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Air-stable n-channel organic thin-film transistors with high field-effect mobility based on N,N-bis(heptafluorobutyl)-3,4,9,10-perylene diimide
High-performance bottom-contact devices based on an air-stable \( n \)-type organic semiconductor \( N,N\text{-bis}(4\text{-trifluoromethoxybenzyl})\)-1,4,5,8-naphthalene-tetracarboxylic di-imide

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\( N,N\text{-bis}(4\text{-trifluoromethoxybenzyl})\)-1,4,5,8-naphthalene-tetracarboxylic di-imide was applied to organic semiconductors for bottom-contact thin-film transistors. The carrier mobility was \( 1.6 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \), the threshold voltage (\( V_T \)) was +5.5 \text{ V}, and the on/off current ratio was \( 8.6 \times 10^5 \). Devices without any further surface treatments were tested in an ambient environment. The threshold voltage shift (\( \Delta V_T \)) was verified by gate bias stress measurements. A prototype compound, \( N,N\text{-bis}(4\text{-trifluoromethylbenzyl})\)naphthalene-1,4,5,8-tetracarboxylic di-imide, shows direct correlation to the bottom-contact device with the varied molecular structure. © 2007 American Institute of Physics. [DOI: 10.1063/1.2741414]

Organic thin-film transistors (OTFTs) have wide applications in low-cost electronic devices such as flexible active displays, rfid tags, smart cards, and logic circuits. Many reports have illustrated the characteristics of OTFTs using pentacene, a well-known material, as the \( p \)-type organic transistor. In order to make complementary metal-oxide semiconductors more efficient, high-performance \( n \)-type organic transistors are needed. To date, several air-stable \( n \)-type materials have been studied. In particular, Katz et al. reported a series of \( n \)-type materials, namely, 1,4,5,8-naphthalene-tetracarboxylic di-imide (NTCDI), which were modified from 1,4,5,8-naphthalene-tetracarboxylic dianhydride using alkyl chain, benzyl, and phenyl structure. Although \( n \)-octyl-NTCDI has a high mobility, it cannot operate in air. The excellent electric properties and stabilization of 1H-1H-perfluorocyclo-NTCDI and 4-trifluoromethyl-NTCDI were established with perfluorinated species. The perfluorinated group also provides resistance, protecting the molecular center from oxygen and moisture.

Most organic \( n \)-type devices are fabricated in a top-contact form. Dholakia et al. showed that bottom-contact devices show larger contact resistance than top-contact devices in some cases. In recent research, self-assembled monolayers (SAMs) were used as buffers to reduce heterogeneous electron transfers between the metal/dielectric and organic layers of the bottom-contact structure. Here, the source and drain electrodes were deposited beforehand on the dielectric layer, and then the organic layer was allowed to evaporate fully. Chemical reagents, including alkyl chains and terminal thionic groups, combined with the gold surface to form SAMs. The drawbacks of SAMs are that they only appear in particular chemical reactions, and the requisite gold electrodes increase the cost of making the transistors.

In this letter, we synthesize an organic \( n \)-type material, \( N,N\text{-bis}(4\text{-trifluoromethoxybenzyl})\)-1,4,5,8-naphthalene-tetracarboxylic-di-imide (NTCDI-OCF\(_3\)) [Fig. 1(a)], and compare its electrical characteristics in a bottom-contact configuration with those of model compound \( N,N\text{-bis}(4\text{-trifluoromethylbenzyl})\)naphthalene-1,4,5,8-tetracarboxylic di-imide (NTCDI-CF\(_3\)) [Fig. 1(b)]. The NTCDI-OCF\(_3\) shows a mobility as high as \( 1.6 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \), which is higher than that of NTCDI-CF\(_3\). Furthermore, all bottom-contact devices were fabricated without any surface treatments, and electric measurements were obtained in air. Table I compares the performance of both OTFTs.

The profile of the bottom-contact device is shown in Fig. 2. A layer of 100-nm-thick indium tin oxide (ITO) served as a bottom gate electrode. The gate dielectric layer was 300 nm thick and made of plasma-enhanced chemical vapor deposition silicon dioxide (SiO\(_2\)). For the top source and drain electrodes, ITO was sputtered on the top of the SiO\(_2\). The defined channel length and channel width were, respectively, 30 and 500 \( \mu \)m. Finally, organic materials were thermally evaporated through a metal shadow mask in a high-vacuum chamber (pressure at \( 2 \times 10^{-6} \) torr). While organic material evaporated, we maintained the optimum substrate temperatures: 40 °C for NTCDI-OCF\(_3\) and 80 °C for NTCDI-CF\(_3\). NTCDI-OCF\(_3\) and NTCDI-CF\(_3\) were prepared

![FIG. 1. Chemical structures of (a) NTCDI-OCF\(_3\) and (b) NTCDI-CF\(_3\).](image-url)
TABLE I. Electrical characteristics of bottom-contact devices with the two semiconductors ($V_D=+50$ V).

<table>
<thead>
<tr>
<th>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>On/off current ratio</th>
<th>Threshold voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTCDI-CF$_3$</td>
<td>$7.9 \times 10^{-4}$</td>
<td>2.3 $\times 10^4$</td>
</tr>
<tr>
<td>NTCDI-OCF$_3$</td>
<td>$1.6 \times 10^{-2}$</td>
<td>8.6 $\times 10^5$</td>
</tr>
</tbody>
</table>

according to well-established procedures.$^{11}$ Materials were purified at least twice sublimation which we use as the semiconductor layer.

As indicated in previous research, the mobility of top-contact devices made from NTCDI-CF$_3$ that use gold as the top electrode was 0.12 cm$^2$ V$^{-1}$ s$^{-1}$. Our repetition of this test returned similar results: the calculated mobility was 0.1 cm$^2$ V$^{-1}$ s$^{-1}$. We found that the performance of the OTFTs dropped off in the bottom-contact form. Although the NTCDI-OCF$_3$ top-contact device showed a slightly lower mobility than previously tested, 0.08 cm$^2$ V$^{-1}$ s$^{-1}$, the transistor of the bottom-contact device showed excellent carrier mobility. Again, we must mention that no further surface treatments were placed on the top electrode or the dielectric layer of this bottom-contact device.

To understand how the bottom-contact devices performed when operated in a series, bias stress tests were performed (in a dark ambient environment). The device was operated with a continuing bias for 3 h and we measured the relative output current for each 5 s period. The biases of the gate voltage and drain voltage were set at a fixed value of +50 V, simulating real use of the transistor. The output current decay shown in Fig. 3 illustrates that NTCDI-OCF$_3$ maintained a significantly higher degree than NTCDI-CF$_3$ during the same bias period. Dholakia et al., as mentioned above, demonstrated that bottom-contact devices have larger contact resistance than top-contact ones. The film growth of organic semiconductors appeared in varying stacking formations between the metal and oxide surfaces, resulting in imperfect molecule arrangements. The surface morphology of NTCDI-CF$_3$ and NTCDI-OCF$_3$, as observed by atomic force microscopy (AFM) (Digital Instruments Nanoscope), is displayed in Figs. 4(a) and 4(b), respectively. As Fig. 4(b) clearly shows, NTCDI-OCF$_3$ has more continuous grain growth, which we believe to be suitable for a bottom-contact device. The NTCDI-OCF$_3$ bottom-contact device shows several advantages over NTCDI-CF$_3$. It allows a further reduction in contact resistance, as well as less attrition of the current during series bias stress.

Gate bias stress may accompany a threshold voltage shift ($V_T$ shift, $\Delta V_T$) due to “charge trapping.”$^{12}$ We measured the transfer characteristics, pristine state, and 1 h after the stress tests, using a semiconductor analyzer HP 4156A in an ambient environment. Results are shown in Figs. 5 and 6. The NTCDI-OCF$_3$ bottom-contact device showed less $\Delta V_T$ than NTCDI-CF$_3$, and it maintained the almost same electrical drain current performance and mobility after bias stress. In other research, no definite mechanism for bias stress has been studied.$^{13,14}$ We focus on $\Delta V_T$, which indicates the degree of the trapped charge and the long-term stability of the devices. The threshold voltage shifts of the transistors with NTCDI-CF$_3$ and NTCDI-OCF$_3$ are, respectively, +16 V (Fig. 5), and +7 V (Fig. 6). The NTCDI-OCF$_3$ bottom-contact devices made from NTCDI-CF$_3$ that use gold as the conductor layer.
contact device demonstrated superior stability under bias stress.

In conclusion, we have fabricated a bottom-contact device with a n-type organic semiconductor $N,N$-bis(4-trifluoromethoxybenzyl)-1,4,5,8-naphthalene-tetracarboxylic di-imide. The electrical characteristics of this device revealed a carrier mobility of $1.6 \times 10^{-2}$ cm$^2$/V·s, a threshold voltage of +5.5 V, and an on/off current ratio of $8.6 \times 10^5$. A continuous arrangement of such molecules may reduce contact resistance and decay current. Our tests of the device under constant bias stress confirmed this. Furthermore, a lower threshold voltage shift means that less charge trapping occurs after gate bias stress.

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