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Communications

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 $\sim$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 ($\sim$3 eV) materials class can also exhibit high electron mobility, environmental stability, and solution

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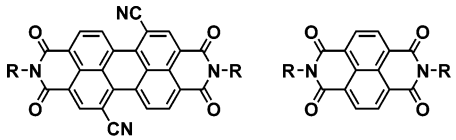
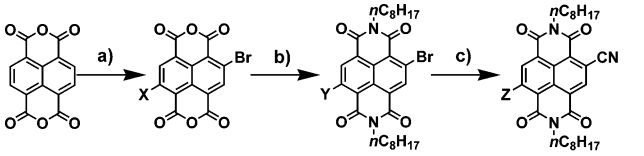


PDI-RCN$_2$ **NDI-R**

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),

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**

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.

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.

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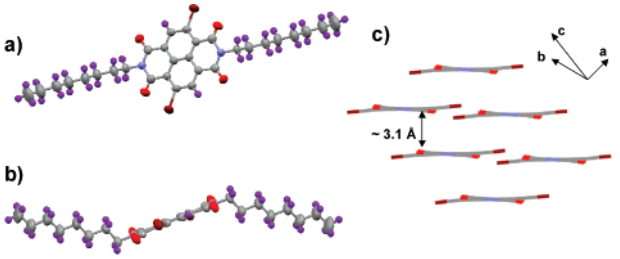

Figure 1. NDI-8Br$_2$ crystal structure depicting (a) the face-on view demonstrating the one substitutional isomer, (b) the side view depicting a nearly planar naphthalene core, and (c) the packing diagram demonstrating the small interplanar intermolecular distance of ~3.1 Å. *N*,*N*′-groups have been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

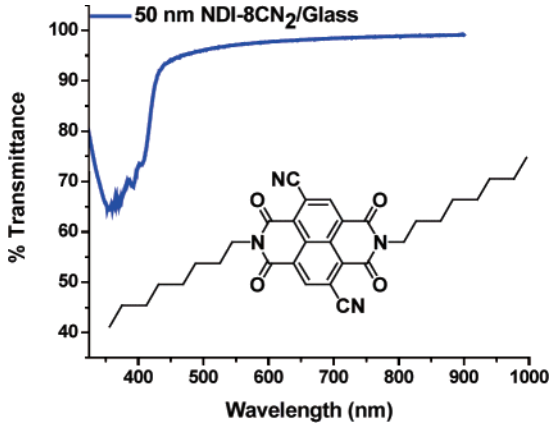

Figure 2. Transmission optical spectrum of a 50 nm vapor-deposited thin film of NDI-8CN$_2$ on glass demonstrating the impressive transparency of this material between 400 and 800 nm.

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

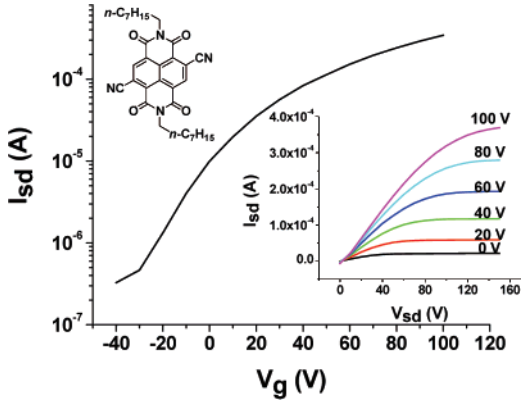

Figure 3. $I-V$ curves measured in air for NDI-8CN_2 films (T_d = 130 °C) on Si/SiO_2 substrates after storage in ambient atmosphere for 5 months. The transfer plot yields an electron mobility of 0.1 $cm^2V^{-1}s^{-1}$ and I_{on}/I_{off} = 10^3. The inset of the output plot demonstrates the well-defined linear and saturation regime at the gate bias (V_g) indicated above the trace.

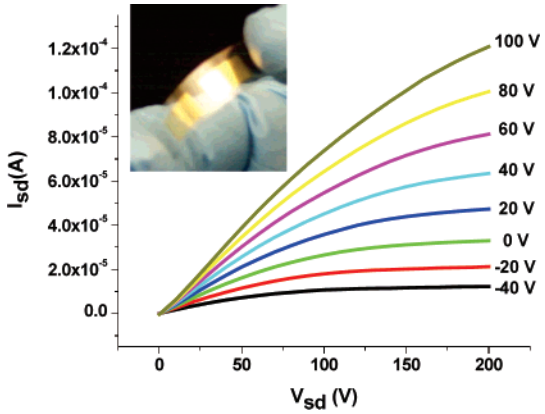

Figure 4. Output plot for a transparent, flexible OFET having a PEDOT:PSS gate, polymer gate dielectric, NDI-8CN_2 semiconductor, and Au source and drain, and exhibiting an electron mobility of 0.03 cm^2 V^{-1} s^{-1} in air. Inset: photograph of an array of ~100 devices fabricated on overhead transparency 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 $\sim10^5$ for NDI-8CN and $\sim10^3$ for NDI-8CN_2 thin films. The lower I_{on}/I_{off} ratio of NDI-8CN_2 is due to high I_{off} ($\sim1 \times 10^{-6}$ 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 $I_{on}/I_{off} \sim10^3$ 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} $\sim10^3$ in ambient atmosphere.

In summary, new NDI core halogenation chemistry yields the first cyano NDIs. Dicyanation affords a similar reduction potential to PDI-RCN_2s 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.