Chapter 1

Introduction and Scope of the Thesis

1.1 Introduction

Photodetector is a device that can convert an optical signal into an electrical signal. The converted electrical signal can be processed for optical communication and computing, environmental monitoring, surveillance, image sensing and many more[1]–[9]. In general, most of the commercial photodetectors are based on inorganic semiconductors materials such as silicon (Si) and III-V materials. Higher carrier mobility, smaller exciton binding energy, higher temperature processing and higher stability may be the major reasons for preferring the inorganic materials over the organic semiconductors for electronic device applications. However, the fabrication process of inorganic materials-based photodetectors requires many expensive sophisticated analytical equipment which, in turn, increases the fabrication and manufacturing costs of these devices[10], [11]. Further, inorganic semiconductors are not suitable for flexible electronic device fabrications due to mechanical rigidity. That is why, a number of researchers have been trying to explore the organic semiconducting compounds for fabricating the optoelectronic devices due to their lower fabrication cost by solution methods, lower temperature processing, lighter weights, and better mechanical flexibility of the organic materials over the inorganic semiconductors during last two decades [12]–[17].

Various types of photodetectors can be fabricated to detect light with wavelengths in the ultraviolet (UV), visible and infrared regions. If the photodetectors are designed to detect light over a narrow-band of wavelengths centered around a main operating wavelength in any of the UV, visible and infrared regions, we generally call them narrow-band photodetectors.

Most of the III-V inorganic materials-based photodetectors operating in the near-infrared regions are used for optical communication, computing and optical imaging systems. On the other hand, the broadband photodetectors are designed to detect lights over a wide-range of wavelengths starting from the ultraviolet (UV) to the near-infrared (NIR) regions for potential applications in biomedicine, imaging, communication, environmental monitoring, health monitoring and night surveillance etc. [18]–[25] Recently, nanocomposites of conducting polymers and inorganic semiconductors have been used for fabricating wideband photodetectors [26]–[28]. In the present thesis, an attempt has been made to explore the relatively less-explored PTB7 organic semiconductor material for broadband photodetection applications.

1.2 Basics of Organic Photodetectors

In general, mostly reported organic photodetectors use two terminal device structures similar to the photovoltaic devices which main consist of an active layer sandwiched between the anode and cathode as shown in the Fig 1.1.

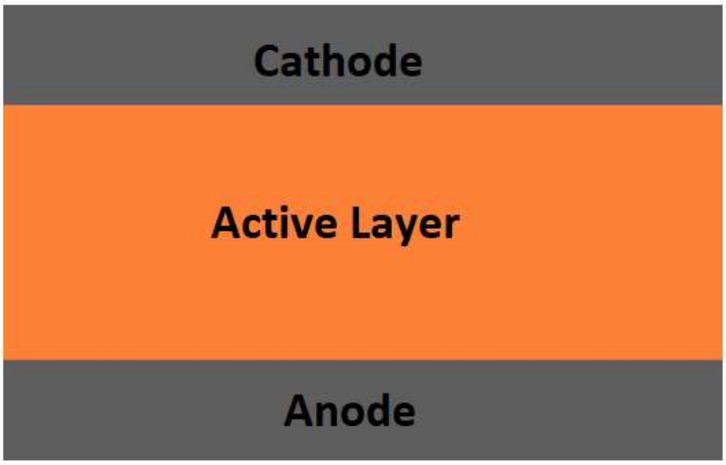

Fig.1.1: Two terminal device architecture of the Organic Photodetectors

In this type of photodetector structure, either the cathode or anode electrode is made to be transparent to the incident light so that light can be entered into the active layer of the device through it. In general, the active layer in an organic photodetector may either be an organic semiconducting material or an inorganic - organic hybrid nanocomposite material. Hybrid inorganic-organic nanocomposites have been reported for highly efficient broadband photodetectors [28], [29]

From the structural point of view, organic photodetectors are mainly classified into three types[30]: phototransistors-based OPDs (PT-OPDs), photoconductors-based OPDs (PC-OPDs), and photodiodes-based OPDs (PD-OPDs) as shown in Fig.1.2. Every device structure has its individual merits and demerits for various applications. The PT-OPDs have normally three-terminals namely source, drain and gate like the field effect transistors (FETs) as shown in Fig.1.2(a). The PT-OPDs provide photocurrent gain due to transistor action. In addition, a photoconductive gain can also be obtained by modulating the conductivity of the channel through the bias voltage applied to the Gate electrode. The PC-OPDs are two-terminal devices like inorganic photoconductors. PC-OPDs can provide photocurrent gain by photocarrier multiplication or photocurrent multiplication or simply photomultiplication (PM) effect, which, in turn, results in the high responsivity, more than 100% external quantum efficiency (EQE) and high detectivity of the PC-OPDs. The basic structure of PC-OPDs is shown in Fig.1.2(b). However, the PC-OPDs have limited applications in high-frequency optical demodulators (e.g. optical mixing) and at microwave frequencies low-detection level, low response speed and low signal-to-noise ratio [30]. The PD-OPDs are again two-electrode (cathode and anode) devices clearly shown in Fig.1.2 (c), these structures are widely used due to their interesting photoresponse characteristics such as low dark current, fast response, and wide linear dynamic range.

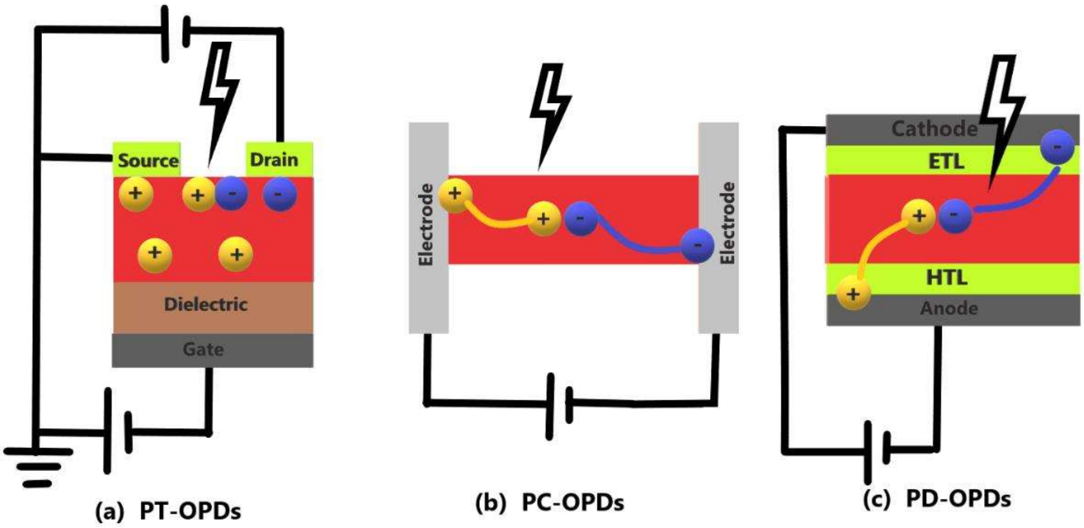

Fig.1.2: Organic photodetectors are mainly classified into three types: (a) Phototransistors-based OPDs (PT-OPDs).(b) Photoconductors-based OPDs (PC-OPDs). (c) Photodiodes-based OPDs (PD-OPDs)

It is always desirable to have high EQE, responsivity and detectivity in any photodetectors. In general, the EQE of more than 100% is easily achievable in the PT-OPDs due to transistor action and in PC-OPDs due to PM effect, PD-OPDs have EQE of less than 100%. It may be mentioned that the PM effect cannot be achieved via avalanche multiplication or impact ionization in the OPDs due to disorder nature and high exciton binding energy of the organic materials[30]. However, the PM effect can be introduced to PD-OPDs by various advanced design strategies, nanostructured material engineering techniques and interfacial modifications to achieve the EQE of beyond 100% at the cost of reduced response speed of the detectors.

We will call them PM-type OPDs. PM-type PD-OPDs have a conventional structure of anode/hole transporting layer (HTL)/active layer/electron transporting layer (ETL)/cathode. An inverted vertical M-type PD-OPD uses an anode/ETL/active layer/HTL/cathode in inverted type where the work functions of the anode and cathode are of different values for the ease of collection of the photogenerated carriers in the active region[30].

1.2.1 Definitions of Some *Key* Parameters of Organic Photodetectors

Some of the important parameters of any photodetectors are as follows:

1.2.1.1 Responsivity (R_λ)

The responsivity (R_λ) is defined as the ratio of the output photocurrent (I_{Ph}) to input incident optical power (P_{in}) on the detector which can be written as[31].

$$R_\lambda\left(\frac{A}{W}\right)=\frac{I_{ph}}{P_{in}} \qquad 1.1$$

1.2.1.2 External Quantum Efficiency (EQE)

The external quantum efficiency is defined as the ratio of number of charge carriers collected by the external circuit to the number of photons incident on the photodetector. This parameter basically represents the capability of electrical signal conversion from optical signal of the device. The EQE is expressed in terms of the photoresponsivity as[32]:

$$EQE(\%)=1240\frac{R_\lambda}{\lambda}*100 \qquad 1.2$$

where, R_λ is the responsivity (A/W) and λ is wavelength (nm) of the incident photons.

1.2.1.3 Detectivity (D)

The Detectivity (D) of a photodetector is defined as the minimum power of the incident optical signal which the device can detect. The mathematical expression for detectivity is given by [30].

$$D = \frac{(A\Delta f)^{1/2} * R_\lambda}{J_n} \qquad 1.3$$

where Δf is the electrical bandwidth of the signal and J_n is termed as the noise current.

The detectivity is normally expressed as Jones. In general, the main contribution to noise signal is the dark current. Thus, the detailed detectivity expression can also be written as[31].

$$D(Jones) = \frac{R_\lambda}{\sqrt{2eJ_d}} \qquad 1.4$$

where J_d is the dark current density (A/cm^2) and e (C) is the electronic charge.

1.2.1.4 Speed of Response

The response speed is normally expressed in terms of rise time (τ_{rise}) and fall time (τ_{fall}) of the photogenerated current corresponding to an incident optical pulse train of certain ON and OFF periods. When the pulse changes its state from OFF to ON state, the photocurrent starts to increase from zero to some certain maximum value. The time required to change the photocurrent from 10 % to 90 % of the maximum value is commonly known as the rise-time of the photodetector. Similarly, when the pulse changes from ON to OFF state, the photocurrent starts to decrease from its maximum towards zero. The time required to decrease the photocurrent from 90 % to 10 % of the maximum value, is called the fall-time of the photodetector. Ideally, zero values of τ_{rise} and τ_{fall} desirable. However, their values are affected by various defect centers and complex recombination process mechanism in the active region of the device.

1.3 Literature review of some photodiode type broadband organic photodetectors

Enormous of progress in the broadband organic photodetectors has been achieved by exploring advanced strategies and/or new device structures. The energy band diagram of the photodiode-type organic photodetectors (PD-OPDs) considered in Fig. 1.2 (c) is shown in Fig. 1.3.

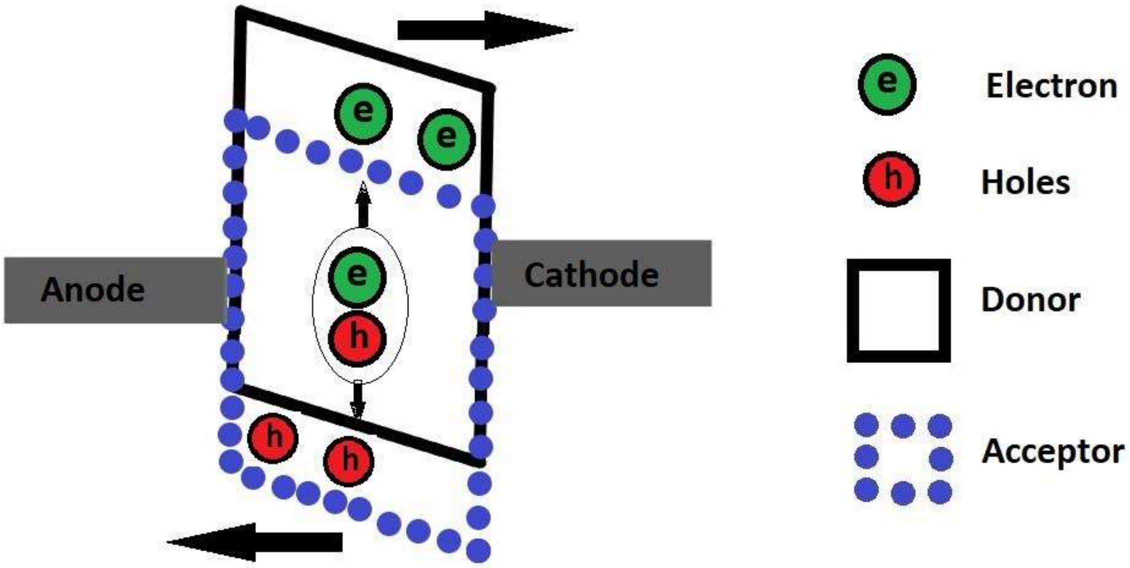

Fig.1.3: Schematic view of energy band diagram of the device operating in photodiode mode.

The active layer comprising donor and acceptor organic materials absorbs photons and generate excitons which are dissociated at the donor/acceptor interface. The generated excitons get separated into electrons and holes which are finally collected by suitable electrodes by applying an electric field to result in a photocurrent. In general, the EQE of the PD-OPDs is usually less than 100 % [30].

1.3.1 Thick Film Broadband Organic Photodetectors

Thick film photodetectors have reduced dark current and broad-spectrum response [33][34]. Reduction in dark current with increased active layer thickness in thick-film devices was experimentally verified by the Wu and his coworkers [35]. Interference model was explored by Ramuz et al. [36] to investigate effect of active layer on the dark current of an ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al structure. It was shown that the dark current density is greatly reduced by optimizing the thickness of the photo active layer at the cost of the EQE to certain extent. Armin et al. [34] obtained a broad-spectral photo-response by increasing the thickness of the active layer. The increased active layer thickness increases interference of light which affect the optical field distribution in the active region thereby reducing the EQE spectral shape of the organic photodetectors [34]. Huang et al. [37] investigated experimentally the effect of active layer thickness on the performance characteristics of thick film technology-based ITO/ZnO/PTB7-Th:CO1-4Cl/MoOx/Ag photodetector. high performance broadband photodetector with low dark current density and high detectivity. Recently, Zeng et al.[38] explored thick film approach for fabricating an ITO/PEDOT:PSS/PNTT:PCBM/PNDIT-PF$_3$N-Br/Al broadband photodetector. The device showed a reduction in the dark current and enhancement of EQE over the complete response spectrum with the increased thickness of the active layer [38].

1.3.2 Ternary Nanocomposites Based Broadband Photodetectors

The blend of ternary compound materials has been widely used for the active region in high efficiency photovoltaics devices [22]. However, they have not been explored much for the active region of broadband photodetectors. Several attempts were made to develop ternary blend based broad band photo detectors in last decades by employing some organic semiconducting materials. Interestingly, it is observed that the use of organic-inorganic hybrid ternary blend in the active layer of the photodetectors not only enhances the photo response spectrum of the device but also improves the other key parameters such as the detectivity and EQE of the photodetectors [40], [41].

Xu et al.[42] fabricated an ITO/ZnO/P3HT:PTB7: PCBM/MoOx/Ag using P3HT:PTB7: PCBM based ternary organic compounds. The dark and photo currents were shown to be optimized by mixing 10 wt % PTB7 in the binary blend of P3HT and PCBM. Li and co-workers [40] mixed ultralow bandgap organic semiconductors namely COi8DFIC non fullerene acceptor with the PTB7-Th: PCBM binary blends for the active layer of the ITO/ZnO/PEIE/active layer/MoOx/Ag photodetectors. The device exhibited a self-powered characteristic with a photo response over a broad spectral range from 400 nm to 1000 nm with the maximum detectivity of 7×10^{11} Jones at zero bias. Liu et al. [41] realized high performance self-powered broadband photodetectors by utilizing ternary blend nanocomposites as the active layer. They demonstrated that, the ternary blend nanocomposites based active layers in the photodetectors not only play a vital role in extending the spectral range of the photoresponse but also their individual compositions play an influencing role in deciding the overall optical performance of the device. For example, the photodetectors with active layer of PTB7-Th: IFIC-i-4F:$PC_{71}BM$(1:0.6:1.2, wt/wt/wt) ternary blend show higher detectivity and wider spectral range than the devices with PTB7-Th: IFIC-i-4F:$PC_{71}BM$(1:1.3:0.5, wt/wt/wt) ternary blends as well as devices with active layers of binary blends of any two of the three in the aforementioned ternary compounds [41]. The extended spectral range in the former device is mainly attributed to the efficient light harvesting capability of the ternary blends while the high detectivity is attributed to suppressed dark current density resulted from the discontinuous channels formed by mixing low IFIC-i-4F content in the ternary blends [41].

1.3.3 Interface Engineering in Broadband Photodetectors

The interface engineering is considered to be one of the most important strategies exercised for performance improvements in organic photodetectors[43], [44]. In this method, the work function of the contact electrodes is modified by employing a suitable interface layer [45], [46]. The interface layer material is so chosen that, in addition to modifying the work function of the electrodes, it can also act as a charge blocking layer to reduction in the dark current density by reducing the carrier recombination in the active layer. The overall effect of the interface engineering strategy is to improve the responsivity and detectivity parameters of the organic photodetectors.

Several works have been reported on the successful demonstration of the aforementioned benefits obtained by interface engineering strategy in the organic photodetectors. Saracco et al. [44] have demonstrated that the work function of the ITO electrode can be modified by using a PEIE interfacial layer. Kim et al. [47] have used C_{60} based hole blocking layer (HBL) for drastic reduction in the dark current of a p-DTS $(FBTTh_2)_2/PC_{71}BM$ photodetector. The HBL interface layer is used to block the hole insertion into the active region by enhancing the hole injection barrier. Zhou et al. [48] have investigated the effects of the poly -TPD as well as PEDOT: PSS based electron blocking layer (EBL) on the performance parameters of a PD-Type OPD. The poly-TPD was shown to be a better EBL than the PEDOT: PSS in their work. Ma and Inganas [49] investigated the role of P3HT based EBL in ITO/ZnO/PBDB-T: PNDI-FT10/P3HT/MoOx/Ag based photodetector structure. The P3HT interface layer was shown to enhance the electron injection barriers for preventing the electron injection from the external circuit into the active layer.

1.3.4 Multilayered Broadband Photodetectors

Multilayer strategy was extensively explored for organic photovoltaic applications[30], [50]. Recently, several research groups have been motivated from the organic photovoltaics to explore the multi-junction active region strategy in the organic photodetectors. This strategy not only suppresses the charge injection to reduce dark current but also offers excellent light harvesting capability by super imposing the photon harvesting of each of the layers incorporated in the active layer of the device[51]–[55]. Menke et al.[52] have reported broadband UV to NIR organic PD-type photodetectors by employing multilayer strategy with three small molecules materials having photon harvesting energy in the UV-NIR region. They [52] have investigated the performance of the device comprising three layers of SubPc:C_{60} (1:1, wt/wt), ClAlPc:C_{60}(1:1, wt/wt) and SnNcCl_2:C_{60}(1:1, wt/wt) stacked together in the active region. The fabricated device showed flat photoresponse over a broad spectral range. Liu et al. [54] reported a PD-type OPD with device structure similar to the PD-OPDs shown in Fig.1.2(c).The fabricated double layered broadband organic photodetector clearly show that the double layer strategy could be used for extending the spectral range of the photoresponse and reducing the dark current of the detector. However, it was noted that proper care needs to be taken while stacking one layer over the other so that the influence of the top layer should not affect the properties of the material in its bottom layer[54].

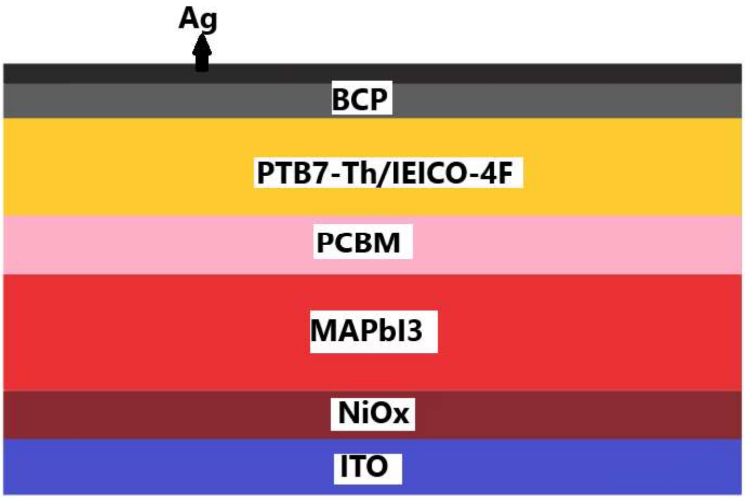

Fig.1.4 : The schematic device structure with MAPbI$_3$ perovskite integrated with the binary organic blend of PTB7-Th: IEICO-4F (1:1.5, wt/wt)

Some researchers have used perovskite materials with high absorbing capacity for fabricating multilayered perovskite/organic hybrid photodetectors [53], [55]. Wu and co-workers [53] have successfully integrated MAPbI$_3$ perovskite with the binary organic blend of PTB7-Th: IEICO-4F (1:1.5, wt/wt) to show superior performance to only-perovskite based photodetectors .The device structure of the fabricated photodetector was similar to Fig.1.4. Li et al.[55] have integrated MAPbI3 perovskite with organic materials to achieve of the perovskite /organic hybrid material based high efficiency broad band photodetectors. Note that such photodetectors have superior performance parameters to the devices consisting of either only perovskite or only organic material due to the combined benefits of high light harvesting capacity of perovskite materials and broad absorption spectra of the organic materials. Table 1.1 compares the key parameters of some broad band organic photodetectors.

Table 1.1 Comparison of some key parameters of broadband organic photodetectors based on photodiode type with different active layers and strategies.

Device Structure **(Year)**	**Detectivity (Jones), Bias (V)**	**Responsivity (AW^{-1}), Spectral Range (nm)**	**EQE (%) , Bias (V)**	**Ref.**
ITO/PEDOT: PSS/P3HT: PCBM/Ca/Al (2008)	$7x10^{12}$, -1	--, 300-650	70, 0	[36]
ITO/MoO3/SubPc:C60/ClAlPc :C60/SnNcCl2:C60/BCP/Al (2012)	5.3×10^{10} −3	0.35, 300-1000	80, -3	[52]
ITO/PEIE/PBDTTT-C: PC70BM/PEDOT: PSS/Ag (2013)	--	--, 350-850	30, -2	[44]
ITO/PEDOT: PSS/PCDTBT: PCBM/Sm/Al 2014,	$2x10^{12}$, -1	--, 300-750	70, -1 V	[34]
ITO/PEDOT: PSS/p-DTS(FBTTh2)2: PC71BM/C60/Al (2015)	2×10^{12}, −0.5	0.4, 300-800	67, -0.5	[47]
ITO/poly-TPD/PDPP3T:PC71BM/Al (2015)	$1.5\times10^{13,}$ −0.5	0.2, 300-1000	0.4, -0.5	[48]
ITO/NiOx/MAPbI3/PCBM/PTB7-Th: IEICO-4F/BCP/Ag (2018)	$5x10^{13}$, -0.1	0.5, 300-1000	78, -0.1	[53]

ITO/ZnO/PBDB-T: PNDI-FT10/P3HT/MoO3/Ag (2018) (2018)	5.8×10^{12}, −3	0.34, 300-850	65, -3	[49]
Device Structure **(Year)**	**Detectivity (Jones), Bias (V)**	**Responsivity (AW^{-1}), Spectral Range (nm)**	**EQE (%), Bias (V)**	**Ref.**
ITO/ZnO/PTB7-Th:CO1-4Cl/MoOx/Ag (2019)	$3.3\text{x}10^{13}$, -0.1	0.45, 400-1100	65, -0.1	[37]
ITO/PEDOT: PSS/PNTT: PC71BM/PNDIT-PF3N–Br/Al (2019)	$1.4\text{x}10^{13}$, -0.1	--, 300-850	59.4, -0.1	[38]
ITO/ZnO/PEIE/PTB7-Th: COi8DFIC:PC71BM/MoOx/Ag (2019)	7×10^{11}, 0	0.35, 400-1000	--, --	[40]
ITO/ZnO/PTB7-Th: IFIC-i-4F:PC71BM/MoO3/Ag (2019)	$1\times10^{14,}$ 0	--, 300-1000	--, --	[41]
ITO/ZnO/PTB7-Th: ITIC/PTB7-Th: FOIC/MoO3/Ag (2020)	$2.6\times10^{11,}$ −0.1	0.48, 300-1000	75, -0.1	[54]
ITO/PTAA/MAPbI3/F8IC:PTB7-Th/C60/BCP/Cu (2020)	$2.6\times10^{11,}$ −0.1	0.43, 300-1000	80, 0	[55]

1.4 Review of Some Photomultiplier (PM) Effect Based Broadband Photodetectors

High responsivity is one of the most important requirements for the high sensitivity photodetectors. In general, most of the polymer based organic photodetectors work in the photodiode mode and have, in general, poor responsivity. However, a tremendous progress has been made in the last decade to improve the responsivity of the organic photodetectors by introducing the strategy of the photocurrent multiplication phenomenon in these devices. The carrier tunneling from the external circuit into the active region is one of the critical requirements to realize the photomultiplication effect in the high gain photodetector structures. Some of the important techniques explored by the researchers for improving the photocurrent in organic photodetectors are discussed below.

1.4.1 Photomultiplication via Traps in the Active Layer of Organic Photodetectors

The first organic photodetector with photomultiplication effect in organic photodetectors was reported by Hiramoto et al.[56] in 1994. The photomultiplication effect in the device was observed due to hole traps formation at the interface of the organic film/gold electrodes. The hole traps triggered the electron injection from the external circuit into the device thereby causing photocurrent multiplication.

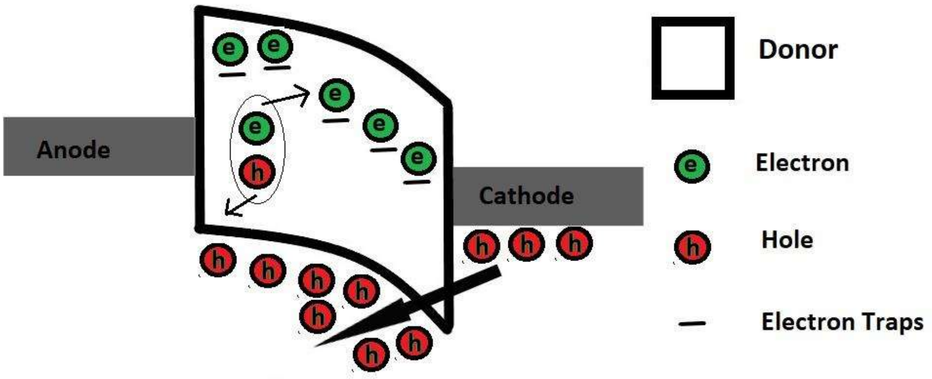

Fig.1.5 : Schematic view of energy band diagram of the device with PM effect realized through traps in the active layer

Later works of Hiramoto et al. [57] also confirmed that the photocurrent multiplication effect in the organic photodetectors were mainly originated from poor contact formation at the organic film/gold electrodes due to the high surface roughness of the organic films [57]. The photocurrent multiplication in a typical broadband organic photodetector realized through traps in the active layer is shown in the Fig 1.5. The traps in the active layer can be from nanoparticles (NPs)[27], quantum dots (QDs)[28] and organic acceptors[58]–[62]. Excitons are generated due to absorption of photons. The majority carriers in the active layer are drifted by the electric field while the part of minority carriers is trapped and accumulated near the injection electrodes to create a coulomb field. This narrows the barrier for the injection of opposite charge carriers to create photomultiplication (PM) in the device.

Based on the mechanism as shown in Fig.1.5 successfully, Chen et al. [63] had reported photocurrent multiplication effect by introducing CdTe nanoparticles (NPs) into the P3HT: PCBM composites based active region .The CdTe NPs were claimed to act as electron traps to trigger the hole injection from the external circuit to cause photocurrent multiplication. Guo and co-workers [27] also achieved photocurrent multiplication in the organic photodetectors by incorporating ZnO NPs into the P3HT based active region of the device. In this, ZnO NPs act as electron traps to induce hole injection from the external circuit to result in the photocurrent multiplication in the photodetector. Dond et al. [28] reported a high gain photodetector by incorporating the quantum dots (QDs) of PbS and ZnO in the P3HT: PCBM composite based active region. The PbS QDs were used for absorbing light in near infrared (NIR) region to extend the spectral range of the photodetector while the ZnO QDs were used to act as electron traps to trigger hole injection from the external circuit to result in the photocurrent multiplication of the detector [28].

However, in recent years, a tremendous of progress has been made in the development of broadband organic photodetectors with photocurrent multiplication feature by using organic semiconductors as traps in the active region of the device[58]–[62]. Li et al. [64] observed the photocurrent multiplication effect in P3HT: PCBM (100:1, wt/wt) photoactive layer-based photodetector due to the large donor traps in P3HT and a very small acceptor traps in PCBM . The fabricated device showed a high EQE of 37500% at 526 nm at large reverse bias of -19V. The used donor traps in P3HT material acted as hole transport channel while the acceptor traps in the PCM material acted as electron transport channel in the active layer of the device. However, the non-flat spectral response and requirement of large reverse bias voltage were the major drawbacks of that device.

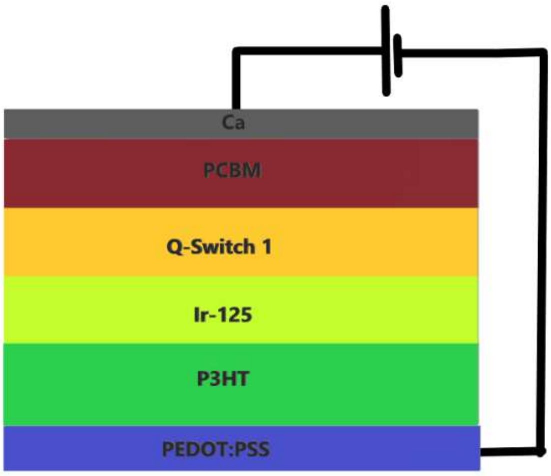

Fig.1.6: Broadband PM-OPDs device structure with traps (Q switch 1 molecules) in the active layer and Ir-125 NIR dye to extend the spectral range to NIR.

In order to achieve a flat photoresponse, Wang et al. [65] made a successful attempt by introducing a third low-bandgap polymer material namely PTB7-Th into the P3HT: PCBM active layer. They obtained a broad response over 320-800 nm with the maximum EQE of about 3800 % but at large reverse bias voltage of -25V. Planar heterojunction-based device with a broad spectral response and high EQE of 120700 % at large reverse bias voltage of -25V was reported by Jang et al. [66]. Later, Jang et al.[67]demonstrated an ultrathin active layer (~ 70 nm) based high performance photodetector by incorporating small molecule organic semiconductor namely 2,2′-((2Z,2′Z)-((4,4,9,9-tetrahexyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b′]dithiophene-2,7-diyl)bis(methanylylidene)) bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)) dimalononitrile (IDIC) as an optical sensitizer with the maximum EQE of 60700% at -19V reverse bias. Cheng et al. [68]observed photocurrent multiplication effect by introducing NIR dye (Ir-125) to perform dual functions of NIR absorber as well as electron traps in the active region. The Chuang et al.[69] extended the photoresponse spectral range by incorporating Ir-125 and a molecule Q-switch 1 into P3HT: PCBM active layer. The corresponding device structure is shown in the Fig.1.6.They also [69] noted that a suitable dye content in the active layer could play a vital role in both the photocurrent multiplication and photoresponse spectral range enhancement of the device.

Some research groups have used the donor organic semiconductors to introduce hole traps in the active layer to attain the photocurrent multiplication effect through electron tunneling injection. Zhao et al.[12] obtained photocurrent gain in ZnO/PCBM: P3HT (100:5, WT/WT) based photodetector due to large acceptor traps in PCBM and a very small donor traps in P3HT. They obtained the maximum EQE of 4900 % at reverse bias of -5V. Zhao and co-workers[17] extended the spectral range by employing double layer strategy in ITO/ZnO/PM6:Y6 (1:1.5, wt/wt)/PCBM: P3HT (100:5, wt/wt)/Au photodetector where the PM6:Y6 (1:1.5, wt/wt) worked as the photo absorbing layer while the PCBM: P3HT (100:5, wt/wt) layer worked as the photocurrent multiplication layer. Yang at al.[70] reported a high gain PBDB-T: Y6 (3:100, wt/wt) based broadband photodetector with the maximum EQE of 18000 % under reverse bias of 1V and at 350 nm wavelength.

1.4.2 Photocurrent Multiplication via Traps at Interfacial Layers Based Photodetectors

In this strategy the photocurrent multiplication can be achieved by interfacial layer other than traps in the active layer. The traps in the interfacial layer may be attributed to the intrinsic properties of the interfacial layer or externally introduced traps [25], [71], [72]. The charge carriers are trapped in the interfacial traps to result in the narrowing of charge injection barrier of the opposite charge carriers for their injection into the active layer from the external circuit to cause the photomultiplication effect in such devices.

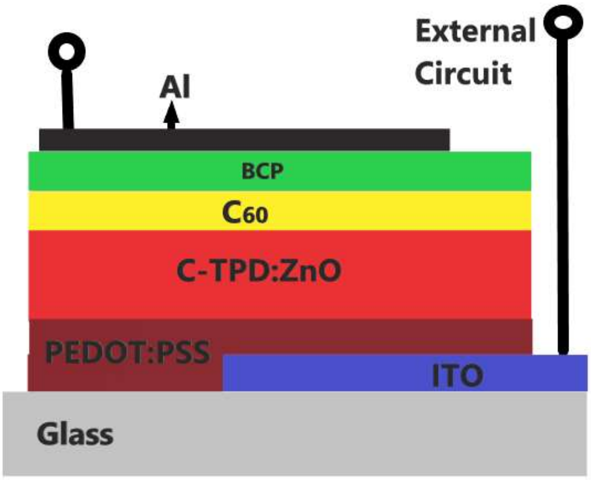

Fig.1.7: Schematic layout of Broadband PM-OPDs device structure having traps in the interfacial layer.

Huang and Yang [73]observed photocurrent multiplication effect in the device with structure ITO/PEDOT: PSS/Pentacene/C_{60}/BCP/Al in this device the multiplication effect was attributed to the electron tunneling injection triggered by hole trapping at the PEDOT:

PSS/C_{60} interface and C_{60} disordered structures. Guo et al. [74] observed photocurrent multiplication by inserting C-TPD layer in between PEDOT: PSS and C_{60} in the device already reported by Huan and Yang [73]. Later, Fang et al.[71] improved the detectivity and photocurrent gain by incorporating ZnO NPs into the C-TPD interface layer of the structure reported by Guo et al.[74] as depicted in Fig.1.7 .They successfully demonstrated that the ZnO NPs incorporated in the C-TPD interfacial layer could act as the additional hole trapping sites to improve the overall performance of the device.

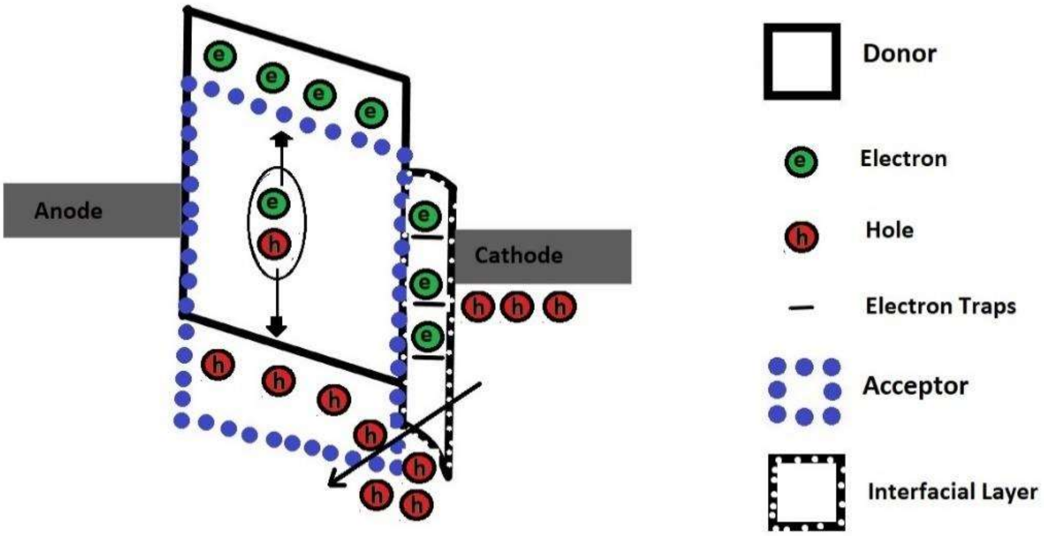

Fig.1.8: Schematic view of energy band diagram of the device with PM effect realized through intrinsic traps in the interfacial layer

The working mechanism of these interfacial-trap-assisted charge carrier injection-based PM-OPDs is illustrated with the help of energy band diagram shown in Fig.1.8.As already discussed, that the main source of traps in the interfacial layer is either from external incorporation or intrinsic traps. As clearly depicted from the Fig 1.8, that electrons are trapped in the interfacial layer and holes are injected from the external circuit to result in the photomultiplication effects in such devices. Zhou and co-workers [25] observed notable photocurrent multiplication gain in device with structure ITO/ZnO/PM6:Y6/PC71BM:P3HT/Au. The fabricated device was shown to work in photodiode mode without any UV light treatment of the ZnO NPs layer but it exhibited photocurrent gain when the NPs layer was exposed to UV light for 30s.Lee et al.[72] observed photocurrent multiplication in colloidal PbS quantum dots (QDs) based photodetector with a device structure of ITO/PEDOT:PSS/PBDB-T:Y6/Al. The device showed a broad spectral range with the maximum EQE of 13800 % at 1200 nm under -12V reverse bias voltage.

1.4.3 Electron /Hole Blocking Layer Based Photodetectors with Photocurrent Gain

Besides the incorporation of traps in the active layer and insertion of interfacial layer for photocurrent gain, the use of suitable charge blocking layers (known as electron blocking layer (EBL) and hole blocking layer (HBL) is another very useful strategy to achieve photocurrent multiplication effect in the organic photodetectors. The energy band diagram of organic photodetectors with charge blocking layers has been shown in the Fig 1.9 [24], [75], [76]. As depicted in the Fig.1.9, the hole blocking layer is inserted between the active layer and the buffer layer. The hole blocking layer (HBL) basically blocks the holes due to the significant HOMO level difference between the HBL and donor. The corresponding hole accumulation near the HBL results in electron tunneling injection from the anode for photocurrent multiplication effects. The EQEs of such device is normally greater than 100% at the cost of slower response speed as compared to the PD-OPDs.

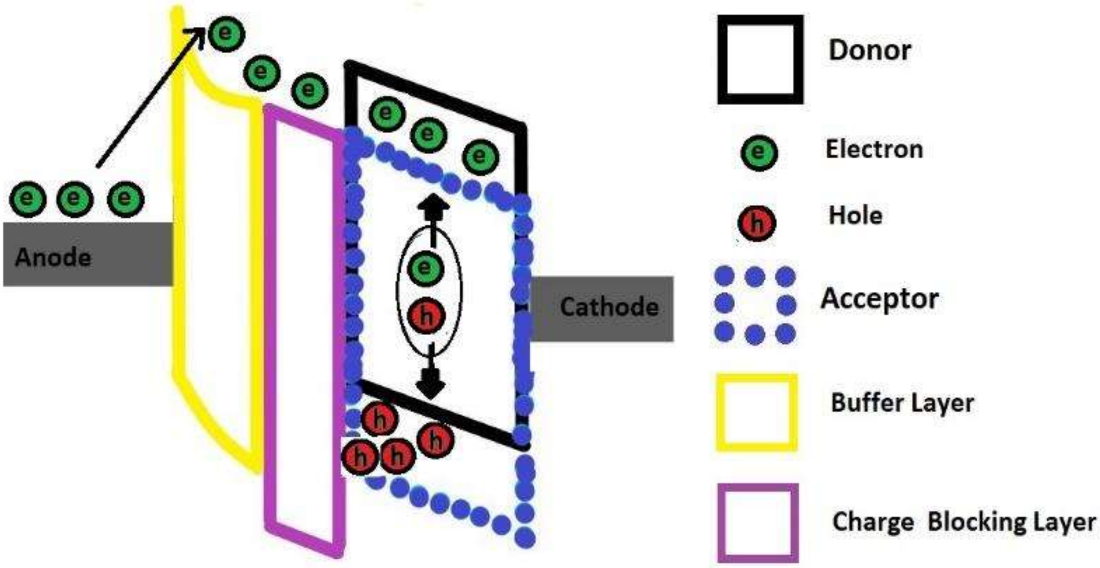

Fig.1.9: Schematic view of energy band diagram of the device with PM effect realized through charge blocking layer

Hammond et al.[75] realized the photocurrent multiplication by utilizing charge blocking layer as illustrated in the Fig.1.9 with the device structure ITO/NTCDA/C_{60}/CuPc: C_{60} (3:7,wt/wt)/BCP/Al. The fabricated photodetector utilizes NTCDA and C_{60} as the hole blocking layer (HBL). Moreover, Han et al. [24] also observed significant photocurrent gain by replacing MoOx by BCP in ITO/AZO: PDIN/polymer: PCBM (1:2, wt/wt)/MoOx/Al structure based broadband photodetector with charge blocking layer phenomenon as illustrated in the Fig.1.9. Some important broadband photodetectors with photocurrent gain are summarized in the Table 1.2.

Table 1.2. Comparison of some key parameters of broad band organic photodetectors based on photocurrent multiplication phenomenon with different active layers and strategies.

Device Structure (Year)	**D (Jones), Bias (V)**	**R (AW^{-1}), Spectral Range (nm)**	**EQE (%), Bias (V)**	**Ref.**
Au/Me-PTC/Au (1994)	--, --	--, 350-700	10000, 16	[56]
ITO/DQ/Ag (1996)	--, --	--, 400-700	2500, 20	[57]
ITO/PEDOT: PSS/P3HT: PCBM: CdTe /Ca/Al (2008)	--, --	--, 350-750	8000, -4.5	[63]
ITO/PEDOT: PSS/P3HT: Ir-125:PCBM/Ca/Al (2010)	--, --	32.4, 300-900	7000, -1.5	[68]
ITO/NTCDA/C60/CuPc:C60/BCP/Al (2010)	--, --	--, 400-800	34000, -4	[75]
ITO/PEDOT:PSS/PVK:TPD-Si2/P3HT: ZnO/BCP /Al (2012)	2.45×10^{14}, -9	52, 300-700	34000, -9	[27]
ITO/PEDOT: PSS/P3HT: PCBM: PbS: ZnO/Al (2014)	1.01×10^{12}, -3	5.6, 320-1000	1600, -4	[77]
ITO/PEDOT: PSS/P3HT:PC71BM/LiF/Al (2015)	--, --	51.7, 300-700	16700, -19	[59]

Device Structure **(Year)**	**D (Jones),** **Bias (V)**	**R (AW^{-1}),** **Spectral Range (nm)**	**EQE (%)** **, Bias (V)**	**Ref.**
ITO/PEDOT: PSS/P3HT:PTB7-Th: PC71BM/Al (2015)	1.91x10^{13}, -25	229.5, 320-800	38000, -25	[65]
ITO/ZnO/PDPP3T:PC71BM/Al (2016)	6.3x10^{12}, -0.5	--, 300-1100	140000, -0.5	[25]
ITO/lysine/PBDTT-DPP: PC71BM/MoO3/Al (2017)	1.03x10^{14}, 1	29.69, 300-900	5008, 1	[76]
ITO/AZO: PDIN/DPP-BBT-DTP: PC71BM/MoO3/Al (2018)	3x10^{11}, -2	9.28, 300-1300	1392, -2	[24]
ITO/PEDOT: PSS/P3HT/PCBM/Al (2018)	1.3x10^{12}, -5	--, 300-700	120700, -19	[66]
ITO/PEDOT: PSS/P3HT/IDIC/Al (2019)	4x10^{12}, -10	--, 300-700	60700, -19	[78]
ITO/ZnO/PC71BM:P3HT/Au (2020)	3.2x10^{12}, -5	23, 300-800	4900, -5	[12]
ITO/ZnO/PM6:Y6/PC71BM:P3HT/Au (2020)	6.8x10^{12}, 10	8.8, 350-950	1200, 10	[17]
ITO/PEDOT: PSS/PZ1/PBDB-T: Y6/Al (2020)	2.13x10^{12}, 2	--, 350-950	8600, 2	[70]

1.5 Motivation of the Thesis

Organic photodetectors (OPDs) have drawn considerable attention in recent times due to low-cost fabrication method, compatibility with flexible electronic devices, light weight and low-temperature processing. Like the conventional inorganic materials-based photodetectors, the OPDs are also supposed to be used for various applications including optical communication, environmental monitoring, biomedical imaging, and sensing[30] . OPDs for operating in the Ultraviolet (UV), visible, and near-infrared (NIR) lights can be realized by using suitable optical bandgap based organic semiconductors and device architectures. The broadband OPDs are widely used in image sensing applications. The details literature survey shows various strategies for enhancing the spectral range of the photoresponse and achieving high current gain[30], [50].

At present, most of the image sensors available in the market use mainly the photodiode (PD) type broadband OPDs[77]. Low sensitivity of PD-type OPDs increases the overall cost and complexity of these organic image sensors since it requires an additional current amplification circuit to enhance the photocurrent of the organic detectors [30], [50]. Thus, it is desirable to develop OPDs of simple architectures for reducing both the complexity and costs of the organic image sensors. The photocurrent multiplication (PM)-type OPDs with high current gain are considered to be the excellent candidates for the organic image sensors due to their high sensitivity to convert weak light signals into electrical signals. Further, the PM-type photodetectors may eliminate the requirement of the extra current amplification system in the organic image sensors.

In general, high quantum efficiency (QE), high responsivity and low noise are mandatory requirements for any broadband photodetector. In the past few decades, tremendous progress in the development of broadband PM-type (with gain) hybrid organic-inorganic photodetectors (PM-type OIPDs) has been observed. Performance optimization of such type of photodetectors have been achieved through device engineering as well as advanced material processing methodologies. The present thesis thus aims to fabricate and characterize some PM effect based organic-inorganic hybrid broadband photodetectors. Three major objectives of the present thesis are

- To develop novel strategies for the performance enhancement of the existing hybrid broadband photodetectors through device engineering
- To explore innovative approaches and novel nanostructured nanocomposites for the fabrication and characterization of the broadband organic photodetectors with photocurrent gain
- To explore new advanced materials for performance improvement of some high gain and low-cost solution processing based broadband photodetectors

1.6 Scope of the Thesis

In this thesis, some organic-inorganic nanocomposites/ZnO Nanorods based broadband photodetectors are fabricated and characterized. Besides the present Chapter, this thesis has FOUR remaining chapters as discussed in the following.

Chapter 2 presents a novel technique for enhancing the responsivity and EQE of a FTO-coated glass/ZnO nanorods arrays (NRAs)/PCDTBT:PCBM:PbS QDs/Ag structure based broadband photodetector. The ZnO NRAs layer acts at the electron transport layer (ETL), the hybrid organic-inorganic nanocomposite layer of the PCDTBT: PCBM: PbS QDs acts as the active layer and the MoOx layer acts as the hole transport layer (HTL) in the photodetector.

The active layer is grown on the ZnO NRAs ETL so that ZnO NRs are penetrated vertically inside the active layer to improve the charge extraction and transportation from the active layer. The PbS QDs in the active layer act as an effective photosensitizer for enhancing the absorption in the visible region of the PCDTBT: PCBM polymer. The combined effects are shown to enhance both the responsivity and EQE drastically, outmatching the majority of organic photodetectors.

Chapter 3 presents a FTO/ZnO NRs/PCDTBT:PCBM:CdSe NCs/MoOx/Ag structure broadband photodetector fabricated on fluorine-doped tin oxide (FTO) coated glass substrate for UV-visible applications. The organic-inorganic nanocomposite of PCDTBT: PCBM and CdSe tetrapod shaped nanocrystals (NCs) is explored for the active material in the proposed device. The tetrapod shaped CdSe NCs is used to act as a sensitizer for visible band while the PCDTBT: PCBM composite polymer is used to serve as functional interfaces for extracting charge carriers from the inorganic sensitizer. The polymers not only facilitate efficient charge extraction from the inorganic NCs but also allow ambipolar transport in the ternary blend nanocomposites-based device. The CdSe tetrapod shaped NCs are shown to improve the performance over the commonly used spherical shaped inorganic NCs.

Chapter 4 presents a simple low-cost approach to fabricate a p-PTB7/n-ZnO nanorods (NRs) heterojunction based high performance wideband photodetector. The main objective of this chapter is to to explore the relatively less-explored PTB7 organic semiconductor material for broadband photodetection applications. The device structure of FTO/ZnO NRs/ poly[[4,8-bis [(2 ethylhexyl) oxy] benzo [1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2ethylhexyl) carbonyl] thieno [3,4-b] thiophenediyl]](PTB7) /MoOx/Ag is fabricated using solution method. The ternary organic-inorganic nanocomposites used in the previous chapters are replaced by a single high quality PTB7 polymer to reduce both the fabrication complexity and cost of the proposed device. The PTB7 polymer has been used for detection of light mainly in the visible region while the ZnO NRs layer is used to detect light mainly in the UV region to realize the proposed wideband UV-visible photodetector. The n-ZnO NRs and p-PTB7 layers also serve as efficient electron transport layer (ETL) and hole transport layer (HTL) in addition to the UV and visible light absorbers, respectively, in the proposed photodetector structure.

Chapter 5 is devoted to summarize the major findings of the present thesis. Finally, some future scopes of works related to this thesis are also outlined in this chapter.