

# Low-Voltage Organic Transistors Based on Tetraceno[2,3-b]thiophene: Contact Resistance and Air Stability

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**Supporting Information** 

**ABSTRACT:** The small-molecule organic semiconductor tetraceno[2,3-*b*]thiophene has been synthesized through an environmentally friendly synthetic route, utilizing NaBH<sub>4</sub>, rather than Al/HgCl<sub>2</sub>, for the reduction of the quinone. Low-voltage organic thin-film transistors (TFTs) have been fabricated using tetraceno[2,3-*b*]thiophene and, for comparison, pentacene and anthradithiophene as the semiconductor. The tetraceno[2,3-*b*]thiophene TFTs have an effective field-effect mobility as large as 0.55 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and a subthreshold swing of 0.13 V/decade. In addition, it has been found that the contact resistance of the tetraceno[2,3-*b*]thiophene TFTs is



substantially smaller than that of the anthradithiophene TFTs and similar to that of the pentacene TFTs. The long-term air stability of TFTs based on all three semiconductors has been monitored over a period of 12 months. The initial charge-carrier mobility of the tetraceno [2,3-b] thiophene TFTs is ~50% smaller than that of the pentacene TFTs, but as a result of the greater ionization potential and better air stability induced by the terminal thiophene ring condensed at the thiophene-*b*-bond, the tetraceno [2,3-b] thiophene TFTs outperform the pentacene TFTs after continuous exposure to ambient air for just 3 months.

### INTRODUCTION

Organic thin-film transistors (TFTs) are a promising technology for the realization of flexible electronic systems, such as rollable or foldable displays or stretchable sensor arrays. The conjugated organic semiconductor that forms the active TFT layer must meet a significant number of requirements, and to date, more than 700 different materials have been evaluated for this purpose.<sup>1</sup> Pentacene was one of the first and remains among the most popular small-molecule semiconductors for organic TFTs, because of its large carrier mobility.<sup>2,3</sup> Electronic systems that have been successfully demonstrated using pentacene TFTs include flexible active-matrix displays,<sup>4</sup> sensor arrays,<sup>5</sup> radio-frequency identification (RFID) tags,<sup>6</sup> and microprocessors.<sup>7</sup>

However, pentacene has a pronounced sensitivity to chemical oxidation in ambient air<sup>8–11</sup> that typically leads to a rapid, irreversible degradation of the electrical performance of pentacene TFTs exposed to ambient air.<sup>12</sup> One strategy for overcoming this problem is to replace pentacene with a material that has a larger ionization potential, i.e., a lower-lying highest occupied molecular orbital (HOMO) level. This can be accomplished, for example, by reducing the size of the conjugated core<sup>13,14</sup> or by replacing some of the benzene rings with fused heteroaromatic rings, such as thiophene.<sup>15</sup>

This study focuses on pentacene analogues with one or both of the terminal benzene rings replaced with thiophene rings condensed at the thiophene-*b*-bond: tetraceno[2,3-*b*]-

thiophene<sup>16–18</sup> and anthradithiophene.<sup>19,20</sup> The reorganization energies ( $\sim 100 \text{ meV}$ ),<sup>18,21–25</sup> the packing structure (herringbone motif), and the lattice parameters<sup>25,26</sup> of these semiconductors are all similar to those of pentacene, which is beneficial in view of efficient charge transport. Compared with pentacene, they provide better oxidation resistance, because of their lower-lying HOMO levels (-4.6 eV for pentacene, -4.7 eV for tetraceno [2,3-b] thiophene, and -4.8 eV for anthradithiophene).<sup>15</sup> To the best of our knowledge, TFTs based on tetraceno [2,3-b] thiophene and anthradithiophene have so far been fabricated only using thermally grown SiO<sub>2</sub> as the gate dielectric, which is unsuitable for flexible electronics because of the high process temperature. In addition, in all previous reports on tetraceno[2,3-b]thiophene and anthradithiophene TFTs, the gate dielectric was quite thick, so that the TFTs had to be operated with relatively high voltages. Also, there are no previous reports of the contact resistance of tetraceno 2,3b]thiophene and anthradithiophene TFTs. Here, we present a comparison of the performance and long-term air stability of TFTs based on tetraceno[2,3-b]thiophene, anthradithiophene, and pentacene with a gate dielectric that is obtained at a sufficiently low temperature to be suitable for flexible plastic

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substrates and is sufficiently thin that the TFTs can be operated at voltages of 3 V.

### EXPERIMENTAL SECTION

The synthesis of tetraceno[2,3-*b*]thiophene is described in the Supporting Information. Pentacene and anthradithiophene (a mixture of the *syn* and *anti* isomers anthra[2,3-*b*:7,6-*b'*]dithiophene and anthra[2,3-*b*:6,7-*b'*]dithiophene) were purchased from Sigma-Aldrich and used as received. *n*-Tetradecylphosphonic acid was purchased from PCI Synthesis (Newburyport, MA).

Organic thin-film transistors were fabricated on doped silicon substrates in the staggered inverted (bottom-gate, top-contact) architecture. A 30 nm thick layer of aluminum was deposited by thermal evaporation in vacuum as a common gate electrode for all TFTs on the substrate. A  $\sim$ 3.6 nm thick aluminum oxide (AlO<sub>x</sub>) layer was generated by a brief oxygen plasma treatment.<sup>27</sup> For the formation of the self-assembled monolayer (SAM), the substrates were immersed in a 2-propanol solution of tetradecylphosphonic acid (HC14-PA) overnight. The substrates were then rinsed with pure 2-propanol and briefly baked on a hot plate at a temperature of 100 °C. The AlO<sub>x</sub>/ SAM gate dielectric has a capacitance per unit area of 700 nF/cm<sup>228,29</sup> (Figure S2 of the Supporting Information). A 25 nm thick layer of the organic semiconductor (tetraceno[2,3-b]thiophene, anthradithiophene, or pentacene) was deposited onto the AlO<sub>x</sub>/SAM gate dielectric by sublimation in vacuum. To obtain the optimal thin-film morphology, the substrate was held at a temperature of 60-80 °C during the semiconductor deposition. A 30 nm thick layer of gold was deposited by thermal evaporation in vacuum through a shadow mask to define the source and drain contacts. All electrical measurements were performed in ambient air at room temperature under weak yellow laboratory light on a Micromanipulator 6200 manual probe station using an Agilent 4156C Semiconductor Parameter Analyzer. The threshold voltages and effective field-effect mobilities were calculated from the measured transfer curves by a linear fit to the  $I_{\rm D}$ versus  $V_{
m GS}$  data (linear regime) or the  $\sqrt{I_{
m D}}$  versus  $V_{
m GS}$  data (saturation regime). Atomic force microscopy (AFM) measurements were performed using a Nanoscope III Multimode instrument in tapping mode equipped with a silicon cantilever (resonance frequency of 204-497 kHz).

#### RESULTS AND DISCUSSION

**Synthesis.** Tetraceno[2,3-*b*]thiophene was synthesized by the method shown in Scheme 1. First, thiophene-2,3-



dicarbaldehyde was obtained from thiophene-3-carbaldehyde<sup>30</sup> and condensed with 1,4-dihydroxyanthracene<sup>31,32</sup> to yield the corresponding tetracenothiophene quinone. Instead of refluxing in pyridine for several hours,<sup>18</sup> the aldol condensation reaction was conducted in a mixture of ethanol and tetrahydrofuran using 15% NaOH as a base.<sup>30,33–35</sup> The quinone was then reduced to tetraceno[2,3-b]thiophene. Here, rather than

following a procedure that requires  $HgCl_{2}$ , <sup>19,36,37</sup> we followed an environmentally friendly method using NaBH<sub>4</sub> for the reduction to the diol, <sup>38,39</sup> followed by deoxygenation with SnCl<sub>2</sub>/10% HCl.<sup>34,40</sup> Finally, tetraceno[2,3-*b*]thiophene was purified by sublimation.

Bottom-gate, top-contact organic TFTs based on all three semiconductors were fabricated on doped silicon substrates, as shown in Figure 1. The TFTs have aluminum gate electrodes, a gate dielectric composed of a thin layer of oxygen-plasma-grown aluminum oxide and a solution-processed tetradecyl-phosphonic acid self-assembled monolayer (SAM), a vacuum-deposited organic semiconductor layer, and vacuum-deposited gold source/drain contacts patterned using a shadow mask. The highest process temperature is 100  $^{\circ}$ C, and the small thickness (5.3 nm) of the AlO<sub>x</sub>/SAM gate dielectric makes it possible to operate the TFTs with gate-source voltages of 3 V.

The optical absorption spectra of vacuum-deposited thin films of tetraceno[2,3-*b*]thiophene, anthradithiophene, and pentacene are shown in Figure S3 of the Supporting Information. The spectra indicate a blue shift as the number of thiophene rings in the molecule is increased. A similar effect was previously observed by Payne et al. upon fusing thiophene rings to alkyne-substituted acenes.<sup>34</sup> The observed blue shifts in the absorption spectra are consistent with calculations performed by Chen et al.<sup>15</sup> that indicate a decrease in the HOMO energy and an increase in the optical gap when one or more of the benzene rings of an acene are replaced with thiophene rings condensed at the thiophene-*b*-bond. In contrast, incorporating thiophene rings condensed at the thiophene-*c*-bond leads to a decrease in the HOMO–LUMO gap and thus to a red shift in the absorption spectrum.<sup>15</sup>

**Thin-Film Morphology.** The morphology of a vacuumdeposited tetraceno[2,3-b]thiophene film with a nominal thickness of 25 nm measured by atomic force microscopy (AFM) in tapping mode is shown in Figure S1 of the Supporting Information. Large ordered domains can be seen, quite similar to the domains typically observed in vacuumdeposited pentacene films.

Transistor Characteristics. The transfer and output characteristics of long-channel TFTs (channel length of 100  $\mu$ m) based on all three semiconductors measured immediately after device fabrication are shown in Figure 2. The effective field-effect mobilities, threshold voltages, subthreshold swings, and on/off current ratios extracted from the transfer curves are summarized in Table 1. The largest effective mobilities we have obtained for tetraceno[2,3-b]thiophene (0.55 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), anthradithiophene (0.14 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), and pentacene (1.14  $cm^2 V^{-1} s^{-1}$ ) in the saturation regime are similar to the highest mobilities reported in the literature for these semiconductors (tetraceno[2,3-b]thiophene, 0.47 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>;<sup>17,18</sup> anthradi-thiophene, 0.09 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>;<sup>19</sup> pentacene,  $\sim 1$  cm<sup>2</sup> V<sup>-1</sup>  $s^{-1}$ ).<sup>41-43</sup> For anthradithiophene, it should be noted that a mixture of syn and anti isomers was employed in our work, as in ref 12. For TFTs based on isomerically pure ADT, Mamada et al.<sup>25</sup> and Nakano et al.<sup>44</sup> reported mobilities of 0.017 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for *syn*-ADT<sup>44</sup> and 0.18 cm<sup>2</sup> V<sup>-1</sup> s<sup>-125</sup> and 0.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-144</sup> for anti-ADT.

**Contact Resistance and Intrinsic Mobility.** Figure 3 shows that for all three semiconductors, the effective field-effect mobility is significantly smaller in TFTs with shorter channel lengths, where the relative influence of the contact resistance on the total device resistance is greater than in long-channel TFTs. By fitting the experimentally measured relationship between the



Figure 1. Schematic cross section of the bottom-gate, top-contact TFTs and chemical structures of the three organic semiconductors investigated in this study (tetraceno[2,3-*b*]thiophene, anthradithiophene, and pentacene).



**Figure 2.** Transfer characteristics in the linear ( $V_{\text{DS}} = -0.1$  V) and saturation ( $V_{\text{DS}} = -1.5$  V) regime and output characteristics of fresh tetraceno[2,3-*b*]thiophene, anthradithiophene, and pentacene TFTs.

effective field-effect mobility  $\mu_{\rm eff}$  and the channel length L to the equation

$$\mu_{\rm eff} = \frac{\mu_0}{1 + \frac{L_{1/2}}{L}} \tag{1}$$

we can obtain the intrinsic channel mobility  $\mu_0$  (which is the field-effect mobility without the influence of the contacts) and the characteristic channel length  $L_{1/2}$  (at which the contact resistance equals the channel resistance).<sup>45,46</sup> The fits to the data in Figure 3 yield intrinsic channel mobilities  $\mu_0$  and characteristic channel lengths  $L_{1/2}$  of 0.31 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 6

 $\mu$ m for tetraceno[2,3-*b*]thiophene, 0.17 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 9  $\mu$ m for anthradithiophene, and 1.18 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 15  $\mu$ m for pentacene, respectively (Figure 3a and Table 1).

The contact resistance (and also the intrinsic channel mobility) can be determined with the transmission line method (TLM).<sup>47–51</sup> In a simple model, the total resistance of a field-effect transistor in the linear regime can be expressed as the sum of contact resistance  $R_{\rm C}$  and channel resistance  $R_{\rm channel}$  ( $R_{\rm total} = R_{\rm C} + R_{\rm channel}$ ). While the channel resistance is proportional to the channel length, the contact resistance is independent of the channel length:

$$R_{\text{total}}W = R_{\text{C}}W + \frac{L}{\mu_0 C_{\text{diel}}(V_{\text{GS}} - V_{\text{th}})}$$
(2)

where  $R_{\text{total}}W$  is the total device resistance normalized to the channel width,  $R_CW$  is the width-normalized contact resistance, L is the channel length,  $\mu_0$  is the intrinsic channel mobility,  $C_{\text{diel}}$  is the gate-dielectric capacitance per unit area,  $V_{\text{GS}}$  is the gate-source voltage, and  $V_{\text{th}}$  is the threshold voltage. In the TLM analysis,  $R_{\text{total}}W$  is plotted as a function of channel length, so that the linear fit yields  $R_CW$  (by extrapolating to L = 0) and the intrinsic channel mobility (from the slope of the linear fit)<sup>47-49</sup> (Figure 3b).

For the TLM analysis, we fabricated TFTs with channel lengths ranging from 2 to 100  $\mu$ m and measured the total resistance at a drain-source voltage of -0.1 V (linear regime). To account for the fact that TFTs based on different semiconductors and/or different channel lengths may have different threshold voltages, only data measured at a fixed gate overdrive voltage [i.e., at a fixed gate-source voltage above threshold ( $V_{\rm GS} - V_{\rm th}$ )] were considered for the first part of the analysis; this assures that only contact resistances obtained under the same bias condition are compared.

In Figure 3b, the width-normalized total resistances of TFTs based on all three semiconductors at a gate overdrive voltage of -1.5 V are plotted as a function of channel length. The linear fits yield width-normalized contact resistances and intrinsic channel mobilities of 1.5 k $\Omega$  cm and 0.29 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for tetraceno[2,3-*b*]thiophene, 5.5 k $\Omega$  cm and 0.15 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for anthradithiophene, and 1.4 k $\Omega$  cm and 1.14 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for pentacene, respectively (Figure 3b and Table 1). These values suggest that there is a correlation between the contact resistance and the intrinsic mobility: When the charge carriers in the gate-induced accumulation channel have a large mobility, the contact resistance tends to be smaller. This can be understood in the context of the current crowding model<sup>47,49,50,52</sup> in which the semiconductor volume underneath

Table 1. Maximal and Average Effective Field-Effect Mobilities, Threshold Voltages, Subthreshold Swings, and On/Off Current Ratios of Tetraceno[2,3-b]thiophene, Anthradithiophene, and Pentacene TFTs with a Channel Length of 100  $\mu$ m in the Saturation Regime and in the Linear Regime, and Intrinsic Channel Mobilities and Width-Normalized Contact Resistances Extracted using TLM (from Figure 3)

	tetraceno[2,3-b]thiophene	anthradithiophene	pentacene		
Saturation Regime ( $V_{\rm DS} = -1.5$ V; $L = 100 \ \mu m$ )					
maximal effective field-effect mobility	$0.55 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$0.14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$1.14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$		
average effective field-effect mobility	$0.41 \pm 0.07 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$0.13 \pm 0.005 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$0.99 \pm 0.17 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$		
threshold voltage	$-1.37 \pm 0.15 \text{ V}$	$-1.11 \pm 0.15 \text{ V}$	$-1.22 \pm 0.07 \text{ V}$		
subthreshold swing	$168 \pm 18 \text{ mV/decade}$	$243 \pm 20 \text{ mV/decade}$	$132 \pm 6 \text{ mV/decade}$		
on/off current ratio	10 <sup>5</sup>	10 <sup>4</sup>	10 <sup>6</sup>		
Linear Regime ( $V_{\rm DS} = -0.1$ V; $L = 100 \ \mu {\rm m}$ )					
maximal effective field-effect mobility	$0.42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$1.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$		
average effective field-effect mobility	$0.35 \pm 0.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$0.10 \pm 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$1.05 \pm 0.19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$		
threshold voltage	$-1.47 \pm 0.13 \text{ V}$	$-1.45 \pm 0.01 \text{ V}$	$-1.33 \pm 0.06 \text{ V}$		
subthreshold swing	$128 \pm 60 \text{ mV/decade}$	$308 \pm 30 \text{ mV/decade}$	$145 \pm 6 \text{ mV/decade}$		
on/off current ratio	10 <sup>4</sup>	10 <sup>3</sup>	105		
Fit to $\mu_{\text{eff}} = f(L)$					
intrinsic mobility $(\mu_0)$	$0.31 \pm 0.005 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$0.17 \pm 0.006 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$1.18 \pm 0.035 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$		
$L_{1/2}$	$5.5 \pm 0.38 \ \mu m$	$8.8 \pm 1.3 \ \mu m$	$15 \pm 1.6 \ \mu m$		
Transmission Line Method ( $V_{GS} - V_{th} = -1.5 \text{ V}; V_{DS} = -0.1 \text{ V}$ )					
intrinsic mobility $(\mu_0)$	$0.29 \pm 0.004 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$0.15 \pm 0.006 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$1.14 \pm 0.037 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$		
width-normalized contact resistance	$1.5 \pm 0.15 \text{ k}\Omega \text{ cm}$	$5.5 \pm 1.2 \text{ k}\Omega \text{ cm}$	$1.4 \pm 0.15 \text{ k}\Omega \text{ cm}$		



Figure 3. (a) Effective field-effect mobility in the linear regime as a function of channel length. The fit to eq 1 yields intrinsic channel mobility  $\mu_0$ . (b) Transmission line method (TLM). Channel width-normalized total resistance as a function of channel length. All resistances were measured at a fixed overdrive voltage ( $V_{CS} - V_{th}$ ) of -1.5 V and a drain-source voltage of -0.1 V. Extrapolation to a channel length of zero yields the width-normalized contact resistance  $R_CW$ , and the inverse of the slope of the linear fit yields the intrinsic channel mobility  $\mu_0$ . (c) Channel width-normalized contact resistance ( $R_CW$ ) as a function of inverse gate overdrive voltage.

the contacts is regarded as a resistor network composed of vertical and horizontal resistors (which can be linked to the contact resistivity and the channel sheet resistance, respectively) (see Figure 4). A larger carrier mobility will lead to a



Figure 4. Schematic cross section of the semiconductor area below the source/drain contacts, illustrating the horizontal and vertical resistances contributing to the contact resistance in the framework of the current crowding model (left) and a schematic of charge injection (right).

smaller sheet resistance (and will likely also lead to a smaller contact resistivity) and hence (all else being equal) to a smaller contact resistance, which is consistent with the results seen in Figure 3b. Note that for anthradithiophene and pentacene, the intrinsic channel mobility extracted from the TLM analysis is indeed greater than (or at least similar to) the effective fieldeffect mobility of the long-channel TFTs in the linear regime, as expected. For tetraceno[2,3-b]thiophene, the intrinsic channel mobility (0.29 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) happens to be smaller than the average effective mobility  $(0.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ , because the measurements were performed on different substrates and are thus subject to certain unavoidable process variations.] The fact that the contact resistance is in part determined by the intrinsic mobility would also explain why the contact resistance does not show a systematic dependence on the HOMO energy, which might have been expected on the basis of energy-barrier considerations alone.

By performing TLM measurements over a wide range of gate-source voltages, we can analyze the dependence of the contact resistance on the gate-source voltage (or on the gate overdrive voltage,  $V_{\rm GS}$  –  $V_{\rm th}$ ). From the literature, it is wellknown that the contact resistance of organic TFTs decreases with increasing gate overdrive voltage.<sup>46,51–55</sup> When the contact resistance is plotted as a function of the inverse of the gate overdrive voltage, the approximately linear relation between these two quantities becomes visible, as seen in Figure 3c. A linear relation between  $R_{\rm C}W$  and  $1/(V_{\rm GS} - V_{\rm th})$  has been previously observed for other organic semiconductors<sup>46,54</sup> and can also be understood in the context of the current crowding model: A larger gate overdrive voltage leads to a greater chargecarrier density in the accumulation channel and thus to a smaller channel sheet resistance, i.e., to a smaller horizontal component of the contact resistance. As a result of the smaller horizontal component of the contact resistance, a larger area underneath the contact becomes available for charge injection (or extraction), and this results in a smaller contact resistance.<sup>54</sup> In addition to the channel sheet resistance, the contact resistivity (i.e., the vertical component of the contact resistance) is likely also reduced when the carrier density in the channel is increased, because a tail of gate-induced carriers

extends above the channel into the bulk of the semiconductor.  $^{\rm 46,54}$ 

Air Stability. On the basis of the fact that the difference in energy between the HOMO level and the vacuum level is greater in tetraceno[2,3-*b*]thiophene and anthradithiophene than in pentacene, as well as from UV–vis absorption measurements in solution,<sup>17,56</sup> it is expected that TFTs based on tetraceno[2,3-*b*]thiophene and anthradithiophene have better air stability than pentacene TFTs,<sup>15,17,18,57</sup> but to the best of our knowledge, this has never been experimentally confirmed. We have therefore monitored the evolution of the charge-carrier mobility of TFTs based on tetraceno[2,3-*b*]thiophene, and pentacene fabricated under identical process conditions (same substrate, gate dielectric, contact metal, film thicknesses, channel length, channel width, etc.) over a period of several months without any protection from ambient air (relative humidity of ~50%). The results are summarized in Table 2.

Table 2. Evolution of the Effective Field-Effect Mobility (averaged over five transistors) of Tetraceno[2,3b]thiophene, Anthradithiophene, and Pentacene TFTs ( $L = 100 \ \mu m$ ) during Continuous Exposure to Ambient Air

time	tetraceno[2,3-b]thiophene	anthradithiophene	pentacene	
Average Effective Field-Effect Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )				
fresh	0.39	0.13	0.89	
1 week	0.30	0.08	0.50	
1 month	0.15	0.052	0.24	
3 months	0.07	n/a	0.05	
4 months	n/a	0.026	n/a	
5 months	0.05	n/a	0.02	
1 year	0.011	0.006	0.005	
HOMO Energy <sup>a</sup> (eV)				
	-4.7	-4.8	-4.6	
<sup>a</sup> Calculated by Chen et al. <sup>15</sup>				

Each value in Table 2 is an average of the results from five TFTs. Immediately after fabrication, the field-effect mobility of the pentacene TFTs is twice as large as that of the tetraceno[2,3-b]thiophene TFTs and close to an order of magnitude larger than that of the anthradithiophene TFTs. However, the rate at which the mobility degrades in air shows the opposite trend: pentacene degrades significantly more rapidly than tetraceno[2,3-*b*]thiophene and anthradithiophene. As a result, the performance of the tetraceno [2,3-b] thiophene exceeds that of the pentacene TFTs after just 3 months in air. Anthradithiophene (having two terminal thiophene rings) is even more stable than tetraceno[2,3-b]thiophene (having just one thiophene moiety), but because the initial mobility of the anthradithiophene TFTs is so small, it takes 1 year for the anthradithiophene TFTs to outperform the pentacene TFTs, and catching up with the tetraceno[2,3-*b*]thiophene TFTs takes even longer. Figure 5 shows the transfer and output characteristics of representative tetraceno[2,3-b]thiophene, anthradithiophene, and pentacene TFTs immediately after fabrication and after continuous exposure to ambient air for 4 or 5 months under weak yellow laboratory light. From these results, tetraceno [2,3-b] thiophene emerges as the best compromise between initial performance and long-term air stability.



**Figure 5.** Electrical performance of the tetraceno[2,3-*b*]thiophene, anthradithiophene, and pentacene TFTs ( $L = 100 \ \mu m$ ) directly after fabrication and after continuous exposure to ambient air for several months. After a few months in air, the tetraceno[2,3-*b*]thiophene TFTs outperform the pentacene TFTs, because of their better air stability.

#### CONCLUSIONS

In summary, the small-molecule organic semiconductor tetraceno [2,3-b] thiophene was synthesized, utilizing NaBH<sub>4</sub>, rather than the more toxic Al/HgCl<sub>2</sub>, for the reduction of the quinone. Low-voltage organic TFTs based on a low-temperature-processed ultrathin gate dielectric were fabricated using tetraceno [2,3-b] thiophene and, for comparison, pentacene and anthradithiophene as the semiconductor. In addition to the effective field-effect mobility extracted from the transfer characteristics, the contact resistance and the intrinsic channel mobility were also determined by employing the transmission line method on TFTs with channel lengths ranging from 2 to 100  $\mu$ m. The contact resistance of the tetraceno[2,3-b]thiophene TFTs was found to be similar to that of the pentacene TFTs and substantially smaller than that of the anthradithiophene TFTs. The long-term air stability of TFTs based on all three semiconductors was monitored over a period of 12 months. The initial carrier mobility of the tetraceno 2,3b]thiophene TFTs is  $\sim$ 50% smaller than that of the pentacene TFTs, but as a result of the greater ionization potential and better air stability induced by the terminal thiophene ring condensed at the thiophene-b-bond, the tetraceno [2,3-b]thiophene TFTs outperform the pentacene TFTs after continuous exposure to ambient air for just 3 months.

### ASSOCIATED CONTENT

### **S** Supporting Information

Experimental procedures, synthesis, and absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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### **Supporting Information**

# Low-voltage Organic Transistors Based on Tetraceno[2,3-*b*]thiophene: Contact Resistance and Air Stability

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- **1.** General procedures
- 2. Synthesis
- 3. Semiconductor thin-film morphology
- 4. Gate-dielectric capacitance measurements
- 5. Absorption spectra
- 6. Additional references

## **1. General procedures**

<sup>1</sup><u>H and <sup>13</sup>C NMR spectra</u> were recorded with a Varian Unity (400 MHz) spectrometer. Proton chemical shifts were referenced to CDCl<sub>3</sub> (7.27 ppm) and to DMSO (2.5 ppm); <sup>13</sup>C shifts were referenced to CDCl<sub>3</sub> (77.0 ppm) and to DMSO (39.51 ppm). The multiplicities are labeled by s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets).

<u>Mass spectra</u> were recorded either using a JEOL JMS-700T in EI mode (70 eV) or a MALDI-TOF-MS Axima Resonance from Shimadzu in LDI-MS mode (laser desorption ionization-mass spectrometry).

<u>Absorption Spectra</u> were recorded using a Lambda 9 Spectrometer from Perkin-ELMER in transmission configuration.

Sample preparation: Organic thin-film transistors were fabricated in the staggered inverted (bottom-gate, top-contact) architecture on doped silicon substrates. Aluminum gate electrodes with a thickness of 30 nm were deposited onto the substrates by thermal evaporation in vacuum. A ~3.6 nm thick aluminum oxide layer was generated by a brief oxygen plasma treatment (30 sccm O<sub>2</sub>, 10 mTorr, 200 W, 30 s). For the formation of the self-assembled monolayer (SAM), the substrates were immersed overnight into a 2-propanol solution with a concentration of ~1 to 2 mmol/l of *n*-tetradecylphosphonic acid (HC<sub>14</sub>-PA) at room temperature. The substrates were then rinsed with pure 2-propanol and annealed on a hotplate at a temperature of 100 °C for about 10 min. The quality of the SAMs was confirmed by static contact angle measurements. The AlO<sub>x</sub>/SAM gate dielectrics have a capacitance per unit area of 0.7  $\mu$ F/cm<sup>2 (28,29)</sup> (see Figure S2). A nominally 25 nm thick layer of the organic semiconductor was deposited onto the AlO<sub>x</sub>/SAM gate dielectric by sublimation in vacuum. During the semiconductor deposition, the substrate was held at a temperature of  $70^{\circ}$ C for tetraceno[2,3-b]thiophene, 80°C for anthradithiophene and 60°C for pentacene, since this was found to provide the largest field-effect mobility for each semiconductor. The TFTs were completed by the vacuum deposition of gold source and drain contacts. All vacuum depositions were carried out with a Leybold UNIVEX 300 vacuum system at a base pressure of about 10<sup>-6</sup> mbar. The film thickness was measured with a quartz crystal microbalance. Aluminum was deposited with a deposition rate of ~9-12 Å/s, the organic semiconductor and the gold contacts were deposited with a deposition rate of 0.2-0.3 Å/s.

Electrical measurements were carried out on a vibration-damped Micromanipulator 6200 probe station with an Agilent 4156C Semiconductor Parameter Analyzer. The measurements were performed in ambient air (humidity ~ 50 %) at room temperature and under yellow lab light. The effective field-effect mobilities and threshold voltages were calculated from the measured transfer curves using a linear fit to the  $I_D$  versus  $V_{GS}$  data in the linear regime and to the  $\sqrt{I_D}$  versus  $V_{GS}$  data in the saturation regime. The values given in Table 1 are for the mean and the standard deviation of parameters obtained from 7 tetraceno[2,3-*b*]thiophene TFTs (4 substrates), 4 anthradithiophene TFTs (1 substrate) and 7 pentacene TFTs (5 substrates). During the air-stability tests, the substrates were stored over a period of several months without protection from ambient air (relative humidity ~50 %) and without protection from the weak yellow laboratory light.

<u>Atomic force microscopy (AFM)</u> was conducted with a Nanoscope III Multimode in tapping mode with silicon cantilevers (resonance frequency: 204-497 kHz) and were processed with WSxM.<sup>[S1]</sup>

### 2. Synthesis

**1.4-Anthracenedione** <sup>[S2]</sup>



5.1 g of sodium borohydride (133 mmol, 4 eq) was added in small portions to an ice-cooled (0°C) stirred solution of 8.0 g (33 mmol) quinizarin (1,4-dihydroxyanthraquinone) in 150 ml methanol under nitrogen atmosphere. The reaction was monitored by working up an aliquot of the reaction mixture and checking for the disappearance of quinizarin by TLC. The mixture was stirred overnight and cooled with an ice bath before quenching slowly with 6N hydrochloric acid (90 ml). The crude product was filtered, washed with water, dried under reduced pressure and purified with a dry silica plug using 1:1 hexanes/DCM first and then DCM to give 6.5 g (94 %) of orange crystals.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.08 (s, 2H, ArH); 7.71 (m, 2H, ArH); 8.08 (m, 2H, ArH), 8.64 (s, 2H, ArH) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 128.35; 128.87, 129.59, 130.22, 134.82, 140.06, 184.68 ppm.

### 1,4-Dihydroxyanthracene <sup>[S2,S3]</sup>



A mixture of 300 ml of dioxane and 100 ml of water was purged with nitrogen for 1 h and then added to a flame-dried, nitrogen-cooled 100 ml RBF. After adding 3.34 g (19 mmol) of sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) and degassing for another 30 min, 1.0 g (4.8 mmol) of 1,4 anthracenedione was added and the mixture was stirred under nitrogen flow. After the addition of another 1.25 g (7 mmol) of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, the mixture was stirred overnight under nitrogen flow at room temperature. The reaction mixture was then poured into 100 ml of nitrogen-purged water that was cooled with an ice bath. After filtering under nitrogen flow, the product was dried under reduced pressure to give 0.79 g (78 %) of a yellow powder.

<sup>1</sup>H-NMR (400 MHz, DMSO-d6):  $\delta$  6.62 (s, 2H, ArH); 7.46 (m, 2H, *J1* = 6.4 Hz, *J2* = 3.3 Hz ArH); 8.08 (m, 2H, *J1* = 6.5 Hz, *J2* = 3.4 Hz, ArH) ppm; 8.67 (s, 2H, ArH); 9.56 (s, 2H, OH) ppm.

ppm. <sup>13</sup>C-NMR (100 MHz, DMSO-d6): δ 105.51, 120.58, 125.25, 128.34, 130.44, 145.34 ppm.

### Thiophene-3-aldehyde ethylene acetal <sup>[S4]</sup>



A 250 ml round bottom flask was charged with 25 g (223 mmol) 3-thiophenecarbaldehyde dissolved in 100 ml of benzene, 15 ml (16.65 g, 268 mmol) of ethylene glycol and a catalytic amount of camphor sulfonic acid. The flask was equipped with a Dean-Stark trap and a reflux condenser to collect the water formed during the reaction, and the reaction mixture was kept at a temperature of 111°C overnight. After cooling to room temperature, the mixture was poured into 100 ml of saturated aqueous sodium bicarbonate solution (NaHCO<sub>3</sub>) and stirred at room temperature for 30 min. The aqueous phase was then extracted 5 times with diethyl ether and the combined organic layers were dried with MgSO<sub>4</sub> and filtered. The solvents were removed under reduced pressure to give 34.4 g (99 %) of a brown oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.95 (m, 4H); 5.88 (s, 1H); 7.18 (d, *J* = 5.2 Hz, 1H); 7.28 (d, *J* = 4.6 Hz, 1H); 7.40 (s, 1H) ppm.

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 64.91, 100.39, 123.58, 125.76, 126.19, 140.38 ppm. MS (EI 70 eV) m/z = 156 (M<sup>+</sup>), 84 (M<sup>+</sup> -C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>).

### Thiophene-2,3-dicarbaldehyde



A flame-dried 250 ml round bottom flask was charged with 15.6 g (100 mmol) of thiophene-3-carbaldehyde ethylene acetal that was dissolved in 100 ml of anhydrous tetrahydrofuran (THF) under nitrogen atmosphere. The reaction mixture was cooled to  $-78^{\circ}$ C under nitrogen. 40 ml (100 mmol) of a 2.5 M solution of *n*-butyllithium in hexanes was then added slowly with a syringe. The mixture was stirred at  $-78^{\circ}$ C for 15 min, whereupon 22 ml (25.19 g, 218 mmol) of *N*-formylmorpholine was added with a syringe. The solution was stirred and allowed to warm up to room temperature overnight. After quenching with water, the reaction mixture was extracted with diethyl ether, dried with MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The material was eluted through a silica gel plug (2:1 hexanes/ethyl acetate), then dissolved in 100 ml of 80 % acetic acid and kept at a temperature of 60°C overnight. After cooling to room temperature, 100 ml of ethyl acetate and 500 ml of water were added. Subsequently, the organic layer was separated from the aqueous layer, washed with water, dried with MgSO<sub>4</sub> and filtered. The solvents were removed under reduced pressure. The crude product was eluted through a silica gel plug (5:1 hexanes/ ethyl acetate), and recrystallized in hexanes to give 7.6 g (54 %) of fluffy yellowish crystals.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.62 (d, 1H, *J* = 5.1 Hz, ArH); 7.72 (dd, 1H, *J*1 = 5.1 Hz, *J*2 = 1.2 Hz, ArH); 10.36 (s, 1H, CHO); 10.46 (d, 1H, *J* = 0.8 Hz, CHO) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 130.06, 133.90, 143.58, 147.24, 182.70, 184.72 ppm.

MS (EI 70 eV)  $m/z = 140 (M^+)$ , 111 ( $M^+$  -CHO).

Tetraceno[2,3-b]thiophene-5,12-dione



0.98 g (7 mmol) of thiophene-2.3-dicarbaldehyde and 1.46 g (7 mmol) of 1,4-dihydroxyanthracene were added to a 250 ml round bottom flask equipped with a stir bar and were dissolved in a hot mixture of 10 ml of THF and 5 ml of ethanol. A few drops of 15% aqueous NaOH solution were then added while stirring until a precipitate was observed. The slurry was stirred for one hour and was subsequently filtered through a Büchner funnel, washed with methanol until the filtrate was colorless, followed by THF and diethyl ether (in this sequence) to give 1.6 g (72 %) of an off-white solid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.63 (d, 1H, *J* = 5.27 Hz, ArH); 7.72 (dd, 2H, *J1* = 6.4 Hz, *J2* = 3.3 H, ArH); 7.81 (d, 1H, *J* = 5.71 Hz, ArH); 8.14 (dd, 2H, *J1* = 6.4 Hz, *J2* = 3.3 Hz, ArH); 8.89 (s, 1H,ArH); 8.93(s, 2H, ArH); 8.97(s, 2H, ArH) ppm.

Tetraceno[2,3-*b*]thiophene<sup>[39]</sup>



In a flame-dried 500 ml round bottom flask equipped with a stir bar, 1.0 g (3.18 mmol) of tetraceno[2,3-*b*]thiophenequinone was dissolved in 60 ml of anhydrous THF. Then, 1.2 g (31.85 mmol, 10 eq) of sodium borohydride was added and the reaction mixture was heated at 60°C for several days until TLC followed by SnCl<sub>2</sub>/HCl treatment revealed that the reaction was complete. 10 % hydrochloric acid and 3.59 g (15.9 mmol, 5 eq) of stannous chloride (SnCl<sub>2</sub>) was added. After stirring for 1 h, the mixture was filtered in the dark under nitrogen flow and washed with degassed methanol to give 0.74 g (82 %) of a purple powder. MS (LDI-MS) m/z = 284.06 (M+, 100%).

### 3. Semiconductor thin-film morphology



**Figure S1.** Semiconductor thin-film morphology: Topography (left) and amplitude (right) images of a tetraceno[2,3-*b*]thiophene thin-film with a nominal thickness of 25 nm measured by atomic force microscopy (AFM) in tapping mode. The images are from the same sample, showing two different magnifications.

### 4. Gate-dielectric capacitance measurements



**Figure S2.** Capacitance per unit area of the  $AlO_x/SAM$  gate dielectric as a function of frequency. The capacitance was measured on  $Al/AlO_x/SAM/Au$  test structures with shadow-mask patterned Al bottom electrodes and Au top electrodes fabricated on a thermally oxidized silicon wafer. Inset: A photograph of one of the test structure with an overlap area of 200 µm x 200 µm.

### 5. Absorption spectra



**Figure S3.** Absorbance of 25 nm thick, vacuum-deposited thin films of anthradithiophene (1), tetraceno[2,3-*b*]thiophene (2) and pentacene (3).

### **<u>6. Additional references</u>**

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