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Solution-Processed Molecular Bis(Naphthalene Diimide) Derivatives with High Electron Mobility

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Supporting Information

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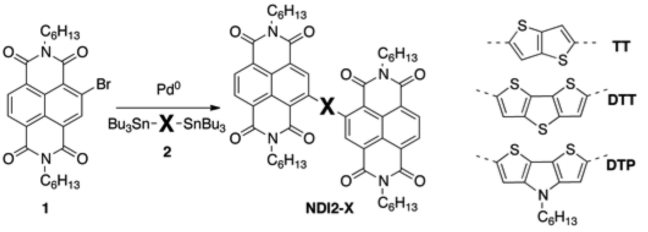
Organic semiconductors have attracted interest for electronic applications because of their potential for use in low-cost, large-area, flexible electronic devices.[1−3] While many examples of organic semiconductors for p-channel and n-channel organic field-effect transistors (OFETs) have been reported in the recent literature,[4−6] there is a paucity of high-performance, solution-processable, small-molecule materials for n-channel OFETs. In order to take advantage of the technological potential of organic semiconducting materials, solution-processable, ideally air-stable, electron-transport (ET) materials with low barriers for charge injection, high charge-carrier mobility values (>1 $cm^2 V^{-1} s^{-1}$), large current on/off ratios ($I_{on}/I_{off} > 10^6$), and low threshold voltages (< ± 2.5 V) are still desirable.

Rylene diimides are interesting candidates and many high-mobility examples have been reported.[7] In particular, materials based on naphthalene-1,8:4,5-bis(dicarboximide)s (NDIs) are among the best organic ET materials to date; some examples show air-stable n-channel mobility values of up to 1.2 $cm^2 V^{-1} s^{-1}$ when incorporated in OFETs by vacuum deposition.[8,9] However, solution-processed ET materials based on NDI derivatives typically exhibit lower mobility values[10] and only recently have values exceeding ∼0.1 $cm^2 V^{-1} s^{-1}$ been reported. An ET copolymer of NDI and bithiophene reported by Facchetti et al.[11] represents the highest mobility example of a solution-processable polymer, with an OFET mobility value of 0.85 $cm^2 V^{-1} s^{-1}$. The highest OFET electron mobility values reported to date for solution-cast small molecules have been measured on core-expanded NDIs reported by Zhu et al.;[12,13] very recently, one of these derivatives was shown to exhibit values as high as 0.55−1.2 $cm^2 V^{-1} s^{-1}$ when appropriately processed,[13] further demonstrating the potential of rylene-based materials for high-performance solution-processed n-channel OFETs. Here, we report that bis(NDI) derivatives with conjugated bridging groups based on fused heterocycle ring systems can be processed from solution into films that exhibit OFET electron mobility values of up to 1.5 $cm^2 V^{-1} s^{-1}$, which is among the highest yet reported for an n-channel OFET based on a solution-processed small molecule.

As shown in Scheme 1, palladium-catalyzed Stille coupling of a brominated NDI, **1**,[14,15] and distannyl fused-ring heterocycle derivatives, **2**,[16,17] yields the bis(NDI) derivatives, **NDI2-X** in 30−60% yield; these compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry, elemental analysis, TGA, and DSC.

Scheme 1. General Synthesis of NDI2-X



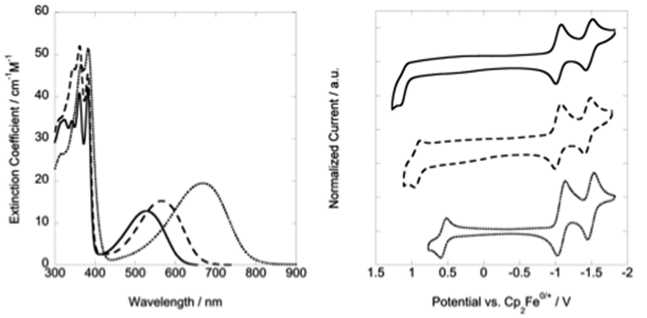


Figure 1. UV−vis absorption in chloroform (left) and cyclic voltammetry (right) of **NDI2-TT** (solid), **NDI2-DTT** (dashed), and **NDI2-DTP** (dotted).

The UV−vis absorption spectra (Table 1, Figure 1) of the **NDI2-X** derivatives in chloroform have maxima at 382−385 nm, similar to that of the corresponding monomeric NDI derivative (383 nm). Additionally, **NDI2-TT**, **NDI2-DTT**, and **NDI2-DTP** exhibit long-wavelength absorption maxima at 543, 566, and 681 nm, respectively. The bathochromic shift of this long-wavelength absorption with increasing electron-richness of the bridging group is suggestive of a charge-transfer (CT) type

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Table 1. Optical, Electrochemical,[a] Thermal, and Field-Effect Transistor Properties[b] of NDI2-X

X	λ_{max}[c] /nm	$\varepsilon^c \times 10^{-3}$ /$M^{-1}cm^{-1}$	$\lambda_{max,solid}$ /nm	$E_{1/2}^{+/0}$ /V	$E_{1/2}^{0/2-}$ /V	$E_{1/2}^{2-/4-}$ /V	T_d[d] /°C	μ_e /$cm^2\ V^{-1}\ s^{-1}$	V_{TH} /V	I_{on}/I_{off}
TT	383	41.7	335	1.10	−1.05	−1.48	400	0.12 ±0.02)	12.3 (±0.7)	1×10^4
	543	12.8	572							
DTT	382	40.5	362	0.93	−1.03	−1.45	402	0.14 (±0.07)	9.0 (±0.3)	2×10^3
	566	14.8	570							
DTP	385	52.9	400	0.56	−1.09	−1.50	409	1.2 (±0.3)	13.0 (±0.9)	[e]
	681	19.9	744							

[a] In CH_2Cl_2/0.1 M $^nBu_4NPF_6$ vs $FeCp_2^{+/0}$. [b] Average n-channel saturation-region field-effect mobility (μ_e), threshold voltage (V_{TH}), and current on/off ratio (I_{on}/I_{off}) for top-gate bottom-contact OFETs based on solution-processed NDI2-X layers. [c] In $CHCl_3$. [d] Defined as temperature at which a 5% mass loss in seen by TGA. [e] Not determined because of ambipolarity of sample.

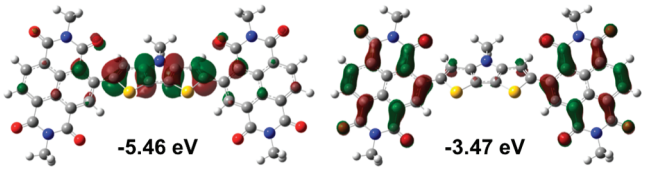

Figure 2. Pictorial representation of the HOMO (left) and LUMO (right) wavefunctions for **NDI2-DTP** as determined at the B3LYP/6-31G** level of theory.

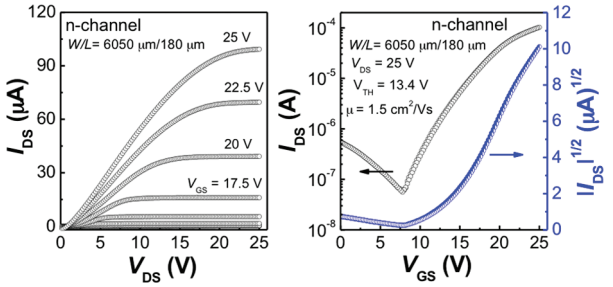

Figure 3. Output (left), and transfer (right) characteristics for n-channel operation of a particular top-gate OFET with **NDI2-DTP** as semiconductor and CYTOP/Al_2O_3 gate dielectric layer with Au source/drain electrodes (W/L = 6050 μm/180 μm).

origin. Moreover, the low-energy band is similar to that seen in other thiophene-substituted NDIs.[11]

Density functional theory (DFT) calculations at the B3LYP/6-31G** level were used to investigate the (gas-phase) neutral ground state, while time-dependent DFT (TDDFT) calculations were used to examine the $S_0 \rightarrow S_n$ vertical ground-to-excited-state transitions. The TDDFT results, using either the B3LYP or long-range-corrected CAM-B3LYP and ωB97X functionals, reveal that indeed the low-lying transitions have charge-transfer-like character.[18] In general, absorption profiles for the visible region generated with the three density functionals are in good agreement. The B3LYP $S_0 \rightarrow S_1$ transition energies were calculated to be 1.95, 1,84, and 1.70 eV (636, 674, and 729 nm) for **NDI2-TT**, **NDI2-DTT**, and **NDI2-DTP**, respectively, with the transitions dominated by electronic excitation from the HOMO → LUMO (98, 88, and 85%, respectively). HOMO and LUMO single-electron wavefunction distributions (B3LYP/6-31G**) are depicted in Figure 2 and Figures S2 and S3 of the Supporting Information. The HOMO wavefunctions are localized on the central electron-rich units for all three **NDI2-X** derivatives. The LUMOs are almost entirely localized on the two NDI segments and their energies are within 0.13 eV of that of an isolated NDI.

Cyclic voltammetry (CV) was used to measure the electrochemical properties of the **NDI2-X** derivatives in CH_2Cl_2/0.1 M $^nBu_4NPF_6$ (Table 1, Figure 1). In each case, a one-electron reversible oxidation process was observed along with two reversible reduction processes, each with approximately twice the current of that found for the oxidation; these are assigned to essentially independent reduction of both NDIs to their radical anions to give a molecular dianion and then a second reduction of both NDIs to give a tetraanion (Table 1, Figure 1). The first half-wave reduction ($E_{1/2}^{0/-}$) potentials are very similar to that of an isolated NDI core ($E_{1/2}^{0/-} = -1.34$ V), consistent with the similarity in the DFT LUMO energies of the **NDI2-X** compounds and isolated NDIs noted above. The half-wave oxidation ($E_{1/2}^{+/0}$) potentials show a difference between the potentials for DTT and DTP, which reflects that between 2,6-dibutyl-4*H*-dithieno[3,2-*b*:2′,3′-*d*]thiophene and 4-(*tert*-butyl)-2,6-dibutyl-4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole ($E_{1/2}^{+/0}$ = 0.69 and 0.23 V, respectively),[19] consistent with DFT data showing the HOMOs to be largely localized on the bridging groups; DFT adiabatic ionization potentials also show similar trends (6.83, 6.65, and 6.35 eV in **NDI2-TT**, **NDI2-DTT** and **NDI2-DTP**, respectively).

Electrical characterization studies (Table 1) were performed on top-gate OFETs with a CYTOP/Al_2O_3 bilayer gate dielectric[20] and Au source/drain electrodes (Supporting Information). **NDI2-X** was spin-coated from 1,2-dichlorobenzene solutions; however, uniform films were not obtained from spin-casting of **NDI2-TT** and **NDI2-DTT** due to reduced solubility of these materials in dichlorobenzene, and so films of these materials were prepared by drop casting.

OFETs fabricated using **NDI2-DTP** showed ambipolar electrical characteristics with dominant n-channel transistor behavior. Devices exhibited electron mobility values of up to 1.5 $cm^2\ V^{-1}\ s^{-1}$ with a rather high threshold voltage of 13.0 V (Figure 3). In p-channel transistor operation (Figure S10 of the Supporting Information), a hole mobility of up to 9.8×10^{-3} $cm^2\ V^{-1}\ s^{-1}$ with a threshold voltage of −14.4 V was observed. The ambipolarity of **NDI2-DTP** means that the transistors are not fully turned off at zero gate bias and that no I_{on}/I_{off} can be measured, which is problematic for applications. On the other hand, decreasing the donor character of the bridge led to purely n-channel device performance and moderate on/off ratios; devices based on **NDI2-TT** and **NDI2-DTT** function solely as n-channel transistors, albeit with lower mobility values than that seen for **NDI2-DTP** and with comparably high threshold voltages. Studies are underway to further

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optimize the properties and device characteristics of this class of materials.

■ ASSOCIATED CONTENT

Supporting Information. Full synthesis and characterization of **NDI2-X**, including OFET device fabrication and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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