

## **Supporting Information**

### **High Performance n-Type Organic Thin-Film Transistors Based on Solution-Processable Perfluoroalkyl-Substituted C<sub>60</sub> Derivatives**

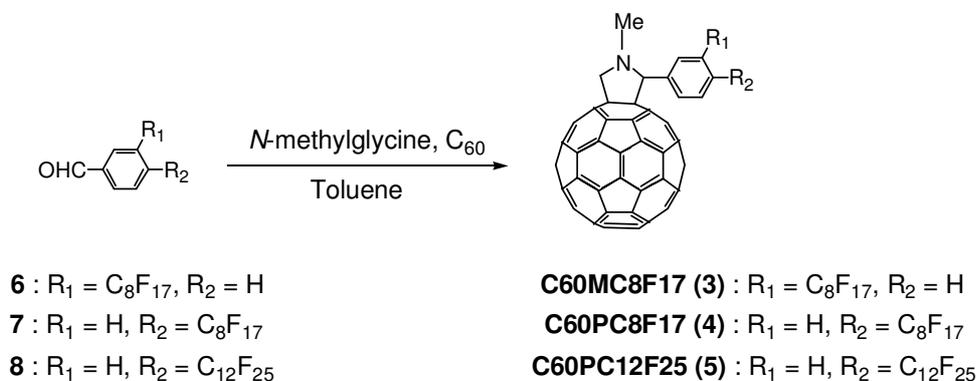
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## Materials and Measurement.

[6,6]-phenyl C61-butyric acid methyl ester (PCBM) was purchased from Frontier Carbon Corporation. Perfluoroalkylbenzaldehydes **6-8** were prepared according to the previously reported procedure (Scheme S1).<sup>S1</sup> Perfluoroalkyl-substituted C<sub>60</sub> derivatives **3-5** were synthesized by the Prato reaction.<sup>S2</sup> C<sub>60</sub>-fused *N*-methylpyrrolidine-*meta*-dodecyl phenyl (C60MC12) was also synthesized by the Prato reaction and reported elsewhere.<sup>S3,S4</sup> Separation of C<sub>60</sub> derivatives from the crude products was performed by high performance liquid chromatography (LC-9104, Japan Analytical Industry Co.) with a Cosmosil Buckyprep Packed Column (Nacalai Tesque Co.) and an UV detector (wavelength: 340nm). C<sub>60</sub> derivatives were purified by a recycling mode of high performance liquid chromatography (HPLC) until only single peak was observed on the chromatogram. <sup>1</sup>H NMR spectra were recorded on a JEOL GSX270 spectrometer, and chemical shift values were given in parts per million (ppm) relative to internal tetramethylsilane. Elemental analyses were performed by Center for Organic Elemental Microanalysis (Kyoto University). Fast atom bombardment mass spectra (FAB-MS) were recorded on a JEOL MS 600H spectrometer using 3-nitrobenzylalcohol as a matrix.

Electrochemical properties of C<sub>60</sub> derivatives were investigated by cyclic voltammetry (CV) using Potentiostat/Galvanostat Model 273A (EG&G PRINCETON APPLIED RESEARCH). The experiments were performed in anhydrous *o*-dichlorobenzene (ODCB) containing tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>, 0.05 M) as the supporting electrolyte at a scan rate of 100 mV/s. A platinum work electrode, platinum counter electrode and Ag/AgCl reference electrode were employed. The ferrocene/ferrocinium (Fc/Fc<sup>+</sup>, E<sub>1/2</sub> = 0.62 V in our system) was used as an internal reference for all measurements.



**Scheme S1.** Synthesis of C<sub>60</sub> derivatives.

**C60-fused *N*-methylpyrrolidine-*meta*-perfluorooctyl phenyl (C60MC8F17, 3).** A mixture of *N*-methylglycine (135 mg, 1.51 mmol), 3-perfluorooctylbenzaldehyde **6** (725 mg, 1.38 mmol) and C<sub>60</sub> (1.00 g, 1.39 mmol) was refluxed in toluene (350 mL) under N<sub>2</sub> atmosphere for 22 h. The crude product was separated and purified by HPLC with Cosmosil Buckyprep Packed Column (Nacalai Tesque Co.). After vacuum evaporation of the solvent, C60MC8F17 was obtained as a brown solid in 9% yield (152 mg, 0.12 mmol). <sup>1</sup>H NMR(270 MHz, CDCl<sub>3</sub>) δ 2.82 (s, 3H), 4.31 (d, *J* = 9.7 Hz, 1H), 5.016 (d, *J* = 9.2 Hz, 1H), 5.020 (s, 1H), 7.58 (d, *J* = 5.1 Hz, 2H), 8.06 (d, *J* = 27.3 Hz, 2H). Anal. Calc. For C<sub>77</sub>H<sub>10</sub>F<sub>17</sub>N: C, 72.71; H, 0.79; N, 1.10. Found: C, 73.20; H, 1.11; N, 1.05%. MS (FAB) *m/z* 1271(M<sup>+</sup>).

**C60-fused *N*-methylpyrrolidine-*para*-perfluorooctyl phenyl (C60PC8F17, 4).** A mixture of *N*-methylglycine (214 mg, 2.40 mmol), 4-perfluorooctylbenzaldehyde **7** (1.13 g, 2.16 mmol) and C<sub>60</sub> (506 mg, 0.70 mmol) was refluxed in toluene (300 mL) under N<sub>2</sub> atmosphere for 19 h. The crude product was separated and purified by HPLC with Cosmosil Buckyprep Packed Column (Nacalai Tesque Co.). After vacuum evaporation of the solvent, C60PC8F17 was obtained as a brown solid in 17% yield (153 mg, 0.12 mmol). <sup>1</sup>H NMR(270 MHz, CDCl<sub>3</sub>) δ 2.82 (s, 3H), 4.31 (d, *J* = 9.7 Hz, 1H), 5.017 (d, *J* = 9.7 Hz, 1H), 5.019 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.97 (s, 2H). Anal. Calc. For C<sub>77</sub>H<sub>10</sub>F<sub>17</sub>N: C, 72.71; H, 0.79; N, 1.10. Found: C, 72.81; H, 0.79; N, 1.07%. MS (FAB) *m/z* 1271(M<sup>+</sup>).

**C60-fused *N*-methylpyrrolidine-*para*-perfluorododecyl phenyl (C60PC12F25, 5).** A mixture of *N*-methylglycine (41 mg, 0.46 mmol), 4-perfluorododecylbenzaldehyde **8** (304 mg, 0.42 mmol) and C<sub>60</sub> (298 mg, 0.41 mmol) was refluxed in toluene (200 mL) under N<sub>2</sub> atmosphere for 19 h. The crude product was separated and purified by HPLC with Cosmosil Buckyprep Packed Column (Nacalai Tesque Co.). After vacuum evaporation of the solvent, C60PC12F25 was obtained as a brown solid in 28% yield (168 mg, 0.11 mmol). <sup>1</sup>H NMR(270 MHz, CDCl<sub>3</sub>) δ 2.82 (s, 3H), 4.30 (d, *J* = 9.7 Hz, 1H), 5.007 (d, *J* = 9.2 Hz, 1H), 5.011 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H). Anal. Calc. For C<sub>81</sub>H<sub>10</sub>F<sub>25</sub>N: C, 66.10; H, 0.68; N, 0.95. Found: C, 66.06; H, 0.69; N, 0.72%. MS (FAB) *m/z* 1471(M<sup>+</sup>).

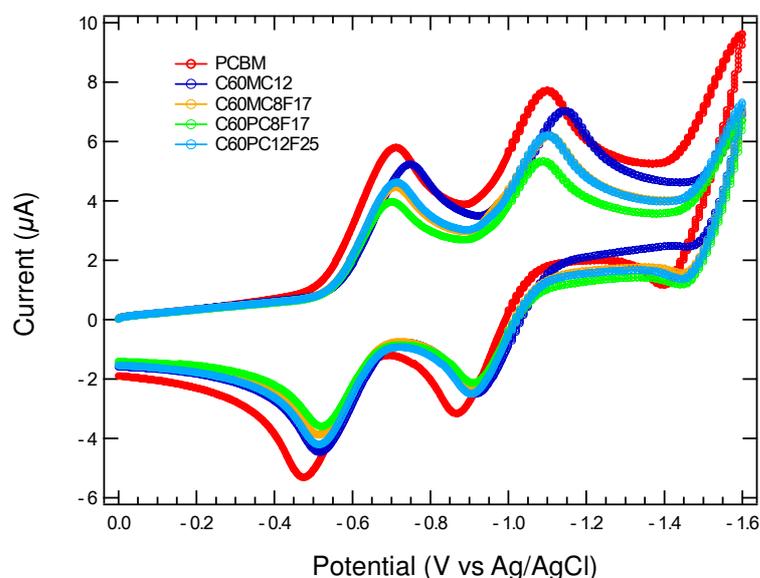
#### References:

- S1. Pozzi, G.; Colombani, I.; Miglioli, M.; Montanari, F.; Quici, S. *Tetrahedron* **1997**, *53*, 6145.
- S2. Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
- S3. Chikamatsu, M.; Nagamatsu, S.; Yoshida, Y.; Saito, K.; Yase, K.; Kikuchi, K. *Appl. Phys. Lett.* **2005**, *87*, 203504.
- S4. Chikamatsu, M.; Itakura, A.; Yoshida, Y.; Azumi R.; Kikuchi, K.; Yase, K. *J. Photoch. Photobio.*

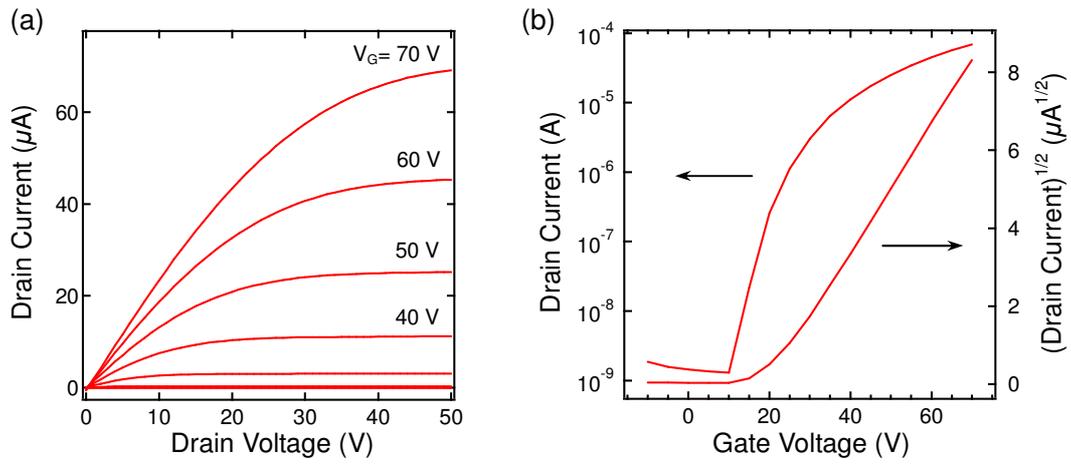
### Device Fabrication and Thin Film Characterization.

The devices were constructed on a highly doped p-type silicon wafer covered with 300-nm thick SiO<sub>2</sub> (a capacitance per unit area of 10 nF/cm<sup>2</sup>). The SiO<sub>2</sub> surface was treated with hexamethyldisilazane (HMDS). Each of C<sub>60</sub> derivatives (**1-5**) was dissolved in chloroform (10 mg/ml), filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter, spin-coated at 2000 rpm. Finally, gold source and drain electrodes were deposited on the films by using a resistive heating evaporation source. A nickel thin-plate patterned with channel lengths (*L*) of 20 μm and channel widths (*W*) of 5 mm was used as a metal shadow mask. For the measurement of the TFT characteristics, Au wires were connected to the device electrodes using silver paste. The devices annealed at 373 K for 15 hours in a vacuum. The TFT characteristics were measured with Keithley 6430 and 2400 source measurement units in a vacuum (10<sup>-6</sup>~10<sup>-7</sup> Torr) and air at room temperature. The field-effect mobility  $\mu$  and the threshold voltage  $V_T$  were estimated from the square root of drain current-gate voltage ( $I_D^{1/2}$ - $V_G$ ) plots, according to the standard equation in the saturation regime,  $I_D = (W/2L) \mu C_i (V_G - V_T)^2$ , where  $I_D$  is the drain current,  $W$  and  $L$  are the conduction channel width and length, respectively,  $C_i$  is the capacitance per unit area of gate dielectric,  $V_G$  is the gate voltage.

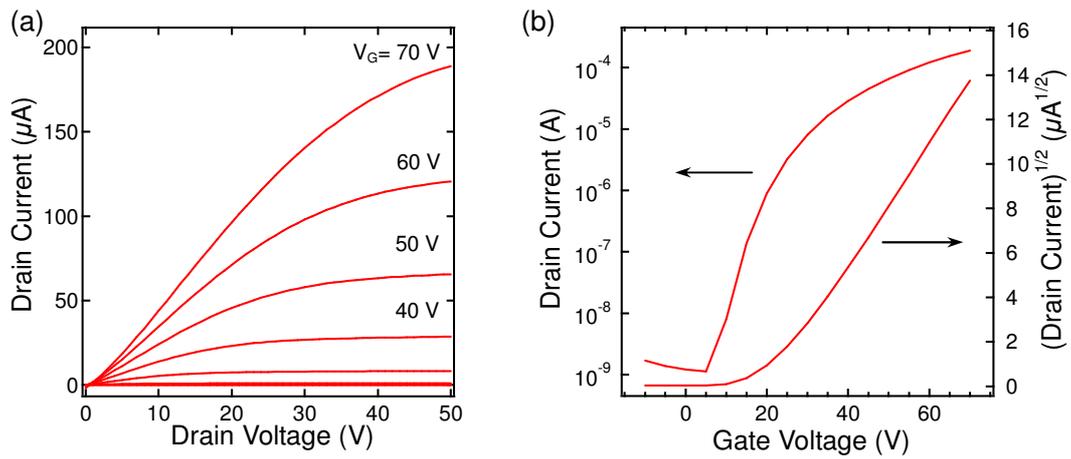
X-ray diffraction (XRD) measurement of the spin coated films was carried out on a Rigaku Denki RU-300 using Cu  $K\alpha$  radiation (40 kV, 200 mA) with a curved graphite monochromator. The diffractions were measured from 2° to 30° in the  $\theta$ -2 $\theta$  scan mode with 0.01°-step in 2 $\theta$  and 1°/min.



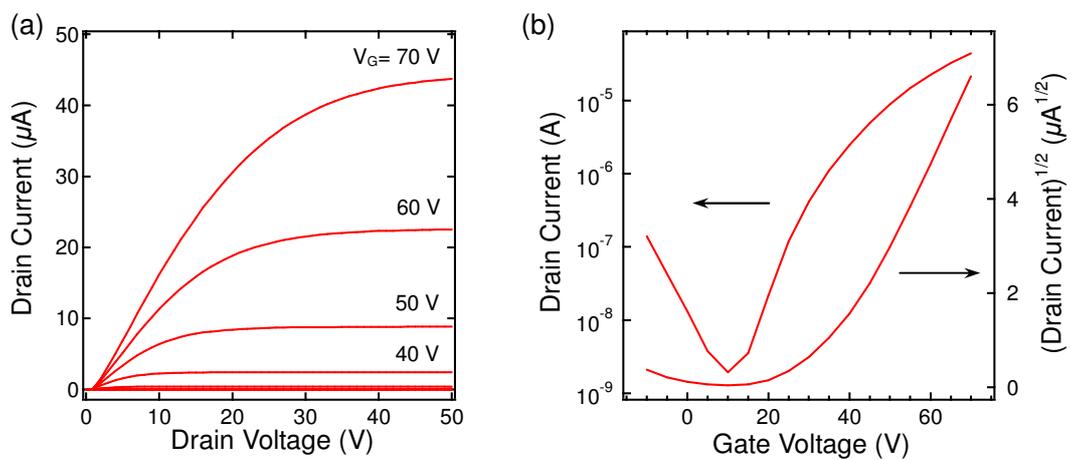
**Figure S1.** Cyclic voltammograms of PCBM, C60MC12, C60MC8F17, C60PC8F17 and C60PC12F25.



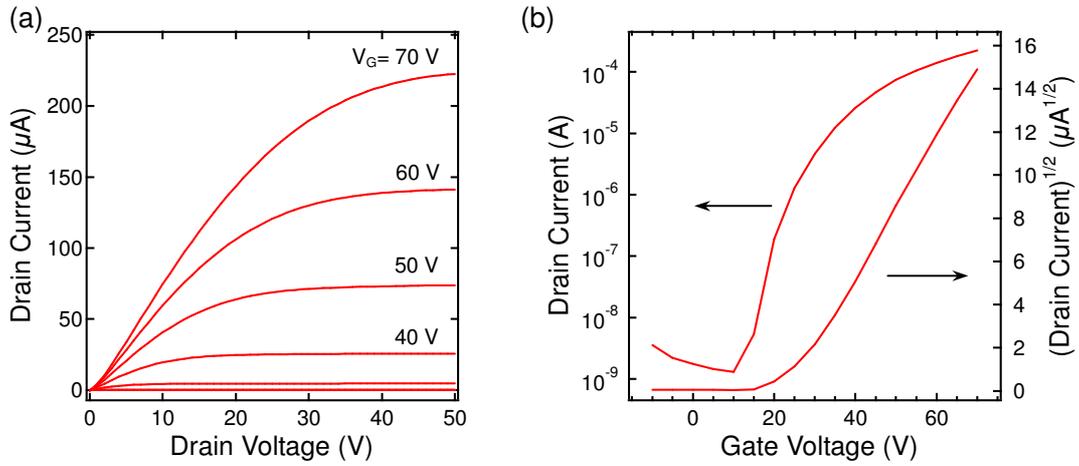
**Figure S2.** Output (a) and transfer (b) characteristics of a TFT based on C60MC8F17 in a vacuum.



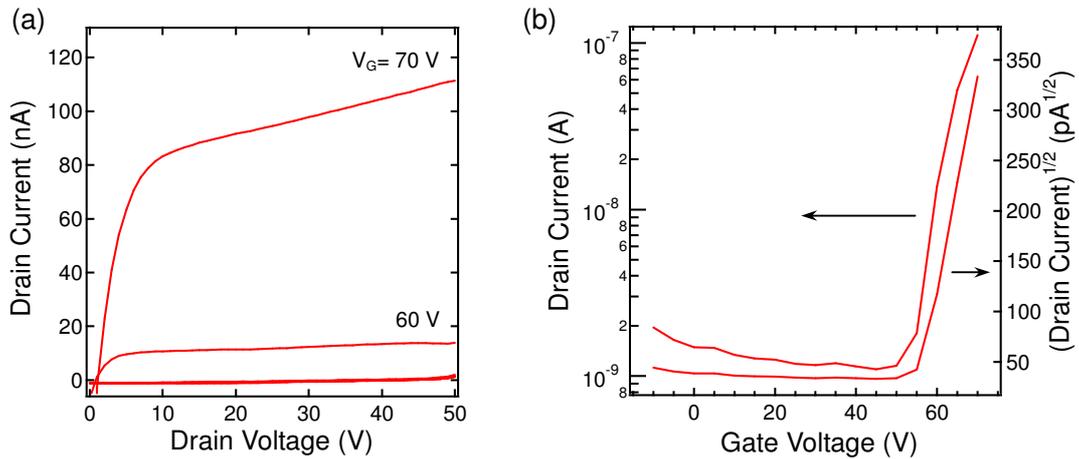
**Figure S3.** Output (a) and transfer (b) characteristics of a TFT based on C60PC8F17 in a vacuum.



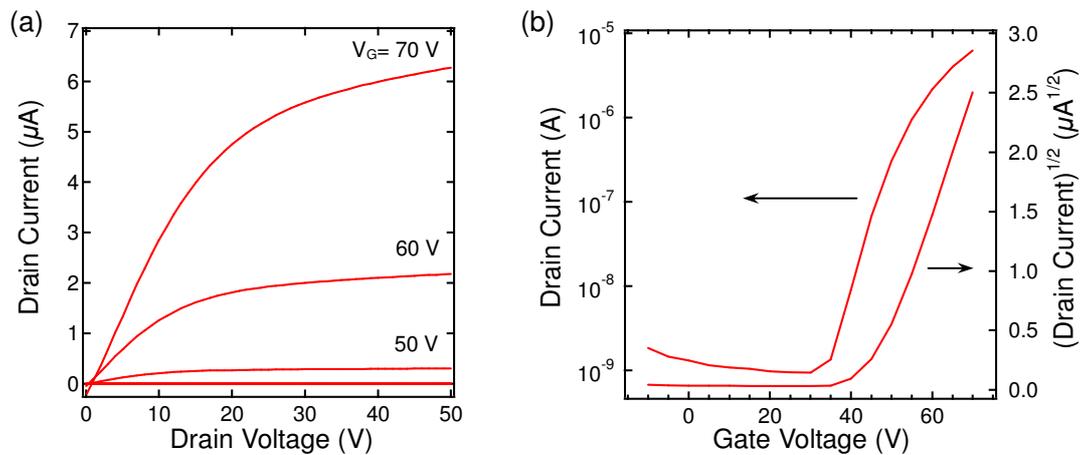
**Figure S4.** Output (a) and transfer (b) characteristics of a TFT based on PCBM in a vacuum.



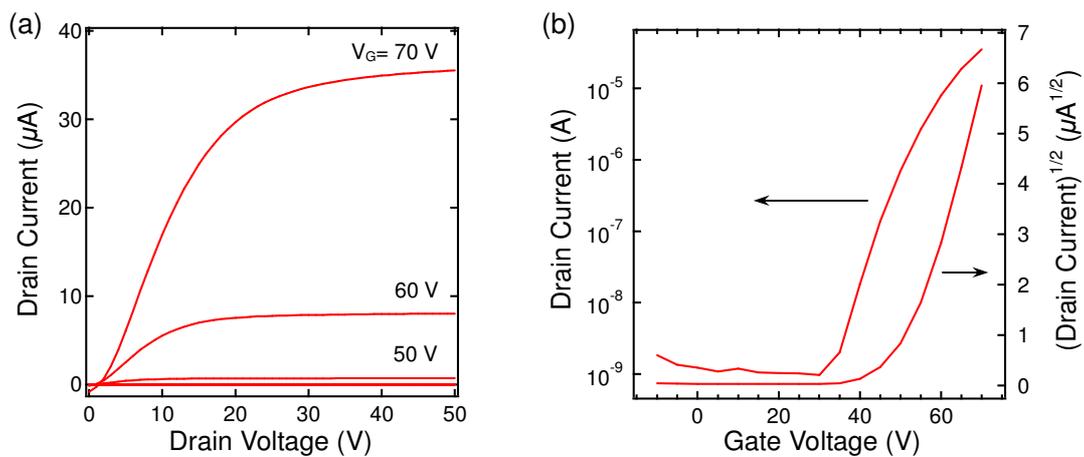
**Figure S5.** Output (a) and transfer (b) characteristics of a TFT based on C60MC12 in a vacuum.



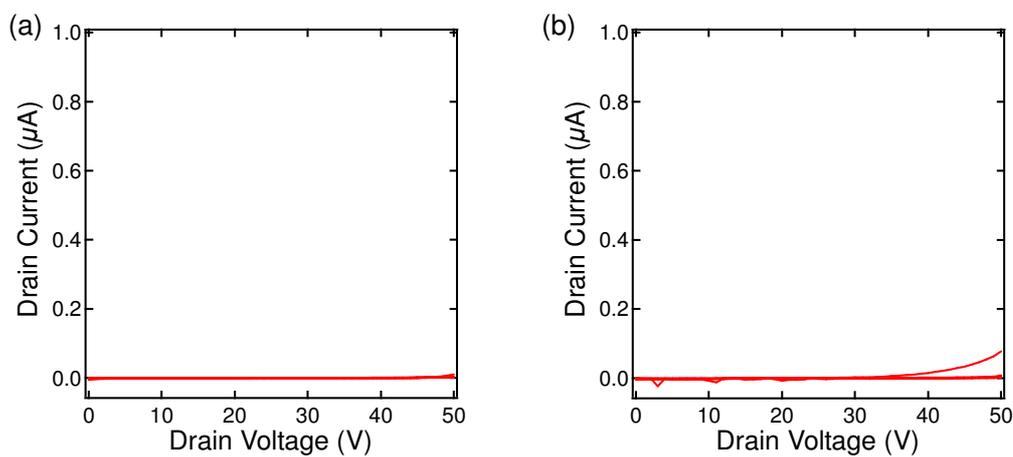
**Figure S6.** Output (a) and transfer (b) characteristics of a TFT based on C60MC8F17 (3) in air (after exposure to air for 5 hours).



**Figure S7.** Output (a) and transfer (b) characteristics of a TFT based on C60PC8F17 (4) in air (after exposure to air for 5 hours).



**Figure S8.** Output (a) and transfer (b) characteristics of a TFT based on C60PC12F25 (5) in air (after exposure to air for 5 hours).



**Figure S9.** Output characteristics of TFTs based on (a) PCBM after exposure to air for 10 minutes and (b) C60MC12 after exposure to air for 2 hours.