Facile fabrication of large area oriented conjugated polymer films by ribbon-shaped FTM and its implication on anisotropic charge transport

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Abstract

Facile fabrication of large area (> 20 long and > 2 cm wide) uniform and oriented thin films of a variety of conjugated polymers (CPs) with minimal material wastage been successfully demonstrated using our newly developed ribbon-shaped floating film transfer method (FTM). Under an identical film fabrication conditions of FTM like hydrophilic liquid substrate consisted of ethylene glycol and glycerol (3:1), temperature of 60°C and polymer concentration 1% (w/w) in chloroform, order molecular orientation was found to be PQT-C12>F8T2>NR-P3HT>PBTTT-C14>PTB7. Depending on the nature of polymeric backbone, CPs exhibited differentia optical anisotropies in their oriented thin films, which was explained in terms of nature and rigidity of polymeric chains in the light of persistent length. Organic field effect transistors fabricated using these CPs exhibited clear p-type behavior and anisotropic charge transport. Amongst various CPs used, PQT-C12 not only exhibits highest optical anisotropy (DR = 5.1) but also highest anisotropic

charge transport ($\mu_{\parallel}/\mu_{\perp} = 7.1$). Ribbon-shaped thin films of PQT-C12 prepared by ribbon-shaped FTM exhibited best device performance with a charge carrier mobility 5.0×10^{-2} Cm^2/Vs and ON/OFF ratio of 10^6 when films were oriented parallel to the channel direction. Interestingly, mobility of parallel oriented thin films prepared by FTM was about two orders of magnitude higher compared to the devices OFETs fabricated using conventional spin coating (6.7×10^{-4} cm^2/Vs).

Introduction

Utilization of conjugated polymers (CPs) and their semiconducting properties for the application in various technological fields like solar cells, organic light emitting diodes and organic field effect transistors (OFETs) make them strong contender amongst organic semiconductors in the area of organic electronics [1-2]. CPs can be functionalized by main chain and side chain substitutions [3-4], which facilitates solution processing and various types of applications [5-7]. Intrinsic one dimensionality and extended π-conjugation of CPs make them susceptible to molecular self-assembly in condensed state. In molecular self-assembly attainment of ordered structure is driven by the different interactions like hydrogen bonding, hydrophobic, electrostatic, van der Waals and π-π stacking etc. Controlling the molecular self-assembly in order to get ordered structure is one of the requirements for providing the high-performance to optoelectronics devices. Alignment of CPs has been reported for enhancing the charge transport, polarized luminescence and electroluminescence [8-11]. At the same time, molecular alignment CPs support in-plane transport owing to the planarity of π-conjugated backbone leading to high-performance in organic OFETs [10]. A number of techniques like mechanical rubbing[12], friction transfer [13], high temperature rubbing [14], drawing [15], strain alignment [16] and solution flow [17] etc. have already been used for the alignment of the CPs. Although these techniques have been found to impart molecular orientation but intriguing problems like mechanical damage, static charge accumulation, solubility of the under layers, material wastage and lack of multilayer formation have to be solved amicably. Apart from these, they use shear force providing face-on orientation, which not much suitable for planer devices like OFETs. On the other hand, deposition of thin film through polymeric solution with slow solvent evaporation result in to thermodynamically favored edge-on orientation, which is highly essential for in-plane charge transport in the planner devices [18-20].

We have developed a new and low-cost method for the fabrication uniform and oriented thin films on the viscous liquid substrate and named as floating film transfer method (FTM) [21-22]. Orthogonality of the solvents used for the preparation of liquid substrate and solution of CPs are important requirements for thin film fabrication under FTM. Application of a drop of polymer solution with low boiling solvent on an orthogonal liquid substrate leads to fabrication of thin floating film via film spreading and solvent evaporation. Competing processes like evaporation of solvent used for polymer solution and viscous force of liquid substrate provide molecular orientation to the floating film. Such floating films can be easily transferred to the desired substrate for further characterization as well as applications. It has been found that film thickness and orientation intensity can be controlled by optimizing film-casting parameters like concentration of the polymer solution, temperature and viscosity of the liquid substrates [23]. Apart from the optimization of film casting conditions during FTM, the nature of the polymeric backbone also plays a dominant role in controlling the molecular orientation and affects the finally attainable optical anisotropies [24]. In order to circumvent issues like non-uniformity and multi-directional film spreading, we have recently reported an improvisation in our conventional FTM [25]. Utilization of a custom-made slider during film spreading for providing directionality to the spreading film in FTM led to the large area (14-20 cm) and highly oriented films formation named as Ribbon- shaped FTM [26].

Present article deals with fabrication and characterization of very large area oriented thin films of CPs using our newly proposed ribbon-shaped FTM. To expedite the investigations pertaining to the nature of the polymeric backbone on molecular orientation, five different CPs (homopolymer and copolymer) belonging to the thiophene family have been taken into

consideration. Molecular orientation in these large areas oriented films have been probed by polarized electronic absorption spectroscopy while anisotropic charge transport has been studied after the fabrication OFETs in the bottom gate top contact device architecture.

2. Materials and Method

Five different CPs such as poly(didodecylquaterthiophene) (**PQT-C12**), poly[(9,9-dioctyl-9H-fluorene-2,7-diyl)-alt-2,2'-bithiophene]-5,5'-diyl)] (**F8T2**), non-regiocontrolled poly (3-hexyl thiophene) (**NR-P3HT**), poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (**PBTTT-C14**) and poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl] (**PTB7**) have been used for present investigation. Chemical structure of the CPs are shown in the Fig. 1.
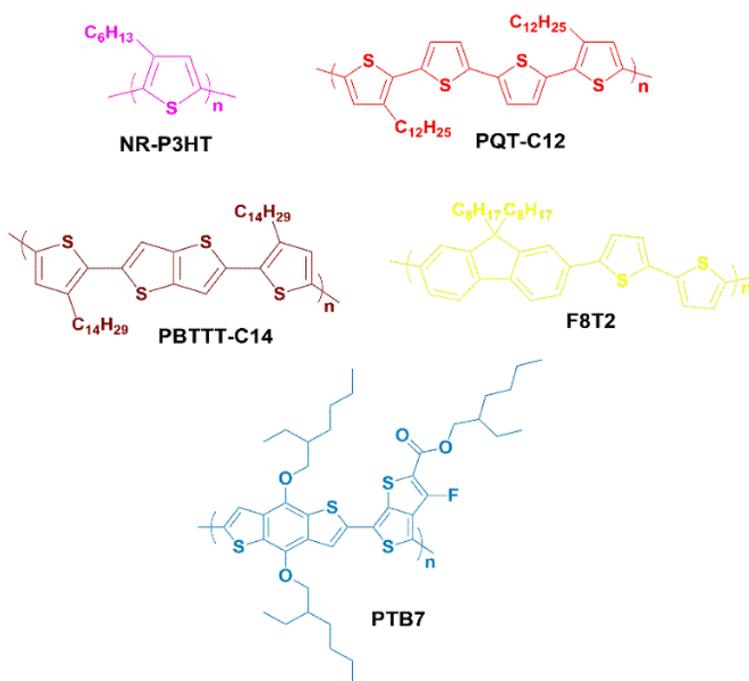

Figure 1. Chemical structure of conjugated polymer utilized for probing molecular orientation and anisotropic charge transport.

NR-P3HT and PQT-C12 were chemically synthesized using FeCl₃ catalyzed oxidative polymerization and purified by soxhlet extraction as per our earlier publications [27-29]. Copolymer F8T2 was synthesized by Suzuki coupling following the method reported by Lim et al [30]. Copolymer PTB7 and homopolymer PBTTT-C14 were obtained from 1-Material and Sigma Aldrich, respectively. Both of these two polymers were used as received without any further purifications. In order to fabricate thin films by FTM, 1 % solution (w/w) of the respective CPs was prepared in the dehydrated chloroform. Oriented thin films of the CPs were prepared using a rectangular tray (23 cm ×15 cm) filled with hydrophilic viscous liquid substrate. The liquid substrate consisted of a binary mixture of ethylene glycol (EG) and glycerol (GL) in the 3:1 ratio. A custom-made slider (PTFE) was placed at one of the longer side of the rectangular tray as schematically shown in the Fig. 2.
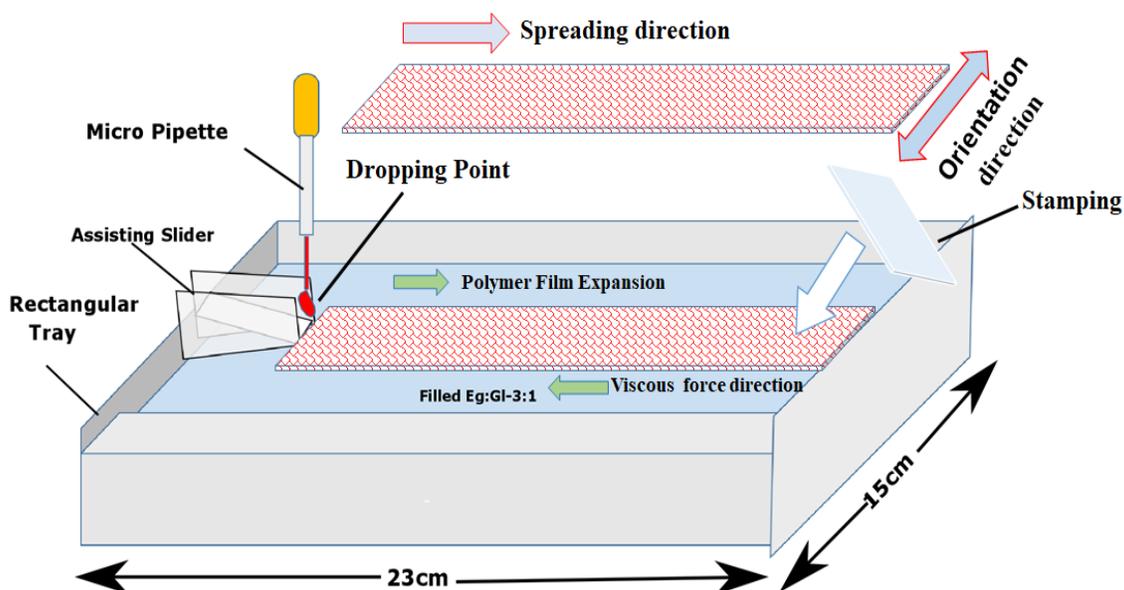

Figure 2. Schematic representation for fabrication of oriented thin film by ribbon-shaped FTM.

About 25 µl solution of respective polymers in dehydrated chloroform was dropped in the center of the slider upon the hydrophilic liquid substrate. Slider assists the spreading of polymer solution in one direction followed by continuous evaporation of chloroform owing to its low boiling point finally leading to large area ribbon-shaped oriented floating film. Film orientation was verified manually by necked eye using a polarizer film and transferred on a glass and Si/SiO$_2$ substrates by stamping for investigations pertaining to the estimation of optical anisotropy and device fabrication, respectively. At the same time, spin-coated films of CPs under investigation were also prepared by using 0.5 % (w/w) polymer solution at spinning speed of 3000 rpm for 120 s to compare their optoelectronic behavior. Polarized electronic absorption spectra were measured by UV-visible NIR spectrophotometer (JASCO-570) attached with Glan Thomson prism. To measure the absorption coefficient, the film thickness was estimated by interference microscope [Nikon Eclipse LV150]. Electrical characterization was made after OFET fabrication in bottom gate top contact device structure using respective CP films fabricated by spin coating as well as FTM. OFET was fabricated upon a highly p-doped silicon having 300 nm of SiO$_2$ insulating layer as a gate dielectric with the capacitance of 10 nF/cm^2. Prior to semiconductor deposition, SiO$_2$ surface was treated with 2 mM solution of octadecyltrichlorosilane (OTS) in dehydrated toluene at 90°C for 2 hours followed by annealing at 130°C for 30 min. to make self-assembled monolayer of OTS on SiO$_2$ surface. 50 nm source and the drain electrodes were then deposited by thermal evaporation at a base pressure of 10^{-6} Torr using Ni as a shadow mask having channel length (L= 20 µm) and width (W=2 mm). Electrical characterization of OFETs thus fabricated was done with computer controlled two-channel source measure unit (Keithley-2612) at pressure of 10^{-3} Torr.

3. Result and Discussion

3.1 Fabricated of oriented thin films CPs by ribbon-shaped FTM

As discussed earlier, orientation intensity in FTM can be controlled by controlling the speed of film spreading and solvent evaporation forming thin film on the viscous hydrophilic liquid substrate. At the same time, extent of orientation and film thickness can also be controlled by controlling the film casting parameters like concentration of the polymer solution along with the temperature and viscosity of the liquid substrate [23]. During FTM, compressive force posed by the viscous liquid substrate and solvent evaporation of polymer solution synergistically assist the molecular alignment. These ribbon shaped films have been found to orient in the tangential direction to the film spreading. An optimized condition such as hydrophilic liquid substrate consisted of EG/GL (3:1), temperature of 60°C and polymer concentration 1% (w/w) in chloroform was found to be optimum for NR-P3HT. Utilization PTFE slider and NR-P3HT, we have recently demonstrated fabrication of very large area (>20 cm long and >2 cm wide), uniform and oriented under ribbon-shaped Film [25]. In order to check versatility of this ribbon-shaped FTM, a number of organic CPs like PQT-C12, F8T2, NR-P3HT, PBTTT-C14 and PTB7 were utilized for the fabrication of thin films. All of the these CPs were subjected to thin film fabrication by under optimized casting condition of NR-P3HT aiming towards implication of nature of polymeric backbone on their optoelectronic properties. Fabricated thin films for various CPs are shown in the Fig. 3. It can be clearly seen from this figure that all of the CPs under investigation form very large area about 2 cm x > 20 cm thin films like a ribbon under FTM similar to that of NR-P3HT as reported by us previously. Observation of these films under polarizer reveals a contrast in the color when polarizer was rotated at 90° indicating that these films are oriented too. Direction of the film orientation was perpendicular to the film spreading direction.
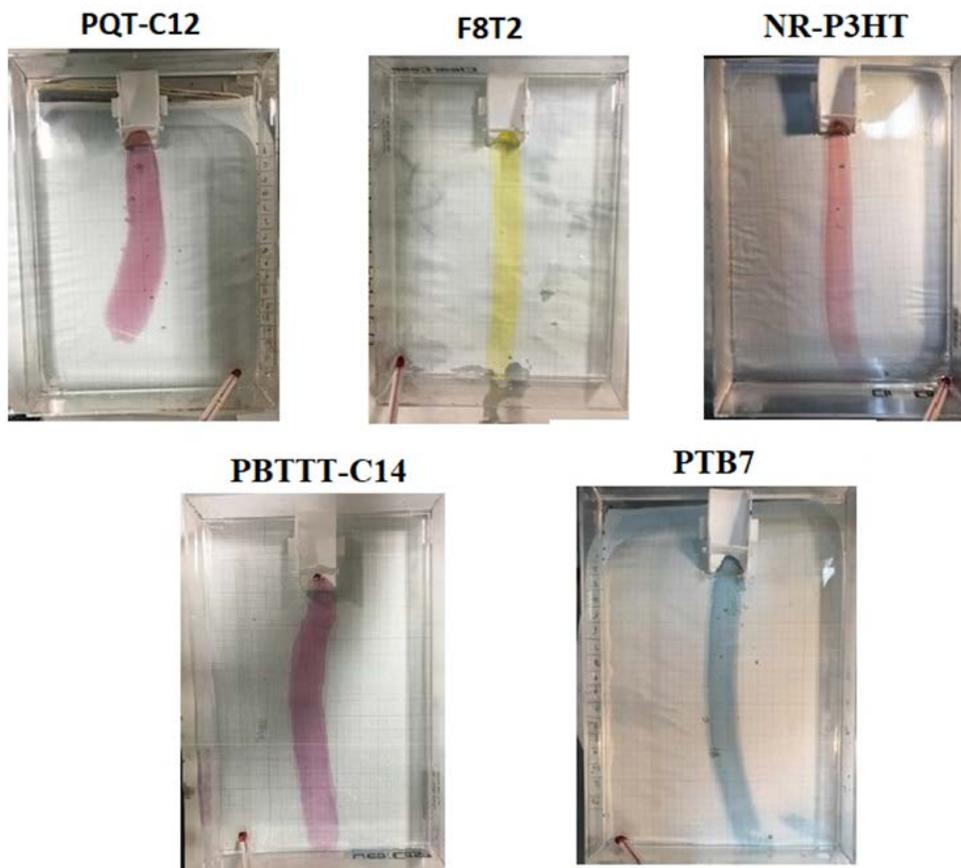
Figure 3. Photographic images of thin films of various CPs fabricated by ribbon shaped FTM under identical casting conditions [liquid substrate-EG: GL (3:1), temperature 60°C, concentration 1 % (w/w) in chloroform]. Relatively dark color shows parallel orientation obtained after rotating the polarizer from 0° to 90°.

Fabrication of homogeneously uniform films is one of the important requirements for utilization of thin film fabrication technology towards their application for devices with high reproducibility. In order to investigate the homogeneity of large area thin films fabricated by ribbon shaped FTM, variation in thickness over centimeter scale was measured by measuring the position dependent absorbance at the respective absorption maximum of the CPs. It is well known

that peak absorbance directly correlates with the thickness, therefore, it was measured using 2-dimensional position scanning of absorbance 1 mm interval. A fixed light source, computer controlled X-Y sample stage and multichannel photodiode array detector were used for the 2-D positional scanning. Results of the 2D-positional mapping of the film uniformity is shown in the Fig. 4. It can be clearly seen that thin films of all of the CPs are highly uniform with standard deviation of (+- * %). Moreover, this film uniformity continues up to cm scale not only in the length but also in the width directions.
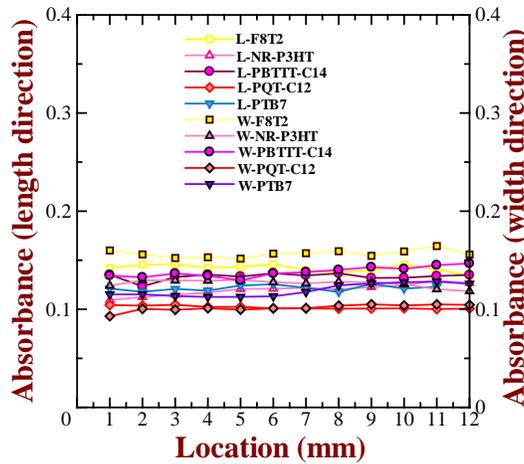

Figure 4. Variation of peak absorption intensity across about 1 cm in the length and width directions for the thin films CPs casted on glass substrate.

3.2 Optical characterizations

3.2.1 Non-polarized electronic absorption spectra

All of the five CPs were first subjected to optical characterization using thin films fabricated by conventional spin coating before the anisotropic optical characterization using oriented thin films fabricated by ribbon-shaped FTM. Solid-state thin film electronic absorption spectra of spin-coated films of CPs under investigation are shown in the Fig. 5 along with summarization of values

of their absorption maxima (λ_{max}) in the table 1. Although all of the CPs belong to the thiophene family but varying absorption spectral features depending the extent π-conjugation.
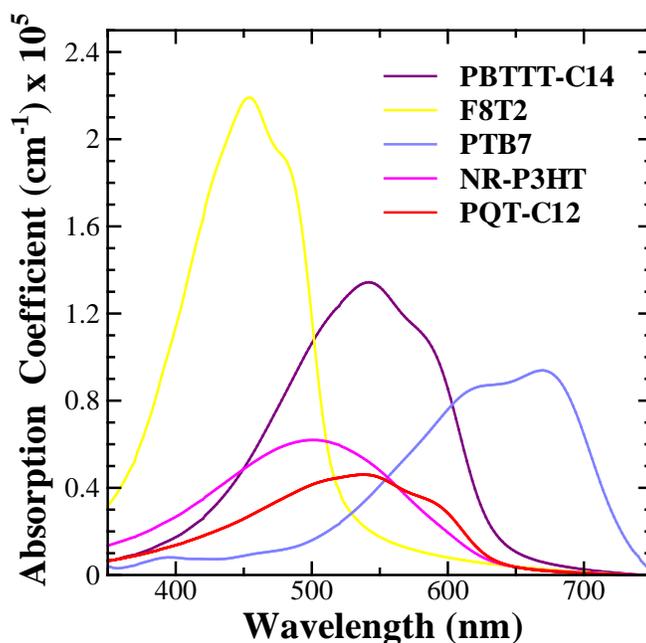

Figure 5. Electronic absorption spectra various conjugated polymers on glass prepared by spin coated method.

Amongst CPs used F8T2 shows most hypsochromically shifted λ_{max} at 454 nm and vibronic shoulder at 482 nm along with highest value of extinction coefficient of 2.27 x 10^5 cm^{-1}. On the other hand, PTB7 exhibits largest bathochromically shifted λ_{max} at 670 nm associated with π-π* electronic transition and vibronic shoulder at 622 nm. Largest extent of π-conjugation in the monomer block along with high planarity is attributed to the observation of larges value of the λ_{max}. Although PQT-C12 and NR-P3HT are structurally very similar but exhibit λ_{max} at 538 nm and 508 nm, respectively. At the same time, we can see a clear vibronic shoulder at 587 nm for PQT-C12 while such vibronic shoulder is absent for NR-P3HT. It is well known that regioregular

P3HT exhibit not only red-shifted λ_{max} but also clear vibronic shoulder due enhanced effective π-conjugation and crystallinity as compared to their non-regiocontrolled counterparts [31]. Therefore, presence of higher extent of regioregularity in PQT-C12 owing to its molecular structure could be responsible for its red-shifted λ_{max} along with clear vibronic shoulder compared to that of NR-P3HT. PBTTT-C14 is a liquid crystalline CP and exhibit λ_{max} at 542 nm associated with π-π* electronic transition along with vibronic shoulder appearing at 586 nm. It is interesting to note that absorption coefficient of NR-P3HT (6.6×10^4 cm^{-1}) is higher than that of PQT-C12 (4.8×10^4 cm^{-1}), which could be explained considering the density or compaction of π-electrons in the polymeric backbone. In an interesting report, Takashima et al have reported that in the regioregular poly(3-alkylthiophenes), absorption coefficients of CPs decreases with the alkyl chain length [32]. Therefore, presence long alkyl chain (dodecyl) in PQT-C12 could be responsible for its lower absorption coefficient as compared to NR-P3HT having relatively smaller alkyl chain (hexyl) substituents. It can be seen that PBTTT-C14 exhibits highest red shift amongst the CPs except PTB7, which is associated with very large effective π-conjugation length and enhanced molecular self-assembly facilitated by its high degree of planarity and presence of fused thienothiophene ring.

3.2.2 Polarized electronic absorption spectra

As mentioned previously, ribbon-shaped FTM not only leads to large area homogeneous thin films but also imparts the molecular orientation. In order to quantitatively analyze the molecular orientation of CPs, oriented polymer films were transferred on to glass substrate and subjected to polarized electronic absorption spectral investigations by measuring the absorbance of the films after rotating the angle of the polarizer at 00° (parallel) and 90° (perpendicular). Figure 5 shows the anisotropic electronic absorption spectra for thin films of PQT-C12, F8T2, NR-P3HT, PBTTT-

C14 and PTB7. At the same time, optical parameters like absorption maxima for parallel/perpendicular orientation, vibronic shoulders and optical anisotropy in terms of dichroic ratio (DR) have been summarized in the table 1. Electronic absorption spectra of PQT-C12 in the parallel orientation exhibits λ_{max} at 547 nm, which is 9 nm red-shifted as compared to non-polarized spin coated film. Apart from red shift, it exhibits vibronic shoulder at 589 nm, which indicates the structural ordering in the condensed state and enhance the π-π stacking [33]. The dichroic ratio $(A_\parallel/A_\perp)$ for this CP was found to be 5.1, which was maximum amongst the CPs used for present investigation.
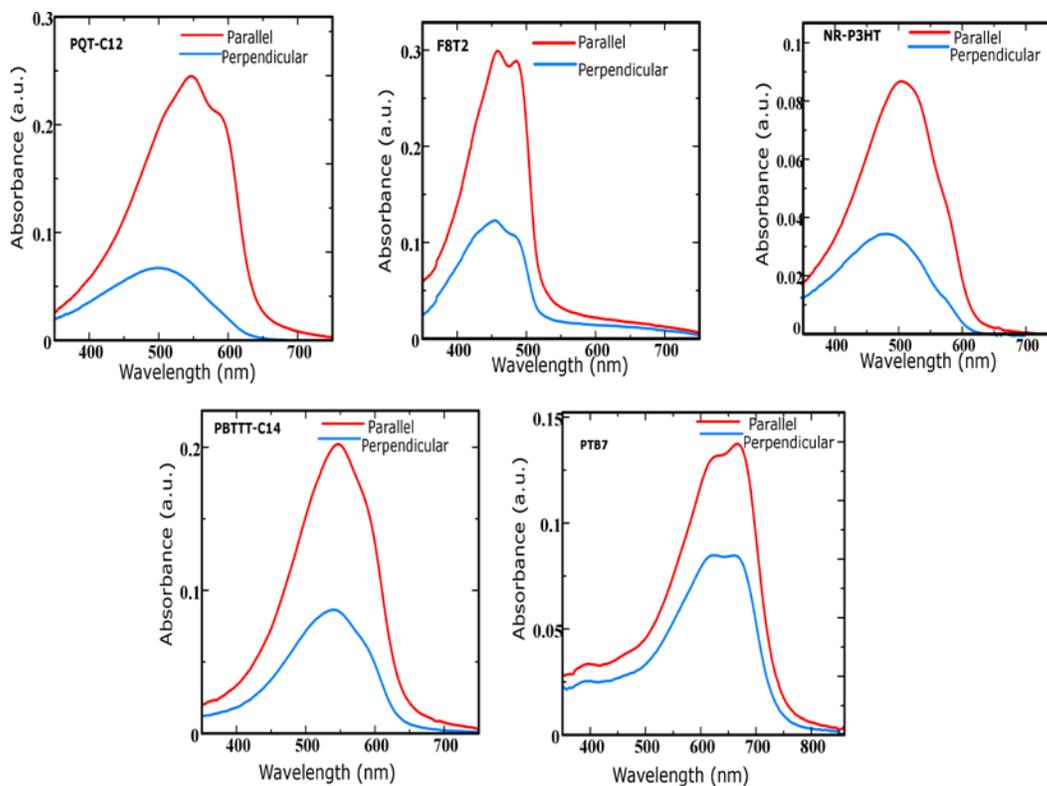

Figure 6. Polarized electronic absorption spectra of oriented CPs on glass substrate prepared by ribbon shaped FTM.

Oriented F8T2 films exhibit an intense absorption associated with shows π-π transition appearing at λ_{max} of 486 nm, which is not only 5 nm red-shifted as compared to spin-coated films but also shows clear vibronic shoulder indicating backbone alignment [11]. Oriented NR-P3HT films exhibited λ_{max} at 520 nm with pronounced red-shift and clear vibronic shoulders at 562 nm and 587 nm, which are very similar to the spectral features of regioregular P3HT and absent in the spin-coated films [27]. PBTTT-C14 shows λ_{max} at 546 nm, which is slightly red-shifted (4 nm) as compared to non-polarized Spin coated films. In spite of molecular rigidity and well known liquid crystalline nature, red-shifted λ_{max} and vibronic shoulder clearly indicates enhanced effective p-electron delocalization in the FTM processed oriented films owing to the applied shear forces during the solidification after film spreading [34-36]. Interestingly, FTM processed PTB7 exhibits nearly similar spectral features as compared to that of spin-coated films and smallest optical anisotropy (DR = 1.7) also supports that polymeric chains are less prone to align further.

A perusal of Fig. 6 and table 1 clearly corroborates that ribbon-shaped FTM is not only able to make large area homogeneous thin films (Figs. 3 & 4) of all of the CPs under investigation but also exhibit optical anisotropy too. Although extent of orientation (represented by DR) is different, which was highest for PQT-C12 and lowest for PTB7. It has been previously reported by us that extent of orientation depends not only on FTM parameters but also on the crystallinity, molecular packing, liquid crystalline behavior and nature of polymeric backbones [23-24, 37]. It has been observed that rigid rod-like crystalline CPs are relatively less prone to orientation under FTM, which can be explained considering the fact molecular orientation is facilitated by viscous dragging force applied during film spreading and solidification on the liquid substrate. This is the

reason why, regioregular (RR) P3HT exhibits relatively small orientation as compared it its non-regiocontrolled NR-P3HT under identical film casting conditions during FTM [**27**].

Tabel-1 Optical parameters for spin coated and ribbon shaped FTM films for various CPs deduced from the solid-state electronic absorption spectra.

Polymer	Film conditions	Absorption Maximum (nm)	Dichroic Ratio (DR)	Vibronic Shoulder (nm)
PQT-C12	Spin Coat	538	5.1	587
	FTM Parallel	547		589
	FTM Perpendicular	502		Absent
F8T2	Spin Coat	454	2.5	482
	FTM Parallel	459		486
	FTM Perpendicular	455		485
NR-P3HT	Spin Coat	508	2.4	Absent
	FTM Parallel	520		602
	FTM Perpendicular	496		Absent
PBTTT-C14	Spin Coat	542	2.2	586
	FTM Parallel	546		594
	FTM Perpendicular	540		590
PTB7	Spin Coat	670	1.7	620
	FTM Parallel	670		624
	FTM Perpendicular	662		618

In an interesting review, Kuei and Gomez discussed in detail about molecular chain conformation of CPs and their implications on the phase behavior and optoelectronic properties

and advocated about the persistent length (L_p) in order to correlate compare the chain conformation of the CPs quantitatively [38]. Actually, L_p is the distance taken by polymeric backbone to bend it by 90° and it smaller value leads to attain flexible coil like conformation while a high L_p represents stiff, rod-like and crystalline polymeric backbone. Using small angle neutron scattering experiments, McCulloch et al reported a small L_p of 0.9 and 1.4 for regiorandom and NR-P3HT, which was much higher for RR-P3HT (2.9) [39]. Therefore, lower value of L_p could be attributed to lower DR under FTM for RR-P3HT reported by us previously and relatively higher for NR-P3HT observed in the present work. At the same time, a L_p value 9.0 and 8.2 have been reported by Zhao et al and Li et al for PBTTT and PTB7, respectively [40]. This indicates that both of these polymers are stiff rigid rod-like and highly crystalline which make them less prone to orient easily during FTM as indicated by their lower values of DR as shown in the table 1. One can argue that in spite of lower Lp for PTB7 (8.2) than PBTTT-C14 (9.0), why it exhibit relatively lower molecular orientation (DR= 1.7) as compared to PBTTT-C14 (DR= 2.2) under ribbon shaped FTM. This can be explained considering the nature of polymeric backbone in to consideration. Although of the PTB7 and PBTTT-C14 both bear fused thienothiophene ring providing enhanced planarity and intermolecular interactions but former has hydrophilic ester group while later has only hydrophobic alkyl chains. We have recently reported that thin films PBTTT-C14 prepared by FTM exhibits edge-on orientation and its hydrophobicity-assisted repulsion from hydrophilic liquid substrate promote this edge-on orientation [41]. Contrary to this, presence of hydrophilic ester group in PTB7 offers attractive interaction of the polymeric main-chain with hydrophilic liquid substrate leading posing hindrance in the orientation leading to drastically reduced DR of 1.7 in the oriented films of PTB7 prepared under ribbon-shaped FTM.

3.4 Anisotropic charge transport

To investigate the effect of molecular orientation on anisotropic charge transport, bottom gate and top contact OFETs were fabricated using thin films of various CPs. Schematic representation of the fabricated OFET is shown in the Fig. 7(a) where, thin film were fabricated by ribbon-shaped FTM along with the spin coating for comparison. In the case of utilization of oriented film for device fabrication, direction of oriented FTM films was first confirmed by polarizer film followed by its transfer on SiO_2/Si substrate in order to assign the orientation. Top source-drain metal contacts were then thermally evaporated using shadow mask by placing the mask in parallel and perpendicular with respect to the orientation direction. Field effect mobility (μ) was calculated from the transfer characteristics when the device reached in the saturation region using the equation 1 as follows:

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

Where, I_{DS}, W, L, μ, C_i, V_{GS} and V_{TH} are, saturated output current, channel width, channel length, charge carrier mobility, capacitance of gate insulator, applied gate bias voltage and threshold voltage respectively. A typical output characteristics as function of varying gate bias voltage for the OFETs using oriented thin films of PQT-C12 fabricated by ribbon-shaped FTM is shown in the Fig. 7(b). It can be clearly seen from the Fig. 7(b) that OFET shows typical p-type semiconducting behaviour since it is being driven upon application of negative gate bias voltages. At the same time, there is pronounced enhancement in the ON current for the OFETs of PQT-C12, when it was oriented parallel to the channel direction.
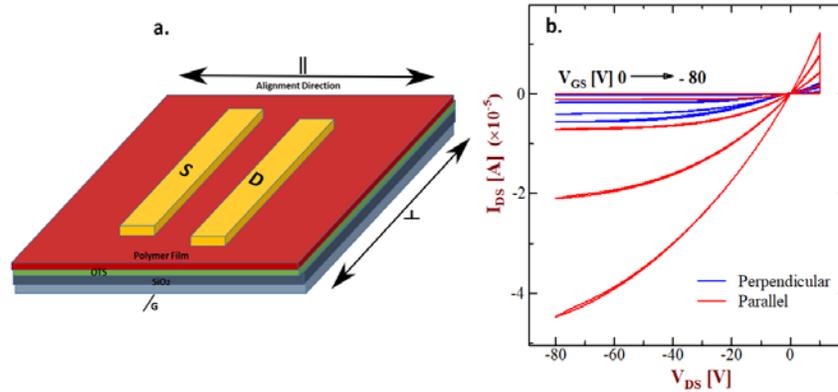
Figure 7. Device architecture (a) and representative output characteristics of OFETs (b) fabricated using parallel and perpendicularly oriented PQT-C12 films at various applied gate bias.

In order to electrical parameters of the OFETs fabricated in this work, cyclic output characteristics ($I_{DS}-V_{DS}$) was utilized to plot transfer curves ($I_{DS}-V_{GS}$) and ($I_{DS}^{1/2}-V_{GS}$) of the OFETs operated at $V_{GS} = -80$ V, which are shown in the Fig. 8. Electrical parameters like μ, ON/OFF ratio, electronic anisotropy etc. deduced from the characteristic curves for all of the CPs along with corresponding isotropic spin coated films (for comparison) have been summarized in the table 2.

Table-2 Anisotropic electrical parameters deduced from OFETs using thin films of different CPs fabricated by ribbon-shaped FTM.

Conducting Polymers	FTM [$\mu_{//}$] ($cm^2.V^{-1}S^{-1}$)	FTM [$\mu_\perp$] ($cm^2.V^{-1}.S^{-1}$)	Spin coated ($cm^2.V^{-1}.S^{-1}$)	($\mu_{||}/\mu_\perp$)	I_{ON}/I_{OFF}	DR
PQT-C12	5×10^{-2}	7×10^{-3}	6.7×10^{-4}	7.1	10^6	5.1
F8T2	1×10^{-3}	7×10^{-4}	2×10^{-4}	1.4	10^4	2.5
NR-P3HT	4.2×10^{-3}	1.2×10^{-3}	1×10^{-5}	3.5	10^4	2.4
PBTTT-C14	7.5×10^{-3}	5×10^{-3}	5.2×10^{-3}	1.5	10^4	2.2
PTB7	1.9×10^{-4}	5.5×10^{-5}	1.1×10^{-4}	3.5	10^3	1.7

A perusal of the transfer characteristics shown Fig. 8 and table 2 corroborates that amongst CPs used PQT-C12 exhibited highest charge carrier mobility of 0.05 cm^2/vs for FTM films oriented parallel to channel direction which was about 7 times higher (7.0 $\times 10^{-3}$ cm^2/vs) as compared to the corresponding FTM films in the perpendicular orientation. An electrical and optical anisotropies of 7.1 and 5.1, respectively, also justifies the implication anisotropic charge transport in the OFETs based on PQT-C12. At the same time, nearly 75 times enhancement in the mobility of parallel oriented PQT-C12 films compared to its spin coated counterparts (6.7 $\times 10^{-4}$ cm^2/vs) portrays the importance of molecular orientation on the highly facile charge carrier transport. Although highest mobility of PQT-C12 in this work is a lower as compared to the benchmark values (> 0.1 cm^2/vs), which could be attributed to optimization of other factors like dielectric interface, molecular weight, polydispersity index, processing conditions and channel length etc. apart from molecular orientation [42]. Parallel FTM oriented F8T2 exhibits although about 5 times higher mobility as compared to its corresponding spin coated films but it is lower than the reported mobility of high performance OFETs (4.3 x 10^{-2} cm^2/vs) for this material by Endo et al [43]. This high mobility was reported for highly anisotropic F8T2 films (DR>10) achieved after thin film fabrication under stringent conditions like annealing at its very high liquid crystalline temperature of 280°C and rubbing alignments. On the other hand, large area ribbon-shaped FTM films fabricated in this work under ambient condition without any high temperature treatments with moderate carrier mobility justifies its usefulness of our method. NR-P3HT based OFETs exhibited maximum charge carrier mobilities of 4.2$\times 10^{-3}$ cm^2/vs, 1.2$\times 10^{-3}$ cm^2/vs and 1.0 $\times 10^{-5}$ cm^2/vs in parallel oriented, perpendicularly oriented and spin coating films, respectively. This indicates that charge transport in parallel oriented thin films of NR-P3HT was $> 10^2$ times facile as compared to its spin-coated thin film counterparts.
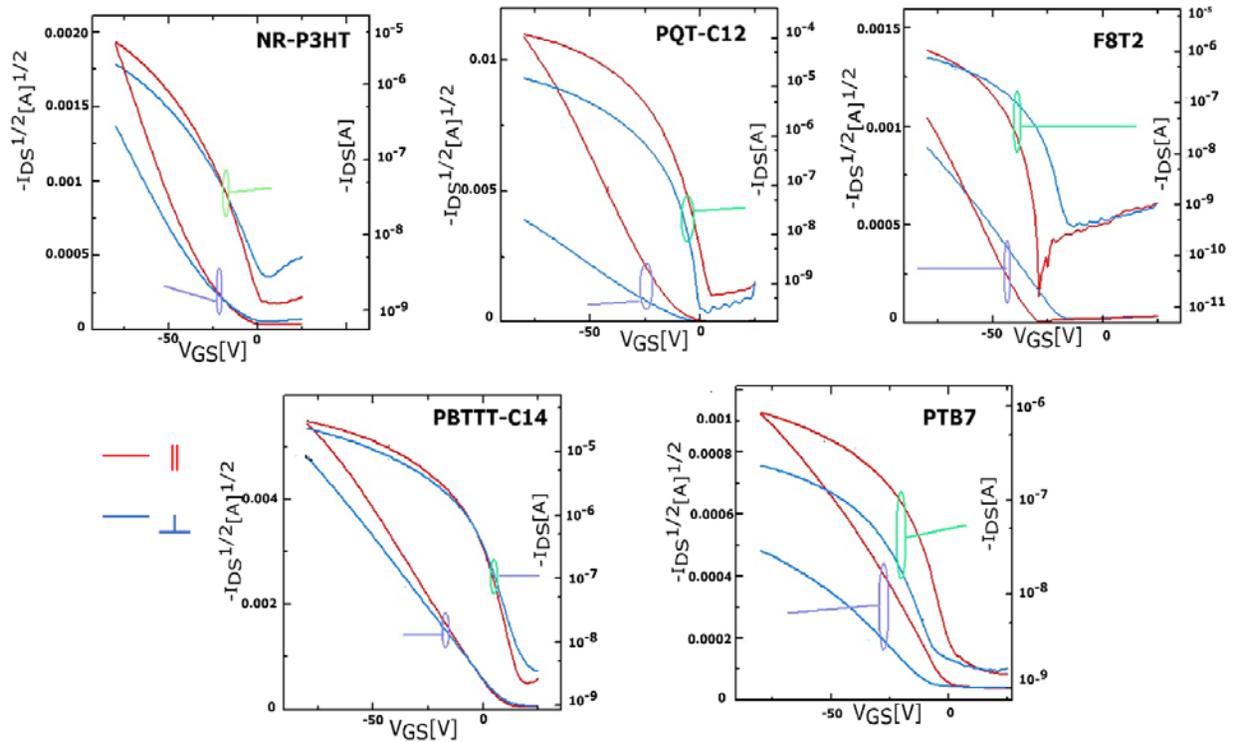
Figure 8. Transfer characteristics of OFETs operated at gate bias voltage of -60 V in parallel and perpendicular orientation for various thin films fabricated using ribbon-shaped FTM.

Charge carrier mobilities in the FTM processed parallel oriented thin films of PBTTT-C14 and PTB7 were slightly higher as than that of their analogous spin coated films and electrical anisotropy follows the trend of optical anisotropy. In spite of large area homogeneous thin films of PBTTT-C14 prepared by ribbon-shaped FTM, mobility of parallel oriented film (7.5×10^{-3} cm^2/vs) was lower than that reported by M. Pandey et al by conventional FTM under optimized condition (0.11 cm^2/Vs) [20]. In this work, similar casting condition was used for the ribbon shaped FTM of all of the CPs in order to structure-property correlation, which might not be optimum of PBTTT-C14, Therefore, lower molecular orientation of this material in the present case might be responsible for hampered value of observed carrier mobility. In line with smallest molecular orientation, parallel oriented FTM films of PTB7 exhibited FET mobility of 1.9×10^{-4} cm^2/vs,

which smallest mobility values observed amongst the CPs used in this work. Although observed mobility is nearly similar to that reported by Xu et al (6.0×10^{-4} cm^2/Vs), smallest value of molecular orientation (1.7) and nearly similar value compared to that of spin-coated film [44] suggest that hindrance in most favorable edge-on orientation owing to its molecular structure could be responsible for hampered charge transport along the channel.

Conclusion

Ribbon-shaped FTM has been successfully used for the fabrication of large area (up to 20 cm in length and 2 cm in width) uniform and oriented thin films. Applicability this technique for homogeneous thin film fabrication was demonstrated using a number of conjugated polymers belonging to polythiophene family. Efficient material utilization during thin film fabrication in ribbon-shaped FTM can be justified considering the fact that by using only one drop (20 µl) of polymer solution, it is possible to fabricate >100 OFETs. Parametric optimization of FTM parameters for a CP is necessary in order to get optimum molecular orientation but under identical casting condition used in this work, order molecular orientation was found to be PQT-C12>F8T2>NR-P3HT>PBTTT-C14>PTB7. Structure-property correlation in terms of polymeric structure and molecular orientation was explained in terms of nature and rigidity of polymeric chains in the light of reported values of persistent length. A clear p-type and anisotropic charge transport was demonstrated by all of the CPs used in this work. Amongst CPs used, PQT-C12 not only exhibits highest optical anisotropy but also highest anisotropic charge transport, best device performance a charge carrier mobility 5×10^{-2} Cm^2/Vs in parallel orientation.

Reference

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