SYNOPSIS

The content of this synopsis report entitled **“Design, development and fabrication of thiophene and benzothiadiazole based conjugated polymers for photovoltaics”** is divided into five chapters. In chapter 1 the respective research area, where design synthesis and fabrication of conjugated polymers, along with the scope and significance of the subsequent chapters are discussed. In chapter 2 photostability enhancement of P3HT-PCBM by using appropriate ratio of MWCNT in ambient conditions have been discussed. Chapter 3 discusses about synthesis of poly(ortho-arylene-vinylene) type of polymer alternating at 5,6-position of BT namely P1 and P2 in the polymer main chain. Chapter 4 demonstrates that on functionalization of methyl acetate group at 5,6-positions of BT red-shift absorbance, lowered the $\text{LUMO}^{\text{optical}}$, improves phase separation in active layer of PSC and hence improves solar cell performance compared to its methyl counterpart. Chapter 5 results in synthesis of newer napthothiadiazole (NT) based D-A polymer and their BHJ solar cell performance.

Chapter 1: Introduction to polymer solar cell

Polymer solar cells (PSCs) have gained much attention owing to its several advantages such as large area solution processability, fine tuning of band gap on polymer backbone and amorphous nature of polymer that allow fabrication on light weight flexible substrates. These properties make CPs attractive for solar cell researchers and a PCE of ~13% has been achieved recently. These polymer solar cells will be cheaper and flexible in nature compared to present commercialized expensive silicon solar cells. Generally a blend of p-type CP (Figure 2) and an n-type acceptor (Figure 2) are used to sandwich between an anode and a cathode (Device geometry and mechanism of a polymer solar cell has been shown in Figure 1).

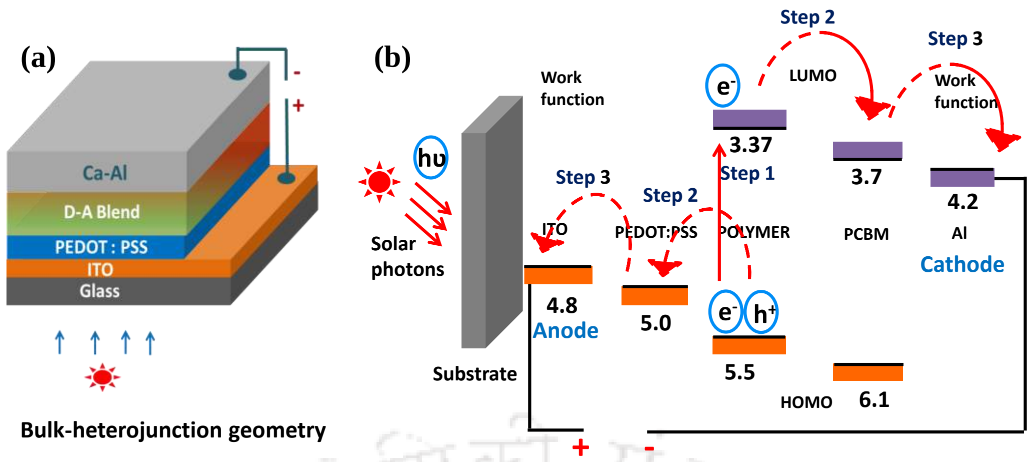

Figure 1 Bulk-heterojunction polymer solar cell (a) device structure (b) mechanism.

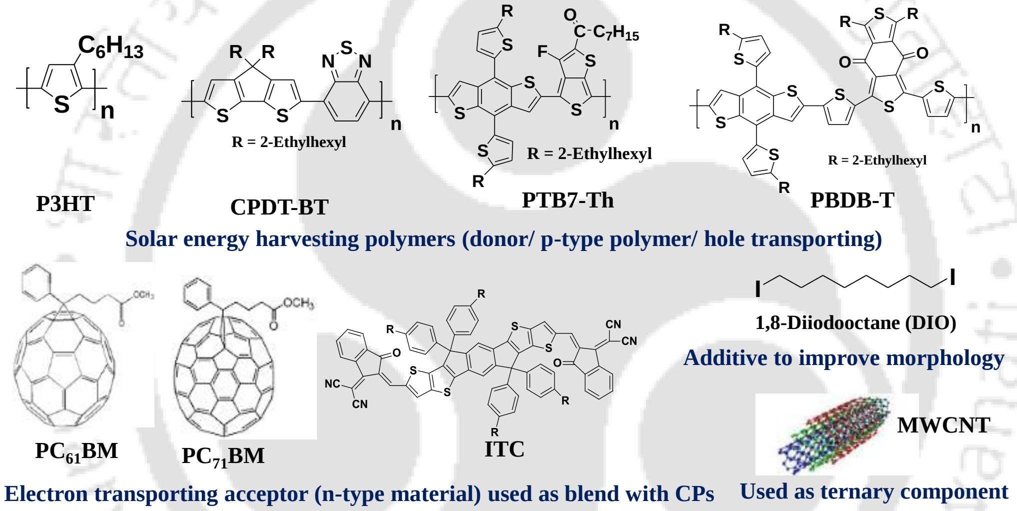

Figure 2 Structure of frequently studied polymers and acceptor units for PSC, along with additive and ternary component.

Generally CPs have been synthesized by the combination of π-electron acceptor, such as [2,1,3-benzothiadiazole (BT), thieno[3,4-b]pyrazine (Tp), quinoxaline (Q)] and π-electron donor, such as [thiophene (Th), cyclopentadithiophene (CPDT), benzo[1,2-b:4,5-b′]dithiophene (BDT), fluorene (FL), carbazole (Cz)] either as D-A, D-A-D or D-π-A (π refers to extended conjugation). D-A combination creates intra molecular charge transfer between donor and acceptor leading to red shift of absorbance, a spectral region where earth receives the most solar photon flux. In the past few years, using these conjugated structures, the desired parameters of molecular structure of a CP for PSCs have been successfully achieved, such as: low dihedral angle along conjugation backbone (a dihedral angle of $< 20^0$ are highly desirable) with high molar extinction coefficient, low band gap of less than 1.8 eV with suitably positioned HOMO and LUMO level (as difference between HOMO of donor and LUMO of acceptor directly proportional to V_{OC}), deeper HOMO level for better air stability, hole mobility in the order of 10^{-2} to 10^{-3} $cm^2V^{-1}s^{-1}$, better solubility along with enhanced film forming property in common organic solvents. All of the above characteristics within a CP directly affect solar cell parameters like Jsc, V_{OC}, FF, PCE (definition given in chapter 1) and significant improvement of PSC performance by modifying structure have been witnessed in recent years. But limiting PCE and photodegradation nature on exposure to ultraviolet radiation in presence of oxygen and moisture limit these CPs to be used for commercial application. Hence detail and progressive study about them are highly essential for in depth understanding of structure property relationship.

Chapter 2: Photo stability enhancement of poly(3-hexylthiophene)-PCBM nano-composites by addition of multi walled carbon nanotubes under ambient conditions

Even though widely used poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT-PCBM) composites for optoelectronic devices, especially bulk-heterojunction (BHJ) solar cells could give efficient polymer solar cells with 4-5% PCE, a major problem of photo stability is associated with it and remains unsolved. P3HT-PCBM composite was found to be degrading on irradiation with ultraviolet radiation or a solar simulator providing AM 1.5G illumination (1000 Wm^{-2}, 72 ± 2 °C or 330 Wm^{-2}, 25 °C), in presence of oxygen and moisture. It is important to stabilize the P3HT-PCBM binary mixture which is the most frequently used composite for BHJ solar cells. Herein, a systematic study has been performed on the photo stability of this binary mixture in the presence of MWCNT at various ratios and optimized the conditions that could be utilized for fabricating photovoltaic devices even under ambient conditions. The P3HT-PCBM binary mixture was converted to a ternary composite by sonicating with MWCNT, (Figure 3a and 4a) maintaining the total amount of carbon nanomaterial (PCBM-MWCNT) within 10% (w/w). It was found that P3HT-PCBM (7%)-MWCNT (3%) is a better photo stable composite than P3HT and P3HT-PCBM (10%) even on extended UV exposure under ambient conditions (Figure 3b and 4a). UV-visible (solution and film), fluorescence spectral analysis and transmission electron micrograph (TEM) with selected area electron diffraction (SAED) pattern have been used as a tool to study the photo stability (Figure 4b and 4c).

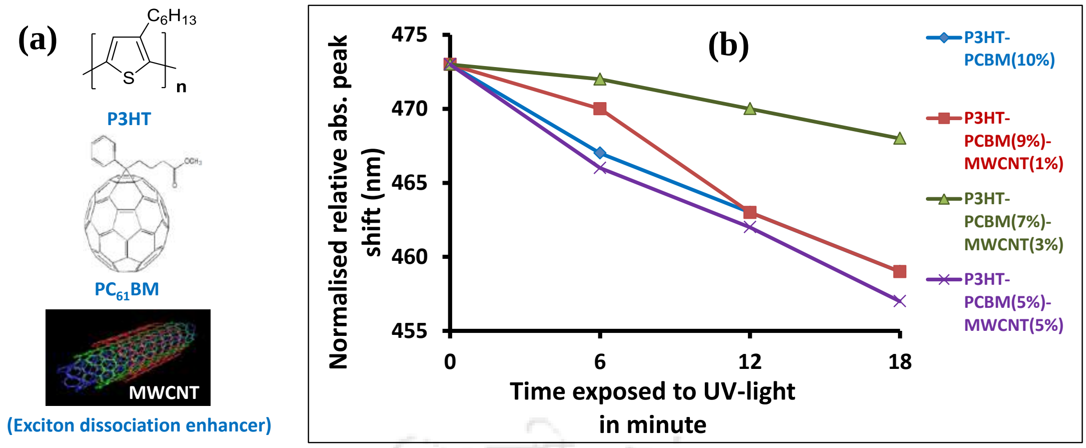

Figure 3 (a) Structures of polymer P3HT, $PC_{61}BM$ and MWCNT used for this study (b) solid state photodegradation comparison of composites of P3HT: PCBM: MWCNT shows high photostability for P3HT-PCBM (7%)-MWCNT (3%).

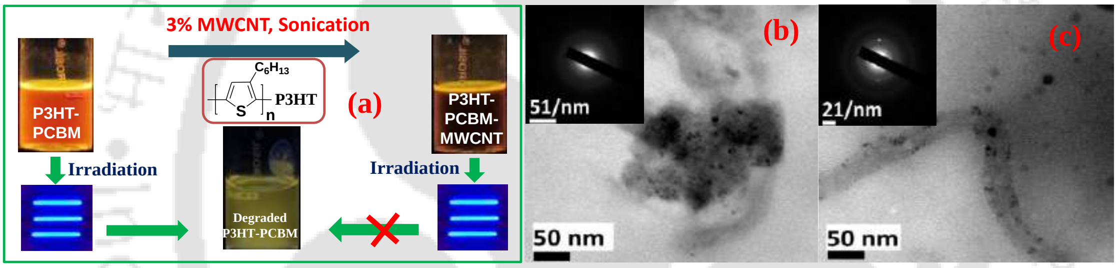

Figure 4 (a) Pictorial representation for photostability enhancement of P3HT-PCBM by MWCNT. TEM image confirming better photostability of composite (b) P3HT-PCBM (7%)-MWCNT (3%) (c) P3HT-PCBM (7%)-MWCNT (3%) degraded up to 20 minutes.

Chapter 3: Insight into the synthesis and fabrication of 5,6-*alt*-benzothiadiazole based D-π-A conjugated copolymers for bulk-heterojunction solar cell

In this approach two poly(o-arylene-vinylene) (POAV) type polymers, where benzothiadiazole (BT) has been attached alternatively to donor via two vinyl-bond (additional π-bond that can extend conjugation and reduce the dihedral angle between donor and acceptor) at 5 and 6 position of BT rather than commonly chosen 4 and 7 have been synthesized. Two extensively used hole transporting donor units: 3-hexylthiophene and 4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-*b*;3,4-*b′*]-dithiophene have been chosen, to obtain 5,6-*alt*-BT based D-π-A type polymers and to give an insight into its potential as a donor in a BHJ solar cell (Figure 5a). POAV polymers show bi-humped UV-visible

(Figure 5b) spectra as like D-A polymers. POAV CPs have been used as donor to fabricate solar cells, with a device structure ITO/PEDOT:PSS/P1orP2-$PC_{61}BM$ or $PC_{71}BM$ /Al or Ca:Al. Without annealing or use of additives, maximum V_{OC} of 0.68 V, fill factor of 30.2%, quantum efficiency of 22% (Figure 6b) and maximum power conversion efficiency (PCE) of 0.76% have been achieved with P2 (Figure 6a). In similar device configuration with P1 PCE was 0.34% (Figure 6a). This approach makes o-arylene kind of (POAV) polymer useful for optoelectronic application with commonly used fullerene/non-fullerene derivatives as acceptor, where an appropriate phase separation between donor and acceptor is an important factor for charge separation.

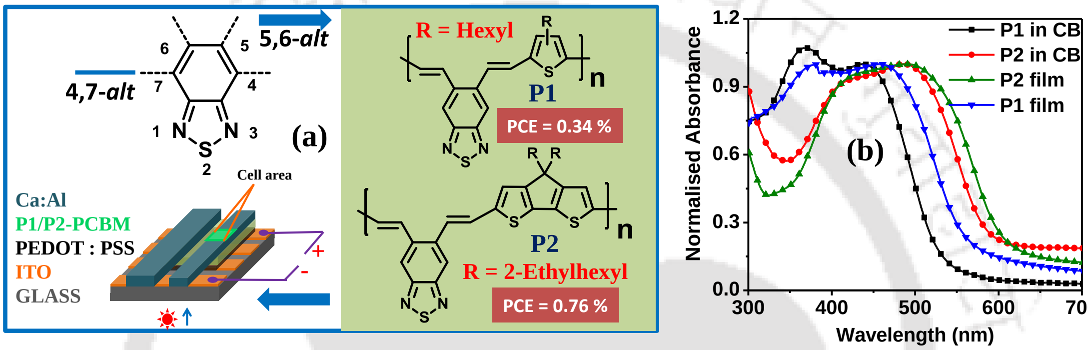

Figure 5 (a) Schematic representation for design, synthesis of 5,6-*alt*-BT-based polymer and its solar cell performance investigation. (b) UV-visible spectra for synthesized POAV type polymer, both in solution and in film state.

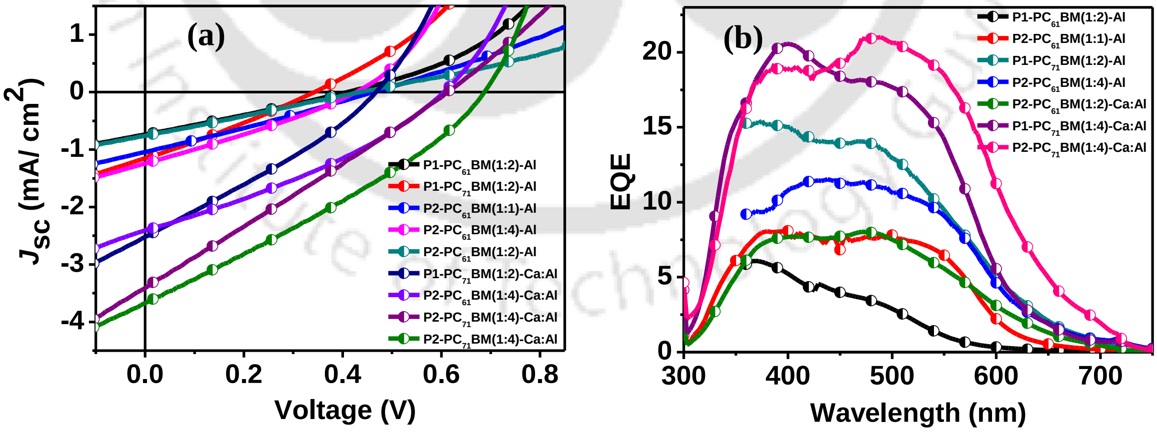

Figure 6 (a) J-V curve (b) external quantum efficiency for POAV type polymer.

Chapter 4: Substituting non-conjugating ester group into side chain of benzothiadiazole improves optical, electrochemical properties, morphology of active layer and solar cell performance of D-A polymer for photovoltaics

Herein, the effect of non-conjugated ester functionalization at 5,6-position of 2,1,3-benzothiadaizole (BT) in donor (D)-acceptor (A) polymer used for photovoltaic devices has been investigated. Position 5 and 6 of BT have been functionalized with methyl acetate group and its structure property relationship have been compared with BT having methyl group at 5,6-positions using four types of D-A polymers (Figure 7a). Alternate co-polymers of newly synthesized methyl and methyl acetate derivatives of BT and Th-BT-Th with commonly used donors such as dithiophene (DTh) and benzodithiophene (BDT) have been synthesized using Stille coupling reaction, namely P(1,2,3,4)-Me and P(1,2,3,4)-Ac. Synthesized ester functionalized polymers stable up to 250 °C (Figure 9a). It has been studied that side chain ester group lowers the dihedral angle, improves optical (Figure 7b) and electrochemical properties of CPs used for PSC, improves phase separation of active layer (Figure 9b to e) and solar cell performance of fabricated PSC compared to its methyl counterpart, as investigated between P(1,2.3,4)-Me and P(1,2,3,4)-Ac. On fabrication of BHJ solar cell with device configuration **ITO/PEDOT:PSS/P-PC$_{71}$BM/LiF/Al**, polymer having methyl acetate functionalization such as P2-Ac, P3-Ac and P4-Ac results in higher PCE of 1.36%, 1.17 % and 0.35% compared to their methyl counterpart P2-Me, P3-Me and P4-Me with PCE of 0.9%, 0.54% and 0.17% respectively (Figure 8a). With 1,8-diiodooctane (DIO) as additive, a PCE of 1.96% has been achieved with P3-Ac with a EQE of 36% (Figure 8b).

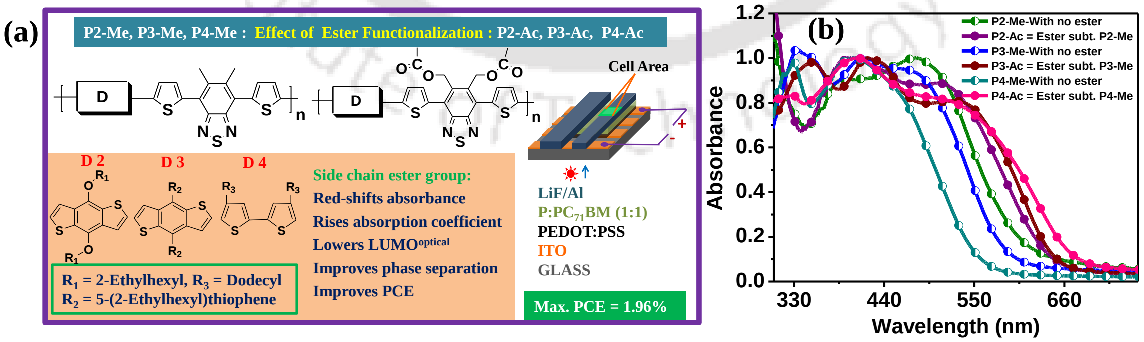

Figure 7 (a) Schematic representation and collective superior performance of ester group at position 5 and 6 of BT as side chain and over methyl (b) thin film UV-visible spectra.

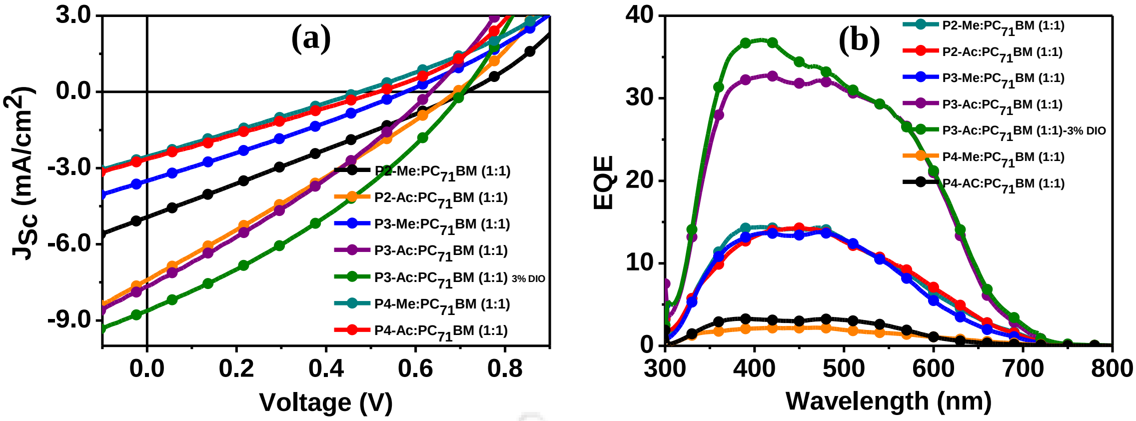

Figure 8 (a) J-V curve for fabricated solar cells (b) external quantum efficiency.

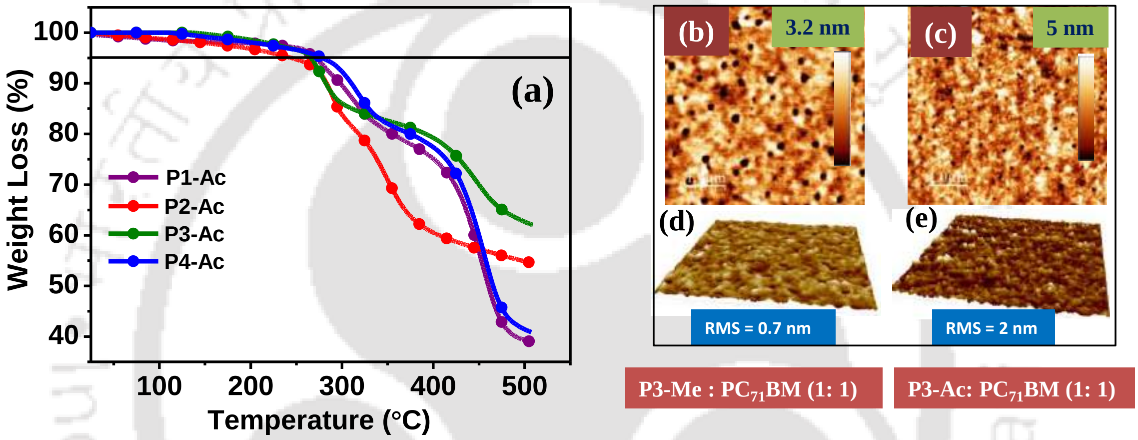

Figure 9 (a) TGA spectra showing thermal stability up to 250 °C for ester substituting polymers. (b to e) improved morphology for methyl acetate substituting polymers compared to their methyl counterpart.

Chapter 5: 6,7-Di(thiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole and 4,6,7,9-tetra(thiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole as new acceptor units for D-A type co-polymer towards fabrication of polymer solar cell

This work emphasize on the synthesis of two new acceptor units for donor (D)-acceptor (A)-based polymers used in photovoltaic devices, namely 4,9-dibromo-6,7-di(thiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole [a derivative of naphtho[2,3-c][1,2,5]thiadiazole (NT), substituted with two thiophene (Th) units on 6 and 7 position of it (NT-Th)] and 4,9-bis(5-bromothiophen-2-yl)-6,7-di(thiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole (Th-NT-Th) with two additional Th units substituted at 4,7 position of NT-Th. Both the NT-based acceptors have been designed using 5,6-position of benzothiadiazole (BT) and synthesized by Wittig coupling reaction. Alternate D-A co-polymer of new NT-based acceptors with commonly used donor 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b′]dithiophene (BDT) via Stille coupling results new conjugated polymers (CPs) namely **P(BDT-NTTh)** and **P(BDT-ThNTTh)**. Newly synthesized acceptor units distinguishes itself from existing literature of naphtho[2,3-c][1,2,5]thiadiazole (NT) acceptor in having additional two Th units attached at 6,7 position of NT, imparting into it a 2-dimensional (2D) type of conjugated structure (Figure 10a). Both **P(BDT-NTTh)** and **P(BDT-ThNTTh)** have ICT band in 700 to 800 nm region (Figure 10b) a necessary requirement for a CP for PSC. Photovoltaic performance of both the CPs has been investigated by fabricating BHJ solar cell with configuration **ITO/PEDOT:PSS/Polymer-PC$_{71}$BM/LiF/Al**, which results a PCE of 0.34% and 1.31% with **P(BDT-NTTh)** and **P(BDT-ThNTTh)** respectively (Figure 11a and 11b). Hole-mobility for blend of **P(BDT-NTTh)** and **P(BDT-ThNTTh)** with PC$_{71}$BM have been calculated using space charge limited current (SCLC) method by fabricating hole only devices with configuration **ITO/PEDOT:PSS/Polymer-PC$_{71}$BM/Cu** and results mobility of $2.2*10^{-6}$ and $1.5*10^{-5}$ cm^{2}V^{-1}s^{-1} respectively.

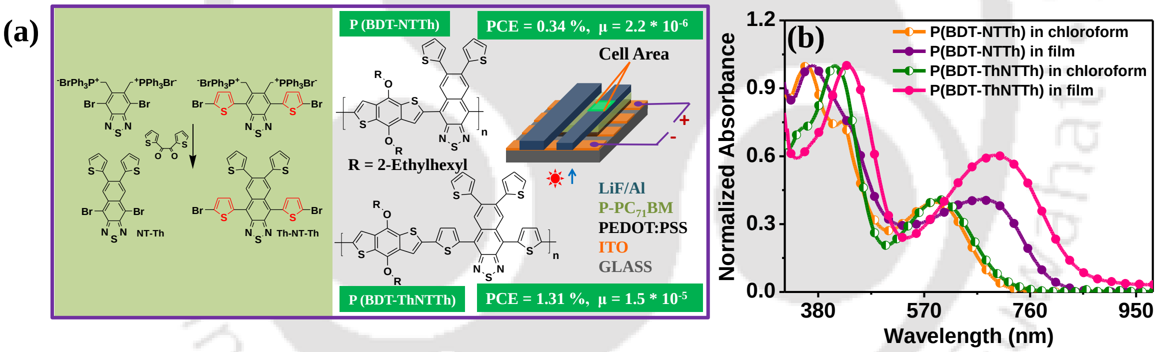

Figure 10 Schematic representations for synthesis of NT-based new acceptors and polymers with PSC performance (a) UV-visible spectra in chloroform and film.

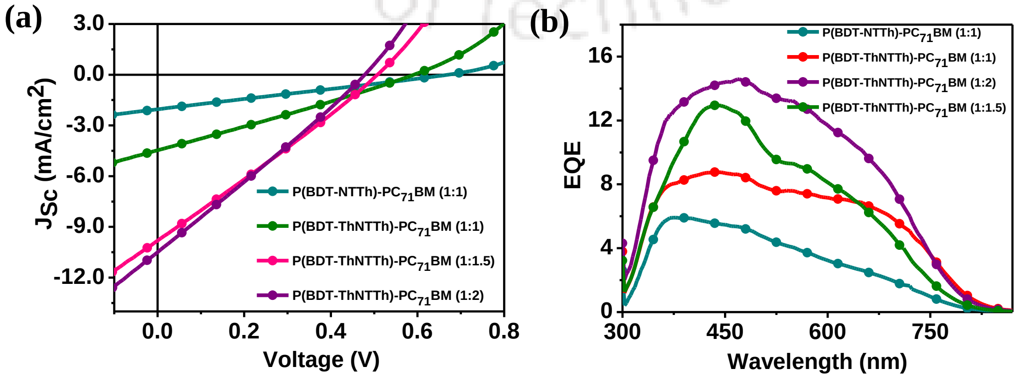

Figure 11 Solar cell performance of NT based polymers (a) J-V curve (b) EQE spectra.

Conclusion and thesis overview

Here effort has been given to investigate further, on structural change leading to change in optoelectronic property by synthesizing newer acceptor units using with 5,6-position of BT. Synthesized acceptor units for donor (D)-acceptor (A)-based conjugated polymers used in photovoltaic devices are 4,9-dibromo-6,7-di(thiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole(NT-Th), 4,9-bis(5-bromothiophen-2-yl)-6,7-di(thiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole (Th-NT-Th) and (4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-diyl)bis(methylene)diacetate. Further efforts have been given towards durability measures for blend of thiophene containing donor polymer and acceptor used for solar cell fabrication (such as PCBM), by preparing composites with MWCNT. Such systems can be used to bring high performance material with improved photo stability for future optoelectronic application.