

# Supporting Information

## Perfluoropentacene: High-Performance p-n Junctions and Complementary Circuits with Pentacene

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**General.** Melting points were obtained on a Büchi melting point apparatus B-540.  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on a JEOL JNM-LA 500 at 500 and 470.4 MHz, respectively. Chemical shifts were reported as  $\delta$  values (ppm) relative to internal tetramethylsilane ( $^1\text{H}$  NMR) or hexafluorobenzene ( $^{19}\text{F}$  NMR). EI mass spectra were collected on a Shimadzu GCMS-QP5050A at 70 eV. UV-vis spectra were recorded on a JASCO V-570 spectrophotometer. Emission spectra were collected on a JASCO FP-6600 spectrofluorophotometer. Differential pulse voltammetries were recorded on a BAS-100B/W electrochemical analyzer. Analytical TLCs were performed on commercial Merck plates coated with silica gel 60 F254. Flash chromatographic separations were carried out on Fuji Silysia FL60D.

**Materials.** Tetrafluorophthalic anhydride (**1**) was prepared by the reaction of tetrafluorophthalic acid with acetyl chloride and purified by sublimation in vacuo at 110 °C. Anhydrous ether was used as received from Kanto Chemicals Co.  $\text{SF}_4$  and HF were obtained from Kanto Denka Kogyo Co. and Morita Chemical Industry Co., respectively. Bromopentafluorobenzene and 2-methoxyfuran were distilled before use. All other reagents and solvents were used without further purification.

**1,2,3,4-Tetrafluoro-5,8-dihydroxyanthraquinone (2).** A mixture of  $\text{AlCl}_3$  (100 g, 750 mmol) and NaCl (20.0 g, 342 mmol) was stirred at 135 °C. To the molten salt was added a mixture of hydroquinone (15.3 g, 139 mmol) and **1** (23.4 g, 106 mmol). The reaction mixture was heated at 200 °C for 1 h, cooled to room temperature, and poured into 1M HCl. After being stirred at 100 °C for 1 h, the red suspension was filtered, washed with  $\text{H}_2\text{O}$ , and dried in vacuo to give a red solid. This was recrystallized from 1,2-dichlorobenzene to afford **2** as red needles (23.6 g, 71%): mp 240-241 °C (lit.<sup>1</sup> mp 230 °C);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  27.12 (d,  $J$  = 7.8 Hz, 2F), 19.02 (d,  $J$  = 7.8 Hz, 2F);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  12.74 (s, 2H), 7.36 (s, 2H); MS  $m/z$  312 ( $\text{M}^+$ , 100).

**5,6,7,8-Tetrafluoro-9,10-dihydroxy-2,3-dihydroanthracene-1,4-dione (3).**<sup>2</sup> To a stirred suspension of **2** (43.0 g, 138 mmol), tin powder (32.8 g, 276 mmol), and acetic acid (350 mL) was added dropwise 37% HCl (80 mL). The reaction mixture was refluxed overnight, cooled to room temperature, and poured into  $\text{H}_2\text{O}$ . The resulting yellow suspension was filtered, washed with 1M HCl and  $\text{H}_2\text{O}$ , and dried in vacuo to afford **3** as a yellow solid (41.4 g, 95%): mp 258-259 °C;  $^{19}\text{F}$  NMR

(CDCl<sub>3</sub>)  $\delta$  26.21 (d,  $J$  = 12.1 Hz, 2F), 12.33 (d,  $J$  = 12.1 Hz, 2F); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  14.04 (s, 2H), 3.10 (s, 4H); MS  $m/z$  314 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>14</sub>H<sub>6</sub>F<sub>4</sub>O<sub>4</sub>: C, 53.52; H, 1.92. Found: C, 53.28; H, 1.87.

**1,2,3,4,8,9,10,11-Octafluoro-5,7,12,14-tetrahydroxypentacene-6,13-dione (4).** A mixture of AlCl<sub>3</sub> (1.53 g, 11.5 mmol) and NaCl (10.0 g, 171 mmol) was stirred at 135 °C. To the molten salt was added a mixture of **1** (5.75 g, 26.1 mmol) and **3** (9.84 g, 31.3 mmol). The reaction mixture was heated at 280 °C for 1 h, cooled to room temperature, and poured into 1M HCl. After being stirred at 100 °C for 1 h, the suspension was filtered, washed with methanol, CH<sub>2</sub>Cl<sub>2</sub>, hot toluene, and ether. The resulting solid was dried in vacuo to give **4** as a dark brown powder (11.5 g, 85%). An analytical sample was obtained by sublimation in vacuo at 320 °C: mp > 300 °C; MS  $m/z$  516 (M<sup>+</sup>, 100), 258 (M<sup>2+</sup>, 29.0). Anal. Calcd for C<sub>22</sub>H<sub>4</sub>F<sub>8</sub>O<sub>6</sub>: C, 51.18; H, 0.78. Found: C, 51.40; H, 1.07.

**1,2,3,4,5,5,6,6,7,7,8,9,10,11,12,12,13,13,14,14-Icosafluoro-5,6,7,12,13,14-hexahdropentacene (5).**

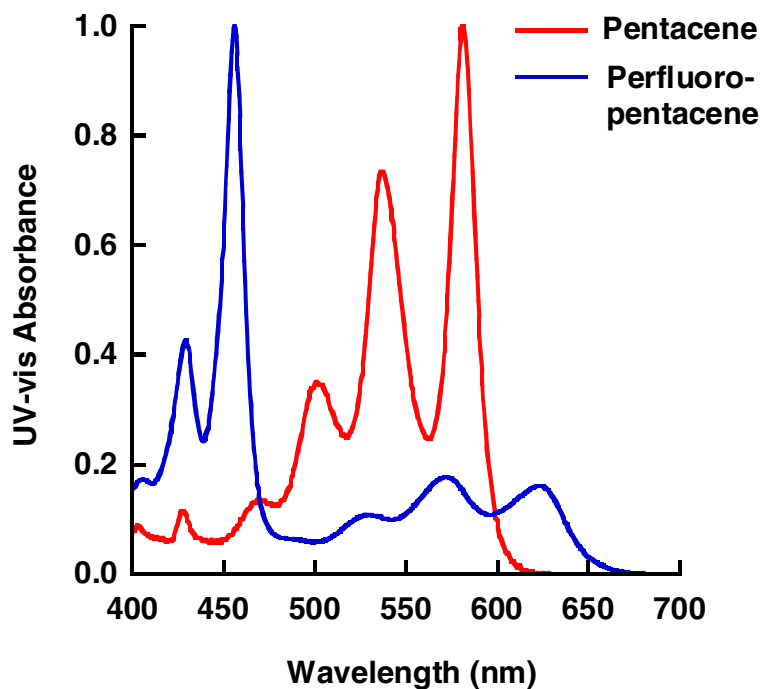
*Caution! A well-ventilated hood connected to an alkaline scrubber is necessary for a handling of HF and SF<sub>4</sub>. The operator should wear a face-shield as well as rubber gloves.*

A 0.5 L stainless steel autoclave was charged with **4** (5.00 g, 9.68 mmol), and the reactor was immersed in a -78 °C bath. HF (100 g) was introduced into the reactor by condensation, followed by SF<sub>4</sub> (28.0 g, 259 mmol). The bath was removed, and the reactor was stirred at 150 °C for 45 h. The reactor was cooled slowly to room temperature. Volatile materials were released slowly into the scrubber. N<sub>2</sub> gas was introduced into the reactor until HF was completely removed. The resulting solid was dissolved in hot CHCl<sub>3</sub> and filtered to remove insoluble materials. The filtrate was treated with activated charcoal, filtered through Celite, and concentrated in vacuo to give a yellow solid. This was recrystallized from CHCl<sub>3</sub> to afford **5** as pale yellow crystals (2.49 g, 40%): mp 267-269 °C; <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  70.73-70.91 (m, 8F), 64.46-64.64 (m, 4F), 25.66-25.86 (m, 4F), 16.70 (d,  $J$  = 12.8 Hz, 4F); MS  $m/z$  644 (M<sup>+</sup>, 100), 625 (M<sup>+</sup>-F, 32.4), 575 (M<sup>+</sup>-CF<sub>3</sub>, 77.2). Anal. Calcd for C<sub>22</sub>F<sub>20</sub>: C, 41.02. Found: C, 40.96.

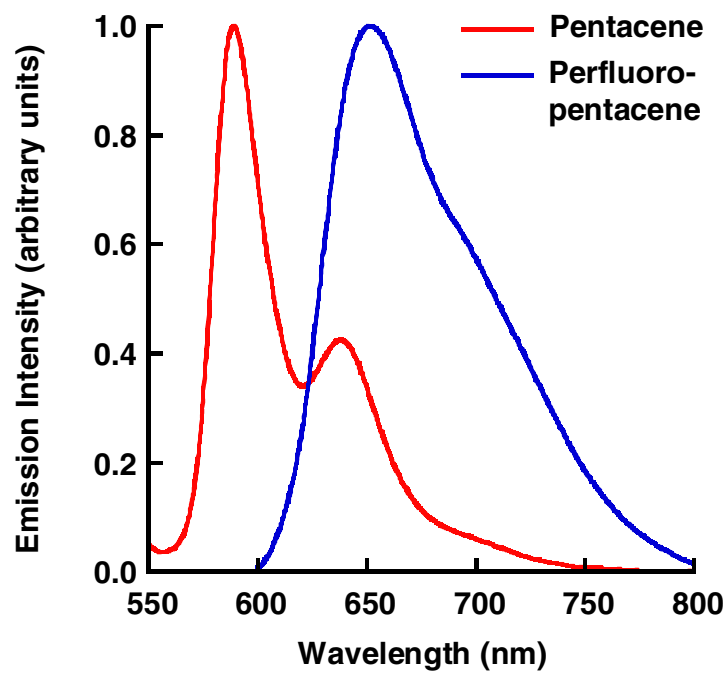
**1,2,3,4,5,6,7,8,9,10,11,12,13,14-Tetradecafluoropentacene (Perfluoropentacene).** A mixture of **5** (1.23 g, 1.91 mmol) and zinc dust (10.8 g, 165 mmol) was heated in an evacuated glass tube at 230 °C for 30 min and then at 280 °C for 3 h. The reaction mixture was poured into 20% HCl and stirred at room temperature overnight. The resulting suspension was filtered and washed with 1M HCl, H<sub>2</sub>O, and methanol to give a dark blue solid. This was sublimed in vacuo at 280 °C to give perfluoropentacene as dark blue crystals (663 mg, 65%). An analytical sample was obtained by train sublimation: mp > 300 °C; MS *m/z* 530 (M<sup>+</sup>, 100), 499 (M<sup>+</sup>-CF, 24.7), 265 (M<sup>2+</sup>, 51.1). Anal. Calcd for C<sub>22</sub>F<sub>14</sub>: C, 49.84. Found: C, 49.56.

**Fabrications of OFETs.** OFETs, bipolar OFETs, and complementary circuits were constructed on heavily doped n-type silicon wafers (< 0.018 Ωcm) covered with 200 nm-thick thermally grown silicon dioxide. The silicon dioxide acts as a gate dielectric layer, and the silicon wafer serves as a gate electrode. We used the multi-vacuum chamber system that consists of an evaporation chamber and a measuring chamber. Perfluoropentacene and pentacene were deposited on the OTS-modified silicon dioxide by vacuum evaporation at a rate of 0.03-0.05 nm s<sup>-1</sup> under pressure of 5 × 10<sup>-5</sup> Pa. The thicknesses of the semiconducting layers were 10-35 nm. For the fabrication of bipolar OFETs, perfluoropentacene and pentacene were evaporated continuously. During the evaporation, the temperature of the substrate was maintained by heating a copper block on which the substrate was mounted. Gold was used as source and drain electrodes and deposited on the organic semiconductor layer through a shadow mask with a channel width (*W*) of 1000 μm and channel lengths (*L*) of 75, 100, and 200 μm. OFETs were transferred to the measuring chamber without exposure to air. The electrical measurements were performed at room temperature under pressure of 10<sup>-5</sup> Pa with Hewlett-Packard 4140A and 4140B models.

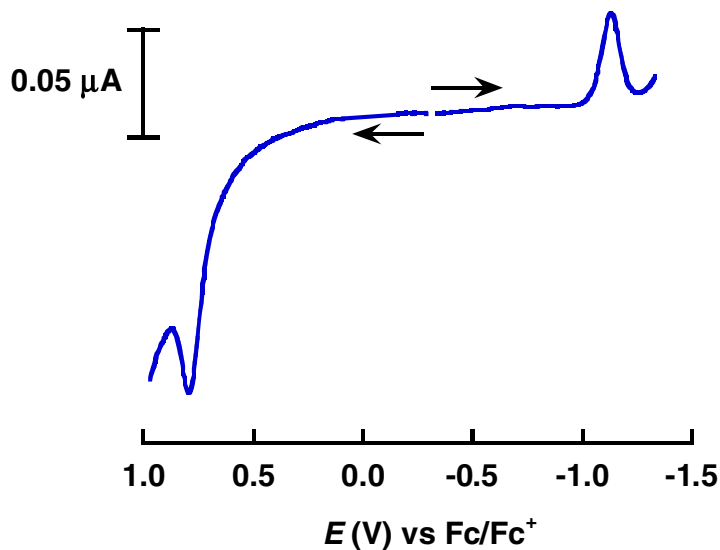
**X-ray Diffraction Studies.** X-ray diffraction (XRD) measurements on perfluoropentacene films were carried out with a JEOL JDX-3530 X-ray diffractometer system. XRD patterns were obtained using Bragg-Brentano geometry ( $\theta$ - $2\theta$ ) with Cu K $\alpha$  radiation as an X-ray source with an acceleration voltage of 40 kV and a beam current of 30 mA.



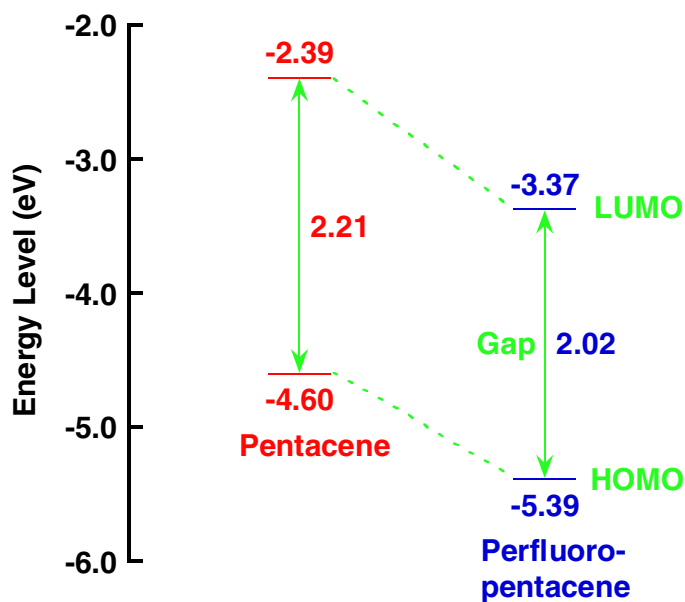
**Figure 1.** Absorption spectra of pentacene and perfluoropentacene in 1,2-dichlorobenzene.



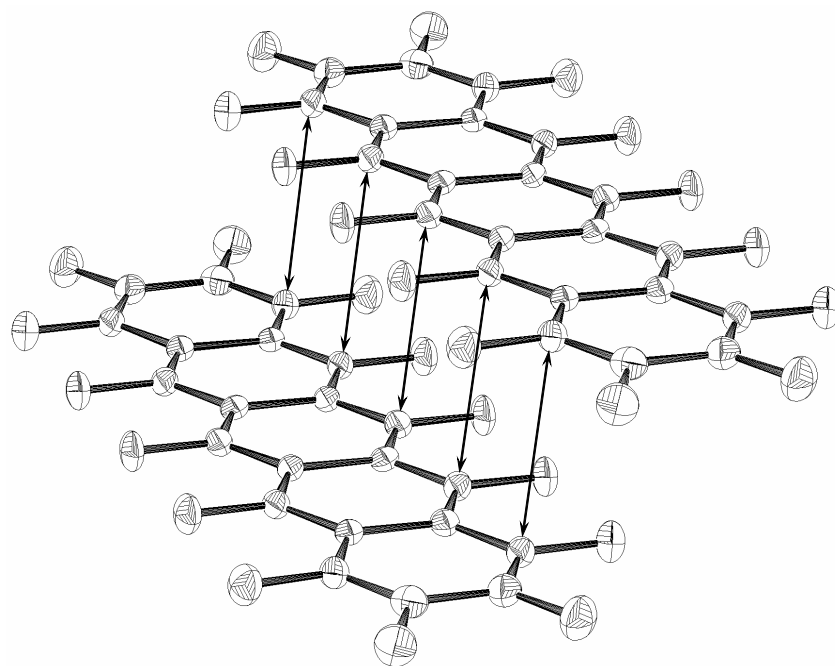
**Figure 2.** Emission spectra of pentacene and perfluoropentacene in 1,2-dichlorobenzene.



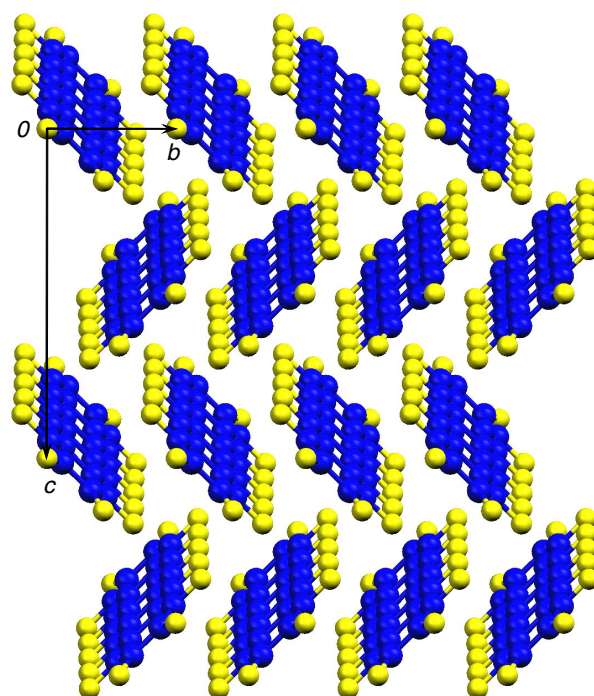
**Figure 3.** Differential pulse voltammogram of perfluoropentacene. Conditions: scan rate, 20 mV s<sup>-1</sup>; 0.1 M (n-Bu)<sub>4</sub>PF<sub>6</sub> in 1,2-dichlorobenzene; working electrode, Pt disk (1-mm diameter); counter electrode, Pt wire; reference electrode, Ag/0.01 M AgNO<sub>3</sub> and 0.1 M (n-Bu)<sub>4</sub>NClO<sub>4</sub> in CH<sub>3</sub>CN.



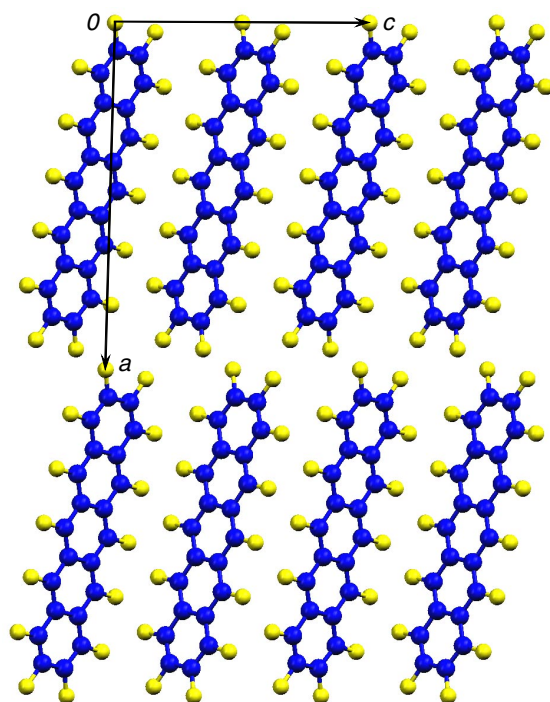
**Figure 4.** Energy diagrams calculated at the B3LYP/6-31G(d) level for pentacene and perfluoropentacene.<sup>3</sup>



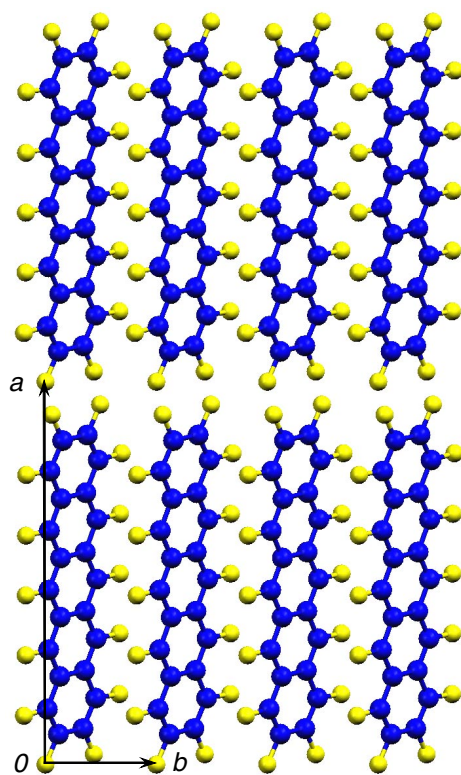
**Figure 5.** Molecular arrangement of perfluoropentacene. The short C-C contacts (3.22-3.25 Å) are indicated by arrows.



**Figure 6.** Molecular packing diagram of perfluoropentacene with a view down the *a* axis.



**Figure 7.** Molecular packing diagram of perfluoropentacene with a view down the  $b$  axis.



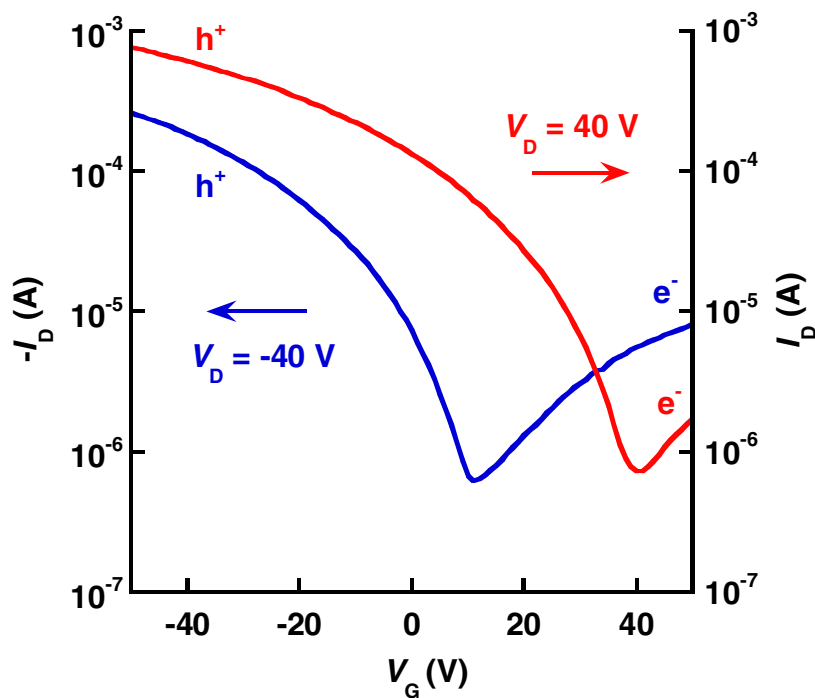
**Figure 8.** Molecular packing diagram of perfluoropentacene with a view down the  $c$  axis.



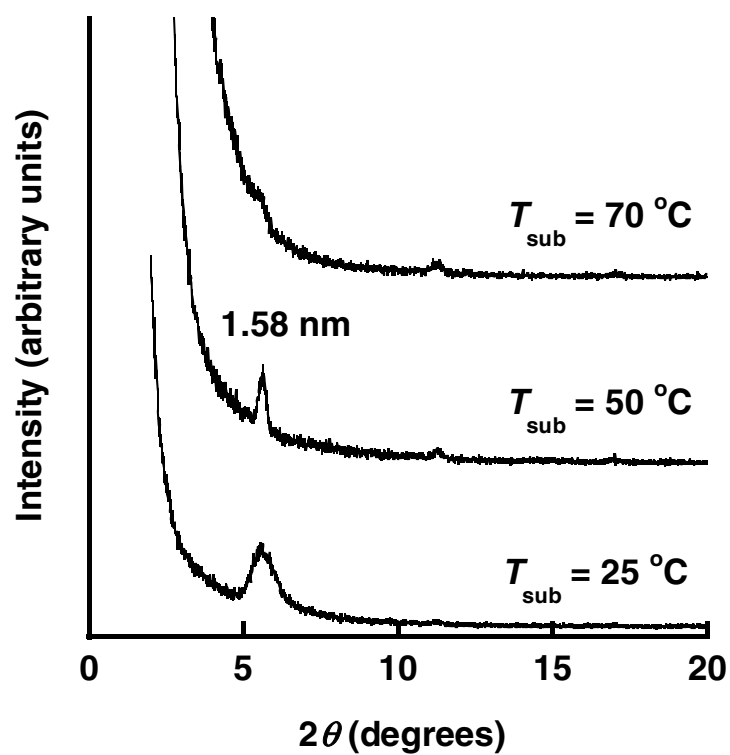
(a)

Gold (Source)	Gold (Drain)
Perfluoropentacene	
Pentacene	
SiO <sub>2</sub> (Insulator)	
n <sup>+</sup> -Si (Gate)	

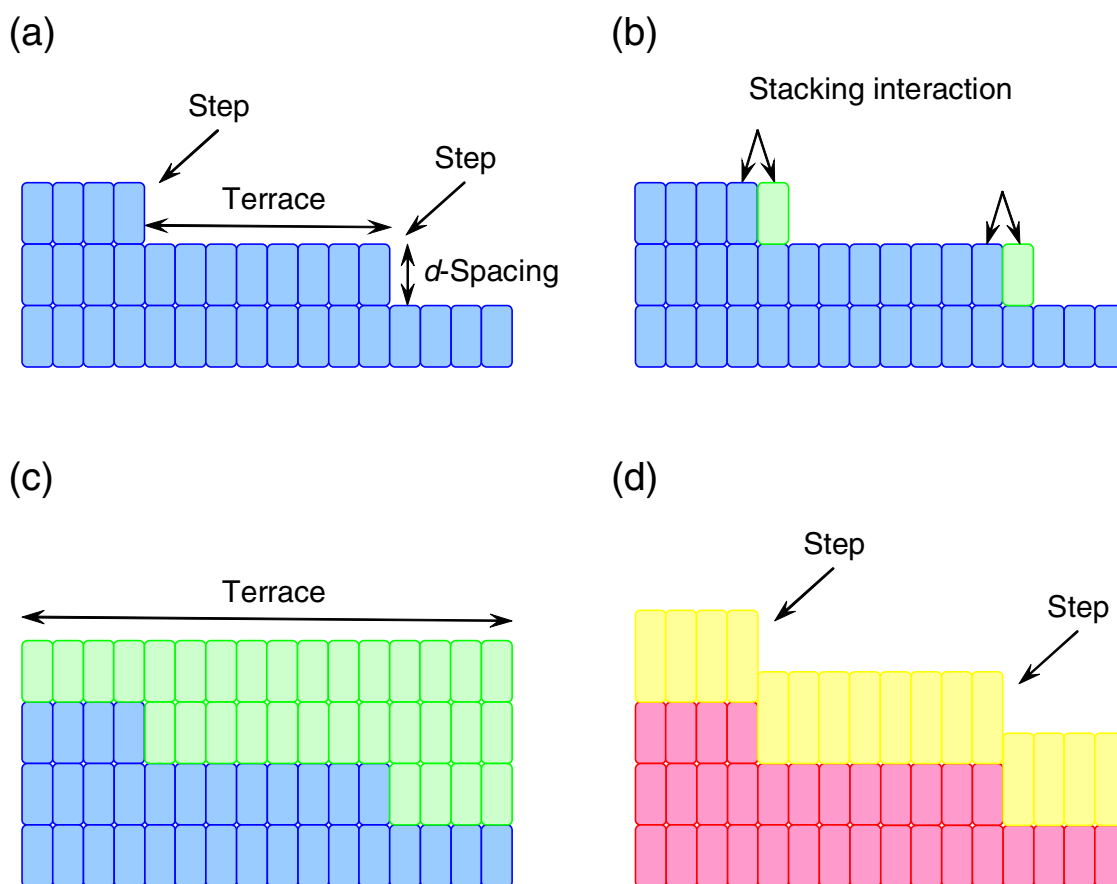
(b)



**Figure 9.** (a) Structure of a pentacene/perfluoropentacene bipolar OFET. The thicknesses of the pentacene and perfluoropentacene layers are 23 nm. (b) Drain current ( $I_D$ ) versus gate voltage ( $V_G$ ) characteristics at drain voltages  $V_D = -40$  and 40 V for a pentacene/perfluoropentacene bipolar OFET. The field-effect mobilities are calculated to be 0.52 and 0.022 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for the p- and n-channel operations, respectively.



**Figure 10.** X-ray diffractograms of perfluoropentacene films on OTS-modified  $\text{SiO}_2/\text{Si}$  fabricated at different substrate temperatures.



**Figure 11.** (a) Schematic illustration of terraces and steps on the surface of the perfluoropentacene (blue) layer. The step height corresponds to the  $d$ -spacing. (b) Stacking interactions between perfluoropentacene and pentacene (green). This allows pentacene molecules to crystallize from the steps, which leads to the continuous crystal growth at the interface. (c) The well-ordered pentacene layer is formed because its  $d$ -spacing is almost the same as that of the perfluoropentacene layer. (d) When the thin-film  $d$ -spacings of two molecules are different (red < yellow), the steps of the first layer are preserved in the second layer. These steps cause smaller grain sizes that reduce the mobility of polycrystalline films.

## References

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- (3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. P.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.