

Zone-Refinement Effect in Small Molecule–Polymer Blend Semiconductors for Organic Thin-Film Transistors

Yeon Sook Chung,[†] Nayool Shin,[†] Jihoon Kang,[†] Youngeun Jo,[†] Vivek M. Prabhu,^{*,#} Sushil K. Satija,[#] R. Joseph Kline,[#] Dean M. DeLongchamp,[#] Michael F. Toney,[§] Marsha A. Loth,[‡] Balaji Purushothaman,[‡] John E. Anthony,^{*,‡} and Do Y. Yoon^{*,†}

Department of Chemistry, Seoul National University, Seoul 151-747, Korea, National Institute of Standards & Technology, Gaithersburg, Maryland 20899, United States, Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, United States, and Stanford Synchrotron Radiation Laboratory, Menlo Park, California 94025, United States

Received September 29, 2010; E-mail: dyyoon@snu.ac.kr; vprabhu@nist.gov; anthony@uky.edu

Abstract: The blend films of small-molecule semiconductors with insulating polymers exhibit not only excellent solution processability but also superior performance characteristics in organic thin-film transistors (OTFTs) over those of neat small-molecule semiconductors. To understand the underlying mechanism, we studied triethylsilylethynyl anthradithiophene (TESADT) with small amounts of impurity formed by weak UV exposure. OTFTs with neat impure TESADT had drastically reduced field-effect mobility ($<10^{-5} \text{ cm}^2/(\text{V s})$), and a disappearance of the high-temperature crystal phase was observed for neat impure TESADT. However, the mobility of the blend films of the UV-exposed TESADT with poly(α -methylstyrene) (P α MS) is recovered to that of a fresh TESADT–P α MS blend ($0.040 \text{ cm}^2/(\text{V s})$), and the phase transition characteristics partly return to those of fresh TESADT films. These results are corroborated by OTFT results on “aged” TIPS–pentacene. These observations, coupled with the results of neutron reflectivity study, indicate that the formation of a vertically phase-separated layer of crystalline small-molecule semiconductors allows the impurity species to remain preferentially in the adjacent polymer-rich layer. Such a “zone-refinement effect” in blend semiconductors effectively removes the impurity species that are detrimental to organic electronic devices from the critical charge-transporting interface region.

Organic semiconducting materials with high field-effect mobility and solution processability have attracted tremendous attention for their potential applications in printable electronic devices including organic thin-film transistors (OTFTs) for flexible displays and radio frequency identification tags and organic photovoltaic solar cells (OPVs). Organic semiconductors can be classified into two different types: small molecules and polymers. Small-molecule semiconductors show high crystallinity, high field-effect mobility, and high stability but often have poor solution processability.^{1–3} On the other hand, polymer semiconductors generally show low crystallinity, low field-effect mobility, and low stability but typically exhibit excellent solution processability, enabling simple fabrication processes such as inkjet patterning.⁴ The “blending” approach of mixing small-molecule semiconductors and polymers has been developed to address the poor solution processability of small molecules, and blend semiconductors have been shown to exhibit both high field-

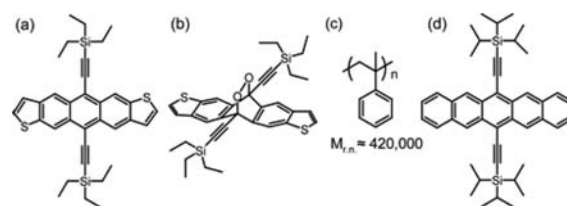


Figure 1. Chemical structures of (a) TESADT, (b) the impurity in light-exposed TESADT, (c) P α MS, and (d) TIPS–pentacene.

effect mobility and good solution processability, together with the necessary stability.^{5–7} Moreover, a number of groups have reported significantly improved electrical properties (field-effect mobility, threshold voltage, and on–off ratio) for blend semiconductors in OTFTs as compared with those of neat small molecules.^{8–13} Previous studies to understand the origin of these surprising experimental results have shown that a vertically phase-separated thin layer of pure small-molecule semiconductors could be formed at the gate interface critical to the charge transport, with segregation characteristics that depend on the blend polymer molecular mass.^{10,11} The vertical phase separation in thin blend films is initiated by the interfacial energy that favors one component over the other at the substrate–semiconductor (for bottom gate) or the semiconductor–air surfaces (for top gate), and it is indeed a necessary condition for obtaining electrical properties of blend semiconductors that are as good as those of neat small molecules. However, vertical phase separation alone is insufficient to explain the observed significant improvements of electrical properties, such as a nearly 6-fold increase in field-effect mobility in OTFTs with blend semiconductors as compared to those with neat small-molecule semiconductors.¹⁰ Therefore, a full understanding of the basic mechanism responsible for the improved performance of blend semiconductors is critically needed in order to take full advantage of small molecule–polymer blend semiconductors for OTFTs and OPVs.

Here we report experimental results centered on a model organic semiconductor, triethylsilylethynyl anthradithiophene (TESADT, Figure 1a),^{14–17} which is known to be unstable upon extended light exposure,¹⁸ and its blends with poly(α -methylstyrene) (P α MS, Figure 1c), an insulating polymer binder often used in preparing blend semiconductors.

Small amounts of impurity, generated by exposure of TESADT powder to a weak ultraviolet (UV) light, were readily incorporated and enabled a systematic study of the impurity effects on the field-effect mobility of neat TESADT and TESADT–P α MS blend films in OTFTs. The OTFT results, matched by the impurity effects on

[†] Seoul National University.

[#] National Institute of Standards & Technology.

[‡] University of Kentucky.

[§] Stanford Synchrotron Radiation Laboratory.

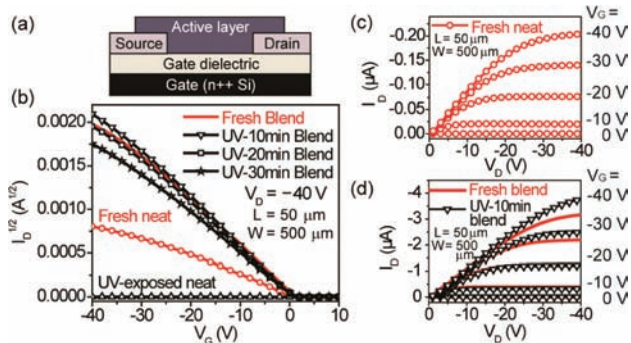


Figure 2. (a) Schematic drawing of bottom-gate/bottom-contact OTFTs. (b) Representative transfer characteristics of bottom-gate/bottom-contact OTFTs for neat and blend films of fresh TESADT and UV-exposed TESADT (neat sample data are practically identical for the three UV-exposed samples), together with representative output characteristics for (c) neat film of fresh TESADT and (d) blend films of fresh and UV 10-min exposed TESADT with P α MS.

phase behavior determined by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD), point to a “zone-refinement effect”, a well-known, practical process in preparing inorganic semiconductors.¹⁹ This zone-refinement effect applies to the blend by transporting the impurity away from the gate dielectric interface into the polymer-rich phase, as the key mechanism for the significantly improved electrical properties of TESADT-P α MS blend films.

The zone-refinement effect model is further corroborated by OTFT measurements on well-known 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene, Figure 1d)-P α MS blends,^{6,9,10} by comparing the results between fresh TIPS-pentacene and “aged” TIPS-pentacene.

TESADT is a soluble p-type organic semiconductor that typically exhibits a field-effect mobility of ca. 0.002 cm²/(V s) in unannealed films, which increases to ca. 0.1 cm²/(V s) upon brief solvent-vapor or extended vacuum annealing in the spin-cast films,^{15–17} but is known to be unstable under light.¹⁸ Exposing TESADT powder to a very weak UV source in the laboratory, a hand-held UV lamp for thin-layer chromatography that emits a weak 314 nm radiation (ca. 29 μ W/cm²), causes a photochemical reaction of TESADT, generating a small amount of impurity. UV-exposed TESADT samples show very slight decreases in their UV-vis absorption spectra (Figure S1, Supporting Information) but no detectable change in NMR due to the low impurity concentration. These UV-exposed samples, obtained with exposure times of 10, 20, and 30 min, enabled the study of the effects of a small amount of impurity on the performance of bottom-gate/bottom-contact OTFT (Figure 2a) and phase behavior of neat films and blend films. The impurity of TESADT was identified as endoperoxide (Figure 1b) by NMR and mass spectroscopy of highly degraded samples (see Supporting Information).

In order to study the impurity effect on the characteristics of OTFTs, OTFT devices were fabricated with thermally grown SiO₂ dielectric and Au electrodes in a bottom-gate/bottom-contact structure. Dielectric and electrodes were treated with hexamethyldisilazane and pentafluorobenzenethiol, respectively. TESADT neat films were deposited by drop-casting from 1% by mass solution in chloroform, followed by solvent evaporation at 75 °C for 3 min in a vacuum oven. The unannealed TESADT neat films exhibit mobility of 0.0053 \pm 0.0024 cm²/(V s), whereas UV-exposed TESADT neat films show no detectable field-effect mobility (Figure 2b and Table 1). Such a drastic effect on field-effect mobility implies that the electrical performance of OTFT is extremely

Table 1. Characteristics of TESADT-Based Semiconductors in Bottom-Gate/Bottom-Contact OTFTs^a

TESADT film	μ_{average} (cm ² /(V s))	V_{th} (V)	$I_{\text{on}}/I_{\text{off}}$
fresh neat	0.0053 \pm 0.0024	1.7 \pm 1.3	3.0 \times 10 ⁴
UV-10 min neat	<10 ⁻⁵		
fresh blend	0.038 \pm 0.009	1.5 \pm 0.8	9.8 \times 10 ⁴
UV-10 min blend	0.040 \pm 0.011	1.0 \pm 0.5	3.0 \times 10 ⁶
UV-20 min blend	0.037 \pm 0.014	1.1 \pm 0.9	1.2 \times 10 ⁶
UV-30 min blend	0.034 \pm 0.013	1.0 \pm 0.6	2.7 \times 10 ⁵

^a Uncertainty in the typical device characteristics is estimated by one standard deviation from the mean obtained from over seven devices.

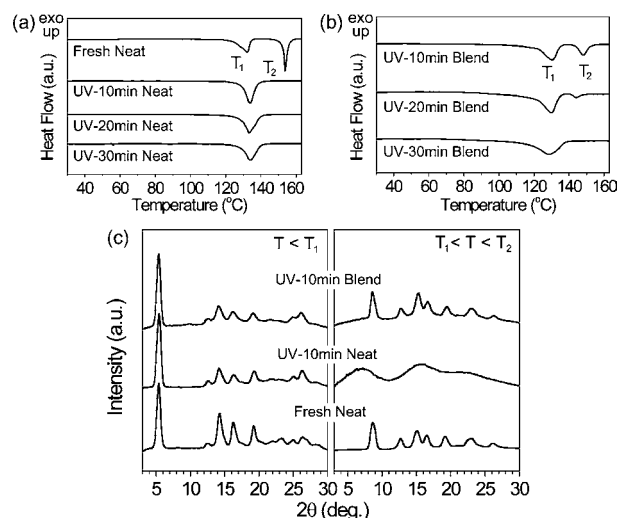


Figure 3. DSC heating traces for (a) neat samples and (b) blend samples. (c) Wide-angle X-ray diffraction results of TESADT samples at two temperatures of $T < T_1$ and $T_1 < T < T_2$ around two phase transitions of fresh TESADT.

sensitive to very small amounts of impurity, very similar to the well-known result for inorganic and organic semiconductors.²⁰ We also studied the effects of the impurity on the structures of the thin films by synchrotron grazing-incidence X-ray diffraction (GIXD, Supporting Information), which shows that the thin-film morphology in ambient conditions is negligibly affected by the small amount of impurity.

The presence of a small amount of impurity is also found to strongly affect the phase transition behavior observed by DSC (Figure 3a) and the temperature dependence of WAXD patterns (Figure 3c). The samples were prepared by peeling off solution-cast and dried films. Fresh TESADT neat film shows two endothermic peaks. The first transition peak at $T_1 = 132$ °C ($\Delta H = 20.3$ J/g) refers to the crystal(1)–crystal(2) transition, and the second peak at $T_2 = 154$ °C ($\Delta H = 21.1$ J/g) is related to the crystal(2)–isotropic melt transition. Interestingly, the UV-exposed TESADT neat films show only one endothermic peak for the crystal(1)–isotropic melt transition around 133 °C, with a transition enthalpy ΔH of 41.2 J/g for 10-min, 40.7 J/g for 20-min, and 39.6 J/g for 30-min exposure, respectively. The transition temperature and the total enthalpy change to the isotropic melt indicate that the impurity component strongly suppresses the high-temperature crystal(2) phase of fresh TESADT.

To investigate the blending effect on OTFT performance of TESADT, bottom-gate/bottom-contact OTFT devices were prepared with the blend films drop-cast from chloroform solutions of fresh TESADT and P α MS of relative number-average molar-mass, $M_{n,r} \approx 420\,000$ g mol⁻¹, in a mass ratio of 7 (TESADT):3 (P α MS) (Figure 2 and Table 1). The OTFT devices fabricated with the blend

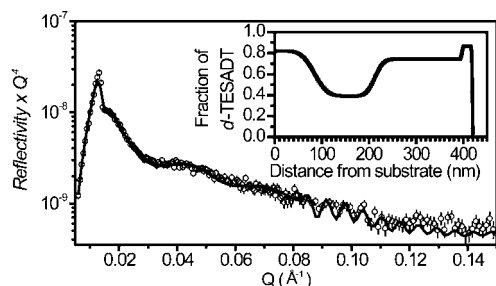


Figure 4. Neutron reflectivity profile and fitted concentration profile (inset) of *d*-TESADT in 7:3 (by mass) blend films of *d*-TESADT and high-molecular-mass P α MS. The experimental and fitted reflectivity curves are shown by circles and line, respectively.

show a mobility of $0.038 \pm 0.0085 \text{ cm}^2/(\text{V s})$, which is nearly 7-fold higher than that of neat TESADT, similar to the 6-fold increase previously reported for the TIPS-pentacene blend case and higher than the value reported for an unannealed TESADT film.^{15,17} Most surprisingly, the mobility values of the blend semiconductor films prepared from UV-exposed TESADT and P α MS (7:3 ratio by mass) are essentially the same as the mobility of fresh TESADT–P α MS blends (Figure 2 and Table 1). That is, not only is the detrimental effect of the impurity in neat TESADT films completely eliminated, but also the improved electrical properties (mobility, threshold voltage, and on/off ratio) observed for fresh TESADT–P α MS blends are similarly reproduced in the blend films prepared with UV-exposed TESADT. Blending the semiconductor with P α MS appears to effectively remove the UV-generated impurity from the critical charge-transport region at the gate interface of the OTFT.

In order to understand the OTFT results, the phase behavior of blend films of UV-exposed TESADT and P α MS was also investigated by DSC (Figure 3b) and WAXD (Figure 3c). The high-temperature crystal phase of TESADT, which disappears in the UV-exposed neat TESADT, is partly recovered in the blend films with P α MS. The transition enthalpy value of the second phase transition, relative to the first, becomes smaller with increasing UV-exposure of TESADT, indicating that the removal of impurity from the UV-exposed TESADT by blending with P α MS does occur but involves only certain portions of the film.

The experimental results of OTFT characteristics, coupled with the phase behavior of UV-exposed TESADT–P α MS blends, point to the formation of a TESADT layer devoid of chemical impurity at the critical gate/semiconductor interface. Such *in situ* purification is very reminiscent of the “zone-refinement” process of inorganic semiconductors,¹⁹ where the exclusion and transport of impurities occurs from the growing crystal upon recrystallization from the melted zone containing impurity. In the blend semiconductors, the vertical phase separation and crystallization upon solvent evaporation from the solvent-cast blend solutions appears to exclude the impurity in the critical charge-transporting region adjacent to the dielectric substrate. The impurity compound, excluded from the crystalline layer of TESADT, would reside miscible in the polymer-rich layer well removed from the gate interface.

The vertical phase separation and the presence of this polymer-rich layer was previously shown by the neutron reflectivity study of the spin-coated thin blend films of deuterated (*d*) TIPS-pentacene and P α MS.¹⁰ Figure 4 shows that TESADT–P α MS blend films (7:3 ratio by mass) exhibit similar vertical phase separation characteristics, as determined by neutron reflectivity experiments of blend films of *d*-TESADT and P α MS (Supporting Information). Such a polymer-rich layer effectively traps the organic impurity, the presence of which at the gate/semiconductor interface will

seriously degrade the charge transport. In other words, the presence of a polymer-rich layer adjacent to the vertically phase-separated crystalline organic semiconductor layer will facilitate the zone-refinement process to exclude the undesirable organic impurities from the critical charge-transport region.

In order to corroborate the zone-refinement effect deduced from the TESADT–P α MS blends, similar OTFT measurements were carried out with “aged” TIPS-pentacene samples that were stored under ambient light conditions for 3 years. Drop-cast films of the “aged” TIPS-pentacene neat film show a mobility of $0.0083 \text{ cm}^2/(\text{V s})$ that is significantly lower than the neat fresh TIPS-pentacene mobility of $0.05 \text{ cm}^2/(\text{V s})$. The blend films of fresh TIPS-pentacene and P α MS (1:1 ratio by mass) were previously reported to exhibit a mobility of $0.3 \text{ cm}^2/(\text{V s})$, about a 6-fold increase over the mobility value of neat fresh TIPS-pentacene.¹⁰ However, upon blending this impure material with P α MS, the mobility of the blend film (1:1 ratio by mass) increases to $0.29 \text{ cm}^2/(\text{V s})$, effectively the same as the mobility of fresh TIPS-pentacene blend with P α MS. Analysis of the aged material by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry showed small amounts of impurities that include mono- and dioxygen adducts (Supporting Information). Therefore, the zone-refinement effect seems to be generally applicable to the blend films of soluble small-molecule semiconductors with polymers.

In summary, in order to understand the improved electrical properties of small molecule–polymer blend semiconductors in OTFTs, we studied TESADT with small amounts of impurity formed by weak UV exposure. OTFTs with neat impure TESADT had drastically reduced field-effect mobility ($<10^{-5} \text{ cm}^2/(\text{V s})$), and a disappearance of the high-temperature crystal phase was observed for neat impure TESADT. However, the mobility of the blend films of the UV-exposed TESADT with P α MS is recovered to that of a fresh TESADT–P α MS blend ($0.040 \text{ cm}^2/(\text{V s})$), and the phase transition characteristics partly return to those of fresh TESADT films. These results are corroborated by OTFT results on “aged” TIPS-pentacene. Coupled with the neutron reflectivity study on blend semiconductor films, these observations indicate that the formation of a vertically phase-separated layer of crystalline small-molecule semiconductors allows the impurity species to remain preferentially in the adjacent polymer-rich layer. Such a “zone-refinement effect” in blend semiconductors effectively removes the impurity species that are detrimental to organic electronic devices from the critical charge-transporting interface region.²¹

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Supporting Information Available: Description of materials characteristics of TESADT impurity; experimental methods and results of OTFT devices, synchrotron GIXD, and neutron reflectivity. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (21) Direct evidence for the removal of organic impurity from the bottom surface of a blend semiconductor film is obtained by the near-edge X-ray absorption fine structure spectroscopy study on a fluorine-substituted TESADT–PtMS blend film; see Figure S11, Supporting Information.

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