

High and Balanced Hole and Electron Mobilities from Ambipolar Thin-Film Transistors Based on Nitrogen-Containing Oligoacenes

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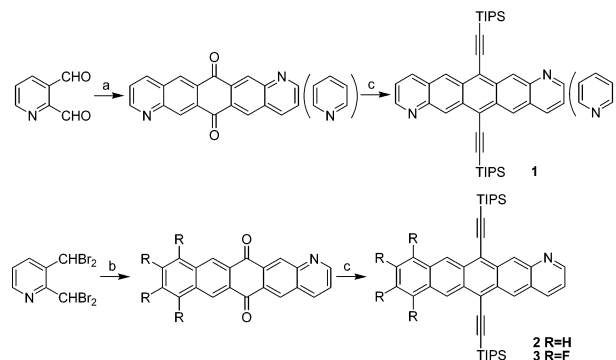
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Abstract: We demonstrate a strategy for designing high-performance, ambipolar, acene-based field-effect transistor (FET) materials, which is based on the replacement of C–H moieties by nitrogen atoms in oligoacenes. By using this strategy, two organic semiconductors, 6,13-bis(triisopropylsilyl)ethynylanthradipyridine (**1**) and 8,9,10,11-tetrafluoro-6,13-bis(triisopropylsilyl)ethynyl-1-azapentacene (**3**), were synthesized and their FET characteristics studied. Both materials exhibit high and balanced hole and electron mobilities, **1** having μ_h and μ_e of 0.11 and 0.15 cm²/V·s and **3** having μ_h and μ_e of 0.08 and 0.09 cm²/V·s, respectively. The successful demonstration of high and balanced ambipolar FET properties from nitrogen-containing oligoacenes opens up new opportunities for designing high-performance ambipolar organic semiconductors.

In recent years, organic semiconductors have attracted considerable attention because of their potential for creating low-cost, portable electronic and optoelectronic devices such as organic light-emitting diodes (OLED), organic field effect transistors (OFETs), flexible displays, and sensors.^{1–3} Most organic semiconductors reported so far, such as oligoacene and oligothiophene derivatives,^{4,5} exhibit p-type transport properties, whereas more efforts have been devoted to the design and synthesis of n-channel materials in recent years. The majority of organic semiconductors give only unipolar FET characteristics, and few organic semiconductors have been found to exhibit ambipolar characteristics.⁶ Moreover, to the best of our knowledge, very few organic semiconductors^{7–9} exhibit balanced hole and electron transport characteristics.

Ambipolar materials are strongly desirable for logic circuit design because they enable the simple fabrication of complementary circuits like inverters without advanced patterning techniques to deposit p- and n-channel materials separately. Moreover, ambipolar materials work for both positive and negative voltages, which simplifies the circuit design. An ideal ambipolar material is expected to give balanced performance in both negative and positive voltage regimes; therefore, it is strongly desired that the ambipolar materials could have balanced n- and p-channel performance. However, among the few reported ambipolar organic semiconductors, their mobilities are either low or unbalanced.^{10–13} For example, Yoon et al. reported that dihexanoylquaterthiophene gave good ambipolar transport behavior, with μ_h and μ_e values of ~0.01 and 0.1 cm²/V·s, respectively, in a vacuum.¹⁴ Recently, Bao et al.⁷ reported a high-performance ambipolar material, fluorinated tetraceno[2,3-*b*]thiophene, which has μ_h and μ_e of up to 0.12 and 0.37 cm²/V·s in air

and in nitrogen, respectively. However, when operated under the same condition, i.e., in a nitrogen glovebox, the hole mobilities were several times lower than the electron mobilities, i.e., down to 0.065 cm²/V·s. Here we demonstrated high and balanced hole and electron mobilities from 6,13-bis(triisopropylsilyl)ethynylanthradipyridine (**1**) and 8,9,10,11-tetrafluoro-6,13-bis(triisopropylsilyl)ethynyl-1-azapentacene (**3**), where **1** has μ_h and μ_e of 0.11 and 0.15 cm²/V·s and **3** has μ_h and μ_e of 0.08 and 0.09 cm²/V·s, respectively.

Scheme 1. Synthetic Route to Molecules **1–3**^a

^a Reagents and conditions: (a) 1,4-cyclohexanedione, KOH, EtOH, 60 °C, 42%; (b) 1,4-anthraquinone or 5,6,7,8-tetrafluoro-1,4-anthraquinone, NaI, DMF, 75 °C, 40%; (c) i, *n*-BuLi, THF, TIPS–acetylene, 0 °C; ii, SnCl₂, 60 °C, 24%.

The molecular design is based on 6,13-bis(triisopropylsilyl)ethynylpentacene (TIPS-PEN), which is one of the most remarkable soluble p-type semiconductors that has high hole-transport performance^{15,16} and improved stability compared to pentacene. Our novel design of high-performance, ambipolar, acene-based FET materials is based on the replacement of C–H moieties by nitrogen atoms in oligoacenes by nitrogen atoms. This is different from the most common approach to obtain ambipolar characteristics through chemical modification of originally p-type materials by introducing electron-withdrawing groups (i.e., –F,⁷ –CN,¹³ –Cl,⁸ alkanoyl¹⁴) to the conjugated cores in order to lower the lowest unoccupied molecular orbital (LUMO) levels and reduce electron injection barriers, hence bringing about n-channel properties. Nitrogen replacement of the C–H moiety in the aromatic rings^{17–19} can efficiently lower the molecule's LUMO level and enhance electron transport properties.¹⁷ Scheme 1 shows our synthetic strategy. The 6,13-anthradipyridinequinone was obtained from 2,3-pyridinedicarbaldehyde and 1,4-cyclohexanedione by aldol condensation.²⁰ The one-nitrogen-containing pentacene-6,13-quinones were synthesized by Diels–Alder reaction²¹ between 2,3-bis(dibromomethyl)pyridine and 1,4-anthraquinone or 5,6,7,8-tetrafluoro-1,4-

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anthraquinone. The one- or two-nitrogen-containing quinones were then reduced by SnCl_2 to give **1**, 6,13-bis(triisopropylsilyl)ethynyl-1-azapentacene (**2**), and **3**. We noticed that the traditional reduction condition (H^+/SnCl_2) was unfavorable in the reduction of nitrogen-containing quinones and could not give the corresponding target compounds, most likely due to the protonation of the nitrogen atoms under acidic conditions. Reducing the quinones under a neutral condition using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ afforded the target compounds in yields of 20–30%. All the nitrogen-containing TIPS-PENs exhibit very good solubility in common organic solvents, like chloroform and toluene, and can be recrystallized from $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$.

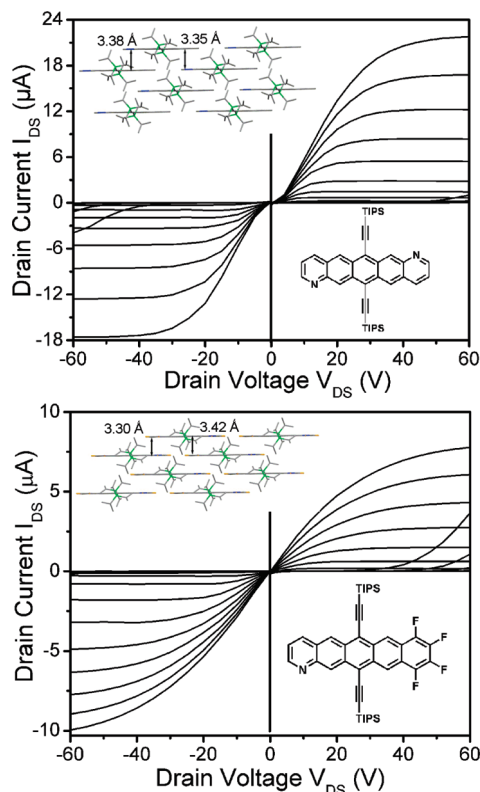


Figure 1. Typical output curves for **1** (top) and **3** (bottom) deposited at 80 °C on OTS-treated SiO_2 for $L = 150 \mu\text{m}$, $W/L = 20$. The gate voltage ranges from -120 to 120 V. Inset: 2D slip-stacks of **1** and **3** in the single-crystal view along the axis that is formed by two ethynyl substituents, which does not correspond to any crystallographic axis.

Single crystals of **1** and **3** have been obtained, and X-ray crystallography revealed that they pack into highly desirable 2D brick-layer structures (Figure 1), similar to TIPS-PEN.² Indeed, introduction of nitrogen atoms at the terminal ring(s) reduced the π – π stacking distance between the conjugated acene backbones. The distances between the aromatic backbones are 3.35 Å for **1** and 3.30 Å for **3**, compared to 3.43 Å for TIPS-PEN.²² The reduced packing distance in the nitrogen-containing TIPS-PENs may be attributed to negatively polarized nitrogen atoms of one molecule located over positively polarized C(H) atoms of another.²³ Atomic force microscope (AFM) images of the thin films deposited on octadecyl(trimethoxy)silane (OTS)-treated SiO_2 surfaces showed grain structures (Supporting Information). The grain sizes increased from tens of nanometers to nearly 1 μm when the substrate temperatures were increased from room temperature to 80 °C. Large grain size is expected to improve the FET properties, which is confirmed by the device characteristics (Table 1).

Top-contact transistors were fabricated on a 400 nm thermally grown SiO_2 layer on a heavily doped Si gate. Some substrates were

Table 1. Summary of Parameters of Top-Contact OFETs Fabricated from **1–3** with Au Electrodes, $W/L = 20$

compd	conditions	$\mu_{\text{h}}, \mu_{\text{e}}$ ($\text{cm}^2/\text{V} \cdot \text{s}$)	on/off	V_{T} (V)	carrier
1	rt, OTS, Ar	0.008	10^3	–50	h
	$T_{\text{c}} > 80$ °C, OTS, Ar	0.11; 0.15	10^4	–55; +70	h; e
2	rt, OTS, Ar	0.02	10^3	–28	h
	80 °C, OTS, Ar	0.22	10^4	–55	h
3	rt, OTS, Ar	0.0015	10^3	–65	h
	80 °C, OTS, Ar	0.08; 0.09	10^4	–60; +75	h; e

treated with octadecyltrimethoxysilane (OTS).²⁴ The molecules (purified by chromatography on silica gel and recrystallized twice) were thermally evaporated onto the substrates under high vacuum (10^{-6} Torr) to a thickness of 40 nm, as measured in situ by a quartz crystal microbalance. Au electrodes were then deposited through a shadow mask. Table 1 summarizes the OFET parameters for compounds **1–3**. The reported mobility data are the average values of around 20 devices for each material, and device statistics are provided in the Supporting Information. As expected, no n-channel behavior was observed on bare SiO_2 , due to the unpassivated hydroxyl groups serving as electron traps.²⁵ Like most n-type organic semiconductors, no n-channel property was obtained in ambient conditions because of the thermodynamic instability of the radical anion toward oxygen in the presence of water.²⁶ However, inside the argon glovebox, on OTS-treated substrates, molecules **1** and **3** exhibit favorable ambipolar characteristics: for **1**, $\mu_{\text{h}} = 0.11 \text{ cm}^2/\text{V} \cdot \text{s}$, $\mu_{\text{e}} = 0.15 \text{ cm}^2/\text{V} \cdot \text{s}$, on/off ratio = 10^4 (Figure 1); for **3**, $\mu_{\text{h}} = 0.08 \text{ cm}^2/\text{V} \cdot \text{s}$, $\mu_{\text{e}} = 0.09 \text{ cm}^2/\text{V} \cdot \text{s}$, on/off ratio = 10^4 . Compared to the previously reported ambipolar compounds,^{7,10–15} our synthesized molecules showed excellent performance in both p- and n-channel conditions and gave similar hole and electron mobilities under the inert atmosphere. Under the same device fabrication conditions, molecule **2** showed high hole transport performance ($\mu_{\text{h}} = 0.22 \text{ cm}^2/\text{V} \cdot \text{s}$, on/off ratio = 10^4) but no electron transport behavior.

Molecular orbital levels were measured using cyclic voltammetry in CH_2Cl_2 at room temperature. UV–vis spectra were recorded in solution and on the thin films (Supporting Information). DFT calculation at B3LYP/6-31G (d) level was used to study the molecular orbital levels. The results are summarized in Table 2. The reason that compounds **1** and **3** showed ambipolar characteristics while compound **2** gave only p-type transport properties could be attributed to their different LUMOs and the highest occupied molecular orbital (HOMO) energy levels (Table 2). The LUMO energy of compound **2** is higher than those of **1** and **3** by 0.11 and 0.27 eV, respectively, as suggested by DFT calculation. Therefore, electron injection to the LUMO of **2** is more difficult than that to **1** and **3**, and hole transport properties are dominant. Actually, using the same top-contact device structure and employing the low work function metal (Ag) as drain and source electrode material, we also observed ambipolar transport from compound **2**, although the electron mobility ($0.005 \text{ cm}^2/\text{V} \cdot \text{s}$) was more than 1 order of magnitude lower than the hole mobility ($0.07 \text{ cm}^2/\text{V} \cdot \text{s}$) (see Supporting Information). This result suggests that precise tuning of the molecular levels is important to achieve high and balanced ambipolar properties, and incorporating a nitrogen atom into the pentacene framework is an effective means to achieve this. The LUMO levels of **1** and **3** are between -3.2 and -3.4 eV. To obtain air-stable electron-transport properties, further reducing the LUMO level is required to avoid quenching of the anions by atmospheric oxidants.²⁶ However, whether further reduction of the LUMO level

will still give balanced hole and electron transport properties needs to be further investigated.

Table 2. Summary of HOMO, LUMO, and Band Gap of Compounds **1–3**

compd	CVs ^a			E_{gap}		DFT ^d		
	LUMO	HOMO	E_{gap}	solution ^b	film ^c	LUMO	HOMO	E_{gap}
1	−3.40	−5.42	2.02	1.84	1.63	−3.24	−5.09	1.85
2	−3.33	−5.31	1.98	1.81	1.57	−3.13	−4.95	1.82
3	−3.46	−5.49	2.03	1.83	1.63	−3.40	−5.25	1.85

^a In CH₂Cl₂ solution (0.1 M Bu₄NBF₄ electrolyte), Pt electrode. Scan rate: 100 mV/s. Fc/Fc⁺ (−4.8 eV to vacuum) internal reference. ^b Band gaps estimated from UV–vis absorption edge in solution. ^c Band gaps estimated from UV–vis absorption edge in a 25 nm thin film on quartz. ^d Computational study at the B3LYP/6-31G(d) level using the Gaussian 03 package. All values are given in eV.

To conclude, we have demonstrated that the incorporation of nitrogen atoms into the framework of TIPS-PEN is an effective strategy to produce oligoacene-based ambipolar OFET materials. Compounds **1** and **3** exhibited high and balanced mobilities and good on/off ratios. Air-stable and solution-processed high-performance ambipolar OFETs are currently being pursued.

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Supporting Information Available: Details of experimental procedures, UV–vis spectra, X-ray diffraction graphs, transfer curves, and AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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