Supplementary Information

Enhancement of Charge Transport Properties of Small Molecule Semiconductors by Controlling Fluorine Substitution and Effects on Photovoltaic Properties of Organic Solar Cells and Perovskite Solar cells

Jae Hoon Yun,[ac] Sungmin Park,[ad] Jin Hyuck Heo,[e] Hyo-Sang Lee,[af] Seongwon Yoon,[b] Jinback Kang,[g] Sang Hyuk Im,[e] Hyunjung Kim,[g] Wonmok Lee,[h] BongSoo Kim,[a] Min Jae Ko,[a] Dae Sung Chung,[b] and Hae Jung Son[acf]**

[a] *Photoelectronic Hybrid Research center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea, E-mail: hjson@kist.re.kr*

[b] *School of Chemical Engineering and Material Science, Chung-Ang University, Seoul 06974, Republic of Korea, E-mail: dchung@cau.ac.kr*

[c] *University of Science and Technology (UST), Daejeon 34113, Republic of Korea*

[d] *Department of Chemistry, Korea University, Seoul 06974, Republic of Korea*

[e] *Functional Crystallization Center (FCC), Department of Chemical Engineering, Kyung Hee University, Yongin-si 17104, Gyeonggi-do, Republic of Korea*

[f] *Green School (School of Energy and Environment), Korea University, Seoul 02792, Republic of Korea*

[g] *Department of Physics, Sogang University, Seoul 04107, Republic of Korea*

[h] *Department of Chemistry, Sejong University, Seoul 05006, Republic of Korea*

General

All of the chemicals were purchased from Aldrich and used without further purification unless stated otherwise. Tetrahydrofuran (THF) and toluene were distilled before use with sodium metal using benzophenone as an indicator. $PC_{71}BM$, 4-bromo-7-(5′-hexyl-[2,2′-bithiophen]-5-yl)benzo-[*c*][1,2,5]thiadiazole (3), 4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene (7), and 7,7′-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene-2,6-diyl)bis(6-fluoro-4-(5′-hexyl-[2,2′-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole) (2F) were purchased from 1-Material Inc.. 4,7-Dibromo-5-

fluorobenzo[*c*][1,2,5]thiadiazole (2) was purchased from TCI and 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (5) was purchased from Sunatech. (5′-hexyl-[2,2′-bithiophene]-5-yl)trimethylstannane (1) and 4-bromo-5-fluoro-7-(5′-hexyl-[2,2′-bithiophen]-5-yl)benzo-[*c*][1,2,5]thiadiazole (4) were synthesized according to previous reports.[S1,S2]

Characterization methods

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Ascend 400 spectrometer. The NMR peaks of each compound were assigned with chemical shifts (δ: ppm) and spectral splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Microwave reactions were performed by a microwave initiator (Biotage). UV-visible (UV-vis) absorption spectra were obtained using an UV/vis spectrometer (Lambda 35, PerkinElmer) over the wavelength from 300 nm to 900 nm. The cyclicvoltammetry (CV) was performed using a CH instruments electrochemical analyzer to study electrochemical properties of the small molecules. Pt disk electrode was used as a working electrode and a platinum (Pt) wire as a counter electrode. A 0.1M deoxygenated tetra-butylammonium hexafluorophosphate (Bu_4NPF_6) solution in dichloromethane was used as an electrolyte at a scan rate of 50mV/s. All potentials were performed versus Ag/AgCl reference electrode. The redox potential of ferrocene/ferrocenium (Fc/Fc+) was used to calibrate under the same conditions. The thermal properties were carried out by a thermogravimetric analysis (TGA, TA instruments Q50 thermal analysis). Atomic force microscopy (AFM) was measured by using an XE-100 (Park system) in a non-contact mode. Transmission electron microscopy (TEM) images were recorded on a FEI (Tecnai F20 G^2). TEM samples were prepared from spin coating the blend solution on ITO/PEDOT:PSS substrate, and then floating the film in water, followed by lifting on a carbon-coated square mesh copper grid. Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed with trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile

(DCTB) as a matrix. Elemental analyses were measured on a FLASH 2000 (Thermo SCIENTIFIC, England).

Synthesis

(5′-Hexyl-[2,2′-bithiophene]-5-yl)trimethylstannane (1)

5-Bromo-5′-hexyl-2,2′-bithiophene (2.01g, 6.11mmol) was dissolved in anhydrous THF (50 mL) under Argon atmosphere. The solution was cooled to -78 °C and n-BuLi (1.6 M in hexane, 4.56 mL, 7.30 mmol) was added dropwise. The reaction mixture was stirred for 2 h at -78 °C and then, a trimethyltinchloride solution(1.0 M in hexane, 8 mL, 8 mmol) was rapidly injected to the solution. After stirring for another 1h at -78°C, the reaction mixture was warmed to R.T. and stirred overnight. This reaction was then quenched with D.I. water and extracted with diethyl ether three times. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. After vacuum drying, dark blue oil compound (1) was obtained (2.26g, 89.6%) The compound (1) was used in the next reaction without further purification.

^{1}H NMR ($CDCl_3$), δ (ppm) : 7.21 (d, 1H), 7.07 (d, 1H), 6.97 (d, 1H), 6.67 (d, 1H), 2.78 (t, 2H), 1.64-1.72 (m, 2H), 1.29-1.40 (m, 6H), 0.90 (t, 3H), 0.38 (s, 9H)

^{13}C NMR ($CDCl_3$), δ (ppm) : 145.2, 143.7, 136.7, 135.9, 135.1, 124.8, 124.4, 123.3, 31.71, 30.30, 28.91, 22.72, 14.22, -8.10.

4-Bromo-5-fluoro-7-(5′-hexyl-[2,2′-bithiophene]-5-yl)benzo[*c*][1,2,5]thiadiazole (4)

Compound (1) (1.52 g, 3.68 mmol), 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (2) (1.15 g, 3.68 mmol), $Pd[PPh_3]_4$ (212.6 mg, 0.184 mmol), and degassed toluene (52.6 mL) were placed in a two-neck flask under argon protection. The reaction mixture was stirred at 80 °C for 40 h and cooled to room temperature. The reaction mixture was concentrated in vacuo to give the crude product that was purified by column chromatography using a hexane/toluene (3:1) to give an orange solid compound (4) (623 mg, 35.1%).

^{1}H NMR ($CDCl_3$), δ (ppm) : 8.04 (d, 1H), 7.68 (d, 1H), 7.18 (d, 1H), 7.12 (d, 1H), 6.73(d, 1H), 2.83 (t, 2H), 1.66-1.74 (m, 2H), 1.28-1.42 (m, 6H), 0.90 (t, 3H).

^{13}C NMR ($CDCl_3$), δ (ppm) : 162.0, 159.5, 154.38, 154.30, 148.9, 146.8, 141.3, 135.1, 134.1, 129.9, 127.39, 127.29, 125.2, 124.4, 123.9, 115.49, 115.19, 95.95, 95.70, 31.70, 31.65, 30.37, 28.91, 22.71, 14.22.

4-Bromo-5,6-difluoro-7-(5′-hexyl-[2,2′-bithiophene]-5-yl)benzo[*c*][1,2,5]thiadiazole (6)

Compound (1) (265 mg, 0.641 mmol), 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (5) (465.8 mg, 1.26 mmol), Pd[PPh_3]$_4$ (37 mg, 0.032 mmol), and degassed toluene (12.6 mL) were placed in a microwave tube under argon protection. The reaction mixture was heated to 160 °C for 1h and cooled to room temperature. The reaction mixture was concentrated in vacuo to give the crude product that was purified by column chromatography using a hexane/toluene (2:1) to give an orange solid compound (6) (194 mg, 60.5%).

^{1}H NMR ($CDCl_3$), δ (ppm) : 8.19 (d, 1H), 7.23 (dd, 1H), 7.16 (d, 1H), 6.74 (d, 1H), 2.82 (t, 2H), 1.67-1.74 (m, 2H), 1.3-1.41 (m, 6H), 0.90 (t, 3H).

^{13}C NMR ($CDCl_3$), δ (ppm) : 153.77, 153.58, 151.22, 151.02, 150.36, 150.16, 149.99, 149.93, 147.76, 147.68, 147.56, 146.89, 142.20, 142.13, 134.0, 132.46, 132.36, 129.01, 125.2, 124.4, 123.2, 113.37, 113.25, 96.62, 96.40, 31.71, 31.64, 30.4, 28.9, 22.7, 14.2.

4,4-Bis(2-ethylhexyl)-2-(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene (8)

4,4-Bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene (7) (2.1 g, 5.01 mmol) was dissolved in anhydrous THF (50 mL) under argon atmosphere. The solution was cooled to -78 °C and n-BuLi (1.6 M in hexane, 3.26 mL, 5.12 mmol) was added dropwise. The reaction mixture was stirred for 20 min at -78 °C, then warmed to R.T.. After 1 h stirring, the reaction flask was again cooled to -78 °C and a trimethyltinchloride solution (1.0 M in hexane, 5.3 mL, 5.3 mmol) was rapidly injected to the solution. The reaction mixture was warmed to R.T. and stirred overnight. The reaction was then quenched with D.I. water and extracted with diethyl ether three times. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. After vacuum drying, a dark blue oil compound **(8)** was obtained (2.70g, 92.5%). The compound (8) was used in the next reaction without further purification.

^{1}H NMR ($CDCl_3$), δ (ppm) : 7.15 (d, 1H), 7.07 (s, 1H), 7.02 (d, 1H), 1.37-1.45 (m, 2H), 1.51-1.31 (m, 16H), 0.87-0.99 (m, 4H), 0.74-0.83 (m, 12H), 0.37 (s, 9H).

^{13}C NMR ($CDCl_3$), δ (ppm) : 154.5, 149.1, 145.8, 143.3, 140.1, 138.1, 134.3, 132.3, 36.16, 36.08, 35.87, 35.84, 29.12, 29.08, 23.15, 17.9, 14.31, 14.29, 10.98, -7.99.

4-(4,4-Bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene-2-yl)-5-fluoro-7-(5′-hexyl-[2,2′-bithiophene]-5-yl)benzo[*c*][1,2,5]thiadiazole (9)

Compound (4) (615 mg, 1.28 mmol), compound (8) (891.2 mg, 1.532 mmol), $Pd[PPh_3]_4$ (73.8 mg, 0.063 mmol), and degassed toluene (8 mL) were placed in a microwave tube under argon protection. The reaction mixture was heated to 160 °C for 1h and cooled to room temperature. After the reaction was completed, the mixture was extracted with ethyl acetate and washed with brine. Organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product then was purified by column chromatography using a hexane/CH_2Cl_2 (19:1) to give a dark blue oil compound (9) (864 mg, 82.6%).

^{1}H NMR ($CDCl_3$), δ (ppm) : 8.28 (t, 1H), 8.03 (d, 1H), 7.73 (d, 1H), 7.27 (d, 1H), 7.19 (d, 1H), 7.12 (d, 1H), 7.08 (d, 1H), 6.73 (d, 1H), 2.82 (t, 2H), 1.67 – 1.74 (m, 2H), 1.15 – 1.51 (m, 24H), 0.96 - 1.07 (m, 4H), 0.88-0.92 (m, 3H), 0.77-0.84 (m, 12H).

^{13}C NMR ($CDCl_3$), δ (ppm) : 158.6, 156.0, 152.14, 152.02, 150.77, 150.70, 148.5, 147.9, 145.2, 142.63, 142.57, 142.52, 141.8, 139.1, 134.8, 133.3, 132.33, 132.25, 132.14, 128.8, 127.8, 124.9, 123.88, 123.37, 123.26, 122.83, 122.58, 114.98, 114.66, 110.51, 110.36, 34.94, 34.91, 34.7, 34.68, 30.56, 30.45, 29.18, 27.95, 27.93, 27.86, 27.83, 27.79, 21.99, 21.97, 21.58, 16.77, 16.71, 16.63, 13.16, 13.13, 13.07, 9.80, 9.77.

4-(6-Bromo-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b′*]dithiophene-2-yl)-5-fluoro-7-(5′-hexyl-[2,2′-bithiophene]-5-yl)benzo[*c*][1,2,5]thiadiazole (10)

In a two-necked flasks under avoiding any light source, compound (9) (991 mg, 1.21 mmol) was dissolved in chloroform (92 mL). The solution was cooled to 0 °C in an ice bath and *N*-bromosuccinimide (NBS) (226.1 mg, 1.27 mmol) was added by small portions. After removing the ice bath, the reaction was stirred for 24 h at R.T.. After the reaction was completed, the mixture was extracted with chloroform and washed with brine and water. Organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product then was purified by column chromatography using a hexane/CH_2Cl_2 (19:1) to give a dark blue oil compound (10) (1.02 g, 94%). ^{1}H NMR ($CDCl_3$), δ (ppm) : 8.26 (t, 1H), 8.03 (d, 1H), 7.72 (d, 1H), 7.18 (d, 1H), 7.12 (d, 1H), 7.04 (s, 1H), 6.72 (d, 1H), 2.82 (t, 2H), 1.68-1.77 (m, 2H), 1.17-1.70 (m, 24H), 0.98-1.03 (m, 4H), 0.88-0.92 (m, 3H), 0.77-0.85 (m, 12H).

^{13}C NMR ($CDCl_3$), δ (ppm) : 159.7, 157.2, 153.0, 152.9, 151.10, 151.04, 149.52, 149.43, 146.2, 143.8, 141.9, 140.3, 135.8, 134.4, 134.08, 134.02, 133.05, 132.94, 132.5, 129.0, 124.9, 124.54, 124.44, 123.9, 123.6, 115.7, 115.4, 112.1, 111.23, 111.08, 36.06, 35.86, 31.72, 31.53, 30.3, 29.08, 29.0, 23.1, 22.7, 17.86, 17. 77, 17.68, 14.32, 14.22, 10.9.

4-(4,4-Bis(2-ethylhexyl)-6-(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b′*]dithiophene-2-yl)-5-fluoro-7-(5′-hexyl-[2,2′-bithiophene]-5-yl)benzo[*c*][1,2,5]thiadiazole (11)

Compound (10) (559 mg, 0.57 mmol, hexamethylditin (932.4 mg, 2.85 mmol), Pd[PPh_3]$_4$ (32.9 mg, 0.028 mmol), and degassed toluene (8 mL) were placed in a microwave tube under argon protection. The reaction mixture was heated to 160 °C for 1h and cooled to R.T.. After the reaction was completed, the mixture was extracted with diethyl ether and washed with brine. Organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. To remove excess hexamethylditin, the mixture was washed with 40 °C methanol thoroughly to give a viscous dark blue oil compound (11) (552 mg, 98.7%).

^{1}H NMR ($CDCl_3$), δ (ppm) : 8.29 (t, 1H), 8.02 (d, 1H), 7.72 (d, 1H), 7.18 (d, 1H), 7.14 (s, 1H), 7.12 (d, 1H), 6.72 (d, 1H), 2.82(t, 2H), 1.68-1.78 (m, 2H), 1.17-1.50 (m, 24H), 0.77-1.08 (m, 19H), 0.46 (s, 9H).

^{13}C NMR ($CDCl_3$), δ (ppm): 159.7, 157.2, 154.7, 153.3, 153.2, 152.0, 149.6, 146.3, 145.3, 143.06, 143.00, 142.90, 140.2, 139.5, 138.1, 136.1, 134.5, 133.62, 133.52, 133.40, 133.31, 128.96, 125.0, 124.38, 124.27, 123.94, 123.72, 116.11, 115.78, 111.79, 111.63, 36.17, 36.08, 35.88, 35.82, 31.73, 31.59, 30.3, 29.14, 29.08, 28.96, 23.2, 22.7, 17.99, 17.95, 14.34, 14.33, 14.23, 11.0, -8.0.

Synthesis of 0F

4-Bromo-7-(5′-hexyl-[2,2′-bithiophene]-5-yl)benzo[*c*][1,2,5]thiadiazole (3) (552.9 mg, 1.19 mmol), 4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b′*]dithiophene (12) (444 mg, 0.59 mmol), Pd[PPh_3]$_4$ (68.9 mg, 0.059 mmol), and degassed toluene (15 mL) were placed in a microwave vial under argon protection. The reaction mixture was heated at 160 °C for 1 h and cooled to room temperature. The mixture was concentrated in vacuo to give the crude product that was purified by column chromatography using a hexane/chloroform gradient. The product fraction was collected and dissolved in chloroform. The chloroform solution was then concentrated under reduced pressure, followed by precipitation using hexane. The solid was collected by filtering and washed with hexane several times. The product was dried under vacuum over 24 h to give a brown solid compound 0F (607 mg, 86%).

^{1}H NMR ($CDCl_3$), δ (ppm) : 8.19 (t, 2H), 7.99 (d, 2H), 7.78 (br s, 4H), 7.16 (d, 2H), 7.09 (d, 2H), 6.71 (d, 2H), 2.81 (t, 4H), 1.68-1.70 (m, 4H), 1.29-1.40 (m, 30H), 1.09-1.24 (m, 4H), 0.81-0.92 (m, 18H).

^{13}C NMR ($CDCl_3$), δ (ppm) : 152.68, 152.61, 146.2, 144.9, 141.3, 139.4, 137.7, 134.9, 130.8, 128.3, 126.2, 125.3, 125.2, 125.1, 124.9, 123.97, 123.88, 36.22, 35.96, 31.76, 31.72, 30.4, 29.18, 29.14, 28.94, 23.2, 22.7, 18.0, 14.36, 14.24, 11.03.

IR (neat, ν_{max} /cm^{-1}): 2958, 2922, 2869, 2854, 1727, 1707, 1631, 1581, 1532, 1487, 1463, 1441, 1426, 1358, 1242, 1179, 1098, 1054, 1001, 960, 880, 849, 791, 753, 726, 613, 518, 495, 475, 449.

MALDI-TOF MS: Calcd for $C_{64}H_{74}N_4S_8Si$ (M $^+$): 1182.34; found: 1181.08.

Elementary Analysis: Calcd for $C_{64}H_{74}N_4S_8Si$ (%): C, 64.93; H, 6.30; N, 4.73; S, 21.66; found C, 65.13; H, 6.27; N, 4.77; S, 21.27.

Synthesis of 1F

Compound (11) (532 mg, 0.54 mmol), compound (3) (263 mg, 0.56 mmol), Pd[PPh_3]$_4$ (31 mg, 0.027 mmol), and degassed toluene (7.7 mL) were placed in a microwave vial under argon protection. 1F was

then prepared using the same procedure for the synthesis of 0F to give a brown solid compound (461 mg, 70.9%).

^{1}H NMR (CDCl$_3$), δ (ppm) : 8.33 (t, 1H), 8.20 (t, 1H), 8.01-8.03 (m, 2H), 7.81-7.82 (m, 2H), 7.72 (d, 1H), 7.17-7.18 (m, 2H), 7.10-7.12 (m, 2H), 6.71-6.73 (m, 2H), 2.80-2.84 (m, 4H), 1.67-1.74 (m, 4H), 1.21-1.43 (m, 30H), 1.05-1.6 (m, 4H), 0.89-0.92 (m, 6H), 0.80-0.85 (m, 12H).

^{13}C NMR (CDCl$_3$), δ (ppm) : 159.8, 157.3, 153.3, 153.19, 152.53, 152.47, 151.99, 151.92, 150.5, 149.7, 146.4, 146.0, 145.2, 143.8, 141.4, 140.4, 139.2, 137.7, 136.2, 134.87, 134.56, 133.42, 133.32, 130.8, 129.1, 128.2, 126.1, 125.12, 125.05, 124.95, 124.73, 124.62, 124.51, 124.09, 123.88, 123.77, 116.21, 115.89, 111.67, 111.51, 36.2, 35.9, 31.74, 31.68, 30.39, 29.21, 29.12, 28.97, 23.25, 22.75, 17.9, 14.39, 14.25, 11.03.

IR (neat, v_{max} /cm^{-1}): 2954, 2922, 2868, 2854, 1733, 1710, 1629, 1568, 1530, 1491, 1460, 1441, 1360, 1345, 1268, 1251, 1179, 1163, 1100, 1050, 965, 923, 879, 825, 794, 783, 753, 724, 613, 517, 495, 472, 453, 441.

MALDI-TOF MS: Calcd for $C_{64}H_{74}N_4S_8Si$ (M $^+$): 1200.34; found: 1198.9

Elementary Analysis: Calcd for $C_{64}H_{74}N_4S_8Si$ (%): C, 63.96; H, 6.12; N, 4.66; S, 21.34; found C, 63.82; H, 6.08; N, 4.68; S, 21.30.

Synthesis of 3F

Compound (11) (552 mg, 0.56 mmol), compound (6) (267 mg, 0.53 mmol), Pd[PPh$_3$]$_4$ (31 mg, 0.027 mmol), and degassed toluene (15 mL) were placed in a microwave vial under argon protection. 3F was

then prepared using the same procedure for the synthesis of 0F to give a brown solid compound (496 mg, 71.6%).

^{1}H NMR ($C_2D_2Cl_4$, 343 K), δ (ppm) : 8.36-8.39 (m, 2H), 8.23 (d, 1H), 8.07 (d, 1H), 7.75 (d, 1H), 7.27 (d, 1H), 7.23 (d, 1H), 7.18 (d, 1H), 7.16 (d, 1H), 6.78-6.80 (m, 2H), 2.85-2.89 (m, 4H), 1.73-1.75 (m, 4H), 1.58-1.64 (m, 2H), 1.28-1.50 (m, 28H), 1.12-1.23 (m, 4H), 0.95-0.98 (m, 6H), 0.87-0.92 (m, 12H).

^{13}C NMR ($C_2D_2Cl_4$, 363 K), δ (ppm) : 159.8, 157.2, 153.2, 153.1, 152.64, 152.58, 151.29, 151.22, 151.05, 150.84, 150.62, 150.55, 150.35, 149.68, 149.63, 148.75, 148.67, 148.5, 148.26, 148.0, 146.49, 146.47, 144.66, 144.31, 141.18, 141.12, 140.4, 136.04, 136.02, 134.72, 134.65, 134.15, 134.08, 134.03, 134.00, 133.31, 133.21, 133.07, 131.57, 131.49, 123.0, 129.1, 124.93, 124.85, 124.14, 124.10, 123.8, 123.2, 116.1, 115.8, 112.0, 111.9, 111.51, 111.35, 110.83, 110.79, 110.71, 36.04, 35.88, 31.31, 31.19, 30.0, 28.98, 28.54, 22.8, 22.3, 18.1, 13.80, 13.74, 10.67.

IR (neat, v_{max} /cm^{-1}): 2954, 2918, 2869, 2850, 1725, 1707, 1629, 1574, 1489, 1463, 1439, 1365, 1340, 1246, 1177, 1102, 1050, 996, 965, 881, 814, 796, 785, 748, 724, 609, 518, 504, 476, 442.

MALDI-TOF MS: Calcd for $C_{64}H_{74}N_4S_8Si$ (M $^+$): 1236.32; found: 1235.66.

Elementary Analysis: Calcd for $C_{64}H_{74}N_4S_8Si$ (%): C, 62.10; H, 5.78; N, 4.53; S, 20.72; found C, 62.16; H, 5.79; N, 4.684 S, 20.81.

Synthesis of 4F

Compound (12) (230 mg, 0.31 mmol), compound (6) (309 mg, 0.62 mmol), Pd[PPh$_3$]$_4$ (35 mg, 0.031 mmol), and degassed toluene (15.4 mL) were placed in a microwave vial under argon protection. 4F was

then prepared using the same procedure for the synthesis of 0F to give a brown solid compound (322 mg, 82.7%).

^{1}H NMR ($C_2D_2Cl_4$, 343K), δ (ppm) : 8.38 (t, 2H), 8.25 (d, 2H), 7.28 (d, 2H), 7.20 (d, 2H), 6.79 (d, 2H), 2.88 (t, 4H), 1.73-1.80 (m, 4H), 1.56-1.62 (m, 2H), 1.28-1.48 (m, 28H), 1.12-1.24 (m, 4H), 0.94-0.98 (m, 6H), 0.86-0.91 (m, 12H).

^{13}C NMR ($C_2D_2Cl_4$, 363 K), δ (ppm) : 152.26, 152.20, 150.77, 150.42, 148.71, 148.62, 148.40, 148.18, 148.05, 146.50, 144.7, 141.31, 141.25, 141.18, 134.14, 134.05, 134.0, 133.9, 133.6, 133.56, 133.52, 131.62, 131.52, 129.99, 129.94, 129.92, 124.84, 124.13, 123.2, 111.86, 111.74, 110.97, 110.85, 36.04, 35.89, 31.31, 31.19, 30.05, 28.98, 28.55, 22.76, 22.29, 18.05, 13.79, 13.74, 10.7.

IR (neat, v_{max}/cm^{-1}): 2954, 2921, 2968, 2852, 1723, 1707, 1655, 1629, 1574, 1561, 1532, 1517, 1487, 1463, 1441, 1421, 1355, 1342, 1242, 1177, 1096, 1045, 1000, 960, 884, 849, 814, 790, 750, 726, 611, 525, 518, 506, 474, 442.

MALDI-TOF MS: Calcd for $C_{64}H_{74}N_4S_8Si$ (M^+): 1254.31; found: 1252.79

Elementary Analysis: Calcd for $C_{64}H_{74}N_4S_8Si$ (%): C, 61.21; H, 5.62; N, 4.46; S, 20.42; found C, 61.19; H, 5.58; N, 4.50 S, 20.48.

Theoretical calculation method

Density functional theory (DFT) calculations using Gaussian 09 at the B3LYP level with a 6-

311G(d,p) basis set was carried out to determine the electronic and conformation properties of the molecules. The dipole moment was calculated from the optimized structure and its magnitude and direction were designated by an arrow from the center of a cross dashed line corresponding to the center of each molecule.

OTFT device fabrication and characterization

Bottom gate / top contact OTFTs were fabricated on a common gate of highly n-doped silicon with a 100-nm-thick SiO_2 dielectric layer. The SiO_2 layer was modified with octyltrichlorosilane(OTS) by dipping in a toluene solution (1:200 v/v). Active layer solutions were prepared by dissolving 0F-4F in chloroform with the concentration of 20 mg/mL. The solutions were spin-coated on the OTS-modified Si substrate at 2000 rpm for 60 s. Au source / drain electrodes (80 nm) were thermally evaporated through a shadow mask, followed by an annealing at 80 °C for 10 min. The electrical characteristics were measured with a 4156A precision semiconductor parameter analyzer (Agilent Technologies). For all measurements, the channel widths and channel lengths were 1500 μm and 150 μm, respectively.

Charge carrier mobility measurement

Space-charge-limited current (SCLC) measurements were performed by using Keithley model 2400 source measuring unit. The single carrier diode were fabricated by using an architecture of ITO/PEDOT:PSS/active layer/Au and ITO/Al/Active layer/Al for hole-only devices and electron only devices, respectively. The *J*-*V* characteristics of the single carrier devices are fitted from Mott-Gurney law as in following equation,

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$$

where ε_0 is the permittivity of a free space, ε_r is the relative permittivity of the material, μ is the carrier mobility, and L is the film thickness of active layer. V is the effective voltage determined by $V = V_{appl} - V_r$

– V_{bi}, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes.[S3,S4]

SMs-OPV devices fabrication

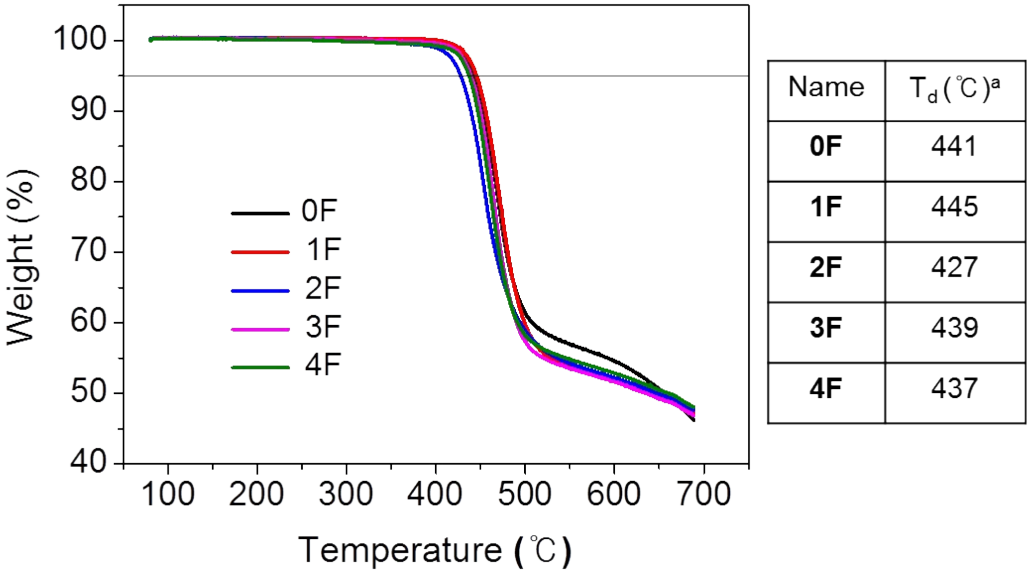
Pre-patterned indium tin oxide (ITO) glass substrates were cleaned by ultrasonication in isopropanol, acetone, and isopropanol sequentially in each step for 10 min and dried under 90 °C oven for 1 h. The ITO glass substrates were then treated with an UV/O_3 cleaner for 20 min. Next, polyethlenimine ethoxylated (PEIE) solution diluted with 2-methoxyethanol to a 0.2 wt% was spin-coated on the ITO substrate at 5000 rpm for 60 s in a N_2 filled glovebox. Active layer solution (for 0F, 1F, 2F and 4F:$PC_{71}BM$ at a weight ratio 3:2 and 3F:$PC_{71}BM$ at a weight ratio 6:5) were prepared by dissolving in a mixture of chlorobenzene and diiodooctane (DIO) (99.6:0.4 v/v). Each concentration of the blend solution was 33 mg/mL for 0F, 1F, 2F and 4F and 38 mg/mL for 3F. All of the solution were stirred on a hot plate at 90 °C for at least 3 h in order to dissolve the materials. During spin-coating, all the solutions should keep warm at 90 °C before dropping onto the substrates. After filtering the solution by using 0.45 μm PTFE filter, the active layers were spin-coated on the top of the ITO/PEIE substrate to afford an optimized thickness of 100 nm. A thin layer (4 nm) of MoO_3/100 nm Ag was thermally evaporated through a shadow mask under high vacuum to complete the devices. The active area of the fabricated devices was 0.12 cm^2.

Perovskite solar cell (PSC) devices fabrication

$CH_3NH_3PbI_3$ ($MAPbI_3$) perovskite solution was prepared according to previous report.[S5] For preparation of $MAPbI_3$ planar hybrid solar cells, about 50 nm-thick dense TiO_2 electron conductor was deposited on a top of the cleaned F-doped SnO_2 (FTO, Pilkington, TEC8) glass substrate by spray pyrolysis deposition (SPD) method with 40 mL of 20 mM of titanium diisopropoxide bis(acetylacetonate)/iso-propanol solution at 450 °C. This was repeated the spraying process about 40 times to spray 40 mL solution manually by using a glass type atomizer. A 0.1 mL of 40 wt% $MAPbI_3$/DMF solution with a HI solution (40 wt% $MAPbI_3$ solution in DMF/HI = 1 mL/0.1 mL) was then spin coated onto the TiO_2/FTO substrate at 3000 rpm for 200 s, followed by drying on a hot plate at 100 °C for 2 min in air under 35 % relative humidity. An HTM layer was prepared by 0F and 2F solution in toluene (60 mg/mL) . The HTM was formed by spin-coating at 2000 rpm for 30 s. Finally, a 60 nm-thick Au layer was formed by thermal evaporation to form the back contact. The active area was fixed to 0.16 cm^2. All precursor preparation and device fabrication were carried out under air condition and humidity of about 35%.

Solar cell measurement

The devices were characterized by using a Keithley model 2400 source meter under AM1.5G at sun light intensity (100 mW/cm^2) in ambient air. A class-A solar simulator with a 1000 W Xenon lamp (Yamashita Denso) was used as a light source. Its light intensity was calibrated by using a NREL-calibrated Si solar cell coupled with KG-5 filter. External quantum efficiencies (EQE) were recorded on incident photon-to-current conversion equipment (Mcscience), calibrated by a G425 silicon photodiode.



Name	T_d (℃)[a]
0F	441
1F	445
2F	427
3F	439
4F	437

Figure S1. TGA curves of 0F–4F with a heating rate of 10 °C/min under N_2 atmosphere.

[a] Temperatures in which 5% weight loss occurs.

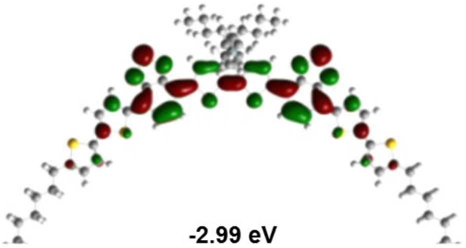
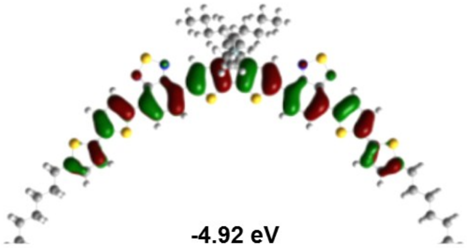
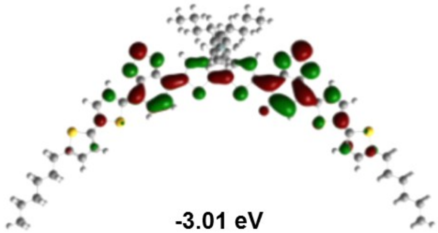
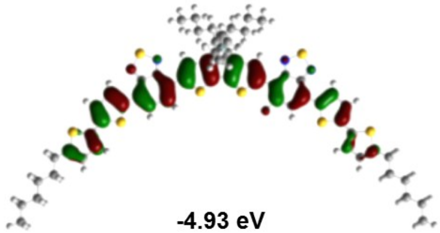
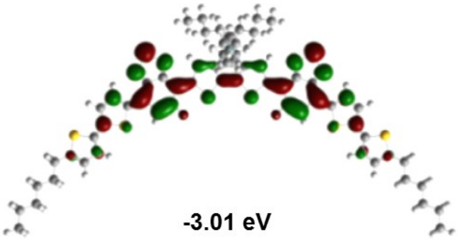
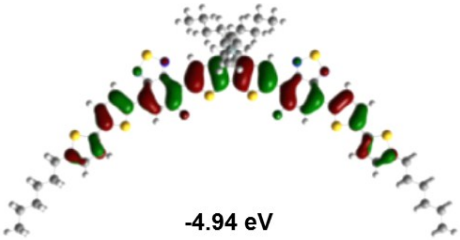
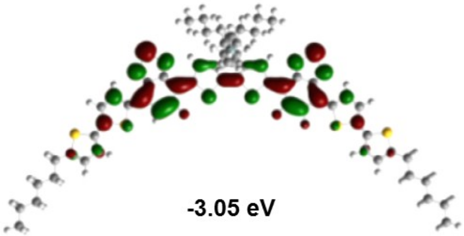
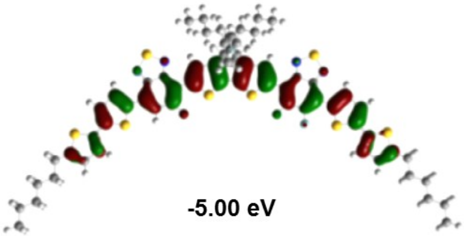
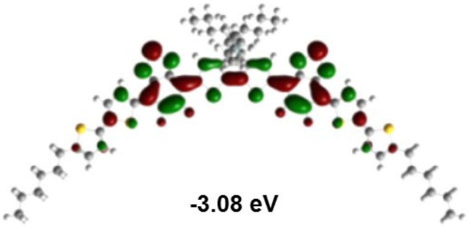
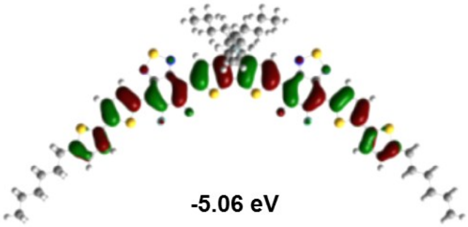
	LUMO	HOMO
0F ΔE = 1.93 eV	 -2.99 eV	 -4.92 eV
1F ΔE = 1.92 eV	 -3.01 eV	 -4.93 eV
2F ΔE = 1.93 eV	 -3.01 eV	 -4.94 eV
3F ΔE = 1.95 eV	 -3.05 eV	 -5.00 eV
4F ΔE = 1.98 eV	 -3.08 eV	 -5.06 eV

Figure S2. HOMO/LUMO energy levels and frontier molecular orbitals obtained from DFT calculations on 0F–4F with optimized geometries. ΔE is an energy bandgap of 0F–4F estimated from difference between the HOMO and LUMO values.

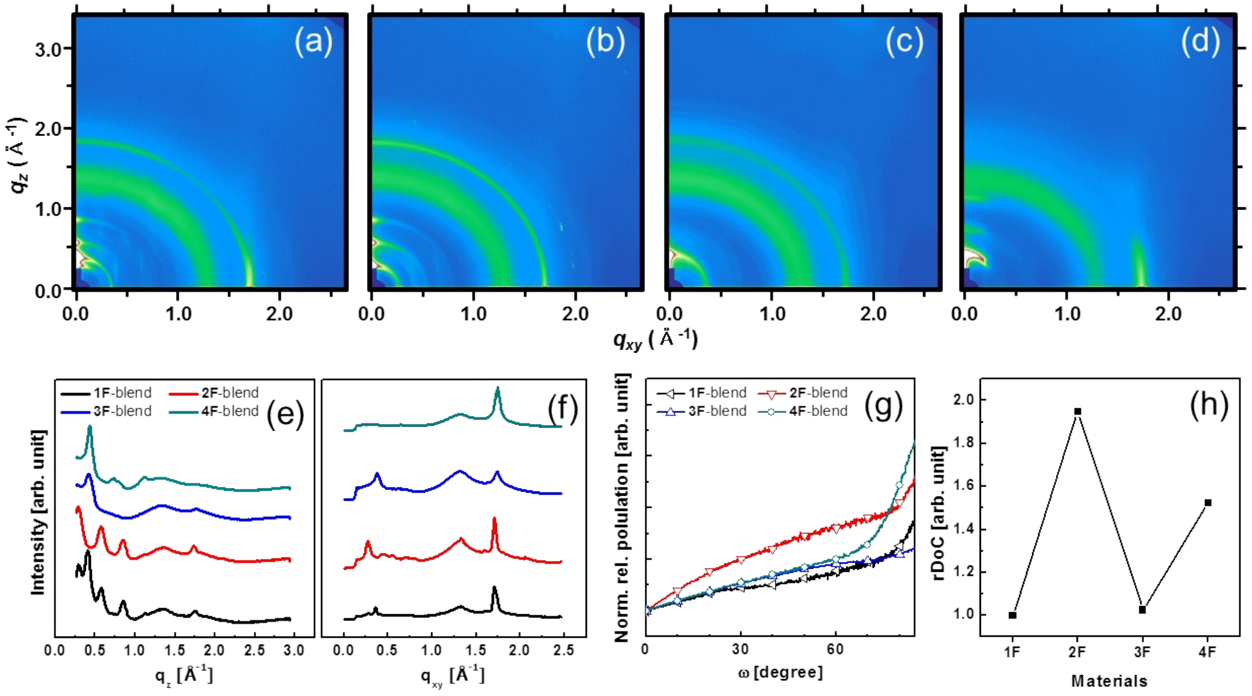


Figure S3. 2D-GIXD patterns of the compound:PC$_{71}$BM blend film of (a) 1F, (b) 2F, (c) 3F, and (d) 4F, GIXD patterns in (e) out-of-plane and (f) in-plane directions, (g) the pole figures multiplied by a factor of sin ω, and (h) the relative degree of crystallinity(rDoC) as a function of the number of fluorine substitutions.

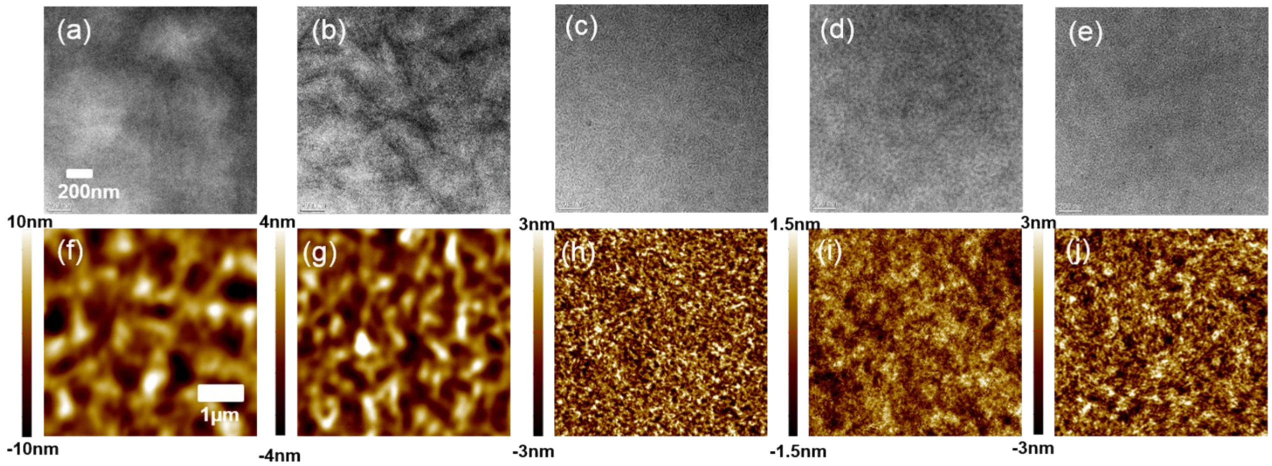


Figure S4. TEM and AFM topography images of the compound:$PC_{71}BM$ blend film of (a,f) 0F, (b,g) 1F, (c,h) 2F, (d,i) 3F, and (e,j) 4F.

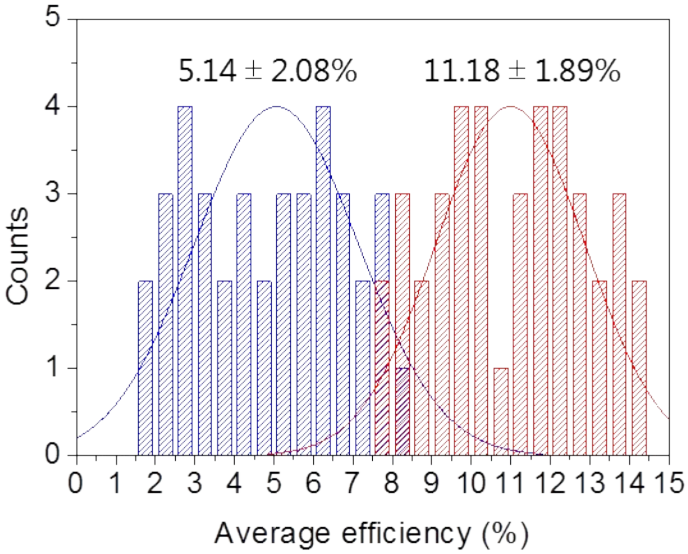


Figure S5. Histograms of efficiencies of the perovskite solar cells based on 0F (blue) and 2F (red).

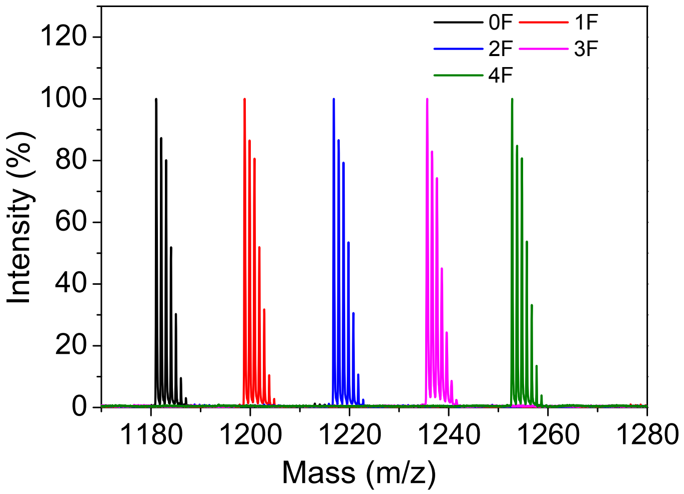


Figure S6. MALDI-TOF mass spectrum of 0F, 2F, 1F, 3F, and 4F.

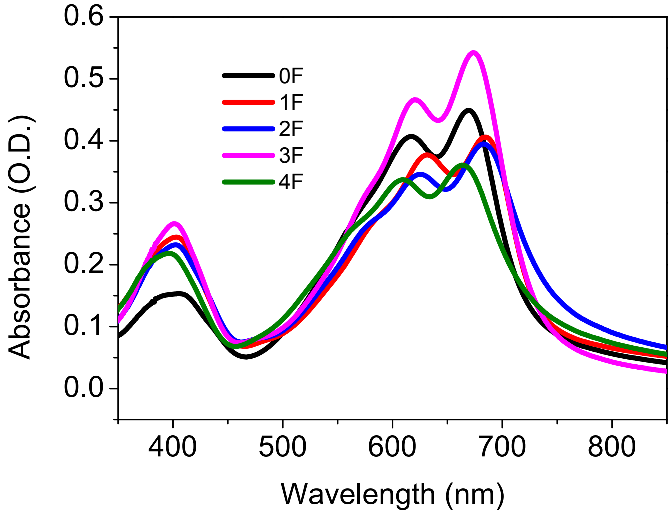


Figure S7. Pristine UV-visible absorption spectra of 0F–4F. The thickness of each film was around 70 ± 3 nm

Reference

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