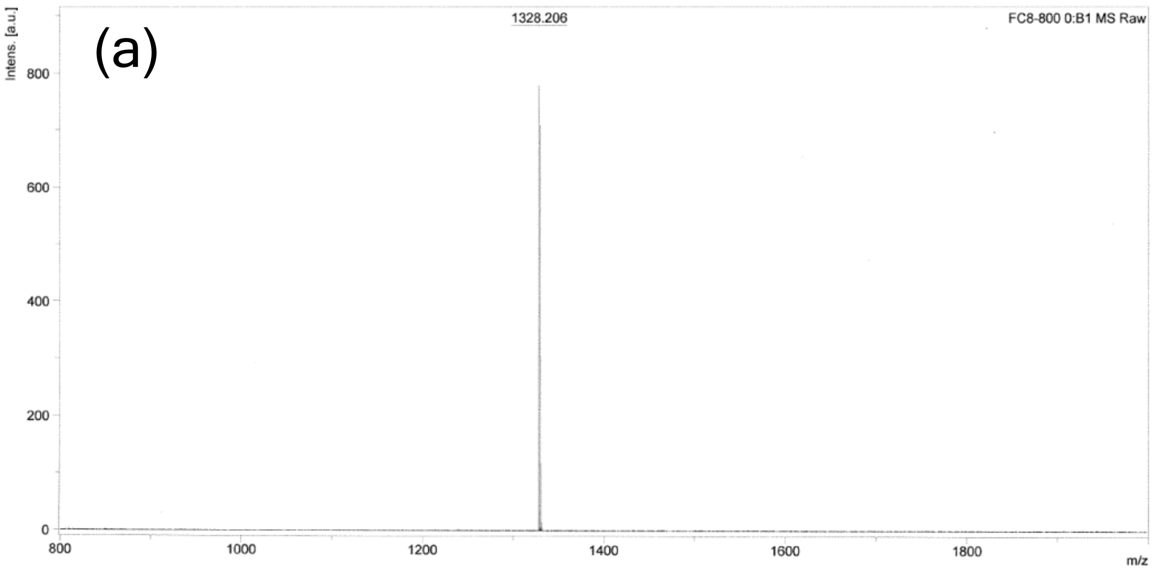
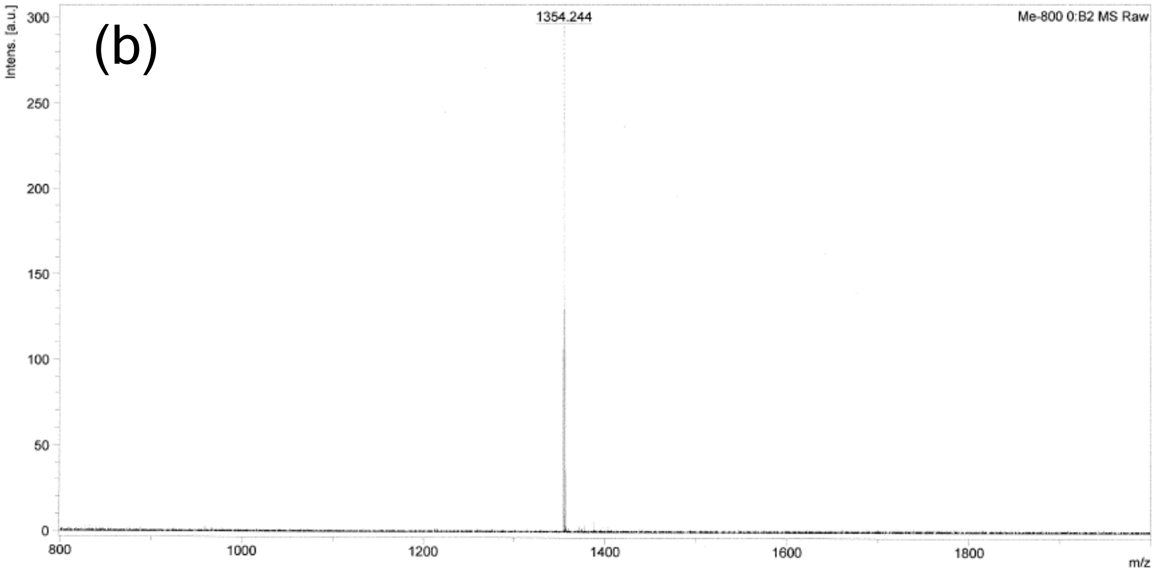


Figure S1. ^{1}H-NMR charts of (a) **F**, (b) **Me**, (c) **Bn**, (d) **A**, (e) **T** and (f) **OH**.


(a)
1328.206
FC8-800 0:B1 MS Raw
Intens. [a.u.]
800
600
400
200
0
800
1000
1200
1400
1600
1800
m/z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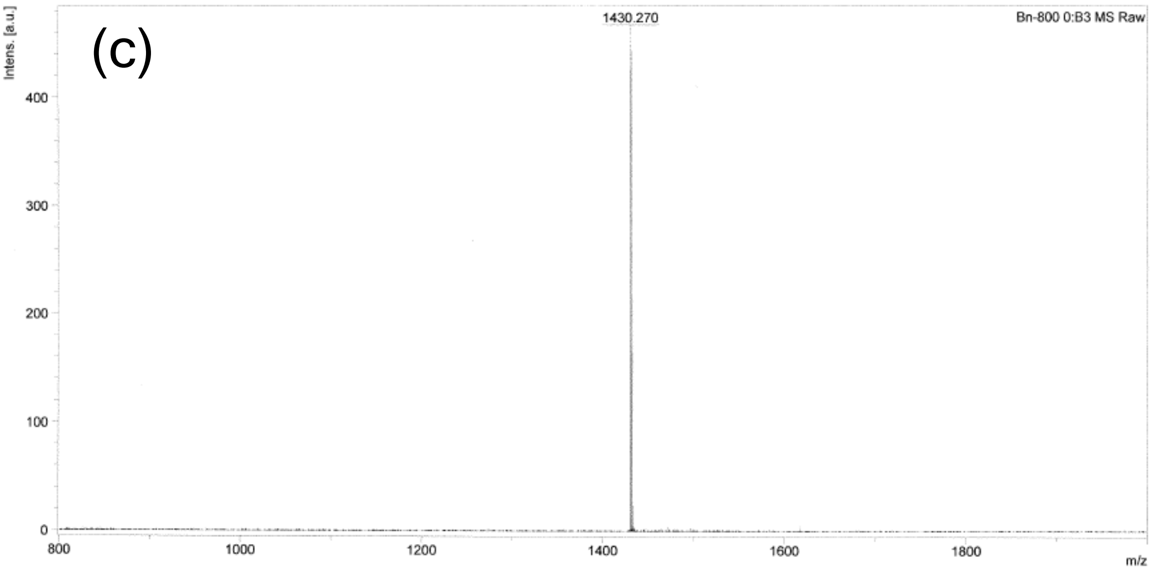
1600
1800
m/z


(c)
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1600
1800
m/z

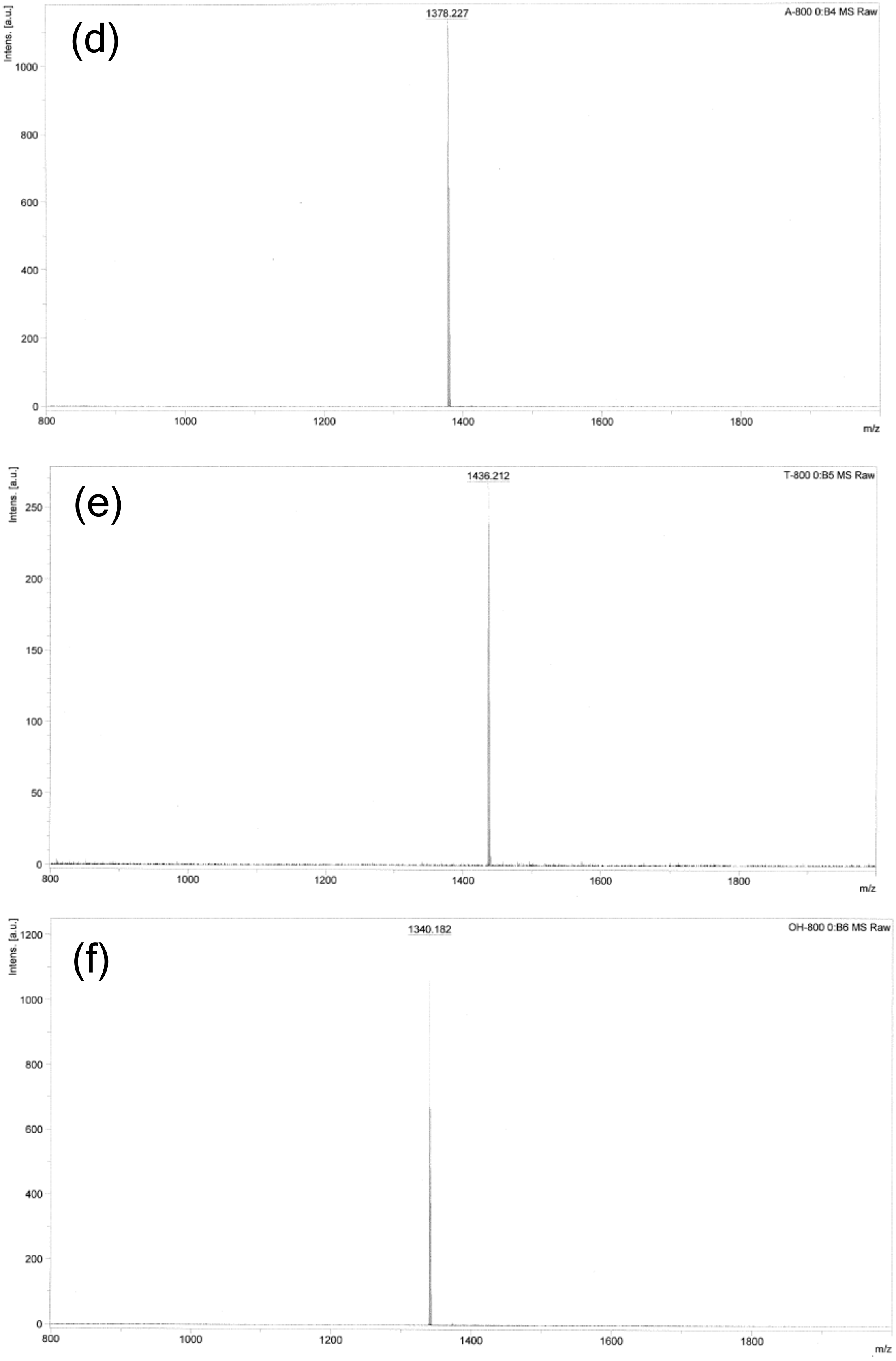

Figure S2. MALDI-TOF-MS charts of (a) **F**, (b) **Me**, (c) **Bn**, (d) **A**, (e) **T** and (f) **OH**.

Film preparation

An indium tin oxide (ITO)-coated glass substrate (sheet resistance: 10 Ω sq^{-1}, Geomatech, Japan) was cleaned by ultrasonication in detergent, water, acetone, and 2-propanol. The substrate was dried, and then exposed to UV-O_3 for 30 min. The solution was prepared by dissolving PCBM (10 mg) and different amounts of **F**, **Me**, **Bn**, **A**, **T**, or **OH** in chlorobenzene (1 mL). The solution was spin coated at 600 rpm for 1 min. The film was annealed at 150 °C under N_2 for 5 min.

Surface analysis

X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) was performed on an AXIS-ULTRADLD spectrometer (Kratos Analytical) and a PHI 5000 Versa Probe II surface analysis instrument (ULVAC-PHI). Monochromated Al *K*α radiation was used in all the XPS measurements. The carbon 1s (non-fluorinated carbon: 282 eV, fluorinated carbon: 288 eV), fluorine 1s (686 eV), and S 2p (162 eV) peaks were used for the characterization. To obtain the XPS depth profile, each sample was etched using an argon ion etcher at an acceleration voltage of 500 V with an etching rate of approximately 0.1 nm/s. He I radiation was used in all the UPS measurements. The static contact angle of a dichlorobenzene solution of modifiers and PCBM on glass substrate and distilled water on the each film was measured on a DMe-201 (Kyowa) and a CA-X contact angle meter (Kyowa) at room temperature.

XPS depth profiles

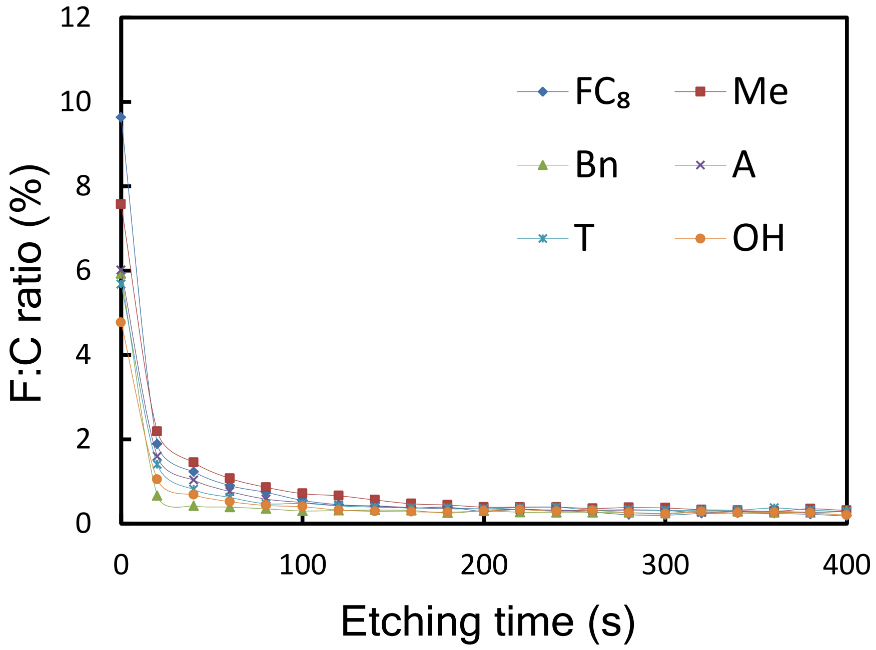

Figure S3. XPS depth profile: the F:C ratio of the films fabricated from 1 g/L solutions of the modifiers.

UPS spectra

The films were prepared from a concentration of 1 g/L for the all modifiers and a PCBM concentration of 10 g/L on ITO substrate. Figure S4a, b and c show the UPS data at whole, cutoff and HOMO regions, respectively, using the He I irradiation. By using the spectrum width determined from the distance between the cutoff to the HOMO edge, the ionization potential (IP) of the films can be extracted. IPs and the positions of HOMO peaks are summarized in Table S1.

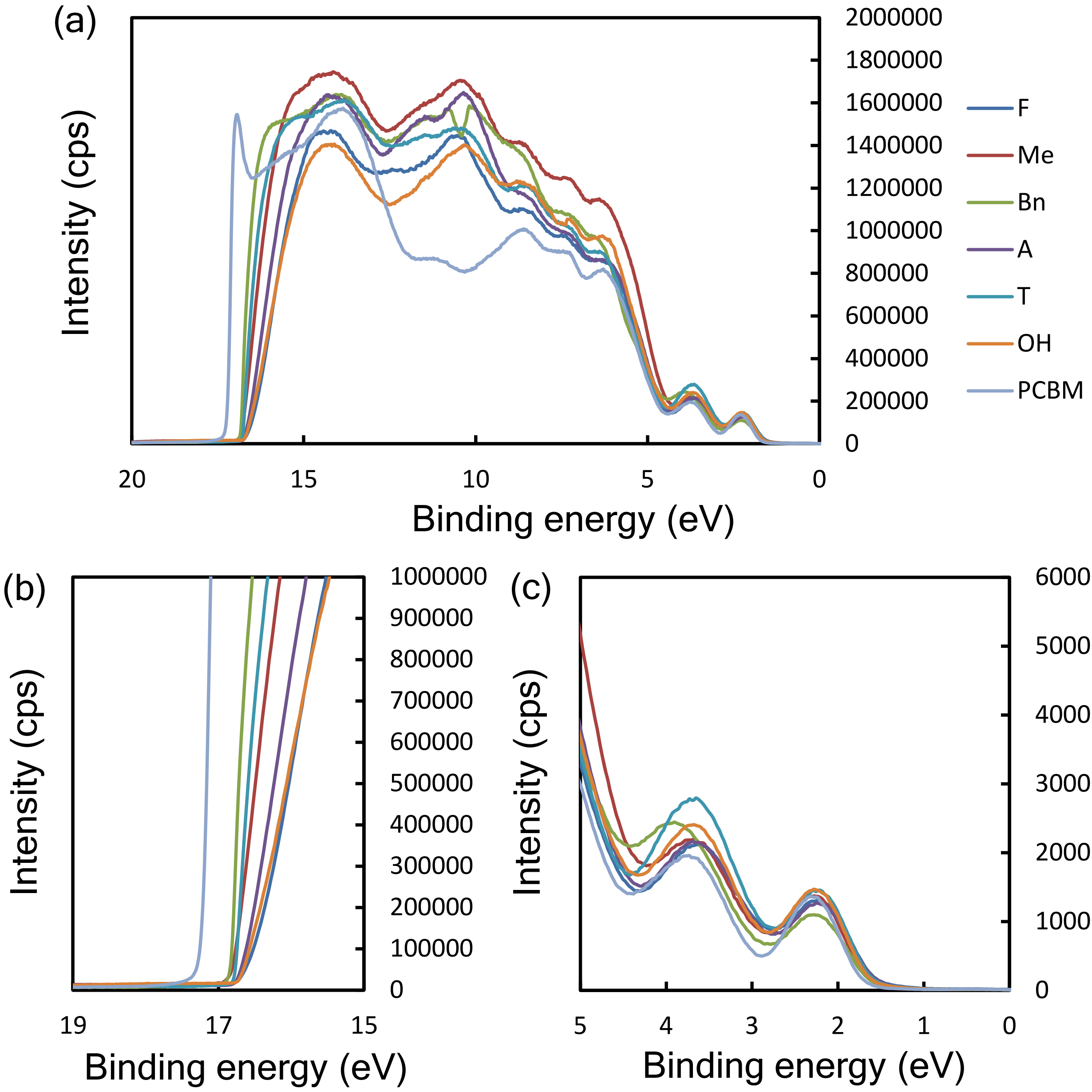
(a)
Intensity (cps)
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
20
15
10
5
0
Binding energy (eV)
F
Me
Bn
A
T
OH
PCBM
(b)
Intensity (cps)
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
19
17
15
Binding energy (eV)
(c)
Intensity (cps)
600000
500000
400000
300000
200000
100000
0
5
4
3
2
1
0
Binding energy (eV)

Figure S4. UPS spectra: the F:C ratio of the films fabricated from 1 g/L solutions of the modifiers. (a) whole spectra, (b) cut off regions, (c) HOMO regions.

Films	**Ionization potentials (eV)**	**HOMO peak positions (eV)**
PCBM	5.66	2.30
F	6.04	2.23
Me	5.93	2.28
Bn	5.91	2.28
A	5.94	2.24
T	5.96	2.24
OH	5.98	2.26

Table S1. Ionization potentials and HOMO peak positions of the films

Estimation of the maximum F/C ratio in XPS

The XPS intensity of specific element can be described as

$$I_{i} = \frac{I^{\circ}_{i}}{\lambda_{i}} \int_{z_1}^{z_2} X_i \exp\left(-\frac{z}{\lambda_{i}}\right) dz \qquad \text{eq. S1}$$

where I_i is the intensity of the signals of element i, I_i^{o} is the relative sensitivity factor of element i, λ_i is the attenuation length of the electrons of element i, z is the signal depth, and X_i is the local atomic concentration of element i.[3] If it is assumed that the modifiers form densely packed uniform monolayers on the surface of PCBM film, the fluorine signal originated from the fluoroalkyl chain layer, and the non-fluorinated carbon signal came from the functional group layer on the top surface and the fullerene layer in the bulk. Therefore, the I_F/I_C and F/C atomic concentration (Γ_{max}^{calc}) can be described as

$$\frac{I_{F}}{I_{C}}=\frac{\frac{I_{F}^{\circ}}{\lambda_{F}}\int_{d_1}^{d_2} X_F \exp\left(-\frac{z}{\lambda_{F}}\right)dz}{\frac{I_{C}^{\circ}}{\lambda_{C}}\int_{0}^{d_1} X_{C_1} \exp\left(-\frac{z}{\lambda_{C}}\right)dz+\frac{I_{C}^{\circ}}{\lambda_{C}}\int_{d_2}^{\infty} X_{C_2} \exp\left(-\frac{z}{\lambda_{C}}\right)dz} \quad \text{eq. S2}$$

$$\Gamma_{max}^{calc}=\frac{I_F/I_F^{\circ}}{I_C/I_C^{\circ}}=\frac{X_F\left\{exp\left(-\frac{d_1}{\lambda_F}\right)-exp\left(-\frac{d_2}{\lambda_F}\right)\right\}}{X_{C_1}\left\{1-exp\left(-\frac{d_1}{\lambda_C}\right)\right\}+X_{C_2}exp\left(-\frac{d_2}{\lambda_C}\right)} \quad \text{eq. S3}$$

where d_1 is the depth of the functional group layer and d_2 is a sum of the depth of functional group layer and fluoroalkyl chain layer, which were obtained from optimized structure in DFT calculation. Previously reported values of $\lambda_F = 2.7$ nm, $\lambda_C = 3.8$ nm were used. Note that $d_1 = 0$ in **F** because there is no functional layer in the fluoroalkyl chain in **F**. X_{C1} and X_{C2} are the local atomic concentrations of carbon in the functional group layer and in the fullerene layer, respectively, and X_F the local atomic concentration of fluorine in the fluoroalkyl chain layer. These values were calculated by the number of atoms divided by the depth of each layer. The details of the derivation of X_{C1}, X_{C2}, and X_F for each film are summarized below.

Derivation of eq. 1 in ARXPS of the T/PCBM film

The relationship between the XPS intensity of specific atoms and the take-off angle can be derived by replacing z with $z/\cos\theta$ in eq. S1, and described as

$$I_{i} = \frac{I_{i}^{\circ}}{\lambda_{i}} \int_{z_1}^{z_2} X_i \exp\left(- \frac{z}{\lambda_{i} cos\theta} \right) dz \qquad \text{eq. S4}$$

θ is the take-off angle.[3] Assuming sulfur atoms are present over the distance d_S from surface with coverage α, and that carbon atoms are distributed uniformly over all regions of the film, the intensity ratio of the sulfur and carbon atom can be described as

$$\frac{I_{S}}{I_{C}} = \frac{\alpha \frac{I_{S}^{\circ}}{\lambda_{S}} \int_{0}^{d_S} X_S \exp\left(- \frac{z}{\lambda_{S} cos\theta} \right) dz}{\frac{I_{C}^{\circ}}{\lambda_{C}} \int_{0}^{\infty} X_C \exp\left(- \frac{z}{\lambda_{C} cos\theta} \right) dz} \qquad \text{eq. S5}$$

Thus, the S/C atomic ratio is

$$S/C atomic\ ratio\ is = \frac{I_S/I_S^{\circ}}{I_C/I_C^{\circ}} = \frac{\alpha X_S}{X_C} \left\{ 1 - exp\left(- \frac{d_S}{\lambda_S cos\theta} \right) \right\} \qquad \text{eq. S6}$$

Derivation of local atomic concentration X_i

d_1 (nm) = 0.367, 0.710, 0.701, 0.570, and 0.238 for **Me**, **Bn**, **T**, **A**, and **OH**, respectively

d_2 (nm) = 1.02, 1.28, 1.63, 1.62, 1.49, and 1.16 for **F**, **Me**, **Bn**, **T**, **A**, and **OH**, respectively

X_{C1} (nm^{-1}) = number of carbons in functional group layer (n_{C1})/d_1, **Me**: n_{C1} = 2, X_{C1} = 5.45, **Bn**: n_{C1} = 8, X_{C1} = 11.3, **A**: n_{C1} = 4, X_{C1} = 7.01, **T**: n_{C1} = 7, X_{C1} = 9.98, **OH**: n_{C1} = 1, X_{C1} = 4.20

X_{C2} (nm^{-1}) = number of carbons in PCBM/length of PCBM = 72/1.29 = 55.8

X_F (nm^{-1}) = number of fluorines in fluoroalkyl chain layer/(d_2 - d_1) = 16/0.917 = 15.7 (except **FC$_8$**)

X_F (nm^{-1}) = number of fluorines in fluoroalkyl chain layer/(d_2 - d_1) = 17/1.02 = 16.7 (**FC$_8$**)

X_S (nm^{-1}) = number of sulfurs/molecular length of thiophene = 1/0.346 = 2.89

X_C (nm^{-1}) = number of carbons in PCBM/length of PCBM = 72/1.29 = 55.8 (assuming that carbon atoms are distributed uniformly in all regions of the film with a local atomic concentration of the fullerene layer)

References

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