

Single-step solution processing of small-molecule organic semiconductor field-effect transistors at high yield

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Single-step solution processing of small-molecule organic semiconductor field-effect transistors at high yield

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Here, we report a simple, alternative route towards high-mobility structures of the small-molecular semiconductor 5,11-bis(triethyl silylethynyl) anthradithiophene that requires one single processing step without the need for any post-deposition processing. The method relies on careful control of the casting temperature of the semiconductor and allows rapid production of transistors with uniform and reproducible device performance over large areas. © 2011 American Institute of Physics. [doi:10.1063/1.3673280]

Soluble pentacenes and anthradithiophenes are promising candidates for organic field-effect transistors (OFETs): among these compounds, 5,11-bis(triethyl silylethynyl) anthradithiophene (TES ADT) is one of the highest performing materials with charge-carrier mobilities μ_{FET} reaching $1 \text{ cm}^2/\text{Vs}$.¹ However, obtaining reproducibly and reliably such a high performance with this small molecule is still challenging. The latter is probably best reflected by the fact that published mobility values span orders of magnitudes, and striking differences in other relevant device characteristics are also found in literature.^{1–3} In order to overcome this undesirable feature of TES ADT, 2,8-difluoro-5,11-bis(triethyl silylethynyl) anthradithiophene (diF-TES ADT) was synthesized, tailored for accelerating molecular assembly in solution through halogen interactions (which result from the introduction of difluoro-moieties into the fused-aromatic backbone).⁴ This adjusted molecular design significantly increased the reproducibility in obtaining thin-film structures of good semiconducting properties, and device performance and uniformity could be enhanced further when the material was blended with a polymer matrix, such as the semiconducting polytriarylamines (PTAAs).⁵ However, high-performance transistors were mostly obtained in top-gate devices, in combination with relatively thick polymer gate dielectrics of a low dielectric constant, where circuitry integration can be complex, and the low capacitance between gate electrode and semiconducting channel implies high driving voltages. The reason for the need for top-gate configuration is that device performance of such blends relies on vertical phase segregation of the small molecule to the top surface (i.e., towards the dielectric interface)—which is usually difficult to control, especially over large areas. Since, in addition, the synthetic route of diF-TES ADT is significantly more intricate com-

pared to the non-fluorinated TES ADT, we revisited the use of TES ADT in OFET applications, focusing on single component systems and the technologically desired bottom-gate/bottom-contact transistor configuration.

Recent work has indicated that following such a strategy of using single component TES ADT active layers in bottom-gate/bottom-contact devices may be a feasible option. Most prominently, Cho *et al.* exploited “aging” (i.e., crystallization over time) of an initial vitreous solid state of low mobility ($\mu_{\text{FET}} \sim 0.002 \text{ cm}^2/\text{Vs}$) to realize well performing structures. However, in order to obtain $\mu_{\text{FET}} \sim 0.1 \text{ cm}^2/\text{Vs}$ with such TES ADT architectures, the material needed to be aged over a period of at least 7 days in vacuum.³

Whilst “aging” (or crystallization in the solid state) does provide an elegant method for studying relevant structure/device performance interrelationships of TES ADT films, it is evident that this protocol may not lead to high-throughput device manufacturing. We, therefore, explored whether the molecular order of TES ADT can be manipulated without the need to rely on time-consuming post-processing procedures. To this end, in a first set of experiments, we fabricated transistor devices on Si (n^{++})/SiO₂ substrates comprising an oxide dielectric of 140 nm-thickness and photo-lithographically patterned Au source/drain electrodes. Prior to device fabrications, a pentafluorobenzenethiol monolayer was deposited onto the Au electrodes.⁶ The SiO₂ was treated with trichlorophenylsilane. Our objective was to investigate if casting at temperatures above the glass transition temperature T_g (see Ref. 3) directly leads to aged structures. For this purpose, we used 4 wt. % TES ADT solutions in chloroform and solution-cast them at $T_{\text{casting}} \sim 30\text{--}40^\circ\text{C}$. Our reasoning was based on the fact that aging is a process that occurs at temperatures close to or above the glass transition temperature T_g of a given material, and thus, high-temperature casting may accelerate this process. [Note that aging at elevated temperatures has been observed to occur in films of other small molecular semiconductors such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine

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(TPD).⁷ It is also commonly found in bulk commodity polymer products.⁸]

Predominantly amorphous structures were obtained when following this processing protocol, which were very similar to the spin-coated, low-mobility films reported by Cho *et al.* The amorphous nature of such “high-temperature cast” TES ADT films is evident from the absence of any birefringence or detectable reflections in, respectively, the optical microscopy and wide-angle x-ray scattering (WAXS) data presented in Fig. 1. As a consequence of the high molecular disorder in such high-temperature cast TES ADT structures, bottom-gate/bottom-contact devices displayed a saturation charge-carrier mobility of only $5 \times 10^{-6} \text{ cm}^2/\text{Vs}$, in agreement with Ref. 3.

We attribute formation of an amorphous structure at least partly to the rapid solvent removal and, hence, limited solidification time of TES ADT. This counter-acts the higher molecular mobility at elevated temperatures that could have led to an improved molecular arrangement in the resulting TES ADT structure. In order to decrease the solidification rate, in a second set of experiments, we, therefore, cast the TES ADT solution at 5°C , which can be expected to reduce the solvent evaporation rate. Highly birefringent TES ADT films were obtained in this manner. These films featured well-defined diffraction peaks of a full-width-at-half-maxima of less than 0.014 \AA^{-1} in agreement with the formation of a high-quality thin film. Most intriguingly, these low-temperature cast TES ADT architectures were homogenous and uniform over the entire substrate area. [Note, casting at 25°C led to a “mixed” microstructure comprised of amorphous domains interspersed in birefringent regions (Fig. 1/ left: middle panel)].

The highly homogenous nature of films cast at 5°C allowed us to fabricate bottom-gate/bottom-contact devices in a single step, with the resulting devices out-performing any single-component OFET based on TES ADT, independent of device architecture¹⁻³ as recorded over 90 transistors (Fig. 2). All transistors displayed steep sub-threshold slopes and high current modulation on the order of magnitude of

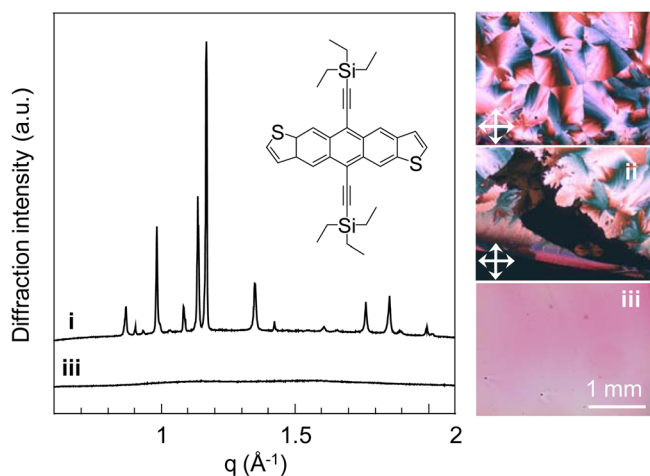


FIG. 1. (Color online) Left: Wide-angle x-ray diffractograms of TES ADT powders obtained from thin films cast at 5°C (i) and 40°C (iii), respectively. In the inset, the chemical structure of TES ADT is shown. Right: Optical micrographs of TES ADT thin films, solution-cast at, respectively, 5°C (top; crossed-polarized - i), room temperature (middle; crossed-polarized - ii), and 40°C (bottom; unpolarized - iii).

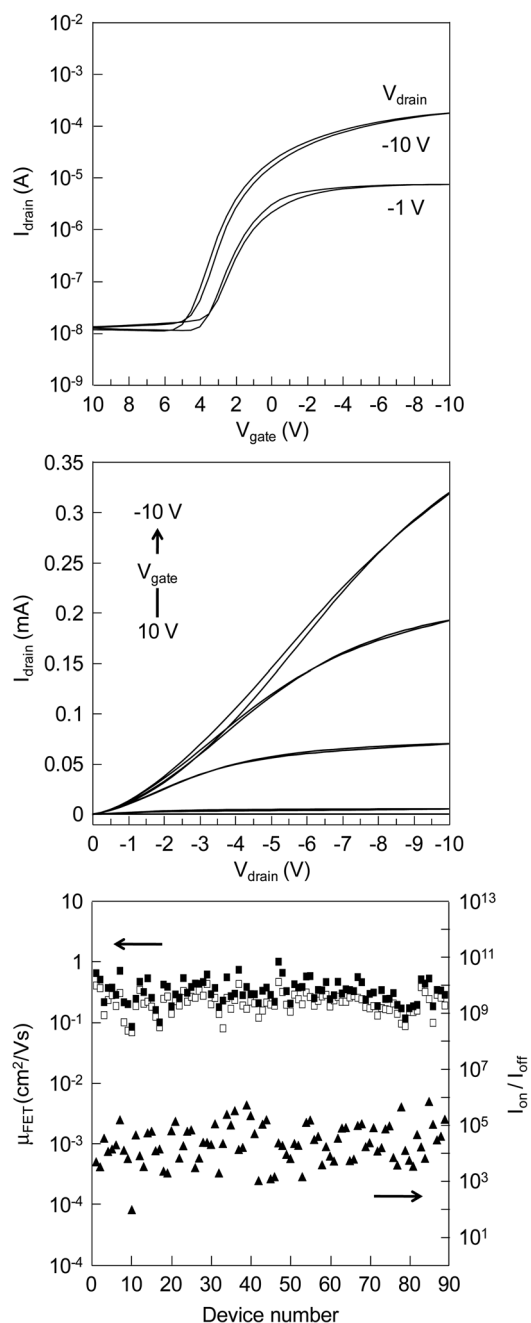


FIG. 2. Top/middle panel: Typical OFET transfer (top) and output (middle) characteristics of “low-temperature”-cast TES ADT thin films, measured in a bottom-contact/bottom-gate configuration. Bottom panel: Charge-carrier mobilities and ON/OFF ratios deduced from 90 devices that had been cast at low temperatures.

10^5 at low operating voltage of -5 V and less desired qualities for applications such as switching devices for display backplanes. We deduce high saturation mobilities of $0.42 \pm 0.19 \text{ cm}^2/\text{Vs}$ and observe stable threshold voltages of $3.6 \pm 0.9 \text{ V}$. The best device reached a saturation mobility of $1.3 \text{ cm}^2/\text{Vs}$. Most beneficially, the device yield is 100%, which promises reliable manufacturing and simplified device integration, especially when considering that our single-step process has already allowed us to produce homogenous films of more than a square centimeter size.

The above transistor data are supported by lateral time-of-flight transient photoconductivity measurements (ITOF), which provide an alternative tool to analyse *in-plane* charge

transport.^{9,10} We applied biases from 200 V to 800 V between co-planar electrodes separated by 160 μm (rather than using a diode structure employed in more conventional TOF). Consistently, charge-carrier mobilities of 0.08 cm^2/Vs for the crystalline, “low-temperature cast” TES ADT films can be deduced from the ITOF data. These values are comparable to the mobilities measured for the bottom-gate/bottom-contact transistors fabricated following the same processing protocol; and the small difference in the observed charge-carrier mobilities can be attributed to the different charge-carrier densities that can be induced in FETs compared to ITOF measurements.¹⁰ For the amorphous structures, cast above the glass transition temperature,³ we measure ITOF mobilities that are four orders of magnitude lower (μ_{TOF} of $6 \times 10^{-6} \text{ cm}^2/\text{Vs}$), again in good agreement with our device data.

In summary, when casting TES ADT solutions in chloroform at temperatures of more than 20 °C below the material’s glass transition temperature, highly crystalline thin films are realized by a single-step process. This allows reliable fabrication of high-performance bottom-gate/bottom-contact transistors as scrutinized based on device data obtained over 90 FET structures. We believe that our strategy is also likely to work for other organic semiconductors and that strict control of processing conditions, such as casting temperature

will lead to further progress in the field of organic transistors.

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¹⁰See supplementary material at <http://dx.doi.org/10.1063/1.3673280> for details on the lateral time-of-flight (ITOF) photoconductivity technique and ITOF data.