Organic n-Channel Thin-Film Transistors Based on Dichlorinated Naphthalene Diimides


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ABSTRACT

Five core-dichlorinated naphthalene diimides (NDIs) bearing several fluoroalkyl-substituents at the imide nitrogens were synthesized, characterized and employed in organic n-channel thin-film transistors with a vacuum-deposited semiconductor layer on 110 nm thick SiO2 (100 nm)/AlOx (8 nm)/SAM (1.7 nm) and 5.7 nm thick AlOx (3.6 nm)/SAM (2.1 nm) gate dielectrics. The electron mobility of the thin-film transistors under ambient conditions is as large as 1.3 cm²/Vs on the thicker gate dielectric. On the thinner gate dielectric the mobility is lower (0.4 cm²/Vs) but enables switching at gate-source voltages of only 3V. Such outstanding performance together with the feasible synthetic access to these compounds make these semiconductors highly promising for low-cost, large-area, and flexible electronics.

Keywords: Organic electronics, organic thin-film transistors, organic n-channel semiconductors, dichlorinated naphthalene diimides, charge transport, air-stability

1. INTRODUCTION

Organic thin-film transistors (TFTs) are today in the focus of many investigations as they are promising components for future low-cost, large-area, and flexible electronics. Nowadays the main challenge lies in finding organic n-channel semiconductors which exhibit both high charge-carrier mobility and good ambient stability for the realization of complementary circuits in combination with already existing organic p-channel semiconductors.

Promising candidates for n-channel OTFTs are naphthalene tetracarboxylic diimides (NDIs) due to their suitable electron affinity and the tunability of their optoelectronic properties by substitution. It is well-known that the substituents at the imide positions of NDI greatly affect the molecular packing motif, the thin-film morphology, and therefore charge-carrier mobility. Several NDI derivatives without core-substitution have shown remarkably high field-effect mobilities (up to 6 cm²/Vs) but often suffered from a lack of stability under ambient conditions which has been attributed to their high-lying lowest unoccupied molecular orbital (LUMO) levels. The ambient stability of OTFTs based on perylene or naphthalene diimide semiconductors can be improved by substituting strong electron-withdrawing groups, such as fluorine, cyano, alkanoyl, perfluorobenzene, and fluoroalkyl groups either in the imide position or at the core. This has yielded air-stable n-channel transistor operation by significantly lowering the LUMO of the resulting molecule to resist ambient oxidation. In addition, the self-segregation of densely packed fluorocarbon chains has been shown to provide a kinetic barrier to the diffusion of ambient oxidants such as oxygen, moisture, and ozone into the active channel area. With these perceptions in mind we have recently synthesized new 2,6-core-dichlorinated 1,4,5,8-naphthalene tetracarboxylic acid diimides bearing 2,2,3,3,4,4,4-
heptafluorobutyl and 2,2,3,3,4,4,5,5,5-nonafluoropentyl substituents at the imide nitrogens (compounds 3 and 4 in Scheme 2). For both compounds very high n-channel mobilities up to 0.91 (3) and 1.43 (4) have been achieved on SiO\(_2\) (300 nm) gate dielectrics. Remarkably, for NDI 3 the highest values were obtained on bare SiO\(_2\) gate dielectrics whilst for NDI 4 the highest values were measured on octadecyltrimethoxysilane (OTS)-treated SiO\(_2\).\(^{[25]}\)

In this work, we have synthesized three additional core-dichlorinated NDI compounds with shorter and longer fluorinated chains in the imide position and have employed them for the fabrication of n-channel OTFTs on different gate dielectrics, i.e. 110 nm thick SiO\(_2\)/Al\(_2\)O\(_x\)/tetradecylphosphonic acid and 5.7 nm thick Al\(_2\)O\(_x\)/octadecylphosphonic acid. We have studied structure-property correlations by investigating the thin-film morphology and field-effect mobilities on substrates with differently thick gate dielectrics.

2. EXPERIMENTAL SECTION

**Instrumentation.** Cyclic voltammetry experiments were performed using a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three-electrode single-compartment cell under argon. Dichloromethane (HPLC grade) was dried over calcium hydride under argon and degassed before use. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared according to literature\(^{[32]}\) and recrystallized from ethanol/water and dried under vacuum. The measurements were carried out in dichloromethane at a concentration of about 10\(^{-4}\) M with ferrocene (Fc) as the internal standard for the calibration of the potential. A Ag/AgCl reference electrode was used and a Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively. UV/VIS spectra were recorded with a Perkin Elmer Lambda 40 UV/VIS spectrophotometer. Solutions were prepared using dichloromethane in ambient condition. A Digital Instruments (DI) MMAFM-2 scanning probe microscope was used to perform tapping-mode atomic force microscopy (AFM) on the samples with a silicon tip of 300 kHz frequency. DI Nanoscope software was used to process the raw AFM images.

**Transistor Fabrication and Characterization.** We have fabricated TFTs with a thick gate dielectric (110 nm thick) that are operated with gate-source voltages (\(V_{GS}\)) of ~40 V, as well as TFTs with a thin gate dielectric (5.7 nm thick) that are operated with \(V_{GS}\) of ~3 V (Scheme 1).

![Scheme 1](image_url)

**Scheme 1.** Cross section of the TFTs with the 110 nm thick SiO\(_2\)/Al\(_2\)O\(_x\)/SAM gate dielectric (left) and of the TFTs with the 5.7 nm thick Al\(_2\)O\(_x\)/SAM gate dielectric (right).

TFTs with 110 nm thick gate dielectric: A heavily doped Si wafer was used as the substrate and gate electrode. The gate dielectric consisted of a 100 nm thick SiO\(_2\) layer (grown by thermal oxidation at a temperature of ~1000 °C) and an 8 nm thick Al\(_2\)O\(_x\) layer (deposited onto the SiO\(_2\) by atomic layer deposition) as well as a 1.7 nm thick self-assembled monolayer (SAM: obtained by immersing the substrate into a 2-propanol solution of n-tetradecylphosphonic acid). The SiO\(_2\)/Al\(_2\)O\(_x\)/SAM gate dielectric has a total thickness of 110 nm and a gate capacitance per unit area (\(C_i\)) of 32 nF/cm\(^2\). A 30 nm thick semiconductor layer was deposited onto the gate dielectric by sublimation in vacuum with a deposition rate of about 0.3 Å/sec. During the semiconductor deposition, the substrate was held at a specific temperature to optimize film growth. Transistors were completed by depositing Au source and drain contacts onto the organic semiconductor by vacuum evaporation through a shadow mask. The channel width was 200 μm and the channel length was 100 μm.

TFTs with 5.7 nm thick gate dielectric: A 20 nm thick Al gate electrode was deposited by thermal evaporation onto a heavily doped Si wafer used as the substrate. The gate dielectric consisted of a 3.6 nm thick Al\(_2\)O\(_x\) layer (obtained by briefly exposing the Al surface to oxygen plasma) and a 2.1 nm thick self-assembled monolayer of n-octadecylphosphonic acid. The Al\(_2\)O\(_x\)/SAM gate dielectric has a total thickness of 5.7 nm and a \(C_i\) of 810 nF/cm\(^2\). A 30 nm thick semiconductor layer was then deposited by vacuum sublimation, followed by Au source and drain contacts. The channel width was 200 μm and the channel length was 100 μm.
The electrical characteristics of the TFTs were measured in ambient air using an Agilent 4156C Semiconductor Parameter Analyzer. Key device parameters, such as field-effect mobility ($\mu$) and on-to-off current ratio ($I_{on}/I_{off}$) were extracted from the drain current ($I_D$) versus $V_{GS}$ characteristics.

3. RESULTS AND DISCUSSION

Synthesis. The NDI derivatives were synthesized according to Scheme 1. Briefly, 2,6-dichloronaphthalene tetracarboxylic acid dianhydride was prepared according to the literature[33] and heated under reflux in acetic acid or mixtures of acetic acid and N-methyl-2-pyrrolidone (NMP) with fluorinated alkyl amines to get yellowish solids 1-5 in yields of 65 to 90%. The NDI compounds were purified by vacuum sublimation in a three-temperature-zone furnace before thin-film deposition.

Electronic Structure Characterization. The energy levels of the core-chlorinated NDIs were investigated in solution at a concentration of $10^{-5}-10^{-4}$ M. Figure 1 exhibits UV/VIS spectra obtained from NDIs in dichloromethane at 298 K. NDIs 1-5 show as expected only minor changes in shape of the absorption band.

Table 1. Summary of the $\lambda_{max}$ of UV/VIS spectra and HOMO/ LUMO in dichloromethane at 298 K of the NDIs.

<table>
<thead>
<tr>
<th>NDI</th>
<th>$\lambda_{max}$ / nm</th>
<th>HOMO / eV</th>
<th>LUMO / eV</th>
<th>$E_g$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>402</td>
<td>−7.10</td>
<td>−4.02</td>
<td>3.08</td>
</tr>
<tr>
<td>2</td>
<td>402</td>
<td>−7.10</td>
<td>−4.02</td>
<td>3.08</td>
</tr>
<tr>
<td>3</td>
<td>402</td>
<td>−7.09</td>
<td>−4.01</td>
<td>3.08</td>
</tr>
<tr>
<td>4</td>
<td>402</td>
<td>−7.07</td>
<td>−3.99</td>
<td>3.08</td>
</tr>
<tr>
<td>5</td>
<td>402</td>
<td>−7.08</td>
<td>−4.00</td>
<td>3.08</td>
</tr>
</tbody>
</table>

$^a\lambda_{max}$ measured in CH$_2$Cl$_2$; $^b$HOMO estimated from LUMO and $E_g$. $^c$LUMO measured by cyclic voltammetry in degassed CH$_2$Cl$_2$ with 0.1M TBAFP as the electrolyte, with respect to a Fe/Fe$^+$ reference (−4.8 eV to vacuum) added after each measurement; $^dE_g$ (eV), band gap in solution obtained from the long wavelength absorption edge.
In the cyclic voltammetry analysis, NDIs exhibited two reversible reduction waves, while no oxidation wave could be observed due to the limited available potential range in the given solvent. Chlorination on the core region lowered the LUMO levels of the NDI derivatives. For instance, NDI without Cl substitution at the core showed a LUMO of $-3.72$ eV (with R = CH$_2$C$_3$F$_7$) while NDI with the same imide substituent and two Cl atoms at the core exhibited a lower LUMO of $-4.01$ eV. As expected, little variation of the LUMO levels and the band gaps are given within the series of NDIs 1-5 (Table 1) which all contain a methylene spacer unit between the NDI core and the perfluorinated alkyl chain.

**OTFT Characterization.** The electrical characteristics of a TFT based on compound 3 with a 110 nm thick SiO$_2$/AlO$_x$/SAM gate dielectric are shown in Figure 2; this TFT has a field-effect mobility of 1.3 cm$^2$/Vs. The electrical characteristics of a TFT based on the same compound (3), but with a 5.7 nm thick AlO$_x$/SAM gate dielectric are shown in Figure 3; this TFT has a mobility of 0.4 cm$^2$/Vs. Compound 3 is the derivative for which we have obtained the largest field-effect mobilities. Compounds 1 and 2 (which have shorter fluoroalkyl substituents) and compounds 4 and 5 (which have longer fluoroalkyl substituents) have mobilities that are significantly smaller than those of compound 3 (see Table 2 for a summary of the mobilities and on/off current ratios measured in TFTs based on all five compounds).

The observation that a fluoroalkyl substituent with a length of four carbon atoms (compound 3) provides the maximum mobility (while shorter and longer substituents lead to distinctly smaller mobilities) is consistent with a very similar observation that was recently reported for a family of dicyano-PDI compounds with various fluoroalkyl substituents.

![Figure 2](http://proceedings.spiedigitallibrary.org/)

**Figure 2.** Electrical characteristics of a TFT based on compound 3 with a 110 nm thick SiO$_2$/AlO$_x$/SAM gate dielectric. The TFT has an electron mobility of 1.3 cm$^2$/Vs and an on/off current ratio of 10$^7$.

![Figure 3](http://proceedings.spiedigitallibrary.org/)

**Figure 3.** Electrical characteristics of a TFT based on compound 3 with a 5.7 nm thick AlO$_x$/SAM gate dielectric. The TFT has an electron mobility of 0.4 cm$^2$/Vs and an on/off current ratio of 10$^5$.  

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Table 2. Summary of the electrical TFT parameters.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Optimum Substrate Temperature</th>
<th>TFTs with 110 nm thick SiO₂/AlOₓ/SAM gate dielectric</th>
<th>TFTs with 5.7 nm thick AlOₓ/SAM gate dielectric</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Optimum Substrate Temperature</td>
<td>Field-effect mobility on/off current ratio</td>
<td>Field-effect mobility on/off current ratio</td>
</tr>
<tr>
<td>1</td>
<td>50 °C</td>
<td>0.0005 cm²/Vs 10⁷</td>
<td>0.0001 cm²/Vs 10⁴</td>
</tr>
<tr>
<td>2</td>
<td>50 °C</td>
<td>0.2 cm²/Vs 10⁶</td>
<td>0.004 cm²/Vs 10⁴</td>
</tr>
<tr>
<td>3</td>
<td>50 °C</td>
<td>1.3 cm²/Vs 10⁷</td>
<td>0.4 cm²/Vs 10⁵</td>
</tr>
<tr>
<td>4</td>
<td>70 °C</td>
<td>0.9 cm²/Vs 10⁷</td>
<td>0.2 cm²/Vs 10⁵</td>
</tr>
<tr>
<td>5</td>
<td>90 °C</td>
<td>0.5 cm²/Vs 10⁷</td>
<td>0.2 cm²/Vs 10⁵</td>
</tr>
</tbody>
</table>

Table 2 also shows that the field-effect mobilities measured in the TFTs with the thick gate dielectric (SiO₂/AlOₓ/SAM, 110 nm) are always larger than the mobilities measured in the TFTs with the thin gate dielectric (AlOₓ/SAM, 5.7 nm). This can be explained by the fact that the carrier mobility in polycrystalline organic semiconductors is a function of both the carrier density and the lateral electric field in the channel. At the maximum gate-source voltage (40 V for the thick gate dielectric, 3 V for the thin gate dielectric) the carrier density in the channel is about the same (~10¹³ cm⁻²), but the lateral electric field is much larger in the TFTs with the thick gate dielectric (4 MV/cm) than in the TFTs with the thin gate dielectric (0.15 MV/cm). For the same carrier density, a larger lateral electric field is expected to produce a larger mobility, since a large lateral field accelerates the release of carriers that have been trapped in defects at the grain boundaries or at the semiconductor/dielectric interface.

Figure 4. AFM amplitude (0-500 mV) and topography (smaller inlay: 0–50 nm) images of 30 nm thick films of compounds 1-5 deposited by vacuum deposition onto AlOₓ/SAM gate dielectric.
AFM Analysis. To elucidate the influence of the fluorinated side chain in imide position on the mobilities of NDIs 1-5 the morphologies of the thin films were studied using AFM. Figure 4 exhibits AFM amplitude and topography images of 30 nm thick films prepared by vacuum deposition of compound 1-5 on AlO_{x}/SAM substrates at optimized substrate temperatures, respectively. Whereas clear grains and presumably the uncovered substrate can be observed for NDIs 1 and 5, the compounds 2, 3, and 4 show a closed layer with grains in the size of about 1-2 μm. The smoothest morphology can be observed for NDIs 3 and 4 with 2,2,3,3,4,4,4-heptafluorobutyl and 2,2,3,3,4,4,5,5,5-nonafluoropentyl as fluorinated side chain. This corresponds well to the results of OTFT performance. It is well known that charge transport takes place predominantly in the first few monolayers of organic semiconductor near the semiconductor/dielectric interface in an OTFT device. The formation of less grain boundaries may explain the higher charge carrier mobility for NDI 3 films deposited at this condition.

4. CONCLUSION

We described the synthesis of five core-chlorinated NDIs 1-5 with fluorinated alkyl chains of different length at the imide nitrogen, characterized their electrical and optical properties as well as the film morphology of the n-channel semiconductors in air. OFETs were fabricated in a bottom gate top contact configuration with either thick (SiO_{2}/AlO_{x}/tetradecylphosphonic-acid SAM: 110 nm thick) or thin gate dielectric (AlO_{x}/octadecylphosphonic acid SAM 5.7 nm thick). The LUMO level and band gap of NDI molecules in solution were not dependent on the chain length of the fluorinated substituent. The AFM investigations of the NDI thin films deposited on top of the thin gate dielectric (AlO_{x}/SAM) under the optimized substrate temperatures revealed the smoothest surface with the least amount of grain boundaries for compounds 3 and 4. NDIs 3 and 4 exhibited the highest field-effect mobilities (up to 1.3 and 0.9 cm²/Vs, respectively) together with the minimal hysteresis and high on-to-off ratios (~10⁷) in air on the thicker substrate which confirms our earlier results on SiO_{2} and SiO_{2}/OTS dielectrics. All analogues with shorter (1, 2) or longer (5) fluorinated side chains yielded lower mobilities. This may be related with the fact that the molecular packings and concomitant charge-transport behaviors are highly sensitive to the relative ratio of the size of endgroup with regard to that of π-conjugated core. For NDIs 3 and 4 our current and recent work shows that high field-effect mobilities > 1 cm²/Vs can be measured on a broad variety of substrates. In this work this feature enabled the realization of TFTs on thin gate dielectrics that afforded transistors with a field-effect mobility of 0.4 cm²/Vs and on/off current ratios of 10⁷ at technologically interesting very low gate-source voltages of 3V. As we will show in a subsequent paper the good combination of molecular properties and packing behavior that provides a favorable barrier to the exclusion of ambient oxidants into the active channel area also enables the preparation of outstanding OTFTs by solution-processing. Accordingly, core-chlorinated NDIs are most promising n-channel organic semiconductors for use in various practical applications.

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