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Interplay of Orientation and Blending: Synergistic Enhancement of Field Effect Mobility in Thiophene-based Conjugated Polymers

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ABSTRACT

Trade-off between mechanical flexibility due to amorphicity and highly facile charge transport emanating from molecular crystallinity demands the orientation of conjugated polymers (CPs) for their utilization as active semiconducting material for flexible organic electronics. We have already demonstrated that it is rather easy to orient non regiocontrolled poly(3-hexylthiophenes) (NR-P3HT) as compared to their highly regioregular counterparts due to very high alkyl chain interdigitation. To provide an amicable solution, efforts have been directed to orient blends of two CPs such as NR-P3HT (amorphous and flexible) and poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) (crystalline and facile charge transport) using a solution based procedure floating film and transfer method (FTM). FTM processed thin films of this blend system exhibited very high field effect transistor (FET) mobility reaching up to $0.1 \text{ cm}^2/\text{V}\cdot\text{s}$, which is much higher than the corresponding individual CPs. In spite of only 10% incorporation of PBTTT in blend of NR-P3HT and PBTTT, there was a synergistically enhanced optical dichroic ratio (4.6 to 7.2) and FET mobility (8-fold) as compared to pristine NR-P3HT. At the same time, there was a 5 fold enhancement of FET mobility when 20% NR-P3HT was added in PBTTT as compared to that of PBTTT. This synergistic enhancement of charge carrier transport in the blend system has been explained by formation of oriented self-assembled fibrous domains of NR-P3HT and facile inter-domain transport in crystalline PBTTT.

1. Introduction

Advent of solution processable conjugated polymers (CPs) and their successful implementation as active semiconducting components have geared the fast development in the area of organic electronics.^{1,2} Apart from most acclaimed spin coating there are number of solution based approaches capable of providing high quality thin films towards the realization of improved performances in organic electronic devices.^{3,4} Charge transport in CPs has captivated a lot of attentions from the scientific community which can be gauged by their tremendous application potentials in the area of organic field effect transistors.^{5,6} Charge transport in CPs are stringently dependent on the overlapping of electron density from their neighboring π -orbitals which in-turn controls the intermolecular associations, molecular stacking, chain alignment etc. Molecular engineering approaches for the in-depth understanding of underlying phenomena have been the center of attention of the research community. Ubiquitous implication of film morphology on controlling the performance of organic field effect transistors (OFETs) make CPs more interesting not only to understand the related transport processes but also efforts towards their control in order to achieve the desired functions.⁷⁻⁹ Molecular orientation in CPs due to their one dimensional character makes them capable of improving their charge carrier mobility,^{5,10,11} which has been witnessed by report of a number of methods for their unidirectional orientation in the recent past.¹²

Among CPs, polythiophenes have been most extensively investigated for device application in the area of organic electronics. Intractability of electro-polymerized materials of this family of CPs led to the attraction for solution processable poly (3-hexyl thiophene) (P3HT) prepared by FeCl_3 catalyzed chemical synthetic methods but their small field effect mobility (μ) led to its repudiation by majority of the researchers.^{11,13,14} In general, they exhibit very small μ ($<10^{-5}$ $\text{cm}^2/\text{V.s}$) when their thin films are prepared by conventional spin coating due to their low

regioregularity,^{11,14} uncontrolled growth of polymer chains and presence of various regio-isomers. The presence of regio-randomness in P3HT leads to the mechanical flexibility owing to their low crystallinity.¹⁵ Recently, flexible OFETs utilizing low regioregular and regiorandom P3HT has also been demonstrated by other groups.^{16,17} Several attempts has been made to increase the crystallinity of CPs in order to increase the performance of OFETs, however, such problems are irresistible due to their semi crystalline nature.¹⁸ In-fact the high crystallinity affects the mechanical pliancy of film thereby making them inadequate for soft electronics device application.¹⁵ Therefore to solve such issues, many methods have been explored in order to improve the transport properties in low crystalline systems and is still perpetuating.^{16,19} In spite of the fact reported μ in CPs are breaking their previous records by molecular design and implementation of various film processing techniques,^{20,21} however, there is no consensus for a widely acceptable charge transport model in semiconducting CPs.²²

Furthermore, in P3HT with reduced regioregularity and apart from the presence of head-to-tail (H-T) coupling, there are sufficient head-to-head (H-H) and tail-to-tail (T-T) coupled fractions in the main polymer chain. Such a mismatch in their regioregularity provides large steric interaction leading to increased torsion.^{23,24} On the other hand, highly regioregular (RR) P3HT exhibits high crystallinity due to their increased inter-chain interactions assisted by high interdigitation of alkyl chains between adjacent macromolecules resulting in relatively high μ in their thin films.¹⁰ Microstructures of highly RR-P3HT consists of semi-ordered and amorphous regions where long polymer chains are mainly responsible for the connecting the adjacent crystallites.^{22,25} Large scale orientation of CPs is a unique solution for improving the in-plane transport of CPs, however, the resulting performance is governed by the kind of orientation of CPs adopted within

their crystallites i.e. edge-on, face-on or mixture of both as shown in Figure 1 (a). Although highly oriented films of RR-P3HT with face-on orientation has been demonstrated through some global orientation methods such as mechanical rubbing and friction transfer techniques.^{26,27} However, the presence of out-of-plane π - π stacking and in-plane alkyl side-chain impede the inter-molecular transport at the interface of insulator and CPs.²⁸ The origin of such edge-on and face-on orientation of the film depends on the different film forming methods. Application of mechanical pressure (shear-forces) on the polymer backbone has been reported to adopt the face-on orientation.^{26,27} Therefore, this highly face-on oriented films does not serve the purpose of improving the in-plane transport and the problems related to the damage occurring to underlying surface while rubbing and friction transfer cannot be ignored also. In this perspective, such orientation methods are certainly not suitable for devices requiring high in-plane transport like OFETs.^{25,29} On the other hand, direct solution casting methods favor slow solvent evaporation, resulting in to thermodynamically favored edge-on orientation with in-plane π - π stacking and π -conjugation favoring facile in-plane charge transport.^{7,29} However, preparation of large scale oriented film of RR-P3HT is difficult through solution based approaches. This could be attributed to the stiffness present in the RR-P3HT due to high intermolecular inter-digitation/interaction, concomitantly imparting relatively lower degrees of freedom for adjacent macromolecules to orient freely.³⁰

In order to provide an amicable solution for both of the issues like flexibility and orientation in P3HT, recently we have shown that using NR-P3HT with moderate regioregularity of (~80%), it is possible to attain good molecular orientation. To accomplish this goal, we have utilized a facile solution based approach of floating film and transfer method (FTM) which is capable of providing large scale orientation of CPs in single direction. FTM basically involves rapid

evaporation of solvent together with orientation and thermodynamically favorable edge-on orientation leading to the remarkably enhanced μ of NR-P3HT by 2-3 order of magnitude reaching $\sim 10^{-3} \text{ cm}^2/\text{V.s.}$ ^{11,31} It has been found that such a large scale unidirectional orientation although leads to high intra-domain charge transport but they still possesses hampered inter-domain transport due to their relatively low crystallinity or π - π stacking. Therefore, it is of utmost importance to provide a logical solution for the facile inter-domain charge transport while maintaining the inherent flexibility which is expected to be a milestone in the area of high performance flexible electronics. Mixing two CPs of different nature to tune resulting μ by varying their mixing ratio has been a focal point of many researchers and many interesting results have also been reported.^{16,32,33} Involving such blending of two CPs with contrasting inherent behaviors by adding a highly crystalline material with pronounced inter-domain transport in the highly oriented domains (with high intra-domain transport) of second polymer would be a prominent approach for solving both flexibility and orientation issues in CPs.

In this article, both of the crystallinity as well as the molecular orientation issues have been amicably taken in to the consideration in order to improve the charge carrier transport in the blends of CPs. We have focused on the most widely studied thiophene based CPs like NR-P3HT as amorphous and poly[2,5-bis(3-tetradecylthiophene-2-yl)thieno[3,2-b]thiophene] PBTTT as a crystalline polymeric materials as depicted in **Figure 1** (b). Using FTM as a highly facile solution based method for the preparation of oriented thin films, the influence of the addition of crystalline CP in the highly oriented NR-P3HT has been investigated together with the charge carrier transport and opto-electrical anisotropy. The orientation in the pristine NR-P3HT is increased drastically by the addition of only 10% of PBTTT and synergistically improved μ with anisotropic charge transport. Transport properties of thin films of different blends and stoichiometry were correlated

with the results obtained from various techniques such as polarized absorption spectroscopy, atomic force microscopy and X-ray diffraction (XRD) patterns etc.

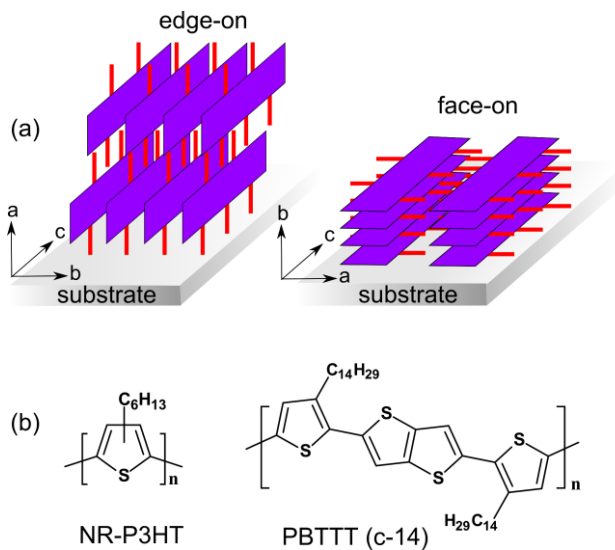


Figure 1. (a) Schematic representation of face-on and edge on orientation in conjugated polymers, (b) structure of NR-P3HT and PBTTT. In (a) a, b, c axis corresponds alkyl-stacking direction, π -stacking and conjugation direction.

2. Experimental Section

2.1 Materials

NR-P3HT has been synthesized by most commonly used FeCl₃ assisted oxidative chemical polymerization and purified by Soxhlet extraction as published earlier.³⁴ Determination of the molecular weight of the synthesized polymer was carried by gel permeation chromatography using polystyrene standards. The molecular weight and polydispersity index (PDI) of the synthesized NR-P3HT was found to be $M_w = 102645$, $M_n = 29849$ and 3.4, respectively. On the other hand, its regioregularity was found to be about 80% as confirmed by with ¹H-NMR spectroscopic investigations.³⁵ PBTTT was purchased from Sigma Aldrich having $M_w = 40,000 - 80,000$ and PDI below 3 and used without any further purification. All of chemicals used in the synthesis were

of reagent grade and used without any purification. Anhydrous chloroform was purchased from Sigma Aldrich which was utilized to dissolve all of the above polymers.

2.2 Thin Film Preparation and Orientation

1% and 0.2% weight by weight (wt/wt) solutions of CPs were prepared in anhydrous chloroform for the fabrication of thin films by FTM and spin-coating, respectively. FTM was utilized as a casting method used for the preparation of the oriented thin film as per our previous publication.³¹ Addition of PBTTT to NR-P3HT has been done in the increasing order of weight percentage in NR-P3HT. All of the solutions were warmed at 60°C to avoid any aggregation and gelation before casting the films on liquid substrate. The oriented FTM films from liquid substrate were finally transferred by stamping on the desired solid substrates either for characterization or OFET fabrication.³¹ For out-of-plane X-ray diffraction, FTM samples were prepared by multilayer coating on hexamethyldisilazane treated silicon wafers in order to have relatively thicker film (~700 nm) in for getting measurable XRD signal intensity without influencing the film morphology as published earlier.³¹

2.3 Thin Film Characterization

The thicknesses of the all the FTM films were measured by interference microscopy (Nikon Eclipse LV150) and found to be in between 20-25 nm (Figure S1, Supporting Information). Polarized electronic absorption spectroscopic measurement was conducted using UV-visible-NIR spectrophotometer (JASCO V-570) equipped with Glan Thompson prism. The polarizer was placed before the detector, and rotated to change the polarization direction. AFM images were done under tapping mode by JEOL SPM5200 with Olympus probe (OMCL- AC200TS-C3). Thin films were annealed at 80 °C to insure similar morphology as used for OFET fabrication prior to AFM. Orientation intensity was quantitatively determined in terms of dichroic ratio (DR) by

polarized absorption spectra. The DR was calculated by using equation $DR = A_{\parallel} / A_{\perp}$, where A_{\parallel} is maximum absorbance when polarization direction was parallel (\parallel) to orientation direction and A_{\perp} is absorbance in the perpendicular (\perp) direction at the wavelength of A_{\parallel} .³⁵

2.4 Fabrication of Organic Thin Film Transistor

Heavily p-doped silicon substrates were used as base substrates having 300 nm of SiO₂ as an insulating layer having capacitance $C_i = 10$ nF/cm²). The SiO₂ surface was spin coated with CYTOP (a highly hydrophobic fluoropolymer) at 3000 rpm for 120 s and baked at 150°C for 1 h to make the surface hydrophobic for better adhesion of the floating films. The resultant C_i after of CYTOP coated substrates were found to be 8 nF/cm². The reference spin coated samples were prepared on base SiO₂ substrates owing to existing problem of spin coating on CYTOP due to its high hydrophobicity.³⁶ The oriented FTM films were stamped on to the prepared substrates. Films were annealed at 80°C prior to electrode deposition. 50 nm thick source and drain were deposited by thermal evaporation of gold (1.5 Å/s) at pressure 10⁻⁶ Torr using nickel mask. Channel length (L) and channel width (W) were 2000 μ m and 20 μ m, respectively. All of the output and transfer characteristics were measured by computer controlled two channel electrometer (Kiethley 2612) and devices were exposed to air prior to measurements. Field effect mobility (μ), threshold voltage (V_{TH}) and on/off ratio was calculated in saturation regime ($V_{DS} = -80$ V) of transfer characteristics following the relation as:

$$I_{DS} = \frac{W}{2L} \mu C_i (V_{GS} - V_{TH})^2 \quad (1)$$

The average μ in the devices were estimated by taking the average of at least 3 devices in each configurations.

3. Results and Discussion

Solid-state electronic absorption spectrum of P3HT thin film exhibits a pronounced optical absorption in the 400 nm-650 nm associated with the π - π^* electronic transition which is parallel to the polymer backbone main-chain axis³⁷ and the extent of their orientation intensity can be easily monitored by polarized absorption spectroscopy. The ratio of the absorbance at absorption maximum (λ_{\max}) obtained from polarized light parallel and perpendicular to the main chain alignment direction gives with extent of orientation intensity as DR.³⁸ Spin coated thin films of NR-P3HT exhibits a featureless absorption spectrum having π - π^* transition around 480 nm,^{31,39} In contrary to this NR-P3HT film processed with FTM exhibits sharp vibronic features along with red-shifted λ_{\max} at 527 nm as shown in the **Figure 2** (a). The red shifted λ_{\max} in the FTM processed film is due to the increased π -conjugation length due to oriented NR-P3HT having the DR of 4.6 which is interestingly higher than that observed for films aligned by mechanical rubbing and almost similar to the observed values for RR-P3HT by strain alignment.^{26,38}

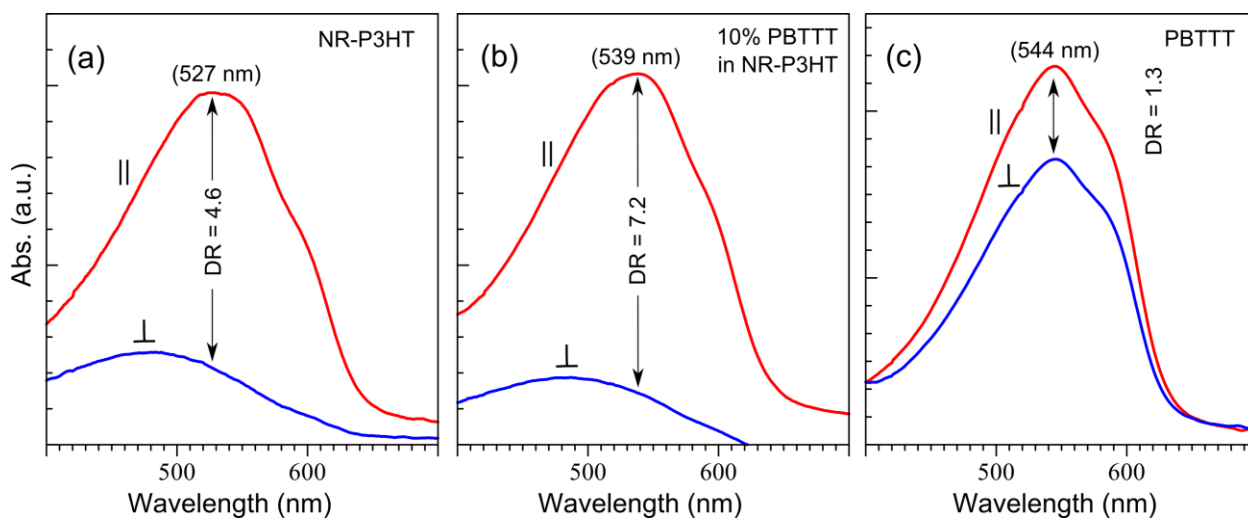


Figure 2. Polarized absorption spectra oriented films prepared by FTM. (a) Pristine NR-P3HT, (b) NR-P3HT having 10% PBTtT and (c) Pristine PBTtT.

Significant works have been done to align the conjugated polymers either by utilizing the nano-confinement during nanoimprinting,⁴⁰ assisting the alignment by pre-patterned layers and polyimide layers as host substrates for deposition.⁴¹⁻⁴³ Such methods utilize the assisted alignment of the guest CP along the in-built direction of the host substrate texture. Unlikely in our case, when we attempted to blend small amount (10%) PBTTT in NR-P3HT there was synergistic improvement in the orientation intensity. It can be clearly seen from the **Figure 2** (b), that there is a net increase in the intensity of orientation intensity, concomitantly increasing the DR value >7. To the best of our knowledge, this could be the first phenomenon observed where the guest is increasing the orientation of the host. One can argue that increased DR is probably due to the orientation of the guest PBTTT, which can't be distinguished due to the overlapping absorption spectra of constituent polymers. Effort was also directed to orient pristine PBTTT with FTM in similar casting condition, but very little orientation of PBTTT was found as shown in **Figure 2** (c). Due to the overlapping wavelength and lack of sharp peaks in the absorption spectra of these individual polymers as can be seen from **Figure 2**, it is quite ambiguous to decide and distinguish the role of individual CP in this blends for this surprising increase in the orientation intensity. One of the plausible solutions to clarify this enhanced net orientation intensity in the blend by logically selecting the guest CP having the absorption in higher/lower wavelength region than that of host CP. Taking this point in to consideration, it has been found that by small addition of polyfluorene (PFO) in NR-P3HT, there was an increase in the orientation intensity of the blend similar to that observed for the blend of NR-P3HT and PBTTT (Figure S2, Supporting Information).

It is reasonable to say that P3HT films having high regioregularity is brittle due to the fish bone structure of their alkyl side chains,³⁰ concomitantly P3HT with low regioregularity is

comparatively flexible due to the entanglement of the polymeric chains, resulting from the discontinuity in head-to-tail configuration.¹⁵ Such materials auspiciously gives the adjacent macromolecules of NR-P3HT to align freely as compared to the highly regioregular P3HT. The possible mechanism for synergistically improved orientation by small addition of PBTTT could be attributed to the fact that the presence of crystalline domains of PBTTT concomitantly reduces the entanglement and provide more freedom to NR-P3HT to align. Such phenomenon related to microstructures rearrangements has been shown schematically in the **Figure 3**. As spin coated films consists of amorphous and randomly distributed polymer chain of NR-P3HT while oriented films processed with FTM are consisted of large scale entangled oriented domains, which tends to form more flat aligned structures with the addition of guest material PBTTT. This proposal is in accordance with results revealed by microstructural investigations using atomic force microscopy (AFM) and will be discussed in next section.



Figure 3. Schematic representation of the thin film microstructures of NR-P3HT coated by (a) as-spun NR-P3HT, (b) FTM coated NR-P3HT and (c) FTM coated NR-P3HT blended with small amount PBTTT (blue stripes).

Effect of post-annealing at 60°C on DR in different blending ratio of PBTTT in NR-P3HT has been shown in **Figure 4**. A perusal of this figure clearly reveals that DR of NR-P3HT first increases by 10 % addition of PBTTT followed by a decrease upon further addition. The cause of such gradual decrease in DR upon blending can be easily understood considering the low DR exhibited by pristine PBTTT. Upon annealing the FTM processed films at 60°C, it has been found that net resulting DR of all the blend films increases, however, extent of this change decreases

with the increasing PBTTT fraction in the blend. One of the probable reasons could be the evaporation of the remaining solvents but it is of worth to notice that higher changes in DR is observed in NR-P3HT.⁴⁴ Such increase in DR is reasonable as macromolecules in the domains of NR-P3HT are less crystalline providing flexibility to the polymeric backbone to reorganize.¹⁵ Such a drastic changes in DR of NR-P3HT is in well agreement with the increment in DR due to small addition of guest polymer.

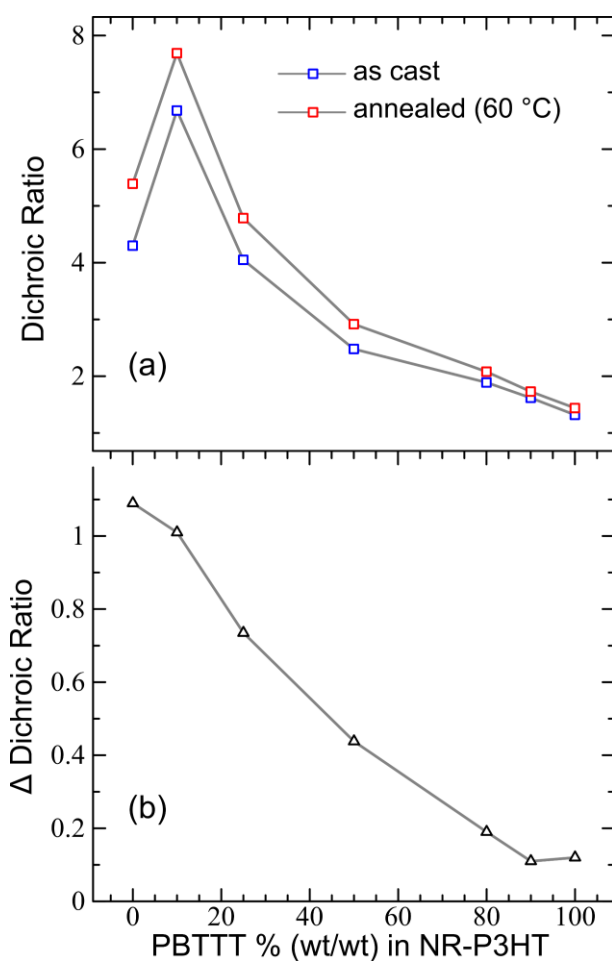


Figure 4. (a) Dichroic Ratio (DR) of the as-cast and annealed oriented FTM films, (b) Increase in the DR (Δ) after annealing at 60°C. Δ DR in (b) was calculated from taking the difference of DR of annealed and as-cast film (average of at least 3 films), respectively. Higher changes in Δ DR with higher content of NR-P3HT in the blend fraction shows that the NR-P3HT macromolecules has more tendency to rearrange due to its flexibility.

For spin coated NR-P3HT, the absorption of NR-P3HT at 480 nm represents π - π^* transitions with featureless absorption and relatively blue shifted λ_{\max} around 480 nm is attributed to the decrease in effective π -conjugation length, concomitantly localizing the wave function of the exciton to higher extent and increasing its energy.⁴⁵ The less resolved fine structures in spin coated films can be attributed to wider distribution of the conjugation lengths. However, when the same films of NR-P3HT was prepared by FTM, λ_{\max} was found to be red shifted to 527 nm representing the increase in the π -conjugation length with and evolution of 0-0 transitions representing the high degree of inter-chain interaction.⁴⁵ In order to visualize the further ordering and increase in the inter-chain interactions by addition of small amount of (PBTTT 10%), Spanos model for the quantitate analysis of inter and intermolecular ordering in CPs was performed.⁴⁶ Electronic absorption spectrum of FTM processed NR-P3HT exhibits vibronic structures showing only 0-0 transitions at 602 nm whereas it becomes more resolved and shows the 0-1 vibronic band also appearing at 539 nm upon addition of PBTTT. The amount of the inter-chain coupling can be estimated by the ratio of 0-0 and 0-1 vibronic bands, which corresponds to free exciton bandwidth (W) of the aggregates. The decrease in the value of W can be attributed to the increase in the conjugation length as well as chain ordering. The value of W was calculated from the relation as,

$$\frac{Abs_{0-0}}{Abs_{0-1}} \approx \left(\frac{1 - 0.24 \frac{W}{E_p}}{1 + 0.073 \frac{W}{E_p}} \right)^2 \quad (2)$$

Where A_{0-0} and A_{0-1} represents the corresponding intensities related to 0-0 and 0-1 transitions obtained from the normalized spectra (Figure S3, Supporting Information) and E_p denotes the vibrational energy at 0.18 eV.^{47,48} The value of W was calculated for both of the pristine FTM

coated NR-P3HT film as well as for blend of NR-P3HT having 10 % PBTTT and results are shown in the **Table 1**. The value of W in pristine NR-P3HT film was found to be 160 meV which was decreased to 148 meV for NR-P3HT having 10% PBTTT reflecting that slight addition of guest crystalline material leads to promotion of the intermolecular ordering in NR-P3HT macromolecules.

Table. 1 Different parameters calculated from absorption spectra of oriented films of NR-P3HT and blending mixture of NR-P3HT and PBTTT.

	DR	A_{0-0}	A_{0-1}	W (eV)
NR-P3HT Pristine	4.6	0.0563	0.1033	0.160
10% PBTTT in NR-P3HT	7.2	0.0591	0.1033	0.148

Previously, we have reported about the formation of aligned fibrous domains like features in NR-P3HT when films were processed with FTM, which were responsible for the optical anisotropy and extended π -conjugation. The nanofibrous domains were well oriented showing clear extended conjugation length confirmed by optical measurement.¹¹ **Figure 5** shows the tapping mode AFM images of the different stoichiometric blends of NR-P3HT and PBTTT. A perusal of the Figure 5(a) clearly corroborates the formation of highly aligned fibrous domains in the pristine NR-P3HT films, however, it exhibits higher roughness giving the idea that the domains of NR-P3HT are highly entangled due to their low regioregularity. Addition of only 10 % PBTTT in NR-P3HT is enough to remove such entanglement between the domains and leading to reduced roughness as shown in the Figure 5(b). Pristine PBTTT itself exhibits very less orientation in this casting condition but play a crucial role for controlling the orientation of blend,³⁰ and increase in

molecular orientation upon the addition of PBTTT (10 %) in NR-P3HT has been already discussed by polarized absorption spectroscopy. At the same time, AFM surface topology for blend film with 80 % PBTTT content exhibits relatively smooth texture (roughness 3.8 nm) as compared to the pristine PBTTT (roughness 5.1 nm). This might associated with presence of relatively amorphous and flexible NR-P3HT as a plasticizer occupying the remaining 3-D space existing between the crystalline domains of PBTTT. This proposal has been well correlated with fact that PBTTT exhibits terrace phase morphology as compared to highly flat surfaces observed with NR-P3HT when spin coated.^{31,49,50}

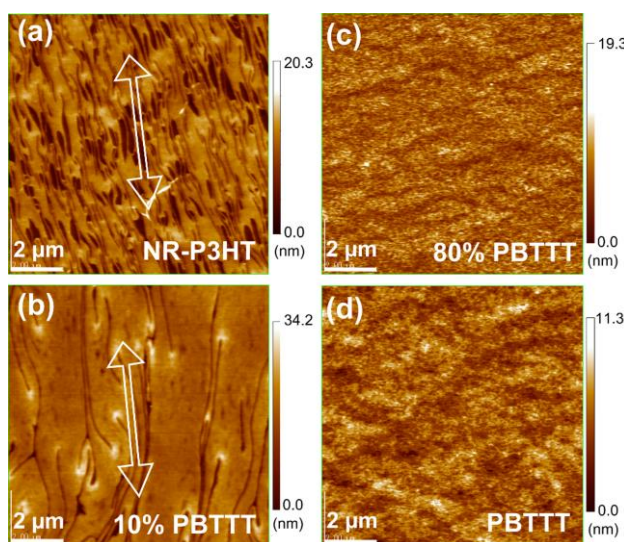


Figure 5. AFM images of FTM films. Pristine NR-P3HT (a), 10 % PBTTT in NR-P3HT (b), 80 % PBTTT in NR-P3HT (c) and (d) Pristine PBTTT. White arrow represents the direction macromolecule orientation as confirmed by polarized absorption spectroscopy.

FTM processed films of pristine NR-P3HT exhibits edge-on orientation with enhanced crystallinity as compared to that of spin-coated films as demonstrated us in our earlier publication.³¹ **Figure 6** shows the out of plane X-ray diffraction of the all of the FTM processed blend films with increasing PBTTT contents in the NR-P3HT. It can be clearly seen that NR-P3HT

exhibits (100) diffraction peak around at 5.3° corresponding to lamella-stacking of its alkyl-side chains representing the edge-on orientation as shown in Figure 1 (a).³¹ The decrease of its intensity upon addition of PBTTT is attributed to the decrease of its relative extent and presence of this diffraction peak is rather more important to decide the microstructure. However, as can be seen that peak at 5.3° still exists in the presence of PBTTT up to 10%. Disappearance of this peak in the presence of higher extent of PBTTT might be associated with the disruption of the alkyl-stacking of NR-P3HT. On the other hand, diffraction peak (100) at 4.04° starts to appear for PBTTT with the addition of PBTTT ($\geq 25\%$) in NR-P3HT. This clearly represents that films microstructure in these films are governed by the NR-P3HT up to 10% PBTTT and after which peak at 5.3° disappear and only peaks corresponding to the alkyl d-spacing of PBTTT at 4.04° appear prominently^{9,49}. Based on the XRD pattern observation of the blend films it could be concluded that majority of crystalline domain formation in microstructures are governed by the PBTTT and NR-P3HT exists as oriented amorphous phase like and play an important role to connect these separated crystalline domains.

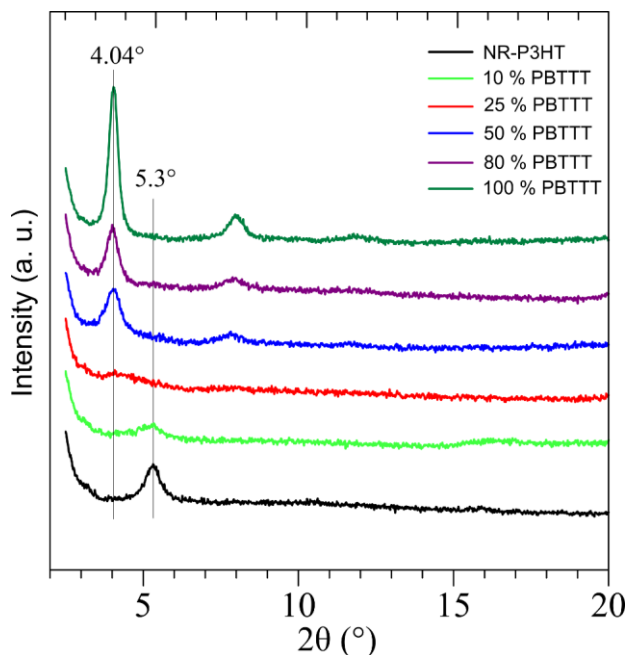


Figure 6. Out-of-plane X-ray diffraction pattern of FTM films with increasing amount of PBTTT in NR-P3HT.

Charge transport properties of NR-P3HT and PBTTT blend thin films were investigated by fabricating bottom gate top contact OFETs. We probed the transport characteristics along the \parallel and \perp to the orientation direction of the polymer. Charge transport in isotropic films were also investigated by spin coating the corresponding blend fractions. The evolution of μ in different configurations along \parallel (μ_{\parallel}), \perp (μ_{\perp}) and spin coated (μ_{sc}) is shown in **Figure 7** (a). As can be seen from **Figure 7** (a), FTM films of NR-P3HT exhibits much improved μ_{\parallel} (> 2 orders of magnitude) as compared to its μ_{sc} , as reported earlier also.¹¹ At the same time, it has also been reported in the literature that spin-coated thin films of PBTTT exhibits rather low μ in the range of ($\sim 10^{-3}$ cm²/V.s) and get pronounced (~ 0.1 cm²/V.s) when heated to its liquid crystalline temperature around 150 °C.⁴⁹

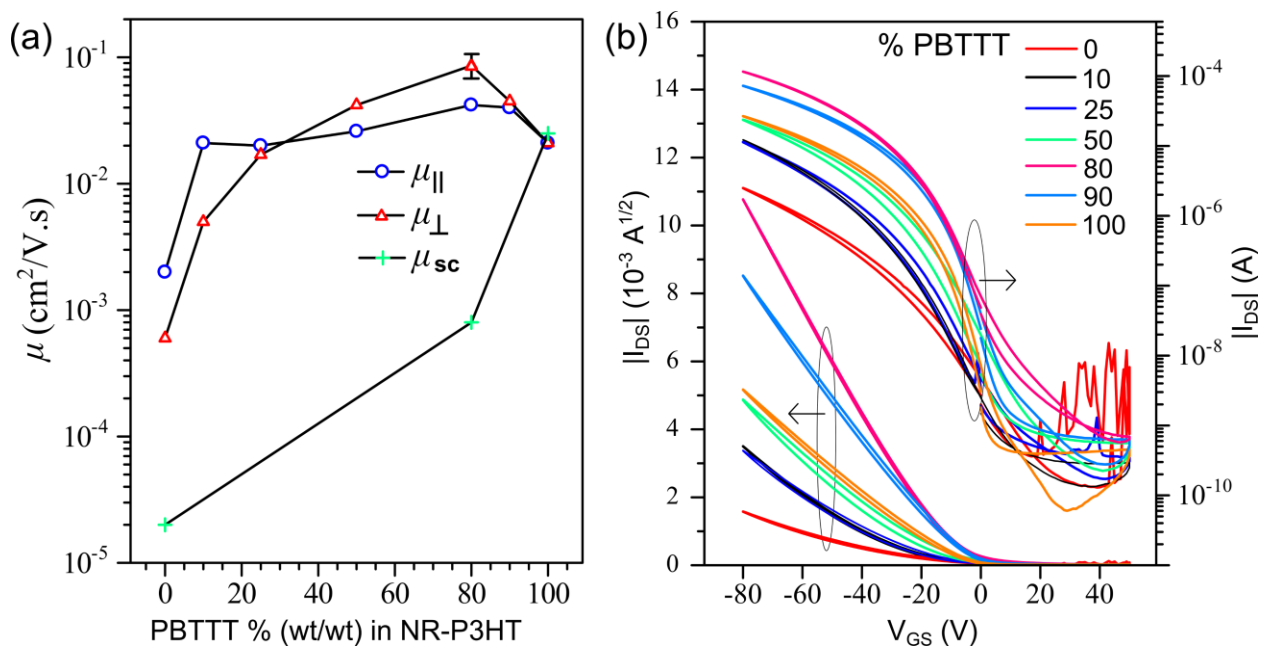


Figure 7. (a) Evolution of μ in bottom-gate top-contact OFETs prepared in blending mixture of NR-P3HT and PBTTT. The μ measured along \parallel and \perp to the orientation direction of the polymer

is $\mu_{||}$ and μ_{\perp} . prepared by FTM. (b) Transfer characteristics of OFETs with increasing amount PBTTT in NR-P3HT having FTM films with orientation \parallel to the channel direction ($V_{DS} = -80$ V). The μ_{sc} in (a) represents the μ in isotropic films prepared by spin coating.

This can be seen from the **Figure 7(a)** that addition of small amount (only 10%) of PBTTT increased the $\mu_{||}$ of FTM processed NR-P3HT films up to $0.02 \text{ cm}^2/\text{V.s}$, which is nearly similar to the $\mu_{||}$ of pristine PBTTT films fabricated by FTM under ambient conditions without any high temperature annealing. The possible reason for such synergistic improvement in the $\mu_{||}$ due to the enhanced orientation exhibited by NR-P3HT having 10% PBTTT as described in polarized absorption spectroscopic investigation, where the DR of 4.6 of NR-P3HT was increased up to 7.2. This pronounced $\mu_{||}$ is also in well agreement with the AFM image where addition of small amount of PBTTT reduces the roughness present in the oriented NR-P3HT films, concomitantly decreased entanglement between the domains of oriented NR-P3HT film. This approximately 8-fold increment in $\mu_{||}$ also suggests that the fibrous domains in NR-P3HT films are capable of very high intra-domain carrier transport and PBTTT as guest macromolecules further facilitates the transport process owing to its very high inter-domain transport. Interestingly, upon further increase in the fraction of PBTTT ($> 25\%$) there was enhancement in the $\mu_{||}$ and μ_{\perp} with respect to the pristine PBTTT as well as NR-P3HT. However, it was found that there is uneven distribution of increment in $\mu_{||}$ and μ_{\perp} as can be seen from the **Figure 7(a)**. The average $\mu_{||}$ at high percentage of PBTTT continues to increase and at 80% the increment in this is about 2 times higher ($0.042 \text{ cm}^2/\text{V.s}$) than that of average $\mu_{||}$ of pristine PBTTT. This can be easily understood from the perusal of transfer characteristics of the \parallel OFETs fabricated with the blend films of NR-P3HT and PBTTT with varying stoichiometric contents as shown in the **Figure 7(b)**.

It is worth to note that unlike RR-P3HT, PBTTT in general exhibits small electrical anisotropy ($\mu_{\parallel}/\mu_{\perp}$) in spite of having high optical anisotropy due to the different structures of grain boundaries and domain boundary limited transport.^{51,52} Therefore, origin of $\mu_{\parallel}/\mu_{\perp}$ in blend due to PBTTT must be negligible as the DR exhibited by pristine PBTTT is very less (Figure 2c). As can be seen from **Figure 7(a)**, for PBTTT rich blends $\mu_{\perp} > \mu_{\parallel}$, blends having 80% contents of PBTTT have shown average μ_{\perp} of 0.086 cm²/V.s with maximum value of 0.11 cm²/V.s exhibiting an increase of almost 5-fold when compared to that of pristine PBTTT. On the other hand, as summarized in Table 2, when same blend fraction having 80% PBTTT as well as pristine PBTTT were spin coated, they exhibited μ_{sc} of 7.0 x 10⁻⁴ cm²/V.s and 0.025 cm²/V.s (Figure S4, Supporting Information). The possible reason for this observed low μ_{sc} in the blends could be attributed to the amorphous and randomly oriented chains of NR-P3HT and connection between the crystalline domains of PBTTT controlling the inter-chain transport as reported previously.¹¹

Table 2. Device parameters (mobility and I_{on}/I_{off}) for different device configurations using different blends of NR-P3HT and PBTTT along with pristine films.

	μ (cm ² /V.s)			I_{on}/I_{off}	
	μ_{\parallel}	μ_{\perp}	μ_{sc}	\parallel	\perp
Pristine NR-P3HT	0.002	0.0006	0.00002	$\sim 10^4$	$\sim 10^2$
10% PBTTT	0.021	0.005	—	$\sim 10^5$	$\sim 10^3$
80% PBTTT	0.042	0.086 (Max. 0.11)	0.0008	$\sim 10^6$	$\sim 10^6$
Pristine PBTTT	0.021	0.021	0.025	$\sim 10^5$	$\sim 10^5$

To the best of our knowledge, this synergistically improved μ in the PBTTT is highest reported so far where no annealing was conducted to their liquid crystalline phase transition temperatures. Reported values of μ_{sc} for PBTTT based OFETs in this range ($0.1 \text{ cm}^2/\text{V.s}$) have only been reached by processing the substrates with octyltrichlorosilane (OTS) followed by the subsequent annealing of the films to the different phase transition temperatures of around $180 \text{ }^\circ\text{C}$ and $275 \text{ }^\circ\text{C}$.^{49,51} Basically OTS treatment of the substrate has been chosen to increase the hydrophobicity of the substrates and when heated on OTS substrates it forms larger domains due to dewetting.⁴⁹ Such increase in the grain size due to annealing decreases the inter-domain resistances offered to the charge carriers to travel from source to drain.^{49,50} It is also worth to mention here that such an enhancement in the OFET performance is possible without compromising with the off-current characteristics and increase in on-current which increases the on-off ratio.

Evolution of V_{TH} along the || direction with different blends shows similar trends to that of orientation (Figure S5, Supporting Information). It was found that there is slight negative shift in the V_{TH} for 10% PBTTT. The possible reason for such negative shift could be associated with their increased orientation, since we have previously reported that highly oriented NR-P3HT exhibits negative shift in V_{TH} as compared to the spin coating.¹¹ Positive shift of V_{TH} observed for further addition of PBTTT can also be correlated with decrease in orientation characteristics as more random film morphology leads to positive shift in V_{TH} which is also reflected in transfer characteristics of spin-coated films too (Figure S4).¹¹ Such characteristics of effective control on threshold voltage in blends of spin-coated films have also been published by other research groups.³² It is worth to note here, that devices were exposed to air atmosphere and their measurements were carried out one by one. Therefore, the possibility of gate bias stress in these

OFETs cannot be ignored, which results in undesirable changes in the transistor characteristics associated with charge trapping.⁵³ However, since the devices were made/measured over the span of months, this obvious trend of V_{TH} observed in this case cannot ignore the role of orientation. However, understanding this behavior more explicitly needs detailed investigation, which is beyond the scope of our present work.

Figure 8 shows the output characteristics || OFETs fabricated utilizing different thin films of the blends consisted of NR-P3HT and PBTTT processed by FTM. Except stoichiometric ratio of NR-P3HT and PBTTT all other device fabrication parameters have been kept constant. A perusal of the output curves clearly reveals p-type charge transport characteristics with well saturated output currents. A Clear higher order of magnitude in output current can be easily seen in the output characteristics in all of the blend system based devices as compared to their corresponding films casted by each of the respective pristine materials.

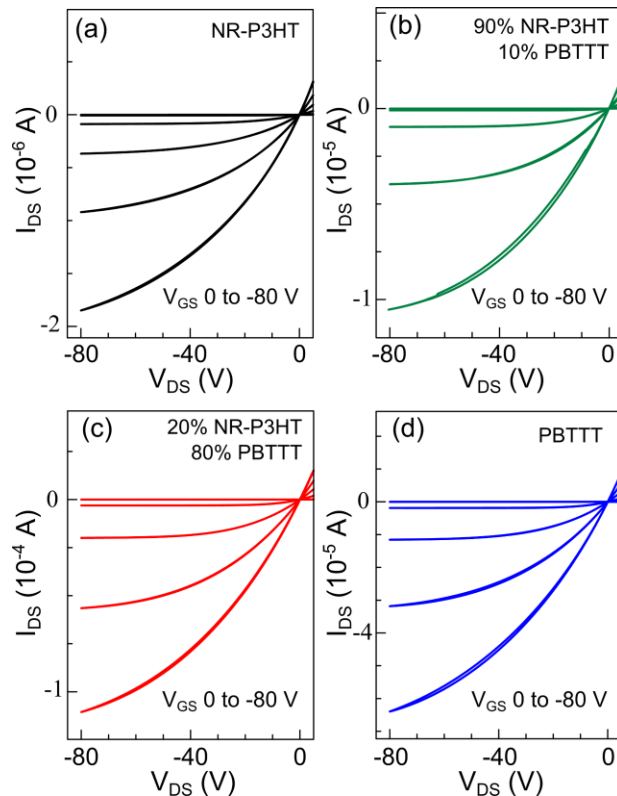


Figure 8. Output characteristics of parallel OFETs. (a) Pristine NR-P3HT, (b) 10% PBTTT in NR-P3HT, (c) 80 % PBTTT in NR-P3HT and (d) Pristine PBTTT.

Figure 9 depicts the schematic representation of two schemes for the synergistic improvement in the OFET characteristics upon blending PBTTT in NR-P3HT. Scheme 1 is related to the improvement of μ when 10% of PBTTT was added in NR-P3HT and this model is well correlated to the above explanation given for improved orientation as shown in **Figure 3**. In this case, presence of small fraction of highly crystalline PBTTT decreases the entanglement present in domains of NR-P3HT as reflected in the AFM images (**Figure 4**). Firstly, the presence of such crystalline material in amorphous oriented films of NR-P3HT not only leads to increased orientation of NR-P3HT by decreasing entanglement. Secondly, they act like a high transport bridge between the domains of the NR-P3HT owing to the high inter-molecular transport. Scheme 2 is proposed in order to explain the improved transport in blend films consisting of higher PBTTT contents (80%) in NR-P3HT. As shown in polarized absorption spectra and AFM images too, these FTM films of blend do not exhibit relatively higher molecular orientation, therefore, orientation present is mainly contributed by the NR-P3HT domains with extended π -conjugation length. Such macromolecules in the domains exhibit a lot of mechanical flexibility to adjust them in to 3-D space of the FTM film, as it was also well reflected in Figure. 4. Possibly this NR-P3HT domains must be filling the vacant spaces between highly crystalline domains of PBTTT and thereby synergistically improving the μ . It has been well accepted that in the case of oriented conjugated polymers, μ in parallel direction is generally higher as compared to its perpendicularly oriented counterparts. Interestingly, a perusal of Figure 7(a) indicates that perpendicular μ or either same or a bit higher than that of their corresponding parallel oriented counterparts especially for the blend films having PBTTT contents in NR-P3HT are $> 25\%$. Although exact reason is not

completely clear but this could be associated with the collective effect of inter-domain and intra-domain carrier transport. Since PBTTT is in higher extent, inter-domain transport is expected to play a dominant role. Contrary to this, NR-P3HT has relatively higher tendency of orientation in the parallel direction, therefore, charge transport in this direction should be governed by hopping through both of the PBTTT and NR-P3HT domains as schematically shown in the Figure 9. Since NR-P3HT exhibits relatively lower electrical conductivity, it will offer higher resistance towards the charge carrier transport in parallel direction.

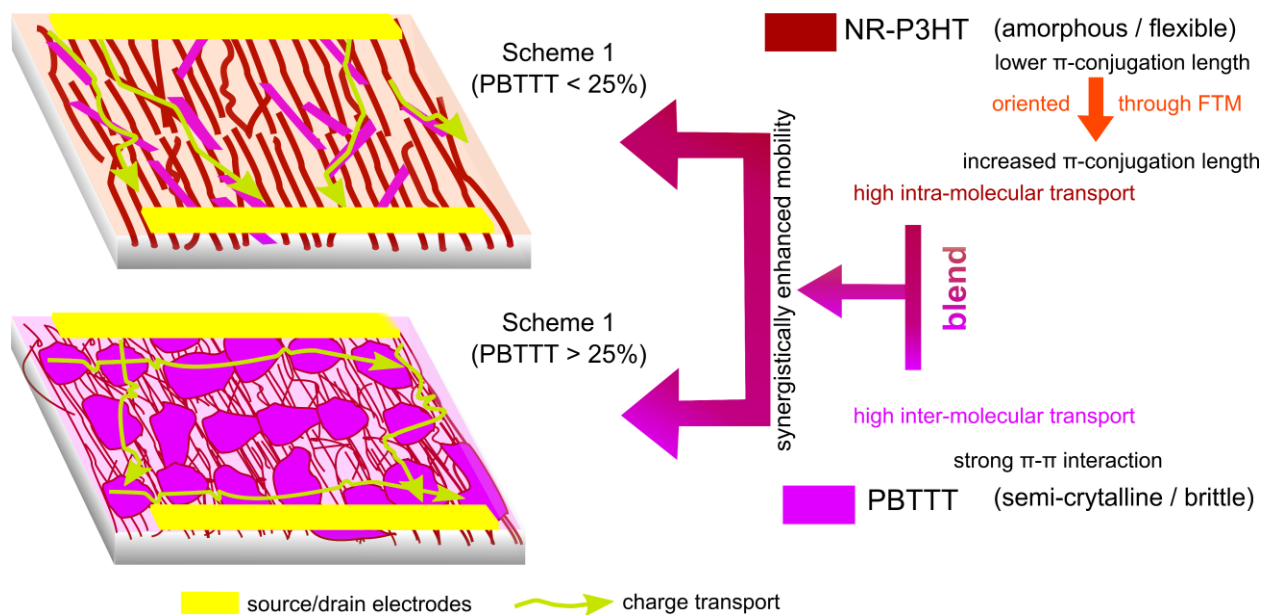


Figure 9. Schematic illustration showing the possible anisotropic charge carrier transport. Scheme 1 is for (PBTTT < 25%) and Scheme 2 is (PBTTT > 25%). Direction of the carrier transport has been shown by green arrows.

It can be argued that whether the charge transport in this present blend system is energetically favorable or not. It has been reported that ionization potential (IP) PBTTT (5.1 eV) is about 0.3 eV lower as compared to P3HT under similar experimental conditions.⁵⁴ It means holes induced within the channel after negative gate bias application in both of the NR-P3HT as

well as PBTTT can be easily injected in to Au electrode. At the same time, holes from PBTTT have another pathway of the transport via NR-P3HT also which is energetically favorable. Device stability is another important criterion for the practical applications. PBTTT has been widely reported as air stable CP owing to its relatively lower IP having stability of 600 h at relative humidity of 4% even for non-encapsulated devices.⁵⁴ However, stability can also be enhanced either by encapsulation or adopting the top gate device architecture.¹⁶ Although, we have not evaluated the long term device stability but it is expected that our blend system should exhibit improved device stability as compared to NR-P3HT. This is attributed to the fact that IP of the blend of two materials lies in between the component CPs and varies nearly linearly as a fraction of blending.³² Therefore, in this present case of blend of NR-P3HT and PBTTT, the IP of the blend should always be lower than NR-P3HT hence device stability should practically be improved.

Conclusion

In conclusion, utilization of FTM as a facile solution based approach for the fabrication of orientated thin films of blends of CPs have been successfully demonstrated. In order to circumvent the trade-off issues between flexibility and high charge carrier transport, a unique strategy of casting oriented films of blends involving the addition of highly crystalline material (PBTTT) in amorphous NR-P3HT which is susceptible to high molecular orientation has been adopted. An increase in the orientation and effective conjugation length of amorphous NR-P3HT by the incorporation of small (10%) crystalline guest CP is well reflected and supported by optical and microstructural characterization. Addition of only 10% of crystalline PBTTT in the oriented NR-P3HT resulted in to pronounced (8-fold) FET μ of the blend reaching similar value to that of

pristine PBTTT. Employing higher percentage of PBTTT in the blend shows synergistically improved charge carrier transport. Thin films fabricated from the oriented blend of CPs consisting 80% PBTTT led to the improved μ by 5 fold and 33 fold compared to that of pristine PBTTT and NR-P3HT based OFETs, respectively. This field effect μ is 3 order of magnitude higher than that of its corresponding spin-coated device counterparts. Finally, attainment of such a high FET μ ($0.11 \text{ cm}^2/\text{V.s}$) along with high on/off ratio (10^6) for oriented blends of PBTTT (80%) and NR-P3HT (20%) fabricated under ambient conditions without annealing to higher liquid crystalline phase temperature ($> 150 \text{ }^\circ\text{C}$) provides a novel strategy for fabrication of the room temperature solution processable OFETs towards the potential applications in the area of next generation flexible electronics.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge. Polarized absorption spectra of oriented FTM films having guest as PFO, Normalized Absorption Spectra of NR-P3HT and PBTTT Blend, Transfer characteristics of spin coated, Variation of threshold voltage of OFET, Variations in film thickness of different FTM film.

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Notes

The authors declares no competing financial interest.

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TOC Graphic

