High Mobility Field-Effect Transistors with Versatile Processing from a Small-Molecule Organic Semiconductor

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Along with excellent potential for commercial applications such as displays or sensors,[1] organic semiconductors offer a versatile platform to understand the fundamental structural and process parameters governing charge transport in carbon-based solids. In earlier work, we demonstrated how the addition of specific functional groups to the anthradithiophene chromophore allowed tuning of the solid-state order of these now soluble materials to enhance hole mobility in thin-film transistors.[2] We later found that the addition of two fluorine substituents both enhanced the stability of the organic material and subtly changed the crystal packing to further enhance charge transport.[2] We report here a further modification—replacing the trialkylsilyl substituent with its trialkygermyl homologue—that again subtly changes the solid-state order and yields a significant improvement in performance, along with permitting processing by an array of methods suitable for large-area deposition.

The triethylgermylenyl-substituted anthradithiophene (diF-TEG ADT, Figure 1 a) is easily prepared as an inseparable mixture of syn and anti isomers by standard chemical synthesis. We have shown in previous studies that the presence of the two isomers does not significantly impact device performance.[6] The molecular structure and representation of the molecular packing, emphasizing the two-dimensional π-stacked arrangement, are shown in Figure 1. The molecules adopt a 2D π-stacking motif (Figure 1 b), similar to triethylsilylene-yl substituted anthradithiophene - diF-TES ADT, with the slight increase in C-Ge bond length compared with the C-Si bond allowing closer interplanar spacing (3.24 Å in diF-TEG ADT compared to 3.37 Å in diF-TES ADT).[5] We also observe other subtle differences between the crystal packing of the diF-TEG ADT and diF-TES ADT compounds, such as a 1.8 Å smaller shift along the long-axis between adjacent molecules, and 11% larger areal molecular overlap for the TEG compound. These variations in molecular arrangement suggest improvement in charge transport properties, as predicted by theoretical studies showing that such differences can strongly affect the intermolecular electronic couplings.[7] XRD measurements performed on thin films deposited from a chlorobenzene solution on an Au surface treated with pentfluorobenzene thiol (PFBT) self-assembly monolayer indicate that the diF-TEG ADT films exhibit a high degree of crystallinity, with the molecules adopting a preferred orientation along the (001) direction (Figure 1 c). This orientation, with the molecular backbones aligned “edge-on” (approximately perpendicular to the surface) and the ab plane parallel to the substrate (Figure 1 d) yields π-π overlap in the plane of the substrate, which is believed critical for high charge carrier mobilities.[8,9]

To explore the transport properties and processing possibilities of this new material, field-effect transistors (FETs) were fabricated by a number of methods. Bottom contact, bottom gate FETs with configuration similar to the one presented in Figure 2 a were fabricated on substrates consisting of highly doped silicon (the gate electrode), and thermally grown SiO2 as gate dielectric. Source and drain Au contacts were defined photolithographically with channel lengths between 5 and 100 μm. The contacts were chemically treated with PFBT prior to film deposition to improve crystallization and charge injection.[8] Initially, the organic semiconductor was deposited on these substrates using drop-casting in a solvent-rich atmosphere (SAC - solvent assisted crystallization).[10] The optical micrograph and electrical properties of a representative device obtained by SAC are depicted in Figure 2 b, c and d respectively. The crystallites forming the films are red, platelet-like (Figure 2 b). The evolution of the drain current (I_D) with the source-drain voltage (V_DS) for several source-gate (V_GS) voltages plotted in Figure 2 c indicates that hole transport is characteristic for this

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material when Au contacts are used. The compression and curvature of $I_D$ in the linear regime of device operation (low $V_{DS}$) is not uncommon in high-mobility organic thin-film transistors (OTFTs), especially at short channel lengths, and arises from the fact that here the charge injection and collection efficiencies at the contacts are challenged by the high current density generated in the transistor channel.\[^{11}\]

In Figure 2d we plot the evolution of the $I_D$ versus $V_{GS}$ in the saturation regime ($V_{DS} = -40\,\text{V}$) for the same device, having channel length $L = 5\,\mu\text{m}$ and channel width $W = 200\,\mu\text{m}$. From the curve on the right axis we estimate the on/off ratio to be $\sim 10^6$ and from the curve on the left axis, we calculate a field-effect mobility $\mu = 5.4\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. This value is significantly higher than the best mobility reported in solution deposited diF-TES ADT: a summary of the highest reported mobilities in diF-TEG ADT (this work) and diF-TES ADT (references included) is compiled in Table 1. The threshold voltage shifts towards positive values when the measurement is performed in ambient conditions, which is qualitatively consistent with an oxidative oxygen
doping and is under investigation, but we were able to mitigate these parasitic currents with vacuum outgassing of the sample and performing the FET characterization in vacuum.

The histogram in Figure 3 reviews the values of the mobility $\mu$ recorded on 104 devices fabricated by SAC. The mean value of the mobility was $2.3 \pm 1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, with the lowest recorded value of $0.14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the highest of $5.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Such a spread in mobilities is quite common in organic FETs, including single crystal devices, and can originate from such effects as the quality of the metal/semiconductor and metal/dielectric interfaces, thin-film structure and morphology, contact resistance and anisotropy in electrical properties along different crystallographic directions. Nevertheless, the fact that 94 devices (90% of the total measured) exhibited mobilities greater than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the best recorded mobility was as high as $5.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, makes diF-TEG ADT one of the highest mobility solution-deposited organic semiconductors reported to date. At the same time, our measurements are influenced by morphological effects that cannot be controlled accurately with solution processing, and which impeded access to intrinsic properties of this material. We are currently pursuing single crystal growth by physical vapor transport to be able to access the ultimate performance of this material.[5]

A recent approach to improve device-to-device performance issues involves blending the small-molecule semiconductor into an insulating or semiconducting polymer.[13] In the case of diF-TES ADT, blends with a poly(triarylamine) led to impressive device performance with excellent reproducibility from spin-coated films.[14] Because of the nature of the phase separation of the two species, best performance is observed in top-gate, bottom-contact devices. Thus, a 1:1 weight ratio blend of diF-TEG ADT and poly(triarylamine) was dissolved in tetralin and spin-cast onto a substrate with pre-patterned PFBT-treated Au source and drain electrodes. The as-spun films were annealed at 100 °C for 5 minutes, during which time the small-molecule semiconductor dried forming crystalline domains in the range 10–100 µm in diameter (Figure 4 a,b). CYTOP was next deposited as gate dielectric followed by the evaporation of Al through a shadow mask to form the gate electrode. Although maximum mobility in this configuration was not as high as observed in the SAC-deposited films, device-to-device variability did appear to decrease, with a mobility of $1.28 \pm 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ being recorded.

As exemplified by the blend work described above, significant progress has been made recently in device processing, resulting in steady improvements in FET properties. Nevertheless, often these properties can only be reproduced over small areas, when deposition methods such as spin-coating, or drop-casting are used and fail when large-areas are employed. Reproducing the performance obtained with conventional deposition techniques is not trivial given its strong dependence on film morphology and microstructure, which in turn are dictated by processing parameters. Recent reports on spray-deposited FETs have generated interest in this inexpensive, unconventional electronic device manufacturing technique, compatible with arbitrary large-area substrates. For example, Chan et al have measured mobilities of 0.023 cm$^2$ V$^{-1}$ s$^{-1}$ in polymer FETs based on airbrushed P3HT.[15] We have demonstrated spray-deposited small-molecule FETs with mobilities of 0.2 cm$^2$ V$^{-1}$ s$^{-1}$ based on diF-TES ADT.[16] Motivated by the remarkable electrical properties of diF-TEG ADT in drop-cast and spin-coated blend devices, we fabricated spray-coated FETs to test the compatibility of this material with methods applicable to large-area electronics. In a bottom-gate, bottom-contact configuration, diF-TEG ADT was deposited by spray deposition of a 0.15 wt% solution in chlorobenzene. Control over the droplet properties was achieved by tuning the pressure of the transporting gas and the distance between the spray nozzle and the substrate. In Figure 5 we plot the device structure and the current-voltage characteristics of one of the best devices, fabricated under ambient conditions, with the Argon propellant set to a pressure of 5 psi, and with the airbrush positioned perpendicular to the device substrate, at a height of 13 cm. A mobility of $\mu = 2.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was calculated from the transfer characteristics in the saturation regime ($V_{DS} = -40 \text{ V}$), plotted in Figure 5a. To the best of our knowledge, this value represents the highest mobility reported to date in spray-coated organic FETs. Other characteristics for this device include a very small threshold voltage ($V_T = 0.5 \text{ V}$) and a good current on/off ratio ($I_{on}/I_{off} \sim 10^4$). An average mobility of $1.1 \pm 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was determined from measuring 36 devices fabricated under similar conditions (Figure 1, SI).

In summary, the replacement of a trialkylsilyl substituent with a triarylgermyl group led to subtle but significant changes in molecular packing, which in turn yielded impressive improvements in device performance. Solution-processed OFETs based on diF-TEG ADT exhibit field-effect mobilities as high as 5.4 cm$^2$ V$^{-1}$ s$^{-1}$. Devices with a record-high mobility of 2.2 cm$^2$ V$^{-1}$ s$^{-1}$ are fabricated using spray-deposition, which highlights the promise of this material for incorporation in low-cost, large-area electronics.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\mu_{\text{drop-Cast}} \left( \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1} \right)$</th>
<th>$\mu_{\text{spin}} \left( \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1} \right)$</th>
<th>$\mu_{\text{spray}} \left( \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>di-F TES ADT</td>
<td>1.5$^{[1]}$</td>
<td>0.4$^{[18]}$</td>
<td>0.2$^{[16]}$</td>
</tr>
<tr>
<td>di-F TEG ADT</td>
<td>5.4</td>
<td>3.7</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Figure 3. Histogram showing the values of mobilities ($\mu$) measured for 104 di-F-TEG ADT devices. The highest mobility is 5.4 cm$^2$ V$^{-1}$ s$^{-1}$, and the average value is $2.3 \pm 1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.
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Figure 4. Polarized light microscopy image of a diF-TEG ADT: poly(tertriarylamine) blend film spin-cast onto glass substrates containing; a Au/PFBT electrode (a–electrode area indicated) and a highest magnification image of the same film onto bare glass area (b). Transfer (c) and output (d) characteristics for transistors fabricated using a 1:1 (by weight) blend of diF-TEG ADT and poly(tertriarylamine), with channel length and width of \( L = 20 \mu m \) and \( W = 1000 \mu m \), respectively.

Experimental Section

Material Synthesis: Triethylgermyl acetylene was prepared by adding 200 mL of 0.5 M (100 mmol) ethynyl Grignard in THF solution to a flame dried 500 mL round bottom flask under nitrogen. Triethylchlorogermane (4.87 g, 25 mmol) was added dropwise at room temperature and the solution was stirred overnight at room temperature. After TLC with potassium permanganate stain confirmed completion, the reaction mixture was quenched with water and 10% HCl solution. After extraction with pentane, the organic layer was dried, filtered, and the solvent removed by simple distillation. Silica chromatography with pentane was used to remove a slight brown color and after distillation of the pentane

Figure 5. Electronic properties of spray-deposited diF-TEG ADT transistors. a) Transfer characteristics in the saturation regime (\( V_{DS} = -40 \) V). Right axis: \( \log(I_D) \) vs \( V_{GS} \). Left axis: \( \sqrt{I_D} \) vs \( V_{GS} \). b) Output characteristics for the same device.
3.54 g (77%) of the desired colorless liquid acetylene was isolated.\textsuperscript{1} H NMR (400 MHz, CDC\textsubscript{3}) \(\delta\) 1.141 (quart, \(J = 7.3\) Hz, 6H), 2.054 (t, \(J = 7.3\) Hz, 9H), 2.533 (s, 1H) ppm.\textsuperscript{13}C NMR (100 MHz, CDC\textsubscript{3}) \(\delta\) 5.683, 8.923, 8.795, 93.385 ppm. MS (EI 70eV/m/z 182, 184, 185, 186, 188 (2.5:3.5:4:5:1, M?): 135, 153, 156, 157, 159 (2.5:3.5:4:5:1, M?): 125, 127, 128, 131 (2.5:3.5:4:5:1, M?): 125-128, 131 (2.5:3.5:4:5:1, M?): 97, 95, 98, 99, 101 (2.5:3.5:4:5:1, M?): 129.768, 129.821, 129.859, 129.904, 130.003, 130.094, 139.431, 139.583, 139.749, 140.031, 140.129 ppm. MALDI-TOF, no matrix.

\textsuperscript{4}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 5.683, 9.586, 103.358, 107.662, 120.324, 120.362, 121.600, 121.653, 123.976, 129.768, 129.821, 129.859, 129.904, 130.003, 130.094, 139.431, 139.583, 140.031, 140.129 ppm. S (MALDI-TOF, no matrix) \(m/z\) 650, 652, 654, 656, 658 (2.5:3.5:4:5:1, M?): 125-128, 131 (2.5:3.5:4:5:1, M?): 129.768, 129.821, 129.859, 129.904, 130.003, 130.094, 139.431, 139.583, 140.031, 140.129 ppm. MALDI-TOF, no matrix.

**Single Crystals**

**X-Ray Diffraction**

X-ray data were collected on a Bruker D8 Discover with D:Vinci diffractometer, in the standard Bragg-Brentano para- focusing configuration utilizing sealed tube CuK\textalpha\ radiation and operated at 40 kV and 40 mA. The sample was mounted on a horizontal sample stage on a 830 mm diameter goniometer on a Bruker D8 Discover with DaVinci diffractometer, in the standard parameter analyzer. Optical micrographs were obtained with an Olympus BH2 UMA microscope, under polarized light.

**Fabrication and electrical characterisation of FETs based on polymer/small molecule blends**

Top-gate, bottom-contact organic blend transistors were fabricated on glass substrates using Au electrodes treated with PFBT. As-prepared devices had channel lengths and widths varying from 20–100 µm and 0.5–2.0 mm respectively. The blend semiconductor was deposited by spin coating at 500 rpm for 10 sec followed by 2000 rpm for 20 sec from 4 wt% 1,2,3,4-tetrahydroxynaphthalene solutions. The resulting films were annealed at 100 °C for 2.5 min to remove excess solvent. Blends consisted of 50:50 by wt% of diTF-EG ADT with poly(triarylmethane)(PTAA). The fluoropolymer CYTOP was deposited as the gate dielectric in nitrogen atmosphere followed by the evaporation of the aluminium gate electrode through shadow masks in high vacuum. Electrical characterisation was performed in a nitrogen atmosphere using a semiconductor parameter analyzer.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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