Solution-Processed Small Molecule-Polymer Blend Organic Thin-Film Transistors with Hole Mobility Greater than 5 cm²/Vs

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The performance level of organic thin-film transistors (OTFTs) has been steadily improving over the past ten years and is now competitive with mainstream inorganic technologies such as hydrogenated amorphous silicon (a-Si:H). Organic semiconductors are attractive because they offer the possibility for device and circuit fabrication over large-area substrates at low-cost using alternative processing paradigms such as solution-based methods. However, it is often the case that obtaining the desirable film microstructure from solution and implementing this in high performance OTFTs and circuits, is very challenging.

Blends of polymers and small molecules have been successful in combining the processability inherent to polymers with the high carrier mobility found in many crystalline molecular solids. Based on this approach, solution processed OTFTs with record breaking hole mobilities (2.4 cm²/Vs) have recently been demonstrated utilizing blends of the small molecule compound 2,8-difluoro 5,11-triethylsilylethynyl anthradithiophene (diF-TES ADT) with the conjugated polymeric matrix poly(triarylamine) (PTAA). Despite the high values, however, the hole mobility derived from blend OTFTs is still well below that obtained from single crystal diF-TES ADT based OTFTs (>6 cm²/Vs). Furthermore, the channel current on/off ratio in these blend based high mobility OTFTs is also low (<10⁴) and makes the technology unsuitable for certain applications such as active-matrix liquid crystal displays (AM-LCDs). Thus, one could in principle attempt to further improve the performance characteristics of blend OTFTs through careful material selection and reproducible film microstructure engineering. Ideal blend systems should exhibit minimal structural defects (i.e., highly crystallinity) without compromising the processing advantage. However, solution processed films containing crystalline components are likely to be polycrystalline and charge transport is often controlled by grain boundary effects. One possible approach to improve the carrier mobility, and potentially the current on/off ratio, in acene:polymer blends, is to increase the intrinsic mobility of the polymer (i.e. the matrix) without affecting the phase separation of the two blend components. Introduction of such a high mobility matrix polymer could in principle mediate conduction across grain boundaries and hence enhance the conduction pathways between acene-rich regions. The latter could improve both the effective carrier mobility as well as device reproducibility.

Here we report the use of a novel small molecule–polymer blend for the fabrication of high performance solution processed OTFTs. Specifically, we study blends of the small molecule diF-TES ADT with the conventional polymeric binder poly(dimethyl triarylamine) [PTAA], as the control material system, and poly(dialkyl-fluorene-co-dimethyl-triarylamine) [PF-TAA] as the alternative matrix polymer. The chemical structures of the organic semiconductors employed in this study: (a) poly(triarylamine) (PTAA), (b) poly(fluorene-co-triarylamine) (PF-TAA) and (c) diF-TES ADT.
structural and electrical properties of the blend films have been studied using a combination of cross-section transmission electron microscopy (TEM), atomic force microscopy (AFM), grazing incidence wide angle X-ray scattering (GIWAXS) and organic thin-film transistor (OTFT) measurements. Despite the similarities between the molecular structures of the two binders, the phase separation in diF-TES ADT:PF-TAA films is drastically different than that observed in conventional diF-TES ADT:PTAA blend films. Importantly, the structural difference in the diF-TES ADT:PF-TAA blend is accompanied by a significant enhancement in the hole transport across the transistor channel resulting in a record breaking field effect mobility of >5 cm²/Vs and channel current on/off ratios of >10⁶.

The blend semiconductors were tested in top-gate OTFTs with several parameters being measured for at least 10 devices to obtain an average of the parameter spread. The OTFT data are summarised in Figure 2 along with a polarised optical microscopy image of the diF-TES ADT:PF-TAA film. In agreement with previously published results, the diF-TES ADT:PTAA blend yields linear and saturation mobilities in the range 2–2.5 cm²/Vs with low device-to-device variation and a threshold voltage of around ~5 V. However, the current on/off ratio is not as high as many single component OFETs while the subthreshold slope (S) is relatively large (~4-5 V/decade) indicating the presence of traps. Detailed treatment of the trap concentration and their energetic distribution in diF-TES ADT:PTAA films has been reported previously. On the other hand, OTFTs based on diF-TES ADT:PF-TAA exhibit striking differences in their electronic properties when compared to PTAA based devices. Figure 3 displays a typical set of the transfer and output characteristics.
of diF-TES ADT:PF-TAA OTFTs while the various transistor parameters are plotted in Figure 2 together with the parameters of diF-TES ADT:PTAA transistors. The diF-TES ADT:PF-TAA OTFTs exhibit peak saturation mobilities of >5.5 cm²/Vs with an average value of 4.2 (±0.7) cm²/Vs while the linear mobility is relatively low and in the range 1-2 cm²/Vs. Most importantly, the OTFTs exhibit greatly improved current on/off ratios, as compared to PTAA based devices, with values exceeding 10⁶. To the best of our knowledge, this is the first report of blend OTFTs that combine exceptionally high hole mobility and current on/off ratio.

In order to understand the difference between the mobilities in the PF-TAA and PTAA blend based devices one has to consider the various materials properties. For instance, one important difference between the two binders is the significantly higher hole mobility of PF-TAA as compared to that of PTAA. This may result to a more efficient transport between the diF-TES ADT crystalline domains and hence a higher hole mobility. Furthermore, the comparable HOMO levels of PTAA and diF-TES ADT may also be the reason for the enhanced linear mobility in the blend since hole transport between the crystalline domains of diF-TES ADT and amorphous polymer remains relatively undisturbed. This however is not the case for PF-TAA since its HOMO level is significantly lower (~5.9 eV) than diF-TES ADT. This relatively large energetic mismatch may be the primary reason for the relatively low linear mobility at low electric fields. The deeper HOMO level of PF-TAA may also be responsible for the less efficient hole injection from the gold source-drain (S-D) electrodes into the HOMO level of the diF-TES ADT:PF-TAA blend because of the existence of a significant potential barrier to injection.

To investigate further the electronic properties of the two blends we have studied the dependence of the linear mobility on the lateral electric field (ξ = V_D/L) using OTFTs with different channel length (L). The results are plotted in Figure S1 in accordance with the Poole-Frenkel model[10] given as:

$$\mu_{lin} = \mu_0 \exp\left(\gamma \sqrt{\xi}\right)$$

where, μ_0 and γ are constants. The diF-TES ADT:PTAA OTFTs show ideal behaviour over a relatively wide range of ξ with a value of γ = 0.0058 (±0.0002) cm¹/V⁰. This weak dependence is consistent with a simple model of electric field assisted barrier lowering with very little disorder in the density of states. On the other hand PF-TAA based blend devices show much stronger field dependence, an increase in mobility with channel length, and a deviation from the Poole-Frenkel model at higher electric fields. The strong channel length dependence suggests that the mobility is being limited by parasitic contact effects. Indeed, contact resistance (R_C) analysis using the transmission line method, yields a R_C in the range 100-200 Ωm for diF-TES ADT:PF-TAA based devices. This is approximately one order of magnitude larger than diF-TES ADT:PTAA transistors and in accordance with the Au/PF-TAA energy level mismatch picture discussed earlier. However, the contact resistance alone cannot explain the dependence of hole mobility on ξ and L. A plausible explanation is that the deeper HOMO level of the PF-TAA (as compared to diF-TES ADT) is leading to the formation of trap states in the solid film and in close proximity to the S-D contacts where a Poole-Frenkel mechanism dominates.[11] Significant energetic disorder in these trap states would lead to a considerable increase in γ. However, as the electric field is increased the parasitic contact effects become less dominant and γ decreases, in agreement with the data presented in Figure S1.

With the aim of improving the performance of PF-TAA blends in the linear regime several concentrations of diF-TES ADT were also studied and plotted in Figure 2. Below 50 wt%
diF-TES ADT mobilities are low, most likely as a result of reduced electronic percolation pathways between crystalline domains. A significant reduction in $V_T$ is also observed with increasing diF-TES ADT concentration, possibly as a result of decreased trap concentration associated with the presence of PF-TAA. However, the subthreshold slope ($S$) shows the opposite trend. This is most likely due to the inherently higher $S$ of diF-TES ADT compared to PF-TAA caused by the presence of deep traps located at the grain boundaries.\(^6\)

Figure S2 displays the temperature dependence of the hole mobility (linear and saturation) in diF-TES ADT:PF-TAA OTFTs. A thermally activated hole transport is observed as in the case of diF-TES ADT:PTAA devices.\(^7\) For $T > 200$ K, however, the diF-TES ADT:PF-TAA OTFTs show higher activation energies possibly indicating the presence of deeper trap states. At lower temperatures the activation energies derived are much lower and most likely attributed to tunnelling of carriers between transport sites. When biased in saturation [Figure S2(b)], a weak dependence of the hole mobility on temperature (activation energies as low as 14 meV) is measured with maximum values $>1$ cm$^2$/Vs even at 80 K. Figure S3 displays the dependence of threshold voltage ($V_TH$) on temperature ($V_TH(T)$) for both PTAA and PF-TAA blend based devices. It can be seen that although the overall areal trap density ($N_tr$) is higher in diF-TES ADT:PF-TAA blends, their energy distribution is different exhibiting a lower activation energy. The latter could be related to the electronic properties of the binder polymer and/or to the resulting microstructure of the phase separated film.

Additional insight into the polymer-molecule blends’ phase separation, microstructure and morphology is necessary to explain the enhanced carrier mobility in PF-TAA based devices as compared to PTAA based OTFTs. Cross-sections of thin films of diF-TES ADT blended with PTAA and PF-TAA were imaged by transmission electron microscopy, as shown in Figures 4(a) and 4(b), respectively. In each case, we show a side-by-side comparison of bright-field (BF) and energy-filtered (EF) microscopy images taken from the raw images (Figure S4). The organic blend can be easily delineated from BF-TEM images as it is sandwiched between the glass substrate and the gold coating applied in advance of focused ion beam sectioning; both inorganic layers appear significantly darker. Since very little contrast is achieved between the small-molecule and polymer components by BF-TEM, we used EF-TEM analysis in the energy range specific to Si in order to locate the diF-TES ADT-rich phase. In both samples, we find evidence for two distinct layers, with a Si-rich (diF-TES ADT-rich) layer topping a Si-poor (polymer-rich) layer coating the glass substrate. Both films exhibit nearly identical thickness, with $85 \pm 3$ nm and $83 \pm 1$ nm as measured from EF-TEM images for blends containing PTAA and PF-TAA, respectively. However, the diF-TES ADT-rich overlayer appears to be ~50% thicker in PF-TAA-based blends ($32 \pm 1$ nm) than the PTAA-based blends ($21 \pm 2$ nm). This difference is significant given the fact that solutions were spin-cast from identical (1:1) blend ratios. This observation suggests the presence of significantly higher amount of binder mixed with the diF-TES ADT-rich overlayer when PF-TAA is used than when PTAA is used. Further comparison of BF and EF microscopy images of the PTAA-based blends reveals a significant discrepancy in the location of the organic-gold interface, suggesting overlap between the Si-rich diF-TES ADT layer and the gold film. By contrast, when PF-TAA is used the gold and organic layers are completely distinct and form an abrupt interface. These observations suggest important differences between the two blends which may well be responsible for the distinct differences observed in the corresponding transistor characteristics. For example, the flatness and long range uniformity of the diF-TES ADT:PF-TAA films may well be the key property responsible for the very high hole mobility observed in this blend. The relatively high content of the PTAA binder at the film surface, on the other hand, may be the reason for the relatively low linear mobility and its strong dependence on the lateral electric fields.

Figure 4. Cross-section bright-field (BF) and energy-filtered (EF) transmission electron microscopy (TEM) images of; (a) diF-TES-ADT:PTAA, and (b) diF-TES-ADT:PF-TAA blended thin films on glass substrate. The EF-TEM images reveal two dimensional distribution of Si in the sample indicating the presence of the small molecule diF-TES-ADT. In the case of diF-TES-ADT:PTAA, Si is observed to segregate at the blend-Au (electrode) interface, indicating the presence of a significantly phase separated system. In the case of the diF-TES-ADT:PF-TAA however, this phase separation is much less pronounced and extends deeper into the film.
ordering in diF-TES ADT crystallites and domains in the presence of the PF-TAA binder, which could in turn explain the significantly improved carrier transport.

TEM and AFM results together with GIWAXS and carrier transport measurements suggest the presence of some polymer binder within the diF-TES ADT rich layer in close proximity to the dielectric, improve the polycrystalline material’s microstructure and surface morphology in favour of enhanced field effect carrier mobility at the semiconductor-dielectric interface. Although detailed understanding of the role of blend film composition and morphology on device performance would require further work, the present study provides, for the first time, evidence that blend-based OTFTs with performance characteristics similar to those obtained from single-crystal organic transistors can be manufactured from solution utilising carefully formulated small molecule-polymer blends.

In summary, we have demonstrated for the first time that significant improvements to the electronic properties of acene:polymer blends can be made by using a higher mobility amorphous polymer semiconductor as the binder. The performances of two blend systems namely diF-TES ADT blended with PTAA and PF-TAA, were studied and compared. Optimized PF-TAA blends show a hole mobility in excess of 5 cm²/Vs, a value approaching that obtained from single crystalline diF-TES ADT based devices. This improved performance is attributed to the improved crystallinity of the small-molecule component and its overall film surface uniformity. The combination of solution processing, high carrier mobility and large current on/off ratio makes this novel semiconductor blend highly promising for a host of future electronic applications.

Further insight into the surface morphology of the samples is provided by topographic and phase image comparisons of the two films via atomic force microscopy. In Figure 5(a) and 5(b), we show topographic images of the surface of PTAA- and PF-TAA-based blends, respectively. The associated distributions of surface height are plotted in Figure 5(c), revealing the PTAA-based film is substantially rougher, with root mean squared roughness of 1.87 nm as compared to 1.02 nm in case of the PF-TAA-based film. In Figure 5(d) and 5(e), we show the phase images of the surface of PTAA- and PF-TAA-based blends, respectively. The associated distributions of surface phase are plotted in Figure 5(f). The latter reveal two phases decorating the surface of the PTAA-based blend, while PF-TAA surface is homogeneous and appears to be single phased. We speculate that the diF-TES ADT-rich layer is coated by a thin, continuous layer of PF-TAA, which prevents diffusion and penetration of Au atoms into the grain and domain boundaries of the diF-TES-ADT phase.

The packing structure and texture of the crystalline diF-TES ADT phases within the blends were evaluated by GIWAXS measurements (Figure S5). In all cases, we find the diF-TES ADT phase to be purely (001)-textured, showing no evidence of other crystalline orientations. The (001) Bragg sheet exhibits the same narrow peak width in both GIWAXS images, indicating that the polycrystalline films have similarly good lamellar structure. However, the in-plane peaks reveal significant differences in their line shape. A close-up view of the diffraction peaks reveals [Figure S5(b),(d)] significantly broader line shape in the plane of the substrate in case of PTAA based blends than in PF-TAA based blends. These observations suggest improved in-plane
Experimental Section

Device fabrication and characterisation: Top-gate, bottom-contact OTFTs were fabricated on glass using gold electrodes treated with a pentfluorobenzene thiol self-assembled monolayer. Devices had channel lengths and widths varying from 20–100 µm and 0.5–2.0 mm respectively. 2,8-Difluoro-5,11-bis(triethylsilylethynyl) anthradithiophene (dF-TESADT), poly(4-fluorophenyl) (2,4-dimethylphenyl) amine (PTAA) and poly[2,3-bisfluorene-co-bis-N,N-(2,4-dimethylphenyl) diphenylamine] (F8-TAA) were prepared by the reported procedures. F8TAA of Mn 28 KDa, Mw 53 KDa, and TAA of Mn 8.5 KDa, Mw 16 KDa were used. The blend semiconductors were deposited by spin coating at 500 rpm for 10 sec followed by 2000 rpm for 20 sec from 4 wt% 1,2,3,4-tetrahydronaphthalene solutions. The resulting films were annealed at 100 °C for 2.5 min to remove excess solvent. Blends consisted of 37.5, 50.0 or 62.5 wt% dif-TES ADT with either PTAA or PF-TAA (Figure 1). The fluoropolymer, CYTOP, was deposited as the gate dielectric and evaporated aluminium as the gate contact. Basic electrical measurements were performed in a nitrogen atmosphere and measurements as a function of temperature were carried out under vacuum using a semiconductor parameter analyser. The electric field dependence of mobility was measured by varying both the channel length, L, and the drain voltage, V_D, in the linear regime from 0.5–10 V. Mobilities were estimated using the standard thin film model in both linear and saturation regimes of the device. The linear TFT mobility was found using:

$$\mu_{LT} = \frac{L}{W} \frac{\partial ID_{lin}}{\partial V_D}$$

whilst the linear effective mobility was calculated using,

$$\mu_{EFF} = \frac{L}{W} \frac{I_{def}}{V_D - V_{on}}$$

where L, W and C_i are the channel length, channel width and geometric capacitance of the dielectric respectively. The onset voltage, V_{on}, was estimated from the transfer characteristics and was usually found to be close to 0 V.

Electron microscopy: A transmission electron microscope operating at 300 kV (Titan Cryo Twin, FEI Company, Hillsboro, OR) was used to acquire cross-section microscopy images using a 4 k x 4 k charged couple device (CCD) camera model US4000 and an energy filter model GIF Tridiem from Gatan, Inc. (Gatan Inc., Pleasanton, CA). The GIF was utilized in energy-filtered TEM (EFTEM) mode to image the Si distribution in the sample. The Si L-edge located at 99 eV was selected close to 0 V.

Supporting Information

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

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