Rapid technological advancements in recent decades have resulted in an increased demand for innovative materials that are not only efficient, but also versatile and sustainable. Organic semiconducting polymers (OSPs), for instance, have come to exploit some exclusive properties- solution processability, mechanical flexibility, and compatibility with low-cost substrates such as plastic, paper, and textiles. Such properties have led to promising applications, ranging from electronic and optoelectronic devices and solar cells to sensors and energy storage systems. Some applications have realized the benefits of the organic-based devices, while others still suffer from limitations in performance and stability. Factors affecting improvement are charge transport, material microstructure, and minimizing operational voltages toward realization of high-performance flexible electronics. Highly oriented thin films are one specific promising strategy to force the molecular structures into sharp alignment, leading towards higher mobility of charge carriers and hence towards stronger efficiency of the whole device. These can bring organic semiconductors closer to commercialization. Another important role is that of the appropriate choice and integration of suitable dielectric materials in ensuring the sustainability of flexibility and low power consumption in organic devices. These new techniques in fabrication and composite materials allow potential improvements in charge transport and stability in operation for more robust and cost-effective technologies. The work developed here explores these ideas in hope of contributing to a better understanding of organic materials and their application in next-generation electronics.

Chapter 1, discusses the very basics of organic π-conjugated systems; particularly their structure, properties, and the mechanisms of charge transport in leading organic devices. Some of the major challenges encountered in the deposition of high-quality organic semiconducting polymer (OSP) thin films are highlighted in the chapter. A number of

strategies designed to address these challenges are brought under discussion, such as backbone engineering, molecular aggregation control, and use of fillers. In addition to this, the thesis also focuses much on special techniques like unidirectional molecular alignment for enhanced performance of devices. This chapter also includes a detailed literature review illustrating the path toward the progress in this field. The importance of understanding for semi-crystalline growth in OSP thin films during self-assembly has also been discussed. This analysis guides me to identify the research objectives in the context of an explicit reason towards advancing the development of high-performing organic electronic devices. The materials and methods that are involved in my PhD study are discussed in detail in **Chapter 2**, It describes the preparation of organic semiconducting ink for various electronics device fabrication. Besides, this chapter discusses the conventional Floating Film Transfer Methods (FTMs) and its modification that led to the development of the Unidirectional Floating Film Transfer Method (UFTM). In addition, the synthesis method of ion-conducting dielectric materials is also discussed. This ion conducting oxide thin film has high areal capacitance and has been used as a gate dielectric of a low operating voltage organic transistor. Some characterization tools are also described in detail and include methods of analysis of film morphology, structure, and electronic properties along with steps in the fabrication of organic electronic devices.

Chapter 3 described the anisotropic carrier transport characteristics of unidirectionally aligned films of poly(4-terthiophen-2-yl-difluorobenzothiadiazole) (P4T2F-HD) that prepared through Unidirectional Floating Film transfer Method (UFTM). This study has been carried out through time-resolved microscopic via optical second-harmonic generation imaging. Through this study I have explored the distinctive charge transport dynamics in different directions of the film which are associated with individual molecular orientations within the material. Direct imaging of the directional dependence of carrier

mobility within the films is enabled in SHG imaging, revealing considerable anisotropy in electronic transport. This method permitted us to observe charge movement in real time and hence make quantitative assessments related to carrier velocity and diffusion along different directions. The findings are indicative of highly directional preference in carrier transport that might be attributed to the molecular orientation and packing within the P4T2F-HD films. This anisotropy is very carefully studied in the context of the electronic structure of the material and molecular orientations in order to have a clear appreciation of all the forces driving charge transport in organic semiconductor materials.

The presented results in **Chapter 3** are opted for the work that is presented in **Chapter 4**. This chapter describes the method of fabrication for ultra-sensitive, flexible organic phototransistors (OPTs) toward advanced wearable and smart home devices. The conventional techniques for the fabrication of OPTs face severe problems mainly arising from the degradation of polymer gate dielectrics resulting from solvents, which significantly impede the device performance. In this regard, the use of a UFTM for the deposition of P4T2F-HD thin films on dielectric film minimized those effects. The phototransistors fabricated through this technique exhibited desirable enhancements where sensitivity equals 167%, with very high responsivity of 292 AW^{-1}, and detectability of 8.5 $\times 10^{13}$ Jones under the illumination strength of 125 μWcm^{-2}. Additionally, these devices demonstrated excellent robustness: they possessed sound performance at a long time and were capable of withstanding cyclic bending in both parallel and perpendicular orientations relative to the channel. The research illustrates the potential of the UFTM to enhance OPT functionality and durability toward real applications in flexible electronics.

Organic phototransistors are out of competition for portable electronics that requires the reduction of the operating voltage of the transistors. **Chapter 5**, deals with the development of low-voltage ($\leq$ 2.0 V) near-infrared (NIR) sensitive organic phototransistors (OPTs)

using the economical UFTM to process poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl) thieno[3,2-b]-thiophene)] (DPP-TTT) as the active layer. To reduce the operating voltage of this OPTs, lithium alumina (Li-Al_2O_3) thin film has been used as a gate dielectric that capable us to operate this device within 2 V due to its high areal capacitance (~410 nF/cm^2). Besides, the uni-directional DPP-TTT polymer film allows faster charge transport, resulting in a saturation mobility of the device of 0.21 $cm^2/V{\cdot}s$ with an on/off ratio ~10^4. This device also shows high NIR photosensitivity of 215% with a photoresponsivity of 28.16 A/W and has a great potential to be incorporated into more energy-efficient optoelectronic systems.

Chapter 6 presents a new strategy that provides a better uni-directional DPP-TTT thin film deposition by dispersing 2D C_3N_5 nanosheets inside the DPP-TTT solution. During this deposition, 2D C_3N_5 nanosheets act as a structural template for improving the organization of the polymer during the thin film deposition through the UFTM. Consequently, these findings confirm that well-ordered arrays of DPP-TTT come with enhanced π–π stacking and intermolecular forces needed for efficient charge transport. The C_3N_5 nanosheets incorporated DPP-TTT thin film-based OFETs exhibit better charge-carrier mobility (0.41 $cm^2/V{\cdot}s$) with similar on/off ratio (~10^4). Additionally, by using TRM-SHG technique it has been identified that C_3N_5 nanosheets increase structural ordering of the DPP-TTT matrix, thus providing more efficient pathways for charge transport and promoting reduction in trap states within the device. Therefore, the synergistic effects of combining Donor-Acceptor (D–A) polymers with 2D organic materials enhanced the device performance very significantly, indicating this composite approach might hold for the development of higher performance organic electronic devices.

Finally, **Chapter 7** draws together a summary of important findings based on this research and reveals potential future directions for this work. A focus has been placed on how the

outcomes from this work can align with and contribute to broader advances within global technology establishing opportunities for the next wave of exploration and innovation in this field.