3

Effect of Solvent Additives on OFET Performance

One of the prime goals of the research work undertaken in this thesis is to improve the device performance by enhancing the crystallinity of the active layer. In order to achieve this objective, strategy for active layer deposition has to be reframed. One of the simplest ways to induce the changes in the degree of crystallinity of a solution processed organic semiconductor is the variation in solvents used. Solvents have great capacity to alter the molecular order in the active layer and ultimately device performance. In this chapter, semiconductor films have been prepared using dual solvent scheme and effect of structural dissimilarity between the component solvents on the crystallinity of the final semiconductor film and corresponding device performance is comprehensively studied, which has been recently published [Bharti and Tiwari, 2016].

3.1 INTRODUCTION

Due to their applicability as the active layer in OFETs, organic semiconductors are extensively studied for their properties and processing styles [Sirringhaus *et al.*, 1999, Tiwari *et al.*, 2010, Giri *et al.*, 2011]. One of the properties, which is desirable for superior charge transport, is the crystalline nature of the deposited semiconductor [Coropceanu *et al.*, 2007, Noriega *et al.*, 2013]. Transport of charge carriers occurs in few monolayers of semiconductor film close to dielectric-semiconductor interface and it is strongly affected by the crystallinity of these monolayers [Brütting and Adachi, 2012, DiBenedetto *et al.*, 2009]. These crystalline layers in OFETs lead to improved device characteristics due to the absence of grain boundaries which cause scattering or trapping of the charge carriers [Sirringhaus *et al.*, , 1999, Noriega *et al.*, 2013]. Crystallinity of the semiconductor layer depends on the deposition procedure. For various vacuum grown semiconductors including pentacene, deposition methods to enhance crystallinity are largely explored [Briseno *et al.*, 2006, Zhang *et al.*, 2009, Tiwari *et al.*, 2012]. To improve the crystalline order in a solution processed semiconductor, various schemes including solvent vapor annealing [Dickey *et al.*, 2006], evaporation controlled fluidic channel [Kim *et al.*, 2014], solvent exchange [Balakrishnan *et al.*, 2005, Do Hwan Kim *et al.*, 2007], and dual solvent [Li *et al.*, 2009, Lada *et al.*, 2011, Hwang *et al.*, 2012, Han *et al.*, 2015, Zhao *et al.*, 2015] have been demonstrated. Dual solvent method is one of the effective and simple techniques to control the time of evaporation of the solvent. Evaporation rate of the solvent and the solvation of the semiconductor depend on molecular structure of the solvent additive. When these additives are added in a certain proportion in to the main solvent, these have a great potential to alter the intermolecular forces between semiconductor molecules, solvent molecules and semiconductor-solvent molecules due to preferential solvation [Agmon, 2002]. Various reports are available in literature for TIPS-pentacene OFETs fabricated using dual solvent scheme [Li *et al.*, 2009, Lada *et al.*, 2011, Hwang *et al.*, 2012, Zhao *et al.*, 2015]; however, the crucial role of the nonsolvent additive and its chemical structure in solvation of an organic semiconductor has not been explored in detail till now.

In this chapter, the effect of structural dissimilarity between several additive solvents and the main solvent on the degree of crystallinity of the organic semiconductor film and the performance of the solution processed TIPS-pentacene OFETs has been demonstrated. A systematic approach has been followed to understand the role played by several active

intermolecular forces in the process of solvation of an organic semiconductor which ultimately affects the crystalline order and the resultant device performance. It was found through this study that increasing structural dissimilarity between the solvent additive and the main solvent enhances the molecular aggregation in the semiconductor due to its weaker ability to overcome the intermolecular forces between molecules of the organic semiconductor; eventually resulting in increased degree of crystallinity, and improvement in device characteristics (field-effect mobility in saturation up to 0.15 cm^2 V^{-1} s^{-1}) [Bharti and Tiwari, 2016].

3.2 SOLUTION DYNAMICS AND SOLUBILITY ANALYSIS

It is important to understand the process of formation of a solution and role played by various intermolecular forces in the solvation of a material. Molecules of a material are held together due to variety of intermolecular forces (such as London dispersive forces, dipolar interactions, hydrogen bonding etc.). In solids and liquids, these forces are relatively stronger. Generally, a smaller amount of a material (the solute) is mixed with a larger amount of the other material (the solvent) in order to form a solution. There are three types of intermolecular interactions in a mixed state of solute and solvent; solute-solute, solvent-solvent and solute-solvent. Levels of all these intermolecular forces in the solution are controlled by the affinity of the solvent for solute molecule. In addition, many significant properties of the final solution and the film formed depend on solute-solvent affinity [Strobl, 2013]. The affinity of a solvent for a solute can be calculated using Hansen's solubility theory [Hansen, 2007]. ∂_d, ∂_p, and ∂_h, are the three Hansen's parameters signifying dispersive, polar and hydrogen bonding component of the intermolecular forces. The role of various intermolecular forces in the determination of the solubility of a solute in a specific solvent is very critical. Hansen's solubility theory can also be pictorially represented in form of Teas graph, a graphical solubility analysis using fractional solubility parameters. Various solvents can be relatively positioned in the graph depending on their solubility parameters, whereas each solute can be represented with a solubility window. The solvents appearing within the solubility window are expected to dissolve the solute. Solvents well in the center of the window are better solvents then the others lying elsewhere in the window. Solute is marginally soluble and non-soluble in solvents which lie on the boundary and outside the solubility window respectively.
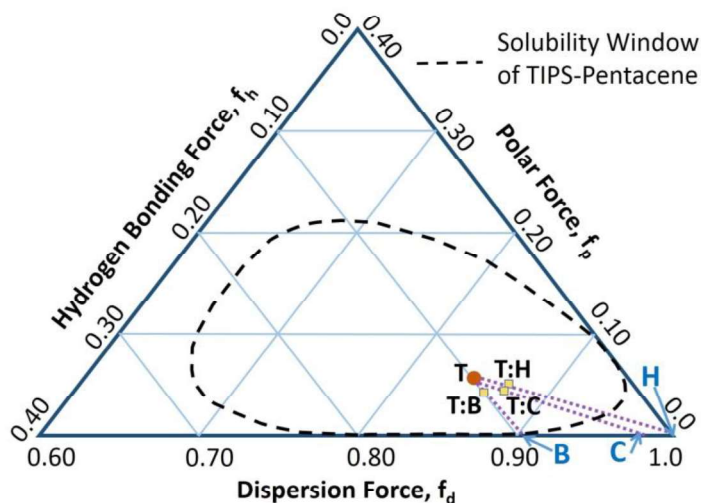

Figure 3.1: A representation of the solubility analysis on Teas graph. Dashed line represents solubility-window of TIPS-pentacene. Various solvents and binary solvent mixtures have been indicated on the graph as H (hexane), C (cyclohexane), B (benzene), T (toluene), T:B (toluene\benzene), T:C (toluene\cyclohexane), and T:H (toluene/hexane).

Figure 3.1 shows Teas graph with solubility window of TIPS-pentacene and relative position of various solvents used. Hexane, which is a nonpolar aliphatic hydrocarbon and having only weak dispersive intermolecular forces, is present in the extreme right bottom of the graph (denoted by H). Cyclohexane, a nonpolar cyclic hydrocarbon, also having weak dispersive forces is present in the right bottom corner of the graph (C). Toluene and benzene, polar and nonpolar aromatic hydrocarbon respectively having relatively larger components of the other two parameters are present farther from the corner (denoted as T and B respectively). Binary mixtures have also been marked on the graph using appropriate methods [Burke, 1984]. As pure hexane and cyclohexane lie outside the solubility window of TIPS-pentacene, these chemicals are pure non-solvent of TIPS-pentacene. Toluene being a good solvent lies inside the window whereas Benzene being a marginal solvent lies on the boundary of the window. All the binary mixtures lie inside the window hence dissolve TIPS-pentacene. A good solubility is expected, if the solvent and solute have similar values of all three Hansen solubility parameters [Lada *et al.*, 2011]. The mismatch in the solubility parameters (R_S) of solute and solvent can be obtained from following equation.

$$R_S = \sqrt{\Delta\partial_d^2 + \Delta\partial_p^2 + \Delta\partial_h^2} \qquad (3.1)$$

Hansen's solubility parameters for TIPS-pentacene have been established by solubility tests [Abu-Sen *et al.*, 2014]. A larger R_S from TIPS-pentacene signifies a lesser solubility. Table 3.1 lists the solubility parameters for various solvents used here and TIPS-pentacene. By observing the values of solubility parameters from the table, it can be deduced that toluene and binary mixture of toluene/benzene are good and almost similar solvents for TIPS-pentacene. However, binary mixtures of toluene/cyclohexane and toluene/hexane are relatively poor solvent systems for TIPS-pentacene due to larger R_s values.

Table 3.1: Hansen's solubility parameters for several solvents and TIPS-pentacene. All the dual solvents have a mixing ratio of 80:20 (v/v).

Solvent/Material	Hansen's Solubility Parameters (M Pa)$^{1/2}$			Mismatch from TIPS-Pentacene (R_S)
	∂_d	∂_p	∂_h	
Toluene	18.00	1.40	2.00	2.04
Benzene	18.40	0.00	2.00	1.69
Cyclohexane	16.80	0.00	0.20	3.96
Hexane	14.90	0.00	0.00	5.32
Toluene/Benzene	18.08	1.12	2.00	1.90
Toluene/Cyclohexane	17.76	1.12	1.64	2.33
Toluene/Hexane	17.00	1.12	1.60	2.78
TIPS-Pentacene	18.80	0.40	3.60	NA

To predict the properties of the resulting organic semiconductor film, understanding of the action of solute-solute, solvent-solvent and solute-solvent intermolecular interactions in absence and presence of additives at various stages of solution formation are desired. Figure 3.2 demonstrates the solution formation process in absence or presence of additives. The relative

height of the arrow indicates the relative strength of the force. In Figure 3.2(a), TIPS-pentacene (solute) and toluene (solvent) molecules are shown in an unmixed state. In this case, solute-solute intermolecular forces are stronger than solvent-solvent forces and there are no solute-solvent interactions at this point. In Figure 3.2(b), TIPS-pentacene and Toluene molecules have been shown in a just-mixed state. In order to form a solution, solvent molecules should be separated from each other. These separated solvent molecules should be able to overcome the intermolecular forces in the solute and surround the solute molecule to form a solvation shell [Hertz, 1970]. With time, Individual interactions between toluene and TIPS-pentacene molecules gradually get weakened and interactions between TIPS-pentacene and toluene molecules becomes stronger. Figure 3.2(c) shows a stage where a solvation shell is formed with very strong interactions between TIPS-pentacene and toluene molecules. At this point, interaction between TIPS-pentacene molecules is not favorable due to presence of highly interacting toluene molecules resulting to a net repulsive force between two TIPS-pentacene molecules. This repulsive force may be felt over range of at most a few solvent molecules neighboring the TIPS-pentacene [Strobl, 2013]. In figure 3.2(d), solvation of TIPS-pentacene is shown with hexane as additive. In the presence of non-solvent (hexane) molecules, toluene molecules are not able to decimate the attractive solute-solute intermolecular interactions resulting to a lesser repulsive force between TIPS-pentacene molecules. An enhanced interaction between TIPS-pentacene molecules is possible in this situation compared to the case of pure toluene, eventually promoting a higher degree of molecular aggregation and better crystallinity in the resulting films.
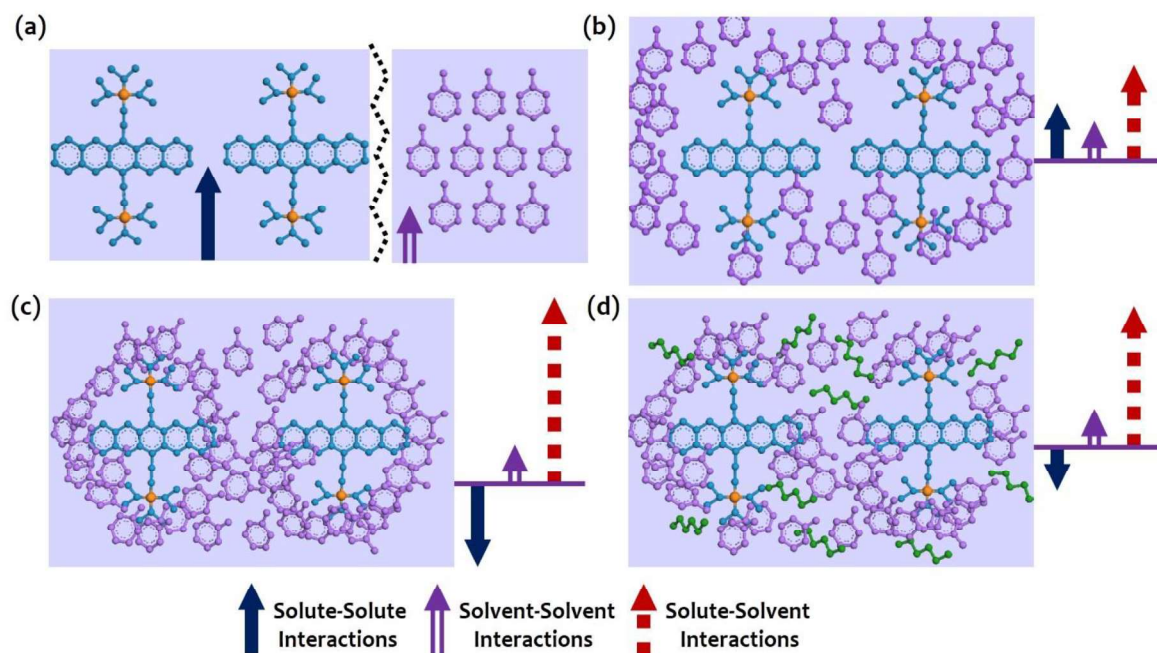

Figure 3.2: A Schematic representation of TIPS-pentacene solution formation. Solute-solute, solvent-solvent, and solute-solvent intermolecular forces are represented by solid, double-lined and dotted arrows respectively. Height of the arrow indicates relative strength of the force. Arrow pointing down indicates attractive forces whereas a down pointing arrow signifies repulsive forces among molecules. **(a)** TIPS-pentacene and toluene in an unmixed state. **(b)** TIPS-pentacene and toluene just mixed with each other. **(c)** Solution is formed with very strong interactions between TIPS-pentacene. **(d)** A solution in the presence of hexane (non-solvent). The presence of non-solvent molecules causes a lesser repulsive force among TIPS-pentacene molecules.

3.3 EXPERIMENTS

OFETs were fabricated in bottom-gate top-contact architecture on highly doped (n-type) Si substrates with a 300 nm thick layer of SiO_2 (C_{ox} = 11 nF/cm^2). Substrates were cleaned by heating and ultra-sonication in solvents of 2-propanol, tri-chloro-ethylene and methanol respectively for 15 minutes each. After cleaning with solvents, substrates were washed in ample amount of de-ionized water, and were dried in a nitrogen blow. TIPS-pentacene solutions (1.0 wt.%) were prepared in toluene, toluene/benzene, toluene/cyclohexane, toluene/hexane solvents with toluene/additive volume ratio of 80/20. Solutions were stirred for 3 h at 70 °C. Solutions were then dispensed on the cleaned substrates inclined at a small angle (~5°). For slow solvent evaporation and to provide a solvent rich environment, substrates were covered with a petri dish. To remove any solvent residuals, substrates were heated at 80 °C after solvent evaporation. 200 nm thick source-drain contacts of Au were deposited under a high vacuum of 10^{-6} torr using shadow masks. The widths and lengths of crystals joining source and drain contacts were considered as W and L of the OFET. Figure 3.3 shows the molecular structure of several solvents used and the OFET device structure. All the solution preparations and sample processing steps were performed in dark and ambient conditions.
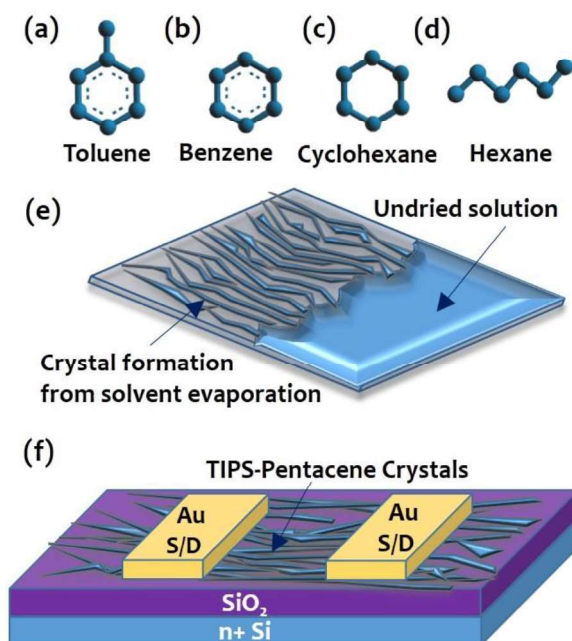

Figure 3.3: Molecular structures of various solvents; toluene **(a)**, benzene **(b)**, cyclohexane **(c)**, and hexane **(d)**. **(e)** The solvent evaporation behavior of TIPS-pentacene drop cast solution. **(f)** Device structure of a bottom-gate top-contact TIPS-pentacene OFET.

3.4 FILM AND DEVICE CHARACTERIZATION

Optical micrographs and AFM images of the resulting crystals obtained by drop casting from different TIPS-pentacene solutions are shown the Figure 3.4. These films contain crystals of very large dimensions with length up to 8000 μm and width up to and 1000 μm. General terracing structure of TIPS-pentacene crystal was confirmed by the AFM images, as also demonstrated by others [Diao *et al.*, 2013, Kim *et al.*, 2014]. The terracing structure of crystals obtained from toluene/benzene solution was similar to that achieved from pure toluene, which was expected from similar values of Hansen's parameters and mismatch in R_S values. Identical molecular interactions in these two cases result in identical terracing structures, which are also confirmed by the similarity of AFM images in Fig. 3.4(e) and (f). As the dissimilarity of the structure of the additive from the main solvent (cyclohexane and hexane) increases, more

irregularities in the terracing structure of TIPS-pentacene are seen. This irregular terracing structure indicates unequal amount of intermolecular forces between molecules of TIPS-pentacene, toluene and the additive.
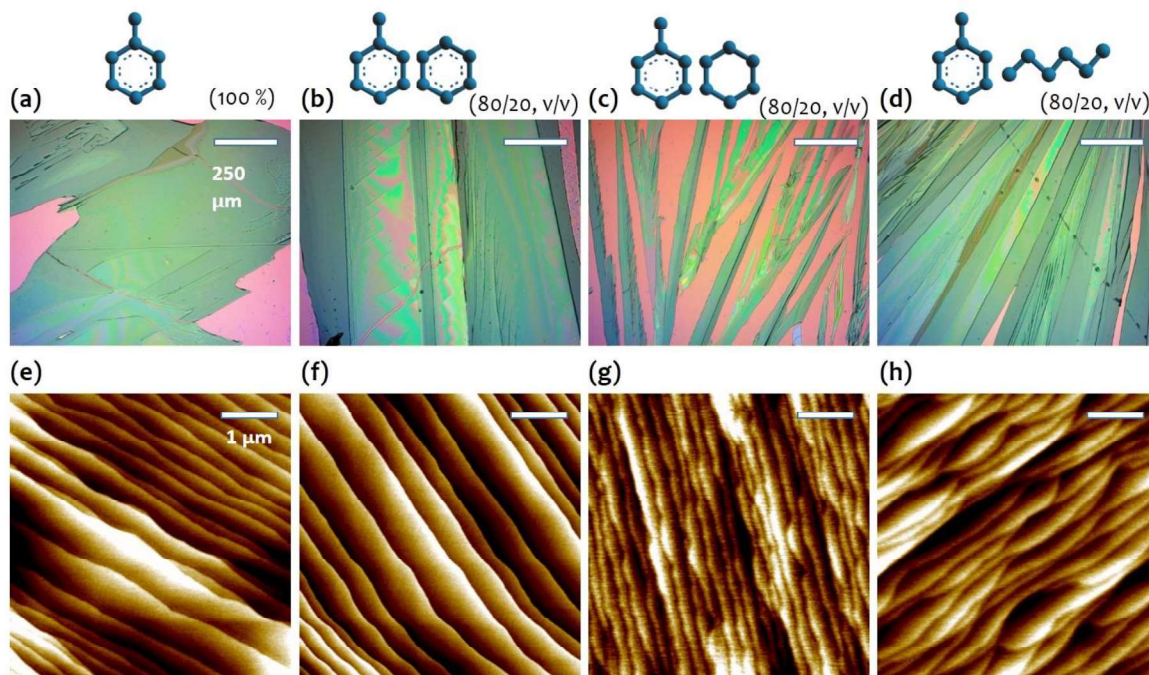

Figure 3.4: Optical micrographs and surface morphologies of TIPS-pentacene crystals obtained by solutions of toluene **(a) & (e)**, toluene/benzene **(b) & (f)**, toluene/cyclohexane **(c) & (g),** and toluene/hexane **(d) & (h)**. Similar surface morphologies of the crystals in the image (e) and (f) confirm similar behavior of the toluene and toluene/benzene solutions. As the dissimilarity between the additive and the main solvent rises, more irregularities in the terracing structure can be observed.
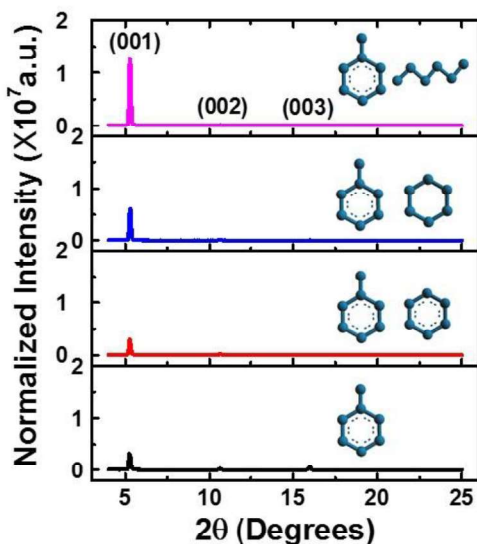

Figure 3.5: X-ray diffractograms for TIPS-pentacene crystals obtained from several solutions. An additive solvent with higher dissimilarity has the least ability to surmount the intermolecular forces between TIPS-pentacene molecules, which causes a higher degree of crystallinity.

Solutions formed using pure toluene and binary mixture of toluene/benzene do not support TIPS-pentacene nucleation well due to strong intermolecular interactions between solvent molecules and TIPS-pentacene, and weaker interaction between TIPS-pentacene molecules. However, as the solvent additive changes from benzene to hexane, nucleation of

TIPS-pentacene increases due to improving interaction among TIPS-pentacene molecules eventually resulting in better crystallinity [Li *et al.*, 2009]. These conclusions are well supported by 1D GIXRD measurements, which are shown in Figure 3.5.

X-ray intensity values are normalized with the ratio of average crystal height and width, to take sample dimension and grain size into account. These XRD patterns reveal that the crystallites obtained from the binary solvent system of toluene/hexane have the highest crystallinity. Films obtained from only toluene solvent exhibited the distinct (002) and (003) peaks. However these peaks emerge due to nonselective crystal growth along these planes. For toluene/hexane film, preferential crystal growth happens along a single (001) plane due to better molecular aggregation. To support these claims with a quantitative measure of degree of crystallinity, integrated intensity ratio and full width at half maximum (FWHM) was calculated. The integrated intensity ratio, $\Phi_{(00l)}$, for a diffraction peak corresponding to (00l) plane is defined by following equation;

$$\Phi_{(00l)} = \frac{I_{(00l)}}{I_F} \quad\quad\quad (3.2)$$

Where $I_{(00l)}$ represents the integrated intensity of the (00l) peak and I_F represents the integrated intensity of the entire X-ray diffractogram. Integrated intensity is determined by calculating the area under the diffraction peak or the X ray diffractogram. Integrated intensity ratio for (001) peak, $\Phi_{(001)}$ were found to follow a rising order with the values of 0.52, 0.54, 0.69 and 0.72 for the crystallites obtained from solutions with toluene, toluene/benzene, toluene/cyclohexane and toluene/hexane respectively. FWHM for (001) peak in toluene/hexane was found to be 2.27×10^{-3} rad as compared to 2.72×10^{-3} rad for toluene only case which also indicates higher degree of crystal growth than toluene only case. A higher and lower value of integrated intensity ratio and FWHM respectively confirm a higher crystalline order in the former case. Table 3.2 summarizes the (001) integrated intensity ratio, full width at half maximum (FWHM), crystal width and height of semiconductor crystals.

Table 3.2: Summary of parameters obtained for TIPS-pentacene crystals and corresponding OFETs.

Solvent	$\Phi_{(001)}$	(001) Peak FWHM (10^{-3}Rad.)	Crystal Width/ Height (µm)	μ_{max} (cm^2 V^{-1} s^{-1})	μ (cm^2 V^{-1} s^{-1})	V_{TH} (V)	I_{ON}/I_{OFF}
Toluene	0.5188	2.72	324±295/ 2.38±0.53	0.05	0.03 ±0.02	6.6 ±4.1	10^3-10^4
Toluene/ Benzene	0.5372	2.67	372±220/ 2.68±1.1	0.05	0.03 ±0.01	1.8 ±1.5	10^4-10^5
Toluene/ Cyclohexane	0.6880	2.34	310±158/ 1.79±0.72	0.03	0.023 ±0.004	6.6 ±5.5	10^4-10^5
Toluene/ Hexane	0.7231	2.27	338±91/ 1.33±0.43	0.15	0.065 ±0.054	7.9 ±7.6	10^4-10^5

Figure 3.6 shows the electrical characteristics for the OFETs obtained by different solutions of TIPS-pentacene. Table 3.2 summarizes the electrical parameters extracted from multiple devices of each type. μ_{max} represents the maximum mobility in saturation regime. The integrated intensity ratios, μ_{max}, and average μ, are also given in bar chart (in Figure 3.7) for all four types of solvents. OFETs with toluene solvent exhibited μ_{max} of 0.05 cm^2 V^{-1} s^{-1} with average of 0.03±0.02 cm^2 V^{-1} s^{-1}. The μ_{max} increased to higher than 0.1 cm^2 V^{-1} s^{-1} for OFETs with

semiconductor films obtained from toluene/hexane solvent due to improved crystallinity, with average μ of 0.065±0.054 cm^2 V^{-1} s^{-1} (9 devices of same batch).
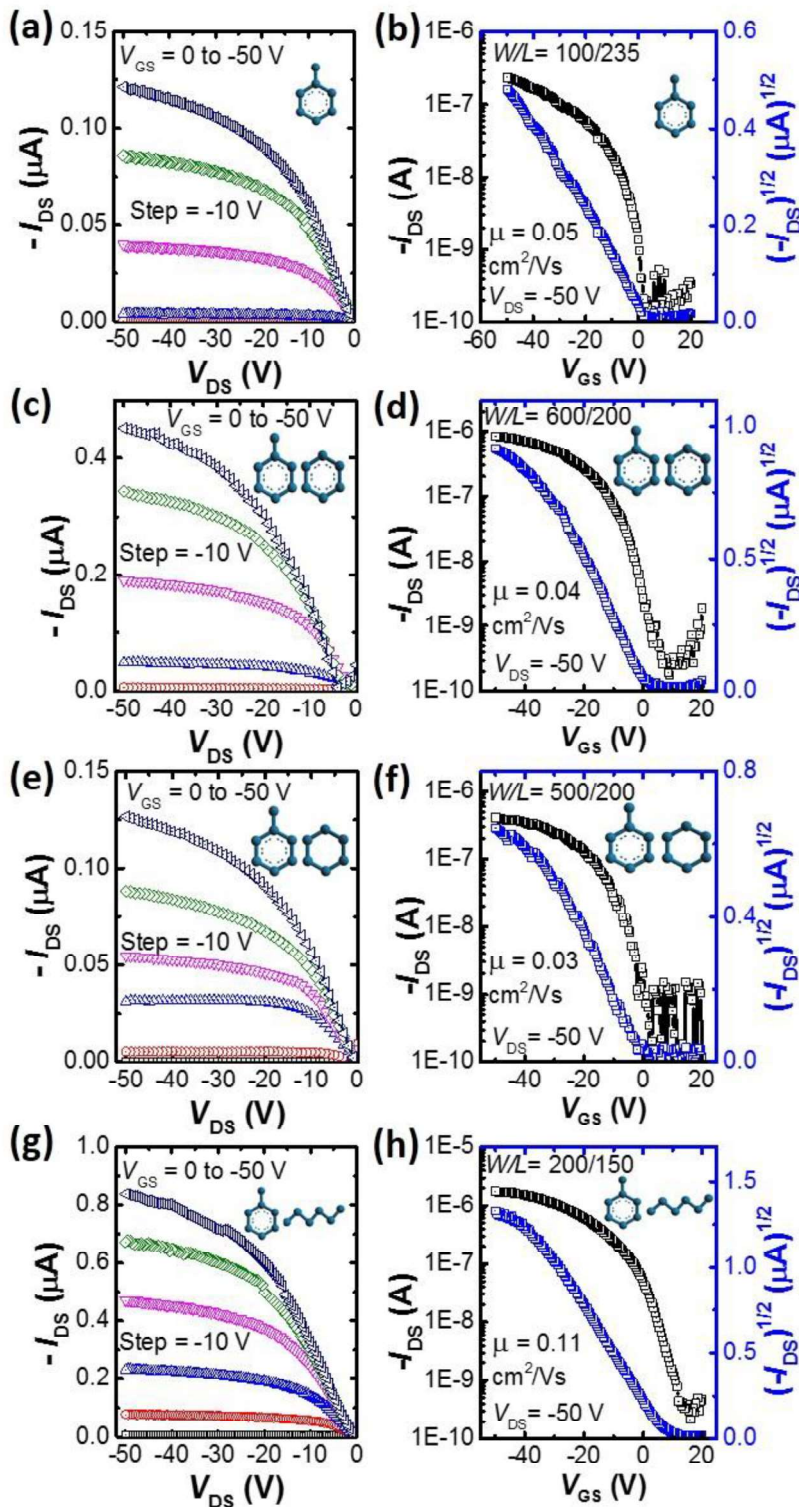

Figure 3.6: Output and transfer characteristics of OFETs obtained from solutions of toluene **(a) & (b)**; toluene/benzene **(c) & (d)**; toluene/cyclohexane **(e) & (f)** and toluene/hexane **(g) & (h)**.

Effect of the addittive solvent in the binary mixture on the crystallinity of the organic semiconductor is very well reflected through the device performance. Average μ for devices

with toluene/benzene solution is very similar to that of toluene, i.e. 0.03 ± 0.02 cm^2 V^{-1} s^{-1}. As the crystallinity increases, μ increases, except for solutions made with toluene/cyclohexane where the crystallinity did not reflect well in device performance in terms of average value of μ (0.023 ± 0.004 cm^2 V^{-1} s^{-1}), probably due to relatively smaller size of crystals and the discontinuity between them. This discontinuity between crystals prevents a uniform channel between source and drain, decreasing the charge carrier mobility for this case [Lee *et al.*, 2010]. However, a systematic trend was observed in overall from solution formation to crystallinity and performance of OFETs.
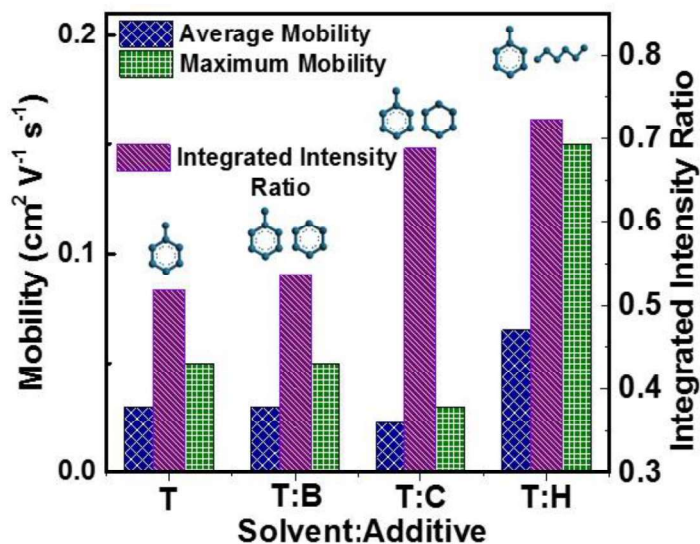

Figure 3.7: Variation in the field-effect mobility and integrated intensity values for OFETs fabricated using various solvents.

3.5 CONCLUSIONS

In this chapter, effect of structural dissimilarity between the additive solvent and the main solvent on the semiconductor solution formation, degree of crystallinity of the resultant crystallites, and final device performance of the organic semiconductor TIPS-pentacene was studied in detail with toluene as the main solvent and benzene, cyclohexane, and hexane as additive solvents. Hansen's solubility theory suggested that toluene/hexane mixture was poorer solvent of TIPS-pentacene than other combinations due to higher dissimilarity between component solvents. A weaker solvent system supports better molecular aggregation leading to higher degree of crystallinity in the TIPS-pentacene crystals. This explanation was well supported by experimental results. The integrated intensity ratio for (001) peak increased with increase in dissimilarity of the additive solvent to the main solvent; improving from 0.52 for toluene to 0.54, 0.69 and 0.72 respectively for toluene/benzene, toluene/cyclohexane, and toluene/hexane. Lower value of FWHM further supported high degree of preferential growth along (001) plane for crystals resulting from toluene/hexane. The field-effect mobility for the OFETs fabricated from toluene/hexane solvent was increased by two times (up to 0.15 cm^2 V^{-1} s^{-1}) compared to that for devices fabricated using toluene solvent due to this improvement in crystallinity.

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