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Anthracenedicarboximides as Air-Stable N-Channel Semiconductors for Thin-Film Transistors with Remarkable Current On−Off Ratios

Zhiming Wang, Choongik Kim, Antonio Facchetti,* and Tobin J. Marks*

Department of Chemistry and the Materials Research Center, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

Received May 18, 2007; E-mail: a-facchetti@northwestern.edu; t-marks@northwestern.edu

Thin-film transistors based on organic semiconductors (OTFTs) have attracted great scientific and technological interest in the quest for "plastic" electronics.[1] The basic OTFT structure includes three contacts (source, drain, gate), a dielectric, and a semiconductor (Figure 1), with the latter functioning as either a *p*-channel (hole-transporter)[2] or *n*-channel (electron-transporter) charge carrier.[3] OTFT *p*-channel semiconductors have been widely studied and have achieved acceptable device performance and stability. For example, OTFTs based on acene films[2d] and single-crystals[4] can attain hole mobilities $\mu_h > 1$ cm^{-2}/(V s) in ambient. In contrast, *n*-channel organic semiconductors remain problematic because of the inherent electron trapping tendencies of many materials, especially at the semiconductor−dielectric interface.[5] In principle, there are three approaches to mobilize/stabilize field-effect-derived electrons:[3,5] (a) use strongly electron-deficient π-conjugated cores; (b) employ *p*-channel materials but eliminate deep electron trapping sites by passivating the dielectric surface; (c) functionalize conventional *p*-channel cores with powerful electron-withdrawing and/or hydrophobic substituents. Indeed, high mobility *n*-channel semiconductors have recently been realized with these approaches.[3c,f] Some of these materials exhibit a combination of excellent TFT performance both in vacuum ($\mu_e \approx 0.3-0.6$ cm^2/(V s); $I_{on}/I_{off} \approx 10^7-10^9$; $V_{th} \approx +30$ to 50 V) and in ambient ($\mu_e \approx 0.1-0.6$ cm^2/(V s); $I_{on}/I_{off} \approx 10^4-10^5$; $V_{th} \approx -30$ to 15 V). However, a critical characteristic of high-mobility air-stable *n*-channel materials has been the relatively low I_{on}/I_{off} ratios and large negative threshold voltage shifts versus the corresponding air-sensitive systems—they are difficult to "turn off".[3,6] The large electron affinities of known air-stable *n*-channel cores which prevent electron trapping also enhance sensitivity to electron-doping from the metal contacts and/or donor sites in the dielectric. An empirical first reduction potential (E_{R1}) window for both stable TFT electron conduction and low doping levels is derived by analyzing the redox properties of several rylene/oligothiophene-based *n*-channel semiconductors developed in our group.[3f,6] When $E_{R1} \lesssim -0.6$ V (vs SCE), the material may be an *n*-channel semiconductor but not air-stable. When $E_{R1} = -0.6$ to -0.4 V, the onset of *n*-channel stability begins. However, for $E_{R1} > 0.0$ V, significant doping becomes evident and device current modulation is difficult to control. Therefore, semiconductors with an E_{R1} ranging from -0.4 to 0.0 V should result in TFTs exhibiting both stable electron transport in air and minimal doping (low I_{off}). Note that semiconductor film morphology optimization may also play a role in stabilization of TFT transport.[7]

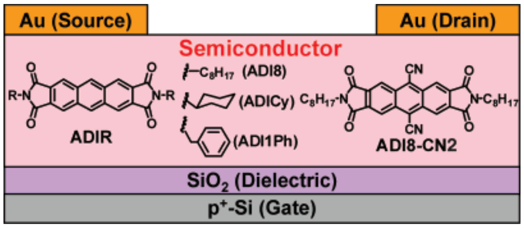

Figure 1. Schematic representation of OTFT device components and chemical structures of the ADI semiconductors.

In this Communication we report a new electron-deficient semiconductor family based on the anthracenedicarboximide (ADI) core. The goal here is two-fold: (1) demonstrate a new *n*-channel semiconductor family for OTFTs; (2) tune electron affinity to achieve air stability while maintaining low I_{off} currents at $V_{SG} = 0.0$ V − enhance I_{on}/I_{off} ratios. This work finds inspiration in the pioneering studies of Miller showing that linear acenedicarboximide cores are easily *n*-dopable electrochemically[8] and those of Wasielewski on cyanated rylenes.[5a,9] The E_{R1} of ADIR (Figure 1), where R = bulky 4-*t*-butylphenyl, was reported to be ca. −1.1 V (vs SCE)[7] and, as in the case of perylenedicarboximide (PDI) derivatives, should be relatively insensitive to N-substitution. From our recent studies,[6] ADIRs should have the electronic energetic characteristics of stable *n*-channel semiconductors but the corresponding OTFTs should not operate in air. However, DFT computations[10] predict that CN functionalization at the anthracene 9,10 positions should displace E_{R1} to ca. −0.2/−0.3 V, more negative than core-cyanated perylenes ($E_{R1} \approx 0.0$ V), but within the air stability window. We report here that this design strategy achieves the aforementioned goals.

The synthesis of core-unsubstituted ADIRs (Scheme 1) involves two simple steps: (a) 1,2,4,5-tetramethylbenzene bromination, (b) Diels−Alder cycloaddition/aromatization of 1,2,4,5-tetrakis(dibromomethyl)benzene with the requisite *N*-alkylmaleimide. The advantages include mild reaction conditions, good yields, and straightforward product purification via reprecipitation/sublimation. The structures and purities of the new ADIRs were verified by elemental analysis, ^{1}H NMR, and mass spectrometry (see Supporting Information).

The electrochemical properties of these new anthracenedicarboximides reveal important aspects of electronic structure and substituent effects (Table 1). Thus, **ADI8**, **ADICy**, and **ADI1Ph** exhibit comparable E_{R1}s (−1.1 to −1.2 V, Figure S2)—much less negative than that of parent anthracene (−1.9 V). As expected, such redox potentials are still close to the overpotentials required for reactions involving O_2 (∼1 V), strongly suggesting that ADIR-based FETs will not operate in ambient conditions.[11]

Top-contact OTFTs were fabricated on p$^+$-Si/SiO$_2$ substrates (Figure 1). Typical current−voltage plots are shown in Figures 2 and S2, with carrier mobilities calculated in saturation from the equation $\mu_{sat} = (2I_{SD}L)/[WC_{ox}(V_{SG} - V_{th})^2]$. The positive gate and source-drain voltages demonstrate that these ADIRs are *n*-channel materials. Tables 1 and S1 summarize TFT response for HMDS-treated and untreated Si/SiO$_2$ substrates, respectively. Electron mobilities as high as 0.02 cm^2/(V s) and $I_{on}/I_{off} \approx 10^7$ are achieved in vacuum. Photoconductivity measurements of anthracene single crystals reveal comparably high hole and electron mobilities[12] but,

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Scheme 1. Synthesis of Anthracenedicarboximides

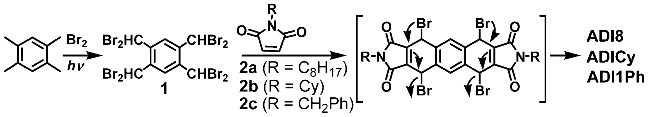


Table 1. Electrochemical[a] and OTFT[b] Data for ADI Derivatives

compound	$E_{(1)}$ (V)	μ ($cm^2/(V\ s)$)	I_{on}/I_{off}	V_{th} (V)	S (V/dec)
anthracene	−1.92	0.02[c]	$\sim 10^4$	−10	
ADI8	−1.17	0.02	4×10^7	+45	2.0
ADICy	−1.17	0.01	5×10^6	+35	2.9
ADI1Ph	−1.12	0.01	2×10^7	+45	4.1
ADI8-CN2	−0.33	0.03 (vac.)	6×10^6	+10	1.9
		0.02 (air)	2×10^7	+15	1.9

[a] In CH_2Cl_2 (vs SCE) solution (0.1 M Bu_4NPF_6 electrolyte), Pt electrode. Scan rate: 100 mV/s. Fc/Fc^+ (0.52 V vs SCE) internal reference. [b] Film growth temperature is 90 °C. [c] Single crystal (ref 13).

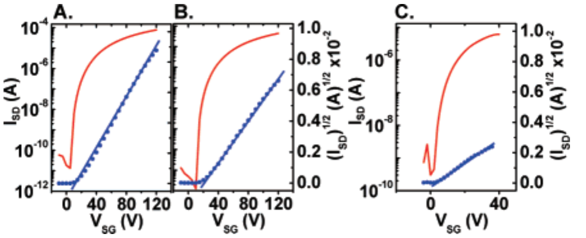
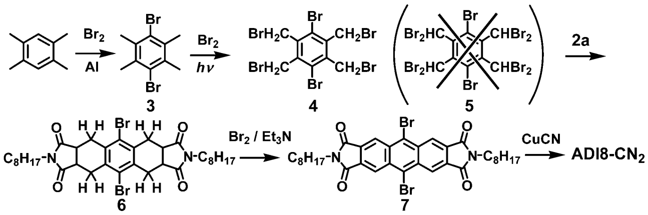


Figure 2. $I-V$ transfer plots for vapor-deposited **ADI8**-CN2 films in vacuum (A) and air (B) on HMDS-treated $Si-SiO_2$ substrates and as solution-cast films on a solution-processed CPB insulator in air (C). $V_{SD} = 100$ V.

Scheme 2. Synthesis of the Core-Cyanated **ADI8**-CN2



in contrast to other acenes,[4b] anthracene-based FETs perform poorly unless single crystals are employed for *p*-channel semiconductor.[12] Therefore, compared to anthracene, introduction of the diimide groups and *N*-hydrocarbon functionalization strongly affects frontier MO energies, enabling *n*-channel conductivity and film self-organization on the insulator for efficient charge transport.

We next synthesized 9,10-core-cyanated ADIs, starting with **ADI8**-CN2. Since attempts to brominate **ADI8** were unsuccessful, we developed a synthesis starting from tetramethylbenzene (Scheme 2). Interestingly, bromination of the dibromotetramethylbenzene does not proceed to the tetrakis(dibromomethyl) derivative (**5**), probably because of steric hindrance. Cycloaddition of **4** with **2a** affords core **6**, which is aromatized with Br_2/Et_3N to **7**, and finally dicyanated to afford **ADI8**-CN2 in 25% overall yield. OTFTs based on **ADI8**-CN_2 operate in air (vacuum) and exhibit $\mu_e = 0.02$ (0.03) $cm^2/(V\ s)$; $I_{on}/I_{off} > 10^7$ ($\sim 10^7$); $V_{th} \approx +15$ (+10 V) (Figure 2). Note the very high I_{on}/I_{off} ratios and positive V_{th} for this system, in agreement with the enhanced electron affinity. $I-V$ hysteresis is negligible (very small) for the devices measured in vacuum (ambient) (Figure S3). From cyclic voltammetry, E_{R1} of **ADI8**-CN2 is −0.33 V (Figure S4), in agreement with theoretical expectations[10] and the ambient TFT stability characteristics. Consequently, these results provide additional evidence that a redox window between $E_{R1} = -0.4$ and 0.0 V is essential to achieve both stable electron transport in air and low I_{off}. Similarly to other rylene TFTs, the present devices are sensitive to the combined action of humidity and sunlight. However, the performance of devices stored in air with exclusion of light remains stable for at least 4 months after fabrication (Figure S5). Finally, ADIR core cyanation strongly enhances solubility. Films of **ADI8**-CN2 can be spin-cast on a solution-processed 100 nm-thick CPB gate dielectric[5a] affording $\mu_e \approx 0.001$ $cm^2/(V\ s)$; $I_{on}/I_{off} > 10^5$; $V_{th} \approx 0$ V.

In summary, we report a new *n*-type TFT semiconductor family based on anthracenedicarboximides. **ADI8**-CN_2–based TFTs exhibit good electron mobility (μ_e up to 0.02 $cm^2/(V\ s)$), very high $I_{on}/I_{off} > 10^7$ in ambient conditions as a consequence of balanced electron affinity. Studies are underway to enhance μ_e by variation of N-substituents. Note that within the core-cyanated perylene family, optimized μ_e varies by >10× with proper N-substitution.[6]

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Supporting Information Available: Synthesis of ADIs, device fabrication details, UV−vis/electrochemical/FET data. This material is available free of charge via the Internet at http://pubs.acs.org.

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