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Cyanated Diazatetracene Diimides with Ultrahigh Electron Affinity for *n*-Channel Field Effect Transistors

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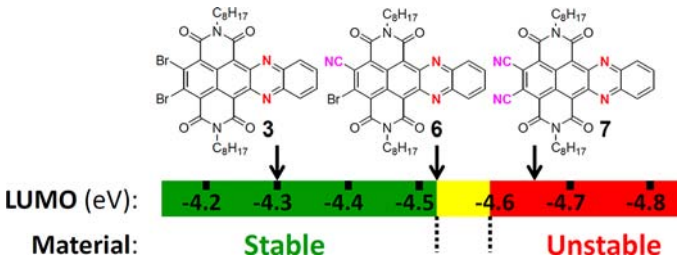
ABSTRACT



Several diazatetracene diimides with high electron affinity (up to 4.66 eV!) were prepared and well characterized. The LUMO energy level of these electron-deficient molecules was found to be closely related to their material stability. Compound 7 with ultrahigh electron affinity suffered from reduction and hydrolysis in the presence of silica gel or water. The stable compounds 3 and 6 showed *n*-channel FET behavior with an average electron mobility of 0.002 and 0.005 $cm^2 V^{-1} s^{-1}$, respectively, using a solution processing method.

The lowest unoccupied molecular orbital (LUMO) energy level of an *n*-type organic semiconductor has been proven closely associated with the organic field effect transistor (OFET) device stability when operated in air.[1] A low-lying LUMO energy level is critical to stabilize the radical anions generated in the OFET device,[2] while on the other hand, the neutral semiconductor molecule tends to be attacked by nucleophiles more easily as the LUMO goes low.[3] Therefore, a good balance of the LUMO would be of great importance if one is to synthesize stable *n*-type semiconductors. Detailed understanding on how LUMO is correlated to both the material stability and device stability is crucial for the further optimization of *n*-type organic semiconductors.[4]

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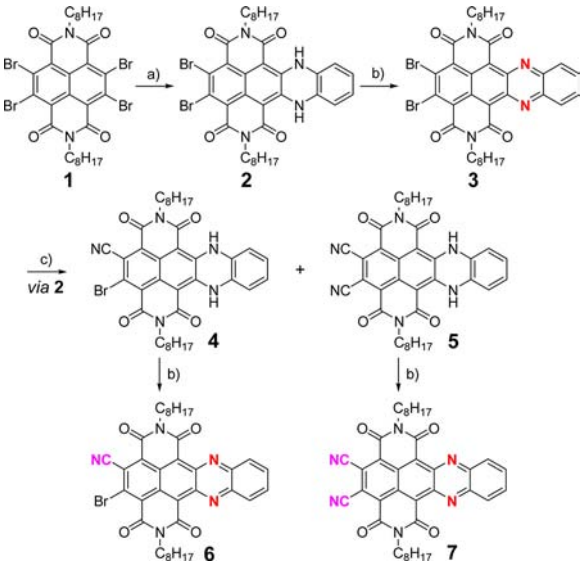
Naphthalene diimides (NDI)[5] are among the most promising candidates for *n*-type OFET materials mainly due to their high electron affinity and versatile functionalization approaches either on the imide position[6] or on the naphthalene core.[7] In the search for high-performance air-stable *n*-type semiconductors based on naphthalene diimides, we recently prepared a series of cyanated NDI with high electron affinity, and stable materials have been achieved with LUMO energy level at −4.4 eV.[3] We also noticed that as the LUMO of the material goes to −4.6 eV, the neutral material tends to become unstable. A borderline of the LUMO energy level therefore has been figured out to guarantee the intrinsic stability of the materials. In order to challenge the lowest possible LUMO for stable n-type molecules and make the borderline more confined, we prepared several diazatetracene diimides (Scheme 1) by expanding the π-conjugation of NDI in the current study. Our strategy to increase the electron affinity is to combine the electron-withdrawing ability of cyanides, imide groups, and pyrazine nitrogens all together,[8] and stable *n*-type diazatetracenes **3** and **6** have been achieved with LUMO energy level as low as −4.53 eV. An unstable species **7** with a LUMO at −4.66 eV is also isolated and well characterized. The charge-transport properties of the stable materials **3** and **6** are characterized in organic field effect transistors.

Scheme 1[a]



[a] Conditions: (a) *o*-phenylenediamine, $CHCl_3$, rt, overnight, 83%; (b) PbO_2, $CHCl_3$, 15 min, quantitative; (c) $Pd_2(dba)_3$, dppf, CuCN, dioxane, 50 °C, overnight, 30% yield for **4** and 24% yield for **5**.

The synthesis of **3**, **6**, and **7** is outlined in Scheme 1. Compound **2** was prepared from tetrabromonaphthalene diimide **1**[9] under very mild conditions ($CHCl_3$, rt) in 83% yield. The reported harsh conditions (DMF, 135 °C)[10] turned out to be troublesome in our hands, and the target molecule was always contaminated with debrominated side products, which made the isolated yield rather low. Oxidation of **2** easily happened in the presence of lead dioxide to afford **3** almost quantitatively. The two bromine atoms in **3** are further activated by the presence of electron-withdrawing imines, and therefore, we also attempted further annulation of one more *o*-phenylenediamine to **3**.[11] Surprisingly, its dihydro form **2** was obtained as the major product, indicating that the imine bonds in **3** were reduced by the diamine. A similar phenomenon was also observed in the cyanation reaction of **3**. As **3** was subjected to cyanation in the presence of $Pd_2(dba)_3$, dppf, CuCN, and dioxane,[12] it was found that a complete conversion to the hydrogenated form **2** occurred after 2 h at 50 °C. Water in the solvent could serve as hydrogen source in this reaction. Further cyanation reaction on the in situ generated **2** went on smoothly, and both the monocyanted product **4** (in 30% yield) and dicyanated product **5** (in 24% yield) were isolated after reaction overnight. Fast oxidation of **4** and **5** by lead dioxide gave **6** and **7**, respectively, in almost quantitative yields. This quantitative oxidation process was evidenced by dynamic NMR monitoring, as shown in Figure S1 in the Supporting Information. Both **4** and **5** had very poor solubility and strong tendency to aggregate in chloroform, and this made the collection of their ^{13}C NMR spectra unsuccessful. However, **6** and **7** showed good solubility in chloroform which could be explained by the structural variation after oxidation (vide infra). Compound **7** was unstable upon contact with silica gel or water due to quick decomposition via nucleophilic attack by water or reduction on the imines (Figure S2, Supporting

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Information). Nevertheless, the quantitative conversion from **5** to **7** made the chromatography purification unnecessary and detailed characterization of **7** was hence achieved.

The UV−vis absorption and photoluminescence of compounds **2**−**7** were measured in diluted chloroform solutions (Figure 1 and Figure S3, Supporting Information). Cyanation on the diazatetracene diimide was found to have a minor influence on the absorption and emission behavior for this series of molecules. However, after oxidation by lead dioxide, e.g., from compound **2** to **3**, vivid differences were observed on the UV−vis spectra. For the dihydro compounds **2**, **4**, and **5**, they all showed an acene-like *p*-band in the region of 550−650 nm (Figure S3, Supporting Information), while for the oxidized species (**3**, **6** and **7**), the absorption in the range of 550−600 nm were much weaker and they all emit in the region 600−700 nm with similar fluorescence patterns. Stokes' shifts were small for these molecules as in agreement with previous results.[11]

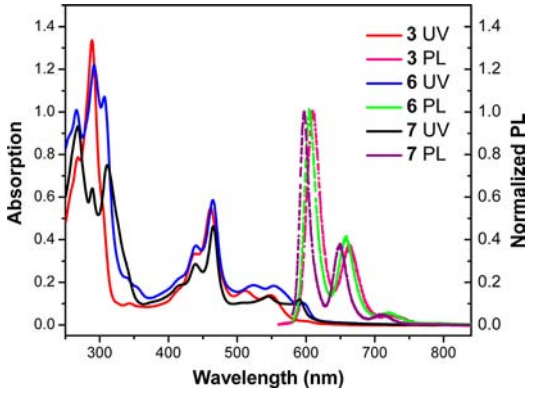

Figure 1. UV−vis absorption spectra of compounds **3**, **6**, and **7** in chloroform and their fluorescence spectra recorded in chloroform.

The electrochemical properties of diaza-tetracenes **2**−**7** were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dry DCM (Figure 2; Figure S4 and Table S1, Supporting Information). A significant decrease of LUMO levels was observed upon oxidation. The LUMO energy level was estimated to be −4.30, −3.53, −3.70, −4.53, and −4.66 eV, respectively, for compounds **3** to **7**. The oxidized products **3**, **6**, and **7** have much lower LUMO energy level than the reported tetracene bisimides and cyanated tetracenes.[8h−j] The ultra-low-lying LUMO energy level of compound **7** (−4.66 eV!) was the lowest LUMO for well-characterized NDI- or aza-acene-based materials reported to date.[3,13] The extremely high electron affinity of compound **7** would account for its intrinsic instability toward water and silica gel. Furthermore, the trend becomes clear now, and the electron-deficient molecules tend to be unstable as the LUMO goes too low (< -4.6 eV).[3a]

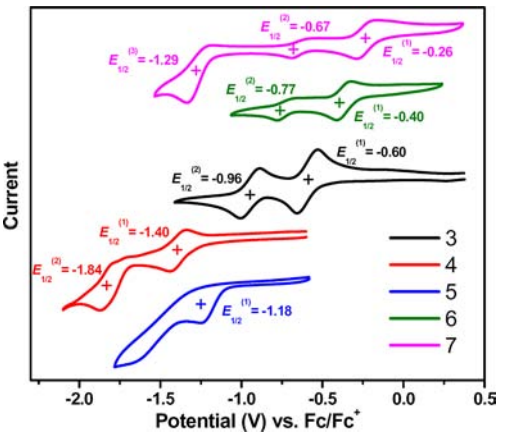

Figure 2. Cyclic voltammograms of compounds **3**−**7**. Compound **4** also showed one oxidation wave; see Figure S4 (Supporting Information).

Time-dependent density function theory (TD-DFT at B3LYP/6-31G*) calculations were conducted on compounds **2** and **3** to better understand their geometric structure and optical properties (Figure 3; Figures S5−S7 and Tables S2−S6, Supporting Information). As shown in Figure 3a, the dihydro compound **2** has almost planar backbone structure with two imide groups on the same plane mainly due to chelating intramolecular hydrogen bonding between the NH and the carbonyls on the imides. However, after removal of the hydrogen by oxidation, compound **3** possesses two possible conformers **3a** and **3b** (Figure 3a), and in both conformers the imide groups are deviated from the central diaza-tetracene plane which is caused by the steric congestion between the carbonyl groups and the lone electron pair on the imine. Such a geometrical change would account for the solubility enhancement after oxidation, i.e., from **2** to **3**. For compound **2**, TD-DFT calculation predicts a major transition at 535 nm (HOMO-0 to LUMO+0, $f = 0.4502$), and for compound **3**, both conformers give similar absorption pattern with one major transition at 429 nm (mainly HOMO-3 to LUMO+0, $f = 0.2452$) and a much weaker transition at 585 nm (mainly HOMO-0 to LUMO+0, $f = 0.0493$) (Figure 3b). This result is consistent with the experimentally measured absorption data for these two compounds.

Bottom-gate top-contact OFETs of **3** and **6** were fabricated on p+-Si/SiO_2 substrates by spin coating 0.8 wt % chloroform solutions onto octadecyltrichlorosilane (OTS) treated substrates.[14] The thin films were then annealed at 150 °C for 30 min in vacuum. Au source/drain electrodes (80 nm) were patterned on the organic layer through a shadow mask to afford the devices. The typical transfer

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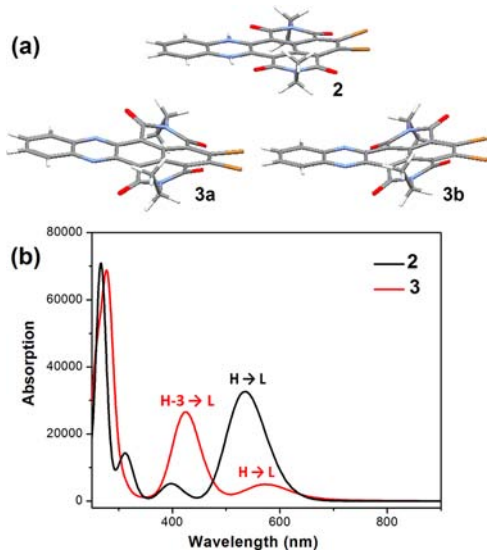

Figure 3. Optimized structure and calculated absorption spectra for compounds **2** and **3** (the octyl group is replaced by ethyl).

and output curves measured in N_2 are shown in Figure 4. The device (as-cast) operated in the *n*-channel region and revealed an average saturation mobility of 0.002 cm^2 V^{-1} s^{-1} (I_{on}/I_{off} = 10^5) for **3** and 0.005 $cm^2V^{-1}s^{-1}$ (I_{on}/I_{off} = 10^5) for **6**. The threshold voltage (V_{th}) was around 10 V for the as-spun thin films. Thermal annealing at 150 °C has little effect on the charge carrier mobility but negatively shifted the V_{th} by about 5 V due to decreased charge traps (solvent residue, etc.). Thin film crystallinity was characterized by X-ray diffraction (Figure S8, Supporting Information). The XRD pattern exhibited the primary peak at 2θ = 5.03° for **3** and 4.94° for **6**, which correspond to a *d*-spacing value of 17.56 Å and 17.87 Å, respectively. Higher XRD intensity of **6** over **3** indicates a better crystallinity of the thin film, which would account for the observed higher mobility of **6**. AFM images (Figure S9, Supporting Information) revealed more homogeneous thin film morphology for compound **6** compared with **3**, indicating that homogeneity of the thin film is essential in achieving high mobility.[3a] When both devices are operated in air, the device performance is reduced with the average electron mobility dropped by 5−10 folds, and the I_{on}/I_{off} value decreased by 2 orders of magnitude, indicating that LUMO energy level is not the sole factor to determine the *n*-type device stability in air. Further effort is needed to better understand this issue.

In summary, diaza-tetracene diimides compounds **3**, **6**, and **7** with high electron affinity have been prepared for

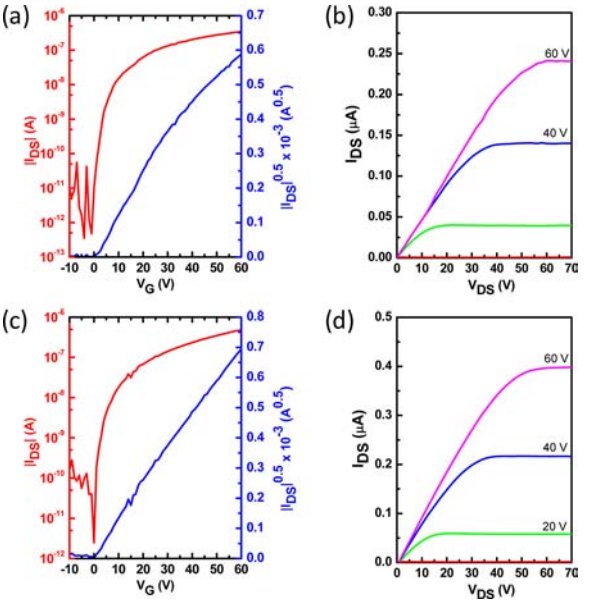

Figure 4. Transfer and output characteristics of FET devices fabricated by solution coating of **3** (a, b) and **6** (c, d) on OTS-treated substrates for thermal annealed (150 °C) thin films under N_2 conditions.

n-channel organic field effect transistors. It is remarkable that compound **7** with an ultrahigh electron affinity of 4.66 eV was isolated and well characterized, although it is very sensitive to water and silica gel. Compounds **3** and **6** were also successfully used for solution processable *n*-channel OFET devices with an average electron mobility of 0.002 and 0.005 cm^2 V^{-1} s^{-1}, respectively. Our studies shed some light on how to control the LUMO energy level of an *n*-type semiconductor to balance the device stability and material stability and to further improve the device performance.

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Supporting Information Available. Synthetic procedures and characterization data for all new compounds. Calculation data for compounds **2** and **3**. Device fabrication and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.