Polymer binder effects on the electrical characteristics of 6, 13-bis(triisopropylsilylethynyl)-pentacene thin-film transistors in different solvents

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ABSTRACT

This paper presents the effects of the polymer binder on the electrical properties of 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene) organic thin-film transistors (OTFTs) which have been fabricated using a variety of 2 wt.% TIPS-pentacene solutions that have been prepared in different solutions, including anisole, toluene, and chlorobenzene. Poly(triarylamine) (PTAA) is added as a polymer binder to help the TIPS-pentacene form a stronger binding, thus improving device performances. By using these materials as the active channel, a molecular guest-host system is formed, with TIPS-pentacene as the host and the PTAA as the guest. Introducing the TIPS-pentacene solutions means that the polymer binder and the solvent dependent electrical characteristics can be investigated to determine if the device exhibits the best performance when the solution is prepared with anisole as the solvent and PTAA as the polymer binder. Consequently, a device made from anisole with PTAA exhibits superior electrical properties in comparison to the devices made with the other solutions including the saturation field-effect mobility (μ_{sat}) of 0.21 cm^2/V·s, current on/off ratios of 5×10^6, and a sub-threshold slope (SS) of 0.46 V/dec at a gate bias $V_{GS} = -40$ V.

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1. Introduction

Organic thin-film transistors (OTFTs) have been widely investigated for their use in various electronic applications, such as active-matrix flat panel displays (AM-FPDs), smart cards, and radio frequency identification (RFID) tags [1–4]. Among the organic semiconductors (OSCs), pentacene is the most preferred material due to its high field-effect mobility and environmental stability [5,6]. However, pentacene is insoluble in organic solvents, which limits its use in producing printed OTFTs that require a soluble process. Recently, soluble OSCs have become preferable for use as the active layers in OTFTs rather than vacuum-deposited ones because of their low-cost, low-processing temperature, and adaptability to flexible technologies [6,7]. Moreover, soluble OSCs enable simple processing techniques, such as spin coating and drop-casting [8,9], and printing processes such as roll-to-roll processing and ink-jet printing [10,11]. A functionalized pentacene, 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene), is the most promising candidate among the soluble OSC materials [12]. The bulky functionalized groups in TIPS-pentacene encourage the molecular ordering with face-to-face interactions, rather than the edge-to-face interactions, thereby leading to improved π-orbital overlaps [13]. However, one of the key issues of TIPS-pentacene is how to obtain a continuous thin film with well-ordered crystalline, in large areas because, in general, TIPS-pentacene is limited in its uniformity over a large-area, and also in its solvent dependency, for which a polymer solvent has to be used. During fabrication of the devices, it is found that these limitations

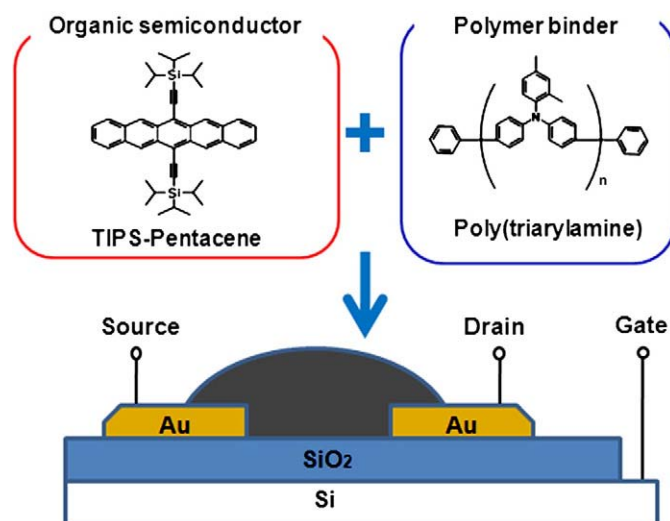Fig. 1. Schematic of a TIPS-pentacene TFT with PTAA.

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E-mail address: bkju@korea.ac.kr (B.-K. Ju).
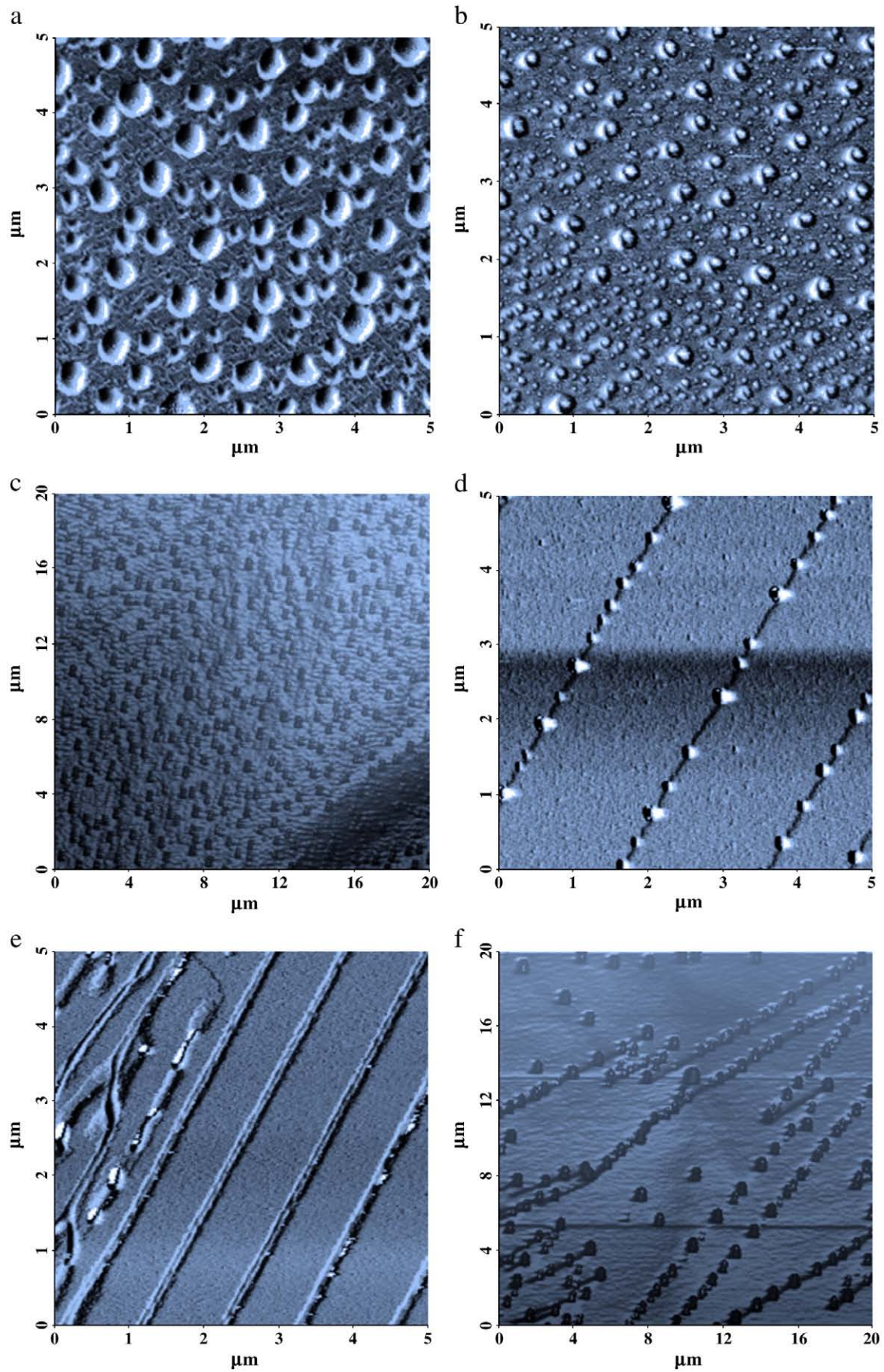
Fig. 2. AFM images of TIPS-pentacene TFTs: (a) from anisole without PTAA (b) from toluene without PTAA (c) from chlorobenzene without PTAA (d) from anisole with PTAA (e) from toluene with PTAA and (f) from chlorobenzene with PTAA.

result in lower electrical performances and field effect mobilities than the theoretical expectations.

This work focuses on two issues — one being the enhanced film morphology obtained by using a molecular guest-host system with a polymer binder and the other being the polymer's binding effect on the TIPS-pentacene under different kinds of solvents. These variables are used to find the best conditions under which enhanced electrical characteristics can be achieved. Poly(triarylamine) (PTAA) is employed as the polymer binder, which helps the TIPS-pentacene form a stronger binding thereby improving the overall device performance [14]. These materials are employed for the design of a molecular guest-host system, based on TIPS-pentacene as the host and PTAA as the guest.

2. Experimental studies

Fig. 1 shows a schematic diagram of the proposed OTFT device fabricated on a highly doped p-type Si wafer, with a thermally grown 500 nm SiO_2 and the 200 nm Au source/drain electrodes are deposited through a shadow mask by using a thermal evaporator (DOV Co., Ltd.). An interdigitated-finger geometry is employed for the electrodes, which improve the electrical properties of the devices [15] and the device's channel length (L) and width (W) are 100 µm and 2500 µm, respectively. The TIPS-pentacene solutions are prepared by mixing PTAA in different solvents, including anisole, toluene, and chlorobenzene and the weight percentage (wt.%) of TIPS-pentacene powder to the solution is 2 wt.% after which the TIPS-pentacene is mixed with PTAA with a 10:1 weight ratio, as reported previously [16]. Next, the active layer is formed by drop-casting the prepared TIPS-pentacene solution, which is then annealed at 90 °C for 10 min. Park et al. reported that TIPS-pentacene film, formed by drop casting, has better molecular order than if it is formed by spin and dip casting, and so drop-casted TIPS-pentacene based OTFT has better device performances compared to other casting methods. The surface morphology of the proposed devices is observed with atomic force microscopy (AFM, Dimension 3100), and the structural analysis is investigated with X-ray diffraction (XRD, D/max 2200 V) spectroscopy in the symmetric reflection coupled $\theta-2\theta$ arrangement with a Cu Kα1 radiation ($\lambda_{K\alpha1} = 1.54$ Å) X-ray source. The electrical characteristics are measured using a semiconductor characterization system (Keithley SCS 4200) in a dark box.

3. Results and discussion

In order to study the surface morphology, the crystallization and molecular ordering of the TIPS-pentacene films are compared under different conditions and Fig. 2(a)–(f) shows the AFM images (5 µm × 5 µm) of each TIPS-pentacene film surface, drop-casted on the SiO_2 dielectric. Note that in Fig. 2, (c) and (f) were measured by the size of 20 µm × 20 µm in order to display the best molecular alignment. As shown in Fig. 2(a)–(c), the TIPS-pentacene film without PTAA shows amorphous TIPS-pentacene clusters, which can lead to poor carrier mobilities due to interference with the flowing carriers in the active layer [16]. As far as uniformity is concerned, these clusters can be a disadvantage for processing large-areas and so it is advisable that these states be removed after the TIPS-pentacene is mixed with the polymer binders thereby forming a host-guest system. As shown in Fig. 2(d)–(f), well-ordered molecules along the semi-crystalline polymer binder line can be observed, which can be explained by semi-crystalline host matrixes, with well-defined insertion sites for the guest, substitutes for the host molecules, thus the host and the guest molecules together form a compatible system [17]. When compared to the images without PTAA, it is clearly demonstrated that molecules are drawn up several lines and the well-organized TIPS-pentacene molecules may also enhance the field-effect mobility of the device because of the better π-orbital overlap among the neighboring TIPS-
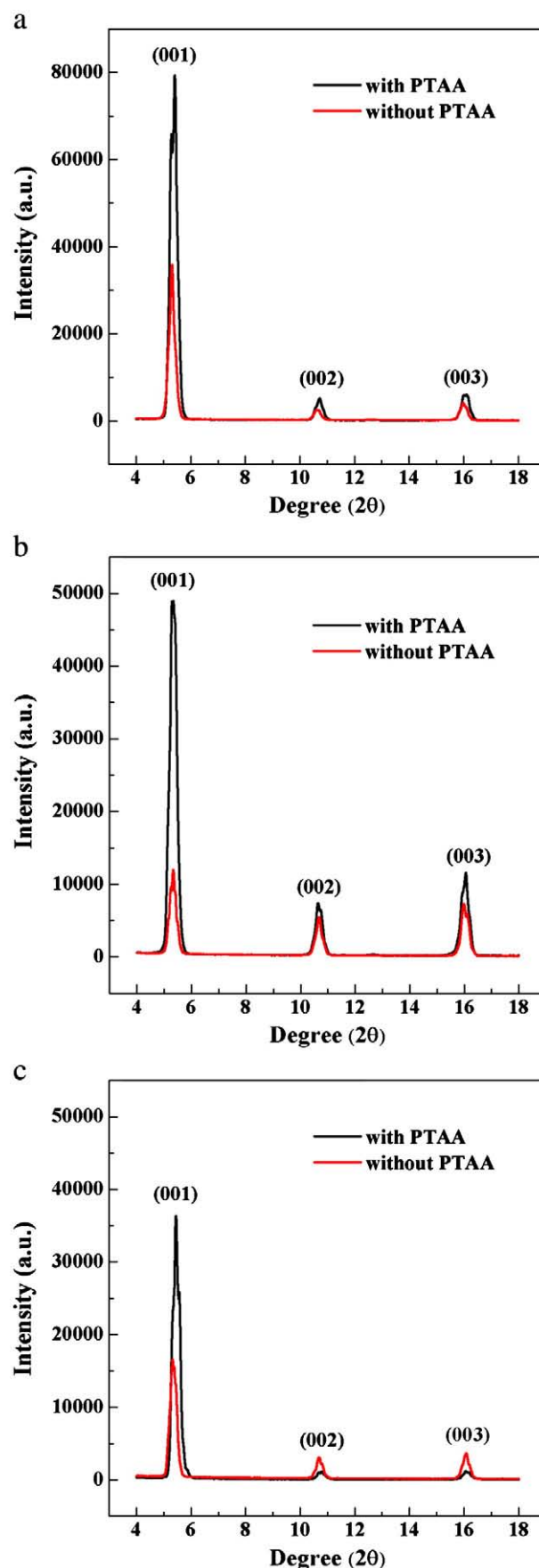
Fig. 3. XRD spectra of TIPS-pentacene TFTs: (a) from anisole (b) from toluene and (c) from chlorobenzene.
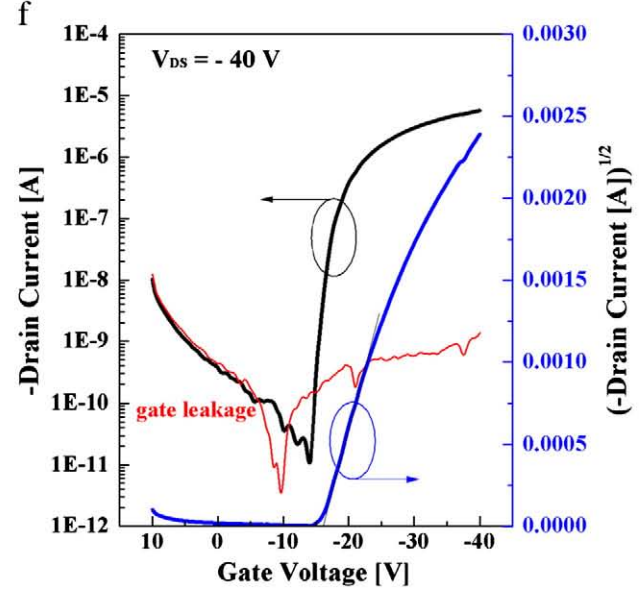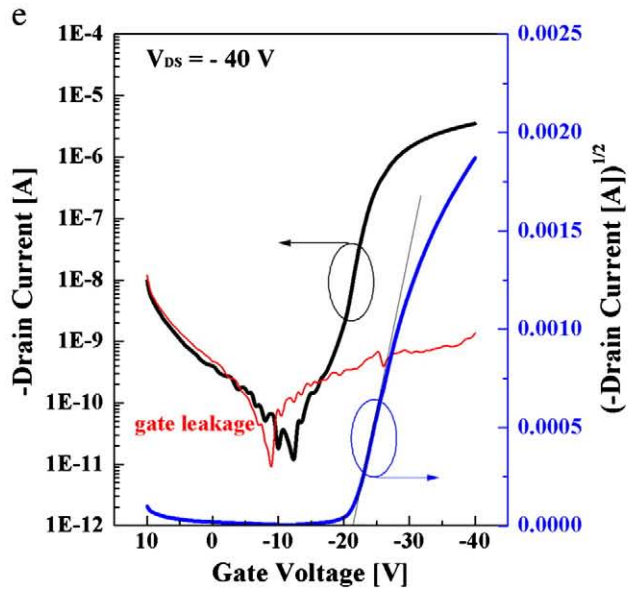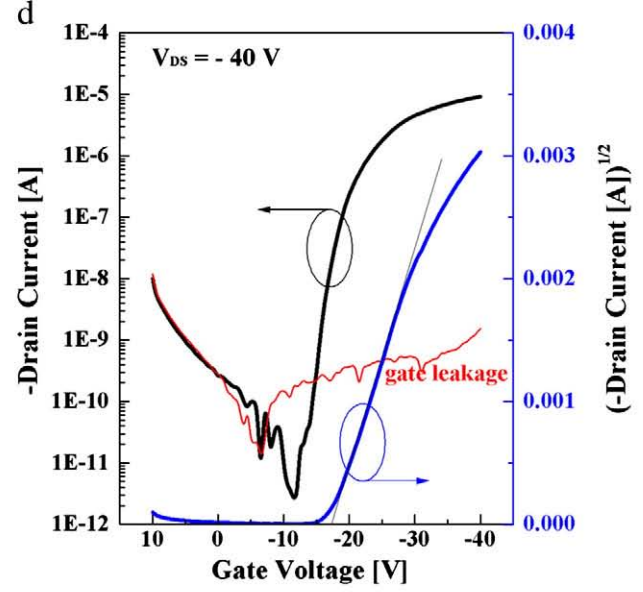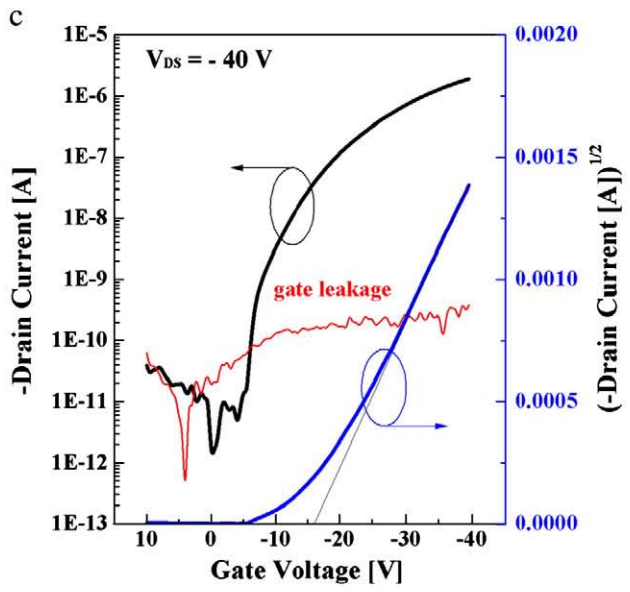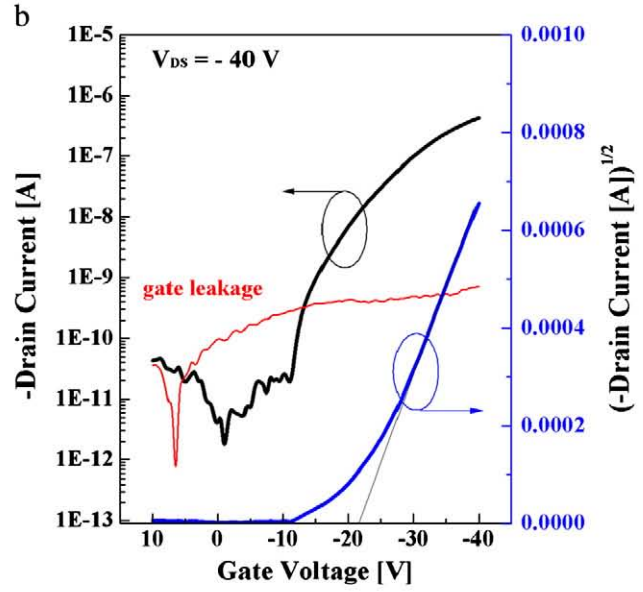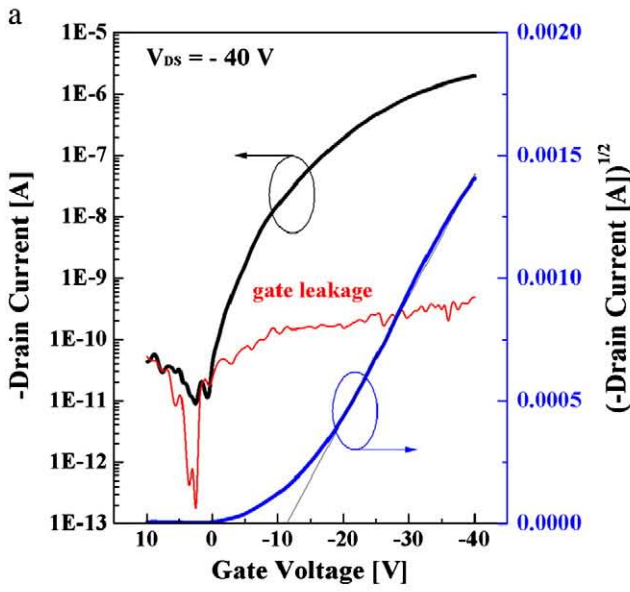
Table 1
The electrical parameters of the proposed devices.

Solvent	Anisole		Toluene		Chlorobenzene	
Binder	With PTAA	Without PTAA	With PTAA	Without PTAA	With PTAA	Without PTAA
Mobility(cm^2/Vs)	0.21	0.029	0.11	0.014	0.12	0.039
On/Off Ratio	5×10^6	2.8×10^5	4.2×10^5	3.9×10^5	8×10^5	1.8×10^6
Sub-threshold Slope (SS)	0.46	1.19	0.50	0.93	0.48	0.69
Vth (V)	-17.5	-12	-21	-21	-16.5	-16

pentacene molecules [18]. In this case, it would appear that the insertion of PTAA may increase the mobilities of the holes between the TIPS-pentacene molecules, instead of the hopping transporting behaviors in the amorphous arrangements.

Fig. 3 shows the XRD spectra of the TIPS-pentacene films from (a) anisole, (b) toluene, and (c) chlorobenzene. The upper spectra exhibits a series of (0 0 *l*) diffraction peaks of the TIPS-pentacene film with PTAA, whereas the lower spectra is exhibited for the TIPS-pentacene film without PTAA. Fig. 3(a)–(c) demonstrate that the XRD peaks of the TIPS-pentacene film with PTAA show higher intensity peaks than those of the film without PTAA and these higher intensity peaks indicate a well-organized molecular structure [19], as confirmed by the AFM images mentioned above. Fig. 3(a) shows the maximum peak of TIPS-pentacene film from toluene with PTAA observed at 5.42°, corresponding to layer-by-layer separation (*d*) of 16.4 Å, which is in very close agreement with the thin film phase reported in the literature [13]. The *d* value has been calculated by Bragg's equation,

$$d = \frac{\lambda_{K\alpha1}}{2\sin\theta},\qquad(1)$$

where θ is half of the measured angle, and $\lambda_{K\alpha1} = 1.54$ Å, which is the wavelength of Cu $K\alpha1$ radiation X-ray source. Similarly, the *d* of TIPS-pentacene film from toluene with PTAA is 16.5 Å at the maximum peak of 5.34°, and the *d* of TIPS-pentacene film from chlorobenzene with PTAA is 16.2 Å at the maximum peak of 5.46°. To investigate the effect of the polymer binder on the electrical characteristics, OTFTs have been fabricated with TIPS-pentacene dissolved in each solvent, with PTAA and without PTAA. Fig. 4(a)–(f) shows the transfer characteristics (log ($-I_{DS}$) *versus* V_{GS} and $\sqrt{-I_{DS}}$ *versus* V_{GS}) of the proposed devices. The saturation field-effect mobility (μ_{sat}), extracted in the saturation regime, is calculated by the following equation,

$$I_D = \frac{WC_i}{2L}\mu_{sat}(V_{GS}-V_{th})^2,\qquad(2)$$

where I_D is the drain current, C_i is the capacitance per unit area, V_{GS} is the gate voltage, and V_{th} is the threshold voltage. For whole devices, the V_{GS} is swept from 10 V to –40 V, and the drain voltage (V_{DS}) is fixed at –40 V. The OTFTs, fabricated from anisole without PTAA, as shown in Fig. 4(a), exhibit μ_{sat} values of 0.029 cm^2/V·s, current on/off ratios of 2×105, sub-threshold slopes (SS) of 1.19 V/dec, and threshold voltages (V_{th}) of -12 V under a gate bias $V_{GS} = -40$ V. After fabricating with PTAA, as shown in Fig. 4(b), the improved electrical characteristics are confirmed, including μ_{sat} of 0.21 cm2/V·s, current on/off ratio of 5×106, SS of 0.46 V/dec, and V_{th} of -17.5 V. These results are consistent with the film surface conditions confirmed in the AFM images and the XRD spectra. A host-guest system influences the binding effect, which enables the TIPS-pentacene to arrange along the crystalline polymer, thus making it easier for the carriers to transport between the molecules. A somewhat high V_{th} is attributed to the charge trapping at the OSC-gate dielectric interface. This phenomenon is commonly observed in a

soluble process because water or some impurities are absorbed at the interface when depositing the OSC [19]. Fig. 4(c)–(f) also shows similar tendencies in improving the electrical performances when PTAA is added. Fig. 4(c)–(d) shows the OTFTs being fabricated from toluene, and Fig. 4(e)–(f) shows an OTFT being fabricated from chlorobenzene; Table 1 gives the electrical parameters of all these devices. Although the enhancements are slightly different depending on the kind of solvents, all the experimental devices indicate that the addition of the PTAA results in a positive effect on improving the electrical characteristics where the μ_{sat} is increased 3–8 times after adding PTAA into the TIPS-pentacene. Moreover, a high current on/off ratio is obtained due to the fairly low off-current and the graphs confirm that the gate current (I_G) of the devices displays a negligible leakage value, hence it could be assumed that I_D is approximately the same as the channel current (I_{CH}), when $I_{CH}/(I_{OFF}+I_G) > 10^3$. The fabricated devices satisfy the given conditions so it is assumed that the μ_{sat} is attributed to the I_{DS}.

It is noted that a solvent with a high boiling point gives a positive effect on the film morphology and a slower solvent evaporation allows structural rearrangement before the film solidifies which helps the film to form a better crystalline structure [20]. The better morphological properties consequently lead to superior electrical characteristics, especially the μ_{sat} [21]. The boiling points of each solvent used are the following: anisole (155 °C), chlorobenzene (132 °C), and toluene (111 °C). As expected, the device with anisole exhibits the best μ_{sat} among the devices fabricated and this being approximately twice that of the devices with anisole and chlorobenzene.

4. Conclusion

In summary, OTFTs have been fabricated with a molecular guest-host system, based on TIPS-pentacene as the host and PTAA as the guest, in different solvents and it has been confirmed that the binding effect of PTAA forms a line of semiconducting material. It has also been found that the binding effect is maximized when the solution is made from a solvent with a high boiling point and hence the improved surface condition is achieved from using the most appropriate solvent, and the polymer binder contributes to the enhancement of the electrical performance. These results show that this guest-host system, based on TIPS-pentacene/PTAA, is a promising application for fabricating large-areas having the advantage of well-ordered uniform morphology and high mobilities. Moreover, devices fabricated with a drop-casting soluble process indicate the best suitability for use in plastic electronics since they are low-cost and require low-temperatures and are easy to fabricate.

Fig. 4. Transfer characteristics (log($-I_{DS}$) *versus* V_{GS} and $\sqrt{-I_{DS}}$ *versus* V_{GS} curves) of TIPS-pentacene TFTs: (a) from anisole without PTAA (b) from toluene without PTAA (c) from chlorobenzene without PTAA (d) from anisole with PTAA (e) from toluene with PTAA and (f) from chlorobenzene with PTAA.

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