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Cyanonaphthalene Diimide Semiconductors for Air-Stable, Flexible, and Optically Transparent n-Channel Field-Effect Transistors

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Organic semiconductors offer potentially inexpensive active components in large-area and flexible optoelectronics such as complementary circuits (CMOS), light-emitting diodes (OLEDs), and photovoltaics (OPVs).[1] Because efficient charge transport in organic semiconductors is thought to proceed via hopping involving delocalized π-orbitals, such materials tend to be highly conjugated and thus excellent chromophores with optical extinction coefficients (ϵ) of $\sim 10^4$ to $\sim 10^6$ M^{-1} cm^{-1}. However, materials for transparent displays or charge-blocking layers in OLEDs/OPVs should ideally be transparent to visible light, requiring a >3 eV band gap.[2] A common strategy for achieving wide band gap chromophores is to compress the molecular conjugation length;[3] however, this frequently depresses charge-carrier mobility.[4] Consequently, attempts to fabricate transparent organic field-effect transistors (OFETs) with high mobility have generally yielded low band gap (<2.5 eV) films with significant visible absorption.[5]

Recent studies of dicyanoperylene diimides (PDI-RCN_2)[6] have demonstrated a unique combination of high electron mobility (as high as 0.6 cm^2 V^{-1} s^{-1}), environmental stability, and solution processability.[6b] Thus, PDI-RCN_2s yield complementary organic logic and frequency-generating devices with unprecedented performance.[6c−e] However, the ~2.4 eV PDI-RCN_2 band gap and $\epsilon = 47000$ M^{-1} cm^{-1} renders 50 nm films intensely red to the eye and unsuitable for transparent organic optoelectronics.[6a,6b]

Previous research on core-unsubstituted naphthalene diimide (NDI) semiconductors demonstrated that this wide band gap (~3 eV) materials class can also exhibit high electron mobility, environmental stability, and solution

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(1) (a) *Printed Organic and Molecular Electronics*; Gamota, D. R., Brazis, P., Kalyanasundaram, K., Zhang, J., Eds.; Kluwer Academic Publishers: New York, 2004; p 695. (b) Malliaras, G.; Friend, R. *Phys. Today* **2005**, *58*, 53−58. (c) Katz, H. E.; Bao, A. *J. Phys. Chem. B* **2000**, *104*, 671−678.

(2) (a) Wang, L.; Yoon, M.-H.; Lu, G.; Yang, Y.; Facchetti, A.; Marks, T. J. *Nat. Mater*. **2006**, *5*, 893−900. (b) Artukovic, E.; Kaempgen, M.; Hecht, D.S.; Roth, S.; Grüner, G. *Nano Lett.***2005**, *5*, 757−760. (c) Hoffman, R. L.; Norris, B. J.; Wager, J. F. *Appl. Phys. Lett.* **2003**, *82*, 733−735. (d) Masuda, S.; Kitamura, K.; Okumura, Y.; Miyatake, S.; Tabata, H.; Kawai, T. *J. Appl. Phys.* **2003**, *93*, 1624−1630.

(3) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; p 628.

(4) (a) Garnier, F.; Deloffre, F.; Horowitz, G.; Hajlaoui, R. *Synth. Met.* **1993**, *57*, 4747−54. (b) Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 2339−2350.

(5) See for example: (a) Ohta, H.; Kambayashi, T.; Nomura, K.; Hirano, M.; Ishikawa, K.; Takezoe, H.; Hosono, H. *Adv. Mater*. **2004**, *16*, 312−316. (b) Choi, J.-M.; Hwang, D. K.; Kim, J. H.; Im, S. *Appl. Phys. Lett.* **2005**, *86*, 123505.

(6) (a) Ahrens, M. J.; Fuller, M. J.; Wasielewski, M. R. *Chem. Mater*. **2003**, *15*, 2684−2686. (b) Jones, B. A.; Ahrens, M. J.; Yoon, M.-H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6363−6366. (c) Jung, T.; Yoo, B.; Wang, L.; Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J.; Dodabalapur, A. *Appl. Phys. Lett.* **2006**, *88*, 183102. (d) Yoo, B.; Jung, T.; Basu, D.; Dodabalapur, A.; Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J., *Appl. Phys. Lett.* **2006**, *88*, 082104. (e) Yoo, B.; Madgavkar, A.; Jones, B. A.; Nadkarni, S.; Facchetti, A.; Dimmler, D.; Wasielewski, M. R.; Marks, T. J.; Dodabalapur, A. *IEEE Electron Device Lett.* **2006**, *27*, 737−739.

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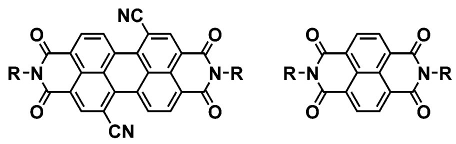
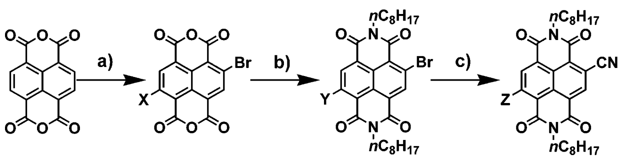


PDI-RCN$_2$ **NDI-R**

processability, but not in a single material.[7] NDI air stability typically requires the presence of fluorous *N*-R groups, which also results in depressed mobility (0.06 cm^2 V^{-1} s^{-1}) relative to *N*-*n*-octyl NDI (0.16 cm^2 V^{-1} s^{-1}).[7b] In this communication, we report two new core-cyanated naphthalene diimide semiconductors, NDI-8CN and NDI-8CN$_2$ (Scheme 1), which represent the first air-stable, high-mobility, and transparent organic n-type semiconductors. Electrical properties are evaluated in bottom-gate (Si/SiO$_2$) top-contact (Au) OFETs, along with thin film microstructure and morphology. Finally, the first visible region transparent OFET channel is fabricated. The syntheses of NDI-8CN and NDI-8CN$_2$ are achieved via a new NDI core bromination, cyanation sequence.

Scheme 1. Synthetic Route to NDI-8CN and NDI-8CN$_2$, Where the Reaction Conditions Are: (a) Br$_2$/I$_2$, Oleum; (b) *n*-octyl Amine, HOAc; (c) CuCN, DMF.



NDA **NDA-Br: X = H** **NDA-Br$_2$: X = Br** **NDI-8Br: Y = H** **NDI-8Br$_2$: Y = Br** **NDI-8CN: Z = H** **NDI-8CN$_2$: Z = CN**

Typically, core-substituted NDIs are accessed via pyrene chlorination;[8] however, in the present work, NDA is brominated with I$_2$/Br$_2$ to yield a mixture of monobrominated (NDA-Br) and dibrominated (NDA-Br$_2$) products. Condensation with *n*-octyl amine is accomplished by refluxing in acetic acid, and the resulting mono- and dibromoimides can be readily separated chromatographically. Interestingly, only a single substitutional isomer of NDI-8Br$_2$ is isolated, as evidenced by ^{1}H NMR and single-crystal X-ray diffraction (Figure 1), whereas perylene dianhydride dibromination yields a mixture of substitutional isomers.[8d] Previous rylene imide cyanations relied on Pd catalysts with Zn(CN)$_2$;[6a,6b] however, cyanation of NDI-8Br and NDI-8Br$_2$ is accomplished with CuCN in DMF to afford NDI-8CN and NDI-8CN$_2$ in ~45% cyanation yield, without air-sensitive Pd catalysts.

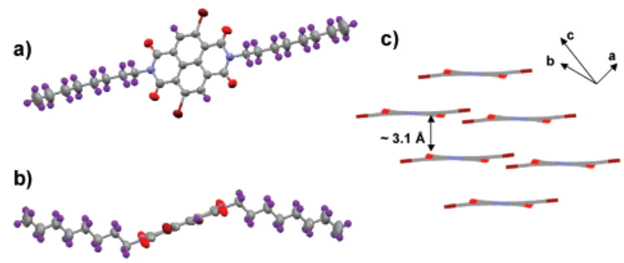


Figure 1. NDI-8Br$_2$ crystal structure depicting (a) the face-on view demonstrating the one substitutional isomer, (b) the side view depicting a nearly planar naphthalene core, and (c) the packing diagram demonstrating the small interplanar intermolecular distance of ~3.1 Å. *N*,*N*′-groups have been removed for clarity.

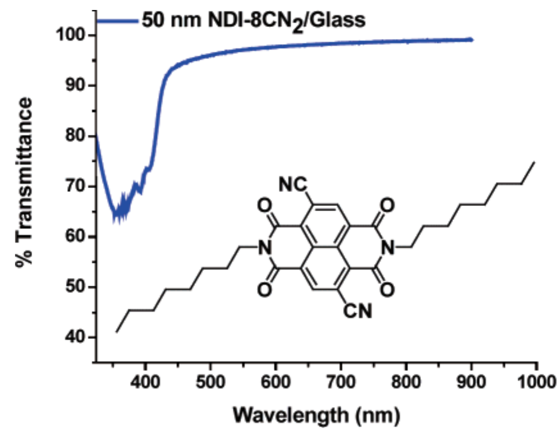


Figure 2. Transmission optical spectrum of a 50 nm vapor-deposited thin film of NDI-8CN$_2$ on glass demonstrating the impressive transparency of this material between 400 and 800 nm.

NDI-8CN and NDI-8CN$_2$ electronic structures were examined by cyclic voltammetry, optical spectroscopy, and photoluminescence. Electrochemical reduction potentials in dichloromethane vs S.C.E. are −0.22 V for NDI-8CN and +0.08 V for NDI-8CN$_2$, consistent with systematic LUMO energy depression with increasing cyanation. Importantly, NDI-8CN$_2$ has a reduction potential similar to that of PDI-RCN$_2$ (−0.07 V vs S.C.E.);[6a−b] therefore, the LUMO/charge-carrier energies in the NDI and PDI materials should be similar. Optical and photoluminescence spectroscopy of these NDI derivatives reveals a band gap of ~3 eV, reflecting the smaller conjugated core dimensions relative to PDIs.[6a,6b] Thus, thin films of these NDIs are transparent in the visible region (Figure 2).

Thin (50 nm) NDI-8CN and NDI-8CN$_2$ films were grown by physical vapor deposition (2 × 10^{-6} Torr, 0.2 Å/s) onto doped Si substrates having a 300 nm thermally grown SiO$_2$ dielectric. During film deposition, the growth temperature (T_d) was varied to optimize the semiconductor film microstructure/morphology. All thin films were characterized by OFET measurements, X-ray diffraction (XRD), and tapping-mode AFM. Top-contact OFETs with 100 μm/5 mm *S*/*D* width/length were fabricated by thermally depositing 50 nm thick gold electrodes onto the NDI films through a shadow mask.

OFET measurements performed in vacuum (~10^{-6} Torr) reveal optimal average electron mobilities for NDI-8CN and NDI-8CN$_2$ films of 4.7 × 10^{-3} cm^2 V^{-1} s^{-1} and 0.15 cm^2 V^{-1} s^{-1}, for T_d values of 130 and 110 °C, respectively. These differences in mobility despite similar chemical structures

(7) (a) Katz, H. E.; Johnson, J.; Lovinger, A. J.; Li, W. *J. Am. Chem. Soc.* **2000**, *122*, 7787−7792. (b) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Seigrist, T.; Li, W.; Lin, Y.-Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478−481. (c) Katz, H. E.; Otsuki, J.; Yamazaki, K.; Suka, A.; Takido, T.; Lovinger, A. J.; Raghavachari, K. *Chem. Lett.* **2003**, *32*, 508−509. (d) Katz, H. E.; Siegrist, T.; Schön, J. H.; Kloc, C.; Batlogg, B.; Lovinger, A. J.; Johnson, J. *ChemPhysChem* **2001**, *3*, 167−172.
(8) (a) Thalacker, C.; Miura, A.; De Feyter, S.; De Schryver, F. C.; Würthner, F. *Org. Biomol. Chem.* **2005**, *3*, 414−422. (b) Würthner, F.; Ahmed, S.; Thalacker, C.; Debaerdemaeker, T. *Chem*−*Eur. J.* **2002**, *8*, 4742−4750. (c) Thalacker, C.; Röger, C.; Würthner, F. *J. Org. Chem.* **2006**, *71*, 8098−8105. (d) Würthner, F.; Stepanenko, V.; Chen, Z.; Saha-Moller, C. R.; Kocher, N.; Stalke, D. *J. Org. Chem.* **2004**, *69*, 7933−7939.

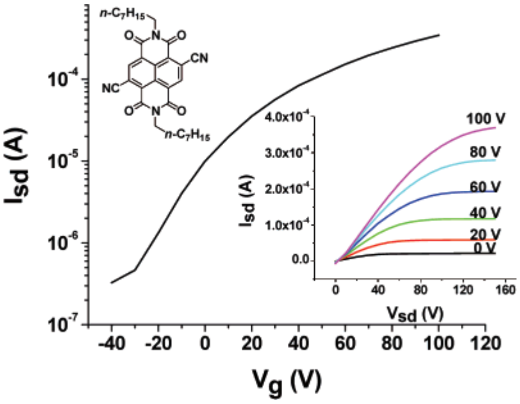


Figure 3. $I-V$ curves measured in air for NDI-8CN$_2$ films (T_d = 130 °C) on Si/SiO$_2$ substrates after storage in ambient atmosphere for 5 months. The transfer plot yields an electron mobility of 0.1 cm^{2}V^{-1}s^{-1} and I_{on}/I_{off} = 10^3. The inset of the output plot demonstrates the well-defined linear and saturation regime at the gate bias (V_g) indicated above the trace.

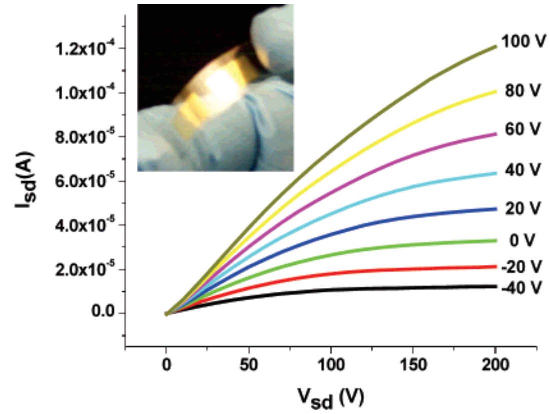


Figure 4. Output plot for a transparent, flexible OFET having a PEDOT:PSS gate, polymer gate dielectric, NDI-8CN$_2$ semiconductor, and Au source and drain, and exhibiting an electron mobility of 0.03 cm^2 V^{-1} s^{-1} in air. Inset: photograph of an array of ~100 devices fabricated on overhead transparency film demonstrating transparency and flexibility.

are discussed with the AFM and XRD data below. Interestingly, OFET operation in ambient atmosphere reveals that the NDI-8CN devices undergo severe degradation of $I-V$ characteristics, whereas the NDI-8CN$_2$ devices exhibit stable operation with only a slightly lower maximum average mobility of 0.11 cm^2 V^{-1} s^{-1} (Figure 3). The NDI-8CN$_2$ robustness suggests that ambient stability can be extended to other rylene diimides via polycyanation to achieve reduction potentials ~0 V vs S.C.E. The current on−off ratios (I_{on}/I_{off}) can be as high as ~10^5 for NDI-8CN and ~10^3 for NDI-8CN$_2$ thin films. The lower I_{on}/I_{off} ratio of NDI-8CN$_2$ is due to high I_{off} (~1 × 10^{-6} A), which is likely due to dopants in the NDI-8CN$_2$ thin films or proximate dielectric layer.

AFM reveals similar polycrystalline morphologies for NDI-8CN and NDI-8CN$_2$ films, with ribbon-like grains until $T_d \approx 90$ °C, and plate-like grains at higher T_d settings. XRD measurements on NDI-8CN and NDI-8CN$_2$ films indicate similar, highly textured microstructures, exhibiting only 00*l* reflections and with a *d*-spacing of 18.2 Å. The primary difference in the film XRD data for the two materials is the presence of a second family of Bragg reflections in NDI-8CN$_2$ films grown at T_d > 90 °C, corresponding to a *d*-spacing of 20.2 Å. However, there is no obvious correlation between mobility and these additional reflections. Given the similar morphologies and microstructures of both NDI-8CN and NDI-8CN$_2$ films, the difference in mobility in vacuum is likely related to in-plane ordering, which cannot be rigorously evaluated with the present $\theta/2\theta$ XRD and AFM data.

Top-contact bottom-gate transparent channel flexible n-type OFETs were fabricated with NDI-8CN$_2$ to demonstrate the unique materials properties. Thin NDI-8CN$_2$ films (50 nm) were vapor-deposited onto overhead transparency film coated with a spin-cast PEDOT:PSS polymeric gate and a P-UV-013 polymer dielectric.[9] Next, 20 nm gold source/drain electrodes were evaporated through a shadow mask onto the NDI-8CN$_2$ films to give an OFET of *S*/*D* width/length = 100 μm/5 mm. This air-stable, flexible, transparent OFET exhibits a mobility of 0.03 cm^2 V^{-1} s^{-1}, $V_{th} = -2$ V, and I_{on}/I_{off} ~10^3 in ambient atmosphere (Figure 4). An analogous rigid device fabricated on an ultrasmooth ITO/glass substrate as a gate gives $\mu = 0.08$ cm^2 V^{-1} s^{-1}, $V_{th} = 4$ V, and I_{on}/I_{off} ~10^3 in ambient atmosphere.

In summary, new NDI core halogenation chemistry yields the first cyano NDIs. Dicyanation affords a similar reduction potential to PDI-RCN$_2$s and imparts air-stability to the fluorine-free semiconductor. Utilizing PEDOT:PSS or ITO as the gate electrode and a polymer dielectric, the first high-mobility, air-stable, n-type transparent channel OFETs were fabricated with NDI-8CN$_2$.

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Supporting Information Available: Experimental details; spectral, electrochemical, film diffraction, AFM, electrical data, OFET fabrication details; CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Details of transparent device fabrication are contained in the Supporting Information.