Supporting Information

High-Performance Low-Cost Organic Field-Effect Transistors with Chemically Modified Bottom Electrodes

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1. Molecular structures of TCNQ, pentacene, CuPc, and F_{16}CuPc

Pentacene, copper phthalocyanine (CuPc) and hexadecafluoro copper phthalocyanine (F_{16}CuPc) (purchased from Aldrich Chemical Co.) were purified by a train sublimation method. Their molecular structures are shown in Figure S1.

![Molecular structures of TCNQ, pentacene, CuPc, and F_{16}CuPc.](image)

*Figure S1. Molecular structures of TCNQ, pentacene, CuPc, and F_{16}CuPc.*

2. Fabrication and characterization of the organic field-effect transistors

Organic field-effect transistors (OFETs) were made both in top- and bottom-contact device configurations. The substrate was the highly n-doped silicon wafer with a 450 nm thermally oxidized SiO\textsubscript{2} dielectric layer. Before deposition of the organic semiconductor, octadecyltrichlorosilane (OTS) treatment was performed on the gate dielectrics in a vacuum oven with OTS at a temperature of 120 °C. Then the treated substrates were rinsed with heptane, ethanol, and chloroform, respectively. Thereafter,
the substrates were dried with nitrogen to form an OTS self-assembled monolayer.

**Fabrication of OFETs with the top-contact configuration:** The organic thin films of 50 nm were deposited onto the n-doped silicon wafers with the OTS-modified SiO₂ dielectric layer at a rate of 0.5 Å s⁻¹ at a base pressure of 4 × 10⁻⁴ Pa. Then, source-drain (D-S) gold contacts were thermally evaporated through a shadow mask. The channel length \( L \) and width \( W \) are 0.05 and 3 mm, respectively. A quartz crystal oscillator placed near the substrates was used to monitor the thickness of the thin films, which were calibrated ex situ using an Ambios Technology XP-2 surface profilometer.

**Fabrication of OFETs with the bottom-contact configuration:** The \( D-S \) metal contacts were thermally evaporated onto the n-doped silicon wafer with the OTS-modified SiO₂ dielectric layer through a shadow mask. Thereafter, 2 mM TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) solution in acetonitrile was dropped onto the substrate with the S-D metal electrodes. The substrate was spun dried quickly, rinsed with additional acetonitrile, and followed by drying under a N₂ stream. Finally, 50 nm organic layers were thermally deposited at a rate of 0.5 Å s⁻¹.

**Characterization of OFETs:** The characteristics of the OFETs were measured by using a Hewlett-Packard (HP) 4140B semiconductor parameter analyzer at the different gate voltages. All of the measurements were performed under ambient atmosphere at room temperature.

3. **SEM measurement**

SEM measurement was performed on a Hitachi S-4300 field emission scanning
electron microscope.

*Figure S2.* (a) SEM images of pentacene deposited onto the surfaces of the (A) SiO$_2$, (B) Cu-TCNQ, and (C) Cu; (b) magnified SEM images of pentacene deposited onto the surfaces of the (A) SiO$_2$, (B) Cu-TCNQ, and (C) Cu.

4. AFM image characteristics

AFM images of the pentacene thin films on the different surface were obtained on a Nanoscope IIIa AFM (Digital Instruments) in tapping mode.
Figure S3. AFM images of pentacene deposited on the surfaces of (a) Ag-TCNQ, (b) Cu-TCNQ, (c) Ag, and (d) Cu.

5. Field-effect performances of the fabricated field-effect transistors

Figure S4. Output characteristics of the pentacene bottom-contact OFETs with (a) the Cu source-drain electrodes and (b) the Cu-TCNQ modified Cu source-drain electrodes.
Figure S5. Output characteristics of the F_{16}CuPc bottom-contact OFETs with (a) the Ag source-drain electrodes and (b) the Ag-TCNQ modified Ag source-drain electrodes.

For the OFETs based both on pentacene and F_{16}-phthalocyanine, modification of the S-D electrodes enhances the field-effect mobilities compared with those of the devices with the metal Cu or Ag electrodes. We suggest that the improved performances for the pentacene- and F_{16}CuPc-based devices result from the different mechanism. The OFETs with the bottom contact S-D electrodes usually exhibit worse electrode/organic layer contacts and low field-effect properties. Our modification method improves the electrode/organic layer contacts. Meanwhile, modification of the S-D electrodes by metal-TCNQ increases work function of the S-D electrodes, which enhances the electron injection barrier from the metal electrodes into F_{16}CuPc and decreases the hole injection barrier from the metal electrodes into pentacene. Therefore, the enhancement of the mobilities for the pentacene-based devices is attributed both to appropriately reduced energy level mismatch and improved electrode/organic layer contacts. For the F_{16}CuPc-based devices with the modified S-D electrodes, improved
electron injection barrier could decrease the field-effect mobilities. Thus, outstanding electrode/organic layer contacts play a dominant role in improving the performances of the F16CuPc-based devices with the modified S-D electrodes. Consequently, the mobilities of the F16CuPc-based devices with the modified S-D electrodes are only 2–3 times higher than those of the devices with the Ag or Cu bottom-contact electrodes, while for the pentacene-based devices, the mobility improvement of 4–10 times is observed.

Table S1. The field-effect mobilities and on/off ratios of fabricated OFETs.

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Electrode</th>
<th>Mobility (cm$^2$/V.s)</th>
<th>On/off ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentacene</td>
<td>Au$^a$</td>
<td>0.15</td>
<td>$10^6$</td>
</tr>
<tr>
<td>Pentacene</td>
<td>Au$^b$</td>
<td>0.10</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Pentacene</td>
<td>Ag$^b$</td>
<td>0.02</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Pentacene</td>
<td>Ag-TCNQ/Ag$^b$</td>
<td>0.18</td>
<td>$10^6$</td>
</tr>
<tr>
<td>Pentacene</td>
<td>Cu$^b$</td>
<td>0.01</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Pentacene</td>
<td>Cu-TCNQ/Cu$^b$</td>
<td>0.1</td>
<td>$10^6$</td>
</tr>
<tr>
<td>CuPc</td>
<td>Au$^a$</td>
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<td>$10^6$</td>
</tr>
<tr>
<td>CuPc</td>
<td>Au$^b$</td>
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<td>$10^4$</td>
</tr>
<tr>
<td>CuPc</td>
<td>Ag$^b$</td>
<td>0.0009</td>
<td>$10^3$</td>
</tr>
<tr>
<td>CuPc</td>
<td>Ag-TCNQ/Ag$^b$</td>
<td>0.016</td>
<td>$10^6$</td>
</tr>
<tr>
<td>CuPc</td>
<td>Cu$^b$</td>
<td>0.0002</td>
<td>$10^3$</td>
</tr>
</tbody>
</table>
CuPc | Cu-TCNQ/Cu\(^b\) | 0.004 | 10\(^3\)  
F\(_{16}\)CuPc | Au\(^a\) | 0.011 | 10\(^6\)  
F\(_{16}\)CuPc | Au\(^b\) | 0.0015 | 10\(^4\)  
F\(_{16}\)CuPc | Ag\(^b\) | 0.003 | 10\(^3\)  
F\(_{16}\)CuPc | Ag-TCNQ/Ag\(^b\) | 0.009 | 10\(^5\)  
F\(_{16}\)CuPc | Cu\(^b\) | 0.0003 | 10\(^4\)  
F\(_{16}\)CuPc | Cu-TCNQ/Cu\(^b\) | 0.001 | 10\(^4\)  

\(^a\)OFET has the source-drain electrodes with a top contact geometry; \(^b\)OFET has the source-drain electrodes with a bottom contact geometry.

6. Contact resistance measurement

After the formation of the thermally oxidized SiO\(_2\) dielectric layer on the \(n\)-doped silicon wafer, the \(S-D\) electrodes (Au, Ag, and Cu) were deposited onto the silicon substrates and patterned (lift off technique). The TFT channel lengths, defined as the distance between the source and drain electrodes, varies from 5 to 50 \(\mu\)m, the channel width (\(W\)) was maintained at 1.4 mm. Then OTS treatment on the SiO\(_2\) dielectric layer was performed. Thereafter, the \(S-D\) metal electrodes were modified by TCNQ. The pentacene layer with a thickness of 500 Å was thermally evaporated onto the \(n\)-doped silicon wafer with the \(S-D\) electrodes at a rate of 1 Å s\(^{-1}\) at a base pressure of 4 \(\times\) 10\(^{-4}\) Pa.

For an OFET, when the space charge limited current (SCLC) effect is neglected, the
ON resistance, $R_{ON}$, in the linear operation regime (source-drain voltage $\ll$ gate voltage), can be expressed as follows:$^1$

$$R_{on} = \frac{\partial V_{SD}}{\partial I_{SD}} \bigg|_{V_{SD} \rightarrow 0} = R_{ch} + R_{p} = \frac{L}{W \mu_i C_i (V_G - V_T)} + R_{p}$$

(1)

where $R_{ch}$ is the channel resistance, $R_{p}$ is the parasitic resistance, $W$ is the channel width, $L$ is the channel length, $C_i$ is the capacitance of the gate dielectric, $I_{SD}$ is the source-drain current, $V_{SD}$ is the source-drain voltage, $\mu_i$ is the intrinsic mobility, $V_G$ is the gate voltage, and $V_T$ is the intrinsic threshold voltage. The parasitic resistance, $R_p$, which is associated with the contacts between $S$-$D$ electrode and semiconductor layer, can be extracted by measuring the ON resistance, $R_{ON}$, from the linear region of the FET output characteristics. Figure S6 shows a plot of $R_{ON}$ as a function of $L$ at the gate voltage of $-40$ V. For the OFETs based on pentacene, we found that the relationship of $R_{on}$ vs $L$ gives straight lines, indicating that the ON resistance is well expressed by Eq. (1). By extrapolating the relationship of $R_{ON}$ vs $L$ to $L = 0$, the contact resistance values can be determined. The contact resistances of the Ag/pentacene, Ag-TCNQ modified Ag/pentacene, Cu/pentacene, Cu-TCNQ modified Cu/pentacene are 1.56 M$\Omega$, 0.12 M$\Omega$, 1.8 M$\Omega$ and 0.21 M$\Omega$, respectively. This indicates that the modification of the $S$-$D$ electrodes by metal-TCNQ decreases the contact resistance and improves carrier injection.
Figure S6. Relationship between the ON resistance and channel length at the gate voltage of –40V for the pentacene based devices with various S-D electrodes.
Figure S7. Output characteristics of the devices based on pentacene with channel length of 5 µm and electrode of (a) Ag, (b) Ag-TCNQ modified Ag, (c) Cu, (d) Cu-TCNQ modified Cu, and (e) Au electrode.

7. Device stability measurement

The stability measurement of the devices based on pentacene with the modified electrode was performed. The devices with channel length of 5 µm were measured more than 100 times continuously. All of the measurements were performed under an ambient atmosphere at room temperature. Figure S8 shows the mobility and on/off ratio changes vs operation cycles. Devices with the modified S-D electrodes exhibit similar performances (mobility and on/off ratio) stabilities compared with those with the Au electrode. The reduction of the device performances results from the poor stabilities of pentacene as reported previously.²
Figure S8. Pentacene-based device performance stabilities (a) mobility and (b) on/off ratio with 100 cycles of measurements.

References
