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High-Performance n-Channel Organic Thin-Film Transistor Based on Naphthalene Diimide

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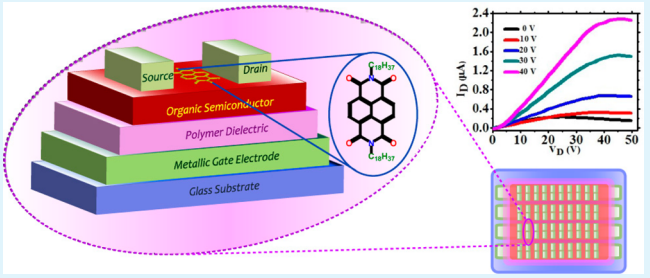
Supporting Information

ABSTRACT: A conjugated molecule comprising 1,4,5,8-naphthalene diimide (NDI) substituted with two octadecylamine (OD) chains has been synthesized (NDI-OD2) in a single step from commercial materials, and its organic thin-film transistor (OTFT) devices on glass substrate have been studied using poly(vinyl alcohol) (PVA) gate dielectric material. Although we utilized the PVA dielectric without any intermediate buffer layer or PVA cross-linkers, excellent electron mobility as high as ~1.0 cm^2V^{-1} s^{-1} are obtained. This NDI-OD2 molecule exhibits comparable optical (E_g^{UV} ~3.1 eV) and electrochemical band gaps (E_g^{CV} ~3.02 eV) with a lowest unoccupied molecular orbital (LUMO) energy levels of ~3.3 eV. When processed by solution method, this material forms rod−shaped crystalline microstructures, whereas, when thermally deposited, it assumes the formation of smooth 2D films. The chemical as well as physical properties and theoretical calculations of NDI-OD2 have been studied and the effect of the C-18 alkyl chain unit has been discussed. The OTFT consisting of NDI-OD2 exhibits excellent performance parameters such as high electron mobility (μ_e) and I_{on}-to-I_{off} ratio. After demonstrating the high performance of NDI-OD2-based TFT devices fabricated with biocompatible PVA dielectric, we have also demonstrated that these devices can be degraded because of the presence of this PVA dielectric when exposed to a high-moisture environment. The systematic degradation of the device activity in a controlled way within 10 days of exposure (>80% moisture) is also presented here. In this study, a conceptually important feature and futuristic aspect that the n-channel TFT devices can also be biodegraded irreversibly is demonstrated. This concept of developing a low cost and biodegradable OTFT device with biocompatible PVA dielectric with excellent electron mobility is expected to have diverse applications in disposable electronic tags, biomedical devices, and food industry packing.



KEYWORDS: *n-channel organic thin film transistor, naphthalene diimide, poly(vinyl alcohol), n-type organic semiconductor, electron transport*

INTRODUCTION

Organic semiconductors (OSCs) have attracted increasing attention because of their important roles in electronics, such as p−n junctions, bipolar transistors, and complementary circuits.[1−9] Among them, organic thin-film transistors (OTFTs) represent one of the important building blocks for developing organic and printed electronics because their transistor performance is comparable to that of Si-TFTs and they have advantages of light weight, flexibility, transparency, facile processing methods, and low manufacturing costs. However, the development of n-channel OTFTs still lags behind that of p-type OTFTs because of their inferior performance, air instability, and few other issues.[10−15] The performance of p-type OTFTs has recently improved substantially and become comparable to that of a Si-TFTs: for example, the hole mobilities of pentacene,[16] and a rubrene single crystal,[17] have been reported to be as high as 3 and 15 $cm^2V^{-1}s^{-1}$ respectively. In contrast, progress in n-type OTFT materials has been inadequate and delayed by several inherent problems.[18−21] It is recognized that the electron carriers in n-type OTFT materials undergo detrimental trapping processes, i.e., they show strong instability[22] when they are exposed to H_2O and O_2 in air.[23] As a consequence, in most cases, the μ_e of n-type OTFT materials dramatically decreases when exposed to air.

Among the rare building blocks useful for producing n-channel OSCs, rylene diimides, especially perylene and naphthalene derivatives, have so far proved to be the most successful electron-transporting (n-type) units.[24−34] Small molecule perylene diimides (PDIs) are good candidates for n-type organic semiconductors because they assemble in π-stacks that enhance the intermolecular π-orbital overlap and facilitate charge transport. Many modifications have been introduced in PDIs that have led to the improved solubility in common solvents, in addition to the improvement in electron mobility and enlarged electron affinity for operation stability in

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air. Naphthalene diimide (NDI) based molecules have also been intensively investigated as n-type semiconductors for organic field effect transistors (OFETs).[35,36] This class of material demonstrates not only a highly planar conjugated backbone, but also easily tunable electronic properties through modification at the core and/or the imide position with electron-withdrawing groups or conjugated units.[37] On the basis of core expansion or core-substitution strategies, several NDI derivatives with symmetrical structures have been designed and synthesized for n-channel OFETs with high electron mobility.[38] The electron-accepting naphthalene diimides (NDI), an analog of PDI, provides a planar conjugated bicyclic structure, which leads to strong $\pi-\pi$ interactions and offers improved charge-transporting properties between the chains. In addition, the introduction of alkyl chains at the N-position of the imide ring allows good control over physical properties such as solubility and processability, crystallization, and self-assembly capability. Moreover, the presence of strong electron-withdrawing groups within the naphthalene moiety also lowers the LUMO level, thereby increasing the air stability of the n-type semiconductor.[39−41]

An additional requirement of OTFT monomer materials is sufficient thermal stability to endure the elevated temperatures of the fabrication steps as well as the heat generated during operation of integrated devices.[42,43] The performances of OTFTs are not only dependent on the organic semiconductors and their molecular arrangement within the active channel of the device but also on the gate dielectric that controls the charge flow. Inorganic oxides such as SiO_2, Al_2O_3, TiO_2, etc. are frequently utilized for OTFT fabrication as gate dielectric materials with higher gate dielectric constant. But most of these high dielectric constant materials suffer from expensive deposition methods. Therefore, organic dielectric materials which can be processed by solution casting methods such as poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), poly(4-vinylphenol) (PVP) are frequently utilized in OTFT device fabrication as well as for biomedical and biodegradable device application.[44]

In this study, we report the development of 1,4,5,8-Naphthalene diimide (NDI) substituted with octadecylamine (OD) chains (NDI-OD2 molecule) and fabricated their efficient OTFT devices. We have exploited the biocompatibility and low-cost design of the devices using pristine PVA as organic dielectric material spin-casted on the glass substrate and used it without further treatment. PVA is very economical, has high dielectric constant and good surface alignment, and is well-known to be compatible with electronic devices; because of the US FDA approval, it has also been utilized extensively in biomedical devices. Despite these advantages, PVA has a fundamental drawback of degrading the devices because of its hygroscopic nature. Hence, this material has not been generally preferred as a dielectric for OTFT devices or if utilized, it must be cross-linked with a linker such as ammonium dichromate or an additional buffer layer is needed to prevent the device degradation. We optimized a well-ordered smooth film of NDI-OD2 by thermal deposition method directly over the pristine PVA layer, such that the fabricated devices demonstrated excellent performances with very low leakage current and excellent mobility. However, it was observed that when NDI-OD2 was processed by solution method, it forms needle-shaped crystalline microstructures, whereas when thermally deposited, it assumes the form of smooth 2D film following Stranski−Krastanov growth pattern. The NDI-OD2 showed typical n-type TFT performance with the maximum electron mobility found to be 1.0 $cm^2\ V^{-1}\ s^{-1}$ under vacuum. Most notably we have been successful in performing experiments which demonstrate that the NDI-OD2 devices can work in the presence of spin-casted pristine PVA, with a conceptually important feature that these n-channel TFT devices can also be biodegraded when exposed to environment having high moisture content because of the presence of this PVA dielectric. We observed that these NDI-OD2 devices exhibit performance loss in a controlled manner followed by complete failure on continuous exposure for few days to high moisture environment. Thus, low-cost and environmentally friendly n-channel OTFT devices with high electron mobility can be achieved utilizing a combination of conjugated small molecules and biodegradable dielectric material such PVA.

RESULTS AND DISCUSSION

Synthesis. NDI−OD2 molecule was synthesized following the procedure reported in literature by the direct condensation of 1,4,5,8-Naphthalene dianhydride with octadecylamine in excellent yields[45] (see the Supporting Information, Figure S1).

DFT Calculated Molecular Geometries and Orbitals. To predict the minimum-energy confirmation of the monomer backbone and the LUMO/HOMO, we performed the DFT calculation (B3LYP/6-31G (d)) on the NDI-OD2 molecule (see the Supporting Information, Figure S2). The dihedral angle between the main NDI core and the neighboring C-18 alkyl unit is calculated to be ∼89.76°. The theoretical HOMO−LUMO position of NDI-OD2 was found to be (−6.984 eV, −3.365 eV), which reveals that the energy gaps reflect the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donate an electron. The geometrically optimized structures and their corresponding HOMO and LUMO structures are shown in Figure 1a−c.

Optical Properties. UV−visible absorption and emission spectra of the molecule were measured in a dilute solution of chloroform (1×10^{-3} M). For solid state study, a thin film of the molecule was thermally deposited on glass substrate under 1×10^{-7} mbar pressure. The UV−visible spectrum of NDI-OD2 shows absorption peaks at 381, 360, and 341 nm due to characteristic $\pi-\pi^*$ transitions.[46] The spectral absorptions of a thin film of NDI-OD2 is red-shifted by about 10 nm as compared to the solution (see the Supporting Information, Figure S3). This shift in the film form is due to the additional intermolecular interactions leading to conformational adjustments of the molecules that impose changes in the conjugation length.[47] The absorption pattern similarity between the thin film and the solution spectra suggests a structurally well-organized molecular system.[48] In $CHCl_3$, the emission spectrum shows peaks at 406 and 431 nm, with a weak blue emission and displaying almost similar mirror image of the absorption spectrum (Figure 2a).[49]

Electrochemical Properties and Band Gap Calculation. The redox properties of the NDI-OD2 were evaluated using cyclic voltammetry. NDI-OD2 film was drop-casted from chloroform solution onto a 2 mm diameter Glassy carbon electrode. The cyclic voltammogram was recorded against Ag/Ag^+ reference electrode in anhydrous acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte at a scan rate of 50 mV/s. The electrochemical potentials were estimated from the onset of the oxidation and reduction sweeps. The voltammogram was calibrated using the

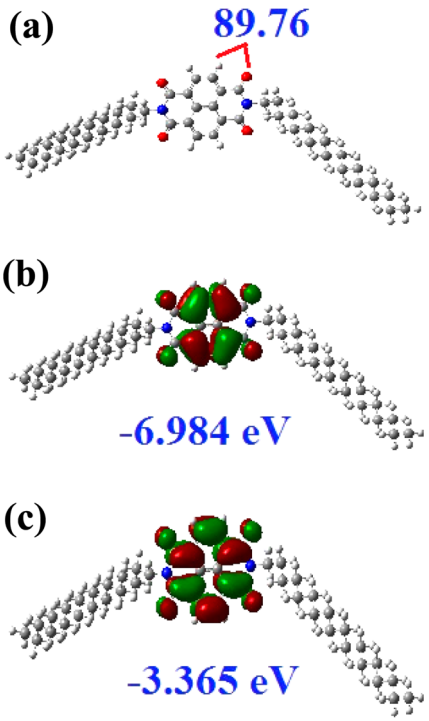

Figure 1. (a) Optimized structure and MO energies ((b) HOMO and (c) LUMO) of the NDI-OD2 molecule, obtained by DFT calculation.

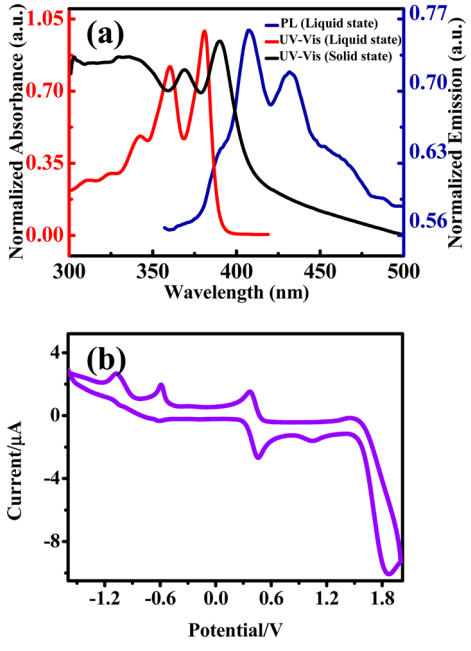

Figure 2. (a) Absorption of NDI-OD2 monomer shows three characteristics absorption peaks at 381, 360, and 341 nm in solution state and a slightly red shift of about 10 nm in solid state as compared to the solution. The emission spectrum shows peaks at 406 and 431 nm, having reasonable mirror image of the absorption spectrum. (b) Cyclic voltammogram of NDI-OD2 monomer as thin film was drop-cast on a Glassy carbon working electrode and tested in anhydrous acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP) solution at a scan rate of 50 mV/s.

Fc/Fc^+ redox couple. The redox potential thus obtained was converted to the corresponding energy levels assuming the absolute HOMO energy level of ferrocene to be −4.8 eV. (eq 1 and eq 2).[50]

$$E_{HOMO} = -(E_{ox\,onset} + 4.8)\ eV \quad (1)$$

$$E_{LUMO} = -(E_{red\,onset} + 4.8)\ eV \quad (2)$$

The estimated HOMO and LUMO energy levels and the electrochemical as well as optical band gap of the NDI-OD2 is summarized in Table 1, whereas the representative scans of the NDI-OD2 thin films are shown in Figure 2b.

Table 1. Summary of Band Gap Calculation Data for NDI-OD2[a]

$E_{HOMO}^{(CV)}$	$E_{LUMO}^{(CV)}$	E_g^{CV}	E_g^{UV}	E_g^{Th}
−6.414	−3.394	3.02	3.18	3.61

[a]Energies are in eV. E_g^{CV}, electrochemical band gap; E_g^{UV}, optical band gap; and E_g^{Th}, theoretical band gap were calculated by using DFT calculation.

Thermal Studies. For any organic device, especially for n-type OTFTs, superior thermal properties are very important since they are directly related to practical issues such as device fabrication, operation and longevity. The thermal stability of NDI-OD2 was investigated with thermo gravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The NDI-OD2 was thermally stable up to 391 °C. The degradation begins at ∼393 °C and complete degradation is observed above 500 °C (Figure 3). Because the maximum

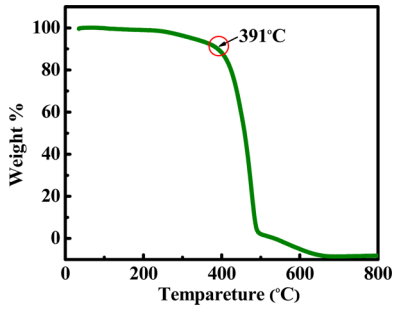

Figure 3. TGA plot of NDI-OD2 with heating rate of 10 °C min^{-1} under nitrogen flow showing the thermal degradation pattern.

deposition temperature attained during the device fabrication (room temperature to ∼230 °C sublimation) (see the Supporting Information, Figure S4) was much below the degradation temperature of the NDI-OD2, its performance remained unaffected as observed from the smooth film formation and the OTFT device data.

Thin Film Microstructure. Different microscopic analysis and XRD studies were utilized to investigate the surface morphologies of the fabricated thin films. Figure 4 shows the optical microscopic images, FESEM and AFM of spin-cast (∼55 nm, 2000 rpm) and thermally deposited (∼60 nm, 1×10^{-7} mbar pressure) NDI-OD2 film at room temperature. In polarized optical microscopy (Figure 4a, i and ii) (see the Supporting Information, Figure S5) and FESEM [Figure 4b, i and ii) (see the Supporting Information, Figure S6) the NDI-OD2 appeared as a sharp single needle-type microstructure when spin-cast by solution method, whereas, the thermally deposited films give highly smooth 2D film following Stranski-Krastanov growth pattern.

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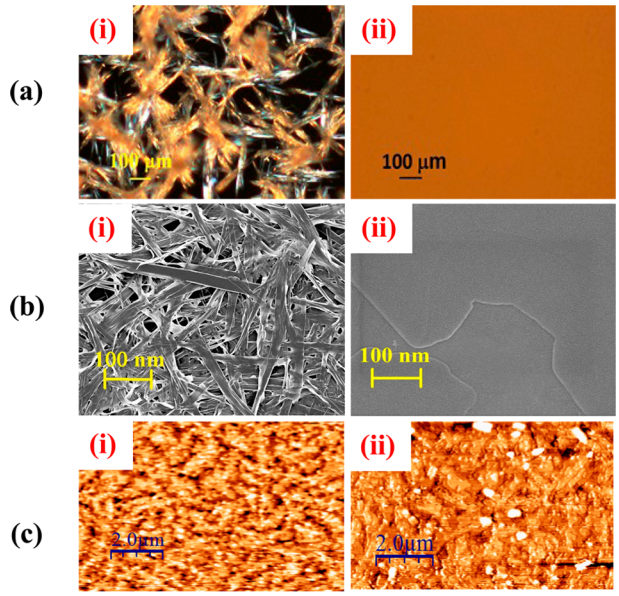

Figure 4. (a) Optical microscopy images, (b) FESEM images, and (c) AFM images of (i) spin-cast and (ii) thermally deposited films of NDI-OD2 showing that the thermally deposited film have better morphology than the spin-cast film of the monomer.

The thermally grown thin film of NDI-OD2 shows a very densely packed smooth film in AFM analysis with RMS roughness of ~5.64 nm (Figure 4c, ii) which is requisite for efficient TFT behavior, whereas, the spin-cast film (Figure 4c, i) shows ~47.90 nm (see the Supporting Information, Figure S7) roughness.

The crystalline nature of NDI-OD2 was confirmed by using high power (18 kW) X-ray diffractometer. Figure 5a displays X-ray diffraction (XRD) patterns for both thin film and powder. It is evident that the sharp peaks observed in the small-angle regions support the formation of molecules that were highly ordered and crystalline in nature. The lamellar *d*-spacing for powder and thin film around $2\theta = 2.4°$ was found to be 36.93 and 37.75 Å, respectively. These values are somewhat smaller than the theoretically predicted value of 53.02 Å (Supporting Information, Figure S2). However, a careful observation of the XRD patterns reveals that (i) majority of the diffraction peaks observed in the powder were also obtained in thin films for $2\theta \leq 15°$ confirming that the thin films have the same molecular packing motif as seen in powders. With increasing $2\theta > 15°$, both powder and thin film exhibit completely different properties, i.e., while the powder sample exhibits more number of diffraction lattice planes giving rise to different Bragg peaks, the thin film displays a broad peak in the 2θ range of 16 to 34°. This could be correlated to the growth nature of the evaporated film on the substrate. This is also in excellent agreement with the earlier reports on similar system.[51] (ii) the XRD peaks of the powder sample exhibits more asymmetry in nature and the broadness of the peaks is observed to be larger in the thin films as compared to the powders. The average size of the crystallites calculated using the Bragg peak at around $2\theta = 14°$ corresponds to 25 and 23 nm for powder and thin film, respectively (see the Supporting Information, Figures S8 and S9). To further investigate the crystalline nature, we obtained high-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) patterns as shown in Figure 5b, c, respectively (see the Supporting Information, Figure S8). Closer observation of the HRTEM image reveals

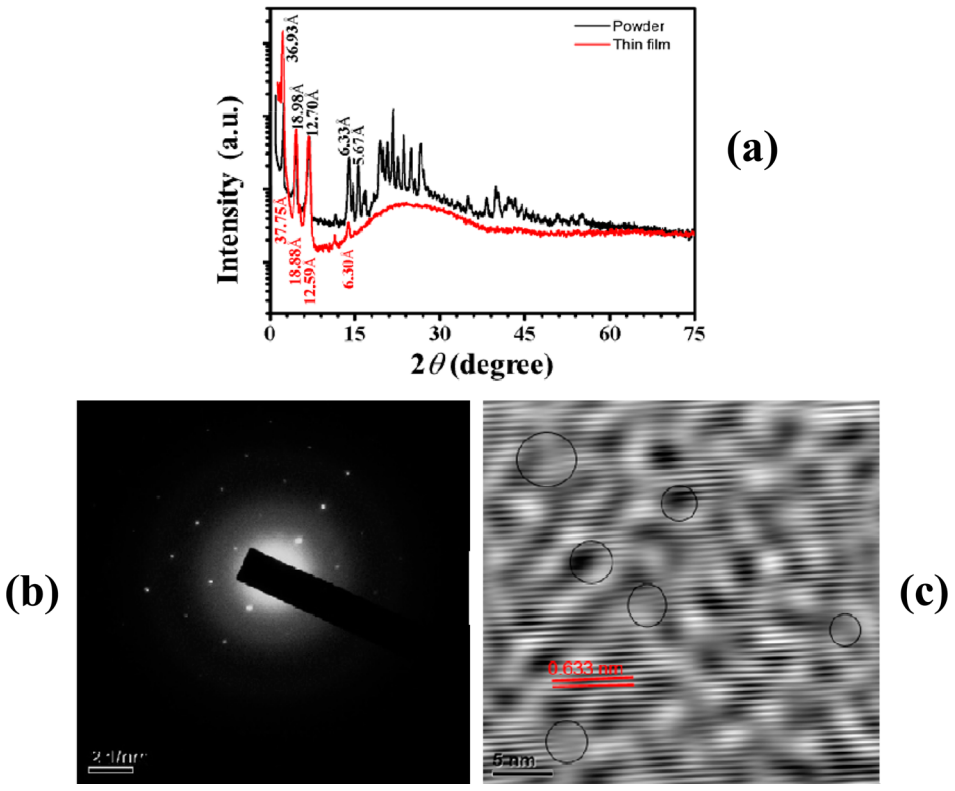

Figure 5. (a) XRD patterns, (b) SAED pattern, and (c) HRTEM of NDI-OD2 confirming the crystalline nature of this molecule. The interplanar spacing determined from HRTEM image is about 6.33 Å, which is in good agreement with the value calculated from the XRD at $2\theta = 14°$.

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the presence of finite dislocations as highlighted by circles causing possible strain and resulting in asymmetric XRD peaks (see Figure 5a). In addition, the interplanar spacing determined from HRTEM image is about 6.33 Å, which is in good agreement with the value calculated from the XRD peak at around $2\theta = 14°$. The crystalline nature of NDI-OD2 is also confirmed from SAED results as shown in Figure 5b.

OTFT Device Fabrication and Characterization. OTFTs based on NDI-OD2 were fabricated with a top contact bottom-gate configuration. A simple glass slide was used as a substrate and aluminum (Al) (100 nm) gate electrode was thermally deposited above it. A spin-coated film of poly(vinyl alcohol) (PVA) thickness ~1 μm (1000 rpm) was used as a dielectric material having capacitance ~8.854 nF cm^{-2}. A 60 nm thick (±10 nm) NDI-OD2 semiconductor film was thermally deposited on the Al coated glass slide (substrate temperature = room temperature), at a pressure of 1×10^{-7} mbar. Al source and drain contacts (100 nm) were deposited on the organic layer through a shadow mask with channel length (L) and width (W) of 50 μm and 1 mm, respectively. All the electrical properties were measured under vacuum using a Keithley 4200-SCS semiconductor parameter analyzer. The mobility of the saturated region was extracted from the following eq 3

$$I_{DS} = C_i \mu_e (W/2L)(V_g - V_T)^2 \quad (3)$$

where I_{DS} is the drain current, C_i is the capacitance per unit area of the gate dielectric layer, μ_e is the field effect electron mobility, W and L are the channel width and length, V_g and V_T are the gate voltage and threshold voltage, respectively. The output and transfer characteristic curves for NDI−OD2 based OTFT are shown in Figure 6a, b (see the Supporting Information, Figures S10 and S11).

The NDI-OD2 molecules in OTFT devices, sublimed at room temperature over pristine PVA dielectric, exhibited excellent electron mobility as high as 1.0 cm^2 V^{-1} s^{-1} (average value for 75 devices was ~0.68 cm^2 V^{-1} s^{-1}) under vacuum with threshold voltage of 16.24 V and current on-to-off ratio 1×10^2. Because the XRD pattern of the evaporated film of NDI-OD2 reveals very good crystalline nature and AFM analysis confirms that these thermally grown thin film shows a very densely packed smooth morphology, such densely packed semiconducting layers tend to exhibit larger off-current levels, resulting in smaller on-to-off current ratios and is in agreement with a recent report.[52] The mobility values which we report here are the highest in a bottom-gated n-type TFT device fabricated on glass substrate using biocompatible PVA dielectric. In addition, the use of PVA dielectric further allowed us to degrade the device in a highly controlled manner on simple exposure to moisture, thereby, further reducing the recycling cost of the product after end use. On exposure of these NDI-OD2 molecule-based devices to an environment having >80% moisture, the drastic degradation of the device commences with observation of loss in mobility followed by complete device failure within 10 days and confirms with conventional knowledge that pristine PVA dielectrics degrade the OTFT devices when exposed to moisture containing environment (see the Supporting Information, Figure S12).

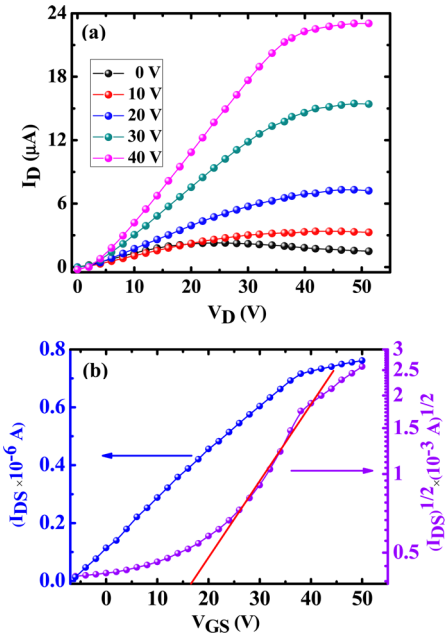

Figure 6. (a) Output and (b) transfer characteristics curves of OTFT device based on NDI-OD2 monomer; I_{DS} was obtained at drain-source voltage V_{DS} = 40 V.

Encouraged by the results of PVA dielectric, the NDI-OD2 molecules were also sublimed over other dielectrics such as PMMA, PVP independently and PMMA as a buffer layer with PVA dielectric and their device characteristics studied. All these combinations, however, exhibited very poor device performance as compared to pristine PVA dielectric due to inferior film formation. The thermally evaporated films of NDI-OD2 molecules on PVA were found to have very good layer structure. PVA is known for its high surface energy compared to other organic dielectric materials due to its hydrophilic nature.[53] Closer inspection revealed that NDI-OD2 forms a very smooth, amorphous-like film on PVA surface with surface roughness of less than ~5.64 nm. Hence, higher mobility values are observed with NDI-OD2 active layer and PVA dielectric here. In addition to the role of dielectric, it is known that the length of the alkyl chains can also effectively improve the OTFT device performance. According to Pei et al., organic materials that possess longer alkyl chains (branched or linear) exhibited higher carrier mobilities.[54] The NDI-OD2 molecule-based material reported here possesses two symmetrical octadecyl chains and demonstrates excellent electron mobility in the presence of low-cost device using commercially available materials such as aluminum and PVA on glass substrate, which allows to scale up the device fabrication and production on larger substrates and quantities.

CONCLUSIONS

We described the synthesis, fabrication, and characterization of alkyl chain-substituted naphthalene diimide molecule, which in combination with a biocompatible PVA dielectric was utilized to fabricate n-type OTFT devices with high electron mobility on glass substrate. The NDI-OD2 material is obtained in a single step from commercially available materials allowing development of these materials up to a large scale. We have also avoided the use of Si-substrates and gold electrodes and instead used glass and aluminum, in addition to the economical PVA as the dielectric material to keep the overall cost of this device very low as well as degradable after use. A combination of several thin film characterizations (Optical microscopy, FESEM, AFM, XRD and TEM) techniques reveals that the thermally deposited NDI-OD2 has significant influence on film morphology and molecular packing which enhanced the charge

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transport properties. This NDI-OD2 material shows a typical n-type TFT performance with excellent electron mobility that were as high as ~1.0 $cm^2 V^{-1} s^{-1}$ indicating that low-cost, high performance n-type TFT devices based on small molecules such as NDI-OD2 can be developed. All these results clearly exhibit that the molecular modulation of the semiconductor structure or modulation of the fabrication technique can provide an effective approach to achieve low-cost, high-performance OTFTs on desired substrates and electrodes even in the presence of biocompatible dielectric material such as PVA and possibly extending these devices to biomedical applications. The use of PVA also allowed the systematic degradation of the device activity in a controlled way within few days of exposure to moisture. The thermal deposition of this material on desired substrate was also possible at room temperature, making them very attractive materials with great potential for organic and bioelectronic devices, sensors, etc. We presume that because of the overall economy of fabricating this OTFT device, in addition to the excellent electron mobility, they can potentially be applied to bioelectronics and medical devices, disposable tags, consumer goods, and grocery industry packing.

EXPERIMENTAL SECTION

Chemicals and Solvents. 1,4,5,8-Naphthalene dianhydride, octadecylamine, quinoline, zinc acetate, were used as received from Sigma-Aldrich.

Instrumentation. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a variant AS400 NMR spectrometer. IR spectrum of NDI−OD2 was recorded on a PerkinElmer FT-IR spectrometer. UV−visible absorption spectra (solution and film both) were recorded on a PerkinElmer Lambda 35 spectrophotometer. Emission Spectra were measured on a Varian-Cary Eclipse spectrophotometer. Field emission scanning electron microscopy images were recorded in a Sigma Carl Zeiss scanning electron microscope. Atomic force microscopy images were taken by Agilent 5500-STM instrument. Transmission electron microscopic studies were done using a Tecnai G2 F20 S-twin JEOL 2100 transmission electron microscope. Electrochemical measurements were done using CH Instrument. Thermo gravimetric analysis (TGA) measurements were performed on Shimadzu thermo gravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C min^{-1}. The powder and thin film X-ray diffraction (XRD) pattern was recorded by high power (18 kW) X-ray diffractometer (Rigaku TTRAX III) with Cu Kα radiation.

ASSOCIATED CONTENT

Supporting Information

Synthesis of NDI-OD2, characterization and the methods used in performing various imaging, electrochemistry, XRD, DFT calculations, and device fabrication experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dotz, F.; Kastler, M.; Facchetti, A. A High-Mobility Electron-Transporting Polymer for Printed Transistors. *Nature* **2009**, *457*, 679−686.

(2) Usta, H.; Facchetti, A.; Marks, T. J. *n*-Channel Semiconductor Materials Design for Organic Complementary Circuits. *Acc. Chem. Res.* **2011**, *44*, 501−510.

(3) Guo, X.; Kim, F. S.; Seger, M. J.; Jenekhe, S. A.; Watson, M. D. Naphthalene Diimide-Based Polymer Semiconductors: Synthesis, Structure−Property Correlations, and n-Channel and Ambipolar Field-Effect Transistors. *Chem. Mater.* **2012**, *24*, 1434−1442.

(4) Guo, Y.; Yu, G.; Liu, Y. Functional Organic Field-Effect Transistors. *Adv. Mater.* **2010**, *22*, 4427−4447.

(5) Chen, H.; Guo, Y.; Mao, Z.; Yu, G.; Huang, J.; Zhao, Y.; Liu, Y. Naphthalene Diimide-Based Copolymers Incorporating Vinyl-Linkages for High-Performance Ambipolar Field-Effect Transistors and Complementary-Like Inverters under Air. *Chem. Mater.* **2013**, *25*, 3589−3596.

(6) Dodabalapur, A. Organic and Polymer Transistors for Electronics. *Mater. Today* **2006**, *9*, 24−30.

(7) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. n-Type Organic Semiconductors in Organic Electronics. *Adv. Mater.* **2010**, *22*, 3876−3892.

(8) Facchetti, A. Semiconductors for Organic Transistors. *Mater. Today* **2007**, *10*, 28−37.

(9) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. Design, Synthesis, and Characterization of Ladder-Type Molecules and Polymers. Air-Stable, Solution-Processable *n*-Channel and Ambipolar Semiconductors for Thin-Film Transistors via Experiment and Theory. *J. Am. Chem. Soc.* **2009**, *131*, 5586−5608.

(10) Maliakal, A. In *Organic Field-Effect Transistor*; Bao, Z., Locklin, J. CRC Press: Boca Raton, FL, 2007; p 229.

(11) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting π-Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics. *Chem. Rev.* **2012**, *112*, 2208−2267.

(12) Zaumseil, J.; Sirringhaus, H. Electron and Ambipolar Transport in Organic Field-Effect Transistors. *Chem. Rev.* **2007**, *107*, 1296−1323.

(13) Newman, C. R.; Frisbie, C. D.; Filho, D. A. S.; Brédas, J. L.; Ewbank, P. C.; Mann, K. R. Introduction to Organic Thin Film Transistors and Design of n-Channel Organic Semiconductors. *Chem. Mater.* **2004**, *16*, 4436−4451.

(14) Shirota, Y.; Kageyama, H. Charge Carrier Transporting Molecular Materials and Their Applications in Devices. *Chem. Rev.* **2007**, *107*, 953−1010.

(15) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y.; Dodabalapur, A. A Soluble and Air-stable Organic semiconductor with High Electron Mobility. *Nature* **2000**, *404*, 478−481.

(16) Klauk, H.; Halik, M.; Zschieschang, U.; Schmid, G.; Radlik, W.; Weber, W. High-Mobility Polymer Gate Dielectric Pentacene Thin Film Transistors. *J. Appl. Phys.* **2002**, *92*, 5259−5263.

(17) Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A. Elastomeric Transistor Stamps: Reversible Probing of Charge Transport in Organic Crystals. *Science* **2004**, *303*, 1644−1646.

(18) Bao, Z. Materials and Fabrication Needs for Low-Cost Organic Transistor Circuits. *Adv. Mater.* **2000**, *12*, 227−230.

(19) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. Effects of Arylene Diimide Thin Film Growth Conditions on n-Channel OFET Performance. *Adv. Funct. Mater.* **2008**, *18*, 1329−1339.

(20) Haddon, R. C. C_{70} Thin Film Transistors. *J. Am. Chem. Soc.* **1996**, *118*, 3041−3042.
(21) Horowitz, G.; Kouki, F.; Spearman, P.; Fichou, D.; Nogues, C.; Pan, X.; Garnier, F. Evidence for n-Type Conduction in a Perylene Tetracarboxylic Diimide Derivative. *Adv. Mater.* **1996**, *8*, 242−245.
(22) Horowitz, G. Organic Field-Effect Transistors. *Adv. Mater.* **1998**, *10*, 365−377.
(23) Jones, B. A.; Facchetti, F.; Wasielewski, M. R.; Marks, T. J. Tuning Orbital Energetics in Arylene Diimide Semiconductors: Materials Design for Ambient Stability of n-Type Charge Transport. *J. Am. Chem. Soc.* **2007**, *129*, 15259−15278.
(24) Wen, Y.; Liu, Y. Recent Progress in n-Channel Organic Thin-Film Transistors. *Adv. Mater.* **2010**, *22*, 1331−1345.
(25) Zhang, F.; Di, C.-a.; Berdunov, N.; Hu, Y.; Gao, X.; Meng, Q.; Sirringhaus, H.; Zhu, D. Ultrathin Film Organic Transistors: Precise Control of Semiconductor Thickness via Spin-Coating. *Adv. Mater.* **2013**, *25*, 1401−1407.
(26) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. Rylene and Related Diimides for Organic Electronics. *Adv. Mater.* **2011**, *2*, 268−284.
(27) Zhang, F.; Hu, Y.; Schuettfort, T.; Di, C.-a.; Gao, X.; McNeill, C. R.; Thomsen, L.; Mannsfeld, S. C. B.; Yuan, W.; Sirringhaus, H.; Zhu, D. Critical Role of Alkyl Chain Branching of Organic Semiconductors in Enabling Solution-Processed N-Channel Organic Thin-Film Transistors with Mobility of up to 3.50 $cm^2\ V^{-1}\ s^{-1}$. *J. Am. Chem. Soc.* **2013**, *135*, 2338−2349.
(28) Würthner, F.; Stolte, M. Naphthalene and Perylene Diimides for Organic Transistors. *Chem. Commun.* **2011**, *47*, 5109−5115.
(29) Suraru, S. L.; Zschieschang, U.; Klauk, H.; Würthner, F. A Core-Extended Naphthalene Diimide as a p-Channel Semiconductor. *Chem. Commun.* **2011**, *47*, 11504−11506.
(30) Oh, J. H.; Suraru, S.-L.; Lee, W.-Y.; Könemann, M.; Höffken, H. W.; Röger, C.; Schmidt, R.; Chung, Y.; Chen, W.-C.; Würthner, F.; Bao, Z. High-Performance Air-Stable n-Type Organic Transistors Based on Core-Chlorinated Naphthalene Tetracarboxylic Diimides. *Adv. Funct. Mater.* **2010**, *20*, 2148−2156.
(31) Jung, B. J.; Tremblay, N. J.; Yeh, M. L.; Katz, H. E. Molecular Design and Synthetic Approaches to Electron-Transporting Organic Transistor Semiconductors. *Chem. Mater.* **2011**, *23*, 568−582.
(32) Li, C.; Xiao, C.; Li, Y.; Wang, Z. Synthesis and Properties of Heterocyclic Acene Diimides. *Org. Lett.* **2013**, *15*, 682−685.
(33) Ye, Q.; Chang, J.; Huang, W. K.; Shi, X.; Wu, J.; Chi, C. Cyanated Diazatetracene Diimides with Ultrahigh Electron Affinity for n-Channel Field Effect Transistors. *Org. Lett.* **2013**, *15*, 1194−1197.
(34) Chen, X.; Guo, Y.; Tan, L.; Yang, G.; Li, Y.; Zhang, G.; Liu, Z.; Xu, W.; Zhang, D. Dithiazole-Fused Naphthalene Diimides Toward New n-Type Semiconductors. *J. Mater. Chem. C* **2013**, *1*, 1087−1092.
(35) Chang, J.; Ye, Q.; Huang, W. K.; Zhang, J.; Chen, K. J.; Wu, J.; Chi, C. Stepwise Cyanation of Naphthalene Diimide for n-Channel Field-Effect Transistors. *Org. Lett.* **2012**, *14*, 2964−2967.
(36) Laquindanum, J. G.; Katz, H. E.; Dodabalapur, A.; Lovinger, A. J. n-Channel Organic Transistor Materials Based on Naphthalene Frameworks. *J. Am. Chem. Soc.* **1996**, *118*, 11331−11332.
(37) Chang, J.; Shao, J.; Zhang, J.; Wu, J.; Chi, C. A Phthalimide-Fused Naphthalene Diimide with High Electron Affinity for a High Performance n-Channel Field Effect Transistor. *RSC Adv.* **2013**, *3*, 6775−6778.
(38) Shao, J.; Chang, J.; Chi, C. Solution-Processable n-Type Semiconductors Based on Unsymmetrical Naphthalene Imides: Synthesis, Characterization, and Applications in Field- Effect Transistors. *Chem.—Asian J.* **2014**, *9*, 253−260.
(39) Lv, A.; Puniredd, S. R.; Zhang, J.; Li, Z.; Zhu, H.; Jiang, W.; Dong, H.; He, Y.; Jiang, L.; Li, Y.; Pisula, W.; Meng, Q.; Hu, W.; Wang, Z. High Mobility, Air Stable, Organic Single Crystal Transistors of an n-Type Diperylene Bisimide. *Adv. Mater.* **2012**, *24*, 2626−2630.
(40) Crone, B.; Dodabalapur, A.; Lin, Y.-Y.; Filas, R. W.; Bao, Z.; LaDuca, A.; Sarpeshkar, R.; Katz, H. E.; Li, W. Large-Scale Complementary Integrated Circuits Based on Organic Transistors. *Nature* **2000**, *403*, 521−523.
(41) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötz, F.; Kastler, M.; Facchetti, A. A High-Mobility Electron-Transporting Polymer for Printed Transistors. *Nature* **2009**, *457*, 679−686.
(42) Junga, Y.; Baeg, K. J.; Kim, D.; Someya, T.; Park, S. Y. A Thermally Resistant and Air-Stable n-Type Organic Semiconductor: Naphthalene Diimide of 3,5-Bis-Trifluoromethyl Aniline. *Synth. Met.* **2009**, *159*, 2117−2121.
(43) Horowitz, G. Organic Thin Film Transistors: From Theory to Real Devices. *J. Mater. Res.* **2004**, *19*, 1946−1962.
(44) Bettinger, C. J.; Bao, Z. Organic Thin-Film Transistors Fabricated on Resorbable Biomaterial Substrates. *Adv. Mater.* **2010**, *22*, 651−655.
(45) Shukla, D.; Nelson, S. F.; Freeman, D. C.; Rajeswaran, M.; Ahearn, W. G.; Meyer, D. M.; Carey, J. T. Thin-Film Morphology Control in Naphthalene-Diimide-Based Semiconductors: High Mobility n-Type Semiconductor for Organic Thin-Film Transistors. *Chem. Mater.* **2008**, *20*, 7486−7491.
(46) Avinash, M. B.; Govindaraju, T. A Bio-Inspired Design Strategy: Organization of Tryptophan-Appended Naphthalenediimide into Well-Defined Architectures Induced by Molecular Interactions. *Nanoscale* **2011**, *3*, 2536−2543.
(47) Pron, A.; Gawrys, P.; Zagorska, M.; Djuradoa, D.; Demadrillea, R. Electroactive Materials for Organic Electronics: Preparation Strategies, Structural Aspects and Characterization Techniques. *Chem. Soc. Rev.* **2010**, *39*, 2577−2632.
(48) Li, J.; Qin, F.; Li, C. M.; Bao, Q.; Chan-Park, M. B.; Zhang, W.; Qin, J.; Ong, B. S. High-Performance Thin-Film Transistors from Solution-Processed Dithienothiophene Polymer Semiconductor Nanoparticles. *Chem. Mater.* **2008**, *20*, 2057−2059.
(49) Bell, T. D. M.; Bhosale, S. V.; Forsyth, C. M.; Hayne, D.; Ghiggino, K. P.; Hutchison, J. A.; Jani, C. H.; Langford, S. J.; Lee, M. A.-P.; Woodward, C. P. Melt-Induced Fluorescent Signature in a Simple Naphthalenediimide. *Chem. Commun.* **2010**, *46*, 4881−4883.
(50) Popere, B. C.; Pelle, A. M. D.; Thayumanavan, S. BODIPY-Based Donor Acceptor π-Conjugated Alternating Copolymers. *Macromolecules* **2011**, *44*, 4767−4776.
(51) Fritz, S. E.; Martin, S. M.; Frisbie, C. D.; Ward, M. D.; Toney, M. F. Structural Characterization of a Pentacene Monolayer on an Amorphous SiO_2 Substrate with Grazing Incidence X-ray Diffraction. *J. Am. Chem. Soc.* **2004**, *126*, 4084−4085.
(52) Fukuda, K.; Takeda, Y.; Mizukami, M.; Kumaki, D.; Tokito, S. Fully Solution-Processed Flexible Organic Thin Film Transistor Arrays with High Mobility and Exceptional Uniformity. *Sci. Rep.* **2014**, *4*, 3947−3954.
(53) Singh, Th. B.; Erten, S.; Gunes, S.; Zafer, C.; Turkmen, G.; Kuban, B.; Teoman, Y.; Sariciftci, N. S.; Icli, S. Soluble Derivatives of Perylene and Naphthalene Diimide for n-Channel Organic Field-Effect Transistors. *Org. Electron.* **2006**, *7*, 480−489.
(54) Lei, T.; Wang, J. Y.; Pei, J. Roles of Flexible Chains in Organic Semiconducting Materials. *Chem. Mater.* **2014**, *26*, 594−603.