Polyacrylate polymer assisted crystallization: Improved charge transport and performance consistency for solution-processable small-molecule semiconductor based organic thin film transistors

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ABSTRACT

In this study, we report an effective approach to modulate crystallization, control charge transport and enhance performance consistency of small-molecule semiconductor based organic thin film transistors (OTFTs) with the addition of a polyacrylate polymer additive poly(2-ethylhexyl acrylate) (P2EHA). 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS pentacene) was used as a benchmark semiconductor to blend with the P2EHA additive, leading to a vertical phase separation between these two components. The resultant TIPS pentacene film exhibited greatly reduced crystal misorientation, enlarged grain width and enhanced film coverage. Bottom-gate, bottom-contact OTFTs based on the TIPS pentacene/P2EHA blends were fabricated and showed an increased average hole mobility of 0.317 ± 0.047 cm²/Vs, as well as a performance consistency factor of 6.72, which is defined as the ratio of the average hole mobility to the standard deviation of mobility. Notably, it leads to a 10-fold and 7-fold enhancement of average mobility and performance consistency as compared to the pristine TIPS pentacene OTFTs. This great improvement of device performance can be attributed to the reduced crystal misorientation, less defects and trap centers at the grain boundaries as a result of the enlarged grain width, as well as increased film coverage, due to the addition of the P2EHA polyacrylate polymer additive.

1. Introduction

In recent years, organic electronics has attracted numerous attention due to its compatibility with high-performance, solution-processable, and low-cost applications on flexible substrates [1,2]. Particularly, significant progress has been achieved in the study of charge transport, air stability and solvent choices of various high-performance, small-molecule organic semiconductors, such as N,N'-1,1'H-perfluorobutyl dicyanoperylenecarboxydiimide (PDIF-CN2) [3–5], 5,11-bis(triethylgermylthethyl) anthradithiophene (dif-TEG-ADT) [6,7], and 6,13-bis (triisopropylsilylethynyl) pentacene (TIPS pentacene) [8,9]. Despite these advances, the crystallization of small-molecule organic semiconductors in solution is still anisotropic by nature, and the organic thin film transistors (OTFTs) based on such misoriented crystals exhibit severe performance variations [10], which has largely restricted the application for high-performance organic electronics devices [11].

In order to address the crystal misorientation issue, different efforts which involve capillary force [12,13], substrate patterning [14,15], and solution-shearing [16,17] based external crystal alignment techniques, have been made to align the small-molecule organic semiconductor crystals. On the other hand, various polymer additives have been studied in order to control the crystallization of the small-molecule semiconductors [18–20]. These polymer addition methods, which take advantages of the uniformity property of polymers and high mobility of semiconductors, can work independently to tune the semiconductor crystallization or be applied along with those external alignment techniques as mentioned above. For example, Chen et al. reported the control of TIPS pentacene thin film morphology by blending with conjugated polymer additives, including a bidodecylthiophene copolymer (PnBT-RRa) and poly(3-hexylthiophene) (P3HT) [21]. It was found
that different polymer additives contributed to distinctively different polymer morphologies, intermolecular interactions, and charge transport modes of TIPS pentacene based OTFTs. Asare-Yeboah et al. demonstrated the addition of poly(3-methyl styrene) (P3MS) polymer, along with a temperature gradient technique, to align TIPS pentacene crystals [22]. The addition of the P3MS polymer was shown to greatly enhance the crystal orientation, eliminate thermal cracks and improve hole mobility of TIPS pentacene based OTFTs. More recently, Bi et al. reported that a P3HT polymer additive was combined with a “controlled evaporative self-assembly” (CESA) method to grow well-orientated 2,5-di-(2-ethylhexyl)-3,6-bis(3”-n-hexyl-2,2’,5,2’‘)terthiophen-5-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (SMDPPEH) semiconductor crystals, leading to controlled crystallization and enhanced device performance of SMDPPEH based OTFTs [23].

In this work, we report the addition of a polycrystalline polymer additive poly(2-ethylhexyl acrylate) (P2EHA) in order to tune the crystallization of small-molecule organic semiconductors. TIPS pentacene was chosen as a benchmark semiconductor to blend with P2EHA, which leads to a vertical phase separation between these two components. By varying the loading ratios of the P2EHA polymer additive, we demonstrate to effectively modulate crystallization, control grain width and reduce crystal misorientation of TIPS pentacene crystals. Since defects are located at the grain boundaries, increased grain width essentially contributes to less trap centers of the charge carriers. The bottom-gate, bottom-contact OTFTs based on the TIPS pentacene/P2EHA blends demonstrated a great enhancement of average mobility of up to 0.317 ± 0.047 cm²/Vs, and an excellent performance consistency factor of 6.72, which is defined as the ratio of average hole mobility to the standard deviation. The effective crystal alignment approach by using the P2EHA additive can be applied to other solution-processed, small-molecule semiconductors and shed light on the high-performance organic electronics applications on flexible substrate.

2. Experiment

TIPS pentacene and P2EHA were purchased from Sigma Aldrich and were used as purchased. Toluene was purchased from VWR and was used without further purification. Bottom-gate, bottom-contact OTFTs were fabricated to test charge transport in the TIPS pentacene/P2EHA blends. Optical photolithography was utilized to pattern the substrate with source and drain contact electrodes. Specifically, the 3-inch silicon wafer substrate with a 100 nm thickness of thermally grown silicon dioxide (SiO₂) was patterned with a thin layer of photoresist, which served as a mask for the following lift-off process. Then, 50 nm of gold was deposited using electron-beam evaporation as source and drain electrodes, followed by lift-off in acetone with ultrasonication. After patterning, each wafer contained a total of 10 bottom-gate, bottom-contact transistor devices, which had a channel width of 500 microns and 1000 microns, and a varied channel length from 5 microns to 50 microns.

Prior to the growth of semiconductor crystals, both pentfluoroobenzonethiol (PBFT) and hexamethyldisilazane (HMDS) treatments were conducted on the patterned bottom-gate, bottom-contact transistor substrate. In particular, HMDS self-assembled monolayers (SAMs) were formed to passivate the hydrophobic SiO₂ surface via vapor deposition at 140 °C, followed by rinsing with isopropanol alcohol (IPA). PBFT treatment was aimed at the gold source and drain electrodes to modify the electrode surface energy, by sintering the patterned substrate in a PBFT/toluene solution with a concentration of 10 mM for 2 h and rinsing with toluene [24].

TIPS pentacene and P2EHA were dissolved in toluene at a concentration of 5 mg/ml, and were then mixed in solution at different weight ratios of 5%, 10%, 20% and 60%. Then the TIPS pentacene/P2EHA blends in toluene were drop casted onto the surface-treated substrate, which was located in a petri-dish and covered with a cap, and TIPS pentacene crystals were formed under a confined solvent evaporation configuration at room temperature. Since there was no external gas applied to navigate the crystal growth, the effect of gas flow on the crystallization of TIPS pentacene can be neglected. A small tilting angle (~5°) was added to the substrate in order to facilitate the formation of oriented TIPS pentacene crystals. The substrate tilting orientation was parallel to the direction from source to drain electrodes of the charge transport channel. After solvent evaporation, the film thickness of the semiconductor layer was approximately 150–200 nm.

To test charge transport in the TIPS pentacene/P2EHA blends, electrical characterization of the bottom-gate, bottom-contact OTFTs was conducted using an Agilent B1500A semiconductor parameter analyzer. From the saturation regime of the slope of the transfer curve (/(IDS)1/2–VGS), the field-effect hole mobility was extracted. All devices were measured for a total of five times to ensure consistency of the extracted field-effect mobilities. Optical micrographs of TIPS pentacene/P2EHA thin films were taken by using a Zeiss Axiosplan optical microscope with a built-in camera.

3. Results and discussion

The molecular structures of TIPS pentacene, P2EHA and toluene are shown in Fig. 1(a–c), respectively. TIPS pentacene was chosen as a benchmark semiconductor to blend with P2EHA in this work because of its high mobility, improved solution solubility and air stability [25–28]. As shown in its molecular structure in Fig. 1(a), the attachment of the two bulky side groups to the aromatic rings of TIPS pentacene disrupts the herringbone packing, which improves its solubility in common solvents [29–31]. In addition, the enhanced face-to-face interaction (π-π stacking) leads to improved charge transport [32]. P2EHA is a polycrystalline polymer which has a weight-average molecular weight MW of 100–120 k and a polydispersity index (PDI) of 3. The hydrophobic side group of P2EHA has eight carbon atoms (Fig. 1(b)).

In order to modulate crystallization and tune charge transport of TIPS pentacene, P2EHA was blended as a polymer additive at different weight ratios of 5%, 10%, 20% and 60% which leads to distinctive TIPS pentacene thin film morphologies as shown in the optical images of Fig. 2. While the pristine TIPS pentacene film exhibited severe crystal misorientation and poor film coverage [33], the loading of P2EHA polymer at 5% weight ratio lightly improved the coverage, although crystal misorientation still existed. At 10% loading, the TIPS pentacene crystals were aligned along the tilted orientation of the substrate (Fig. 2b). Furthermore, the addition of the P2EHA additive at 20% dramatically improved both crystal orientation and film coverage, as shown in Fig. 2(c). Finally, when the P2EHA weight ratio increased to 60%, all TIPS pentacene crystals were aligned along a uniform orientation and the film coverage reached to nearly 100%, leading to a thin film morphology of TIPS pentacene as demonstrated in Fig. 2(d).

In order to quantitatively characterize the change of crystal orientation with the addition of the P2EHA polymer, we measured the misorientation angle as a function the P2EHA loading ratio. As shown in the inset of Fig. 3(a), the misorientation angle (θ) is defined as the angle between the long axis of a TIPS pentacene crystal and a baseline crystal. While the pristine TIPS pentacene film exhibited randomly-oriented crystals with a misorientation angle of 41.4° ± 27.1° [34], the loading of P2EHA at 5%, 10%, 20% and 60% reduced the misorientation angle to 40.2° ± 33°, 12.5° ± 4.3°, 11.5° ± 2.9°, and 4.1° ± 1.8°, respectively. It is noted that the loading of P2EHA at 60% has greatly reduced the misorientation angle to...
Fig. 1. Molecular structure of (a) small-molecule organic semiconductor 6,13-bis (triisopropylsilylethynyl) pentacene (TIPS pentacene), (b) polyacrylate polymer additive poly(2-ethylhexyl acrylate) (P2EHA) and (c) toluene.

Fig. 2. Polarized optical images of TIPS pentacene/P2EHA blend films with different ratios of the P2EHA additive: (a) 5%, (b) 10%, (c) 20% and (d) 60%. The tilted blue rods represent the TIPS pentacene molecule backbones. The yellow arrows imply the long axis direction of TIPS pentacene. The white triangles mark the bare substrate. Image (a–d) share the same scale bar of 100 μm as shown in (d).

Fig. 3. Plot of the average misorientation angle and grain width of the TIPS pentacene film as a function of the loading ratio of the P2EHA polymer additive. (a) The misorientation angle (θ) is defined as the angle between the long axis of TIPS pentacene crystals. (b) The grain width \( W_g \) is defined as the domain width along the short axis of the TIPS pentacene crystals. The standard deviation of both average misorientation angle and grain width are based on 8 measurements.
below 5°, which indicates a significant improvement of crystal orientation as compared to pristine TIPS pentacene film.

In addition to the reduction of crystal misorientation, the loading of P2EHA polymer additive also modulated the grain width of the TIPS pentacene crystals, as shown in the optical images of Fig. 2. The average grain width was measured as a function of the P2EHA loading ratio, and the result was presented in Fig. 3(b). Here we define grain width, or \( W \), as the domain width along the short axis of the TIPS pentacene crystals, as shown in the inset. While pristine TIPS pentacene exhibited an average grain width of 91 ± 20 \( \mu \text{m} \) [34], the loading of P2EHA at 5%, 10%, 20% and 60% led to an average grain width of 62.17 ± 40.26 \( \mu \text{m} \), 60.51 ± 61.28 \( \mu \text{m} \), 40.59 ± 9.18 \( \mu \text{m} \), and 140.44 ± 19.82 \( \mu \text{m} \), respectively. Specially, it is noted that the average grain width was significantly increased at the loading ratio of 60%. Since defects are located at the grain boundaries, the enlarged grain width indicates a reduction of grain boundaries, and consequently, less trap centers of charge carriers, which is beneficial for charge transport and device performance of the TIPS pentacene based OTFTs [35].

Bottom-gate, bottom-contact OTFTs were fabricated to test charge transport in the TIPS pentacene crystals. The representative output and transfer characteristics of OTFTs are shown in Fig. 4(a, b), respectively, and the device configuration of OTFTs is illustrated in Fig. 4(c). The mobility was calculated from the square root curve of the transfer characteristic in the saturation region, which is based on the following traditional MOSFET equation (1):

\[
I_{DS} = \mu C_i \frac{W}{2L} (V_{GS} - V_T)^2
\]  

(1)

where \( \mu \) is the mobility, \( C_i \) is the capacitance of SiO\(_2\) gate dielectrics, \( W \) and \( L \) are the width and length of the semiconducting channel, respectively, and \( V_T \) is the threshold voltage.

The average mobility of OTFTs based on pristine TIPS pentacene crystals and TIPS pentacene/P2EHA blends (with 60% loading ratio) is compared in Fig. 4(d). Without the addition of P2EHA additive, the pristine TIPS pentacene based OTFTs exhibited an average hole mobility of 0.03 ± 0.04 cm\(^2\)/V\(\cdot\)s [34], which indicates great variations in the charge carrier mobilities and performance consistency. In comparison, the devices with 60% loading of P2EHA showed an average hole mobility of 0.317 ± 0.047 cm\(^2\)/V\(\cdot\)s. This clearly indicates that loading of the P2EHA polymer additive has greatly enhanced the charge carrier mobility. It’s worth noting that, as compared to the pristine TIPS pentacene based OTFTs, the addition of P2EHA at the weight ratio of 60% remarkably contributed to a 10-fold enhancement of the average mobility of TIPS pentacene based OTFTs, which can be attributed to the combination effect of improved crystal orientation, reduced defects and charge trap centers as a result of enlarged grain width, as well as an enhanced film coverage.

In addition to the enhancement of average hole mobility, the loading of the P2EHA polymer additive also significantly reduced the variations in the charge carrier mobility of the TIPS pentacene based OTFTs. To better demonstrate mobility variation, we define the ratio of average mobility to standard deviation of mobility (\( \mu_{AVE}/\mu_{STDEV} \)), as a metric to quantitatively evaluate the device performance consistency. While pristine TIPS pentacene based OTFTs exhibited performance consistency factor (\( \mu_{AVE}/\mu_{STDEV} \)) of I, the loading of P2EHA polymer additive at 60% weight ratio increased the \( \mu_{AVE}/\mu_{STDEV} \) factor to 6.72, as shown in Fig. 4(d). Particularly, it resulted in a 7-fold enhancement of the performance consistency factor, as compared to that of the pristine TIPS pentacene based OTFTs.

Finally, we use a schematic picture to better illustrate the change of the thin film morphology of TIPS pentacene as a result of the addition of P2EHA polyacrylate polymer additive. As shown in Fig. 5(a), the pristine TIPS pentacene film exhibited severe crystal misorientation and poor coverage, which is responsible for anisotropic charge transport and severe variations of device performance consistency of OTFTs. On the other hand, when P2EHA was added (i.e. at a weight ratio of 60%) to tune the crystallization and thin film morphology, as shown in Fig. 5(b), the TIPS pentacene crystal misorientation was significantly reduced, and both the grain width and film coverage were greatly enhanced, favoring charge transport and device performance of TIPS pentacene based OTFTs.
Based on the Flory-Huggins theory [36], the Gibbs free energy of mixing ($\Delta G$) for a binary blend of solute and solvent is expressed by equation (2):

$$\frac{\Delta G}{RT} = \sum_{i=1}^{2} n_i \ln \phi_i + n_1 \phi_2 \chi$$

(2)

where $n_i$ is the molar number of each component in the binary system, $\phi_i$ the volume fraction parameter, and $\chi$ the interaction parameter of the two components. On the right side of equation (2), the first term $\sum_{i=1}^{2} n_i \ln \phi_i$ represents the combinatorial entropy change, whereas the second term $n_1 \phi_2 \chi$ is associated with contact dissimilarity. Similarly, $\Delta G$ for a ternary blend system is expressed by equations (3) and (4) [37]:

$$\frac{\Delta G}{RT} = \sum_{i=1}^{3} n_i \ln \phi_i + \Gamma(T, \varphi, N)$$

(3)

$$\Gamma(T, \varphi, N) = n_1 \varphi_2 g_{12} + n_1 \varphi_3 g_{13} + n_2 \varphi_3 g_{23} + n_1 \varphi_2 \varphi_3 g_{123}$$

(4)

where $\sum_{i=1}^{3} n_i \ln \phi_i$ in equation (3) accounts for the combinatorial entropy, $\Gamma(T, \varphi, N)$ represents the non-combinatorial entropy and enthalpy changes, $g_{12}$, $g_{13}$, and $g_{23}$ are the interaction parameter of a composition-related binary system, and $g_{123}$ is the interaction parameter in a ternary system. $\Gamma$ is considered to be related to the degree of polymerization ($N$) in a ternary blend system that contains a polymer component (i.e. P2EHA).

Based on the thermodynamics point of view, equations (3) and (4) provide an insight into the kinetic interaction among the components existing in a ternary blend system (i.e. TIPS pentacene, P2EHA and toluene as in this work). The long side group of P2EHA polymer additive with eight carbon atoms is anticipated to contribute to a moderate decrease of the combinatorial entropy ($\sum_{i=1}^{3} n_i \ln \phi_i$) [36–38], but to a great reduction of $\Gamma(T, \varphi, N)$ of the TIPS pentacene/P2EHA blends, presumably due to a large enthalpy change. This facilitates the ternary system to form a phase separation during the initial stage of crystallization (when $\Delta G < 0$). Since crystallization plays a critical kinetic part in phase separation, a layer rich of the semiconducting TIPS pentacene is firstly formed on the top. The residual solution with a greatly increased P2EHA concentration facilitates the formation of a middle layer rich of P2EHA. At last, the remaining TIPS pentacene forms a bottom layer as the toluene solvent dries out. Therefore, the vertical phase separation between TIPS pentacene and P2EHA through the kinetic interplay provides an important confinement of the anisotropic crystallization. This leads to the growth of well-aligned TIPS pentacene crystals with enhanced crystal orientation, as illustrated in Fig. 5(b).

Since an effective vertical phase separation between TIPS pentacene and P2EHA depends on the remaining concentration of P2EHA in solution after a top TIPS pentacene-rich layer is formed, blending only a small amount of P2EHA with TIPS pentacene (i.e. at 5% weight ratio) resulted in a weak vertical phase separation, which provided very limited confinement of TIPS pentacene crystallization, and consequently, negligible alignment of randomly-oriented crystals. In contrast, as the loading ratio of P2EHA increased to 10%, 20% and 60%, stronger vertical phase separation occurred as a result of the elevated P2EHA concentration in solution, leading to more effective confinement of crystallization and greater enhancement of crystal orientation, as evidenced by the reduction of misorientation angles as presented in Fig. 3(a).

4. Conclusion

In summary, we have demonstrated an effective approach to control crystallization, tune charge transport and improve performance consistency of TIPS pentacene based OTFTs by blending P2EHA as a polycrylate polymer additive. Vertical phase separation occurred between TIPS pentacene and P2EHA, resulting in an effective confinement of the anisotropic crystallization and charge transport of the semiconductor. At a loading ratio of 60%, an average misorientation angle of $4.1 \pm 1.8^\circ$ and grain width of $140.44 \pm 19.82 \mu$m were obtained. Increased grain width indicates reduced grain boundaries and, correspondingly, less defects and trap centers of charge carriers. Bottom-gate, bottom-contact OTFTs based on the TIPS pentacene/P2EHA blends were fabricated and exhibited an improved average mobility of $0.317 \pm 0.047$ cm²/Vs and performance consistency of 6.72 (defined as the ratio of average mobility to standard deviation of mobility), which is a 10-fold and 7-fold enhancement as compared to the pristine TIPS pentacene.

![Figure 5](image-url)
OTFTs. Such a remarkable improvement in charge transport and device performance of OTFTs can be attributed to the combination effect of reduced crystal misorientation, enlarged grain width, and enhanced film coverage of the TIPS pentacene film as a result of P2EHA polyacrylate polymer additive.

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