Effects of $p$-(Trifluoromethoxy)benzyl and $p$-(Trifluoromethoxy)phenyl Molecular Architecture on the Performance of Naphthalene Tetracarboxylic Diimide-Based Air-Stable n-Type Semiconductors

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Supporting Information

ABSTRACT: $N,N'$-Bis(4-trifluoromethoxyphenyl) naphthalene-1,4,5,8-tetracarboxylic acid diimide (NDI-POCF$_3$) and $N,N'$-bis(4-trifluoromethoxybenzyl) naphthalene-1,4,5,8-tetracarboxylic acid diimide (NDI-BOCF$_3$) have similar optical and electrochemical properties with a deep LUMO level of approximately 4.2 eV, but exhibit significant differences in electron mobility and molecular packing. NDI-POCF$_3$ exhibits nondetectable charge mobility. Interestingly, NDI-BOCF$_3$ shows air-stable electron transfer performance with enhanced mobility by increasing the deposition temperature onto the octadecyltrichlorosilane (OTS)-modified SiO$_2$/Si substrates and achieves electron mobility as high as 0.7 cm$^2$ V$^{-1}$ s$^{-1}$ in air. The different mobilities of those two materials can be explained by several factors including thin-film morphology and crystallinity. In contrast to the poor thin-film morphology and crystallinity of NDI-POCF$_3$, NDI-BOCF$_3$ exhibits larger grain sizes and improved crystallinities due to the higher deposition temperature. In addition, the theoretical calculated transfer integrals of the intermolecular lowest unoccupied molecular orbital (LUMO) of the two materials further show that a large intermolecular orbital overlap of NDI-BOCF$_3$ can transfer electron more efficiently than NDI-POCF$_3$ in thin-film transistors. On the basis of fact that the theoretical calculations are consistent with the experimental results, it can be concluded that the $p$-(trifluoromethoxy) benzyl (BOCF$_3$) molecular architecture on the former position of the naphthalene tetracarboxylic diimides (NDI) core provides a more effective way to enhance the intermolecular electron transfer property than the $p$-(trifluoromethoxy) phenyl (POCF$_3$) group for the future design of NDI-related air-stable n-channel semiconductor.

KEYWORDS: organic thin-film transistor, air-stable, n-type organic semiconductor, naphthalene diimide, trifluoromethoxy

1. INTRODUCTION

Organic thin-film transistors (OTFTs) have attracted great attention due to their considerable potential applications in organic electronics such as complementary circuits, sensors, and display backplanes. In fact, the hole mobilities of p-channel organic semiconductors have been significantly improved beyond the hydrogenated amorphous silicon. However, the development of n-type materials was far behind that of p-type materials due to the difficulty of strong electron-withdrawing group development and the instability in ambient air. To design a molecule with high electron mobility and excellent air stability is still challenging for n-type organic semiconductors.

Naphthalene tetracarboxylic diimides (NDIs) are one of the typical imide-based core structures for the utilization of n-channel organic semiconductors due to the simplicity of synthesis and high electron affinity. Up to now, the highest electron mobility of NDIs has reached 6.2 cm$^2$ V$^{-1}$ s$^{-1}$ in Ar.
and 3.5 cm² V⁻¹ s⁻¹ in ambient air. For the rational design of air-stable n-type semiconductors based on NDI core, many efforts have been made such as investigating alkyl chain lengths, and introducing fluoro and oxygenated groups. The trfluoromethoxy group (OCF₃) is considered to be a strong electron-withdrawing and π-donating substituent based on three fluoro atoms and an oxygen lone pair. As a practical matter, the introduction of p-(trfluoromethoxy) benzyl (BOCF₃) in NDI (Figure 1) can form air-stable n-type semiconductor material with mobility of 3.58 × 10⁻² cm² V⁻¹ s⁻¹ without surface treatment in the air. Detailed studies on the effects of benzyl and phenyl groups have not been elucidated.

In this study, we intend to modify the molecular packing of NDI-BOCF₃ by replacing the BOCF₃ substituent with p-(trfluoromethoxy) phenyl (POCF₃) substituent at the former position of NDI to obtain a new compound of NDI-POCF₃ (Figure 1), and investigate the differences of those two materials systematically. Interestingly, the substituent variety slightly affects the electrochemical and optical properties (Table 1) of those two materials, but significantly changes the charge transfer and molecular packing characteristics. The OTFT performance of NDI-BOCF₃ could be improved drastically by increasing the deposition temperature during vacuum evaporation and by using octadecyltrichlorosilane (OTS)-modified SiO₂/Si substrate. The highest electron mobility of 0.7 cm² V⁻¹ s⁻¹ was obtained in air, which is approximately 20 times higher than previously reported data. However, the OTFTs for NDI-POCF₃ did not work. The reason was clarified by the analysis of thin films using X-ray diffraction (XRD) and atomic force microscope (AFM), and the calculation of intermolecular transfer integral of LUMO based on the single-crystal data using Amsterdam density functional (ADF).

2. EXPERIMENTAL SECTION

Synthesis. The detailed synthesis routes and chemophysical characterizations of NDI-POCF₃ and NDI-BOCF₃ are described in the Supporting Information.

OTFT Device Fabrication. Organic thin-film transistors with top contact/bottom gate configuration were fabricated by the vapor deposition process. The heavily doped silicon wafers with oxide thickness of 300 nm were first cleaned with acetone, deionized water, and isopropanol in the ultrasonic bath, respectively. These substrates were then dried by nitrogen gas and further cleaned in oxygen plasma for 15 min. It was then treated in 0.03 g/mL concentration of octadecyltrichlorosilane (OTS) solution in toluene at 60 °C for 20 min to form a self-assembled monolayer. The OTS-modified SiO₂/Si substrates were rinsed with fresh toluene in the sonic bath for 1 min and dried by nitrogen gas. The organic active layer was then evaporated onto these substrates to a thickness of approximately 35 nm under the pressure of 1 × 10⁻⁴ Pa for each substrate temperature condition. Gold source and drain electrodes (W/L = 10) were deposited on the organic active layer using a shadow mask. Electrical characteristics of the OTFT devices were measured by Agilent B1500A in ambient air. The electron mobility (μe) was obtained from the saturation regime using the following equation:

\[ I_{ds} = C(V/2L)(V_{gs} - V_{th})^2 \]  

In the above equation, \( I_{ds} \), \( W \), \( L \), \( V_{gs} \), \( V_{th} \), and \( C \) represent the drain-source current, channel width, channel length, gate voltage, threshold voltage, and the capacitance per unit area of the gate dielectric layer, respectively.

3. RESULTS AND DISCUSSION

The electrochemical property and UV–vis absorption spectra of those two materials were analyzed in dichloromethane solution and in thin film/solution (Figure 2). The related results are summarized in Table 1, and similar optical and electrochemical characteristics were observed. The absorption edge of NDI-BOCF₃ and NDI-POCF₃ was measured to be 416 and 411 nm in thin film and 390 and 389 nm in solution (Figure 2b). According to the optical characteristics of thin film, the band gap was calculated to be 2.98 and 3.02 eV for NDI-BOCF₃ and NDI-POCF₃, respectively. On the basis of the calibration of redox potentials of an internal ferrocene reference (\( F / F^+ \)), the thermally evaporated thin films of those two materials on GCE electrode were prepared for the cyclic voltammograms (CV) measurements. According to the onset of CV reduction peaks, the deep LUMO levels of NDI-BOCF₃ and NDI-POCF₃ were estimated to be −4.22 and −4.17 eV, respectively. The low LUMO energy levels promise the candidates for the application of n-channel OTFTs with excellent air stability.

On the basis of the LUMO level and energy band gap confirmations, the highest occupied molecular orbital (HOMO) levels of NDI-BOCF₃ and NDI-POCF₃ were obtained to be −7.20 and −7.19 eV, respectively. In addition, the thermogravimetric analysis (TGA) showed good thermal stability with onset decomposition temperature up to 352 and 394 °C for NDI-BOCF₃ and NDI-POCF₃, as seen in Figure S1.

Interestingly, benzyl and phenyl-related NDI-BOCF₃ and NDI-POCF₃ have similar optical and electrochemical characteristics, but presented significant differences in intermolecular electron transport. Figure 3 shows the typical transfer and output curves of OTFTs for NDI-BOCF₃ deposited at substrate temperatures of room temperature (Figure 3a and b) and 70 °C (Figure 3c and d), respectively. The detailed

Table 1. Electrochemical and Optical Properties of NDI-POCF₃ and NDI-BOCF₃

<table>
<thead>
<tr>
<th></th>
<th>( E_{\text{onset, red vs Fc/Fc}^+} ) (V)</th>
<th>( E_{\text{LUMO}} ) (eV)</th>
<th>( E_{\text{HOMO}} ) (eV)</th>
<th>( \lambda_{\text{dil. film}} ) (nm)</th>
<th>( \lambda_{\text{sat.}} ) (nm)</th>
<th>( E_g ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDI-BOCF₃</td>
<td>−0.88</td>
<td>−4.22</td>
<td>−7.20</td>
<td>416</td>
<td>390</td>
<td>2.98</td>
</tr>
<tr>
<td>NDI-POCF₃</td>
<td>−0.93</td>
<td>−4.17</td>
<td>−7.19</td>
<td>411</td>
<td>389</td>
<td>3.02</td>
</tr>
</tbody>
</table>

*a) Estimated from electrochemical determination versus \( F / F^+ \). \( b) E_{\text{LUMO}} = -(E_{\text{onset, red vs Fc/Fc}^+} + 5.1) \) (eV). \( c) E_{\text{HOMO}} = E_{\text{LUMO}} - E_g \). d) Estimated from thin-film absorption spectra. e) Solution absorption spectra in chloroform. f) Energy band gap calculated from the absorption edge of the as-cast thin film.
Device performances were summarized in Table 2. As can be seen, the electron mobility of NDI-BOCF3 increased from 0.23 to 0.70 cm² V⁻¹ s⁻¹ as the substrate temperature increased from rt to 70 °C, but decreased to 0.16 cm² V⁻¹ s⁻¹ after the substrate temperature increased to 100 °C. In contrast, NDI-POCF3-based OTFTs showed nondetectable charge mobility despite having properties similar to those of NDI-BOCF3 (Table 1).

To clarify the differences of the OTFT characteristics between NDI-BOCF3 and NDI-POCF3, we first analyzed the temperature-dependent crystal phase evolutions using thin-film X-ray scattering (XRD). Figure 4a shows XRD patterns of NDI-BOCF3 thin films deposited on the OTS-modified SiO₂/Si substrates by a vacuum evaporator with various substrate temperatures.

Table 2. Device Performance of NDI-POCF3 and NDI-BOCF3

<table>
<thead>
<tr>
<th>polycrystalline thin-film device</th>
<th>Tₘₐₜ (°C)</th>
<th>ionic mobility (cm²/(V s))</th>
<th>max mobility (cm²/(V s))</th>
<th>ionic mobility/10 V</th>
<th>Vₑ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDI-BOCF3</td>
<td>rt</td>
<td>0.22 ± 0.01</td>
<td>0.23</td>
<td>1.5 × 10⁶</td>
<td>−4.4</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.28 ± 0.05</td>
<td>0.37</td>
<td>4.2 × 10⁵</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.62 ± 0.06</td>
<td>0.70</td>
<td>3.9 × 10⁵</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.15 ± 0.01</td>
<td>0.16</td>
<td>2.4 × 10⁵</td>
<td>−2.1</td>
</tr>
<tr>
<td>NDI-POCF3</td>
<td>rt, 70</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Figure 2. Electrochemical (a) and UV–vis absorption spectra (b) of NDI-POCF3 and NDI-BOCF3.

Figure 3. Typical OTFT characteristics (transfer curve and output curve) for NDI-BOCF3 thin films grown on the OTS-modified SiO₂/Si substrates. (a) and (b) were obtained at Tₘₜ = rt. (c) and (d) were obtained at Tₘₜ = 70 °C.

Figure 4. XRD patterns for (a) NDI-BOCF3 and (b) NDI-POCF3 polycrystalline thin films deposited on the OTS-modified SiO₂/Si substrates at different temperatures. Sharp Bragg reflections up to third order were clearly seen, suggesting high degrees of crystallinity for NDI-BOCF3. On the basis of the single-crystal data, the peak at 2θ = 4.54° corresponds to (100) plane, and the other two peaks are successive orders of reflections, (200) and (400) planes, respectively. Thus, NDI-BOCF3 thin film has
the spacing distance \(d_{100}\) of 1.95 nm, which is close to both the interplane distance of 2.09 nm in a-axis direction of the single crystal and the step height of approximately 2.0 nm obtained from AFM images. This result indicates that the a-axis direction of NDI-BOCF3 molecules (Figure 6a) was aligned nearly perpendicular to OTS-modified SiO\(_2\)/Si substrate. Furthermore, the intensity of each peak increased gradually as the substrate temperature increased. This result suggests that crystalline quality was improved, which is consistent with OTFT mobility results increasing from room temperature to 70 \(^\circ\)C as shown in Table 2. In contrast, NDI-POCF3 thin film deposited at a substrate temperature of 70 \(^\circ\)C showed two diffraction peaks at 2\(\theta\) = 9.9\(^\circ\) and 18.4\(^\circ\) that correspond to (001) and (002) planes with weak intensity (Figure 4b), suggesting the poor crystallinity of the thin film that results in nondeectable mobility of NDI-POCF3. Besides, the corresponding spacing distance \(d_{001}\) of the primary diffraction peak is calculated to be 0.98 nm, which is equal to the interplane distances of 0.98 nm in c-axis direction of the single crystal. This result may suggest that the c-axis direction of NDI-POCF3 (Figure 6c) crystallites in the thin film is perpendicular to that of the OTS-modified SiO\(_2\)/Si substrate.

Temperature-dependent thin-film morphology of two materials was analyzed by AFM and exhibited quite disparate results. Figure 5a–d shows NDI-BOCF3 thin films deposited at the substrate temperature of rt, 50, 70, and 100 \(^\circ\)C, respectively. Rod-like grains were observed for the NDI-BOCF3 thin films at all deposition temperatures. The grain size was increased from several hundred nanometers to approximately 2 \(\mu\)m by increasing the substrate deposition temperature from rt to 100 \(^\circ\)C. This result supports our OTFT mobility observations (Table 2). In general, well-defined thin film with large grain size and high crystallinity provides a positive effect on the carrier mobility,\(^{26–30}\) suggesting that the highest mobility should be obtained at a substrate temperature of 100 \(^\circ\)C. However, the device performance decreased when the temperature was increased to 100 \(^\circ\)C. On the basis of the XRD and AFM results, it is possible that the larger grains with highly crystallinity formed at higher substrate temperatures impinged upon each other and generated voids, which affects the continuity of the thin film.\(^{31}\) In contrast, a completely different phenomenon was observed in the AFM images of NDI-POCF3 thin films, as shown in Figure 5e,f. The grain size did not change after increasing the substrate temperature. Besides, a higher RMS roughness of \(~\sim15\) nm (Figure 5e) was detected, which is approximately 5 times larger than that for NDI-BOCF3 thin film at the same substrate temperature (Figure 5a). The thin film with smaller grain size and large RMS roughness was found to be detrimental to the device performances.\(^{26,30}\) The XRD and AFM results suggest that NDI-POCF3 thin films have a different crystal structure from NDI-BOCF3 thin films. The electron mobility of NDI-BOCF3 is expected to be higher than that of NDI-POCF3 due to the well-defined thin-film morphologies with enhanced crystallinities.

To further understand the effect of BOCF3 and POCF3 molecular architecture on the performance of NDI-based semiconductors, the intermolecular transfer integrals were processed by importing the single-crystal data in a modeling software, amsterdam density functional (ADF),\(^{32}\) which uses density function theory for the calculation of principal electronic structure. The electronic couplings \((V)\)\(^{33}\) between neighboring molecules in the single crystal can be calculated to predict the benefit of BOCF3 and POCF3 substitutions at former positions of NDI. It was performed by generalized gradient approximation with the PW91 functional (GGA:PW91) and the basis set of triple-Z 2 plus polarization functions (TZ2P) in the ADF program.\(^{32,34,35}\) However, the single-crystal data of NDI-POCF3 and NDI-BOCF3 were required for the calculation of transfer integrals of LUMO. Thus, the single crystals of those two materials were grown by the physical vapor transport method\(^{36}\) and analyzed by X-ray
crystallography. The detailed molecular packing of those two materials was shown in Figure 6.

As expected, significant differences of molecular packing and intermolecular relationships are observed for those two materials. For the NDI-BOCF3, the interplane distances of \( a = 20.905 \, \text{Å} \), \( b = 4.649 \, \text{Å} \), and \( c = 14.258 \, \text{Å} \) were demonstrated by X-ray crystallography. The short interplane distances provide strong face-to-face intermolecular interactions and large transfer integral of LUMO. Therefore, the strongest transfer integral of LUMO was calculated to be 79.7 meV in \( b \)-axis direction for NDI-BOCF3 (Figure 6b). Besides, the opposite directions between two neighboring molecules with dihedral angle of approximately 95° were investigated and caused the herringbone-like packing structure (Figure 6b). The intermolecular orbital overlaps of LUMO between two opposite neighboring molecules in this direction were calculated to be 14.1 meV (Figure 6a,b), which indicates a one-dimensional (1D) electronic structure for NDI-BOCF3. In contrast, an approximately parallel molecular orientation in different molecules (Figure 6d) was demonstrated for NDI-POCF3. The interplane distances of NDI-POCF3 were found to be \( a = 5.122 \, \text{Å} \), \( b = 24.503 \, \text{Å} \), and \( c = 9.786 \, \text{Å} \), respectively. The largest transfer integral of NDI-POCF3 in the \( a \)-axis direction was calculated to be 42.9 meV, which is smaller than NDI-BOCF3. Large intermolecular orbital overlaps are good for the efficient carrier transport in OTFTs. In addition, the transfer integrals of LUMO in other directions were close to 0 meV (Figure 6c and e), which leads to highly 1D electronic structure. However, highly 1D electronic structure of active materials is not preferred in OTFTs due to the arbitrary orientations of the crystalline grains in the thin film and the incapability of the highly interactive electronic structure over the thin film. On the basis of the thin-film characteristics and the calculated transfer integral of LUMO, we can conclude that NDI-BOCF3 can transport electron more efficiently than NDI-POCF3 in OTFTs. The results are consistent with our measurements of OTFT devices.

Figure 6. Molecular packing structure and intermolecular transfer integrals of LUMO in the single crystal of NDI-BOCF3 (a,b) and NDI-POCF3 (c–e).

NDI-BOCF3-based OTFTs exhibited excellent device performances in the air. The BOCF3 group not only protects the molecular center from oxygen and moisture due to the perfluorinated groups, but also provides a strong electron-withdrawing and \( \pi \)-donating substituent based on three fluorine atoms and an oxygen lone pair. In addition, it also provides a more effective way to control overall thin-film morphology, crystalline quality, and molecular packing than the POCF3 group in NDI, leading to an excellent electron mobility in n-channel OTFTs. Moreover, the introduction of POCF3 group into NDI decreases the intermolecular transfer integral of LUMO, which should be the main factor causing the lack of performance of NDI-POCF3. Especially, the calculated transfer integrals of LUMO are negligible (\(~0\) meV), except in the direction of close face-to-face intermolecular interaction. It not only causes a highly 1D electronic structure, but also leads to inefficient electron transport in OTFTs. Furthermore, highly 1D electronic structure will lead to arbitrary orientation of crystallites in thin film, which results in negative effects on the film morphology and device performance. The results indicate the great potential of the BOCF3 group on the future design of NDI-related air-stable n-channel semiconductors.

4. CONCLUSIONS

In this study, the effect of BOCF3 and POCF3 molecular architecture on the performance of NDI-based n-channel semiconductor has been systematically studied. The substituent variety of those two materials only has a slight effect on the electrochemical and optical properties, but significantly changed the intermolecular electron transport and molecular packing behaviors. NDI-POCF3 thin films showed poor film morphology and crystallinity with nondetectable mobility. In contrast, NDI-BOCF3 thin films exhibited good film morphology and crystallinity with detectable mobility. Furthermore, highly 1D electronic structure will lead to arbitrary orientation of crystallites in thin film, which results in negative effects on the film morphology and device performance.
substrate with a temperature of 70 °C. Furthermore, the electronic structure in the solid state can efficiently explain the differences in device characteristics. The theoretical calculations based on single-crystal data revealed that the intermolecular orbital overlaps of NDI-BOCF$_3$ were larger than those of NDI-POCF$_3$. From the results, we concluded that BOCF$_3$ substitution at the former position of NDI is a type of promising molecular modification for the further development of NDI-related materials.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b04753.

Synthesis routes of NDI-POCF$_3$ and NDI-BOCF$_3$, and chemophysical characterizations including $^{1}$H, $^{13}$C NMR spectroscopy, EI-mass spectroscopy, elemental analysis, and TGA measurements (PDF)

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**Notes**

The authors declare no competing financial interest.

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