Organic semiconducting polymers (OSPs) received appreciable attention in the past three decades to meet the growing technological appeal in pursuit of sophistication and sustainable development of human civilization. OSPs are known for their striking features of solution-processing compatibility, easy functionalization, and mechanical flexibility, which means they can be processed on low-cost substrates, such as – plastic, paper, and even on our clothes. These unique properties make OSPs suitable for vast applications- from electronic and photovoltaic to gas sensors, energy harvesting, electrochemical and bio-related applications. However, only a few devices like PEC and PLED found their way out from the laboratory level to industries owing to exceptional cost-to-performance ratio. Other electronic devices still lack performance, stability, reproducibility, and competitive operational lifetime. Thus, to make OSP-based devices commercially viable, there are two most suitable approaches: one is to reduce the manufacturing cost, and second, to improve device performance. Developing low-cost and facile processing techniques that facilitate the fabrication of organic devices over large-area substrates without any processing-induced defects is, therefore, the need of the hour. Now, there are two facets in addressing the issues mentioned earlier: understanding the mechanism behind the growth of semicrystals in conjugated polymer thin films through exploring fundamental properties and then utilizing the knowledge to improve the film microstructure and molecular orientation.

Given this, **chapter 1** introduces the organic π-conjugated systems and their fundamentals. It consists of the charge transport mechanism in present state-of-the-art organic devices and challenges in their practical implementations in terms of film fabrication. The detailed description of several approaches from backbone engineering, molecular aggregation, and filler addition to unidirectional molecular orientation aiming towards the realization of

high-performing organic devices has also been described in this chapter with a literature survey. Further, the need for a comprehensive understanding of the OSP semicrystal growth in thin films during the self-assembly process has been discussed in detail with a proper justification for the thesis objectives.

Chapter 2 briefs the utilized materials, preparation of organic semiconducting ink, conventional "*floating-film transfer methods*" (FTMs), the development of novel FTMs through interface engineering, and then organic device fabrication steps. Several characterization techniques viz. Atomic Force Microscopy, X-Ray Diffractometer, Transmission Electron Microscopy, UV-vis spectroscopy, Cyclic Voltammetry, and I-V measurements have also been presented in short.

Chapter 3 explains the mechanism of 'edge-on' oriented semicrystal growth in thin films of OSPs self-assembled at the air-liquid interface in terms of convective Marangoni flow, compressive viscous force, divergent evaporation flux, and high conformational degrees of freedom of OSPs. In this regard, major polythiophene derivatives P3HT, PQT, and PBTTT were collectively employed as model OSPs, and their films were examined using multiple characterization techniques. The degree of paracrystalline disorder along (*h*00) direction and the local in-plane orientation of the polymer chains in crystalline domains along the π–π stacking direction in three different polymer backbone structures have been investigated. Further, the charge transport properties in all three directions (out-of-plane and in-plane viz. along and across the polymer chains) of the thin solid polymeric films using vertical and planar device architectures have been thoroughly studied. By considering the obtained results from different characterizations and all possible flow processes, the exact growth mechanism of these thin films has been proposed in this chapter.

Next, **chapter 4** deals with the engineering at the air/solution interface, utilizing the understanding from chapter 3, aiming towards improving overall film crystallinity. This chapter reports a unified approach harnessing the key advantages of the FTM along with the effect of solvent vapor-assisted controlled evaporation of the solvents to fabricate a high-quality active semiconducting layer for organic field effect transistor (OFET) applications. In this work, rr-P3HT has been used as model OSP, and the fabricated films were thoroughly characterized using several tools to understand the structure-property correlation by exploring the fundamental properties. Oriented thin films thus fabricated exhibited highly 'edge-on' oriented molecular packing with reduced interlamellar spacing, d_{h00}, extended π-conjugation length, and lower exciton bandwidth. Moreover, quantum dot-like aggregated nano-structuring within the crystalline domains forms a network of interconnected conductive pathways, resulting in enhanced field-effect mobility along the polymer backbone, $\mu_{\|} = 0.0498$ $cm^2V^{-1}s^{-1}$, around five times higher than the thin films prepared by conventional FTM.

After that, **chapter 5** reports a novel subphase-modified floating-film transfer method (SM-FTM) harnessing the key advantages of the existing ribbon-FTM along with an interfacial engineering approach for molecular rearrangement in polymer thin films. Dodecyl benzene sulfonic acid (DBSA) has been used to tune the surface energy of the base hydrophilic liquid substrate that alters the molecular backbone stacking proximate to the solution-liquid interface. The molecular arrangements in microcrystalline domains, electronic band structures, and the evolution of surface texture at the solution-liquid interface have been investigated through multiple characterization tools. After that, the electrical performances of Schottky barrier diodes (SBDs) were studied in an ITO/P3HT/AlOx/Al sandwiched structure, and a dramatic enhancement of rectification ratio up to 8.2×10^6 at ±6V was

achieved. Further, an analytical model for SM-FTM, developed using lubrication theory and thin-film dynamics, has also been presented to elucidate the polymer spreading dynamics and the mechanism of molecular rearrangement at the interface.

Chapter 6 presents a band engineering approach, where a synergistic effect between a high-mobility p-type OSP with a rigid backbone, PBTTT, and DPPCN, a NIR dye molecule, has been systematically investigated, aiming towards developing high-performing OFETs and organic phototransistors (OPTs). An optimum percentage (2%) of DPPCN blended/doped in the PBTTT matrix shows improvement in overall film crystallinity, along with an enhanced uniaxial molecular orientation. The optimum hybrid system, PBTTT/DPPCN(2%), shows enhanced average saturation mobility up to 0.2 $cm^2V^{-1}s^{-1}$ compared to 0.16 $cm^2V^{-1}s^{-1}$ in the pristine one. Moreover, the presence of a NIR-sensitive molecule in the system causes the inception of NIR sensitivity in the order of 10^3 and almost one order enhancement in photosensitivity for the red light, ~10^4.

Finally, **chapter 7** summarizes the overall thesis and the future scopes of this research work to meet global technological advancements.