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## Ambipolar, High Performance, Acene-Based Organic Thin Film Transistors

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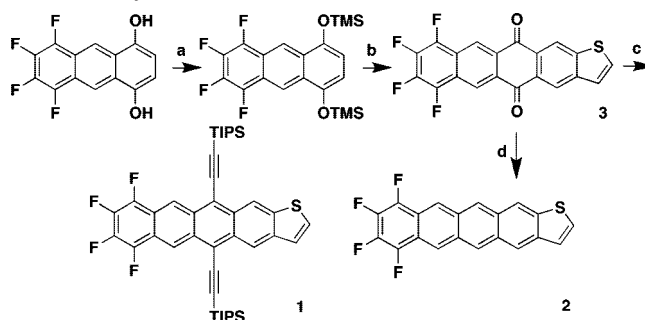
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Organic semiconductors may be a viable alternative to amorphous silicon technology in low-cost, large-area, flexible displays or sensors. With regards to organic field-effect transistors (OFETs), many molecules<sup>1,2</sup> have surpassed the benchmark performance of pentacene, by virtue of being soluble and/or stable at ambient while having high FET mobility. Most of these materials give unipolar transistors (i.e., only hole or electron transport has been observed). However, there is no fundamental reason for organic transistors to be unipolar.<sup>3</sup> Indeed, it has been demonstrated that once traps at the semiconductor dielectric interface are eliminated electron transport is observable.<sup>4</sup> Ambipolar behavior has been shown for pentacene,<sup>5–7</sup> and *n*-channel operation was observed for perfluoropentacene.<sup>8</sup> Here, we demonstrate a high performance, ambipolar, acene-based field-effect transistor, which is soluble and stable, with both hole and electron mobilities,  $\mu_h$  and  $\mu_e$ , respectively,  $>0.1$  cm<sup>2</sup>/V·s.

Ambipolar semiconductors are important for complementary-like inverters that enable robust, low-power circuits with wide noise margins without using advanced patterning techniques to selectively deposit *n*- and *p*-channel materials.<sup>9</sup> More recently, they have been found useful for making light-emitting transistors.<sup>3</sup> Previous attempts for ambipolar OFETs centered on organic bilayers<sup>10</sup> and blends of small molecules<sup>9</sup> and polymers.<sup>11</sup> While complementary-like inverters were achieved, the mobilities were moderate. Due to their scarcity, ambipolar transistors are also interesting from an academic point of view. The few examples in literature are mainly low band gap semiconductors that reduce the charge injection barriers for both holes and electrons. For example, quinoidal terthiophene<sup>12</sup> has an electron mobility,  $\mu_e$ , up to 0.2 cm<sup>2</sup>/V·s, but hole mobility,  $\mu_h$ , and  $\mu_e < 10^{-4}$  cm<sup>2</sup>/V·s at substrate temperatures  $>137$  °C, while squarylium dyes,<sup>13</sup> nickel dithiolenes,<sup>14</sup> and fullerenes<sup>3</sup> have  $\mu_h$  and  $\mu_e$  values of  $\sim 10^{-3}$ – $10^{-5}$  cm<sup>2</sup>/V·s. A single organic material exhibiting good ambipolar transport is dihexanoyl-quartherthiophene,<sup>15</sup> which has  $\mu_h$  and  $\mu_e$  values of  $\sim 0.01$  and 0.1 cm<sup>2</sup>/V·s in vacuum. Here, we present two molecules, 7,8,9,10-tetrafluoro-5,12-bis(TIPSethynyl)tetraceno-tetraceno[2,3-*b*]thiophene, **1**, and 7,8,9,10-tetrafluoro[2,3-*b*]thiophene, **2**, where **1** has  $\mu_h$  and  $\mu_e$  of up to 0.12 and 0.37 cm<sup>2</sup>/V·s in air and in nitrogen, respectively.

We functionalized the asymmetric tetraceno[2,3-*b*]thiophene<sup>16</sup> core with fluorine atoms, both to improve oxidative stability and to induce electron transport by lowering the molecular orbital energies. Scheme 1 shows our synthetic strategy. We found that the Mukaiyama aldol condensation,<sup>17</sup> in the presence of the Lewis acid catalyst tris(pentafluoro)phenylboron, resulted in the formation of 7,8,9,10-tetrafluoro-tetraceno[2,3-*b*]thiophene-5,12-dione, **3**, in 75% yield on a multigram scale. Conventional aldol condensations, or the Diels–Alder reaction,<sup>16</sup> resulted in 10–20% yields similar

Scheme 1. Synthetic Route to Molecules **1** and **2**<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) TMSCl, HMDS, CH<sub>3</sub>CN, rt, 73%; (b) i, 2,3thiophenedicarbaldehyde, tris(pentafluorophenyl)boron, CH<sub>2</sub>Cl<sub>2</sub>, rt; ii, CF<sub>3</sub>CH<sub>2</sub>OH, reflux, 75%; (c) i, *n*BuLi, ether, TIPSacetylene, 60°C; ii, SnCl<sub>2</sub>·H<sub>2</sub>O, 60°C, 70%; (d) Al, HgCl<sub>2</sub>, CBr<sub>4</sub>, CyOH, reflux, 53%.

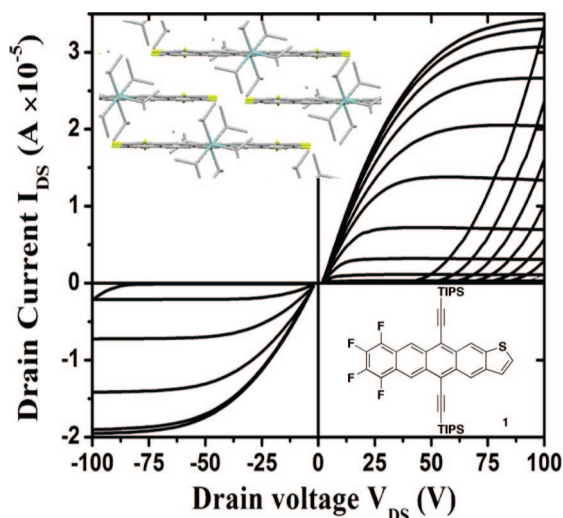
to those obtained for linear acene quinones containing a fused terminal tetrafluorophenyl ring.<sup>18,19</sup> **3** was reduced by standard methods to give 7,8,9,10-tetrafluoro-tetraceno[2,3-*b*]thiophene, **2**, that was further purified by sublimation under high vacuum in a three-zone furnace. 7,8,9,10-Tetrafluoro-5,12-bis(TIPSethynyl)tetraceno[2,3-*b*]thiophene, **1**, was made by adapting known methods<sup>20</sup> and recrystallized twice in degassed hexanes.

Single crystals of **1** have been obtained, and they show the molecule packs in the highly desirable 2D bricklayer structure, similar to 6,13-TIPSethynylpentacene.<sup>20</sup> As with the tetrafluoro- and octafluoro-TIPS-ethynylpentacenes,<sup>19</sup> introduction of fluorine atoms at the terminal ring(s) reduced the  $\pi$ – $\pi$  stacking distance between the conjugated acene backbones. The distance between the aromatic backbones is 3.32 Å for **1**, compared to 3.40 Å for 5,12-bis(TIPSethynyl)tetraceno[2,3-*b*]thiophene (unpublished data). This may be due to the molecular quadrupole<sup>21</sup> interactions between the electron-rich benzene rings and the electron-deficient tetrafluorophenyl ring. Comparing the single crystal data to the out-of-plane peaks (OOP) measured in X-ray diffraction (XRD) for thin films grown on device wafers, **1** appears to pack edge on with the long axis of the conjugated backbone parallel to the substrate. The OOP *d*-spacing of 16.8 Å is almost the same as the 16.81 Å for the *c*-axis in single crystal form. Up to the (007) peak is observed on evaporated thin films on various substrates (see Supporting Information, SI), indicating highly crystalline films. Atomic force microscope (AFM) images of the thin films show micron-sized grains on octadecyl(trimethoxy)silane (OTS)-treated surfaces (see SI).

Top-contact transistors<sup>22</sup> were made by evaporating the molecules under high vacuum ( $10^{-6}$  Torr) to a thickness of 45 nm, as measured in situ by a quartz crystal microbalance. Devices were made on a 300 nm thermally grown SiO<sub>2</sub> layer on a heavily doped Si gate. Some substrates were treated with OTS. As expected, no *n*-channel behavior was observed on bare SiO<sub>2</sub>, due to the

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**Figure 1.** Typical output curves for **1** at 60 °C on OTS-treated SiO<sub>2</sub> for  $L = 100 \mu\text{m}$ ,  $W/L = 20$ . The gate voltage ranges from  $-100$  to  $+180$  V. Inset: 2D slip-stacks of **1** in the single crystal viewed down the  $c$ -axis.

**Table 1.** Summary of Top-Contact OFETs Fabricated from **1**, with Au Electrodes,  $W/L = 20$ ,  $L = 50$  or  $100 \mu\text{m}$

condition	$L$ ( $\mu\text{m}$ )	$\mu$ ( $\text{cm}^2/\text{V}\cdot\text{s}$ )	on/off	$V_T$ (V)	carrier
rt OTS, N <sub>2</sub>	100	$0.133 \pm 0.007$	1E+05	+70	e
		$0.0970 \pm 0.009$	3E+02	+10	h
rt OTS, air	50	$0.113 \pm 0.01$	7E+05	+30	h
rt SiO <sub>2</sub> , air	100	$(9.14 \pm 3) \text{E}-04$	5E+04	-60	h
60 °C OTS, N <sub>2</sub>	100	$0.216 \pm 0.08$	3E+05	+55	e
		$0.0569 \pm 0.007$	5E+02	+20	h
60 °C OTS, air	50	$0.0921 \pm 0.02$	1E+05	+30	h

unpassivated hydroxyl groups serving as electron traps.<sup>4</sup> We did not observe  $n$ -channel transistors in ambient either, perhaps due to atmospheric oxidants<sup>14</sup> such as water and oxygen. However, inside the nitrogen glovebox, on OTS-treated substrates, up to  $0.37 \text{ cm}^2/\text{V}\cdot\text{s}$  electron mobility was observed, with a good on/off ratio of  $10^5$ . The threshold voltage was around  $+70$  V. In inert atmosphere, hole mobilities were several times lower than electron mobilities, up to  $0.065 \text{ cm}^2/\text{V}\cdot\text{s}$ . With negative source-drain bias, the device has low on/off ratios of  $<10^3$  (Figure 1). Interestingly, measuring the same devices in ambient resulted in hole mobilities up to  $0.12 \text{ cm}^2/\text{V}\cdot\text{s}$ , perhaps due to doping by molecular oxygen. Good on/off ratios of  $\sim 10^5$  were also obtained because electrons were quenched. Theoretically, it has been shown that the transfer integral for hole and electron conduction need not be the same for a given molecule, due to the different symmetry of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).<sup>23</sup> All the devices showed higher contact resistance at channel length  $L = 50 \mu\text{m}$ , hence better mobilities were reported for  $L = 100 \mu\text{m}$ . Table 1 summarizes the OFET parameters for compound **1**.

Molecule **2** packs with a OOP  $d$ -spacing of  $15.2 \text{ \AA}$  in thin film, which is slightly larger than that measured for tetraceno[2,3- $b$ ]thiophene ( $14.8 \text{ \AA}$ ). Though the thin film of this molecule shows up to 6 orders of  $(00n)$  diffraction, it forms disconnected grains  $10$ – $15 \mu\text{m}$  in length, hundreds of nanometers in height. These rod-like grains appear to be single crystal under the light microscope. These disconnected films explain the low mobilities of  $\mu_h/\mu_e \sim 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$  measured for this molecule in the nitrogen glovebox.

Molecular orbital levels were measured using cyclic voltammetry in dichloromethane at  $45 \text{ }^\circ\text{C}$ . UV–vis was performed in solution

**Table 2.** Electrochemical<sup>a</sup> Data and UV–Vis Absorption of the Molecules in Solution<sup>b</sup> and UV–Vis of a  $45 \text{ nm}$  Thin Film on Quartz

Molecule	HOMO/eV	LUMO/eV	UV–vis edge <sup>b</sup> /eV	$E_g$ /eV
<b>1</b>	$-5.39^a$	$-3.35^a$	2.00	1.82
<b>2</b>	$-5.33^a$	$-3.20^b$	2.20	2.06

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution (0.1 M Bu<sub>4</sub>NPF<sub>6</sub> electrolyte), Pt electrode. Scan rate:  $100 \text{ mV/s}$ . Fc/Fc<sup>+</sup> ( $0.4 \text{ V}$  vs SCE) internal reference. <sup>b</sup> LUMO estimated from UV–vis absorption edge in solution.

and of the thin films (Supporting Information). The results are summarized in Table 2. It seems that the LUMO levels between  $-3.2$  and  $-3.4 \text{ eV}$  render electron transport susceptible to quenching by atmospheric oxidants, consistent with other reports.<sup>24</sup>

To conclude, we have shown that functionalized acenes can make ambipolar OFETs with high mobilities and good on/off ratios. Air-stable, high performance ambipolar OFETs are currently being pursued.

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

## References

- (1) Murphy, A. R.; Frechet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066–1096.
- (2) Bao, Z.; Locklin, J., Eds. *Organic Field-Effect Transistors (Optical Science and Engineering Series)*; CRC Press: Boca Raton, FL, 2007.
- (3) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296–1323.
- (4) Chua, L. L.; Zaumseil, J.; Chang, J. F.; Ou, E. C. W.; Ho, P. K. H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194–199.
- (5) Benson, N.; Schidleja, M.; Melzer, C.; Schmechel, R.; von Seggern, H. *Appl. Phys. Lett.* **2006**, *89*, 182105.
- (6) Singh, T. B.; Meghdadi, T.; Gunes, S.; Marjanovic, N.; Horowitz, G.; Lang, P.; Bauer, S.; Sariciftci, N. S. *Adv. Mater.* **2005**, *17*, 2315–2320.
- (7) Yasuda, T.; Goto, T.; Fujita, K.; Tsutsui, T. *Appl. Phys. Lett.* **2004**, *85*, 2098–2100.
- (8) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138–8140.
- (9) Meijer, E. J.; De Leeuw, D. M.; Setayesh, S.; Van Veenendaal, E.; Huisman, B. H.; Blom, P. W. M.; Hummelen, J. C.; Scherf, U.; Klapwijk, T. M. *Nat. Mater.* **2003**, *2*, 678–682.
- (10) Wang, H. B.; Wang, J.; Yan, X. J.; Shi, J. W.; Tian, H. K.; Geng, Y. H.; Yan, D. H. *Appl. Phys. Lett.* **2006**, *88*, 133508.
- (11) Babel, A.; Zhu, Y.; Cheng, K. F.; Chen, W. C.; Jenekhe, S. A. *Adv. Funct. Mater.* **2007**, *17*, 2542–2549.
- (12) Chesterfield, R. J.; Newman, C. R.; Pappenfus, T. M.; Ewbank, P. C.; Haukaas, M. H.; Mann, K. R.; Miller, L. L.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1278–1282.
- (13) Smits, E. C. P.; Setayesh, S.; Anthopoulos, T. D.; Buechel, M.; Nijssen, W.; Coehoorn, R.; Blom, P. W. M.; de Boer, B.; de Leeuw, D. M. *Adv. Mater.* **2007**, *19*, 734–738.
- (14) Anthopoulos, T. D.; Anyfantis, G. C.; Papavassiliou, G. C.; de Leeuw, D. M. *Appl. Phys. Lett.* **2007**, *90*, 122105.
- (15) Yoon, M. H.; DiBenedetto, S. A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 1348–1349.
- (16) Tang, M. L.; Okamoto, T.; Bao, Z. N. *J. Am. Chem. Soc.* **2006**, *128*, 16002–16003.
- (17) Ishihara, K.; Hanaki, N.; Funahashi, M.; Miyata, M.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1721–1730.
- (18) Chen, Z. H.; Swager, T. M. *Org. Lett.* **2007**, *9*, 997–1000.
- (19) Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G. *Org. Lett.* **2005**, *7*, 3163–3166.
- (20) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482–9483.
- (21) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593–598.
- (22) Locklin, J.; Roberts, M. E.; Mannsfeld, S. C. B.; Bao, Z. *J. Macromol. Sci., Part C: Polym. Rev.* **2006**, *46*, 79–101.
- (23) Coropceanu, V.; Cornil, J.; da Silva, D. A.; Olivier, Y.; Silbey, R.; Bredas, J. L. *Chem. Rev.* **2007**, *107*, 926–952.
- (24) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259–15278.

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