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Citation: *Appl. Phys. Lett.* **109**, 143302 (2016);

View online: <https://doi.org/10.1063/1.4963911>

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# Blending crystalline/liquid crystalline small molecule semiconductors: A strategy towards high performance organic thin film transistors

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(Received 28 June 2016; accepted 20 September 2016; published online 3 October 2016)

Solution processed small molecule polycrystalline thin films often suffer from the problems of inhomogeneity and discontinuity. Here, we describe a strategy to solve these problems through deposition of the active layer from a blended solution of crystalline (2-phenyl[1]benzothieno[3,2-b][1]benzothiophene, Ph-BTBT) and liquid crystalline (2-(4-dodecylphenyl) [1]benzothieno[3,2-b]benzothiophene, C12-Ph-BTBT) small molecule semiconductors with the hot spin-coating method. Organic thin film transistors with average hole mobility approaching  $1 \text{ cm}^2/\text{V s}$ , much higher than that of single component devices, have been demonstrated, mainly due to the improved uniformity, continuity, crystallinity, and stronger intermolecular  $\pi$ - $\pi$  stacking in blend thin films. Our results indicate that the crystalline/liquid crystalline semiconductor blend method is an effective way to enhance the performance of organic transistors. *Published by AIP Publishing.*  
[\[http://dx.doi.org/10.1063/1.4963911\]](http://dx.doi.org/10.1063/1.4963911)

Organic thin film transistors (OTFTs) have drawn much attention from both academic and industrial communities mainly due to their potential use for mass production of cost-effective electronics. Compared to their high vacuum processed inorganic counterparts, polycrystalline thin films of OTFTs can be easily processed from solution by coating or printing techniques, such as spin-coating, ink-jet printing, and screen-printing, which drastically reduce the cost. Great progress has been achieved recently in solution processed OTFTs. High hole and electron mobility exceeding  $5 \text{ cm}^2/\text{V s}$ , from both solution processed small molecules and polymer semiconductors, have been reported.<sup>1-5</sup>

For practical applications, uniformity of the thin films is an important requirement because transistors are often used in arrays. It is vital to minimize the difference from device to device. However, solution processed small molecule polycrystalline OTFTs often suffer from the problems of inhomogeneity and discontinuity, resulting in low mobility and large variation.<sup>6-8</sup> Several strategies have been proposed to solve these problems. One method is to blend small molecule semiconductors with soluble polymer semiconductors or insulators.<sup>4,9-15</sup> But the improvement is sometimes modest due to the difficulty in controlling the micro-structure. Another more effective method is to use liquid crystalline small molecule semiconductors combined with the hot spin-coating technique.<sup>16,17</sup> However, this method only works for liquid crystalline materials. Other methods are needed to further address the inhomogeneity and discontinuity problems for solution processed small molecule polycrystalline OTFTs.

In this letter, we propose a strategy to solve the inhomogeneity and discontinuity problems, fully taking advantage of the good film-forming ability of liquid crystalline materials. By blending an appropriate amount of crystalline material 2-phenyl[1]benzothieno[3,2-b][1]benzothiophene (Ph-BTBT)

with liquid crystalline material 2-(4-dodecylphenyl) [1]benzothieno[3,2-b]benzothiophene (C12-Ph-BTBT) (the weight ratio is pre-optimized to be 1:2.5, denoted as BLEND2.5 in this letter), we obtained high quality polycrystalline thin films using the hot spin-coating method and demonstrated a high average mobility exceeding  $0.8 \text{ cm}^2/\text{V s}$ .

The chemical structures of Ph-BTBT and C12-Ph-BTBT and their differential scanning calorimetry (DSC) curves are presented in Figure 1. The synthesis of these two materials and their other physicochemical properties are reported elsewhere.<sup>18</sup> As seen from the DSC curve, C12-Ph-BTBT exhibits many smectic phases. We exploited the smectic phase between  $65.5^\circ\text{C}$  and  $135.2^\circ\text{C}$  in this study. We characterized the field-effect properties of the Ph-BTBT, BLEND2.5, and C12-Ph-BTBT with top-contact bottom-gate OTFTs. Substrates of heavily doped n-type silicon wafer with 250 nm  $\text{SiO}_2$  ( $\text{n}^+\text{-Si/SiO}_2$ ) were cleaned with acetone, deionized

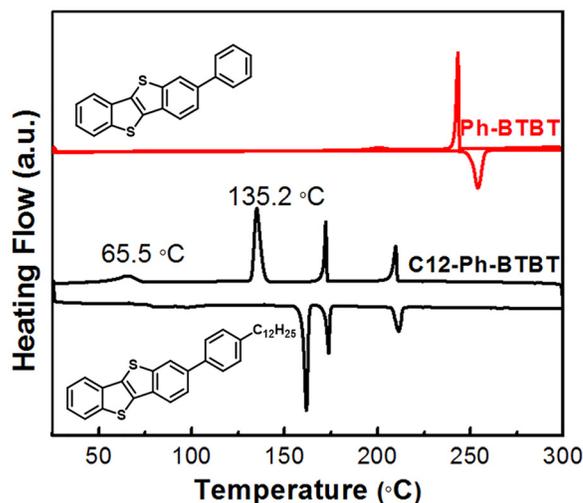


FIG. 1. DSC curves of Ph-BTBT and C12-Ph-BTBT. Insets are their chemical structures.

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TABLE I. The performance of OTFTs based on Ph-BTBT, BLEND2.5, and C12-Ph-BTBT. Note: all values are averaged over at least five devices.

	$\mu_{\text{sat}}$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$I_{\text{on}}/I_{\text{off}}$	$V_{\text{th}}$ (V)	SS (V/decade)
Ph-BTBT	$(5.52 \pm 3.55) \times 10^{-4}$	$(2.96 \pm 2.27) \times 10^1$	$-33.9 \pm 0.7$	$7.5 \pm 0.9$
BLEND2.5	$0.85 \pm 0.10$	$(3.50 \pm 0.70) \times 10^5$	$-21.4 \pm 1.3$	$4.7 \pm 0.5$
C12-Ph-BTBT	$0.24 \pm 0.04$	$(1.21 \pm 0.38) \times 10^5$	$-15.3 \pm 1.4$	$4.6 \pm 0.6$

water, and isopropyl alcohol, respectively, for 10 min in an ultrasonicator. Compounds of Ph-BTBT and C12-Ph-BTBT were dissolved in *o*-dichlorobenzene with the concentration of 10 mg/ml at 70 °C. For BLEND2.5 solution, we blended totally dissolved Ph-BTBT and C12-Ph-BTBT solutions together with the volume ratio of 1:2.5. Polycrystalline thin films with thickness of about 30 nm were obtained by spin-coating the hot solutions onto pre-UV/ozone treated clean Si/SiO<sub>2</sub> substrates, at the spin speed of 1600 rpm for 30 s and then 2000 rpm for 10 s. The spin-coating temperature was maintained at 70 °C to ensure C12-Ph-BTBT in the liquid crystal phase. In order to totally remove the solvent, thin films were pre-annealed at 80 °C for 30 min in a N<sub>2</sub> glove box before moving to the evaporation chamber. No further annealing process was involved during the whole device fabrication process. Gold for source and drain electrodes was deposited onto the resulting polycrystalline thin films by thermal evaporation through a metal mask under pressure below  $3 \times 10^{-4}$  Pa, with a thickness of about 40 nm. The channel width/length (W/L) were 980/98, 780/78, 580/58, and 380/38  $\mu\text{m}$ . The device characteristics were measured using a semiconductor parameter analyzer (Agilent B1500A) in air at

room temperature with relative humidity around 60%. The mobility was calculated from transfer curves in the saturation regime at  $V_{\text{DS}} = -30$  V.<sup>19</sup>

Table I shows the detailed device performance, and Figure 2 shows the corresponding transfer and output characteristics. As seen from the table, Ph-BTBT OTFTs exhibit low mobility below  $0.001 \text{ cm}^2/\text{V s}$  with large mobility variation. C12-Ph-BTBT OTFTs show moderate mobility of  $0.24 \text{ cm}^2/\text{V s}$ . Surprisingly, an average hole mobility over  $0.85 \text{ cm}^2/\text{V s}$  with the best exceeding  $0.9 \text{ cm}^2/\text{V s}$  is demonstrated for BLEND2.5 devices, which is nearly three orders of magnitude higher than that of Ph-BTBT devices and three times higher than that of C12-Ph-BTBT devices. The saturation drain current for BLEND2.5 devices is also obviously increased, so is the on/off ratio, as seen from the transfer and output curves. The threshold voltages and sub-threshold swings are not satisfying in all three types of devices, which should be ascribed to the high humidity during device fabrication and characterization.<sup>20</sup>

In order to find the origins for the improved device performance of BLEND2.5 OTFTs, we first examined the surface morphology of thin films. Figures 3(a)–3(c) show the

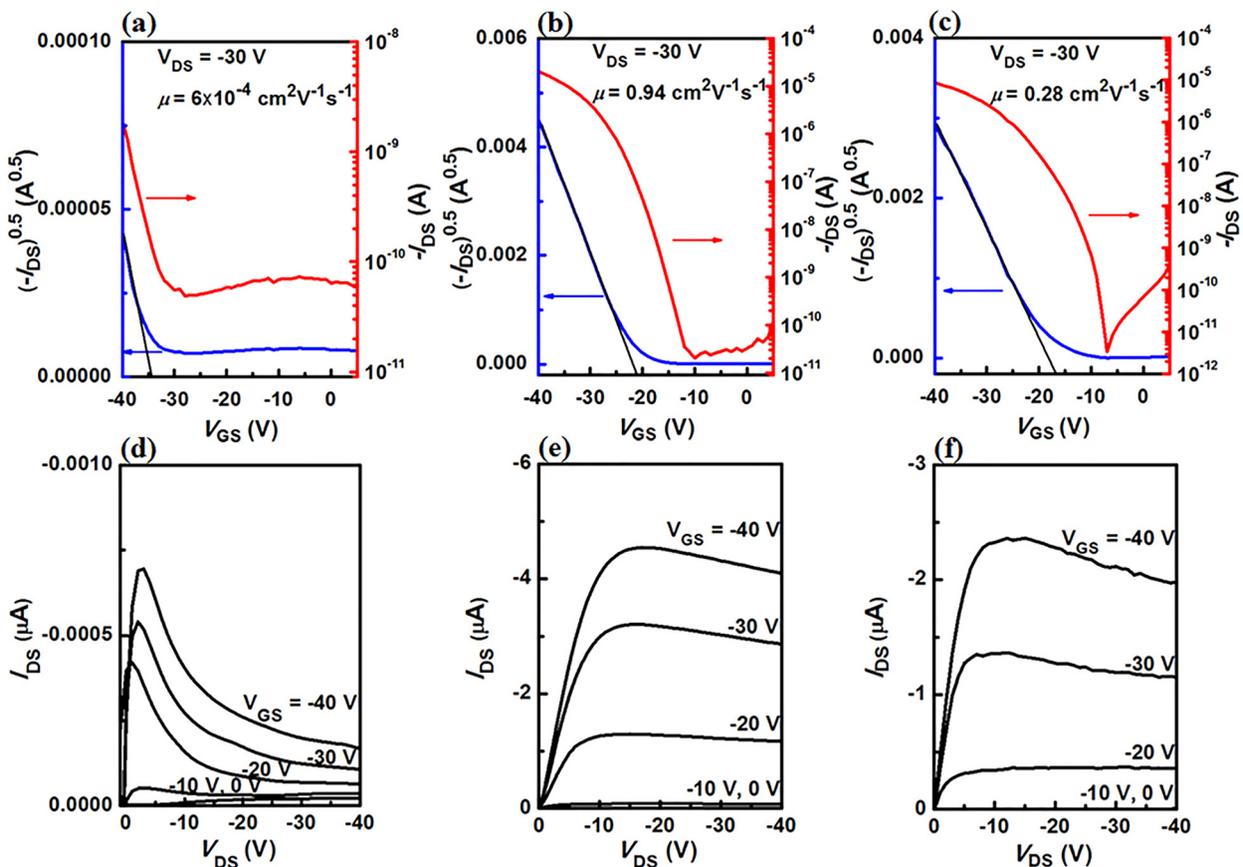


FIG. 2. (a)–(c) Transfer curves of OTFTs based on Ph-BTBT, BLEND2.5, and C12-Ph-BTBT, respectively. (d)–(f) Corresponding output curves.

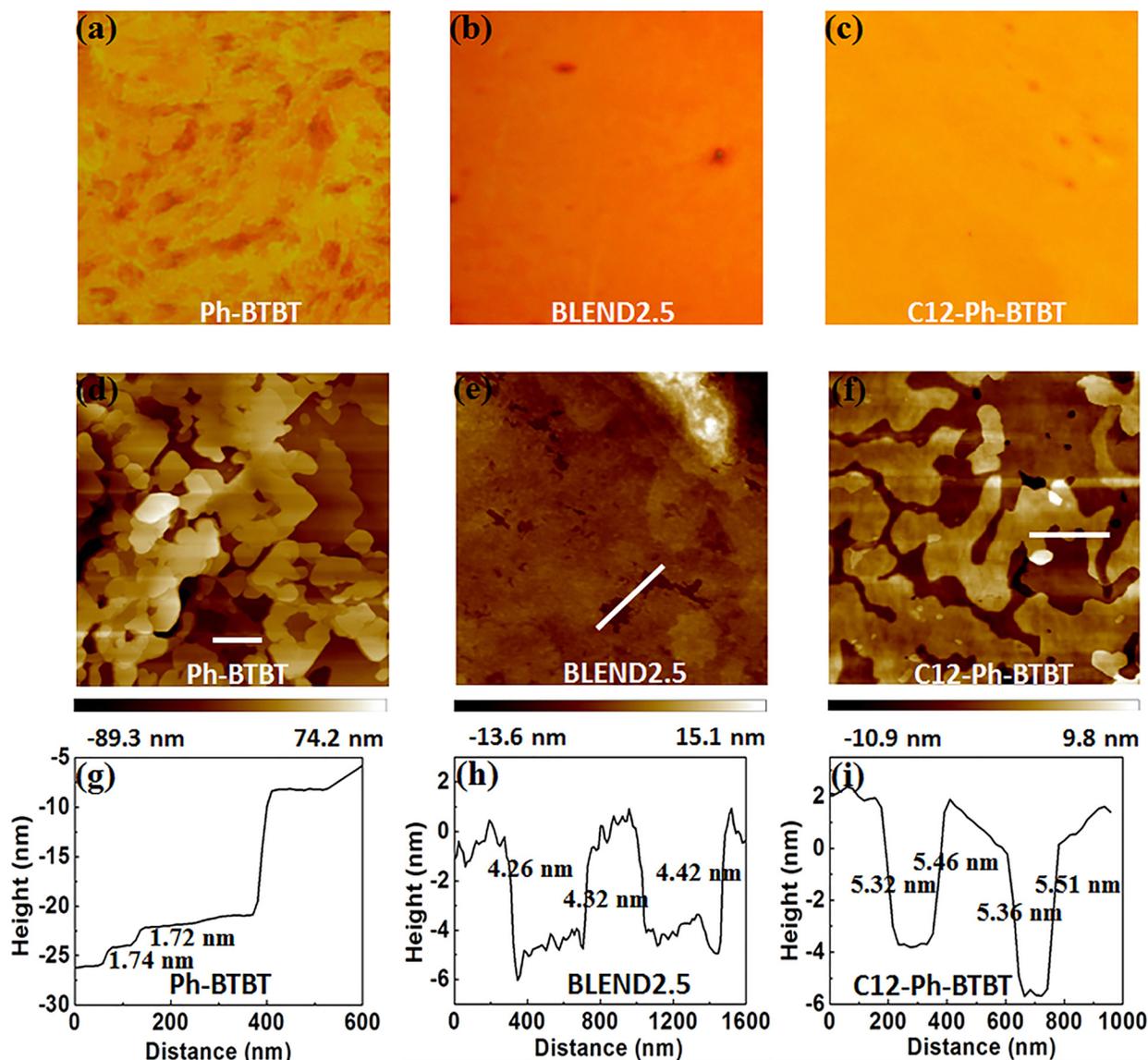


FIG. 3. (a)–(c) Optical microscopy images ( $50\ \mu\text{m} \times 50\ \mu\text{m}$ ) of Ph-BTBT, BLEND2.5, and C12-Ph-BTBT thin films on the Si/SiO<sub>2</sub> substrate, respectively. (d)–(f) Tapping mode AFM height images ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ) of Ph-BTBT, BLEND2.5, and C12-Ph-BTBT thin films on the Si/SiO<sub>2</sub> substrate, respectively. (g)–(i) Cross-sectional profiles along the white lines in images (d)–(f).

optical microscope textures of Ph-BTBT, BLEND2.5, and C12-Ph-BTBT thin films on the silicon substrate. As seen from the images, the morphology of Ph-BTBT is inhomogeneous and discontinuous, with many high isolated islands. In contrast, the morphology of BLEND2.5, similar to that of C12-Ph-BTBT, is quite uniform on the micrometer scale. This morphology improvement is also confirmed by the AFM measurement. Figures 3(d)–3(f) present the tapping-mode AFM height images of Ph-BTBT, BLEND2.5, and C12-Ph-BTBT thin films, respectively. As expected, the surface of BLEND2.5 films becomes much smooth (RMS = 2.65 nm), even smoother than that of C12-Ph-BTBT (RMS = 3.16 nm). On the contrary, the surface of Ph-BTBT films is rather rough (RMS = 22 nm) and less ordered, mainly due to the fast recrystallization rate and low viscosity of Ph-BTBT solution. Furthermore, we examined the cross-sectional profiles of the thin films (Fig. 3(g)–3(i)). A clear step-terrace structure is observed in Ph-BTBT, BLEND2.5, and C12-Ph-BTBT thin films. The step height is about 1.7 nm for Ph-BTBT, equivalent to its

molecular length ( $\sim 1.78$  nm). For C12-Ph-BTBT thin films, the step heights range from 5.3 to 5.5 nm, correlating with twice of the molecular length of C12-Ph-BTBT ( $\sim 2.7$  nm). This means that the molecules stand on the substrate with a monolayer structure in Ph-BTBT thin films but with a bilayer structure in C12-Ph-BTBT thin films. It is noteworthy that typical step heights of approximately 4.4 nm are also found in BLEND2.5 thin films, which corresponds to the sum of the length of Ph-BTBT and C12-Ph-BTBT molecules. This indicates an edge on the structure and bilayer structure of Ph-BTBT and C12-Ph-BTBT formed in BLEND2.5 thin films. In addition, the grain size in BLEND2.5 thin films is obviously increased, with large size up to  $5\ \mu\text{m}$  compared to below  $1\ \mu\text{m}$  for Ph-BTBT and  $\sim 2\ \mu\text{m}$  for C12-Ph-BTBT thin films. Apparently, the larger grains contribute to the enhancement in hole mobility.

To further investigate the molecular packing structures and correlate them with device performance, we performed X-ray diffraction (XRD) analysis on Ph-BTBT, BLEND2.5,

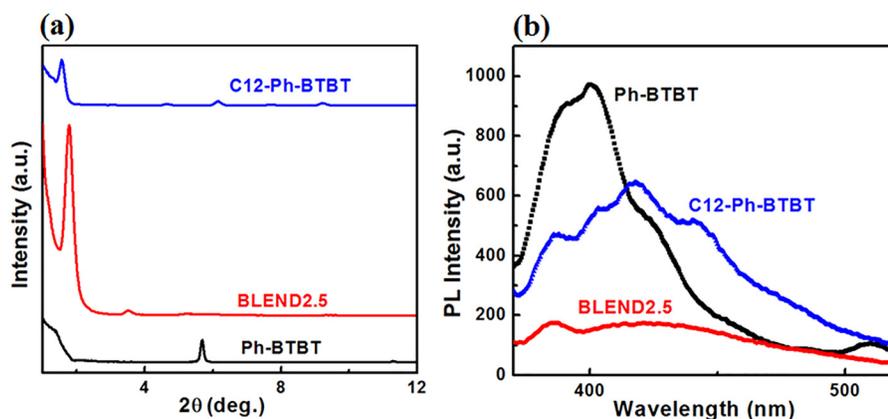


FIG. 4. (a) XRD patterns of Ph-BTBT, BLEND2.5, and C12-BTBT thin films on the Si/SiO<sub>2</sub> substrate. (b) PL spectra of Ph-BTBT, BLEND2.5, and C12-BTBT thin films.

and C12-Ph-BTBT thin films. The results are shown in Figure 4(a). Clear diffraction peaks assignable to (00 $l$ ) reflections are observed in all the three thin films.<sup>21</sup> The first reflection peaks are found at  $2\theta = 5.7^\circ$ ,  $1.8^\circ$ , and  $1.6^\circ$  for Ph-BTBT, BLEND2.5, and C12-Ph-BTBT thin films, respectively. The corresponding d-spacing values are 15.5 Å, 49.6 Å, and 55.4 Å, agreeing well with the step heights from AFM images. The stronger reflection intensity and narrower line width indicate higher degree of crystallinity in BLEND2.5 thin films, possibly due to the strong intermolecular interaction between Ph-BTBT and C12-Ph-BTBT. We also compared the photoluminescence (PL) spectra of Ph-BTBT, BLEND2.5, and C12-Ph-BTBT thin films. The results are shown in Figure 4(b). Ph-BTBT and C12-Ph-BTBT thin films render strong fluorescent emission with the maximum at 400 nm and 420 nm, respectively. In contrast, the emission intensity drastically decreases in BLEND2.5 thin films. The aggregation induced quenching (AIQ) phenomenon implies stronger  $\pi$ - $\pi$  stacking in BLEND2.5 thin films.<sup>22</sup> Due to the lack of single crystal data, it is not possible to analyze the molecular packing and orientation in depth. Great efforts are being made to obtain the single crystal data.

In summary, through blending crystalline (Ph-BTBT) and liquid crystalline (C12-Ph-BTBT) small molecule semiconductors together, we have improved the uniformity and continuity of small molecule polycrystalline thin films with the hot spin-coating method and demonstrated OTFTs with high mobility over  $0.85 \text{ cm}^2/\text{Vs}$ . After analyzing the thin films with AFM, XRD, and PL, we attributed the mobility enhancement to not only improved uniformity and continuity but also better crystallinity and stronger intermolecular  $\pi$ - $\pi$  stacking in blend thin films. We believe that higher mobility can be achieved through the fine selection of the combination of crystalline/liquid crystalline small molecule semiconductors and prolonged understanding of the blending mechanism.

This work was financially supported by the Shenzhen Key Laboratory of Organic Optoelectromagnetic Functional Materials of Shenzhen Science and Technology Plan (ZDSYS20140509094114164), the National Natural Science Foundation of China (Grant No. 51603003), the Shenzhen Peacock Program (KQTD2014062714543296), Nanshan Innovation Agency Grant (No. KC2015ZDYF0016A), Guangdong Talents Project, Guangdong Key Research

Project (Nos. 2014B090914003 and 2015B090914002), Guangdong Academician Workstation (2013B090400016), National Basic Research Program of China (973 Program, No. 2015CB856500), and Natural Science Foundation of Guangdong Province (2014A030313800).

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